



Sediment Equilibrium and Diffusive Fluxes in Relation to Phosphorus Dynamics in the Turbid Minnesota River

by William F. James

PURPOSE: Much is known regarding the importance of surface and subsurface runoff from agricultural watersheds in the regulation of soluble phosphorus (P) concentration in large river systems. However, in-stream processes such as equilibrium P flux from suspended sediment and diffusive P flux from deposited sediment stored in river channels may also play a role in soluble P control. Ranges in equilibrium partitioning between aqueous and exchangeable particulate P pools associated with suspended and deposited sediment are needed in order to estimate mass transfer coefficients (k_d ; $L \cdot kg^{-1}$ and k_e ; $m \cdot d^{-1}$) for watershed and receiving water Nutrient Sub-Module (NSM) development within the System-Wide Water Resources Program (SWWRP) of the U.S. Army Engineer Research and Development Center (ERDC). The objectives of this research are 1) to examine sediment equilibrium and diffusive P fluxes and mass transfer coefficients for suspended and deposited sediment loads, and 2) to place these fluxes within the context of phosphorus dynamics and regulation of soluble P in the Minnesota River.

BACKGROUND: Excessive phosphorus (P) loading is a leading cause of eutrophication and water quality impairment of large floodplain rivers (i.e., $> 10,000 \text{ km}^2$; Caraco et al. 2003), impoundments, and coastal marine environments (Guildford and Hecky 2000; Chételat et al. 2006; Schindler 2006; Smith 2006; Sylvan et al. 2006). A large body of literature exists regarding the important role that watershed point and nonpoint P sources play in the eutrophication of receiving water bodies (Carpenter et al. 1998). Point source contributions from municipal wastewater treatment plants are largely in a soluble form that is directly available for biotic uptake and can comprise a significant portion of the watershed total P load under low discharge conditions (Mainstone and Parr 2002). As watershed size and anthropogenic land management increases, nonpoint sources of P comprise a greater percentage of the load at higher discharge and, thus, have a regulating influence on P concentration (Peierls et al. 1991; Cole et al. 1993; Howarth et al. 2002). For agricultural watersheds, soil fertilization in excess of crop P uptake requirements has resulted in a buildup in soil P concentration over time (Sharpley et al. 1984; Zhang et al. 1995, 2004; Bennett et al. 2001). Numerous studies have shown positive linear relationships between soil P and P in runoff, indicating a link between soil management practices, source soil P concentrations in the landscape, and tributary P load and concentration (Sharpley 1995; Pote et al. 1996, 1999; Fang et al. 2002; Torbert et al. 2002; Davis et al. 2005). However, less is known about P dynamics and transformations as loads are conveyed in the main channel of large rivers to receiving waters (House 2003). This information is needed in order to better predict mass balance P flux through large tributary networks (Alexander et al. 2000).

Much of the current understanding of in-stream P dynamics comes from nutrient spiraling research on small tributaries under base discharge conditions (Meyer 1979; Newbold et al. 1981). While the same processes apply to larger river systems, there are differences in scale and magnitude due to increasing channel width and depth, increased flow velocity, and variation in residence time (Soballe and Kimmel 1987). Under lower discharge conditions and higher residence time, biological uptake by phytoplankton can play an important role in P retention and transformation (Van Nieuwenhuysse and Jones 1996; Gosselain et al. 1998; Reynolds and Glaister 1993; Reynolds 2006). Deposited sediment within main, side, and backwater channels in rivers can also regulate P concentration and productivity via diffusive flux and equilibrium reactions (House and Denison 1998, 2000). P dynamics and concentration are influenced more by abiotic processes such as P equilibrium between suspended sediment and soluble P under higher discharge conditions (Froelich 1988). Transport also dominates at higher discharge (Alexander et al. 2000) versus biological uptake and transformation due to greater turbidity, lower residence time, and phytoplankton washout (Soballe and Kimmel 1987). Thus, seasonal variation in discharge is an important driver influencing biogeochemical processes and P dynamics during transport in large river systems.

Knowledge and prediction of eutrophication response can be improved by considering the susceptibility of P loads transported by large rivers to recycling pathways after deposition. Soluble P is directly available for biotic uptake. However, most of the total P load transported by large rivers is in particulate form (Howarth et al. 1995). While only a small portion of this particulate load is directly available for biological uptake (Sharpley et al. 1991; Ekholm 1994; Uusitalo and Turtola 2003; Uusitalo et al. 2003), a significant percentage is recyclable as deposited sediment and can be transformed to soluble P via eH-pH reactions, equilibrium processes, and bacterial transformation (Gächter et al. 1988; Nürnberg 1988; Berner and Rao 1994; Howarth et al. 1995; Jensen et al. 2006). Internal P recycling from deposited sediment can buffer water column P concentration and enhance productivity during periods of lower loading and higher residence time. Information on the size of the exchangeable particulate P pool and recycling potential for suspended sediment loads of large river systems is therefore needed in order to better target P source and transport processes for management.

Nutrient loads from tributaries of the Upper Mississippi River (i.e., above Cairo, IL USA) contribute substantially to eutrophication and hypoxia of the northern Gulf of Mexico (Goolsby and Battaglin 2001). While much is known about nitrogen (N) retention and transport in this system (Alexander et al. 2000), less information is available regarding P. The Minnesota River (550 km length) drains the agricultural heartland of Minnesota (44,000-km² watershed) and discharges turbid loads into the Upper Mississippi River at Navigation Pool 2 that are high in both total and soluble P concentration. Nonpoint sources of P are derived from bank erosion and landscapes that are intensely managed for row crop production (>75 percent of the watershed; Meyer and Schellhaass 2002). P dynamics are also influenced by point source inputs from wastewater treatment plants servicing the metropolitan areas of Minneapolis-St. Paul (population 2.9 million), Mankato (population 35,000), and other cities in Minnesota. Inputs from the Minnesota River dominate overall suspended sediment, N, and P loads to downstream navigation pools of the Mississippi River and play an important role in eutrophication (James and Barko 2004). In particular, diffusive P flux from deposited sediments originating from the Minnesota

River basin is high and contributes to phytoplankton blooms and hypoxia during low discharge periods in these pools.

Concerns over high algal biomass and dissolved oxygen depletion during low discharge periods, deposition of nutrient-rich sediment, and excessive loads of nitrogen (as nitrate and ammonium) and phosphorus to the system have led to an assessment of water quality and the development of a eutrophication model for use in establishing goals for load reduction of point and nonpoint sources and evaluation of management scenarios to improve current water quality conditions in the system. The Metropolitan Council of St. Paul, Minnesota, was the lead sponsor of this research. Information on the project and research design can be found at:

<http://www.metrocouncil.org/environment/Water/LMRM/index.htm>

<http://www.metrocouncil.org/environment/Water/LMRM/lrmReports/Minnesota-River-Model-Project-Description.pdf>.

Other sponsors of the project were the lower Minnesota River Watershed District; the Metropolitan Airports commission; the Minnesota Pollution Control Agency; the U.S. Army Engineer District, St. Paul; the U.S. Geological Survey; and the Engineer Research and Development Center (ERDC). The objectives of this portion of the research were to quantify major point and nonpoint source P loads entering this reach and examine P dynamics as affected by biotic (phytoplankton uptake) and abiotic (equilibrium and diffusive fluxes) processes in relation to hydrology of the system. Extraction techniques were used to further partition particulate P (PP) loads into functional groupings that were either biologically labile (i.e., direct biotic uptake or subject to recycling pathways) or refractory (i.e., low recycling potential and subject to burial) in order to better understand the impact that PP has on downstream eutrophication after deposition. Finally, mass transfer coefficients were estimated for use in Nutrient Sub-Model (NSM) development within the System-Wide Water Resources Program (SWWRP) of the ERDC.

STUDY SITE: The Minnesota River basin drains a flat topography with calcareous soil parent material created by glacial retreat during the last ice age (Waters 1977). The upstream-downstream boundary of the study site was located between river miles (RM) 39.4 and 3.5, where the Metropolitan Council has maintained long-term sampling stations for more than 40 years (Figure 1). River bathymetry changes below RM 14.7 due to maintenance of a 3-m-deep by 30-m-wide channel for commercial barge navigation. Nonpoint sources of P within the study site include 12 small monitored creeks. There are numerous point source discharges from industrial facilities and small wastewater treatment plants (WWTP) that collectively represent a very minor portion of the P budget. Two larger WWTPs, representing the third and fourth largest plants in the State of Minnesota, discharge (average discharge = $1.8 \text{ m}^3 \text{ s}^{-1}$) at effluent P concentrations of 1.5 mg L^{-1} or less. A 538-megawatt power generating plant (Blackdog GP) pumps water from the Minnesota River at RM 8.8 for cooling condensers. The heated water is then routed into a cooling pond before being discharged back into the river at RM 10.7 and RM 7.5. This circulation pattern is significant during lower discharge periods, representing > 30 percent of the discharge when Minnesota River discharge is $< 50 \text{ m}^3 \text{ s}^{-1}$ (i.e., primarily during late autumn and winter). Meyer and Schellhaas (2002) reported high mean annual

flow-weighted concentrations of 93 mg L^{-1} suspended sediment, 0.3 mg L^{-1} total phosphorus, and $56 \text{ } \mu\text{g L}^{-1}$ total chlorophyll for the lower Minnesota River (i.e., downstream of RM 40) over a 20-year period.

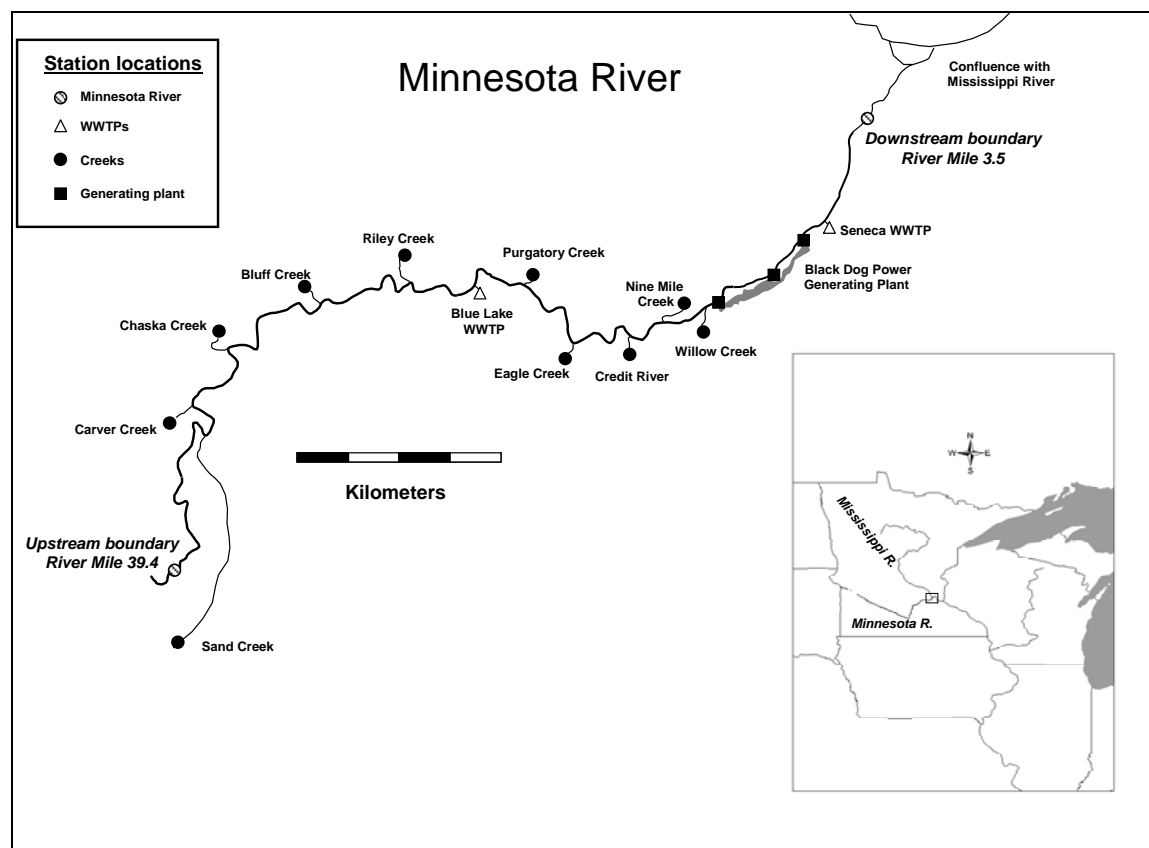


Figure 1. Monitoring stations on the lower portion of the Minnesota River, Blue Lake and Seneca wastewater treatment plants (WWTP), the various creeks, and the Black Dog power generating plant.

METHODS:

Biologically Labile and Refractory Particulate Phosphorus Pools of Suspended Sediment.

Sampling stations were established on the lower Minnesota River at RM 39.4 (near Jordan, MN) and RM 3.5 (upstream of the confluence with the Mississippi River) to determine concentrations of biologically labile and refractory particulate P (PP) fractions (Figure 1). At each station, 20L of river water were collected via surface grab sampling during periods of high discharge (i.e., $> 200 \text{ m}^3 \text{ s}^{-1}$) and suspended sediment concentration in 2005 and 2006 (five events during each year between May and September). In the laboratory, a portion of the sample was filtered onto $0.45\text{-}\mu\text{m}$ membrane filters and dried at $105 \text{ }^\circ\text{C}$ to a constant weight to determine total suspended solids (TSS; American Public Health Association (APHA) 1998). Another portion was filtered through a $0.45\text{-}\mu\text{m}$ filter for soluble reactive P (SRP) determination. Suspended sediment in the remainder of the sample was concentrated by settling and centrifugation at 500 g and preserved with 0.5 mL of 0.1-percent chloroform and refrigeration at $4 \text{ }^\circ\text{C}$. Analyses were conducted within two weeks of sample collection. Sequential fractionation

of PP (Table 1) was conducted according to Hjieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) to determine ammonium-chloride-extractable PP (i.e., loosely bound PP), bicarbonate dithionite-extractable PP (i.e., iron-bound PP), sodium hydroxide-extractable PP (i.e., aluminum-bound PP), and hydrochloric acid-extractable PP (i.e., calcium-bound PP). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable PP (Psenner and Puckso 1988). Labile organic PP was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable PP. PP remaining after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid to determine refractory organic PP. Each extraction was adjusted to pH 7 and analyzed for SRP using the ascorbic acid method (APHA 1998).

Table 1		
Operationally defined particulate phosphorus (PP) fractions. Biologically labile = Subject to recycling pathways. Biologically refractory = Low recycling potential and subject to burial		
Variable	Extractant	Recycling Potential
Loosely bound PP	1 M ammonium chloride	Biologically labile; recycled via eH and pH reactions and equilibrium processes
Iron-bound PP	0.11 M sodium bicarbonate-dithionate	Biologically labile; recycled via eH and pH reactions and equilibrium processes
Labile organic PP	Persulfate digestion of the NaOH extraction	Biologically labile; recycled via bacterial mineralization of organic P and mobilization of polyphosphates stored in cells
Aluminum-bound PP	0.1 N sodium hydroxide	Biologically refractory
Calcium-bound PP	0.5 N hydrochloric acid	Biologically refractory
Refractory organic PP	Persulfate digestion of remaining particulate P	Biologically refractory

Phosphorus Equilibrium Characteristics of Suspended Sediment. Phosphorus equilibrium characteristics between particulate and aqueous phases were examined for periods of high discharge and TSS loading in 2005. Aliquots (~500 mg L⁻¹ dry weight equivalent) of the concentrated suspended sediment were subjected to SRP (KH₂PO₄) standards ranging from 0 to 1.0 mg L⁻¹ for examination of P adsorption and desorption over a 24-hr period. Time series analysis confirmed that equilibrium was achieved within 24 hr (*see below*). Untreated local tap water (groundwater) was used as the water medium because it was low in phosphate concentration and similar in ionic strength to Minnesota River water. KCl, NaCl, and MgSO₄ were added to the tap water to adjust its ionic composition to more closely approximate water from the Minnesota River (Fang and Brezonik 2002). Tubes containing TSS, amended tap water, and known concentrations of SRP were shaken uniformly in a darkened environment, then filtered and analyzed for SRP. The suspended sediment slurries were maintained under oxic conditions at a pH of ~ 8.0 to 8.3 and a temperature of ~ 20 °C during the shaking and equilibration process.

The change in SRP mass (i.e., initial SRP - final SRP; mg) was divided by the dry mass equivalent of TSS to determine the mass of P desorbed or adsorbed (S; mg P kg⁻¹ sediment).

These data were plotted as a function of the equilibrium SRP to determine the partition coefficient (k_d ; $L\ kg^{-1}$) and the equilibrium P concentration (EPC; $mg\ P\ L^{-1}$; the point where net sorption is zero; Froelich 1988). The k_d and EPC were calculated via regression analysis (Statistical Analysis System (SAS) 1994) from linear relationships between final SRP concentration and the quantity of P adsorbed or desorbed at low equilibrium concentrations. Data were also fitted to a two-surface-layer Langmuir regression model using a spreadsheet developed by Bolster and Hornberger (2007) to estimate the sorption maximum (S_{max}) of TSS. The general linearized model is

$$\frac{C}{S} = \left[\frac{1}{S_{max_1} K_1} + \frac{C}{S_{max_1}} \right] + \left[\frac{1}{S_{max_2} K_2} + \frac{C}{S_{max_2}} \right] \quad (1)$$

where C equals the equilibrium SRP concentration and K represents the binding strength coefficient ($L\ kg^{-1}$). Because P desorption occurred at low equilibrium SRP, the concentration of the exchangeable P pool ($mg\ kg^{-1}$) had to be taken into account in the calculation of S_{max} . The NH_4Cl -extractable loosely bound and the bicarbonate-dithionite- extractable iron-bound P fractions were chosen as an estimate of this pool. Various extraction and extrapolation techniques have been used to quantify exchangeable P; however, there is uncertainty regarding its estimation and caution needs to be used in interpretation of S_{max} (Aminot and Andrieux 1996; Bolster and Hornberger 2007). The degree of P saturation (DSP) was calculated as the sum of extractable loosely bound and iron-bound P divided by S_{max} .

For kinetic studies, sediment ($\sim 500\ mg\ L^{-1}$ dry weight equivalent) was subjected to water that contained either zero P or $0.750\ mg\ P\ L^{-1}$. Assay systems were uniformly shaken over a period of five days and subsamples for SRP analysis were collected at various time intervals. SRP concentration was plotted as a function of time to examine uptake or release of P due to adsorption or desorption.

Deposited Sediment Characteristics and Diffusive Fluxes. Sampling stations were established between RM 0 and RM 26 for collection of sediment cores in late September 2005 and early October 2006. Difficulties in navigation prevented sediment core sampling above RM 26. Station selection was based on a survey conducted by the U.S. Geological Survey (USGS) that identified sediment textural (sand-gravel, sand-silt, silt-clay) features between RM 0 and RM 26 using hydroacoustic and ground-truthing techniques. This stretch of the river was divided into upper (i.e., RM 12 to 26) and lower (i.e., RM 0 to 12) sections for sediment sampling purposes. Sampling within each section was further stratified to capture sand-silt sediment in 60 percent of the cores, silt sediment in 30 percent of the cores, and sand sediment in 10 percent of the cores based on general compositional features measured a priori by the USGS. Thus, sediment sampling stations were established randomly within these stratification schemes. Sediment textural distribution maps constructed by the MCES were used to approximately locate an area likely to contain sand-silt, silt, or sand sediment at the randomly assigned river mile.

During each year, two sediment cores (i.e., one for oxic and one for anoxic nutrient release) were collected at each of 12 stations (6 stations in the upper section and 6 stations in the lower section) to determine rates of P release from sediments. One additional core was collected at these same

stations and at an additional 12 randomly selected stations to determine sediment compositional characteristics. All sediment cores were collected intact using a Wildco sediment coring device, and preserved on ice for transport. In the laboratory, the cores used to determine rates of P release were drained of overlying water and the upper 10 cm of sediment were extruded to a smaller acrylic core liner (6.5-cm dia and 20-cm ht) using a core remover tool. Water collected from the Minnesota River was filtered through a glass fiber filter (Gelman A-E) with 300 mL, then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. Sediment incubation systems consisted of the upper 10 cm of sediment and filtered overlying water contained in acrylic core liners that were sealed with rubber stoppers. The sediment incubation systems were placed in a darkened environmental chamber and incubated at a constant temperature (20 °C) for a two-week period. The oxidation-reduction environment in each system was controlled by purging with either air (oxic) or nitrogen (anoxic) through an air stone placed just above the sediment surface. Bubbling action ensured complete mixing of the water column, but did not disrupt the sediment.

Water samples were collected from the center of each sediment incubation system using an acid-washed syringe and immediately filtered through a 0.45- μm membrane syringe filter prior to analysis. Soluble reactive P was determined using the ascorbic acid method (APHA 1998). The water volume removed from each system during sampling was replaced by addition of filtered river water preadjusted to the proper oxidation-reduction condition. Sampling was conducted at daily intervals for eight days, then every other day for an additional eight-day period. Rates of P release from the sediment ($\text{mg m}^{-2} \text{d}^{-1}$) were calculated as the linear change in concentration in the overlying water divided by time and the area of the incubation core liner.

To determine sediment compositional characteristics, the upper 10 cm of sediment were extruded and homogenized for analysis. Organic matter content was estimated as loss-on-ignition (LOI) by combusting sediment at 500 °C for 24 hr. The percentage of sand ($> 63 \mu$), silt (between 2 μ and 63 μ) and clay ($< 2 \mu$) was determined using a combination of sieving and pipette techniques (Plumb 1981). Total sediment P was analyzed colorimetrically following block digestion with sulfuric acid, potassium sulfate, and red mercuric oxide (Plumb 1981). Sequential fractionation of P was conducted as described above.

Water Chemistry and Loading Analysis. Discharges were monitored continuously between 2003 and 2006 at stations established on 12 small creeks discharging into the lower Minnesota River, the Minnesota River at RM 39.4 and RM 3.5, the two WWTPs, and the inflow and two discharges associated with the Blackdog GP (Figure 1). Inflows and discharges associated with the power generating plant were only monitored during 2005 and 2006. Water samples were collected weekly to biweekly over the three-year period at the creek stations, weekly or less at the Minnesota River stations, and daily at the WWTPs. Additional event-composited samples were collected at the creek stations and at RM 39.4. Water samples were collected at the Blackdog GP inflow and outlet structures only during lower discharge periods in 2005 and 2006. River samples were collected at mid-channel 1 m below the surface and analyzed for TSS, LOI, total Kjeldahl N, nitrate+nitrite-N, ammonium-N, total P, total soluble P, SRP, viable chlorophyll, and pheaophytin following standard analytical procedures by MCES staff. Sample was passed through a 0.45- μm membrane filter to determine soluble N and P species. Total N and P species were digested with persulfate prior to analysis. N and P were determined

using standard automated colorimetric procedures (Lachat QuikChem A/E, Hach Co., Loveland, CO, USA). Particulate P (PP) was calculated as total P minus total soluble P. A known volume of sample was filtered through a combusted (500 °C) glass fiber filter (Gelman A/E; 2-µm nominal pore size), dried to a constant weight at 105 °C, and combusted at 500 °C determination of TSS and LOI, respectively. Additional sample filtered onto a glass fiber filter was extracted with 90 percent acetone to determine viable chlorophyll and phaeophytin. Concentrations of LOI, chlorophyll, and PP were divided by TSS concentration to calculate percentages with respect to TSS.

Annual loading was estimated via flow-weighted averaging and regression techniques using the software program FLUX (Walker 1996). SRP input-output budgets were also constructed for various discharge regimes in order to quantify SRP uptake (or export) within the reach under differing chlorophyll concentrations and TSS loading conditions. Representative two-week periods exhibiting relatively constant low discharge or bracketing a discharge peak or trough on the hydrograph were chosen for budgetary analysis to account for variation in travel time.

Statistical Analyses. Regression relationships between variables were analyzed using the Statistical Analysis System (SAS 1994). Hypothesis testing for significant differences in the slope of the regression equation between stations was analyzed using the SAS General Linear Modeling (GLM) and Regression (REG) Procedures.

RESULTS:

Equilibrium and Diffusive P Fluxes. TSS collected during periods of higher discharge was composed of equal percentages of extractable biologically labile and refractory PP forms (Table 2). Loosely bound and iron-bound PP, assumed to approximate the exchangeable PP pool, collectively represented 85 percent and 43 percent of the biologically labile and total PP, respectively. Calcium-bound (53 percent) and refractory organic PP (31 percent) accounted for most of the refractory PP.

Variable		Mean	S.E.	Percent
Biologically labile PP	Loosely bound	138	7	18.2
	Iron-bound	186	6	24.5
	Labile organic	56	4	7.4
Refractory PP	Aluminum-bound	59	3	7.8
	Calcium-bound	203	14	26.8
	Refractory organic	116	18	15.3

Phosphorus desorption from TSS occurred at very low aqueous SRP, while adsorption occurred above an EPC of 0.117 mg L⁻¹ (±0.012 standard error; Figure 2). In addition, the EPC was equivalent to the mean ambient SRP in the river determined at the time of TSS collection

($0.116 \text{ mg L}^{-1} \pm 0.003$ standard error), suggesting equilibrium control of SRP by TSS loads during higher discharge periods. The k_d and S_{max} were 332 L kg^{-1} (± 31 standard error) and 608 mg kg^{-1} (± 16 standard error), respectively. The DSP was high at 69 percent.

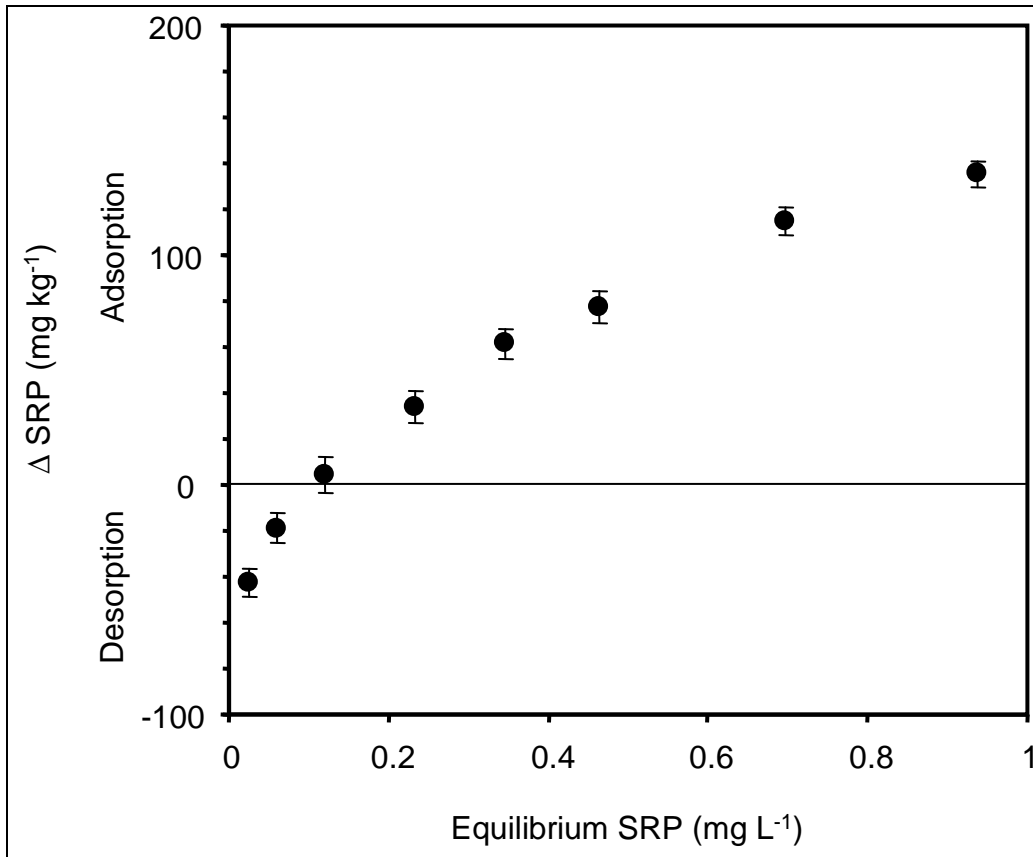


Figure 2. Means (± 1 SE; $n=10$) for soluble reactive phosphorus (SRP) desorption or adsorption versus equilibrium SRP

Kinetic flux exhibited a biphasic pattern (Figure 3). At low ambient SRP, phosphorus desorption was linear and rapid during the first 300 minutes due to deviation below the EPC. The rate of P desorption declined and was constant between 300 and 7200 min. Under conditions of high ambient SRP, adsorption was very rapid between zero and 60 min and lower between 60 and 720 min.

As per the a priori stratification scheme, surface sediments collected in the lower Minnesota River were dominated primarily by sand and silt; clay accounted for less than 17 percent of the particle size composition (Figure 4 and Table 3). The sand content ranged between 4 and 98 percent and silt content ranged between 2 and 75 percent over all stations. Moisture content of the sediment was positively related to the silt and clay content while the inverse pattern occurred for sand content versus moisture content (Figure 4). Sediment density versus particle size distribution relationships exhibited a pattern opposite to that of moisture content. Thus, both moisture content and sediment density were good predictors of the particle size distribution of the sediments.

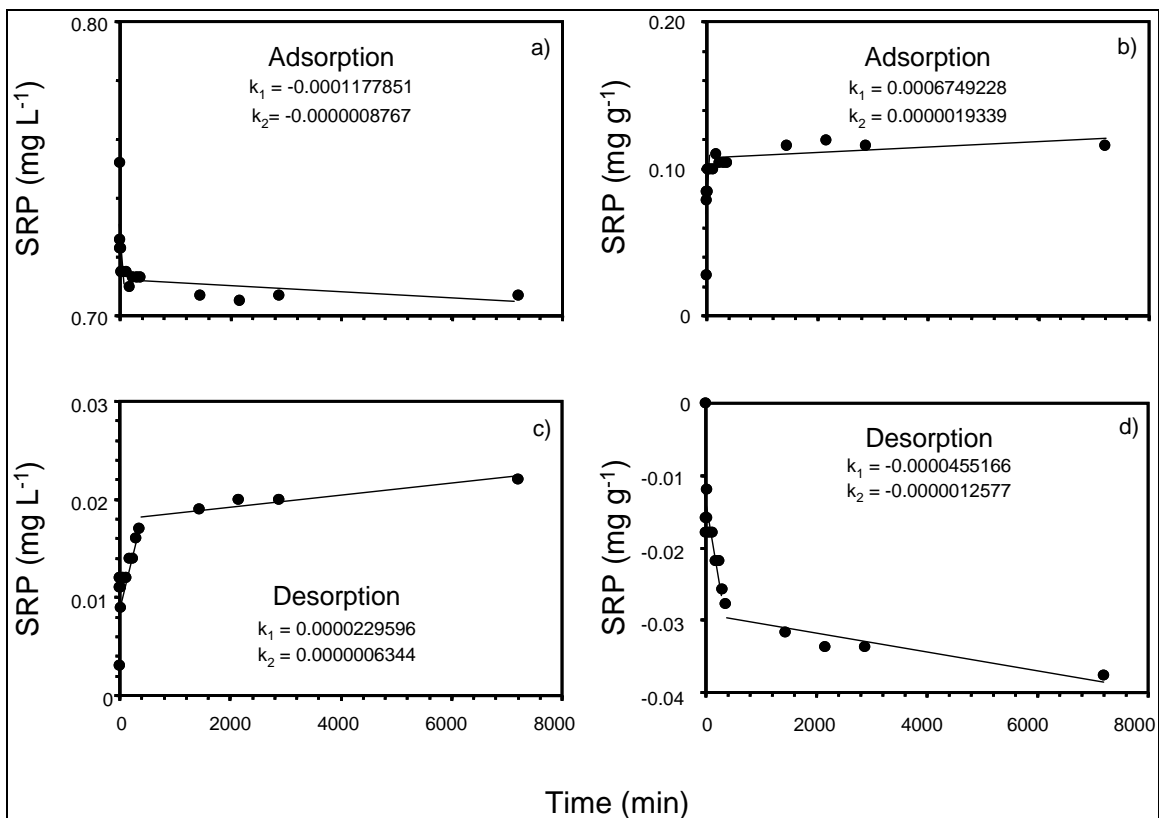


Figure 3. Variations in adsorption (panels a and b) and desorption (panels c and d) of soluble reactive phosphorus (SRP) as a function of time for suspended sediment collected at RM 3.5 in May 2005. k_1 represents rapid kinetics; k_2 represents slow kinetics

Table 3
Means and standard errors (S.E.; n = 24) for physical properties of the upper 10 cm of surface sediments collected in the lower Minnesota River in 2005 and 2006

Variable	2005		2006	
	Mean	S.E.	Mean	S.E.
Moisture content (%)	34.6	1.4	31.7	1.8
Density (g/mL)	1.05	0.03	1.20	0.05
Sand content (%)	53.9	3.4	67.2	4.2
Silt content (%)	37.4	2.8	25.6	3.4
Clay content (%)	8.7	0.7	7.2	0.9

Total P of the sediment varied as a function of sediment physical characteristics. The concentration was positively related to sediment moisture content, silt content, and clay content, and negatively related to sediment density and sand content (Figure 5). These results suggested that the more flocculent sediments composed of finer particles were associated with a higher P concentration. Overall, refractory P (i.e., sum of aluminum-bound, calcium-bound, and residual organic P) constituted the majority of sediment total P and it was dominated by calcium-bound

and residual organic P (Figure 6). The iron-bound P fraction accounted for most of the biologically available sediment P (i.e., sum of loosely bound, iron-bound, and labile organic P).

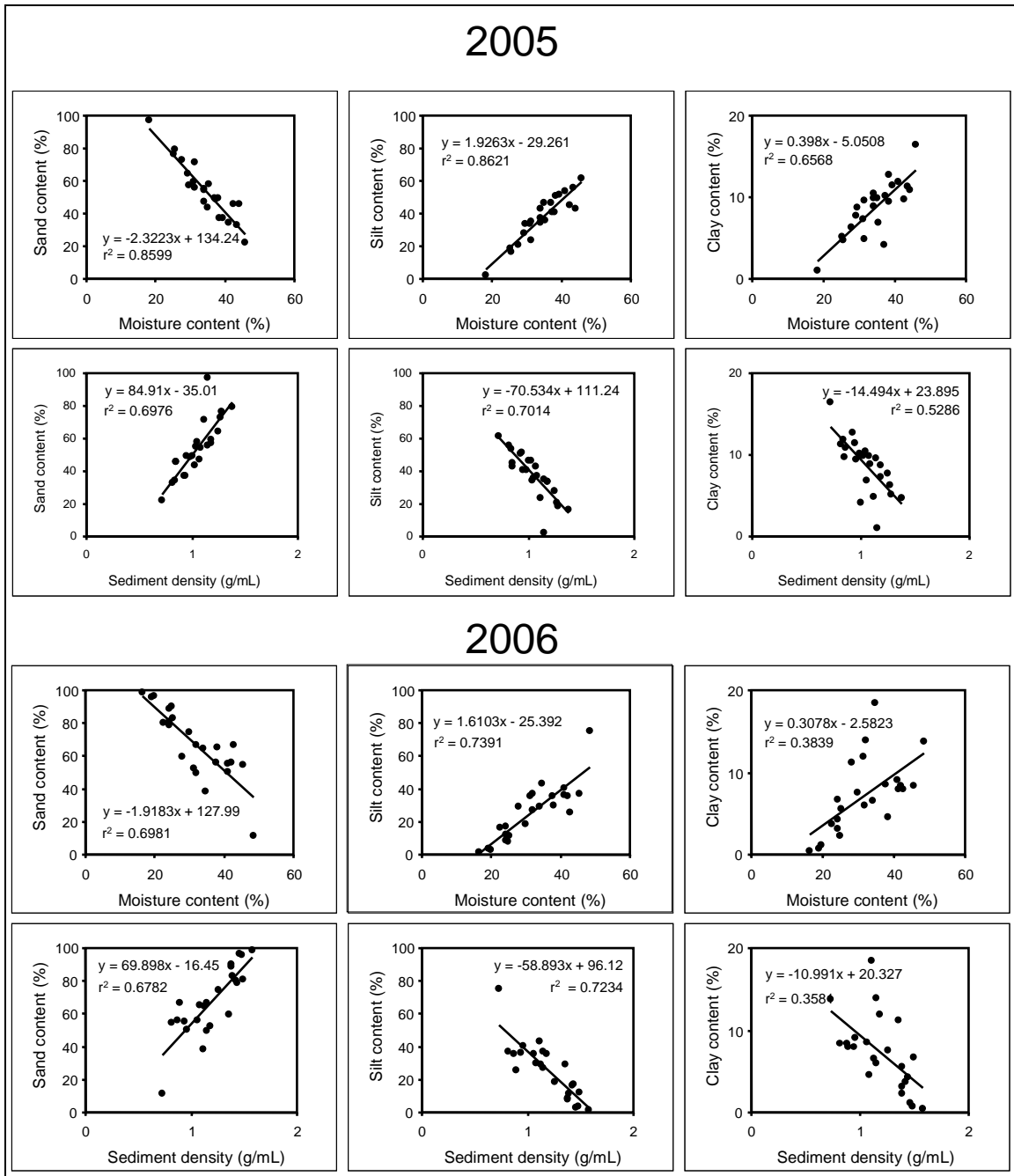


Figure 4. Linear relationships between particle size, moisture content, and sediment density for the upper 10 cm of bottom sediment collected in the lower Minnesota River in 2005 and 2006.

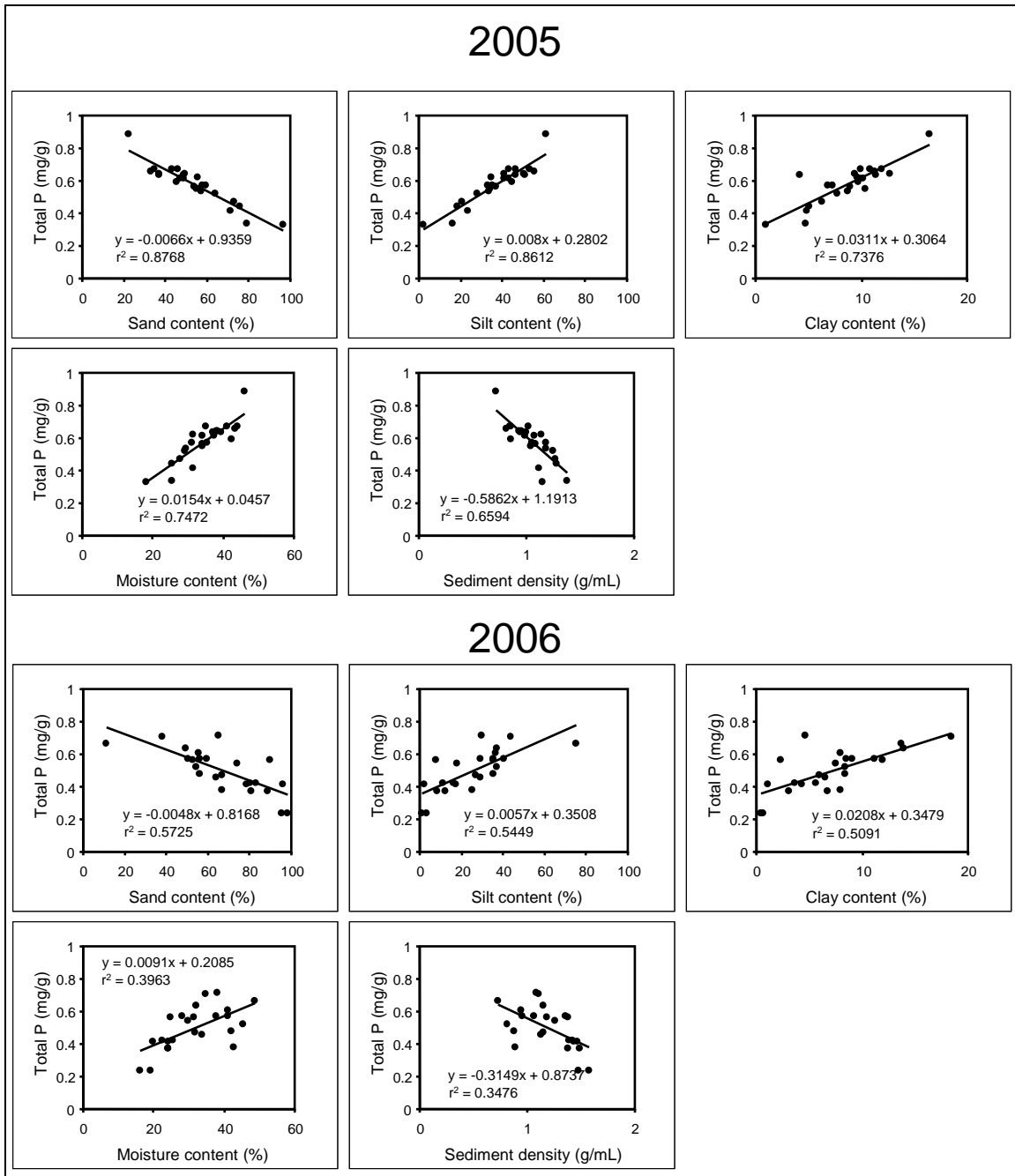


Figure 5. Linear relationships between particle size, moisture content, and sediment density versus total phosphorus (P) for the upper 10 cm of bottom sediment collected in the lower Minnesota River in 2005 and 2006.

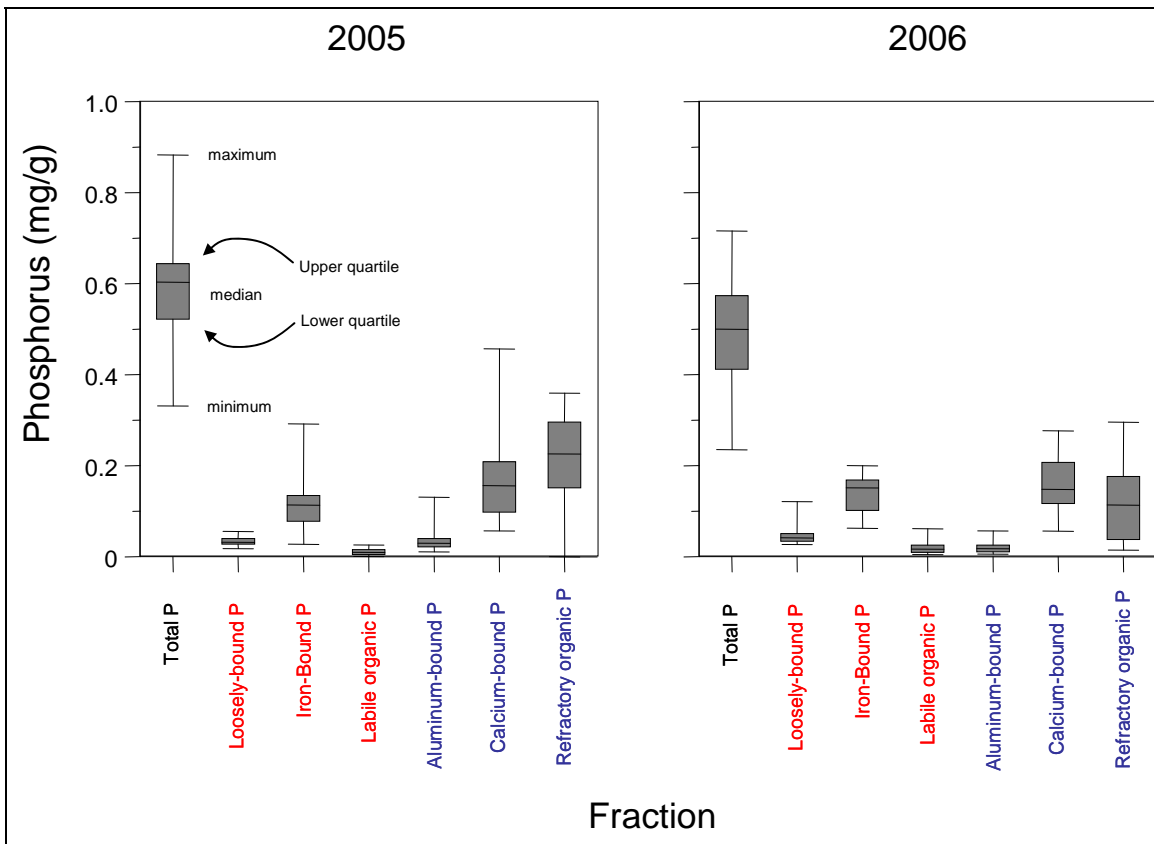


Figure 6. Box and whisker plots of total sediment phosphorus (P), biologically available (red fonts) P, and refractory P for the upper 10 cm of bottom sediment collected in the lower Minnesota River in 2005 and 2006.

Rates of P release from sediment were high under both oxic and anoxic conditions and there was a strong linear relationship between the two variables (Figure 7). Rates were approximately 3.7 to 4.8 times greater under anoxic conditions versus oxic conditions. Under oxic conditions, rates of P release from sediment ranged between 0.5 and 6.5 mg m⁻² d⁻¹. The greatest rate under anoxic conditions of 31 mg m⁻² d⁻¹ was measured from sediment collected at RM 17.6 in 2006. Rates under both oxic and anoxic conditions were positively related to iron-bound P, suggesting that Fe-P interactions were important in driving diffusive fluxes of P out of the sediment (Figure 7).

To estimate internal P loading via P release from sediment during the summer, hydroacoustic analysis of sediment texture throughout the lower Minnesota River was used in conjunction with regression relationships developed between independently determined sand and silt content, iron-bound P, and rates of P release from sediment (Figure 8). Means from hydroacoustic data for percent sand-gravel, silt-sand, and silt content of sediment between RM 0.0 and RM 26.5 are shown in Table 4. For budgetary purposes, it was assumed that dissolved oxygen concentrations in the bottom water were above 1 mg L⁻¹ and that P release from sediment was regulated by oxic conditions. The mean rate of P release over the lower 26-mile stretch of the Minnesota River was approximately 4.0 mg m⁻² d⁻¹ under oxic conditions and 21.3 mg m⁻² d⁻¹ under anoxic conditions (Table 4). Extrapolation of the oxic release rate over the entire 39-mile stretch between Jordan

and the confluence with the Mississippi River resulted in an estimated sediment P release rate of 23 kg d^{-1} (i.e., area-weighted mean $4.0 \text{ mg m}^{-2} \text{ d}^{-1} \times 5.77 \text{ km}^2$, approximate surface area between RM 0 and RM 39.4). This rate represented < 1 percent of the total P load at RM 3.5 for discharges $> 200 \text{ m}^3 \text{ s}^{-1}$ (Figure 9). The relative percentage increased logarithmically with decreasing discharge but represented < 10 percent of the total P load, even for the lowest summer discharges. Although the release rate was high under both oxic and anoxic conditions, relative contributions from sediment flux to the P budget were minor in relation to the much larger inputs from other point and nonpoint sources.

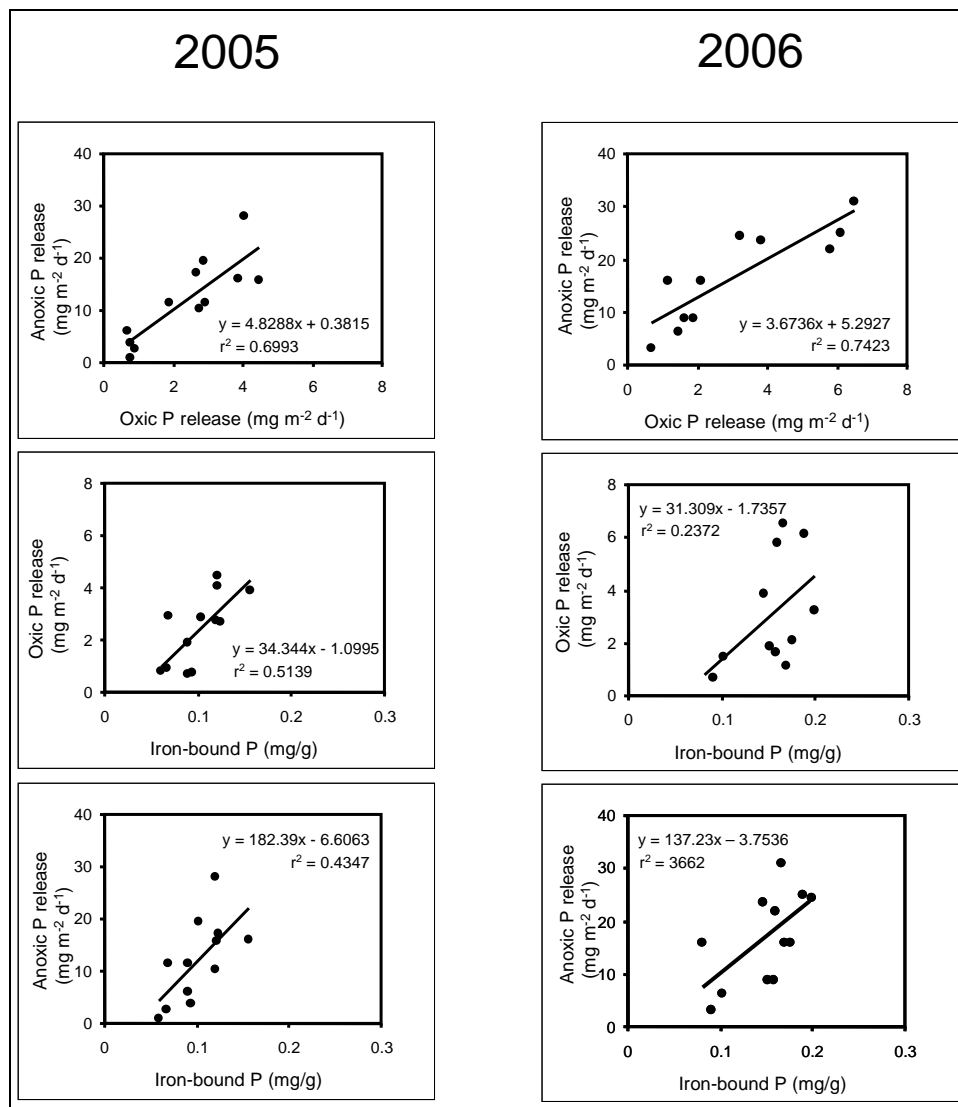


Figure 7. Linear relationships between rates of phosphorus (P) release from sediment under oxic versus anoxic conditions (upper panels) and the iron-bound sediment P concentration versus rates of P release from sediment under oxic and anoxic conditions (middle and lower panels).

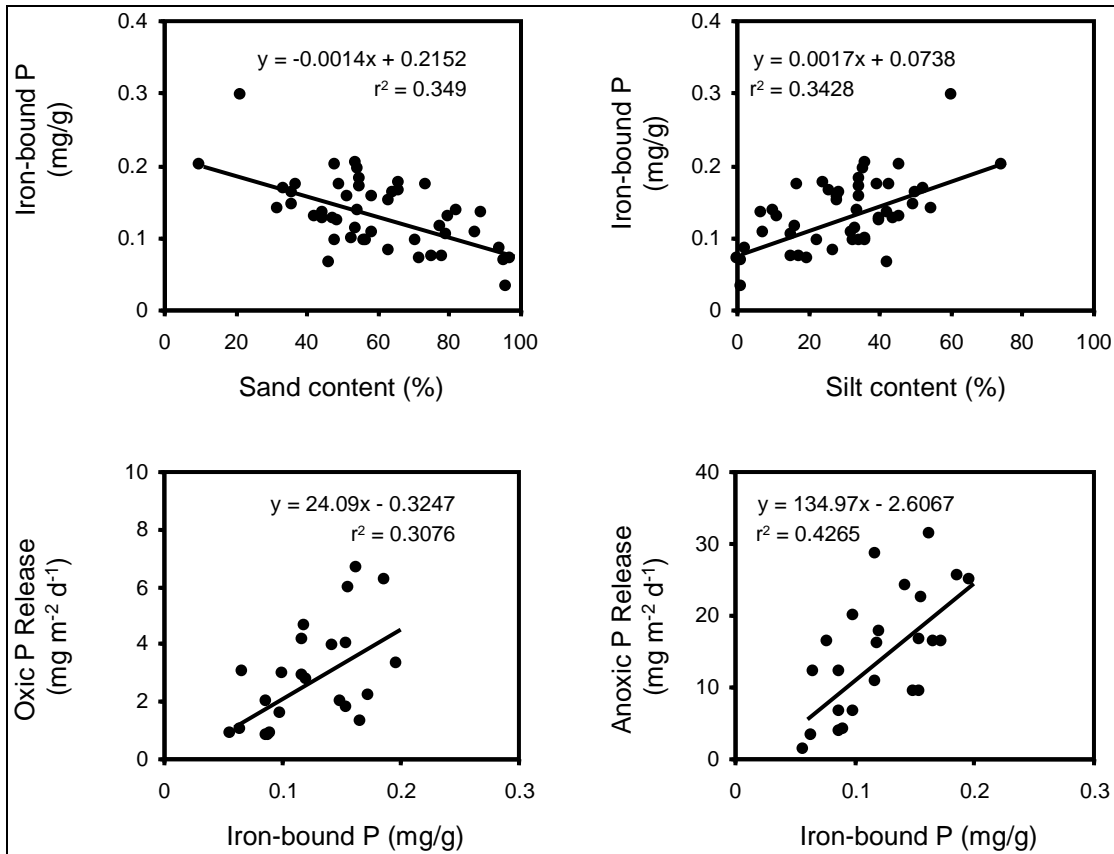


Figure 8. Relationships between sand or silt content and iron-bound P (upper panels) and iron-bound P versus phosphorus (P) release from sediments (lower panels).

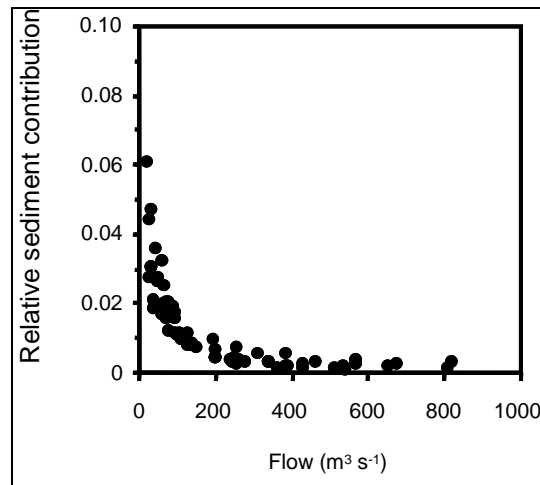


Figure 9. The relative contribution of phosphorus (P) release from sediment under oxic conditions to the P budget of the lower Minnesota River versus flow. The relative sediment P contribution was calculated as the system-wide rate of P release divided by total P loading at RM 3.5.

Table 4

Predicted concentrations of iron-bound phosphorus (P) in the sediment and rates of P release under oxic and anoxic conditions for river mile sections of the lower Minnesota River. Sediment textural categories determined by the U.S. Geological Survey (Mr. T. Winterstein, U.S. Geological Survey, 2004, unpublished data) were used in conjunction with regression relationships developed between sand or silt content versus iron-bound P and iron-bound P versus rates of P release under oxic or anoxic conditions (Figure 8)

River Mile	Sediment Texture		Iron-bound P (mg/g)	Sand-gravel		Iron-bound P (mg/g)	Sand-Silt	
	Sand-Gravel (%)	Sand-Silt (%)		Oxic P Release (mg m ⁻² d ⁻¹)	Anoxic P Release (mg m ⁻² d ⁻¹)		Oxic P Release (mg m ⁻² d ⁻¹)	Anoxic P Release (mg m ⁻² d ⁻¹)
0.5	69	31	0.119	2.5	13.4	0.127	2.7	14.6
1.5	39	62	0.161	3.5	19.1	0.181	4.0	21.8
2.5	21	78	0.186	4.2	22.5	0.208	4.7	25.5
3.5	29	71	0.175	3.9	21.0	0.196	4.4	23.9
4.5	32	68	0.170	3.8	20.4	0.191	4.3	23.2
5.5	28	72	0.176	3.9	21.1	0.198	4.4	24.1
6.5	38	62	0.162	3.6	19.3	0.181	4.0	21.8
7.5	74	26	0.112	2.4	12.5	0.119	2.5	13.4
8.5	44	47	0.154	3.4	18.1	0.155	3.4	18.3
9.5	60	28	0.131	2.8	15.1	0.122	2.6	13.9
10.5	51	48	0.144	3.1	16.8	0.156	3.4	18.5
11.5	20	80	0.187	4.2	22.7	0.212	4.8	25.9
12.5	25	75	0.180	4.0	21.7	0.203	4.6	24.8
13.5	22	77	0.184	4.1	22.3	0.206	4.6	25.3
14.5	36	64	0.165	3.6	19.6	0.184	4.1	22.2
15.5	61	39	0.130	2.8	14.9	0.141	3.1	16.4
16.5	27	72	0.177	3.9	21.3	0.198	4.4	24.1
17.5	25	75	0.180	4.0	21.7	0.203	4.6	24.8
18.5	20	80	0.187	4.2	22.7	0.212	4.8	25.9
19.5	46	54	0.151	3.3	17.7	0.167	3.7	19.9
20.5	57	43	0.135	2.9	15.7	0.148	3.2	17.3
21.5	6	95	0.207	4.7	25.3	0.237	5.4	29.4
22.5	23	77	0.183	4.1	22.1	0.206	4.6	25.3
23.5	15	85	0.194	4.4	23.6	0.220	5.0	27.1
24.5	0	100	0.215	4.9	26.4	0.246	5.6	30.6
25.5	23	77	0.183	4.1	22.1	0.206	4.6	25.3
26.25	27	73	0.177	3.9	21.3	0.200	4.5	24.3
Average (1 SE)	34 (3.6)	65 (3.8)	0.168 (0.005)	3.7 (0.1)	20.0 (0.7)	0.186 (0.006)	4.2 (0.2)	22.5 (0.9)

Regression relationships were developed between rates of P release from sediment ($\text{mg m}^{-2} \text{s}^{-1}$) and iron-bound P volumetric concentration {i.e., iron-bound P (mg g^{-1}) sediment density (g m^{-3})} to estimate a mass transfer coefficient, k_e (m s^{-1}) for use in NSM algorithm development (Figure 10). Under oxic conditions, the k_e was 3.365 m s^{-1} ($\pm 0.728 \text{ S.E.}$). k_e was nearly four times greater under anoxic conditions at 12.818 m s^{-1} (± 3.125).

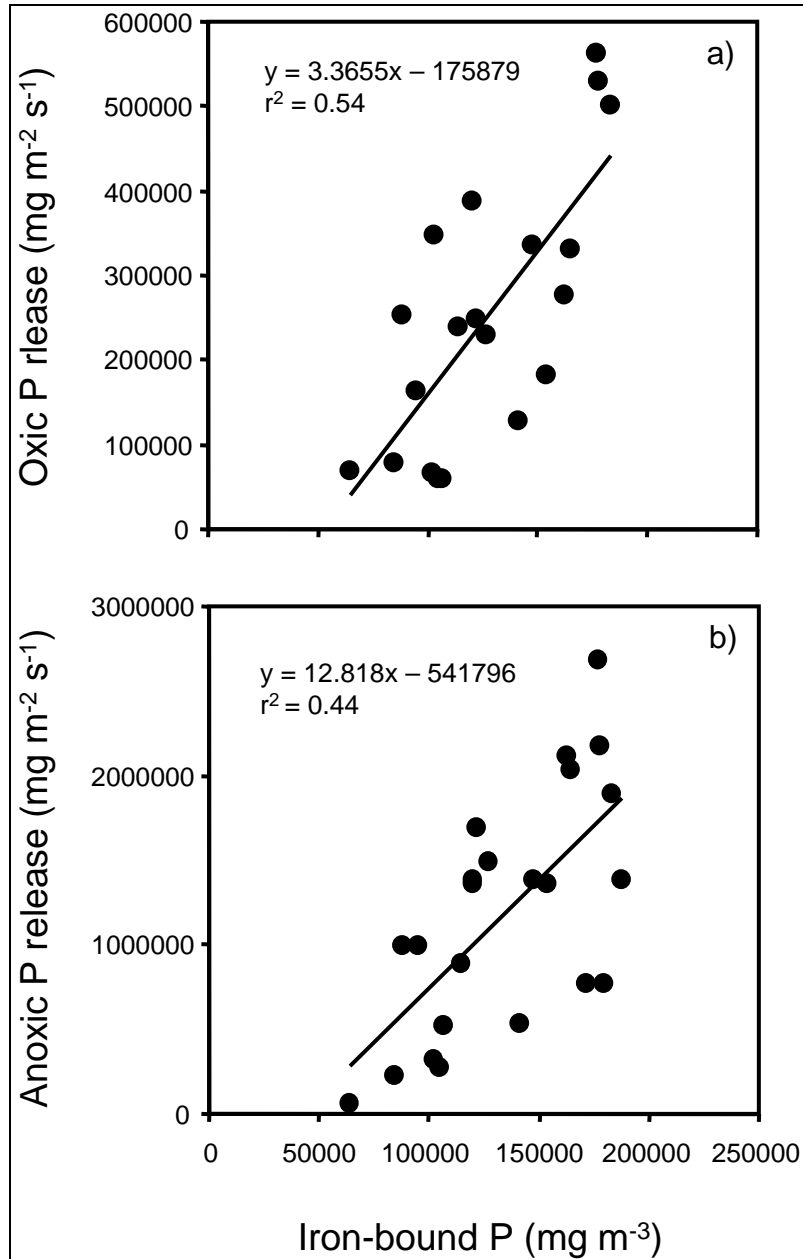


Figure 10. Relationships between volumetric iron-bound phosphorus (P) concentration and (a) the rate of P release under oxic conditions and (b) the rate of P release under anoxic conditions

Phosphorus Dynamics. Concentrations of TSS were lowest at RM 39.4 and RM 3.5 during extended low-discharge periods in winter and late summer and usually increased in conjunction with elevated discharges, with peaks occurring on the rising side of the hydrograph (Figures 11a and 11b). An exception occurred during a period of snowmelt and high discharge in March through late April, 2006, when TSS concentrations were low despite a very high discharge. Regression relationships were significant, but weak, due to the pattern of hysteresis between TSS concentration and discharge during storm discharge periods ($\ln \text{TSS}_{\text{RM39.4}} = 0.352 \cdot \ln \text{Discharge}_{\text{RM39.4}} + 3.002$, $r^2 = 0.27$, $p < 0.0001$; $\ln \text{TSS}_{\text{RM3.5}} = 0.425 \cdot \ln \text{Discharge}_{\text{RM3.5}} + 2.265$, $r^2 = 0.44$, $p < 0.0001$). Chlorophyll concentrations were lowest during the winter months of December through March (Figure 11c). For other months, chlorophyll was highest during periods of lower discharge and declined as a result of higher discharge ($\ln \text{CHLA}_{\text{RM39.4}} = -0.484 \cdot \ln \text{Discharge}_{\text{RM39.4}} + 6.602$, $r^2 = 0.52$, $p < 0.0001$; $\ln \text{CHLA}_{\text{RM3.5}} = -0.381 \cdot \ln \text{Discharge}_{\text{RM3.5}} + 5.950$, $r^2 = 0.33$, $p < 0.0001$). The slope of the TSS-discharge regression equation was significantly greater for RM 3.5 than RM 39.4 ($p < 0.0001$), while the opposite occurred for chlorophyll versus discharge ($p < 0.0001$), resulting in lower predicted TSS and chlorophyll at RM 3.5 versus RM 39.4 as a function of decreasing discharge. These patterns were probably attributable to net retention at low discharge. Seasonal variations in PP were more complex as concentrations were elevated during periods of higher discharge and also during periods of lower discharge and high chlorophyll concentration (Figure 11d). As a result, the PP concentration was not significantly related to discharge for either station ($p < 0.26$).

The concentration of SRP exhibited a complex seasonal pattern that was related to variations in relative loading contributions by point and nonpoint sources, equilibrium processes, and chlorophyll concentration. Overall, SRP declined toward zero as a function of increasing chlorophyll (Figure 12). High chlorophyll concentration coincided with periods of low discharge when point sources from within the reach increasingly dominated P loading, primarily as SRP (Figure 13). SRP also decreased on the falling limb of hydrograph peaks in conjunction with increases in chlorophyll (Figure 11e). Examples of these inverse patterns occurred in May, July, and August 2004; May, June, August, and November 2005; and April, June, July, and August 2006. The molar TN:TP and DIN:DIP (i.e., dissolved inorganic N and P) ratios were > 50 , suggesting potential P limitation during these periods.

Subsequent increases in discharge resulted in declines in chlorophyll and increases in the concentration of TSS (Figures 11b and 11c). Concentrations of SRP were similar at both stations and near the EPC under these conditions (Figure 11e). For instance, SRP averaged 0.115 mg L^{-1} during discharge peaks and high TSS loading that occurred in early June, mid-July, mid-August, and late September 2004. SRP concentration approached the EPC during other high discharge periods in March, early April, early May, and June 2005, and April and early June 2006. Overall, SRP concentrations approached the EPC at both stations as a function of increasing TSS and PP loading (Figure 14). The concentration declined toward zero under conditions of low TSS and PP loading (Figure 14).

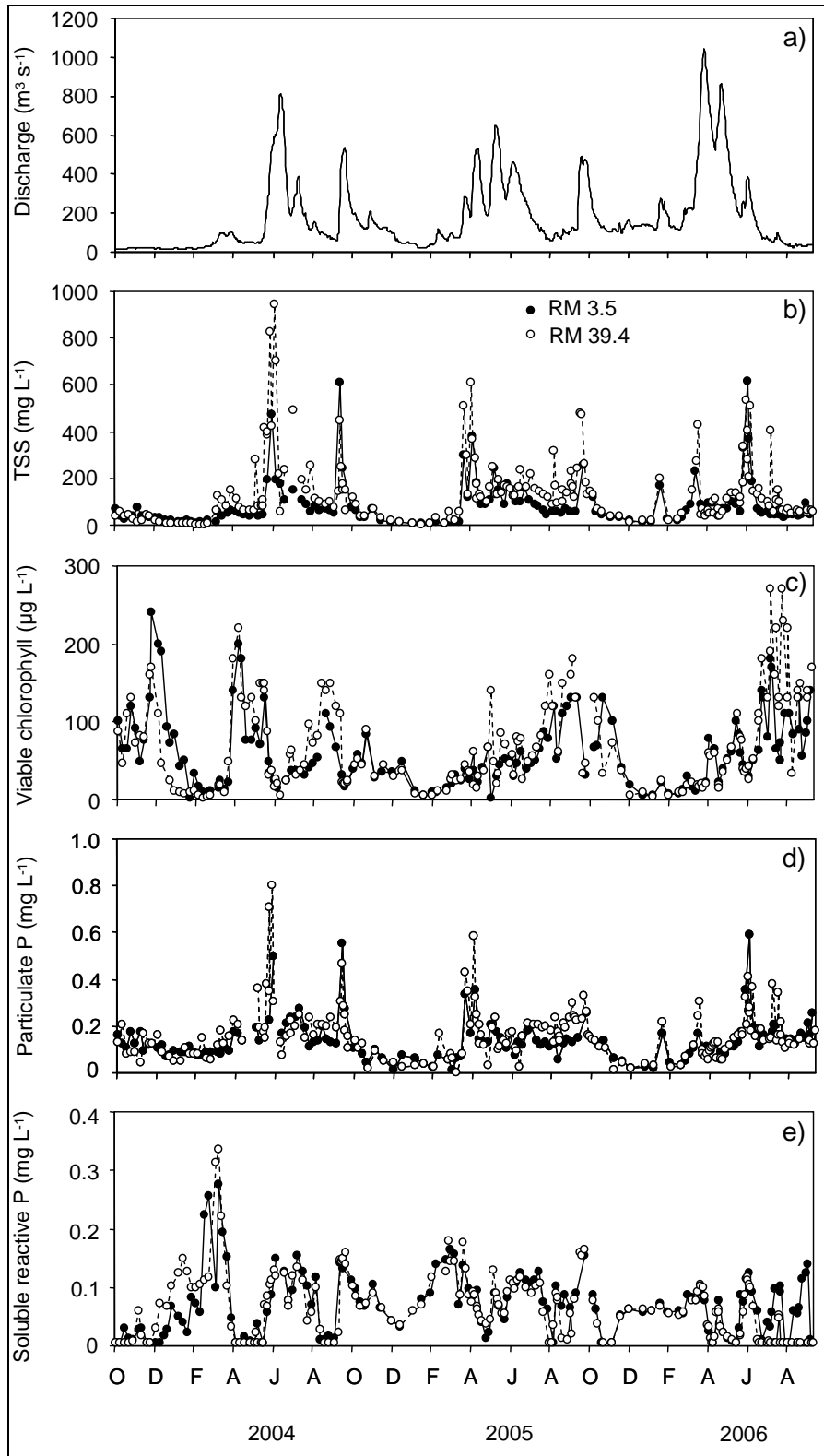


Figure 11. Seasonal variations in a) discharge at river mile (RM) 3.5, b) total suspended solids (TSS), c) viable chlorophyll a, d) particulate phosphorus (P), and e) soluble reactive P at RM 3.5 and 39.4 of the lower Minnesota River during October 2003 through September 2006.

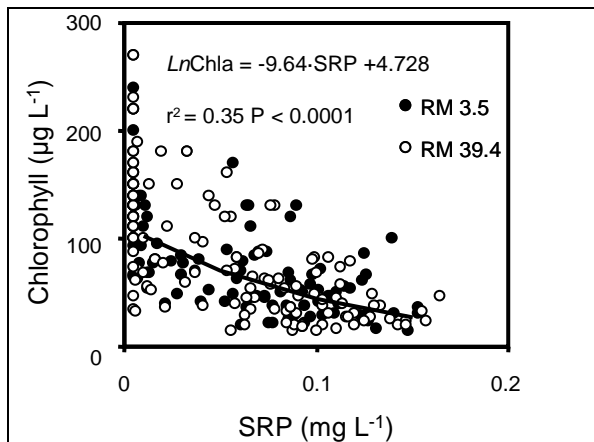
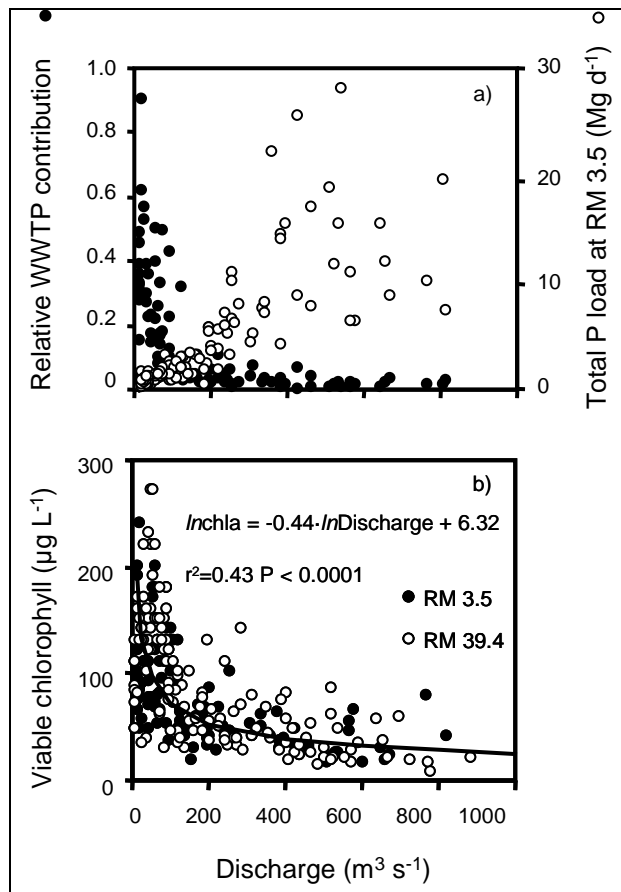


Figure 12. Relationships between soluble reactive phosphorus (SRP) and viable chlorophyll a. Data from river mile (RM) 3.5 and RM 39.4 were combined for regression analysis.

Figure 13. Relationships between discharge and a) relative wastewater treatment plant (WWTP) contributions (solid circles) for total phosphorus (P) load (open circles) for the Minnesota River at river mile (RM) 3.5 and b) viable chlorophyll concentration for the April through November period, 2004-2006. Data from RM 3.5 and RM 39.4 were combined to estimate regression equations.



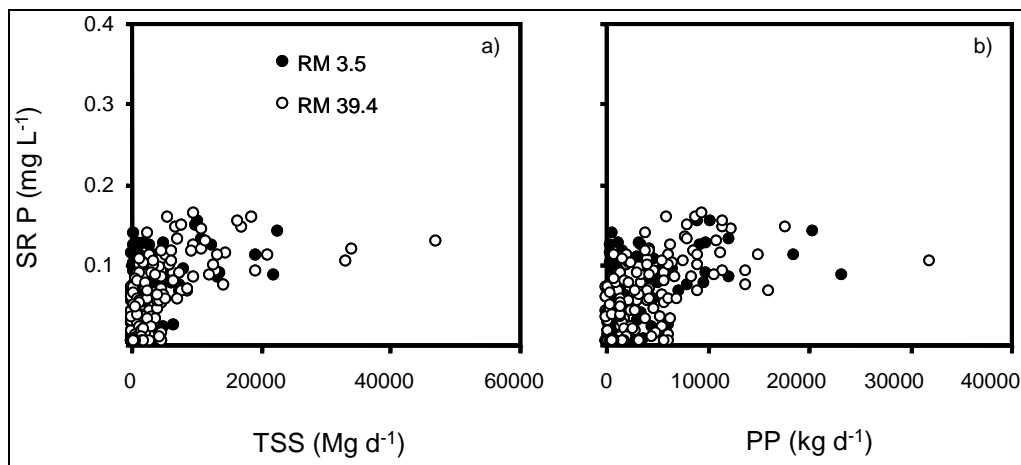


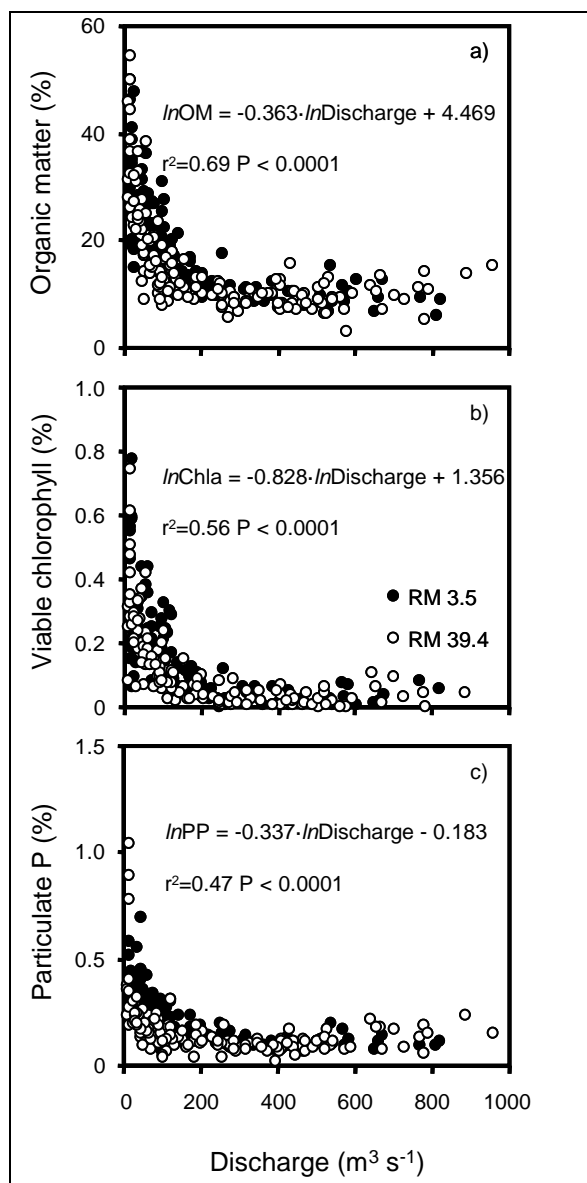
Figure 14. Variations between soluble reactive phosphorus (SRP) concentration and a) total suspended solids (TSS) and b) particulate phosphorus (PP) loading for the April through November period, 2004-2006.

During a period of extended low discharge in September 2006, SRP increased to peak concentrations at RM 3.5 versus concentrations near zero at RM 39.4 (Figure 11e). Diffusive P flux from sediments was high at $3.9 \text{ mg m}^{-2} \text{ d}^{-1}$ in the vicinity of RM 3.5,¹ but a mass balance analysis (not shown) indicated that this source was minor (< 10 percent) and that phytoplankton senescence combined with WWTP point sources located below RM 39.4 were largely responsible for SRP increases at RM 3.5 (WWTP contribution = 31 percent and 75 percent of the total P and SRP loading, respectively). During low discharge winter months, SRP ranged between 0.1 and 0.3 mg L^{-1} with similar concentrations at both stations (Figure 11e). These patterns suggested that SRP inputs originating upstream of RM 39.4 were contributing to the P budget of the river with little transformation to particulate forms due to very low chlorophyll.

Differences in the composition of TSS versus discharge (Figure 15) were used to delineate allochthonous and autochthonous sources of TSS loads for various discharge periods in order to gain further insight into processes regulating P dynamics in the lower Minnesota River. Organic matter (expressed as LOI) and chlorophyll content increased logarithmically as discharge declined at both stations, suggesting that TSS composition was increasingly dominated by phytoplankton at lower discharges (Figures 15a and 15b). The organic matter content ranged between 40 and 60 percent for discharges $< 20 \text{ m}^3 \text{ s}^{-1}$, which was within ranges reported for freshwater diatoms (mean = 58.6 percent; Reynolds 1984). TSS composition was increasingly dominated by inorganic components of allochthonous origin when discharge exceeded $\sim 200 \text{ m}^3 \text{ s}^{-1}$, and phytoplankton biomass indicators declined to an asymptotic minimum with increasing discharge (LOI ~ 9.7 percent and chlorophyll ~ 0.03 percent). PP content exhibited a similar logarithmic pattern (Fig. 15c). It was highest under low discharge conditions in conjunction with TSS composed of phytoplankton biomass and decreased logarithmically with increasing discharge, reaching a minimum of ~ 0.11 percent.

¹ Unpublished data, 2007, William F. James, Research Aquatic Biologist, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Figure 15. Relationships between discharge and a) organic matter (as loss-on-ignition), b) viable chlorophyll, and c) particulate P content (as a percentage of total suspended solids) for the April through November period, 2004-2006. Data from RM 3.5 and RM 39.4 were combined for regression analysis.



Variations in the organic matter content of TSS were used to estimate the loading of allochthonous TSS and PP, exchangeable PP (i.e., loosely bound and iron-bound PP), and equilibrium P flux (i.e., adsorption or desorption) when the concentration of SRP deviated from the EPC. It was assumed that an organic matter content endpoint of 40 percent represented TSS composed of primarily phytoplankton biomass, while an endpoint of 10 percent reflected allochthonous loading originating upriver of RM 39.4. Concentrations lying between these endpoints were assumed to be a mixture of phytoplankton biomass and allochthonous material. These fractions were estimated as $C_{LOI} = (X \cdot C_{phyto}) + ((1-X) \cdot C_{alloch})$, where C_{LOI} was the observed organic matter content, C_{phyto} and C_{alloch} were organic matter content endpoints for phytoplankton or allochthonous material, respectively, and X was the relative proportion. Loading of TSS and PP were partitioned into phytoplankton versus allochthonous material based on these relative proportions. The exchangeable PP load was estimated as 43 percent of the allochthonous TSS load (Table 2). Equilibrium P flux (kg d^{-1}) between the exchangeable PP pool

and water was calculated as $[(EPC - SRP_{Ambient}) \cdot k_d] \cdot Allochthonous\ TSS\ Load$, where EPC was the equilibrium phosphate concentration, $SRP_{Ambient}$ was the observed concentration in the river, and k_d was the linear adsorption coefficient. Equilibrium P flux was estimated for summer months only because temperature effects were not factored into the equilibrium experiments (Barrow 1979).

The exchangeable PP load increased in conjunction with peaks in total P and SRP loading (Figure 16). Adsorption P flux occurred in June 2004, April and May 2005, and June 2006, when ambient SRP concentration was slightly greater than the EPC. During other summer periods, ambient SRP concentration was less than the EPC, resulting in desorption P flux. Although desorption P flux often exceeded 100 kg d^{-1} , it was low compared to total P and SRP loading, representing only ~ 1-2 percent of these loads. Desorption P flux decreased as a function of decreasing discharge ($\ln\text{ Desorption P Flux}_{RM39.4} = 0.970 \cdot \ln\text{ Discharge}_{RM39.4} - 1.80$, $r^2 = 0.47$, $p < 0.0001$; $\ln\text{ Desorption P Flux}_{RM3.5} = 1.621 \cdot \ln\text{ Discharge}_{RM3.5} - 5.827$, $r^2 = 0.77$, $p < 0.0001$). It approached zero at very low discharge in late summer in conjunction with negligible exchangeable PP loading as most of the PP was phytoplankton biomass during these periods. The slope of the desorption P flux-discharge regression equation was significantly greater for RM 3.5 than RM 39.4 ($p < 0.0001$), resulting in lower predicted desorption P flux at RM 3.5 than RM 39.4 as discharge declined. This pattern was similar to TSS-discharge patterns and may have been attributable to deposition of exchangeable PP loads at very low discharge while in transit between RM 39.4 and RM 3.5. Overall, there was an inverse relationship between chlorophyll versus the exchangeable PP load and desorption P flux (Figure 17), due to influences of discharge on chlorophyll.

Budgetary Analysis. During a period of nearly constant low discharge in mid-August, 2006, SRP inputs to the reach were dominated by loading from the WWTPs (Table 5). Discharge output approximately balanced discharge inputs. SRP output loading was considerably less than SRP input loading during this period, resulting in a very high SRP uptake efficiency (> 90 percent). Flow-weighted SRP concentration within the reach was very low relative to the EPC, indicating the potential for desorption P flux. However, this flux was minor relative to other SRP inputs due to low exchangeable PP loading from allochthonous sources during the period. Instead, PP in transit was primarily associated with phytoplankton biomass, as suggested by an organic matter content of 34 percent for TSS and high chlorophyll concentrations in excess of $100\ \mu\text{g L}^{-1}$. A similar budgetary imbalance (SRP uptake efficiency = 67 percent; SRP uptake rate = 126 kg d^{-1}) occurred during a low discharge period in August 2004 in conjunction with chlorophyll concentrations in excess of $140\ \mu\text{g L}^{-1}$ and SRP concentrations $< 0.033\text{ mg L}^{-1}$ at RM 39.4 (not shown). Since exchangeable PP loading equilibrium P fluxes were minor during these periods, and chlorophyll concentrations were high, the high SRP uptake efficiencies during these low discharge periods are attributed to biotic uptake of SRP and transformation to PP.

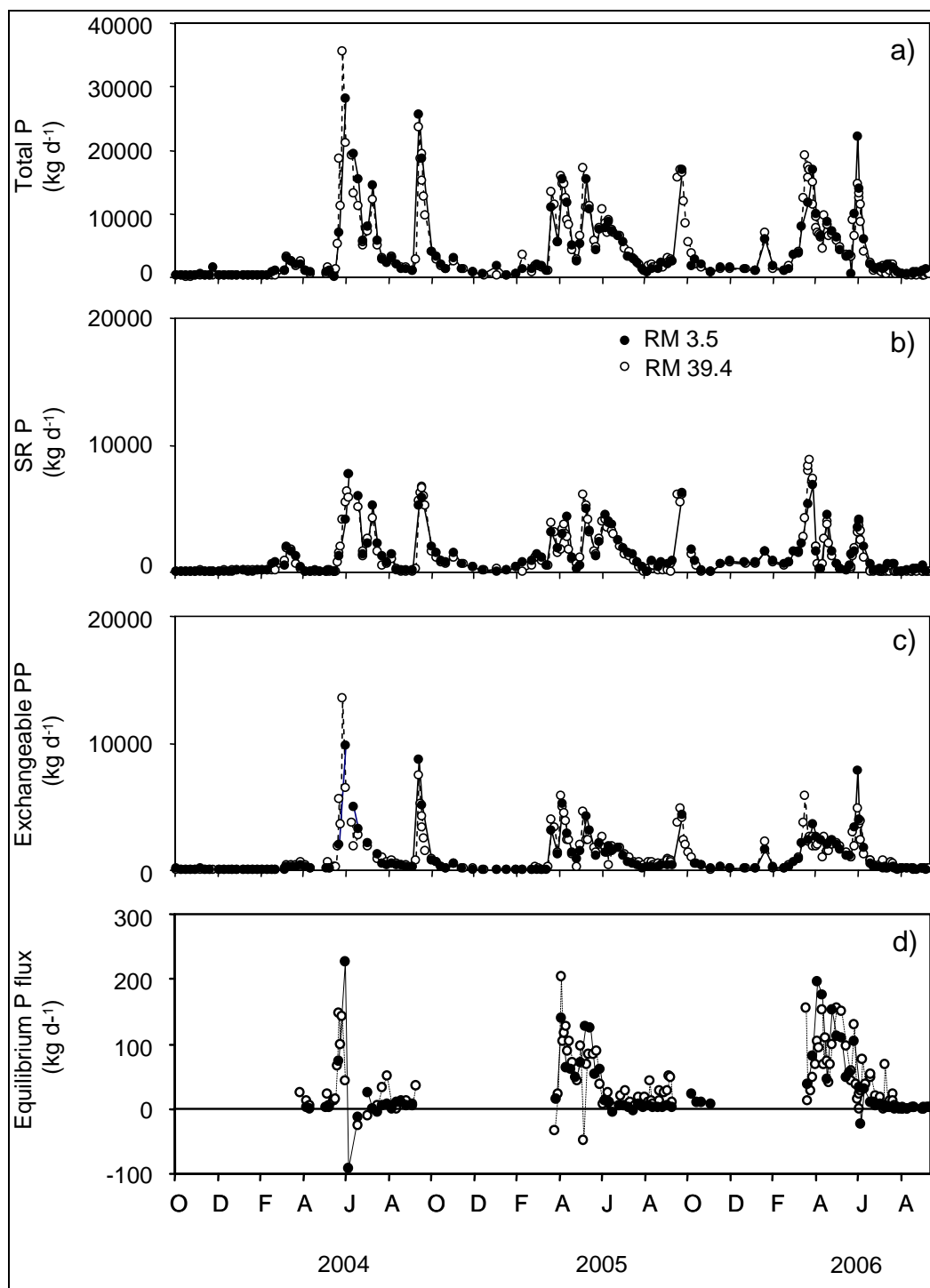


Figure 16. Variations in (a) total phosphorus (P) loading, (b) soluble reactive P (SRP) loading, (c) exchangeable particulate P (PP) loading (i.e., loosely bound and iron-bound PP), and (d) equilibrium P flux between particulate and aqueous phases. A positive equilibrium P flux represents desorption from exchangeable PP to the water column while a negative flux represents adsorption of P onto the exchangeable PP pool.

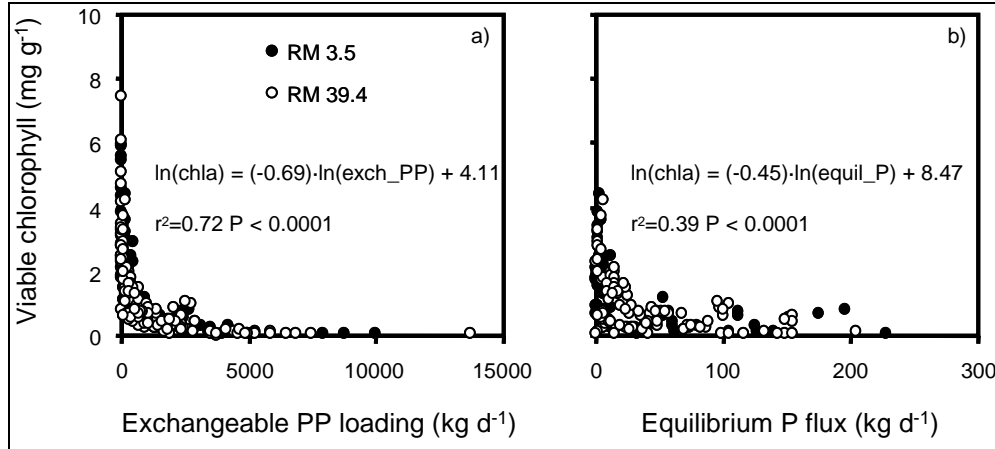


Figure 17. Relationships between viable chlorophyll mass concentration and a) exchangeable particulate P (PP) loading (i.e., loosely bound and iron-bound PP) and b) equilibrium P flux (as desorption of P from particulate to aqueous phases) for the April through November period, 2004-2006.

During a period of peak discharge in June 2004, SRP input loads were dominated by the Minnesota River at RM 39.4, while WWTP loads were negligible by comparison (Table 5). SRP output loading was ~3 percent lower than input loading under these conditions, resulting in minor SRP uptake that was well within the range of analytical and discharge measurement error (Bukaveckas et al. 2005). SRP concentration in the Minnesota River was slightly greater than the EPC during this period, driving abiotic uptake of SRP via adsorption onto suspended sediment particles. Adsorption P flux more than accounted for the SRP uptake during this period. Concentrations of chlorophyll were $< 20 \mu\text{g L}^{-1}$, supporting a contention that biotic uptake was negligible.

During periods of intermediate discharge in June 2005 and 2006, the Minnesota River at RM 39.4 accounted for > 90 percent of the SRP input to the system. The SRP uptake rate was high relative to other periods (Table 5), but represented < 10 percent of the input loading. Abiotic uptake of SRP via adsorption did not occur because flow-weighted SRP concentrations fell below the EPC during these periods. The SRP input-output loading imbalance was more likely attributable to biotic uptake as chlorophyll concentrations were high, ranging between 41 and 72 $\mu\text{g L}^{-1}$. Although desorption P flux occurred during these periods, it was minor in relation to SRP loading inputs from the Minnesota River because ambient SRP concentrations were near the EPC.

On an annual basis, the Minnesota River dominated hydrological inputs to the system during the 3-year period and discharge inputs approximately balanced outputs (Table 6). Nonpoint sources dominated total P and SRP loading to the lower Minnesota River and SRP accounted for 28 to 33 percent of the total P loading. Annual total P loading from WWTPs was minor in relation to nonpoint total P loading. However, they represented a larger percentage of the SRP loading to the system, ranging between ~6 and 13 percent.

Table 5
Soluble reactive phosphorus (SRP) input, output, and uptake loading for various two-week periods between 2003 and 2006¹

Period	Input					Output			Uptake	
	Discharge (m ³ s ⁻¹)	SRP (kg d ⁻¹)	SRP (mg L ⁻¹)	WWTP (%)	Equil. SRP (kg d ⁻¹)	Discharge (m ³ s ⁻¹)	SRP (kg d ⁻¹)	SRP (mg L ⁻¹)	SRP (kg d ⁻¹)	SRP (%)
8/16/06	38	159 (22)	0.040	76.7	2.1	36	5 (1)	0.023	154	96.8
6/16/06	294	2838 (157)	0.105	4.3	41.4	296	2584 (196)	0.101	254	8.9
6/9/05	420	3867 (207)	0.106	3.3	24.9	424	3621 (138)	0.099	246	6.4
6/6/04	711	7185 (285)	0.123	2.0	-364	687	7109 (810)	0.120	223	3.0

¹ SRP input loading is calculated as the sum of mean SRP loads from the lower Minnesota River at river mile (RM) 39.4, 12 small creeks, two wastewater treatment plants (WWTP), and equilibrium SRP flux. The lower Minnesota River at RM 3.5 represents mean SRP output loading from the reach. The standard error (shown in parentheses) of mean SRP input-output loading reflects sampling and analytical error (error associated with flow measurement is not included). SRP input loads from WWTPs are represented as percentages of the total SRP input load. A positive equilibrium SRP flux represents desorption phosphorus (P) flux from particulate to soluble forms, while a negative equilibrium SRP flux indicates adsorption P flux from aqueous to particulate phases. SRP uptake is calculated as SRP input loading minus SRP output loading. SRP uptake efficiency (%) is estimated as SRP uptake divided by SRP input loading and multiplied by 100.

Table 6 Annual input, output, and retention of total and soluble reactive P (SRP) loads in the lower Minnesota River between river mile (RM) 39.4 and RM 3.5 for the years 2004-2006							
Variable	Load Source	Discharge		Total P		SRP	
		m ³ s ⁻¹	%	kg/y	%	kg/y	%
2004							
Inputs	Minnesota River at river mile 39.4	115.4	92.0	1362796	92.2	389698	89.9
	Creeks	5.3	4.2	74058	5.0	18417	4.2
	Point sources	4.7	3.8	40464	2.7	25422	5.9
Outputs	Minnesota River at river mile 3.5	126.3		1405095		412217	
Retention		-0.9	100.8	72222	4.9	21320	4.9
2005							
Inputs	Minnesota River at river mile 39.4	165.1	94.1	1402904	91.3	461762	88.7
	Creeks	5.6	3.2	66869	4.4	19835	3.8
	Point sources	4.8	2.7	66776	4.3	39205	7.5
Outputs	Minnesota River at river mile 3.5	178.5		1381346		513897	
Retention		-3.0	101.7	155203	10.1	6905	1.3
2006							
Inputs	Minnesota River at river mile 39.4	222.7	95.0	1505394	88.4	427398	82.9
	Creeks	8.4	3.6	125661	7.4	22813	4.4
	Point sources	3.4	1.5	71890	4.2	65583	12.7
Outputs	Minnesota River at river mile 3.5	237.0		1517663		450477	
Retention		-2.5	101.1	185282	10.9	65317	12.7

Annual total P loadings for the lower Minnesota River (i.e., combined average of RM 39.4 and RM 3.5) were further partitioned into PP and soluble P fractions. Biologically labile and refractory PP fractions determined for TSS collected during high discharges were assumed to be a constant percentage of the annual PP load. This assumption was reasonable since greater than 70 percent of the loading occurred for discharges > 200 m³ s⁻¹. Over the 3-year period, soluble P (i.e., equivalent to total soluble P), biologically labile PP, and refractory PP each represented about one third of the total P budget (Figure 18). The combined soluble P and biologically labile PP accounted for an average 67 percent (range = 64 to 70 percent) of the total P load discharged into the Upper Mississippi River.

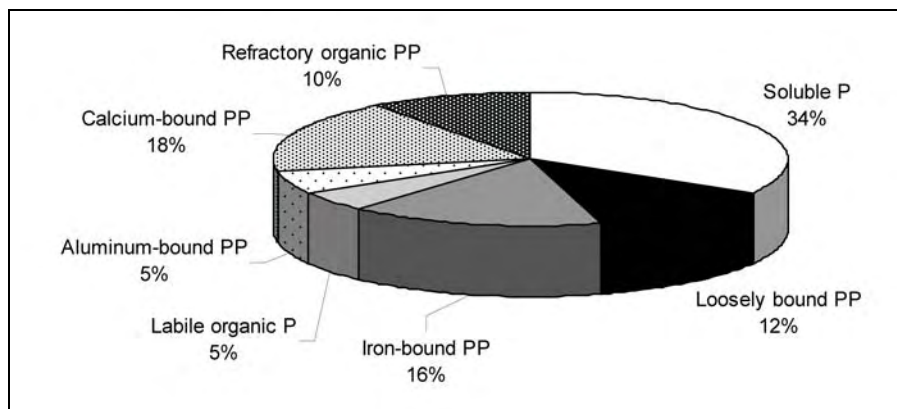


Figure 18. Contribution of biologically labile (solid shades) and refractory (dotted shades) phosphorus (P) fractions to the annual average (i.e., between 2004 and 2006 for RM 39.4 and RM 3.5 combined) annual total P load of the lower Minnesota River

DISCUSSION: Equilibrium P assays demonstrated that P buffering occurred between aqueous and particulate phases, resulting in an EPC of 0.117 mg L^{-1} . SRP concentration in the lower Minnesota River converged with the independently measured EPC as TSS and PP loading increased due to higher discharge. The strong correspondence between measured EPC and ambient SRP indicated that equilibrium reactions between TSS of allochthonous origin and aqueous phases were regulating SRP at higher discharge and TSS loading. This finding falls in line with other evidence demonstrating equilibrium control of SRP by suspended particulate material in overland runoff and in turbid river systems (Mayer and Gloss 1980; Froelich 1988; Carignan and Vaithyanathan 1999; Fang et al. 2002; James et al. 2002; James and Barko 2005). The EPC for TSS in the lower Minnesota River was high relative to EPC values reported for some other systems (Table 7). The DSP was also high and within ranges reported in Fang et al. (2005) for agricultural soils within the Minnesota River Basin. These observations could be related to management practices that result in a buildup of P in soils, unlike unmanaged forested watersheds like Bear Brook, as both the EPC and concentrations of soluble P in runoff have been shown to increase as a function of increasing soil P and DSP for soils of the Minnesota River basin (Fang et al. 2002). However, more information is needed in order to definitively associate source PP contributions to the EPC of TSS loads in large rivers. For instance, sediment erosion in the Minnesota River Basin has been strongly correlated to row crop area, population, and river discharge, with row crop area explaining 84 percent of the variation in sediment loss (Mulla et al. 2000). These relationships support the hypothesis that agricultural land use practice and PP erosion from the landscape are dominant contributors to Minnesota River loads. However, there is also evidence that stream bank erosion has increased in the past decade and represents a much larger proportion of the TSS load than once thought (Sekely et al. 2002).

The k_d for allochthonous TSS loads was moderate but within ranges reported for other river systems (i.e., average of approximately 500 L kg^{-1} ; Froelich 1988), suggesting well-buffered conditions. For instance, Wauchope and McDowell (1984) estimated a k_d of 400 L kg^{-1} for floodplain sediments of the lower Mississippi River. k_d ranged between 250 and $1,380 \text{ L kg}^{-1}$ for TSS in rivers of South America (Carignan and Vaithyanathan 1999). Mayer and Gloss (1980) reported a k_d of 600 L kg^{-1} for TSS of the Colorado River. Higher percentages of fine sand with

lower P affinity may have been a factor contributing to lower k_d for TSS of the lower Minnesota River (House 2003).

Table 7 Comparison of equilibrium phosphorus concentration (EPC) estimates for suspended and deposited sediments of various rivers		
System	EPC (mg L⁻¹)	Reference
Lower Minnesota River (USA)	0.117	Present study
Lake Pepin sediment (USA)	0.155	James and Barko (2004)
Redwood River (USA)	0.070	James et al. (2002)
Eau Galle River (USA)	0.129	James and Barko (2005)
Colorado River (USA)	0.040	Mayer and Gloss (1980)
Bermejo River (Argentina)	0.060	Carignan and Vaithyanathan (1999)
Paraguay River (Argentina)	0.020-0.090	Carignan and Vaithyanathan (1999)
Paraná River (Argentina)	0.005-0.021	Carignan and Vaithyanathan (1999)
Bear Brook (USA)	0.002	Meyer (1979)
NY wooded streams (USA)	<0.002	Klotz (1985)
Lower Mississippi River (USA)	0.108	Wauchope and McDowell (1984)
Xiangxi River (China)	0.100	Chang-Ying et al. (2006)

Total sediment P was positively related to sediment moisture content, silt content, and clay content and negatively related to sediment density and sand content, suggesting that the more flocculent sediments composed of finer particles were associated with a higher total sediment P concentration. Refractory P (i.e., sum of aluminum-bound, calcium-bound, and residual organic P) constituted the majority of sediment total P and it was dominated by residual organic P and calcium-bound P. The iron-bound P fraction accounted for most of the biologically labile sediment P (i.e., sum of loosely bound, iron-bound, and labile organic P) and concentrations were positively correlated with rates of P release from sediment under both oxic and anoxic conditions. These patterns coupled with higher rates of P release under anoxic conditions suggested that Fe-P interactions were important in P flux from sediments. Although the release rate was high under both oxic and anoxic conditions, relative contributions from sediment flux to the P budget were minor in relation to the much larger inputs from other point and nonpoint sources.

Regulation of SRP at high concentrations via equilibrium processes has much relevance to eutrophication and phytoplankton bloom potential for navigation pools of the Upper Mississippi River. Increasing channel width and depth caused by impoundment result in higher residence time, favoring phytoplankton growth and P uptake (Soballe and Kimmel 1987). It may be argued that high concentrations of soluble P are probably not limiting phytoplankton growth in agriculturally managed systems like the Minnesota and Upper Mississippi River. Indeed, bioavailable soluble P forms can account for nearly half of the total P in large rivers

(Turner et al. 2003) and concentrations are often in excess of $100 \mu\text{g L}^{-1}$ (Mainstone and Parr 2002). Yet, phytoplankton growth is still generally limited by P in these systems and productivity can increase in response to increased P loading (Van Nieuwenhuysse and Jones 1996; Mainstone and Parr 2002). This unusual trend may be linked to fertilizer use patterns that result in maintenance of a Redfield DIN:DRP ratio much greater than 16:1 (Howarth et al. 1996; Vitousek et al. 1997; Turner et al. 2003). Under these nutrient ratio conditions, buffering of SRP concentration by equilibrium processes with TSS can represent an important P source for phytoplankton growth in large river systems (James and Barko 2004).

Discharge variation was an important determinant in SRP dynamics in the lower Minnesota River by means of regulating phytoplankton biomass and P transformation. Unlike lakes and reservoirs with greater residence times, inter-relationships among discharge, loading, turbidity, and light penetration regulate phytoplankton biomass and growth in addition to nutrient limitation (Soballe and Kimmel 1987; Van Nieuwenhuysse and Jones 1996). There were many instances when chlorophyll increased with concomitant declines in SRP on the falling limb of the hydrograph or between discharge peaks, suggesting P desorption flux in response to phytoplankton uptake. However, an inverse relationship occurred between chlorophyll concentrations versus exchangeable PP or desorption P flux, due to probable influences of discharge and travel time on phytoplankton growth. Loading of exchangeable PP was low during periods of low discharge, and budgetary analysis indicated that SRP dynamics were regulated more by P loading from WWTPs and transformation to phytoplankton PP than by equilibrium reactions with TSS. As discharge and loading increased, SRP dynamics were controlled by buffering with TSS. Thus, biotic control of SRP and transformation to particulate P dominated under very low TSS loading while abiotic regulation of SRP and downstream transport occurred under higher TSS loading conditions.

Concentrations of loosely bound and iron-bound P were high and represented 43 percent of the PP load of the lower Minnesota River, which is in agreement with ranges reported for other agriculturally managed watersheds (Pacini and Gächter 1999; James et al. 2002; Uusitalo et al. 2003; James and Barko 2005; Jensen et al. 2006). These extractable PP fractions have been linked to sediment diffusive P flux under both oxic and anoxic conditions (Boström et al. 1982; Nürnberg 1988; Jensen and Thamdrup 1993; Peticrew and Arocena 2001; Søndergaard et al. 2003; Pilgrim et al. 2007) and, therefore, represent a quantifiable surrogate metric for estimating redox-sensitive PP loading and recycling potential in receiving water bodies. Transport of redox-sensitive PP derived from the Minnesota River and deposition in navigation pools of the Upper Mississippi River has implications for P dynamics, eutrophication, and recovery of these systems after management of point and nonpoint sources. For instance, Minnesota River TSS loads (20-year mean = $6 \times 10^5 \text{ Mg y}^{-1}$; Meyer and Schellhaass 2002) currently represent greater than 80 percent of sediment deposition rate in Lake Pepin of Navigation Pool 4 (1.5 cm y^{-1} ; Kelley and Nater 2000). Loosely bound and iron-bound P transported by the Minnesota River translate into a very high potential anoxic diffusive P flux of approximately $17 \text{ mg m}^{-2} \text{ d}^{-1}$, based on regression relationships developed by Nürnberg (1988). This estimate represents a minimum because differential deposition of sands versus silts and clays during transport probably results in some PP enrichment (e.g. Evans et al. 2004) and was not considered in the calculation. Intermittent stratification and development of anoxia above the sediment interface occur during periods of low discharge in navigation pools of the Upper Mississippi River (James and Barko

2004). In Lake Pepin (~60 km downstream in Navigation Pool 4), sediment diffusive P flux can account for greater than 30 percent of the P budget under these conditions (Larson et al. 2002) and is an important factor driving phytoplankton productivity.

Inter-relationships between discharge variation and the composition of Minnesota River PP loads also implied alternate recycling pathways during transport through large river systems (e.g. Carpenter 2005). Under low discharge conditions and increasing relative input by WWTP sources, transformation of P from soluble to particulate forms via biotic uptake and eventual senescence during transport and represented a rapid recycling pathway (Hupfer and Lewandowski 2005), analogous to a short nutrient spiraling length (Newbold 1992). In contrast, PP derived from watershed runoff undergoes slower recycling and diagenetic processes as deposited sediment and is subject to longer retention time and nutrient spiraling lengths, particularly for regulated rivers with locks and dams, fluvial tributary systems, and coastal marine environments. Overall, SRP regulation and recycling potential of both suspended and deposited TSS loads is high from agricultural watersheds like the Minnesota River and can contribute to long-term productivity and eutrophication of sensitive coastal systems.

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POINTS OF CONTACT: This technical note was written by William F. James of the Eau Galle Aquatic Ecology Laboratory, Environmental Laboratory (EL), U.S. Army Engineer Research and Development Center (ERDC). For additional information, contact the manager of the System-Wide Water Resources Research Program (SWWRP), Dr. Steven A. Ashby (601-634-2387, Steven.A.Ashby@usace.army.mil). This technical note should be cited as follows:

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