

Phosphate Reactivity in Long-Term Poultry Litter-Amended Southern Delaware Sandy Soils

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ABSTRACT

Eutrophication caused by dissolved P from poultry litter (PL)-amended agricultural soils has been a serious environmental concern in the Delaware–Maryland–Virginia Peninsula (Delmarva), USA. To evaluate state and federal nutrient management strategies for reducing the environmental impact of soluble P from long-term PL-amended Delaware (DE) soils, we investigated (i) inorganic P speciation; (ii) P adsorption capacity; and (iii) the extent of P desorption. Although the electron microprobe (EMP) analyses showed a strong correlation between P and Al/Fe, crystalline Al/Fe-P precipitates were not detected by x-ray diffraction (XRD). Instead, the inorganic P fractionation analyses showed high levels of oxalate extractable P, Al, and Fe fractions (615–858, 1215–1478, and 337–752 mg kg⁻¹, respectively), which were susceptible to slow release during the long-term (30-d) P desorption experiments at a moderately acidic soil pH_{water}. The labile P in the short-term (24-h) desorption studies was significantly associated with oxalate and F extractable Fe and Al, respectively. This was evident in an 80% reduction maximum in total desorbable P from NH₄ oxalate/F pretreated soils. In the adsorption experiments, P was strongly retained in soils at near targeted pH of lime (≈6.0), but P adsorption gradually decreased with decreasing pH near the soil pH_{water} (≈5.0). The overall findings suggest that P losses from the can be suppressed by an increase in the P retention capacity of soils via (i) an increase in the number of lime applications to maintain soil pH_{water} at near targeted pH values, and/or (ii) alum/iron sulfate amendments to provide additional Al- and Fe-based adsorbents.

PHOSPHATE IS A MAJOR nonpoint source contaminant in surface water in the Inland Bays Watershed, a national estuary located in southern Delaware, USA (Andres, 1991; Sims and Ritter, 1993). Annually applied PL (a mixture of manure and woodchips or sawdust used as bedding materials in the poultry houses) has increased both total and bioavailable P in surface and subsurface soil horizons (Mozaffari and Sims, 1994; Sims et al., 2000). Several studies reported that >90% of DE agricultural soils, which were used in the studies, are agronomically high- to excessive-P soils (i.e., >100 mg kg⁻¹ based on operationally defined extractable P using Mehlich 3 extraction) (Daniel et al., 1998; Mozaffari and Sims, 1994; Sims and Wolf, 1994; Sims et al., 1998; Tisdale et al., 1993). Seasonal P release via surface-runoff, surface-erosion, and preferential flow are suspected potential causes for eutrophication and outbreaks of *Pfies-*

teria in Atlantic Coastal water bodies (Burkholder and Glasgow, 1997; Daniel et al., 1998; Stamm et al., 1998). An increased risk for nonpoint P pollution has been a serious environmental concern on the Delmarva Peninsula (Sharpley et al., 1996; Sims et al., 1998). In recent years, laws to mandate nutrient management plans have been passed in the Mid-Atlantic States. Under the Delaware Nutrient Management Act of 1999, the P application rate cannot exceed a 3-yr crop removal rate (Sims, 1999). The Maryland Water Quality Improvement Act of 1998 suggested that the P based nutrient management plans should be implemented by 2005 for all sources of P input (e.g., manure, fertilizers, municipal biosolids, compost) (Simpson, 1998). Cessation or reduction in PL applications and remediation via alum amendments on PL have been considered in future state and federal nutrient management guidelines and laws to reduce the negative impact of soluble P transport to neighboring aquatic environments. To validate these options, we seek answers for the following questions about the P reactivity (retention and release) in high P Delmarva agricultural soils: (i) If PL applications ceased, to what extent will P continue to desorb from the P-rich soils? And, if so, what fraction of P (i.e., operationally defined extractable P) is mostly likely to be desorbed? (ii) If PL were continued to be applied at the current or reduced amendment rates, do the soils have any retention capacity under fluctuating soil pH (before and after liming)?

To fulfill the answers to the questions above, the objectives of this study were to investigate P adsorption capacity, P desorbability, and its relation to operationally defined P fractions using the following comprehensive laboratory experiments. First, the PL-amended DE soils were well characterized using indirect and direct approaches (e.g., sequential inorganic P fractionation and EMP analyses). Second, the relationships between desorbable P fractions and operationally defined P fractions defined as major chemical components in the Mehlich 3 chemical extraction (e.g., NH₄ oxalate and NH₄F) in the P-rich DE soils were investigated by combining short- and long-term desorption experiments and chemical extractions. While short-term (24-h) P desorption experiments were conducted on the soils that have been pretreated with specific chemical reagent treatments, long-term (30-d) P desorption experiments were performed without any chemical pretreatment. Third, to better predict the P partitioning processes in the soils,

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Abbreviations: CEC, cation exchange capacity; DE, Delaware; Delmarva, Delaware–Maryland–Virginia Peninsula; EDS, energy dispersive spectrometer; EMP, electron microprobe; Ev, Evesboro; ICP–AES, inductively coupled plasma–atomic emission spectroscopy; OM, organic matter; Os, Osier; PL, poultry litter; Pm, Pocomoke; PZSE, point of zero salt effect; Sf, Sassafras; WDS, wavelength dispersive spectrometer; XRD, x-ray diffraction.

the effect of pH (4.5–7.5) and initial P concentrations (0.1–1 mM) on P retention capacity were investigated in the PL-amended DE soils using batch adsorption experiments.

MATERIALS AND METHODS

Four long-term PL-amended DE topsoils (0–20 cm) were collected from the Inland Bays Watershed in southern Delaware, USA (Fig. 1). The sites have been cultivated and PL-amended for more than three decades. The soil samples were collected from the well-drained soils Evesboro (Ev) loamy sand (mesic, coated Typic Quartzipsamments) and Sassafras (Sf) sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults), and from the poorly drained soils Osier (Os) loamy sand (siliceous, thermic Typic Psammaquents) and Pocomoke (Pm) sandy loam (coarse-loamy, siliceous, active, thermic Typic Umbraquults). All soils were air dried and passed through a 2-mm sieve for further analyses.

Physicochemical Characterization of Soils

Soil pH_{water} was determined in deionized water using a soil/solution ratio of 1:1. Loss-on-ignition and hydrometer methods were used to measure percentage organic matter (OM) and particle size, respectively (Sims and Heckendorn, 1991). Cation exchange capacity (CEC) was measured using an unbuffered salt extraction method (Grove et al., 1982). The point of zero salt effect (PZSE) of four amended topsoils and three nonamended topsoils were also measured using the potentiometric titration method (Zelazny et al., 1996). The PZSE, which is defined as the suspension pH at which soil has a net charge of zero, was derived from the intersection of two or more potentiometric curves. Total P fractions (i.e., organic and inorganic P phases) were differentiated using an acid-base extraction method described by Bowman (Bowman, 1989). Approximately 2.0 g of air-dried soil samples (2-mm sieved) were mixed with 3 mL of reagent-grade concentrated H_2SO_4 , and the mixtures were gently swirled for 10 min with an addition of 4 mL of deionized water (1 mL at a time). While acid extracts were recovered with 0.45- μm membrane filters, filtrates were further extracted with 100 mL of 0.5 NaOH in 250-mL polypropylene bottles. The mixtures were shaken at 150 rpm for 2 h, and then filtered using 0.45- μm membrane filters. Extractants were analyzed for phosphate (i.e., molybdate active) using the modified Mo blue method (He et al., 1998) and total P using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The modified Mo blue method, which is the original method (Murphy and Riley, 1962) with excess ammonium molybdenum, was used to overcome the interference from dissolved organic acids in the extracts.

Mineralogical Analyses

Organic matter and metal oxides were removed from the soils using sodium hypochlorite and citrate-bicarbonate-dithionite methods, and then sand, silt and clay fractions were obtained using centrifugation-sedimentation methods described by Jackson (1956). Freeze-dried samples were finely ground using a mortar and pestle for further use. Powder XRD measurements were made to determine the bulk mineralogy. The data were collected from 5 to 95° 2 θ with a Philips x-ray powder diffractometer (graphite monochromatized $\text{Cu K}\alpha$ radiation, 0.05° 2 θ step size, and 4 s count time per step). All samples were analyzed as random mounts using the back-packed procedure. The detection limit for crystalline phases by bulk XRD analysis is approximately 2% by weight.

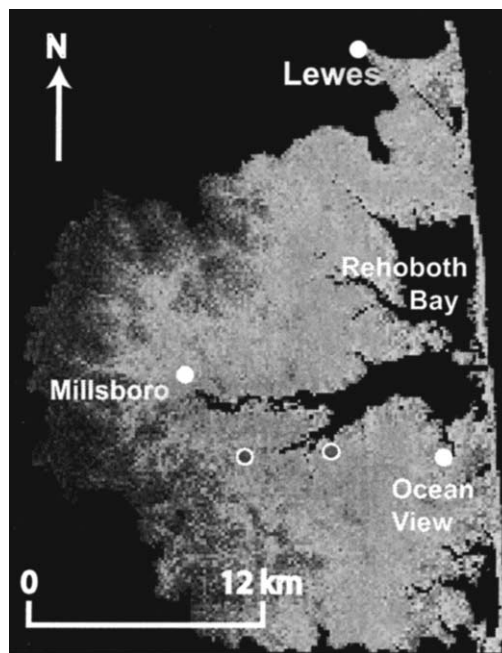


Fig. 1. The locations of two sampling sites (indicated by filled circles), and their relation to the Inland Bays Watershed in southern Delaware. This hillshaded relief map, which was created from a digital elevation model, was modified after <http://www.udel.edu/FREC/spatlab/> (verified 7 Jan. 2005) from Spatial Analysis Laboratory, University of Delaware, with permission.

Inorganic Phosphorus Fractionation

Bulk soil samples were ground using a mortar and pestle before chemical extractions. The inorganic P fractionation method described by Kuo (1996) was slightly modified to optimize the extraction processes by removing Ca from limed agricultural soils.

Inorganic P fractions were divided into soluble P, P in the amorphous Al-Fe oxide fraction, P in crystalline Al oxides and/or variscite (AlPO_4) like phases, and P in crystalline Fe oxide and/or strengite-like (FePO_4) and/or hydroxyl apatite-like phases. During the extraction processes, all tubes were shaken at 250 rpm on an end-over shaker. After the extraction, the samples were passed through 0.45- μm membrane filters before total P analyses using ICP-AES. Since most of the extracts could contain >1 mM of inorganic or organic ligands that interfere with the original ammonium molybdenum analyses (He et al., 1998), ICP-AES for total P was chosen over a molybdenum reactive P analysis. Between each extraction step, samples were washed with 50 mL of 0.1 M NaCl solution three times, and centrifuged at 268 g for 5 min to recover the paste for the next extraction steps.

Figure 2 shows the sequential inorganic P fractionation Steps (a–e). In Step (a), soluble P fractions were extracted using 0.7 g of oven-dried soils (<2 mm) that were suspended in 50 mL of 1 M NH_4Cl solutions for 30 min. Paste samples were then pretreated with 1.0 M ammonium acetate (pH 5.5) for 1 h to remove exchangeable Ca that could readily precipitate out as Ca oxalate during the oxalate extraction. In Step (b), P adsorbed on amorphous Fe and Al oxides and/or amorphous Al, Fe-P components (e.g., variscite and strengite) were fractionated after Step (a) using the ammonium oxalate extraction method (Loeppert and Inskeep, 1996). In Step (c), P sorbed on crystalline aluminum oxides and/or AlPO_4 fractions was extracted using 50 mL of 0.5 M NH_4F (pH 8.2) solution for 1 h. In Step (d), P in crystalline iron oxides and/or strengite-

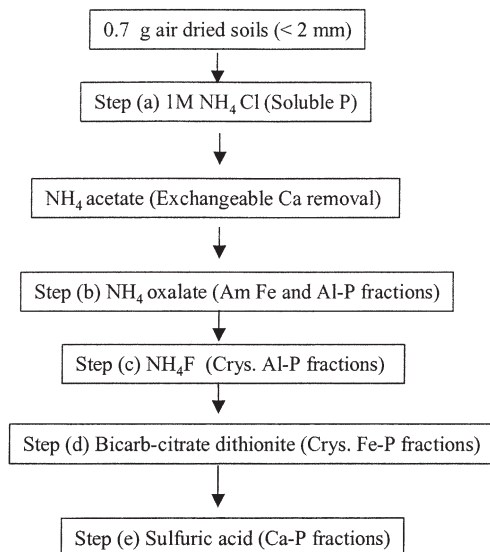


Fig. 2. A flow chart of the modified sequential inorganic P fractionation procedure. Each operationally defined inorganic P fraction with respect to specific extractant is shown in parentheses.

like phases were extracted after Steps (a) and (b) using the dithionite-citrate-bicarbonate method. In Step (e), P-Ca fractions (e.g., hydroxyl apatite phases) were extracted in 50 mL of 0.25 *M* H₂SO₄ for 1 h after which the samples were treated in Steps (a, b and d).

Electron Microprobe Analyses

The Ev and Pm soils, representing a low- and high-OM soil, respectively, were chosen to semiquantitatively investigate the P elemental correlation in the soil matrices using EMP analyses. Thin sections were prepared in two steps. First, the samples were embedded in electrical resin and cured in a constant temperature oven at 70°C for 48 h. Second, the hardened resin embedded samples were cut and polished into thin sections (≈30 μm thick) mounted on quartz slides (2.54-cm diam. and 1.6 mm thickness) using methyl 2-cyanoacrylate adhesive. Selected materials and media were chosen to minimize trace metal or metalloid contamination. Analyses were performed on the thin sections using an electron microscope operating at 15 kV potential and a 30 nA beam current. Eight 128 by 128 pixel x-ray maps (pixel size: 0.91 mm) were obtained with a 1-s dwell covering 117 by 117 μm². Elemental analyses for Si and Fe were collected using a Be window energy dispersive spectrometer (EDS), while Al, S, Ca, and P were collected with wavelength dispersive spectrometers (WDSs). Maps were obtained at a magnification of ×750 to avoid WDS defocusing. The EDS x-ray spectra were also collected at points of interest.

Phosphorus Adsorption Experiments

Phosphate retention capacity has been often evaluated at a fixed pH value (e.g., pH_{water}) and an initial phosphate concentration. However, such results are often difficult to interpret in predicting the fate and transport of P in agricultural soils since (i) soil pH values fluctuate before and after liming, and (ii) dissolved P concentrations in the surface soils can vary before and after PL amendments at current or reduced application rates. For these particular DE soils, recommended target pH values are generally ≈6.0 for Ev, Sf, and Os soils and ≈5.6 for the Pm soil (Sims and Gartley, 1996). To better understand P adsorption capacities on the long-term PL-amended soils, we investigated the P adsorption behavior as a function of pH

(3.0–8.0) and initial P concentrations (0–1 mM). It is difficult to select an ideal dissolved P concentration range in the laboratory experiments to evaluate the P adsorption capacity in PL-amended soils since PL is randomly broadcast on agricultural fields (i.e., nonuniform applications). We suspect the dissolved [P] is not uniformly distributed throughout the field. Instead of estimating the ideal dissolved [P] range based on the PL application rate, the upper [P] limit (i.e., 1 mM ≈ 31 mg L⁻¹) in this experiment was chosen based on the [P] range that was reported in laboratory studies. Shreve et al. (1996) previously reported that dissolved P concentrations from PL-amended loamy soils, which were amended at a rate of 0.5 g of PL in 50 g of soils, decreases from 25 to 7 mg L⁻¹ at pH ≈ 5.0 with increasing time (0–300 d) (Shreve et al., 1996). Since the application rate that was used in Shreve's study is slightly higher than the typical PL application rate on DE soils (i.e., 0.2 g of PL in 50-g soils; equivalent to 9 Mg ha⁻¹), the reported upper limit of dissolved [P] (≈31 mg L⁻¹) in our experiment should be sufficient to simulate the field conditions in DE soils.

Air-dried soil samples (i.e., 1.2 g of the amended Ev, Os, Pm, and Sf) and 24 mL of 0.1 *M* NaCl were shaken at 100 rpm on an orbital shaker for 20 h at 25 ± 2°C. Each soil sample was adjusted to the field pH_{water} using 0.1 *M* HCl and NaOH. An appropriate amount of the NaH₂PO₄ stock solutions (i.e., 1 and 5 mM in 0.1 *M* NaCl at pH 5.0) was added to ensure initial P concentrations of 1 mM, 0.5 mM, and 0.1 mM. The pH was readjusted every 6 to 12 h by adding 0.1 *M* HCl or 0.1 *M* NaOH. After 48 h, the soil suspensions were centrifuged at 478 *g* and passed through a 0.45-μm filter. The modified ammonium molybdenum method (He et al., 1998) was used to analyze concentrations of dissolved orthophosphate. The same method was also used to analyze concentrations of dissolved orthophosphate in the following the desorption experiments. Total adsorbed P (mg kg⁻¹ of soil) was estimated based on differences between [P_{initial}] and [P_{remaining}] with respect to the amount of soils (in kilograms) used in the experiments.

Long-term Phosphorus Desorption Experiments

A batch replenishment method was used to investigate long-term (30-d) P desorption. Air-dried soils (1.2 g) were placed in 50-mL high-speed polycarbonate centrifuge tubes. Thirty milliliters of 0.1 *M* NaCl solutions were added that were adjusted to the soil pH_{water} values. The soil suspensions were shaken on an end-over-end shaker at 200 rpm. Every 24 h, the tubes were centrifuged at 11 950 *g* for 5 min, and the supernatants were replaced with the same P-free 0.1 *M* NaCl solutions. This process was repeated 30 times (for a 30-d period).

In addition to the Mo active P analyses, the filtrate was also analyzed for total Fe and Al using ICP-AES.

Short-Term Phosphorus Desorption Experiments

A stirred-flow method was chosen for the short-term desorption study. In this technique, the adsorbents were exposed to a greater mass of ions than in a static batch system, and the flowing solution continuously removed reaction products (desorbed and detached species) (Sparks, 1989). Air-dried soils (0.6 g) were placed on a stirred flow chamber assembled with a 0.45-μm membrane filter (Sparks, 1989), and 7.6 mL of 0.1 *M* NaCl solution at the soil pH were added. The soil suspensions were preequilibrated for 24 h at 100 rpm before the desorption experiments. The influent solution was pumped at a flow rate of 0.3 mL min⁻¹ into the reaction chamber that was mixed at 300 rpm. Nine-milliliter effluents were collected every 30 min using a fraction collector. Filtrates were analyzed for dissolved

P as described earlier. The desorption experiment was also repeated on the same soil samples which had received three different sequential chemical extractions, namely NH_4Cl , NH_4Cl + ammonium oxalate, and NH_4Cl + NH_4F as described in the inorganic P fractionation methodology section. Oxalate and fluoride ligands represent major chemical components (e.g., ammonium oxalate and ammonium fluoride) in the Mehlich 3 chemical extraction. The NH_4 oxalate and F extractions were performed after the NH_4 -acetate pretreatment to remove exchangeable Ca, since oxalate and F are known to precipitate out with exchangeable Ca in soils (Smillie and Syers, 1972). While the NH_4F extraction was performed after the NH_4Cl + NH_4 oxalate extractions in the previous inorganic P fractionation analyses to remove only operationally defined crystalline Al-P fractions (e.g., crystalline variscite and P sorbed crystalline aluminum oxides), the NH_4F extraction in these experiments was performed right after the NH_4Cl treatment to remove both amorphous and crystalline Al-P fractions in soils. After these chemical treatments, the soils were washed twice with 30 mL of 0.1 M NaCl solutions adjusted to the soil pH, and freeze-dried for the desorption experiments. The combined techniques (i.e., chemical treatment and desorption) were employed to investigate the relationships between operationally defined inorganic P fractions and the desorbable P fractions.

RESULTS AND DISCUSSION

Physicochemical and Mineralogical Characterization

Table 1 shows the particle size and mineralogical properties of the soils. The texture of the Ev and Os soils was a loamy sand, while the Pm and Sf soils were sandy loams. Bulk density of all soils is approximately 1.20 Mg m^{-3} . Major mineral components, confirmed by XRD and micropetrographic analyses, were quartz and albite in the sand fraction, and quartz was the predominant mineral in the silt fractions in all soils. Kaolinite was present in all soils, and different types of 2:1 aluminosilicate minerals (i.e., illite, chlorite and vermiculite) were distributed in the soil clay fractions. The soil OM content was greatest in the Pm soil, followed by the Os soil. The Ev and Sf soils had relatively low OM contents (<1.8%). Strong P adsorption on illite and kaolinite and OM (i.e., Al-peat complexes) have been previously reported (Bar-Yosef et al., 1988; Bloom, 1981; Chen et al., 1973; Edzwald et al., 1976), and these soil inorganic and organic components might be important in controlling P retention in the soils. On the basis of the XRD analyses, there were no specific peaks indicating the presence of strengite- (FePO_4), variscite- (AlPO_4), and apatite-like (Ca_3PO_4) minerals in any of the fractions in the four amended soils. This suggests that these minerals were

either absent or <5% by weight (i.e., approximate detection limit of XRD).

Table 2 shows chemical properties of the PL-amended soils. Soil pH_{water} was moderately acidic to acidic. An increase in the concentration of exchangeable Ca is especially pronounced in the low-OM Ev, Sf, and Os soils. The CEC values that were observed in the amended high-P soils might also be attributed to specifically adsorbed P on inorganic and organic soil components that subsequently increase the net negative charge, electrostatically attracting dissolved cations in these soils.

The long-term PL amendments have resulted in total P values (i.e., inorganic and organic P) to $>900 \text{ mg kg}^{-1}$ in all soils, and the P species are predominantly inorganic P (i.e., Mo active) (Table 2). The PZSE ranged from 3 to 4 in all soils. This may be ascribed to specific anion (i.e., phosphate) adsorption on the soil components that decreases PZSE values of the variable charge mineral surfaces in the soils. For example, phosphate adsorption on Al-Fe oxides is known to decrease the isoelectric point of oxide surfaces (Anderson and Malotky, 1979; Arai and Sparks, 2001; Bleam et al., 1991; Hansmann and Anderson, 1985; Tejedor-Tejedor and Anderson, 1990).

Inorganic Phosphorus Fractionation

The results of the inorganic P fractionation of the PL-amended soils are summarized in Table 3. The total inorganic P values for each soil (i.e., summation of each inorganic P fraction measured using the modified Mo blue method) were slightly less than the total P values in Table 2, but greater than the total inorganic P values that were estimated by the method described by Bowman (1989). This is probably because of the use of latter ICP in the analyses. This highlights the importance of the inorganic P fraction in the long-term PL-amended soils. The predominance of inorganic P fractions in the long-term PL-amended soils was previously observed by other researchers (Sharpley and Smith, 1995).

In the amended soils, the ammonium oxalate extractable fraction (i.e., P associated with amorphous Al-Fe) predominated (60–78% of the total inorganic P), while crystalline Al-Fe associated P fractions, using NH_4F and bicarbonate-citrate-dithionite extractants, were <19% of the total inorganic P fractions. Several researchers reported that a transformation from amorphous to crystalline iron and aluminum oxides were significantly suppressed by specific anion (e.g., P) adsorption (Anderson et al., 1985; Biber et al., 1994; Hsu, 1989). This would en-

Table 1. Texture, organic matter, and mineralogical analyses of surface soils (0–20 cm) from southern Delaware.

Soil type	Texture	Sand	Silt	Clay	OM†	Sand fraction‡	Silt fraction‡	Clay fraction‡¶
Evesboro	loamy sand	85.75	8.05	6.20	1.0	Q, A	Q	K, C
Osier	loamy sand	83.74	8.05	8.21	1.8	Q, A	Q	K, I, C
Pocomoke	sandy loam	77.73	12.06	10.21	8.2	Q, A	Q	K, I
Sassafras	sandy loam	65.5	25.3	9.2	0.8	Q, A	Q	I, C, K, V

† OM, organic matter measure by loss-on-ignition.

‡ Mineralogy determined by powder x-ray diffraction. Mineral abbreviations: A, K-albite; C, chlorite; I, illite; K, kaolinite; Q, quartz; V, vermiculite.

¶ Sims et al. (1996).

Table 2. Physicochemical properties of poultry litter-amended southern Delaware soils.

Sample†	pH _{water}	PZSE‡	Total inorganic P§	Total P§	CEC¶	Exchangeable cations#		
						Al	Ca	Mg
			mg kg ⁻¹		cmol _c kg ⁻¹	cmol kg ⁻¹		
A-Evesboro	5.32	3.08–3.45	984	1152	1.05	0.05	1.19	0.28
A-Osier	5.69	3.50	764	933	2.74	BD	2.25	0.73
A-Pocomoke	5.03	3.80–3.67	735	923	2.21	0.03	2.55	0.84
A-Sassafras	5.52	3.10–3.69	914	1120	1.23	0.02	1.41	0.31

† A = long-term poultry litter-amended soil.

‡ PZSE = point of zero salt effect.

§ Total inorganic P and total P (i.e., inorganic and organic P fractions) is measured by the method described by Bowman (1989). Values are significant at the 0.05 probability level.

¶ CEC = cation exchange capacity. Values are significant at the 0.01 probability level.

Values are significant at the 0.01 probability level.

hance the presence of P adsorption complexes on amorphous Al-Fe oxide-like precipitates in the DE soils. Amorphous Fe and Al oxides in these soils are known to have a large P retention capacity (Arai and Sparks, 2001; Bleam et al., 1991; Parfitt, 1989; Veith and Sposito, 1977). The high correlation between oxalate extractable P and Al-Fe oxides has been well documented in acid soils (Lookman et al., 1996; Vadas and Sims, 2002; van Riemsdijk et al., 1984).

The chloride anion extractable P (i.e., weakly held P) ranged from ≈22 to ≈49 mg kg⁻¹ after the long-term amendments in all soils. Although these values are small with respect to total inorganic P, this increased chloride anion extractable P fraction could have a significant impact on eutrophication since the typical eutrophication inducible P level is as low as 0.04 mg L⁻¹ (Sims et al., 1996). Several field studies have indicated a strong correlation between water extractable soluble P and rainfall simulated dissolved P or runoff (Pote et al., 1999; Sharpley and Moyer, 2000).

While the ammonium oxalate extractable P comprises >60% of the total P, the Ca-P fractions remained consistently low (<5% of total inorganic P). Although the Ca concentrations in PL are generally high (i.e., >15 000 mg kg⁻¹) (Arai et al., 2003), the acidic soil pH might have suppressed the formation of alkaline earth metal phosphate precipitates (e.g., apatite) that are generally thermodynamically favored at neutral to alkaline pH.

Electron Microprobe Analyses

Electron microprobe images of Al, Si, S, P, Ca, and Fe in the Ev and Pm soils are shown in Fig. 3a and Fig. 3b,

respectively. In the low-OM Ev soil (Fig. 3a), P is generally associated with Al and Fe (Regions 1 and 2 indicated by arrows), and to a much lesser extent with Ca (as indicated by a Region 3 circle). In the high-OM Pm soils (Fig. 3b), Fe and S are associated with P. While P and S oxyanion adsorption on Fe based adsorbents (e.g., iron oxide and pyrite) can be speculated, the P-S association might also indicate P retention on S-rich soil humic components. Phosphorus is known to strongly react or associate with organic carbon components in soils (Bloom, 1981; Hens and Mercks, 2001; McDowell and Sharpley, 2001). As observed in the Ev soil, Ca is poorly correlated with P in the Pm soil (as indicated by Region 5). To semiquantitatively investigate the relative concentration of elements, energy dispersive x-ray spectra were taken at the P hot spots (indicated as Regions 2 and 4 in Fig. 3a and Fig. 3b, respectively). The most intense peak was from Si followed by Al, K, P, and Fe peaks were also observed (Fig. 4a and Fig. 4b). These Al and Si peaks might be attributed to a mixture of quartz and albite that were previously confirmed via XRD analysis (Table 1) and/or other aluminosilicate minerals such as kaolinite and illite. Although anions (e.g., arsenate) are known to weakly adsorb on quartz at acidic pH (Xu et al., 1988), large quantities of quartz and albite might retain a substantial amount of P overall in these sandy soils. The strong P association with Al and Fe probably represents P adsorption complexes on Al-Fe oxides and/or Al-Fe-P bulk and coprecipitates and/or chelated complexes on metal-humic components. In Fig. 4a and Fig. 4b, intensity of P peaks at the P hot spot is much stronger in the Ev soils than in the Pm soils, suggesting that the P

Table 3. Inorganic P fractionation of long-term poultry litter-amended southern Delaware soils. Values shown in parentheses are the percentage fraction with respect to total inorganic P values of each soil. Within-column values are statistically different at the 0.05 probability level.

Soils†	Soluble P‡	P _{ox} §	Al _{ox} §	Fe _{ox} §	Crys-Al-P¶	Crys-Fe-P#	Ca-P††	Total inorganic P‡‡
								mg kg ⁻¹
A-Evesboro	44.1 (4.0)	858 (77.98)	1478	353	48.6 (4.41)	119 (10.83)	30.4 (2.76)	1100
A-Osier	21.9 (2.37)	668 (72.45)	1363	752	39.4 (4.27)	169 (18.34)	23.6 (2.56)	923
A-Pocomoke	24.9 (2.83)	615 (69.96)	1555	337	59.2 (6.74)	163 (18.57)	16.7 (1.90)	878
A-Sassafras	48.6 (4.67)	634 (60.85)	1215	590	144 (13.82)	131 (12.57)	49.9 (4.79)	1042

† A = long-term poultry litter-amended soil.

‡ Soluble P = NH₄Cl extractable P.

§ P_{ox} = ammonium oxalate extractable P; Al_{ox} = ammonium oxalate extractable Al; Fe_{ox} = ammonium oxalate extractable Fe.

¶ Crys-Al-P = NH₄F extractable P after NH₄Cl and NH₄ oxalate extraction.

Crys-Fe-P = dithionite-citrate-bicarbonate extractable P after NH₄Cl and NH₄ oxalate extraction.

†† Ca-P = H₂SO₄ extractable P (e.g., hydroxyl apatite-like phases) after NH₄Cl, NH₄ oxalate and dithionite-citrate-bicarbonate extractions.

‡‡ Total inorganic P = the summation of each inorganic P fraction in Table 3.

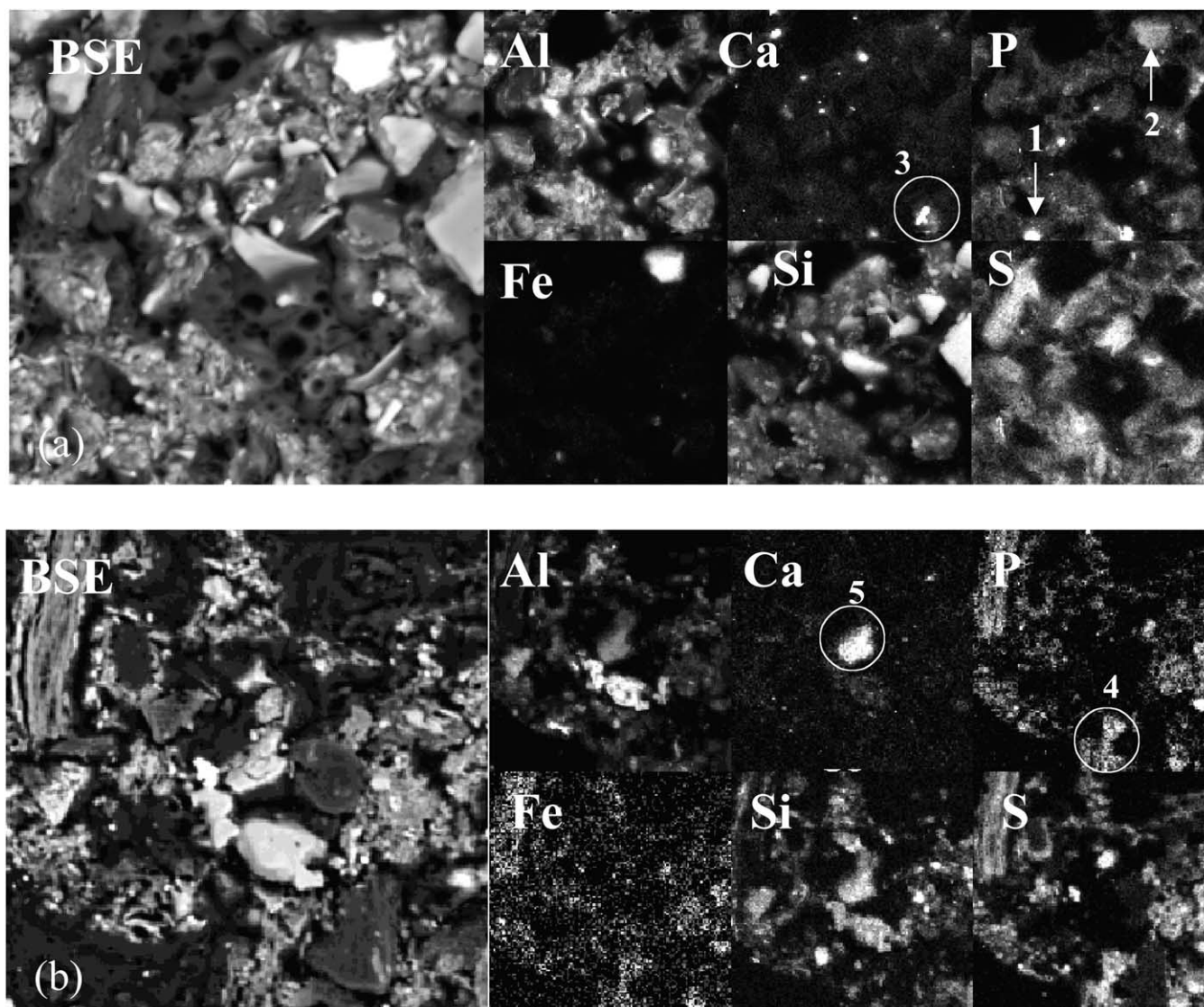


Fig. 3. (a) Electron microprobe images ($117 \times 117 \mu\text{m}^2$) of Al, Ca, P, Fe, Si, and S in Ev loamy sand and (b) in Pm sandy loam soils. The left image is a backscattered electron image (BSE) of the thin section. The brightest colors indicate concentration of high-Z (atomic number) elements.

speciation in the low- and high-OM soils are different. If one assumes that bulk and coprecipitation mechanisms are predominant in these high P ($>800 \text{ mg kg}^{-1}$ of total P) soils, a possible explanation for the different P localization in low- and high-OM soil matrices would be the organic acid suppressed amorphous Fe- and Al-P precipitation mechanisms. Several researchers have reported the organic acid-suppressed Al- and Fe-P precipitation reactions (Struthers and Sieling, 1950; Swenson et al., 1949). Whereas P is readily precipitated out in low-OM soils, the precipitation reactions were suppressed in high OM, resulting in more evenly distributed adsorbed species in soil matrices. Since the release of P is highly influenced by the solid-state P speciation, P precipitates in low-OM soils might be more susceptible than sorption complexes in high-OM soils on changes in the P concentration gradient in soil solutions. Overall, the EMP analyses agree with the results of inorganic P fractionation

that P is generally associated with Al and Fe and to a lesser extent with Ca.

Phosphate Adsorption Experiments

Figure 5 shows the P adsorption envelopes as a function of the initial P concentrations ($[P]_0$). After 24 h of equilibration, the dissolved $[P]$ in the aliquots were subtracted from the $[P]_0$, and total adsorbed P values were normalized with respect to total P values shown in Table 1. In Fig. 5a to 5d, the net negative adsorption indicates that the concentrations of P in the supernatant after 24 h were greater than the $[P]_0$, suggesting that P desorption occurred despite P additions. It seems that chloride exchangeable P is readily available as previously reported in the inorganic P fractionation analyses (described as “soluble P” in Table 3).

In the Ev soil (Fig. 5a), P adsorption increased from pH 3.0 to 5.5, and gradually decreased as pH increased

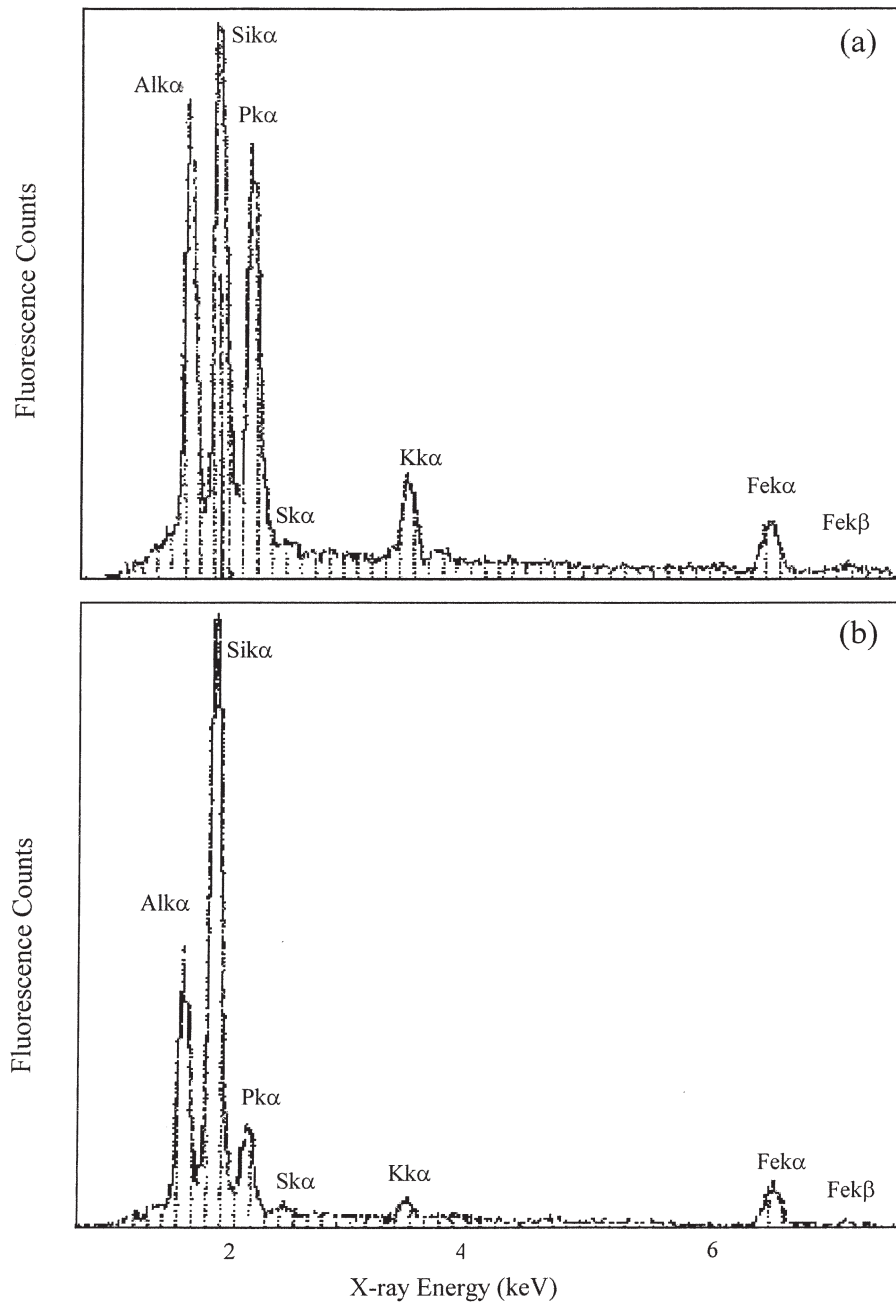


Fig. 4. (a) Energy dispersive x-ray spectrum of Region 2 in Fig. 2a, and (b) Energy dispersive x-ray spectrum of Region 4 in Fig. 2b.

up to 8.0 regardless of the $[P]_0$. The decreasing adsorption behavior at $\text{pH} > 6.0$ is similar to that found for amorphous single mineral component systems (e.g., ferrihydrite and boehmite) (Arai and Sparks, 2001; Blear et al., 1991; Chen et al., 1973), suggesting that these minerals might be important for retaining dissolved P in the Ev soil at $\text{pH} > 6.0$. Similar pH-dependent adsorption reactions were also observed in the other three soils (Fig. 5b–5d). If one assumes that metal oxide absorbents are contributing to the P retention, maximum P adsorption should be observed over an acidic pH range (3.0–5.0); however, the maximum P retention peaked out at pH 6.0 to 7.0 in all soils, indirectly suggesting that ligand exchange P adsorption mechanisms on metal oxides

might be less significant in affecting the maximum P adsorption in these P-rich DE soils.

There was also a trend in all soils for overall adsorption to increase with increasing $[P]_0$ at pH values of 3.0 to 8.0 (Fig. 5a–5d). Interestingly, net positive adsorption was only observed at pH 4.2 to 6.2 in the Ev soil that was spiked with 1 mM P, and at 4.2 to 7.3 in the Os soil that was spiked with ≥ 0.5 mM P. When the Sf and Pm soils were spiked with $[P]_0 > 0.1$ mM, the soils exhibited net positive adsorption at pH values 4.8 to 7.0 and 4.2 to 7.0, respectively. Unlike the Ev soil, the Sf, Pm, and Os soils showed a net positive adsorption capacity at similar pH ranges even when the soils were spiked with $[P]_0 = 0.5$ mM. A possible explanation for the positive

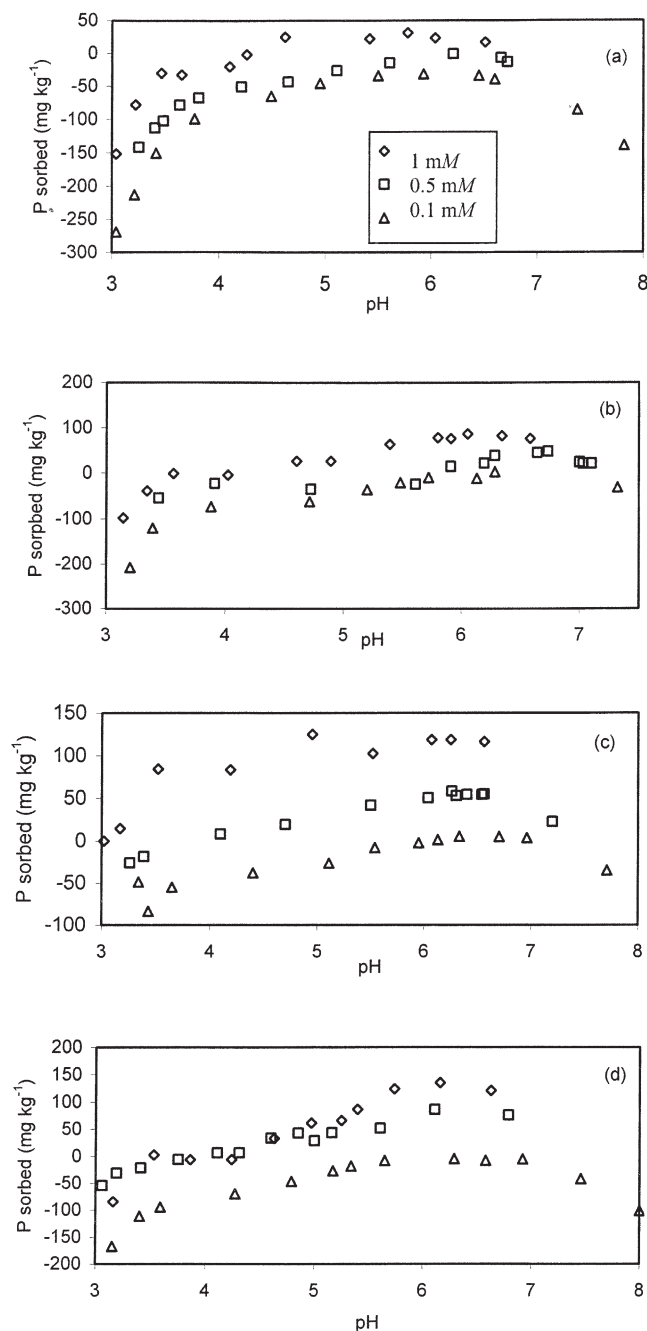


Fig. 5. Phosphorus adsorption on long-term poultry litter-amended soils. (a) Evesboro sandy loam (Ev); (b) Sassafras sandy loam (Sf); (c) Osier loamy sand (Os); and (d) Pocomoke loamy sand (Pm) as a function of pH and initial P concentrations (0.1–1.0 mM).

adsorption at these pH ranges could be the formation of amorphous Mg/Ca- PO_4 precipitates, which are generally thermodynamically stable at $\text{pH} > 5.5$. However, one can expect that those amorphous Ca- PO_4 minerals rapidly undergo dissolution processes when the soils are buffered back to an acidic soil $\text{pH}_{\text{water}} (\approx 5)$. The previous chemical extraction and EMP analyses indicate the absence of Ca- PO_4 minerals in these soils. At moderately acidic pH values (< 5.0), most of the soils (except for the Os soil) did not show any significant adsorption capacity—even the soils that were spiked with high $[\text{P}_0]$

(i.e., 1 mM). This suggests that the P sinks in these soils have nearly reached their maximum P sorption capacities. The average net negative surface charge density at $\text{pH}_{\text{solution}} > \text{PZSE}$ of the soils (3.08–3.67, Table 2) might be repulsing the negatively charged P solution species (i.e., H_2PO_4^-). However, the actual P release mechanisms are difficult to postulate based on these macroscopic data alone since several minerals simultaneously undergo dissolution at acidic pH.

Long-term Phosphate Desorption Experiments

Results of the long-term P desorption are shown in Fig. 6a. After 30 replenishment processes, total desorbable P was highest in the Pm which had the lowest total inorganic P (Table 3), followed by Ev, Sf, and Os. The degree of P desorbability is not correlated with differences in the amount of inorganic P, suggesting a complex desorption mechanism in these soils. It seems that the extent of P desorption in these soils are different. Phosphate desorption in the low-OM soils (e.g., Ev and Sf) decreases after 25 replenishments (i.e., time); however, there were steady and continuous desorption reactions in the higher-OM soils (e.g., Pm) at > 25 replenishments. Slow P desorption behavior from the inorganic soil components (i.e., ferrihydrite, goethite, and kaolinite) have been extensively reported by many researchers (Bar-Yosef et al., 1988; Madrid and Posner, 1979; Ryden et al., 1977). These results indirectly suggest that these mineral components might retain the labile P fractions in low-OM soils like Ev and Sf. However, there is no straightforward explanation to support the continuous P desorption reactions observed in the higher-OM soils.

On the basis of the results of the previous inorganic P fractionation (i.e., correlations with oxalate extractable P and Al/Fe), we subsequently monitored the extent of Al and Fe dissolution during P desorption, and the results are presented in Fig. 6b and 6c. In this figure, continuous Fe and Al dissolution reactions was observed in most of the soils except for the Ev soil, and this macroscopic evidence supports the results of the EMP analyses (i.e., a semiquantitative correlation between P and Al/Fe). The extent of Al and Fe release from the Ev soil remains near constant after 10 replenishments. Interestingly, the order of total desorbed Al and Fe does not match with the order of total desorbed P in the four soils. Whereas the total Fe dissolution was highest at $\approx 100 \text{ mg kg}^{-1}$ in the Sf soil, total Al release was as high as 400 mg kg^{-1} in the Pm soils, suggesting that each soil has different P release mechanisms associated with Al and Fe. There are some consistencies in the molar ratios of total desorbed P with respect to the Fe and Al release after 30 d. The P/Fe and P/Al ratios are 7.33 and 0.94 in Ev, 4.32 and 1.00 in Sf, 4.54 and 0.68 in Os, and 8.78 and 0.66 in Pm, respectively. While the P/Al ratios remain ≤ 1 in all soils, the P/Fe ratios are consistently higher (i.e., > 4) than the P/Al ratios, indirectly suggesting that the major labile P fractions might be associated with Fe more than Al. Several researchers have reported a similar relationship; that is, labile P in runoff is more correlated with oxalate extract-

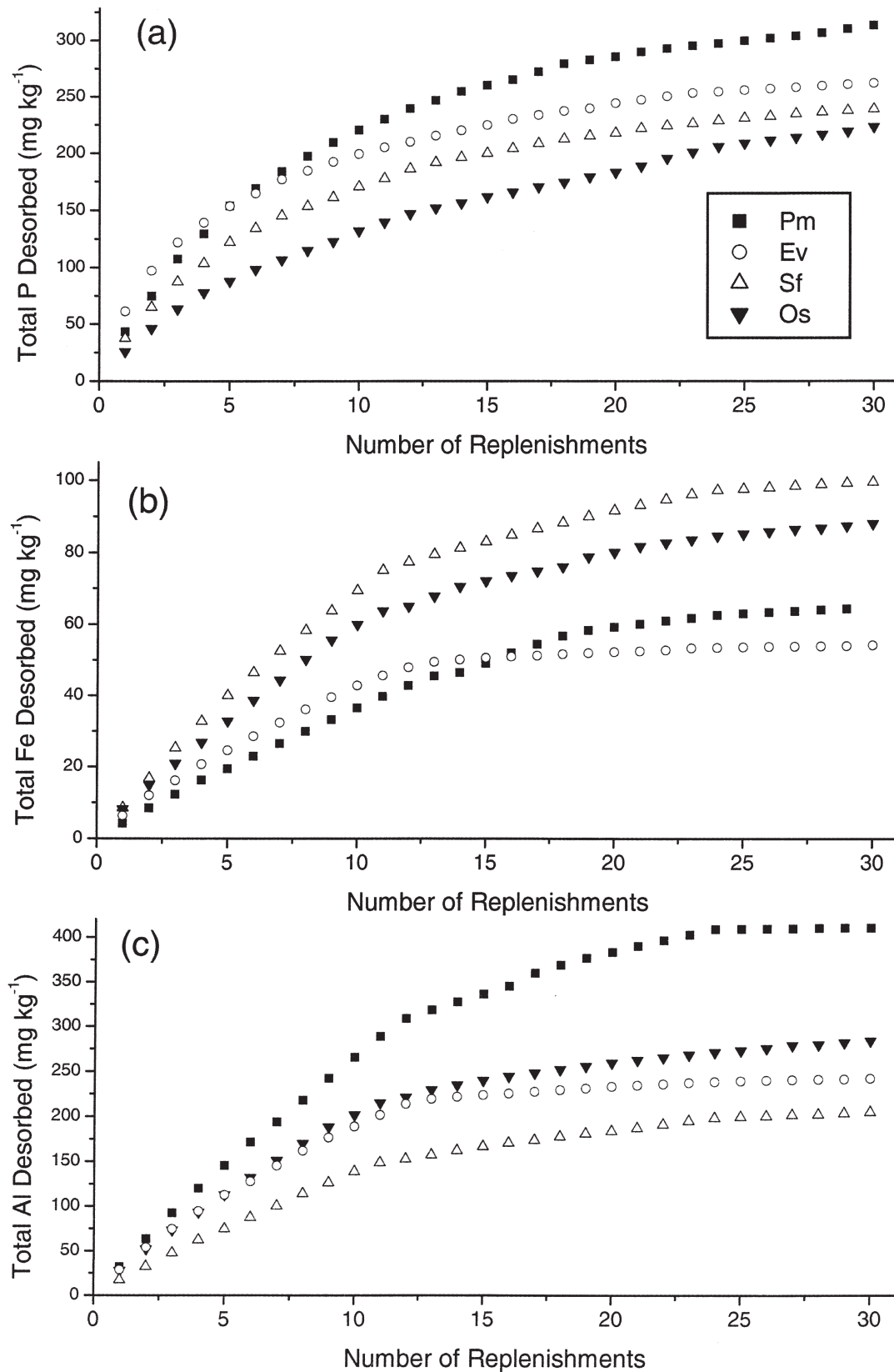


Fig. 6. (a) Long-term (30-d) P desorption from long-term amended soils. (b) Long-term (30-d) Fe desorption from long-term amended soils. (c) Long-term (30-d) Al desorption from long-term amended soils. Ev, Evesboro sandy loam; Sf, Sassafras sandy loam; Os, Osier loamy sand; and Pm, Pocomoke loamy sand.

able Fe_{ox} than Al_{ox} (Schroeder et al., 2004). The previous XRD analyses did not detect any Al-P and Fe-P precipitates in these soils. This suggests that the simultaneous P, Al, and Fe release might be attributed to (i) dissolution of P sorbed on the Fe and Al based or complexed adsorbents (e.g., metal oxides) and/or (ii) desorption of ternary Al/Fe- PO_4 complexes on soil components. Several indirect macroscopic studies have postulated the formation of mixed metal (Al, Cu, and Zn)-P complexes on soils and soil components (Bleam et al., 1991; Bolland et al., 1977; Clark and McBride, 1985).

Short-Term Phosphate Desorption Experiments

The continuous-flow method was also used to measure the extent of P desorption reactions in the well-drained soils (e.g., Ev and Sf). Results of the short-term desorption are presented in Fig. 7a to 7d. The short-term desorption experiments were conducted not only on the PL-amended soils, but also on chemically pretreated PL-amended soils. The chemical treatments were NH_4Cl , $\text{NH}_4\text{Cl} + \text{NH}_4\text{F}$, and $\text{NH}_4\text{Cl} + \text{NH}_4$ oxalate extractions that are previously described in the inorganic P fractionation section. The desorption curves after each treatment show different P desorbability from remaining P fractions.

In all soils, the most P release occurring at 57 chamber volumes (i.e., ≈ 24 h) was observed in the untreated soils followed by the NH_4Cl treated, $\text{NH}_4\text{Cl} + \text{NH}_4\text{F}$ treated, and $\text{NH}_4\text{Cl} + \text{NH}_4$ oxalate treated soils. This indirectly suggests that the operationally defined chloride, fluoride, and oxalate extractable P fractions might be controlling the P release in these soils. Although the poorly drained Os and Pm soils released >200 mg kg^{-1} of total inorganic P, <170 mg kg^{-1} was released from the well-drained Ev and Sf soils. As we observed in the EMP analyses, different solid-state P species are likely to be present in the well-drained Ev soil and the poorly drained Pm soil. Different solid-state P species might be a limiting factor causing the different P release behavior in these soils.

The NH_4Cl treatment resulted in a small reduction in total desorbable P in most of the soils (i.e., Ev, Os, and Pm soils). It seems to appear that a significant reduction (i.e., $\approx 40\%$ of total desorbable P of the untreated sample) was occurring in the Sf soil (Fig. 7b); however, the reduction in the total desorbable P is not significantly different from the other soils when we compare the mass basis values of the reduction in total desorbable P after NH_4Cl treatment in Fig. 7 and the NH_4Cl extractable P in Table 3 for each soil. The reduction in total desorbable P after NH_4Cl treatment is approximately 30, 65, 50, and 15 mg kg^{-1} for the Ev, Sf, Os, and Pm soils, respectively; whereas for the NH_4Cl extractable P in Table 3, total desorbable P is about 44, 49, 22, and 25 for Ev, Sf, Os, and Pm soils, respectively. This suggests that remaining P species after the NH_4Cl extraction in all soils behaved in a similar fashion.

The $\text{NH}_4\text{Cl} + \text{NH}_4\text{F}$ treatment resulted in the second highest P release from all soils. While it resulted in $\approx 50\%$ reduction in total desorbable P in the low-OM Ev and Sf soils, it had the most significant impact (i.e., $>73\%$

reduction) on the poorly drained and high-OM Os and Pm soils, suggesting that the role of Al with respect to the P release is more important in high-OM soils (Os and Pm soils) than low-OM soils (Ev and Sf soils). This result possibly infers the presence of labile OM-Al-P complexes in high-OM soils as previously reported by some researchers (Hens and Mercks, 2001; McDowell and Sharpley, 2001). Furthermore, fluoride extractable pools indicate both crystalline and amorphous Al-P materials in the soils since the NH_4F chemical treatment was employed before the oxalate treatment. If one assumes the fluoride ions were effectively extracting these Al-P fractions, the reduction in the P release via the fluoride treatment indicates that total desorbable P in these soils is controlled by Al. The simultaneous release of Al was also observed in the previous long-term P desorption experiments. Maguire and co-workers have previously reported a similar correlation between Al-associated P and the bioavailable P in biosolid-amended Atlantic Coastal Plain soils (Maguire et al., 2000).

We have reported the results for the important labile Fe-P fractions in the previous long-term desorption experiments, and the results from the short-term desorption study seem contradictory. We suspect that the different findings (i.e., labile Fe-P vs. Al-P fraction) could be due to differences in the desorption experimental techniques. Whereas the batch replenishment technique in the long-term desorption experiments simulates poorly drained conditions, possible readsorption reactions of desorbed species can occur in the closed reaction vessels. The continuous flow-through system that was used in the short-term desorption experiments simulates well-drained conditions, resulting in minimal readsorption processes during the experiment. It may be possible that the different drainage properties of these soils might cause different P release mechanisms that are associated with Fe and Al.

Interestingly, the desorption results from the fluoride treated soils show a small quantity (≈ 52 – 60 mg kg^{-1} of total desorbable P at 57 chamber volumes) of desorbable P in all soils. Since the previous XRD data showed no clear evidence for the presence of crystalline Fe-P, Al-P, and Ca-P, it is possible that crystalline phases contribute little to P desorption. Rather, the amorphous Fe phases (i.e., oxalate extractable Fe) control the P desorption after the fluoride treatment. When the total desorbable P after the fluoride treatment was compared in low-OM Ev and Sf soils, this suspected amorphous Fe-P fraction seems to release more P in the Sf soil than in the Ev soil. The previous inorganic fractionation data showing that Fe_{ox} was greater in the Sf (590 mg kg^{-1}) than the Ev soil (353 mg kg^{-1}) (Table 3) supports the hypothesis that bioavailable amorphous Fe-P fractions are greater in the Sf than in the Ev soil.

Similarly, when the total desorbable P after the fluoride treatment was compared in the high-OM Os and Pm soils, the effect of fluoride on total desorbable P cannot be explained by the differences in the remaining amorphous Fe-P content. On the basis of Fe_{ox} concentrations in the inorganic fractionation data (Table 3) that the Pm soil has less Fe_{ox} content than in the Os soil (337

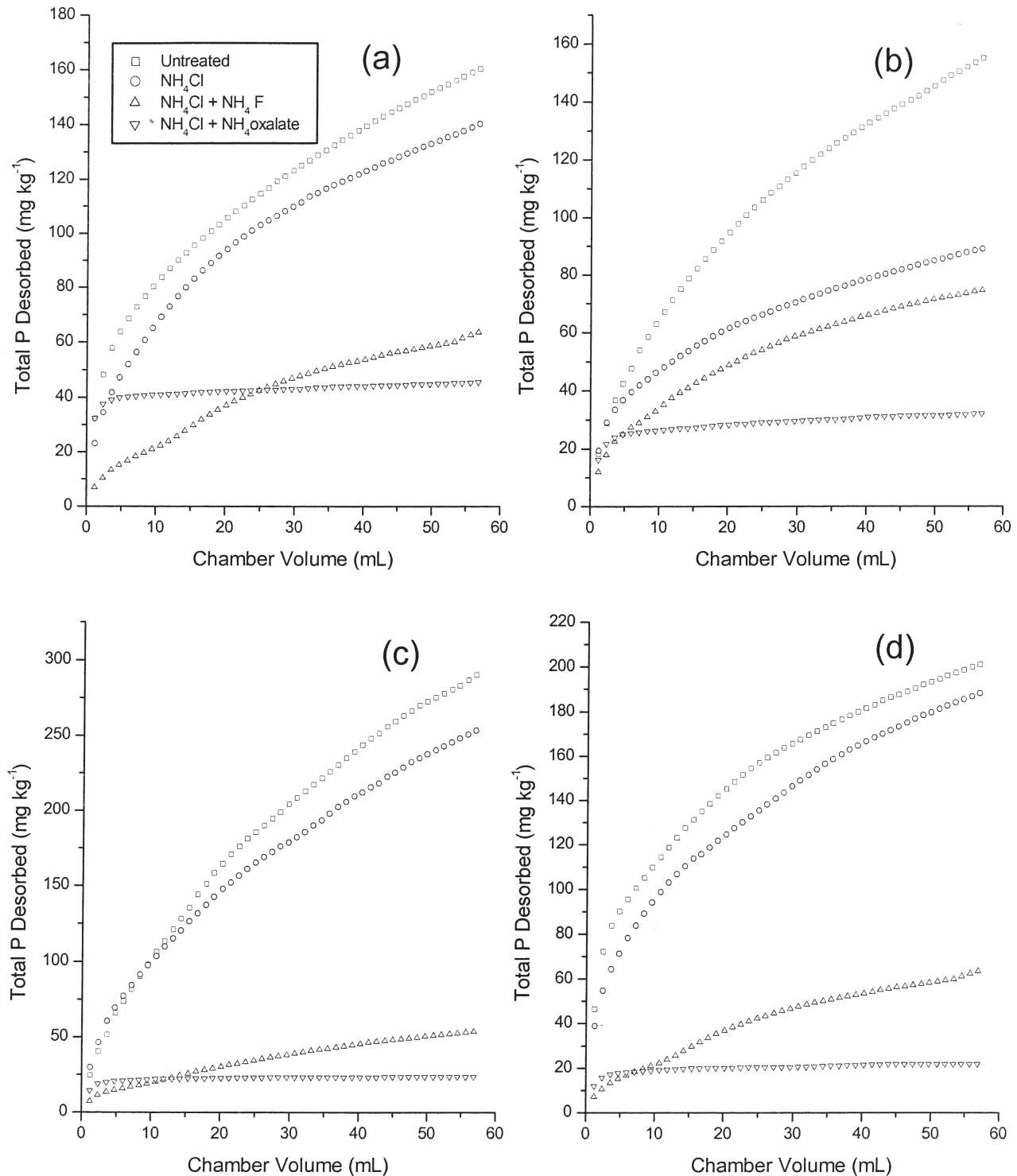


Fig. 7. (a) Short-term P desorption from chemically untreated and treated Evesboro sandy loam (Ev) soils. (b) Short-term desorption from chemically untreated and treated Sassafras sandy loam (Sf) soil. (c) Short-term desorption from chemically untreated and treated Osier loamy sand (Os) soil. (d) Short-term desorption from chemically untreated and treated Pocumoke loamy sand (Pm) soil.

and 752 mg kg⁻¹, respectively) (Table 3), the Pm soils should release less P from the amorphous Fe-P fraction that is left after the F treatment. However, this is not the case. The total desorbable P values after F treatment in the Os and Pm soils are almost equal (i.e., ≈60 mg kg⁻¹) after 57 chamber volumes (Fig. 7c and Fig. 6d). The Pm soil is unexpectedly releasing more P even though the

Fe_{ox} content is almost half of the Os soils (Table 3). This may be because the Pm soil is more poorly drained (thus its much greater OM in Table 1), resulting in more periodic saturated conditions than found in the Os soils. The reduced conditions in the Pm soils might have promoted greater P association with amorphous Fe minerals that are newly formed under the simultaneous reduc-

tive dissolution and reprecipitation reactions during the reduction or reoxidation reaction. Vadas and Sims (1999) previously suggested similar P retention mechanisms to explain enhanced P retention capacity on the A horizon of Pm soils after reduction or reoxidation reactions (Vadas and Sims, 1999).

Implications for Selecting the Best Nutrient Management Plans for the Phosphorus-Rich Delaware Soils

In these P-rich soils, we found that P was still strongly retained near targeted pH values of lime (i.e., ≈ 6.0 for Ev, Sf, and Os soils and ≈ 5.6 for the Pm soil), however, P adsorption gradually decreased with decreasing pH near soil pH_{water} (≈ 5). As a result of long-term PL amendments, there was no evidence, based on XRD analyses, for the presence of crystalline Al and Fe phosphate precipitates and apatite phases. Instead, the inorganic P fractionation analyses showed high levels of oxalate extractable P, Al, and Fe fractions ($\text{P} = 615\text{--}858 \text{ mg kg}^{-1}$; $\text{Al} = 1215\text{--}1478 \text{ mg kg}^{-1}$; $\text{Fe} = 337\text{--}752 \text{ mg kg}^{-1}$) that are susceptible to slow or continuous P desorption at moderately acidic soil pH_{water} along with soluble P fractions (i.e., operationally defined chloride extractable P). Various soil P tests [e.g., water soluble P, ammonium oxalate extraction based extractions (Mehlich 1 and 3)] have been often used to predict the desorbable P fractions from PL-amended P-rich soils. Although these soil P tests were originally developed for agronomic purposes, the results were often positively correlated to dissolved P in runoff and leachates (Pote et al., 1996). These indirect evidences, which were based on simple batch extractions and linear regressions analyses, suggest that soil test P might potentially be utilized to predict the labile P (Chardon and van Faassen, 1999; Pautler and Sims, 2000; Sims et al., 2002; van der Zee and van Riemsdijk, 1988). Our study results provide additional credence evidence to the previous findings.

On the basis of our research findings, several remediation or nutrient management methods on surface soils can be considered or reevaluated for providing the most environmentally feasible and effective ways to reduce the labile P concentrations from the P-rich soils. These include (i) maintaining soil pH_{water} near neutral, and (ii) having effective adsorbents (e.g., amorphous Al and Fe minerals) that can help in retaining soluble P to suppress the P desorption processes.

Perhaps the best way to minimizing future losses of P from high P Delmarva soils is to stop amending them with PL. However, this is not a reasonable solution in view of the large quantity of PL that must be disposed of. Additional and realistic remediation or nutrient management methods are needed to reduce soluble P in the immediate future. If PL application continues at the current or reduced rates, it seems that alkaline characteristics of PL would potentially neutralize the soil pH; however, the soil pH is unlikely to remain at near targeted pH of limed soils because (i) randomly broadcasted PL will not uniformly raise pH throughout the entire agricultural field, and (ii) soil pH strongly buf-

fered back to moderately acidic pH. An increase in the number of lime application would be an environmentally feasible choice to raise soil pH_{water} values without increasing P input in soils only if it does not facilitate the macronutrient (e.g., Mn and Zn) deficiency for crops. One can expect that an increased lime application would effectively maintain soil pH at near neutral in low-OM soils (e.g., Ev and Sf soils); however, it seems less effective for high-OM soils (i.e., Pm and Os soils) since weakly acidic soil OM strongly buffered at moderately acidic pH. As the EMP analyses indicated, different P solid-state speciation were already present in low- and high-OM soils (e.g., possibly precipitates vs. adsorption complexes, respectively). Accounting for the different P speciation (i.e., different release mechanisms) in the high and low-OM soils, additional nutrient management practice (e.g., chemical amendments) should be recommended in addition to an increase in lime.

Chemical amendments [e.g., alum $[\text{Al}_2(\text{SO}_4)_3]$ and iron sulfate] can provide additional adsorbents for soluble P in soils (e.g., amorphous Al/Fe minerals), resulting in suppressed P release. Both of these chemical amendments have been shown to effectively reduce the soluble P runoff from PL-amended Arkansas soils (Shreve et al., 1995; Shreve et al., 1996). Alum amendment on PL has been currently evaluated as a potential remediation or nutrient management method to reduce the soluble P in the Atlantic Coastal Plain soils. The recent studies indicated that alum-amended PL on soils has some potential in reducing the bioavailable P in acidic sandy DE soils (Sims and Luka-McCaffery, 2002; Staats et al., 2004) and P adsorption complexes on amorphous Al-oxides in the alum-amended PL are likely to be controlling the P release (Peak et al., 2002). Addition of alum to moderately acidic Atlantic Coastal Plain soils will need further investigation to determine the long-term stability of P and the impact of soil acidity resulting from the Al inputs. On the contrary, the iron sulfate amendment might be used in DE sandy soils without jeopardizing future soil acidity in soils. Assuming that amorphous Fe oxyhydroxide is controlling the P release as results of iron sulfate amendments, the reductive dissolution of Fe-oxides under seasonally reduced conditions could possibly induce the P release. Field and laboratory scale studies must be conducted to evaluate the redox sensitivity of the FeSO_4/PL -amended DE soils with respect to P release.

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