

Alum Amendment Effects on Phosphorus Release and Distribution in Poultry Litter-Amended Sandy Soils

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ABSTRACT

Increased poultry production has contributed to excess nutrient problems in Atlantic Coastal Plain soils due to land application of poultry litter (PL). Aluminum sulfate [alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$] amendment of PL effectively reduces soluble phosphorus (P) in the PL; however, the effects of these litters when added to acidic, sandy soils are not well understood. The objective of this study was to investigate the efficacy of alum-amended poultry litter in reducing P release from three Delaware Coastal Plain soils: Evesboro loamy sand (Ev; excessively drained, mesic, coated Typic Quartzipsammets), Rumford loamy sand (Ru; well drained, coarse-loamy, siliceous, subactive, thermic Typic Hapludults), and Pocomoke sandy loam (Pm; very poorly drained, coarse-loamy, siliceous, active, thermic Typic Umbraquults). Long-term (25 d) and short-term (24 h) desorption studies were conducted, in addition to chemical extractions and kinetic modeling, to observe the changes that alum-amended versus unamended PL caused in the soils. The Ev, Ru, and Pm soils were incubated with 9 Mg ha^{-1} of alum-amended or unamended PL. Long-term desorption (25 d) of the incubated material resulted in approximately 13.5% (Ev), 12.7% (Ru), and 13.3% (Pm) reductions in cumulative P desorbed when comparing soil treated with unamended and alum-amended PL. In addition, the P release from the soil treated with alum-amended litter was not significantly different from the control (soil alone). Short-term desorption (24 h) showed 7.3% (Ev), 15.4% (Ru), and 20% (Pm) reductions. The overall implication from this study is that the use of alum as a PL amendment is useful in coarse-textured soils of the Coastal Plain. With increased application of alum-amended PL, more significant decreases may be possible with little or no effect on soil quality.

IN 2002, 68% OF DELAWARE'S cash farm income was attributed to commercial broiler production (Delmarva Poultry Industry, 2000). Approximately 74 million chickens are raised each year in the Inland Bays watershed (Sussex County, Delaware) alone (Sallade and Sims, 1997). Because land adjacent to these confined animal feeding operations (CAFOs) is often used to produce feed for the birds, much of the greater than 50 000 Mg of animal waste generated annually from poultry production is land applied to meet nutrient requirements for these small grain crops (Mozaffari and Sims, 1996). Until as late as 1995, some states were still basing litter application rate recommendations on N requirements for the crops and its content in the waste material (Shreve et al., 1995), without regard to P. The discovery of the importance of P in degradation of sur-

face water quality has initiated much research on PL and its chemical properties.

The extensive application of PO_4 -rich PL has resulted in approximately 85% of soils sampled in Sussex County, Delaware testing agronomically high or excessive (ranging from 25 to $>50 \text{ mg kg}^{-1}$) in Mehlich-1 soil test P (Vadas and Sims, 1998). Long-term poultry manure application coupled with excess P input (P added is greater than crop removal) and strong P retention mechanisms in soils (inner-sphere complexation via a ligand exchange mechanism) are responsible for accumulation of soil P. However, when soils reach their capacity for PO_4 adsorption, subsequently added PO_4 anions are held loosely (possibly via electrostatic interaction on variably charged mineral surfaces) and P is more easily desorbed and transported to surface water (Haustein et al., 2000).

Erosion, runoff, and subsurface flow are considered to be the main transport processes of P to surface waters. Because of the sandy, low organic matter soils and an extensive network of drainage ditches in agricultural fields, surface waters in the Inland Bays watershed are highly susceptible to nutrient influxes. Aquatic ecosystems in this region have been seasonally damaged by cycles of eutrophication, overgrowth, and decay of algal blooms, and subsequent depletion of dissolved oxygen. These P-limited processes, also linked to the presence of the toxin-producing dinoflagellate *Pfiesteria piscicida* (Kratch, 1997), decrease the recreational, aesthetic, and environmental value of the affected water bodies.

Alum has been used, in addition to other chemical amendments such as ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), calcium hydroxide [$\text{Ca}(\text{OH})_2$], and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), to change poultry litter chemistry and reduce environmental impacts of land application of the manure. Acidity produced by the dissociation of alum reacts with NH_3 in the litter to form NH_4^+ (a nonvolatile species), reducing volatilization of the toxic gas. Ammonium then reacts with the SO_4^{2-} to form $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulfate) (Moore et al., 1999), increasing the N to P ratio and nutrient value of the litter. When broadcast as a manure fertilizer to forage crops (Moore et al., 2000; Shreve et al., 1995) or incorporated with soil samples (Shreve et al., 1996), those systems with alum-amended litter release less soluble reactive P and trace metals (Moore et al., 1998) to runoff waters than those with unamended litter. Recently, Sims and Luka-McCafferty (2002), on a large-scale field study, showed that water-soluble P, As, Cu, and Zn were significantly lower in alum-amended litter compared with unamended litter. Since Al is not subject to redox changes or detrimental

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Abbreviations: al-lit, alum-amended poultry litter; Ev, Evesboro loamy sand; lit, control poultry litter; PL, poultry litter; Pm, Pocomoke sandy loam; Ru, Rumford loamy sand.

to bird health (unlike Fe), and has a more dramatic effect on the reduction of water-soluble P, it is preferred over other litter amendments as a best management practice in the broiler industry (Moore et al., 1996). In addition, since Al-oxides contribute greatly to P retention in acidic soils, the use of an Al-based amendment is logical, in comparison with Ca. However, the use of amended litters as incorporated crop fertilizers in Coastal Plain soils has not been investigated.

The long- and short-term release of phosphorus as it relates to alum-amended litters is important in determining effects of land application of such materials. Many studies have been conducted on the kinetics of phosphate desorption from soils and clay minerals using anion exchange resins (Evans and Jurinak, 1976), dialysis membrane tubing (Lookman et al., 1995), and batch replenishment methods (Lookman et al., 1996). In these studies, first-order kinetics, the Elovich equation, and the parabolic diffusion equation have been used to model the relationship between time and P release. Attempts have also been made to create modified equations to relate soil properties to constants in these equations (Sharpley, 1983; Vadas and Sims, 2002). Phosphorus release studies have shown that desorption is usually rapid in initial stages, followed by a slower release. This biphasic trend has been attributed to distinct P pools that have different stabilities and/or dissolution rates. Using models to describe these release phenomena can be useful in determining land management parameters. Because previous studies were conducted with heavier, loam soils or on the litter material alone, there has been no investigation on P release kinetics in sandy soils treated with alum-amended poultry litter.

Recent studies have helped to elucidate some of the chemical reactions that are occurring in the alum-amended PL. Using X-ray absorption near edge structure (XANES) spectroscopy, Peak et al. (2002) suggested that the addition of alum to poultry litter results in P being adsorbed onto aluminum oxides, instead of precipitating as aluminum phosphates. In addition, Hunger et al. (2004) investigated the efficacy of sequential chemical extractions, through the use of nuclear magnetic resonance (NMR) spectroscopy, to show the relationships between aluminum- and calcium-bound phosphate in alum-amended litters. However, the stability of the P complexes observed in these studies, as it relates to P lability in the environment, is uncertain.

To further address and understand the poor health of the Inland Bays watershed and surface waters on the Delmarva Peninsula, small-scale P desorption studies were conducted to investigate the efficacy of aluminum sulfate (as a PL amendment) in immobilizing P in acidic, sandy Coastal Plain soils. Accordingly, the objectives of this study were to (i) investigate the effects of alum amendments on P release from long-term PL-amended sandy Coastal Plain soils (from Delaware) using two desorption techniques, (ii) indirectly infer changes in P chemistry of soils treated with alum-amended and unamended litter through chemical extractions, (iii) correlate desorption data with chemical extraction results to understand P-Al interactions, and (iv) apply kinetic

equations to the data to qualitatively compare PO_4 desorption rates from the different systems.

MATERIALS AND METHODS

Soils and Poultry Litter

Three surface soils (0–30 cm) were used: Pm sandy loam, Ru loamy sand, and Ev loamy sand. The soils were air-dried and passed through a 2-mm sieve.

Poultry litter and soil samples were supplied by Dr. J.T. Sims at the University of Delaware Department of Plant and Soil Sciences. Control PL samples were taken from houses in which no chemical amendments were added. Alum application occurred in the poultry houses, between flocks, at a rate of approximately 0.91 Mg per 10 000 birds (approximately 10% by weight of alum to litter) (alum-amended PL). This was sufficient to achieve an Al to P ratio of approximately 1. Litter was oven-dried (at 65°C), ground, and then kept at room temperature until the experiments were performed.

Sample Preparation and Characterization

The soils and litter materials were microwave-digested in 20% nitric acid (HNO_3) solution and the digested solution was analyzed for total P, Fe, and Al using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (TJA-Enviro II; Thermo Electron, Franklin, MA).

Soil pH was measured using a glass electrode and pH meter and adjusted by addition of reagent-grade calcium carbonate (CaCO_3). The amount of CaCO_3 needed to adjust soil pH to a value of 6.0 was calculated by the Adams Evans buffer pH method of determining lime requirement (Sims, 1996). After addition of lime, the pH_{water} (1:1 solid to water mixture) was measured weekly, for 3 wk, to ensure equilibration. A pH value of 6.0 was chosen because this is a target pH value for optimum crop nutrient availability in Delaware soils. Organic matter content was estimated using the loss-on-ignition method (Ben-Dor and Banin, 1989).

Fifty grams of each soil (Ev, Ru, and Pm) were incubated with 0.2 g of alum-amended or control litter in the laboratory. This is roughly equivalent to 9 Mg ha^{-1} on a dry basis. However, tons acre^{-1} is a unit commonly used by farmers when land-applying manures. Our application rate corresponds to 4 tons acre^{-1} , which is a common rate for PL use (Maguire et al., 2001; Penn and Sims, 2002). These mixtures were shaken on an end-over-end shaker at 300 rpm for 1 wk at 10% (on weight basis) moisture content.

Inorganic Phosphorus Fractionation

Sequential extractions (Chang and Jackson, 1957) were performed on 1 g of the samples described above: soil, soil + control PL (soil + lit), and soil + alum-amended PL (soil + al-lit). Between each step, the samples were centrifuged at 2500 rpm for 10 min. The samples were then washed twice with 40 mL of 1 M NaCl solution before proceeding to the next extraction step.

The order of the extractions is as follows: 1 M ammonium chloride (NH_4Cl) shaken for 30 min (loosely bound P); 0.5 M ammonium fluoride (NH_4F) for 1 h (P associated with aluminum); 40 mL of 0.3 M sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), 5 mL of 1 M sodium bicarbonate (NaHCO_3), and 1 g of $\text{Na}_2\text{S}_2\text{O}_4$ (sodium dithionate) heated in a water bath (85°C) for approximately 45 min total (reduce Fe^{3+} and solubilize associated P); and 45 mL of 0.25 M sulfuric acid (H_2SO_4) for 1 h (P associated with Ca). All extracts were analyzed for total P by ICP-AES.

To further understand how Al is associated with P in soils

before and after the application of alum-amended litters, one additional extraction was performed independently of the others. Ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4, \text{pH } 3]$ was used to remove exchangeable and organically complexed Al and amorphous mineral components (Loeppert and Inskeep, 1996). The procedure is as follows: 0.5-g samples were mixed with 30 mL of 1 M ammonium acetate ($\text{NH}_4\text{-OAc}$, pH 5.5) and allowed to react for 1 h in a ventilated container with frequent mixing. The pH was adjusted to 5.5 with addition of 2 M acetic acid until it remained constant for 1 h. All samples were then centrifuged for 10 min at 3000 rpm, washed twice with deionized water, and allowed to air-dry. At this point, all of the tubes were covered with foil, to prevent exposure of the solution to light. Then, 30 mL of 0.175 M ammonium oxalate and 0.1 M oxalic acid were added to the dried samples, and tubes were placed on a reciprocating shaker for 2 h. After centrifugation, the supernatant was decanted and diluted 1:1 with deionized water. Samples were analyzed using ICP–AES.

Long-Term Batch Desorption

One gram of soil or soil–litter mixture (soil + lit or soil + al-lit) was transferred into a 50-mL polycarbonate high speed centrifuge tube and suspended in 30 mL of desorptive solution [2 mM 2-(4-morpholino)-ethane sulfonic acid (MES) buffer and 0.098 M NaCl (pH 6)]. All samples were done in triplicate. The tubes were placed on an end-over-end shaker at 200 rpm at room temperature. Every 24 h, for 25 d, the tubes were centrifuged for 15 min at 1800 rpm and aliquots were decanted and replaced with fresh NaCl–MES desorptive solution. Aliquots were analyzed for dissolved P using the modified ascorbic acid–molybdenum blue method (He et al., 1998). Long-term batch reactions capture all reaction products until the new desorptive solution is introduced, at which point they are removed. This method may be suitable for describing the types of reactions that occur in more poorly drained soils where water may pond, therefore not moving downward through the profile to leach nutrients.

Short-Term Desorption

Short-term desorption was conducted using a stirred-flow technique, modified from Carski and Sparks (1985). Due to the continuous-flow nature of this method, desorption products are removed, so that there is no accumulation in the reaction vessel. This may be particularly suited to simulate conditions that are occurring in well-drained soils. Air-dried soil (0.4 g) was placed in an 8-mL stirred flow reaction chamber with 7.6 mL of NaCl–MES desorptive solution. The solution was injected into the chamber with a previously calibrated 10-mL automatic pipette. A rubber O-ring was placed around the top of the chamber, under a 0.2- μm filter paper, to prevent solution or the soil mixture from escaping the chamber. The soil was suspended in the desorptive solution and hydrated for 24 h with slow stirring (200 rpm) with a magnetic stir bar. After the hydration period, stirring was continued and new phosphate-free solution was continuously pumped into the reaction vessel at a flow rate of 0.15 mL min^{-1} , regulated with a peristaltic pump. Samples were collected hourly for a 24-h period with an Isco (Lincoln, NE) Foxy Jr. fraction collector. All samples (one replicate for each soil and soil + PL mixture) were analyzed for dissolved P using the modified ascorbic acid–molybdenum blue method (He et al., 1998).

Kinetic Modeling

Three kinetic models were applied to the desorption data to better understand the effects of alum-amended PL and time on the desorption process. The three equations are as follows.

Parabolic diffusion law:

$$(C_t/C_\infty) = Rt^{1/2} \quad [1]$$

where C_t is the amount of P desorbed at time t , C_∞ is the total amount of P, and R is the overall diffusion coefficient (Sparks, 1986).

Elovich equation:

$$q = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \quad [2]$$

where q is the amount of P released, α is the initial reaction rate, and β is a constant (Chien and Clayton, 1980).

First-order kinetics:

$$\log(C/C_0) = k'_d t \quad [3]$$

where C is the amount of ion released at time t , C_0 is the total amount of ion that could be released at equilibrium, and k'_d is the apparent desorption rate constant (k_d) divided by 2.303 (Sparks, 1986, 2003).

These equations have been widely applied in desorption studies of soils and soil components, although the equations are empirical and yield, at best, only apparent rate parameters. Because of the heterogeneous nature of soil and PL, finding a meaningful model that can accurately describe these data, specifically, would be difficult. Therefore, the use of these models in this study was only for qualitative comparison between soil and litter combinations.

For statistical analyses, the PROC GLM procedure was used, with Tukey's test being used to evaluate the differences between the means of the control and treatments. A probability (P) less than 0.05 was considered significant. All analyses were completed using SAS Version 8.2 (SAS Institute, 1999).

RESULTS AND DISCUSSION

Physicochemical Properties of Soils

Table 1 displays physical and chemical characteristics of the soil and PL samples. Organic matter content is approximately 1.7, 2.8, and 3.3 g kg^{-1} in the Ev, Ru, and the Pm samples, respectively. The poor drainage of the Pm soil may contribute to organic matter accumulation. In addition, the Pm soil contained much less total Al, Fe, and P than the other two soils (Ru had the highest totals). Although Pm had the highest percentage of bioavailable Al, Fe, and P (Table 1), (as determined by Mehlich-3 soil test), all three soils are rated as "environmental" with respect to P ($>150 \text{ mg kg}^{-1}$) (Sims et al., 2002). Measurement of the Al and Fe concentrations during the inorganic P fractionation (discussion below) showed that Pm samples had the highest percentage of oxalate-extractable Al and Fe (Ev, 14 and 11%; Ru, 10 and 9%; and Pm, 27 and 26% Al and Fe, respectively) in soil alone. The Ev sample displays the lowest percentage of Na-DCB-extractable Fe while Ru had the highest Al and Fe from this extraction (Ev, 6 and 17%; Ru, 11 and 41%; and Pm, 5 and 33% Al and Fe, respectively).

Inorganic Phosphorus Fractionation

Phosphorus distribution of treated and untreated Ev, Ru, and Pm, as determined by chemical extractions, is presented in Table 2. Regardless of differences in other soil properties (i.e., texture and organic matter content), all three soils showed similar trends in the relative amounts of P removed by each extraction: $\text{NH}_4\text{F} \approx \text{NH}_4\text{-}$

Table 1. Physicochemical properties of Coastal Plain surface soils and poultry litter (PL) samples.

Soil	Texture	pH [†]	Organic matter [‡] g kg ⁻¹	Total [§]			Mehlich-3			Water-soluble	
				Al	Fe	P	Al	Fe	P	Al	P
				%			mg kg ⁻¹				
Evesboro (Ev)	loamy sand	5.8	17	0.83	0.29	0.12	1000 (12)	114 (4)	671 (56)		
Rumford (Ru)	loamy sand	6.0	28	1.7	0.78	0.12	1043 (6)	160 (2)	497 (42)		
Pocomoke (Pm)	sandy loam	6.0	82	0.29	0.10	0.06	681 (23)	128 (13)	467 (78)		
Control PL	—	7.6	—	0.06	0.11	2.4				2	2568
Alum-amended PL	—	6.9	—	2.2	0.16	2.0				19	542

[†] Measured in H₂O.

[‡] Measured by loss on ignition.

[§] Determined by microwave digestion.

^{||} Values shown in parentheses are a percent with respect to the measured total P, Al, and Fe in the soil.

oxalate \gg Na-DCB $>$ H₂SO₄ \approx NH₄Cl. Although extractions do not provide direct speciation information, as they are, at best, operationally defined, these data suggest that most of the P in the samples is associated with Al (as aluminum phosphate, mineral, and amorphous phases) and Fe (as amorphous and, to a lesser extent, crystalline oxides), while a smaller amount is complexed with Ca (3–5% of total P) and in loosely bound forms (1–6%). Because the soils used in this study have moderately acidic pH values, metals such as Fe and Al should be controlling P speciation (Vadas and Sims, 1998), which corroborates our extraction conclusions. In addition, if the NH₄F extraction constitutes nonoccluded P (Sharpley et al., 1984) and the relative proportion of oxalate-extractable P to Al and Fe is an indication of the potential for P loss from soils to surface waters (Maguire and Sims, 2002), these extractions would indicate that a large proportion of P in these systems is environmentally labile. In terms of the extractions, soils that have been treated with alum-amended PL (soil + al-lit) do not differ significantly from those that are treated with control PL (soil + lit). The NH₄F extraction of Evesboro soil is the only extraction that showed a significant difference between treatments. Evesboro is the sandiest soil and also has the lowest organic matter content; therefore, it may respond more to treatments than the other two soils. However, because the treatments largely do not change the P distribution, P release is a concern, because it appears (based on macroscopic observations) that the P speciation is not changing with a treatment of al-lit.

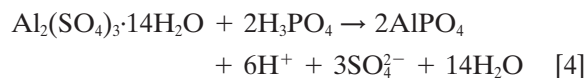
In our study, only one PL application event occurred, whereas in an agronomic setting, multiple additions occur over decades; therefore, the amount of P that we added may not have been large enough to alter the P

distribution, considering the already high P content of these soils. In addition, the relatively small amount of PL (compared with soil) that was added may not have been enough to overcome the bulk soil properties, in terms of these sequential extractions.

Long-Term Phosphorus Desorption

Figure 1 represents data collected as P is released from treated and untreated soils during long-term desorption. A biphasic trend [fast initial desorption (<6 d) followed by slower release (>7 d)] was visualized in all of the long-term desorption curves. As expected, when comparing the control (soil alone) with the soil amended with control litter (soil + lit), all three of the soil + lit samples released significantly more P. When Ev (Fig. 1A), Ru (Fig. 1B), and Pm (Fig. 1C) were treated with unamended versus alum-amended litter, the cumulative amount of desorbable P after 25 d was reduced from 251 to 217 mg kg⁻¹ (approximately 14% decrease), 411 to 359 mg kg⁻¹ (approximately 13% decrease), and 413 to 358 mg kg⁻¹ (13% decrease), respectively. Interestingly, the mean P release values for the soil treated with al-lit and the control soil are not significantly different. This supports the use of alum-amended PL as a potential nutrient management practice due to its efficacy in decreasing P loss from manured soils.

The mechanism by which P release is reduced may be the result of precipitation or sorption reactions represented by the following equations:



OR

**Table 2. Inorganic phosphorus (P) fractionation of Coastal Plain soils amended with control and alum-amended poultry litter.[†]**

Sample [‡]	NH ₄ Cl, labile	NH ₄ F, Al-P [§]	Na-DCB, crystalline oxides	H ₂ SO ₄ , Ca-P	Oxalate, amorphous oxides
Ev	16 (1)	830 (72) ^a	117 (10)	36 (3)	798 (69)
Ev + lit	22 (2)	912 (73) ^b	139 (11)	35 (3)	912 (73)
Ev + al-lit	12 (1)	945 (77) ^c	146 (12)	46 (4)	819 (67)
Ru	8 (1)	746 (60)	348 (28)	64 (5)	919 (74)
Ru + lit	29 (2)	745 (56)	370 (28)	50 (4)	937 (70)
Ru + al-lit	29 (2)	793 (60)	338 (26)	50 (4)	977 (74)
Pm	37 (6)	676 (112)	67 (11)	28 (5)	536 (89)
Pm + lit	39 (6)	679 (98)	74 (11)	24 (3)	543 (78)
Pm + al-lit	34 (5)	666 (98)	92 (13)	31 (5)	651 (96)

[†] With the exception of oxalate P, other extractions were performed sequentially on 1-g subsamples of incubated mixtures used for desorption studies.

[‡] Ev, Evesboro loamy sand; Ru, Rumford loamy sand; Pm, Pocomoke sandy loam; lit, control poultry litter; al-lit, alum-amended poultry litter.

[§] Within-column values followed by different letters are statistically different at the 0.05 probability level.

^{||} Values shown in parentheses are percentages with respect to the measured total P values in the soil or calculated total P in the soil-litter mixture.

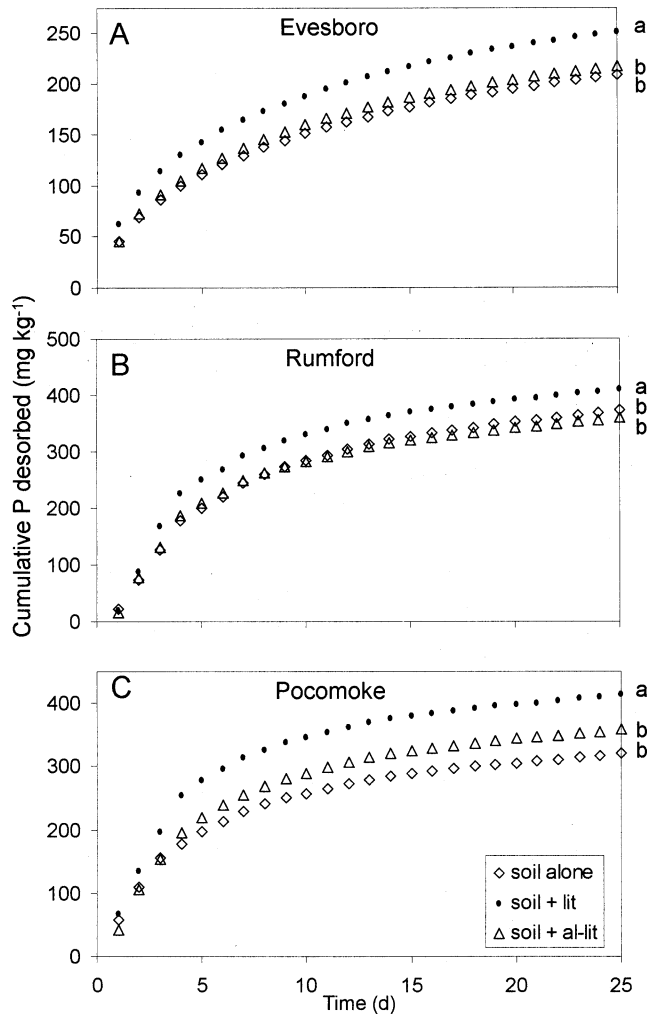


Fig. 1. Long-term (25 d) phosphorus release from poultry litter (PL)-treated and untreated Coastal Plain soils (pH 6) after 1 wk of incubation as determined by the batch desorption technique using 2 mM 2-(4-morpholino)-ethane sulfonic acid (MES) buffer and 0.098 M NaCl (pH 6) desorptive solution with a 1:30 solid to solution ratio. Soil + lit, soil incubated with control litter; soil + al-lit, soil incubated with alum-amended litter. Significant differences between the mean cumulative P release are denoted by different letters at the end of the desorption curve. (A) Evesboro loamy sand, (B) Rumford loamy sand, and (C) Pocomoke sandy loam.

Equation [4] shows that precipitation of an aluminum phosphate would be the reason for decreased P lability in alum-amended PL. According to Peak et al. (2002), in situ, spectroscopic evidence suggests that the nature of the complex is controlled by P sorption onto amorphous aluminum surfaces. This sorption reaction is represented in Eq. [5]. Aluminum hydroxides, which form as a dissolution product of alum, provide the surface for P binding.

All of these results show that alum decreases the amount of P desorption from the Coastal Plain sandy soils used in this study. With repeated application over a longer time scale, the effects of adding alum-amended versus unamended PL may become greater.

Short-Term Phosphorus Desorption

A nearly linear relationship of P release versus time was observed in the stirred-flow samples (Fig. 2); however,

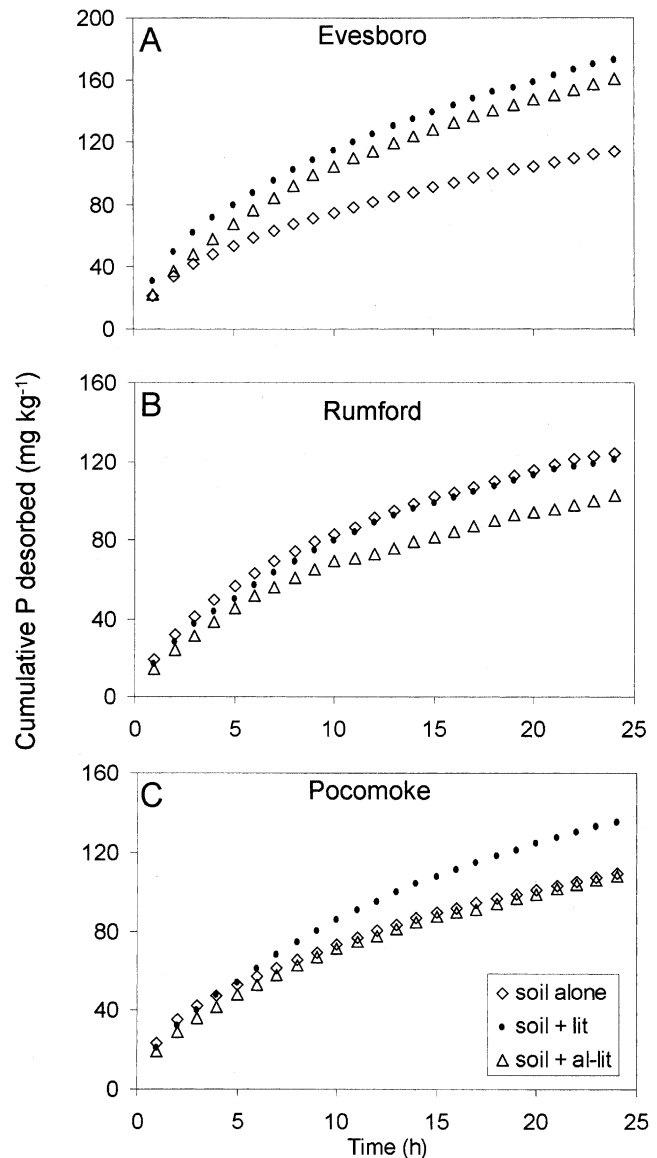


Fig. 2. Short-term (24 h), stirred-flow phosphorus release from poultry litter (PL)-treated and untreated Coastal Plain soils (pH 6) after 1 wk of incubation and 24 h of hydration in 2 mM 2-(4-morpholino)-ethane sulfonic acid (MES) buffer and 0.098 M NaCl (pH 6) desorptive solution with a 0.4:7.6 solid to solution ratio. Soil + lit, soil incubated with control litter; soil + al-lit, soil incubated with alum-amended litter. Experiments were not replicated for the short-term study. (A) Evesboro loamy sand, (B) Rumford loamy sand, and (C) Pocomoke sandy loam.

the same relationship of P release, increasing from soil alone to soil + lit and decreasing from soil + lit to soil + al-lit, still remains. A comparison of soil + lit to soil + al-lit samples shows a 13, 19, and 27 mg kg⁻¹ decrease in desorbed P as a result of addition of alum to the manure (Ev, Ru, and Pm respectively). These values correspond to 7% decrease for Ev, 15% for Ru, and 20% for Pm. Although the soil + al-lit sample released less P than the control in the Ru and Pm soils, statistical analyses of these differences would not be meaningful due to the lack of replications.

The linear trend of P release, unlike the results of the long-term desorption experiments, is probably due

Table 3. Kinetic modeling parameters calculated from long-term release curves for soils incubated with alum-amended and unamended poultry litter.

Sample†	Parabolic diffusion		Elovich			First-order				
	<i>R</i>	<i>r</i> ²	α	β †	<i>r</i> ²	1–5 d		6–25 d		
						k'_d ‡	<i>r</i> ²	k'_d ‡	<i>r</i> ²	
						d ⁻¹	d ⁻¹			
Long-term										
Ev + lit	0.82	0.98	80.71	1.45	0.99	8.61	0.91	1.04	0.93	
Ev + al-lit	0.76	0.98	63.47	1.58	0.99	9.64	0.91	1.13	0.93	
Ru + lit	1.41	0.88	133.22	0.749	0.98	25.8	0.83	0.82	0.89	
Ru + al-lit	1.28	0.90	120.71	0.839	0.98	26.5	0.82	0.89	0.90	
Pm + lit	2.36	0.87	116.35	0.855	0.97	15.0	0.90	0.65	0.90	
Pm + al-lit	2.29	0.90	114.14	0.912	0.99	17.0	0.86	0.81	0.88	
Short-term										
						1–8 h		8–24 h		
						k'_d	<i>r</i> ²	k'_d	<i>r</i> ²	
						h ⁻¹		h ⁻¹		
Ev + lit	0.38	1.00	1.53	2.08	0.97	5.52	0.96	1.38	0.97	
Ev + al-lit	0.38	1.00	1.46	2.10	0.97	6.36	0.97	1.37	0.98	
Ru + lit	0.27	1.00	1.18×10^{-3}	2.73	0.97	5.76	0.96	1.24	0.97	
Ru + al-lit	0.22	0.99	2.60×10^{-4}	3.33	0.97	6.59	0.95	1.29	0.99	
Pm + lit	0.56	1.00	4.76×10^{-2}	2.49	0.96	5.90	0.98	1.45	0.97	
Pm + al-lit	0.44	1.00	2.30×10^{-3}	3.27	0.96	5.10	0.96	1.25	0.98	

† Ev, Evesboro loamy sand; Ru, Rumford loamy sand; Pm, Pocomoke sandy loam; lit, control poultry litter; al-lit, alum-amended poultry litter.

‡ The calculated values were multiplied by 10^2 to obtain the reported numbers.

to the continuous replenishment of desorptive solution in the stirred flow method. As previously mentioned, minimized re-adsorption processes, due to continual removal of desorption products, may better simulate the P desorption behavior in the well-drained soils such as Ev and Ru.

Overall, the alum amendment resulted in a reduction in P release under the reaction conditions we studied. To further assure the effectiveness of the alum amendment, the results of short- and long-term P desorption were modeled using several kinetic equations, the parameters of which are discussed below.

Kinetic Modeling

The use of kinetic models was for qualitative comparison of data sets. Often, multiple models can fit the same set of kinetic data (Ogwada and Sparks, 1986; Onken and Matheson, 1982); therefore, we wanted only to investigate the efficacy of these models in pointing out differences in P release trends. Table 3 gives the values of kinetic variables in the three equations applied to both the long- and short-term data.

The parabolic diffusion model (Eq. [1]) seemed to best fit the Ev systems; however, linear relationships, an indicator that desorption processes are diffusion controlled (Toor and Bahl, 1999), are evident in the other two soils as well. In the long-term desorption study, the diffusion coefficient (*R*) is greater in the soils with a slightly finer texture (Ru) and higher organic matter content (Pm), as soils with more heterogeneity are more likely to have an increase in transport-limited processes. Calculated diffusion coefficients were lower for soil + al-lit systems, indicating that diffusion rates were slower. In the short term study, the diffusion coefficients are much lower; however, the model still yields a straight line. While this may suggest that diffusion influenced P desorption to a smaller extent than in the long-term

study, we cannot determine the type of diffusion that is taking place in either system.

The Elovich equation (Eq. [2]), previously shown to describe P desorption kinetics in soils where a simple first-order model was not suitable (Chien and Clayton, 1980), fit all of the soil + lit and soil + al-lit samples ($r^2 \geq 0.96$). With the presence of alum in the litter, the value of β consistently increased, by a minimum of approximately 6% (Pm), while α consistently decreased in all samples (21, 10, and 2% for Ev, Ru, and Pm, respectively, for long-term data). A decrease in α indicates a reduction in the desorption reaction rate (Chien and Clayton, 1980), while an increase in β correlates to a higher extractable Al content and decreased rate of desorption (Sharpley, 1983; Toor and Bahl, 1999). The information provided by α and β suggested that the presence of alum in PL will slow P release; however, these parameters are dependent on soil type and reaction conditions, and give no fundamental chemical information about the effects of alum-amended PL application on soil chemistry.

A single first-order equation did not describe the entire long- or short-term desorption data as accurately as the other two models (lower r^2), even though the raw data for the stirred-flow study appeared to be more linear in nature. Therefore, for the first-order model (Eq. [3]), the data were broken into two regions where a change occurred in the slope of the desorption curves (after initial 5 d or 8 h for the long- and short-term experiments, respectively), and the model was fit to each region separately. For the long-term study, the r^2 values for this equation were still lower than the other two kinetic models. In the first five and eight data points (of the long- and short-term study, respectively), the k'_d values were greater than in the longer time periods, indicative of a much faster rate of release. The largest k'_d values were observed in the Ru + lit and Ru + al-

lit samples and the k'_d was larger in samples containing alum.

All of the models fit the data well, and each has a set of assumptions for the different physical and chemical properties of the systems to which they are being applied. From the use of these equations we see that the short- and long-term studies yield different magnitudes for the calculated variable, but the relationships between the soil + lit and soil + al-lit samples and their effect (i.e., increase or decrease) on these variables are the same.

CONCLUSIONS

Long-term desorption shows that, across all soils, the mean P release between the control and the soil + al-lit is not statistically different. Short-term desorption studies show that the alum amendment was most effective (determined by the greatest reduction in desorbed P between soil + lit and soil + al-lit) in the Pm soil mixtures, which contain the largest percentages of ammonium oxalate-extractable P, Al, and Fe. This suggests that amorphous aluminum and iron phases may be important in the reduction of desorbed P. Because Pm is a higher-organic-matter soil, it could more specifically suggest that the amorphous phases associated with organic substances are the fraction of soil Al that is responsible for this reduction.

Our results predict that the use of alum as a best management practice is beneficial in Coastal Plain soils. Because soil, especially with the addition of PL (an already complex system), is so heterogeneous, more controlled (pH, temperature, etc.) studies would contribute to a better understanding of the basic chemistry in this system. It has been shown that an adsorbed P phase, onto $\text{Al}(\text{OH})_x$ complexes, is present in the litter (Peak et al., 2002); however, it is unclear what intermediate products are forming or being transformed while the litter remains in the poultry house. Further spectroscopic analysis of litter material may yield more definitive results about these chemical reactions.

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