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Developing a Remediation Strategy for Phosphorus Immobilization: Effect of Co-blending, Al-residual and Ca-Mg Amendments in a Manure-Impacted Spodosol

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A remediation strategy called “co-blending” was developed for rapid phosphorus (P) immobilization. Immobilization was achieved through the combination of an Al-based water treatment residual (Al-WTR) with Ca-Mg-based materials (Slag and magnesium oxide) for use in incubation and leaching experiments. Al-WTR was co-blended with Slag and MgO as “Al-WTR+Slag” and “Al-WTR+MgO,” respectively. Sequential extraction was used to delineate P species into operationally defined fractions: soluble or exchangeable, Al-Fe, and Ca-Mg-bound pools. Results from soils used in the incubation experiment showed that Al-amended material tended to sequester P bound (~26%) to the Al-Fe pool. On the other hand, Ca-Mg-based materials tended to sorb (~70%) of P greatly associated to the Ca-Mg pool. Amendments were applied at 2% or 20 g kg⁻¹ as Al-WTR, MgO, and Slag and at 1%+1% or 10 g kg⁻¹+10 g kg⁻¹ as co-blended Al-WTR+MgO and Al-WTR+Slag, respectively, on mass basis. Results from leaching data suggest that treatment effects on pH are significant at (p < 0.0001) and also significant (p < 0.01) with weeks of leaching. A similar significant (p < 0.0001) trend was observed for effects of treatment on redox potential (Eh). However, treatment effects on weeks of leaching were not significant. Cumulative soluble P (mg) of leachate showed linear reduction (96%) from the control (without amendments) using a regression model. Potential co-blended material selected was Al-WTR+Slag (1%+1%) due to less P in leachates, moderate effect on pH, and fewer amounts of Al-WTR and Slag used compared with 2% Al-WTR and Slag, respectively. In addition, the RMSE of Al-WTR+Slag data fitted to a regression model was the least. Results suggested that the metal cations Al, Ca, and Mg tended to bind different forms of total P at any given pH. Through co-blending, less soluble P may be lost to the environment than using sorption materials independently.

Keywords co-blending, manure-impacted soil, drinking water treatment residual, remediation, immobilization, Ca-Mg-based materials

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Introduction

The potential risk of surface and groundwater contamination by phosphorus (P) is an environmental issue in much of the United States. It is of particular concern in South Florida (Lake Okeechobee watershed) due to the soil hydraulic conditions and low soil P retention capacities (He et al., 1999). Approximately 64% of the soils in Okeechobee County are Spodosols that exhibit low P retention capacity due to negligible amounts of secondary minerals and organic matter (Harris et al., 1996). The flat topography of the watershed coupled with abundant pasture and rangeland use minimizes surface-runoff contamination. However, significant amounts of P can be leached or transported to surface water via sub-surfaced lateral flow. Leaching in these soils takes place when fluctuating water tables, mostly during the summer rains, transport the P from the impacted surface soil to shallow groundwater tables.

The area dairy industry has been identified as a significant source of P loading into the Lake Okeechobee watershed by way of manure deposition. Repeated manure applications have resulted in P-saturated conditions (Pant et al., 2002). The use of chemical amendments containing Fe, Al, and Ca has been suggested as a means to mitigate P losses to water bodies. Although low activity magnesium oxide (MgO) has received little attention for use in P immobilization, blast furnace slag (slag) is being considered (Yamada et al., 1986; Drizo et al., 2002; Xu et al., 2006; Cucarella and Renman, 2009). Slag is a by-product of iron production. Slag material is composed of a calcium aluminosilicate, and it has the potential to sorb toxic compounds (Dimitrova 1996; Cope and Benson, 2009). Conversely, MgO is a product of calcinations of magnesium hydroxide in which different grades of MgO are generated, depending on the prescribed temperature (Van de Walle et al., 1993; Lanin et al., 2008). The effects of the thermal conditions affect the surface area, porosity, and reactivity of MgO. The grades of MgO products are known as “dead burned,” “hard burned,” and “light burned.” One advantage of MgO is that by changing the surface area through temperature modifications, highly reactive products can be generated that contain fewer toxic elements, as compared to slag (Van de Walle et al., 1993).

Another soil P retention option that has attracted recent attention is the use of a by-product from drinking water treatment plants, referred to as aluminum water treatment residual (Al-WTR) (Elliott et al., 2002; Makris et al., 2004; Agyin-Birikorang et al., 2007; Oladeji et al., 2009). The main advantages of Al-WTR are the high P sorption capacity due to Al hydr(oxides) content and the free cost of the material. However, in applying Al-WTR for P sorption, slow sorption kinetics have been observed with long equilibration times (Makris et al., 2004). In addition, large quantities are required for application in heavily impacted soils. This large amount usage was attributed to competition of soluble organics in the manure-impacted soil for water treatment residual (WTR) exchange sites, thus reducing the efficiency of WTR's ability to retain P (Lane, 2002). Other researchers, however, attributed the large quantities of WTR required for immobilization to its bottleneck-shaped micropores that limit P diffusion rates (Makris et al., 2004). Ippolito et al. (2003) further suggested that sorption process is in two stages; the initial P adsorption reaction is quick and occurs as an outer-sphere complex, while the second stage is much slower as P becomes more strongly adsorbed as an inner-sphere complex onto WTR particles.

Florida's Spodosols are acidic and sandy in nature and lack sufficient Al-Fe in the A-horizon. Applying Al-WTR has shown some promise (Silveira et al., 2006). However, it has been observed that high application rates are needed to completely immobilize P. Moreover, these high application rates (15% w/w) have resulted in significant soil acidification (Novak and Watts, 2005), which may cause plant-Al toxicity symptoms if low acidity and Al³⁺ activity continue (Shann and Bertsch, 1993; Delhaize and Ryan, 1995). Using a one-time

application at moderate rates, only about 50% of soluble P in manure-impacted soils was found immobilized after 7.5 years, with the majority of P immobilized within the first year (Agyin-Birikorang et al., 2007). There is therefore a need to optimize the use of Al-WTR for P sorption in manure-impacted soils.

Continuous manure deposition has been reported to increase soil native pH (Nair et al., 1995; Whalen et al., 2000; Eghball, 2002). Leaching the soil for more than 30 weeks have also recorded alkaline pH (Silveira et al., 2006). The alkaline conditions ($\text{pH} \geq 8.3$) were attributed to a continuous release of soluble Ca and Mg bi/carbonates from the manure, leading to fluctuations in pH, as observed in the native soil (Miyittah et al., 2006; Silveira et al., 2006). In addition to soil chemistry, phosphorus chemistry, available moisture and solution pH are the principal factors controlling P binding onto a chemical amendment. An ideal amendment should effectively remove labile P under prevailing soil conditions, including a fluctuating soil pH. However, this ideal amendment is somewhat difficult to obtain due to the fact that several P species may co-exist in soil solution at any given pH. For example, a 1 unit decrease in pH leads to ~ 10 -fold increase in the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ratio. As the soil pH fluctuates, some amendments will better sorb soluble P. As observed in alkaline environments, a Ca-Mg-containing material has been suggested to control P in the solid phase, whereas Al-Fe-based amendments were suggested to control P under acidic conditions (Bohn et al., 2001). A need therefore exists for an amendment that can effectively immobilize P in manure-impacted soils under fluctuating pH conditions.

Sequential extraction of manure-impacted soils revealed that dominant P forms were loosely associated with Ca-Mg (60%-70%) rather than Al-Fe ($\sim 20\%$ -30%) (Sharpley et al., 2004; Silveira et al., 2006). These large pools of alkaline forms of Ca-Mg components loosely associated with P tended to be responsible for periodic P release with changing pH (Miyittah et al., 2006). Other researchers have hypothesized that longer term P desorption is associated with a metastable pool that continuously replenishes solution via diffusion (Hansen and Strawn 2003; Koopmans et al., 2004). Simultaneously, immobilization of soil P, associated with Ca-Mg and Al-Fe P fractions using combinations of different amendments, may hold some promise.

The three objectives of this study were: 1) to bind additional soil labile P by using Ca-Mg with Al-WTR as co-blended products in comparison with single Al-WTR usage; 2) to reduce the amount of Al-WTR used in soils liable to acidity; and 3) to increase the sorption kinetics of P uptake in manure-impacted soil with the use of co-blending of amendments.

Materials and Methods

Soil and Amendment Characterization

A manure-impacted sample of Immokalee fine sand (sandy, siliceous, hyperthermic Arenic Haplaquod) was obtained from a field site on a dairy cattle ranch located in the Lake Okeechobee County watershed. This soil was selected for its high total P due to long-term manure application and/or fecal deposition, as well as the soil's geographic extent in South Florida. Random samples were collected from the A horizons (0–15 cm), and were thoroughly mixed to yield a composite sample. The soil was air-dried and sieved through a 2 mm stainless steel screen. Soil pH was measured in a 1:2 (w: v) aqueous suspension. Soil was fractionated into KCl-P, NaOH-P, and HCl-P. The fractionation procedure is described in Silveira et al. (2006) and also elaborated below under incubation and sequential extraction section. Oxalate-extractable Al and Fe were determined by extraction with 0.2M oxalic acid plus 0.2M ammonium oxalate solution at pH 3 (McKeague et al., 1971).

The Al-WTR was collected from a drinking water treatment plant in Bradenton, Florida. In characterizing the amendments, pH was measured in a 1:2 (w: v) aqueous suspension as reported elsewhere (Silveira et al., 2006). Redox potential (Eh as mV) was measured using two electrodes connected to the pH meter (Accument XL60, Fisher Scientific, USA). The reference electrode and temperature sensor were connected to an interface multi-channel (pH-meter/redox meter), which enabled simultaneous readings of pH and Eh. After every 10 samples, Eh monitoring was evaluated to avoid drifts in voltage for good quality control/assurance (Rabenhorst, 2009).

The Al-WTR samples were air-dried and sieved through $< 850 \mu\text{m}$ screen to minimize slaking and increase reactivity (Dayton and Basta, 2005). Two Ca and/or Mg products, low activity magnesium oxide (MgO), and slag were characterized in a similar manner as Al-WTR. Total recoverable Fe, P, Al, Ca, and Mg were determined using Inductively Coupled Plasma Optical-Emission Spectrometry (ICP-OES, Perkin Elmer Plasma 2100DV, Perkin Elmer Inc., Waltham, MA, USA), following digestion according to EPA Method 3050B (USEPA, 1996).

Incubation and Sequential Extraction

Sufficient amendments were mixed well with the soil at the rate of 0%, 1%, and 2% to the weight (d.w.) of the soil. The treatments were placed into triplicate 100-mL glass bottles and placed in a temperature-controlled incubator chamber at temperature and relative humidity of $22^\circ\text{C} \pm 3$, 45% to 52% respectively. During incubation, all bottles were maintained at moisture content of 10% to 15% to represent typical soil moisture content at field capacity for sandy top soil (Rawls et al., 1982). Soil and amendments were incubated for four weeks, and sequentially extracted P was measured according to Chang et al. (1983), using a 1:20 soil/solution ratio, with modification as in Silveira et al. (2006).

The sequential extraction procedure utilized: 1) 1M KCl to determine the soluble or exchangeable P—this fraction is easily leachable; 2) 0.1M NaOH to determine the chemisorbed P onto oxides and hydroxides of Fe, Al, and Mn; 3) 0.5M HCl to determine P associated with Ca-Mg complexes (Hieltjes and Lijklema, 1980; Ruttenberg, 1992; Stumm and Morgan, 1996). However, the recalcitrant P was not analyzed as reported by Silveira et al. (2006).

Co-blending and Column Leaching

The soil was packed in a revolving container (of vol. $\sim 150 \text{ cm}^3$) that allowed it to mix well and to allow for air exchange when required. Amendments were applied at 0%, 1%, and 2% by mass to the weight (d.w.) of the soil. Oxygen-free water was used to inundate 40% to 100% soil pore spaces while maintaining an air-tight environment. The inundated soil was to simulate dynamics in soil hydraulic conditions, including the worse case scenario of periodic soil saturation for a 10-day cycle. After 10 days, the soil was allowed to air-dry by opening the container. The first amendment was applied and then put through another hydraulic cycle. After 10 additional days, the second amendment was applied to make a pair, while maintaining a soil-moisture content of 10% to 15%. Finally, the periodic hydraulic cycle was repeated for an additional 10 days, and then the soil was air-dried prior to use for the column leaching tests.

The soil column design was similar to that reported by Silveira et al. (2006). Amendments used were Al-WTR, slag, and MgO at (20 g kg^{-1} or 2%), respectively. The samples obtained from the co-blending process above were Al-WTR+MgO, and Al-WTR+Slag

at (10 + 10 g kg⁻¹ or 1% + 1%), or (10 + 10 g kg⁻¹ or 1% + 1%), respectively. The co-blending resulted in all soils receiving a total of 20 g kg⁻¹ of amendments. A soil without amendment was used as a control. All treatments were replicated three times in a completely randomized design. Leaching consisted of the application of 100 mL of DDI water (adjusted to pH 5 to mimic the pH of rainfall in South Florida) to each column weekly for five weeks. Each leaching event corresponded to 1 pore volume. Leachates were analyzed for soluble P with ICP-OES.

Statistical Analysis

Statistical tests were performed using the Proc GLM and Proc REG model SAS version 9.1.3 (SAS Institute, 2003, Cary, NC). Differences within each P fraction were examined using an ANOVA at a significant level (α) of 0.05, with mean separation determined using Tukey's Studentized Range (HSD) Test. Repeated measures analysis was performed with Proc GLM at a significant level (α) of 0.05. Significant differences in the cumulative P mass were determined using Fisher's Protected LSD procedure at a significant level (α) of 0.05. A Root Mean Square Error (RMSE) was calculated to evaluate the model's fitness and performance. Analytical and instrument quality assurance and quality control (QA/QC) were evaluated for all laboratory analyses by including 5% repeats, 5% spikes, and blanks. Standard calibration curves, as well as a quality control check standard, were prepared for each session. Background signal drift was consistently <1% for all instruments. Spike recoveries were within an acceptable range of 90% to 110%.

Results and Discussion

Amendments and Soil Properties

The physicochemical properties of Al-WTR taken from Bradenton, Florida, showed 86 g kg⁻¹ Al content and 2.3 g kg⁻¹ Fe content (Table 1). The relatively high Al content suggests that it might achieve reasonably high P sorption (Grubb et al., 2000; Arias et al., 2006). The slag contained Ca, Mg, and Al (598, 106, 156 g kg⁻¹), respectively. In comparison, MgO had a greater Mg content (897 g kg⁻¹) than slag. The pH of Al-WTR was 6.3, which was consistent with values reported elsewhere (6.0–8.4) (Makris and O'Connor, 2007). The Al-WTR had P concentration of 0.02 g P kg⁻¹, which was slightly below the range reported for Al-WTRs (0.3–4.0 g P kg⁻¹) (Dayton et al., 2003; Makris and O'Connor, 2007). The MgO and slag amendments had alkaline pH values of 10.9 and 11.5, respectively, consistent with values reported by Cucarella and Renman (2009). The soil pH was 7.1. Oxalate-extractable Fe and Al are usually associated with amorphous phases of oxides and suggest that P will be attached to the sesquioxides and other forms of hydr(oxides) present in the soil (Table 1). Total P in the Okeechobee test soil (Table 1) was approximately 2800 mg kg⁻¹, indicating a high P load (Nair and Graetz, 2002). In the soil, most of the reactive P was associated with Ca-Mg, representing 62% of total reactive P, whereas P associated with Al-Fe was 23%, and easily leachable P ~15% (Table 1). The previous fractionation data are consistent with results from Nair et al. (1995); Sharpley et al. (2004). The results showed that Ca-Mg-bound P dominated P forms in a manure-impacted soil. The total P concentration of MgO was below the instrument's detection limits, and slag P content was approximately 0.03 g P kg⁻¹.

Table 1
General properties of amendments and soil

Properties ^a	Total Elemental (g kg ⁻¹)						
Amendments	P	Fe	Ca	Mg	Al	pH	
Al-WTR	0.02	2.3	4.6	0.5	86	6.3	
Slag	0.03	14	598	106	156	11.5	
MgO	^b BDL	2.0	9.0	897	2.0	10.9	
	Sequential extracted P					Oxalate extractable	
mg kg ⁻¹						
#Soil	pH	^c KCl	^d NaOH	^f HCl	Total P	Fe	Al
A-horizon	7.1	400	640	1720	2800	348	210

^aValues are means of triplicate. ^bBDL (below detection limits of 1 * 10⁻³ mg L⁻¹). ^{c,d,f}Soil fractionations (KCl-P (soluble or exchangeable P), NaOH-P (extractable P bound to Al-Fe) and HCl-P (extractable P bound to Ca-Mg) determined using the method of Chang et al., 1983. [#]Okeechobee soil.

Sequential Extractions of Incubated Soils

Sequential extractions from amended soils after 4 weeks of incubation are presented in Figures 1 to 3. In general, the amendments had effects on distribution of P fractions with respect to the extracting reagents. The 1 M KCl extraction, labile or soluble P consists of the significant smallest portion (3%-14%) of the total P pool (*P* < 0.05) (Figure 1). The control

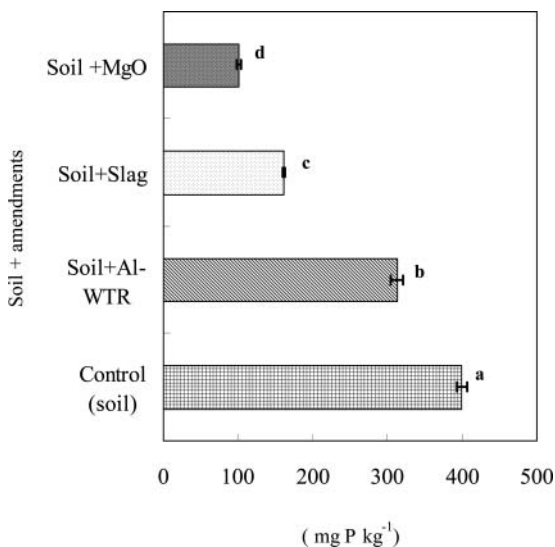


Figure 1. (KCl-P extraction) or soluble/extractable P sequentially extracted from amended and unamended soil after 4 wks of incubation. Error bars indicate SE of triplicate. Means of the same letters are not significantly different at significant level (α) of 0.05, determined by Tukey's Studentized Range (HSD) test.

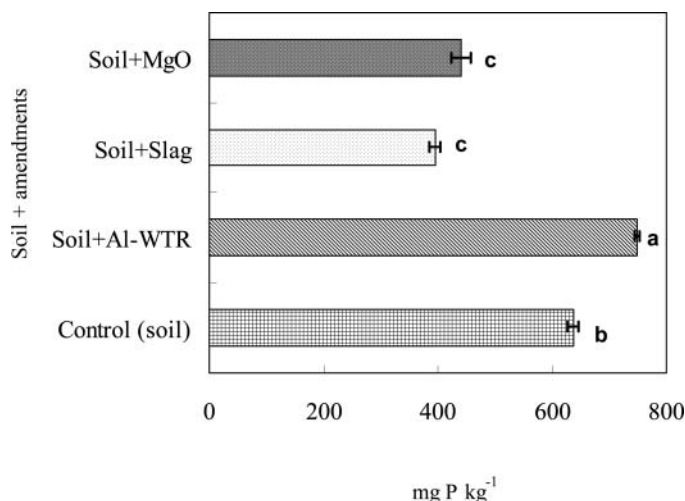


Figure 2. (NaOH-P extraction) or Al-Fe bound P sequentially extracted from amended and unamended soil after 4 wks of incubation. Errors bars indicate SE of triplicate. Mean of the same letter are not significantly different at significant level (α) of 0.05 determined by Tukey's Studentized Range (HSD) test.

had the largest release (400 mg kg^{-1}) of soluble P (14%) of total P. On the other hand, Al-WTR, slag, and MgO had a lower soluble P of 11%, 5%, and 3%, respectively, of total P indicating that amendments application led to reduction in readily labile or exchangeable P. The 0.1M NaOH extraction as reactive Al-Fe-bound P or chemisorbed P ranged from 14%-26% of the total P (Figure 2). Al-amended soil had the largest portion (750 mg kg^{-1}) of reactive Al-Fe-bound P (26%) of total P, and showed an increment of 4% compared to the control. In contrast, slag (395 mg kg^{-1}) and MgO (440 mg kg^{-1}) contributed 14% and 15% of Al-Fe-bound P, respectively, of total P. Therefore, the addition of Al did lead to an increase of Al-bound P pool, thus suggesting the effects of Al on sequestration of P associated with Al-Fe (Malecki-Brown and White, 2009). On the other hand, Ca-Mg-based amendments addition had a decrease ($\sim 8\%$) of Al-Fe-bound P compared to the control (Figure 2). The 0.5M HCl extraction quantified as Ca-Mg-bound P comprised of a significant dominant portion 31%-70% of the total ($P < 0.05$) (Figure 3). Slag and MgO amendments had the largest Ca-Mg-bound P, 67% and 70%, respectively, of the total P. That is, a significant amount of P was bound to slag and MgO at 1980 and 1900 mg kg^{-1} , respectively (Figure 3). On the other hand, Al-based amendment had 31% of Ca-Mg-bound P of total P, a decrease of $\sim 36\%$ relative to slag, a Ca-Mg amendment. Clearly, addition of slag and MgO amendments significantly increased the Ca-Mg-bound P ($\sim 10\%$) compared to the control (Figure 3).

Overall, addition of amendments (Al-Fe, Ca-Mg-based) to the soil tended to sorb P differentially in relation to the fractionated pools. The addition of Ca-Mg-based materials to the loosely associated Ca-Mg-bound P may have initiated a binding response to stabilize largely Ca-Mg associated P. Similarly, to immobilize mainly Al-Fe-bound P, Al-WTR had the most influential effect. The combination or mixing (co-blending) of Al-WTR or slag and MgO amendments containing Al or Ca-Mg hold the promise of immobilizing significant P fraction relative to the cations present for rapid P uptake. Although residual P (organo-complex P) was not analyzed for mass balance, anecdotal evidence suggests that Ca-Mg-based amendments extract greater residual P than Al-based amendment.

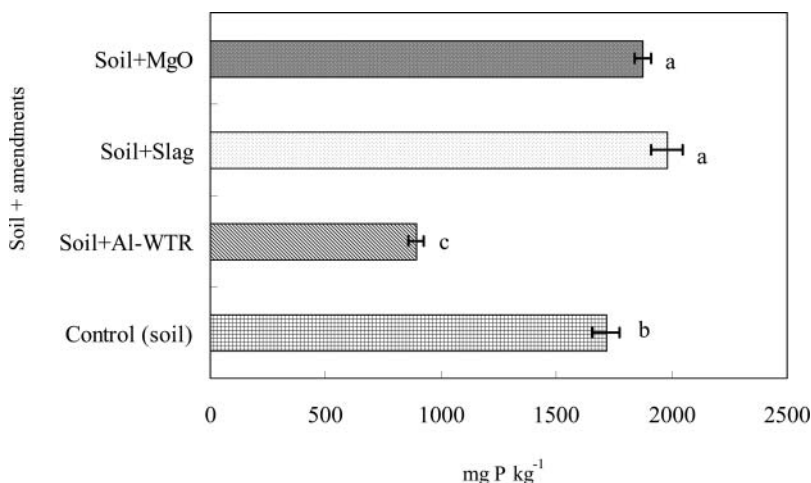


Figure 3. (HCl-P extraction) or Ca-Mg associated P sequentially extracted from amended and unamended soil after 4 wks of incubation. Error bars indicate SE of triplicate. Means of the same letters are not significantly different at $\alpha = 0.05$ determined by Tukey's Studentized Range (HSD) test.

Sequential extraction is a semi-quantitative tool used for tracking the mobility of phosphate species. The procedure may result in overlap and transfer of some P species from one extraction step to another. The procedure can therefore lead to under and/or over predictions of the P species within an extraction. However, the results provided some information on the forms of P immobilized by different metals singly or in combination.

pH, Eh, and Leachate P Analysis

The control composite soil sample "as is" had pH of 7.1. The pH of the native amendments were 6.3, 11.5, and 10.9 for Al-WTR, slag, and MgO, respectively (Table 1). The pH of the leachate samples without any chemical amendments fluctuated, ranging from 7.7 to 8.26 during the five weeks of leaching (Table 2). The progressively weekly alkaline pH observed for the control may be attributed to the release of soluble Ca and Mg bi/carbonates from the manure.

Leachate pH of MgO ranged from 9.4 to 9.7 and that of slag ranged from 8.3 to 8.7 indicating that the amendments were alkaline. Similarly, leachate pH for soil amended with Al-WTR (20 g kg⁻¹) ranged from 7.7 to 8.5 (Table 2). The fluctuating pH environment may tend to make Al-WTR preferentially mask certain P species since the pH affects the types of species of HPO₄²⁻ and H₂PO₄⁻ reaction onto a metal oxide. The variability in soil pH and P species masking by Al-WTR may probably explain the long months and years it took Al-WTR to completely sorb P as reported (Silveira et al., 2006; Agyin-Birikorang et al., 2007). The preferential masking or selective P removal by amendments led to the suggestion that the P species of H₂PO₄⁻ and HPO₄²⁻ in solution were affected by the types of amendments incorporated (i.e. metal cations availability). For instance, at the existing pH of ~8, fewer HPO₄²⁻ species are favored in solution compared to H₂PO₄⁻. In addition, aluminum-based WTR behaving as an amorphous hydr(oxide) may form insoluble polymeric Al(OH)₃ and result in P inactivity when the pH is < 8. On the other hand, above pH of 8, aluminate ions [Al(OH₄⁻)] may dominate. Since Al is amphoteric, there is a possibility of releasing the bound P (Cooke et al., 1993; Upadhyay et al., 2002; Essington,

Table 2
Mean weekly pH for amended and unamended soils during leaching

Treatments	Week 1	Week 2	Week 3	Week 4	Week 5
Control soil (0%)	7.71 ± 0.01	8.11 ± 0.09	7.91 ± 0.07	7.94 ± 0.06	8.26 ± 0.25
Soil + MgO (2%)	9.52 ± 0.04	9.79 ± 0.03	9.67 ± 0.07	9.76 ± 0.05	9.42 ± 0.33
Soil + Slag (2%)	8.45 ± 0.01	8.73 ± 0.02	8.56 ± 0.03	8.73 ± 0.05	8.35 ± 0.31
Soil + Al-WTR (2%)	7.74 ± 0.05	8.12 ± 0.07	7.95 ± 0.03	8.04 ± 0.04	8.49 ± 0.38
Soil + Al-WTR + MgO (1% + 1%)	9.13 ± 0.05	9.48 ± 0.04	9.13 ± 0.02	9.20 ± 0.04	9.35 ± 0.16
Soil + Al-WTR + Slag (1% + 1%)	8.18 ± 0.05	8.48 ± 0.03	8.35 ± 0.02	8.46 ± 0.04	8.43 ± 0.08
Repeated Measures Analysis	<i>p</i>				
Treatments	<0.0001				
Weeks	<0.01				
Treatments * Weeks	0.958				

Weekly values are means of three replicates. Repeated measures analysis performed with PROC GLM, significance at $p < 0.05$.

± indicates standard error of the mean.

2004). This amphoteric nature of Al as pH changes and the effects of competing soluble organics may be responsible for a large amount of Al-WTR usage and the slow P sorption reactions in manure-impacted soils. The observation of the slow P sorption may suggest that Al-WTR tended to preferentially select or mask certain P species as pH fluctuates from 7 to > 8. This masking effect may indicate that certain species of orthophosphate are selected to react with Al while other species remain unreacted. The overall effect shows that the immobilization or sorption process is prolonged.

Leachate pH of soil amended with MgO + Al-WTR ranged from 9.1 to 9.5, while the leachate pH of soil amended with Al-WTR + Slag ranged from 8.2 to 8.5 (Table 2). The lower pH of Al-WTR+Slag compared to MgO+Al-WTR may be due to low Mg content in the slag. The differential change in pH of the co-blended materials (MgO+Al-WTR and Al-WTR+Slag) thus suggests that the amount of cations available greatly affects the pH. Repeated measures analysis showed clearly that the treatments' effects on pH were significant ($p < 0.0001$) as well as with respect to weeks of leaching events ($p < 0.01$). However, interactions between the treatments' effect and weekly leaching events were not significant, thus showing that the type of amendments used significantly influences the observable pH with respect to time.

The control composite soil sample "as is" had Eh (redox potential) = +300 mV. The Eh of the leachate samples ranged from -46 to -169 mV. The negative Eh of leachate samples suggest that the soils became anoxic during the co-blending process (Table 3). All soils, unamended and co-blended, had Eh values below the reported critical redox potential for the reduction of Fe (Eh = +300 to -100 mV; at pH 6-8 (Gotoh and Patrick, 1974; Olila and Reddy, 1997). The redox reaction suggests reduction of Fe³⁺ to Fe²⁺ with the corresponding release of P. Consequently, the released P sequestered to Fe³⁺ might have been recaptured by other metal cations in the co-blended products due to the change in Eh from positive to negative potential. This differential change in Eh may have contributed to the release of

Table 3
Mean weekly Eh (mV) for amended and unamended soils

Treatments	Week 1	Week 2	Week 3	Week 4	Week 5
Control soil (0%)	-46.3 ± 2.04	-69.1 ± 5.30	-64.7 ± 3.96	-61.5 ± 1.44	-64.1 ± 1.18
Soil + MgO (2%)	-158.2 ± 10.7	-166.2 ± 1.85	-169.9 ± 3.99	-167.7 ± 3.81	-164.0 ± 4.14
Soil + Slag (2%)	-103.9 ± 15.7	-104.8 ± 0.86	-103.6 ± 2.02	-104.8 ± 3.33	-102.6 ± 3.97
Soil + Al-WTR (2%)	-48.7 ± 2.53	-69.9 ± 3.91	-67.4 ± 2.16	-66.9 ± 2.07	-70.1 ± 1.50
Soil + Al-WTR + MgO (1% + 1%)	N/A	-148.7 ± 2.64	-137.5 ± 1.75	-133.3 ± 1.35	-131.5 ± 3.01
Soil + Al-WTR + Slag (1% + 1%)	N/A	-90.9 ± 1.49	-91.3 ± 1.37	-90.5 ± 2.40	-89.1 ± 2.38
Repeated Measures Analysis	<i>p</i>				
Treatments	<0.0001				
Weeks	0.19				
Treatments * Weeks	0.99				

N/A indicates data not available. Weekly values are means of triplicate. Negative Eh (mV) values showing anoxic condition due to co-blending. Repeated measures analysis performed with PROC GLM, significance at $p < 0.05$.
± indicates standard error of the mean.

P and subsequent binding under variations of reducing conditions. Furthermore, repeated measures analysis suggested clearly that Eh (mV) effects were significant ($p < 0.0001$) with respect to the treatments, thus suggesting that the amendments used in the co-blending process had an important role in creating anoxic conditions.

This resulting change in Eh occurred for the control, Soil+Slag, Soil+Al-WTR, and Soil+Al-WTR+Slag samples, with pH between 7.71 to 8.46, and Eh of -46.3 to -104.8 mV. Consequently, the decrease in solution P content at low Eh may be attributed: 1) to a combined effect of changes in the dissolution capacity of Fe-hydr(oxides) (Willett and Cunningham, 1983); 2) precipitation of P by Ca and Mg elements in the co-blended samples (Lindsay, 2001); and 3) the slow sorption of P that followed after initial fast reaction believed to be by ligand exchange onto surface hydroxyl groups (Sparks, 2002), provided by amorphous Al in the co-blended process. On the other hand, Soil+MgO and Soil+Al-WTR+MgO had pH (9.1 to 9.8), and corresponding Eh of -132 to -170 mV (Tables 3 and 4) with resulting low P concentration in the leachate. A similar low P content was observed by Patrick et al. (1973) for strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$)-rich soils when the pH was alkaline. The low P suggested that strengite is increasingly stable with increasing soil pH, thereby locking P into the strengite structure. Additionally, at pH 9.1, Fe levels in solutions have shown little variation with changing Eh from $+300$ to -400 mV (Pratt et al., 2007). Alternatively, P has been observed to be released from slag filters under reducing condition at pH of 9.1. The release of P was attributed to desorption of P from Fe-hydr(oxides) at high pH as the surface becomes negatively charged, preventing phosphate anions at high pH to be sorbed onto the surface (Baker et al., 1998). Although the mineral phases in the co-blended samples (e.g. Soil+Al-WTR+MgO, Soil+Al-WTR+Slag) are unknown, similar reactions as observed for strengite-rich soils may tend to occur due to variations in pH and Eh. In effect, single and/or multiple mechanisms of sorption, desorption, ligand exchange, and precipitation may have governed the reduction of the observed soluble P.

Cumulative soluble P (Table 4) illustrates the effects co-blended amendments had on leachate P. Linear regression analysis was performed on cumulative P mass as a function of leaching events. All data plotted (not shown) had correlation coefficients $R^2 > 0.92$. The regressions show a significant ($p < 0.0001$) slope reduction (96%) from control 5.32 to 0.21 as amendments were co-blended (Table 4). Slopes were reduced 68% from 1.73 to ~ 0.2 for Al-WTR vs. slag or MgO. The equations for soil amended with Al-WTR+Slag, MgO+Al-WTR had $P \text{ (mg)} = 0.28x - 0.187$, $R^2 = 0.98$, and $P \text{ (mg)} = 0.21x + 0.05$, $R^2 = 0.93$, respectively (Table 4). The root mean square error (RMSE) analysis was used to differentiate the treatment effects having the most significant influence since R^2 values were too close. A lower value of RMSE (0.071) for Soil+WTR+Slag suggested that its model fits the data well in terms of the least mass (mg) of P measured from the cumulative P loss during the leaching events (Table 4), thus suggesting that Soil+Al-WTR+Slag could be recommended as a candidate material for co-blending to immobilize P from manure-impacted soils in a rapid manner. Slag and MgO single application equally immobilized P comparatively to Al-WTR+Slag (Table 4). However, other factors need to be considered when selecting materials for co-blending such as the cost and the elemental contents of Al, Fe, Ca, and Mg, which are needed for sorption of P, as well as soil pH and buffering capacity. Overall, Al-WTR+Slag was selected as a potential co-blended material due to less P in leachates, moderate effect on pH and fewer amounts of Al-WTR and Slag used compared to 2% Al-WTR and slag, respectively. In addition, the Al-WTR+Slag regression model had the least RMSE. In effect, co-blending may be one approach to optimize the use of Al-WTR in acid soils such as Spodosols.

Table 4
Cumulative mean mass (mg) of soluble P in column leaching study

Treatments	Week 1	Week 2	Week 3	Week 4	Week 5	Regression model	R ²	RMSE
Control soil (0%)	2.64 ± 0.10	7.79 ± 0.43	13.51 ± 0.56	18.87 ± 0.64	23.71 ± 0.68	$S_p = (5.32x - 2.66)$ a	0.99	0.255
Soil + MgO (2%)	0.39 ± 0.02	0.82 ± 0.02	0.98 ± 0.03	1.13 ± 0.03	1.28 ± 0.05	$S_p = (0.21x + 0.29)$ c	0.93	0.102
Soil + Slag (2%)	0.07 ± 0.00	0.41 ± 0.00	0.51 ± 0.01	0.62 ± 0.01	0.74 ± 0.02	$S_p = (0.16x + 0.01)$ c	0.92	0.082
Soil + Al-WTR (2%)	0.79 ± 0.02	2.31 ± 0.04	4.11 ± 0.12	5.88 ± 0.23	7.66 ± 0.32	$S_p = (1.73x - 1.04)$ b	0.99	0.093
Soil + Al-WTR + MgO (1% + 1%)	0.14 ± 0.00	0.56 ± 0.01	0.71 ± 0.01	0.85 ± 0.01	1.01 ± 0.02	$S_p = (0.21x + 0.05)$ c	0.93	0.099
Soil + Al-WTR + Slag (1% + 1%)	0.02 ± 0.01	0.47 ± 0.02	0.68 ± 0.02	0.94 ± 0.03	1.20 ± 0.04	$S_p = (0.28x - 0.187)$ c	0.98	0.071

Weekly cumulative P values are means of three replications. Means of the same letter are not significantly different, at significant level (α) of 0.05, determined by Fisher's Protected Least Significant Difference (LSD). RMSE indicates root mean square error. S_p represents the cumulative mass (mg) of soluble P; using the model equation of cumulative P mass as ordinate and the weekly leaching events (x) as abscissa.
± indicates standard error of the mean.

It is also expected that reduction in soil pH may occur over time due to the low pH (~5.0) of rainfall and high rainfall of the area. A gradual reduction of pH as envisaged may elicit the response by activating the dormant surface properties of the amorphous Al within the co-blended products due to the changes in pH. Thus co-blending may provide the stable and safe boundary conditions for P immobilization. Depending on the amount of Ca-Mg and Al-based materials used, it is expected that P may be immobilized best within the pH range of 5 to 8. In further support of co-blending, co-application of biosolids with WTR has been found to reduce bioavailable P in runoff with an increase in corn yield in alkaline soils of Egypt (Mahdy et al., 2009).

Conclusions

The findings showed that by co-blending Al-WTR with Ca-Mg-based amendments, P leaching was significantly and rapidly reduced. A lower amount of aluminum residual (1%) was used in “co-blending” to achieve low soluble P, rather than 2% of single Al-WTR application. In additional support, this finding is consistent with observations from Ippolito et al. (1999), Bayley et al. (2008), and Mahdy et al. (2009) on P reduction when Al-WTR is co-applied (a type of co-blending) with biosolids containing some form of calcium.

A remediation approach of co-blending an Al and Ca-Mg-based materials has been designed to capture major P forms in manure-impacted Spodosol. Amendments such as MgO, slag, and Al-WTR were found to remove certain portion of the P fractions. Al-WTR tended to greatly immobilize P associated with Al-Fe than P associated with the dominant Ca-Mg forms. Recent findings (Josán et al., 2005; Silveira et al., 2006) underscore the fact that there is undersaturation of Mg-P minerals in abandoned dairy manure-impacted soils. The undersaturation may easily promote dissolution of metastable Mg-P compounds and the release of P, and perhaps also explain the re-emergence of P after single amendments application (Al-WTR) in manure-impacted Spodosols.

On the other hand, Ca-Mg-based materials tended to immobilize P associated with Ca-Mg forms. However, single application of MgO and slag had incremental effects on pH, which may not be desirable if the soil is to be used for plant cultivation. The remediation strategy of co-blending could provide a stable boundary for P immobilization within pH range of 5 to 8, depending on the types of amendment used. The co-blending of Soil+Al-WTR+Slag; 1% + 1% achieved the pH of ~8, close to the native soil during the leaching process, and to a greater extent it had the least P leached during the five-week period. On the contrary, Al-WTR single amendment application had pH of ~8, but with more P losses compared to the co-blended ones.

In spite of the inherent difficulty in comparing our data to field conditions, the results of the leaching study suggest the potential of co-blending to immobilize P. A significant amount of P was immobilized by the co-blended samples within a short period of time (five weeks) used for the study. The study, therefore, suggests that for rapid immobilization of P in manure-impacted soil, sorption materials could be used in combination. In this way, excess loss of P into water bodies could be prevented in a rapid and a safe manner. However, caution should be exercised in the choice of amendments, since the data provided are based on a short-term study. Future efforts are therefore needed for repeated applications, long-term studies, and using geochemical modeling to assess the solid phases controlling P solubility.

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