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Phosphorus Availability from Phosphorus-Amended Water Treatment Residual

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ABSTRACT

Water treatment residual (WTR) is a by-product generated from drinking water treatment facilities that often contains considerable amounts of aluminum (Al) or iron (Fe). Application of WTR to agricultural land can cause deficiencies in soil phosphorus (P). Amendment of WTR with P before application to agricultural land may eliminate the problem of P deficiencies in plant growth. The objective of this field study was to estimate the amount of P required to make WTR a supplier of P to plants. A Fe-based WTR that

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contained a cationic polymer was collected from a sand-bed lagoon of a Connecticut water treatment facility in the spring of 1996 and 1997. The WTR was amended with P at rates of 19.4, 38.8, 62.0, and 77.4 g P kg⁻¹ WTR in 1996, and 0.0, 4.9, 9.7, 14.6, 19.4, 38.8, and 62.0 g P kg⁻¹ WTR in 1997. Fertilizer P was applied at rates of $0-486 \text{ kg P ha}^{-1}$ for the calculation of fertilizer P equivalents of the P-amended WTR. Sorghum-sudangrass (Sorghum sudanenese "Ciba FP-5") was planted in 1996 and 1997 in a Paxton fine sandy loam soil (coarse-loamy, mixed, mesic, subactive oxyaquic Dystrudepts). The experimental design was a randomized complete block with four replications. A P rate between 14.6 and 19.4 g Pkg⁻¹ WTR was sufficient to make this WTR a supplier of P. The rate of P addition to the WTR was much less than predicted based on the amount of P adsorbed by the WTR in a laboratory study. The rate likely was less than predicted due to the release of P from the cationic polymer used in the coagulant. Amendment of WTR with P when the WTR contains a cationic polymer may provide a beneficial use for the WTR.

INTRODUCTION

Drinking water treatment facilities produce a filtering by-product that contains large amounts of Al or Fe. This material, known as water treatment residual (WTR), was commonly discharged directly into water bodies before the Clean Water Act of 1972. After passage of the Act, the most common method of disposal was placement in a landfill. Some alternative ideas for using WTR in a beneficial manner have included addition of WTR to cement aggregate or to road paving material, use as a landscape fill, potting mixture, buffer strip, soil substitute, or application of WTR to agricultural land to reduce labile phosphorus.^[1-4]

Research about the land application of WTR has intensified in the past decade because of increased economic, regulatory, and legal pressures on water treatment facilities for alternative waste management. The results of some of the research has been compiled in a publication written by the US Environmental Protection Agency, The American Water Works Association and the American Society of Civil Engineers.^[5] Major areas addressed in the publication include the characterization of WTR, land site assessment, application and storage of WTR, and environmental monitoring. Some of the benefits of land application of WTR have included improvement of the physical properties of potting soils and field soils,^[2,6]increases in pH,^[7,8] a supplier of macro- and micronutrients,^[9] and most recently to decrease excessive P in agricultural soils.^[3,7,10–16]

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A major problem in soils amended with WTR has been the propensity of WTR to reduce soil P levels to concentrations that limit plant growth.^[2,5,6,8,9,16–20] Water treatment residual reduces soil P concentrations because it consists largely of Al or Fe hydroxides. The Al and Fe chemically bond to soil solution and labile P and form sparingly soluble Al and Fe phosphates, which reduces available soil P and plant growth.^[19]

Amending WTR with P before the WTR is applied to agricultural land to make it a supplier of P would greatly increase the value of WTR. One problem may be the large quantity of P necessary to produce a WTR that will supply P at a rate similar to rates of P applied as fertilizers. In a laboratory study with an Fe-based WTR, Butkus et al.^[21] showed that approximately $77.4 \,\mathrm{gP \, kg^{-1}}$ WTR was required to saturate the WTR with P. This is equivalent to a land application of about $3400 \text{ kg P} \text{ ha}^{-1}$ if WTR is applied at a rate $(44.8 \text{ Mg} \text{ ha}^{-1})$ commonly used by farmers. Field studies with WTR, however, have demonstrated that much less P is needed to overcome P deficiencies in studies where unamended WTR was added to the soil. An application of only $20-45 \text{ kg P ha}^{-1}$,^[18] or doubling the recommended rate of P fertilizer,^[2,19] was sufficient to overcome P deficiencies where unamended WTR was applied at application rates of 22.4–44.8 Mg ha⁻¹. These data suggest that the amount of P required to make WTR a supplier of P may be much less for field conditions compared with laboratory conditions. The objective of this field study was to estimate the amount of P required to make WTR a supplier of P for plant growth.

MATERIALS AND METHODS

Water treatment residual was collected from the sand-bed lagoon at the Gaillard water treatment facility in North Branford, CT in early June, 1996, and the middle of April, 1997. The WTR was 34% dry matter in 1996 and 44% dry matter in 1997. The coagulant used shortly before the WTR was collected and included FeCl₂, at a dose of 4.45 mg L^{-1} , or Fe(SO₄)₂, at a dose of 10.4 mg L^{-1} . A cationic polymer, Magnafloc 572C, a 50% quaternary polyamine solution, was added at a dose of 2.3 mg L^{-1} , and an anionic polymer, Magnafloc 1849A, a 30% polyacrylamide solution, was added to the backwash water at a dose of 0.1 mg L⁻¹. These polymers are thought to be flushed to the lagoons and become a part of WTR when the filters are backwashed. The WTR contained 71.2% sand in 1996 and 74.3% in 1997. The sand became part of the WTR when a backhoe loaded the WTR and some of the sand from the drying bed onto



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a dump truck. The organic matter (OM) content of the WTR, based on loss on ignition at 375° C for 16 h,^[22] was 17.3% in 1996 and 22.0% in 1997.

Total metal analysis of the WTR was accomplished using a $HF/HNO_3/HCl$ microwave digestion procedure developed at the Environmental Research Institute, University of Connecticut. Tracemetal grade reagents and Milli-Q[®] deionized water were used for these preparatory procedures. Inductively coupled plasma atomic emission spectroscopy was used to determine concentrations of Al, calcium (Ca), chromium (Cr), copper (Cu), Fe, nickel (Ni), P, and zinc (Zn); graphite furnace atomic adsorption was used to determine concentrations of arsenic (As), cadmium (Cd), lead (Pb), and selenium (Se); cold-vapor atomic adsorption was used to determine the concentration of mercury (Hg).

Sorghum-sudangrass (Sorghum sudanenese "Ciba-FP-5") was planted at the University of Connecticut Department of Plant Science Teaching and Research Facility in Storrs, CT in 1996 and 1997 to estimate the P fertilizer value of P-amended WTR. The experiments were established in different locations in the same field on a Paxton fine sandy loam soil with an extremely low extractable P concentration (modified-Morgan extractable P of 0.5 mg P kg^{-1}). The previous crop in the field was a grass hay crop that had not been fertilized for at least 20 years. The experimental design was a randomized complete block with four replications. The plot dimensions were 1.52 by 3.05 m.

The P-amended WTR treatments were created by combining the WTR with various rates of P from reagent grade $(NH_4)_2PO_4$ in 68 L plastic tubs. The amount of WTR added to the tubs was equivalent to an application rate of 7.8 Mg ha⁻¹ (dry weight, adjusted for sand content) to the experimental plots. The amount of WTR added to the plot was adjusted for sand but the amount of P added to the WTR was not adjusted for sand because Butkus et al.^[21] has shown that the sand in this WTR adsorbed a negligible amount of P. Distilled water, sufficient for thorough mixing, was added to each tub, and the suspension was vigorously mixed for five minutes a day for one week using a paddle mixer attached to a 1.3 cm drill. One week was deemed sufficient for P equilibration because kinetic studies with this WTR indicated that equilibrium would be obtained within 2 days.^[21] Liquid samples (50 mL) were collected from each tub for the determination of aqueous phosphate by ion chromatography (Dionex Corp., series 4000, Sunnyvale, CA).

In 1996, the rates of P added to the WTR were: 19.4, 38.8, 62.0, and 77.4 $g P kg^{-1}$ WTR. Based on our 7.8 Mg ha⁻¹ rate of WTR application, the amount of P applied to the plots for each treatment was 152, 304, 486,

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and 608 kg P ha⁻¹. In 1997, the rates of P added to the WTR were: 0, 4.9, 9.7, 14.6, 19.4, 38.8, and 62.0 g P kg⁻¹ WTR. The amount of P applied to the plots with the WTR for each treatment was 0, 38, 76, 114, 152, 304, and 486 kg P ha⁻¹. Fertilizer P treatments were applied in separate plots as triple superphosphate in 1996 at 0, 49, 98, 147, and 196 kg P ha⁻¹. In 1997, the fertilizer P was applied as $(NH_4)_2PO_4$ at 0, 38, 76, 114, 152, 304, and 486 kg P ha⁻¹.

The WTR-P treatments and the fertilizer P treatments were mixed with the soil by hand using shovels in 1996 and by use of a rototiller in 1997. Nitrogen, as urea, was applied to all plots at 196 kg N ha^{-1} in 1996. In 1997, differential rates of urea were applied so that each plot received the same amount of N (439 kg ha⁻¹) as supplied by the highest (NH₄)₂PO₄ rate in the WTR-P mixture. The rate of potassium (K) fertilizer was based on a soil test recommendation by the Soil Testing Laboratory at the University of Connecticut. The N and K fertilizers were uniformly applied and disked into the experimental area before application of the treatments.

The sorghum-sudangrass was planted on 29 July and harvested on 1 October 1996. In 1997, the planting date was 2 July and the harvest date was 23 September. The sorghum-sudangrass was seeded in 25.4-cm wide rows at $44.8 \text{ kg} \text{ ha}^{-1}$. Weeds were controlled by application of Bicep at $0.9 \text{ L} \text{ ha}^{-1}$ and Accent at 7.99 mL ha⁻¹ across the entire experimental area. Yields were determined by hand-harvesting a 0.61 m by 1.52 m area in the center of each plot. Harvest yields were corrected for moisture content and reported as total dry matter ha⁻¹. All statistical analyses were completed using the Statistical Analysis System (SAS) software.^[23] An alpha value of 0.05 was used to denote statistically significant treatments. Analysis of variance, using PROC GLM in SAS, and means separation by LSD were used to determine differences in the yields of the P-amended WTR plots. The yield responses to fertilizer P in 1996 and 1997 were described using linear regression (PROC REG in SAS). Fertilizer P equivalents^[24] for the P-amended WTR treatments were calculated using the regression equations from the fertilizer P response curves.

Soil samples were collected from each plot before application of the treatments. Samples were collected from the 0 to 15-cm, and the 15 to 30-cm depths. Each sample was composed of 6, 2.2-cm diameter cores. The soils were air-dried, passed through a 2-mm sieve, and stored in airtight plastic bottles. The extractable P concentrations were determined using the modified-Morgan extracting procedure.^[25] The OM content of the soil was determined by loss on ignition at 375°C for 16 h.^[22] The pH of the soil was measured in a 1:1 soil to distilled water mix with a Fisher Scientific Accumet 925 pH meter using a combination glass electrode (Fisher 13-620-285).



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RESULTS AND DISCUSSION

The total metal concentrations of the regulated metals in the WTR for both years were well below the EPA 503 regulatory levels (Table 1). Metal concentrations of WTR are not regulated by the EPA 503 statute for sewage sludge and domestic septage, but there are similar concerns about the accumulation of metals in soils from WTR, and for this reason many states invoke the 503 regulations for WTR (5). In both years, the regulated metal concentrations in the WTRs were similar to the concentrations in the soil, except for Cu (Table 1). The Cu concentrations were elevated in the 1997 WTR from applications of CuSO₄ to the reservoir for the control of algae (personal communication, John Hudak, South Central Regional Water Authority, New Haven, CT). Previous research has shown that the concentrations of metals in WTR usually are low,^[2,8,9,16,17,19] and that the concentrations of metals in WTR are controlled by the purity of the coagulant used to treat the water.^[28] The elevated concentration of Cu in the 1997 WTR suggests that the use of copper sulfate for algal control in reservoirs should be monitored when considering land application of WTR.

The rates of P added to the WTR in 1996 were guided by information from the adsorption isotherm shown in Butkus et al.^[21] The WTR that

	Soil (0–15 cm)	Soil (15–30 cm)	WTR 1996	WTR 1997	Part 503 regulation ^a	Common range for soils ^b
Element				$(\mu g/g)$		
As	4.5	4.5	3.3	ND ^c	41	1-50
Cd	ND	ND	ND	3.03	39	0.036-0.78
Cr	53	55	56	62	1200	1 - 1000
Cu	15.5	13.5	72	298	1500	3.8-94.9
Hg	0.05	0.05	0.07	0.06	17	0.01 - 0.30
Ni	27.5	30	30.3	25	420	4.1-56.8
Pb	15	11.5	9	9.5	300	4.0-23.0
Se	ND	ND	ND	3	36	5-50
Zn	43.5	37.5	20.8	61	2800	8.0-126.0

Table 1. Selected elemental concentrations of the soil at two depths and the water treatment residual applied in 1996 and 1997.

^aEPA Part 503 land application pollutant concentration limits for sewage sludge. ^bLinsday;^[26] Holmgren et al.^[27]

^cNondetectable.



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Butkus et al.^[21] used was collected from the same water treatment facility as the material used in this study, and the rates of Fe and cationic polymer in the coagulant were identical. At the lowest rate of P amendment $(19.4 \text{ g P kg}^{-1} \text{ WTR})$ the isotherm indicated that all of the P should be adsorbed to the Fe. At the highest rate $(77.4 \text{ g P kg}^{-1} \text{ WTR})$ of P amendment, the isotherm indicated that the Fe should be nearly saturated with P, and a relatively small amount of aqueous P should be in solution. When the aqueous P concentrations in the tubs were measured, the concentrations were much greater than the predicted values from the isotherm. The greater than predicted concentrations of aqueous P demonstrated that the WTR was not adsorbing P in the expected amounts. The WTR was analyzed and found that it was 71.2% sand by weight. This was unexpected because the sand content was assumed to be low (3-5%), and the sand was not visible due to Fe and organic matter coatings. We corrected the amount of WTR added to the tubs for the mass of sand, and the aqueous concentrations of P in the tubs decreased to within a few percent of the concentrations predicted by the laboratory isotherm. The close agreement of the P adsorped by the WTR in the tubs with the predicted adsorption by the isotherm suggests that the Fe and Al oxides were controlling the adsorption of the P and that the sand was adsorbing little to no P.^[21]

Sorghum-sudangrass yields showed a significant linear increase ($\alpha = 0.05$) with P fertilizer treatments in 1996 (Fig. 1). The lowest rate



Figure 1. Relationship between the dry matter yield of sorghum-sudan, various rates of P fertilizer, and P mixed with 7.8 Mg ha^{-1} WTR in 1996.



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Table 2. Amount of P added to the water treatment residual (WTR), the total P, and the aqueous P applied in the WTR-P mix, and the fertilizer P equivalents for the WTR-P treatments in 1996 and 1997.

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Treatment g P kg ⁻¹ WTR	Total P $(kg P ha^{-1})$	Aqueous P^a (kg P ha ⁻¹)	Fertilizer P equivalent $(kgPha^{-1})$
1996			
19.4	152	0	127
38.8	304	5	127
62.0	486	26	127
77.4	620	66	127
1997			
0.0	0	0	0
4.9	38	0	0
9.7	76	0	0
14.6	114	0	0
19.4	152	2	56
38.8	304	1	85
62.0	486	10	UD^{b}

^aThe portion of the total P not adsorbed in the mixture by the WTR. ^bUndetermined.

 $(19.4 \text{ g P kg}^{-1} \text{ WTR})$ of P added to the WTR was equivalent to an application of 152 kg P ha^{-1} if all of the P were available to the crop. The calculated fertilizer P equivalent for this treatment was 127 kg P ha^{-1} (Fig. 1, Table 2). This is almost 83% of the total P added to the WTR, which was much greater than the amount of P expected to be released from the WTR. It was expected that only a small amount of P would be desorbed from the Fe-P complexes. The WTR amended at P rates greater than 19.4 g P kg^{-1} WTR produced yields that were statistically similar to the 19.4 g P kg^{-1} WTR treatment (Fig. 1). It is uncertain why the WTR amended at higher rates of P did not result in a greater release of P, but from a practical standpoint the reason for the similar P fertilizer equivalents for the WTR-P treatments in 1996 is not important. The higher rates of P amendment would not be necessary because the objective is to amend the WTR with the minimum amount of P required to make WTR into a material that supplies a small amount of P to plants. These data show that the lowest rate of amendment provided a fertilizer P equivalent of 127 kg P ha^{-1} , which is greater than the typical rate of P fertilizer $(10-40 \text{ kg P ha}^{-1})$ applied to most agronomic crops.



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The experiment in 1997 included four rates of P with less than $19.4 \,\mathrm{g} \,\mathrm{Pkg}^{-1}$ WTR added to the WTR. After mixing the P and the WTR in the tubs, there was no P in solution for P amendment rates less than $19.4 \,\mathrm{g} \,\mathrm{Pkg}^{-1}$ WTR, and only insignificant amounts of aqueous P were measured at the 19.4 and $38.8 \,\mathrm{g} \,\mathrm{Pkg}^{-1}$ WTR treatments (Table 2). The yields of the sorghum-sudan for the P amendment rates from 4.9 and $14.6 \,\mathrm{g} \,\mathrm{Pkg}^{-1}$ WTR were not statistically different from the application of unamended WTR (Fig. 2). This indicates there was little to no release of P from the WTR. The first significant yield increase came from the $19.4 \,\mathrm{g} \,\mathrm{Pkg}^{-1}$ WTR treatment. The fertilizer P equivalent for this treatment was $56 \,\mathrm{kg} \,\mathrm{Pha}^{-1}$ (Table 2). This is less than the amount of P released from the same treatment in 1996, however, the rate is still considerable in terms of agronomic rates of P application.

A P amendment rate between 14.6 and 19.4 g kg^{-1} seems to be the minimum rate of P amendment required to make this WTR a supplier of P. A P amendment rate within this range may make this WTR a supplier of P because it is about the rate of P amendment where the cationic polymer starts to adsorp P.^[21] A rate of about 12.7 g P kg⁻¹ WTR had no adsorption of P onto the polymer,^[21] but at higher rates of P, up to 40% of the P was adsorbed onto the cationic polymer in the WTR. Results from our field study show that little to no P was released when the WTR was amended with 14.6 g P kg⁻¹ WTR (Fig. 2). Almost all of the P should



Figure 2. Relationship between the dry matter yield of sorghum-sudan, various rates of P fertilizer, and P mixed with 7.8 Mg ha^{-1} WTR in 1997.

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have been adsorbed onto the Fe at this amendment rate,^[21] and only a small portion of the P would be released because most of the P should have formed strong covalent bonds with the iron. At the 19.4 g P kg^{-1} WTR amendment rate some P should be on the polymer and some on the Fe. It was speculated that most of the P available to the sorghum-sudan grass was released from the cationic polymer because the polymer forms weak electrostatic bonds with P whereas the Fe forms strong covalent bonds.

The amount of P released from the amended WTR at the $19.4 \,\mathrm{gP \, kg^{-1}}$ rate was different in each year (Table 2). Because this experiment was not designed to determine a mechanism for the rate of P release from the WTR, we cannot explain the different rates of release in the two years. Some factors that could have affected the release of P are the differences in the dry matter content and organic matter content of the WTRs, and the Fe and Al content of the WTRs. The WTR dry matter content was 34% in 1996 and 44% in 1997. Changes in the dry matter content can change the surface area of the WTR, which would change the adsorption-desorption properties of the WTR.^[29] The organic matter content was 17.3% in 1996 and 22.0% in 1997, and the Fe and Al content of the WTRs were slightly different in the two years (Table 3). Because the organic matter content and the metal content can change the adsorption-desorption properties of WTR, and because these components would likely interact with changes in surface area caused by the different dry matter contents, it is not surprising that there were different amounts of P released from the WTR in the two years.

Accurate predictions of the amount of P released from a WTR-P mixture likely will require more experiments to quantify the factors affecting the adsorption–desorption of P from WTR. These data suggest that for this WTR, a P amendment rate of 19.4 g P kg^{-1} WTR P was sufficient to make the WTR into a supplier of P and an amendment rate

	1996	1997
	$(\mu g/g)$	$(\mu g/g)$
Al	31,452	40,920
Ca	846	no value
Fe	54,396	53,990
Р	793	784

Table 3.	Total Al, Ca, Fe, and P concentrations for th	ıe
WTR in	1996 and 1997.	





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of 14.6 g P kg⁻¹ WTR supplied little to no P to the plants. Recent work by Pautler and Sims^[30] indicates that acid ammonium oxalate-extractable P (P_{ox}) may accurately predict P availability from materials like WTR that contain large amounts of Al and Fe.

The cost to amend this WTR with P would be much less than the cost to place the WTR in a landfill. The cost to amend WTR that contains 35% dry matter with triple superphosphate fertilizer (at 1.50 kg^{-1} P) is 10.18 Mg^{-1} for a rate of $19.4 \text{ gPkgWTR}^{-1}$. The tipping fee for placing WTR in a landfill in Connecticut is about 60 Mg^{-1} . If we assume the trucking costs are the same for delivery to a landfill as to a farmer's field, amending WTR with P would save about 50 Mg^{-1} . This savings assumes that the WTR contains no sand. If the WTR contains sand in similar amounts as the WTR delivered to us (71.2% in 1996 and 74.3% in 1997), the cost to amend the WTR with P would be incurred by the water treatment facility for equipment to mix P with WTR, but this simplified economic analysis suggests that amendment of some WTRs with P may be economically feasible.

CONCLUSIONS

Phosphorus mixed with WTR at a rate between 14.6 g P kg^{-1} WTR and 19.4 g P kg^{-1} WTR was sufficient to make this WTR a supplier of P for plant growth. The rate of P required to make this WTR a supplier of P was much less than predicted based on the amount of P adsorbed by the WTR in laboratory isotherms. The rate likely was less than predicted due to the adsorption and release of P from the cationic polymer used in the coagulant. The cost to amend this WTR with P was much less than the cost to place the WTR in a landfill. The cost of amending WTR with P will vary with the Fe, Al, and cationic polymer concentrations, the dry matter content and the sand content of the WTR. Amending a WTR that contains a cationic polymer with P may create a beneficial use for WTR as a source of P for plant growth.

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