



Exchangeable Phosphorus Pools and Equilibrium Characteristics for River Sediment as a Function of Particle Size

by William F. James

PURPOSE: The System-Wide Water Resources Program-Nutrient Sub-Model (SWWRP-NSM) represents a library of algorithms for simulating nutrient cycling, transformation, and flux in terrestrial and aquatic systems. One feature of SWWRP-NSM is the capability of simulating phosphorus (P) equilibrium fluxes between exchangeable particulate and soluble P pools in the aquatic water column as a function of particle size class. The objectives of this research were to quantify exchangeable particulate phosphorus (P) pools and equilibrium with soluble P as a function of river sediment particle size distribution for use in initializing model parameters for simulating P adsorption and desorption in river systems.

BACKGROUND: In agricultural watersheds, fertilizer application in excess of crop P uptake requirements can result in the enrichment of soil P levels over time (Sharpley et al. 1984; Zhang et al. 1995, 2004; Bennett et al. 2001). Numerous studies have shown that P concentration increases with decreasing soil particle size, due to greater surface area per volume and higher composition of iron (Fe) and aluminum (Al) compounds that provide sorption sites for P in finer silt and clay soils (Day et al. 1987; Agbenin and Tiessen 1995; Sinaj et al. 1997). In contrast, P content is much lower in sands and associated primarily with calcium minerals (Gburek et al. 2005). Field runoff of particulate P during storms and transport to receiving tributaries is governed by particle size and density, as sandier soils tend to become redeposited in the field while the finest particles remain suspended in overland flow. The combined result of these erosion and transport processes is enrichment of suspended particulate loads with P due to movement of finer silts and clays off the landscape (Sharpley 1985).

During transport through the river network, eroded particulate P can play an important role in regulating soluble P via abiotic processes such as P equilibrium between particulate and soluble phases (Froelich 1988). Differential sedimentation due to particle size and density differences can lead to transport of predominantly fine-grained sediment exhibiting a relatively high exchangeable particulate P concentration. Equilibrium processes can, thus, result in high soluble P that influences algal productivity and eutrophication, particularly as particulate loads are discharged into impounded river reaches and coastal marine environments. River network models need to consider particle size distribution during transport in order to better predict P biogeochemical cycling and influences on biota.

The SWWRP-NSM considers in-stream processes for modeling P dynamics, including algorithms describing P adsorption and desorption for a range of particle size classes (Johnson et al. 2008, 2009). Model parameterization requires partitioning of P into soluble and adsorbed fractions as,

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$$P_{sol} = \frac{1}{1 + \sum_{n=1}^N K_d C_s^n} \quad (1)$$

$$P_{part}^n = \frac{K_d C_s^n}{1 + \sum_{n=1}^N K_d C_s^n} \quad (2)$$

where, P_{sol} and P_{part} are the soluble P and particulate exchangeable P fractions (as a fractional percentage), respectively, C_s is the suspended sediment concentration ($M L^{-3}$), and K_d is the linear partition coefficient ($L^3 M^{-1}$), for particle size class n . P_{part} and P_{sol} are directly related to K_d according to the equation,

$$P_{part} = K_d \cdot P_{sol} \quad (3)$$

For sands and coarse-grained silts, we would expect P_{part} and P_{sol} at equilibrium (i.e., no net adsorption or desorption) to be relatively low due to minimal binding sites for P (Figure 1). K_d values should be low as well for these particle size classes because P binding is weak, resulting in poor buffering between soluble and particulate phases due to P disequilibrium. In contrast, finer-grained silts and clays should exhibit much higher concentrations of P_{part} and P_{sol} at equilibrium due to greater P binding potential. K_d is expected to be much higher for finer p-grained particles, reflecting greater P buffering as a result of P disequilibrium (Figure 1). Because particle size distribution in river suspended sediment loads is dynamic during transport, models are needed that weight P equilibrium processes with respect to particle size class, density, and concentration in order to more accurately predict soluble P. The objectives of this research were to quantify exchangeable particulate P pools and equilibrium characteristics as a function of river sediment particle size distribution for use in initializing model parameters for SWWRP-NSM.

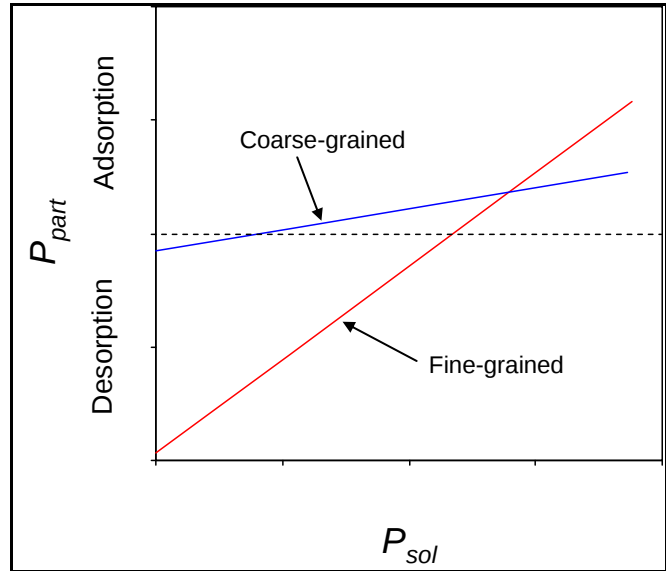


Figure 1. Conceptual diagram showing relationships between exchangeable particulate phosphorus (P_{part}) and soluble phosphorus (P_{sol}) for coarse- and fine-grained particles. The slopes of the red and blue lines represent the linear partition coefficient (K_d). The dotted line depicts zero net P adsorption onto or desorption from P_{part} . The intercept of the lines with the y-axis represents the concentration of the native P_{part} pool ($mg\ kg^{-1}$). The P_{sol} concentration at the point where net P sorption is equal to zero (i.e., intersection of the red or blue line with the dotted line) is the equilibrium phosphorus concentration (EPC). The EPC is estimated as P_{part}/K_d .

METHODS: Deposited sediment was collected from the Minnesota River approximately 10 miles upstream of its confluence with the Mississippi River at St. Paul, Minnesota, in October 2008. In the laboratory, the sediment was diluted (10:1) with tap water (groundwater) amended with P to a concentration of 0.120 mg L^{-1} to maintain in situ P equilibrium conditions (reported in James and Larson 2008). The solution was gently mixed on a shaker table at 20°C in a darkened environmental chamber before initiation of separation into various particle size class ranges (Table 1). Sieving and pipette techniques (Plumb 1981) were used to separate sediment into particles $> 63 \mu$, $< 63 \mu$, $< 31.2 \mu$, 15.6μ , $< 7.8 \mu$, and $< 4 \mu$. Further separation was achieved in a sedimentation chamber by allowing particles to settle through a 100 cm water column at 20°C (Figure 2). The sedimentation chamber consisted of 7 cm diameter acrylic tubing that was attached to a ball valve. A glass sedimentation jar was placed at the bottom of the chamber and secured with a rubber stopper to seal the system. Particles were gently shaken for 24 h in P amended tap water prior to sedimentation. With the valve closed, the sediment mixture was poured into the upper portion of the chamber and gently mixed. The valve was then opened and sediment was allowed to settle for various time periods, based on fall velocities that were computed using Stokes Law. Finer particles remaining suspended in the chamber at the end of the desired time period were removed by pulling a stopper located above the collection jar and allowing the water to drain into a basin. The drain hole was small (1 cm diameter) to minimize turbulence above the sedimentation jar. Settled particles were centrifuged, poisoned with chloroform to inhibit biological activity (0.1 mL 1% solution to 50 mL sample), and stored in a refrigerator at 4°C until analysis.

Table 1. Particle Size Classes

$> 63 \mu$
31.2 to 63 μ
15.6 to 31.2 μ
7.8 to 15.6 μ
3.9 to 7.8 μ
$< 3.9 \mu$

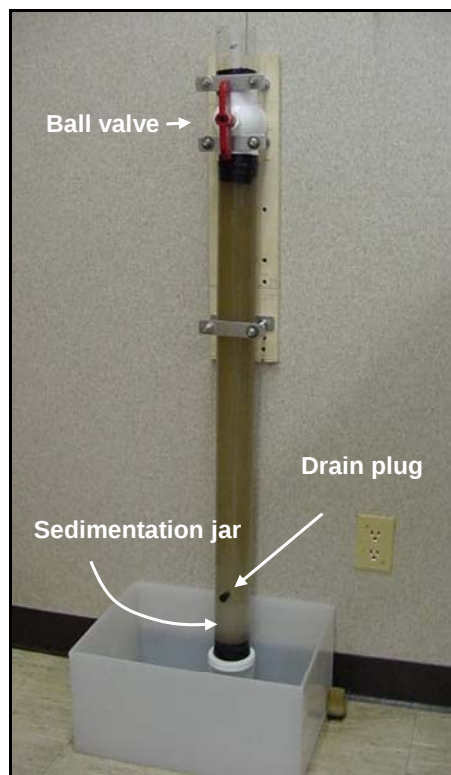


Figure 2. Sedimentation chamber used for separating river sediment into various particle size classes.

Sequential fractionation of particulate P was conducted according to Hjieltjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) to determine ammonium-chloride-extractable P (i.e., loosely-bound P), bicarbonate dithionite-extractable P (i.e., iron-bound P), sodium hydroxide-extractable P (i.e., aluminum-bound P), and hydrochloric acid-extractable P (i.e., calcium-bound P). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable P (Psenner and Puckso 1988). Organic P was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P. Each extraction was adjusted to pH 7 and analyzed for soluble reactive P (SRP) using the ascorbic acid method (American Public Health Association 2005). A portion of loosely-bound, iron-bound, and, to a lesser extent, the aluminum-bound P fractions are believed to be associated with equilibrium P exchanges with the water column. Total P was calculated as the sum of all measured extractable P forms. Total iron (Fe) and aluminum (Al) were measured using atomic absorption spectrometry after digestion with nitric and hydrochloric acid (American Public Health Association 2005).

Aliquots ($\sim 500 \text{ mg L}^{-1}$ dry weight equivalent to simulate suspended sediment concentrations in the lower Minnesota River) of the concentrated suspended sediment isolated for each particle size class were also subjected to phosphate (as KH_2PO_4) standards ranging from 0 to 1.0 mg L^{-1} for determination of P adsorption and desorption over a 24 hour period. Tap water was used because it was low in phosphate concentration and similar in ionic strength to Minnesota River water. Assay tubes containing sediment, tap water, and known concentrations of phosphate were shaken uniformly in a darkened environment then filtered and analyzed for SRP. The sediment slurries were maintained under oxic conditions at a pH of ~ 8.0 to 8.3 and a temperature of $\sim 20^\circ\text{C}$ during the shaking and equilibration process.

The change in SRP mass (i.e., initial SRP minus final SRP; mg) was divided by the dry mass equivalent of sediment to determine the mass of P desorbed or adsorbed (i.e., exchangeable particulate P, P_{part} ; mg P kg^{-1} dry mass sediment). These data were plotted as a function of the equilibrium SRP (i.e., the final SRPO concentration after shaking for 24 hours) to determine the linear partition coefficient (K_d ; L kg^{-1}) and the equilibrium P concentration (EPC) under conditions where net sorption was zero (i.e., the P_{sol} at the EPC; Froelich 1988). The K_d and P_{sol} at the 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. The intercept of the regression equation represented P_{part} . Data were also fitted to a Langmuir regression model using a spreadsheet developed by Bolster and Hornberger (2007) to estimate the P_{part} sorption maximum ($P_{part-max}$). The degree of P_{part} saturation (DPS) was calculated as P_{part} divided by $P_{part-max}$.

RESULTS AND DISCUSSION: Concentrations of total P, loosely-bound P, iron-bound P, aluminum-bound, and organic P increased with decreasing particle size class (Figure 3). In contrast, calcium-bound P concentrations were relatively constant over the range of particle sizes. Total P was composed primarily of calcium-bound P for larger particle size classes (i.e., $> 31.2 \mu$, Figure 4). This percentage declined with increasing particle size because the calcium-bound P fraction remained constant while the loosely-bound, iron-bound, and aluminum-bound P concentration increased as particle size class decreased. For other P fractions, percent composition generally increased with decreasing particle size class. Iron-bound P accounted for the greatest percentage of total P as particle size class decreased followed by aluminum-bound

P > loosely-bound P > organic P. Total Fe and Al concentrations also increased with decreasing particle size class (Figure 5). These trends suggested linkages between metal hydroxides in river sediment and extractable P forms involved in P equilibrium reactions (Gburek et al., 2005).

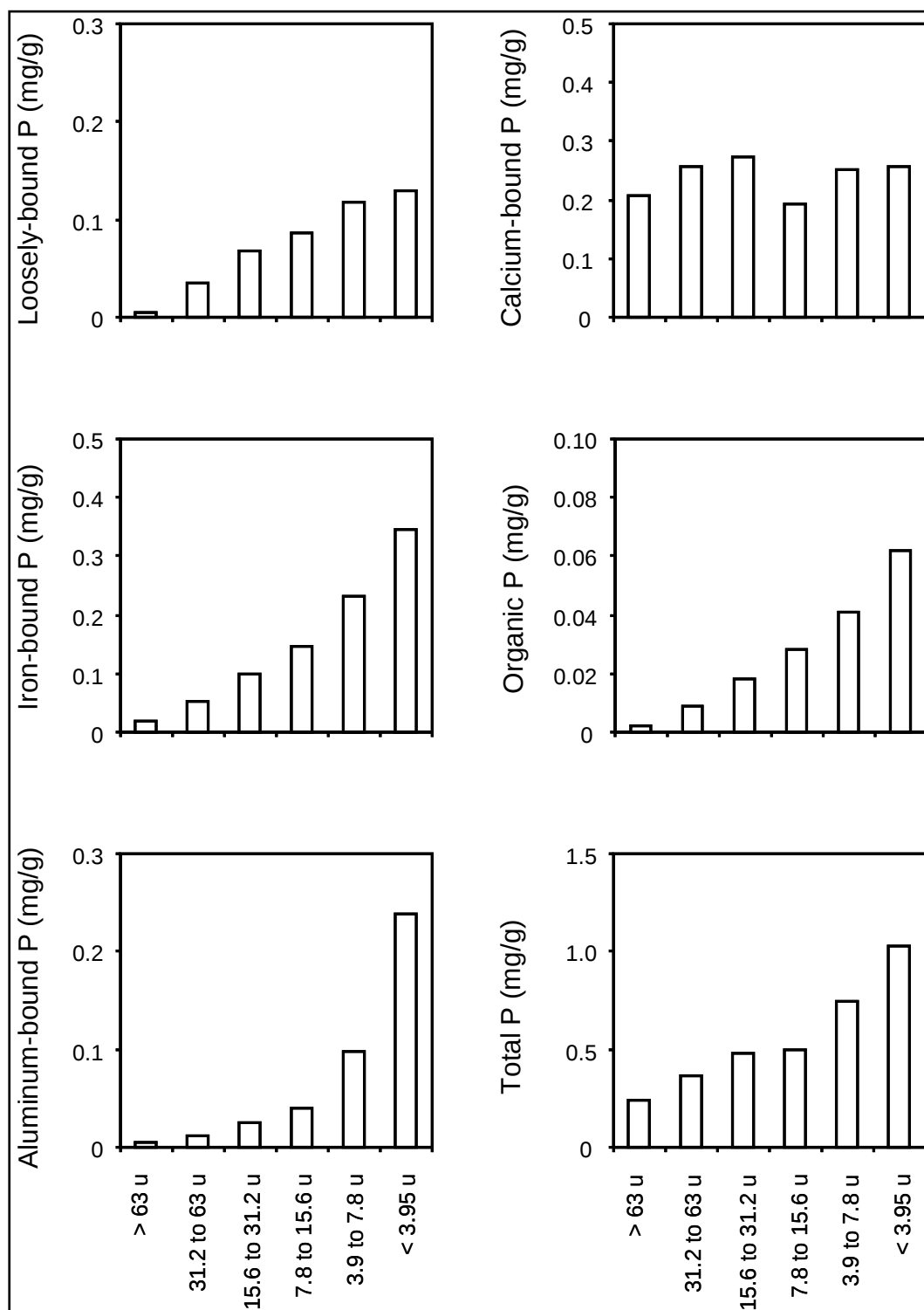


Figure 3. Variations in loosely-bound, iron-bound, aluminum-bound, calcium-bound, organic, and total phosphorus (P) as a function of particle size class.

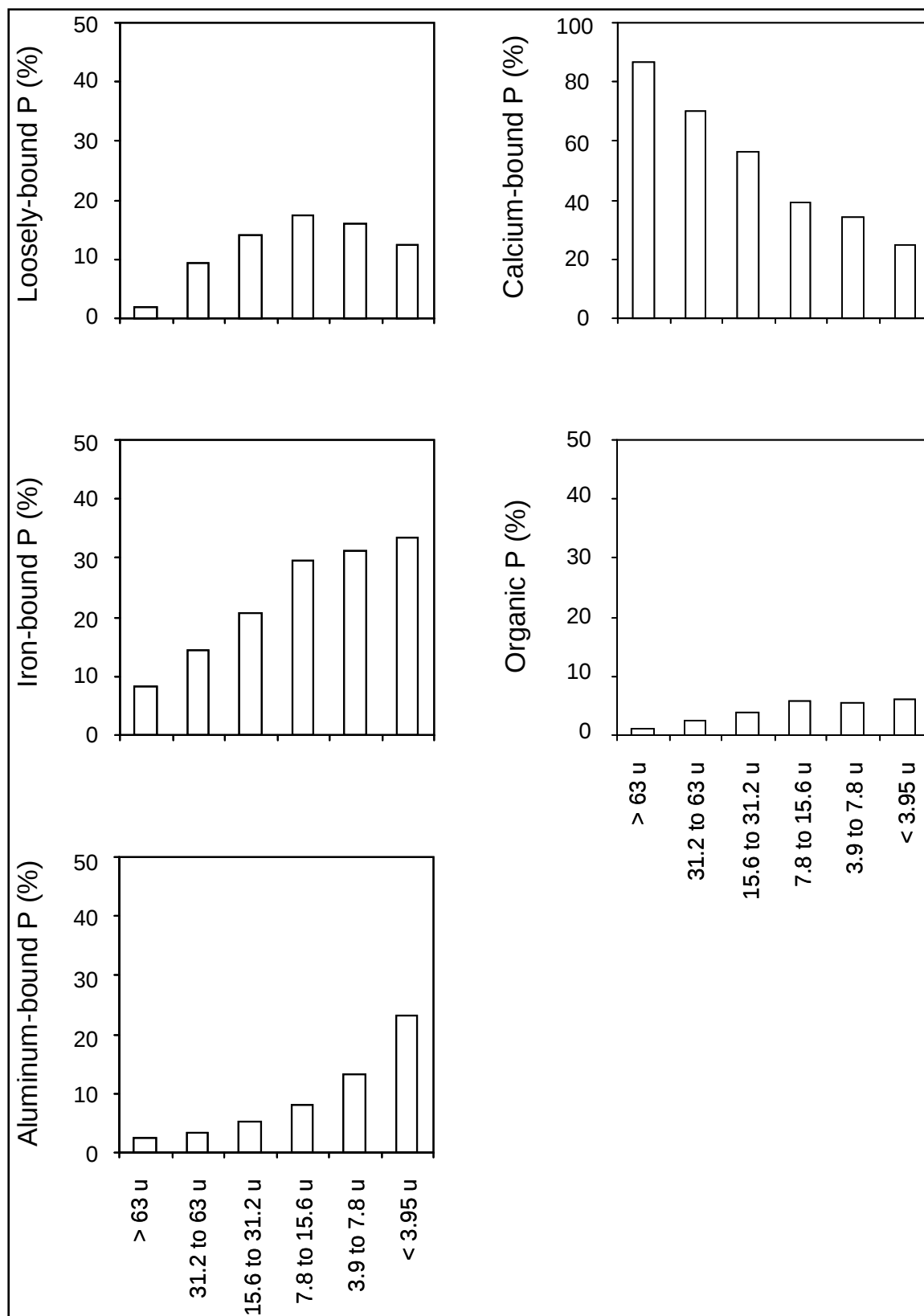


Figure 4. Variations in the percentage of total phosphorus (P) that is loosely-bound, iron-bound, aluminum-bound, calcium-bound, and organic P as a function of particle size class.

Variations in adsorption and desorption from the P_{part} pool versus P_{sol} for various particle size classes are shown in Figure 6. Generally, desorption from P_{part} occurred at low P_{sol} and adsorption to P_{part} occurred as P_{sol} increased above 0.2 mg L^{-1} . The magnitudes of P_{part} desorption and adsorption also increased as a function of decreasing particle size class. Similar to iron- and aluminum-bound P patterns, P_{part} increased significantly with decreasing particle size class, indicating that the exchangeable P pool was considerably larger for fine silts and clays versus sands (Figure 7). For particles less than 63μ , the P_{sol} at the EPC was high and comparable to suspended sediment P equilibrium characteristics in agriculturally-dominated systems (James and Larson 2008). The P_{sol} at the EPC was $\sim 0.09 \text{ mg L}^{-1}$ for particles ranging between 31.2μ and 63μ and increased to $\sim 0.23 \text{ mg L}^{-1}$ for particles less than 4μ (Figure 7). The $P_{part-max}$ and the DPS tended to be inversely related to particle size class (Figure 8). These patterns may be related to greater concentrations of Fe and Al on smaller particles with increased binding sites for P adsorption. The K_d also increased as a function of decreasing particle size, suggesting greater buffering of P between solid and aqueous phases for finer- versus coarser-grained particles (Figure 7).

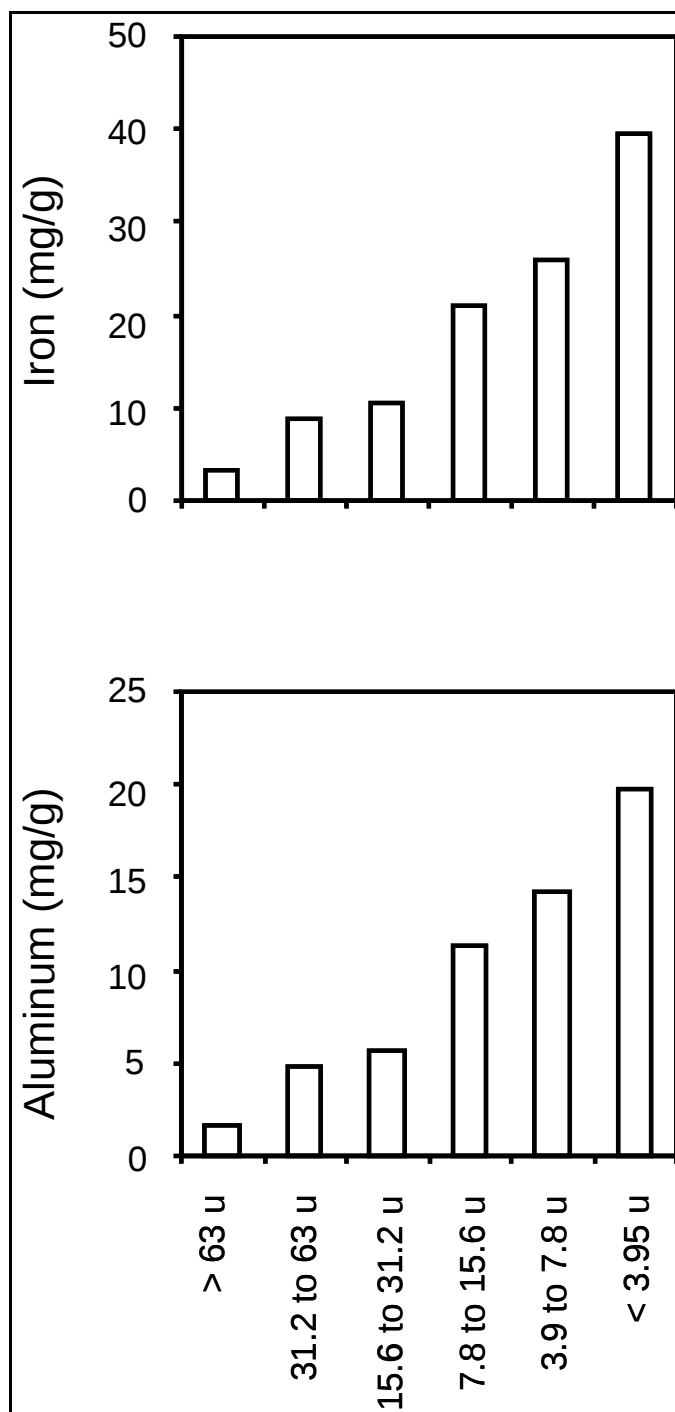


Figure 5. Variations in total iron and aluminum as a function of particle size class.

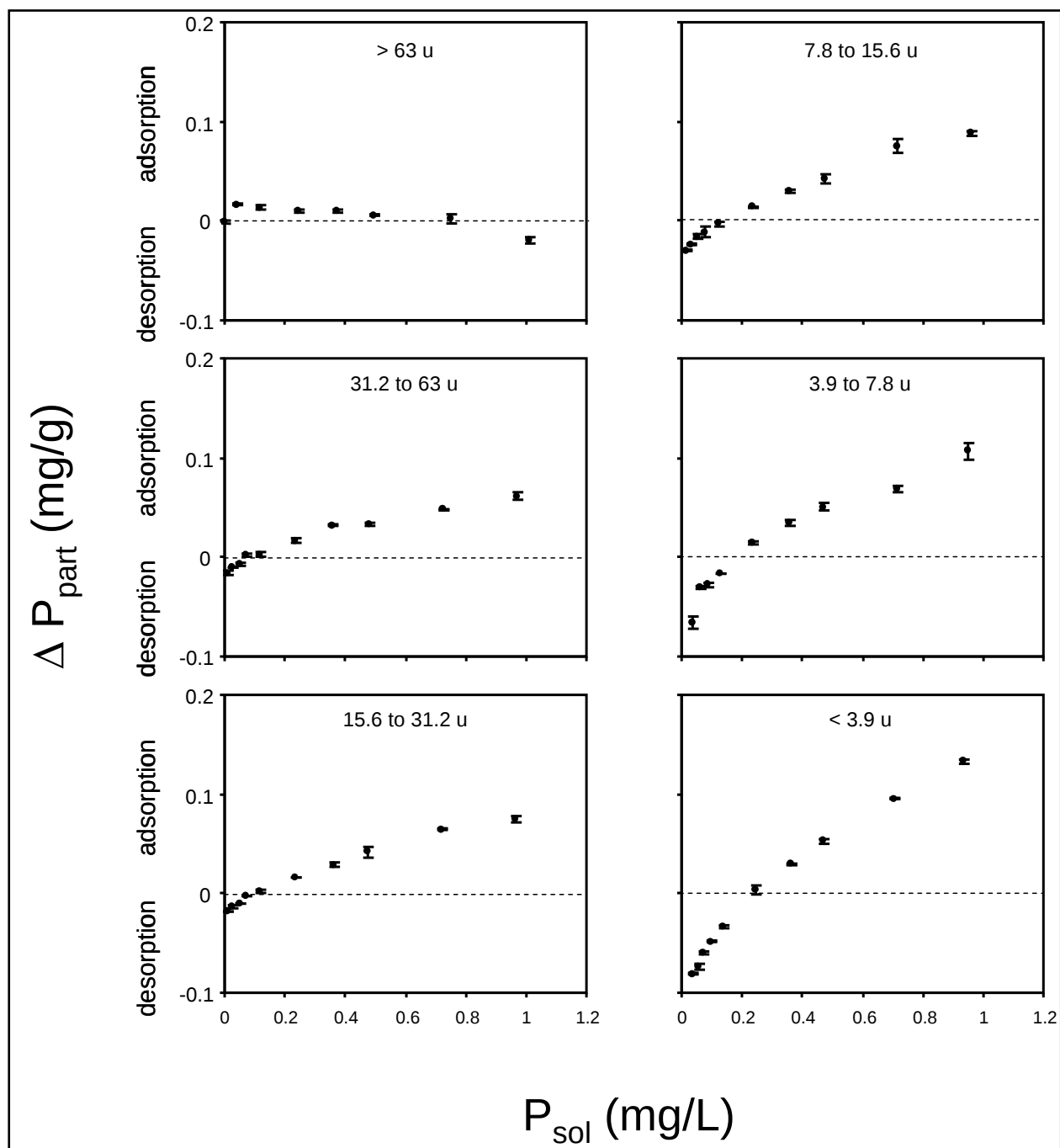


Figure 6. Relationships between mean ($n=3$) exchangeable particulate phosphorus (P_{part}) and soluble phosphorus (P_{sol}) for various particle size classes. Dotted lines depict zero net phosphorus adsorption or desorption. Vertical lines represent plus or minus 1 standard error of the mean.

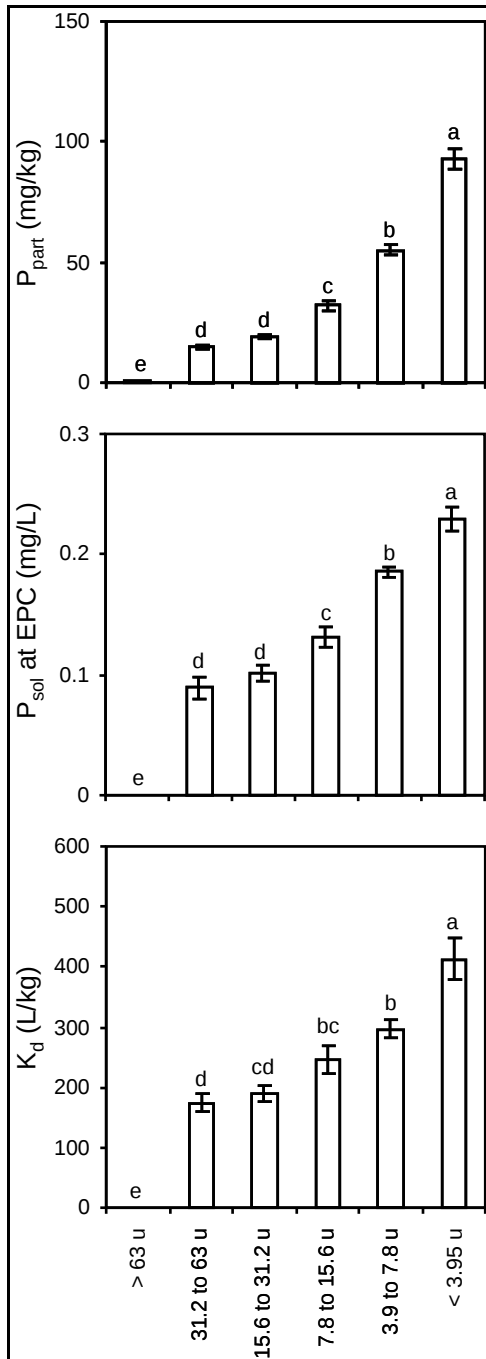


Figure 7. Variations in mean ($n = 3$) exchangeable particulate phosphorus (P_{part}), soluble phosphorus (P_{sol}), and the linear partition coefficient (K_d) as a function of particle size class. Vertical lines represent plus or minus 1 standard error of the mean. Different letters represent significant differences ($p < 0.05$) in the mean based on ANOVA (Duncan-Waller; Statistical Analysis System 1994).

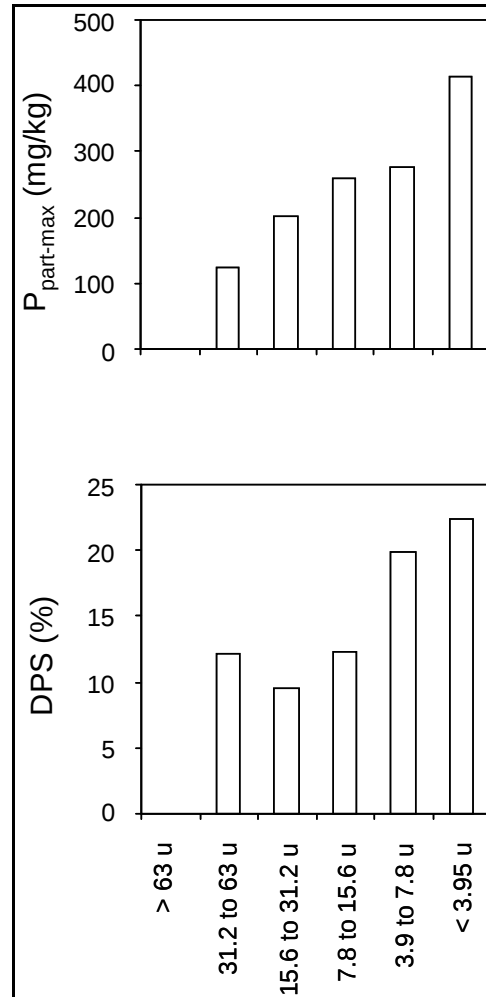


Figure 8. Variations in the theoretical adsorption capacity for exchangeable particulate phosphorus ($P_{part-max}$) and the degree of phosphorus saturation (DPS) for the exchangeable particulate phosphorus pool as a function of particle size class.

Implied from these results is the important role that smaller particle size classes can play in regulating soluble P concentrations via equilibrium processes in rivers during transport. Clays and finer silts have a greater reactive surface area and higher Fe and Al concentration than sands and, therefore, greater potential for adsorbing P. In the watershed, finer particles enriched with adsorbed P can be preferentially transported to receiving tributaries during runoff due to lower density and settling velocity (Sharpley 1985). In large river systems, particle-density size differences result in the deposition of sands and coarse silts and transport of finer silts and clays during high flow events, which can influence soluble P concentrations. For the Minnesota River, relatively high concentrations of P_{part} and P fractions associated with Fe and Al for finer particles were associated with a P_{sol} at the EPC that exceeded 0.10 mg L^{-1} . James and Larson (2008) found that the P_{sol} at the EPC for suspended sediment in the Minnesota River was $\sim 0.12 \text{ mg L}^{-1}$ during periods of runoff and high flow, which is consistent with results reported here. Uptake of soluble P loads generated by equilibrium processes can lead to eutrophication and high phytoplankton bloom potential, particularly as loads enter impounded river reaches. 2-D and 3D river models that simulate river channel P dynamics can be improved by considering P equilibrium reactions and mass transfer as a function of particle size during transport (Johnson et al. 2008, 2009).

ADDITIONAL INFORMATION: This technical note was prepared by William F. James, Research Aquatic Biologist, Eau Galle Aquatic Ecology Laboratory, Environmental Laboratory, U.S. Army Engineer Research and Development Center. The study was conducted as an activity of the Nutrient Algorithms work unit of the System-Wide Water Resources Program (SWWRP). For information on SWWRP, please consult <https://swwrp.usace.army.mil/> or contact the Program Manager, Dr. Steven L. Ashby at Steven.L.Ashby@usace.army.mil. This technical note should be cited as follows:

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