A Method for Determining the Phosphorus Sorption Capacity and Amorphous Aluminum of Aluminum-Based Drinking Water Treatment Residuals

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ABSTRACT

A high amorphous aluminum or iron oxide content in drinking water treatment residuals (WTRs) can result in a high phosphorus (P) sorption capacity. Therefore, WTR may be used beneficially to adsorb P and reduce P loss to surface or ground water. The strong relationship between acid ammonium oxalate–extractable aluminum (Al_{ox}) and Langmuir phosphorus adsorption maximum (P_{max}) in WTR could provide a useful tool for determining P_{max} without the onus of the multipoint batch equilibrations necessary for the Langmuir model. The objectives of this study were to evaluate and/or modify an acid ammonium oxalate extraction of Al_{ox} and the experimental conditions used to generate P adsorption isotherms to strengthen the relationship between Al_{ox} and P_{max}. The oxalate extraction solution to WTR ratio varied from 40:1, 100:1, and 200:1. Batch equilibration conditions were also varied. The WTR particle size was reduced from <2 mm to <150 μm, and batch equilibration was extended from 17 h to 6 d. Increasing the solution to WTR ratio to 100:1 extracted significantly greater Al_{ox} at levels of >50 mg Al kg^{-1}. No additional increase was found at 200:1. Reducing WTR particle size from <2 mm to <150 μm increased P_{max} 2.46-fold. Extending the equilibration time from 17 h to 6 d increased P_{max} by a mean of 5.83-fold. The resulting empirical regression equation between the optimized Al_{ox} and P_{max} ($r^2 = 0.91$, significant at the 0.001 probability level) may provide a tool to estimate the P_{max} of Al-based WTR simply by measuring Al_{ox}. The accurate determination of WTR P_{max} and Al_{ox} is essential in using WTR effectively to reduce P loss in runoff or to reduce the solubility of P in agricultural soils or organic waste materials (biosolids, manure).

THE ROLE OF EXCESSIVE agricultural P in the degradation of surface water has been well documented (Correll, 1998; Daniel et al., 1998; Parry, 1998; Sharpley et al., 1994, 2003). Current strategies used to reduce P in agricultural runoff water (i.e., buffer strips, cover crops, terracing), though well suited for reducing sediment in runoff, may not be as effective at reducing dissolved P (Sharpley et al., 1994, 2003).

Because of their high P sorption capacity, many researchers have proposed the use of drinking water treatment residuals to reduce P loading into surface or ground water (Dayton et al., 2003; Gallimore et al., 1999; Novak and Watts, 2004). Drinking water treatment residuals are often rich in amorphous Fe or Al oxides because of the use of Fe or Al salts for coagulation of source water to remove turbidity and taste and to speed sedimentation. The American Society of Civil Engineers (1996) reported

that WTRs often contain 50 to 150 g amorphous oxide kg^{-1}. Several best management practices (BMPs) using WTR to reduce nonpoint source P pollution have been proposed. One is to surface-apply WTR to remove dissolved P from agricultural runoff water (Basta and Storm, 1997; Dayton et al., 2003; Gallimore et al., 1999; Haustein et al., 2000; Peters and Basta, 1996). Another beneficial use of WTR is to incorporate it into soil to reduce P solubility and prevent P leaching (Codling et al., 2000; Elliott et al., 2002a, 2002b; Novak and Watts, 2004; O'Connor et al., 2002; Peters and Basta, 1996). Beneficial use of WTR has also been expanded to reduce the solubility of P in organic soil amendments, such as manure or biosolids, by co-blending with WTR (Codling et al., 2000; Elliott et al., 2002b; Ippolito et al., 1999). Although all of these application methods have been successful in reducing P risk to water quality, a method is needed to determine the application amount of WTR required to achieve target reductions in P runoff or risk. Accurately determining WTR P sorption maximum is essential to effectively use it to reduce soluble P in agricultural runoff water, to reduce the solubility of P in agricultural soils or organic waste materials (biosolids, manure), and to calibrate WTR application.

The P sorption capacity of WTR varies widely due to differences in amorphous Al or Fe oxide content. Each treatment plant uses different source water and different treatment chemicals and processes, producing WTR with different chemical compositions and P sorption capacities. Dayton et al. (2003) examined the WTR components and/or chemical processes (precipitation, adsorption) that were thought to contribute to WTR P sorption. Using batch equilibration, P sorption isotherms were generated for 21 Al-based WTRs, and the linearized P_{max} was determined. A significant ($r^2 = 0.69$, significant at the 0.01 probability level) nonlinear relationship between the P_{max} and Al_{ox} content was found. No significant relationship was found between P_{max} and either soluble Ca ($r^2 = 0.008$) or clay content ($r^2 = 0.063$). In a simulated rainfall study using a subset of 11 of the Al-based WTRs, a significant relationship between runoff P reduction and Al_{ox} ($r^2 = 0.44$, significant at the 0.05 probability level) and P_{max} ($r^2 = 0.44$, significant at the 0.05 probability level) was also found (Dayton et al., 2003). Though significant, the low correlation coefficient for the relationship between P_{max} and Al_{ox} precluded it being a strong predictive tool for estimating P_{max}. Further, the nonlinearity of the relationship suggested that the amorphous metal oxide content may have

Abbreviations: Al_{ox}, acid ammonium oxalate–extractable aluminum; Fe_{ox}, acid ammonium oxalate–extractable iron; P_{max}, Langmuir phosphorus adsorption maximum; P_{ox}, acid ammonium oxalate–extractable phosphorus; PSI, phosphorus saturation index; WTR, water treatment residual.
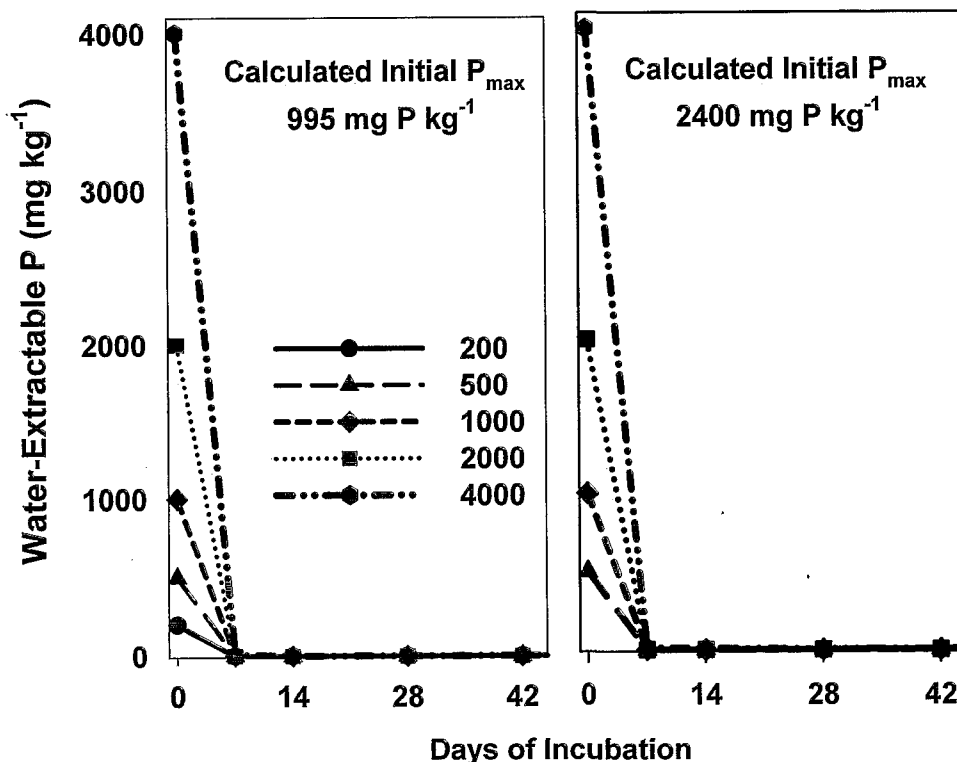
Fig. 1. Soluble P in two water treatment residuals (WTRs) spiked with KH_2PO_4 solutions and incubated up to 42 d. Initial Langmuir phosphorus adsorption maximum (P_{max}) values were obtained using batch equilibration of WTR (<2 mm) with standard P solutions ranging from 0 to 100 mg P L^{-1} for 17 h.

been underestimated. Additionally, a subsequent incubation study where 100 g WTR was equilibrated with P (KH_2PO_4) solutions to supply from 0 to 4 g P kg^{-1} WTR showed that, based on soluble P, WTR sorbed substantially more P than the calculated P_{max} predicted (Fig. 1).

Determining P_{max} from adsorption multipoint isotherms is a laborious procedure. An easier approach is to use a single WTR extraction with acid ammonium oxalate to estimate amorphous (e.g., reactive) Al oxide in WTR. In Al-based WTR, the relationship between amorphous Al and P_{max} could provide decision makers with a strong tool to easily estimate the P_{max} of any Al-based WTR to calibrate WTR application. However, accurately determining both P_{max} and amorphous Al are important to ensure that the relationship will be meaningful. Routine soil tests need to be examined and possibly modified to consider the unique properties of WTR. The beneficial use of WTR may provide an economic benefit to utilities and economic and environmental benefits to communities by preserving surface water quality.

PHOSPHORUS SORPTION MAXIMUM

Olsen and Watanabe (1957) proposed using the linearized Langmuir model to determine the P_{max} in soil. Since then, many researchers have reported the use of the Langmuir model to determine P adsorption maxima in soil. However, the experimental protocol used to measure P_{max} is not standardized. Nair et al. (1984) proposed a standard procedure for generating P sorption

isotherms for soil. They recognized that, while no single procedure is correct, sorption data could be compared between studies by standardizing a procedure. Their procedure recommended using 0.5 to 1 g soil and equilibrating (shaking) with 25-mL P solutions (in 0.01 M $CaCl_2$) ranging from 0 to 10 mg L^{-1} for 24 h at room temperature. Soil particle size was not specified (Nair et al., 1984). Using a 7-d equilibration and a <2-mm particle size, Borggaard et al. (1990) found a significant relationship between P_{max} and oxalate-extractable Al in 14 Danish soils. McLaughlin et al. (1981) also used a 7-d equilibration to examine the P sorption capacity of a variety of Fe- and Al-based materials of varying degrees of crystallinity. O'Connor et al. (2002) found that using a single point sorption isotherm with a 24-h equilibration was inadequate to express the sorption capacity of Fe and Al WTR. They conducted additional studies using multipoint isotherms with an 8-d equilibration and found that the P loading (5000 mg P kg^{-1}) was insufficient for the Al WTR and that the Fe WTR had a P sorption capacity of 3400 mg P kg^{-1} (O'Connor et al., 2002). Syers et al. (1973) used a 72-h equilibration and <2-mm particle size to generate P sorption isotherms. Fox and Kamprath (1970) found that an equilibration time of 6 d was necessary for P sorption stabilization in a highly weathered Hawaiian soil containing a large amount of Al_{ox}. Pautler and Sims (2000) found that in 41 agricultural soils the relationship between the total P sorption capacity and amorphous Al and Fe content was significant (r = 0.61, significant at the 0.01 probability level). After a 20-h equilibration, Börling et al. (2001) found

a highly significant ($r = 0.83$, significant at the 0.01 probability level) relationship between P_{max} and (Al_{ox} + Fe_{ox}) (where Fe_{ox} is acid ammonium oxalate–extractable iron) in 10 Swedish soils.

AMORPHOUS ALUMINUM

Because of their strong affinity for oxyanions, including phosphate, amorphous metal oxides are often used to predict P retention or mobility in soil. A P saturation index is often used to quantify P risk to surface water from agricultural soils. The phosphorus saturation index (PSI) is expressed as:

$$PSI = P_{ox}/(Al_{ox} + Fe_{ox}) \qquad [1]$$

where P_{ox}, Al_{ox}, and Fe_{ox} are oxalate-extractable P, Al, and Fe, respectively in mol kg^{-1} (Sims et al., 1998). This index has been widely adopted and is a useful tool to characterize potential P risk.

Pautler and Sims (2000) found that, in 41 agricultural soils in Delaware, P solubility increased significantly ($r^2 = 0.70$) as soil P saturation increased. Elliott et al. (2002b) found that the P sorbing ability of different types of WTR (Al-, Fe-, or Ca-based), when added to a sandy soil amended with biosolids, could be predicted based on the (Al_{ox} + Fe_{ox}) of the WTR, with Al > Fe > Ca. Many other researchers have observed a relationship between soil P saturation and labile or runoff P (Maguire et al., 2001; Maguire and Sims, 2002; Pote et al., 1996; Sharpley, 1995; Sharpley et al., 2003). Hooda et al. (2000) found that the degree of soil P saturation was significantly related to soil P desorption. Similarly, Lookman et al. (1995) found that after 880 h, soil P desorption for 44 German soils was inversely related to soil (Fe_{ox} + Al_{ox}). Lu and O'Connor (2001) found increased P retention in a sandy, low P sorbing Florida soil by the addition of biosolids high in oxalate-extractable (Al + Fe). Decreasing the PSI of an organic waste by

co-blending with a WTR high in amorphous oxide is a potentially useful way to decrease the PSI and therefore P solubility in the waste material.

The strong relationship between Al_{ox} and P_{max} can be a useful tool in utilizing WTR effectively. Routine methods are available for determining Al_{ox} in soil. However, amorphous metal oxide is often considerably higher in WTR (>50 g kg^{-1}) than in soil. Routine soil tests must be evaluated to discern their ability to accurately measure the amorphous Al, Fe, or P in WTR. Standardizing the experimental conditions used to measure amorphous Al, Fe, and P in WTR would allow for comparisons to be made between WTR studies. The aim of this study is to propose a method using Al_{ox} to predict the sorption capacity of WTR. Specific objectives of this study are to (i) evaluate and/or modify the acid ammonium oxalate extraction method for accurate determination of Al_{ox} in WTR, (ii) evaluate and/or modify experimental conditions used to generate P adsorption isotherms to accurately measure P sorption maxima in WTR, and (iii) identify experimental conditions that strengthen the relationship between Al_{ox} and P_{max}.

MATERIALS AND METHODS

Eighteen WTRs were collected from utilities in Oklahoma and Pennsylvania. All WTRs were air-dried and crushed to <2.0 mm. All chemical analyses and determination were performed in triplicate. Blanks and check samples were included for all chemical determinations to meet quality assurance and quality control (QA/QC) requirements.

Chemical and Physical Characterization

A summary of WTR chemical and physical characteristics is presented in Table 1. Residual pH was determined in a 1:2 WTR to 0.01 M CaCl$_2$ solution using a glass electrode (McLean, 1982). Electrical conductivity (EC) was determined in a 1:2 WTR to deionized water solution (Rhoades, 1996). Total nitrogen and carbon were determined by the Dumas method

Table 1. Chemical and physical characteristics of drinking water treatment residuals (WTRs).

WTR	pH	EC†	N‡	C‡	Sand	Silt	Clay	Fe§	P§	PSI¶
		dS m^{-1}	—— g kg^{-1} ——		—————— % ——————			—— g kg^{-1} ——		%
1	7.1	0.63	10.1	80.0	10.9	61.8	27.3	1.91	1.16	1.04
2	7.7	0.54	7.10	75.0	80.3	14.5	5.20	1.46	0.66	0.64
3	7.0	1.09	18.4	128	76.4	15.7	7.90	10.4	0.82	1.19
4	7.8	0.60	8.20	69.0	81.7	13.1	5.20	6.27	1.99	2.70
5	7.8	1.08	12.1	65.0	70.4	27.8	1.80	5.75	1.44	0.99
6	7.6	0.37	1.30	17.0	43.1	16.9	40.0	0.99	1.13	2.19
7	7.0	0.27	5.60	46.0	84.8	9.80	5.40	9.13	0.58	1.17
8	6.9	0.40	4.80	62.0	76.6	14.5	8.90	11.4	0.94	1.60
9	5.3	0.43	5.90	78.0	84.9	11.1	4.00	5.04	0.30	0.25
10	7.5	1.03	14.6	149	66.4	27.0	6.60	3.49	2.21	6.24
11	7.2	0.67	7.90	86.0	81.9	10.6	7.50	3.10	0.97	6.34
12	7.3	0.87	0.05	47.8	60.8	30.3	8.90	0.12	0.37	0.79
13	7.0	0.22	7.30	60.0	91.2	7.10	1.70	4.35	1.86	2.05
14	7.0	0.80	7.90	63.0	83.1	11.4	5.50	3.68	1.94	2.80
15	6.6	0.22	2.80	23.0	59.1	17.8	23.1	2.57	0.46	2.62
16	7.1	1.23	7.41	100	66.9	31.8	1.30	9.98	0.67	0.37
17	7.0	2.60	8.08	100	75.6	18.5	5.90	12.3	1.45	1.06
18	7.2	0.96	6.37	72.7	22.9	67.1	10.0	1.19	6.02	3.73
Minimum	5.3	0.22	0.05	17.0	10.9	7.10	1.30	0.12	0.30	0.25
Maximum	7.8	2.60	18.4	149	91.2	67.1	40.0	12.3	6.02	6.34
Mean	7.1	0.79	7.55	73.4	67.6	22.6	9.79	5.17	1.39	2.10

† Electrical conductivity.
‡ Total content, dry combustion.
§ Oxalate-extractable, using a 100:1 oxalate solution to WTR dilution.
¶ Phosphorus saturation index.

using a Carlo Erba (Milan, Italy) 1500 series dry combustion analyzer (Bremner and Mulvaney, 1982). Particle size analysis was determined using the pipet method (Gee and Bauder, 1986). Extractable Fe (Fe_{ox}) and P (P_{ox}) were determined by acid ammonium oxalate extraction (McKeague and Day, 1993) using a 100:1 oxalate solution to WTR ratio. Inductively coupled plasma atomic emission spectroscopy (ICP–AES) was used for subsequent analysis of Fe and P. The PSI was determined as previously shown in Eq. [1] (Sims et al., 1998).

Amorphous Aluminum

Amorphous Al (Al_{ox}) was determined by variations of an acid ammonium oxalate extraction (McKeague and Day, 1993). The extraction was performed with a buffered solution of 0.2 M ammonium oxalate [$(NH_4)_2C_2O_4$] and 0.2 M oxalic acid ($H_2C_2O_4$) adjusted to pH 3. All WTRs were crushed to <150 μm, and an extraction time of 4 h was used. The amount of extractable Al was compared at three oxalate solution volume to WTR mass ratios. The three ratios used were the recommended 40:1 and also 100:1 and 200:1. Extracted Al, Fe, and P were quantified using ICP–AES.

Phosphorus Sorption Capacity

Phosphorus sorption isotherms were generated by batch equilibration with standard phosphorus solutions using reagent-grade KH_2PO_4 in deionized water on an end-on-end shaker (1 g WTR to 10 mL P solution). Standard P solutions ranged from 0 to 3.5 g P L^{-1}. The P_{max} was determined using the linearized Langmuir model (Sparks, 1995). The conditions of the batch equilibration were varied for the determination of P_{max}. Residual particle size was reduced from the initial <2 mm (Dayton et al., 2003) to <150 μm. A separate study using five WTRs was conducted to determine when pseudo-equilibrium between WTR and P equilibration solution was established. In this study, WTRs (1 g, <150 μm) were equilibrated with P (KH_2PO_4) solutions (10 mL P solution) by shaking from 1 to 19 d. All solution P measurements were made using ICP–AES.

Serial Desorption

To evaluate the final calculated P_{max}, five WTRs were used in a desorption study. The WTR (1 g, <150 μm) was equilibrated with 10 mL of P solution for 6 d to produce a WTR containing slightly larger amounts of sorbed P than the calculated P_{max}. The P-spiked WTRs were subjected to serial extractions with 25 mL of 0.1 M KCl at 10 min, 2 h, 24 h, and then daily through 5 additional days. The cumulative P desorbed was measured and subtracted from the initial P concentration to calculate final P sorbed to WTR.

RESULTS AND DISCUSSION
Chemical and Physical Characterization

An overview of the chemical and physical characteristics of the 18 WTRs is presented in Table 1. Residual pH ranged from 5.3 to 7.8 with a mean of 7.1. A neutral pH is to be expected since pH adjustment is routinely done during drinking water treatment. The electrical conductivities (EC) were all well below the 4.0 dS m^{-1} associated with saline soil (Brady and Weil, 1996) for salt-sensitive plants. The WTR EC ranged from 0.22 to 2.60 with a mean of 0.79. Total N ranged from 0.05 to 18.4 g kg^{-1} with a mean of 7.55 g kg^{-1}. Total carbon ranged from 17 to 149 g kg^{-1} with a mean of 73.4.

Table 2. Comparison of acid ammonium oxalate–extractable aluminum (Al_{ox}) content and the Langmuir phosphorus adsorption maximum (P_{max}) measured under different conditions.

| WTR† | Al_{ox} | | P_{max} | | |
	40:1‡	100:1‡	Initial§	Crushed¶	Final#
	g kg^{-1}		g P kg^{-1}		
1	75.3	98.5	3.54	9.20	27.1
2	71.2	104.5	2.40	9.35	30.6
3	52.9	54.9	2.04	6.90	24.1
4	57.3	63.6	1.63	6.82	20.1
5	73.6	124	2.82	9.37	27.5
6	37.9	42.0	1.22	12.5	15.6
7	40.1	38.8	0.85	2.40	19.5
8	43.9	45.3	1.33	2.66	16.4
9	NA††	101	5.14	6.71	30.0
10	30.2	31.0	2.54	2.54	18.6
11	30.7	24.6	1.03	3.63	14.2
12	44.5	32.5	2.70	3.68	17.3
13	53.3	58.8	1.00	3.14	21.0
14	55.5	58.7	0.72	6.93	20.2
15	15.3	13.9	0.66	1.84	10.4
16	79.3	165	9.60	28.3	37.0
17	80.0	114	16.5	28.7	29.3
18	84.0	144	15.0	29.5	33.5
Minimum	15.3	13.9	0.66	1.84	10.4
Maximum	84.0	165	16.5	29.5	37.0
Mean	54.5	73.1	3.93	9.68	22.9

† Water treatment residual.
‡ Oxalate solution to WTR ratio.
§ <2-mm Fraction, 17-h equilibration.
¶ <150-μm Fraction, 17-h equilibration.
\# <150-μm Fraction, 6-d equilibration.
†† Not available.

The high total C levels found in many WTRs may be attributed to carbonate additions for pH adjustment, polymer addition during water treatment or dewatering, or perhaps to additions of activated carbon, which is used to remove taste and odor from source water. The clay content of the 18 WTRs ranged from 1.30 to 40.0% with a mean of 9.79%. The oxalate-extractable Fe_{ox} ranged from 0.12 to 12.3 g kg^{-1} with a mean of 5.17 g kg^{-1}. By comparison, the mean Al_{ox} content (Table 2) is higher than the Fe_{ox} by a factor of 29.3 on a molar basis. The WTR oxalate-extractable P_{ox} ranged from 0.30 to 6.02 g kg^{-1} with a mean of 1.39 g kg^{-1}. Not surprisingly the WTR P saturation index was low, ranging from 0.25 to 6.34% with a mean of 2.10%.

Amorphous Aluminum

McKeague and Day (1993) recommended an oxalate solution to soil ratio of 40:1 for soil suspected of being high (>20 g kg^{-1}) in amorphous Al or Fe. However, the procedure used by Dayton et al. (2003) for measuring Al_{ox} (40:1) and P_{max} (initial P_{max}) for the 18 materials in this study resulted in a significant ($r^2 = 0.68$, significant at the 0.001 probability level) nonlinear relationship between initial P_{max} and amorphous Al (40:1) (Fig. 2). The relationship between initial P_{max} and Al_{ox} becomes highly nonlinear at >75 g kg^{-1} Al_{ox}, suggesting that at high WTR Al concentrations the oxalate in the extraction solution may be limiting and not capable of extracting all of the amorphous Al in the WTR. This was confirmed by adjusting the oxalate solution to WTR ratio used in the extraction. Amorphous Al extracted (Table 2) with the suggested solution to WTR ratio of 40:1 ranged from 15.3 to 84.0 g Al kg^{-1} with a mean of
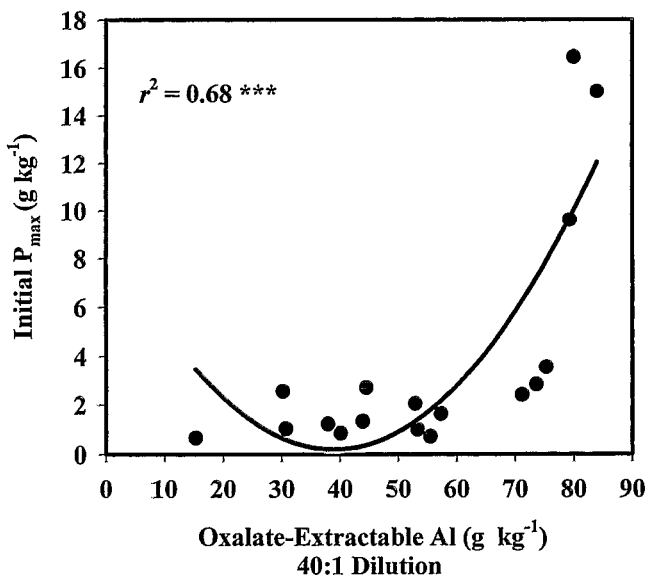
Fig. 2. Relationship between initial Langmuir phosphorus adsorption maximum (initial P_{max}, <2 mm, and 17-h equilibration) and acid ammonium oxalate-extractable aluminum (Al_{ox}, 40:1 solution to water treatment residual [WTR] ratio) for 18 Al-based WTRs.

54.5 g kg^{-1}. By increasing the solution to WTR ratio (Table 1) to 100:1, the Al_{ox} ranged from 13.9 to 165 g kg^{-1} with a mean of 73.1. Figure 3 shows that at oxalate-extractable Al levels below 50 g kg^{-1} the slope is approximately unity and there is little difference between the Al_{ox} measured using the two conditions. However, at higher levels of Al (>50 g kg^{-1}), the slope is >1 (Fig. 3) showing that more Al_{ox} is extracted with a solution to WTR ratio of 100:1 than 40:1.

To determine if a further increase in the solution to WTR ratio of >100:1 would result in additional Al_{ox} extraction, a solution to WTR ratio of 200:1 was also
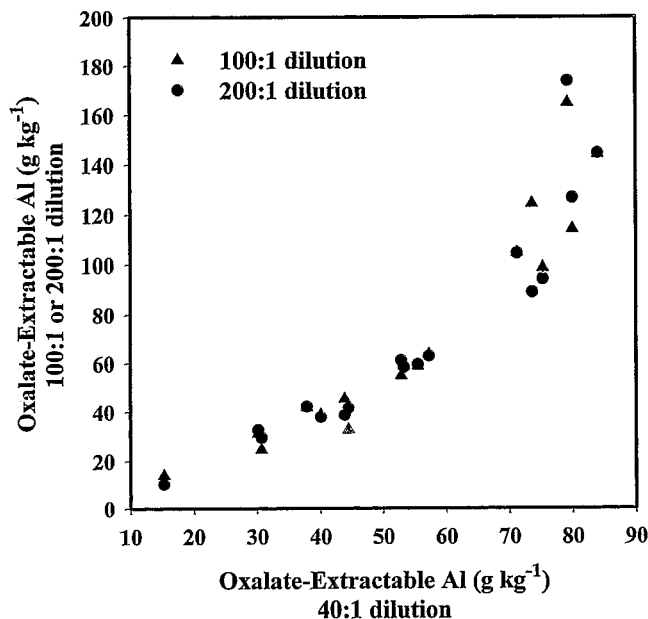

Fig. 3. Relationship between oxalate-extractable Al (100:1 or 200:1 solution to water treatment residual [WTR] ratio) and oxalate-extractable Al (40:1 solution to WTR ratio) for 18 Al-based WTRs.
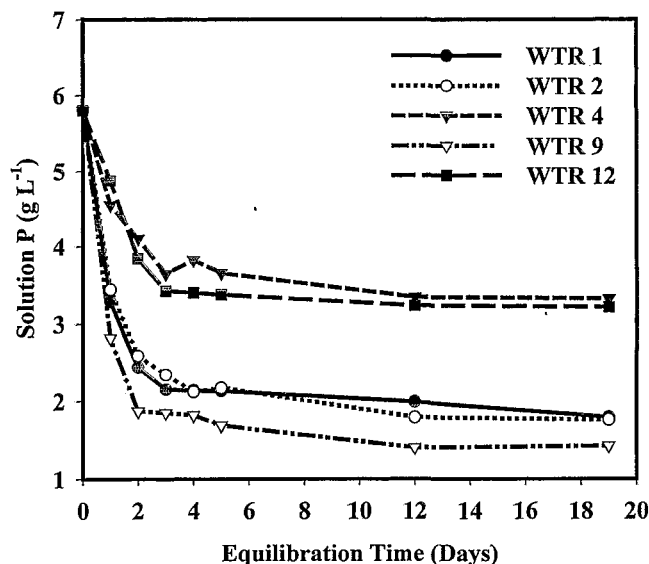

Fig. 4. Solution phosphorus versus time for five Al-based water treatment residuals (WTRs) equilibrated for 19 d.

included. Increasing the solution to WTR ratio to 200:1 did not significantly increase the amount of Al_{ox} extracted compared with Al_{ox} extracted by the solution to WTR of 100:1 (Fig. 3). The McKeague and Day method was designed for use on soil and should be modified to account for the often considerably greater amorphous oxide content (>50 g kg^{-1}) found in most WTRs.

A more accurate determination of Al_{ox} will improve the relationship between P_{max} vs. Al_{ox} and may allow an easy and reliable way to predict P_{max}. Accurate measurement of amorphous oxide is also important in co-blending WTR with an organic waste (biosolids, manure) or mixing WTR into high P soil. Decreasing the PSI of an organic waste or high P soil by blending with WTR high in amorphous oxide is a potentially useful way to decrease P solubility. An accurate Al_{ox} measurement is essential to predict the PSI of blended Al-based WTR.

Phosphorus Sorption Capacity

Improving the relationship between P_{max} vs. Al_{ox} in Al-based WTR is a prerequisite for using Al_{ox} to predict P_{max} without the onus of the batch equilibration required to generate P sorption isotherms. The P_{max} values were determined using the linearized Langmuir model (Sparks, 1995) and using the initial batch equilibration conditions to generate P sorption isotherms (initial P_{max}, <2-mm WTR and an equilibration time of 17 h) described by Dayton et al. (2003). Under these initial conditions, the initial P_{max} ranged from 0.66 to 16.5 g P kg^{-1} with a mean of 3.93 g kg^{-1} (Table 2) for the 18 WTRs in this study. However, in a subsequent incubation study (Fig. 1) of WTR incubated with added P solutions, considerably more P than predicted by the calculated initial P_{max} was sorbed by the WTR. Some of the variation found by Dayton et al. (2003) in the relationship between the initial P_{max} and Al_{ox} (40:1 solution to WTR) ($r^2 = 0.69$, significant at the 0.01 probability level) may have been due to observed differences in WTR slaking when ex-
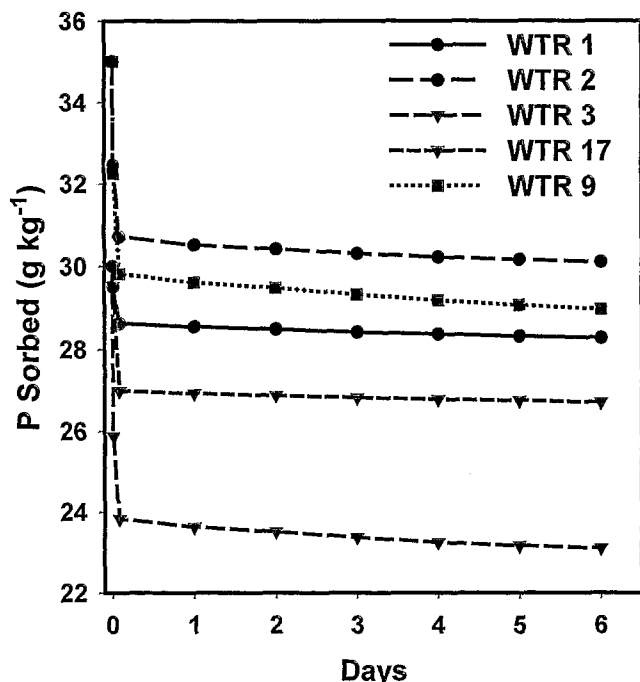
Fig. 5. Phosphorus sorbed versus time for five Al-based water treatment residuals (WTRs) extracted periodically with 0.1 M KCl over 6 d.

posed to equilibration solutions used to generate P sorption isotherms. Slaking may increase the surface area available to react and increase P sorption. Slaking of WTR occurs naturally due to weathering in the field, but differences in slaking during a short-term batch equilibration may be a source of variability. To mitigate the effect of slaking, WTRs were crushed and sieved to <150 μm. Using the same 17-h equilibration time, the P_{max} after crushing (crushed P_{max}) ranged from 1.84 to 29.5, representing a mean increase of 2.46-fold (Table 2) over the initial P_{max}.

To ensure adequate time is allowed to establish pseudo-equilibrium during the batch equilibration, P sorption was examined on a subset of five WTRs using equilibration times of from 1 to 19 d. Solution P decreased rapidly for the first 4 d of equilibration and then remained relatively constant (Fig. 4). Figure 4 shows that the 17-h equilibration time used in Dayton et al. (2003) underestimated WTR P sorption capacity. Little change in P sorption occurred after 5 d of equilibration (Fig. 4). Six days were selected as the equilibration time for generating P sorption isotherms to be used to generate P_{max} (final P_{max}). With the reduced particle size (<150 μm) and the time for equilibration increased to 6 d, the final P_{max} ranged from 10.4 to 37.0 g P kg^{-1} with a mean of 22.9 g kg^{-1} (Table 2), representing a mean increase by a factor of 5.83 over the initial P_{max}.

A serial desorption study (Fig. 5) was used to corroborate that the calculated final P_{max} represented stable oxide-bound P and was not the result of less stable surface precipitation or exchangeable P. Most of the desorbable P was removed in the 10-min rinse step and at 2 h (Fig. 5). Very little P was removed through subsequent extractions. The P retained by the WTR after 6 d of serial desorption ranged from within 91 to 104% of the calcu-
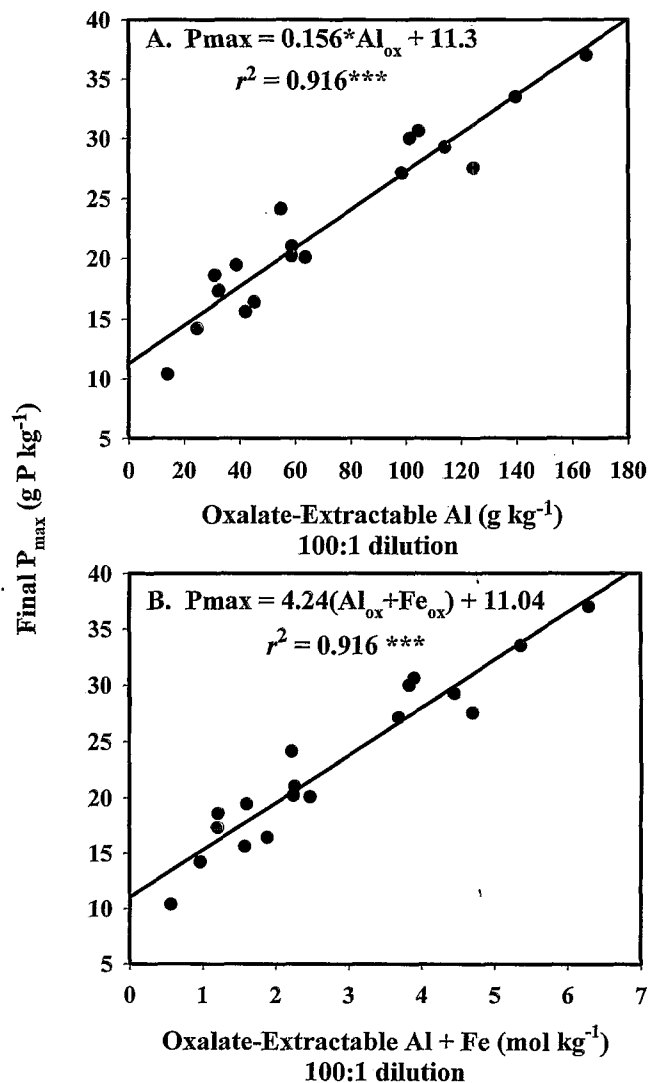

Fig. 6. Relationship between final Langmuir phosphorus adsorption maximum (final P_{max}, <150 μm and 6 d equilibration) and (A) acid ammonium oxalate–extractable aluminum (Al_{ox}, 100:1 to solution to water treatment residual [WTR] ratio) and (B) acid ammonium oxalate–extractable aluminum + iron (Al_{ox} + Fe_{ox}), 100:1 to solution to WTR ratio for 18 Al-based WTRs.

lated final P_{max} (Fig. 5). This demonstrates the stability of P binding and corroborated the final P_{max} measurement.

With Al_{ox} measured at a solution to WTR ratio of 100:1 and P_{max} measured on the <150-μm particle size and using a 6-d equilibration, the relationship P_{max} vs. Al_{ox} improved substantially ($r^2 = 0.916$, significant at the 0.001 probability level) (Fig. 6A). The empirical regression equation:

$$P_{max} \ (g \ kg^{-1}) = 0.156 \times Al_{ox} \ (g \ kg^{-1}) + 11.3 \quad [2]$$

for this data set may provide a tool to estimate the P_{max} of Al-based WTR simply by measuring Al_{ox}. For this data set, the addition of Fe_{ox} (Al_{ox} + Fe_{ox}) did not improve ($r^2 = 0.916$, significant at the 0.001 probability level) the relationship (Fig. 6B). Many more WTRs will need to be examined and certainly field-testing will need to be done to validate these proposed procedures.

CONCLUSIONS

The strong relationship between Al_{ox} and P_{max} can be a useful tool in utilizing WTR effectively. The accurate determination of WTR P_{max} and Al_{ox} is essential in using WTR effectively to reduce soluble P in agricultural run-off water, to reduce the solubility of P in agricultural soils or organic waste materials (biosolids, manure), to enhance the utility of PSI, and to calibrate WTR application. Often, WTR amorphous metal oxide is considerably higher (>50 g kg^{-1}) in WTR than in soil and so is the P sorption capacity. Routine soil tests should be evaluated to discern if they are suitable to measure WTR P sorption parameters. Standardizing the experimental conditions used to measure P sorption parameters in WTR would allow for comparisons to be made between WTR studies. Optimizing the measurement of Al_{ox} and P_{max} should enhance the usefulness of WTR as a tool to reduce the risk posed by agricultural P to surface water.

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