

Phosphate Sorption and Release in a Sandy-Loam Soil as Influenced by Fertilizer Sources

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Soil phosphate ($\text{PO}_4\text{-P}$) sorption and release is affected by reactions at the solution–soil surface interface. The objective of this study was to determine how the net negative surface charge and phosphate adsorption/desorption processes in a sandy-loam soil were affected by cattle manure and inorganic fertilizer applications. The soil came from a field experiment where manure and triple superphosphate (TSP) were applied annually on an equivalent plant-available P basis. After 4 yr, manured soils had 37% more negative surface charge in soil suspensions from pH 4 to 7 than TSP-fertilized soils. Phosphate adsorption was 23% lower in soils receiving manure than TSP. The phosphate adsorption data (adsorption of added phosphate + native adsorbed phosphate) was modeled with the Langmuir 2-surface equation, which revealed that the binding strength for phosphate, including native adsorbed phosphate, was about 50% less in the manured soils than the TSP-fertilized soils. These results suggest that manure applications that increase the net negative surface charge also reduce the soil phosphate adsorption capacity. The cumulative desorbed phosphate was twofold greater from manured soils than TSP-fertilized soils. This confirmed the results from phosphate adsorption isotherms showing that phosphate was weakly bound in manured soils, compared with TSP-fertilized soils. We found that manuring not only decreased phosphate retention by the soil but also increased phosphate release into the soil solution, and thus may lead to greater transport of phosphate from agricultural land to waterways.

Abbreviations: DOC, dissolved organic carbon; OM, organic matter; TSP, triple superphosphate.

Phosphate release and retention by soils play a crucial role in both crop production and environmental protection. As early as the 1840s, P was identified as an essential plant nutrient. The application of P fertilizers has contributed to the high yields and quality of modern crop cultivars. Although animal manure is often used as a P fertilizer, many studies have shown that manured soils have less capacity to retain phosphate (Sims et al., 1998; Sharpley et al., 2001), placing frequently manured soils in a higher risk category for environmental pollution than soils that receive manure rarely or not at all.

Manuring is known to affect the chemical reactions that control phosphate adsorption and desorption between the soil solution and solid phases. In soil solution, low-molecular-weight organic acids and soluble humic and fulvic acids released during the decomposition of organic residues reduced the adsorption of added phosphate by competing for binding sites on soil colloids (Sibanda and Young, 1986; Bhatti et al., 1998; Haynes and Mokolobate, 2001). In the soil solid phase, the decomposition of organic residues often causes a transitory increase in soil pH that can have contradictory effects on phosphate adsorption. If the increase in soil pH increases the negative charge on Al and Fe oxide surfaces, less phosphate adsorption is expected, but if the increase in soil pH leads to enhanced hydrolysis of hydroxyl-Al associated with organic matter, more phosphate adsorption may occur (Haynes and

Mokolobate, 2001). In acidic tropical Ferralic Cambisol soils (initial pH = 4.4), the application of green manure increased the soil pH to between 5.6 and 6.1, while oxalate-extractable Al declined to almost zero during a 49-d incubation. The soil phosphate supply was greater when soils received green manure, suggesting that these changes in soil solution pH and extractable Al may have inhibited phosphate adsorption (Cong and Merckx, 2005).

Manuring also alters some soil physiochemical properties important for phosphate diffusion, namely soil porosity (related to the tortuosity factor, Nye, 1968), soil surface area and soil surface charge. In a long-term study from Denmark, total porosity and the number of macropores were not affected by long-term (100 yr) manure applications, but the pore organization (continuity) in the plow layer tended to be greater in manured soil than inorganically fertilized or unfertilized soils (Schjønning et al., 2005). In contrast, manuring generally increases the proportion of water-stable macroaggregates (Aoyama et al., 1999), suggesting that manured soils will have less surface area for binding phosphates than non-manured soils. Linquist et al. (1997) found that phosphate sorption was linearly related to aggregate mass, and increased from 55 to 245 mg P kg^{-1} soil as the mean aggregate diameter decreased from 3.4 to 0.375 mm. Little is known about how manuring affects the soil surface charge, a key determinant of the strength and number of bonds formed between phosphate molecules and soil surfaces. In laboratory incubations, adding plant residues to soils increased the amount of negative surface charge, which may lead to more repulsive forces toward phosphate anions and thus reduce the amount of phosphate adsorbed on surfaces (Easterwood and Sartain, 1990; Cong and Merckx, 2005). It is not known whether surface charge

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in field soils can be altered by manuring, and how this might affect phosphate adsorption and release under field conditions.

There is interest in comparing phosphate adsorption and release in manured and inorganically fertilized soils in the selection of fertilizer sources to meet the goal of crop production and environmental protection. One way to compare fertilizer sources is to select soils that received approximately the same amount of soluble phosphate in all treatments. In a laboratory study, Øgaard (1996) found that at equivalent soluble phosphate addition between 4 and 26.4 mg P kg⁻¹ soil, phosphate adsorption increased as follows: fresh manure < composted manure < KH₂PO₄ chemical fertilizer. Jiao et al. (2004) found that more dissolved reactive phosphate leached from soils receiving composted cattle manure than those fertilized with TSP under equivalent available phosphate application (45 kg P ha⁻¹ yr⁻¹ for 3 yr). These studies suggest that phosphate adsorption will be lower in manured than inorganically fertilized soils receiving an equivalent soluble phosphate input. Yet, how such experimental findings are linked to the alteration of soil physicochemical properties by manuring has not been investigated.

The objective of this study was to evaluate the net negative surface charge and phosphate adsorption/desorption properties in a sandy-loam soil from a field experiment with manure and TSP treatments.

MATERIALS AND METHODS

Soils

Soil samples were collected from a field experiment located on the Macdonald Research Farm, Ste. Anne de Bellevue, Quebec, Canada (45°28' N, 73°45' W, elevation 35.7 m). Annual temperature at the nearby Dorval climate station averages 6.1°C, with mean annual precipitation of 967 mm. The soil is a fine, mixed, frigid Typic Endoaquent, classified as sandy-loam of the Courval series, with a pH of 6.1 in the 0- to 15-cm layer. Conventionally tilled plots under continuous corn production received either manure (composted cattle manure) or inorganic fertilizers (ammonium nitrate and TSP). The input of plant available phosphate (45 kg Mehlich-3 P ha⁻¹ yr⁻¹ from manure or 45 kg P ha⁻¹ yr⁻¹ from 100% water-soluble TSP) was assumed to be equivalent. Mehlich-3 extractable P was about 56% of the total P in manure, similar to the proportion of water-extractable P (43 to 60% of the total P) in beef and dairy manure reported by Kleinman et al. (2005). Applying manure at a rate of 45 kg Mehlich-3 P ha⁻¹ yr⁻¹ supplied 80 kg total P ha⁻¹ yr⁻¹ to manured soils. We assumed that the Mehlich-3 extractable P in manure represented the phosphate that would be slowly released through desorption, dissolution, and mineralization throughout the growing season.

Soil samples were collected from four replicates of each treatment to the depth of 10-cm in October 2003 after harvest, air-dried and gently crumbled to pass through a 2-mm sieve. Soils were analyzed for pH (1:2 soil/water) and total C and N with a Carlo-Erba Flash EA CN analyzer (Milan, Italy). The total P in soils was determined in hydrogen peroxide/sulfuric acid digests (Parkinson and Allen, 1975). Total inorganic phosphate was measured in 0.5 M H₂SO₄ extracts (O'Halloran, 1993). Mehlich-3 extractable phosphate, Fe and Al were determined using the method described by Tran and Simard (1993). Labile phosphate, collected with an anion-exchange resin, and water-extractable phosphate were also measured (Sibbesen, 1977); the difference between labile phosphate and water-extractable phosphate was considered to represent the native adsorbed phosphate in soils (Holford et al., 1974; Wolf et al., 1986). Composted cattle manure

was analyzed for Mehlich-3 phosphate following the same procedure as for soils. Phosphate in digests and extracts was quantified colorimetrically with the ammonium molybdate-ascorbic acid method (Murphy and Riley, 1962) on a Lachat Quik-Chem AE flow-injection autoanalyzer (Lachat Instruments, Milwaukee, WI). Mehlich-3 Fe and Al were analyzed by atomic absorption spectrometry (AAS). Characteristics of soil from manured and TSP-fertilized plots are provided in Table 1.

Soil Surface Charge

A back-titration method was used to evaluate the soil surface charge (Duquette and Hendershot, 1993). Briefly, it involved two procedures. First, sample titration: 2 g of soil was mixed with 30 mL of 0.01 M KCl solution as the supporting electrolyte. The suspension was titrated with standardized 0.1 M HCl to pH 3. Then, a back-titration was performed with standardized 0.02 M KOH at a rate of 0.2 mL min⁻¹ to pH 10. The pH and the volumes of acid and base added were recorded. Second, reference titration: a second soil suspension was prepared and titrated to pH 3 following the procedure in the sample titration. Then the suspension was transferred into a 50-mL centrifuge tube and centrifuged at 7800 × g for 20 min. The supernatant was filtered using 0.45-µm Millipore polycarbonate membrane into a 100-mL preweighed beaker. The filtrate was weighed and back-titrated to pH 10. During both sample and reference titrations, the suspension or solution was agitated continuously by a magnetic stirrer and purged with ultrapure N₂ gas. The back-titration measurement provides data for relative surface charge (ΔQ), which was calculated by subtracting the OH⁻ consumption of the reference titration from the sample titration at the same pH.

Phosphate Adsorption

A batch adsorption experiment was performed to assess phosphate adsorption in manure-amended and TSP-fertilized soils. Two-gram soil samples were treated with 30 mL of solution containing 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 or 1.0 mM P from KH₂PO₄ and 0.01 M [K], which was balanced by adding 0.1 M KCl. The highest concentration, 1.0 mM P, was chosen based on the assumption of Holford et al. (1974) that adsorption would be the dominant retention mechanism at concentrations < 1 mM P. Above that, precipitation processes would increasingly control the phosphate concentration in soil solution. Although 1 mM P may not

Table 1. Soil chemical properties as influenced by fertilizer sources.

Parameter	Man.-soil†	TSP-soil‡	t test (n = 4): Pr > t (Man.-soil vs. TSP-soil)
pH (water)	6.03 ± 0.09§	5.16 ± 0.06	0.0002
Total nutrients, g kg ⁻¹			
C	27.6 ± 3.5	18.3 ± 2.0	0.0339
N	2.68 ± 0.40	1.85 ± 0.39	0.0080
P	1.21 ± 0.09	1.16 ± 0.08	0.4919
Inorganic P	1.09 ± 0.05	1.02 ± 0.06	0.0145
Mehlich-3, mg kg ⁻¹			
P	188 ± 33	156 ± 26	0.0771
Fe	266 ± 31	281 ± 42	0.5226
Al	1180 ± 37	1250 ± 65	0.1232
Labile-P, mg kg ⁻¹	120 ± 14	86.0 ± 12.0	0.0232
Water-P, mg kg ⁻¹	20.4 ± 5.7	7.25 ± 3.07	0.0177
Qnat.P, mg kg ⁻¹ ¶	99.6 ± 9.1	78.4 ± 10.5	0.0394

†Man.-soil: manured soil. Application rate was 45 Mg (wet weight) ha⁻¹ yr⁻¹, which supplied 45 kg plant-available phosphate (Mehlich-3 P) ha⁻¹ yr⁻¹.

‡TSP-soil: triple superphosphate-fertilized soil. Application rate was 45 kg P ha⁻¹ yr⁻¹.

§Mean ± standard error of four replicate soils from the field experiment.

¶Native adsorbed phosphate.

be a definite limit for adsorption and precipitation processes, it has been generally concluded that at P solution concentrations in the millimolar range, adsorption reactions predominate in soils other than calcareous and highly weathered soils (Holford et al., 1974). The initial solution with different phosphate concentrations was adjusted to pH 6 with 0.1 M KOH. The phosphate adsorption of one replicate soil from each treatment was determined with the same range of phosphate concentrations, but adjusted to pH 3 (with 0.1 M HCl) and pH 10 (with 0.1 M KOH). The soil-phosphate solution mixture was shaken on an end-to-end shaker (15 cycles min⁻¹) at 22 ± 1°C for 24 h. The suspension was centrifuged at 7800 × g for 20 min at 10°C. After measuring pH, the supernatant was filtered through a 0.45-µm membrane. The filtrate was analyzed for phosphate (Murphy and Riley, 1962). The adsorption of added phosphate was calculated as the difference between the amount of phosphate added and the phosphate remaining in solution.

The Langmuir 2-surface equation (Langmuir, 1918; Holford et al., 1974) was used to generate phosphate adsorption parameters.

$$Q = Q_{\max 1} \frac{K_1 C}{1 + K_1 C} + Q_{\max 2} \frac{K_2 C}{1 + K_2 C} \quad [1]$$

where Q = phosphate adsorbed (mg P kg⁻¹) = adsorption of added phosphate + native adsorbed phosphate, Q_{\max} = adsorption maxima (mg kg⁻¹), K = adsorption constant, C = phosphate concentration in equilibrium solution (mg P L⁻¹), and subscripts 1 and 2 denote the high-energy surface and the low-energy surface, respectively.

The distribution of native adsorbed phosphate on the high-energy surface and the low-energy surface ($Q_{\text{nat.P1}}$ and $Q_{\text{nat.P2}}$) was calculated based on parameters (Q_{\max} and K) generated from Eq.[1] and solution phosphate concentration (C) obtained by $Q = Q_{\text{nat.P}}$ (Table 1).

Phosphate Desorption

Phosphate desorption was investigated using a flow method. Ten-grams of soil was placed in a 20-mL polyethylene filtration tube with frits at both ends. Artificial rainwater (Jiao et al., 2004) was continuously passed through the vertical soil column at 3 mL h⁻¹ with a peristaltic pump. This was performed for 6 h d⁻¹ for 10 consecutive days (10 desorption events) at 6°C, which represents the average annual field temperature and also suppresses the microbial activity. The desorption solution collected on each day was analyzed for phosphate, Fe and Al, as described above, and

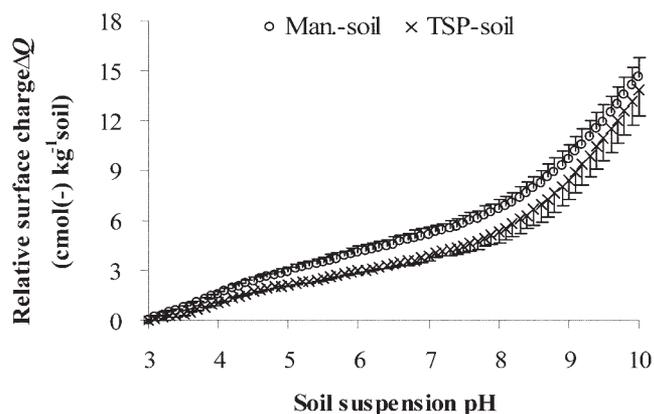


Fig. 1. Soil relative surface charge in manured soil (Man.-soil) and triple superphosphate-fertilized soil (TSP-soil). Data were pooled from four replicates of the field experiment. The vertical bars represent standard error.

for dissolved organic carbon (DOC) using a Shimadzu TOC-V analyzer (Shimadzu Corporation, Kyoto, Japan).

Statistical Analysis

The paired t test in the SAS program (SAS Institute, 1999) was used to test the differences in soil properties, phosphate adsorption and DOC released between manure and TSP treatments. The SAS nonlinear procedure (PROC NLIN) was used to generate the Langmuir 2-surface model.

RESULTS AND DISCUSSION

Soil Properties

Before P fertilizer application, the soil pH in the selected plots averaged 5.79. It increased to pH 6.03 after 4 yr of manure amendment. Similar results were reported in an 8-wk long incubation study, where soil pH increased from 5.5 to 6.3 with the addition of 40 g cattle manure kg⁻¹ soil (Whalen et al., 2000). After 4 yr of applying the fertilizer treatments, the mean measured pH of the manured soil was 6.03, significantly ($P < 0.05$) greater than TSP-fertilized soils, which had a pH of 5.16 (Table 1). The TSP-fertilized soils also received ammonium nitrate each year. Ammonium nitrate is an acidic fertilizer, requiring 0.59 Mg per Mg of N applied to neutralize the acidity (Follett et al., 1981), but TSP-fertilized soils were not limed during this study. Similarly, Koopmans et al. (2003) reported that a sandy-loam soil with an initial pH (KCl) of 4.4 had a lower pH value in the NPK fertilized plots (pH = 4.1) than in the manure-amended plots (pH = 5.4 to 6.5) after 11 yr of applying fertilizer treatments.

The manure treatment increased total C by 51% and total N by 45% compared with TSP fertilizer treatment (Table 1), due to greater C and N inputs to soil from manure than chemical fertilizers. We supplied about the same amount of plant-available phosphate to manure and TSP treatments (45 kg Mehlich-3 P ha⁻¹ yr⁻¹), but the total P input was higher in manured soils, about 80 kg total P ha⁻¹ yr⁻¹. There were numerically higher total P and Mehlich-3 P concentrations in manured soils than TSP-fertilized soils, but these were not statistically different (Table 1). Manuring increased the labile phosphate by 40% and water-extractable phosphate by 181% (Table 1). If phosphate desorption, dissolution and mineralization from manure was greater in soils than predicted from Mehlich-3 extracts, then the manured soils would have contained more water-soluble phosphate than those receiving TSP. Another explanation is assumed on the phosphate binding strength. Manure-P weakly interacts with soil Fe/Al hydroxides forming bonds on the external surface due to its association with organic macromolecules. Such macromolecules may be subject to gradual P decomposition by microbes, releasing P into solution. On the other hand, TSP-P may be strongly sorbed onto the functional groups of Fe/Al hydroxides or diffuse into soil particles, thus limit P availability with time (Linquist et al., 1997).

Soil Surface Charge

Manured soils had more negative surface charge than TSP-fertilized soils in soil suspensions from pH 3 to 10 (Fig. 1). For example, at a soil suspension pH of 6, the relative surface charge

in manured soils was $4.05 \text{ cmol}(-) \text{ kg}^{-1}$, about 37% greater than in TSP-fertilized soils, where the relative surface charge was only $2.96 \text{ cmol}(-) \text{ kg}^{-1}$. We speculate that manuring generates organic acids, which bind to soil surfaces, thus increasing the net negative charges on the surface of soil particles. This is consistent with the higher pH value in manured soils than TSP-fertilized soils (Table 1), which indicates more negative charge on the particle surface of soils amended with manure than TSP.

Phosphate Adsorption

Manured soils had significantly lower phosphate adsorption than the TSP-fertilized soils (Table 2). Additionally, we also tested one replicate soil for phosphate adsorption with solutions adjusted to pH 3 and 10, which would be representative of soil solution pH immediately after acid-forming fertilizers or lime was applied. At normal (pH = 6.0) or extreme conditions (pH 3 or 10), manured soils demonstrated lower phosphate adsorption than TSP-fertilized soils (Fig. 2a, b, c). One explanation for the decrease in phosphate adsorption in manure-amended soils is that some phosphorus adsorption sites in the manured soils were occupied by the negatively charged organic acids, as indicated more negative charges on the surface of manured soils (Fig. 1).

To investigate phosphate binding strength, a Langmuir 2-surface model was used to fit adsorption data for manured and TSP-fertilized soils (Fig. 2). The parameters generated from the 2-surface model showed that phosphate adsorption took place on two types of surface: one is a high-energy surface (SOH_2^+ discussed in Jiao, 2005), which has high binding strength (K_1) but low adsorption maxima ($Q_{\text{max}1}$); another is low-energy surface (SOH discussed in Jiao, 2005), which has low binding strength (K_2) but high adsorption maxima ($Q_{\text{max}2}$) (Table 3). The binding strength on the high-energy surface (K_1) was about 50 times greater than on the low-energy surface (K_2). Thus, more than 90% of the native adsorbed phosphate ($Q_{\text{nat.p}}$) was distributed on the high-energy surface (Table 3). The obvious difference between manure and TSP fertilizer treatments lies in the binding strength (K_1 and K_2) on both energy surfaces. The

K_1 and K_2 values were about 50% lower for manured soils than TSP-fertilized soils (Table 3). Since the K_1 and K_2 values reflect not only the binding strength of observable adsorbed phosphate but also that of native adsorbed phosphate, we suggest that native adsorbed phosphate ($Q_{\text{nat.p}}$) in manured soils is less strongly retained, thus more easily released into soil solution.

Numerous studies have suggested that phosphate adsorption is an inner sphere specific adsorption process, involving ligand exchange with anions such as OH^- (Hingston et al., 1967; Bhatti et al., 1998). Theoretically, phosphate adsorption should be accompanied by the release of OH^- , thus the solution pH value should increase. This was observed when phosphate solution with pH of 10 was added to soil (Fig. 3c), but not with solutions having pH 3 (Fig. 3a) and pH 6 (Fig. 3b). When a KH_2PO_4 solution with pH 3 was added, 85% of the

Table 2. Adsorption of added phosphate as affected by fertilizer sources.

Phosphate added [†] <i>mM</i>	Adsorption of added phosphate	
	Man.-soil [‡]	TSP-soil [§]
	mg P kg ⁻¹	
0	-6.75 ± 2.66 ¶	-1.93 ± 0.82
0.1	32.2 ± 4.0	41.7 ± 1.8
0.2	66.6 ± 5.2	83.4 ± 3.0
0.3	94.1 ± 7.3	121 ± 4
0.4	121 ± 8	155 ± 5
0.5	142 ± 9	186 ± 6
0.6	161 ± 10	211 ± 6
0.7	183 ± 11	236 ± 6
0.8	200 ± 12	255 ± 9
1.0	229 ± 12	295 ± 11
t-test (2-sample paired, <i>n</i> = 40): Man.-soil vs. TSP-soil		
<i>Pr</i> > <i>t</i>	<0.0001	

[†]Phosphate solution pH = 6.0.

[‡]Man.-soil: manured soil.

[§]TSP-soil: triple superphosphate-fertilized soil.

¶ Mean ± standard error of four replicate soils from the field experiment.

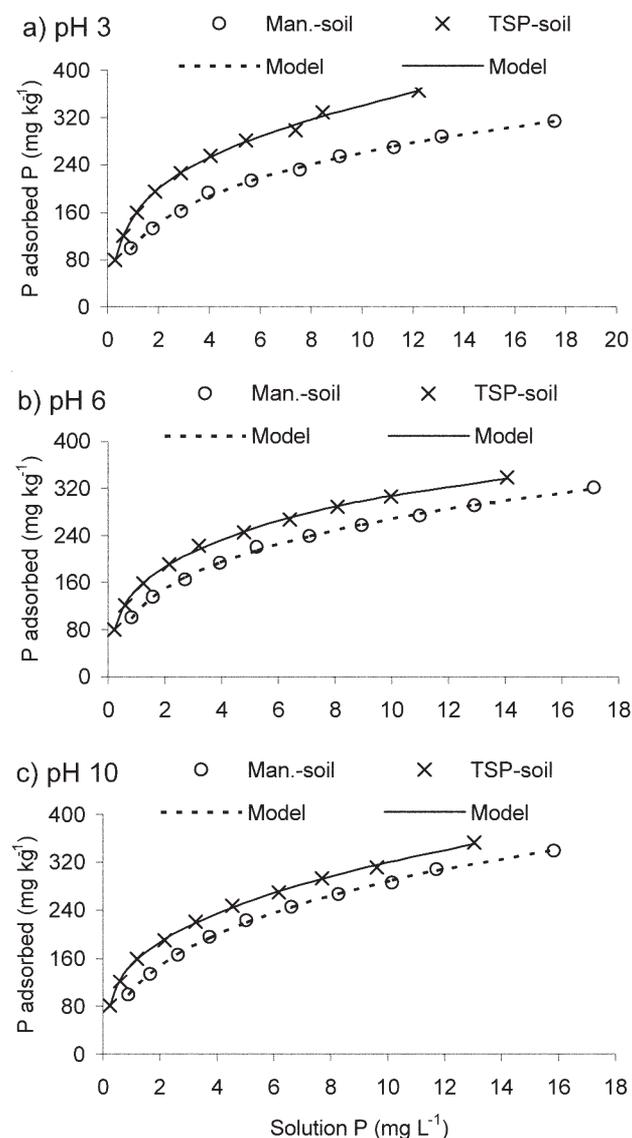


Fig. 2. Phosphate adsorption (adsorption of added phosphate + native adsorbed phosphate) in manured soil (Man.-soil) and triple superphosphate-fertilized soil (TSP-soil) from phosphate solutions adjusted to (a) pH 3; (b) pH 6; and (c) pH 10. Dashed and solid lines were fitted using a Langmuir 2-surface model. Data points were from one replicate soil.

Table 3. Parameters obtained from the Langmuir 2-surface model for P adsorption data.[†]

Parameter	Man.-soil [‡]	TSP-soil [§]
<u>High-energy surface</u>		
K_1	2.161	4.082
Q_{max1} , mg kg ⁻¹	173	202
$Q_{nat.P1}$, mg kg ⁻¹ ¶	91	74
<u>Low-energy surface</u>		
K_2	0.045	0.088
Q_{max2} , mg kg ⁻¹	390	352
$Q_{nat.P2}$, mg kg ⁻¹ #	9	4
Model R^2	0.9999	0.9999

[†]Data of four replicate soils from the field experiment.

[‡]Man.-soil: manured soil.

[§]TSP-soil: triple superphosphate-fertilized soil.

¶ Native adsorbed phosphate on high-energy surface.

Native adsorbed phosphate on low-energy surface.

phosphate is $H_2PO_4^-$ and 15% is H_3PO_4 according to phosphate speciation calculated with Visual Minteq (Gustafsson, 2004). After 24-h reaction with soils, solution pH reached 5.17 with manured soils and 4.46 with TSP-fertilized soils (Fig. 3a). The pH change would shift all the solution phosphate to $H_2PO_4^-$ and release H^+ from H_3PO_4 into the solution. The release of H^+ from the dissociation of H_3PO_4 may compensate for the OH^- released from phosphate adsorption, thus there was no change in solution pH (Fig. 3a) despite the increase of

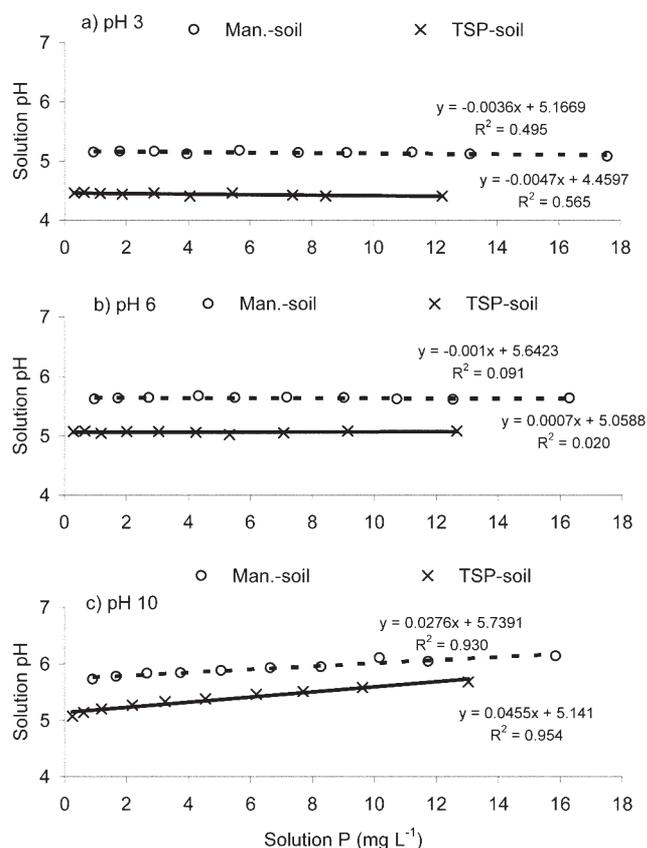


Fig. 3. The relationship between pH and phosphate concentration in the equilibrium solution from phosphate adsorption study. Manured soil (Man.-soil) and triple superphosphate-fertilized soil (TSP-soil) are the same as in Fig. 1, and results are from one replicate soil. The added phosphate solution pH was: (a) pH 3; (b) pH 6; and (c) pH 10.

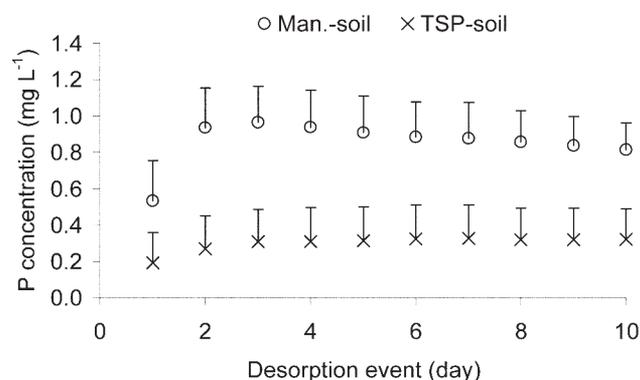


Fig. 4. Phosphate concentrations in desorption solutions collected from manured soil (Man.-soil) and triple superphosphate-fertilized soil (TSP-soil) on 10 consecutive days. Data points are the means (n = 4) and vertical bars are standard errors of the mean.

phosphate adsorption at higher phosphate concentration in equilibrium solutions (Fig. 2a).

Phosphate Desorption

Manured soils produced higher phosphate concentrations in each desorption event than the TSP-fertilized soils (Fig. 4). The phosphate concentration in collected solutions increased from the first to third desorption event and then tended to decrease in manured soil but remained stable in TSP-fertilized soils (Fig. 4). The results indicate that native adsorbed phosphate in manured soil was more easily released into the soil solution than that in the TSP-treated soil, as suggested by the K_1 values calculated in Table 3.

Soils receiving annual applications of manure released more phosphate during the 10 desorption events than soils receiving TSP fertilizer (Fig. 5). For example, after five events, the concentration of phosphate desorbed from manured soils (4.28 mg kg⁻¹) was about three times the desorbed phosphate concentration in TSP-fertilized soils (1.34 mg kg⁻¹) (Fig. 5). The phosphate desorption data was described with a simple linear equation (Fig. 5), and the slope can be considered to be the desorption rate. Manured soils had a desorption rate of 0.89 mg P kg⁻¹ d⁻¹, almost three times of TSP-fertilized soils where the desorption rate was 0.30 mg P kg⁻¹ d⁻¹ (Fig. 5). Similarly, Laboski and Lamb (2003) reported that when the same amount of total P (144 and 288 mg P kg⁻¹ soil) was added to soil and incubated for up to 9 mo, soils receiving liquid swine manure had significantly higher soil test P (Bray-1) than soils receiving KH_2PO_4 fertilizer.

We propose that organic acids from manure decomposition contributed to the greater phosphate desorption from manured soils than from the TSP-fertilized soils. The DOC concentration in the desorption solution was significantly greater ($P < 0.0001$) in manured soils than TSP-fertilized soils (Fig. 6). Since DOC is an indicator of di/tricarboxylic acids (Strobel et al., 1999), this suggests that more organic acids were present in manured than TSP-fertilized soils. Organic acids could affect phosphate desorption in two ways. First, they may chelate Fe and Al oxides and bring them from the soil surface into solution, thus reducing the number of phosphate binding sites. It was found that Fe and Al concentrations in the phosphate desorption solution averaged 0.84 mg Fe L⁻¹ and 0.56 mg Al L⁻¹ in manured soils,

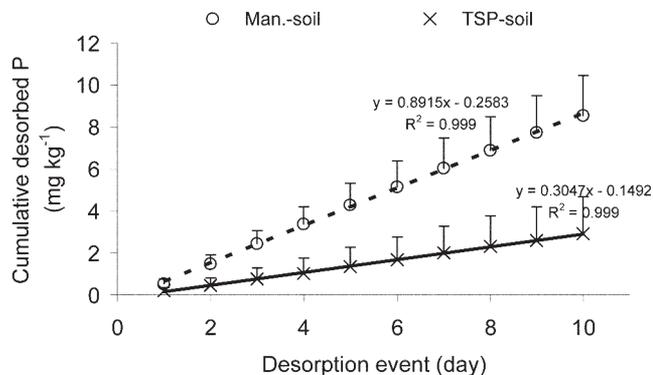


Fig. 5. Phosphate desorption in manured soil (Man.-soil) and triple superphosphate-fertilized soil (TSP-soil). Data points are the means of four soil replicates from field experiment and vertical bars are standard errors of the mean.

which were significantly greater ($\alpha = 0.05$) than in TSP fertilized soils, which contained $0.57 \text{ mg Fe L}^{-1}$ and $0.43 \text{ mg Al L}^{-1}$. Second, organic acids may compete with $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ for the binding sites (positively charged Fe and Al oxides) on the surface of soil particles and replace the loosely adsorbed $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ from the binding sites, thus enhancing the release of phosphate to the solution, as observed by Bolan et al. (1994) and Bhatti et al. (1998).

Other Considerations

We measured more negative charge on soil particle surfaces and greater DOC concentrations in phosphate desorption solutions of manured than TSP-fertilized soils. These results lead us to speculate that negatively charged organic acids from manure may be responsible for the lower phosphate adsorption and higher phosphate desorption capacities in manured soils. How organic acids affect phosphate adsorption/desorption reactions is not well known, but could be evaluated by measuring soil OM pools. Manuring can increase the soil OM significantly within a few years, as we have shown in this study. Sims et al. (1998) noted that soils with a high OM content have a greater potential to lose phosphate via subsurface leaching than soils with a low OM content. However, the change in soil OM due to manuring is likely affected by the type and quantity of manure applied, as well as soil factors that influence the decomposition and stabilization of OM from manure. Further work is needed to evaluate the relationship between soil OM and phosphate adsorption/desorption processes, as these are critical for calculating manure application rates that provide sufficient plant-available phosphate for crops, without compromising environmental objectives.

CONCLUSIONS

In a conventionally tilled soil under continuous corn production, manure applications increased the net negative charge on soil particle surface, compared with TSP fertilizer. This may have caused more repulsion of phosphate anions and thus reduced the amount of phosphate adsorbed on surfaces of manure soils, relative to TSP-fertilized soils. Fitting phosphate adsorption data to the Langmuir 2-surface model revealed that the native adsorbed phosphate in manured soils was loosely

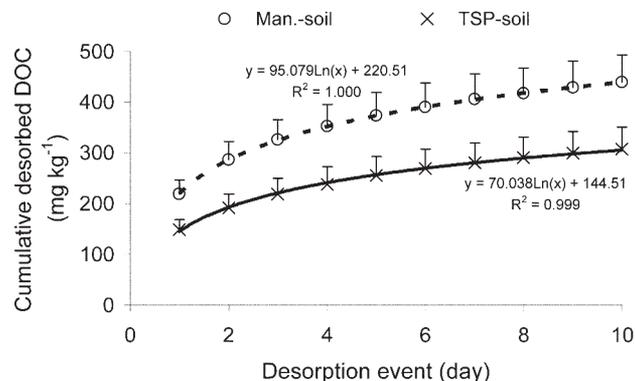


Fig. 6. Cumulative dissolved organic carbon (DOC) released from manured soil (Man.-soil) and triple superphosphate-fertilized soil (TSP-soil) during 10 desorption events. Data points are the means of four soil replicates from field experiment and vertical bars are standard errors of the mean.

retained compared with TSP-fertilized soils. Thus, manured soil had a greater phosphate desorption capacity and would release more phosphate into soil solution than TSP-fertilized soils. We propose that manuring alters soil physiochemical properties in a way that elevates the soil solution phosphate level, making it a more efficient source of plant-available P than TSP when added on an equivalent soluble phosphate level to a high fertility soil. Whether phosphate adsorption/desorption reactions are similar on low fertility soils and with other types of manure remains to be studied.

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