

## Soil Exchangeable Phosphorus Pools, Equilibrium Characteristics, and Mass Distribution Coefficients for Eight-Mile Run Watershed, Wisconsin

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**PURPOSE:** This research experimentally determined phosphorus mass distribution coefficients (i.e., relationship between soil exchangeable and soluble phosphorus), exchangeable phosphorus pools, and soluble phosphorus in the interstitial water for soils exhibiting a range of phosphorus concentrations. The research also developed relationships between these variables and commonly measured, crop-available soil phosphorus for use in establishing initial soil P parameters in the System-Wide Water Resources Program-Nutrient Sub-Model (SWWRP-NSM).

**BACKGROUND:** Mass transfer of soluble phosphorus (P) between soil and laminar overland flow can be described as:

$$S_d = k_e \left( \frac{C_{d2}}{\phi - C_d} \right) \quad (1)$$

where

- $S_d$  = the mass transfer flux ( $M \cdot L^{-2} \cdot T^{-1}$ )
- $C_d$  = the concentration of soluble P in the water column ( $M \cdot L^{-3}$ )
- $C_{d2}$  = the concentration of soluble P in the soil interstitial water ( $M \cdot L^{-3}$ ; also referred to as the equilibrium P concentration or EPC, Froelich 1988)
- $k_e$  = the mass transfer coefficient ( $L \cdot T^{-1}$ )
- $\phi$  = the porosity (dimensionless; Wallach et al. 1988; Chapra 1997; Gao et al. 2004).

$C_{d2}$  can rapidly (i.e., hours) exchange with P that is reversibly adsorbed to soil constituents (primarily on Al and Fe hydroxides) until an approximate equilibrium is achieved between particulate and aqueous phases as:



where  $C_{p2}$  = the soil adsorbed inorganic P pool ( $M \cdot M^{-1}$ ; Barrow 1983; Van Riemsdijk et al. 1984). In general,  $C_{p2}$  represents a small fraction of the total adsorbed inorganic P pool and a smaller fraction of the total potential capacity for soils to adsorb P. Shifts in P equilibrium due to crop uptake or fertilizer application can result in rapid (on the order of minutes to hours) exchanges between the particulate and aqueous phases. For example, P desorption from soil

occurs when  $C_{d2}$  declines below equilibrium conditions and  $P$  adsorption to soil occurs when  $C_{d2}$  exceeds equilibrium conditions.

The total concentration of this exchangeable inorganic  $P$  pool ( $C_{T2}$ ;  $M \cdot L^{-3}$ ) in the surface soil layer can be divided into two components as:

$$C_{T2} = (1 - \varphi) \cdot \rho \cdot C_{p2} + \varphi C_{d2} \quad (3)$$

where  $\rho$  = the soil density ( $M \cdot L^{-3}$ ).  $C_{d2}$  and  $C_{p2}$  are related to an equilibrium partition coefficient as:

$$C_{p2} = k_{d2} \cdot C_{d2} \quad (4)$$

where  $k_{d2}$  = the mass distribution coefficient ( $L^3 \cdot M^{-1}$ ). Equations 3 and 4 can be combined as:

$$C_{T2} = C_{d2} \cdot (\alpha + \varphi) \quad (5)$$

where

$$\alpha = (1 - \varphi) \cdot \rho \cdot k_{d2} \quad (6)$$

Alternatively, Equation 4 can be solved for  $C_{d2}$  and combined with Equation 3 as:

$$C_{T2} = C_{p2} \cdot (\alpha + \varphi) \cdot k_{d2}^{-1} \quad (7)$$

In order to model soluble  $P$  transfer between soil and overland flow,  $C_{T2}$ ,  $C_{p2}$ ,  $C_{d2}$ , and  $k_{d2}$  need to be initialized in SWWRP-NSM. This information is not readily available and usually must be determined experimentally via Langmuir isotherm assays. Numerous studies have shown that  $P$  mass transfer varies positively as a function of the concentration of various adsorbed  $P$  pools and the degree of soil  $P$  saturation (Pote et al. 1996; McDowell et al. 2001; Torbert et al. 2002; Vadas et al. 2005), indicating relationships between  $P$  mass transfer and soil management practices. In addition, extraction techniques have been used to approximate ranges in  $C_{d2}$  and  $C_{p2}$  (see review by McGrechan 2002). Finally, Fang et al. (2002) demonstrated relationships between the EPC and adsorbed  $P$  pools. Little is known about variations in  $k_{d2}$  as a function of adsorbed soil  $P$  (Lewis and McGrechan 2002). However, this information is critical for soil mass transfer modeling, since  $C_{T2}$ ,  $C_{p2}$ ,  $C_{d2}$ , and  $k_{d2}$  are inter-related (i.e., Equations 5 and 7). In particular,  $k_{d2}$  may not be constant, but rather declines with increasing soil  $P$  concentration due to decreasing availability of unoccupied adsorption sites. The objectives of this research were to 1) estimate  $C_{T2}$ ,  $C_{p2}$ ,  $C_{d2}$ , and  $k_{d2}$  for soils with widely ranging  $P$  concentrations, and 2) develop empirical relationships between these variables and commonly measured Bray and Mehlich  $P$  (i.e., extractable crop-available  $P$ ) for use in establishing initial soil  $P$  parameters for SWWRP-NSM (Johnson et al. 2008).

**METHODS:**

**Study Site.** Eight-Mile Run is a 264-ha sub-watershed located in the Upper Eau Galle River Basin, west-central Wisconsin (Figure 1). Livestock (dairy) pasture and associated barnyards represent approximately 6 percent of the watershed. This land use is located immediately adjacent to the tributary in the lower portion of the watershed. Alfalfa and corn production represent approximately 49 percent, and grass, CRP, and wooded land uses occupy approximately 45 percent of the watershed. Crop production occurs in the northern, eastern, and southeastern regions of the watershed. Grass, CRP, and wooded areas are located in the north-central and western portions of the watershed. The watershed is bisected into approximately equal areas by a railroad and U.S. Route 12. Grass, CRP, and wooded areas account for 61 percent while livestock and crop production represent 69 percent of the land use in the upper and lower portions of the watershed, respectively.

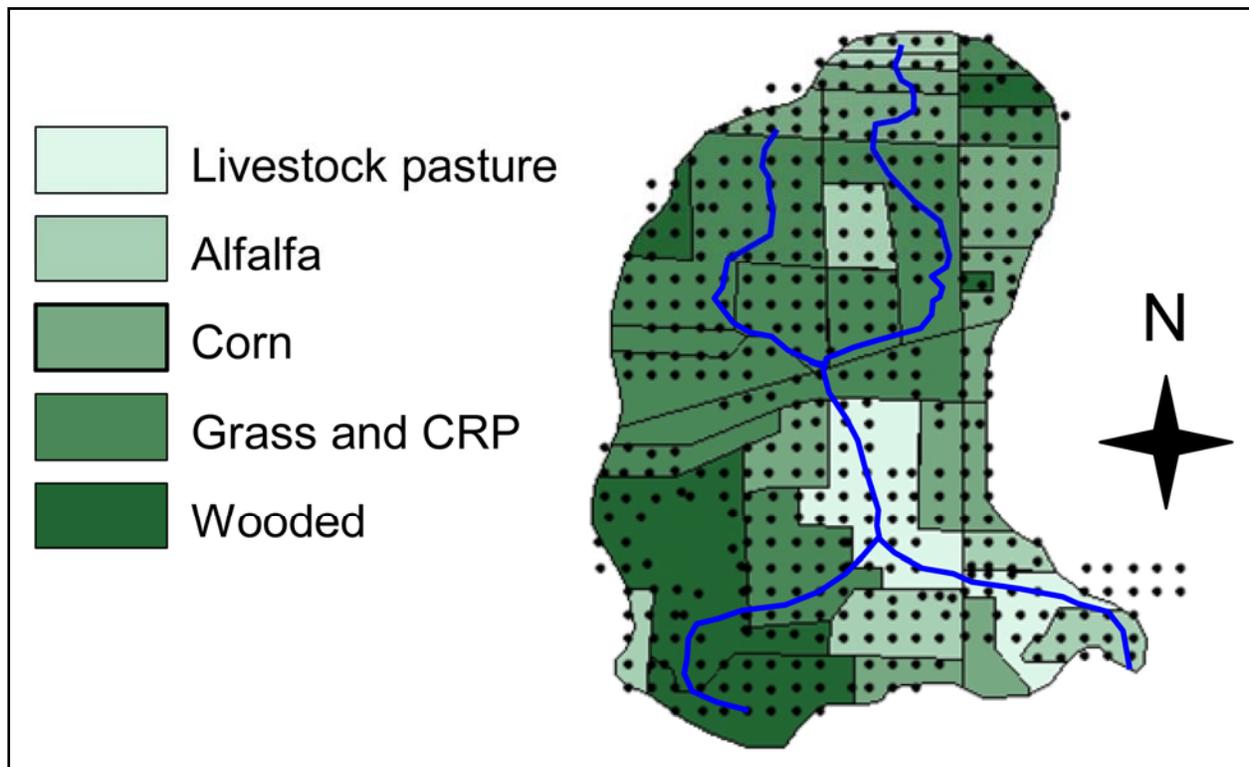


Figure 1. A map of the Eight-Mile Run watershed showing various land uses. Solid circles represent soil sampling locations.

**Field Soil Collection Procedures.** A 75-m sampling grid was established in the Eight-Mile Run watershed for soil sampling between June and early July, 2006 (Figure 1). Stations were located using high resolution digital orthophotographs and differential GPS (Garmin model 72; Garmin International, Olathe, KS, USA). Vegetation was clipped to ground level at each sampling point and six 5-cm-deep soil cores were collected around a 2-m-diam circle. The soil cores collected at each station were combined into one composited sample. Land use was recorded at the time of sampling. In the laboratory, soils were passed through a 2-mm mesh screen to remove root material and air dried at 25 °C. Overall, approximately 430 composited

soil samples were collected from the Eight-Mile Run watershed. The dried soil samples were further composited for chemical analyses as a function of 37 fields exhibiting homogeneous land uses (Figure 1).

**Soil Phosphorus Pools and Equilibrium Characteristics.** Soil was extracted in 0.025 M HCl and 0.03 M NH<sub>4</sub>F and a solution containing 0.2 M CH<sub>3</sub>COOH, 0.25 M NH<sub>4</sub>NO<sub>3</sub>, 0.015 M NH<sub>4</sub>F, 0.013 M HNO<sub>3</sub>, and 0.001 M EDTA for determination of crop-available Bray and Mehlich-3 P, respectively (Pierzynski 2000). Langmuir isotherm assays were conducted according to methods described in Nair et al. (1984). Soils were subjected to initial P (as KH<sub>2</sub>PO<sub>4</sub>-P in a 0.01 M CaCl<sub>2</sub> solution) concentrations of 0, 0.125, 0.25, 0.50, 1, 5, 10, 25, 50 and 100 mg·L<sup>-1</sup> using a soil:solution ratio of 1:25 (40 g·L<sup>-1</sup>). The soil solution tubes were gently shaken in a darkened environment at 20 °C over a 24-hr period. The equilibrated samples were centrifuged at 500 g and filtered through a 0.45-μ filter for soluble reactive P (SRP) determination (American Public Health Association (APHA) 1998).

The change in SRP mass [(initial C<sub>d2</sub> - final C<sub>d2</sub>)·solution volume] was divided by soil mass to determine the mass of P desorbed or adsorbed from soil (ΔC<sub>p2</sub>; mg·kg<sup>-1</sup>). ΔC<sub>p2</sub> was plotted as a function of final C<sub>d2</sub> (i.e., equivalent to C<sub>d2</sub> in Equation 1) to determine the mass distribution coefficient (k<sub>d2</sub>; L·kg<sup>-1</sup>), the equilibrium phosphorus concentration (EPC, the point where net sorption is zero and equivalent to C<sub>d2</sub>; Froelich 1988), and the concentration of the initial adsorbed P pool (C<sub>p</sub>; mg·kg<sup>-1</sup>). k<sub>d2</sub>, C<sub>d2</sub>, and C<sub>p2</sub> (i.e., equivalent to C<sub>p2</sub> in Equation 1) were calculated via regression analysis (Statistical Analysis System 1994) from linear relationships between final C<sub>d2</sub> and ΔC<sub>p2</sub> near the point where net sorption was zero (i.e., crossover point; Figure 2). k<sub>d2</sub> was equal to the slope of the regression line and C<sub>p2</sub> was estimated as the intercept. This calculation was modified for soils with very high P content because the ΔC<sub>p2</sub> versus C<sub>d2</sub> relationship was nonlinear near the crossover region and linear regression of these data would have resulted in an underestimate of C<sub>p2</sub> (Figure 3). Under these conditions, C<sub>p2</sub> was estimated via regression analysis at very low C<sub>d2</sub> and k<sub>d2</sub> was calculated as the slope of the line between C<sub>p2</sub> and positive ΔC<sub>p2</sub> (i.e., net adsorption of P) nearest the crossover point.

The P sorption capacity (PSC; M·L<sup>-3</sup>) was estimated as ΔC<sub>p2</sub> for soils subjected to a 100 mg·L<sup>-1</sup> solution (Nair et al. 1998). The degree of P saturation index (DPS<sub>Index</sub>; %) was calculated as:

$$DPS_{Index} = 100 \bullet \left[ \frac{P_{Adsorbed}}{PSC + P_{Adsorbed}} \right] \quad (8)$$

where  $P_{Adsorbed}$  was either Bray or Mehlich P.

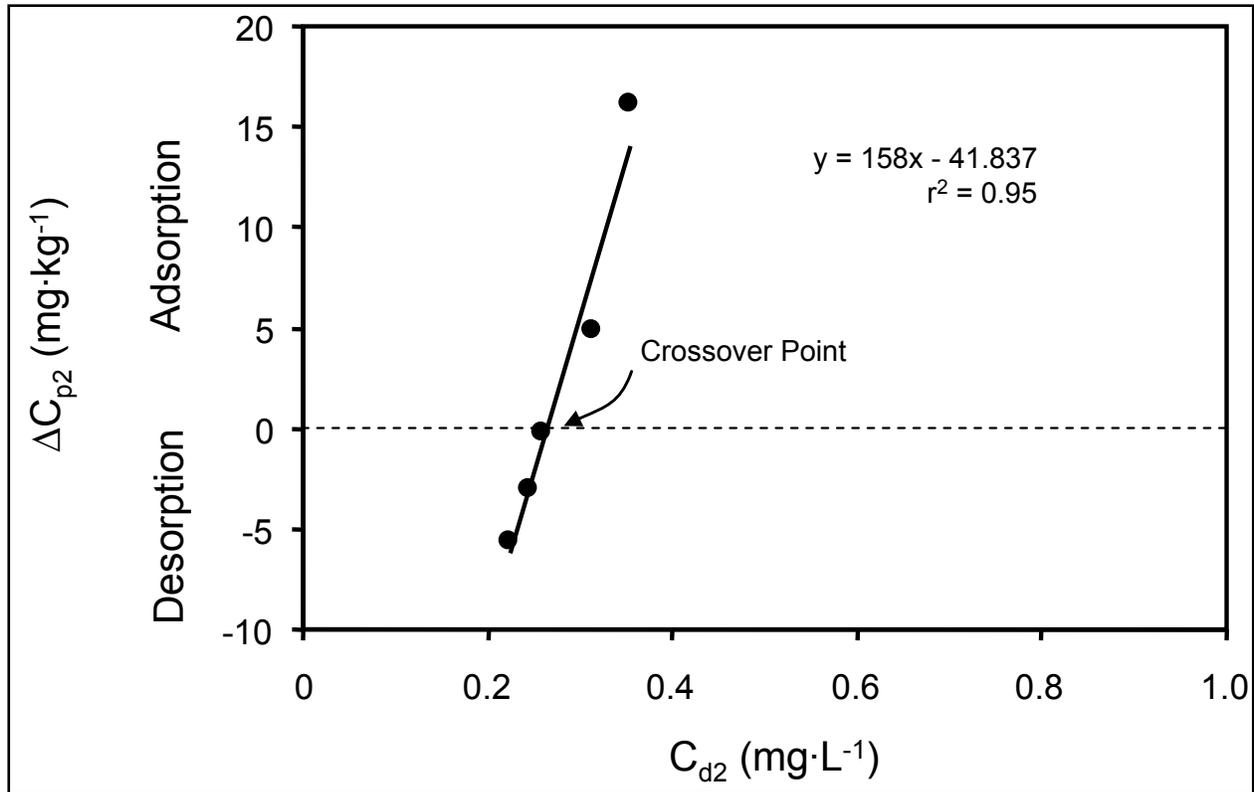


Figure 2. An example of an adsorption-desorption isotherm.  $C_{d2}$  represents the concentration of soluble reactive phosphorus in the aqueous phase after continuous shaking with soil over a 24-hr period.  $\Delta C_{p2}$  represents the change in soluble reactive phosphorus concentration after the 24-hr shaking period (initial  $C_{d2}$  - final  $C_{d2}$ ) normalized with respect to soil mass. A negative  $\Delta C_{p2}$  indicates desorption of phosphorus from soil to the aqueous phase while a positive  $\Delta C_{p2}$  represents adsorption of aqueous phosphorus onto soil particles. The crossover point is equivalent to the equilibrium phosphorus concentration (EPC). The slope of the regression equation near the crossover point is the mass distribution coefficient ( $k_{d2}$ ; L·kg<sup>-1</sup>). The intercept of the regression equation represents initial adsorbed soil phosphorus concentration ( $C_{p2}$ ; mg·kg<sup>-1</sup>).

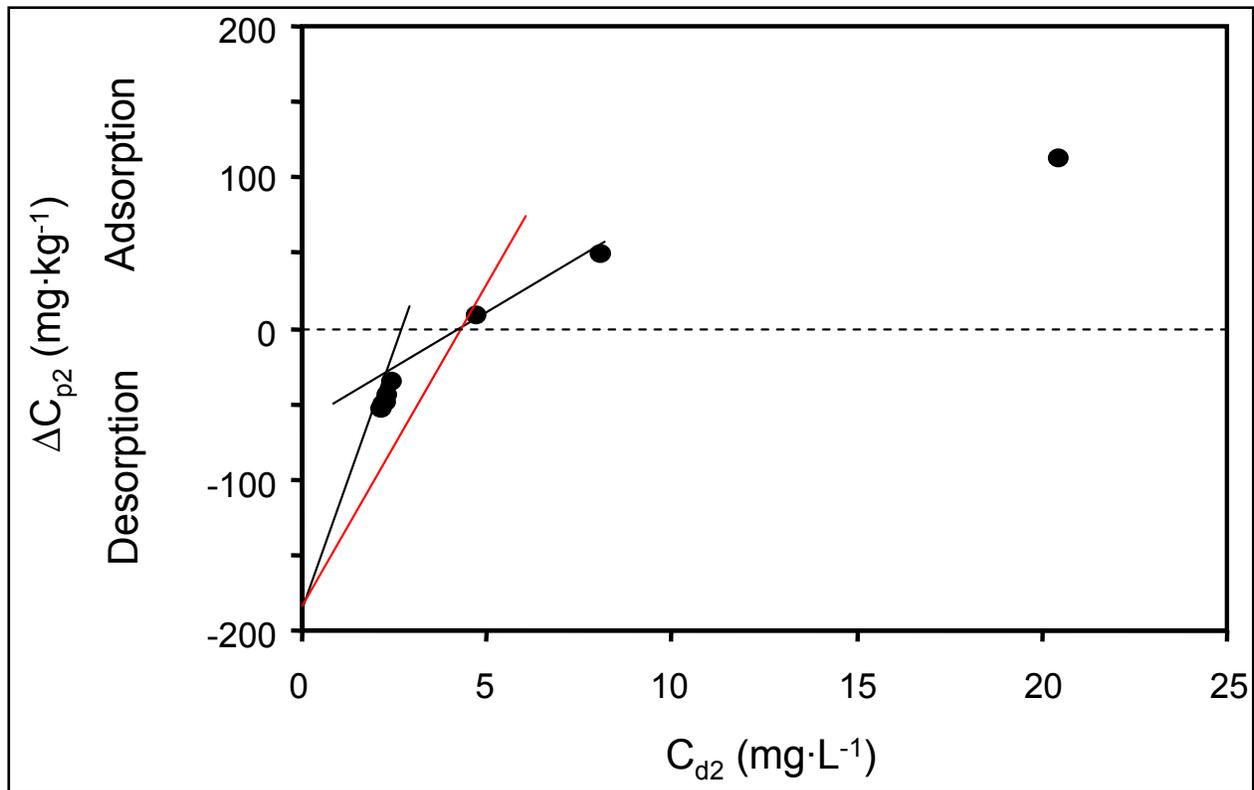


Figure 3. Adjustment used to determine  $k_{d2}$ ,  $C_{d2}$ , and  $C_{p2}$  for soils with very high soil Bray and Mehlich-3 P concentrations and nonlinear patterns near the crossover point.  $C_{p2}$  is estimated as the intercept for the linear portion of the isotherm at low  $C_{d2}$  concentrations.  $k_{d2}$  is calculated as the slope of a line passing through  $C_{p2}$  and the first data point above the crossover (i.e., positive  $\Delta C_{p2}$ ). The red line represents the adjusted  $k_{d2}$  slope.

**RESULTS AND DISCUSSION:** Bray and Mehlich P exceeded  $30 \text{ mg}\cdot\text{kg}^{-1}$  and  $50 \text{ mg}\cdot\text{kg}^{-1}$  (optimum for crop growth), respectively, primarily in the lower portion of the watershed in conjunction with crop and livestock production land use practices (Figure 4). CRP, grasses, and woodlot land uses were associated with Bray and Mehlich P concentrations that were at or below optimum levels for crop uptake.

Examples of  $\Delta C_{p2}$  versus  $C_{d2}$  are shown for four fields in Figure 5. High  $k_{d2}$  was associated with low  $C_{d2}$ , crop-available P, and  $C_{p2}$ . It declined in conjunction with higher soil P concentrations. For all fields,  $k_{d2}$  covaried nonlinearly as a function of crop-available P (Figures 6a and 6b). It was greatest for soils with low Bray and Mehlich P and declined in a negative logarithmic pattern with increasing soil P. These patterns may be related to differences in the degree of P saturation of sorption sites (Kleinman et al. 2000). For instance, the soil buffering capacity to adsorb P under conditions of P disequilibrium would decline as DPS increases due to a lower number of unoccupied adsorption sites, resulting in lower P sorption efficiency (see below and Figure 7).

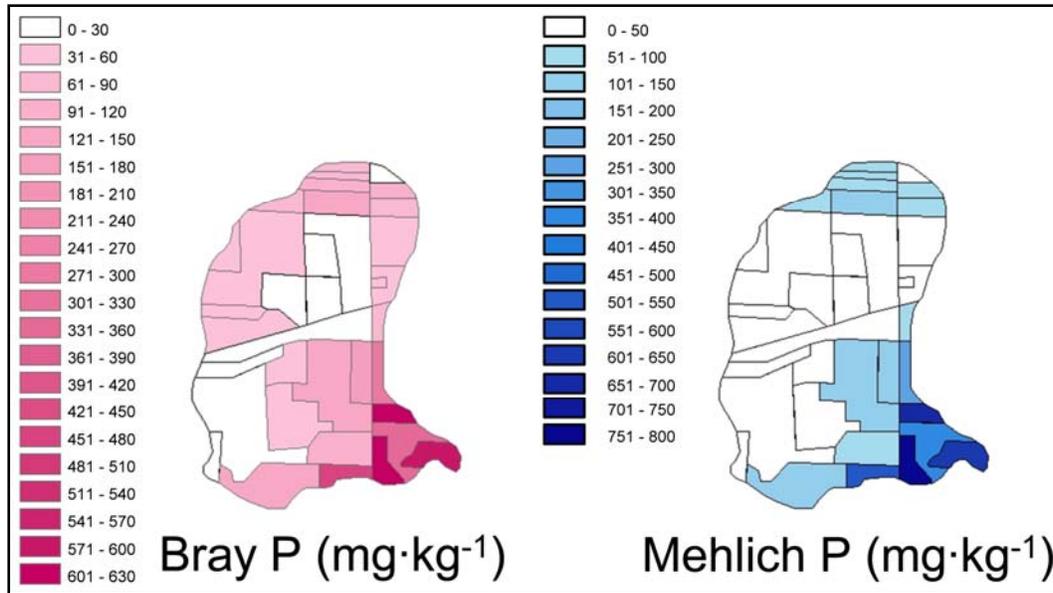


Figure 4. Spatial variations in soil Bray and Mehlich-3 P concentrations in Eight-Mile Run in 2006.

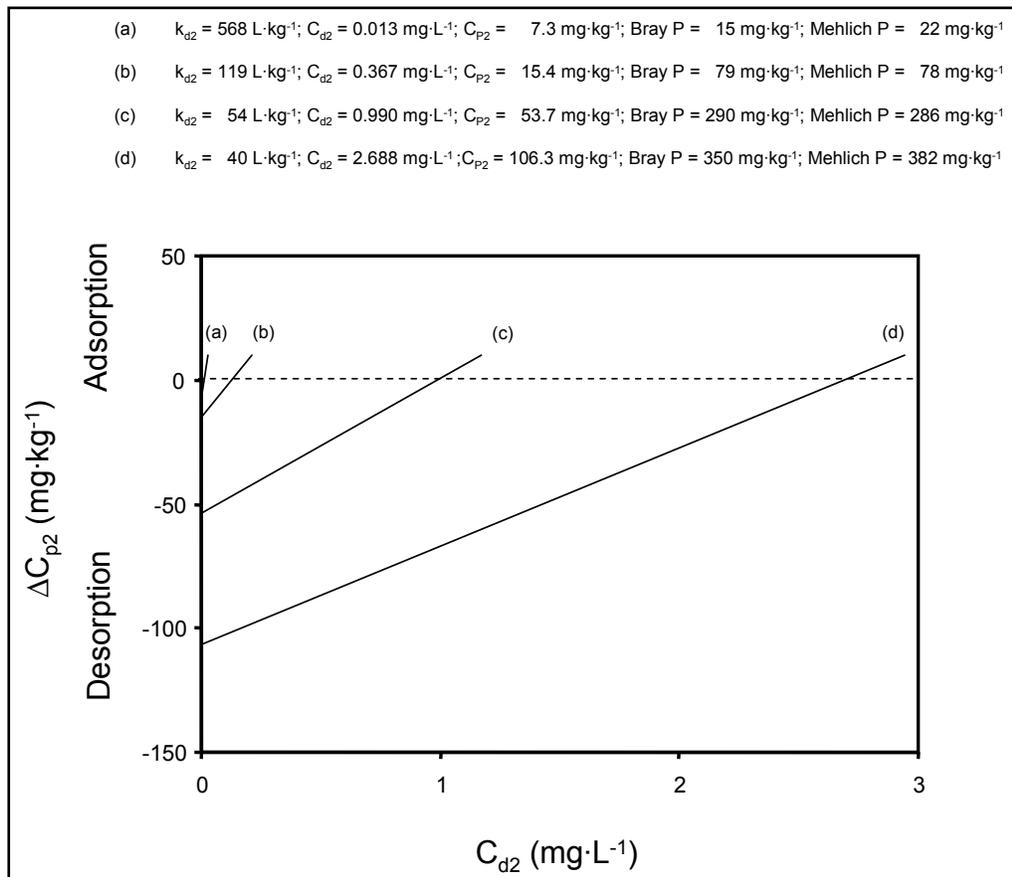


Figure 5. Variations in the soil mass distribution coefficient ( $k_{d2}$ ), equilibrium soluble phosphorus concentration ( $C_{d2}$ ), and soil adsorbed phosphorus concentration ( $C_{p2}$ ) for four soils exhibiting different Bray and Mehlich-3 phosphorus concentrations.

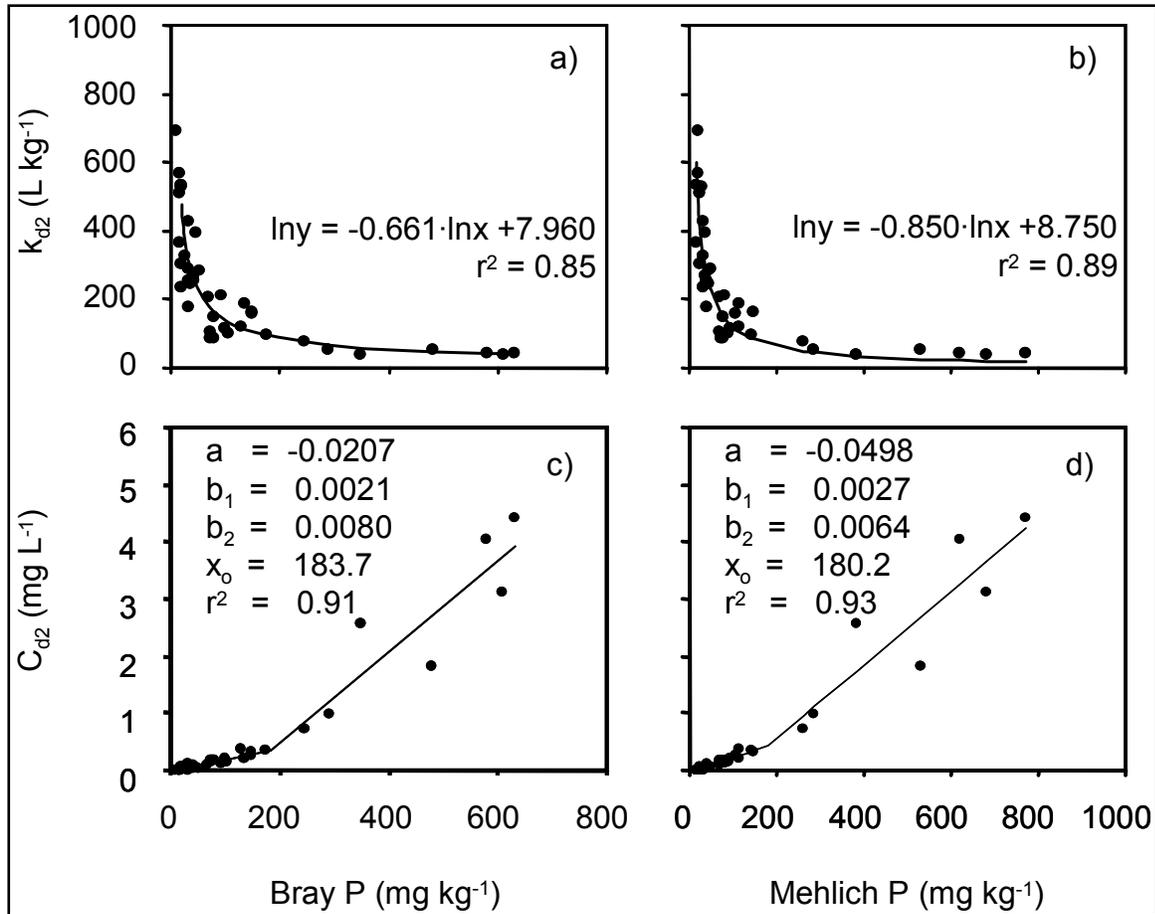


Figure 6. The soil mass distribution coefficient ( $k_{d2}$ ; panels a and b) and the equilibrium soluble phosphorus concentration ( $C_{d2}$ ; panels c and d) versus soil Bray and Mehlich-3 phosphorus. The NLIN procedure (Statistical Analysis System 1994) was used to estimate the coefficients  $a$ ,  $b_1$ ,  $b_2$ , and  $X_0$ . See Equations 7 and 8 for a description.

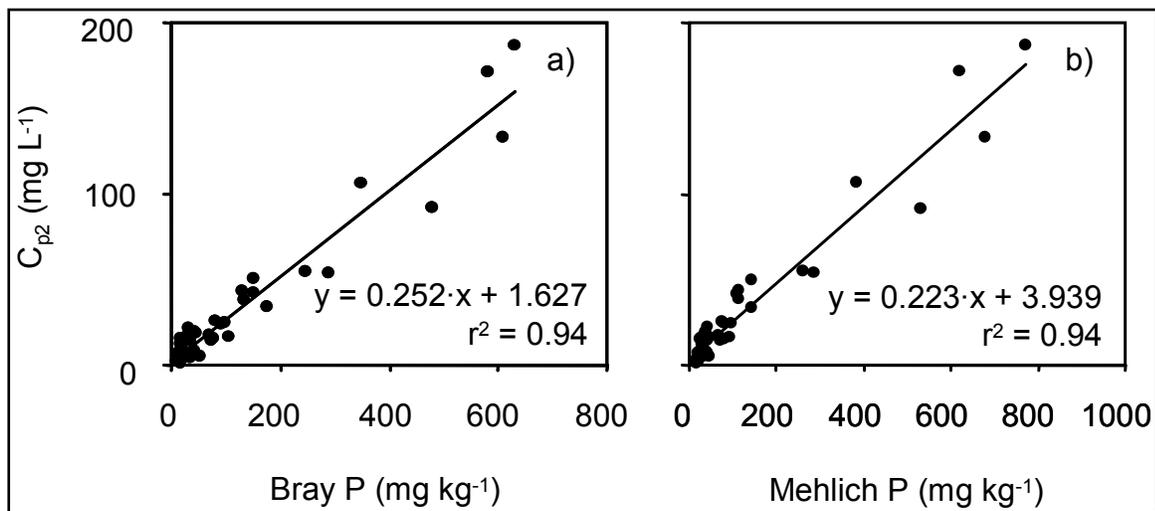


Figure 7. Initial adsorbed soil phosphorus ( $C_{p2}$ ) versus soil Bray and Mehlich-3 phosphorus.

$C_{d2}$  exhibited a biphasic linear increase as a function of crop-available P (Figures 6c and 6d). These patterns could be interpreted using a segmented linear-linear regression analysis (NLIN; Statistical Analysis System 1994) that estimates a threshold between regression lines (Kleinman et al. 2000). Linear models are:

$$y = a + (b_1 \cdot x) \tag{9}$$

$$y = a + (b_1 \cdot x_o) + b_2 \cdot (x - x_o) \tag{10}$$

where  $a$ ,  $b_1$ , and  $b_2$  are constants and  $x_o$  is the Bray or Mehlich P threshold concentration.  $x_o$  was similar for Bray and Mehlich P at 183.7 and 180.2  $\text{mg}\cdot\text{kg}^{-1}$ , respectively. At these threshold levels,  $C_{d2}$  was  $\sim 0.4 \text{ mg}\cdot\text{L}^{-1}$  for Bray and Mehlich P, respectively. Above these levels, the rate of change in  $C_{d2}$  with respect to Bray or Mehlich P increased (Figures 6c and 6d). Similar to  $k_{d2}$ , these patterns are likely related to increasing DPS. As sorption sites become increasingly saturated, buffering capacity declines, resulting in greater equilibrium  $C_{d2}$ . Strong linear relationships were observed between Bray or Mehlich P and  $C_{p2}$  (Figure 7). Overall,  $C_{p2}$  represented approximately 25 percent of the Bray and Mehlich P concentration.

Land uses associated with crop and livestock production in the lower portion of the watershed exhibited the highest  $\text{DPS}_{\text{Bray}}$  and  $\text{DPS}_{\text{Mehlich}}$  (Figure 8). Both indices approached 80-percent saturation in conjunction with high Bray and Mehlich P (Figure 4).  $k_{d2}$ ,  $C_{d2}$ , and  $C_{p2}$  covaried similarly with increasing  $\text{DPS}_{\text{Bray}}$  and  $\text{DPS}_{\text{Mehlich}}$  (Figure 9).  $k_{d2}$  declined logarithmically while  $C_{d2}$  increased in a linear biphasic pattern with increasing  $\text{DPS}_{\text{Bray}}$  and  $\text{DPS}_{\text{Mehlich}}$ . Threshold values for  $\text{DPS}_{\text{Bray}}$  and  $\text{DPS}_{\text{Mehlich}}$  were 37.3 percent and 39.1 percent, respectively, coinciding with a  $C_{d2}$  of  $\sim 0.4 \text{ mg}\cdot\text{L}^{-1}$ . Regression relationships between  $C_{p2}$  and  $\text{DPS}_{\text{Bray}}$  or  $\text{DPS}_{\text{Mehlich}}$  were linear and positive (Figure 9).

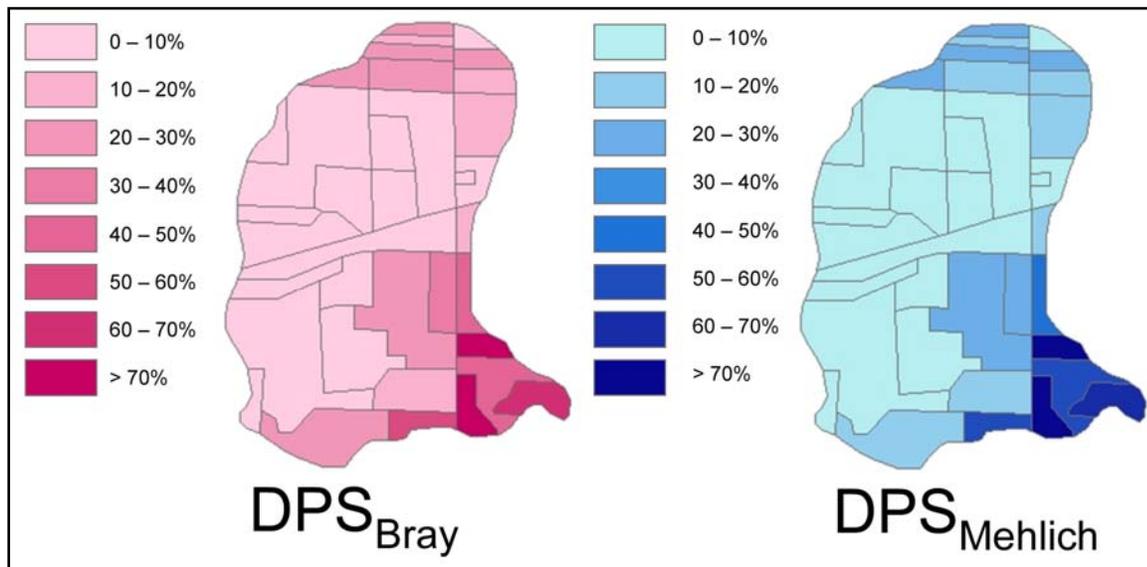


Figure 8. Spatial variations in the degree of phosphorus saturation (DSP), based on soil Bray and Mehlich-3 phosphorus concentration.

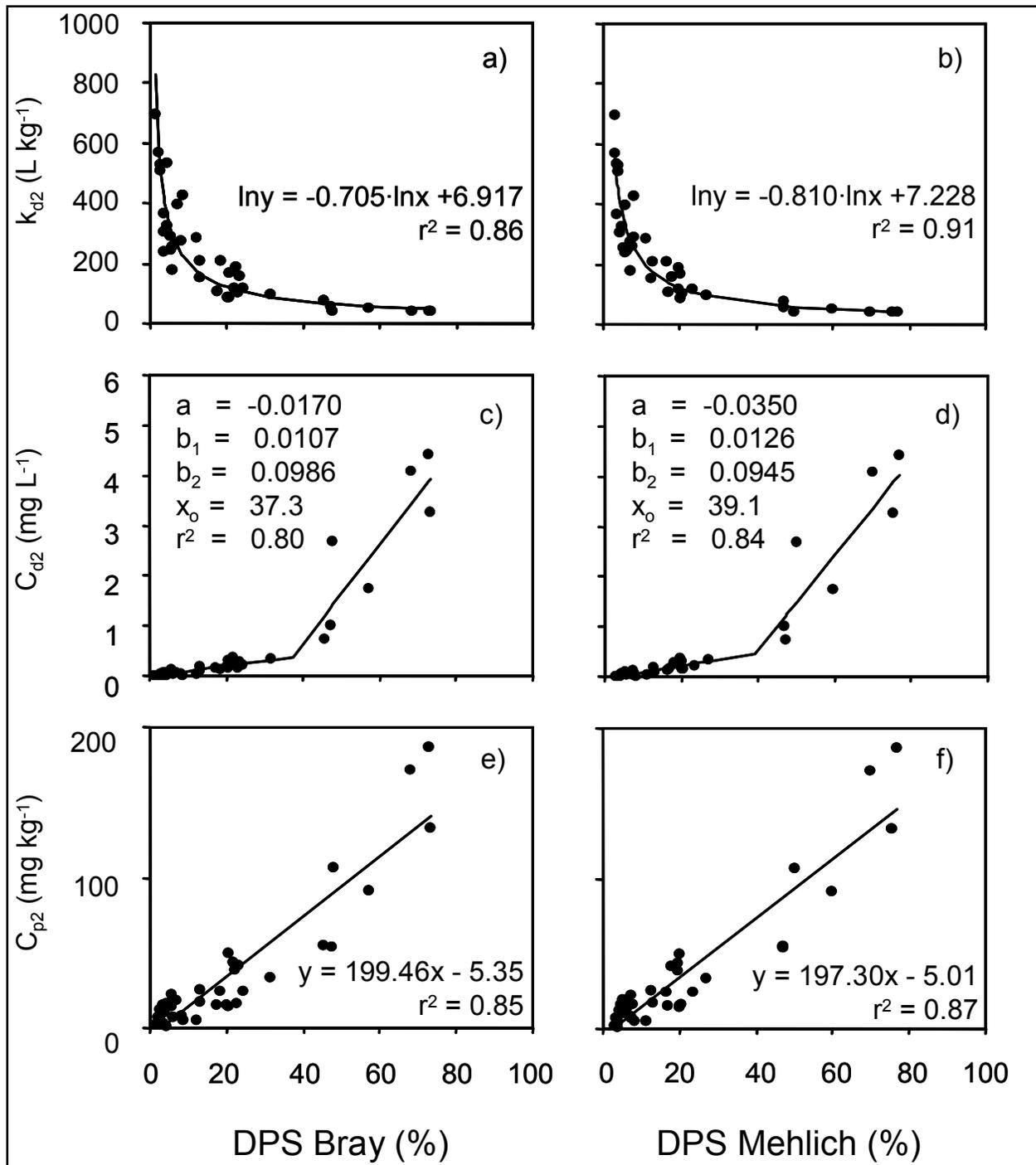


Figure 9. The soil mass distribution coefficient ( $k_{d2}$ ; panels a and b), equilibrium phosphorus concentration ( $C_{d2}$ ; panels c and d), and the initial adsorbed soil phosphorus concentration ( $C_{p2}$ ; panels e and f) versus the degree of phosphorus saturation (DPS) based on soil Bray and Mehlich-3 phosphorus concentration.

An important finding of this study is that commonly measured crop-available P can be used to initialize  $C_{p2}$ ,  $C_{d2}$ , and  $k_{d2}$  in SWWRP-NSM. Empirical regression equations are summarized in Table 1. Relationships between observed and predicted variables were highly significant and slopes were near 1.0 (Figure 10).  $C_{T2}$  can be estimated from Equation 3. Additional information on  $C_{p2}$ ,  $C_{d2}$ , and  $k_{d2}$  is needed for a variety of soil types in order to develop general empirical patterns for initializing these variables in SWWRP-NSM.

<b>Table 1</b> <b>Empirical Equations for Initializing <math>k_{d2}</math>, <math>C_{d2}</math>, and <math>C_{p2}</math> in SWWRP-NSM Using Commonly Measured Soil Bray or Mehlich-3 Phosphorus (<math>P</math>).</b> <b><math>x</math> = Bray or Mehlich <math>P</math> (mg/g)</b>		
Dependent variable, $y$	Bray $P$ regression equations	Mehlich $P$ regression equations
$k_{d2}$ , L·kg <sup>-1</sup>	$\ln(y) = -0.661 \cdot \ln(x) + 7.960$ For $x \leq 183.7$ mg·kg <sup>-1</sup> Bray P $- 0.02067 + 0.00208 \cdot x$	$\ln(y) = -0.850 \cdot \ln(x) + 8.750$ For $x \leq 180.2$ mg·kg <sup>-1</sup> Mehlich P $- 0.04982 + 0.00267 \cdot x$
$C_{d2}$ , mg·L <sup>-1</sup>	For $x > 183.7$ mg·kg <sup>-1</sup> Bray P $0.36118 + 0.0080 \cdot (x - 183.7)$	For $x > 180.2$ mg·kg <sup>-1</sup> Mehlich P $0.4297 + 0.0064 \cdot (x - 180.2)$
$C_{p2}$ , mg·kg <sup>-1</sup>	$y = 0.252 \cdot x + 1.627$	$y = 0.223 \cdot x + 3.939$

**SUMMARY:** Langmuir-type isotherm soil assays were conducted to estimate the mass distribution coefficient ( $k_{d2}$ ), the soil adsorbed inorganic P pool ( $C_{p2}$ ), and the soluble P pool in the soil interstitial water ( $C_{d2}$ ) over a range of soil P concentrations for use in initializing soil P compartments in SWWRP-NSM.  $k_{d2}$  was not constant; but rather, varied in a negative logarithmic pattern as a function of increasing crop-available P concentration. This pattern may be attributable to declining soil buffering capacity for P as DPS increases and availability of unoccupied adsorption sites decreases.  $C_{p2}$  increased in a linear pattern, while  $C_{d2}$  exhibited a biphasic linear increase, in conjunction with increasing crop-available P. The latter pattern may also be related to the DPS.

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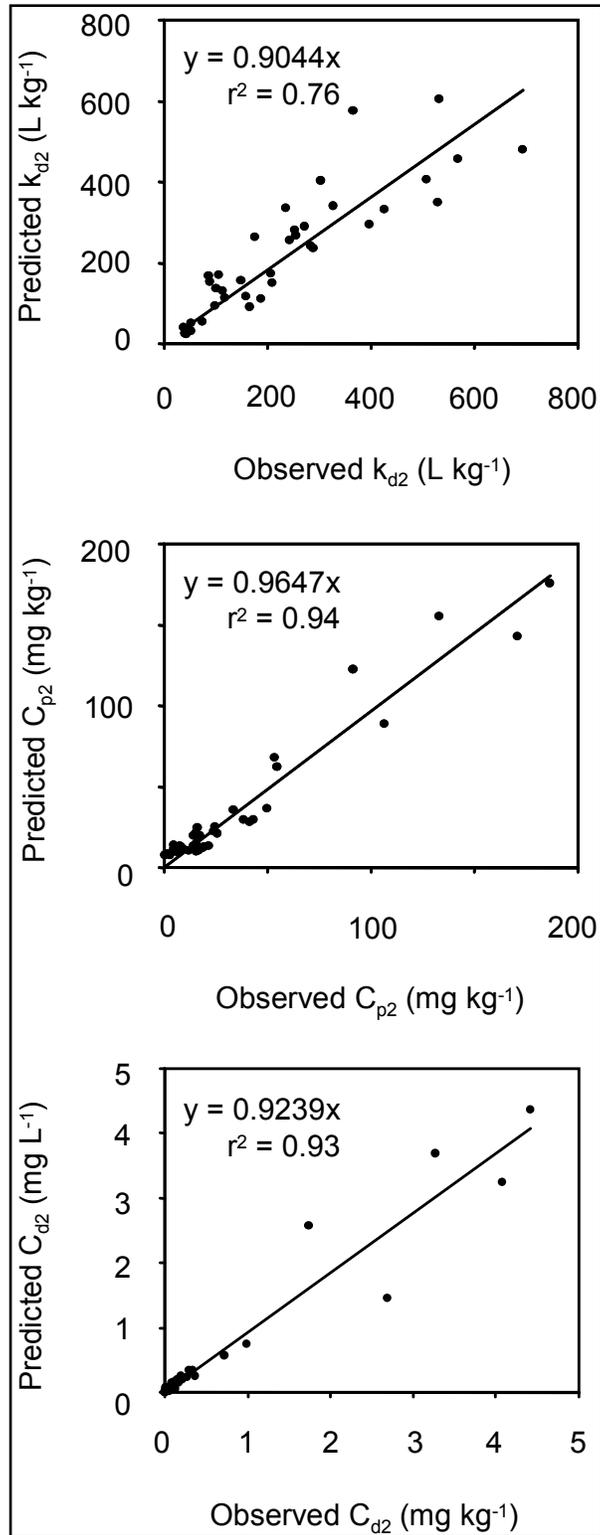


Figure 10. Predicted versus observed soil mass distribution coefficient ( $k_{d2}$ ), initial adsorbed soil phosphorus ( $C_{p2}$ ), and equilibrium phosphorus concentration ( $C_{d2}$ ).

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