

Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico

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Abstract

The annual surface water flux of total reactive (i.e., potentially bioavailable) particulate P from the Mississippi River was estimated by measuring the reactive (including labile, iron, organic, and calcium bound) and nonreactive (detrital) P phases in suspended particulates in the Mississippi River. In addition, the transformation of the major sediment P phases resulting from seasonal channel storage and resuspension was examined. Samples were collected during five cruises over 1 yr at marine and riverine sites. Solid-phase and pore-water nutrients were quantified, and solid-phase P pools were measured using a sequential extraction technique. These results indicate that the Mississippi River exports 134×10^6 kg yr⁻¹ of total reactive P via surface water. Seasonal hydrological forcing controlled the variability in major P phases found in channel sediments through hydrodynamic sorting. Although the 6–9-month time period during which sediments were stored in the river channel was sufficient to see evidence of early diagenesis in the pore waters, no significant net effect was seen on major P phase distribution. The loss of a significant percentage of labile and iron-bound P appears to be occurring only as these riverine sediments are deposited and reworked on the continental shelf.

Phosphorus is an important macronutrient that is thought to limit marine primary productivity, particularly on geological timescales (Holland 1994; Tyrell 1999). For this reason, the marine P budget has been the subject of intense study over the past 3 decades, and much effort has gone into estimating inventories and source and sink terms in the budget (Froelich et al. 1982; Meybeck 1982; Froelich 1988; Ruttenger 1991, 1993; Berner and Rao 1994; Filippelli 1997; Delaney 1998). Riverine flux constitutes the majority of the source term in the reactive (i.e., potentially bioavailable) P budget, with atmospheric input representing <10% of riverine flux (Duce et al. 1991; Delaney 1998). To maintain steady state, riverine flux should be roughly equal in magnitude to the burial of reactive P in oceanic sediments ($8\text{--}18 \times 10^{10}$ mol yr⁻¹; Ruttenger 1993), the mechanism for the ultimate removal of P from the oceans. Estimates of global dissolved P flux from rivers ($0.1\text{--}0.4 \times 10^{10}$ mol yr⁻¹; Froelich et al. 1982) are generally an order of magnitude smaller than the estimate of reactive P burial, so the burial term can only be balanced by riverine input if some fraction of particulate P is included. The question is, how much of this particulate P is reactive and can ultimately support marine productivity?

The large range in estimates of global riverine reactive P flux ($3\text{--}15 \times 10^{10}$ mol yr⁻¹; Froelich et al. 1982; Berner and Rao 1994) is due to two factors: (1) the dominance of par-

ticulate P relative to dissolved P in the estimate and (2) the uncertainty in the degree to which P is solubilized from particles as they are cycled through estuaries and deposited on continental shelves (Froelich 1988). Dissolved reactive P adsorbs to particles such as amorphous ferric hydroxides in freshwater and then is released as salinity increases (Carritt and Goodgal 1954; Lebo 1990). Dissolved reactive P can also be remobilized from sediments as a result of iron or sulfate reduction (Caraco et al. 1990). Thus, riverine flux of total reactive P can be better constrained with improved data on the percentage of particulate P that is reactive in large river systems such as the Mississippi River. In addition, it is important to better understand the physical and geochemical controls on the size of the reactive P pool in sediments and suspended matter in large river systems.

The seasonal storage and remobilization of sediments in rivers potentially influences the size and flux of the reactive particulate P pool. This phenomenon has been observed in rivers ranging in size from small streams (Emmett et al. 1983) to the Amazon, the world's largest river (Meade et al. 1985). Sediment deposition rates in the Mississippi River are high during the sediment storage phase and the resulting deposits remain undisturbed for periods of months (Demas and Curwick 1988). These conditions and timescales are conducive to a number of significant chemical transformations within riverbed sediments that control P remobilization to the water column, including (1) the remineralization of organic carbon and the accompanying generation of diagenetic products in pore waters and (2) the reduction of iron, manganese, and other redox-sensitive elements and accompanying transformations between particulate and dissolved phases. Stored sediments are subsequently resuspended during high discharge phases, and the particulate and dissolved phases are exported to the coastal ocean. Approximately 90% of sediment currently eroded off the land surface of continental United States is stored within the river system, on a timescale of decades (Meade and Parker 1985). This

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storage and remobilization process is likely to play an important role in controlling the reactive P flux from rivers.

We used a sequential extraction technique to determine the major P reservoirs in suspended matter and sediments in the lower Mississippi River and continental shelf of the Gulf of Mexico. Our objective was to understand how seasonal hydrological forcing, sediment storage, and diagenesis affected the chemical forms of P in suspended matter, sediments, and sediment pore waters. The lower Mississippi River, which has the sixth largest water discharge and the seventh largest suspended load among world rivers (Milliman 1991), is an excellent location to study this question. Seasonal sediment storage and remobilization has been well documented for the lower 500 km of the river (Meade and Parker 1985; Demas and Curwick 1988). In addition, increases in riverborne nutrients have resulted in hypoxic bottom waters extending over a 9,500-km² area in the Gulf of Mexico west of the mouth of the Mississippi River (Rabalais et al. 1996). Physical and geochemical controls on the reactive P pool regulate sources of P for biological productivity in eutrophic marine ecosystems and thereby influence the development of hypoxia.

Materials and Methods

The Mississippi River drains two thirds of the continental United States and strongly influences coastal processes in the northern Gulf of Mexico, a permanently stratified, subtropical sea. Approximately 60% of the total suspended matter and 66% of the total dissolved materials transported from the North American continent to the ocean are carried by the Mississippi River (Presley et al. 1980). It has an average freshwater discharge of 380 km³ yr⁻¹, an average sediment discharge of 150×10^9 kg yr⁻¹, and average total N and P fluxes of 1.5×10^9 kg N yr⁻¹ and 0.13×10^9 kg P yr⁻¹ (Goolsby et al. 1999, 2001).

The effects of sediment storage and remobilization were examined in the lower 150 km of the Mississippi River (Fig. 1). Because of extensive leveeing of the lower river, sediments can only enter from upstream, thus simplifying the comparison of surface water and sediment properties between upstream and downstream sites. About 30% of the total discharge is diverted to the Atchafalaya River just above Tarbert Landing, the site of the old river-control structure. Downstream of this point, channel cross-section increases with downstream distance. Significant resuspension and net remobilization of sediments occurs during periods of high discharge ($>20,000$ m³ s⁻¹), January–July (Demas and Curwick 1988). Periods of sediment storage typically occur in a 4–8-month period of lower discharge ($<14,000$ m³ s⁻¹), July–January.

Field methods—Our sampling program consisted of both surface water and sediment sampling in the lower Mississippi River and on the Gulf of Mexico shelf during high and low discharge periods. In April 1999, surface water particulate and dissolved nutrients and organic carbon samples were collected every ~10 km along freshwater (salinity, <2) and estuarine (salinity, ≥ 2) transects from Sta. 1–4 in the Gulf of Mexico (Fig. 1). In November 1999, river discharge

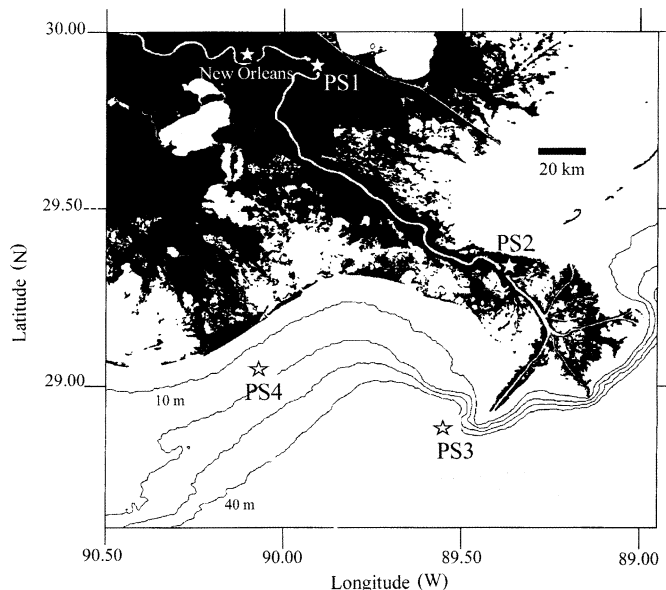


Fig. 1. Map of study area showing river stations (Sta. 1 = PS1 and Sta. 2 = PS2) and Gulf of Mexico stations (Sta. 3 = PS3 and Sta. 4 = PS4).

was at a 20-yr low ($<5,000$ m³ s⁻¹). Salinities of 19–24 were recorded in bottom waters beginning 50 km downstream of Sta. 1. For this reason, both freshwater and estuarine transects for this sampling period were contained within the river itself. Therefore, November 1999 surface water samples with salinities >2 were grouped with estuarine transect samples for analysis. Surface and bottom water column samples were collected using a rosette array of Niskin bottles. Samples were filtered with a precombusted 25-mm glass-fiber filter (0.7 μ m pore size) and frozen for the analysis of total suspended sediment (TSS), chlorophyll *a*, particulate organic carbon (POC), particulate nitrogen (PN), and bulk phosphorus (PP). An additional particulate sample on a 25-mm glass-fiber filter was frozen for the sequential extraction of PP phases. Filtered water was frozen immediately for later analysis of ammonium (NH₄⁺), nitrate (NO₃⁻), nitrite (NO₂⁻), soluble reactive phosphorus (SRP), and total dissolved nitrogen (TDN), phosphorus (TDP), and organic carbon (DOC).

Sediment samples were collected at Sta. 1, 2, and 4 in April 1999, Sta. 2, 3, and 4 in July 1999, and Sta. 1 and 2 in November 1999 and February and May 2000. Mean discharge during the sampling periods spanned a range from a high of 17,000 m³ s⁻¹ in April 1999, intermediate values of ~13,000 m³ s⁻¹ in July 1999 and May 2000, and low discharge of 4,000–7,000 m³ s⁻¹ in November 1999 and February 2000. Samples were collected with a box corer (0.5 \times 0.5 m cross-sectional area) that routinely retrieves undisturbed cores ~50 cm deep. Box cores were subcored immediately on collection. Cores were taken for the analysis of solid-phase and pore-water nutrients and organic carbon, the sequential extraction of solid phase P pools and radionuclides ⁷Be and ²¹⁰Pb for sediment geochronology. The core taken for analyses of nutrients and carbon was extruded immediately in a glove box under nitrogen gas, to prevent oxidation artifacts. The core was sectioned vertically in 1–2

Table 1. The SEDEX procedure (Ruttenberg 1992).

Target phase	Symbol	Extractant
Loosely bound+exchangeable P	Labile	1 mol L ⁻¹ MgCl ₂ (pH 8) 2×2 h; water washes 2×2 h
Iron-bound P	Fe-P	0.3 mol L ⁻¹ Na ₃ -citrate+1 mol L ⁻¹ NaHCO ₃ (pH 7.6)+0.675 g Na ₂ S ₂ O ₄ 1×8 h (CDB solution) for sediments and 0.225 g Na ₂ S ₂ O ₄ for filters; 1 mol L ⁻¹ MgCl ₂ (pH 8) 1×2 h; water wash 1×2 h
Biogenic+CaCO ₃ bound P	Ca-P	1 mol L ⁻¹ Na-acetate buffered to pH 4 with acetic acid 1 × 6 h; 1 mol L ⁻¹ MgCl ₂ (pH 8) 2×2 h; water wash 1×2 h
Detrital apatite+other iorganic P phases	Detr-P	1 mol L ⁻¹ HCl 1×16 h
Organic P	Org-P	Dry oxidation at 550°C for 2 h; 1mol L ⁻¹ HCl for 16 h

cm intervals, centrifuged, and the pore-water centrate filtered with a 0.2- μ m polycarbonate filter. Pore waters were immediately frozen for the analysis of NH₄⁺, NO₃⁻, NO₂⁻, SRP, TDN, TDP, and DOC. Field blanks for all surface- and pore-water analyses consisted of Milli-Q deionized water filtered through the same apparatus as was done for the samples.

Analytical methods—Surface- and pore-water samples were assayed for dissolved inorganic nutrients using the wet chemical methods of Solorzano (1969) for the analysis of NH₄⁺, the method of Strickland and Parsons (1972) for the analysis of NO₂⁻, and the method of Koroleff (1976) for the analysis of SRP. NO₃⁻ was analyzed using a Dionex DX-500 ion chromatograph with an AS9-HC column and a 9-mmol L⁻¹ sodium carbonate eluent. DOC was determined via high-temperature catalytic combustion using a Shimadzu 5000 TOC Analyzer (EPA Method 415.1). TDN was digested to NO₃⁻ using the persulfate oxidation method (Valderrama 1981) and analyzed by ion chromatography. Total P (TP) was digested by combustion and hydrolysis as in Solorzano and Sharp (1980). Dissolved organic nitrogen and phosphorus (DOP) were calculated by subtracting the dissolved inorganic nutrient concentration from TDN or TDP. Pore-water salinity was recorded using a refractometer. TSS was analyzed using the gravimetric technique described by Banse et al. (1963), and Chl *a* was measured with a Waters high-performance liquid chromatograph using the method of Bianchi et al. (1996). Suspended-matter particulate and sediment samples were acidified to remove carbonates and analyzed for organic carbon and nitrogen using a CHNS-O elemental analyzer. Sediment TP was digested by high temperature ashing and leaching with 1 mol L⁻¹ HCL (Aspila et al. 1976). Sand, silt, and clay grain size fractions were

determined by wet sieving the sample through a 62- μ m sieve to separate coarse and fine fractions and then analyzing the fine fraction using the pipette method (Milner 1962).

The major forms of solid-phase P in water column particulates and sediments were investigated using the SEDEX sequential extraction method of Ruttenberg (1992). There are five target phases that are isolated by this extraction method: (1) exchangeable + loosely bound P (labile-P), (2) iron-bound P (Fe-P), (3) biogenic apatite + calcium carbonate-bound P (Ca-P), (4) detrital apatite + other remaining inorganic P phases (detr-P), and (5) organic P (org-P). Of these, labile-P, Fe-P, Ca-P, and org-P could potentially contribute to the reactive P pool, whereas detr-P is considered to be the refractory pool. Table 1 summarizes the SEDEX procedure. The procedure was performed on replicate sediment samples of ~0.3 g dry weight that were freeze dried and ground to <125 μ m. Sediment samples were extracted in a 50-ml centrifuge tube. Extractant volumes were 30 ml, except in the Fe-P extraction step, where 27 ml of citrate bicarbonate was used. Particulate matter on filters was dried, weighed, and placed in 10-ml centrifuge tubes. Extraction volumes for filters were 10 ml, except in the Fe-P extraction step, where 9 ml of citrate bicarbonate was used. Field blanks (filters through which deionized water was passed) were also carried through the sequential extraction procedure.

All supernatant solutions resulting from the labile-P, Ca-P, detr-P, and org-P extraction steps were analyzed for P spectrophotometrically in triplicate by the standard phosphomolybdate blue method (Koroleff 1976). This method could not be used for the supernatants from the Fe-P step, because citrate dithionate-bicarbonate (CDB) interferes with the molybdate blue reagent. To correct for this, the supernatant was reacted with a 1% vol/vol FeCl₃ solution (Lucotte and d'Anglejan 1985), extracted with isobutanol, and analyzed for P by spectrophotometer (Watanabe and Olsen 1962; Ruttenberg 1992). The analysis of Fe in the supernatant from this extraction step was analyzed by ICP-MS (inductively coupled mass spectrometry).

The reproducibility and efficiency of total SEDEX P extraction were evaluated by tabulating relative variances of particulate and sediment replicates and by comparison of SEDEX extraction results with analyses of particulate and sediment TP on duplicate samples (Table 2). SEDEX extractions on replicate sediment samples showed high reproducibility, with coefficients of variance of 2.4–9.6%. Coefficients of variation increased with each progressive step.

Table 2. Reproducibility of the SEDEX method, based on replicate samples of sediments and suspended particulates.

Step	Sediments, mean % relative error (n=114)	Suspended particulates mean % relative error (n=14)
Labile-P	2.4	13.1
Fe-P	4.0	16.7
Ca-P	3.2	15.5
Detr-P	2.9	14.3
Org-P	9.1	19.5
TP	2.6	14.6

Table 3. April and November 1999 mean particulate and dissolved phosphorus, TSS, and particulate C:N atomic ratio data for freshwater transects. Subscripts with different letters (a, b, c) designate significant differences among concentration means at $p < 0.05$ ($\alpha = 0.05$, $df_{\text{num}} = 1$, $df_{\text{denom}} = 13$). Numbers in parentheses represent 95% confidence interval estimates for concentration means.

Consistent	April 1999		November 1999	
	Surface	Bottom	Surface	Bottom
Depth (m)	2 (0)	21 (9)	2 (0)	25 (13)
Salinity	0.3 (0)	0.3 (0)	0.6 (0.5)	0.5 (0.5)
SRP ($\mu\text{mol L}^{-1}$)	1.8 (0.2) _a	1.8 (0.2) _a	3.2 (0.2) _b	3.1 (0.1) _b
DOP ($\mu\text{mol L}^{-1}$)	0.6 (0.3) _a	0.5 (0.3) _a	0.5 (0.2) _a	0.5 (0.2) _a
PP ($\mu\text{mol L}^{-1}$)	2.9 (0.3) _a	3.2 (0.3) _a	0.5 (0.1) _b	0.7 (0.1) _b
Particulate C:N ratio	12 (1) _a	12 (1) _a	8 (1) _b	9 (1) _b
TSS (mg L^{-1})	99 (18) _a	113 (16) _a	16 (4) _b	19 (4) _b

These numbers were slightly higher for the SEDEX extraction of suspended particulates (13.1–19.5%), which had smaller sample sizes. Comparison of sediment TP concentration as measured with the SEDEX method versus that of Aspila et al. (1976) indicated a relative difference of 16%, with the SEDEX-produced values tending to be lower than those obtained by the Aspila et al. (1976) method. The percentage difference was higher for suspended particulate analysis, where SEDEX-produced values averaged 26% lower than those obtained by the Solorzano and Sharp (1980) method. This larger difference may be due to the difficulty in sequentially extracting filters.

The geochronology of sediments sampled in the present study was determined using radioactive isotopes of ^{210}Pb , ^7Be , and ^{137}Cs . The ^{210}Pb activities (half-life, 22 yr) were determined by α -particle spectrometry methods. ^{210}Po , the radiometric granddaughter of ^{210}Pb , was counted using methods described in Nittrouer et al. (1979), McKee et al. (1983), and DeMaster et al. (1985). Activities of ^7Be (half-life, 53 d) and ^{137}Cs (half-life, 30 yr) were determined by γ -spectrometry using a low-energy germanium planar detector coupled with a low-background cryostat and shielding. Energy peaks at 477.6 and 661.6 KeV were used to determine ^7Be and ^{137}Cs activities, respectively. Sedimentation rates were determined from the down-core distribution of excess ^{210}Pb activities using a non-steady-state initial concentration model, as described in Appleby and Oldfield (1992). Statistical analyses consisted analyses of variance used to test for differences in mean constituent concentration between surface and bottom waters and by sampling period and differences in TP and major P phase by station and sampling date (SAS 1989).

Results

Surface-water dissolved and particulate phosphorus: freshwater transect—In the freshwater transects sampled for surface water in April and November 1999, significant seasonal differences were found in the mean concentrations of SRP, TSS, and particulate nutrients and DOC (Table 3). The mean SRP was higher in November, and PP, the C:N ratio, and TSS were lower. DOP was relatively similar between the two periods. No consistent differences were found between surface and bottom waters, nor were there consistent

longitudinal trends for any of the bulk constituents (Table 3, Fig. 2).

For both seasons sampled, DOP was the smallest component of the TP in the lower Mississippi River, with mean concentrations of 0.5–0.6 $\mu\text{mol L}^{-1}$. PP concentrations (3.0 $\mu\text{mol L}^{-1}$) exceeded SRP concentration (1.8 $\mu\text{mol L}^{-1}$) during April 1999, whereas, in November 1999, mean PP concentrations were less than one third of SRP. PP, POC, and PN concentrations were correlated with TSS concentration (Fig. 2).

The mean P content of TSS was significantly higher in November than April 1999 (36.2 and 29.0 $\mu\text{mol g}^{-1}$ dry wt TSS, respectively, $p < 0.05$). The mean C:N ratio of TSS was lower in November than in April (Table 3). During the two sampling periods, the reactive P pool comprised ~98% of the total bulk PP pool. The Fe-P fraction represented the highest percentage (40–43%), followed by labile-P (30–33%), Ca-P (18%), and org-P (5%). Detr-P constituted only 2% of total bulk PP (Fig. 3). The mean contents of labile-P, Fe-P, and org-P in TSS were significantly higher in November than April 1999, whereas no significant differences between Ca-P and detr-P were seen during these two sampling periods (Fig. 3). The contents of PP and the major P phases in TSS were highly spatially variable along the freshwater transect for both sampling periods, but no consistent longitudinal trend was observed (Fig. 4).

Surface-water dissolved and particulate phosphorus: estuarine transect—The environmental conditions sampled in the April and November 1999 estuarine transects were quite different. During the April 1999 sampling period, the estuarine mixing zone was located just offshore of the river mouth on the adjacent continental shelf of the Gulf of Mexico. In November 1999, because of low river discharge, the mixing zone was contained within the physical boundaries of the river channel, and conductivity and temperature data revealed a zone of turbulent mixing and fluidized mud in the bottom waters beginning ~80 km downstream of Sta. 1.

SRP and PP declined with increasing salinity in the April and November 1999 transects, whereas TSS, POC, PN, and DOP were highly variable and showed no discernable trends. Although the partitioning of the PP pools was highly variable over the salinity transect, the overall trends between the freshwater and marine end members were consistent for both

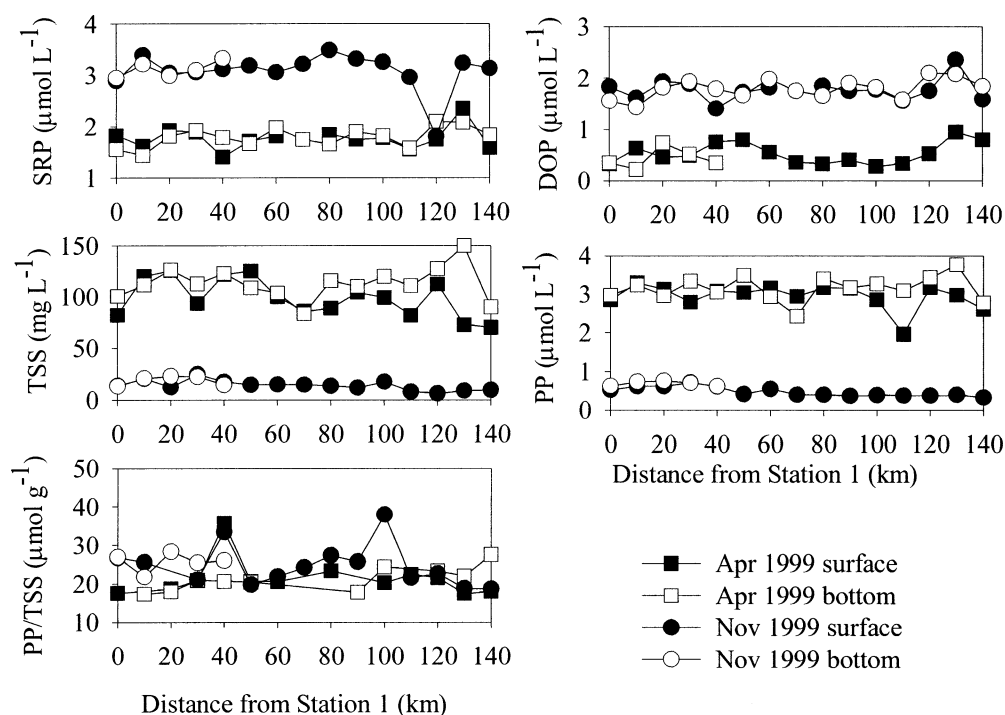


Fig. 2. SRP, DOP, TSS, and PP concentrations and P content of TSS along freshwater transects for April and November 1999. The X-axis is the distance from Sta. 1. Km 140 marks Sta. 2, downstream.

April and November 1999 (Fig. 5). The relative percentage of Fe-P decreased from 40–46% of PP at 0 salinity to a nondetectable amount at salinities of 23–27. Labile-P initially increased from 29–33% of PP at 0 salinity to 55–63% at salinities of 23–27. It then decreased to 26% at a salinity of 35. Org-P and Ca-P increased over this salinity range from 5–12% and 17–60% of PP, respectively.

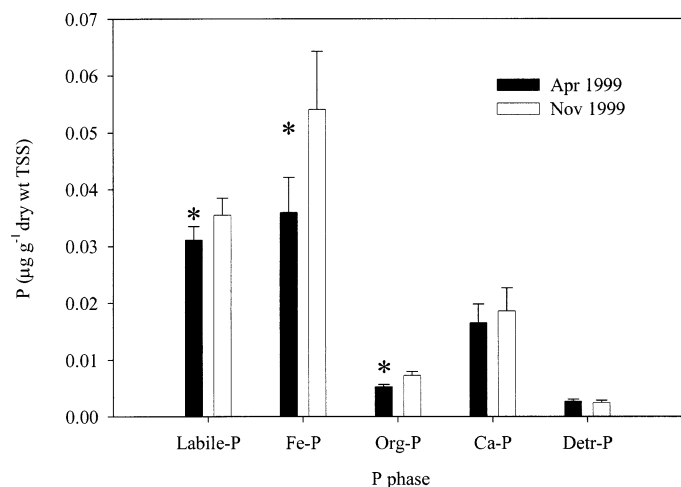


Fig. 3. Mean concentrations of the P phases in TSS for the April and November 1999 sampling periods. Error bars represent 95% confidence intervals. Asterisk: a significant difference in mean concentration between sampling periods with a $p < 0.05$ ($\alpha = 0.05$, $F_{\text{num}} = 1$, $F_{\text{denom}} = 23$).

Bulk sediment characteristics—Vertical profiles of bulk sediment characteristics showed strong seasonal variability, as well as spatial differences between the riverine (Sta. 1 and 2) and marine stations (Sta. 3 and 4). The pore-water salinity of Sta. 1 sediments demonstrated that this is a permanently freshwater station (Fig. 6). Station 2 was variably estuarine, with peak pore-water salinities of 36 in February 2000 and residual salinities of 10 at 30 cm depth even during the high and intermediate discharge periods of April and July 1999. In contrast, sediment pore waters from Sta. 3 and 4 have a permanently marine salinity regime.

The grain size distribution of sediments also showed spatial and temporal variability. The river stations (Sta. 1 and 2) both exhibited a large range in grain size (Fig. 6), although Sta. 2 sediments tended to be finer than those of Sta. 1. Station 3 and 4 sediment contained mostly fine-grained sediment with 70–80% clay. In the river, sediments sampled during high and intermediate discharge periods (April and July 1999 and May 2000) showed the coarsest grain size distribution. Low discharge periods, such as November 1999 and February 2000, exhibited the highest percentages of fine sediment (60–80% silt and clay).

Sediment grain size was strongly correlated with seasonal and vertical variations in sediment percentage of organic carbon (%OC), C:N ratios, and TP content, particularly in river sediments (Fig. 6). As with grain size, river sediments exhibited a large range in %OC (0.3–1.8%), TP (0.6–1.4 mg g^{-1}), and C:N ratio (7–24:1). High discharge periods showed lower %OC and bulk P and higher C:N ratios than low flow periods. The percentage of clay in sediments ex-

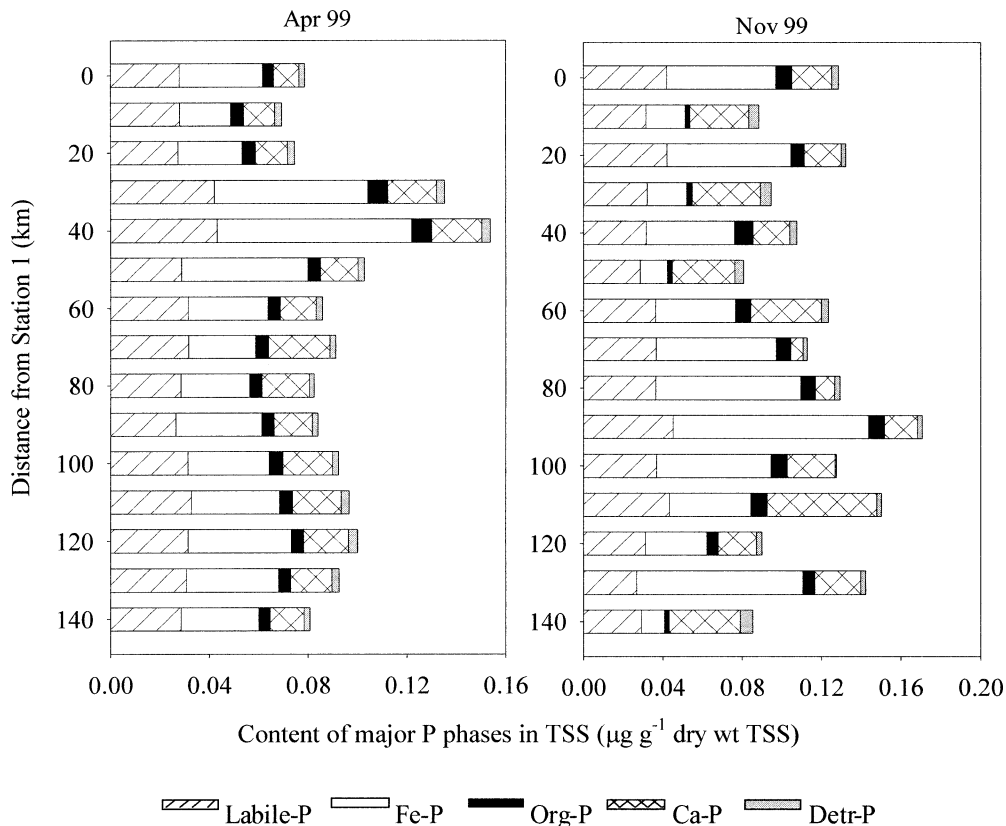


Fig. 4. Content of P phases in TSS along the freshwater transect in the April and November 1999 samplings.

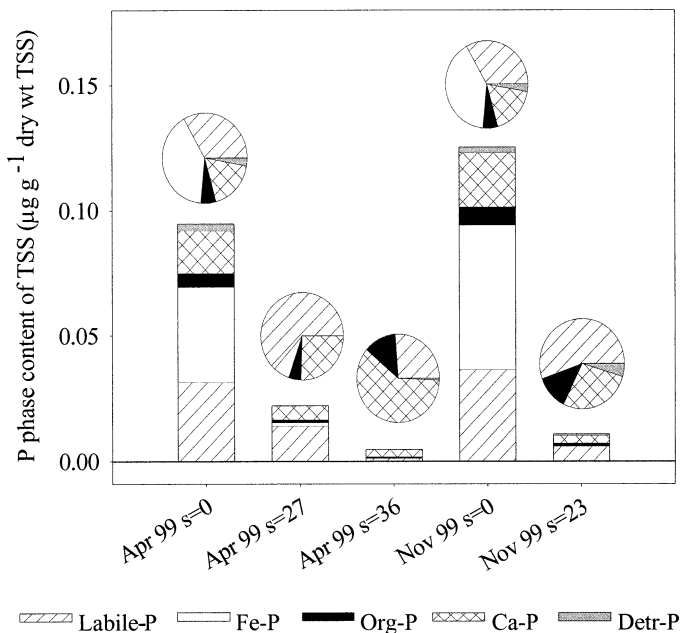


Fig. 5. Content of major P phases in TSS along the estuarine transect in the April and November 1999 sampling periods. Salinity of the samples is designated as "s =." Each bar represents a minimum of two samples analyzed to yield a mean concentration for that salinity and season. The pie chart above each bar represents the percentage composition of each P phase.

plained 63% of the variability in %OC and 60% of variability in TP and C:N ratios for Sta. 1–3.

Stations 3 and 4 showed much less vertical variation than the river stations with respect to %OC, TP, and C:N ratio. In July 1999 (the only period for which these stations were sampled), Sta. 3 averaged 1.2% OC, 0.8 mg g⁻¹ TP, and 13:1 C:N. TP and %OC contents in Sta. 4 sediments were generally the lowest of all stations and seasons, with an average of 0.8% OC, 0.5 mg g⁻¹ TP, and 12:1 C:N. Despite pore-water salinity data showing that Sta. 3 sediments have a marine salinity regime, bulk sediment chemistry data illustrate that the sediments from this station have more in common with the two river stations.

The ²¹⁰Pb and ⁷Be data indicate that the upper 40+ cm of sediments at Sta. 1–3 were deposited within 1 yr of sampling, which indicates very high rates of deposition (Fig. 7). For these stations, there was no appreciable decay of excess ²¹⁰Pb, and excess ⁷Be was measurable to the bottom of the core. Therefore, short-term deposition was likely in the tens of centimeters during seasons of high river discharge. Graphs of excess ²¹⁰Pb illustrate that there is measurable decay only for Sta. 4, the only truly marine station. Excess ⁷Be for this station decayed to zero within the first 10 cm (Fig. 7). On the basis of these data, the sedimentation rate for this site was calculated to be ~0.15 cm yr⁻¹, with a 10-cm mixed layer on the surface.

Pore-water profiles—In general, pore-water DOC, NH₄⁺, and SRP concentrations in Sta. 1 and 2 sediments were low-

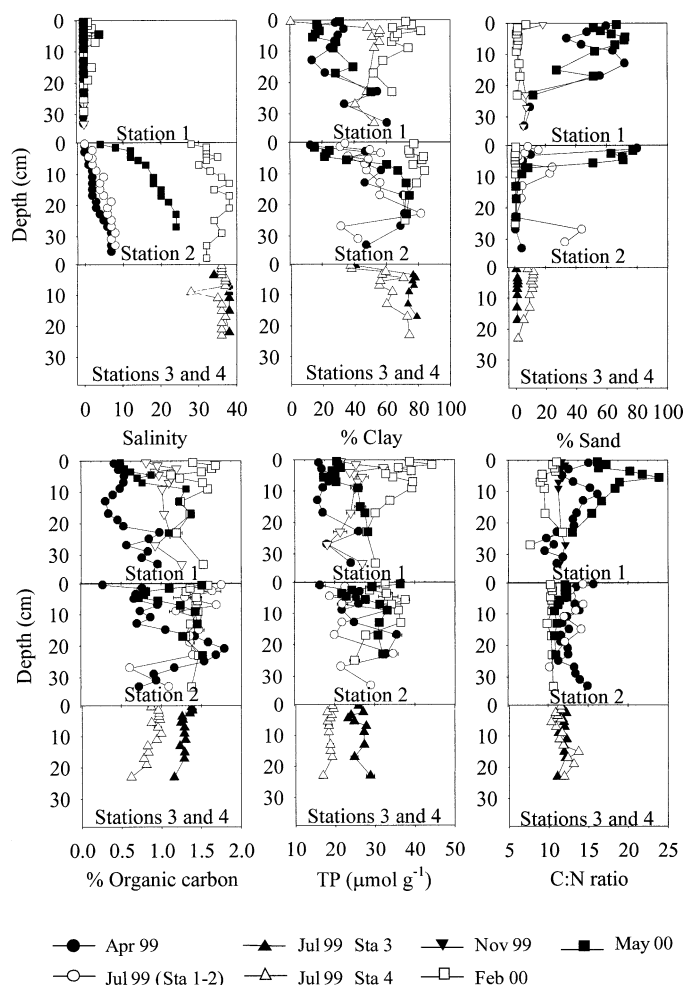


Fig. 6. Vertical profiles of pore-water salinity, grain size, %OC, TP concentration, and C:N ratio in bulk sediments for Sta. 1–4 on five sampling dates.

est in concentration during periods of high discharge and highest during low discharge periods (Fig. 8). Pore-water DOC concentrations in Sta. 1 sediments ranged from a high of $7,000 \mu\text{mol L}^{-1}$ in November 1999 to a low of $1,500 \mu\text{mol L}^{-1}$ in April 1999. Pore-water DOC concentrations were also very high in Sta. 2 and 3 sediments in July 1999, ranging $4,000$ – $8,000 \mu\text{mol L}^{-1}$. Pore-water DOC concentrations in Sta. 4 were lower ($2,000$ and $4,000 \mu\text{mol L}^{-1}$). Ammonium and SRP concentrations also followed this same pattern, with the notable exception that Sta. 2 and 3 profiles had higher concentrations than Sta. 1. Particularly in the case of SRP, Sta. 1 profiles generally remained between 1 and $20 \mu\text{mol L}^{-1}$, regardless of season. Station 2 and 3 pore-water SRP profiles reached concentrations of 50 – $90 \mu\text{mol L}^{-1}$ during July 1999 and February and May 2000, which corresponded with finer grain size and higher pore-water salinity during those periods. This relationship did not hold for Sta. 4 sediments, which had pore-water concentrations of 5 – $20 \mu\text{mol L}^{-1}$, despite a high clay fraction and high pore-water salinity during the July 1999 sampling period.

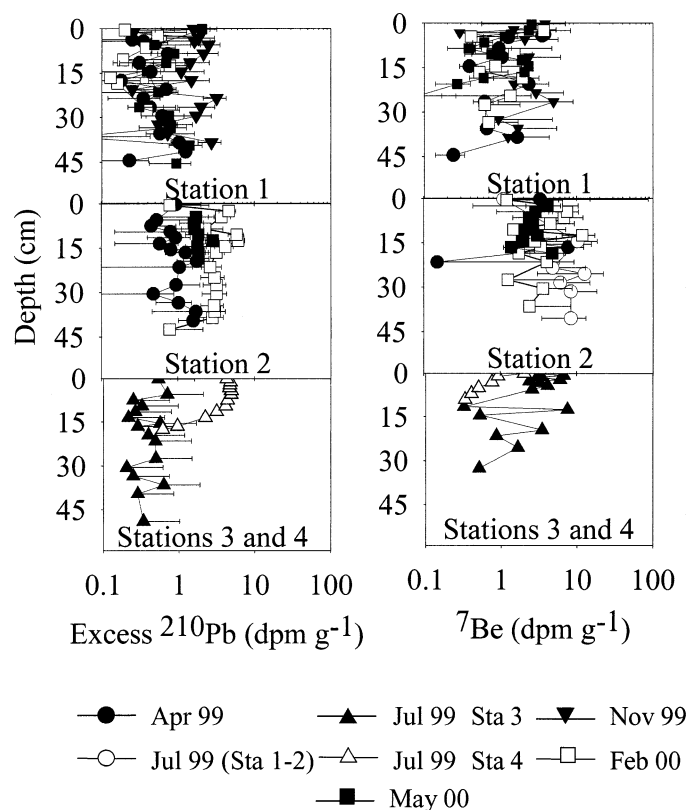


Fig. 7. Vertical profiles of ^7Be and ^{210}Pb for Sta. 1–4 on six sampling dates.

Sediment P phases—River sediments exhibited a large range in content of labile-P (2 – $7 \mu\text{mol g}^{-1}$), Fe-P (5 – $23 \mu\text{mol g}^{-1}$), org-P (1 – $8 \mu\text{mol g}^{-1}$), Ca-P (4 – $8 \mu\text{mol g}^{-1}$), and det-P (2 – $4 \mu\text{mol g}^{-1}$), with highly variable but no consistent vertical trends (Fig. 9). Station 3 P phase concentrations fell within the range exhibited by the river sediments, whereas

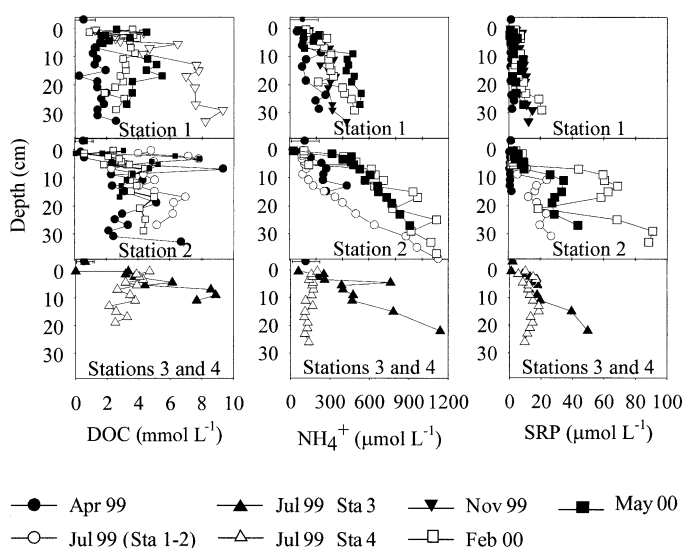


Fig. 8. Vertical profiles of pore-water DOC, NH_4^+ , and SRP concentration for Sta. 1–4 on five sampling dates.

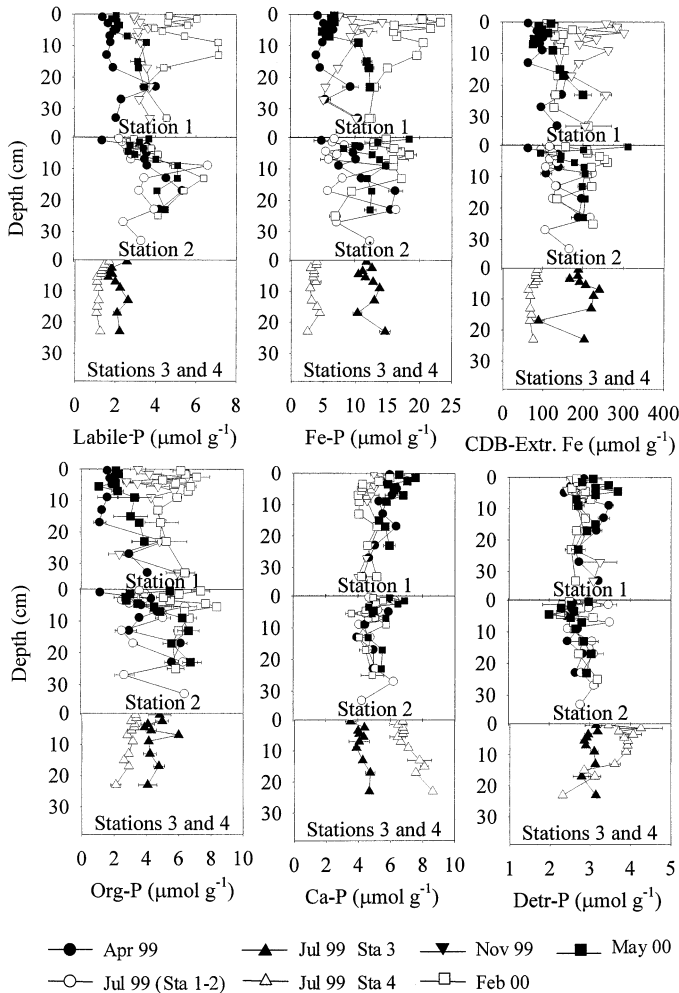


Fig. 9. Vertical profiles of P phase content (labile-P, Fe-P, org-P, Ca-P, and detr-P) and CBD-extracted Fe for Sta. 1–4 on five sampling dates.

Sta. 4 exhibited the lowest mean concentrations of labile-P ($1.7 \mu\text{mol g}^{-1}$) and Fe-P ($4 \mu\text{mol g}^{-1}$) of all stations. In contrast, at Sta. 4, the mean Ca-P and detr-P content was the highest of all stations (6 and $4 \mu\text{mol g}^{-1}$, respectively).

Figure 10 shows the trends in percentage composition of the five major P phases, computed by averaging results of P phase concentration of the top 6 cm over all sampling seasons. Although the percentage org-P of TP stayed relatively constant throughout (15–17%), the percentage of labile-P steadily decreased from 13% in the river sediments to 8% and 7% at Sta. 3 and 4, respectively. The percentage of Fe-P increased from 38 at Sta. 1 to 47% at Sta. 4, then declined rapidly to 19% at Sta. 4. Station 4 had much higher Ca-P (39%) and detr-P (19%) than Sta. 1–3 (16–23% and 10–12% for Ca-P and detr-P, respectively).

As with the bulk sediment characteristics, sediment grain size was strongly related to seasonal and vertical variations in the major P phases in the sediment (Figs. 6, 9). High discharge periods corresponded with higher levels of labile-P, Fe-P, and CBD-extracted Fe and lower org-P, a result that is consistent with sediment of coarser grain size. The per-

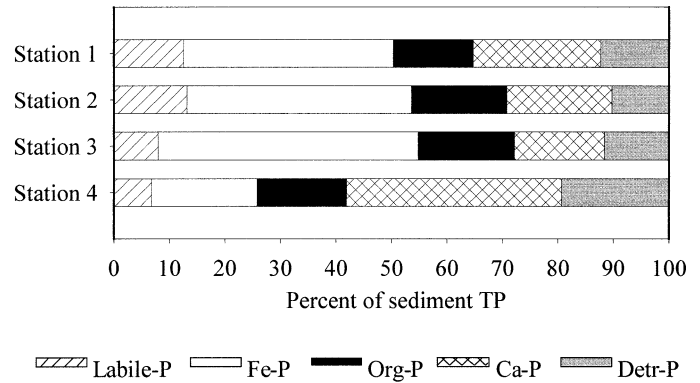


Fig. 10. Mean percentage composition of major P phases in the top 6 cm of sediment in Sta. 1–4, averaged over all sampling dates.

centage of clay in river sediments explained 51–89% of the variability in these phases.

Discussion

Effect of seasonal sediment storage and resuspension on reactive P pools—Total reactive P is derived from terrestrial organic sources and from the chemical weathering of phosphate minerals. Approximately 91% of the $22 \times 10^9 \text{ kg P yr}^{-1}$ delivered by rivers to the oceans is particle bound (Meybeck 1982, 1993; Berner and Berner 1996). Thus, the hydrological and biogeochemical processes acting on riverine suspended and bed sediments may exert a major control on the amount of reactive P transported to coastal oceans. We found that seasonal hydrological forcing controlled the major P phases found in suspended particulate and bed sediments through hydrodynamic sorting (and the relationship of P phase to grain size). The time period of months in which sediments were stored in the river channel was sufficient enough to see evidence of early diagenesis in the pore waters; however, no significant net effect was seen on the relative seasonal distribution of labile-P, Fe-P, or org-P pools in the sediments within the freshwater portion of the river. A significant loss of labile-P and Fe-P fractions only appears to be occurring as these sediments are deposited and reworked within the estuarine portion of the river and on the continental shelf.

The seasonal hydrological control of sediment storage and remobilization and channel bottom geomorphology in the Mississippi River has been well characterized with a Lagrangian transport model that reasonably reproduces the rate and timing of storage and remobilization (Demas and Curwick 1988; Mossa 1996). At low discharge, there are large differences in cross-sectional area between upriver and downriver locations, and the downstream deepening of the channel results in decreased velocities, which promotes sediment deposition (Mossa 1996). Demas and Curwick (1988) observed that the suspended sediment concentration decreased by 80% downriver of Tarbert Landing during flows of $7,300\text{--}7,600 \text{ m}^3 \text{ s}^{-1}$, with $54 \times 10^6\text{--}81 \times 10^6 \text{ kg d}^{-1}$ of sediment deposited as bed sediments during this period. The upstream-downstream difference in cross-sectional area results in a distinct fining of grain size downstream. Nordin

and Queen (1972) found that bed sediments in the lower Mississippi River ranged from 1% silt-clay and 96% sand at Tarbert Landing to 70% silt-clay and 30% sand at Belle Chase (Sta. 1) and 80% silt-clay and 20% sand at Venice (Sta. 2). During higher discharges ($>14,000 \text{ m}^3 \text{ s}^{-1}$), the differences in upriver-downriver cross-sectional area are much smaller. Increased current velocities are accompanied by steeper downstream surface-water gradients, resulting in bottom shear stresses that surpass threshold values for resuspension (Mossa 1996). For example, Demas and Curwick (1988) observed that, for flows of $25,000\text{--}28,000 \text{ m}^3 \text{ s}^{-1}$, sediment resuspension rates of $127 \times 10^6\text{--}163 \times 10^6 \text{ kg d}^{-1}$ resulted in a 30% increase in suspended sediment concentrations downriver of Tarbert Landing.

Seasonal hydrodynamic sorting of sediments during deposition and resuspension events in the Mississippi River exerted a major control on sediment grain size distributions. This, in turn, influenced the concentrations of bulk and reactive P found in suspended and bed sediments. During the high discharge periods of April 1999 and May 2000 (when sediments are actively resuspended), channel sediments were coarse (60–80% sand), had low %OC (0.3–1.5%), and had high C:N ratios (12–20:1). The suspended sediment load was high ($100\text{--}110 \text{ mg L}^{-1}$), with %OC and C:N ratios reflective of channel sediments. During the low discharge periods of November 1999 and February 2000, channel sediments were finer grained (50–80% clay), with high %OC (1.0–1.5%) and lower C:N ratios (7–12:1). Sediments in Sta. 2 also had a greater percentage of fine sediment than Sta. 1 sediments. This finding is consistent with that of Nordin and Queen (1972), who reported that the downstream fining of sediments is associated with a downstream increase in channel cross-sectional area. These fine-grained sediments and suspended load that results from their suspension in the downstream reach during low discharge periods had up to four times higher content of bulk and labile-P, Fe-P, and org-P, which can be explained by the greater adsorption of P to clay particles. These particles have a surficial armoring of reactive iron and aluminum hydroxyoxides and, thus, a higher capacity for adsorbing phosphorus (Carritt and Goodgal 1954; McLaughlin et al. 1981; Froelich 1988). In addition, sediments with finer grain sizes tend to have a higher organic matter content.

Subsequent to deposition, riverbed sediments undergo a number of diagenetically controlled transformations as the decomposition of organic matter proceeds through a well-established sequence of terminal electron acceptors: O_2 , NO_3^- , MnO_2 , FeOOH , SO_4^{2-} , and CO_2 (Froelich et al. 1979). From April 1999 to February 2000, pore-water SRP, NH_4^+ , and DOC concentrations in Sta. 1–3 increased up to a factor of 4, which indicates that the 8–9-month sediment storage period was sufficient to allow for processes of early diagenesis to take place. The large variation in pore-water salinities at Sta. 2 indicates that transport processes (i.e., advection and diffusion) occurred subsequent to deposition (Fig. 6). The concentrations of these solutes in freshwater and marine surface waters are much lower than the pore-water concentrations, regardless of season. Thus, the in situ production of diagenetic products is the major process responsible for the magnitude of the pore-water concentrations measured.

Although the rate of buildup of diagenetic products in pore waters is biogeochemically controlled, the extent of transformation is determined by the duration of storage and the quantity and quality (i.e., grain size and organic matter content) of material deposited (Bernier 1980; Klump and Martens 1983). Sediment grain size and C:N ratio predicted 41–69% of the variability in pore-water NH_4^+ and DOC concentration at Sta. 1–3. This makes it difficult to separate the effect of diagenesis during sediment storage versus sediment quality (i.e., grain size) on pore-water concentrations—both are likely important.

The degree of P release from sediments to the water column in Mississippi River sediments is likely dependent, in part, on whether sulfate reduction is occurring in the underlying sediments. Carbon-normalized sediment P remobilization rates are, on average, fivefold higher in high-sulfate marine systems than in relatively low-sulfate freshwater systems (Caraco et al. 1990). Roden and Edmonds (1997) found that direct microbial Fe(III) reduction solubilized only 3–25% of initial solid-phase P during sulfate-free sediment incubation experiments and that much of the PO_4^{3-} released was captured by solid-phase reduced iron compounds like Fe(II)-hydroxide- PO_4 complexes and/or Fe(II)- PO_4 minerals. Extensive P remobilization to pore waters will take place if sediment Fe(III) is first reduced and then the Fe(II) is converted to Fe-sulfides via reaction with sulfide produced by sulfate reduction (Roden and Edmonds 1997). We found low pore-water SRP concentrations ($0.5\text{--}20 \mu\text{mol L}^{-1}$) in freshwater riverine sediments, where high concentrations of reduced Fe and Mn species showed metal oxide reduction to be active (B.A.M., unpubl. data). We speculate that the binding of Fe with sulfides during sulfate reduction may be a major reason why high pore-water SRP concentrations ($60\text{--}85 \mu\text{mol L}^{-1}$) were present at Sta. 3 (marine) and during low flow periods at Sta. 2, where pore-water salinities reflect an estuarine regime inside the river.

In the freshwater portion of the lower Mississippi River, the net effect of seasonal storage and resuspension on the distribution of the major P pools is probably limited. Although the 8–9-month storage period was sufficient to see a release of P from the solid phase to pore-waters, we did not observe major changes in the relative distribution of solid-phase P pools in the seasonally stored sediments of Sta. 1. Within the freshwater portion of the river, labile-P released from pore waters is likely to be incorporated into the mineral matrix of suspended particulate Fe(III) oxides in surface waters. Low light conditions in the turbid lower Mississippi River limit the primary producer uptake of P (Fox et al. 1985). The transfer of P released from the Fe and labile phases to the organic P phase could occur through uptake by heterotrophic bacteria, but this pathway does not appear to have a significant effect on the org-P content in sediments in this physically dominated system.

Importance of sediment storage and resuspension for P budget of the Gulf of Mexico shelf—The net effect of seasonal sediment storage, diagenesis, and remobilization is likely to be much more important in the Mississippi River estuary, where light limitations on primary productivity decrease as suspended sediment concentrations drop. Through-

out estuarine portions of the river and the inner shelf, P released from anoxic sediments is likely to play a major role in the water column primary productivity for a number of reasons. First, as evidenced by three- to fourfold higher pore-water SRP concentrations at Sta. 2 and 3 versus Sta. 1, sediment P release from high-sulfate estuarine and marine systems is, on average, fivefold higher than in relatively low-sulfate freshwater systems (Caraco et al. 1990). Second, the shelf depositional environments of large river systems are highly energetic and are repeatedly subject to processes of physical mixing and sediment reworking that affect diagenetic reactions occurring in surface sediments and the composition of the buried material (McKee et al., in press). Repeated oxidation, reoxidation, and metabolite exchange promote efficient remineralization in these environments, leading Aller (1998) to refer to them as “sub-oxic fluidized bed reactors.” Sta. 3, which is located in this highly energetic mixing zone, had lower bulk P (25 vs. 32 $\mu\text{g g}^{-1}$), labile-P (average, 2.1 vs. 4.4 $\mu\text{g g}^{-1}$), and org-P (4.2 vs. 4.8 $\mu\text{g g}^{-1}$) contents than sediments of Sta. 2. This indicates that sediment P is more efficiently remobilized at this shelf site. The range of DOC concentrations in both river and shelf stations was also considerably higher than that found in other estuarine systems (Burdige and Homstead 1994; Argyrou et al. 1997), which further supports the efficiency of organic matter decay in these sediments (Fig. 8). Third, the Mississippi River estuary has been shown to have a “phosphorus buffering” behavior of water column particulate P (Fox et al. 1985). Phosphorus buffering is the process by which P is desorbed from sediments to balance low seawater SRP concentration, as a result of anionic competition on surface adsorption sites or SRP biological uptake (Carritt and Goodgal 1954; Fox et al. 1985; Froelich 1988). Our results show a decrease in the P content of TSS, a decrease in the labile-P and Fe-P, and an increase in the org-P and Ca-P components of particulate P (Fig. 5) with increasing salinity—a result that is consistent with the premise of phosphorus buffering.

Enhanced P remobilization from sediments in the estuarine, high-energy, depositional environment of the Gulf of Mexico continental shelf, coupled with phosphate buffering, increases supply of labile-P to water column that supports higher primary and secondary production. Increased eutrophication and deposition of phytoplankton-derived organic carbon resulting from increases in nutrient inputs from the Mississippi and Atchafalaya Rivers is suspected as the primary reason for the occurrence of large-scale hypoxic events in the Gulf of Mexico shelf (Rabalais et al. 1996). Over the broad shelf area influenced by the Mississippi River discharge, N is the most limiting nutrient to primary production, but P may become limiting seasonally or along spatial gradients (Lohrenz et al. 1999).

Riverine flux of reactive P to the Gulf of Mexico: relevance to the global P budget—Estimating the sources and sinks of total reactive P in the global marine P budget has been the subject of intense study during the past three decades, because of the importance of P in controlling marine primary productivity and, ultimately, the oceanic carbon cycle (Froelich et al. 1982; Meybeck 1982; Froelich 1988; Rut-

tenberg 1991; Ruttenger and Berner 1993; Berner and Rao 1994; Filippelli 1997; Delaney 1998). Riverine flux constitutes most of the source term in the global reactive P budget. Therefore, the magnitude of this term can be better constrained with improved data on the percentage of particulate P as reactive P in a large river system such as the Mississippi River (Berner and Rao 1994).

Quantification of the amount of P solubilized from riverine particulates and sediments that contributes to the global marine P budget is difficult. Uncertainty exists in the amount of reactive P that is liberated to surface waters versus that permanently buried in oceanic sediments (Berner and Rao 1994; Meybeck 1982). The method of summing the reactive P components of particulate or sediment TP (labile-P, Fe-P, org-P, and Ca-P), with the assumption that, over geological timescales, all reactive P will be solubilized, provides the most liberal estimate of the contribution of riverine particulate reactive P. On the basis of this method, 92% by weight of Mississippi riverine bottom sediment TP and 98% of suspended particulate TP potentially contributes to the reactive P pool (Table 4). Using this method, the Mississippi River exports an average of $134 \times 10^6 \text{ kg yr}^{-1}$ of total reactive P to the Gulf of Mexico (Tables 4, 5). A more conservative estimate, demonstrated by Berner and Rao (1994), calculates the difference in TP content between freshwater riverine particulates and marine shelf sediments as means of constraining the quantity of reactive P solubilized from riverine particulates (Table 4). On the basis of this method, 58% by weight of riverine particulate TP and 31% of riverine sediment TP contributes to the total reactive particulate P flux of the Mississippi River. This translates to an average riverine export of total reactive P of $87 \times 10^6 \text{ kg yr}^{-1}$.

These numbers underestimate total reactive P flux, because they are based on surface water TP flux alone (Mayer et al. 1998). The remobilization of channel sediments and deposition to the Gulf of Mexico shelf during pulsing events is likely to play an important role of P budget of Gulf of Mexico shelf and are generally not included in estimates of riverine flux. Overall, there was a 31% reduction in TP content between riverine sediments and Sta. 4 (the marine shelf station least influenced by riverine depositional processes). The majority of this reduction in bulk P was lost from the labile-P and Fe-P phases (Table 4). The release of P from riverine particulates and sediments can affect coastal productivity by changing the timing of nutrient flux (Mayer et al. 1998). Although riverine dissolved nutrient flux could be expected to have its maximum effect during maximum discharge (generally in the spring), the release of P and N from particulates may be delayed until periods of higher organic matter decomposition, governed by temperature (Mayer et al. 1998; Rudnick and Oviatt 1986).

Using the method of Berner and Rao (1994), we can also calculate the present-day global riverine reactive P flux using data from the present study. Under the assumption that 91% of the $22 \times 10^9 \text{ kg TP}$ exported by rivers to the global ocean is particulate (Berner and Berner 1996; Meybeck 1982) and that the percentage of particulate TP as reactive P (48%) found in the present study is applicable to all rivers, an estimate of the total riverine reactive P flux to the oceans is presently $11.6 \times 10^9 \text{ kg P}$, or $37 \times 10^{10} \text{ mol P yr}^{-1}$. Although

Table 4. TP and distribution of major P pools in particulate matter and sediments of the Mississippi and Amazon rivers and their adjacent coastal margins. All values are in $\mu\text{g g}^{-1}$ unless otherwise noted. Numbers in parentheses represent 95% confidence intervals.

Source and type	Major P phase					
	Labile-P	Fe-P	Org-P	Ca-P	Detr-P	TP
This study						
Mississippi River particulates ($n=34$)	337 (20)	469 (68)	62 (5)	190 (31)	25 (3)	1,085 (78)
Mississippi R. sediments Sta. 1-2 ($n=91$)	108 (12)	339 (40)	136 (15)	160 (7)	87 (3)	829 (57)
Gulf of Mexico shelf sediments Sta. 4 ($n=10$)	37 (2)	107 (9)	90 (6)	225 (12)	109 (10)	569 (11)
Total particulate reactive P (LP+Fe-P+Org-P+Ca-P)	1,023 (98%) of riverine particulate TP					
Total particulate reactive P ($\text{TP}_{\text{RIVER TSM OR SED}} - (\text{TP}_{\text{SHELF SED}})$)	516 (48%) of riverine particulate TP; 260 (31%) of riverine sediment TP					
Ruttenberg and Berner 1993						
Gulf of Mexico shelf sediments	38	166	154	143	76	557
Berner and Rao 1994						
Amazon R. particulates		217	217	118	99	651
Amazon shelf sediments		233	133	112	31	508
Difference ($\text{P}_{\text{RIVER TSM}} - \text{P}_{\text{SHELF SED}}$)	142 (22%) of riverine particulate TP					

Table 5. Annual surface water flux of total reactive P (in kg) from the Mississippi river to the Gulf of Mexico. The value of reactive particulate P flux in the present study was 48% (based on difference between riverine particulates and Gulf of Mexico sediment TP) or 98% (Labile-P+Fe-P+Org-P+Ca-P of particulate P is potentially reactive and therefore could be released into the water column).

Source and fraction	Annual flux (kg)
Goolsby et al. 1999 (Mean of 1980–1996)	
Dissolved P	41.77×10^6
Particulate P	94.73×10^6
Total P	136.50×10^6
This study	
Reactive particulate P (48%)	45.74×10^6
Total reactive P (48%)	87.24×10^6
Reactive particulate P (98%)	92.84×10^6
Total reactive P (98%)	134.61×10^6

the TP content of Mississippi River particulate matter ($1.1 \pm 0.1 \text{ mg g}^{-1}$) is appreciably higher than that of the Amazon River (0.6 mg g^{-1}), it is within the $1.1\text{--}1.5 \text{ mg g}^{-1}$ global average for rivers (Meybeck 1982; Meybeck and Helmer 1989), making it appropriate for calculation of a present-day flux estimate. However, this number is appreciably higher than current estimates of P burial flux to the oceans ($8\text{--}18 \times 10^{10} \text{ mol P yr}^{-1}$; Ruttenberg 1993), because $37 \times 10^{10} \text{ mol P yr}^{-1}$ represents a present-day reactive P flux that has been enhanced by human activities (Berner and Berner 1987; Berner and Rao 1994).

The combined processes of hydrologically controlled sediment storage and remobilization and the diagenetic transformation of stored sediments control the relative distribution of the major pools of P found in riverine and inner continental shelf suspended and bed sediments. Seasonal hydrodynamic sorting of channel sediments affects the sediment organic matter content, as well as the concentrations of bulk and reactive P found in suspended and bed sediments. An 8–9-month storage of sediments in the river channels was sufficient to see substantial release of P from the solid phase to pore waters, particularly in estuarine sediments, where sulfate reduction results in sequestration of Fe in sulfide minerals and consequent P release from the Fe-P pool. Resuspension of lower Mississippi River bed sediments is sufficiently deep during remobilization that diagenetic products are efficiently transferred to the water column. However, the duration of seasonal sediment storage is generally not long enough to observe major changes in the relative distribution of solid phase P pools in freshwater and estuarine sediments. Enhanced P remobilization from sediments in the estuarine, high-energy, depositional environment of the Gulf of Mexico continental shelf, coupled with phosphate buffering, increases the supply of labile-P to the water column and can support higher primary and secondary production. Eutrophication and deposition of phytoplankton-derived organic carbon, resulting from increases in nutrient inputs from the Mississippi and Atchafalaya rivers, is linked to the occurrence of large-scale hypoxic events in the Gulf of Mexico shelf.

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