Influence of Water Treatment Residuals on Phosphorus Solubility and Leaching

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ABSTRACT

Laboratory and greenhouse studies compared the ability of water treatment residuals (WTRs) to alter P solubility and leaching in Immokalee sandy soil (sandy, siliceous, hyperthermic Arenic Alaquod) amended with biosolids and triple superphosphate (TSP). Aluminum sulfate (Al-WTR) and ferric sulfate (Fe-WTR) coagulation residuals, a lime softening residual (Ca-WTR) produced during hardness removal, and pure hematite were examined. In equilibration studies, the ability to reduce soluble P followed the order: Al-WTR > Ca-WTR ≈ Fe-WTR ≫ hematite. Differences in the P-fixing capacity of the sesquioxide-dominated materials (Al-WTR, Fe-WTR, hematite) were attributed to their varying reactive Fe- and Al-hydrous oxide contents as measured by oxalate extraction. Leachate P was monitored from greenhouse columns where bahiagrass (*Paspalum notatum* Flugge) was grown on Immokalee soil amended with biosolids or TSP at an equivalent rate of 224 kg P ha^{-1} and WTRs at 2.5% (56 Mg ha^{-1}). In the absence of WTRs, 21% of TSP and 11% of Largo cake biosolids total phosphorus (P$_T$) leached over 4 mo. With co-applied WTRs, losses from TSP columns were reduced to 3.5% (Fe-WTR), 2.5% (Ca-WTR), and <1% (Al-WTR) of applied P. For the Largo biosolids treatments all WTRs retarded downward P flux such that leachate P was not statistically different than for control (soil only) columns. The phosphorus saturation index (PSI = [P$_{ox}$]/[Al$_{ox}$ + Fe$_{ox}$], where P$_{ox}$, Al$_{ox}$, and Fe$_{ox}$ are oxalate-extractable P, Al, and Fe, respectively) based on a simple oxalate extraction of the WTR and biosolids is potentially useful for determining WTR application rates for controlled reduction of P in drainage when biosolids are applied to low P-sorbing soils.

L ONG-TERM APPLICATION of manures and biosolids typically results in soil P levels in excess of crop needs. While buildup of P generally does not harm fertility (Peterson et al., 1994), incidental loss of P to water bodies is a major concern receiving much recent attention. Phosphorus moves from agricultural fields either in dissolved or particulate (attached to soil particles) forms. Because P transported from agricultural land is primarily bound to soil particles, erosion control often prevents off-site P movement (Sharpley and Beegle, 1999). However, many agricultural soils have excessive soil test P levels and off-site transport of soluble P may contribute to water quality degradation.

Unlike the case with nitrogen, leaching of P to ground water has not traditionally been a major transport process. In many soils, high P-sorbing oxide components keep leachate P levels well below eutrophication thresholds (0.01 to 0.05 mg L^{-1}, Sims et al., 1998). While this applies in many parts of the country, vertical flux of P is potentially significant in areas with shallow ground water and coarse-textured soils with little P-sorbing ca-

pacity (Eghball et al., 1996). Areas of intense animal agriculture of the Atlantic Coastal Plain are particularly susceptible to deep leaching of P (Sims et al., 1998; Novak et al., 2000). Because leached constituents can move to surface water via lateral subsurface flow, controlling labile P in porewaters is important in managing eutrophication of surface waters.

Increased emphasis on soluble P losses from cropland has spawned the use of chemical amendments to immobilize P in soils and land-applied wastes. Aluminum, Fe, and Ca salts have been used to decrease P solubility in poultry manure and runoff from manure-amended soils (Moore and Miller, 1994; Moore et al., 1999). Because alum (aluminum sulfate) and Fe salts are used to remove turbidity and color from surface water supplies, residuals produced in drinking water treatment contain reactive hydrous oxides with substantial P-fixing capacity (Elliott et al., 1990). These water treatment residuals (WTRs) have been used to reduce P bioavailability and runoff potential in soils (Peters and Basta, 1996; Cox et al., 1997; Gallimore et al., 1999). Ippolito et al. (1999) studied the effects of co-applying WTRs and biosolids on P uptake and biomass production in range grasses. They concluded that a WTR to biosolids mass ratio of 8:1 will sorb all soluble biosolids P but higher ratios may immobilize plant-available P and induce P deficiency in crops. The relative effectiveness of WTRs in reducing labile P depends on source water characteristics, treatment operational methods (Hyde and Morris, 2000), and storage conditions prior to land application.

Several byproduct materials are generated in drinking water purification processes, but two major types of WTRs are produced in large quantities and have potential for P immobilization. Conventionally, sedimentation–flocculation processes produce residuals using either Al salts (e.g., alum) or Fe salts (e.g., ferric chloride) as the primary coagulant. These residuals are herein referred to as Al-WTRs and Fe-WTRs. The other major residual type, Ca-WTR, is produced in water-softening facilities where lime is used for hardness removal. For at least 60 yr water-softening residuals have been used for liming agricultural fields (American Water Works Association, 1951), but their use in P retention has not been widely investigated.

While the role of WTRs in reducing P in surface runoff from high-P soils has been recently researched (Gallimore et al., 1999; Haustein et al., 2000), their effect on P leaching has received limited attention. Therefore, the aim of this study was to investigate the ability of

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WTRs to sorb P and influence downward movement of biosolids P in a sandy soil material of low P-sorbing capacity. Batch equilibrium studies were used to investigate the influence on soluble P of WTRs incorporated at various rates into biosolids–soil suspensions. Greenhouse column experiments were conducted to quantify WTR effects on leaching of biosolids P in a crop growth environment. While P leaching is negligible for most biosolids-amended soils (Peterson et al., 1994; Elliott et al., 2002), our ultimate objective was to determine the effect of WTRs co-applied with biosolids in a system where drainage P is a justifiable concern.

MATERIALS AND METHODS

Residuals and Phosphorus-Source Materials

Two WTRs were obtained from the Manatee County Water Treatment Plant in Bradenton, FL where they had been stockpiled following removal from storage lagoons. This plant generates two residuals, one from a conventional coagulation-filtration process using alum (Al-WTR), and one from a lime softening process (Ca-WTR). The iron residual (Fe-WTR) was produced at the Hillsboro River Water Treatment Plant in Tampa, FL, where ferric sulfate is used as primary coagulant. A commercially available Fe_2O_3, identified as hematite by X-ray diffraction (XRD) analysis, was included for comparison with the amorphous components of the Fe-WTR material. Chemical characteristics of all materials are given in Table 1.

Four biosolids materials from three municipalities were employed as sources of P (Table 2). The selected biosolids represent a variety of processes expected to influence P behavior (e.g., chemical addition for P removal, biological phosphorus removal [BPR], and pelletization). The Baltimore biosolids are produced in a conventional activated sludge process where the solids are anaerobically digested and mechanically dewatered before pelletization. Notably, Fe is used for P removal in the wastewater treatment process. Tarpon Springs and Largo both employ BPR in wastewater treatment along with aerobic digestion of solids, but Tarpon Springs uses alum for supplemental P removal. Major compositional properties are given in Table 2. Triple superphosphate (TSP) was obtained from a local fertilizer distributor and was listed as being 46% citric acid soluble P_2O_5 (20% P).

The WTRs and P sources were analyzed for total P, Fe, Al, Ca, and Mg by inductively coupled plasma atomic emission spectroscopy (ICP) following USEPA Method 3050A digestion (USEPA, 1986). Total C and N were determined by combustion at 1010°C using a Carlo Erba (Milan, Italy) NA-1500 CNS analyzer. Organic matter contents were determined by loss on ignition, oxalate-extractable P (P_{ox}), Fe (Fe_{ox}), and Al (Al_{ox}) by the McKeague et al. (1971) method, and pH (1:2 solid to solution) and percent solids by standard methods (Page, 1982). In addition, the P chemistry of all materials was extensively characterized. Analysis included organic P (Saunders and Williams, 1955), oxalate P, Mehlich 1-P, and various operationally defined P forms (Chang et al., 1983): exchangeable P (KCl), Fe- and Al-P (NaOH), and Ca- and Mg-P (HCl).

Equilibration Studies

Batch equilibration studies were conducted using Immokalee sand. Selected properties are presented in Table 3. The soil has little native P (22.4 mg P kg⁻¹), contains only 125 mg kg⁻¹ oxalate-extractable Fe + Al [Al_{ox} + Fe_{ox}], and has a

Table 1. Characterization of the water treatment residuals (WTRs) and iron oxide.

Description	Total elemental								Organic matter (LOI†)	pH	Solids	Organic P (% of total P)	Sequentially extracted P				Mehlich-1 P	Oxalate extractable			PSI§
	C to N ratio	C	N	Fe	Al	Ca	Mg	P					KCl	NaOH	HCl	Sum		P	Fe	Al	
		— g kg⁻¹ —		—	—	— g kg⁻¹ —			%				— mg kg⁻¹ —					— g kg⁻¹ —			
Al-WTR	26.3	191	7.3	3.66	89.1	15.2	0.117	2.79	24.1	5.25	58.5	3	<0.41‡	231.5	473.7	2788	4.35	2.66	1.66	71.9	0.032
Fe-WTR	16.5	154	9.4	328	8.45	16.4	0.736	4.36	35.6	6.25	88.9	30	<0.41‡	890.1	2030	2920	16.6	1.31	54.2	3.82	0.039
Ca-WTR	346	114	0.33	0.390	0.590	352.3	9.36	0.043	2.26	8.93	100	10	0.75	0.92	49.38	50.0	0.12	0.044	0.345	<0.005‡	0.23
Iron oxide	–	–	–	754	<0.005‡	–	–	0.010	0	6.35	100	10	3.20	1.16	4.69	9.0	0.78	0.008	9.85	<0.005‡	0.0014

† Loss on ignition.
‡ Less than method detection limit.
§ Phosphorus saturation index.

Table 2. Characterization of the P source materials.

Source	Form	C	N	C to N ratio	Total elemental Fe	Al	Ca	Mg	P	Solids	Organic matter (LOI†)	pH	Organic P (% of total P)	Sequentially extracted P KCl	NaOH	HCl	Sum	Mehlich-1 P	Oxalate extractable P	Fe	Al	PSI‡
		—— g kg⁻¹ ——			—————— g kg⁻¹ ——————					%	%			—————— g kg⁻¹ ——————				mg kg⁻¹	—————— g kg⁻¹ ——————			
Baltimore	Pellets	330	52.2	6.32	62.0	21.3	10.3	2.66	27.1	86.8	63.3	6.29	12	0.14	20.2	5.47	25.8	443	24.2	38.9	15.1	0.62
Tarpon Springs	Cake	334	58.0	5.77	9.29	30.2	15.3	4.42	29.6	66.2	66.8	8.11	22	1.99	19.8	6.95	28.7	575	17.4	9.86	27.6	0.47
Largo	Pellets	408	68.8	5.93	6.74	6.60	22.6	5.67	27.5	93.2	78.1	5.62	15	3.51	8.81	7.25	19.6	1 580	11.3	6.51	4.73	1.3
Largo	Cake	380	67.7	5.61	7.83	7.90	14.7	4.10	31.2	14.2	77.8	7.85	17	9.34	10.8	3.06	23.2	11 200	21.1	7.23	9.58	1.4
TSP	—	—	—	—	15.7	10.0	137	6.15	209	100	20.9	5.88	14	180	22.1	5.66	208	120 000	186	11.0	6.85	13

† Loss on ignition.
‡ Phosphorus saturation index.

Table 3. Selected properties of the soil materials used.

Parameter†	Immokalee (A horizon)	Myakka (E2 horizon)
pH	5.29	5.06
Organic matter, %	0.7	0.02
P_{ox}, mg kg⁻¹	13.1	3.7
Fe_{ox}, mg kg⁻¹	85.6	10.1
Al_{ox}, mg kg⁻¹	40.1	12.5
PSI	0.14	0.19
RPA	5.3	3.2
Total P, mg kg⁻¹	18.8	5.6
Organic P, % of total P	79	48
Mehlich-1 P, mg kg⁻¹	1.7	0.92
KCl-P, mg kg⁻¹	1.9	1.8
NaOH-P, mg kg⁻¹	3.3	1.2
HCl-P, mg kg⁻¹	0.9	0.6
Sequential sum, mg kg⁻¹	6.1	3.6

† Al_{ox}, Fe_{ox}, and P_{ox}, oxalate-extractable Al, Fe, and P, respectively; PSI, phosphorus saturation index; RPA, relative phosphorus adsorption (fraction of 400 mg P kg⁻¹ soil load sorbed × 100; Harris et al., 1996).

correspondingly low P-sorbing capacity. Suspensions of Immokalee soil fertilized with various P sources at equivalent P_T concentrations of 100 mg P kg⁻¹ and amended with WTRs were prepared in 0.01 M KCl at a 1:1 soil to solution ratio, using 10 g soil. The suspensions were reacted at room temperature (23 ± 2°C) for 24 h, filtered, and centrifuged, and the supernatant was filtered again (0.45 micron). The various WTR rates (0, 0.1, 0.5, 1.0, 2.0, and 5.0%, by weight) were chosen based on preliminary sorption data (O'Connor and Elliott, 2000) and effectiveness demonstrated in previous studies (Elliott et al., 1990; Lucas et al., 1994). Besides TSP, the following biosolids were used as P sources: Tarpon Springs cake, Largo pellets, and Baltimore pellets.

Greenhouse Experiment

Thirty-six columns were prepared for the greenhouse investigation as part of a larger study comparing P behavior in biosolids-amended sandy soils (O'Connor et al., 2000). Each column consisted of 15-cm-diameter × 45-cm-long PVC tubing fitted with netting to prevent soil loss and a PVC cup to collect drainage. The columns contained 15 cm of the A horizon of Immokalee sand over 28 cm of a sand (E horizon of the Myakka series [sandy, siliceous, hyperthermic Aeric Alaquod]) of negligible P-retention capacity (Table 3). The Immokalee soil was amended with P (224 kg P ha⁻¹ rate) as either TSP or Largo cake biosolids. This biosolids was chosen because of its high potential to leach as indicated by the relatively high KCl-P (Table 2). Appropriate control columns were also included, and all treatments were replicated three times. Bahiagrass was grown over the summer, with four monthly harvests and leaching events (approximately 0.25 pore volumes each). The greenhouse experiment was designed to identify potential WTR effects on P bioavailability to bahiagrass (reported in O'Connor et al., 2000) and P leaching in a low P-sorbing soil (reported here).

All WTRs were incorporated into the Immokalee soil at a 2.5% rate, while the hematite was applied at a loading rate of 1.01%, an iron-equivalent rate to the Fe-WTR. Besides being typical of rates used in previous studies (Elliott et al., 1990; Lucas et al., 1994), a 2.5% WTR application rate of the same Fe-WTR significantly reduced P leaching with minimal negative effect on P uptake by bermudagrass (Brown and Sartain, 2000). An added advantage to this WTR loading is that the 2.5% rate of Fe-WTR (4.36 g kg⁻¹ P_T) is equivalent to an application of 220 kg P ha⁻¹, essentially identical to the P loading rate used for the P sources (224 kg P ha⁻¹). Thus, the leachability of the P in the WTR could be compared with that of TSP and biosolids on an equal P_T basis. Leachate P_T was

determined by colorimetric analysis (Murphy and Riley, 1962) following persulfate digestion in an autoclave. Phosphorus analysis of undigested drainage water, from this (data not presented) and other biosolids-amended soil leaching studies (Elliott et al., 2002) showed little effect of digestion. Thus, leached P existed almost exclusively as inorganic P. Digested leachate P values are nevertheless reported to quantify total P leached, and to compare with total P applied.

RESULTS AND DISCUSSION

Biosolids and Water Treatment Residual Properties

The chemical characteristics of the WTRs and hematite are presented in Table 1. The Al-WTR is acidic (pH = 5.25) and is dominated by Al (Al_T = 89.1 g kg^{-1}), of which approximately 80% is amorphous (i.e., extractable by acid ammonium oxalate; McKeague et al., 1971). The Fe-WTR is slightly acidic (pH = 6.25) and predominantly Fe (Fe_T = 33%), but only about one-sixth of this Fe was oxalate extractable. Both coagulation WTRs contain appreciable Ca (15.2 to 16.4 g kg^{-1}), probably reflecting the use of lime to promote Al and Fe hydroxide precipitation. The Ca-WTR is basic (pH = 8.9) as it is produced in a lime softening process. This material has a calcium carbonate equivalent of approximately 30%, indicating that its liming potential is an important consideration in land application. The iron oxide contained 754 g kg^{-1} Fe_T, of which only 1% was oxalate extractable, consistent with its identification as pure hematite (α-Fe_2O_3) by X-ray diffraction.

Loss on ignition (LOI) values for the Al-WTR and Fe-WTR were 24 and 36%, respectively. These values are too high to be reflective of the humic matter content in typical surface waters. Elliott et al. (1990) compared total organic carbon (TOC) and LOI of several WTRs and concluded that LOI overestimates organic content since water bound to hydrous oxides is also removed during ignition.

While P_T contents of the Ca-WTR and hematite are negligible, those of the Al-WTR and Fe-WTR (2.79 and 4.36 g kg^{-1}, respectively) are sufficient to affect P loadings to the columns. However, this P has limited solubility as indicted by KCl-P values of <0.41 mg kg^{-1} and low Mehlich 1–extractable P values. Significant portions of P_T in the Al- and Fe-WTR were oxalate-extractable, suggesting that the P in these residuals exists as amorphous Al-P and Fe-P solids with limited solubility.

All biosolids had total N levels (average N_T = 62 g kg^{-1}) and P levels (average P_T = 28.9 g kg^{-1}) within the normal range of biosolids produced nationally (USEPA, 1986). Inorganic P forms dominated all P sources (approximately 80–90%, Table 2). Even the Tarpon Springs and Largo materials, generated by BPR processes, contained predominantly (78–85%) inorganic P. Major elemental concentrations (Al_T, Fe_T, Ca_T, and Mg_T) were also representative of biosolids produced nationally, and reflected individual wastewater and sludge treatment processing. Thus, Fe_T or Al_T concentrations were generally <10 g kg^{-1}, unless chemicals were added to the waste stream (e.g., ferric chloride [Baltimore] or alum [Tarpon Springs] salts for P removal).

Biosolids varied widely in the amount of labile P estimated from the P extracted in the first (KCl) step of the sequential extraction (Table 2). The relatively high KCl-P of the Largo biosolids reflects BPR wastewater treatment combined with a lack of chemical addition for precipitation of metal phosphates (Elliott et al., 2002). Phosphorus extracted by KCl was shown in previous work (O'Connor and Sarkar, 2000) to reflect reasonably the relative bioavailable and leachable P for three biosolids. For example, the Largo pelletized biosolids (KCl-P = 3.5 g kg^{-1}) provided much greater bioavailable and leachable P than the high Fe Baltimore pellets (KCl-P = 0.14 g kg^{-1}) (O'Connor and Sarkar, 2000). Inorganic P was dominantly in Fe- and Al-associated forms (NaOH extract). The sum of sequentially extracted P forms is usually taken to represent total inorganic P. Given the dominance of biosolids P_T by inorganic forms, we expected the good correlation (r^2 = 0.94) found between the sum of sequential extracts and P_T (Elliott et al., 2002).

The Mehlich-1 soil test was also applied to biosolids (Table 2). Previous work (O'Connor and Sarkar, 2000) suggested that Mehlich-P in biosolids was at least qualitatively related to bioavailable and leachable P, although not as indicative as KCl-P. Mehlich-P was poorly correlated (r^2 = 0.13) to P_T for the biosolids examined. The P_{ox} was well correlated (r^2 = 0.76) with P_T, indirectly confirming the dominance of Fe- and Al-P forms in most biosolids materials (Soon and Bates, 1982; Elliott et al., 2002). Oxalate extracts noncrystalline Fe and Al and, thus, is expected to release P associated with amorphous Fe and Al solids.

Equilibration Studies

The amount of soluble P remaining after suspension equilibrium is shown in Fig. 1 through 4 for the Al-WTR, Fe-WTR, Ca-WTR and hematite, respectively. Addition of all WTRs and hematite reduced the soluble P levels, and the effect varied as follows: Al-WTR > Ca-WTR ≈ Fe-WTR > hematite. For any given amendment, differences in equilibrium soluble P values were almost entirely a function of initial P source solubility as indicated by KCl-P (Table 2). Solubility of P sources
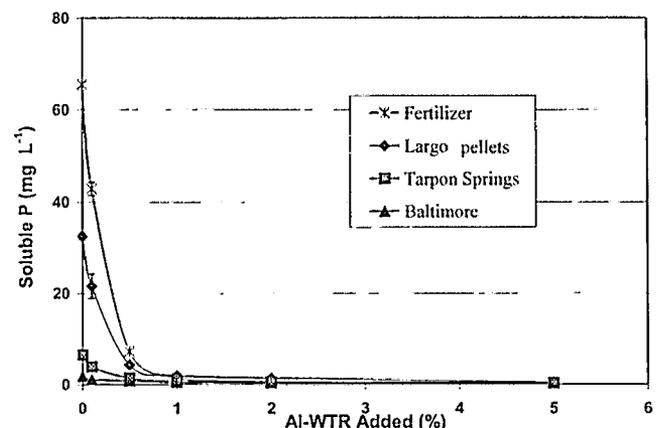

Fig. 1. Soluble P in suspensions of Immokalee soil amended with various P sources and various rates of water treatment residual generated using alum (Al-WTR).
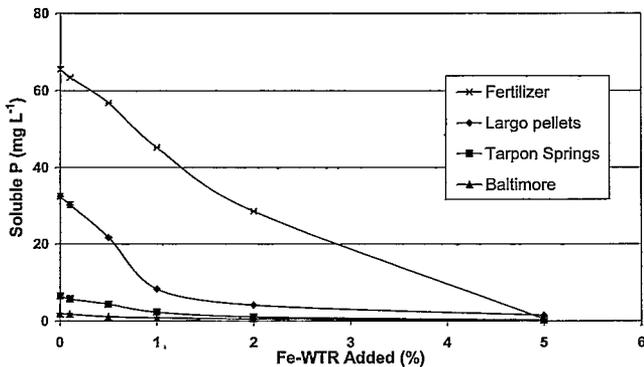
Fig. 2. Soluble P in suspensions of Immokalee soil amended with various P sources and various rates of water treatment residual generated using iron salts (Fe-WTR).

varied consistently as follows: TSP > Largo pellets > Tarpon Springs > Baltimore.

The data in Fig. 1 through 4 demonstrate the appreciable P-retention capacities of WTRs and hematite. The maximum P sorption capacity (P_{max}) was determined from single point isotherms (Harris et al., 1996) to be approximately 3500 mg P kg^{-1} for Fe-WTR and >5000 mg kg^{-1} for the Al-WTR (O'Connor and Elliott, 2000). Heil and Barbarick (1989) reported adsorption capacities of WTR ranging from 737 to 3570 mg P kg^{-1}. Remarkably similar values (P_{max} = approximately 700–3600 mg P kg^{-1}) were recently reported for 18 alum WTRs using a Langmuir isotherm model (Dayton et al., 2000).

Differences in the equilibrium soluble P supported by the three sesquioxide-based materials (Al-WTR, Fe-WTR, and hematite; Fig. 1, 2, and 4, respectively) are explicable in terms of the reactivity of the oxide components of each material. The P-sorbing potential of Al and Fe hydrous oxides is strongly influenced by their crystallinity. Freshly precipitated X-ray amorphous Fe and Al gels sorb 10 to 100 times more inorganic P than their crystalline analogues (McLaughlin et al., 1981). Noncrystalline oxides are often measured by oxalate extraction (McKeague et al., 1971). Thus, the oxalate-extractable Al + Fe [Al_{ox} + Fe_{ox}] serves as a useful index of WTR P-sorbing capacity. The [Al_{ox} + Fe_{ox}] for Al-WTR, Fe-WTR, and hematite were 2.7, 1.1, and 0.18
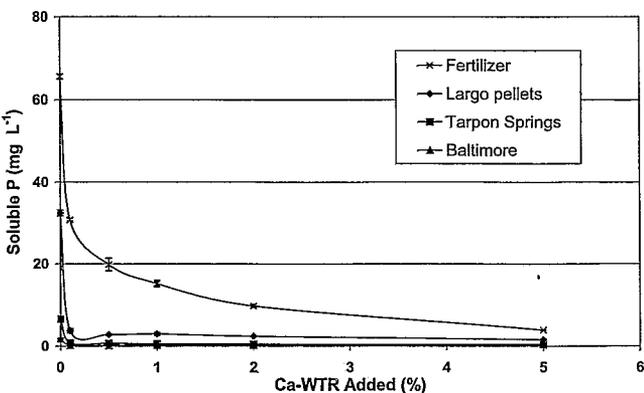

Fig. 3. Soluble P in suspensions of Immokalee soil amended with various P sources and various rates of water treatment residual generated in a lime softening process (Ca-WTR).
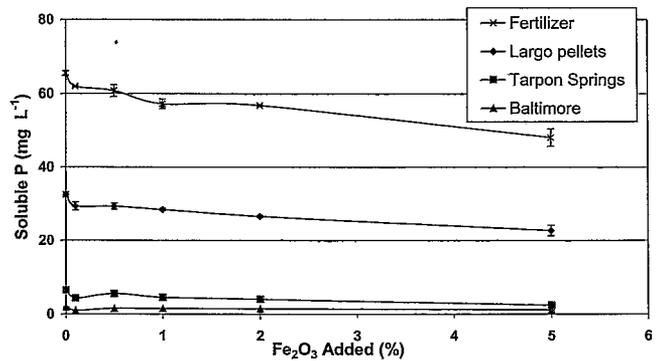

Fig. 4. Soluble P in suspensions of Immokalee soil amended with various P sources and various rates of Fe_2O_3.

mol kg^{-1}, respectively. The Al-WTR was therefore more effective in decreasing soluble P than Fe-WTR, while the hematite was comparatively ineffective. Clearly, total elemental analyses are unreliable predictors of P sorbing capacity: the hematite (Fe_T = 754 g kg^{-1}) was considerably less effective than Fe-WTR (Fe_T = 329 g kg^{-1}) for the same amendment rate. Gallimore et al. (1999) concluded that the amorphous, rather than total, Al content of WTRs determines their ability to reduce P in surface runoff.

Basta and colleagues (Basta et al., 2000; Dayton et al., 2000) reported Al_{ox} and Fe_{ox} for several WTRs. The Al_{ox} content of 18 alum WTRs ranged from 0.1 to 1.8 mol kg^{-1}, with a mean value of approximately 0.9 mol kg^{-1} (Dayton et al., 2000). The strong P-fixing ability of the Al-WTR in this study (Fig. 1) is consistent with its high [Al_{ox} + Fe_{ox}] content (2.7 mol kg^{-1}). The P-fixing capacity of WTRs is influenced by a host of factors. For example, the water source turbidity and coagulant dosage determine the relative proportions of surface water sediment and coagulant hydroxide precipitate in the resulting WTR. The P sorbing capacity of the WTR is expected to vary directly in proportion to its reactive hydrous oxide content. Hyde and Morris (2000) reported that the method of dewatering also influenced the ability of WTRs to decrease extractable P in amended soils.

Additions of Ca-WTR dramatically reduced soluble P concentrations from the various P sources (Fig. 3), and there was little difference in effect at rates of 0.1 to 2%. Phosphorus source solubilities were arrayed in the same order as with the sesquioxide-based materials (Fig. 1, 2, and 4), but only the TSP maintained appreciable soluble P in the presence of Ca-WTR addition. While soluble P was decreased as Ca-WTR was added, the effect was expected to be less than that observed with the other WTRs based on the paucity of Al_{ox} and Fe_{ox} in the Ca-WTR (Table 1). It should be noted that the P sorption behavior of the Ca-WTR is mechanistically distinct from WTRs arising from coagulation–filtration processes where Al- and Fe-hydrous oxides are precipitated. The Ca-WTR material tended to dissolve under circumneutral pH conditions, and its alkaline nature (Table 1) resulted in higher pH values (6.5 to 7.1) for the Ca-WTR equilibrium soil suspensions, compared with the other systems (pH 4.8 to 6.4). The greater pH values and greater soluble Ca concentrations of the

Table 4. Phosphorus leached from triple superphosphate (TSP)- and biosolids-amended Immokalee soil (data from Elliott et al., 2002).

P source	KCl-P	Mean total P leached	P leached (% of total, mean ± standard error)
	g kg^{-1}	mg	%
TSP	180	75.7a†	20.7 ± 2.2
Largo cake	9.34	40.6b	11.1 ± 0.9
Largo pellets	3.51	9.2c	2.5 ± 0.6
Tarpon Springs cake	1.99	0.27c	0.07 ± 0.02
Baltimore pellets	0.14	0.30c	0.08 ± 0.02
None	0.002	0.29c	NA‡

† Means followed by the same letter are not significantly different according to LSD (0.05).
‡ Not applicable.

Table 5. Influence of water treatment residuals (WTRs) on leachate P of triple superphosphate (TSP) and Largo cake columns.

P source	Treatment	Mean total P leached	Applied P leached (mean ± standard error)	PSI† (of applied materials)
		mg	%	
TSP	–	75.7a‡	20.7 ± 2.2	13.3
TSP	Al-WTR	2.60cd	0.73 ± 0.38	0.061
TSP	Fe-WTR	12.8c	3.5 ± 1.1	0.18
TSP	Ca-WTR	9.1cd	2.5 ± 1.2	–
TSP	Hematite	73.1a	20.0 ± 2.9	1.6
Largo cake	–	40.6b	11.1 ± 0.9	1.4
Largo cake	Al-WTR	0.19d	0.067 ± 0.026	0.07
Largo cake	Fe-WTR	0.27d	0.074 ± 0.017	0.12
Largo cake	Ca-WTR	0.57d	0.16 ± 0.03	–
Largo cake	Hematite	0.36d	0.999 ± 0.006	0.69
None	Fe-WTR	0.16d	0.049 ± 0.012	0.039
None	–	0.29d	NA§	–

† Phosphorus saturation index. For mixtures, PSI is a mass-weighted composite of the individual values for the P source and WTR.
‡ Means followed by the same letter are not significantly different according to LSD (0.05).
§ Not applicable.

Ca-WTR systems probably precipitated calcium phosphates that did not form in the lower pH (Fe- and Al-WTRs) equilibration suspensions. Limited equilibrium modeling (data not presented) of the solution chemistries suggested saturation with respect to hydroxyapatite (a Ca-P solid) in the Ca-WTR systems. The important point is that removal of soluble P in the Ca-WTR system was probably a manifestation of precipitation and not solely adsorption.

Greenhouse Leaching Study

Leaching over 4 mo (cumulatively, approximately one pore volume of drainage) from columns amended with TSP and biosolids in the absence of WTRs is given in Table 4. The data show that the P leached from biosolids is less than that from a highly soluble source like TSP. The relative amount of leachable P in biosolids was a reflection of the labile P as measured by KCl extraction. Thus, the biosolids with the most P leached (Largo cake) also had the highest KCl-P. Detailed discussion of the biosolids-P treatments in the absence of WTRs is presented elsewhere (Elliott et al., 2002).

In order to examine the ability of WTRs to alter P leaching from applied biosolids, TSP and the Largo cake were selected for study because of the substantial leaching potential in the absence of WTRs as reflected in KCl-P (Table 2). Total cumulative P leached over the 4-mo period is expressed as a percentage of P$_T$ applied

in Table 5. For TSP, all the WTR materials significantly reduced leaching, whereas hematite did not. For the Largo biosolids, all WTR amendments and hematite effectively eliminated P leaching.

Given the determinant nature of Al and Fe hydrous oxides in controlling P solubility in soils and the predominance of Fe-P and Al-P forms in biosolids (Soon and Bates, 1982), we explored the P saturation index (PSI = [P$_{ox}$]/[Al$_{ox}$ + Fe$_{ox}$]) of the amendment as a predictor of leaching behavior in the Immokalee soil (Elliott et al., 2002). Conceptually, the PSI is the molar ratio of total sorbable P to the amorphous Al and Fe components capable of P fixation. For PSI < 1, there is more reactive Fe and Al than necessary to bind P, while PSI > 1 indicates excess P beyond the material's P retention capacity. The trendline and associated data points in Fig. 5 show the P leached for eight biosolids materials applied at 224 kg P ha^{-1} to the Immokalee soil as a function of the biosolids PSI. The four biosolids discussed in this study are labeled on Fig. 5. Data for the other biosolids were previously reported (Elliott et al., 2002).

Substantial leaching of biosolids P occurred only when the biosolids PSI was greater than unity. The Largo cake
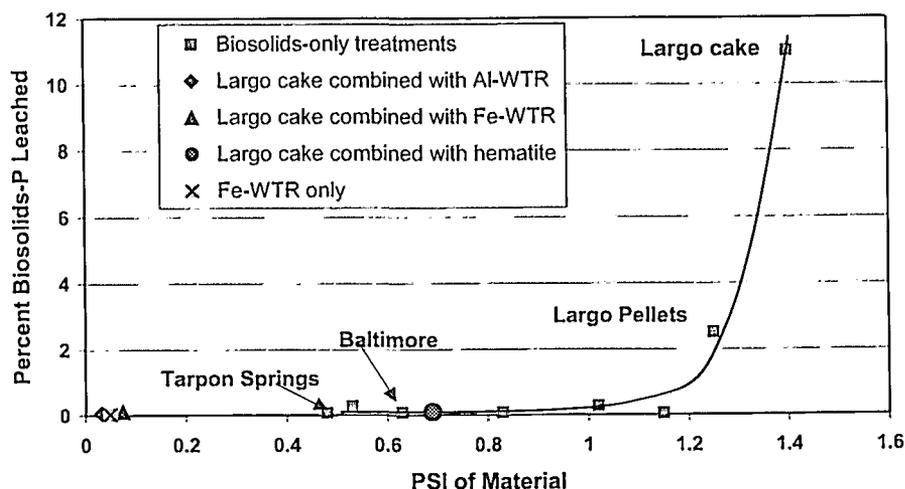

Fig. 5. Biosolids P leached (percent of total applied) as a function of the phosphorus saturation index (PSI) of the material.

had a PSI of 1.4 (Table 5) and exhibited the highest leaching among the biosolids. When the Largo cake was mixed (co-applied) with the Al-WTR or Fe-WTR, the composite PSI for the mixture was lowered to 0.07 and 0.12, respectively. Accordingly, the amount of P leached was negligible and not statistically ($p = 0.05$) different than control (soil only) columns (Table 5). These Largo biosolids–WTR treatments are plotted in Fig. 5.

The PSI concept is useful for explaining why hematite had no effect on P leaching from the TSP-amended soil yet was extremely effective in suppressing P in drainage from the Largo biosolids treatments (Table 5). In the absence of WTRs, both TSP and Largo cake exhibited substantial P leaching. Because of the large P_{ox} of the TSP (Table 2) and the modest Fe_{ox} of the hematite compared with its P_T (Table 1), the composite PSI for TSP–hematite is 1.6. This is well above the threshold PSI (approximately 1.1) associated with substantial P leaching (Fig. 5). The P_{ox} of the TSP is approximately 89% of P_T; however, only 36% of the P_T in the Largo cake is oxalate extractable. Thus, for the Largo–hematite treatment, the composite PSI is 0.69, below the leaching threshold value (see Fig. 5). These comparisons help validate the predictive capability of the PSI of an amendment (or mixture of amendments) as a measure of potential P leaching in waste-amended soils of low P-sorbing capacity.

Although the P_T content of the WTRs themselves (Table 1) is small (<4.36 g kg^{-1}) compared with biosolids, large application rates (e.g., 56 Mg ha^{-1}) can result in appreciable soil applications of P. Average P_T content of WTRs is about 2 to 3 g kg^{-1} (USEPA, 1996). In this study, a 56 Mg ha^{-1} loading of the Fe-WTR ($P_T = 4.36$ g kg^{-1}) corresponded to the addition of 220 kg P ha^{-1}. Yet less than 1% of P_T in the Fe-WTR was extractable by Mehlich-1 and the P was not extracted to any significant extent by KCl (Table 1). Thus, P was expected to be nonleachable from the soil amended only with Fe-WTR. This was, in fact, the case (Table 5). Nonleachability is also predicted from the PSI of Fe-WTR alone (0.039), and clearly illustrated in Fig. 5.

The limitations of the PSI must be appreciated. First, it is most useful in systems where the characteristics of the amendment dominate P chemistry. The behavior exhibited in Fig. 5 applies to the Immokalee sand with very low P-sorbing capacity. For the predominant agricultural soils of the USA, P leaching will be negligible regardless of the amendment PSI, at least if the soil P-sorbing sites are not already saturated prior to spreading. Second, the index applies to Al- and Fe-based WTRs where sesquioxide components determine P-fixing capacity. Because of the aforementioned differences in P removal mechanisms for Ca-based WTRs, [Al_{ox} + Fe_{ox}] is not a reliable measure of P-fixing capacity for softening residuals. In practice, the liming potential of Ca-based softening residuals will probably dictate application rates on acid sandy soils.

Finally, a single high WTR application rate was used in this study. The data are insufficient to ascertain if the composite PSI of WTR–biosolids combinations exhibits the same threshold behavior (Fig. 5) as the PSI of biosolids alone. This is the subject of further investigation that will be reported subsequently.

CONCLUSIONS

While the ability of WTRs to reduce P in surface runoff has been previously investigated (Gallimore et al., 1999; Haustein et al., 2000), this study evaluated the ability of WTRs to alter P solubility and leaching in a sandy soil material amended with biosolids and TSP. In batch equilibration studies, Al-WTR, Fe-WTR, and Ca-WTR were all effective in adsorbing P released from TSP– and biosolids–soil suspensions. In contrast, hematite (α-Fe_2O_3) was relatively ineffective in immobilizing P because of the lower P-sorbing capacity of crystalline versus X-ray amorphous oxides. The Ca-WTR from water softening probably reduced soluble P through precipitation of Ca-P solid phases. Its substantial calcium carbonate equivalent means its liming potential must be considered in use as a soil amendment.

Because Al and Fe salts are used in wastewater treatment and solids dewatering, leaching of P is quite small for most biosolids, even when applied in excess of crop P requirements to soils with limited P-sorbing capacity. Thus, for several biosolids materials, leaching was not significantly (p = 0.05) different than controls (soil only columns) even in the absence of WTRs (Elliott et al., 2002). For biosolids and fertilizers with meager Al and Fe and appreciable leachable P (e.g., TSP and Largo cake), co-application with WTRs dramatically reduced vertical movement of P through the soil profile.

Biosolids to WTR mixing ratios based on total compositional parameters (e.g., Colorado Department Public Health and Environment, 1994) are probably poorly correlated with P bioavailability or environmental mobility. Therefore, mass-based guidelines for specific biosolids–WTR combinations (Ippolito et al., 1999) are unlikely to be generally applicable to the wide range of materials produced nationally. A quantitative approach using coagulation WTRs to reduce P flux from biosolids-amended soils should be based on ensuring sufficient reactive Al + Fe in the WTR to immobilize leachable P in the biosolids. Oxalate extraction can be used to measure both the P-fixing capacity of the sesquioxides in the WTRs and the potentially releasable P in the biosolids. The phosphorus saturation index ($[P_{ox}]/[Al_{ox} + Fe_{ox}]$), employed as a risk indicator of soil-P loss (Chardon et al., 2000), also appears useful for determining amendment rates of WTRs needed to control drainage P in land-based biosolids recycling programs.

REFERENCES

American Water Works Association. 1951. Water quality and treatment. 2nd ed. AWWA, New York.
Basta, N.T., R.J. Zupanic, and E.A. Dayton. 2000. Evaluating soil

tests to predict bermudagrass growth in drinking water treatment residuals with phosphorus fertilizer. J. Environ. Qual. 29:2007–2012.

Brown, E., and J. Sartain. 2000. Phosphorus retention in United States Golf Association (USGA) greens. Soil Crop Sci. Soc. Florida Proc. 59:112–117.

Chang, A.C., A.L. Page, F.H. Sutherland, and E. Grgurevic. 1983. Fractionation of phosphorus in sludge-affected soils. J. Environ. Qual. 12:286–290.

Chardon, W.J., O.F. Schoumans, and G.F. Koopmans. 2000. Soil phosphorus saturation index: Background, applications, and limitations. p. 321. In 2000 Annual Meeting abstracts. ASA, CSSA, and SSSA, Madison, WI.

Colorado Department Public Health and Environment. 1994. Beneficial use of water treatment sludge and fees applicable to the beneficial use of sludge. 5 CCR 1003-7. CDPHE, Denver.

Cox, A.E., J.J. Camberato, and B.R. Smith. 1997. Phosphate availability and inorganic transformation in an alum sludge-affected soil. J. Environ. Qual. 26:1393–1398.

Dayton, E.A., N.T. Basta, and C.A. Jakober. 2000. Phosphorus sorption capacity of drinking water treatment residuals for potential use as a phosphorus sorbent to protect water quality. p. 403. In 2000 Annual Meeting abstracts. ASA, CSSA, and SSSA, Madison, WI.

Eghball, B., G.D. Binford, and D.D. Baltensperger. 1996. Phosphorus movement and adsorption in a soil receiving long-term manure and fertilizer application. J. Environ. Qual. 25:1339–1343.

Elliott, H.A., B.A. Dempsey, D.W. Hamilton, and J.R. DeWolfe. 1990. Land application of water treatment sludges: Impact and management. Am. Water Works Assoc. Res. Foundation, Denver, CO.

Elliott, H.A., G.A. O'Connor, and S. Brinton. 2002. Phosphorus leaching from biosolids-amended sandy soils. J. Environ. Qual. 31: 681–689.

Gallimore, L.E., N.T. Basta, D.E. Storm, M.E. Payton, R.H. Huhnke, and M.D. Smolen. 1999. Water treatment residual to reduce nutrients in surface runoff form agricultural land. J. Environ. Qual. 28:1474–1478.

Harris, W.G., R.D. Rhue, G. Kidder, R.B. Brown, and R. Little. 1996. Phosphorus retention as related to morphology of sandy coastal plain soil materials. Soil Sci. Soc. Am. J. 60:1513–1521.

Haustein, G.K., T.C. Daniel, D.M. Miller, P.A. Moore, Jr., and R.W. McNew. 2000. Aluminum-containing residuals influence high-phosphorus soils and runoff water quality. J. Environ. Qual. 29:1954–1959.

Heil, D.M., and K.A. Barbarick. 1989. Water treatment sludge influence on the growth of sorghum-sudangrass. J. Environ. Qual. 18: 292–298.

Hyde, J.E., and T.F. Morris. 2000. Phosphorus availability in soils amended with dewatered water treatment residual and metal concentrations with time. J. Environ. Qual. 29:1896–1904.

Ippolito, J.A., K.A. Barbarick, and E.F. Rendte. 1999. Co-application of water treatment residuals and biosolids on two range grasses. J. Environ. Qual. 28:1644–1650.

Lucas, J.B., T.A. Dillaha, R.B. Reneau, J.T. Novak, and W.R. Knocke. 1994. Alum sludge land application and its effect on plant growth. J. Am. Water Works Assoc. 86:75–83.

McKeague, J.A., J.E. Brydon, and N.M. Miles. 1971. Differentiation of forms of extractable iron and aluminum in soils. Soil Sci. Soc. Am. Proc. 35:33–48.

McLaughlin, J.R., J.C. Ryden and J.K. Syers. 1981. Sorption of inorganic phosphate by iron- and aluminum-containing components. J. Soil Sci. 32:365–377.

Moore, P.A., T.C. Daniel, and D.R. Edwards. 1999. Reducing phosphorus runoff and improving poultry production with alum. Poultry Sci. 78:692–698.

Moore, P.A., and D.M. Miller. 1994. Decreased phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. J. Environ. Qual. 23:325–330.

Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural water. Anal. Chim. Acta 27:31–36.

Novak, J.M., D.W. Watts, P.G. Hunt, and K.C. Stone. 2000. Phosphorus movement through a coastal plain soil after a decade of intensive swine manure application. J. Environ. Qual. 29:1310–1315.

O'Connor, G.A., and H.A. Elliott. 2000. Co-application of biosolids and water treatment residuals. Final report. Florida Dep. of Environ. Protection, Tallahassee.

O'Connor, G.A., and D. Sarkar. 2000. Fate of land applied residuals-bound phosphorus. Contract no. WM-661. Final report. Florida Dep. of Environ. Protection, Tallahassee.

O'Connor, G.A., D. Sarkar, H.A. Elliott, and D.A. Graetz. 2000. Characterization of forms, solubilities, bioavailabilities, and mineralization rates of phosphorus in biosolids, commercial fertilizers, and manures. Annual report. Water Environ. Res. Foundation, Alexandria, VA.

Page, A.L. 1982. Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Peters, J.M., and N.T. Basta. 1996. Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial wastes. J. Environ. Qual. 25:1236–1241.

Peterson, A.E., P.E. Speth, R.B. Corey, T.W. Wright, and P.L. Schlecht. 1994. Effect of twelve years of liquid digested sludge application on the soil phosphorus level. p. 237–247. In C.E. Clapp (ed.) Sewage sludge: Land utilization and the environment. SSSA, Madison, WI.

Saunders, W.H.M., and E.G. Williams. 1955. Observations on the determination of total phosphorus in soil. J. Soil Sci. 6:254–267.

Sharpley, A.N., and D. Beegle. 1999. Managing phosphorus for agriculture and the environment. Coop. Ext. Serv., Pennsylvania State Univ., University Park.

Sims, J.T., R.R. Simard, and B.C. Joern. 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. J. Environ. Qual. 27:277–293.

Soon, Y.K., and T.E. Bates. 1982. Extractability and solubility of phosphorus in soils amended with chemically treated sewage sludges. Soil Sci. 134:89–96.

USEPA. 1986. Acid digestion of sediment, sludge and soils. Ch. 3. In Test methods for evaluating solid waste. SW-846. USEPA, Cincinnati, OH.

USEPA. 1996. Management of water treatment plant residuals: Technology transfer handbook. USEPA, Office of Res. and Development, Washington, DC.