Phosphorus Release from a Manure-Impacted Spodosol: Effects of a Water Treatment Residual

M. L. Silveira,* M. K. Miyittah, and G. A. O'Connor

ABSTRACT

Long-term depositions of animal manures affect P dynamics in soils and can pose environmental risks associated with P losses. Laboratory studies were done on P solubility characteristics in a manure-impacted Immokalee soil (sandy, siliceous, hyperthermic Arenic Alaquod) and the effectiveness of water treatment residual (WTR) in controlling P leaching. Soil samples with contrasting initial total P concentrations were prepared by mixing samples of a manure-impacted surface A horizon and a minimally P-impacted E horizon. Effects of mixing various ratios of A and E horizons, WTR rates (0, 25, 50, and 100 g kg^{-1}), and depths of WTR incorporation (mixed throughout the soil column or partially incorporated) on P leaching were determined. Between 62 and 77% of total P was released from the soil mixes by successive water extractions, suggesting a considerable buffering capacity of this manure-impacted soil to resupply P into solution. Between 224 and 408 mg kg^{-1} P were leached during the 36-wk leaching period in the absence of WTR. Mixing WTRs with soil reduced soluble P concentration in leachates by as much as 99.8% compared with samples without WTR. Thoroughly mixing WTR with the entire soil column (15 cm) was much more efficient than mixing WTR with only the top 7.5 cm of soil. Calcium- and Mg-P forms appear to control P release in soils without WTR, whereas sorption–desorption reactions probably determine P leaching in WTR-treated samples. Soil P distribution in various chemical forms was affected by WTR additions. Data suggest that WTR-immobilized P is stable in the long term.

Environmental concerns have caused Florida to implement regulatory programs and best management practices in the Lake Okeechobee watershed to reduce P transport and subsequent loads to the lake. The intrinsic characteristics of the Lake Okeechobee watershed (hydraulic conditions associated with sandy soils) create favorable conditions for P losses (Allen, 1988). Approximately 64% of the soils in Okeechobee County are Spodosols and 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 minimizes surface-runoff P contamination; however, significant amounts of P can be leached. The poorly P-sorbing soils are often associated with shallow ground water intercepted by canals that can easily transport to water bodies P leached from agricultural fields or pasture systems amended with fertilizer or manure application.

Beef cattle and dairy farms have been identified as significant sources of P loading in the lake Okeechobee watershed (Allen, 1988). In general, cattle diets exceed the animal nutrition requirements for P by 25 to 40% (Knowlton and Kohn, 1999), and a significant fraction of the P is excreted in the feces. Continuous manure depositions result in P accumulation in surface soil, which eventually overcome the low soil P-sorption capacity. In addition, the majority of the large dairies farms in the Lake Okeechobee watershed are concentrated in a relatively small area, which increases the environmental concerns associated with P losses.

Soil properties and P dynamics can be significantly affected by continuous manure depositions (Cooperband and Good, 2002; He et al., 2004; Zheng et al., 2004). Chemical reactions controlling P dynamics are complex, and depend on a variety of factors (i.e., P source, concentration, availability). Therefore, detailed characterization of the stability and nature of the chemical phases with which P is associated and the kinetics of P release are critical to understanding and predicting long-term P retention and transport in manure-impacted soils.

Manure chemical characteristics are determined by numerous factors, such as diet composition, animal species, and how the sampling is performed (Ward et al., 1978). In general, manure contains both inorganic and organic P and the characteristics of this material play a major role in controlling P dynamics. For instance, Ward et al. (1978) found an average P concentration in 63 manure samples of ~5.4 g P kg^{-1}. The organic fraction of P in manures is composed principally of myo-inositol phosphomonoesters and, in smaller proportions, phospholipids and orthophosphate diesters (Dao, 2004). However, the majority of the P present in manure is inorganic, and the relative proportion of inorganic P (P_i) is substantially increased in soils receiving manure (He et al., 2004; Kashem et al., 2004). Zheng et al. (2004) observed an increase in total labile P (resin-P and $NaHCO_3$–P_i) after 10 annual liquid dairy manure applications. They suggested that, although total soil P increased during the 10 yr irrespective of P source (manure or fertilizer), total labile P pools were greater in soil receiving manure because of the contribution of soil C to biological transformation from organic P (P_o) to P_i. According to Laboski and Lamb (2003), the greater P availability in soils receiving manure (compared with fertilizer-amended soils) is due to the presence of organic acids in the manure, which inhibit P sorption on the soils. Cooperband and Good (2002) found that water-soluble P_i was controlled by sorption–desorption processes in dairy-manure-amended soils in a laboratory incubation

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Abbreviations: DDI, distilled deionized water; DOC, dissolved organic carbon; EC, electrical conductivity; P_i, inorganic phosphorus; P_o, organic phosphorus; SRP, soluble reactive phosphorus; WTR, water treatment residual.

study. Conversely, Hansen and Strawn (2003) suggested that P release from calcareous soils amended with manure was initially controlled by octacalcium phosphate and β-tricalcium phosphate minerals. After the more soluble P phases were dissolved, P release from manure-amended soils could be controlled by more chemically stable forms of P such as hydroxyapatite and fluorapatite.

One approach to reduce P losses from manure-impacted soils is to add chemical amendments that reduce P solubility and increase specific P sorption. Aluminum and Fe salts [e.g., $Al(SO_4)_3$, $FeCl_3$] significantly reduced P solubility and considerably decreased P in runoff from manure-amended soils (Coale et al., 1994; Moore and Miller, 1994; Moore et al., 1999). Iron and Al oxides play an important role in P sorption in Spodosols (Reddy et al., 1998), and P retention in these soils is increased when Fe and Al salts are applied (Anderson et al., 1995). However, the costs and the possibility of Al toxicity associated with Al salts complicate their field use. On the other hand, water treatment residual (WTR), a byproduct of drinking water purification, can be a reasonable alternative to control off-site P transport.

Water treatment residuals contain appreciable amounts of reactive hydrous oxides with significant P-sorbing capacity (Elliott et al., 1990; O'Connor et al., 2002; Novak and Watts, 2004). Aluminum water treatment residuals (Al-WTR) have successfully mitigated P solubility and mobility in soils (Peters and Basta, 1996; Cox et al., 1997; Gallimore et al., 1999; Elliott et al., 2002) with minimal negative impacts on plant nutrition (Brown and Sartain, 2000). Laboratory studies have shown that Al-WTRs adsorb large amounts of P and increase the P-sorbing capacity of selected Florida soils, thereby decreasing P leaching (Elliott et al., 2002; O'Connor et al., 2002). Codling et al. (2000) observed that Al-WTRs could reduce water-soluble P by up to 88%, and the more effective amendment rates varied between 10 and 25 g kg^{-1}. O'Connor et al. (2002) showed that the sorption capacity of some Al-WTRs was ≥5000 mg P kg^{-1}, and that the P sorption by WTR was essentially irreversible.

Previous studies (Makris et al., 2004) suggested that P retention by Al-WTR is by surface P chemisorption in micropores, and that most P sorbs to WTR following intraparticle diffusion in three-dimensional fashion toward the interior of the WTR particles. Thus, soluble P proximity to a WTR particle may be an important factor in determining the kinetics and extent of P sorption in WTR-amended soils. For instance, when Al-WTRs were surface applied to a Florida sandy soil impacted by long-term manure additions, soluble P concentrations remained high and unaffected in soil below the zone of amendment incorporation (Miyittah-Kporgbe, 2004). Studies have also shown that dissolved organic carbon (DOC) can reduce WTR's efficiency to retain P by competing for reactive adsorption sites (Lane, 2002). This effect can be especially important in soils receiving continuous manure deposition, with high DOC concentrations.

Improved understanding of the P dynamics in soils impacted by manure and alternatives to control P losses are essential to predict the fate of P in the environment. Although extensive research has been done in manure-amended soils (Graetz and Nair, 1995; Harris et al., 1996; Nair and Graetz, 2002), some questions remain unanswered. Phosphorus sorption and desorption reactions are particularly distinctive in Florida Spodosols impacted by manure deposition, mainly due to the lack of reactive organic and mineral components responsible for soil P retention (Harris et al., 1996). Additionally, the manure component can play an important role in these soils, influencing P retention and distribution into the various chemical forms. The objectives of this study were to examine (i) P chemical distribution in unimpacted and manure-impacted samples of a Florida Spodosol, (ii) P solubility and release rates from soil samples with different initial P concentrations, and (iii) effectiveness and long-term stability of WTR amendment in controlling P leaching.

MATERIALS AND METHODS

Manure-Impacted and Native Soil Sample Collection

A manure-impacted sample of an Immokalee fine sand was obtained from a field site on a beef cattle ranch located in the Lake Okeechobee County watershed. This soil was chosen because it was expected to exhibit high total P concentration due to long-term manure deposition and low P-sorbing capacity, and the soil's geographical abundance in South Florida. Native Immokalee soil samples not contaminated by manure depositions were collected from the University of Florida Research and Education Center in Immokalee, FL. Multiple random samples of the impacted and native soils were collected from the A horizons (0–15 cm), and were thoroughly mixed to yield a composite sample for each site. Samples of a minimally P impacted E horizon were also collected from the E2 horizon of Myakka sand (sandy, siliceous, hyperthermic Aeric Alaquod). The E horizon samples exhibited insignificant P concentration and negligible P retention capacity (Nair et al., 1998; O'Connor et al., 2004).

Soil samples with contrasting initial total P concentrations were prepared by mixing various amounts of the E horizon soil with the manure-impacted surface soil. Because the E horizon material contained very low P and negligible amounts of Fe and Al, mixing essentially diluted the P concentration in the impacted surface horizon, and decreased soil P sorbing capacity due to the reduction in the amount of reactive compounds (oxalate-extractable Fe and Al). Mixing high-P surface soils with low-P subsoil samples also mimics the effects of deep tillage on P distribution within the soil profile. Besides the decrease in soil extractable and total P, DOC concentration is also expected to be significantly reduced by the mixing process, therefore WTR efficiency to retain P can be affected.

Air-dried soil samples of surface impacted A horizon (0–15 cm) and E horizon (~40 cm) were mixed in ratios of 100:0, 50:50, and 33:67 (percentage wt. basis). The various soil mixes of 100% A horizon (S_1), 50:50 A/E horizon (S_2), and 33:67 A/E horizon (S_3) were thoroughly homogenized, moistened to 80% of field capacity and allowed to equilibrate for 1 wk at room temperature in plastic bags. Following equilibration, a subsample was collected and air dried for P analysis, and corresponded to time zero samples.

Chemical Characteristics of the Manure-Impacted and Native Soil Samples

Air-dried soil samples were ground and passed through a 2-mm sieve before analysis. Total C concentrations were

determined by combustion at 1010°C using a Carlo Erba (Milan, Italy) NA-1500 CNS analyzer. Samples were analyzed for total P by the ash method (Anderson, 1976). Mehlich-1 extractable P was obtained using a 1:4 soil/solution ratio (Mylavarapu and Kennelley, 2004). Oxalate-extractable Al, Fe, and P were determined by extraction with 0.2 *M* oxalic acid + 0.2 *M* ammonium oxalate solution at pH 3 (McKeague et al., 1971). The suspension was equilibrated for 4 h (in the dark) with continuous shaking, centrifuged, filtered through a 0.45-μm filter, and analyzed by inductively coupled plasma spectrometry. Sequentially extracted P was assessed according to Chang et al. (1983), using a 1:20 soil/solution ratio. However, the "soluble and exchangeable P" pool (first step of the sequential extraction procedure) was modified, substituting 1 *M* KCl for NH_4Cl. The sequential extraction procedure extracted P from the following fractions: (i) soluble and exchangeable P (1 *M* KCl), (ii) Fe- and Al-bound P, (iii) P_o (0.1 *M* NaOH), (iv) Ca- and Mg-bound P (0.5 *M* HCl), and (v) residual P (6 *M* HCl digestion). Organic P in the NaOH extract was estimated by difference between total P (potassium persulfate/H_2SO_4 digestion) and P_i. At the end of the sequential extractions, P mass balance was calculated. The rates of P release from unimpacted (native) and manure-impacted soils were measured by shaking 2 g of soil with 20 mL of distilled deionized water (DDI) water in a reciprocating shaker at a rate of 100 strikes min^{-1} at room temperature (24 ± 2°C). The mild vigor of shaking was intended to avoid soil aggregate disruption and particle abrasion (Koopmans et al., 2004). The shaking time varied from 30 min to 96 h. After shaking, samples were centrifuged at 3200 × *g* for 10 min and filtered through a 0.45-μm pore-size filter membrane. Extracts were analyzed for soluble reactive P (SRP) using the colorimetric molybdate blue method (Murphy and Riley, 1962). Quality assurance and quality control protocols included 5% repeats, spikes, certified samples and blanks for each procedure.

Potentially Leachable Phosphorus Pool in Manure-Impacted Soil Samples

A batch method was used to measure the amount of P potentially available for leaching in manure-impacted soils. Two grams of air-dried soil mix samples (S_1, S_2, and S_3) were placed in centrifuge tubes and DDI water was added to attain a 1:10 soil/solution ratio. The extractions were performed in triplicate. The suspensions were shaken on an orbital shaker at a rate of 200 strikes min^{-1} at room temperature (24 ± 2°C) for 1 h. After shaking, the samples were centrifuged at 3200 × *g* for 10 min. The supernatant was filtered (0.45-μm), and P concentrations were measured according to Murphy and Riley (1962). The residual soil was then resuspended in sufficient DDI water to reestablish the 1:10 soil/solution ratio. The extraction process was repeated until extractable P was below the detection limit (<0.05 mg L^{-1}) or for a total of 60 extractions. The remaining residue was weighed, digested for total P, and P mass balance was calculated.

The cumulative amounts of P desorbed during the repeated water extractions were fitted to an empirical equation:

$$x = kBn/(1 + kn) \quad [1]$$

where x = cumulative P released (mg kg^{-1}), k = empirical constant, B = release maximum (mg kg^{-1}), and n = number of extractions.

Small Column Leaching Study

Treatments and Experimental Design

Each of the three soil mixes (S_1, S_2, and S_3) also received four Al-WTR amendment rates (0, 25, 50, and 100 g kg^{-1} equivalent to field application rates of ~0, 56, 112, and 224 Mg ha^{-1} incorporated to a soil depth of 15 cm). The WTR rates were chosen based on previous studies (Elliott et al., 2002; O'Connor et al., 2002; 2005). The Al-WTR was obtained in 2003 from the Bradenton water treatment facility in Bradenton, FL. The material was thoroughly characterized in previous studies (O'Connor and Elliott, 2000); a description of the chemical characteristics of the WTR is presented in Table 1. Total elemental analysis was determined by inductively coupled plasma atomic emission spectroscopy following USEPA Method 3050A digestion (USEPA, 1996). Total C and N concentrations were determined by combustion at 1010°C using a Carlo Erba (Milan, Italy) NA-1500 CNS analyzer. Oxalate-extractable P, Fe, and Al were determined by the McKeague et al. (1971) method. Sequential P extraction was assessed according to Chang et al. (1983). Mehlich-1 extractable P was obtained using a 1:4 soil/solution ratio (Mylavarapu and Kennelley, 2004). The Al-WTR is slightly acidic and contains appreciable amounts of Al, mainly in amorphous forms (oxalate-extractable Al), which can effectively fix soluble P in soils. The low (≪1) P saturation index [moles oxalate P/moles oxalate (Fe + Al)] indicates the potential of this amendment to retain and, hence, control P movement. Although the WTR contains large amounts of organic C, the majority of these organic compounds is apparently not accessible for microbial degradation due to physical and chemical protection mechanisms, and little mineralization is expected (Makris et al., 2004).

To evaluate the effect of the method of incorporation on WTR's efficiency in retaining P, the amendment was either mixed with only half of the soil (representing the top 7.5 cm of 15-cm soil columns), or was thoroughly mixed with the entire soil column volume.

The various soil mixes, each amended with the various WTR rates, were moistened, thoroughly mixed, and equilibrated in plastic bags for 7 d at room temperature (24 ± 2°C). The samples were equilibrated at 80% of field capacity, and bags were opened daily to avoid development of anaerobic conditions. All treatments were replicated three times in a completely randomized design. After the incubation, subsamples (20 g) were collected for sequential fractionation and total P analysis and represented the initial sample conditions. The remaining samples were used for the small column study.

Table 1. Selected chemical properties of the Al water treatment residual (Al-WTR).

		Total elemental								Oxalate extractable‡				Sequentially extracted P			
Description	pH†	C	N	Fe	Al	Ca	Mg	P	Solids	Fe	Al	P	PSI§	KCl	NaOH	HCl	Mehlich-1 P
		g kg^{-1}												mg kg^{-1}			
Al-WTR	5.3	191	7.3	3.7	89.1	15.3	0.1	2.8	660	1.7	71.9	2.7	0.03	0.4	231.5	473.7	4.3

† At a soil/water ratio of 1:2.
‡ At a soil/solution ratio of 1:60.
§ Phosphorus saturation index (PSI) = [oxalate P/(oxalate Fe + oxalate Al)]; elemental concentrations in moles.

Samples (WTR-treated and control soils) were uniformly packed into PVC columns (5 cm i.d. × 17 cm long) to a depth of 13 cm at a bulk density of ~1.33 g cm^{-3}. Samples were gently tapped into the column to ensure uniform distribution and hydraulic conductivity. Columns were equipped with a 2-cm drainage hole at the base, covered with screening to prevent soil loss.

The study was performed under laboratory conditions and included 75 columns (3 soil mixes × 4 WTR rates × 2 depths of incorporation × 3 replicates + 3 columns of 100% E horizon material). Columns were supported on racks and loosely covered with clear plastic wrap to reduce moisture loss between leachings.

Leaching Protocol

One hundred milliliters of DDI (adjusted to pH 5 to mimic the pH of rainfall in South Florida) were added to each column weekly. A total of 3.5 L (~44.6 cm) was leached through each soil column during the 36-wk study period. Each leachate volume (~100 mL) corresponded to ~1 pore volume. Control samples of the E horizon material also received 1 pore volume (in this case ~55 mL) of distilled water per leaching event. Leachate was collected and the volume measured. The volume of water added was adjusted weekly to yield a uniform cumulative outflow among treatments. Leachate was filtered (0.45-μm membrane) immediately after discharge and stored at 4°C until analysis. Soluble reactive P (SRP) analysis (Murphy and Riley, 1962), pH, and electrical conductivity (EC) measurements were performed on the leachates within 48 h of collection. Total P was determined on the unfiltered leachates by acid digestion with potassium persulfate/H_2SO_4 (USEPA Method 365.1, USEPA, 1993).

At the end of the leaching experiment, small soil cores (2.5-cm diameter) from each soil column were taken from the top 7.5 cm of the column and the soil subjected to sequential fractionation and total P analysis. The soil samples collected from the columns after the leaching protocol represented the final sample conditions.

Chemical Analyses and Speciation of Leachates

Selected leachates were analyzed for Ca, Mg, and Al by atomic absorption spectrophotometry. Nitrate, sulfate, and chloride concentrations were analyzed according to Mylavarapu and Kennelly (2004). Dissolved organic C was measured by TOC-5050A (Shimadzu) (Method 5310A, APHA, 1992). The data were used to calculate chemical speciation (including possible controlling solid-phase formation) using the Visual MINTEQ version 2.31 program under an open system (Gustafsson, 2005).

Statistical Analysis

The effects of WTR rate, method of WTR incorporation, and time on P leached were evaluated using repeated-measures ANOVA (SAS Proc Mixed, SAS Institute, 1999). The data were log-transformed to meet the assumption of equal variance. Mean separation of treatment differences was evaluated by Tukey's HSD test. Repeated-measures analysis was performed to test differences in P concentrations as a function of leaching events.

RESULTS AND DISCUSSION

Chemical Characteristics of the Manure-Impacted and Native Soil Samples

Long-term manure deposition changed chemical properties of the Immokalee soil (Table 2). There were significant increases in soil pH, total organic C, and total P compared with values in the unimpacted native soil. The alkaline pH of the manure-impacted surface soils probably resulted from the high base saturation of the animal residue (Hansen and Strawn, 2003). Mehlich-1 and oxalate-extractable P concentrations increased in manure-impacted soils. The overall increase in soil P fractions associated with the very low P-sorbing capacity of the Immokalee sand suggests the potential for environmental impacts associated with incidental P losses.

Phosphorus distribution and storage in the soil was also affected by the manure additions (Table 2). The majority of the P (~51% of total P) in the manure-impacted A horizon was associated with Ca and Mg forms, whereas in the unimpacted A horizon, Ca- and Mg-associated P represented ~5% of total P. In the unimpacted soil, residual P (mainly recalcitrant organic P) accounted for 68% of the total P. Similar shifts in P distribution due to repeated manure depositions were also observed by Nair et al. (1995). They suggested that the greater P concentration in the HCl extracts could be attributed to the abundant Ca and Mg present in the animal manure. In the unimpacted soil, inorganic P (estimated by the sum of KCl-, NaOH-, and HCl-extracted P) accounted for ~32% of the total P, whereas in the manure-impacted soil, 82% of the total P was inorganic P.

Negligible P concentrations (both soluble and total) were found in the E horizon and the inorganic fraction (sum of KCl-, NaOH-, and HCl-extracted P) represented ~65% of total P. The E horizon has a low P-sorbing capacity (Harris et al., 1996) and allows ready movement of P (Li et al., 1999).

Phosphorus release from the unimpacted soil was initially rapid, but slowed appreciably after ~48 h (Fig. 1A)

Table 2. Selected soil chemical properties.

Soil	pH†	TC‡	Total P	Mehlich-1 P§	Oxalate extractable¶			Sequentially extracted P			
					Fe	Al	P	KCl	NaOH	HCl	Residual
		g kg^{-1}	mg kg^{-1}								
Immokalee (A horizon), native	5.6	0.7	19	15	85	40	12	2	3	1	13
Immokalee (A horizon), manure-impacted	7.7	50	1380	882	468	110	1160	212	216	714	250
Myakka (E horizon)	5.1	0.2	6	0.9	10	12	4	2	1	1	2

† At soil/water ratio of 1:2.
‡ TC = total carbon, determined by dry combustion.
§ At solid/solution ratio of 1:4.
¶ At soil/solution ratio of 1:60.

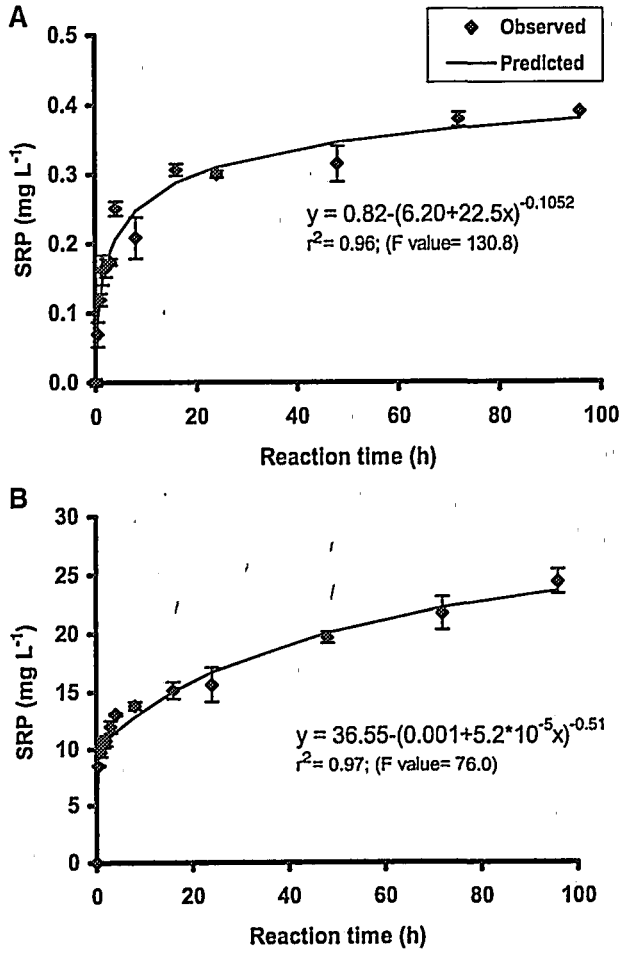

Fig. 1. Phosphorus release kinetics from (A) native and (B) manure-impacted surface soils (note scale differences).

and appeared to plateau thereafter. Phosphorus release from the manure-impacted soil (Fig. 1b) was also initially rapid and slowed after the first few hours, but increased continuously with time, and did not appear to approach a plateau during the 96-h incubation. Hansen and Strawn (2003) also found fast P release from soils amended with manure, followed by subsequent slow release that continued for up to 504 h. After 96 h, SRP concentrations were 0.39 mg L^{-1} for the unimpacted Immokalee soil and 24.4 mg L^{-1} for the manure-impacted Immokalee soil. Although P desorption from the unimpacted and impacted soils occurred at different rates and magnitudes, ~2% of total P was released after 96 h in both samples.

The extracts from the manure-impacted soils were dark brown, suggesting the presence of humic acids, whereas the unimpacted soil extracts were clear. Organic P accounted for ~13–35% of total P in the extracts for the unimpacted soil and 2% of total P for the manure-amended soil. The larger proportion of P_i found in the extracts of the impacted samples reflects the effect of the manure on soil/solution P distribution. Despite the large amount of organic C present in the manure-amended soil, P_o is not the most important phase controlling P release in this system.

Potentially Leachable Phosphorus Pool in Manure-Impacted Soil Samples

The relationship between the amount of P released after repeated water extraction and the total pool of P sorbed in the soil can be used to estimate the total amount of available P and the buffer capacity of the soil in replacing P to the solution. Phosphorus extracted from the A horizon and the mixtures of A and E horizon (50/50 and 33/67 A/E) showed a biphasic pattern (Fig. 2). Higher SRP concentrations were observed in the first three extractions (rapid-release phase), followed by much lower P concentrations in subsequent extractions (slow-release phase). Small variations in SRP trends with time occurred during the repeated water extraction study, such as the increases in SRP observed in extractions 17 and 25 (Fig. 2). The increases were associated with larger intervals (>1 wk) between consecutive extractions, which probably favored greater P desorption.

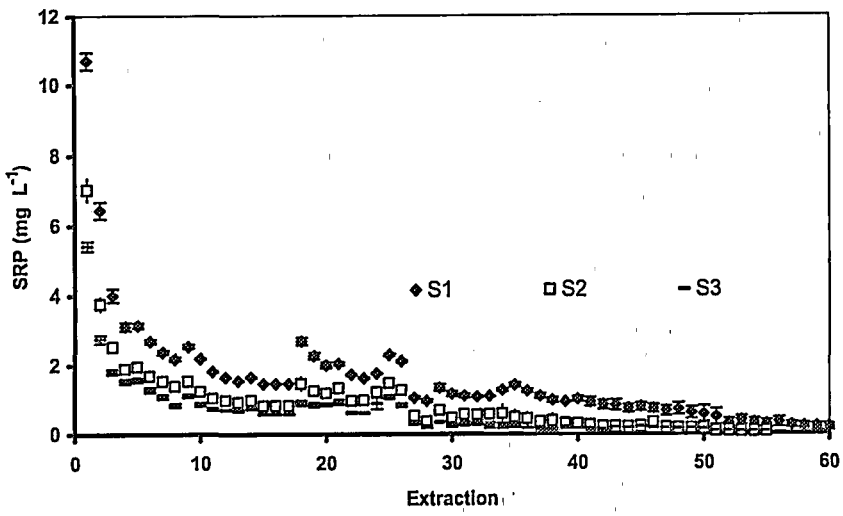

Fig. 2. Water-extractable P released from different soil mixes with repeated extractions. S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.

The initially high P concentrations in the extracts indicate the presence of highly soluble P in the soils. Lower P concentrations in subsequent extracts suggest less soluble solid phases or slower reactions controlling P solubility. Hansen and Strawn (2003) suggested that, following an initial release of readily available and highly soluble P from manure-amended soils, subsequent P desorption is associated with a pool that continuously releases P at low concentrations until depletion. Koopmans et al. (2004) suggested that P is initially desorbed from readily available surface sites, and then continuously replenished into solution by the diffusion of P from the outer layers of the soil aggregates.

Significant amounts of P were released from the manure-impacted Immokalee soil throughout the successive water extractions (Fig. 3). The undiluted S_1 (total P = 1400 mg kg^{-1}) continued to release measurable P through 60 extractions. The soil mixes S_2 (total P = 650 mg kg^{-1}) and S_3 (total P = 400 mg kg^{-1}) released undetectable P (<0.05 mg L^{-1}) after 55 extractions. The data, and release kinetics discussed above, suggest that a small fraction of the P was rapidly released into solution during the initial water extractions (15–25% of total P in the first three extractions), and that more stable (less soluble) solid phases controlled long-term, steady-state P release. The continuous P release revealed the considerable buffering capacity of these soils to resupply P lost (extracted), and the possible long-term effects on water quality associated with the dissolution of these P solids. In contrast, the SRP concentration from the unimpacted soil was below the detection limit after only five water extractions (data not shown),

Table 3. Phosphorus released with repeated water extractions.

Soil mixes†	Extractions	Initial total P	P extracted	P removed
	no.	mg kg^{-1}		% of total
S_1	60	1382	861 a‡	62
S_2	55	650	455 b	70
S_3	55	409	315 c	77

† S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.
‡ Means with the same letter are not significantly different (Tukey's HSD test, $P < 0.001$).

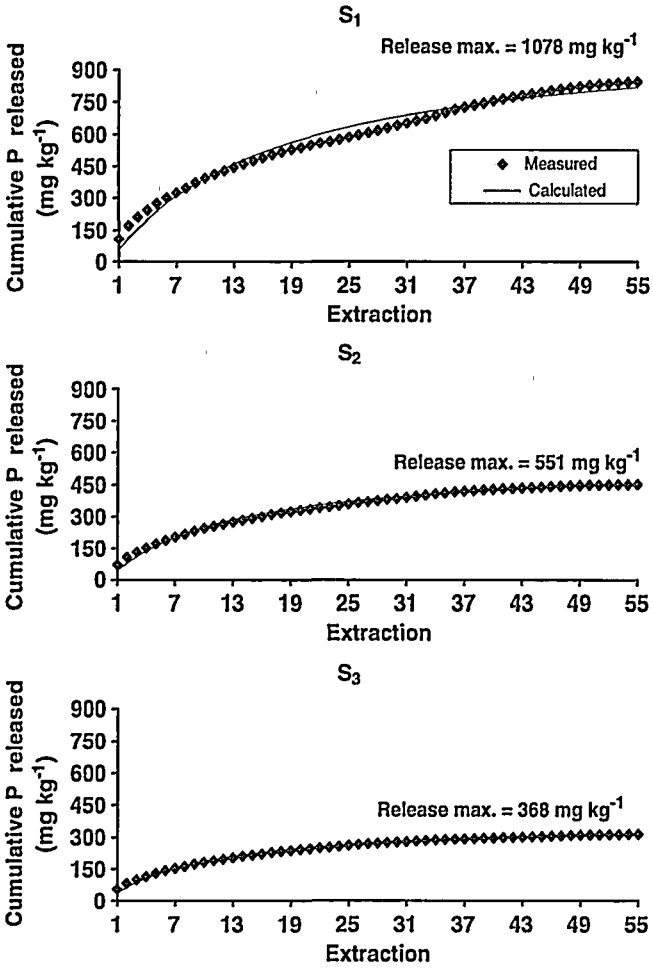

Fig. 3. Measured and calculated P release from soil mixes. S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.

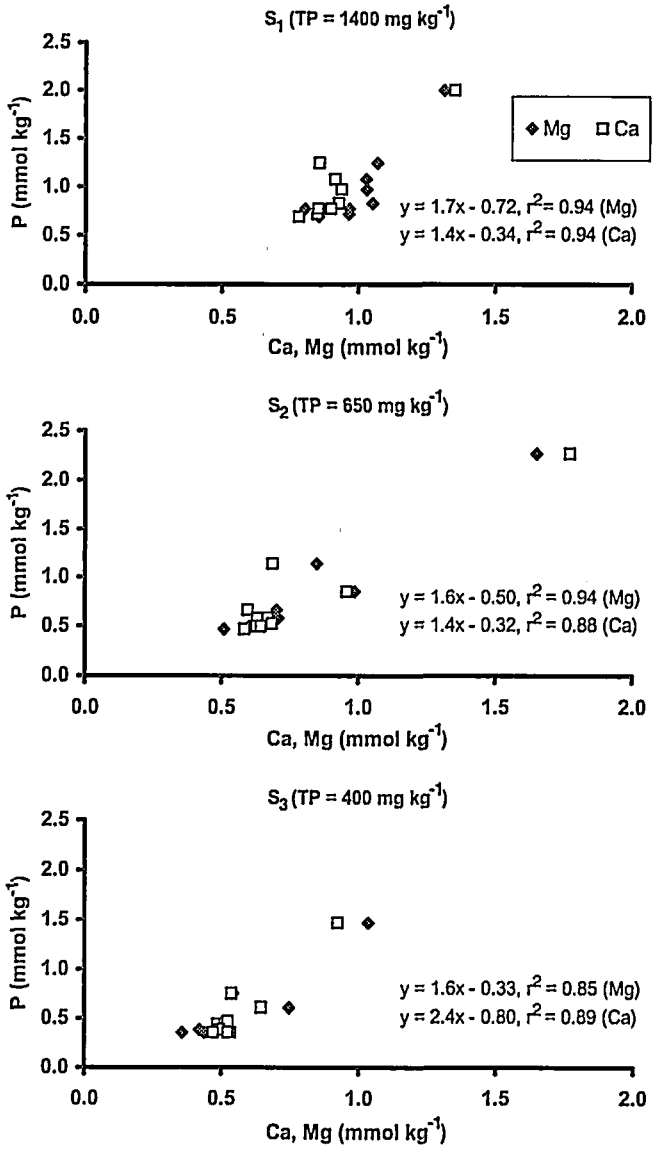

Fig. 4. Phosphorus concentration as a function of Ca and Mg concentrations measured in 1/10 (w/v) water extracts (10 repeated water extractions).

suggesting the poor buffering capacity of this soil to supply P into solution. Presumably, manure-born components regulate the fate of P in the heavily impacted soil. Graetz and Nair (1995) observed that dairy-manure-impacted soils released ~2 to 18% of total P in 10 repeated water extractions. They also suggested that the A horizon of these soils could continuously release P with successive water extractions, as observed in our study.

Surface-impacted samples (S_1) released more P than the soil mixes (S_2 and S_3), and the cumulative P masses released after the repeated water extractions were significantly ($P \leq 0.001$) different (Table 3). The greatest percentage of the total P was removed from S_3 followed by S_2 and S_1. At the end of the experiment, approximately 77, 70, and 62% of total P was removed after the consecutive water extractions for S_3, S_2, and S_1 samples, respectively. These results suggest that total P solubility in water dictates the amount of P extracted, but other factors may be involved. Because the extraction soil/solution ratio (1:10) was similar for all treatments, the water/soluble P ratio for the samples with less total P (S_2

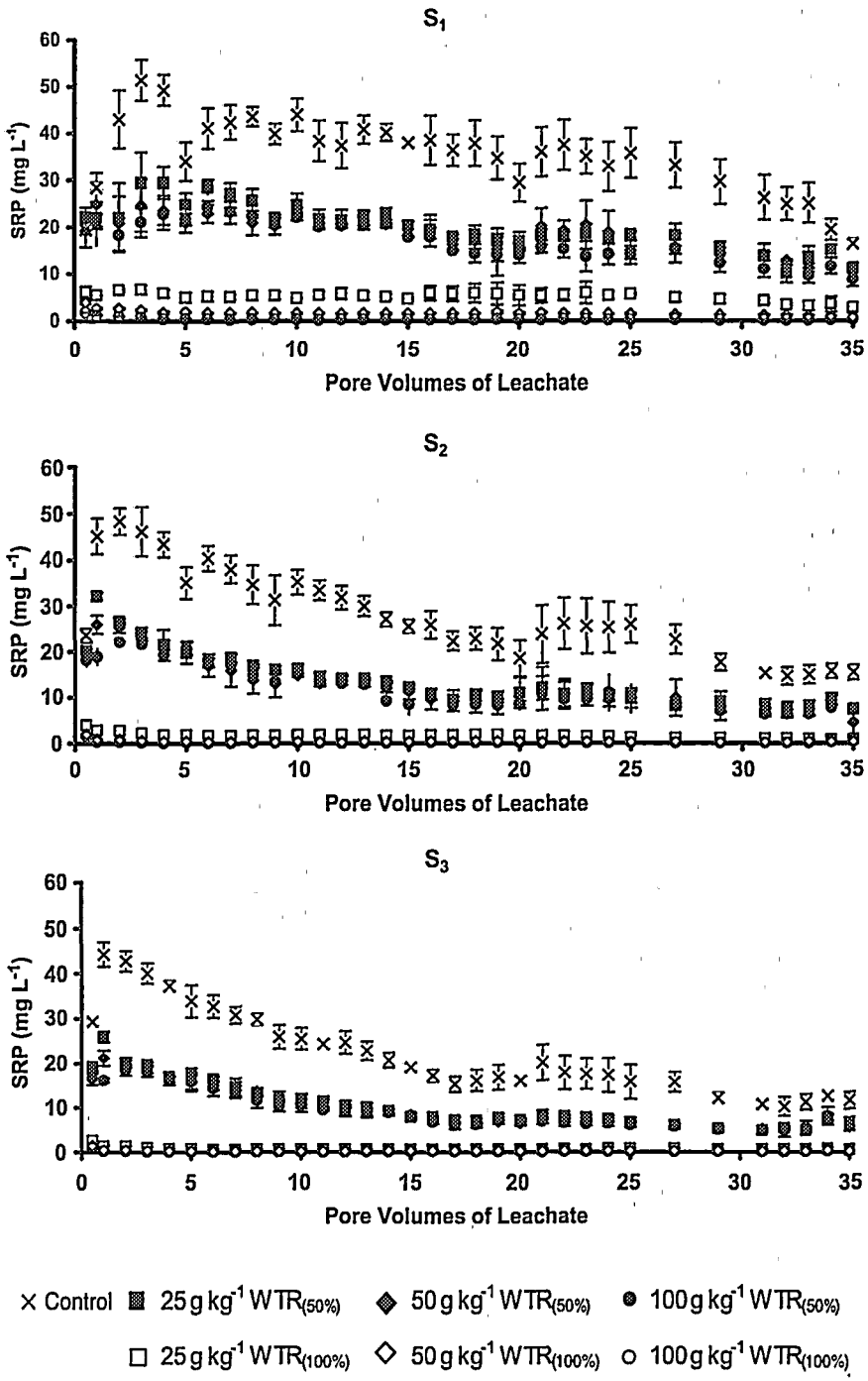

Fig. 5. Phosphorus concentration in leachates of control and samples treated with water treatment residue (WTR) (fully incorporated with the soil mass [100%] and mixed with half of the soil mass [50%]). S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.

and S_3) was much greater than that for samples with high total P concentration (S_1). The greater water/soluble P ratio probably favored P release.

Cumulative P mass released with repeated water extractions (Fig. 3) was well described by the empirical Eq. [1] (S_1: $r^2 = 0.98$, $P < 0.001$, S_2: $r^2 = 0.99$, $P < 0.001$, S_3: $r^2 = 0.99$, $P < 0.001$). Maximum P release was related to total P concentration in the soils. The P release capacities (varying from 368 to 1078 mg kg^{-1}) indicate that as much as 90% of total P in these soils can be potentially released over time.

Calcium and Mg concentrations in the water extracts were highly correlated ($P < 0.001$) with P release (Fig. 4), suggesting that Ca-P or Mg-P minerals, or both, controlled P release from these soils. Because a variety of factors could affect the amounts P of extracted (e.g., vigor and time of shaking or soil/solution ratio), the complete characterization of the solution and the chemical equilibrium modeling was done on the leachates.

Small Column Leaching Study

Chemical Analyses of Leachates

Column experiments were conducted on manure-impacted top soils mixed with various amounts of WTR. Approximately 3.5 L (~35 pore volumes) of DDI water leached through each soil column during the 36-wk leaching period. The control 100% E horizon samples also leached ~35 pore volumes of water in each column; however, the total volume of water leached was ~2 L. The pH values of leachates were higher than that of the applied DDI water (pH 5), ranging from 7.1 to 8.3 (data not shown). The high pH could be due to the alkaline components (i.e., Ca and Mg) present in the manure (Ward et al., 1978; Nair et al., 1995). Leachate pH was not affected by WTR application. Leachate EC values (not shown) remained relatively high even after 35 pore volumes (300–600 μS cm^{-1}), but decreased with successive leaching events, possibly reflecting depletion of salts associated with the manure component.

Most (86–100%) of the total P leached from the soil columns was SRP. Thus, subsequent discussion focuses on the dissolved inorganic P forms. High P concentrations were leached during the 36-wk leaching period in the absence of WTR (Fig. 5). For these control samples, SRP concentrations decreased progressively with time and, at the end of the experiment, were 16.3 mg L^{-1} for S_1, 15.4 mg L^{-1} for S_2, and 11.4 mg L^{-1} for S_3. Leachate SRP concentrations fluctuated for one to six pore volumes in control S_1 samples, were not statistically different up to 27 pore volumes, and decreased significantly ($P < 0.05$) from pore volumes 27 to 35. For control S_2 and S_3 samples, SRP concentrations decreased throughout the 35 pore volumes of leachate. It appeared that after ~20 pore volumes, SRP concentrations from S_2 and S_3 decreased at a constant rate. Although total P in the S_2 soil mix was only one-half of that in S_1 (Table 3), SRP concentrations in the leachates representing the 35th pore volume (Fig. 5) were not significantly different ($P < 0.01$). Thus, total soil P analyses were clearly insufficient to explain P losses. The large amounts of P leached from the control samples are consistent with the results of the repeated water extractions and emphasize the capacity of this manure-impacted soil to release P into solution for long periods. In spite of the wide range of initial total P concentrations (400–1400 mg kg^{-1}), the potential "leachable" P pools of the various soil mixes were uniformly large and were not exhausted throughout the leaching trial.

Mixing WTRs into the soil columns significantly ($P < 0.05$) reduced SRP concentrations in leachates (Fig. 5). The effect of the amendment on controlling P leached was greater when WTR was fully incorporated into the entire soil volume than when only the top half of the soil volume was treated. For instance, from pore volumes 6 to 27, the mean SRP concentration for the control S_1 samples was ~38 mg L^{-1}, whereas in the presence of WTR, SRP decreased to a mean value of 19 mg L^{-1} when WTR was applied to the top half of the soil column, and 2 mg L^{-1} when thoroughly mixed with the whole soil mass. Clearly, the depth of incorporation significantly impacted soluble P immobilization. The results suggest that WTR controlled P release from the soil mass that was in direct contact with the amendment, and the remaining untreated soil mass continued to leach P. Treatments receiving WTR only in the top half of the column released about twice the soluble P as the treatments where WTR was incorporated throughout the soil column. When WTR was mixed through the soil column, SRP concentrations in the leachates were significantly reduced compared with control samples and (nearly) constant with time across the 35 pore volumes. This suggests the long-term stability of the P immobilized by the WTR and stability of the reactions responsible for P retention.

The cumulative P leached differed significantly among the soil mixes and WTR treatments (Table 4). In the control samples, between 31 and 48% of the total P was leached in 35 pore volumes of drainage. Across the three WTR rates, cumulative P leached decreased by 86% (S_1, 25 g kg^{-1} WTR) to 99.4% (S_3, 100 g kg^{-1} WTR)

Table 4. Cumulative P mass (% of total) leached after 36-wk leaching period.

Water treatment residual (WTR) treatments		Cumulative P leached†		
Rate	Method of incorporation‡	S_1§	S_2	S_3
g kg^{-1}	%	mg kg^{-1}		
0	–	408.5 a¶ (31.5)	286.2 a (47.6)	217.3 a (47.6)
25	50	230.3 b (13.3)	139.6 b (20.4)	101.1 b (18.2)
50	50	210.5 b (12.6)	129.0 b (15.3)	97.1 b (15.3)
100	50	194.4 b (10.0)	122.5 b (11.8)	90.5 b (10.9)
25	100	58.8 c (4.2)	17.1 c (2.7)	6.8 c (1.6)
50	100	17.7 d (1.0)	4.1 d (0.5)	2.3 d (0.4)
100	100	4.4 e (0.3)	1.8 e (0.2)	1.2 e (0.2)

† Means of three replicates.
‡ 50% incorporation = WTR incorporated with half of soil column (top 7.5 cm of soil), and 100% incorporation = WTR incorporated with the entire soil column (15 cm of soil).
§ S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.
¶ Means with the same letter in a column are not significantly different (Tukey's HSD test, $P < 0.01$).

of the control for the fully incorporated WTR treatments, and by 44% (S_1, 25 g kg^{-1} WTR) to 58% (S_3, 100 g kg^{-1} WTR) for the top 7.5 cm WTR incorporation. The WTR efficiency was improved by mixing E horizon (S_2 and S_3 samples), possibly due to the "dilution" of DOC. Mixing WTR with the whole soil column was much more effective in reducing P leaching at all rates than mixing with only the top half of the column (Table 4). This was apparently due to the incomplete contact of WTR with about half of the soluble P in the soil. Effectiveness of Al-WTR was, thus, limited by the method of application and failure to react with soluble P beneath the zone of incorporation.

There were no significant WTR rate differences when the amendment was mixed into the top half of the soil column. When WTR was fully incorporated into the soil column, however, cumulative P released significantly ($P < 0.01$) decreased with increasing rate (25 g kg^{-1} > 50 g kg^{-1} > 100 g kg^{-1}). Codling et al. (2000) incubated poultry-litter-amended soils with WTR for 7 wk and found that the amounts of water-soluble P immobilized by WTR were similar at amendment rates varying from 10 to 50 g kg^{-1}.

Chemical Speciation of Leachates

Phosphorus chemical speciation was calculated only for the leachates collected from sample S_1 (control and WTR application rates of 25 and 100 g kg^{-1}). Leachate samples from A horizon soil mixed with E horizon (S_2 and S_3) were assumed to behave similarly to S_1, and were not included in the modeling effort. Leachates were arbitrarily selected (those representing 12, 16, 20, 24, 28, and 34 pore volumes) for analysis and equilibrium modeling.

For all treatments, the major chemical P species in solution were HPO_4^{2-} (~50% of total soluble P), and Mg-P [$MgHPO_{4(aq)}$] and Ca-P ($CaPO_4^-$) complexes (~30 and 13% of total soluble P, respectively). Aluminum-P species were not predicted to occur in the leachates, because of the alkaline conditions (pH ≥ 7.5) and undetectable (<0.03 mg L^{-1}) Al concentrations. Even at the highest WTR rate (100 g kg^{-1}), the amount of soluble Al was <0.03 mg L^{-1}, indicating the stability of WTR during the 36-wk leaching period. Although concerns about Al plant toxicity have been raised when WTRs are used, our data show that when alkaline conditions are maintained, negligible amounts of Al are dissolved from the WTR material.

For all treatments, leachates were supersaturated (positive saturation indices) with respect to hydroxyapatite (Table 5), indicating that this mineral is not playing a major role in P release. On the other hand, leachate samples were undersaturated (negative saturation indices) with respect to $CaHPO_4$, $CaHPO_4{\cdot}2H_2O$, $Mg_3(PO_4)_2$, and $MgHPO_4{\cdot}3H_2O$, and the saturation indices became more negative with increasing WTR rate. In fact, our data (here and elsewhere [Makris et al., 2004]) suggest that sorption–desorption reactions determine P leaching in WTR-treated samples rather than mineral solubility. Calcium- and Mg-P minerals appear to control P release for the control samples, which is consistent with the conclusions of previous studies using similar manure-impacted soils (Wang et al., 1995; Hansen and Strawn, 2003; Josan et al., 2005).

Sequential Phosphorus Fractionation of Samples Before and After Leaching Protocol

Although the total P concentration of the Al-WTR was relatively low (Table 1), high application rates (e.g., 100 g kg^{-1}) substantially increase soil P concentrations (Table 6). Similar results were found by Elliott et al. (2002) studying biosolids amended with the same WTR. Because the WTR exhibited a remarkably lower phosphorus saturation index (PSI; Table 1) than the manure-impacted soil (PSI ~3), negligible P concentrations are expected to release from this material.

Table 5. Saturation indices† calculated by Visual Minteq for selected leachates.

Pore volume	$Ca_3(PO_4)_2$ (β)	$Ca_4H(PO_4)_3{\cdot}3H_2O$	$CaHPO_4$	$CaHPO_4{\cdot}2H_2O$	Hydroxyapatite	$Mg_3(PO_4)_2$	$MgHPO_4{\cdot}3H_2O$
			Control				
12	2.8	1.6	−0.1	−0.4	11.6	−2.1	−1.0
16	2.6	1.4	0.0	−0.3	10.9	−3.0	−1.1
20	2.3	0.9	−0.3	−0.5	10.7	−2.3	−1.0
24	2.9	1.6	−0.1	−0.4	11.6	−2.4	−1.1
28	2.6	1.4	−0.1	−0.4	11.2	−2.8	−1.2
34	2.5	1.2	−0.2	−0.5	11.1	−3.1	−1.3
			Water treatment residual application rate = 25 g kg^{-1}				
12	2.3	0.4	−0.8	−1.1	11.2	−3.0	−1.8
16	1.3	−0.7	−0.9	−1.2	9.3	−3.9	−1.8
20	1.7	−0.4	−0.9	−1.2	10.1	−3.6	−1.9
24	2.2	0.3	−0.8	−1.1	11.0	−3.3	−1.9
28	1.7	−0.3	−0.9	−1.2	10.1	−3.9	−2.0
34	0.9	−1.4	−1.2	−1.5	8.7	−4.6	−2.2
			Water treatment residual application rate = 100 g kg^{-1}				
12	−0.3	−3.5	−2.1	−2.4	7.3	−5.8	−3.1
16	−0.5	−3.6	−2.0	−2.2	6.8	−6.1	−3.0
20	−0.6	−3.8	−2.1	−2.4	6.7	−6.1	−3.1
24	−0.3	−3.5	−2.1	−2.4	7.3	−6.1	−3.3
28	−0.4	−3.7	−2.1	−2.4	7.0	−6.3	−3.3
34	−0.8	−4.2	−2.3	−2.5	6.4	−6.8	−3.5

† Saturation index = log ion activity product (IAP) − log solubility product (K_{ps}).

Table 6. Phosphorus distribution into the various soil fractions.

Soil mixes†	Water treatment residual (WTR) treatments		Sequentially extracted P§				
	Rate	Method of incorporation‡	1 *M* KCl	0.1 *M* NaOH	0.5 *M* HCl	Residual	Total P
	g kg^{-1}	%	mg kg^{-1}				
S_1	0	–	240	275	660	205	1380
S_1	25	50	164	366	711	271	1699
S_1	50	50	118	466	662	227	1589
S_1	100	50	75	725	660	225	1772
S_1	25	100	170	303	627	280	1373
S_1	50	100	150	428	725	251	1656
S_1	100	100	103	421	548	209	1579
S_2	0	–	165	125	166	91	640
S_2	25	50	84	329	267	100	710
S_2	50	50	84	459	221	96	855
S_2	100	50	84	677	212	97	1002
S_2	25	100	115	217	233	86	660
S_2	50	100	73	323	232	89	829
S_2	100	100	58	449	242	119	961
S_3	0	–	148	100	108	52	470
S_3	25	50	53	262	106	44	558
S_3	50	50	32	417	96	57	623
S_3	100	50	14	546	133	59	780
S_3	25	100	81	206	120	66	439
S_3	50	100	54	277	149	63	643
S_3	100	100	30	373	102	72	693

†S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.
‡50% incorporation = WTR incorporated into half of soil column (top 7.5 cm of soil), and 100% incorporation = WTR incorporated into the entire soil column (15 cm of soil).
§Means of three replicates.

Sequential P fractionation revealed distinctly different P distributions in the control and WTR-amended soils at the beginning of the leaching study (Table 6). The sum of the fractions was quite similar to the total P concentrations determined independently, and mass balance recoveries varied from 89 to 100%. For all treatments involving WTR, KCl-extractable P (labile P) was considerably reduced, whereas NaOH-extractable P was increased two- to fivefold compared with control samples. The shifts in the KCl-P fraction are particularly important because this fraction is thought to represent the labile pool of inorganic P (Reddy et al., 1995), and is typically well correlated with P losses (Zhang et al., 2002). The majority (>90% of total P) of the P associated with the NaOH pools consisted of inorganic P, and clearly indicates the effect of Al hydrous oxides of the WTR in complexing with soil P. Because this fraction is assumed to represent primarily Al- or Fe- bound P (Otani and Ae, 1997), the fraction was expected to distinctively reflect the characteristics of the amendment-dominated P chemistry.

The differences between control and amended soils were particularly dramatic for the treatments where WTR was incorporated into only half of the soil mass. In this case, the actual WTR rates for the top 7.5 cm soil samples were twice those where the WTR was fully incorporated and, consequently, the shifts in P forms were more distinct. The HCl-extractable P (Ca- and Mg-bound P) and residual fraction did not change considerably when WTR was applied.

For the control samples, HCl-extractable P was the dominant P form in S_1 (Fig. 6A). However, when the E horizon was mixed (S_2 and S_3), the P concentration in this fraction decreased (Table 6). This may be due to the "dilution" of Ca and Mg components (present in the manured samples) by added E horizon. At the same time, because the E horizon did not have significant amounts of reactive compounds (i.e., Ca, Mg, Fe, and Al), P concentrations in the more labile fractions (e.g., KCl- and NaOH-extractable) increased.

In the absence of WTR, there was a good agreement between the sum of KCl- and NaOH-extractable P (Table 7) and cumulative P leached during the 35-pore-volume leaching event (Table 4). Thus, in this case, sequential fractionation could be used as an approach to estimate the "leachable" P pool. Based on the results of the repeated water extractions, however, it is expected that subsequent leaching events (>35) will continuously release P, until the pools controlling P desorption are completely depleted and sequential fractionation may not be a good indicator of total leachable P. For instance, repeated water extractions removed ~861, 455, and 315 mg P kg^{-1} from S_1, S_2, and S_3, respectively, and even after 60 consecutive extractions, the soils continued releasing P. The amounts of P released by the repeated water extraction were much greater than that assessed by the KCl and NaOH extractions (Table 3), which suggests the complexity in quantifying P sorption and transport process in this soil. While several studies have reported good correlation between P losses and soil tests (Kleinman et al., 2002; Maguire and Sims, 2002; Djodjic et al., 2004), our results suggest that the ability of a single water extraction–sequential fractionation to estimate potential leachable P in manure-impacted soils is questionable.

The amounts of P extracted in the KCl and NaOH fractions (Table 7) were also poor predictors of total P mass leached for the WTR-treated samples. Phosphorus associated with amorphous Al surfaces (NaOH extracts) was the dominant fraction in the WTR-amended soils,

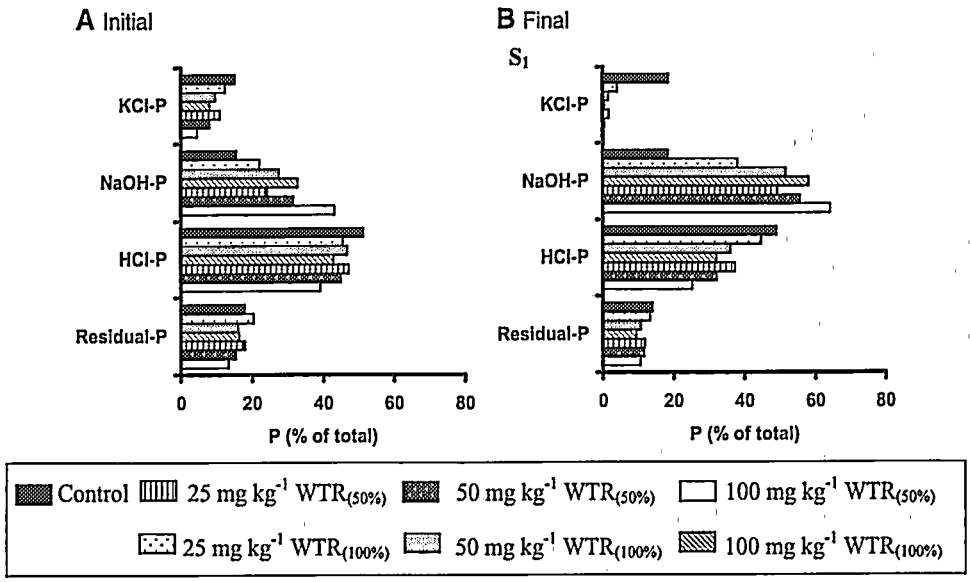

Fig. 6. Phosphorus relative distribution among the various soil fractions. Initial and final = samples before and after the leaching trial, respectively. S_1 = 100% impacted A horizon. $WTR_{(50\%)}$ = water treatment residue mixed with half (7.5 cm) of the soil column, and $WTR_{(100\%)}$ = WTR fully incorporated (15 cm) into the entire soil column.

accounting for 38 to 81% of total P across all treatments. Although the NaOH-P pool has been suggested to be potentially labile and subject to P loss (Zhang et al., 2002), P immobilized by WTR and extracted in the NaOH fraction is not subject to leaching. This association was markedly stable during the 36-wk leaching period. This pattern could be due to intra-aggregate diffusion of P into WTR particles, which reduces P availability with time (Makris et al., 2004). Therefore, this mechanism may be very important for controlling the transport of P from manure-impacted soils amended with WTR.

Leaching during 36 wk markedly affected P distributions across the various chemical forms in the S_1 soil (Fig. 6). Similar results were found for soil mixes S_2 and S_3 with time (not shown). Overall, total P decreased with time, especially for the control samples. For WTR-amended samples, KCl- and HCl-P fractions became smaller with leaching, while NaOH-P became larger. No substantial changes in the residual fractions were observed. In contrast, there was a considerable decrease in all P fractions with successive leaching for the control samples. Apparently, P was redistributed among the various fractions with leaching. Although P concentration in all extracted fractions decreased for the control samples, the relative P distribution after the leaching trial remained similar to that at the beginning of the experiment (Fig. 6). Surprisingly, even the residual P fraction (identified as recalcitrant P forms [Reddy et al., 1995]), decreased by the end of the leaching experiment for the control samples. Thus, there was no evidence that a discrete P fraction controls P leaching, as suggested by previous studies (Graetz and Nair, 1995; Nair et al., 1995). Our results suggest that the more labile P fractions (KCl and, perhaps, NaOH fractions) could be buffering P in solution, followed by redistribution of the resistant P forms into the more labile solid phases. In this case, leaching affects the overall P distribution in the soils. The moderately labile P forms (HCl and residual pools) seem to act as slow-release P sources, contributing to the long-term P release. After each leaching event, the various P forms reestablish a new "quasi-equilibrium," which remains relatively stable until the solution is depleted due to subsequent leaching events.

Table 7. Phosphorus concentrations in selected soil fractions after the 36-wk leaching period.

Water treatment residual (WTR) treatments		KCl-P + NaOH-P†		
Rate	Method of incorporation‡	S_1§	S_2	S_3
g kg^{-1}	%	mg kg^{-1}		
0	–	428	291	248
25	50	531	413	315
50	50	584	512	450
100	50	799	703	560
0	100	474	332	287
25	100	579	396	331
50	100	524	507	402

† Sum of KCl⁻ and NaOH-extractable P from the sequential fractionation procedure.
‡ 50% incorporation = WTR incorporated into half of soil column (top 7.5 cm of soil), and 100% incorporation = WTR incorporated into the entire soil column (15 cm of soil).
§ S_1 = 100% impacted A horizon; S_2 = 50% impacted A horizon, 50% E horizon; S_3 = 33% impacted A horizon, 66% E horizon.

CONCLUSIONS

Soil properties (pH, total organic C, and total P) were affected by long-term deposition of animal manure. In manure-impacted samples, P was mainly (~48% of total P) associated with Ca and Mg forms, whereas in the unimpacted A horizon, residual P (mainly recalcitrant organic P) accounted for 68% of the total P.

A significant fraction (between 62 and 77%) of soil P was released after repeated water (1:10 soil/solution ratio) extractions, and P release patterns were well

correlated with Ca and Mg release throughout extractions. The larger proportion of P_i found in the extracts of the impacted samples reflects the effect of the manure on soil/solution P distribution.

In spite of the inherent difficulty in comparing our data to field conditions, the results of the leaching study suggest the potential for long-term P losses from soils impacted by years of manure depositions. Significant amounts of P (mainly dissolved P_i) were leached from small columns of soil during 36 wk (total 35 pore volumes of drainage). Aluminum-WTR significantly reduced rates and cumulative amounts of P leached. When incorporated thoroughly with the entire soil mass in the column, WTR was much more efficient at controlling soluble P than when only the top half of the soil volume was treated. The method of incorporation clearly impacted P immobilization by WTR, and the efficiency of WTR to retain P was limited due to the incomplete contact of the amendment with the soluble P in the soil. Thus, WTR should be in direct contact with soluble P, and applied at the soil depth where most of the soluble P is present. When WTR was mixed through the soil column, SRP concentrations in the leachates were low (0.1–0.3 mg L^{-1} at 100 g kg^{-1} WTR rate) and nearly constant with time across the 35 pore volumes, suggesting the long-term stability of the P immobilized by the WTR. Furthermore, mixing the surface impacted A horizon (S_1) with unimpacted E horizon (S_2 and S_3) increased WTR effectiveness, possibly due to the decrease in DOC, which may affect WTR sorption capacity.

Chemical modeling of leachates collected from the columns suggests that P leaching from control samples (no WTR additions) was primarily controlled by Ca and Mg solid phases, whereas sorption–desorption reactions, rather than mineral solubility, determined P leaching in WTR-treated samples.

Phosphorus distributions in the control and WTR-amended soils were different. For all treatments involving WTR, labile P (KCl-extractable P) was considerably reduced, while NaOH-P (inorganic P associated with amorphous Al hydroxides) was the predominant P fraction in WTR-treated samples. The sum of KCl- and NaOH-P was a good estimate of potential "leachable" P pools and cumulative P leached during the 35-pore-volume leaching event for control samples. Contrarily, sequential extraction pools were poor predictors of total P mass leached for the WTR-treated samples, possibly due to the intra-aggregate diffusion of P into WTR particles.

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