WATER TREATMENT RESIDUALS AGGREGATE SIZE INFLUENCES PHOSPHORUS SORPTION KINETICS AND P_{MAX} VALUES

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Drinking water treatment residuals (WTRs) are used as a soil amendment to minimize off-site P movement and increase a soil's phosphorus (P) sorption capacity. The aggregate size of WTRs may affect sorption kinetics and P sorption maxima (P_{max}) values. We hypothesize that finer-sized WTRs aggregates will have higher kinetic sorption rates and P_{max} values than coarser-size aggregates. The objectives were to determine WTRs aggregate size effects on kinetic rates of P sorption, on the magnitude of P_{max} values, and the time necessary to reach equilibrium with P. A WTR sample was ground and sieved into five aggregate size ranges (<0.5, 0.5 to 1.0, 1.0 to 2.0, 2.0 to 4.0, and >4 mm). Phosphorus sorption isotherms for each aggregate size range were determined as a function of time (between 24 and 120 h). Reaction rate constants (k) were determined by using a first-order reaction equation and P_{max} values for each aggregate size range were calculated from the linear form of the Langmuir equation. The <0.5-mm WTRs aggregates had the highest k values, and the rates decreased with an increase in aggregate size. All isotherms showed that aggregate size ranges reached equilibrium between 72 and 96 h. There was a strong linear (r^2 between 0.78 and 0.96) and significant ($P < 0.05$) relationship between C (C = mean equilibrium P conc.) and C Q^{-1} (Q = P sorbed). Coarse-sized WTR aggregates (between 1.0 and >4.0-mm) had P_{max} values of <94 mg g^{-1}, whereas fine-sized (<1.0-mm) aggregates had values >98 mg g^{-1}. Aggregate size has an important influence on WTRs P sorption characteristics; therefore, it is recommended that aggregate size should be strongly considered when determining P isotherms or using residuals as a soil amendment to reduce non–point source P contamination of surface water bodies. (Soil Science 2005;170:425–432)

Key words: Aggregates, alum, soil amendment, phosphorus sorption, water treatment residuals.

P HOSPHORUS movement into nutrient-sensitive surface waters can result in eutrophication and lower water quality. To lower the incidence of eutrophication, novel chemical-based best management practices (BMPs) that reduce off-site P movement from P-enriched soils have been successfully used. Chemical-based

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BMPs, such as seeding the soil with inorganic amendments capable of sorbing P, have been demonstrated to reduce runoff P losses (Codling et al., 2002; Daniels et al., 1999; Dayton et al., 2003) and to reduce soil extractable P concentrations (Dayton et al., 2003; Peters and Basta, 1996) from manure treated soils. The inorganic amendments used in these studies were water treatment residuals (WTRs), a byproduct produced during drinking water purification of ground and surface water. Water treatment residuals are formed when silt and clay-size particles are flocculated by adding alum or Fe-salts to raw water. Using these chemicals caused the WTRs surfaces to be enriched in Al- and Fe-oxide and hydroxides functional groups.

This enrichment increases the WTRs affinity and capacity to sorb P (ASCE, 1996; Dayton et al., 2003).

The P_{max} values of alum-based WTRs can vary substantially. Novak and Watts (2004) reported high P_{max} values (85 to 175 mg P g^{-1}) for Al-based WTRs, whereas Dayton et al. (2003) reported lower P_{max} values (0.3 to 5.1 mg P kg^{-1}). The heterogeneity in WTRs P_{max} values is not uncommon considering that water treatment facilities will vary concentrations of alum, depending on the quality of the raw water (Gallimore et al., 1999; Novak and Watts, 2004).

In the reports cited above, P sorption studies were conducted by using WTR aggregates that were 2 mm or less in diameter. Aggregates in this size range are commonly used in laboratory sorption experiments because this threshold diameter separates soil particles from the rock fraction (Gee and Bauder, 1986; Soil Survey Staff, 1951). Using this aggregate size fraction in sorption experiments may introduce some bias in the results. Phosphorus maxima values obtained from a sample composed of heterogeneous aggregate size ranges can be corrected for the conditions. However, the results may not be a true indication of their full P sorption potential. For instance, the increase in crystallinity of hydrous ferric oxide (e.g., goethite) results in a surface area decrease causing lower P sorption (Lijkema, 1980; McLaughlin et al., 1981). Therefore, it can be argued that the surface area of a clay or silt-sized particle with oxide and hydrous oxide functional groups will increase with a decrease in aggregate size. If this is a valid premise, then the WTRs P_{max} values should increase as the WTRs aggregate size decreases.

The P sorption process in well-aggregated soils is generally described by an initial rapid adsorption reaction on surfaces followed by slower kinetic reactions (Linquist et al., 1997; Wilson et al., 2004). The fast reaction is due to electrostatic interactions between P and charged functional groups on solid phases. The slower reactions are due to intraparticle diffusion in meso- and micropores of particles (Makris et al., 2004a; 2004b) and by the high kinetic nature of P sorption by oxide and hydroxide surfaces (Wilson et al., 2004). Diffusional processes into smaller pore spaces contained within larger-size aggregates will increase the time required for a uniform distribution of sorbed P (Linquist et al., 1997; Makris et al., 2004a; 2004b). This finding

means that in well-aggregated field soils, larger-sized aggregates can have vastly different rates of P equilibration compared with smaller-sized aggregates.

Alum-based WTRs have been used as a soil amendment to reduce off-site P movement and improve the P sorption capacity of sandy soils. The P sorption capability of these alum-based WTRs has been assessed under common laboratory conditions using 2-mm and less sieved material and 24-h incubation periods. Alum-based WTRs, composed of different aggregate sizes, may have distinct P sorption capabilities. We hypothesize that the kinetic rates and P_{max} values of WTRs will increase with a decrease in WTR aggregate size and that the larger aggregates will require more time to reach P equilibrium than smaller aggregates. Our objectives were to determine the effects of WTR aggregate size ranges on P sorption kinetic rate constants, on the magnitude of P_{max} values, and the time necessary to reach equilibrium with P.

MATERIALS AND METHODS

Collection of WTRs, Sieving of Aggregates, and Background P Extraction

A WTR sample was collected from a North Carolina water treatment facility in April 2002. The treatment facility withdraws raw water from the Nuese River and uses liquid alum to flocculate impurities. Details concerning the raw water chemistry, alum concentrations used during the process, and chemical properties of the purified water and WTR have been published (Novak and Watts, 2004).

A bulk WTR sample was air-dried and ground. After grinding, the aggregates were passed through a series of sieves to collect aggregates in the >4.0, 2.0 to 4.0, 1.0 to 2.0, 0.5 to 1.0, and <0.5-mm in diameter. The total phosphorus (TP) content of each aggregate size range was quantified by using the $CuSO_4$ + H_2SO_4 digestion method of Gallaher et al. (1976), and P was measured by using the ascorbic acid procedure (Greenberg et al., 1992) with a Technicon AutoAnalyzer (Tarrytown, NY).

P Sorption Kinetic Rate Constants and P Equilibration Times

Kinetic rate constants and P equilibration time periods for the WTRs aggregates were determined by setting up a series of triplicate 25-ml glass tubes containing 1 g of aggregates that were horizontally shaken for 24, 48, 72, 96, and

120 h with a 20-g P L^{-1} (made from KH$_2$PO$_4$) solution dissolved in 0.01M CaCl$_2$. This P concentration was chosen to ensure measurable P in the equilibrium solution because lower P concentrations were almost 100% sorbed in previous WTRs P sorption experiments (Novak and Watts, 2004). After shaking, the tubes were centrifuged at 680g for 10 minutes, and the supernatant was passed through a 0.45-μm nylon syringe filter. Phosphorus concentrations in the equilibrium solution were quantified by using the colorimetric method of Murphy and Riley (1962) on a Technicon AutoAnalyzer. The mean amount of P sorbed by each aggregate size range per incubation period was calculated, and significant differences between these means were compared by using a least significance difference test, using SAS v. 8.0 (SAS Inst., Cary, NC). The aggregates were judged to be at equilibrium with P when there were no significant differences in the mean P sorption values between time periods.

The kinetic rate constants for P sorption by aggregates were determined by using the integrated form of the first-order equation (Sparks, 1995):

$$\log_{10}[A]_t = \log_{10}[A]_o - kt/2.303 \qquad (1)$$

where, $[A]_o$ = initial P equilibrium concentration, and $\log_{10}[A]_t$ = P equilibrium concentration at time t (expressed in h), and k = kinetic

rate constant. To ascribe a first-ordered model to the P sorption reactions, the $\log_{10}[P]_t$ vs t was plotted, and the slope of the regression line was tested for linearity using a Student's t test (Zar, 1999). A true first-order kinetic relationship between these variables should plot as a straight line (Sparks, 1995).

P Sorption Isotherms and P_{max} Determination

Statistical analyses of the P sorption means versus incubation time showed that three of five aggregates size ranges reached equilibrium conditions after 72 h. Consequently, the P_{max} values for each WTRs aggregate size range were determined by using a modified batch equilibration technique (Nair et al., 1984), which involved conducting the incubation for 72 instead of 24 h. One gram of aggregates were placed into triplicate 25-ml glass centrifuge tubes, and 10 ml of P solution (10 to 35 g P L^{-1}) was added. The P sorption isotherms were plotted by using the mean quantity of P sorbed (Q mg g^{-1}) and the mean equilibrium P concentration (C, mg L^{-1}). The sorption data were also plotted by using the linear version of the Langmuir equation:

$$CQ^{-1} = (1/P_{max})(C) + 1/(k)(P_{max}) \qquad (2)$$

where P_{max} (mg g^{-1}) is the P sorption maxima, and k (L mg^{-1}) is a sorption constant relative to P binding energy (Olsen and Watanabe, 1957).
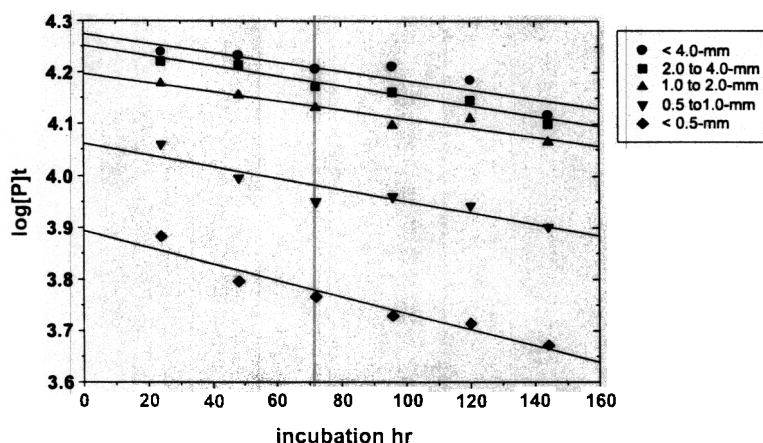

Fig. 1. Log$_{10}$ [P]$_t$ versus incubation hours for the water treatment residuals aggregate size range and linear regression relationship between these variables.
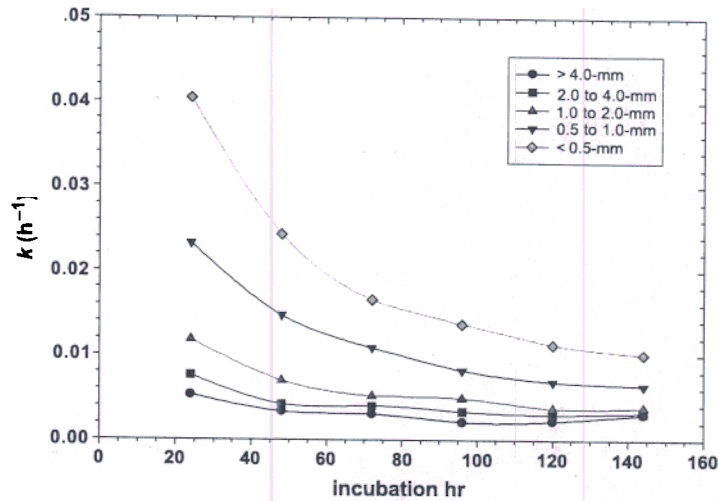
Fig. 2. P sorption rate constants (k) for each aggregate size range during incubation time course.

A linear regression analyses was performed between C and C Q^{-1}, and P_{max} values were calculated from the inverse of the slope from the regression equation. Previously sorbed P (as TP) was subtracted from all isotherms values before plotting to obtain corrected P_{max} values. The regressions were determined by using SigmaStat version 3.0 software (SSPS Corp., Chicago, IL).

RESULTS AND DISCUSSION

P Equilibration Kinetics With WTR Aggregates

To establish if the kinetic relationships of WTR aggregate P sorption were correctly described by using a first-ordered reaction model, plots of $log_{10}[P]_t$ versus t were constructed, and the slopes for these relationships were tested for linearity. This relationship for all aggregate size ranges is shown in Fig. 1. The linear regression relationship between $log_{10}[P]_t$ versus t were all significant ($P < 0.05$) and fit the data very well (r^2 values between 0.83 to 0.95). The slope values from the five regression equations were found to be significantly linear (Student's t test, $P < 0.05$). This finding indicates that the kinetic reaction between P and the WTR aggregates under the experimental conditions imposed was correctly ascribed by using a first-order model (Sparks, 1995).

The soil P sorption process is generally described as an initial rapid reaction primarily on surfaces followed by a slower set of reactions due to P migration into interstitial pores within aggregates (Makris et al., 2004a; 2004b; Wilson

et al., 2004). Phosphorus sorption data presented here follows those trends, in that initial P sorption was kinetically rapid (high k values), followed by a slowing kinetic rate (Fig. 2). The k values for all aggregate size ranges throughout the entire time course ranged between 0.04 and 0.002. The finer-sized aggregates (<0.5 and 0.5 to 1.0 mm) had higher k values that the coarser-sized aggregates (>1.0 mm), with the k value for the <0.5-mm aggregates 8-fold higher that the larger >4.0-mm aggregates at 24 h. This trend is related to the higher surface area of the finer-size aggregates simply having more surface area to rapidly sorb P compared with the coarser-sized aggregates. All k values decline through the time course, which may be due to saturation of surface P binding sites and the slower migration into interstitial aggregate pores.

| TABLE 1

Mean P sorbed by water treatment residuals aggregate size ranges with significance determined by least significant difference test

Aggregate Size	Mean P Sorbed (mg g⁻¹) at h					
	24	48	72	96	120	LSD

P Equilibration Time Periods for the WTR Aggregates

The three largest aggregate size classes (>4.0, 2.0 to 4.0, and 1.0 to 2.0 mm) had mean P sorption values that were not significantly different at 24 and 48 h (Table 1). For the >4.0-mm size aggregates, P equilibrium was confirmed at 48 h because there were no significant differences in mean P sorbed when compared with values at 72 and 96 h. The 2.0 to 4.0-mm aggregates had reached equilibrium after 72 h because mean P sorbed was not significantly different compared with values at 96 and 120 h. Aggregates in the 1.0- to 2.0-mm

size range reached P equilibrium at 96 h, with no significant differences in mean P sorbed when compared with values at 120 h. For the finer aggregate size ranges (<0.5 and 0.5 to 1.0 mm), P sorption continued to increase between 24 and 48 h. Equilibrium with P was achieved after 72 h for the smallest aggregate size ranges.

Most aggregates size ranges (3 of 5) required 72 h of incubation to reach equilibrium with P. Only the 1.0- to 2.0-mm aggregate size range required 96 h of incubation to reach equilibrium. The extra 24 h required by this aggregate size range to reach equilibrium with P may be
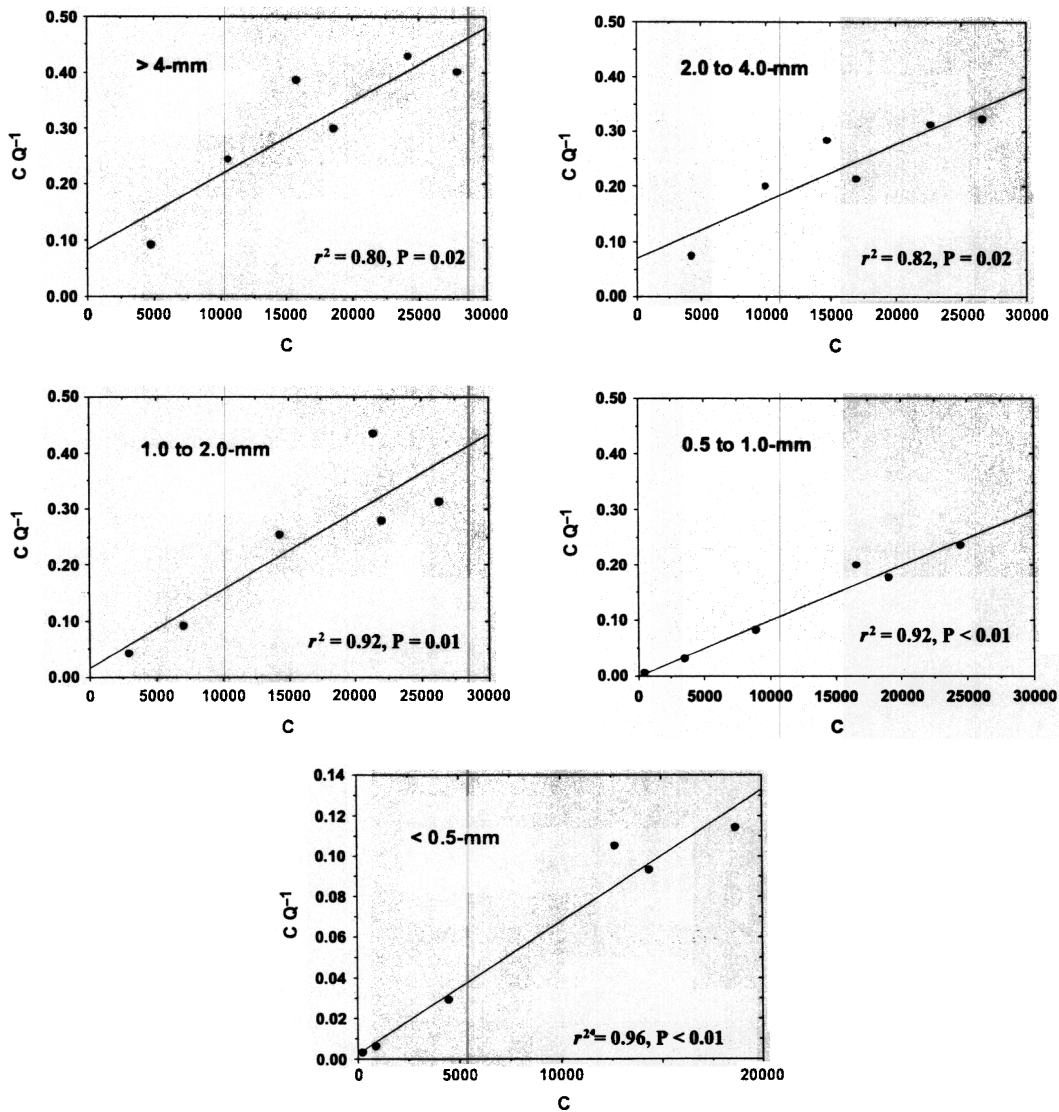

Fig. 3. Phosphorus sorption isotherms showing regression relationships between C and C Q^{-1} for each aggregate size range (note scale change on <0.5-mm graph).

due to restrictions in P diffusion into small pores caused by pore blockages or due to chemical differences in surface P binding sites (Wilson et al., 2004). As a conservative measure, the subsequent P_{max} experiment was limited to 72 h of incubation because the majority (60%) of aggregate size ranges reached P equilibrium at this time.

Because of the time dependence observed in reaching equilibrium with P and the high kinetic nature of the sorption data by the aggregates, results from this study call into question the 24-h period of equilibration commonly used in most laboratory P sorption isotherm experiments. It is conceivable that under some experimental conventions, an equilibration time period of 24 h can be acceptable to produce satisfactory results. Results from this study, however, show that P sorption by WTR aggregates can require incubation time periods >24 h to reach equilibrium.

P Sorption by WTR Aggregates and P_{max} Values

Correcting for previously bound P, background TP concentrations were subtracted from each aggregate size range P sorption value before plotting. The TP concentration in the <0.5-mm fraction was 3.6 mg g^{-1} and between 3.2 to 3.3 mg g^{-1} for the remaining ranges. Linear regression relationships between C and C Q^{-1} for each aggregate size were significant (*P* < 0.05) and fit the data very well (r^2 values between 0.78 and 0.96; Fig. 3).

Our hypothesis was that pulverizing WTRs into finer aggregate size ranges would significantly increase their P_{max} values. As shown in Fig. 4, as aggregate size decreased from >4.0 to <0.5 -mm, in general, the P_{max} value increased. These results are similar to P sorption results by soil aggregates (Linquist et al., 1997), where smaller-sized soil aggregates had a greater "reactive mass" (i.e., higher surface area) compared with larger-sized aggregates. Ippolito et al. (2003) also reported a higher P sorption capacity by smaller-size WTR aggregates (0.1 to 0.3 mm) compared with a nonfractionated sample. The <0.5-mm aggregates had the highest P_{max} value (150 mg g^{-1}), followed by the 0.5- to 1.0-mm aggregate size class (98 mg g^{-1}), and this was attributable to an increase in surface area and thus reactive sites. The <0.5-mm aggregates in the equilibration time experiment also sorbed the most P (Table 1). The P_{max} values for the remaining aggregate size ranges vary between 73 to 94 mg g^{-1} and do not follow the clean trends in P sorbed as displayed in Table 1.

It is possible that the large P_{max} value measured in the 2.0- to 4.0-mm and the 1.0- to 2.0-mm aggregate size range is a result of variations in the aggregate size distribution pattern contained within the incubation tubes. This explanation is plausible, based on triplicate results from experiments to determine aggregate-size distribution patterns contained within 2.0 to 4.0 and <2-mm sieved WTRs. Eighty-gram portions of 2.0- to 4.0-mm sieved WTRs
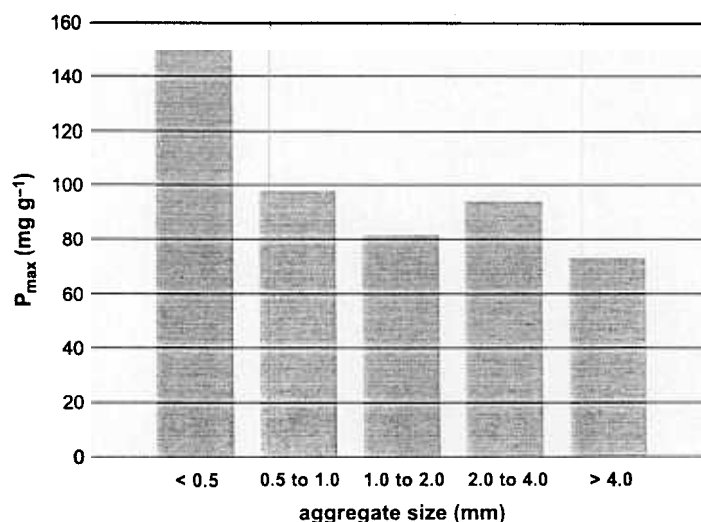

Fig. 4. Aggregate size range and P sorption maxima.

were passed through a 2.83-mm sieve, and the size distribution patterns were determined in the 2.83- to 4.0- and 2.0- to 2.83-mm ranges. The relative percentage difference in the 2.83- to 4.0- and 2.0- to 2.83-mm size ranges between the first and second sieving were almost 31 and 22%, respectively. Similarly, experiments showed that the percentage of aggregates by weight in the 1.0- to 2.0- and <0.5-mm size range can vary between 33 to 57%.

To exemplify potential result bias through conducting P sorption experiments using <2.0-mm sieved WTRs, the P_{max} results from this experiment were compared with results from Novak and Watts (2004). They reported a P_{max} value of 85 mg g^{-1}, using <2-mm sieved aggregates from this same WTR. Although this reported P_{max} value for the <2-mm aggregates is similar to the P_{max} value (82 mg g^{-1}) of the 1.0- to 2.0-mm aggregates, it is much smaller than the P_{max} values measured for the 0.5- to 1.0- and < 0.5-mm aggregates (98 and 150 mg g^{-1}, respectively). This comparison suggests that P sorption isotherm experiments on WTRs may vary greatly, depending on which aggregate size range is used. It is clear that higher P_{max} values can be obtained in P sorption isotherm experiments by using smaller-sized WTR aggregates.

CONCLUSIONS

The utilization of WTRs as a soil amendment to reduce off-site P movement and diminish extractable soil P concentrations has been well established in the literature. Recent researcher has shown that WTRs are effective P binding agents with very little P desorbed. These facts have been commonly determined after a 24-h equilibration period, using WTRs sieved to a 2-mm diameter aggregate size. There has been minimal concern in the literature about longer time periods to reach P equilibrium and pulverizing WTRs into smaller particle sizes to maximize the amount of sorbed P. Results from this laboratory project clearly show that P sorption was time-dependent, and crushing WTRs into smaller diameter aggregates can increase their P_{max} values between 1- and 2-fold. Results from this study also call into question the use of a 24-h equilibration period as the standard method since larger-sized aggregates required between 72 and 96 h to reach equilibrium with P. Aggregate size has an important influence on WTRs P sorption characteristics; therefore, it is suggested that aggregate size should be strongly considered when determining P isotherms or using residuals as a soil amendment to reduce P movement.

REFERENCES

ASCE. 1996. Management of Water Treatment Plant Residuals. Am. Soc. Civil Eng., NY and Am. Water Works Assoc., Denver, CO.

Codling, E. E., C. L. Mulchi, and R. L. Chaney. 2002. Biomass yield and phosphorus availability to wheat grown on high phosphorus soils amended with phosphate inactivating residue: II, Iron Rich Residue. Commun. Soil Sci. Plant. Anal. 33:1063–1084.

Daniels, T.C., G. Hausten, P. A. Moore, and D. Nichols. 1999. Effect of land applied alum residuals and HCA on runoff phosphorus concentrations from high-P soils. In: WEF/AWWA Joint Residuals and Biosolids Management Conference Abstracts, San Diego, CA.

Dayton, E. A., N. T. Basta, C. A. Jakober, and J. A. Hattey. 2003. Using treatment residuals to reduce phosphorus in agricultural runoff. J. Am. Water Works Assoc. 95:151–158.

Gallaher, R. N., C. O. Weldon, and F. C. Baswell. 1976. A semiautomated procedure for total nitrogen in plant and soil samples. Soil Sci. Soc. Am. J. 40:887–889.

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

Gee, G. W., and J. W. Bauder. 1986. Particle-size analysis. In: Methods of Soil Analyses: Part 1-Physical and Mineralogical Methods. 2nd ed. A. Klute (ed.). Soil Sci. Am. Madison, WI, pp. 383–412.

Greenberg, A. E., L. S. Clesceri, and A. D. Eaton. 1992. Standard Method for the Examination of Water and Wastewater. 18th ed. American Public Health Association, Water and Environment Federation, Washington, DC.

Ippolito, J. A., K. A. Barbarick, D. M. Heil, J. P. Chandler, and E. F. Redente. 2003. Phosphorus retention mechanisms of a water treatment residual. J. Environ. Qual. 32:1857–1864.

Lijkema, L. 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. Environ. Sci. Technol. 14:537–541.

Linquist, B. A., P. W. Singleton, R. S. Yost, and K. G. Cassman. 1997. Aggregate size effects on the sorption and release of P in an Ultisol. Soil Sci. Soc. Am. J. 61:160–166.

Makris, K. C., W. G. Harris, G. A. O'Connor, and T. A. Obreza. 2004b. Phosphorus immobilization in micropores of drinking-water treatment residuals:

Implications for long-term stability. Environ. Sci. Technol. 38:6590–6596.

Makris, K. C., H. E. Shall, W. G. Harris, G. A. O'Connor, and T. A. Obreza. 2004b. Intraparticle phosphorus diffusion in a drinking water treatment residual at room temperature. J. Colloid Interface Sci. 277:417–423.

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.

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

Nair, P. S., T. J. Logan, A. N. Sharpley, L. E. Sommers, M. A. Tabatabi, and T. L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. J. Environ. Qual. 13:591–595.

Novak, J. M., and D. W. Watts. 2004. Increasing the phosphorus sorption capacity of southeastern Coastal Plain soils using water treatment residuals. Soil Sci. 169:206–214.

Olsen, S. R., and F. S. Watanabe. 1957. A method to determine phosphorus adsorption maximum in soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Proc. 21:144–149.

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

Soil Survey Staff. 1951. Soil Survey Manual. U.S. Dept. Agr. Handbook No. 18. U.S. Govt. Printing Office. Washington, DC.

Sparks, D. L. 1995. Environmental Soil Chemistry. Academic Press, New York, NY.

Wilson, G. V., F. E. Rhoton, and H. M. Salim. 2004. Modeling the impact of ferrihydrite on adsorption-desorption of soil phosphorus. Soil Sci. 169:271–281.

Zar, J. H. 1999. Biostatistical analyses. 4th ed. Prentice Hall. Upper Saddle River, NJ.