# **Phosphorus Retention Mechanisms of a Water Treatment Residual**

J. A. Ippolito,\* K. A. Barbarick, D. M. Heil, J. P. Chandler, and E. F. Redente

## ABSTRACT

Water treatment residuals (WTRs) are a by-product of municipal drinking water treatment plants and can have the capacity to adsorb tremendous amounts of P. Understanding the WTR phosphorus adsorption process is important for discerning the mechanism and tenacity of P retention. We studied P adsorbing mechanism(s) of an aluminum-based [Al2(SO4)3.14H2O] WTR from Englewood, CO. In a laboratory study, we shook mixtures of P-loaded WTR for 1 to 211 d followed by solution pH analysis, and solution Ca, Al, and P analysis via inductively coupled plasma atomic emission spectroscopy. After shaking periods, we also examined the solids fraction by X-ray diffraction (XRD) and electron microprobe analysis using wavelength dispersive spectroscopy (EMPA-WDS). The shaking results indicated an increase in pH from 7.2 to 8.2, an increase in desorbed Ca and Al concentrations, and a decrease in desorbed P concentration. The pH and desorbed Ca concentration increases suggested that CaCO<sub>3</sub> controlled Ca solubility. Increased desorbed AI concentration may have been due to Al(OH), formation. Decreased P content, in conjunction with the pH increase, was consistent with calcium phosphate formation or precipitation. The system appeared to be undersaturated with respect to dicalcium phosphate (DCP; CaHPO4) and supersaturated with respect to octacalcium phosphate [OCP; Ca<sub>4</sub>H(PO<sub>4</sub>)<sub>3</sub>. 2.5H<sub>2</sub>O]. The Ca and Al increases, as well as OCP formation, were supported by MINTEQA2 modeling. The XRD and EMPA-WDS results for all shaking times, however, suggested surface P chemisorption as an amorphous Al-P mineral phase.

WATER TREATMENT RESIDUALS are a waste product of drinking water treatment. Alum  $[Al_2(SO_4)_3$ · 14H<sub>2</sub>O] is commonly used in the treatment process for particulate flocculation and water clarification and is a component of WTR. Landfill disposal of this material is common practice. However, as landfill space becomes less available and more costly, municipalities are likely to seek out beneficial reuse of WTR.

Land application of WTR is one method of beneficial recycling. The potential benefits of WTR land application are increased plant available N and total organic C (Lin, 1988; Dempsey et al., 1989; Elliott et al., 1990; Elliott and Dempsey, 1991), and increased aggregate stability, water retention, aeration, and drainage capacity (El-Swaify and Emerson, 1975; Scambilis, 1977; Rengasamy et al., 1980; Bugbee and Frink, 1985). The amorphous hydrous oxides in WTR may benefit coarse-textured soils by increasing cation exchange capacity (American Society of Civil Engineers et al., 1996). Alkaline WTR may also be used as a liming agent.

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The single greatest disadvantage of WTR land application is its adsorption of plant-available soil P. Heil and Barbarick (1989) noted severe P-deficiency symptoms associated with an excessive rate (25 g WTR kg<sup>-1</sup> soil) of WTR addition, but they were able to increase sorghum-sudangrass [Sorghum bicolor (L.) Moench Sorghum X drummondii (Steudel) Millsp. & Chase] production by increasing the rate of P fertilizer application. Ippolito et al. (1999) decreased P concentrations in blue grama [Bouteloua gracilis (H.B.K.) Lag. ex Steud.] by increasing WTR rates. Rengasamy et al. (1980) reduced P uptake in maize (Zea mays L.) with WTR addition, while Elliott and Singer (1988) and Bugbee and Frink (1985) found reduced P concentrations in tomato (Lycopersicon esculentum L.) and lettuce (Lactuca sativa L.) grown in WTR-amended potting media.

Results of studies designed to determine mechanism(s) of P retention by WTR are inconclusive. One hypothesis is that P adsorption occurs at the WTRhydrous aluminum oxide interface. Phosphate replaces singly coordinated OH<sup>-</sup> groups and then reorganizes into a very stable binuclear bridge between cations (Bohn et al., 1985). This chemisorption process is coupled with the release of OH<sup>-</sup> ions; thus the process is favored by low pH values (Stumm, 1987). Cox et al. (1997) studied low-pH WTR addition to acid soil, observed P immobilization, and associated it with Albound phosphate. Van Riemsdijk et al. (1975) reported aluminum phosphate precipitation from mixing a phosphate solution with amorphous Al(OH)<sub>3</sub> at pH 5.

Tools such as X-ray diffraction (XRD), electron microprobe analysis, and chemical speciation software such as MINTEQA2 may be used to help speculate as to possible P adsorption mechanisms. For example, Karathanasis (1991) used XRD to help determine phosphate mineral distribution of two Kentucky soils. Kumar (1994) recovered apatitic grains from a fertilized soil and, using XRD and electron microprobe analysis, showed no difference between the grains and original fertilizers. Iron, Si, K, Ca, and Al soil distribution (Golden et al., 1997), trace element partitioning within Fe-Mn soil nodules (Palumbo et al., 2001), and Pb mineralogy of mixed, mine overburden soils (Davis et al., 1992; Ruby et al., 1992) all have been studied using electron microprobe analysis. Sloan et al. (1995) and Alva et al. (1991) used MINTEQA2-derived saturation indices to identify possible solid phases in soil amended with five P fertilizer rates and in soil amended with phosphogypsum solution, respectively. Sloan and Basta (1995) used MINTEQA2 to determine Al speciation in acid soils amended with alkaline biosolids.

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Abbreviations: EMPA-WDS, electron microprobe analysis using wavelength dispersive spectroscopy; OCP, octacalcium phosphate  $[Ca_4H(PO_4)_3 \cdot 2.5H_2O]$ ; TCP, tricalcium phosphate  $[Ca_3(PO_4)_2]$ ; WTR, water treatment residual; XRD, X-ray diffraction.

Our research objectives were to (i) investigate slightly basic, aluminum-containing WTR effectiveness in removing P from solution; (ii) determine the ease of P removal from a P-loaded WTR; (iii) evaluate the longterm changes in solution pH, Ca, Al, and P concentrations of a P-loaded WTR; and (iv) determine the mechanism(s) of solution P removal by WTR.

We tested three hypotheses. First, WTR will adsorb >2000 mg P kg<sup>-1</sup> WTR, as calculated by previous research (Ippolito, 2001). Second, long-term chemicalphase changes of P will be associated with WTR Ca, as calcium phosphates precipitate due to the slightly alkaline nature of the WTR (pH = 7.6). The presence of these phosphate mineral phases will be determined by comparing observed data with values calculated from equilibrium constants and by the chemical speciation model MINTEQA2, and by XRD and electron microprobe analysis using wavelength dispersive spectroscopy (EMPA–WDS). Third, P-loaded WTR will readily desorb P when placed in solution, thus acting as a P supplier as suggested by Butkus et al. (1998).

### **MATERIALS AND METHODS**

The WTR used in this study was obtained from the Englewood, CO water treatment facility. The influent water source is the South Platte River and is typically at pH 7.5 to 8.0. The water treatment facility routinely adds an anionic polymer to the WTR for conditioning before belt pressing.

We air-dried the WTR and then sieved it to the 0.1- to 0.3-mm size fraction. We collected the 0.1- to 0.3-mm size fraction because this was the smallest size fraction of which we could collect large enough quantities for the experiment. The elemental composition of the Englewood WTR is presented in Table 1. We determined total elemental composition of the fractionated WTR by a HClO<sub>4</sub>-HNO<sub>3</sub>-HF-HCl digestion (Soltanpour et al., 1982) and analyzed the digest using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). We determined total N via LECO-1000 (LECO Corp., St. Joseph, MI) analysis (Nelson and Sommers, 1996), NH<sub>4</sub>-N and NO<sub>3</sub>-N in a 2 M KCl extract (Mulvaney, 1996),

Table 1. Properties of the 0.1- to 0.3-mm size fraction of water treatment residual (WTR) obtained from Englewood, CO.

Property	: ·	Value
Total N, g kg <sup>-1</sup>		6.2
Organic N, g kg <sup>-1</sup>		5.5
NHN, mg kg <sup>-1</sup>		6.6
NO <sub>5</sub> -N, mg kg <sup>-1</sup>		711
Ca, g kg <sup>-1</sup>		41.9
K, g kg <sup>-1</sup>	-	3.1
P, g kg <sup>-1</sup>		2.3
Al, g kg <sup>-1</sup>		64.1
Fe, g kg <sup>-1</sup>		17.6
Cu, mg kg <sup>-1</sup>		4110
Zn, mg kg <sup>-1</sup>	1	137
Ni, mg kg <sup>-1</sup>		137
Mo ma ka <sup>-1</sup>		
Mo, mg kg <sup>-1</sup>	1 ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) (	3.7
Cd, mg kg <sup>-1</sup>	1	1.77
Cr, mg kg <sup>-1</sup>		14.3
Pb, mg kg <sup>-1</sup>	1 ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) (	14.4
As, mg kg <sup>-1</sup>		9.0
Se, mg kg <sup>-1</sup>	1	1.5
Hg, mg kg <sup>-1</sup>		0.06
pH		7.6
ĒC†, dS m⁻¹		6.9
CEC‡, cmol, kg <sup>-1</sup>		49.8

† Electrical conductivity.‡ Cation exchange capacity.

and organic N via subtraction of inorganic from total. The pH and electrical conductivity (EC) were determined using a saturated paste extract (Rhoades, 1982b) and cation exchange capacity (CEC) via the method of Rhoades (Rhoades, 1982a).

#### **Phosphorus Sorption–Desorption Study**

We added multiple 20-g samples of WTR (dry weight basis) to 800 mL of 0.1 *M* KCl containing 300 mg P L<sup>-1</sup> into 1000-mL Nalgene bottles (Nalge Nunc Int., Rochester, NY). The solutions were placed on a reciprocating shaker for 24 h, decanted, and filtered through Whatman (Maidstone, UK) no. 42 filter paper, and the decantate was saved. A 24-h shaking period was used to be consistent with our previous P adsorption studies (Ippolito et al., 1999). We then added 800 mL of distilled-deionized H<sub>2</sub>O to the WTR, shook vigorously, let the suspension settle overnight, decanted, filtered, saved the second decantate, and analyzed both decantates for P using ICP– AES. Adsorbed P was calculated by difference between initial and final concentrations.

The P-loaded WTR was air-dried, then triplicate 4-g (dry weight basis) subsamples were weighed into 50-mL centrifuge tubes. We added 20 mL of 0.01 M CaCl<sub>2</sub> solution to buffer ionic strength and shook the tubes for 1, 2, 4, 7, 14, 28, 84, and 211 d. After shaking, we decanted, filtered the liquid, and analyzed it for pH and Ca, Al, and P using ICP-AES. We converted solution concentrations (mg L<sup>-1</sup>) from ICP-AES to a weight basis (mg kg<sup>-1</sup> WTR) using a dilution factor of five (4 g WTR per 20 mL 0.01 M CaCl<sub>2</sub>) to express the amount of Ca, Al, or P desorbed from a given quantity of WTR.

Activities of the Ca and Al were calculated based on each time period's desorbed concentration values, and potential calcium phosphate species were determined based on individual shaking period pH values and desorbed values for Ca and P. We also calculated the  $CO_2$  partial pressure to determine which carbonate minerals were potentially present. We compared these activities with activities calculated from equilibrium constants found in Lindsay (1979). The equilibrium speciation model MINTEQA2 (Allison et al., 1991) was used to compare results. Using the observed activities data from 211 d, we entered a fixed pH of 8.15, entered amorphous Al(OH)<sub>3</sub> and calcite as finite solids converted from Al and Ca concentrations, respectively, found in the WTR, and excluded all crystalline Al hydroxide species as well as hydroxyapatite for MINTEQA2 input. We recognized that our system was not in equilibrium and that we were not using pure, crystalline materials (as assumed in MINTEQA2); we used MINTEQA2 for comparison and estimation purposes only.

Data were analyzed using regression analysis and analyses of variance and tested at the 0.01 probability level (p) (Steel and Torrie, 1980). The results will be referred to in the Results and Discussion section as "observed" for data calculated from actual values, "predicted" for data calculated from Lindsay (1979) equilibrium constants, or "MINTEQA2" for data calculated by MINTEQA2.

# X-Ray Diffraction and Electron Microprobe–Wavelength Dispersive Spectroscopy Analysis

After the various shaking periods, we examined the solids fraction using XRD and EMPA–WDS. We used two or three replicates from the 1-, 28-, 84-, and 211-d samples for XRD and EMPA–WDS analysis, respectively. For XRD analysis, the samples were ground with a porcelain mortar and pestle before placing them in the XRD holder. The samples were packed as dry powder mounts into a 2.54-cm-diameter by 0.32cm-deep holder, and analyzed from 5 to 55°20. The XRD (SCINTAG Model XDS 2000 XGEN-4000; Thermo ARL, Ecublens, Switzerland) had a copper target. Box car smoothing was used and K- $\alpha$ -2 stripping was performed using K- $\alpha$ -1 and K- $\alpha$ -2 as 1.540562 Å and 1.544390 Å, respectively.

For EMPA-WDS analysis, samples were placed in a very thin layer in the bottom of individual 0.7-cm-long by 1.6-cmwide by 1-cm-deep plastic boats. We gently poured Acrylimet epoxy (South Bay Technology, San Clemente, CA) over the samples and let them cure for 24 h at room temperature and 138 kPa of pressure. After curing, the epoxy-coated samples were removed from the plastic boats and wet wheel-polished with an Exakt 400CS microgrinder (Exakt Technologies, Oklahoma City, OK) using 800- and then 1200-grit polishing paper to remove approximately 0.15 mm of material. The amount of material removed was approximately equal to half the diameter of the sample particles. The samples were carboncoated in a vacuum evaporator and analyzed using a JEOL JXA-8900 electron microprobe analyzer (JEOL USA, Peabody, MA) at an accelerating voltage of 15 keV and a magnification between 300 and 550x. We used backscattered electrons for collecting images of the specimen surface and wavelength dispersive spectroscopy to generate dot maps of P, Al, and Ca.

### **RESULTS AND DISCUSSION**

### **Phosphorus Sorption–Desorption Results**

Our initial WTR P-loading experiment indicated that 250 mg P was adsorbed, which was equivalent to 12 500 mg P adsorbed kg<sup>-1</sup> WTR  $\pm$  70 mg kg<sup>-1</sup>, or 1.25% by weight. Previous research (Ippolito, 2001) indicated a much lower adsorption capacity of 2178 mg P adsorbed kg<sup>-1</sup> of Englewood WTR (0.22% adsorbed by weight). However, this previous work was a WTR and biosolids co-mixing study where the WTR was not fractionated, P was supplied only by biosolids, and the biosolids bio-available P was held constant. We expected higher adsorption capacities with the smaller WTR size fractions described in this manuscript because of greater specific surface area and because all of the solution P was available for adsorption.

The results of the desorption study showed that as shaking time increased, the solution pH increased to a maximum of 8.15 after 211 d (Fig. 1). However, this pH value was not significantly different (LSD = 0.15) than the pH value measured after 84 d. The time predicted to attain a maximum pH of 8.15 was 135 d. This prediction indicates that after 135 d a solid phase was controlling pH. Since our measured pH values did not change significantly after 84 d, this may also indicate that a solid phase was controlling pH after 84 d in our study.

The desorbed Ca concentration increased to 1680 mg kg<sup>-1</sup> WTR with increased shaking (Fig. 2) and did not approach a maximum by the end of the study (LSD = 43). The observed and predicted Ca concentration at 211 d, when converted to activity, equaled  $10^{-2.43}$  and  $10^{-2.93}$ , respectively. The MINTEQA2 approach calculated a similar Ca activity of  $10^{-2.98}$ . Based on the observed pH and Ca data, we calculated a CO<sub>2</sub> partial pressure equal to 0.023 kPa.

An average maximum pH of 8.15 and Ca desorption results support the hypothesis that  $CaCO_3$  controls Ca concentration at a partial pressure of  $CO_2$  slightly less

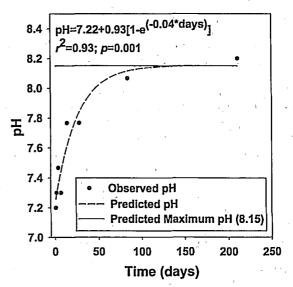
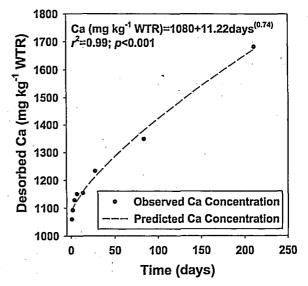
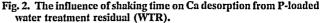


Fig. 1. The influence of shaking time on P-loaded water treatment residual (WTR) solution pH.

than atmospheric (0.02 versus 0.03 kPa). This decrease from atmospheric  $CO_2$  levels may indicate  $CaCO_3$  precipitation since the subsamples were closed to atmospheric exchange. Although no lime was added during the water treatment process, the treatment plant influent water source is the South Platte River, which has a pH of approximately 7.5 to 8.0, and the WTR Ca content = 41.9 g kg<sup>-1</sup>. This suggests that the pH of the influent water is controlled by carbonate solid phases, CaCO<sub>3</sub>.

The addition of the 0.01 M CaCl<sub>2</sub> ionic strength solution may have influenced Ca equilibrium. However, the 0.01 M CaCl<sub>2</sub> solution might have only contributed to the formation of CaCO<sub>3</sub>, since Ca activity at 211 d appears to be controlled by the presence of CaCO<sub>3</sub>, not CaCl<sub>2</sub>. Furthermore, we compared MINTEQA2 output, using the input variables as described in the Materials and Methods section, to similar input but altering the





CaCO<sub>3</sub> and CaCl<sub>2</sub> to either (i) CaCO<sub>3</sub> as a finite solid and  $10^{-600}$  *M* CaCl<sub>2</sub> (to prevent a phase rule violation) or (ii) no CaCO<sub>3</sub> and 0.01 *M* CaCl<sub>2</sub>. The MINTEQA2 program predicted solid CaCO<sub>3</sub> precipitation for the no CaCO<sub>3</sub> and 0.01 *M* CaCl<sub>2</sub> system, and the difference in MINTEQA2 solution Ca activity output for all three subsamples was <0.0001%.

The desorbed Al concentration increased with increased shaking time (Fig. 3). The LSD = 0.31, and indicated that solution Al concentration was increasing drastically from 84 to 211 d. This may be caused by dissolution of amorphous Al(OH)<sub>3</sub> and formation of the solution species Al(OH)<sub>4</sub>, as shown by the observed, predicted, and MINTEQA2 Al activity ( $10^{-4.91}$ ,  $10^{-5.47}$ , and  $10^{-4.89}$ , respectively). We expected an increase in desorbed Al content, since Al undergoes hydrolysis as pH increases and hydroxy Al complexes dominate above pH 7. The lower Al concentrations associated with 1 to 84 d are also probably Al(OH)<sub>4</sub><sup>-</sup> since solution pH was between 7.2 and 8.1.

Hem and Roberson (1967) reported Al(OH) $_{4}^{-}$  as the predominant dissolved form of Al in the pH range of 7.5 to 9.5. Schecher and Driscoll (1988) also reported the primary Al species was Al(OH) $_{4}^{-}$  above pH 5.5. Schecher and Driscoll (1987) presented Al species equilibrium constants, their standard deviations, and a measure of uncertainty. Their paper supports the contention that the thermodynamic equilibrium constants contain uncertainty. This explains the discrepancy in our observed, predicted, and MINTEQA2 Al activity values.

Desorbed P concentration decreased with increased shaking time, indicating continued sorption (Fig. 4). The LSD = 0.59, which indicated that P concentration continued to decrease from 84 to 211 d. Initial concern arose from filtering through Whatman no. 42 filter paper, undoubtedly due to possible colloidal P material in our filtered solutions. Although this may be the case, the decrease in P content clearly illustrates that soluble P is decreasing with increasing shaking time. If colloidal

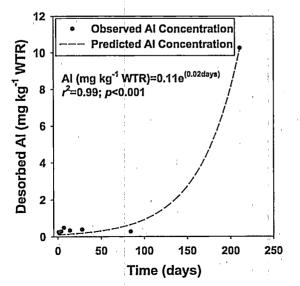


Fig. 3. The influence of shaking time on Al desorption from P-loaded water treatment residual (WTR).

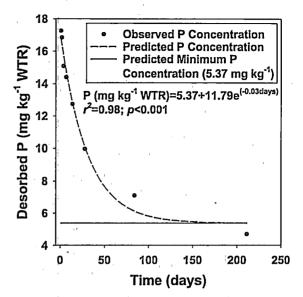
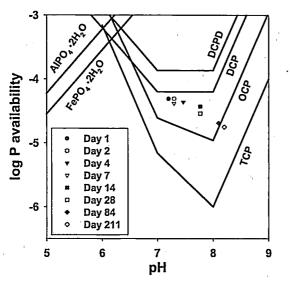


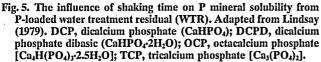
Fig. 4. The influence of shaking time on P desorption from P-loaded water treatment residual (WTR).

materials passed through the filter paper, we would have invariably observed an increase in solution P concentration with increasing shaking time associated with colloidal P. The decrease can be explained as P finding more reactive sites in micropores, becoming more strongly adsorbed at individual surface sites, layered surface precipitation, or the formation of calcium phosphate precipitates. Griffin and Jurinak (1973) studied P adsorption on calcite and speculated that P adsorption occurs, in part, as a multilayer phenomenon on specific sites on the calcite surface. They interpreted their data as the onset of heterogeneous nucleation of calcium phosphate crystallites on the calcite surface.

The data in Fig. 4 show an initial fast, almost linear decrease in P sorption from 1 to 28 d followed by a slower decrease afterwards. Castro and Torrent (1998) studied P sorption by calcareous soils and described sorption as a two-step process; an initial linear region associated with P adsorption on variable charge surfaces and a latter linear region corresponding to the precipitation of calcium phosphates. The two regions observed in our study may be due to a similar P sorption mechanism. The somewhat linear region from 1 to 28 d suggests possible adsorption, and the gradual transformation from 28 to 211 d suggests conversion from more to less soluble calcium phosphate minerals.

Our system appears to be undersaturated with respect to dicalcium phosphate and trending toward the formation of octacalcium phosphate [OCP; Ca<sub>4</sub>H(PO<sub>4</sub>)<sub>3</sub>· 2.5H<sub>2</sub>O] (Fig. 5). The MINTEQA2 model results also suggest the formation of OCP. The formation of OCP, as well as the possibility of Ca being controlled by the presence of CaCO<sub>3</sub>, indicates that our findings are similar to those of Griffin and Jurinak (1973). In addition, the system appears to be progressing from a more to a less soluble mineral form, slightly less soluble than dicalcium phosphate to equilibrium with OCP, as suggested by Castro and Torrent (1998). The data for 211 d show that the solid phase controlling solution P appears





to be slightly less soluble than OCP. This suggests that an additional transformation from OCP to tricalcium phosphate  $[TCP; Ca_3(PO_4)_2]$  is beginning at about 211 d.

Our P findings are in direct opposition to the suggestion of Butkus et al. (1998) of adding P to WTR as a pretreatment to convert WTR from a phosphate consumer to a P supplier. Our results indicate that P is highly sorbed, and given time, is further chemisorbed to the WTR or Ca fraction or is precipitating as OCP, which would make it a poor P supplier. Bowman et al. (1998) concluded that reactive Fe and Al oxide surfaces, along with CaCO<sub>3</sub>, play a role in determining transitional or intermediate P levels. Given time, a more resistant P pool is formed. The specific binding of P has been discussed by Bohn et al. (1985), whereas adsorption occurs at the hydrous aluminum oxide interface with phosphate replacing singly coordinated OH<sup>-</sup> groups and then reorganizing into a very stable binuclear bridge between cations. Hingston et al. (1972) proposed specific adsorption of phosphate ions at the oxide interface, where the formation of coordination complexes occur. Peak et al. (2002), using X-ray absorption near edge structure spectroscopy, showed a conversion of alum to an amorphous Al(OH)<sub>3</sub> precipitate in alum-amended poultry litter. The amorphous Al(OH)<sub>3</sub> then reacted with poultry litter-borne P via an adsorption mechanism. These mechanisms may also hold true for P adsorption on aluminum-containing WTR.

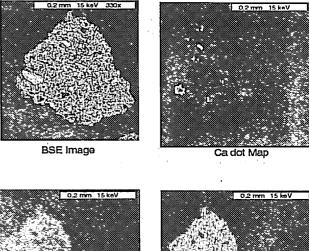
Phosphorus solubility diagrams like those of Lindsay (1979) suggest that variscite, dicalcium phosphate, and OCP can coexist at a pH of 6 to 6.5. Below this pH range, the Al species variscite controls P solubility. Above this pH range, and as suggested in our study, the calcium phosphate minerals control P solubility. Pierzynski et al. (1990a) showed soil sample supernatants at pH greater than 6.8 exhibited solubility relationships between that of OCP, TCP, and hydroxyapatite [Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH].

Fixen and Ludwick (1982) verified the presence of P minerals in the solubility range between that of OCP, TCP, and hydroxyapatite in several calcareous soils. O'Connor et al. (1986) gave evidence that TCP controlled P solubility in a calcareous soil with a history of P fertilization.

## X-Ray Diffraction and Electron Microprobe–Wavelength Dispersive Spectroscopy Results

The results of XRD analysis of the 1-, 28-, 84-, and 211-d samples were similar and did not show accumulation of calcium phosphate mineral species (data not shown). However, the XRD analysis did show the presence of calcite in the WTR, which supports our suggestion that CaCO<sub>3</sub> controlled Ca activity in our desorption study. The lack of evidence of phosphate minerals does not rule out their presence in the system because XRD detection limits for most mineral phases are approximately 1 to 5% by weight and our samples only contained 1.25% P by weight.

We used EMPA–WDS analysis to identify elemental associations with P. We also did not detect any major differences among any of the EMPA–WDS results. Therefore, we chose to illustrate the EMPA–WDS results from one sample replicate from 1 d and from 211 d (Fig. 6 and 7). The Ca and P dot maps clearly show there is no visible association between these elements. This is evident by the black areas on the P dot map, which appear as white areas on the Ca dot map. However, P does appear to be more closely associated with the Al fraction of the WTR. This P is most likely surface



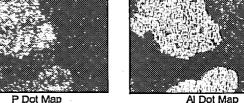


Fig. 6. Backscattered electron (BSE) image and wavelength dispersive spectroscopy dot maps of Ca, P, and Al of sample Day 1. The light-colored portions on the dot maps indicate the presence of Ca, P, or Al.

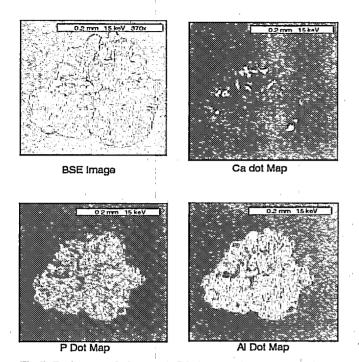


Fig. 7. Backscattered electron (BSE) image and wavelength dispersive spectroscopy dot maps of Ca, P, and Al of sample Day 211. The light-colored portions on the dot maps indicate the presence of Ca, P, or Al.

chemisorbed to Al throughout the WTR particle (can be inferred because the samples were polished to remove half the material) primarily due to the porous nature of the WTR (backscattered electron [BSE] images, Fig. 6 and 7). The EMPA-WDS data does not support the results of the solution chemistry that suggest the presence of calcium phosphate minerals. This may be due to the fact that this method has detection limits near approximately 1% by weight and our samples contained only 1.25% P by weight.

Previous studies may help explain the results from our WTR system. Galarneau and Gehr (1997) examined P removal from wastewaters using WTR and concludedthat the minimum residual orthophosphate concentration required to be in equilibrium with  $Al(PO_4)$  would be 2244 mg P L<sup>-1</sup> at pH 7. Our final P concentration was much lower than this value, suggesting other mechanisms of P sorption.

Samadi and Gilkes (1999) studied P transformations in calcareous soils using scanning electron microscopy in conjunction with energy dispersive spectroscopy and found no evidence of P association with other soil elements. However, Sawhney (1973), using electron microprobe analysis, found P associated with Al, Fe, and Si throughout particles from Connecticut soils. Castro and Torrent (1995) studied P solubility in calcareous soils and noted that soils containing a higher ratio of clays and Fe oxides may occlude P. Holford and Mattingly (1975) noted high-energy P adsorption in calcareous soils appeared to be mainly associated with surfaces of Fe compounds or perhaps, more generally, with all the hydrous oxides present.

Pierzynski et al. (1990b) studied P chemistry in exces-

sively fertilized soils and concluded that the elemental makeup of P-rich particles contained several cations in association with P; aluminum was the predominant cation association regardless of soil pH. In a followup study, Pierzynski et al. (1990c) studied the P-rich particles using scanning transmission electron microscopy equipped with an energy dispersive X-ray analyzer. They concluded that the P-rich particles were an amorphous mix of Al, Si, and P, and compared it with an amorphous analog of variscite and allophane.

Based on our results and these other findings, we speculate P retention by WTR in our study may be due to surface chemisorption, as P may initially be adsorbed as an outer sphere complex or found in the diffuse ion swarm near individual WTR particles. As time passes, P may become more strongly adsorbed as an inner sphere complex onto WTR, eventually forming a solid phase similar to amorphous variscite. The MINTEQA2 results, from the shaking experiment, indicated that the system was undersaturated with respect to crystalline variscite. The version of MINTEQA2 we used did not contain equilibrium constants for amorphous variscite, and therefore we cannot verify its presence.

Calcium phosphate mineral phases also may be controlling P solubility in our system. These minerals may be present in very low quantities as a surface precipitate on calcite, which EMPA–WDS could not detect due to relatively high detection limits and the particle size that we sampled.

## CONCLUSIONS

We accepted the hypothesis that WTR will adsorb greater than 0.2% P by weight. The Englewood WTR phosphorus adsorptive capacity was approximately 12 500 mg P kg<sup>-1</sup> WTR, or 1.25%. We used the 0.1- to 0.3-mm size fraction for this determination, which would have a higher P adsorption capacity than a nonfractionated sample because it has greater reactive surface area.

Incubation of a P-loaded WTR in 0.01 M CaCl<sub>2</sub> solution showed the pH increased from 7.2 to 8.2 and desorbed Ca concentration increased from 410 mg kg<sup>-1</sup> WTR at 1 d to 1680 mg kg<sup>-1</sup> WTR at 211 d. The final pH and the observed and predicted Ca activities suggest the system was in equilibrium with CaCO<sub>3</sub>. The desorbed Al concentration also increased with shaking time and suggests that amorphous Al(OH)<sub>3</sub> inherent in WTR is forming the solution species Al(OH)<sub>4</sub>, particularly above pH 7 where hydroxy Al complexes, such as Al(OH)<sub>4</sub>, dominate.

We rejected the hypothesis that P-loaded WTR will readily release P to solution. The amount of P desorbed from the P-loaded WTR decreased with increased shaking time, from 17.3 to 4.7 mg kg<sup>-1</sup> WTR. This decrease could be caused by P finding more occluded Al surface sites to react with, becoming more strongly sorbed at individual Al surface sites, undergoing layered surface precipitation, or forming calcium phosphate precipitates.

The desorption experiment supports the contention that P is sorbed by  $CaCO_3$  with subsequent calcium

phosphate precipitation. Specifically, we observed evidence of transformation from a more to less soluble calcium phosphate mineral species; from dicalcium phosphate to OCP. The system also shows limited evidence of an additional transformation, from OCP to TCP. The MINTEQA2 results supported these findings, advocating the hypothesis that long-term P chemical phase changes are associated with the Ca fraction of WTR.

We further researched possible mineral phases and P associations using XRD and EMPA-WDS. Neither verified the presence of calcium or aluminum phosphate mineral precipitates, although they may be present in amounts less than detection limits or in an amorphous mineral form. The XRD results lacked any P mineral phase, but revealed the presence of mainly 1:1 and 2:1 type clays as well as calcite. The EMPA-WDS results showed that P is associated with the Al fraction of the WTR. This association may be due to surface P chemisorption, or precipitation of an amorphous aluminum phosphate. Based on this information, we cannot accept our hypothesis with regard to a P-Ca association.

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