Biogeochemistry (2008) 90:75–92
DOI 10.1007/s10533-008-9232-5

ORIGINAL PAPER

Phosphorus dynamics and loading in the turbid Minnesota River (USA): controls and recycling potential

William F. James · Catherine E. Larson

Received: 7 March 2008 / Accepted: 7 August 2008 / Published online: 30 August 2008

Abstract Phosphorus (P) dynamics in the agriculturally-dominated Minnesota River (USA) were examined in the lower 40 mile reach in relation to hydrology, loading sources, suspended sediment, and chlorophyll to identify potential biotic and abiotic controls over concentrations of soluble P and the recycling potential of particulate P during transport to the Upper Mississippi River. Within this reach, wastewater treatment plant (WWTP) contributions as soluble reactive P (SRP) were greatest during very low discharge and declined with increasing discharge and nonpoint source P loading. Concentrations of SRP declined during low discharge in conjunction with increases in chlorophyll, suggesting biotic transformation to particulate P via phytoplankton uptake. During higher discharge periods, SRP was constant at $\sim$0.115 mg l^{-1} and coincided with an independently measured equilibrium P concentration (EPC) for suspended sediment in the river, suggesting abiotic control over SRP via phosphate buffering. Particulate P (PP) accounted for 66% of the annual total P load. Redox-sensitive PP, estimated using extraction procedures, represented 43% of the PP. Recycling potential of this load via diffusive sediment P flux under anoxic conditions was conservatively estimated as $\sim$17 mg m^{-2} d^{-1} using published regression equations. The reactive nature and high P recycling potential of suspended sediment loads in the Minnesota River has important consequences for eutrophication of the Upper Mississippi River.

Keywords Equilibrium phosphorus concentration · Phosphorus · Redox-sensitive phosphorus · Rivers · Soluble phosphorus · Suspended sediment

W. F. James (✉)
Engineer Research and Development Center, Eau Galle Aquatic Ecology Laboratory, W. 500 Eau Galle Dam Rd., Spring Valley, WI 54767, USA
e-mail: william.f.james@erdc.usace.army.mil

C. E. Larson
Metropolitan Council Environmental Services, 390 Robert St. North, St. Paul, MN 55101-1805, USA
e-mail: cathy.larson@metc.state.mn.us

Introduction

Excessive phosphorus (P) loading is a leading cause of eutrophication and water quality impairment of large floodplain rivers (i.e., >10,000 km^2), 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 our understanding of in-stream P dynamics comes from nutrient spiraling research on small tributaries under base flow 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 travel time (Soballe and Kimmel 1987). Under lower discharge conditions and higher travel time, biological uptake by phytoplankton can play an important role in P retention and transformation (Van Nieuwenhuyse 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 become 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 travel time, and phytoplankton washout and dilution (Soballe and Kimmel 1987; Reynolds 2006). 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 through 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 discharge and loading. 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 km^2 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 (>73% of the watershed; Meyer and Schellhaass 2002). P dynamics are also influenced by point source inputs from wastewater treatment plants (WWTPs) servicing the metropolitan areas of Minneapolis-St. Paul (pop. 2.9 million), Mankato (pop. 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 during low discharge periods and development of hypoxic conditions in these pools.

Concerns over high P loading from the Minnesota River and influences on downstream receiving pools of the Mississippi River led to an investigation of P dynamics in the lower 40 miles (63 km) of the river flowing through the metropolitan area of Minneapolis-St. Paul, Minnesota. Our objectives were to quantify the major point and nonpoint source P loads entering this reach and to examine the P dynamics, as affected by biotic (phytoplankton) and abiotic (equilibrium) processes, in relation to hydrology of the system. We hypothesized that soluble P is regulated by equilibrium processes with suspended sediment of allochthonous nonpoint source origin during higher discharge periods, with little transformation via phytoplankton uptake due to rapid flushing, cellular washout, and dilution. During periods of lower discharge, soluble P concentrations may be influenced by greater relative contribution from WWTP sources and transformation to particulate forms via phytoplankton uptake. 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.

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, a regional agency, has maintained long-term sampling stations for more than 40 years (Fig. 1). River bathymetry changes below RM 14.7 due to the 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 WWTPs 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 for each = 1.8 $m^3\ s^{-1}$) at effluent P concentrations of 1.5 mg l^{-1} or less. A 538-megawatt power generating plant (Black Dog GP) pumps water from the Minnesota River at RM 8.8 for cooling condensers. The heated water is then routed into a cooling lake 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% of the volumetric flow when Minnesota River discharge is <50 $m^3\ s^{-1}$ (i.e., primarily during late autumn and winter). Meyer and Schellhaass (2002) reported high mean annual flow-weighted concentrations of 93 mg l^{-1} suspended sediment, 0.3 mg l^{-1} total phosphorus, and 56 μg l^{-1} total chlorophyll for the lower Minnesota River (i.e., downstream of RM 40) over a 20-year period. Diatoms (primarily *Cyclotella* sp.) account for >80% of the phytoplankton assemblage during the summer.

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) for determination of concentrations of biologically labile and refractory PP fractions (Fig. 1). Twenty liters of river water were collected at each station via surface grab sampling during periods of high discharge (i.e., >200 $m^3\ s^{-1}$) and suspended sediment concentration in 2005 and 2006 (five events during each year). A portion of the sample was filtered in the laboratory onto 0.45 μm membrane filters and dried at 105°C to a constant weight for the determination of total suspended solids (TSS; American Public Health Association 1998). Another portion was filtered through a 0.45 μm 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% chloroform and refrigeration at 4°C for determination of PP fractions. Analyses were conducted within 2 weeks of sample collection. Sequential fractionation of PP (Table 1) was conducted according to Hjieltjes and Lijklema (1980), Psenner and Puckso (1988), and

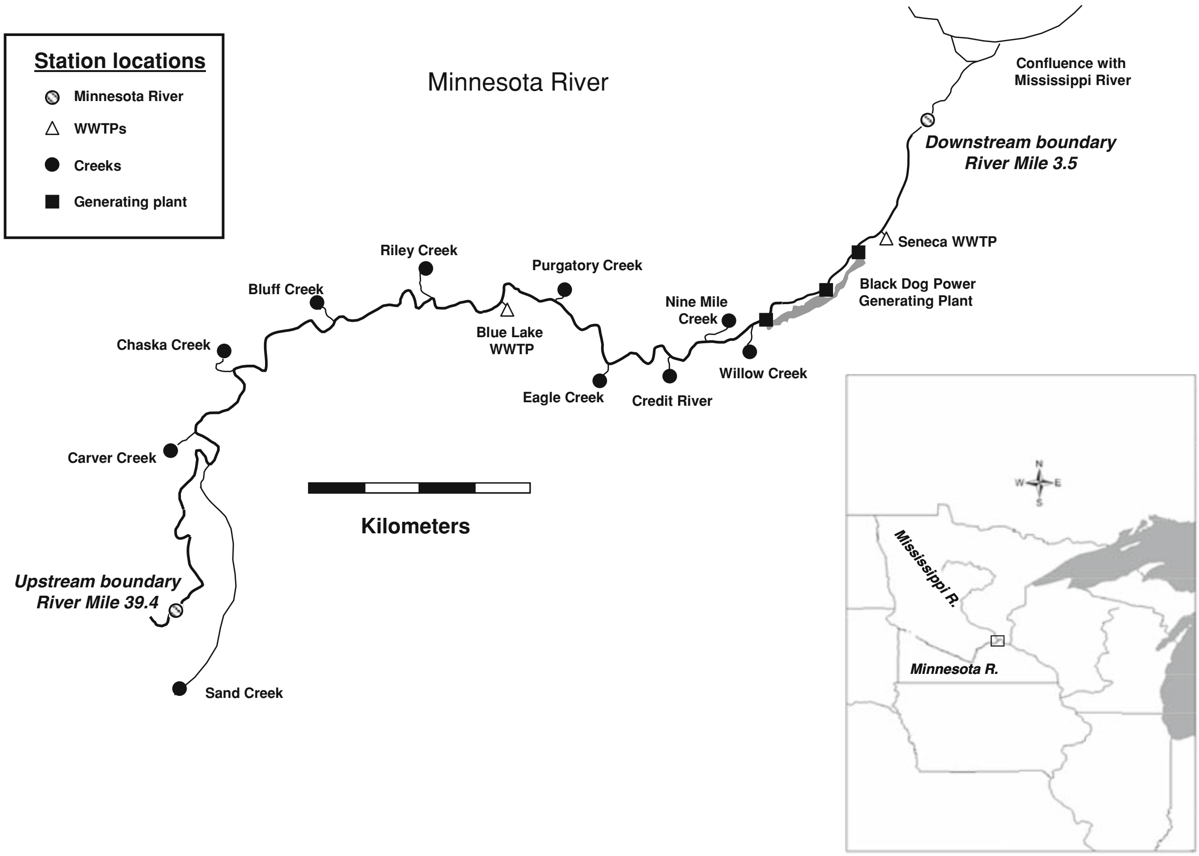

Fig. 1 Monitoring stations located on the lower portion of the Minnesota River, Blue Lake and Seneca wastewater treatment plants (WWTP), the various creeks, and the Black Dog power generating plant

Table 1 Operationally-defined particulate phosphorus (PP) fractions

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

Biologically labile = Subject to recycling pathways; Biologically refractory = Low recycling potential and subject to burial

Nürnberg (1988) for the determination of 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 for determination of refractory organic PP. Each extraction was adjusted to pH 7 and analyzed for SRP using the ascorbic acid method (American Public Health Association 1998).

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 same concentrated suspended sediment used for determination of PP fractions were subjected to SRP (KH_2PO_4) standards ranging from 0 to 1.0 mg l^{-1} for examination of P adsorption and desorption after 24 h. Time series analysis confirmed that equilibrium was achieved within 24 h. 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 $MgSO_4$ 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 ~8.0–8.3 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 final equilibrium SRP to determine the linear adsorption 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 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 P sorption maximum (S_{max}) of TSS. The general linearized model is

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

where C equals the equilibrium SRP concentration and K represents the binding strength coefficient (l kg^{-1}). Because P desorption occurred at a 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 loosely-bound and 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}.

Water chemistry and loading analysis

Stage elevation and discharges were monitored continuously between 2003 and 2006 at stations established on 12 small creeks draining into the lower Minnesota River, the Minnesota River at RM 39.4 and RM 3.5, the two WWTPs, and the inflow and two outflow structures associated with the Black Dog GP (Fig. 1). Travel time between RM 39.4 and RM 3.5 was estimated over different discharges at RM 39.4 using the model Hydrologic Engineering Centers River Analysis System (HEC-RAS; Warner et al. 2008) and relationships developed between discharge at RM 39.4 and flow velocity based on dye tracer studies (US Geological Survey and Minnesota Pollution Control Agency, unpubl. data). Water samples were collected biweekly to monthly over 3 years at the creek stations, weekly to biweekly at the Minnesota River stations, and five per week at the WWTPs. Additional event-composited samples were collected at the creek stations and at RM 39.4. Water samples were collected at the Black Dog GP inflow and outflow 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, loss-on-ignition organic matter (LOI), total Kjeldahl N, nitrate plus nitrite-N, ammonium-N, total P, total soluble P, SRP, viable chlorophyll, and pheaophytin following standard analytical procedures (American Public Health Association 1998). Sample was passed through a 0.45 μm membrane filter for determination of 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 for determination of TSS and LOI, respectively. Additional sample filtered onto a glass fiber filter was extracted with 90% acetone for determination of viable chlorophyll and phaeophytin. Concentrations of LOI, chlorophyll, and PP were divided by TSS concentration to calculate constituent 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 2 week periods exhibiting relatively constant low discharge or bracketing a discharge peak or trough on the hydrograph were chosen for budgetary analysis.

Statistical analyses

Regression relationships between variables were analyzed using the Statistical Analysis System (1994). Hypothesis testing for significant differences in the slope of regression equations developed for stations RM 39.4 and RM 3.5 was analyzed using the Statistical Analysis System (1994) General Linear Modeling (GLM) and Regression (REG) Procedures.

Results

Particulate phosphorus composition and equilibrium characteristics

The 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% and 43% of the biologically labile and total PP, respectively. Calcium-bound (53%) and refractory organic PP (31%) accounted for most of the refractory PP.

Phosphorus desorption from TSS occurred at very low aqueous concentrations of SRP while adsorption occurred above an EPC of 0.117 mg l^{-1} (±0.012 S.E.; Fig. 2). In addition, the EPC was equivalent to the

Table 2 Biologically labile and refractory particulate phosphorus (PP) fraction means (mg kg^{-1}; $n = 20$), standard errors (S.E.), and percent composition for allochthonous TSS loads in the lower Minnesota River, 2005–2006

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

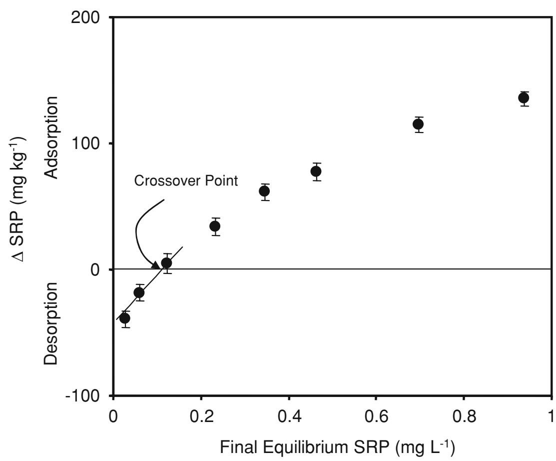

Fig. 2 Adsorption–desorption isotherm for allochthonous total suspended solids collected from the lower Minnesota River during periods of high discharge (<200 m^3 s^{-1}). Mean (±1 S.E.; $n = 10$) final equilibrium soluble reactive phosphorus (SRP) represents the concentration in the aqueous phase after continuous shaking over 24 h. ΔSRP is the change in the SRP concentration per TSS dry mass after 24 h. A negative ΔSRP indicates desorption and a positive ΔSRP represents adsorption. The crossover point is equal to the equilibrium phosphorus concentration

mean ambient concentration of SRP in the river determined at the time of TSS collection (0.116 mg $l^{-1} \pm 0.003$ S.E.), suggesting equilibrium control of SRP by TSS loads during higher discharge periods. The k_d and S_{max} were 332 l kg^{-1} ($\pm$31 S.E.) and 608 mg kg^{-1} ($\pm$16 S.E.), respectively. The DSP was high at 69%.

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 (Fig. 3a, b). 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 flow periods ($ln\ TSS_{RM39.4} = 0.352 \cdot ln\ Discharge_{RM39.4} + 3.002$, $r^2 = 0.27$, $p < 0.0001$; $ln\ TSS_{RM3.5} = 0.425 \cdot ln\ Discharge_{RM3.5} + 2.265$, $r^2 = 0.44$, $p < 0.0001$). Chlorophyll concentrations were lowest during the winter months of December through March (Fig. 3c). For other months, chlorophyll was highest during periods of lower discharge and declined as a result of higher discharge ($ln\ CHLA_{RM39.4} = -0.484 \cdot ln\ Discharge_{RM39.4} + 6.602$, $r^2 = 0.52$, $p < 0.0001$; $ln\ CHLA_{RM3.5} = -0.381 \cdot ln\ Discharge_{RM3.5} + 5.950$, $r^2 = 0.33$, $p < 0.0001$). 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 concentrations at RM 3.5 versus RM 39.4 as a function of decreasing discharge. These patterns were most likely 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 (Fig. 3d). 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 (Fig. 4). High chlorophyll concentrations also coincided with periods of low discharge when point sources from within the reach increasingly dominated P loading, primarily as SRP (Fig. 5). In addition, SRP decreased on the falling limb of hydrograph peaks in conjunction with increases in chlorophyll (Fig. 3e). 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 (Fig. 3b, c). Concentrations of SRP were similar at both stations and near the EPC under these conditions (Fig. 3e). 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 (Fig. 6). The concentration declined toward zero under conditions of low TSS and PP loading (Fig. 6).

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 (Fig. 3e). Diffusive P flux from sediments was high at 3.9 mg $m^{-2}\ d^{-1}$ in the vicinity of RM 3.5 (W. F. James, unpubl. data), but a mass balance analysis (not shown) indicated that this source was minor (<10%) in relation to other inputs and that phytoplankton senescence combined with WWTP sources located below RM 39.4 were largely responsible for SRP increases at RM 3.5 (WWTP contribution = 31% and 75% 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 (Fig. 3e). 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.

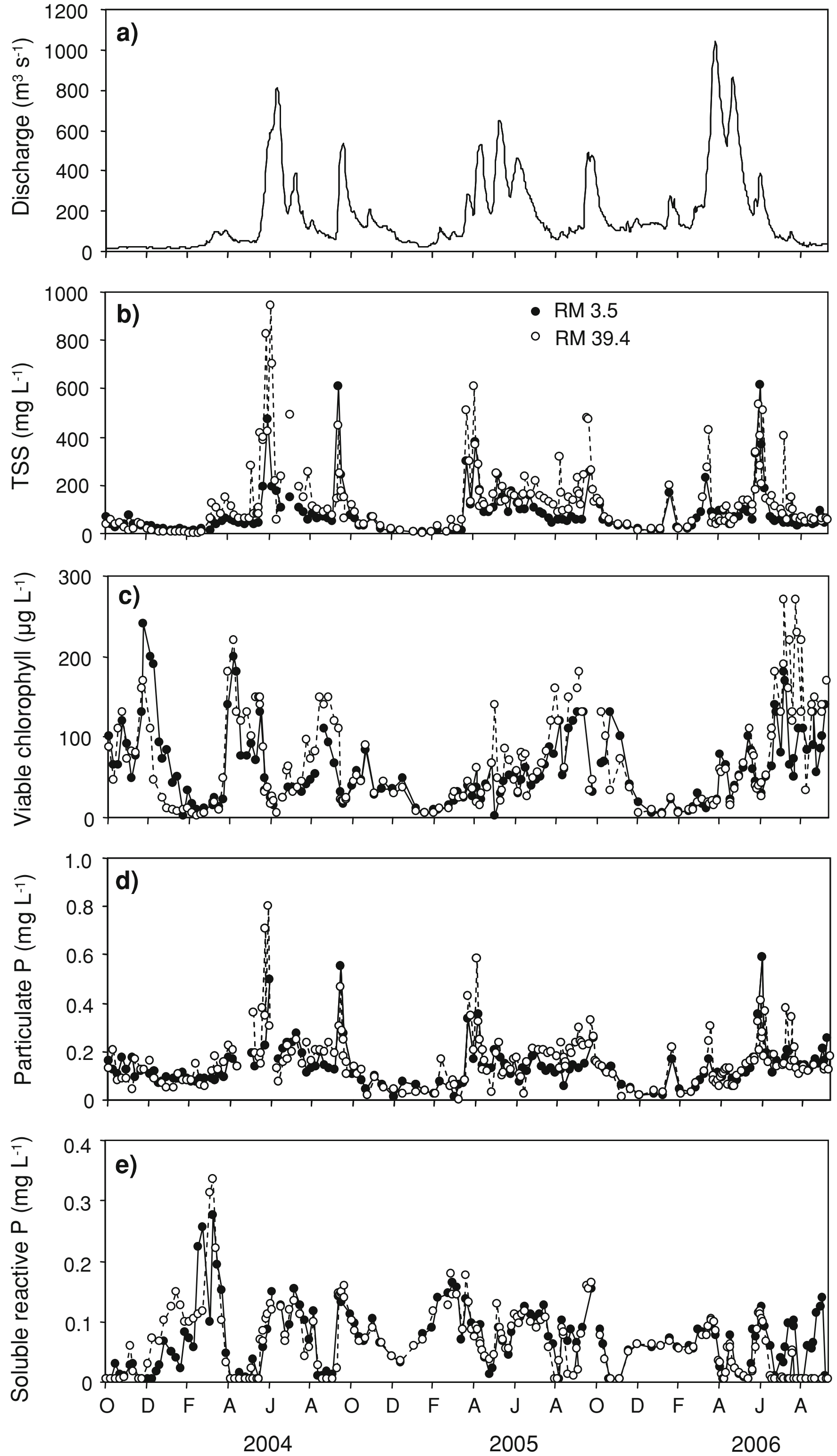

Fig. 3 Seasonal variations in (**a**) discharge at river mile (RM) 3.5, (**b**) total suspended solids (TSS), (**c**) viable chlorophyll a, (**d**) particulate phosphorus (P), and (**e**) soluble reactive P at RM 3.5 and 39.4 of the lower Minnesota River during October 2003 through September 2006

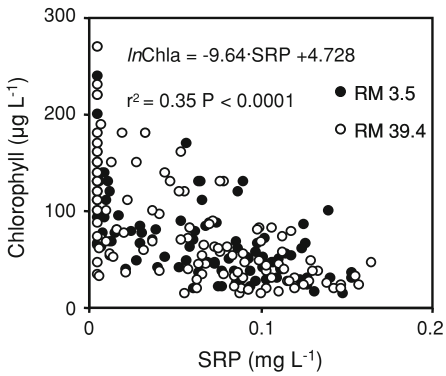

Fig. 4 Relationships between soluble reactive phosphorus (SRP) and viable chlorophyll a concentration. Data from river mile (RM) 3.5 and RM 39.4 were combined for regression analysis

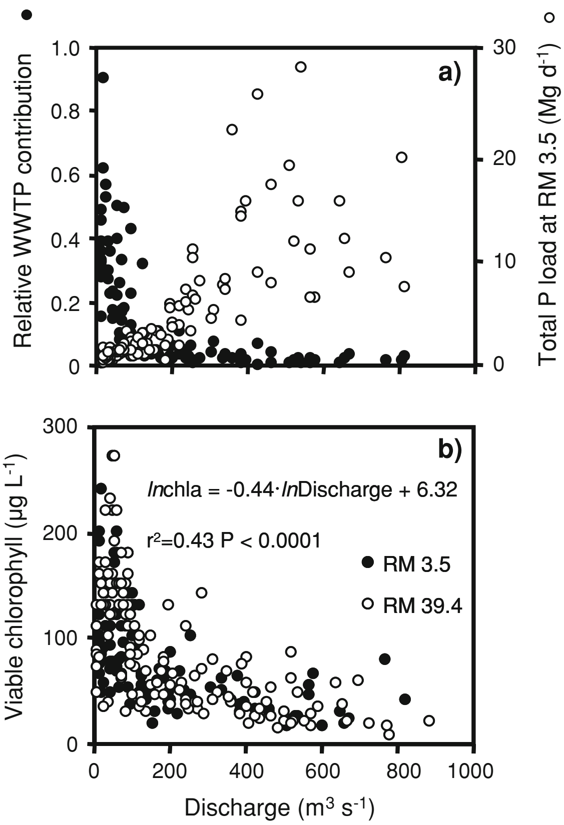

Fig. 5 Relationships between discharge and (**a**) relative wastewater treatment plant (WWTP) contributions (solid circles) or total phosphorus (P) load (open circles) for the Minnesota River at river mile (RM) 3.5 and (**b**) viable chlorophyll a concentration for the April through November period, 2004–2006. Data from river mile (RM) 3.5 and RM 39.4 were combined for regression analysis

Differences in the composition of TSS versus discharge (Fig. 7) were used to delineate allochthonous and autochthonous sources of TSS loads for different 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 biomass at lower discharges (Fig. 7a, b). The organic matter content ranged between 40% and 60% (mean = 41.5% ± 1.9 S.E.) for discharges <20 $m^3\ s^{-1}$ (travel time > 5 days), which fell within ranges reported for freshwater diatoms (45–58.6%; Reynolds 1984). TSS composition was dominated by inorganic components of allochthonous origin when discharge exceeded ~125 $m^3\ s^{-1}$ (travel time <1.3 days) and phytoplankton biomass indicators declined to an asymptotic minimum with increasing discharge (LOI = 9.7% and chlorophyll = 0.03%). PP content exhibited a similar logarithmic pattern (Fig. 7c). 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%.

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., P adsorption or desorption) when the concentration of SRP deviated from the EPC. We assumed that an organic matter content endpoint of 40% represented TSS composed of primarily phytoplankton biomass, while an endpoint of 10% reflected allochthonous loading originating upstream 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. Loadings of TSS and PP were partitioned into phytoplankton versus allochthonous material based on these relative proportions. The exchangeable PP load was estimated as 43% of the allochthonous TSS load (Table 2). Equilibrium P flux (kg d^{-1}) between the exchangeable PP pool and

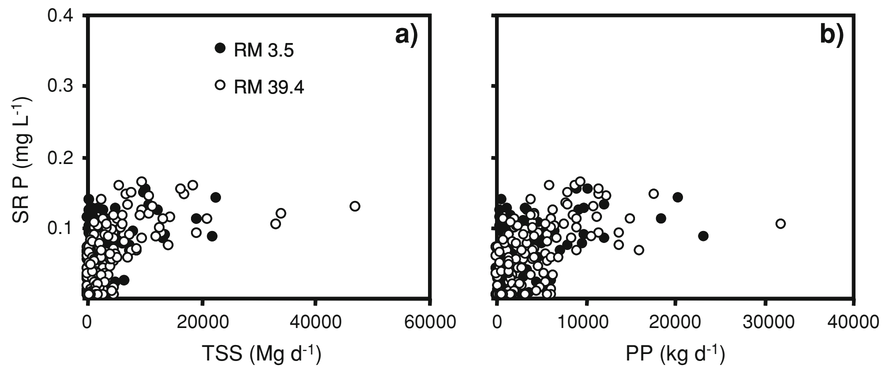

Fig. 6 Variations between soluble reactive phosphorus (SRP) concentration and (**a**) total suspended solids (TSS); (**b**) particulate phosphorus (PP) loading for the April through November period, 2004–2006

water was calculated as, $[(EPC - SRP_{Ambient})k_d]$ *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 (Froelich 1988). We estimated equilibrium P flux for summer months only because temperature effects were not factored into the equilibrium experiments (Barrow 1979).

The exchangeable PP load increased in conjunction with discharge and peaks in total P and SRP loading (Fig. 8). 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% of these loads. Desorption P flux decreased as a function of decreasing discharge (ln Desorption P $Flux_{RM39.4} = 0.970 \cdot ln$ $Discharge_{RM39.4}$–1.80, $r^2 = 0.47$, $p < 0.0001$; ln Desorption P $Flux_{RM3.5} = 1.621 \cdot ln$ $Discharge_{RM3.5} - 5.827$, $r^2 = 0.77$, $p < 0.0001$). 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 (ln chlorophyll $= -0.69 \cdot ln$ exchangeable PP load $+ 4.11$, $r^2 = 0.72$, $p < 0.0001$) and desorption P flux (ln chlorophyll $= -0.45 \cdot ln$ desorption P flux $+ 8.47$, $r^2 = 0.39$, $p < 0.0001$) due to influences of discharge on chlorophyll concentration.

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 (76% of the input load; Table 3). Discharge output approximately balanced discharge inputs and travel time between RM 39.4 and RM 3.5 was ~3 days. SRP output loading was considerably less than SRP input loading during this period, resulting in a very high SRP uptake efficiency (>90%). 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 (2.1 kg d^{-1}) relative to total 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% for TSS and high chlorophyll concentrations in excess of 100 μg l^{-1}. A similar budgetary imbalance (SRP uptake efficiency = 60%; SRP uptake rate = 121 kg d^{-1}) occurred during another low discharge period (69 m^3 s^{-1}; Fig. 3) in August, 2004, in conjunction with chlorophyll concentrations in excess of 140 μg l^{-1} and SRP concentrations <0.033 mg l^{-1} at RM 39.4 and near the detection limit of 0.005 mg l^{-1} at RM 3.5 (not shown). Since exchangeable PP loading and equilibrium P fluxes were minor, and chlorophyll concentrations were high, we attribute

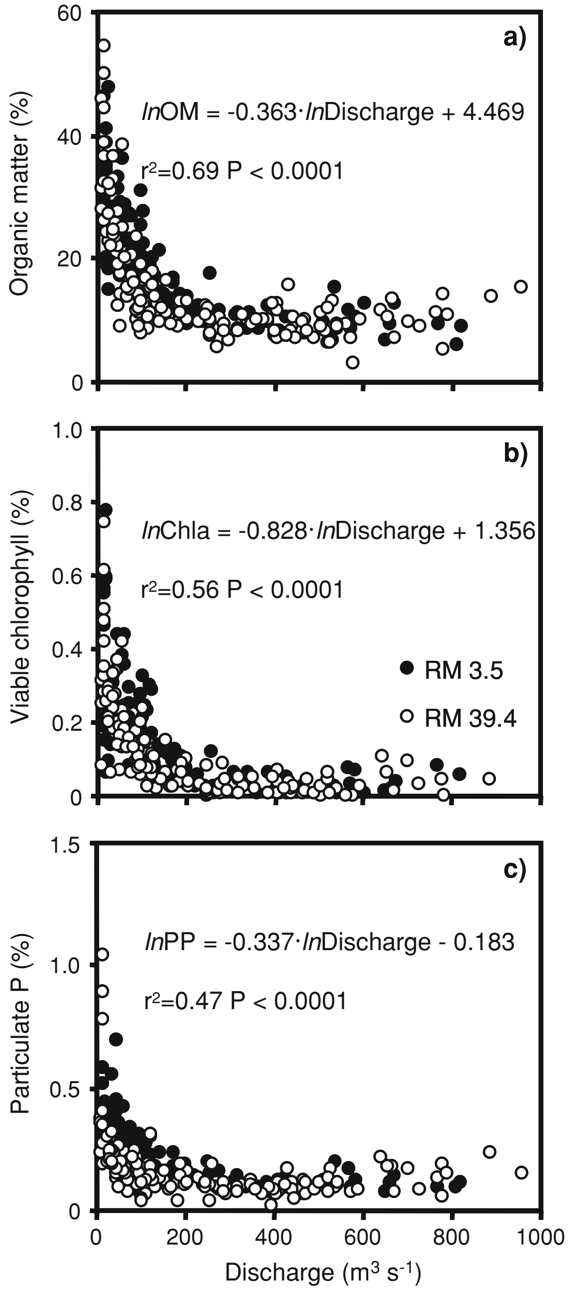

Fig. 7 Relationships between discharge and (**a**) organic matter (as loss-on-ignition), (**b**) viable chlorophyll a, and (**c**) particulate P content (as a percentage of total suspended solids) for the April through November period, 2004–2006. Data from RM 3.5 and RM 39.4 were combined for regression analysis

the high SRP uptake efficiencies during these low discharge periods to biotic uptake of SRP and transformation to PP.

During a period of peak discharge in June, 2004 (Table 3), travel time between RM 39.4 and RM 3.5 was <1.6 days. SRP input loads were dominated by the Minnesota River at RM 39.4 (97% of the input load), while WWTP loads were negligible by comparison (<2% of the input load). SRP output loading was $\sim$3% lower than input loading under these conditions, resulting in minor SRP uptake that was well within the range of analytical and flow measurement error (Bukaveckas et al. 2005). SRP concentration in the Minnesota River was slightly greater than the EPC during this period (i.e., 0.120 mg l^{-1} versus 0.117 mg l^{-1}), driving abiotic uptake of SRP via adsorption onto suspended sediment particles. The estimated adsorption P flux of 364 kg d^{-1} more than accounted for the SRP uptake during this period. Concentrations of chlorophyll were <20 μg l^{-1}, which also suggested that biotic uptake was negligible.

During periods of intermediate discharge and travel times ranging between 1.2 and 1.4 days in June, 2005 and 2006 (Table 3), the Minnesota River at RM 39.4 accounted for >90% of the SRP input to the system. Inputs from WWTPs represented only 3–4% of the total SRP input loading during these periods. The SRP uptake rate was high relative to other periods, but represented <10% 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 (Table 3). The loading imbalances were more likely attributable to biotic uptake as chlorophyll concentrations were high, ranging between 41 and 72 μg l^{-1}. Although, desorption P fluxes of 41 and 25 kg d^{-1} occurred in June of 2005 and 2006, respectively, they were minor in relation to SRP loading inputs from the Minnesota River because ambient SRP concentrations (range = 0.099–0.106 mg l^{-1}) were near the EPC.

On an annual basis, the Minnesota River at RM 39.4 dominated hydrological inputs to the system during the 3-year period and discharge inputs approximately balanced outputs (Table 4). RM 39.4 also accounted for most of the total P and SRP loading to the lower Minnesota River and SRP represented 28–33% of the total P loading. Annual total P loading from WWTPs was minor in relation to river and creek total P loading. However, WWTP inputs represented a larger percentage of the SRP loading to the system, ranging between $\sim$6 and 13%. Annual total P and SRP uptake rates were negligible in relation to input during the 3-year period.

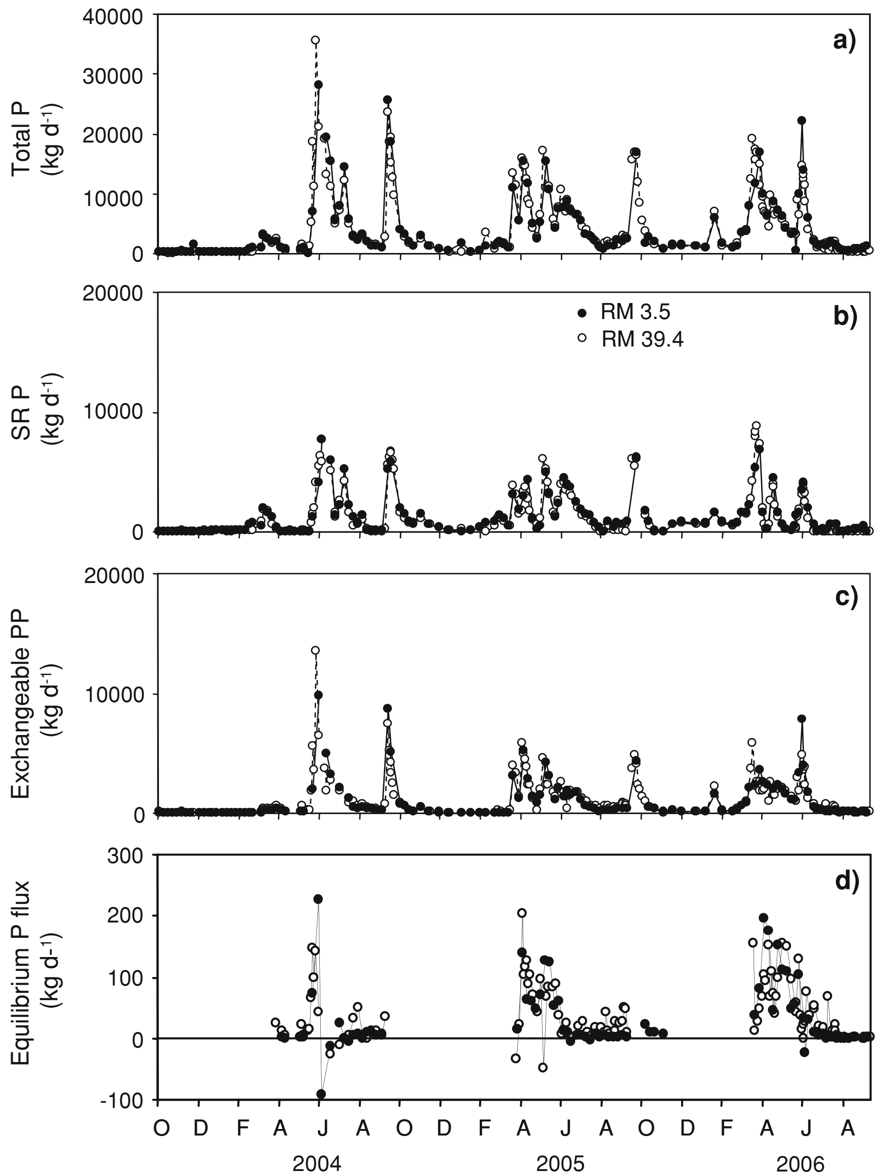

Fig. 8 Variations in (**a**) total phosphorus (P) loading, (**b**) soluble reactive P (SRP) loading, (**c**) exchangeable particulate P (PP) loading (i.e., loosely-bound and iron-bound PP), and (**d**) equilibrium P flux between particulate and aqueous phases. A positive equilibrium P flux represents desorption from exchangeable PP to the water column while a negative flux represents adsorption of P onto the exchangeable PP pool

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. We assumed that biologically labile and refractory PP fractions determined for TSS collected during high discharges were a constant percentage of the annual PP load. This assumption was reasonable since greater than 70% of the loading occurred for discharges > 200 m^3 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 (Fig. 9). The combined soluble P and biologically labile PP accounted for an average 67% (range = 64–70%) of the total P load discharged into the Upper Mississippi 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}. The SRP concentration in the lower Minnesota River converged with the independently measured EPC as

Table 3 Soluble reactive phosphorus (SRP) input, output, and uptake loading for various 2 week periods between 2003 and 2006

Two-week period beginning	SRP input			SRP output			SRP uptake	
	Discharge ($m^3\ s^{-1}$)	Load[a] ($kg\ d^{-1}$)	Conc.[b] ($mg\ l^{-1}$)	Discharge ($m^3\ s^{-1}$)	Load ($kg\ d^{-1}$)	Conc. ($mg\ l^{-1}$)	Load[c] ($kg\ d^{-1}$)	Efficiency[d] (%)
8/16/06	38	159 (22)	0.040	36	5 (1)	0.023	154	96.8
6/16/06	294	2838 (157)	0.105	296	2584 (196)	0.101	254	8.9
6/9/05	420	3867 (207)	0.106	424	3621 (138)	0.099	246	6.4
6/6/04	711	7185 (285)	0.123	687	7109 (810)	0.120	223	3.0

SRP input loading was 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, and equilibrium SRP flux. The lower Minnesota River at RM 3.5 represented SRP output loading from the reach

[a] Standard error shown in parentheses

[b] Flow-weighted mean SRP concentration

[c] Calculated as SRP input minus output loading

[d] SRP uptake loading divided by SRP input loading and multiplied by 100

Table 4 Annual input, output, and uptake 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	
		($m^3\ s^{-1}$)	(%)[a]	($kg\ year^{-1}$)	(%)[a]	($kg\ year^{-1}$)	(%)[a]
2004							
Inputs	Minnesota river—RM 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—RM 3.5	126.3		1405095		412217	
Net change	Retention or export[b]	−0.9	100.8	72222	4.9	21320	4.9
2005							
Inputs	Minnesota River—RM 39.4	165.1	94.1	1381346	91.2	461762	88.7
	Creeks	5.6	3.2	66869	4.4	19835	3.8
	Point sources	4.8	2.7	66776	4.4	39205	7.5
Outputs	Minnesota river—RM 3.5	178.5		1381346		513897	
Net change	Retention or export[b]	−3.0	101.7	133645	8.8	6905	1.3
2006							
Inputs	Minnesota river—RM 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—RM 3.5	237.0		1517663		450477	
Net change	Retention or export[b]	−2.5	101.1	185282	10.9	65317	12.7

[a] Percentage of total input

[b] Positive rate indicates retention while a negative rate represents export

TSS and PP loading increased because of higher discharge. The strong correspondence between measured EPC and ambient SRP concentration indicated that equilibrium reactions between TSS of allochthonous origin and aqueous phases were regulating concentrations of SRP at higher discharge and TSS loading. This finding is consistent with other evidence demonstrating equilibrium control of SRP by suspended particulate material in overland runoff and in turbid river systems (Mayer and Gloss 1980;

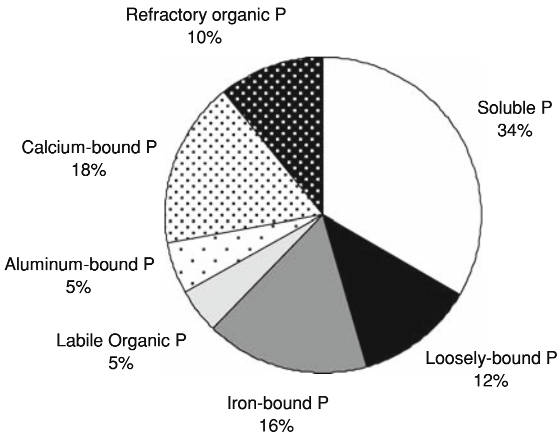

Fig. 9 Contribution of biologically labile (solid shades) and refractory (dotted shades) phosphorus (P) fractions to the annual average (i.e., between 2004 and 2006 for RM 39.4 and RM 3.5 combined) total P load of the lower Minnesota River

Froelich 1988; Carignan and Vaithiyanathan 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 5). 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 agricultural management practices that result in a buildup of P in soils, unlike unmanaged forested watersheds like Bear Brook, because 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, 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 value for k_d was moderate but within ranges reported for other river systems (i.e., average of $\sim$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 l kg^{-1} for TSS in rivers of South America (Carignan and Vaithiyanathan 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).

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). However, 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 Rivers. 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

Table 5 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 Vaithiyanathan (1999)
Paraguay River (Argentina)	0.020–0.090	Carignan and Vaithiyanathan (1999)
Paraná River (Argentina)	0.005–0.021	Carignan and Vaithiyanathan (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)

excess of 100 μg 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 Nieuwenhuyse 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 and fate 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 Nieuwenhuyse 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 generally occurred between chlorophyll concentrations versus exchangeable PP loading or desorption P flux, due to probable negative influences of greater discharge and higher turbidity 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 represented 43% 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; Petticrew 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, the Minnesota River TSS loads (20-year mean = 6×10^5 Mg $year^{-1}$; Meyer and Schellhaass 2002) currently represent >80% of sediment deposition rate in Lake Pepin of Navigation Pool 4 (1.5 cm $year^{-1}$; 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 $\sim$17 mg m^{-2} d^{-1}, based on regression relationships developed by Nürnberg (1988). This estimate represents a minimum because differential deposition of sands versus silts and clays during transport probably results in some particulate P enrichment (e.g., Evans et al. 2004) and was not considered in our calculation. Intermittent stratification and development of anoxia above the sediment interface occur during periods of low discharge in navigation pools of the Upper Mississippi River (James and Barko 2004). In Lake Pepin ($\sim$60 km downstream in Navigation Pool 4), sediment diffusive P flux can account for >30% 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 PP loads in the Minnesota River also implied alternate recycling pathways (e.g., Carpenter 2005) during transport through large river systems. 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 represents 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 distributary 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.

Acknowledgements Metropolitan Council Environmental Services (MCES) of St. Paul, MN, and the US Army Engineer District, St. Paul (USAE St. Paul), are gratefully acknowledged for funding this research. We thank H. Eakin and L. Pommier of the Engineer Research and Development Center (ERDC) Eau Galle Aquatic Ecology Laboratory, K. Jensen, S. Schellhaass, and personnel of MCES for sampling, chemical analyses, and database compilation, A. Buesing (USAE St. Paul) and D. Smith (ERDC) for modeling travel time, and anonymous reviewers for helpful comments that improved this manuscript. Additional funding was provided by the Engineer Research and Development Center System-Wide Water Resources Program. Permission to publish this information was granted by the Chief of Engineers.

References

Alexander RB, Smith RA, Scharz GE (2000) Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 503:758–761. doi:10.1038/35001562

American Public Health Association (1998) Standard methods for the examination of water and wastewater, 20th edn. Washington, DC

Aminot A, Andrieux F (1996) Concept and determination of exchangeable phosphate in aquatic sediments. Water Res 30:2805–2811. doi:10.1016/S0043-1354(96)00192-3

Barrow NJ (1979) Three effects of temperature on the reactions between inorganic phosphate and soil. Eur J Soil Sci 30:271–279. doi:10.1111/j.1365-2389.1979.tb00984.x

Bennett EM, Carpenter SR, Caraco NF (2001) Human impact on erodable phosphorus and eutrophication: a global perspective. Bioscience 51:227–234. doi:10.1641/0006-3568(2001)051[0227:HIOEPA]2.0.CO;2

Berner RA, Rao J-L (1994) Phosphorus in sediment of the Amazon River and estuary: implications for the global flux of phosphorus to the sea. Geochim Cosmochim Acta 58:2333–2339. doi:10.1016/0016-7037(94)90014-0

Bolster CH, Hornberger GM (2007) On the use of linearized Langmuir equations. Soil Sci Soc Am J 71:1796–1806. doi:10.2136/sssaj2006.0304

Boström B, Jansson M, Forsberg C (1982) Phosphorus release from lake sediments. Arch Hydrobiol Beih Ergebn Limnol 18:5–59

Bukaveckas PA, Guelda DL, Jack J, Koch R, Sellers T, Shostell J (2005) Effects of point source loadings, sub-basin inputs and longitudinal variation in material retention on C, N and P delivery from the Ohio River Basin. Ecosystems (NY, Print) 8:825–840. doi:10.1007/s10021-005-0044-3

Carignan R, Vaithiyanathan P (1999) Phosphorus availability in the Paraná lakes (Argentina): influence of pH and phosphate buffering by fluvial sediments. Limnol Oceanogr 44:1540–1548

Carpenter SR (2005) Eutrophication of aquatic ecosystems: bistability and soil phosphorus. Proc Natl Acad Sci USA 102:10002–10005. doi:10.1073/pnas.0503959102

Carpenter SR, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VH (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol Appl 8:559–568. doi:10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2

Chang-Ying F, Fang T, Sheng Deng N (2006) The research of phosphorus of Xiangxi River nearby Three Gorges, China. Environ Geol 49:923–928. doi:10.1007/s00254-005-0124-x

Chételat J, Pick FR, Hamilton PB (2006) Potamoplankton size structure and taxonomic composition: influence of river size and nutrient concentrations. Limnol Oceanogr 51:681–689

Cole JJ, Peierls BL, Caraco NJ, Pace ML (1993) Nitrogen loading of rivers as a human-driven process. In: McDonnell MJ, Pickett STA (eds) Humans as components of ecosystems: the ecology of subtle human effects and populated areas. Springer-Verlag, Berlin

Davis RL, Zhang H, Schroder JL, Wang JJ, Payton ME, Zazulak A (2005) Soil characteristics and phosphorus level effect on phosphorus loss in runoff. J Environ Qual 34:1640–1650. doi:10.2134/jeq2004.0480

Ekholm P (1994) Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland. Hydrobiol 287:179–194

Evans DJ, Johnes PJ, Lawrance DS (2004) Physico-chemical controls on phosphorus cycling in two lowland streams. Part 2—the sediment phase. Sci Total Environ 329:165–182. doi:10.1016/j.scitotenv.2004.02.023

Fang F, Brezonik PL (2002) Phosphorus retention by river suspended sediment in the Minnesota-Mississippi Rivers system. Thesis, University of Minnesota

Fang F, Brezonik PL, Mulla DJ, Hatch LK (2002) Estimating runoff phosphorus losses from calcareous soils in the Minnesota River Basin. J Environ Qual 31:1918–1929

Fang F, Brezonik PL, Mulla DJ, Hatch LK (2005) Characterization of soil algal bioavailable phosphorus in the Minnesota River Basin. Soil Sci Soc Am J 69:1016–1025

Froelich PN (1988) Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. Limnol Oceanogr 33:49–668

Gächter R, Meyer JS, Mares A (1988) Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnol Oceanogr 33:1542–1558

Goolsby DA, Battaglin WA (2001) Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. Hydrol Process 15:1209–1226. doi:10.1002/hyp.210

Gosselain V, Viroux L, Desey J-P (1998) Can a community of small-bodied grazers control phytoplankton in rivers? Freshw Biol 39:9–24. doi:10.1046/j.1365-2427.1998.00258.x

Guildford SJ, Hecky RE (2000) Total nitrogen, total phosphorus, and nutrient limitation in lakes and oceans: is there a common relationship? Limnol Oceanogr 45:1213–1223

Hjieltjes AH, Lijklema L (1980) Fractionation of inorganic phosphorus in calcareous sediments. J Environ Qual 8:130–132

House WA (2003) Geochemical cycling of phosphorus in rivers. Appl Geochem 18:739–748. doi:10.1016/S0883-2927(02)00158-0

House WA, Denison FH (1998) Phosphorus dynamics in a lowland river. Water Res 32:1819–1830. doi:10.1016/S0043-1354(97)00407-7

House WA, Denison FH (2000) Factors influencing the measurement of equilibrium phosphate concentrations in river sediments. Water Res 34:1187–1200. doi:10.1016/S0043-1354(99)00249-3

Howarth RW, Jensen HS, Marino R, Postma H (1995) Transport to and processing of P in near-shore and oceanic waters. In: Golterman HL, Serrano L (eds) Phosphate in sediments. Backuys Publ., Leiden

Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K et al (1996) Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35:75–139. doi:10.1007/BF02179825

Howarth RW, Sharpley A, Walker D (2002) Sources of nutrient pollution to coastal waters in the United States: implications for achieving coastal water quality goals. Estuaries 25:656–676

Hupfer M, Lewandowski J (2005) Retention and early diagenetic transformation of phosphorus in Lake Arendsee (Germany)—consequences for management strategies. Arch Hydrobiol 164:143–167. doi:10.1127/0003-9136/2005/0164-0143

James WF, Barko JW (2004) Diffusive fluxes and equilibrium processes in relation to phosphorus dynamics in the Upper Mississippi River. River Res Appl 20:473–484. doi:10.1002/rra.761

James WF, Barko JW (2005) Biologically labile and refractory phosphorus loads from the agriculturally-managed Upper Eau Galle River watershed, Wisconsin. Lake Res Manage 21:165–173

James WF, Barko JW, Eakin HL (2002) Labile and refractory forms of phosphorus in runoff of the Redwood River Basin, Minnesota. J Freshw Ecol 17:297–304

Jensen HS, Thamdrup B (1993) Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. Hydrobiologia 253:47–59. doi:10.1007/BF00050721

Jensen HS, Bendixen T, Andersen FØ (2006) Transformation of particle-bound phosphorus at the land-sea interface in a Danish estuary. Water Air Soil Pollut Focus 6:547–555. doi:10.1007/s11267-006-9038-1

Kelley DW, Nater EA (2000) Historical sediment flux from three watersheds into Lake Pepin, Minnesota, USA. J Environ Qual 29:561–568

Klotz RL (1985) Factors controlling phosphorus limitation in stream sediments. Limnol Oceanogr 30:543–553

Larson CE, Johnson DK, Flood RJ, Meyer ML, O'Dea TJ, Schellhaass SM (2002) Lake Pepin phosphorus study, 1994–1998. Effects of phosphorus loads on the water quality of the Upper Mississippi River, Lock and Dam 1 through Lake Pepin. Final Report Metropolitan Council Environmental Services, St. Paul, MN, USA

Mainstone C, Parr W (2002) Phosphorus in rivers—ecology and management. Sci Total Environ 282–283:25–47. doi:10.1016/S0048-9697(01)00937-8

Meyer JL (1979) The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. Limnol Oceanogr 24:365–375

Mayer LM, Gloss SP (1980) Buffering of silica and phosphate in a turbid river. Limnol Oceanogr 25:12–25

Meyer ML, Schellhaass SM (2002) Sources of phosphorus, chlorophyll, and sediment to the Mississippi River upstream of Lake Pepin: 1976–1996. Metropolitan Council Environmental Services, St Paul, MN

Newbold JD (1992) Cycles and spirals of nutrients. In: Calow P, Petts GE (eds) The rivers handbook, vol 1. Blackwell Scientific, Oxford

Newbold JD, Elwood RV, O'Neill RV, Van Winkle W (1981) Measuring nutrient spiralling in streams. Can J Fish Aquat Sci 38:860–863

Nürnberg GK (1988) Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments. Can J Fish Aquat Sci 44:960–966

Pacini N, Gächter R (1999) Speciation of riverine particulate phosphorus during rain events. Biogeochemistry 47:87–109

Peierls BL, Caraco NF, Pace ML, Cole JJ (1991) Human influence on river nitrogen. Nature 350:416–419. doi:10.1038/350386b0

Petticrew EL, Arocena JM (2001) Evaluation of iron-phosphate as a source of internal lake phosphorus loadings. Sci Total Environ 266:87–93. doi:10.1016/S0048-9697(00)00756-7

Pilgrim KM, Huser BJ, Brezonik PL (2007) A method for comparative evaluation of whole-lake and inflow alum treatment. Water Res 41:1215–1224. doi:10.1016/j.watres.2006.12.025

Pote DH, Daniel TC, Sharpley AN, Moore PA, Edwards DR, Nichols DJ (1996) Relating extractable soil phosphorus to phosphorus losses in runoff. Soil Sci Soc Am J 60:855–859

Pote DH, Daniel TC, Nichols DJ, Sharpley AN, Moore PA, Miller DM et al (1999) Relationship between phosphorus levels in three utisols and phosphorus concentrations in runoff. J Environ Qual 28:170–175

Psenner R, Puckso R (1988) Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. Arch Hydrobiol Biol Erg Limnol 30:43–59

Reynolds CS (1984) The ecology of freshwater phytoplankton (Cambridge studies in ecology). Cambridge University Press, Cambridge

Reynolds CS (2006) The ecology of phytoplankton. Cambridge University Press, Cambridge

Reynolds CS, Glaister MS (1993) Spatial and temporal changes in phytoplankton abundance in the upper and middle reaches of the River Severn. Arch Hydrobiol Suppl 101 Large Rivers 9:1–22

Schindler DW (2006) Recent advances in the understanding and management of eutrophication. Limnol Oceanogr 51:356–363

Sekely A, Mulla DJ, Bauer DW (2002) Streambank slumping and its contribution to the phosphorus and suspended

sediment loads of the Blue Earth River, Minnesota. J Soil Water Conserv 57:243–250
Sharpley AN (1995) Dependence of runoff phosphorus on extractable soil phosphorus. J Environ Qual 24:920–926
Sharpley AN, Smith SJ, Stewart BA, Mathers AC (1984) Forms of phosphorus in soil receiving cattle feedlot waste. J Environ Qual 13:211–215
Sharpley AN, Troeger WW, Smith SJ (1991) The measurement of bioavailable phosphorus in agricultural runoff. J Environ Qual 20:235–238
Smith VH (2006) Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. Limnol Oceanogr 51:377–384
Soballe DM, Kimmel BL (1987) A large-scale comparison of factors influencing phytoplankton abundance in rivers, lakes, and impoundments. Ecology 68:1943–1954. doi:10.2307/1939885
Søndergaard M, Jensen JP, Jeppesen E (2003) Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia 506–509:135–145. doi:10.1023/B:HYDR.0000008611.12704.dd
Statistical Analysis System (1994) SAS/STAT Users Guide Version 6, 4th edn. SAS Institute, Cary, NC
Sylvan JB, Dortch Q, Nelson DM, Maier Brown AF, Morrison W, Ammerman JW (2006) Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation. Environ Sci Technol 40:7458–7553. doi:10.1021/es061417t
Torbert HA, Daniel TC, Lemunyon JL, Jones RM (2002) Relationship of soil test phosphorus and sampling depth to runoff phosphorus in calcareous and noncalcareous soils. J Environ Qual 31:1380–1387
Turner RE, Rabalais NN, Justic D, Dortch Q (2003) Global patterns of dissolved N, P, and Si in large rivers. Biogeochemistry 64:297–317. doi:10.1023/A:1024960007569
Uusitalo R, Turtola E (2003) Determination of redox-sensitive phosphorus in field runoff without sediment preconcentration. J Environ Qual 32:70–77
Uusitalo R, Turtola E, Puustinen M, Paasonen-Kivekäs M, Uusi-Kämppä J (2003) Contribution of particulate phosphorus to runoff phosphorus bioavailability. J Environ Qual 32:2007–2016
Van Nieuwenhuyse EE, Jones JR (1996) Phosphorus-chlorophyll relationship in temperate streams and its variation with stream catchment area. Can J Fish Aquat Sci 53:99–105. doi:10.1139/cjfas-53-1-99
Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW et al (1997) Human alteration of the global nitrogen cycle: sources and consequences. Ecol Appl 7:737–750
Walker WW (1996) Simplified procedures for eutrophication assessment and prediction: user manual. Instruction Report W-96-2, September, 1996, US Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, USA
Warner JC, Brunner GW, Wolfe BC, Piper SS (2008) HEC-RAS, river system applications guide. Version 4.0, March 2008. US Army Corps of Engineers Hydrologic Engineering Center. http://www.hec.usace.army.mil/software/hec-ras/
Waters TF (1977) The streams and Rivers of Minnesota. University of Minnesota Press, Minneapolis, MN
Wauchope RD, McDowell LL (1984) Adsorption of phosphate, arsenate, methanocarsonate and cacodylate by lake and stream sediments. Comparisons with soils. J Environ Qual 13:499–504
Zhang TQ, MacKenzie AF, Liang BC (1995) Long-term changes in Mehlich-3 extractable P and K in a sandy clay loam soil under continuous corn (*Zea mays* L.). Can J Soil Sci 75:361–367
Zhang TQ, MacKenzie AF, Liang BC, Drury CF (2004) Soil test phosphorus and phosphorus fractions with long-term phosphorus addition and depletion. Soil Sci Soc Am J 68:519–528