LABILITY OF DRINKING-WATER TREATMENT RESIDUALS (WTR) IMMOBILIZED PHOSPHORUS: IMPLICATIONS FOR LONG-TERM STABILITY

By

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This PhD dissertation is dedicated to my family.

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To God be the glory for the great things he has done in my life.

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Drinking-water treatment residuals (WTR) are by-products of the drinking-water treatment process and are physical mixtures of aluminum or iron hydr(oxides) that originate from flocculant (aluminum or iron salts) additions made during the processing of drinking-water. Short-term studies have demonstrated WTR efficacy in reducing soluble phosphorus (P) concentrations in runoff and leaching from P-impacted soils. However, the long-term stability of P sorbed by WTR has only been qualitatively addressed in laboratory experiments. Field experiments and other approaches to accurately quantify P lability were needed to test WTR efficacy in reducing soluble P concentrations and to confirm trends observed in, or inferred from, laboratory studies. We artificially aged WTR amended soils either through repeated wetting and drying for two years, or via elevated temperatures (46 and 70 degree Celsius) for 4.5 years, to simulate natural long-term weathering processes that could influence the stability of sorbed P. Then using a modified isotopic dilution technique, coupled with a stepwise acidification procedure, we evaluated the changes in lability of WTR immobilized P due to aging and changes in pH. We also monitored the longevity of WTR effects on P lability for 7.5 years from one-time WTR amended manure-impacted soils at two sites. Amendment with WTR reduced labile P concentration in the artificially-aged sample by at least 70% and in field sites by at least 60%.

The WTR immobilized P was stable within pH range of 4 – 7 throughout the aging and monitoring periods. The combined data from the field study and the laboratory aging experiments suggest that WTR amendment should reduce P losses from P-impacted soils, and do so for a long time. To confirm this, we investigated P losses in runoff and leachate from P-impacted soils, 7.5 years after WTR application. Amendment with WTR decreased total dissolved P and bioavailable P masses in runoff and leachate by more than 50%. From the various studies, we conclude that WTR is an effective amendment to control labile P in P-impacted soils and that WTR immobilized P is stable and will remain fixed for a long time, independent of common soil pH values.

CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

Intense agricultural activities often result in excessive phosphorus (P) inputs to soils. Large P inputs rarely have negative agronomic effects, but can degrade water quality. Phosphorus loss from soils is one of the major factors responsible for accelerated eutrophication of surface waters in many locations in Florida and other eastern states of USA where soils that retain P poorly are abundant. These sandy (coarse-textured) soils not only sorb P poorly, but are often accompanied by high water tables. The combination of these characteristics makes such soils vulnerable to P losses and negative impacts on water quality (He et al., 1999; Novak et al., 2000). The Lake Okeechobee and Kissimmee watersheds, for example, have prolonged history of using P sources such as P fertilizers, manures and biosolids to increase soil fertility and crop yields. Applications of organic sources of P are typically based on crop nitrogen (N) requirements, which usually provide P in excess of crop needs. Off-site migration of P to surface waters is a major concern because P is the limiting nutrient for eutrophication of most freshwaters, leading to algal blooms and growth of aquatic weeds (Elliott et al., 2002 a,b). Besides being unsightly and rendering surface waters unfit for recreation, aquatic plants can clog water treatment filters and, upon plant death and subsequent decomposition, cause fish kills due to decreased oxygen levels in the fresh water. Some algae produce toxins that can result in death if ingested by animals (Sharpley et al., 1994). Fish kills have also resulted from outbreaks of the bacteria *Pfiesteria piscicida* (Kratch, 1997). These dinoflagellates cause lethal lesions on fish and have been linked to skin rashes, respiratory problems, and memory loss among people who come in contact with water containing these algae. Usually the microbes are not toxic, but excessive P loadings into water bodies promote the production of the toxic form of *Pfiesteria* (Kratch, 1997). In the fall of 1997, after a particularly bad outbreak of Pfiesteria along the east coast, the popular press blamed the

poultry producers and land application of poultry manure for accelerated eutrophication of surface waters (Kratch, 1997).

Soils in the Lake Okeechobee and Kissimmee watersheds (e.g., Immokalee sand and Myakka sand) sorb P poorly and, thus, there is concern that large P inputs to the soils represent an increased risk for nonpoint-source pollution of surface waters (Elliott et al., 2002 a,b; O'Connor et al., 2002). One suggested way to mitigate this problem is to increase the P sorption capacity of soils in the watershed by amending the soils with drinking-water treatment residuals (WTRs), the residues from municipal water treatment plants (O'Connor et al., 2002; Makris and O'Connor, 2006).

Drinking-water treatment facilities produce millions of liters of potable water every day. The process of producing potable water from surface water supplies typically involves coagulation and flocculation of suspended solids. The precipitated material is separated by filtration or gravity and the solid material is known as drinking-water treatment residual (WTR). Common coagulants include aluminum sulfate ($A1_2(SO_4)_3$), ferric chloride ($FeC1_3$), ferric sulfate ($Fe_2(SO_4)_3$) and calcium carbonate ($CaCO_3$). Although new drinking-water treatment technologies (membrane separation, ion exchange, precipitative softening, granular activated carbon, and disinfection/UV) have emerged, there are still over 1000 drinking-water treatment plants in the United States which use alum, $Al_2(SO_4)_3 \cdot 14H_2O$, as a coagulant for efficient removal of particulate solids and colloids from surface water supply. More than 2 million metric tons of WTR are generated daily from drinking-water treatment plants (Prakash and SenGupta, 2003). Alum is converted during the coagulation process into insoluble aluminum hydroxide, a major component (50-75%) of the solids in WTR, along with suspended inorganic particles, natural organic matter, and trace amounts of heavy metal precipitates (Prakash and SenGupta,

2003). Drinking-water treatment residuals can be disposed: a) directly to a receiving stream; b) to sanitary sewers; c) to a landfill, assuming that the residual contains no free-draining water and does not have toxic characteristics as defined by the TCLP test; and d) by land application (Chwirka et al., 2001). A 1991 survey of 612 utilities serving populations of > 50,000 showed that landfill disposal was the predominant disposal method followed by land application > sanitary sewer disposal > direct stream discharge > lagooning (Kawczyinski and Achtermann, 1991). In the state of Florida, the most acceptable long-term disposal method of WTRs is landfilling (Townsend et al., 2001) and land application (O'Connor et al., 2005). The disposal (via landfill) cost of non-hazardous WTRs is estimated at < \$50 Mg^{-1} (Meng et al., 2001). Land application is an attractive and less expensive alternative means of WTRs disposal and may have the added benefit of immobilizing P in poorly P-sorbing soils. Land application of WTRs can be a cost-effective treatment for effectively sorbing excess levels of labile P in soils. The high amorphous aluminum (Al) or iron (Fe) content of the WTRs can increase a soil's P sorption capacity (Elliott et al., 1990; Novak and Watts, 2004; Dayton and Basta, 2005; Rhoton and Bigham, 2005). Land-application of WTRs can significantly reduce runoff-P from agricultural fields. Haustein et al. (2000) documented decreasing soluble P concentrations in runoff from fields excessively high in soil test P following amendment with an Al-WTR (rates up to 18 Mg ha^{-1}). Gallimore et al. (1999) applied an Al-WTR to poultry litter-amended soils, and reduced soluble P in surface runoff. Peters and Basta (1996) significantly reduced (~ 50 % of the initial values) soil test-extractable P concentrations of an acidic and a calcareous soil incubated with high loading rates of two Al-WTRs (~ 60 and 200 Mg ha^{-1}).

Because of the wide variation among the drinking-water treatment procedures and source waters, each WTR is unique, making it difficult to predict P sorption based on water treatment

method alone. A better approach is to identify the WTR components responsible for P sorption. A comprehensive study (Dayton et al., 2003), generated by a 17 hour batch equilibration, using 21 Al-based WTR from Oklahoma utilities, examined WTR chemical components related to P sorption. The P sorption maxima (P_{max}) of the WTRs were related to amorphous Al-oxide (Al_{ox}) concentrations (Dayton et al., 2003). However, further studies showed these short-term equilibration studies greatly underestimated the true adsorption capacity of WTRs (Ippolito, et al., 2003; Dayton and Basta, 2005; Makris et al., 2005).

O'Connor et al. (2002) showed that P movement from P-enriched sandy soils to freshwater supplies is reduced when the soils were treated with WTRs. The primary purpose of their study was to investigate the ability of three WTRs produced in Florida to reduce soluble P levels in Florida soils amended with fertilizer, manure, and biosolids-P sources. Phosphorus was hypothesized to be immobilized by specific adsorption and /or precipitation. The Al-WTR used had an especially large P-sorption capacity of at least 5000 mg P kg^{-1}. Sorption of P by the Al-WTR and a Fe-WTR was independent of pH (4-8), and essentially irreversible. The combined data suggested that WTRs could be effective amendments to improve P retention in poorly P-sorbing Florida soils when applied at practical rates of several Mg ha^{-1}. Brown and Sartain (2000) showed that a 25 g kg^{-1} Fe-WTR application rate significantly reduced P leaching from applied fertilizer P, with minimal negative impact on bermudagrass (*Cynodon dactylon)* P uptake. Thus, WTR can be a cost-effective amendment for immobilizing P in contaminated sites.

Elliott et al. (2002b) compared the ability of water treatment residuals {aluminum sulfate (Al-WTR), and ferric sulfate (Fe-WTR), a lime softening residual (Ca-WTR)} and pure hematite to alter P solubility and leaching in low P-sorbing, Immokalee sand amended with dewatered biosolids and triple superphosphate (TSP) fertilizer. In the absence of WTRs, 21% of TSP total P

and 11% of biosolids total P leached from laboratory columns over 4 months. When co-applied with WTRs, the losses from TSP treated columns were reduced to 3.5% (Fe-WTR), 2.5% (Ca-WTR) and < 1% (Al-WTR) of applied P. For the biosolids treatments, all WTRs retarded downward P flux such that leachate P was not statistically different from those of the control (soil only) columns.

Alum additions to poultry litter are known to reduce P solubility and reduce P losses from poultry litter-amended soils (Peters and Basta, 1996; Moore, 1998; Gallimore et al., 1999). Aluminum-WTR was expected to be equally effective and less expensive than alum. Laboratory work confirmed that alum and Al-WTR, on a per mole of oxalate-extractable Al basis, were equally effective in controlling P solubility (Makris et al., 2005c). Thus, when Al-WTR is available, its use can reduce costs associated with alum, and when Al-WTR is in short supply, alum may be substituted to meet the Al demand for P solubility control.

Phosphorus sorption kinetics by WTRs exhibit a slow phase that followed a rapid initial phase, as typically occurs with metal hydroxides (Makris et al., 2005a, b; Makris and Harris, 2006). The slow phase continued for at least 80 d, and suggested continued slow penetration of P into the WTR structure. Electron microprobe analysis of cross-sectional, P-treated particles suggested three-dimensional P sorption that was time-limited by P diffusion through abundant microporosity in the WTRs (Makris et al., 2004a). Estimates of the effective P diffusion coefficient were very small (Makris et al., 2004b) and consistent with the slow P-sorption kinetics once surface sites (fast kinetics) were occupied.

Two main concerns with the land application of WTRs are the potential for induced plant P deficiencies and Al toxicity (Basta et al., 2000). Studies have shown that application of WTR > 10g WTR kg^{-1} (~20 Mg WTR ha^{-1}) reduced tissue P concentrations, but did not induce other

nutrient deficiencies or toxicities (Elliott and Singer, 1988; Heil and Barbarick, 1989; Cox et al., 1997). Harris-Pierce et al. (1993) reported minimal negative effects of WTR (5.6 to 22.4 Mg ha^{-1}) and biosolids (11.2 Mg ha^{-1}) co-applied on native rangeland vegetation. Gallimore et al. (1999) found that land application of WTR at rates of 11.2 and 44.8 Mg ha^{-1} did not increase dissolved solids or Al in surface runoff. Haustein et al (2000) reported no significant increase of dissolved Al in surface runoff of Al-WTR amended soils (2.2 to 18 Mg ha^{-1}). Equilibrium soluble Al concentrations in the Al-WTR systems were usually less than 1 mg L^{-1} (and decreased further as Al-WTR rates increased), suggesting minimal Al phytotoxicity hazard.

Short-term lab, greenhouse, and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P concentrations in runoff (Basta and Storm, 1997; Dayton et al., 2003; Novak and Watts, 2004; 2005; Dayton and Basta, 2005; Elliott et al., 2005), and leaching (Elliott et al., 2002a; Silveira et al., 2006) from soils impacted with animal manure. Concentrating the WTRs in strips of land, rather than applying the residuals to an entire watershed, reduces the amount of WTR needed while protecting surface waters from P pollution (Basta et al., 2003). The authors concluded that such buffer strips are a best management practice to reduce surface water pollution, and the effectiveness of the strips can be greatly improved by amendment with WTRs (Basta et al., 2003). Silveira et al. (2006) reported that mixing WTRs with a manure-impacted Spodosol reduced soluble P concentration in leachates by as much as 99.8%, compared with samples without WTR.

The long-term stability of sorbed P on soil oxide components, however, is an issue that has not been thoroughly explained or documented. Time constraints associated with conducting long-term (> 20 years) field experiments to test the stability of soil metal oxides inhibit improved understanding of the fate of sorbed oxyanions in soils. Investigations of the long-term P

immobilization capacity of WTRs are necessary, as well as studies of management practices that will enhance stable immobilization of P without adversely affecting the productivity of agricultural soils.

Several approaches can be used to address the long-term stability of solid phase-immobilized contaminants, including chemical extractions, spectroscopic measurements, equilibrium (modeling) calculations, and the use of radioisotopes to quantify contaminant lability. The various approaches require samples of various "ages" to address long-term stability.

The use of radioisotopes has significantly assisted in the study of the behavior of both nutrient and toxic elements in soil (Hamon et al., 2002). Many elements have useful radioisotopes that can be used to study retention and plant uptake processes in soil. Several researchers have used the isotopic dilution methodology to quantify element partitioning between labile and non-labile pools (Fujii and Corey, 1986; Gao et al., 2004). The isotopic exchange (E-value) method has been applied successfully to investigate the stability of solid-phase associations of various elements (Fujii and Corey, 1986; Hamon et al., 2002; 2004; Lombi et al., 2003; Gao et al., 2004). Isotopic dilution techniques can provide insight into changes in the distribution of P between labile (isotopically exchangeable) and fixed (nonisotopically exchangeable) pools following incorporation of remediation materials.

The use of isotopes to assess the solid $\Leftrightarrow$ solution phase partitioning of elements in soils relies on the following principles: (a) that addition of the isotope does not perturb the equilibrium of the system because only a negligible quantity of isotope is introduced and (b) that the isotope behaves exactly as the natural element in the soil (Hamon et al., 2002). Assuming these principles hold, an isotope introduced to a soil will partition such that, at time $t = \infty$, $C_s/C_{tot} = I_s/I_{tot}$, where C and I are the concentrations of element and introduced isotope, respectively, in

solution (s) and total (tot) in the soil. At any given time $t<\infty$, the extent of isotope partitioning to the solid phase indicates the exchangeability (lability or E value) of the element associated with the solid phase (Hamon et al., 2002).

Several researchers have used the isotopic exchange and dilution techniques as useful tools to examine the lability of metals in soils (Fujii and Corey, 1986; Hamon et al., 2002; 2004; Lombi et al., 2003; Gao et al., 2004). When isotopic tracers are added to soil solution, they rapidly exchange with the surface-bound metal that is in direct equilibrium with the soil solution. In contrast, metals tightly held in crystalline mineral precipitates or occluded in mineral lattices are only very slowly exchangeable (Hamon et al., 2002; Lombi et al., 2003). The labile pool (E_a) of the metal is calculated as follows

$$E_a = (C_{sol} / C^{\S}_{sol}) * R * (V/W) \quad (1)$$

where C_{sol} is the concentration of the metal in solution (μg mL^{-1}), $C^{\S}sol$ is the concentration of radioisotope (Bq mL^{-1}) remaining in solution after the equilibration time, R is the total amount of the radioisotope that was added to the sample (Bq mL^{-1}), and V/W is the ratio of solution to sample. The amount of isotopically exchangeable metal associated specifically with the solid phase (E_e) is calculated as follows

$$E_e = (C_{sol} / C^{\S}_{sol}) * (R - C^{\S}_{sol}) * (V/W) \quad (2)$$

The samples to evaluate long-term stability of WTR immobilized-P can be obtained from long-term field studies or from laboratory studies of artificially-aged materials. Artificial aging can be accomplished using elevated temperatures (Ford et al., 1997; Makris et al., 2005c), or repeated wetting and drying cycles, (Kennedy et al., 2004). Incubation at elevated temperatures or repeated wetting and drying results in dissolution, crystallization and re-crystallization of metal oxides (Ma and Uren, 1997). Aging results in the transformation of the metal oxides, and

eventually affects their sorption capacities. Temperature controls the transformation of amorphous to crystalline solid phases. Hematite formation is optimum at temperatures > 90°C, whereas goethite can be optimally synthesized at temperatures < 40°C (Schwertmann and Cornell, 1991). Work done by Kennedy et al. (2004) showed that repeated wetting and drying induces structural changes in metal oxides.

Makris (2004) utilized both field and artificially-aged (through thermal incubation) samples and applied chemical extractions and spectroscopic approaches to study the stability of WTR- immobilized P. His work showed that adsorption of P by WTRs was strongly hysteretic. Once sorbed in the internal micropores of WTR, P release is unlikely because of very high bonding energy of P to surfaces and structural limitations to P movement through "bottle-necks" consisting of complex metal-organic C assemblages (Makris, 2004). Samples of WTRs and WTR amended soils were thermally incubated to artificially "age" the materials, and to encourage reactions expected to occur in the field in the long-term. Both spectroscopic and chemical (extractants) techniques were utilized to characterize the "aged" samples. Collectively, the data supported earlier conclusions that immobilized-P is stable; in particular, there were no indications that heat-induced reorganization of amorphous WTR structures caused P to be excluded (released) from the structure (Makris, 2004). Though spectroscopic studies showed no crystallinity of the WTR aged at elevated temperatures, Makris (2004) suggested that elevated temperatures accelerated diffusion of the sorbed P into the micropores of the WTR and that structural changes prevented the sorbed P from being released. The thermal incubation data, however, did not show any pronounced differences in spectroscopic characteristics between the samples incubated at room temperature (23 ^{o}C) and those incubated at elevated temperatures (70 ^{o}C). Chemical analysis of field samples of both the control (unamended) and the WTR

treatments showed a reduction in desorption of the sorbed P. These results suggest that a different approach is needed to determine the solubility of the sorbed P over time to precisely predict the long-term stability of the WTR-sorbed P.

Additional approaches include the use of radioisotopes (^{32}P) to investigate the lability of the WTR-sorbed P as a function of soil pH; chemical equilibrium modeling to predict possible solid phases (if any) controlling the solubility of the WTR immobilized P, and runoff studies (via rainfall simulation) to determine the longevity of WTR immobilization of P. This additional information should improve our ability to predict the long-term stability of the WTR-sorbed P.

Appropriate hypotheses were formulated as follows:

- **H1**. Soil amendment with WTR will reduce P solubility in P impacted soils under natural (field) conditions.
- **H2**. Aging will induce changes in the nature of WTR-P binding that will prevent desorption of WTR immobilized P.
- **H3**. Sorbed P will remain unaffected by reasonably anticipated changes in important soil parameters (e.g. pH).
- **H4**. WTR application will reduce labile P concentrations in runoff and leachate, thus improving runoff and leachate quality.
- **H5**. Stable Al- and Fe-phosphate minerals will control solubility of WTR immobilized P, thus ensuring that WTR immobilized P remains stable in the long-term.

The overall objective is to assess the long-term stability of WTR immobilized P. Specific objectives addressed in this dissertation are to:

- evaluate changes in lability of WTR immobilized P with time
- determine pH effect on lability of WTR immobilized P
- assess the stability and longevity of WTR immobilized P under field conditions
- evaluate long-term effectiveness of WTR in improving leachate and runoff quality
- predict solid phases controlling solubility of WTR immobilized P, and evaluate the stability of the predicted solid phases.

CHAPTER 2
CHARACTERISTICS OF FOUR DRINKING-WATER TREATMENT RESIDUALS AND THREE SOILS

Introduction

Drinking-water treatment plants use different water sources and different chemicals (types and rates) as coagulants. Thus, the WTRs produced by different drinking-water treatment plants and at different times by the same drinking-water treatment plants can have widely different physical characteristics, elemental compositions and sorption capacities (Makris and O'Connor, 2006). Drinking-water treatment residuals are commonly characterized by broad particle size distributions. Very coarse fragments (> 2 mm) exist in small numbers, and the greatest number of WTR particles is usually found in the micrometer (1 - 5 μm) size range (Makris and O'Connor, 2006). The broad size distribution is evidenced by the predominance of large amounts (% number distribution) of small particles (0.1 - 10 μm) (Makris, 2004).

Elliott et al. (2002b) explained differences in P-fixing capacities of an Al- and a Fe-WTR by variations in the reactive Fe- and Al-hydroxide contents, as measured by oxalate extraction. Their results indicated that an Al-WTR was more effective in sorbing P than a Fe-WTR. Dayton et al. (2003) found that variations in oxalate-extractable Al concentrations of 20 Al-WTRs explained differences in runoff-P reductions by WTRs ($r^2 = 0.69$, quadratic model). However, Dayton et al. (2003) used short (15 h) equilibration times and modest initial P loads (up to 2,500 mg kg^{-1}). A recent attempt to improve P sorption maxima predictions for the same Al-WTRs utilized a different solid:solution ratio (1:100), smaller size aggregates (< 150 μm), and longer equilibrations times (6-d), and resulted in a significant ($r^2 = 0.91$) linear relationship between oxalate-extractable Al and P sorption maxima (P_{max}) for Al-WTRs (Dayton and Basta, 2005). Similar work was not conducted for either Fe-, or Ca-based WTRs. Surprisingly, the linear model reported by Dayton and Basta (2005) suggests significant P retention (11.3 g kg^{-1}) at zero

oxalate extractable Al. Thus, the empirical regression model predicts that a material with negligible oxalate-extractable Al concentrations would sorb more than 1 % soluble P (1.1 %). In a long-term (up to 80 days) P sorption study utilizing P loads of 10,000 mg kg^{-1} and 7 Fe-, and Al-based WTRs (< 2-mm), no significant correlation existed between oxalate-extractable Fe +Al concentrations with P sorption maxima for the 7 WTRs, despite the high oxalate extractable Fe and Al levels (Makris et al., 2005a). Oxalate-extractable [Fe+Al] accounted for 50 to 65 % of total [Fe+Al] for the Fe-WTRs and 80 to 90 % of total [Fe+Al] for Al-WTRs (Makris et al., 2005a).

Phosphorus sorption maxima differ among WTRs with contrasting physicochemical properties. Dayton et al. (2003) reported a wide range in P sorption among 21 WTRs (0.5 - 5.0 g kg^{-1}). The authors suggested that the large variability in WTR sorption was probably due to differences in water treatment processes (i.e. how much coagulant was used) and differences in particle size distribution (Dayton et al., 2003). Phosphorus sorption experiments (25 ^{o}C) with one Al-WTR showed a maximum P sorption capacity of 12.5 g kg^{-1} (Ippolito et al., 2003). Butkus et al. (1998) were able to load a Fe-WTR with ~ 20 % P by wt. (200 g kg^{-1}). Makris (2004) reacted Al- and Fe-WTR particles with inorganic P solutions at P loads up to 10 g P kg^{-1}. Almost all of the added P was sorbed by most WTRs, although some WTRs sorbed little P.

There are two contrasting views about P sorption kinetics by WTRs. Makris et al. (2005a) suggested that P sorption kinetics of WTRs are usually biphasic. Novak and Watts (2005), on the other hand, suggested that first order kinetics adequately describe the reactions. Nevertheless, both models suggest that P sorption reactions with < 2-mm WTR particles may not reach equilibrium in short contact times (up to 1 or 2 days).

The WTRs utilized in the study were obtained from different drinking-water treatment plants, and the WTRs were expected to have different physicochemical characteristics and different P sorption kinetics. The objectives of this work were, therefore, to characterize the WTRs used in this study, ascertain their P sorption kinetics and characterize the soils used to know their initial physicochemical properties before applying any amendment.

Materials and methods

Collection of WTRs and Soils Used

Four WTRs were used in this study: three were Al-based, and one was Fe-based. The Al-WTRs were obtained from one water treatment plant in Bradenton, Florida, one plant in Holland, Michgan, and one plant in Lowell, Arkansas. The Fe-WTR was obtained from a plant in Cocoa Beach, Florida.

The Bradenton WTR was used in a joint South Florida Water Management District (SFWMD) and Florida Department of Environmental Protection (FDEP) project in Kissimmee watershed, FL, seeking to control P loss in surface runoff and leachates. The material was obtained from the Manatee Co. water treatment plant in Bradenton, FL. Samples of the WTR, similar (in chemical characteristics) to the one that was land-applied in the field study were shipped to our laboratory in 2004. Another Al-WTR used came from the Holland, MI water treatment plant. This material is produced by alum addition to raw water. The material was used in a field experiment at Holland, MI to evaluate the longevity (~7.5 years) of WTR effects in waste-amended soils high in soil test P levels. Subsamples were transferred to our laboratory from the initial stockpile that was land-applied in 1998 (Jacobs and Teppen, 2000). The third Al-WTR came from the Beaver Water treatment plant in Lowell, AR. This material was successfully used to reduce runoff-P in rainfall simulation plots of soils (Haustein et al., 2000) with high soil test P levels. However, a different batch than the one used by Haustein et al.

(2000) was shipped to us, as was later evidenced by differences in chemical composition. The Fe-based WTR came from the Taylor Creek Surface water treatment plant, Cocoa Beach, FL, where iron sulfate is coupled with powdered activated carbon (PAC), (100 tonnes) and polymer (7 tonnes) additions, annually.

Soils from three field sites were used for the various studies: One site located at Immokalee, FL and two field sites (sites 1 and 2) located in western Michigan were used for this study. Native Immokalee sand (sandy, siliceous, hyperthermic Arenic Alaquods) samples not contaminated by manure depositions and having 'very low' soil test P and very coarse texture were collected from the University of Florida Research and Education Center in Immokalee, FL. Multiple random samples were collected from the A horizons (0-15 cm), and were thoroughly mixed to yield a composite sample. The two test sites in Michigan (Jacobs and Teppen, 2000) were selected in 1998 for evaluation of WTR effects on P extractability in soils having "very high" Bray-1 soil test P concentrations. Soils from both sites have a long-term (> 10 yr) history of heavy chicken manure applications (actual application rates unknown). Soil at site 1 was a Granby fine sandy loam (sandy, mixed, mesic Typic Endoaquolls) with "very high" Bray-1 soil test P levels of 265 mg kg^{-1}. Soil at the second site was Granby loamy sand (sandy, mixed, mesic Typic Endoaquolls) with an even greater soil test P value of 655 mg kg^{-1}.

Characterization of WTRs and Soils Used

Samples of both soils and WTRs were air-dried and passed through a 2 mm sieve before analyses. Particle size distribution of the samples was determined by the pipette method (Day, 1965). The pH of both WTR and soil samples was determined in a 1:2 WTR to 0.01 *M* $CaCI_2$ solution using a glass electrode (McLean, 1982). Electrical conductivity (EC) of the WTR was determined in a 1:2 WTR to deionized water solution (Rhoades, 1996). Total C and N of both WTR and soil samples were determined by combustion at 1010 ^{o}C using a Carlo Erba NA-1500

CNS analyzer. Soluble reactive P (SRP) in the WTR was measured in a 0.01 M KCl solution at a 1:10 solid:solution ratio, after 40 days reaction, whereas the SRP of the soil samples was measured after reaction for 24 hours. Extracts were filtered (Whatman No 42) and analyzed colorimetrically for P with the Murphy and Riley (1962) method. Total P, Fe, and Al in both WTR and soil samples were determined by ICP-AES (Perkin-Elmer Plasma 3200) following digestion according to the EPA Method 3050A (USEPA, 1986). Oxalate (200 mM) extractable P, Fe, and Al of both the WTR and soil samples were determined by ICP-AES after extraction at a 1:60 solid:solution ratio, following the procedures of Schoumans (2000). Oxalate-extractable Fe and Al represent noncrystalline and organically complexed Fe and Al present in the solid (McKeague et al., 1971). Values of the P saturation ratio (PSR) (Maguire et al., 2001), and P saturation index (PSI) (Elliott et al., 2002a) were calculated for the soils and WTRs, respectively. These indices are similar to the degree of P saturation (DPS) index, but omit the saturation factor, α ($\alpha = 0.3$-0.5) in the ratio (Schoumans, 2000). Small PSR and PSI values (< 0.1) suggest excess P sorption capacity and limited P lability.

Typical QA / QC protocols of matrix spike (5 % of the set) recoveries were used in all the experiments. Method reagent blanks, certified check standard analyses, and new standard curves for each set of samples were used.

Phosphorus Sorption Isotherms and P_{max} of WTR Determination

Statistical analyses of the P sorption means versus incubation time showed that three of the four WTRs reached equilibrium conditions after 96 hours. Consequently, the P_{max}, values for each WTR were determined by using a modified batch equilibration technique (Nair et al., 1984), which involved conducting the incubation for 96 instead of 24 hours. One gram (oven-dry equivalent) samples of each air-dry WTR (<2mm diameter) were respectively placed into triplicate 25-ml glass centrifuge tubes. Ten milliliter of solution containing the appropriate

amount of inorganic P (250 to 1000 mg P L^{-1}) was added to each tube. The inorganic P solutions were made from KH_2PO_4 dissolved in 0.01 M $CaC1_2$. After the 96-hour equilibration, solutions were filtered through a 0.45µm filter membrane and P was determined colorimetrically (Murphy and Riley, 1962). The P lost from the initial solution was assumed to be sorbed to the soil. 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:

$$C/Q = (1/P_{max})(C) + 1/(k)(P_{max})$$

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).

A linear regression analyses was performed between C and C/Q, and P_{max} values were calculated from the inverse of the slope from the regression equation. Previously sorbed P was subtracted from all isotherms values before plotting to obtain corrected P_{max} values.

Phosphorus Sorption Kinetics by WTRs Used

Representative air-dried (< 2 mm) samples of the WTRs were reacted for 1, 7, 14, 21, 28, 35 and 42 days with P solutions that resulted in P loads of 2,500 to 10,000 mg P kg^{-1} in a 1:10 WTR:0.01 M KCl suspensions. The same tests allowed determination of P sorption capacities and kinetics of P retention by the materials at 23 ± 2 ^{o}C. The selection of the above range of P loads was based on sorption experiments reported by Dayton et al. (2003), Makris et al. (2005b) and Novak and Watt (2005). Initial P concentrations far exceed those typically found in P-enriched soils, but were selected to account for cases where repeated annual P-source applications or dairy-impacted systems occur. The pH was not controlled and suspensions were not shaken during the equilibration period. No mechanical energy (shaking) was applied to the samples since shaking is not a field process and Makris (2004) observed no significant difference

in P sorption after 10 days between shaken and non-shaken samples. Following the reaction periods, suspensions were centrifuged, filtered (0.45 μm), and analyzed for P colorimetrically using the method of Murphy and Riley (1962).

Results and Discussion

Physicochemical Characterization of the WTRs

The WTRs were analyzed for selected physicochemical properties (Table 2-1). All the WTRs had large percentage of coarse (> 0.02 - 2 mm) size fraction. However, the Al-WTRs had relatively high percentage of fine (< 0.02 mm) size fraction. The relatively high percentage of the fine-sized fraction of the Al-WTRs implies that such WTRs will have greater surface area to rapidly sorb P than the coarse-textured Fe-WTR aggregates. Novak and Watts (2005) observed that WTR aggregate size was inversely related to the P_{max} of the WTR. Thus, crushing WTRs into smaller diameter aggregates can increase the P_{max} values between 1- and 2-fold (Novak and Watts, 2005). The pH of Al-WTRs was circumneutral (6.5- to 7.1), within the normal range for soils (Bohn et al., 1985), and may result from pH adjustment with alkaline materials (i.e., calcium hydroxide) during drinking-water treatment. Makris and O'Connor (2006) observed that pH of Al-WTRs is commonly circumneutral (5.0 - 7.0), although some WTRs exhibit pH values as great as 8.2. The EC values of the Al-WTRs ranged from 1.02 to 1.49 dS m^{-1}, well below the 4.0 dS m^{-1} associated with soil salinity problems (Brady and Weil, 2002). The KCl-P represented only a small fraction of total P, and ranged from 0.3- to 0.6 % of total P. Phosphorus solubility (KCl-extractable P) in WTRs is typically low and represents only a small fraction (< 0.2 to 0.7 %) of total P for all three WTR classes (Makris and O'Connor, 2006). The KCl-extractable P is considered the most available pool of P and varies among different P sources (Elliott et al., 2002b). The very low amounts of KCl-P in WTRs implies that they would be poor sources of P in soils and can serve as additional sinks for P immobilization in poorly P-sorbing soils.

Table 2-1. General physicochemical properties of drinking-water treatment residuals used. Numbers are mean values of six replicates ± one standard deviation.

Source	Bradenton	Holland	Lowell	Cocoa
Form	Al-based	Al-based	Al-based	Fe-based
Sand-size (%)	72.5	76.0	80.4	86.5
Silt-size (%)	12.7	11.8	11.5	12.4
Clay-size (%)	14.8	12.2	8.13	1.14
pH	6.5	7.1	6.8	5.1
EC (dS m^{-1})	1.49	1.21	1.02	1.32
Total C (g kg^{-1})	102 ± 12.1	168 ± 42.4	182 ± 63.1	116 ± 31.2
Total N (g kg^{-1})	7.72 ± 1.32	3.61 ± 0.91	7.21 ± 0.83	11.4 ± 1.41
KCl-P (mg kg^{-1})	5.08 ± 0.8	5.62 ± 0.4	5.26 ± 1.1	6.25 ± 0.9
Total P (g kg^{-1})	3.42 ± 0.2	1.84 ± 0.2	0.83 ± 0.1	0.71 ± 0.2
Total Al (g kg^{-1})	90.1 ± 12.2	68.2 ± 16.2	77.1 ± 18.1	2.24 ± 0.3
Total Fe (g kg^{-1})	6.24 ± 0.6	8.71 ± 0.4	10.7 ± 2.6	2.42 ± 3.62
Oxalate P (g kg^{-1})	2.98 ± 0.1	1.66 ± 0.1	0.74 ± 0.1	0.61 ± 0.1
Oxalate Al (g kg^{-1})	79.1 ± 12.1	54.3 ± 6.2	68.2 ± 8.4	1.92 ± 0.4
Oxalate Fe (g kg^{-1})	5.24 ± 1.1	7.22 ± 0.8	16.8 ± 1.3	1.41 ± 1.64
PSI[†]	0.02	0.03	0.02	0.03

[†] P saturation index

Total C values for the Al-WTRs varied from 102 to 182 g kg^{-1}. Total C measured values agreed with the range of C found for Al-WTRs (23- to 205 g kg^{-1}; Dayton et al., 2003; Makris, 2004). Total C determinations may overestimate organic C content since the combustion method (temperature 1010 °C) measures both organic and inorganic C. Total C values for the Al- and Fe-WTRs vary widely depending on the raw water source (surface- or ground-water). Often, however, total C values are high, reaching levels on the order of 200 g kg^{-1} regardless of the WTR class (Makris and O'Connor, 2006). 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 used to remove taste and odor from source water (Dayton et al., 2003). Total P values were typical of Al-WTRs (0.3- to 4.0 g P kg^{-1}; Dayton et al., 2003; Makris, 2004). Phosphorus in WTRs originates from the raw water treated in drinking-water treatment plants and ultimately becomes a part of the WTR structure. The

relatively high total P content of the Al-WTRs is probably due to concentration in the WTR after removal from contaminated raw water during treatment. As the KCl-extractable P data show, most of the P in WTRs is insoluble in aqueous suspensions. Other data (Makris et al., 2004b) showed that the P is occluded in the WTR structure and is minimally released over time. Total Al ranged from 38 to 90 g Al kg^{-1}, within normal ranges reported by others (15- to 177 g Al kg^{-1}; Dayton et al., 2003; Makris, 2004; 15 to 300 g Al kg^{-1}; Makris and O'Connor, 2006). The great variability in total Al and Fe concentrations in the WTRs can partially be explained by the fact that different drinking-water treatment facilities add different amounts of Al / Fe salts in the treatment of raw waters, and by differences in the chemical composition of inorganic colloids suspended in the raw water. Aluminum (hydr)oxides are sorbents for oxyanions such as phosphate, thus the high Al content of the WTR suggests that they will be major sorbents for P. Oxalate-extractable Al values were close to total Al (80-90 % of the total), suggesting an amorphous nature of the Al- WTRs. This is consistent with the findings of O'Connor et al. (2001) that the traditional 200 mM oxalate-extractable P, Al and Fe concentrations are typically 80-90 % of the respective WTRs' total elemental concentrations. X-ray diffraction analysis of Fe- and Al-WTRs (Makris, 2004) suggests that amorphous Al or Fe hydroxides dominate the Al- and the Fe-WTRs, respectively, with no apparent crystalline components (Makris, 2004). Oxalate-extractable P, Fe, and Al are usually associated with the amorphous phase of the particles. Oxalate-extractable Al values are highly variable, but typically represent 30-90 % of total Al of Al-WTRs (Dayton et al., 2003; Makris, 2004, Dayton and Basta, 2005), which supports the amorphous model of Al-WTRs. Phosphorus retention is strongly related to amorphous Fe and Al concentrations. Gallimore et al. (1999), Dayton et al. (2003) and Dayton and Basta (2005) concluded that the amorphous (oxalate-extractable), rather than the total Al

content of WTRs, determines their effectiveness in reducing runoff-P. Thus, the high oxalate-extractable metal percentage in Al-WTRs suggests high P sorption effectiveness. This suggestion is consistent with the very small PSI values (~0.02), which gives an indication that the Al-WTRs can be effective sorbents for P.

The Fe-based WTR (Cocoa WTR) had acidic pH (5.1). Typically, Fe-based WTRs are alkaline (pH values 7.2 - 9.2; Makris and O'Connor, 2006) although the pH values for two Fe-WTRs investigated by Makris (2004) were 4 and 5.6. Similar to the Al-WTRs, KCl-P in the Fe-WTR represented only a small fraction (0.3 %) of total. Total C value was 198 g kg^{-1}, within the range of organic C values measured in Al-WTRs (23- to 205 g kg^{-1}, Dayton et al., 2003, Makris, 2004). The Fe-WTR had C:N ratio of 19, suggesting an abundant N pool for plant uptake. Total P content was 0.7 g P kg^{-1}, whereas total Fe was 242 g Fe kg^{-1}. Total Fe measurements were above typical values found for WTRs (50 to150 g kg^{-1}, ASCE, 1996). Large total Fe values may not necessarily correlate well with elemental bioavailability or increased P sorption capacities. Oxalate-extractable Fe accounted for 58.6 % of the total Fe concentration, suggesting an amorphous nature of the WTR. X-ray diffraction analysis (Makris, 2004) suggested that amorphous Fe (hydr)oxides dominated all Fe-WTRs, with no apparent crystalline Fe (hydr)oxides. Iron-based WTRs had reduced oxalate-extractable Fe values as a percentage (45 to 64 %; Makris and O'Connor, 2006) of total Fe compared with the Al-WTRs. This difference might suggest reduction in P sorption effectiveness of the Fe-WTRs compared with Al-WTRs. However, the low PSI value (0.03) suggests that the Fe-WTR can also be an effective P sorbent.

Soil Characterization

The soil samples collected from both sites of the Michigan field study have near neutral pH (Table 2-2). Soil collected at site 2 had greater (1.2 g kg^{-1}) total P than site 1 (0.7 g kg^{-1}) soil. The high total P values reflect the long history of poultry manure application to the fields (Jacobs and

Teppen, 2000). The KCl extractable P accounted for 3.3 and 4.2 %, respectively, of the total P contents at sites 1 and 2. The high KCl-P concentrations at both sites suggest that the soils can contribute significantly to P loss in runoff. The soil from site 1 had greater total Fe and Al content than site 2, suggesting that site 1 had greater potential to sorb excess soil P than the soil from site 2. Soil from site 2 had a relatively high PSR value (> 1), which suggest that site 2 could contribute significant amounts of P in surface runoff. The PSR value of site 1 was relatively low (~ 0.3) and less than one-third of the PSR value of site 2. Site 2 had about twice the STP and one-half the total Fe and Al concentrations of site 1 (Table 2-1). Despite the low PSR value of site 1, a value of 0.3 suggests that the site can contribute some amount of P in runoff from the site.

Table 2-2. Selected physicochemical properties of the Michigan soils (sites1 and 2) and the Immokalee sand. Units for all measurements (except pH and particle size values) are expressed in mg kg^{-1}. Numbers are mean values of six replicates ± one standard deviation.

	Michigan site 1	*Michigan site 2*	*Immokalee Sand*
Sand	60 %	76 %	89 %
Silt	28 %	16 %	5 %
Clay	12 %	8 %	6 %
pH	6.4 ± 0.2	6.8 ± 0.2	5.6 ± 0.3
Total C	18200 ± 334	24000 ± 586	7400 ± 59.4
KCl-P	22.1 ± 2.3	58.1 ± 5.1	4.36 ± 1.4
Oxalate P	512 ± 27.5	970 ± 81.3	11.7 ±2.6
Oxalate Al	2400 ± 221	710 ± 38.5	42.1 ± 9.1
Oxalate Fe	730 ± 48.3	290 ± 12.8	84.2 ± 8.2
Total P	710 ± 47.1	1200 ± 24.3	23.8 ± 4.21
Total Al	7000 ± 235	3400 ± 32.5	61.3 ± 12.3
Total Fe	2700 ± 198	1800 ± 6.7	114 ± 21.6
PSR[†]	0.32 ± 0.11	1.14 ± 0.04	0.09 ± 0.02

[†] P saturation index

The Immokalee fine sand collected from the University of Florida Research and Education Center in Immokalee for the study is acidic (pH = 5.6) and contains small amounts of total carbon and Fe and Al (Table 2-2). The soil contains low amounts of total P, but KCl-P

represents ~ 18 % of total P, a likely consequence of the soil's low Al and Fe contents, which are major sorbents of P. The soil has a PSR value of < 0.1, suggesting that the soil will not be source of P supply in runoff.

Phosphorus Sorption by WTRs

The alum-based WTRs (Bradenton, Holland, and Lowell) have vastly different P sorption characteristics than the Fe-based WTR (Cocoa) (Figure 2-1). All the WTRs sorbed 100% of the initial P in solution at concentrations < 500 mg P L^{-1}. Isotherms were conducted using solutions containing greater initial P concentrations (> 500 mg P L^{-1}) to obtain suitable isotherm points for plotting (Figure 2-1). At the greatest initial P load, the Bradenton material sorbed the greatest amount of P, followed by Holland, Lowell, and Cocoa in that order. Langmuir-sorption maxima could not be determined for the Bradenton and Holland WTRs because isotherms did not exhibit obvious equilibrium conditions. Langmuir-sorption maxima were determined for only the Lowell (alum-based) and Cocoa (Fe-based) WTRs. Both of these WTRs had significantly different P sorption isotherms (Figure 2-1) and there was a 5-fold difference in P_{max} values between the WTRs. The linear form of the Langmuir equation (linear regression relationships between C and C Q^{-1}) fits the data sets of the two WTRs very well (both $r^2 = 0.99$, $p < 0.001$). The slopes of the regression equations for the Lowell and Cocoa WTRs were 0.133 and 0.667, respectively, corresponding to P_{max} values of 7.5 and 1.5 g P kg^{-1}, respectively. The much greater P_{max} values for the Lowell Al-WTR is consistent with its elevated oxalate extractable metal content (Table 2-1). Dayton et al. (2003) reported that WTRs P_{max} values were statistically correlated to their Al_{ox} content. The greater P_{max} of the Lowell WTR can also be related to its greater percentage of fine aggregate sizes (Table 2-1). Novak and Watts (2005) showed that as aggregate size decreased from > 4.0 to < 0.5 mm P_{max} values generally increased, and attributed the change to increased surface area and numbers of reactive sites. Ippolito et al. (2003) also reported a greater P sorption

capacity by smaller-size WTR aggregates (0.1 to 0.3 mm) compared with a non-fractionated sample.

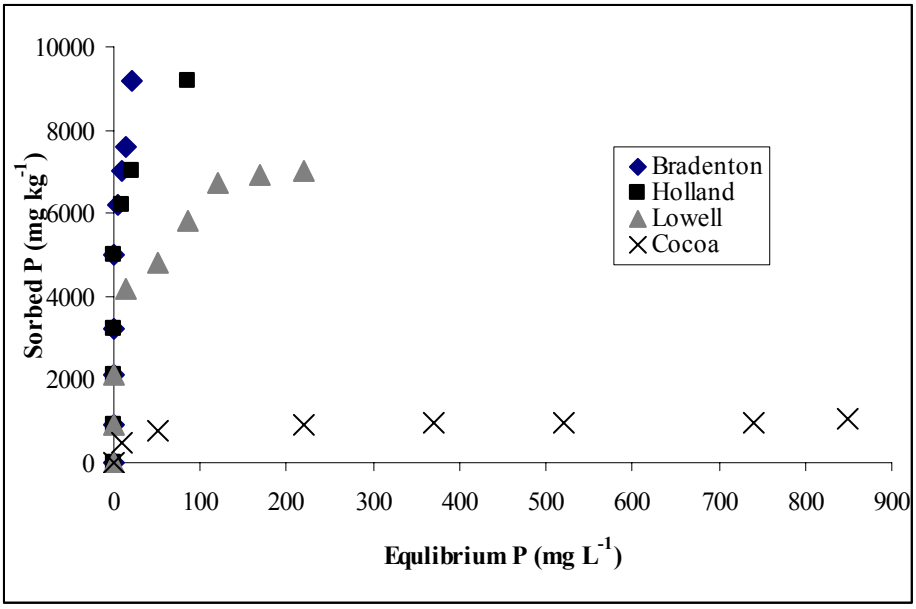


Figure 2-1. Drinking-water treatment residuals' phosphorus sorption isotherms

The Cocoa WTR on the other hand had a lower P sorption capacity due possibly, to the greater percentage of large particle size fraction, lower oxalate extractable Fe+Al concentration, and the acid pH. Traditional measurements of oxalate extractable P, Fe and Al in organic wastes, soils, WTRs and their mixtures have been used to explain trends in runoff-P (Gallimore et al., 1999) and P leaching losses in soils amended with organic P sources and/or WTRs (Elliott et al., 2002). The oxalate-extractable [Fe+Al] accounted for < 60 % of total [Fe+Al] for the Fe-WTRs, whereas for Al-WTRs it accounted for ranged from 80- to 98 % of total [Fe+Al]. This result suggests a smaller reactivity of the Cocoa WTR compared with the Al-WTRs. Elliott et al. (2002) explained differences in P-fixing capacities of an Al- and a Fe-WTR by their varying reactive Fe- and Al-hydroxide content, as measured by oxalate extraction. Their results indicated that the Al-WTR was more effective in sorbing P than the Fe-WTR. The reduced affinity for P exhibited by Cocoa-WTR may also be attributed to the acidic nature of the WTR. Makris (2004)

reported that low pH values (< 5.5) affected organic molecules configuration on the surface of WTRs. Low pH leaves the majority of surface functional groups unionized, such that molecules may lie flat on the surface and block the free transfer of water or solutes in and out of pores, which reduce P accessibility to sorption sites (Makris, 2004). Makris et al. (2005) showed that adjusting the pH to 7 doubled the P sorption capacity of the Cocoa material.

The difference in P_{max} values between the Lowell WTR and the Cocoa-WTR exemplifies the P sorption potential of Al-WTRs (Makris, 2004). The Lowell Al-WTR P_{max} value (7.5 g kg^{-1}) is greater than P_{max} values reported for alum-based WTR produced in Oklahoma (0.30 to 5.14 g P kg^{-1}, Dayton et al., 2003) and in Florida (5 g P kg^{-1}, O'Connor et al., 2002), but lower than some Al-WTRs produced in North Carolina (8.5 g P kg^{-1}, Novak and Watts, 2004). Heterogeneity in residuals P_{max} values is expected, as water treatment facilities vary the concentrations of added alum or other flocculating agents (e.g., Ca or Fe cationic salts), depending on the quality of the raw water (Gallimore et al., 1999).

Phosphorus Sorption Kinetics by WTRs

The Bradenton and Holland WTRs had the greatest and most rapidly expressed affinity for P. Within 7 days, the WTRs sorbed 84 and 91 %, respectively, of the initial load of 10,000 mg P kg^{-1} (Table 2-3). By 14 days, both Al-WTRs sorbed essentially all P from solution. Given enough time (42 days), the Lowell WTR also sorbed a substantial amount (~ 70 % of initial P load) of P from solution. The Cocoa WTR sorbed the least amount of P of all WTRs after 42 days (~12 %).

The WTR-P sorption process is generally described as an initial rapid reaction (primarily on external surfaces), followed by a slower reaction representing P migration into interstitial micropores within aggregates (Makris et al., 2004a,b; Wilson et al., 2004). Phosphorus sorption data presented here (Table 2-3) followed those trends. Initial P sorption was rapid, followed by

slower P sorption. Phosphorus sorption by other WTRs (Makris et al., 2005a) was also initially fast, and was followed by a slow P sorption stage. The fast stage of P sorption presumably characterized P retention on highly accessible surfaces like particle exteriors and macropores (Van Riemsdjik and Lyklema, 1980). The slower stage has been characterized as P association, via diffusion, in micropores (Axe and Trivedi, 2002; Makris et al., 2004b). Phosphorus sorption kinetics by metal hydroxides and soils are well characterized and generally show a fast sorption phase, followed by a slower reaction rate where sorption may never reach true equilibrium (Bolan et al., 1985).

Table 2-3. P sorbed by four drinking-water treatment residuals with time. (Initial P load = 10,000 mg kg^{-1}).

WTR source	1 day	7 days	14 days	21 days	28 days	35 days	42 days
	P sorbed† by WTRs (mg kg^{-1})						
Bradenton	4820	9100	10000	10000	10000	10000	10000
Holland	4560	8400	10000	10000	10000	10000	9980
Lowell	3790	5200	5800	6250	6550	6700	7000
Cocoa	720	835	910	1020	1090	1150	1200

† P sorbed was assumed to be P lost from the initial solution

The fast reaction is ascribed to low-energy, external surface site binding via ligand exchange (Bolan et al., 1985). The slow reaction between P and metal hydroxides proceeds for days, months, and even years, and has been attributed to continuing surface precipitation reactions (Van Riemsdijk and Lyklema, 1980; Nooney et al., 1998) or intraparticle diffusion into micropores (Axe and Trivedi, 2002; Makris et al., 2004a). Makris et al. (2004a) identified the latter mechanism as prominent in the retention of P by WTRs, and suggested that P immobilized by WTRs should be essentially irreversibly bound.

Novak and Watts (2005) suggested that first order kinetics adequately describe P sorption reactions by WTRs, but kinetic data for all the Al-WTRs examined in this study were best fit to a second order reaction rate model (Table 2-4), suggesting a biphasic nature of P sorption. Azizian

(2004) and Makris et al. (2005a) reported similar results and indicated that P sorption reactions by WTRs are best described by second order kinetics. However, P sorption kinetic data for the Fe-WTR (Cocoa WTR) did not fit either a first- nor second order reaction rate model, possibly, due to limited P sorption of the Cocoa WTR (Table 2-4). This result is consistent with the observation of Makris et al. (2005a). The second order reaction rate coefficients increased with the P sorption capacities of the WTRs. The faster the reaction, as suggested by larger rate 2nd order coefficients, the greater the amount of P sorbed. The Bradenton and Holland WTRs had the greatest second order rate coefficients, suggesting little effect of the slow P stage on the overall P reaction with the solid. The two WTRs exhibited the fastest removal of P from solution and depleted all of the added soluble P within 14 days. The Cocoa material exhibited the smallest 2nd order rate coefficient, suggesting a greater effect of the slow P sorption stage compared with the other Al-WTRs. The slow P stage in the Cocoa material was rate limiting for P sorption.

Table 2-4. Determination coefficients (r^2) of the reaction rates and 2nd order rate constants for the drinking-water treatment residuals used.

Source	Form	Rate fit (r^2)		Rate constants (k)
		1st order	2nd order	(L s^{-1} mg^{-1})
Bradenton	Al-based	0.82	0.96	$1.36 * 10^{-4}$
Holland	Al-based	0.89	0.97	$1.59 * 10^{-4}$
Lowell	Al-based	0.90	0.96	$2.82 * 10^{-5}$
Cocoa	Fe-based	0.34	0.49	$7.25 * 10^{-9}$

The Al-WTR P sorption data conflict with the suggestion of Butkus et al. (1998) that adding P to WTR as a pretreatment converts WTR from a P consumer to a P supplier. Our results indicate that P is highly sorbed, over time becomes strongly chemisorbed to the WTR, and would represent a poor P supplier. Bowman et al. (1998) concluded that reactive Fe and Al oxide surfaces, along with $CaCO_3$, play a role in determining transitional or intermediate P levels. Over time, a more resistant P pool is formed. The specific binding of P has been described by Bohn et

al. (1985), where adsorption occurs at the hydrous aluminum oxide interface with phosphate replacing singly coordinated OH- groups and then reorganizes 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) used X-ray absorption near edge structure spectroscopy, and showed a conversion of alum to an amorphous $Al(OH)_3$ precipitate in alum-amended poultry litter. The amorphous $Al(OH)_3$ then reacted with poultry litter-borne P via an adsorption mechanism. Similar mechanisms may also describe P adsorption on aluminum-containing WTR.

CHAPTER 3
STABILITY OF WTR IMMOBILZED PHOSPHORUS: KISSIMMEE FIELD STUDY

Introduction

Phosphorus loss from agricultural cropland is one of the major factors responsible for accelerated eutrophication of surface waters in many locations in the USA, including the Great Lakes, Chesapeake and Delaware Bays, Lake Okeechobee, and the Everglades (Sharpley et al., 1996; Daniel et al., 1998; Sims et al., 1998; Sims et al., 2000; Maguire et al., 2001). Lake Okeechobee, the major aquatic resource for water storage, wildlife, and recreation in south Florida, is threatened by cultural eutrophication from excessive P loading in the surrounding basins. The Kissimmee watershed has a prolonged history of using P sources such as P fertilizers, manures and biosolids to increase soil fertility and crop yields. However, applications of organic sources of P are typically based on crop N requirements, which provide P in excess of crop needs. Eghball and Power (1999) showed a significant accumulation of plant available P in the top 15 cm of soil following N-based beef cattle manure or compost application, but no accumulation occurred with P-based applications. Phosphorus build-up in the soil is not detrimental to crops, but off-site migration to surface waters is a major concern because P is the limiting nutrient for eutrophication of most freshwaters (Elliott et al., 2002 a; O'Connor and Chinault; 2006). Soils in the Kissimmee watershed (e.g. Immokalee sand and Myakka sand) sorb P poorly, and there is concern that such high-P soils represent an increased risk for nonpoint-source pollution of surface waters (Elliott et al., 2002a; O'Connor et al., 2002). Concerns about P pollution from biosolids, in particular, have resulted in land application guidelines that limit application rates to those based on crop-P removals (typically, ≤ 2 Mg ha^{-1}). Such rates are so low (uneconomical and impractical) that the beneficial recycling of biosolids to lands in the watershed is seriously threatened (O'Connor and Chinault, 2006).

Excessive soluble P concentrations can be controlled with environmentally-benign and cost-effective P-sorbing amendments such as alum (Moore, 1998) or drinking-water treatment residuals (WTRs) (Elliott et al., 2002b). Numerous P sorption-desorption studies and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P from P-impacted soils (Elliott et al., 2002a; Dayton et al., 2003; Makris, 2004; Makris et al., 2004a,b). Although in the short term, WTR is effective in reducing soluble P levels, field studies to ascertain the long-term stability of WTR immobilized P are scarce. The stability of sorbed P by WTRs has been qualitatively addressed in lab experiments (Makris et al., 2004a,b). The lab experiments suggested that intraparticle P diffusion into the WTRs, coupled with minimal (highly hysteretic) P desorption represented irreversible P sorption by the WTRs. Field experiments are needed to test WTR efficacy in reducing soluble P concentrations and to confirm trends observed in, or inferred from, lab studies.

The initial objective of this study was to determine the effects of WTR on P losses to surface and groundwater from land amended with different P sources (biosolids, manure and inorganic fertilizer) applied at P- and N-based rates. However, this objective could not be pursued to its logical conclusion due to a natural disaster. The fall of 2004 was an especially busy hurricane season in south FL, and the experimental plots were heavily flooded and berms separating the plots were breached. The flooding appears to have contaminated (moved soil and associated treatments) across plots, which forced early termination of the experiment. In view of this mishap, we also modified the initial objective of our study to focus on the effectiveness of WTRs as a best management practice to minimize P solubility in P-amended, low P sorbing Florida soil, and to assess the stability of WTR immobilized P when the hydrology of WTR amended soil changes.

Materials and Methods

Field layout and Amendments Application

The study was carried out at a cattle-pasture (Kirton Ranch) located on the eastern border of Okeechobee County, seven miles (11.3 km) northeast of Okeechobee, and north of Lake Okeechobee. The soil at the project site is the Immokalee fine sand, a typical Spodosol, classified in the Arenic Alaquods taxonomic group, with a distinct A, E and Bh horizons.

The experimental design was a 48-plot randomized complete block design (RCBD) consisting of three blocks with each block evaluating four P-sources: A) two biosolids: a "moderate-soluble P" source from Pompano Beach, FL, and a "high-soluble P" source from Boca Raton, FL, B), poultry manure from Indiantown, FL, and C) inorganic fertilizer (TSP). The P sources were applied with and without WTR (aluminum-based, obtained from Manatee Co. Water Treatment Plant in Bradenton). An extra plot per block was left untreated as the “control”. The pasture was fenced to prevent cattle from entering the study field. Two application rates for the P sources were utilized to attain P-based and N-based nutrient management. The 39.6 kg P ha^{-1} rate represents the IFAS recommended rate for bahiagrass (Hanlon, 1995). The plots receiving this nutrient rate represent the P-based rate treatment. Similarly, the 179 kg N ha^{-1} rate represents the recommended (Hanlon, 1995) N-based rate. The TSP fertilizer N-based rate was 128 kg P ha^{-1}, and approximates the rate of P applied when biosolids or manure are applied at an N-based rate. The N and P concentrations and the percent solids of the biosolids, and the poultry manure (Table 3-1) were used to calculate the quantities of materials to be applied. The Al-WTR (10 g kg^{-1}, 22.4 Mg ha^{-1}) was applied on May 9-13, 2003. The two biosolids were applied from May 13-14, 2003. The poultry manure was applied on May 14, 2003. The TSP fertilizer was applied on May 19, 2003. Ammonium nitrate was applied from May 23-26, 2003, to the P-based treatments of the biosolids and the manure to equalize the N supplied by the amendments that

differ in total N levels. No ammonium nitrate was applied to the N-based treatments except for the TSP. The study field was mowed a week prior to application of materials. The study continued for two growing seasons (terminated Dec 2004), but amendments were applied only in 2003.

Soil and Amendment Characterizations

General and P-specific characterization was done on the soil samples and the amendments (materials actually applied). Portions of the applied amendments were air-dried and ball-milled for analysis. The soil samples were air-dried and passed through a 2 mm sieve before analysis. The amendments and soil samples were analyzed for total P, Fe, Al, Ca, Mg by ICP-AES following digestion according to the EPA Method 3050A (USEPA, 1986). Oxalate (200 mM) extractable P, Fe, Al, Ca, and Mg were determined by ICP-AES after extraction at a 1:60 solid:solution ratio, following the procedures of Schoumans (2000). Total C and N of the amendments were determined by combustion at 1010 °C using a Carlo Erba NA-1500 CNS analyzer. Total C, but not N, was analyzed for representative soil samples, and pH measurements were performed on fresh materials (1:2 solid or soil:solution ratio). Percent solids were determined by drying materials at 105 °C (Sparks, 1996).

Periodic Soil Sampling and Analysis

Composite soil samples (formed by mixing twenty 2.5-cm-diameter core samples) were obtained from each plot of the study site. Soil sampling to characterize initial conditions of the field after amendment application occurred in June, 2003. A second sampling occurred in January 2004 (8 months after the material application). For both samplings, samples were taken from the upper 5 cm of the A horizon, the middle of the E horizon (~ 45-55 cm from the top); and the top 10 cm of the Bh horizon. The impact of the amendments on the P chemistry in the entire A horizon (0-15 cm) was determined in another sampling in March 2004. A final sampling

was done in December 2004, following the termination of the field study. Samples were taken from the A horizon (0-5 cm and 0-15 cm), the middle of the E horizon (~ 45-55 cm), and the top 10 cm of the Bh horizon, to provide comparisons with the samples taken previously. Soil samples were air-dried and passed through a 2-mm sieve before analysis.

The samples were analyzed for total- and oxalate extractable P, Al and Fe as described above. The degree of phosphorus saturation (DPS) was calculated for the soil samples, and represents the moles of oxalate P divided by the sum of moles of oxalate-200mM (Fe + Al), assuming a saturation factor (α) value of 0.55 as suggested by Nair et al., (2004) for Florida soils. The DPS of surface soils is a measure of P loss potential from the soil, and a critical value of 25% has been suggested for FL soils (Nair et al., 2004). The soil samples were also analyzed for Mehlich 1-P, Iron-strip P and water extractable P as measures of available P. Water extractable P was determined by reacting the soil samples with deionized water at a ratio of 1:10 soil:solution ratio for one hour (Kuo, 1996). The P concentration was analyzed colorimetrically with the Murphy and Riley method (1962). Mehlich 1-P was determined on the samples by shaking the soil samples with 0.0125 M H_2SO_4 in 0.03 M HCl solution at a ratio of 1:4 soil:solution ratio for 5 minutes (Hanlon et al., 1997). Extracts were filtered through Whatman N° 42 filter paper and analyzed colorimetrically (Murphy and Riley, 1962). The Iron-strip P was determined by reacting the soil samples with Fe-impregnated (0.65 M $FeCl_3$ in 0.6 M HCl) filter paper and then extracting the P adsorbed with 0.1 M H_2SO_4 (Van der Zee, 1987). The extractable P was analyzed colorimetrically (Murphy and Riley, 1962).

Quality Control

All sample collection/handling/chemical analysis was conducted according to a standard QA/QC protocol. For each set of samples, a standard curve was constructed ($r^2 > 0.998$). Method reagent blanks were appropriately used, as well as certified standards from a source other than

normal calibration standards. Percent recovery ranged from 97-103% of values obtained by the calibration curve. A 5% matrix spike of the set was used to determine the accuracy of the data obtained, with recoveries ranging from 96-103% of the expected values. Another 5% of the set was used to determine the precision of the measurements (triplicates). Analyses that did not satisfy the above QA/QC protocol were rerun.

Statistical Analyses

Differences among treatments were statistically analyzed as a factorial experiment with a randomized complete block design (RCBD), using the general linear model (GLM) of the SAS software (SAS Inst., 1999). The means of the various treatments were separated using a single degree of freedom orthogonal contrast procedure.

Results and Discussion

The samples collected from the field in June, 2003 and Jan and Mar, 2004 (before the occurrence of the hurricanes) enabled us to assess the impacts of the P sources and rates of application on the P chemistry of the soil and to evaluate the effectiveness of the applied WTR in reducing soluble P levels under field conditions. Although the hurricanes precluded continuing the study, sufficient data were collected to evaluate the stability of WTR immobilized P over time.

Soil and Amendments Characteristics

The soil and organic amendments were analyzed for selected chemical properties (Tables 3-1 and 3-2). The pH values of the P sources ranged from 6.8 for the poultry manure to 8.2 for the Boca Raton biosolids. The percent solids also varied with amendment; the biosolids (Boca Raton and Pompano biosolids) had similar values (~ 14 %), whereas the manure had ~27 %. Boca Raton biosolids had the greatest amount of total P (39 g kg^{-1}), followed by the Pompano biosolids (24.1 g kg^{-1}). These values are consistent with values reported for most biosolids (~3 -

40 g kg^{-1}, Elliott et al., 2002a,b; O'Connor et al., 2004). The poultry manure had the least total P content, but the observed value (18.9 g kg^{-1}) is close to the average value (20 g kg^{-1}) reported for chicken manure total P by Barnett (1994). The Boca Raton biosolids had the greatest 'available' P (water-, iron strip-, and Mehlich-1 extractable P) value, consistent with the total P content of the P sources. However, unlike the trends in total P values, poultry manure had greater 'available' P than the Pompano biosolids. The lower 'available' P content of the Pompano biosolids probably reflects the relatively high Fe + Al content of the material. The high total and 'available' P content of the Boca Raton biosolids, coupled with the low C:N ratio of the material suggests that the Boca Raton Biosolids will be a good P supplier and is likely to pose environmental problems if applied in excess of the crop P requirement. The total Al + Fe concentrations varied among the organic P sources and ranged from ~2.5 g kg^{-1} (poultry manure) to ~ 42 g kg^{-1} for the Pompano biosolids. Total Fe + Al contents in the range of (~2 – 80 g kg^{-1}) have been reported for biosolids (Elliott et al., 2002a,b; O'Connor et al., 2005). The poultry manure had little total Al and Fe (2.4 g kg^{-1}) and was dominated by calcium (102 g kg^{-1}), a basic ingredient of poultry diet (Barnett, 1994). Oxalate extractable P, Fe, and Al are usually associated with the amorphous phase of particles. Oxalate extractable Fe + Al in the Boca Raton biosolids was ~26 g kg^{-1}, and ~32 g kg^{-1} for the Pompano biosolids, well within the typical range (10-80 g kg^{-1}) for biosolids (Elliott et al., 2002a,b; O'Connor et al., 2005). We also calculated the phosphorus saturation index (PSI = [Pox]/ [Al_{ox} + Fe_{ox}]) of the P sources (Elliott et al., 2002a; Schoumans, 2000) from the moles of oxalate- extractable P, Fe, and Al data (Table 3-1). The index is used here as an indication of the degree to which biosolids P is potentially bound with Fe and Al in the biosolids. Thus, PSI values of < 1 suggest excessive Fe and Al for binding of P (little available P), whereas values of > 1 suggest abundant P not associated with Fe and Al

precipitates (abundant available P). Soil oxalate-extractable Fe and Al can affect P phytoavailability once biosolids are land-applied, but the PSI value of biosolids has been suggested as an *a priori* index of biosolids P lability (Elliott et al., 2002a). Since only oxalate-extractable P, Fe, and Al are considered, the index is not as useful for Ca-dominated materials. The PSI qualitatively identified the Boca Raton material as a good "labile" P source. The Pompano (high Fe) material is qualitatively identified as a poor labile P source.

Table 3-1. Selected chemical properties of amendments (oven dry basis) utilized in the Kirton Ranch field study. Units for all measurements (except pH, % Solids and PSI) are expressed in g kg^{-1}. Numbers are mean values of six replicates ± one standard deviation

Form	Manure	Biosolids		Al-WTR
Source	Indiantown	Boca Raton	Pompano	Bradenton
pH	6.8	8.2	7.9	5.6
Total C	32.0	34.7	36.6	13.9
Total N	8.4	8.0	7.03	0.7
% Solids	27.0 ± 4.2	13.4 ± 1.6	15.4 ± 3.4	40.6 ± 6.2
Total P	18.9 ± 3.8	38.7 ± 2.3	24.1 ± 4.2	4.69 ± 0.7
Total Al	0.94 ± 0.1	9.37 ± 0.4	9.26 ± 1.4	107 ±- 8.3
Total Fe	1.53 ± 0.3	24.3 ± 3.1	32.8 ± 6.4	6.08 ± 0.4
Total Ca	102 ± 11.2	27.5 ± 1.1	47.0 ± 5.5	1.53 ± 0.1
Total Mg	5.82 ± 0.8	10.0 ± 0.8	4.15 ± 0.6	0.44 ± 0.02
Oxalate P	10.4 ± 1.2	26.4 ± 3.9	28.5 ± 3.2	4.33 ± 0.8
Oxalate Al	0.79 ± 0.1	6.50 ± 0.9	7.41 ± 0.6	84.3 ± 6.2
Oxalate Fe	0.82 ± 0.3	19.4 ± 2.3	24.7 ± 4.2	5.16 ± 1.0
Oxalate Ca	4.25 ± 0.1	19.7 ± 3.1	43.7 ± 6.1	0.36 ± 0.1
Oxalate Mg	4.27 ± 0.3	8.93 ± 0.6	3.24 ± 0.3	145 ± 8.9
Mehlich 1-P	4.90 ± 1.2	8.76 ± 2.4	2.30 ± 0.4	-
Fe strip P	1.34 ± 0.3	6.42 ± 1.2	1.05 ± 0.2	-
Water P	0.85 ± 0.1	2.59 ± 0.6	0.34 ± 0.1	-
PSI†	21.7 ± 0.6	1.44	0.7	0.02

† Phosphorus saturation index ‡ Not applicable

The WTR used for the study had ~ 40 % solids. With the exception of the total C and total- and oxalate-extractable P and Al contents, which were all greater in the WTR actually applied, all the other chemical characteristics were similar to those determined for the Bradenton WTR (Table 2-1) utilized in other studies. The slight differences in the chemical contents of the WTRs from the same drinking-water treatment plant collected at different times can be attributed to differences in quality of the water source, which can influenced the treatment procedure (rates of coagulant used and the level of pH adjustment).

General chemical characteristics of the Immokalee fine sand collected from the project site are given in Table 3-2. The A-horizon soil samples used in this experiment had characteristics similar to the unimpacted Immokalee soil characterized previously (Table 2-1). The measured values obtained for the lower horizons (E and Bh) are similar to those observed for another Spodosol (Myakka) located in the Okeechobee watershed (Nair et al., 1995). However, the data generated for the 3 horizons showed that the soil of the project site was very heterogeneous, which was reflected in the large variability among chemical measurements of the same treatments.

Effects of Phosphorus Sources and Rates of Application

Mean values of total- and oxalate (200 mM) extractable P, Fe and Al for the A (0-5 cm) horizon sampled from the field in June 2003 and January 2004 are provided in Table 3-3; values of soils sampled from the A (0-15 cm) in March 2004 are presented in Table 3-4. The general chemical characteristics of the E, and Bh horizons sampled from the field in June 2003 and January 2004 were similar to those sampled to initially characterize the field (Table 3-2) and are not presented.

The greatest absolute total- and oxalate extractable P values from the A horizon were found in the Boca Raton biosolids-treated plots, followed by Pompano-, poultry manure- and the

TSP fertilizer-treated plots (Tables 3-3 and 3-4). As expected, the plots treated with N-based rates of amendments had greater absolute total- and oxalate extractable P values than plots treated at P-based amendment rates. The total- and oxalate extractable P concentrations of the samples taken in June 2003 through March 2004 were significantly greater than values of the initial soil samples (before the amendments were applied) taken to characterize the site (Table 3-1). Clearly, the application of the amendments significantly increased the P load of the soil. Although the values of Mehlich extractable P concentrations for the various treatments were significantly lower that the respective total- and oxalate extractable P values, Mehlich 1 extractable P data followed the same trend as the total-and oxalate extractable P data (data not presented).

Table 3-2. Selected chemical characteristics of the Immokalee soil (oven dry basis) used in the field study. Units for all measurements (except pH and DPS) are expressed in mg kg^{-1}. Numbers are mean values of six replicates ± one standard deviation

Chemical characteristics	Horizons		
	A (0-10cm)	E (~ 40 -45 cm)	B_h (top 10 cm)
pH	5.5	5.9	5.1
Total P	24.5 ± 5.46	7.9 ± 4.56	24.5 ± 11.3
Total Al	72 ± 23.3	33.6 ± 7.55	1280 ± 170
Total Fe	101 ± 39.6	38.5 ± 6.21	94.8 ± 23.2
Oxalate P	10.0 ± 2.95	3.76 ± 2.76	23.8 ± 13.7
Oxalate Al	54.8 ± 6.74	15.8 ± 5.35	970 ± 418
Oxalate Fe	61.7 ± 8.52	13.0 ± 5.98	39.0 ± 5.08
Mehlich 1-P	13.3 ± 6.54	1.88 ± 1.33	12.1 ± 2.82
WEP†	4.07 ± 0.78	0.77 ± 0.32	3.31 ± 0.5
Fe-strip-P	9.6 ± 0.11	1.36 ± 0.12	16.4 ± 3.2
DPS‡	0.10	0.14	0.02

† Water extractable P ‡ Degree of phosphorus saturation

Table 3-3. Total- and oxalate (200 mM) extractable P, Fe and Al concentrations† of soil samples collected from the A horizon (0-5 cm) in June 2003 and Jan. 2004. All values are expressed in mg kg^{-1}.

Treatments	Total P	Total Al	Total Fe	Oxalate P	Oxalate Al	Oxalate Fe
Controls	72.8 ± 9.5	142 ± 23.9	101 ± 23.5	60.8 ± 15.8	130.4 ± 46.5	126 ± 47.2
Manure-N, no WTR	128 ± 29.3	184 ± 17.1	129 ± 10.6	104 ± 11.9	147 ± 13.24	106 ± 8.49
Manure-N, WTR	211 ± 21.2	590 ± 60.5	213 ± 96.1	159 ± 47.7	460 ± 41.0	158 ± 88.7
Manure-P, no WTR	123 ± 15.1	212 ± 19.3	131 ± 17.2	81.4 ± 38.4	182 ± 14.7	125 ± 49.4
Manure-P, WTR	185 ± 52.0	520 ± 58.9	196 ± 44.7	124 ± 90.7	410 ± 84.0	131 ± 68.3
Boca-N, no WTR	232 ± 28.3	214 ± 22.8	248 ± 23.1	118 ± 49.0	204 ± 96.3	151 ± 28.3
Boca-N, WTR	290 ± 30.9	910 ± 28.3	437 ± 24.9	243 ± 15.4	760 ± 39.8	326 ± 38.2
Boca-P, no WTR	191 ± 42.7	181 ± 36.3	220 ± 19.7	116 ± 25.7	107 ± 41.6	211 ± 36.0
Boca-P, WTR	274 ± 35.0	890 ± 99.7	344 ± 75.6	240 ± 47.1	620 ± 47.0	227 ± 99.7
Pompano-N, no WTR	167 ± 51.5	307 ± 31.7	363 ± 28.3	81.7 ± 18.0	196 ± 26.0	117 ± 14.4
Pompano-N, WTR	247 ± 41.8	970 ± 34.4	484 ± 25.9	221 ± 64.1	790 ± 13.6	419 ± 79.8
Pompano-P, no WTR	135 ± 36.7	227 ± 57.1	359 ± 40.4	96.6 ± 14.4	186 ± 35.2	237 ± 18.5
Pompano-P, WTR	211 ± 35.1	920 ± 20.5	491 ± 91.6	167 ± 10.1	750 ± 90.2	398 ± 41.7
TSP-N, no WTR	147 ± 20.7	194 ± 39.4	131 ± 18.6	85.2 ± 34.1	102 ± 41.8	107 ± 36.1
TSP-N, WTR	227 ± 80.0	530 ± 60.7	193 ± 26.0	188 ± 30.5	470 ± 37.8	123 ± 13.4
TSP-P, no WTR	102 ± 22.0	177 ± 15.3	118 ± 9.23	73.5 ± 10.6	133 ± 19.8	83.4 ± 6.13
TSP-P, WTR	170 ± 37.2	490 ± 61.9	186 ± 41.2	104 ± 76.2	370 ± 58.3	117 ± 41.7

† Numbers are the average of six samples (2 x three replicated plots) ± one standard deviation.

The greatest absolute values of the total- and oxalate extractable Fe + Al concentrations were found in plots treated with Pompano biosolids, followed by Boca Raton biosolids treatments. There were no differences between the Fe + Al concentrations of the manure and TSP treated plots (Tables 3-3 and 3-4). In general, the Fe +Al concentrations of the samples taken in June 2003 through March 2004 were significantly greater than those of the samples initially taken to characterize the site (Table 3-1).

The lower horizons (E and Bh) had similar total- and oxalate extractable P concentrations in all the plots, at all sampling times (data not presented). The values were not different among the P sources- and P rates-treated plots. The concentrations of Fe + Al were also similar in all the plots. Similar values were obtained for P, Fe and Al in the initial samples taken to characterize the site (Table 3-1), suggesting no impact of the surface applied amendments on the lower horizons.

Table 3-4. Total- and oxalate (200 mM) extractable P, Fe and Al concentrations† of soil samples collected from the A horizon (0-15 cm) in March 2004. All values are expressed in mg kg^{-1}.

Treatments	Total P	Total Al	Total Fe	Oxalate P	Oxalate Al	Oxalate Fe
Controls	17.3 ± 6.3	52.6 ± 7.93	58.1 ± 9.51	12.1 ± 3.44	51.9 ± 9.92	57.3 ± 12.0
Manure-N, no WTR	74.9 ± 16.7	53.3 ± 11.0	62.1 ± 11.7	75.8 ± 9.31	52.7 ± 11.5	61.3 ± 9.52
Manure-N, WTR	101.4 ± 9.5	361 ± 27.4	78.0 ± 16.5	97.7 ± 9.02	324 ± 43. 5	76.7 ± 12.4
Manure-P, no WTR	47.2 ± 10.7	52.7 ± 9.49	59.8 ± 9.07	46.3 ± 8.67	52.1 ± 11.2	59.0 ± 9.89
Manure-P, WTR	59.9 ± 11.1	360 ± 27.4	75.4 ± 13.0	58.3 ± 6.83	313 ± 36.1	74.5 ± 8.67
Boca-N, no WTR	122 ± 15.2	179 ± 18.3	98.4 ± 16.7	81.3 ± 21.2	177 ± 17.7	73.3 ± 45.8
Boca-N, WTR	266 ± 18.3	686 ± 18.7	313 ± 19.6	154 ± 20.8	678 ± 55.4	209 ± 43.6
Boca-P, no WTR	99.3 ± 11.1	80.6 ± 10.0	135 ± 21.1	95.9 ± 10.8	89.5 ± 6.03	90.2 ± 29.0
Boca-P, WTR	242 ± 19.1	588 ± 35.1	249 ± 18.4	117 ± 12.5	581 ± 36.1	147 ± 28.0
Pompano-N, no WTR	138 ± 17.9	182 ± 19.1	213 ± 18.6	63.2 ± 10.4	180 ± 18.3	84.7 ± 26.8
Pompano-N, WTR	182 ± 22.2	690 ± 32.2	430 ± 32.1	174 ± 16.4	695 ± 30.5	324.1 ± 49.9
Pompano-P, no WTR	93.1 ± 11.8	134 ± 18.0	194 ± 28.6	89.8 ± 10.5	136 ± 12.6	291.2 ± 36.0
Pompano-P, WTR	105 ± 10.5	601 ± 35.1	419 ± 26.4	101 ± 10.9	594 ± 52.9	216.5 ± 23.5
TSP-N, no WTR	91.5 ± 10.5	55.1 ± 12.0	58.6 ± 12.7	68.3 ± 9.28	54.5 ± 11.1	57.9 ± 15.0
TSP-N, WTR	119 ± 14.5	494 ± 25.1	100 ± 16.0	114 ± 11.5	288 ± 52.9	99.2 ± 9.50
TSP-P, no WTR	84.2 ± 11.1	53.9 ± 9.10	58.2 ± 11.1	61.3 ± 10.4	53.2 ± 10.5	57.5 ± 9.13
TSP-P, WTR	101 ± 11.4	471 ± 39.8	100 ± 8.02	97.2 ± 9.26	279 ± 52.9	98.9 ± 10.5

† Numbers are the average of three replicated plots ± one standard deviation.

Impacts of WTR on Phosphorus Solubility

The total- and oxalate extractable P concentrations of the WTR amended plots were significantly greater than the P concentrations of the plots not treated with WTR, suggesting that the extractants were sufficiently rigorous to extract P otherwise immobilized by, or contained in, the WTR (Tables 3-3 and 3-4). The same trend was observed with the Mehlich-1 extraction data (data not presented).

The effect of WTR amendment on surface soil P chemistry is most dramatic when the oxalate extractable P concentrations (in moles) are divided by the corresponding oxalate Fe and Al values (in moles) times a saturation coefficient (α) value of 0.55. The resulting value is the Degree of P saturation - DPS (Nair et al., 2004) and correlates negatively with expected P losses from a site. Pautler and Sims (2000) found that P solubility increased significantly ($r^2 = 0.70$) as soil P saturation increased in 41 agricultural soils in Delaware. Hooda et al. (2000) found that the degree of soil P saturation was significantly related to soil P desorption. The critical DPS values for FL soils is 0.25 (25 %) (Nair et al., 2004); soils with DPS values > 25% are expected to release significant P to surface runoff or leaching, whereas soils with DPS values < 25 % are not. Amendment with WTR significantly ($p < 0.001$) reduced DPS values in surface soils amended with any P-source at any rate (Figure 3-1).

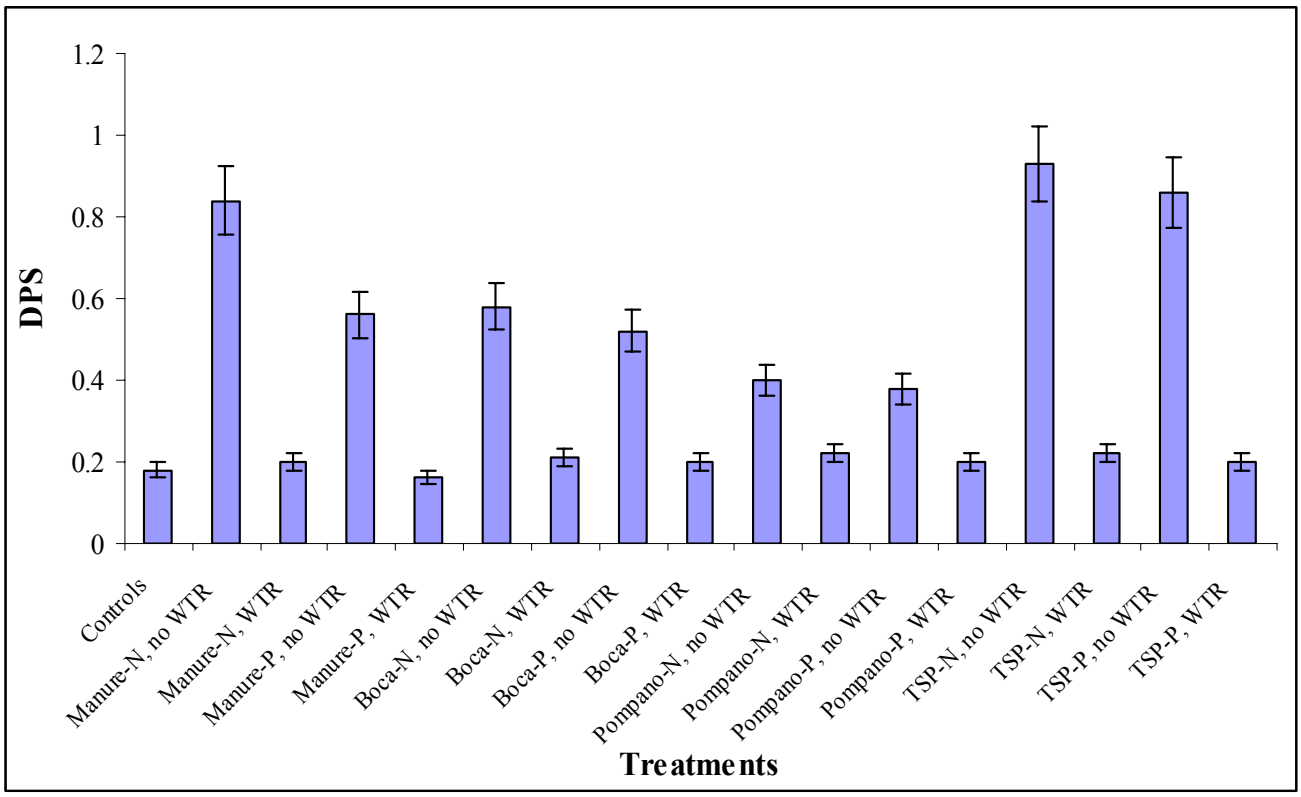
The DPS values of the WTR amended plots from the TSP treated plots decreased by 86 % (N-based) and 82 % (P-based) relative to the same treatments without WTR amendment. Similarly, DPS values of the manure-treated plots decreased by 83 % (N-based) and 82 % (P-based). The decrease of the DPS values from the WTR amended plots treated with biosolids was also significant ($p = 0.013$). For the plots treated with Boca Raton biosolids, the reduction in the DPS values ranged between 49 % (N-based) to 60 % (P-based). For the Pompano biosolids-treated plots, the reduction ranged from 48 % (N-based) to 53 % (P-based). The magnitude of

DPS reduction due to WTR effect was less in the biosolids-amended plots because the biosolids contained moderate amounts of Fe and Al. For example, Boca Raton biosolids contained 9.4 g Al kg^{-1} and 24.3 g Fe kg^{-1} and the Pompano biosolids contained 9.2 g Al kg^{-1} and 32.8 g Fe kg^{-1} (Table 3-1). The poultry manure (N-based) - and the TSP-treated plots, without WTR amendments, had DPS values of 84 to 93 %, respectively, which suggest that these treatments could contribute significant amounts of P in runoff and/or leaching.

Plots amended with WTR also had significantly lower water extractable P (Figure 3-2) concentrations than the plots without WTR amendment. Similar trends were observed for the Fe-strip extractable P concentrations (data not presented). Thus, the effectiveness of WTR in reducing soluble P levels was observed with Fe strip and water extraction data. For all P sources and rates of application, WTR amended plots released significantly less P (had lower WEP values) than the plots not treated with WTR (Figure 3-2). Immobilization of P by WTR also masked differences in P-source and P-rate. There were no differences in soil WEP values among the P sources and the rate of application (N-based and P-based) when the soil was amended with WTR. In the absence of WTR, there were differences among both the P sources and between the rates of application.

As expected, the total- and oxalate extractable Fe+Al concentrations of the samples were significantly greater in the WTR amended plots than the plots not amended with the WTR (Figure 3-3). Iron and Al hydroxides are major sorbents for oxyanions in soil. An increase in the sorbent content of the amended plots is expected to increase the P sorption capacity of the amended plots. Dayton et al. (2003) found a significant relationship (r^2 = 0.69, p = 0.01) between oxalate extractable Al concentration (Al_{ox}) and the maximum P sorption capacity (P_{max}). Elliott et al. (2002b) found that the P sorbing ability of different types of WTR (Al-or Fe-based),

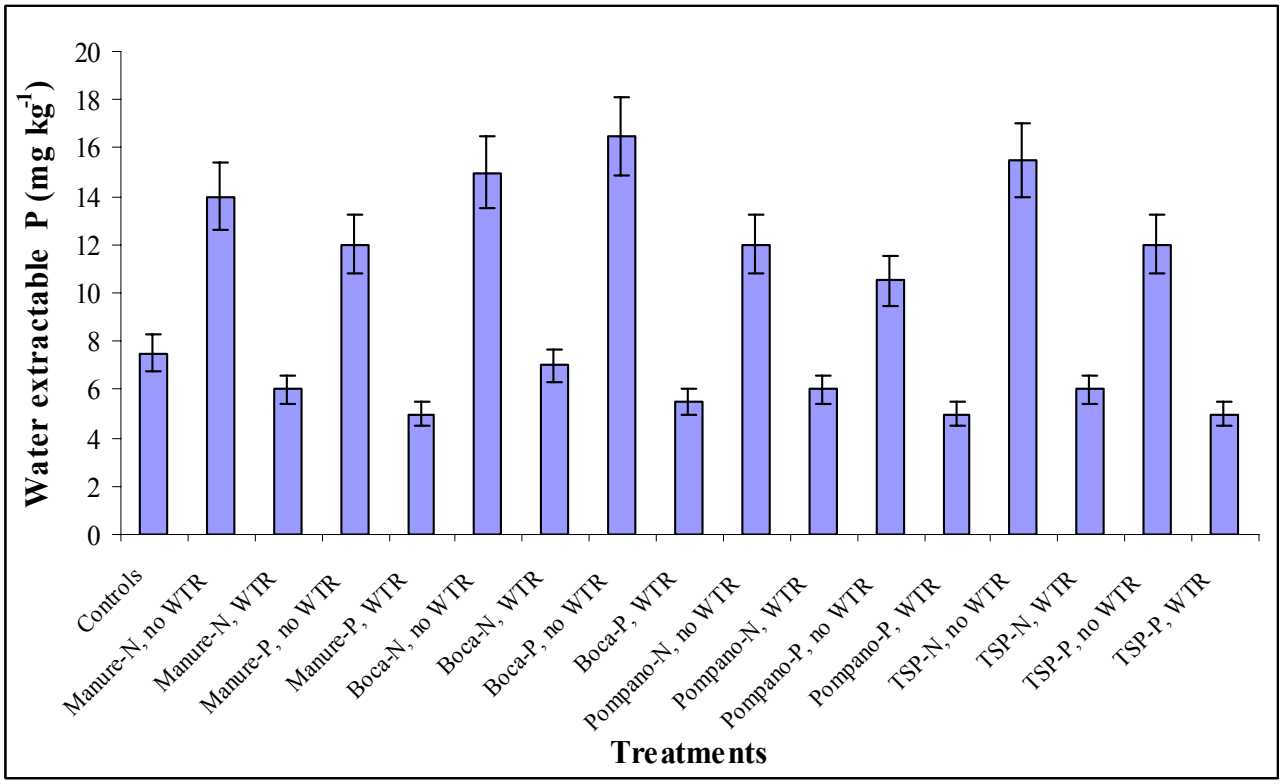
when added to a sandy soil amended with biosolids, could be predicted based on the amorphous metal oxide content of the WTRs. Similarly, Lookman et al. (1995) found that after 880 hours, soil P desorption from 44 German soils was inversely related to soil (Fe_{ox} + Al_{ox}). The increased Fe and Al concentrations in the soils studied here were reflected in the DPS analysis, which showed significantly ($p < 0.001$) lower DPS values for the WTR amended plots than for the unamended plots (Figure 3-1). The lower DPS values indicate the potential of WTR amendments to immobilize soluble P and to reduce P-source impacts on water quality.



WTR amended vs. control	**NS**
Plots without WTR vs. control	***
Plots without WTR vs. WTR amended	***
WTR amended N rate vs. P rate	**NS**
n	**102**

*** indicates significance at $p < 0.001$; **NS** indicates non-significant

Figure 3-1. Differences in degree of phosphorus saturation (DPS) in A horizon (0-5 cm) samples taken in June 2003 and Jan. 2004. Error bars denote one standard deviation.



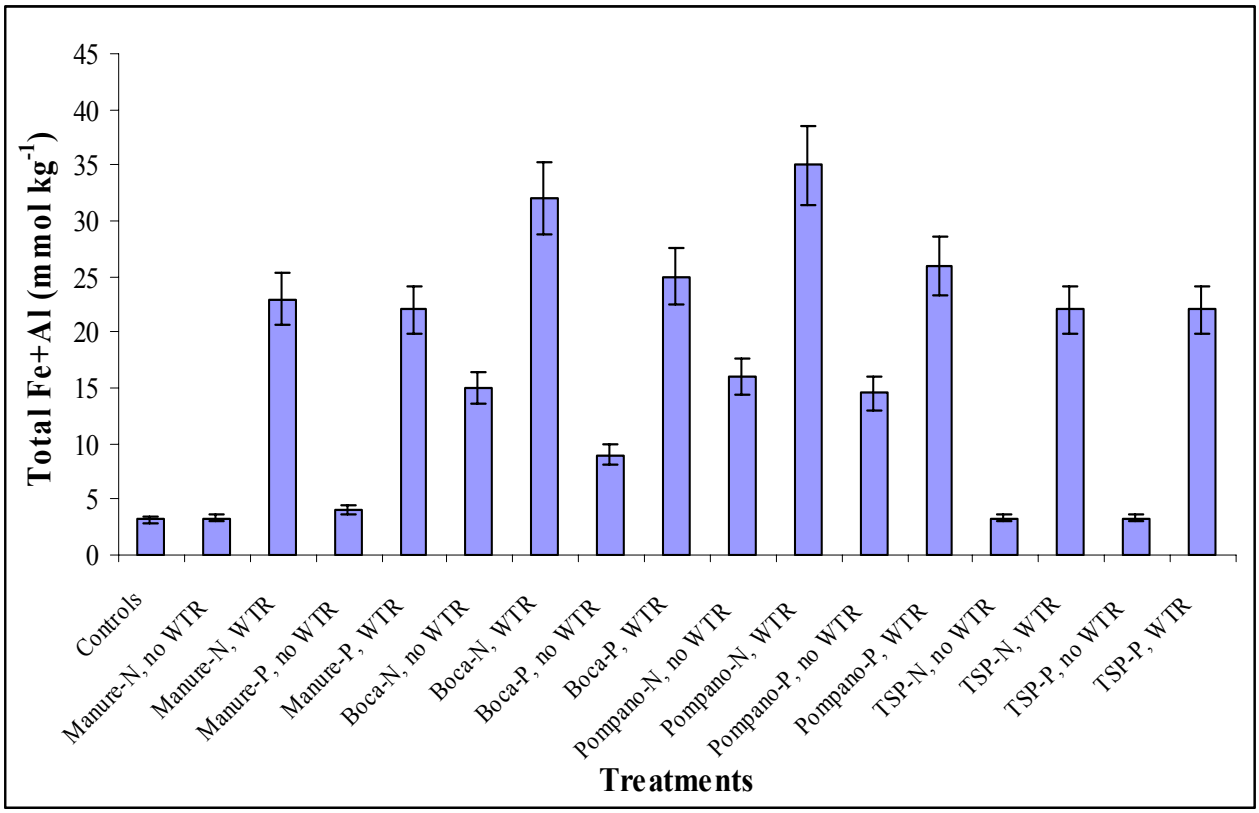
WTR amended vs. control	**NS**
Plots without WTR vs. control	***
Plots without WTR vs. WTR amended	***
WTR amended N rate vs. P rate	**NS**
n	**102**

*** indicates significance at $p < 0.001$; **NS** indicates non-significant

Figure 3-2. Differences in water extractable P values in A horizon soil samples (0-5 cm) taken in June 2003 and Jan. 2004. Error bars denote one standard deviation.

Total- and oxalate extractable -P, Fe and Al values for the E and Bh horizon samples from plots with and without WTR amendments were similar for various amendments (data not presented), and similar to values from the samples collected to initially characterize the site (Table 3-2). The data suggest no impact of the surface applied amendments on the lower horizons. The samples taken in January 2004 showed a slight increase in both total- and 200 mM oxalate extractable P in the Bh horizons of the plots treated with poultry manure or TSP without WTR amendments (data not presented). Although these increases in P contents were not statistically significant, they may suggest P losses from the A horizon and subsequent

accumulations in the Bh horizon. The relatively high DPS values (> 0.8) of the A horizon samples of the two treatments (Figure 3-1) suggested the potential of P losses from both plots.



WTR amended vs. control	***
Plots without WTR vs. control	**NS**
Plots without WTR vs. WTR amended	***
WTR amended N rate vs. P rate	**NS**
n	**102**

*** indicates significance at $p < 0.001$; **NS** indicates non-significant

Figure 3-3. Differences in the total Fe+Al concentrations of the WTR amended and unamended plots of the A horizon samples (0-5 cm) taken in June 2003 through Jan. 2004. Error bars denote one standard deviation.

The data for the lower horizons suggest no significant effect of any treatment (P-sources, P-rate, or WTR) on the P soil chemistry of these horizons. The data also clearly indicate a lack of significant leaching of P from any WTR amended plots or from plots treated with the biosolids to the E and Bh horizons in the 8 months following treatment application. Some leaching from the poultry manure and TSP treated plots without WTR amendment may have occurred, but either

the effect was small and insignificant or the leached P was not captured in the depths or frequency of sampling.

The data from the Kirton Ranch field study support the conclusions made from the lab study (chapter 2) and some other studies (Elliott et al., 2002b; Dayton et al., 2003; Makris et al., 2004a,b; 2005abc; O'Connor et al, 2005) that WTR is effective in immobilizing P. The field data suggest that application of alum-based WTRs to P-impacted soils could serve as a practical chemical-based BMP. Applying alum-based WTRs to soils can increase soil P sorption capacity, thereby, potentially reducing off-site P movement from fields via runoff and leaching. Reducing off-site P transport may lower P loads into nutrient sensitive surface water systems, thereby minimizing the occurrence of eutrophication. However, the magnitude of the soil P sorption increase will depend on the P binding effectiveness of the WTRs. Different WTRs have widely different characteristics (chapter 2), therefore for such field studies, it is imperative to identify effective WTRs through preliminary lab studies.

Evidence of Field Contamination through Hurricane-induced Flooding

The soil P-related measurements taken in the samples collected after the hurricanes in fall 2004 (Dec. 2004) were not consistent with those observed for the samples collected in June 2003, Jan 2004, or March 2004. The total P concentrations of the A horizon (0-5 cm) soil samples taken from the WTR amended plots in Dec. 2004 were significantly less ($p = 0.02$) than those taken in June 2003 and Jan. 2004 (Figure 3-4). The reduction of P concentrations in the WTR amended plots cannot be attributed to WTR immobilization because similar reductions were observed for total Fe + Al concentrations (Figure 3-5) and oxalate extractable Fe + Al concentrations in the WTR amended plots of A horizon (both 0-5 cm) soil samples (data not presented). Conversely, total P concentrations increased in the control plots and the plots not amended with WTR (Figure 3-4). There were no intentional P applications to these plots after the

initial amendments, so the significant increases in the total P concentrations in the control plots and the plots without WTR amendments must have come from other sources. This P input may have originated from material movement onto the plots as a result of flooding caused by hurricanes in the fall of 2004. The pH of the soil (5.5) is sufficient to prevent the solubilization of Fe and Al. Therefore, the significant reduction in the total- and oxalate extractable Fe and Al concentrations can only result from the physical movement of the soil and soil amendments from the WTR amended plots to the plots without WTR amendments, and vice versa, due to the flooding of the field by the hurricanes.

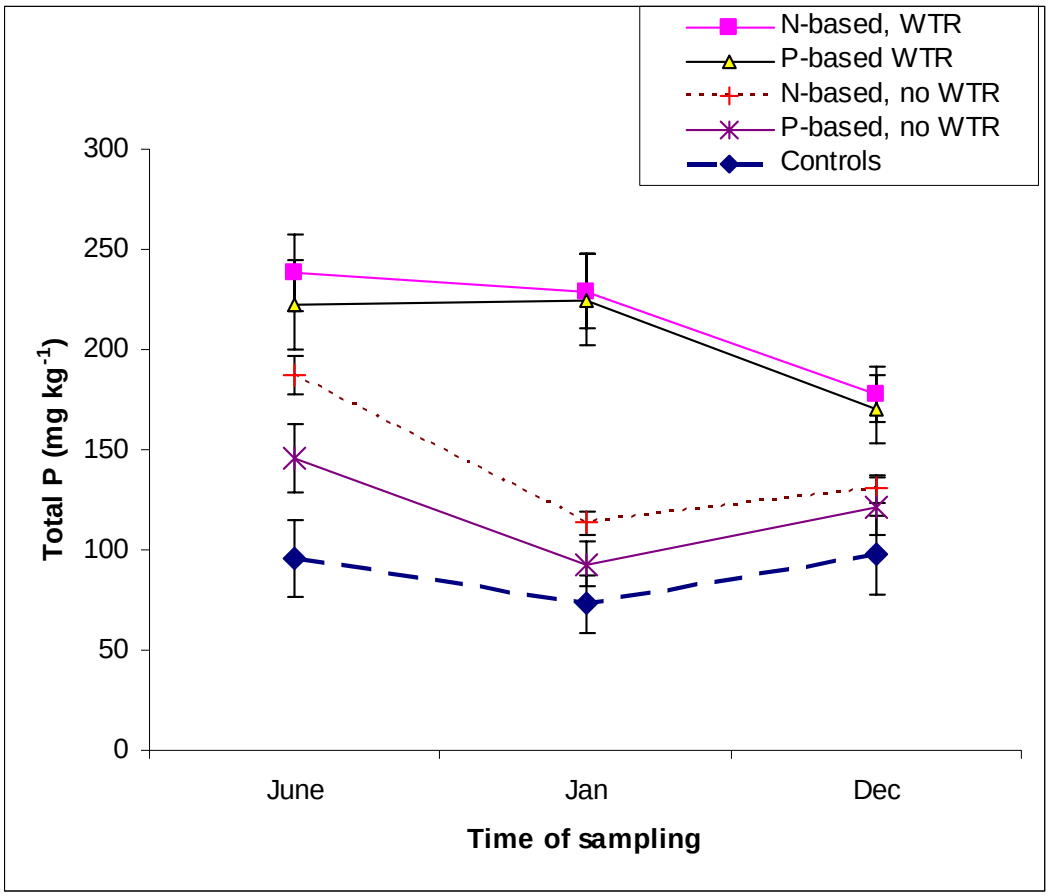


Figure 3-4. Changes in total P of the A horizon (0-5 cm depth) of the soil samples with time (June 2003 - Dec 2004). Error bars denote one standard deviation.

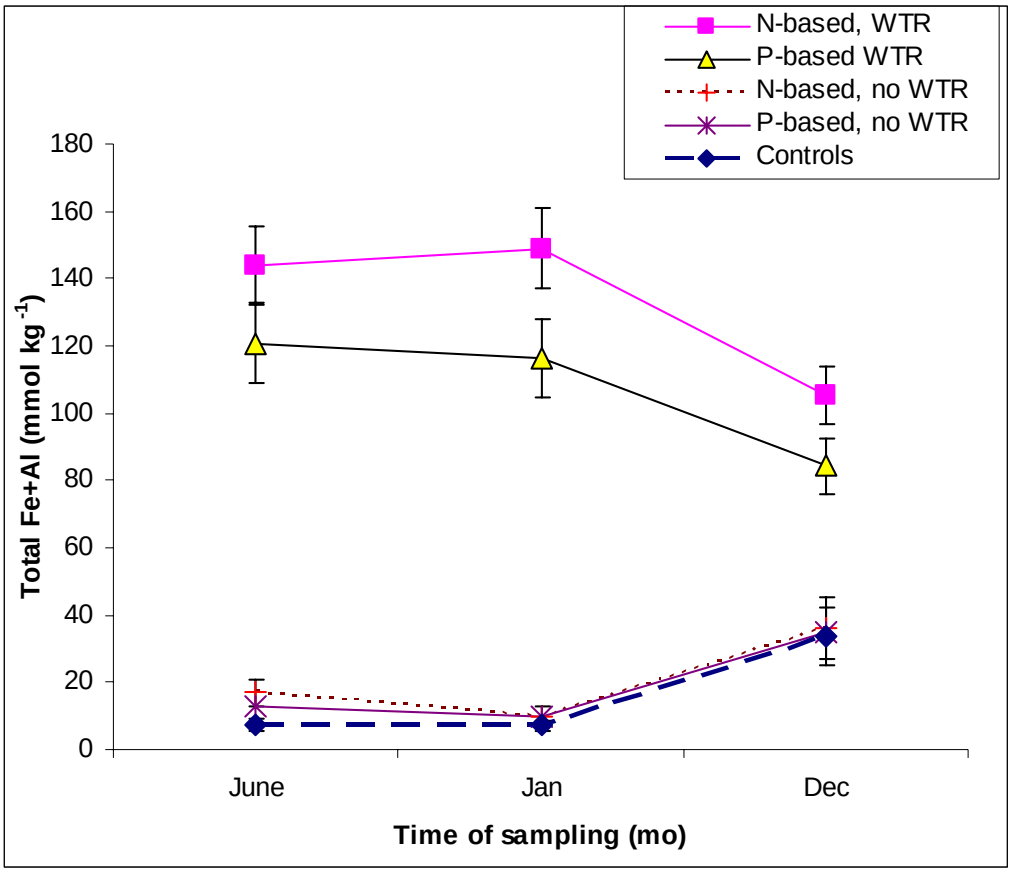


Figure 3-5. Changes in total Al + Fe of the A horizon (0-5 cm depth) of the soil samples with time (June 2003 - Dec 2004). Error bars denote one standard deviation.

Compared to data from the June 2003 and Jan. 2004 samples**,** the Mehlich 1- (M1-P), Iron strip- (ISP), and water extractable P (WEP) values of the samples taken in Dec. 2004 showed greater variability. The M1-P, ISP, and WEP values of the samples taken from the A (0-5 cm) horizon in Dec. 2004 (Table 3-5) showed inconsistent trends among the respective P values (compared to samples taken in June 2003 and Jan. 2004). The M1-P and the ISP values of the WTR amended plots sampled in Dec. 2004 were significantly greater than values in Jan. 2004 samples, but not statistically different from the results of the June 2003 samples (data not presented). The reduction of the ISP in the Jan 2004 samples of the WTR amended plots (compared to June 2003 samples) was attributed to P immobilization by WTR. The sudden

increase (Dec 2004) in ISP values of the WTR amended plots is difficult to explain since there had not been any intentional P application to the fields.

Table 3-5. Water-, iron strip- and Mehlich 1 extractable P concentrations of soil samples collected from the A horizon (0-5 cm) in Dec. 2004. All values are expressed in mg kg^{-1}.

Treatments	WEP	ISP	M-1P
Controls	11.1 ± 1.31†	10.5 ± 0.94†	18.4 ± 13.5††
Manure-N, no WTR	14.5 ± 11. 5††	21.3 ± 14.2††	29.7 ± 22.9††
Manure-N, WTR	4.45 ± 3.15††	10.8 ± 3.51†	28.6 ± 2.81††
Manure-P, no WTR	12.0 ± 1.20†	17.4 ± 6.11††	43.5 ± 23.4†
Manure-P, WTR	7.71 ± 9.91††	25.7 ± 15.9††	40.4 ± 16.8††
Boca-N, no WTR	21.0 ± 7.10†	25.2 ± 3.60†	25.7 ± 4.42†
Boca-N, WTR	2.59 ± 0.64†	16. 6 ± 7.52††	72.4 ± 33.9††
Boca-P, no WTR	25.6 ± 15.6†	28.2 ± 12.6††	26.0 ± 18.0††
Boca-P, WTR	3.79 ± 3.02††	10.5 ± 4.73†	32.0 ± 14.1†
Pompano-N, no WTR	17.1 ± 1.33†	19.9 ± 1.60†	24.7 ± 11.7†
Pompano-N, WTR	5.65 ± 7.21††	12.8 ± 8.21††	41.7 ± 27.9†
Pompano-P, no WTR	17.5 ± 12.9†	16.3 ± 14.5†	39.8 ± 20.1†
Pompano-P, WTR	5.07 ± 3.89†	12.2 ± 5.32†	26.5 ± 2.44†
TSP-N, no WTR	14.6 ± 7.03†	16.5 ± 12.4†	21.3 ± 19.1†
TSP-N, WTR	5.98 ± 3.44†	13.5 ± 0.54†	27.3 ± 12.8†
TSP-P, no WTR	12.4 ± 4.50†	11.2 ± 3.02†	24.9 ± 3.83†
TSP-P, WTR	5.78 ± 6.14†	9.71 ± 4.10†	28.3 ± 18.1†

† Numbers are the average of three replicated plots ± one standard deviation.
†† Numbers are the average of six samples (two samples each from three replicated plots) ± one standard deviation.

The absolute values of the ISP and M1-P values of the samples from plots without WTR amendments were slightly increased from those observed in Jan. 2004, but the increase was not significant. The control plots, however, showed a continuous decrease in ISP concentrations from June 2003 through Dec. 2004, but an increase in M1-P values in Dec. 2004 samples (compared to Jan. 2004 samples). The water extractable P (WEP) values showed a similar behavior to the ISP values, but the increases in the WEP values from the Jan. 2004 data were not significant. The inconsistencies observed in the M1-P, ISP and WEP values are difficult to explain, but are consistent with the contention that physical movement of soil and soil

amendments occurred in the field as a result of the flooding, which affected P chemistry of the field sites.

Stability of WTR immobilized Phosphorus

Despite the hurricane-induced flooding of the field that resulted in the contamination of the individual plots, some P values of the samples collected after the hurricanes still showed the effectiveness of WTR in reducing soluble P levels. The ISP and WEP values measured from the A (0-5 cm) horizon plots amended with WTR were significantly lower ($p = 0.03$ and 0.01, respectively) than values from the plots without WTR amendments (Figures 3-6 and 3-7). Similar behavior was observed in the A (0-15 cm) soil samples (data not presented). The ISP and WEP data suggest that, despite the flooding of the field, most of the WTR immobilized P remained stable.

The persistent effect of the WTR amendment was also clearly shown in the increase of Fe+Al concentrations of the plots of the surface (0-5 cm) horizon (Figure 3-8). There was a highly significant ($p = 0.01$) increase of total Fe+Al content of the WTR amended plots, across P-sources and source-rate treatments. The consistently high Al and Fe content of the WTR amended plots suggests that those plots maintained the capacity to sorb P.

The DPS values of the WTR amended plots sampled in Dec. 2004 were significantly ($p = 0.01$) smaller than those of the plots without WTR amendments (Figure 3-9). The DPS values of the WTR amended plots from the TSP treated plots decreased by 74 % (N-based) and 72 % (P-based) compared to the same treatments without WTR. Similarly, DPS values of the manure-treated plots decreased by 70 % (N-based) and 78 % (P-based). The decrease of the DPS levels from the WTR amended plots treated with biosolids was also significant ($p = 0.020$). For the plots treated with Boca Raton biosolids, the reduction in the DPS values ranged between 53 % (N-based) to 46 % (P-based).

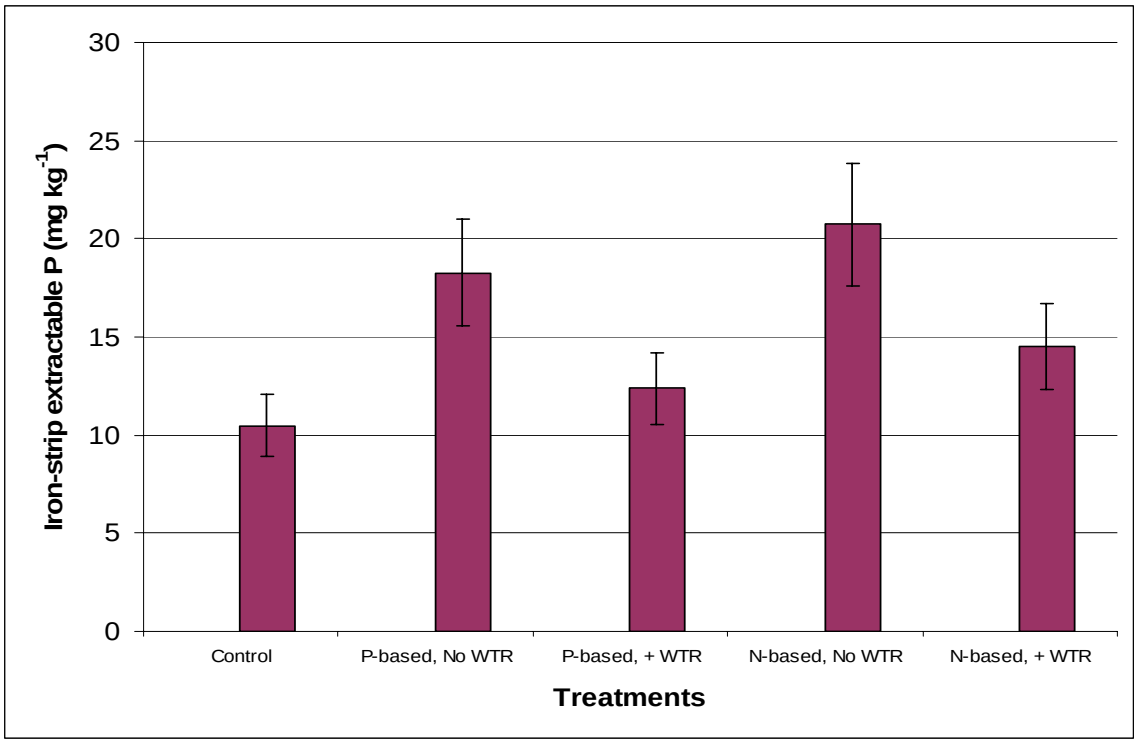


Figure 3-6. Differences in iron strip P values from the A horizon (0-5 cm) of the soil samples taken in Dec. 2004. Error bars denote one standard deviation.

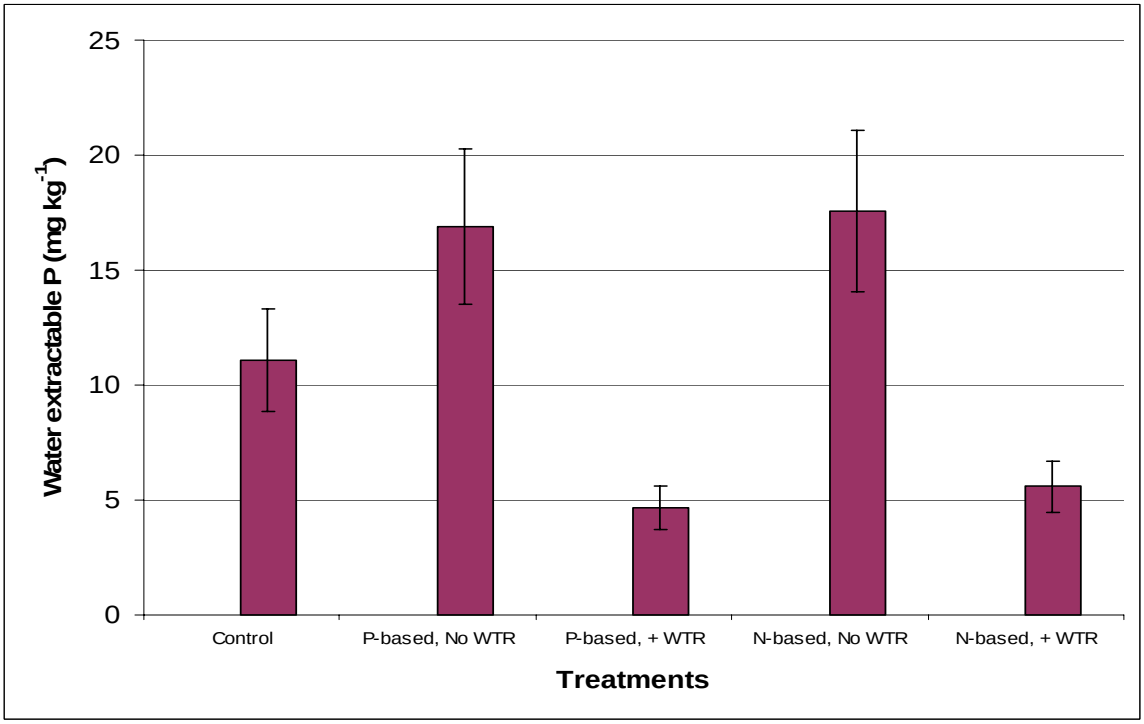


Figure 3-7. Differences in water extractable P values from the A horizon (0-5 cm) of the soil samples taken in Dec. 2004. Error bars denote one standard deviation.

For the Pompano biosolids-treated plots, the reduction ranged from 55 % (N-based) to 51 % (P-based). The loss of P (through leaching and/or runoff), coupled with the "mixing" of treatments in the soil surface resulted in a significant reduction of the DPS values in the control plots and the plots without WTR amendments, compared to the DPS values obtained for the June 2003 to March 2004 soil samples (Figure 3-1). Nevertheless, the DPS values of the WTR amended plots remained below the threshold value of 25% (Nair et al., 2004). This suggests that, despite the flooding of the field, the WTR amended plots retained the capacity to retard P movement.

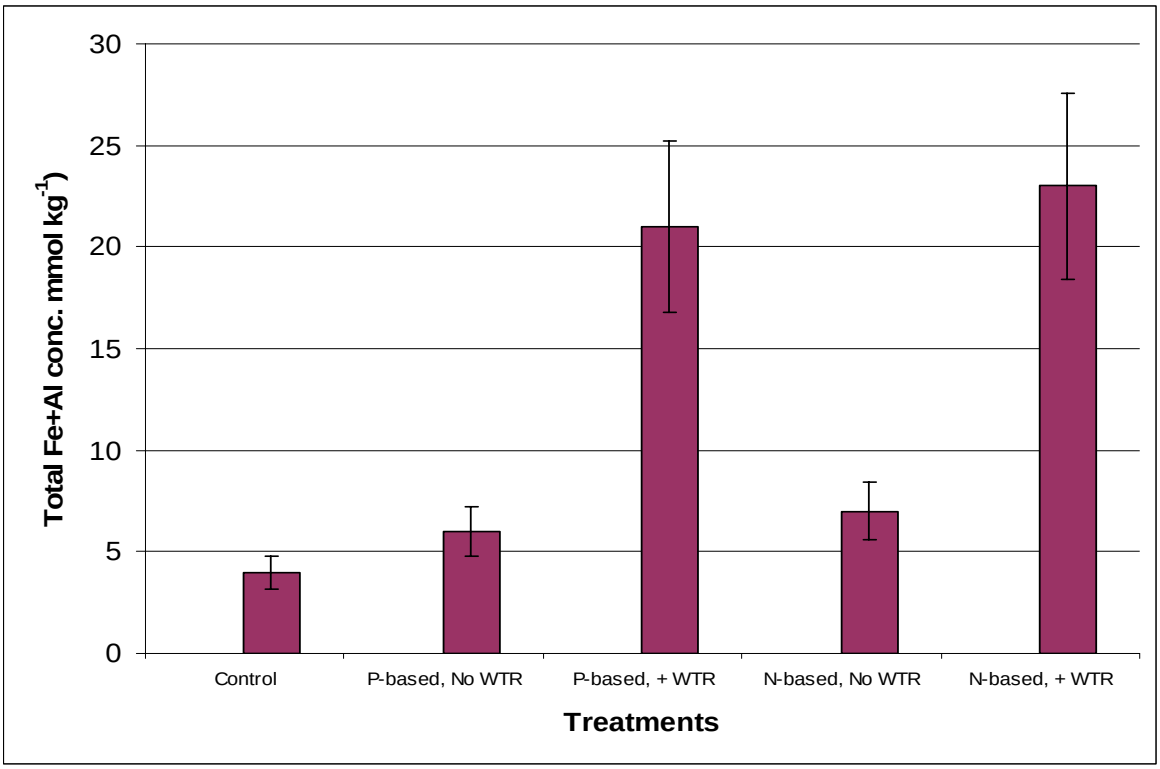


Figure 3-8. Differences in total Fe + Al concentrations from the A horizon (0-5 cm) soil samples taken in Dec. 2004. Error bars denote one standard deviation.

The E horizons had similar total- and oxalate extractable P concentrations among all the plots sampled in Dec. 2004 (data not presented). The respective P concentrations obtained with the other extractants (Water, Iron-strip and Mehlich 1) were also similar among the P sources- and P rates-treated plots, with and without WTR amendment (data not presented). The total- and

oxalate extractable Fe and Al concentrations were similar in all the plots as well (data not presented). Similar values were obtained for P, Fe and Al in the samples taken in June 2003 and Jan 2004, suggesting that there were no impacts of the surface applied amendments on the E horizon. If P leached, P movement was unrestricted through the E horizon.

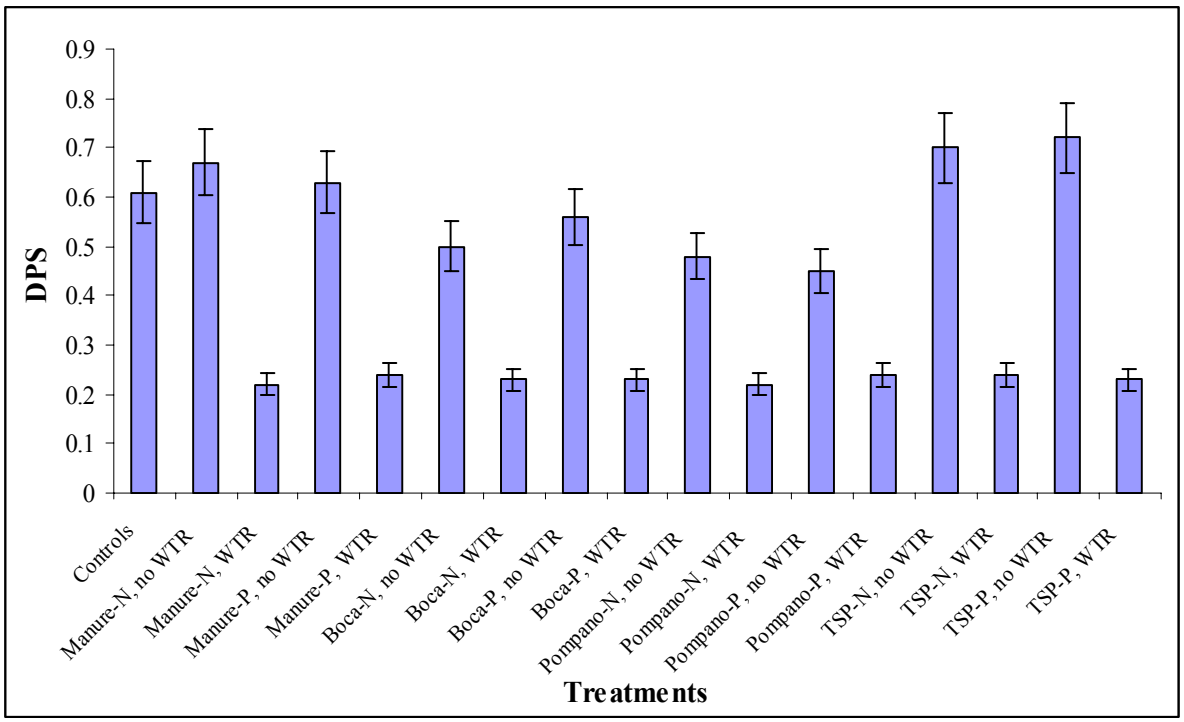


Figure 3-9. Differences in DPS values of the WTR amended and unamended plots of the A horizon (0-5) samples taken in Dec. 2004. Error bars denote one standard deviation of three replicates.

The absolute values of the total- and oxalate extractable P concentrations of the samples taken in the Bh horizon were greater in the control plots and the plots without WTR amendments than those found in the WTR amended plots (data not presented). Similar behavior was observed for the water extractable P, Fe-strip P and Mehlich 1- P data (data not presented). Comparing the WEP values with those observed previously (June 2003 and Jan. 2004), a significant ($p = 0.03$) increase in the WEP values was observed in the control plots and the plots without WTR amendments (Figure 3-10). The WEP values of the WTR amended plots did not significantly increase, although the absolute values increased slightly. Similar behavior was observed for the

results obtained with the other extractants. The data suggest P leaching from the surface horizon and subsequent accumulation in the Bh horizon. The greatest P leaching apparently occurred in the plots without WTR amendments and the control plots; very little or no P leaching occurred in the WTR amended plots.

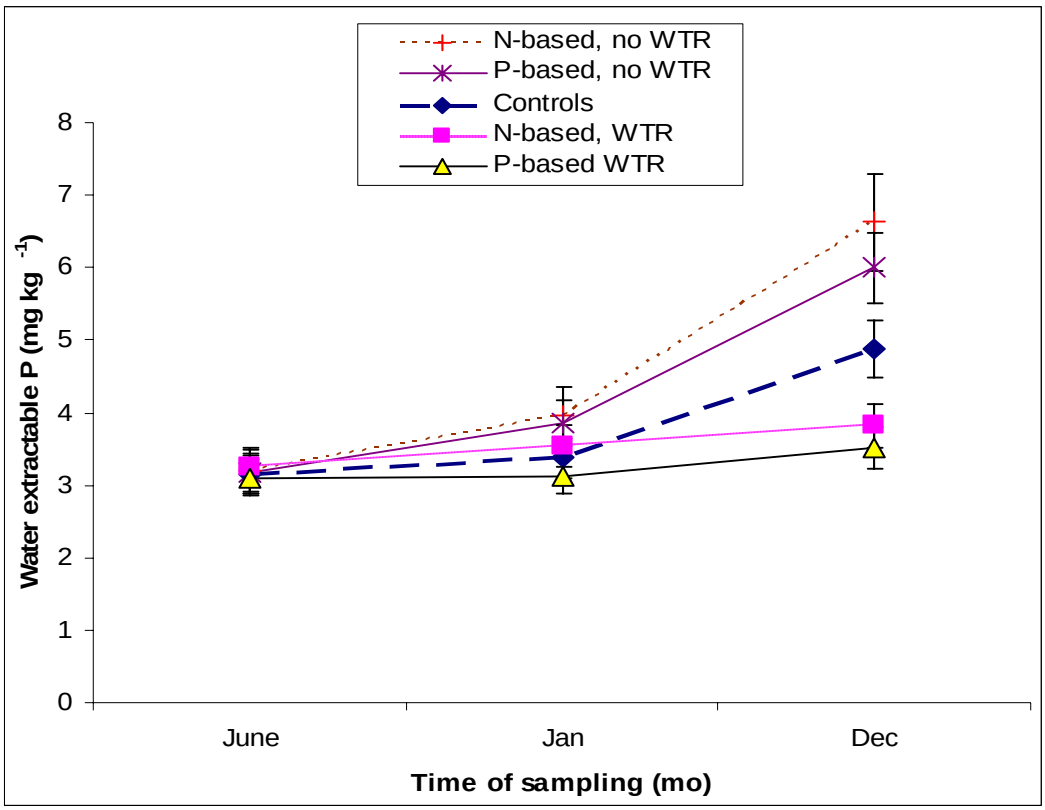


Figure 3-10. Changes in total P concentrations of the Bh horizon of the soil samples with time (June 2003 - Dec 2004). Error bars denote the standard deviation.

Total- and oxalate extractable Fe and Al concentrations were similar among the Dec. 2004 samples taken from the Bh horizon from all the plots. That is, the Fe + Al concentrations were not different among the P sources- and P rates-treated plots, with and without WTR amendments in the Bh horizon (data not presented). The concentrations of Fe + Al in the Bh were similar to the values obtained from the samples taken in June 2003 and Jan 2004 and to those collected initially to characterize the site (Table 3-2). Thus no vertical movement of Fe and Al occurred in the field. The pH of the soil was sufficient to prevent solubilization and subsequent leaching of

Fe and Al into lower horizons. This observation suggests that the increased P content of the Bh horizon may have occurred through leaching from the overlying A horizon. The data suggest that there was significant leaching of P from the surface horizon following the hurricane-induced flooding of the field. The amounts of P leached from the plots without WTR amendments were significantly greater than from WTR amended plots. Thus, despite the extensive flooding of the fields, the WTR was able to retain the immobilized P, and prevent excessive P leaching.

The combined data from this field study strongly suggest that WTR is effective in reducing P mobility and could be relied upon to reduce P movement in surface runoff and leachates. In a column leaching study, Silveira et al. (2006) observed that Al-WTR continued to reduce the concentration of P leached for 36 weeks, and concluded that WTR immobilized P is stable. Based on the results of spectroscopic studies, Makris and O'Connor (2006) concluded that once P reaches the WTR microsites, very strong adsorption, and highly hysteretic desorption apparently occurs. Thus, once immobilized by the WTR particles, the P is likely irreversibly bound, unless the structure of the WTR is destroyed under very extreme conditions.

CHAPTER 4
AGING AND pH EFFECTS ON LABILITY OF DRINKING-WATER TREATMENT RESIDUALS (WTR) IMMOBILIZED PHOSPHORUS

Introduction

The use of drinking-water-treatment residuals (WTRs) to control excessive soluble P concentrations in highly P-impacted soils has received increased attention in recent years. Short-term laboratory, greenhouse, and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P concentrations in runoff and leaching from areas amended with animal manure, biosolids and/or inorganic P fertilizers (Peters and Basta, 1996; Basta and Storm, 1997; Elliott et al., 2002a,b; O'Connor et al., 2002; Dayton et al., 2003; Makris, 2004; Makris et al., 2004a,b; Novak and Watts, 2004; Dayton and Basta, 2005; Elliott et al., 2005; Makris et al., 2005a,b,c; Novak and Watts, 2005; Silveria et al., 2006). The long-term stability of WTR immobilized P, however, is an issue that has not been thoroughly explained or documented. Time constraints associated with conducting long-term (> 20 years) field experiments to test the stability of WTR sorbed P inhibit improved understanding of the fate of sorbed P in soils. One approach to overcome this constraint is to artificially "age" freshly amended soil samples to infer the long-term stability of WTR immobilized P. Artificial aging of fresh WTR amended soil samples can be achieved through incubation at elevated temperatures or through repeated wetting and drying. Aging transforms metal oxides (dissolution, crystallization and re-crystallization) and affects their sorption capacities (Ma and Uren, 1997; Frau, 2000; Kennedy et al., 2004; Makris et al., 2005c).

Contrasting theories exist for the solubility of aged suspensions of ions sorbed onto Fe and Al oxides. The classic theory holds that structural reorganization of an amorphous solid phase results in the incorporation of a sorbed ion into the solid structure of the metal oxide forming a "solid solution" (Spadini et al., 1994). The solubility of long-range ordered oxides is orders of

magnitude less than that of the amorphous solid, and the vulnerability of these oxides to microbial iron reduction is also reduced (Postma and Jakobsen, 1996). Martinez and McBride (1998) synthesized aged Cd, Cu, Pb and Zn coprecipitates with amorphous iron hydroxides at 70 °C thermal heating for 2 months. The aging process decreased Cd and Zn solubility when the coprecipitate was formed by slow titration (0.03 mL min^{-1}). Ainsworth et al. (1994) observed the incorporation of Co and Cd into the hydrous iron oxide structure after 20 weeks of aging at room temperature.

The classic theory of decreasing metal solubility as pure minerals or soil solid phases age with time, however, does not apply to all metals. Martinez et al. (1999) demonstrated that Pb initially sorbed onto soil oxides and ferrihydrite [$Fe(OH)_3.xH_2O$], was released into solution after thermally-treating the minerals for 2 months at 70 °C. Ford et al. (1997) conducted an aging experiment (pH 6, heating at 40-70 °C for 2-6 weeks) and attributed Pb desorption from an amorphous Fe solid phase to the reduction in available sorption sites due to crystallization of an iron (hydr)oxide structure. Martinez et al. (2001) studied Pb solubility at 70 ºC after prolonged aging (1.5 years) of suspensions of soil samples containing noncrystalline aluminosilicates and oxides of Fe and Al as predominant reactive surfaces. Crystallization of the Fe phases to goethite occurred and Pb was released into solution

Kennedy et al. (2004) showed that repeated wetting and drying can induce structural changes in metal oxides. The researchers dried synthetic MnO at 37 ^{o}C for 24 hours, and then hydrated it for 24 hours, with wetting and drying cycles repeated three times, over 7 days. Repeated wetting and drying resulted in a non-reversible decrease in particle size. After the seven-day incubation period, total proton binding capacities determined by acid-base titrations decreased with cyclically re-wetting and drying. However, visual inspection by scanning electron

microscopy revealed fine-grained, amorphous particles and XRD results indicated no crystallinity (Kennedy et al., 2004). The authors therefore concluded that detectable bulk changes in crystallinity would only occur over longer timescales in natural low temperature surface environments. Frau (2000) also reported that precipitation and dissolution cycles of some secondary iron and manganese oxides are strongly influenced by seasonal wetting and drying cycles, and accelerate structural changes. In an incubation study, drying and rewetting cycles led to irreversible formation of a hydration layer on goethite that accounted for stability of goethite crystals deposited from aqueous suspension (Frau, 2000).

Misra and Teixera (2001) used soil phenomenon to explain the structural changes occurring as a result of wetting and drying, and suggested that the entry of water into a dry soil produced internal and external forces that promoted aggregate breakdown. Internal forces due to water entry may arise from the release of entrapped air (Marshall et al., 1996). Aggregate breakdown can change soil structure by modifying the size and stability of aggregates and soil porosity. Upon drying, soil material may reorganize leading to coalescence of neighboring soil material. The process of aggregate breakdown and reorganization resulting from cycles of wetting and drying may induce similar structural changes in WTRs.

Drinking-water treatment residuals are enriched in amorphous Fe or Al hydroxides, and aging is expected to produce similar physicochemical transformations as observed for metal oxides. Makris (2004) observed decreased specific surface area (SSA) of an Al-WTR thermally incubated at 46 ^{o}C and 70 ^{o}C for 2 years. We hypothesized that the structural reorganization associated with aged metal oxides contained in the WTRs would stabilize immobilized P, even when important soil properties (e.g. pH) change. This study was, therefore, conducted to (i) evaluate the changes in lability of WTR immobilized P in artificially aged WTR amended soil

samples, and (ii) determine the effect of pH on the lability of WTR immobilized P using a modified isotopic dilution technique coupled with a stepwise acidification procedure.

Materials and Methods

Sample Preparation

Four WTRs, three alum-based with high P sorption capacities (Bradenton, Lowell and Holland WTRs) and one iron-based (Cocoa WTR) with a low P sorption capacity (chapter 2) were utilized for this study. Subsamples (< 2 mm) of each WTR were reacted for 7 days with P solutions at a P load of 10,000 mg P kg^{-1} in 1:10 WTR:0.01 M KCl suspensions (P-impacted WTRs). The pH was not controlled and the suspensions were not shaken during the equilibration period. After equilibration with added P, the WTRs were air dried. Non-treated (no added P) WTR samples were also included in an incubation experiment, described later.

Unamended surface soil from the Immokalee fine sand (sandy, siliceous, hyperthermic Arenic Alaquods) and collected from the University of Florida Research and Education Center in Immokalee, FL, was used for incubation studies. (Detailed descriptions of the soil and WTR properties are presented in chapter 2). The soil was air-dried and passed through a 2 mm sieve before amending with 25 g kg^{-1} of air-dried subsamples of the four WTRs (not P-impacted) described above. Phosphorus was added as triple superphosphate (TSP) solution at three rates: zero, low, and high to roughly mimic field application rates. The "low rate" of 43 mg P kg^{-1} (~86 kg ha^{-1}) still exceeds the range (44-65 kg P ha^{-1}) recommended for pasture grass raised for hay on P deficient soils (Adjei and Mislevy, 2001). The "high" P rate equals 100 mg P kg^{-1} soil, and represents a highly P-impacted soil. Fertilizer-P was dissolved in 0.01 M KCl and added to generate a solid:solution ratio of 1:10. The soil-WTR suspensions were reacted for 7 d at room temperature, without stirring. After the equilibration the amended soil suspensions were centrifuged and the supernatants were decanted.

Three replicates were used and a total of forty-five samples were studied. The experimental design was a completely randomized design (CRD) with treatments as:

no P, no WTR	low P, no WTR	high P, no WTR
no P, WTR (BR)	low P, WTR (BR)	high P, WTR (BR)
no P, WTR (HL)	low P, WTR (HL)	high P, WTR (HL)
no P, WTR (LW)	low P, WTR (LW)	high P, WTR (LW)
no P, WTR (CO)	low P, WTR (CO)	high P, WTR (CO)

where letters in parentheses are abbreviations for the four WTRs: BR = Bradenton, HL = Holland, LW = Lowell and CO = Cocoa WTRs.

Thermal Incubation

Subsamples of the equilibrated samples (both the WTR and WTR amended soil samples) were placed in incubators maintained at 23, 46, and 70 ^{o}C. P-treated and untreated samples of the four WTRs were incubated in the lab for 4.5 years. No attempt was made to control soil moisture during incubation. The heat treatment was applied to encourage structural changes that might mimic long-term weathering reactions in the field. We hypothesized that elevated temperatures would provide the necessary thermal energy for structural rearrangements with time. The changes in particle conformation, towards a lower free energy of the system, would either exclude or occlude sorbed P by the Al-WTR. Two batches of samples were thermally incubated concurrently. The first batch was started in spring 2002 for spectroscopic studies, detailed by Makris (2004), but the incubation was allowed to continue for the current P lability study. Since no lability data for the samples had been generated in the first years of incubation, a second batch of identically prepared samples were incubated, beginning in summer 2005, to measure the 'initial' labile P concentrations. Subsamples were collected at time zero, 1 month, 5 months, 1 year (for the 'second batch' samples), and at 3.5, 4 and 4.5 years (for the 'first batch' samples) after the initiation of the incubation. Subsamples were analyzed for labile P concentrations using a modified isotopic dilution technique coupled with a stepwise acidification procedure.

Wet-and-Dry Incubation

Phosphorus-equilibrated samples (both the WTR and WTR amended soil samples) were placed in an incubator at 23 ^{o}C and kept wet (~ 80 % of water holding capacity) for 7 days, and then allowed to dry for 7 d. The wet and dry cycles (54) continued for 2 years. Representative samples were taken at time zero, 5 months, 1 year, 1.5 years, and 2 years of incubation and analyzed for labile P concentrations using a modified isotopic dilution technique coupled with a stepwise acidification procedure.

Determination of Labile Pools of Phosphorus

Two grams (oven-dry equivalent) of each soil or WTR sample was placed in centrifuge tubes to which 20 mL of deionized water was added, giving a solid-to-solution ratio of 1:10, as suggested by Morel and Torrent (1997). Two drops of toluene were added to each suspension and appropriate aliquots of diluted HCl and NaOH were added daily to the samples to provide a series of 5 pH levels (3-7) for each treatment. The soil suspensions were equilibrated for 4 days in an end-over-end shaker. The samples were then spiked with 50 µL of a solution containing ^{32}P (500 kBq mL^{-1}) and returned to the shaker to isotopically equilibrate for 3 days. After equilibration, samples were centrifuged at 4200 x g for 10 min and filtered through 0.2-µm filters (Sartorius). Activities of radioactive P in the filtrates were assessed using liquid scintillation (Beckman LS 5801) counting. Water extractable P was determined colorimetrically using the method of Murphy and Riley (1962). All analyses were performed in triplicate and included blanks. The total activity introduced in each sample was determined by analyzing spiked solutions, without soil, in parallel with the soil suspensions (Lombi et al., 2003). The labile pools (*E*) of P were determined as reported in Hamon et al. (2002):

$$E = (C_{sol}/C^{\S}_{sol})\ R * (V/W) \qquad [1]$$

where C_{sol} is the concentration of water extractable P in solution (μg mL^{-1}), $C^{\$}_{sol}$ is the activity of radioisotope remaining in solution after equilibration (Bq mL^{-1}), R is the total activity of radioisotope added to each sample (Bq mL^{-1}), and V/W is the ratio of solution to sample, which in this case was 10 mL g^{-1}.

The percent labile P (% E) recovered was calculated as:

$$\% E = E / (\text{total P at 'native' pH of soil}) * 100 \quad [2]$$

where E is the labile pool of P calculated from equation [1]

Total P was determined using ICP-AES following digestion with the USEPA 3050A method (USEPA, 1986).

Preliminary experiments were conducted to determine the suitability of the isotopic dilution technique to assess P lability in WTRs and WTR amended soils. The effects of soil (or WTR):solution ratio, equilibration time, filter size, and centrifuge speed on the P concentrations in solution were also determined.

Determination of Oxalate Extractable Phosphorus

Two oxalate extract concentrations (5 and 200 mM) in buffered solutions (Schoumans, 2000) were utilized to determine the P concentrations of the sampled WTR and amended soil. A 1:60 soil (or WTR):solution ratio, shaken for 4 hours in the dark and filtered (0.45 μm), were analyzed for P, Al, and Fe by ICP-AES (Perkin-Elmer Plasma 3200. The insensitivity of the 200 mM oxalate treatment in extracting P from WTRs prompted us to also use a milder extractant (5 mM oxalate). The 5 mM oxalate extract has also been used to assess P availability in soils (Bhatti et al., 1995).

Quality Control

All sample collection/handling/chemical analysis was conducted according to a standard QA/QC protocol. For each set of samples, a standard curve was constructed ($R^2 > 0.998$).

Method reagent blanks were appropriately used. A 5% matrix spike of the set was used to determine the accuracy of the data obtained, with recoveries ranging from 96-103% of the expected values. Another 5% of the set was used to determine the precision of the measurements (triplicates). Analyses that did not satisfy the above QA/QC protocol were rerun.

Statistical Analyses

Data were analyzed as a factorial experiment with the completely randomized design (CRD) using the general linear model, PROC GLM, procedure of the SAS software (SAS Inst., 1999). The means of the various treatments were separated using a single degree of freedom orthogonal contrast procedure. Correlation analysis, with the PROC CORR procedure of the SAS software (SAS Inst., 1999), was used to evaluate the relationship between the two incubation (thermal and wet-and-dry) methods.

Results and Discussion

The isotopic dilution technique has been widely employed for estimating the total available pool of P in soils, often termed the 'E-value' (e.g. Talibudeen; 1957; Tran et al., 1988; Morel and Plenchette, 1994), as well as P availability in different fertilizer sources (e.g. Hendricks and Dean, 1947; Frossard et al., 1996). However, preliminary studies showed that the isotopic dilution technique was not appropriate for determining the labile pools of P in WTRs. The high P-sorption capacity of the WTRs led to sorption of the added ^{32}P, instead of isotopic exchange with the WTR-P (^{31}P), which over-estimated the labile P pools of the WTRs. The oxalate extraction procedure (5 and 200 mM) was used instead to assess the effect of aging on P extractability from the WTRs.

Relative Effectiveness of the WTRs

Incubations were performed with four WTRs (Holland, Bradenton, Lowell, and Cocoa), and soils amended with these four WTRs, with and without prior P addition (P-impacted WTR).

Oxalate (5 mM) extractable P concentrations for the P-impacted WTRs at the initial and final sampling of the thermally (70 ^{o}C) incubated samples, and those incubated via wetting and drying are presented in Table 4-1. The oxalate (5 mM) extractable P and labile P concentrations of the highly (100 mg kg^{-1}) P-impacted soils (with WTR amendment) for the thermally (70 ^{o}C) incubated samples and those aged through wetting and drying are presented in Tables 4-2 and 4-3, respectively.

Table 4-1. Oxalate (5 mM) extractable P concentrations (mg P kg^{-1}) measured from the artificially-aged, P-impacted[§] WTRs at the initial and final incubation periods. Values are means of three samples ± one standard deviation.

	Thermal[§§] incubation			wet-and-dry incubation	
WTR	Time zero	1 year	4.5 years	Time zero	2 years
Bradenton	7090 ± 830	1940 ± 240	1910 ± 56.2	7110 ± 1100	1980 ± 54.7
Cocoa	8890 ± 920	7580 ± 440	7520 ± 520	8940 ± 920	7580 ± 589
Holland	7200 ± 520	2020 ± 159	1960 ± 69.3	7080 ± 645	2025 ± 103
Lowell	7610 ± 615	2070 ± 142	1990 ± 62.4	7520 ± 680	2070 ± 78.4

[§] P load = 10000 mg kg^{-1} [§§] Thermally incubated at 70 ^{o}C

The 5 mM oxalate extractable P data show that at the end of the sampling period for both the thermally incubated and the wet-and-dry incubated samples, the Al-WTRs immobilized ~ 80 % of the initially added P (Table 4-1). No significant differences were found between the 3 Al-based WTRs in the amount of P sorbed at the final incubation period (both thermal and wet-and-dry incubation). The P sorption studies performed earlier with these 3 WTRs (chapter 2) suggested that the P sorption capacities of the Bradenton and Holland WTRs were superior to the Lowell WTRs. However, data from the incubated samples suggest that given sufficient reaction time, P sorption of the 3 WTRs was similar. Consistent with the P sorption studies (chapter 2), the Fe-based (Cocoa) WTR was the least effective P immobilizer. At the end of the incubation periods, Cocoa WTR immobilized < 25 % of the initially added P for both the thermally incubated and the samples incubated via wetting and drying (Table 4-1).

The oxalate (200 mM) data did not show any treatment and time effect. No significant time and treatment interaction effect was also observed using this extractant (data not presented). Unlike the data generated with the oxalate 5 mM extractant, no significant differences were observed among the different WTRs. The extractable P values measured in the samples at time zero were not significantly different from those measured during the experimental period and the final measurement. As observed previously (chapter 3), 200 mM oxalate was rigorous enough to extract P contained in the WTRs; hence, no WTR effect was detected.

Consistent with the data for the WTRs, the oxalate (5 mM) extractable P and the labile P concentrations of the P-impacted soils suggest that the Al-WTRs were more effective in reducing P mobility than the Fe-WTR (Tables 4-2 and 4.3). At the end of the incubation period, the Al-WTRs reduced oxalate (5 mM) extractable P and labile P concentrations for both the thermally incubated and wet-and-dry incubated samples by > 70 %, whereas the reductions due to the Fe-WTR was ≤ 20 %. The combined data suggest that the Al-WTRs were more effective in P immobilization than Fe-WTR, consistent with the P sorption kinetics data presented in chapter 2 of this dissertation.

Table 4-2. Oxalate (5 mM) extractable P concentrations (mg P kg^{-1}) of the artificially-aged, high P-impacted[§] WTR amended soil, measured at the initial and final incubation periods. Values are means of three samples ± one standard deviation.

	Thermal[§§] incubation			wet-and-dry incubation	
Treatment	Time zero	1 year	4.5 years	Time zero	2 years
No-WTR	107 ± 8.4	99.8 ± 4.4	99.4 ± 6.3	105 ± 5.8	102 ± 7.1
ABR[†]	93.4 ± 6.1	27.4 ± 2.1	24.4 ± 2.1	89.2 ± 5.3	30.2 ± 2.6
ACO[‡]	99.2 ± 3.9	86.3 ± 5.2	82.1 ± 5.2	99.8 ± 4.2	75.4 ± 7.2
AHL[††]	92.5 ± 4.1	30.8 ± 3.8	26.4 ± 3.2	94.3 ± 4.9	35.1 ± 4.1
ALW[‡‡]	94.2 ± 3.6	39.6 ± 3.4	35.4 ± 2.8	95.2 ± 6.1	37.6 ± 2.8

[§] P load = 100 mg kg^{-1}
[§§] Thermally incubated at 70 °C
[†] Soil amended with Bradenton WTR
[††] Soil amended with Holland WTR
[‡] Soil amended with Cocoa WTR
[‡‡] Soil amended with Lowell WTR

Table 4-3. Labile P concentrations (mg P kg^{-1}) of the artificially-aged, high P-impacted[§] WTR amended soils, measured at the initial and final incubation periods. Values are means of three samples ± one standard deviation.

	Thermal[§§] incubation			wet-and-dry incubation	
Treatment	Time zero	1 year	4.5 years	Time zero	2 years
No-WTR	103 ± 8.3	101 ± 7.2	98.6 ± 6.2	107 ± 5.6	101 ± 7.4
ABR[†]	92.5 ± 4.2	18.9 ± 2.1	17.3 ± 1.4	94.6 ± 6.2	19.2 ± 1.2
ACO[‡]	99.8 ± 4.2	80.1 ± 5.4	78.4 ± 3.6	99.4 ± 7.8	79.6 ± 4.9
AHL[††]	98.3 ± 3.6	20.4 ± 2.3	18.6 ± 2.1	93.6 ± 6.8	21.7 ± 2.2
ALW[‡‡]	96.1 ± 5.6	21.7 ± 4.2	20.8 ± 1.8	98.9 ± 7.1	22.4 ± 3.2

[§] P load = 100 mg kg^{-1}
[§§] Thermally incubated at 70 ^{o}C
[†] Soil amended with Bradenton WTR
[††] Soil amended with Holland WTR
[‡] Soil amended with Cocoa WTR
[‡‡] Soil amended with Lowell WTR

Aging and pH Effects on Phosphorus Lability

Despite the differences in the physicochemical properties and P sorption kinetics of the four WTRs (chapter 2), their effects on soluble P over time followed similar trends. Therefore, only the data for the Holland Al-WTR material are presented here. The Holland WTR was the material utilized for the Michigan field study (chapter 5), and showed the clearest treatment effects on lability.

Phosphorus Extractability of Thermally Incubated WTRs

The effects of thermal aging on P extractability were assessed through chemical extraction using 5 and 200 mM oxalate extractants. The 200 mM oxalate extractant extracted ~ 90 % of the P spiked onto the WTR (Figure 4-1) suggesting that the extractant was sufficiently rigorous to extract P otherwise immobilized by, or contained in, the WTR. Oxalate (200 mM) extractable P concentrations were relatively constant from the samples taken at time zero through 3.5 years of thermal incubation. However, there was a significant reduction of the extractable P of the thermally (46 and 70 ^{o}C) incubated samples taken 4 and 4.5 years after the initiation of the incubation. Conversely, no significant difference in extractable P was detected over time for the control (those incubated at 23 ^{o}C) WTR samples.

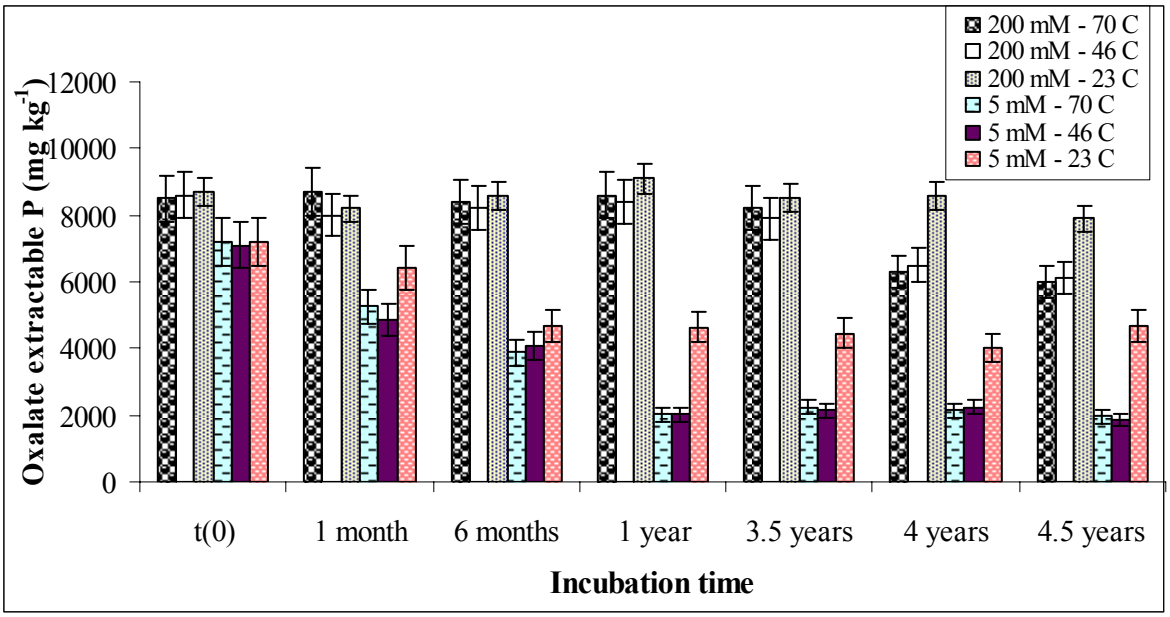


Figure 4-1. Changes in the mean oxalate (200 and 5 mM)-extractable P concentrations with incubation time at 23, 46 and 70 ^{o}C of the P impacted Al-WTR.

Particle surface transformations due to temperature or sorbate additions would be difficult to detect using a high concentration of oxalate (200 mM), so we also used a weaker (5 mM) concentration. The 5 mM oxalate extractant extracted significantly ($p<0.001$) less P from the WTR than 200 mM oxalate at all incubated temperatures over the incubation period (Figure 4-1). For the P-impacted WTR, 5 mM oxalate-extractable P significantly ($p = 0.015$) decreased 1 month after thermal (46 and 70 °C) incubation (Figure 4-1). Extractable P continued to decrease as the thermal incubation continued for another 11 months; thereafter, the system appeared to be at steady state. In contrast, 200 mM oxalate extracted significantly less P only after 4 years of thermal incubation. Although the absolute values of 5 mM oxalate-extractable P in the control samples (those incubated at 23 ^{o}C) decreased after 1 month, the reduction was not significantly different from the values of the extracted P at the initial sampling. The reduction in extractable P values of the control samples became significant after 6 months of incubation and stabilized thereafter (Figure 4-1). Untreated WTR (no P added) had oxalate (5 mM)-extractable P levels close to the instrument's detection limit of 0.03 mg P L^{-1} (data not presented). Phosphorus

indigenous to the WTR (no P added treatment) was apparently an integral part of the internal WTR structure, and little was accessible to the weaker extractant (5 mM oxalate).

Labile Phosphorus Concentration of Thermally Incubated WTR Amended Soil

Soils amended with WTRs represent the most realistic system to assess long-term P stability of sorbed P by WTRs applied to soils. This study evaluated the stability of WTR immobilized P in thermally aged P-impacted (43 or 100 mg kg^{-1}) Immokalee soil samples. Effects of pH on the lability of WTR immobilized P were also assessed.

There was a significant effect of WTR amendment, aging, and pH on P lability in all the samples. The labile P concentrations of the WTR amended soil samples that were highly impacted with P (100 mg kg^{-1}) and thermally aged at 46 and 70 ^{o}C significantly ($p < 0.001$) decreased at all pH levels (3 – 7) after 4.5 years of thermal incubation (Figure 4-2). Data for samples incubated at either 46 or 70 ^{o}C were similar, and only the 70 ^{o}C data are presented. Amendment with Al-WTR decreased labile P concentrations by ~ 70 % relative to the samples without WTR amendment. Similar trends were observed in the samples taken previously (1 year, 3.5 and 4 years). However, until 6 months of thermal incubation, the reductions in labile P concentrations were observed only in the samples equilibrated at pH 4-7 (discussed later). In the earlier samplings (0-6 months), no significant WTR effect on labile P values was observed in the samples equilibrated at pH 3. Similar behavior was observed for the thermally aged 'low' impacted (43 mg P kg^{-1}) samples and those without P addition (data not presented).

Compared to the thermally aged soil samples, labile P concentrations of the 'high' impacted P control soil samples (incubated at 23 ^{o}C) were significantly ($p = 0.025$) greater at all pH levels (Figure 4-2). Similar behavior was observed for the 'low' impacted P samples and the samples without P addition (data not presented). The significant aging effect supports the contention of Makris et al. (2004 a,b) that the applied thermal energy enhances diffusion of P

into the micropores of the WTR and that the possible structural reorganization of the WTR during the aging process increases the stability of the WTR immobilized P. Labile P concentrations measured at the various P loading rates and pH levels were similar when the samples were incubated at 46 ^{o}C and at 70 ^{o}C, suggesting that the enhanced aging of the samples at 46 ^{o}C was equally effective as the aging at 70 ^{o}C.

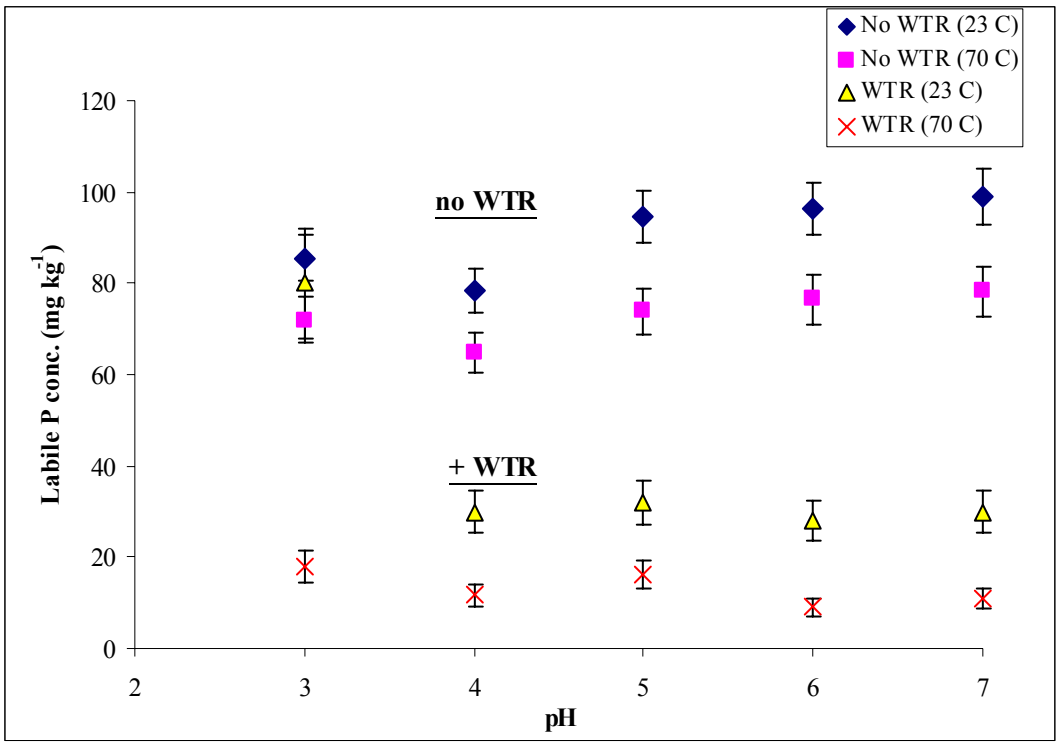


Figure 4-2. Changes in labile P concentrations of thermally incubated (4.5 years) Immokalee soil samples initially spiked with 100 mg P kg^{-1}, as a function of pH.

For the soil samples without WTR amendments, the smallest labile P concentrations were observed at pH 4 at all impacted P levels in both the thermally aged and the control soil samples (Figures 4-2 and 4-3). The greatest labile P concentrations, on the other hand, occurred at pH 7 at all impacted P levels in both the thermally aged and the control soil samples (Figures 4-2 and 4-3). The data suggest that P fixation was greatest at pH 4, whereas P was desorbed at pH 7. Several researchers (Nwoke et al., 2004; Olsson and Tyler, 2004; Wang et al., 2004) reported P availability increases at near-neutral to neutral pH.

Soil samples receiving the greatest concentration of added P (100 mg P kg^{-1}), without WTR amendment, had the greatest labile pools of P, followed by the samples spiked at 43 mg P kg^{-1}. The least labile P concentrations occurred in the samples without P addition, in the thermally aged and the control soil samples (Figures 4-3 and 4-4). WTR amendment, coupled with the aging of the samples, masked the P addition effect (Figure 4-4). In the thermally aged soil samples, the labile P concentrations in the WTR amended P-impacted soil samples and the soil samples without P addition were similar.

The labile P concentrations of the WTR amended control soil samples (those incubated at 23 ^{o}C) incubated for 4.5 years decreased at all impacted P levels when the labile P concentrations were determined at pH 4–7 (Figure 4-3). Within this pH range, amendment with Al-WTR decreased the labile P concentrations by ~ 60 % relative to the samples without WTR amendments. However, at pH 3, labile P concentrations of the WTR amended soil samples and the samples without WTR amendments were similar at each impacted P levels (Figure 4-3). This suggests that the WTR was destabilized at pH 3 and immobilized P was desorbed. Similar trends were observed from the samples taken throughout the incubation period.

WTR amendment, coupled with the thermal incubation significantly decreased labile P concentration of the WTR amended soil one month after thermal incubation at all pH levels except at pH 3 (Figure 4-5). A further significant reduction was observed after 6 months. Within the pH range of 4-7, reductions in labile P due to WTR amendment persisted throughout the incubation period. Measurements taken after 1 year of thermal incubation showed that labile P concentration of the samples equilibrated at pH 3 decreased significantly, and the decrease persisted thereafter (Figure 4-5). After 3.5 years of thermal incubation, no significant differences were observed in labile P concentrations among all WTR amended samples (pH 3-7).

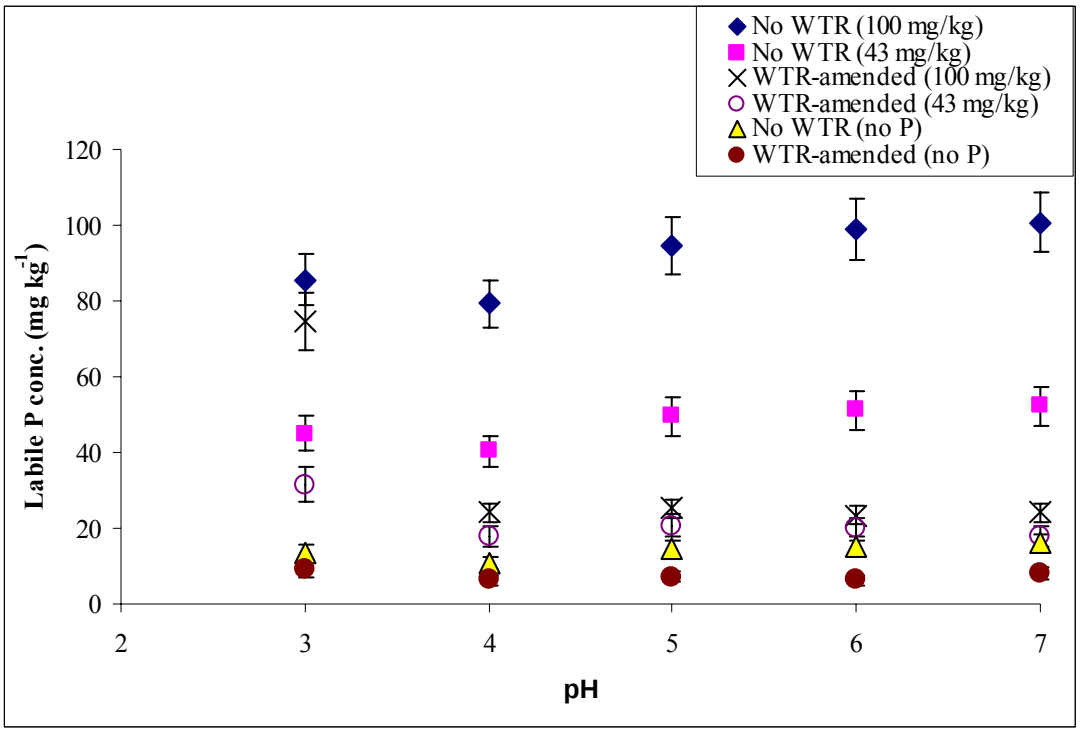


Figure 4-3. Changes in labile P concentrations of P impacted Immokalee soil samples incubated for 4.5 years at 23 ^{o}C (with and without and WTR amendments) measured as function of pH.

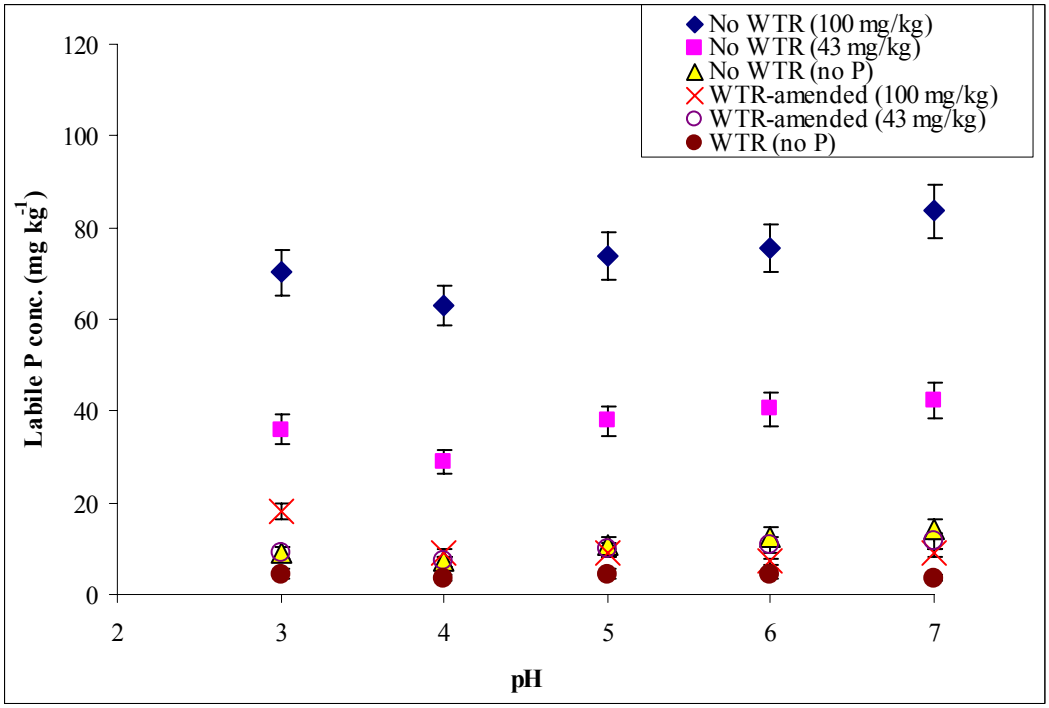


Figure 4-4. Changes in labile P concentrations of P impacted Immokalee soil samples incubated for 4.5 years at 70 ^{o}C (with and without and WTR amendments) measured as function of pH.

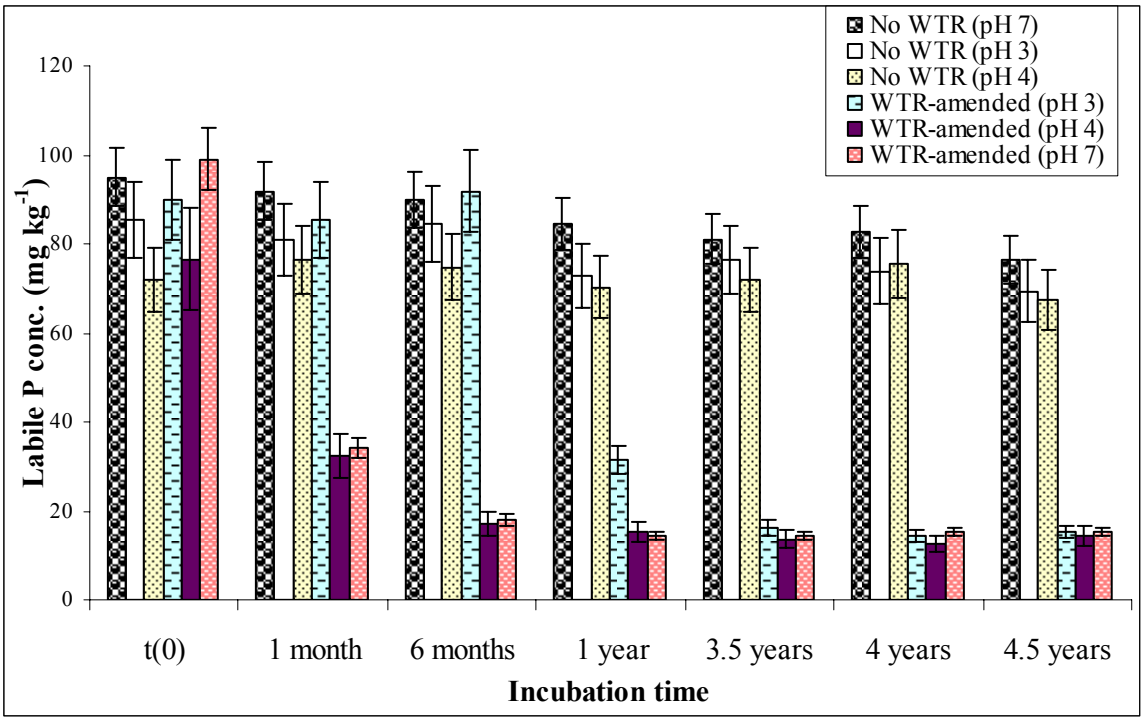


Figure 4-5. Changes in labile P concentrations with time, of the Immokalee soil samples spiked with 100 mg P kg^{-1} and thermally incubated at 70 ^{o}C for 4.5 years.

After 4.5 years of thermal incubation, a significant decrease in labile P pools was still observed at all pH values, including pH 3. Thus, if thermal incubation truly predicts long-term aging under field conditions (Postma and Jacobsen, 1996; Ford et al.,1997; Martinez et al., 2001), not only will the WTR immobilized P remain fixed for a long time in soils with typical pH values, but the destabilization of the WTR immobilized P at pH 3 will also be eliminated over time.

Oxalate extractions were also performed on soil samples collected over time during the incubation period. The 5 mM oxalate extractable P data also showed significant WTR amendment and aging effects (Figure 4-6). After one month of thermal incubation, the extractable P concentrations of the WTR amended soils spiked with 'high' P load significantly decreased in the samples incubated at 23 or 70 ^{o}C. The extractable P concentration continued to decline for 6 months, but no significant decrease occurred thereafter. The rate of decrease in the

values of extractable P concentration in samples incubated at 70 °C was, however, greater than the rate for samples incubated at 23 °C. Heat treatment apparently enhanced the immobilization process by hastening diffusion of P into the micropores of the WTR, as suggested by Makris et al. (2004a,b).

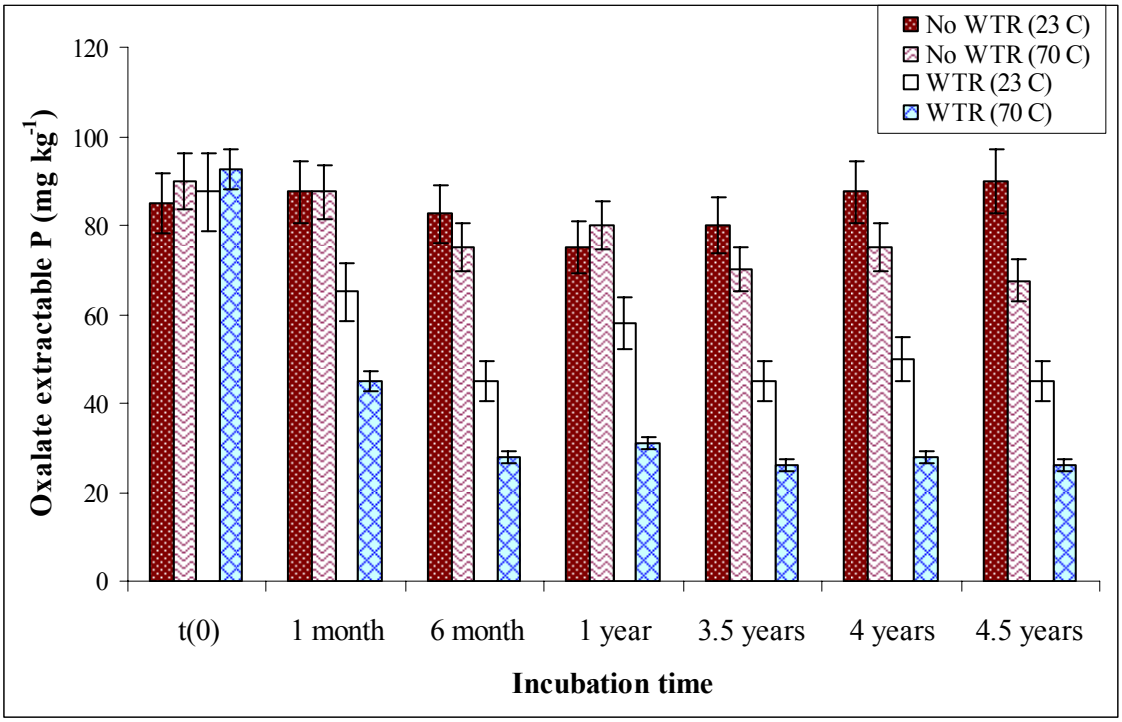


Figure 4-6. Changes in oxalate (5 mM)-extractable P concentrations with incubation time at 23, and 70 °C of WTR amended and unamended (no WTR) Immokalee soil samples that received 'high' (100 mg kg^{-1}) P load.

The oxalate-200 mM P concentrations in soils not amended with WTR or TSP did not change with time at any incubation temperature (data not presented). The unamended (no WTR) soil samples with high (100 mg P kg^{-1}) P treatment showed a similar trend except that the absolute values of the thermally incubated samples declined after 1 year of incubation, but the decreases in extractable values were not significant (data not presented). The WTR amended, P-impacted soil samples, however, showed significant incubation time and temperature interaction effects. For the control samples (those incubated at 23 °C), the 200 mM oxalate extractable P values did not change with time, but the absolute values of the extractable P concentration of the

thermally incubated samples decreased slightly after 1 year of incubation. The reduction of the extractable P concentrations of the thermally incubated samples became significant after 4.5 years. The decrease in the extractable P concentrations of the WTR amended samples could not be attributed to WTR effects because similar trends were observed in the thermally incubated unamended (no WTR) samples.

Phosphorus Extractability of Wet-and-Dry-Incubated WTRs

As with the thermally incubated P-impacted WTR samples (Figure 4-1), 200mM oxalate extractant extracted most of the 10,000 mg kg^{-1} P spiked onto the WTR and were unaffected by aging via wetting and drying (Figure 4-7). For the P-treated WTR, 5 mM oxalate-extractable P values significantly ($p = 0.025$) decreased after 5 months incubation (10 wet/dry cycles), in contrast to the 200 mM oxalate P values, which were unchanged even after 2 years of incubation (Figure 4-7).

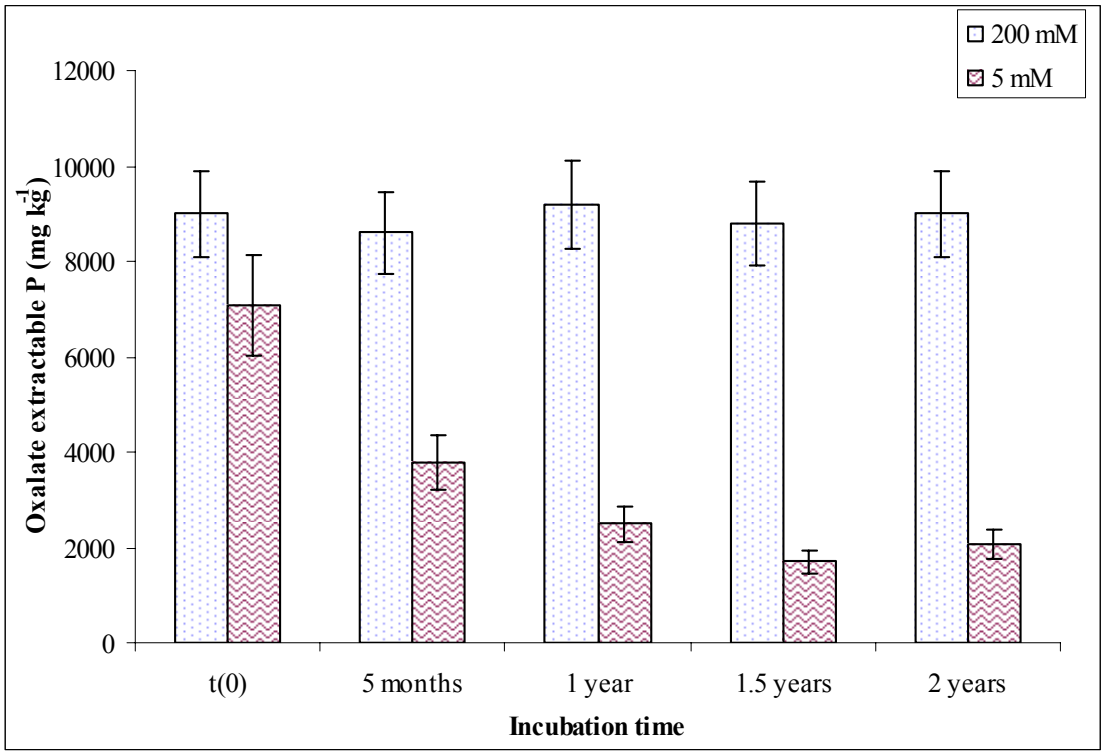


Figure 4-7. Changes in the mean oxalate (200 and 5 mM)-extractable P concentrations with incubation time of the P impacted Al-WTR (incubation through wetting and drying).

The oxalate 5 mM extractable P values continued to decline significantly for another 1 year. No differences were observed in the extractable P values of the samples taken after 1.5 and 2 years of wetting and drying, suggesting that the system apparently became stable after 1.5 years of aging.

Similarly to the thermally incubated samples, the untreated WTR had oxalate (5 mM)-extractable P values close to the instrument detection limit (0.03 mg P L^{-1}), and the values were independent of incubation time (data not presented).

Labile Phosphorus Pools of WTR amended Soil Aged via Wetting and Drying

Amendment with WTR, aging, as well as their interaction, significantly decreased P lability at all P loads. In the 'high' (100 mg P kg^{-1}) P-impacted soil, WTR application decreased labile P concentrations at all pH values except pH 3 (Figure 4-8).

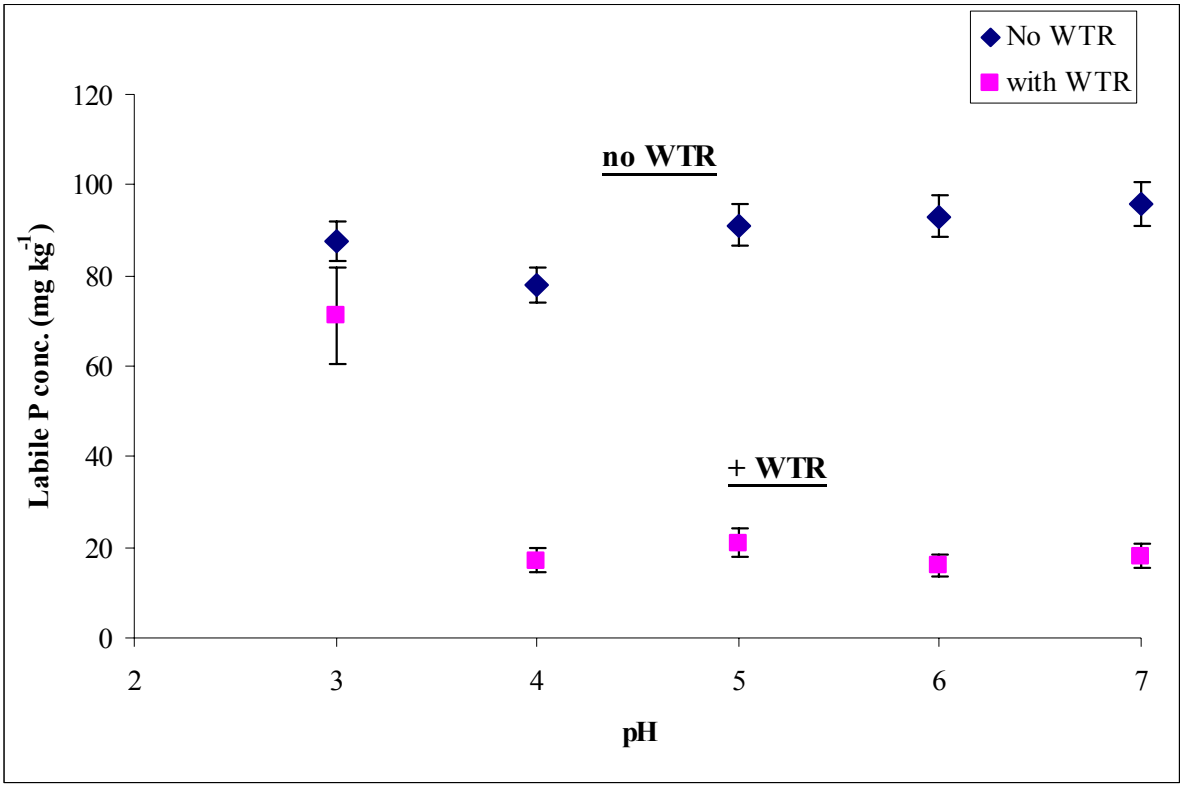


Figure 4-8. Changes in labile P concentrations as a function of pH for the Immokalee soil samples spiked with 100 mg P kg^{-1} and incubated via wet-and dry cycles for 2 years.

Within the pH range of 4 - 7, labile P concentrations were ultimately reduced by ≥ 75 %, relative to the no-WTR (control) samples. However, at pH 3, much of the sorbed P was desorbed, and labile P was about three times of that measured at pH 4-7. Similar results were observed in the 'low' (43 mg P kg^{-1}) P-impacted and the samples without P addition (data not presented). The results suggest that WTR immobilization of P is most effective within the pH range of 4 - 7, and that the WTR immobilized P is stable within this pH range. As with the thermally incubated samples and within the pH range of 4 - 7, amendment with WTR and aging through wetting and drying cycles masked the P load effect (Figure 4-9). Significant reductions in labile P of the WTR amended soil samples were observed over time with repeated wetting and drying cycles (Figure 4-10) within pH range of 4 - 7.

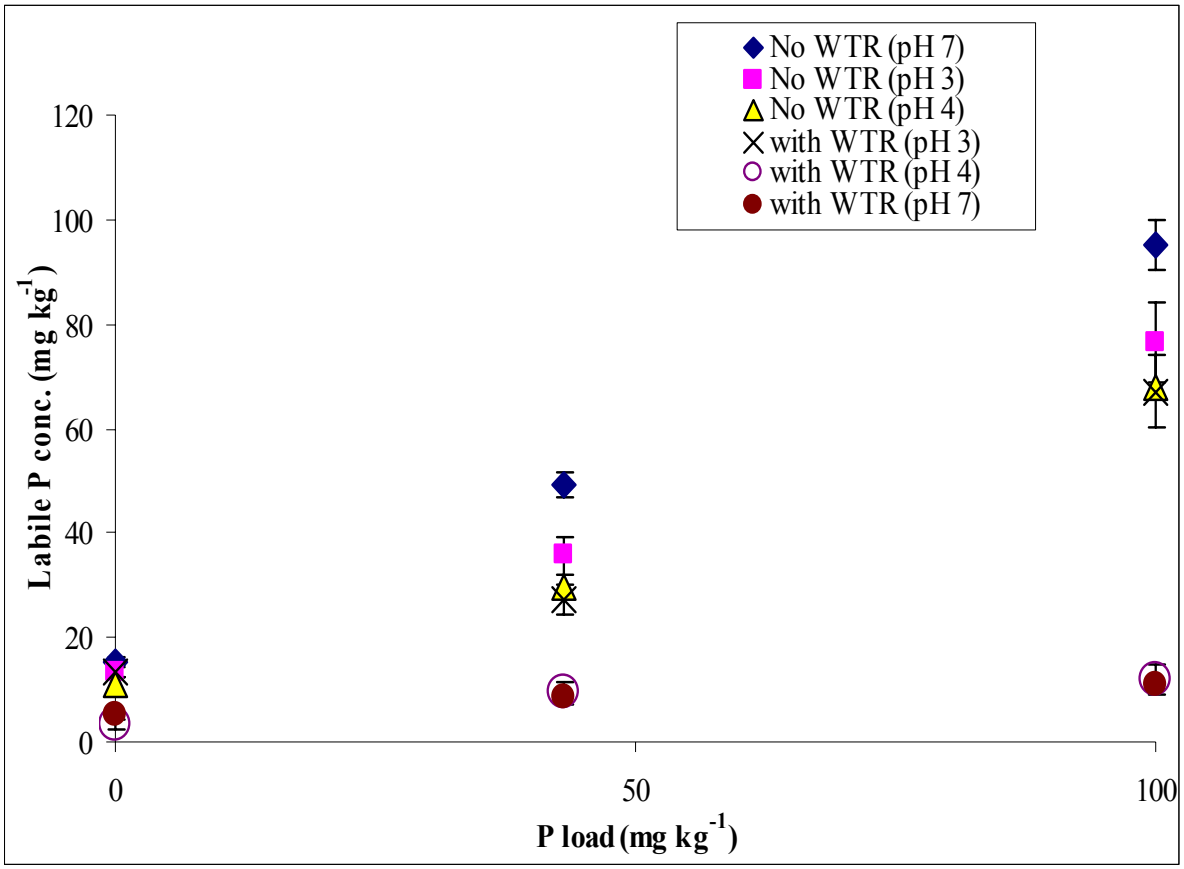


Figure 4-9. Changes in labile P concentrations as a function of impacted P levels for Immokalee soil samples artificially aged via wet-and dry cycles for 2 years.

Without WTR amendment, labile P concentrations of the soil samples remained high and relatively stable over time in the pH 4 - 7 range. Amendment with WTR significantly decreased labile P after 5 months of incubation, and the decrease continued with additional wetting and drying cycles until apparent equilibrium at 1 to1.5 years (~ 40 wet and dry cycles). No reductions in labile P concentrations were observed for the WTR amended samples when the determinations were conducted at pH 3. This suggests that the WTR was destabilized at pH 3 and released P otherwise incorporated in the WTR.

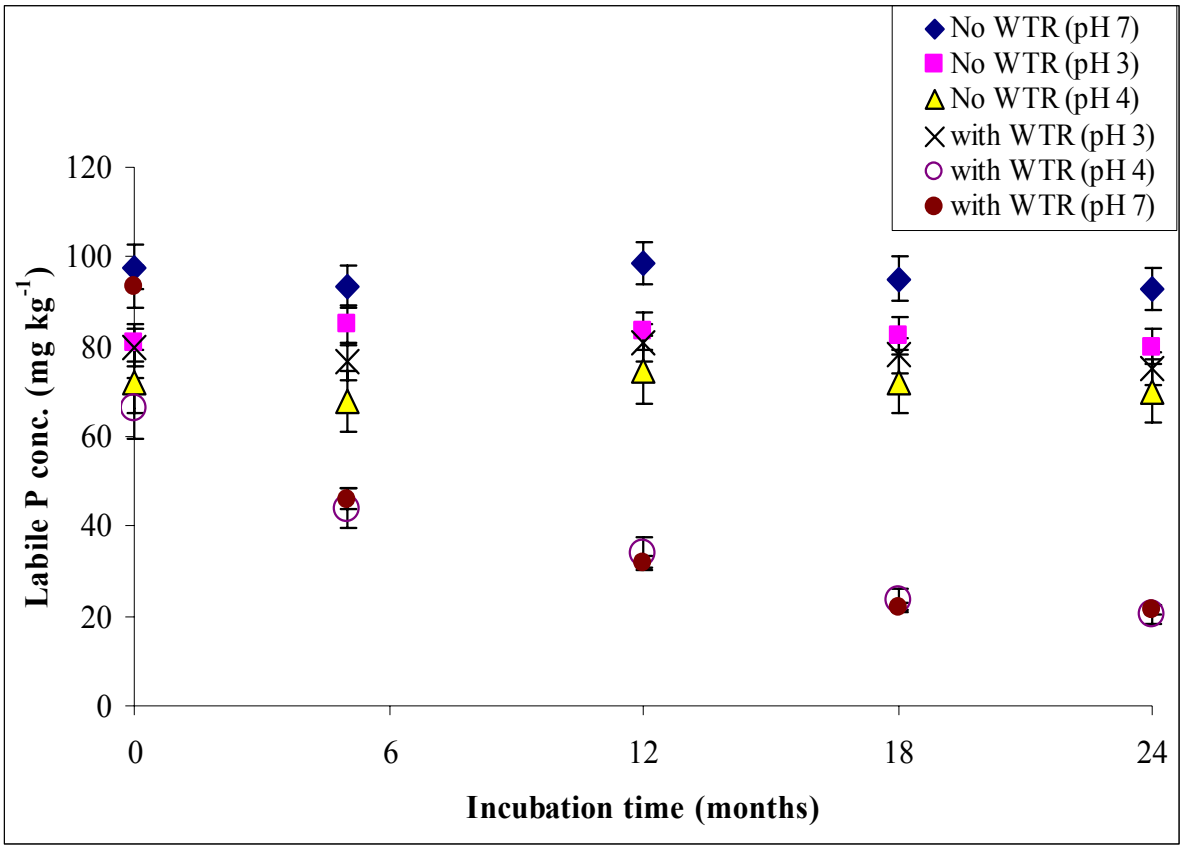


Figure 4-10. Changes in labile P concentrations with time in Immokalee soil samples spiked with 100 mg P kg^{-1} and artificially aged through wet-and dry cycles.

Oxalate extractions were also performed on soil samples incubated through repeated wetting and drying cycles. As with the thermally incubated soil samples, oxalate-200 mM P concentrations from the samples without P and WTR amendment did not change with time (data

not presented). Similarly to the data of the Kissimmee field study (chapter 3), the WTR amended soil samples had significantly greater oxalate (200mM)-extractable P concentrations than the soil without WTR amendments. This suggests that the extractant was rigorous enough to extract P otherwise immobilized and/or contained in the WTR. Using the weaker oxalate (5 mM) extractant, a significant WTR effect became obvious. Amendment with WTR, coupled with the wetting and drying, decreased the extractable P concentration from ~ 90 mg kg^{-1} to 55 mg kg^{-1}, 5 months after incubation and then to ~ 35 mg kg^{-1} after 1 year (Figure 4-11). Thereafter, the decrease in extractable P concentrations was no longer significant and appeared to have stabilized. Thus, the 5 mM oxalate extractant showed the beneficial effect of aging and WTR amendment in reducing P solubility in P-impacted soils.

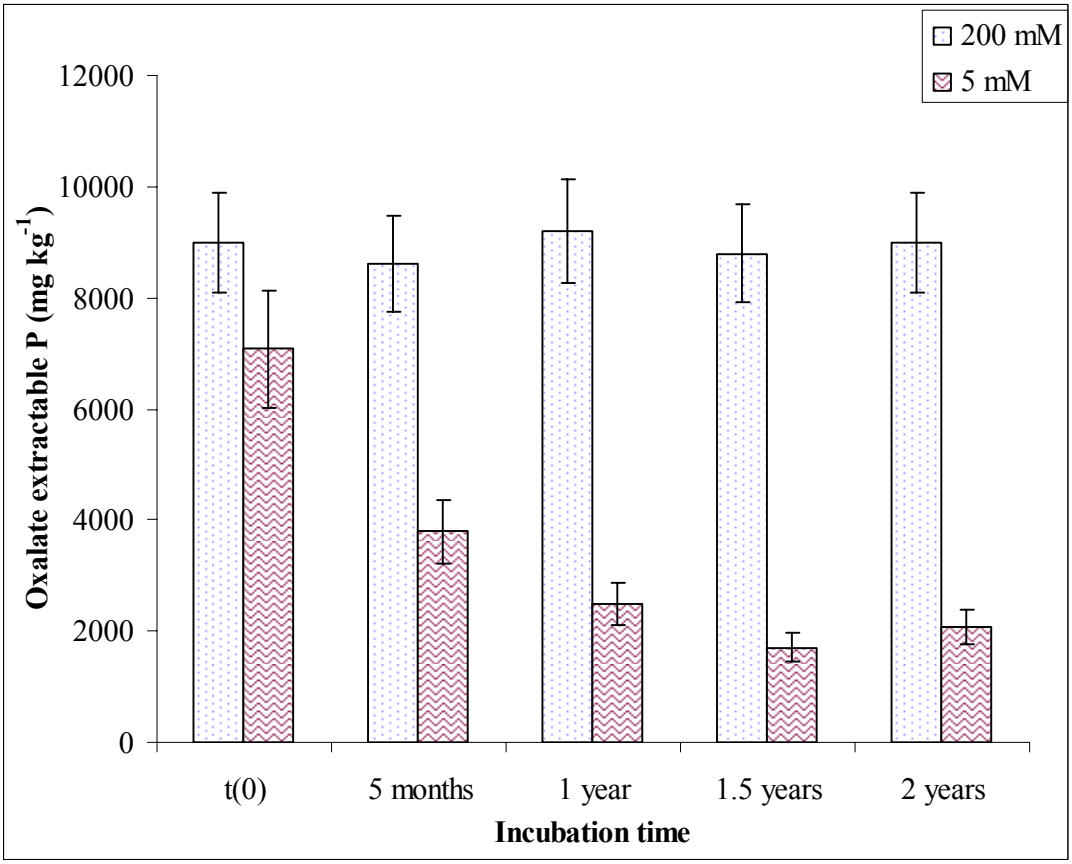


Figure 4-11. Changes in oxalate (5 mM)-extractable P with incubation time of WTR amended and unamended (no WTR) Immokalee soil samples that received 'high' (100 mg kg^{-1}) P load.

The incubation data for both WTR alone, and WTR amended soils show that WTR effectively reduces soluble P levels, and suggest that P would remain immobilized in the long-term. There was no release of P from WTRs or WTR amended soils, upon aging via thermal or wet-and-dry incubation. The data suggest that sorbed P will remain indefinitely immobilized unless particle dissolution occurs at extreme pH values ≤ 3. Happily such extreme pH conditions are rarely encountered in agricultural soils.

Evaluation of the Aging Techniques

Artificial aging of metal oxides through repeated wet-and-dry cycles represents a cost effective means of obtaining aged samples that mimics aging under natural environments (Frau, 2000; Kennedy et al., 2004). Results obtained from the samples aged through wet-and-dry cycles closely mirrored those obtained from the thermally incubated soil samples. Within the pH range of 4-7, the thermally incubated WTR amended samples appeared to stabilize at 6 months, whereas the samples incubated via wetting and drying apparently reached equilibrium about 1.5 years after incubation. When the data generated from time zero until the apparent 'stabilized' times of the two aging techniques were analyzed, a very strong ($r \sim 0.96$) and highly significant ($p < 0.001$) correlation was observed between the two aging techniques (Figure 4-12). Similarly when all the data generated (between pH 4 - 7) from the two aging techniques over the incubation period were analyzed together there was a significant ($p = 0.01$) correlation ($r^2 = 0.74$) between the two techniques (data not presented). No significant correlation ($r^2 = 0.24$, $p > 0.05$) was observed between the data of the samples equilibrated at pH 3 over the incubation period by the two aging techniques (data not presented).

Time series analysis suggests that equilibrium labile P levels (~ 20 mg kg^{-1}) of the high P-impacted (100 mg kg^{-1}) WTR amended soil samples were achieved after~ 6 months of thermal incubation, and after ~1.5 years of wet-and-dry incubation. The data suggest that the aging

process is slower with the wet-and dry incubation technique. This observation supports the hypothesis that the elevated temperatures enhanced the diffusion of P into the micropores of the WTR (Makris et al., 2004 a,b). Schwertmann and Cornell (1991) reported that temperature controls the transformation of amorphous solid phase of metal oxides (e.g. hematite) and that structural reorganization is enhanced at elevated temperatures. Nevertheless, the data suggest that given time, the slower aging through wet-and-dry cycles is ultimately equally as effective as through thermal incubation.

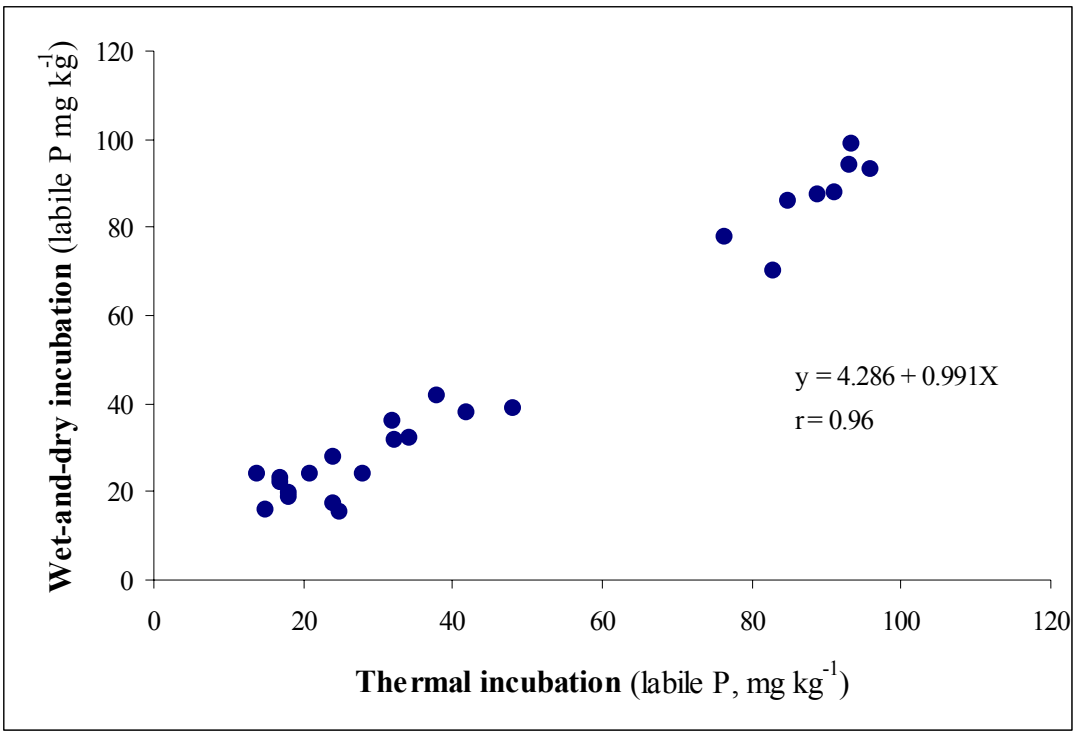


Figure 4-12. Relationship between labile P concentrations of the WTR amended P-impacted (100 mg kg^{-1}) samples incubated either thermally or via wetting and drying. Measurements were taken until time to apparent equilibrium.

CHAPTER 5
LONG-TERM PHOSPHORUS IMMOBILIZATION BY A DRINKING-WATER TREATMENT RESIDUAL: MICHIGAN FIELD STUDY

Introduction

Excessive soluble P concentrations in poorly P-sorbing soils can be controlled through the additions of P-sorbing amendments, such as alum (Moore et al., 1998) or drinking-water treatment residuals (WTRs) (Elliott et al., 2002b; Makris et al, 2004a,b; Novak and Watts, 2004; O'Connor et al., 2004; Novak and Watts, 2005 Silveira et al., 2006). Drinking-water treatment residuals are by-products of the drinking-water treatment process and are physical mixtures of Al or Fe hydr(oxides) that originate from flocculant (Al or Fe salts) additions made during the processing of drinking-water (O'Connor et al., 2002). Drinking- water treatment residuals are usually disposed of in landfills and can be obtained at minimal or no cost from drinking-water treatment facilities.

Short-term lab, greenhouse, and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P concentrations in runoff (Dayton et al., 2003; Dayton and Basta, 2005; Elliott et al., 2005), and leaching (Elliott et al., 2002a) from areas amended with animal manure. The long-term stability of the P sorbed by WTRs has been qualitatively addressed in laboratory experiments (Makris et al., 2004 a,b). The authors suggested that intraparticle P diffusion into the WTRs, coupled with the minimal P desorption (80 days), represented irreversible P sorption by the WTRs. Makris (2004) observed that adsorption of P by WTRs was strongly hysteretic and essentially independent of pH. Once sorbed in the internal micropores of WTR, P release is unlikely because of very high bonding energy of P to surfaces and steric limitations to P movement through "bottle-necks" consisting of complex metal-organic C assemblages. The combined Makris (2004) data suggest that WTRs can be effective sorbents for P and that the immobilized P would be stable in the long-term. However, long-term field

experiments are needed to test WTR efficacy in reducing soluble P concentrations and to confirm trends observed in, or inferred from, laboratory studies. Time constraints associated with conducting long-term field experiments are the major drawbacks in evaluating the long-term fate of sorbed P in WTR amended soils, and few researchers have conducted such studies.

Some field studies (Moore et al., 1998; Lu and O'Connor, 2001) have monitored soluble P concentrations in high P-containing soils, treated with amendments similar in chemical composition to WTRs (i.e., high in amorphous Fe or Al content, such as alum salts, or biosolids relatively high in total Al and Fe). Most Fe- or Al-WTRs resemble Fe or Al hydroxides in chemical composition, and literature pertaining to Fe/Al hydroxide effects on soluble P concentrations can be used to predict the long-term fate of sorbed P by WTRs (Makris et al., 2005). Self-Davis et al. (1998) studied tall fescue grass plots treated with alum-amended poultry litter for 3 years and showed no differences in soil water-soluble P (WSP) and Mehlich III-P concentrations when compared to an unfertilized control. However, WSP in the untreated (no alum) poultry litter-amended plots linearly increased each year (Self-Davis et al., 1998). Lu and O'Connor (2001) showed that biosolids (containing 27–109 g kg^{-1} total Fe + Al) applied to a poorly P-sorbing soil, increased P sorption initially, but the effect was minimal after 4 years.

Based on the short-term effectiveness of WTRs in reducing soluble P concentrations in soils, we hypothesized that (i) WTR application would significantly reduce soil P extractability and (ii) aging of WTR in the field would inhibit P desorption in the long-term, based on the intraparticle diffusion concept used to describe the hysteretic long-term (up to 80-days) P sorption by WTRs (Makris et al., 2004a,b). Samples from a long-term WTR field application experiment were utilized to test our hypotheses. Our objectives were (i) to assess the long-term effectiveness of alum WTR (Al-WTR) in reducing P extractability and labile pools in field soils

with long histories of poultry manure applications and (ii) to assess the effect of pH changes on the lability of WTR immobilized P in field-aged samples using a modified isotopic dilution technique coupled with a stepwise acidification procedure.

Materials and Methods

Field Layout and Amendments Application

Two field sites (sites 1 and 2) located in Western Michigan (Jacobs and Teppen, 2000) were selected in 1998 for evaluation of WTR effects on P extractability in soils having "very high" soil test P concentrations. Both soils had a long-term (> 10 years) history of heavy poultry manure applications (actual application rates unknown). Soil at site 1 was a Granby fine sandy loam (sandy, mixed, mesic Typic Endoaquolls) with Bray P1 test levels (265 mg P kg^{-1}). Soil at the second site was Granby loamy sand (sandy, mixed, mesic Typic Endoaquolls) with Bray P1 test values of 655 mg P kg^{-1}.

A randomized, complete block design was established at each site with four replications per treatment and a plot size of 14 m x 30 m. The Al-WTR, obtained from the Holland, MI water treatment plant, was used in this study. The material was removed from lagoon storage, and stockpiled for drying. The dried Al-WTR was applied (114 dry Mg ha^{-1}) to plots using a Knight ProTwin Slinger, model 8030 V-box spreader, by making three passes on each side of the plot, or three round trips. All plots, including the untreated controls, were disked (10-15 cm) twice following WTR application. Additionally, site 1 was chisel-plowed and field cultivated prior to planting on May 5, 1998. Site 2 was moldboard plowed (20-25 cm) before planting on May 4, 1998. Both sites were moldboard plowed prior to planting in 1999. In April/May, 2000, both sites were rototilled prior to planting to promote more thorough mixing of WTR, then moldboard plowed. Moldboard plowing was used each spring, 2001-2004, at each site prior to planting. Field corn (*Zea mays* L.) was planted each year at both sites. Herbicides and insecticides for

weed and pest control typically used by cooperating farmers were applied at planting. Fertilizer nitrogen and potash were applied as needed. The study continued for 7 years, but the WTR amendment was applied only in 1998. Details of the field study are given in Jacobs and Teppen (2000).

Soil Sampling

Surface soils of control and WTR amended plots from the two field sites were first sampled in spring 1998 (time zero) by compositing 20 cores (2.54 cm diameter) from the top 20 cm depth of each plot. Soil surface samples were similarly collected each fall in 1998, 1999, 2000, 2001, 2002, 2003 and 2004 for analyses to monitor changes in labile pools of P following the WTR application. In fall 2005, surface soils of the control and the WTR amended plots from both sites were bulk sampled (~ 20 kg) from the top 20 cm depth of each plot for use in a rainfall simulation study. Samples were air-dried and passed through a 2 mm sieve before analyses.

Laboratory Analyses

Phosphorus extractability in soils was monitored as a function of time in the field with several P extraction schemes to identify the extraction method that adequately assessed P lability in WTR amended soils. Additionally, extractable Fe and Al concentrations were monitored over time.

Total P (USEPA, 1986) and oxalate (200 mM) extractable P (Schoumans, 2000) determinations were performed as described in chapters 2 and 3. The insensitivity of the 200 mM oxalate treatment in extracting P from WTRs led us to also use a milder extractant (5 mM oxalate). The 5 mM oxalate extract has also been used to access P availability in soils (Bhatti et al., 1998). Water-soluble P (WSP) in soils was determined by reacting soil samples with deionized water at a 1:10 soil:solution ratio for 24 h, modified from Kuo (1996). Bray P1 concentrations were determined by reacting the soil samples with 0.025 M HCl in 0.03 M NH_4F

solution at a ratio of 1:10 soil:solution ratio and shaken for 5 min (Brown, 1998). Extractions were filtered (Whatman No 42) and analyzed colorimetrically for P concentration with the Murphy and Riley (1962) method. Phosphorus saturation ratio (Maguire et al., 2001) was calculated for the soils. This index is similar to the degree of P saturation (DPS) index, but omits the saturation factor, α (α = 0.3-0.5) in the ratio (Schoumans, 2000). The labile pools of P, as a function of time and pH, were determined using the modified isotopic dilution technique coupled with stepwise acidification procedure described in the previous chapter. Standard QA / QC protocols of matrix spike (5 % of the set) recoveries were used in all the experiments, including sample collection/handling/chemical analysis. Method reagent blanks, certified check standard analyses, and new standard curves for each set of samples were used. (Detailed description of this procedure is presented in chapter 3.

Statistical Analyses

Differences among treatments were statistically analyzed as a factorial experiment with a randomized complete block design (RCBD), using the general linear model (GLM) of the SAS software (SAS Inst., 1999). The means of the various treatments were separated using a single degree of freedom orthogonal contrast procedure.

Results and Discussion

The field study was conducted primarily to assess the long-term phosphorus immobilization by WTR under natural conditions to confirm conclusions made from laboratory sorption and incubation studies. We utilized several commonly used soil P extractants to assess the effect of WTR on P extractability over time. We utilized the modified isotopic dilution technique, coupled with stepwise acidification procedure to evaluate lability of WTR immobilized P as a function of pH in field-aged WTR amended samples, as a confirmation of observations garnered from the artificially aged sample studies.

Extractable Phosphorus, iron and Aluminum over Time

We hypothesized that application of WTRs to soils with excessive P concentrations will reduce extractable P concentrations and decrease the amount of P available for surface movement to surface water. Determining the most appropriate P extraction method for WTR amended soils is of paramount importance for determining or predicting P losses. In this regard, we utilized five soil P extraction procedures [total P extractant, oxalate (200 and 5 mM), Bray-1, and water] to evaluate WTR effectiveness in reducing P extractability.

The absolute values of the total-P concentrations from the WTR amended plots were consistently greater than the control plots from both sites (especially, site # 2), over the sampling period (Figure 5-1), consistent with those observed in the Kissimmee field study in (chapter 3). This trend was mirrored by the oxalate (200 mM) extractable P concentrations (Figure 5-2). Both the extractants were rigorous enough to extract P contained in the WTR and the immobilized P by the WTR. The total- and oxalate extractable P decreased over time, although the decreases were not statistically significant. The decrease in total- and oxalate (200 mM)-extractable P concentrations over time could not be directly attributed to P sorption by the Al-WTR, since similar changes were also observed in the control plots. The decrease may, however, be attributed to P loss either through plant uptake of runoff. This observation suggests that the expected P immobilization by WTR cannot be assessed with these two extractants to directly measure extractable P concentration.

However, the oxalate (200 mM) extractant could be used indirectly to evaluate WTR effect on the P sorption capacity of poorly P sorbing soils by evaluating the oxalate extractable Fe and Al. Dayton and Basta (2005) reported that oxalate (200 mM) extractable Al content is strongly and positively correlated with the maximum P sorption capacity (P_{max}) of soils and soil amendments.

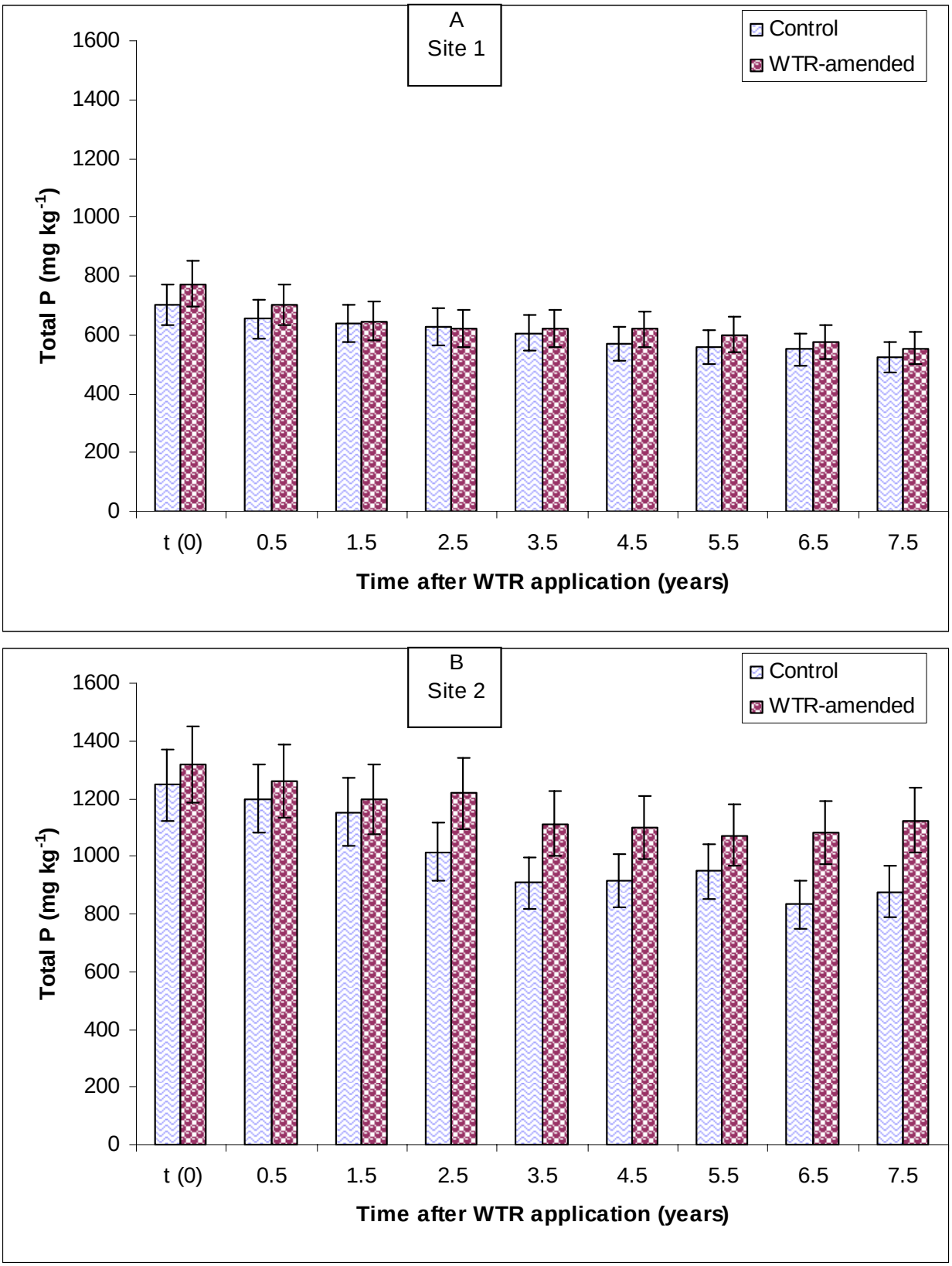
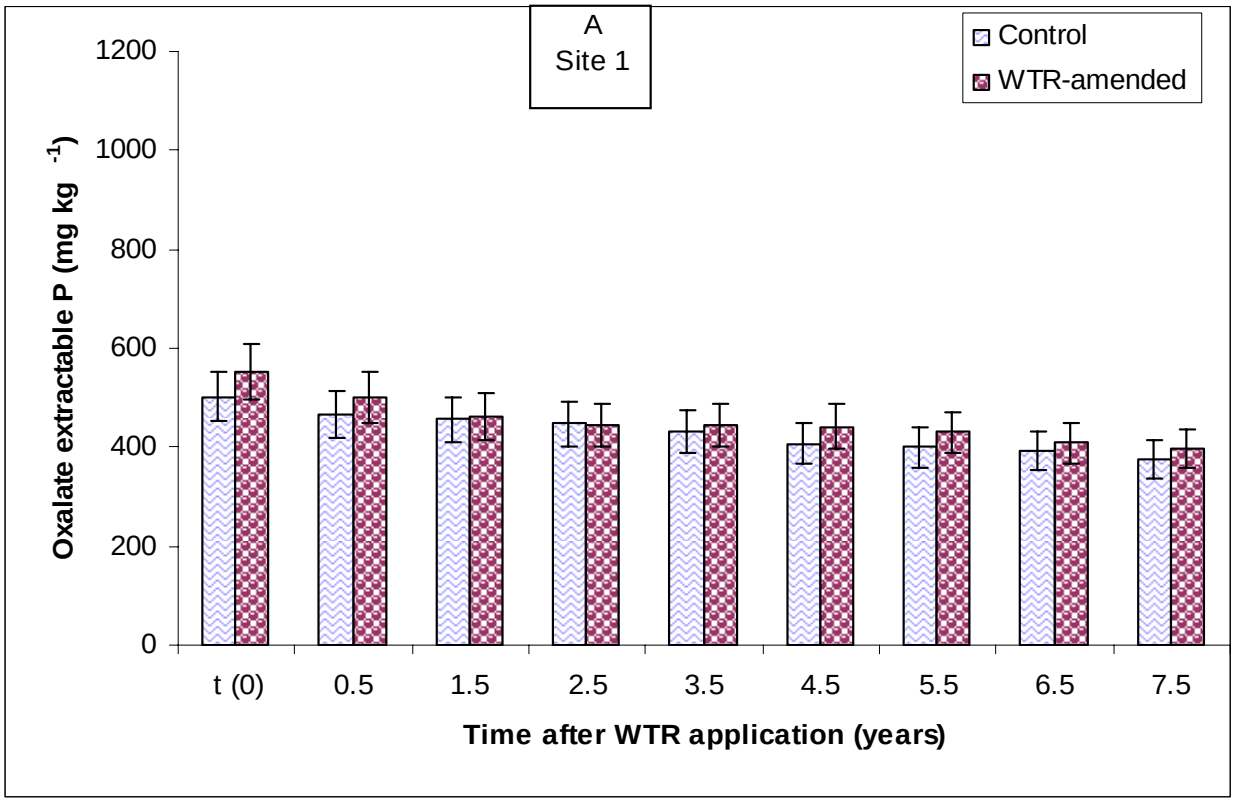


Figure 5-1. Changes in total-P concentrations with time for A) site 1 and B) site 2, of the Michigan field study. Error bars denote one standard deviation.



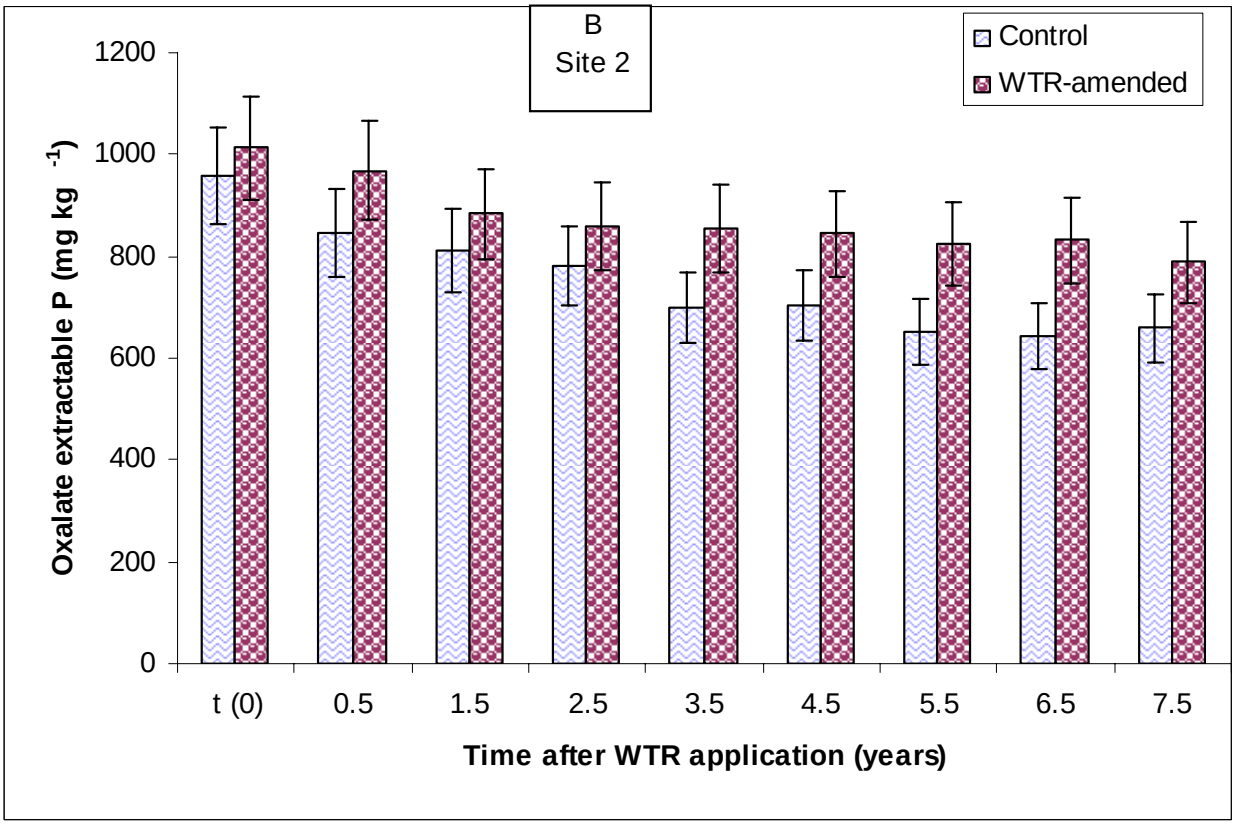


Figure 5-2. Changes in oxalate (200 mM) - extractable P concentrations with time for A) site 1 and B) site 2, MI field study. Error bars denote one standard deviation.

Elliott et al. (2005) showed that as Fe and Al content of biosolids increased, soluble P levels of the materials decreased. For both sites, the concentrations of total- and oxalate (200 mM)-extractable soil Al and Fe concentrations in the WTR amended plots increased ($p<0.03$) over time, although the data exhibited some variability. The WTR amended plots of site 2 exhibited a greater increase in total- and oxalate (200 mM)-extractable Al and Fe concentrations than at site 1, possibly due to lower native Al and Fe concentrations of the site 2 soil (Table 2-2). The variability in total- (data not presented) and oxalate extractable Al and Fe, and P concentrations over time (Figure 5-3) is attributed to sampling variability. Iron and Al hydroxides, especially Al forms in Al-WTR, can be major sorbents for oxyanions in soils, such as P (Dayton and Basta, 2005; Elliott et al., 2005; Makris et al 2005a). Therefore changes in the magnitude of the sorbent pool with time are expected to influence the P sorption capacity of the amended soil.

The variability in the oxalate-extractable Fe and Al concentrations observed with time from both sites (Figure 5-3) prompted normalizing the data by dividing the oxalate-extractable P by the corresponding oxalate Fe and Al concentrations (in moles). This normalization yields a term, the P saturation ratio (PSR) (Maguire et al., 2001), similar to the degree of P saturation (DPS) index, but omits the saturation factor, α ($\alpha = 0.3$-0.5) in the ratio (Schoumans, 2000). Small PSR values (< 0.1) suggest excess P sorption capacity and limited P lability. The PSR values for both sites were calculated and statistically analyzed to evaluate subtle differences between treatments over time.

For site 1, PSR values of the WTR amended plots did not significantly differ at the 95 % confidence level from the control (no WTR) plots (Figure 5-4A). Similarly, aging in the field had no significant effect on the PSR values for WTR amended plots even 7.5 years after WTR

application; the PSR values remained low and relatively constant (~ 0.3) throughout the monitoring period.

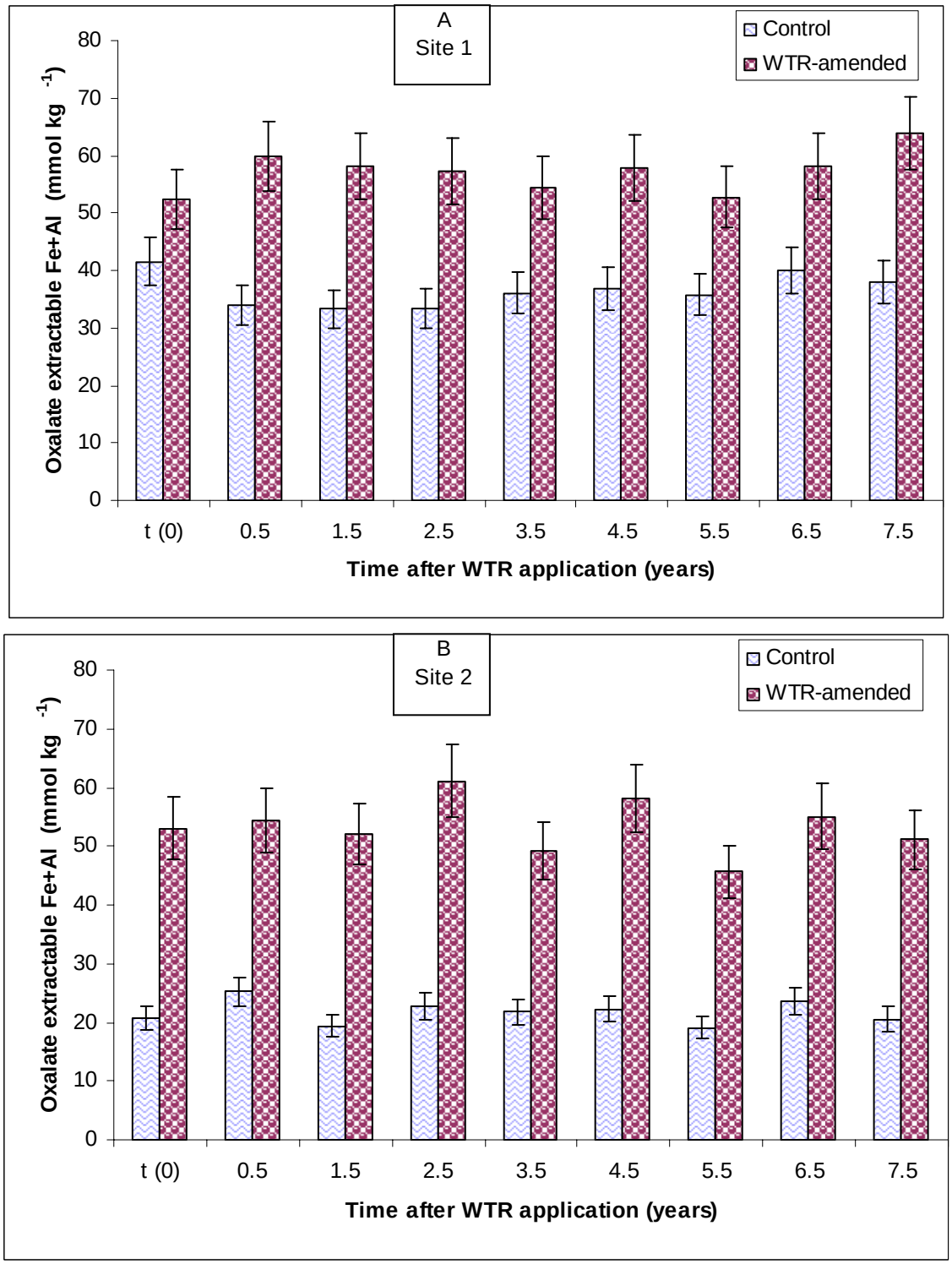


Figure 5-3. Changes in oxalate-extractable Fe and Al concentrations with time for A) sites 1 and B) site 2 of the Michigan field study. Error bars denote one standard deviation.

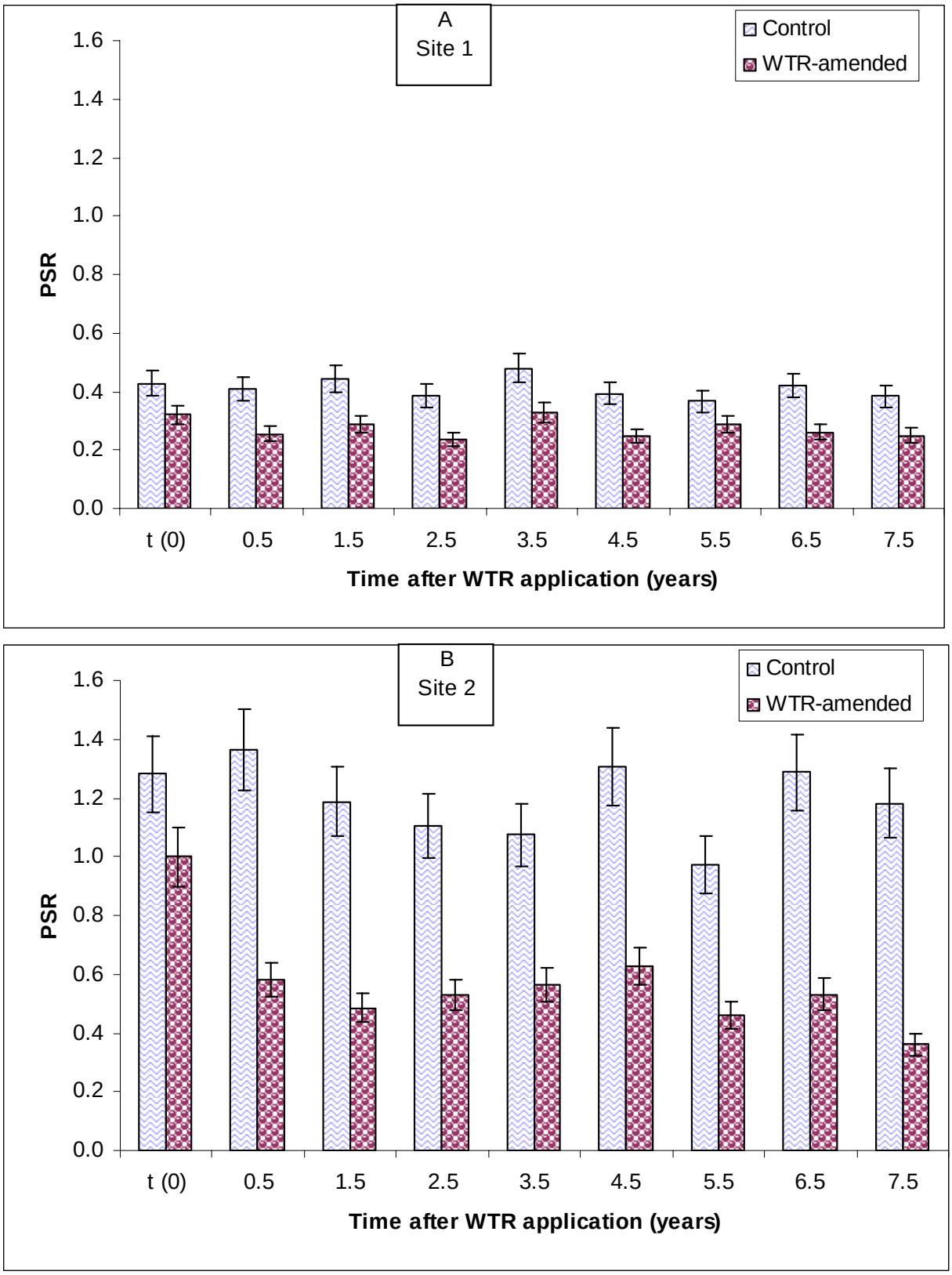


Figure 5-4. Phosphorus saturation ratio (PSR) changes with time for A) site 1 and B) site 2 of the Michigan field study. Error bars denote one standard deviation.

For site 2 (Figure 5-4B), PSR values were at least double those of site 1 for both control and WTR amended plots, because site 2 had about twice the STP and one-half the total Fe and Al concentrations (Table 2-2). Control plots of site 2 had relatively high PSR values (> 1), which suggest that site 2 could contribute significant amounts of P in surface runoff. Amendment with the WTR significantly ($p = 0.015$) decreased PSR values 6 months after application and, thereafter, remained relatively constant (Figure 5-4B) at PSR values < 50 % of the PSR values of the control samples. Since there was no significant change over time, the data suggest little potential for time-dependent P release from WTR amended plots. Low native total soil Al and Fe concentrations in the site 2 soil (Table 2-2) may have contributed to the positive WTR effect on reducing P extractability, as expressed by the PSR concept. In contrast, site 1 soil had relatively high amounts of native total Al and Fe concentrations; thus, the WTR application rate used was not sufficient to dramatically increase total soil Al levels or to significantly change PSR values.

Bray-1 soil P extractant was also used to assess the effectiveness of WTR in reducing P extractability in soils. Bray-1 extractant is the commonly used extractant in Michigan to measure STP (Dr. L.W. Jacobs, Michigan State University, personal communication). The composition of the extractant is a dilute acid and fluoride, which is used primarily to extract P from soils and sediments. Contrary to the total- and oxalate (200 mM) extractable P, Bray-1 extractable P from the WTR amended plots was not significantly different from those of the control plots over time (Figure 5-5). Thus, the hypothesized effectiveness of WTR in reducing P extractability in soil could not be detected with Bray-1 extractant. Kuo (1996) reported that the fluoride in Bray-1 extractant enhances P release from aluminum phosphate by decreasing Al activity in solution through the formation of various Al-F complexes. Fluoride is also effective at suppressing re-adsorption of solubilized P by soil colloids. The acidic nature of the extractant (pH < 3) also

contributes to dissolution of P from Al, Ca, and Fe-bound forms in most soils. Consequently, Bray-1 extractant, like the total and oxalate extracts, will not be effective in assessing P extractability in soils amended with Al-WTR.

Unlike the other three soil P extractants discussed above, the oxalate (5 mM) extractant extracted significantly ($p < 0.01$) less P from the WTR amended plots than from the control plots at both sites (Figure 5-6). Makris (2004) used oxalate (5 mM) extractant to desorb P from WTR, based on the assumption that this oxalate concentration mimics natural conditions where land-applied WTRs could release sorbed P via organic ligand mineral dissolution. Similarly Bhatti et al. (1998) found oxalate (5 mM) as an effective extractant to desorb P from some spodic horizon soils.

At site 1, oxalate (5 mM) extractable P was reduced from ~ 200 to ~ 100 mg kg^{-1} 6 months after WTR amendment, but thereafter, no significant reduction was observed. Although the reduction in extractable P values did not decrease significantly over time after the initial 6 month period, the overall reduction in extractable P over the experimental period was > 50%, relative to the control plots. For site 2, oxalate (5 mM) extractable P decreased from ~ 400 to ~ 280 mg kg^{-1} relative to the control plots, 6 months after WTR amendment and the reduction continued significantly for another year. Thereafter, the extractable P levels remained almost constant, with no significant reduction. Interestingly, no P was released back into solution after 7.5 years of field aging from both sites. Thus, the effectiveness and longevity of WTR in P immobilization was observed with this extractant and suggests that the oxalate (5 mM) could be used to assess the effectiveness of WTR in reducing extractable P levels in soils. Oxalate (5 mM) extractable Fe and Al concentrations from the WTR amended plots were also significantly than the control plots

(data not presented). The trends of the oxalate (5 mM) extractable Fe and Al were similar to those observed for the oxalate (200 mM) extractant.

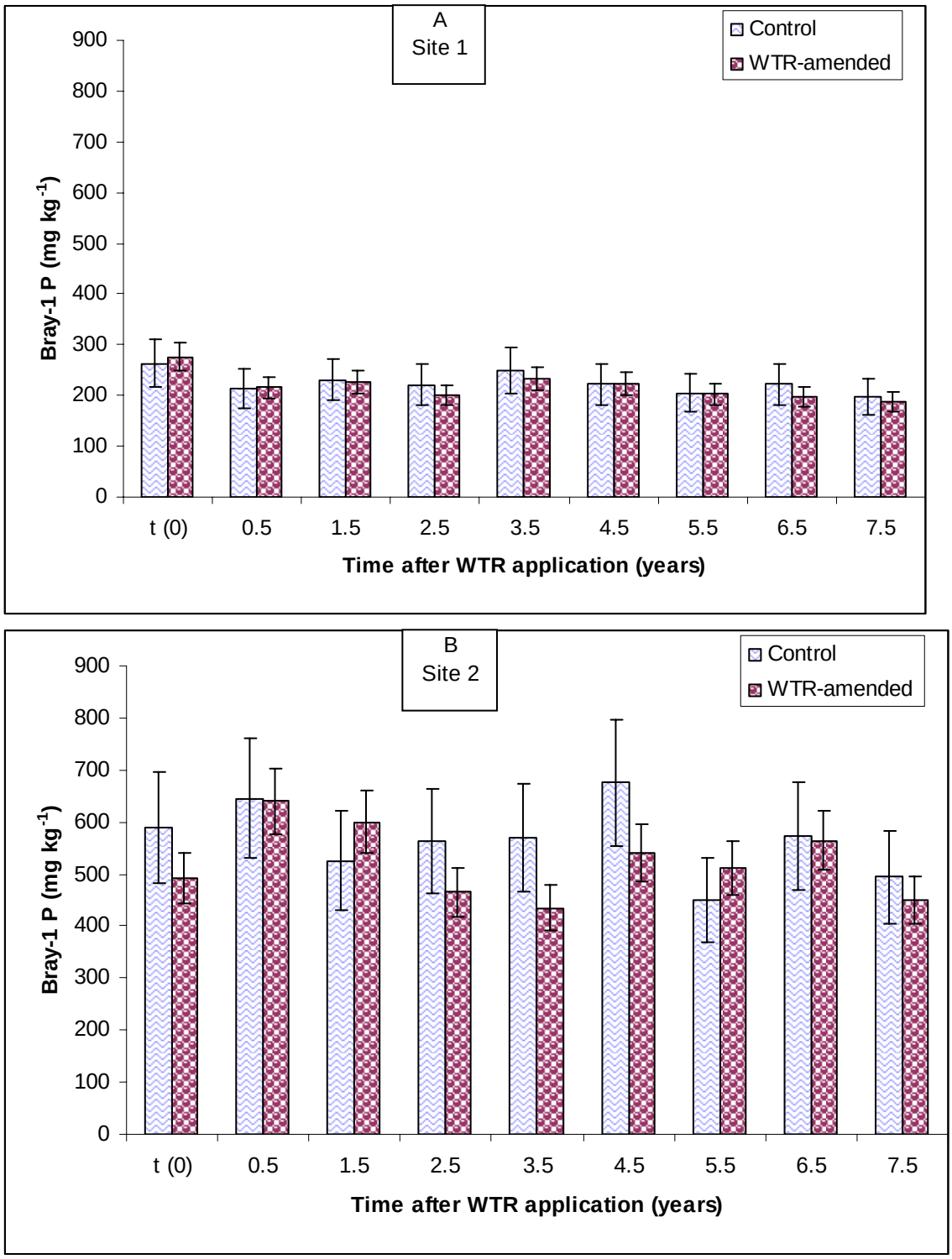


Figure 5-5. Changes in Bray-1 P levels with time in the field for: A) site 1 and B) site 2 of the Michigan field study. Error bars denote one standard deviation.

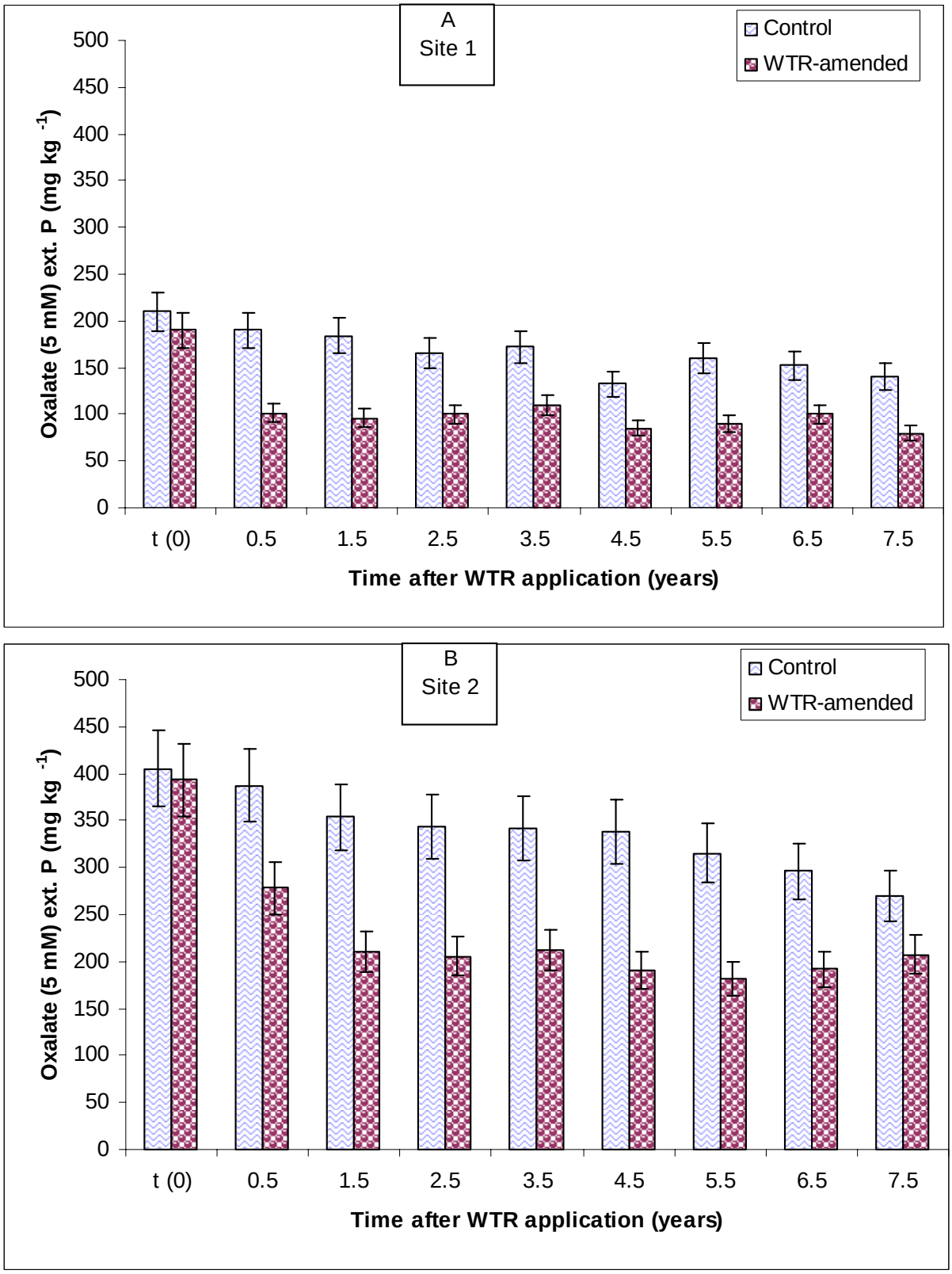


Figure 5-6. Changes in Oxalate (5mM) extractable P levels with time in the field for: A) site 1 and B) site 2 of the Michigan field study. Error bars denote one standard deviation.

Changes in Water Soluble Phosphorus with Time

Water soluble P has been used to successfully characterize P phytoavailability and solubility in soils amended with Al-WTR (Di et al., 1994; Codling et al., 2000; Ippolito and Barbarick. 2006). Measured WSP levels in the control plots did not change significantly with time in the field, and were ~ 22 and 30 mg P kg^{-1} for site 1 (Figure 5-7A) and site 2 (Figure 5-7B), respectively. Site 2 had greater amounts of WSP, consistent with greater soil test P levels and coarser soil texture (Table 2-2). The high, and nearly constant, WSP levels in the control plots reflect the history of heavy manure applications to these soils, and portend that soils from both sites could continuously supply large amounts of soluble P in runoff over many years.

Amendment with Al-WTR significantly ($p = 0.015$) reduced WSP concentrations at both sites (Figure 5-7). At site 1 (Figure 5-7A), WTR application reduced WSP values from ~ 22 to 15 mg P kg^{-1} 6 months after WTR application, and WSP levels continued to decline for another 2 years. Time series analysis suggests that an equilibrium WSP level (~ 6 mg P kg^{-1}) was reached about 2.5 years after WTR application. Similar WTR effects were obtained for site 2 (Figure 5-7B). Amendment with Al-WTR reduced WSP values within 6 months, and the reduction continued for another 4 years. Time series analysis suggested that an equilibrium WSP level (~ 13 mg P kg^{-1}) was reached about 4.5 years after WTR application. The greater time (4.5 years) required at site 2 for the equilibration of WTR effect on WSP probably reflects the greater initial soil test P level, compared to site 1 (Table 2-2).

Nevertheless, WTR amendment of either manure-impacted site significantly reduced WSP levels (at all times) below the excessive levels in the control soils. The reduction in WSP due to WTR application is expected to reduce P loss and P pollution potential for these soils. Notable also is the longevity of the WTR effect. There was no evidence of release of WTR immobilized P over time as measured by the WSP values. The WSP data demonstrate delayed, but steady,

reduction in soluble P with time, and ultimate reductions of ~ 60 to 70 % relative to the control soils.

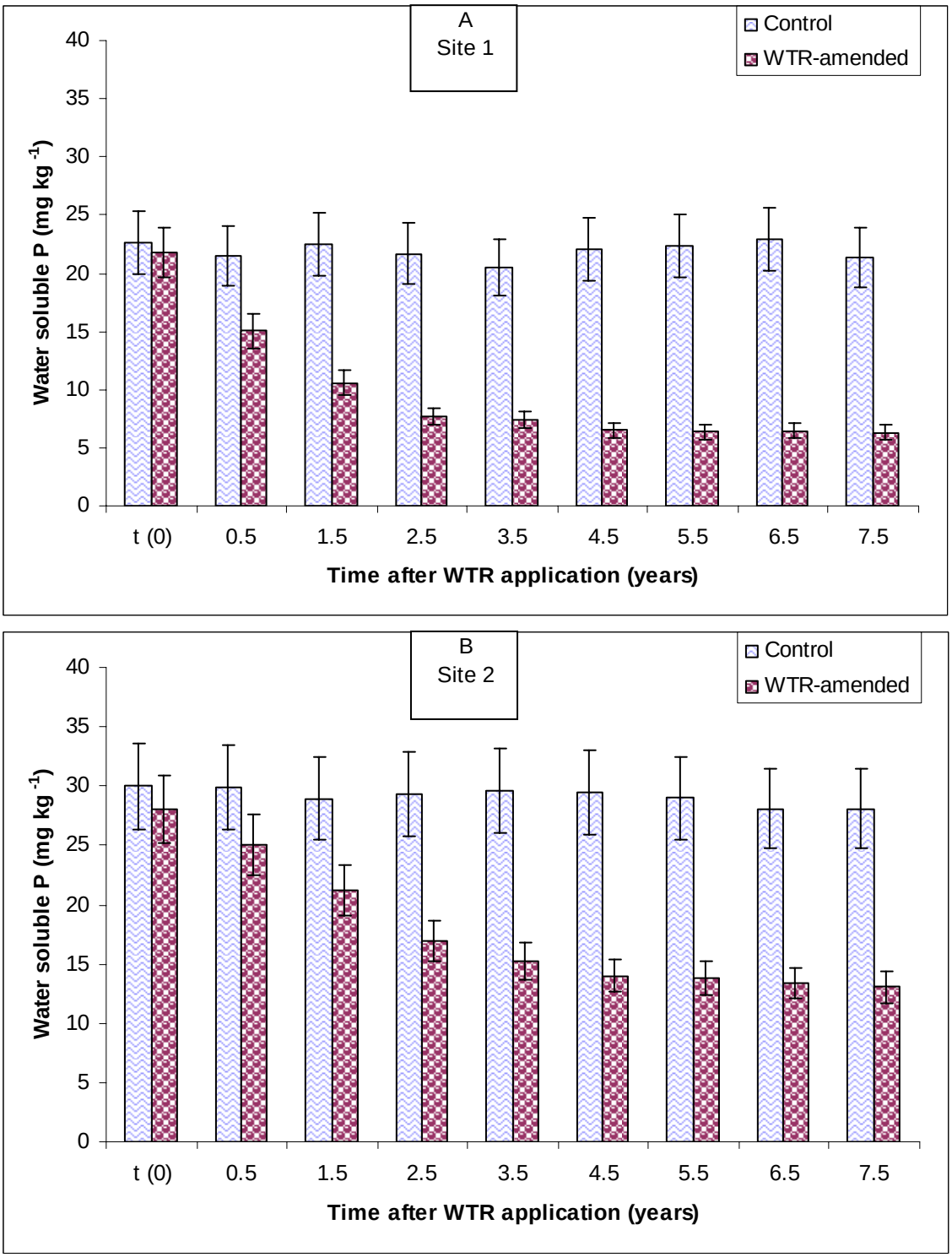


Figure 5-7. Changes in water soluble P levels with time in the field for: A) site 1 and B) site 2 of the Michigan field study. Error bars denote one standard deviation.

Labile Pools of Phosphorus as a Function of pH

The labile P concentrations were determined for all the samples collected from both sites from 1998 to 2005, at 5 pH levels (3 – 7). However for explanatory purposes, only the labile P pools measured at pH 3 and 6 are discussed in terms of the longevity of WTR effect. Similar trends in P lability behavior were observed over the pH range of 4 – 7, whereas lability behavior at pH 3 was different from the others. Similarly, for explanatory purposes for pH effect on P lability, data of the samples taken in 2005 are presented in this dissertation. Similar trends of pH effects were observed in samples taken over the entire sampling period.

Labile Phosphorus in Control Plots

Site 2 had greater amounts of labile P than site 1 at all pH values (Figure 5-8), consistent with greater soil test P values (more than double those of site 1, Table 2-2). The high labile P concentrations in the control plots reflect the long history of heavy manure applications to these soils, and suggest that soils from both sites could continuously supply large amounts of P for plant and microbial uptake and to runoff over many years. Apparently, sufficient manure-P remains to support high P lability in the surface soils despite termination of manure additions. As with the data of the artificially-aged samples in the previous chapter, the lowest labile P concentrations in the control plots were observed at pH 4 at both sites (Figure 5-9), ranging from an average of ~ 45 mg P kg^{-1} to ~ 85 mg P kg^{-1} for sites 1 and 2, respectively. The greatest labile P concentrations were measured at pH 7 at both sites (~ 110 mg P kg^{-1} and ~ 200 mg P kg^{-1} at sites 1 and 2, respectively). This is consistent with the observation of several researchers (Nwoke et al., 2004; Olsson and Tyler, 2004; Wang et al., 2004) that P availability increases at near-neutral to neutral pH. Labile P measured at both sites followed the order: pH 7 ≥ pH 6 = pH 5 > pH 3 > pH 4 across the study period (1998-2005) (Figure 5-9). The data suggest that more P was fixed at pH 4 than at pH 3. Lindsay (1979) reported that at pH values ≤ 4, Al-P minerals

dissolution can be considerable and some sorbed P may be released via particle dissolution. Typical oxalate (200 mM) extractions are commonly performed at pH 3 (Schoumans 2000), which dissolves noncrystalline Fe and Al components of the WTRs. Although a pH of 3 is rarely encountered in natural systems, measurements at pH 3 represent a worst-case scenario for release of immobilized P to solution.

Effects of WTR Amendments of Labile Phosphorus

Significant effects of WTR application, time, and pH, as well as their interactions on P lability were observed at both field sites. The labile P concentrations of the WTR amended plots decreased with time, when the labile P concentrations were determined within pH range of 4–7. However, at pH 3, no significant difference ($p = 0.672$) in labile P was observed between the control plots and the WTR amended plots at both sites.

Amendment with Al-WTR significantly ($p < 0.001$) reduced labile P concentrations at both sites for pH 4-7 (Figure 5-9). Within this pH range, no increases in labile P concentrations from the WTR amended plots from both sites were observed with time suggesting that the WTR immobilized P remained intact. At site 1, labile P concentrations measured 6 months after WTR application were reduced at all pH levels (except pH 3). The labile P concentrations continued to decline for another 2 years, consistent with the trend observed with WSP measurements. Time series analysis suggests that an equilibrium labile P concentration (~ 25 mg P kg^{-1}) was reached ~ 2.5 years at pH 6 (1.5 years at pH 5) after WTR application (Figure 5-8).

As expected, the labile P concentrations of the samples from both sites, under different treatments were greater than the WSP concentrations. The isotopic dilution technique measures all WSP (easily available) in addition to other loosely bound P that is not extracted with water (exchangeable), which would eventually become 'available' in the soil solution (Hamon et al., 2002). Despite the significant differences in the concentrations of labile P and WSP, the trend of

labile P measurements (at pH 4-7) were consistent with trends of WSP values for the same treatments over time. Correlation analysis using the SAS software PROC CORR (SAS, 1999) suggests a very strong ($r^2 > 0.9$) and significant ($p < 0.001$) correlation between the two P measurement procedures.

At pH 3, however, there was no significant difference between the labile P concentration of the WTR amended plots and the control plots, suggesting that the immobilized P was desorbed at this pH level (Figure 5-10). Most probably, the WTR structure was destabilized at pH 3 and the immobilized P as well as some P contained in the WTR was released.

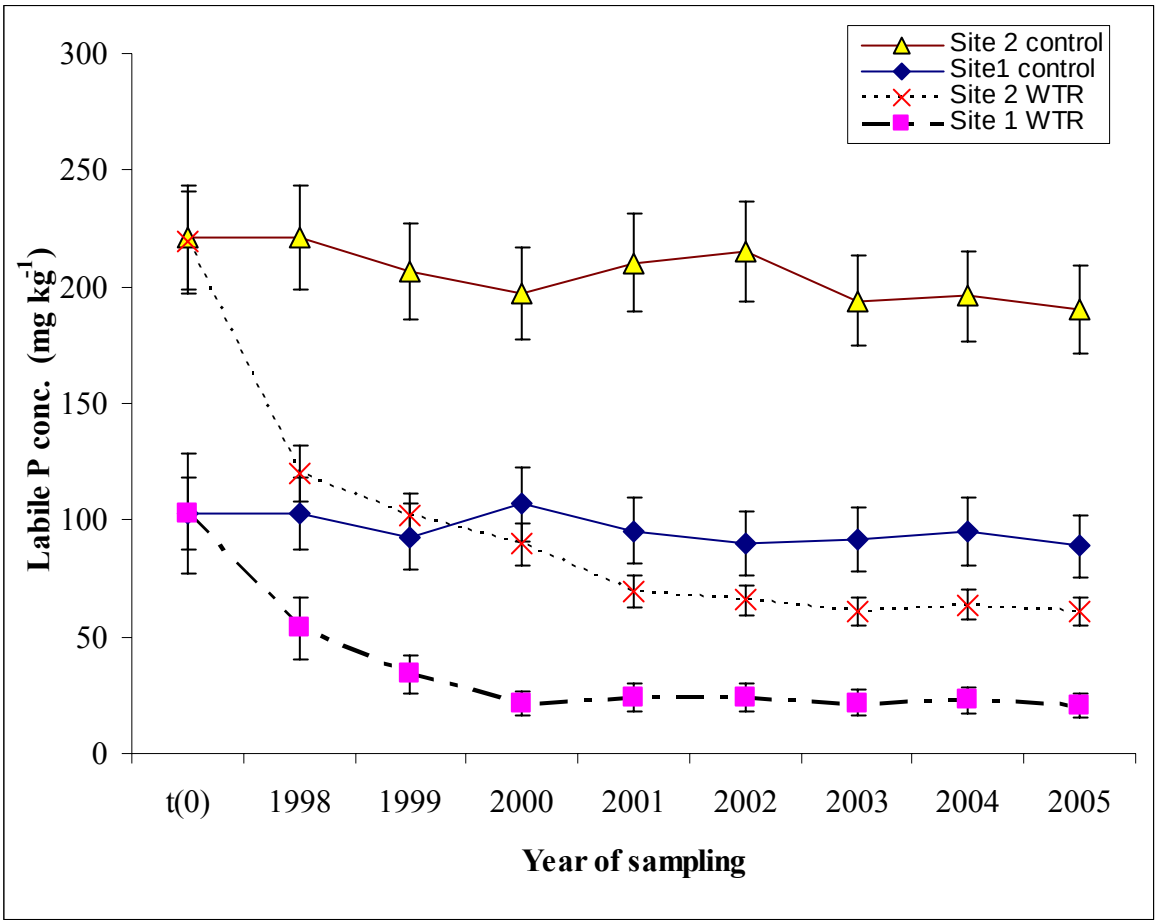


Figure 5-8. Changes in labile P concentrations with time for the Michigan field samples equilibrated at pH 6 for both the control and WTR amended plots taken from both sites.

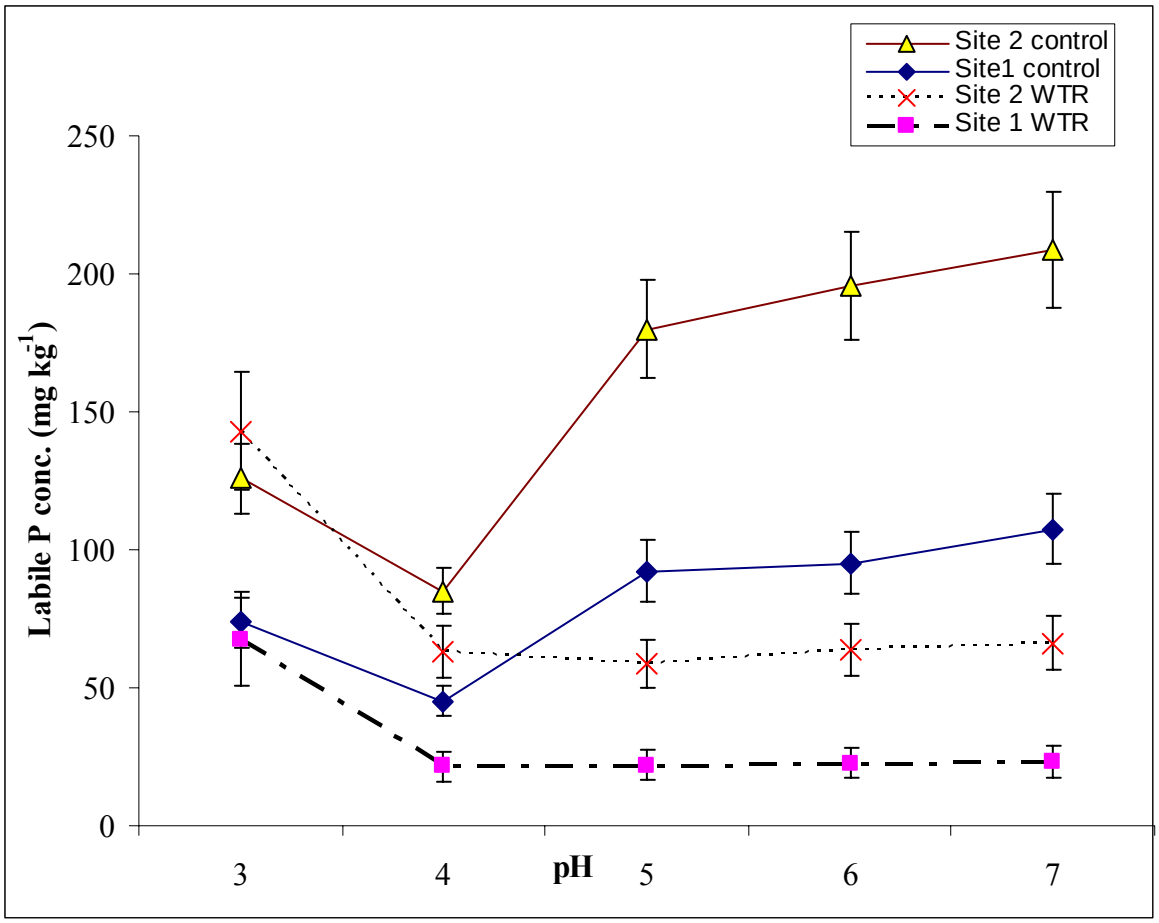


Figure 5-9. Changes in labile P concentrations as a function of pH for the Michigan field samples taken in 2005 from both the control and WTR amended plots at sites1 and 2.

Similar labile P behavior with time was observed for the site 2 samples. Amendment with Al-WTR reduced labile P concentrations within 6 months (at pH 4-7), and the reductions continued for another 3 to 4 years (Figure 5-8). Time series analysis suggests that an equilibrium labile P concentration (~ 65 mg P kg^{-1}) was reached after 3.5 years (for pH 4-6) and 4.5 years (for pH 7). The greater time (3.5 - 4.5 years) required at site 2 than for site 1 (~ 2.5 years) is consistent with the trend observed with the WSP measurements and reflects the greater soil test P values of site 2 than site 1 (Table 2-2). The reduction in labile P due to WTR application is expected to reduce P loss and P pollution potential for these soils. Despite the reduction in labile P concentrations by WTR amendments, the data suggests that the labile P concentrations of the

WTR amended plots are still high enough to constitute P mobility problems at both sites. Perhaps, a greater amount (> 114 Mg ha^{-1}) of WTR is needed to reduce labile P concentrations to levels that are not potentially harmful to the environment.

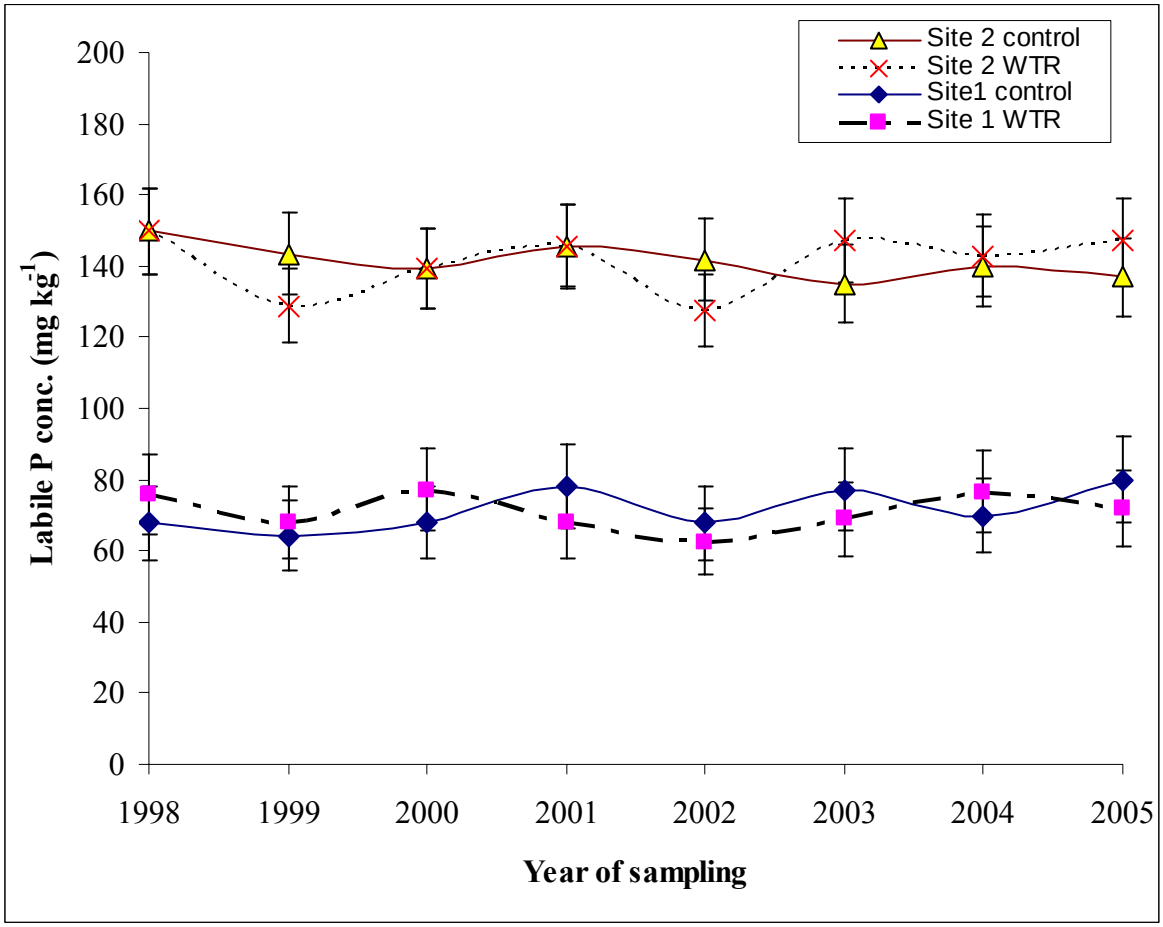


Figure 5-10. Changes in labile P concentrations with time measured at pH 3 in both the control and WTR amended plots at site1 and 2.

Consistent with the WSP data, again, is the longevity of the WTR effect. There was no evidence of release (increased lability) of WTR immobilized P over time at pH range of 4-7. The data demonstrate a steady reduction in labile P with time, and ultimate reductions of ~ 65 to 75 % relative to the control soils at pH 5-7 and ~ 35 to 50 % at pH 4. The lower percentage of reduction in labile P concentration observed at pH 4 is a reflection of the low labile P concentration measured for the control plots at pH 4 (Figure 5-9).

Data trends from this study were consistent with data from the artificially-aged soil samples (chapter 4). Within pH range of 4-7, WTR immobilized P was stable. However, at pH 3, WTR was destabilized and the immobilized P was released back into soil solution. Fortunately, such pH levels are rarely encountered in soils. Thus, WTR is an effective amendment to reduce labile P in P-impacted soils and WTR immobilized P will remain fixed for a long time, independent of common soil pH values.

CHAPTER 6
LONG-TERM EFFECTS OF A DRINKING-WATER TREATMENT RESIDUAL ON RUNOFF AND LEACHATE QUALITY

Introduction

Surface runoff of nutrients nitrogen (N) and phosphorus (P) from manured agricultural land can be an important source of water quality impairments in surface waters in the United States (Parry, 1998). The USEPA (1986b) reported that accelerated eutrophication, the biological enrichment of surface waters stemming from anthropogenic inputs of nutrients, is the most common surface water impairment in the United States. Applications of animal manure in amounts that exceed agronomic P rates (typically, based on the N requirement for crop production) result in increased loss of P from agricultural land in surface runoff and potential eutrophication of surface waters (Sharpley et al., 1994). The role of P in runoff water (Sharpley et al., 1994; Correll, 1998; Daniel et al., 1998; Pote et al., 1999) and leaching (Ward and Summers, 1993; Sims et al., 1998) from agricultural land in the eutrophication of surface water is well documented. Excessive concentration of soluble P is the most common source of eutrophication in fresh surface waters (Correll, 1998).

As a result of increased concern, many states are developing manure application limits to protect surface water quality (Sims et al., 1999). Common strategies used to reduce P transport to surface water include conservation tillage, crop residue management, cover crops, buffer strips, contour tillage, runoff water impoundment, and terracing. These strategies are effective in controlling particulate P but not dissolved P in runoff (Sharpley et al., 1994; Daniel et al., 1998). Drinking-water treatment residuals (WTR) that contain Al or Fe oxides can be beneficially used as a best management practice (BMP) to protect surface water quality by removing dissolved P from agricultural runoff water.

Incorporating WTRs into soil reduces excessive soluble P resulting from manure application (Cox et al., 1997; Dayton et al., 2003; Elliott et al., 2005; Silveira et al., 2006). Similar studies showed that phosphorus solubility in biosolids was reduced by co-application with WTRs (Ippolito et al., 1999; Elliott et al., 2002). O'Connor et al. (2002) showed that P movement from P-enriched soils to freshwater supplies was reduced when the soils were treated with WTRs. The primary purpose of their study was to investigate the ability of three locally produced WTRs to reduce soluble P levels in sandy Florida soils amended with fertilizer, manure, and biosolids-P sources. Phosphorus was hypothesized to be immobilized by adsorption and /or precipitation. Gallimore et al. (1999) utilized WTRs as a buffer strip (44.8 Mg WTR ha^{-1}) applied to a portion of a pasture treated with poultry litter. Surface runoff P was reduced by WTR from an average of 15 to 8.1 mg L^{-1}. Large differences (16 and 47%) in soluble P reduction were found between the WTRs from two treatment plants that were used in the study. The authors concluded that the most effective surface application of WTR was as a buffer strip (Gallimore et al., 1999).

The results of the various studies presented in this dissertation (chapters 2 to 5) suggest that WTRs could be effective amendments to reduce labile P levels in P-impacted soils and that WTR immobilized P is stable. The combined data of the Michigan field study, in particular, (chapter 5) suggest that a one-time Al-WTR application is capable of reducing labile P for as long as 7.5 years after the soil is amended with Al-WTR. The long-term effects of WTR on labile P need to be confirmed with a runoff and/or leaching study to assess expected improvement in water quality. The objective of this study was therefore to evaluate the long-term effectiveness of Al-WTR in reducing dissolved P in runoff and leachate from field soils with long histories of poultry manure applications using rainfall simulation techniques.

Several studies have used simulated rainfall onto packed soil boxes and field plots to evaluate P transport in surface runoff (Kleinman and Sharpley, 2003; Kleinman et al., 2004; Elliott et al., 2005). Runoff dissolved P concentrations from simulated rainfall have been found to be correlated to the water extractable Phosphorus (WEP) content of soil and organic P source (Kleinman et al., 2002; Brandt and Elliott, 2003). Kleinman et al. (2004) reported that runoff boxes, typically packed with soil and subjected to simulated rainfall, allow greater control of confounding variables than do field runoff plots, as soils can be homogenized to minimize significant variability in physical and chemical characteristics. Recently, a series of findings, primarily from packed box studies, provided the quantitative basis for developing P availability coefficients in some P site assessment indices (Sharpley et al., 2003).

Materials and Methods

Soils and Sampling

The soils used for the study were collected from one-time WTR amended fields (2 sites) in Western Michigan (Jacobs and Teppen, 2000). (Detailed description of soils and field layout are presented in chapter 5). In fall 2005 (7.5 years after WTR amendment), surface soils of the control and the WTR amended plots from both sites were bulk sampled from the top 20 cm depth of each plot for use in this study.

Rainfall Simulation Experiment

The rainfall simulation was carried out as prescribed in the U.S. National Phosphorus Research Project indoor runoff box protocol (National Phosphorus Research Project, 2001). However, the design of wooden runoff boxes (100 cm long, 20 cm wide, and 7.5 cm deep) was modified to quantify leaching of P in addition to runoff P by adding a second (empty, water-tight) box under the first in a double-decker design. This design allows collection of runoff and leachate simultaneously. The upper boxes were packed with 5 cm of soils to a bulk density of 1.4

g cm^{-3}. Soils collected from the study sites were pre-wetted to near saturation to control for antecedent moisture and to promote runoff in the subsequent rainfall simulation. Rainfall simulations were conducted three times, at one-day intervals between rainfall events. Boxes were sloped at 3 % and rainfall was delivered at 7.1 cm hr^{-1} from a height of 3 m above the boxes. For each rainfall event, 30 minutes of runoff, and leachate generated continuously during the entire rainfall, was collected from each box and the volumes recorded. Subsamples of the runoff were immediately filtered (0.45 μm) for analysis. A representative well-mixed sample of the unfiltered runoff and leachate (~ 250 mL) was also taken from each replicate for further analysis.

Leachate and Runoff Analyses

Leachate and runoff pH and EC was determined on each sample. The soluble reactive P (SRP) was determined on the filtered runoff and the leachate samples colorimetrically (Murphy and Riley, 1962). Total dissolved phosphorus (TDP) was measured on the filtered runoff and the leachate samples after digesting 10 mL of the samples with 0.5 mL 11 N H_2SO_4 and 0.15g of potassium persulfate in an autoclave for 1 hour (Pote and Daniel, 2000a,b). Total P in the unfiltered runoff samples was determined by digesting 5 mL of the samples with 1 mL of 11 N H_2SO_4 and 0.3g of potassium persulfate on a digestion block and then diluting with 10 mL of water (Pote and Daniel, 2000b). All digested samples were analyzed for P colorimetrically (Murphy and Riley, 1962). The iron-oxide impregnated paper strip method (Myers and Pierzynski, 2000) was used to estimate bioavailable P (BAP) in unfiltered runoff waters.

Particulate phosphorus (PP) was calculated by subtracting TDP from the TP of each sample. Dissolved organic P (DOP) was assumed to be the difference between SRP and TDP. Flow-weighted P concentrations were determined for the runoff and the leachate by summing the product of the P concentrations and volumes for the three runs (P load) and dividing the P load by the total volume of the runs. The masses of runoff and leachate P losses (mg) were calculated

as the product of flow-weighted concentrations (mg L^{-1}) and the runoff and leachate volumes (L), respectively. Total P losses were determined by summing the masses of runoff and the leachate P loss.

Statistical Analysis

The data showed great variation about the means with coefficient of variation > 50 %. This prompted testing for normal distribution of the data using the Kolmogorov-Smirnov Procedure and the normal probability plots of the Statistical Analysis System (SAS Institute, 1999). The P concentration data were not normally distributed, and a plot of residuals vs. predicted values showed that the 'constant variance' assumption of analysis of variance was violated; therefore typical analysis of variance could not be used. Instead, the NPAR1WAY procedure of the SAS software with the Kruskal-Wallis test was used. The NPARIWAY procedure is a nonparametric procedure that tests whether the distribution of a variable has the same location parameter across different groups. The Kruskal-Wallis procedure tests the null hypothesis that the groups are not different from each other by testing whether the rank sums are different based on a Chi-square distribution (Hollander and Wolfe, 1999). The nonparametric procedure is a powerful and robust statistical test that is insensitive to variation among data and the presence of outliers (Hollander and Wolfe, 1999).

Results and Discussion

The rainfall simulation study was conducted to confirm WTR effects on WSP and labile P concentrations in the two Michigan soils observed in previous studies. Soils used represented samples from one-time WTR amended fields in Western Michigan, 7.5 y after WTR amendment. The masses (mg) of the various forms of P lost in runoff and leachate from soil samples collected from both sites are given in Table 6-1, and the pH and EC values are presented in Table 6-2.

Table 6-1. Masses of the various P forms measured in runoff and leachate from both sites of the Michigan field study. All values are expressed in mg. Numbers are flow-weighted means of 4 replicates in 3 rainfall events ± one standard deviation

TREATMENT		*RUNOFF*						*LEACHATE*			*TOTAL P LOSS (Runoff + Leachate)*	*TOTAL[§§] BAP LOSS (Runoff + Leachate*
		TDP[†]	SRP[‡]	DOP[††]	PP[‡†]	BAP[‡‡]	T P[§]	TDP[†]	SRP[‡]	DOP[††]		
Site 1	CTRL	43.6±31.6	40.6±31.2	3.01±2.2	51.9±43.6	52.4±21.4	95.5 ± 52.1	29.0±4.9	12.7±9.32	16.3±11.5	124±88.9	81.4±53.8
	WTR	17.9±8.32	16.0±11.3	1.94±1.37	83.7±77.8	22.1±10.9	102 ± 66.3	13.3±8.65	5.82±3.96	7.49±5.48	115±79.9	35.8±16.4
Site 2	CTRL	65.5±47.3	60.6±46.1	4.85±2.99	87.4±53.6	76.7± 41.6	153 ± 101	44.5±29.5	20.4±16.7	24.1±18.9	197±131	121± 87.6
	WTR	34.1±26.9	31.3±19.8	2.85±2.04	158±112	39.2± 24.7	193 ± 89.6	18.7±11.2	7.12±5.34	11.6±8.74	211±156	57.2±23.7

[†] Total Dissolved P [‡] Soluble Reactive P [††] Total Dissolved P
[‡†] Particulate P [‡‡]Bioavailable P [§] Total P
[§§] Total BAP loss = runoff BAP + leachate TDP

Table 6-2. pH and EC values[†] measured in runoff and leachate from both sites of the Michigan field study

		RUNOFF		*LEACHATE*	
Treatment		pH	EC (μS cm^{-1})	pH	EC (μS cm^{-1})
Site 1	CTRL[‡]	6.70 ± 0.16	375 ± 2.96	6.78 ± 0.21	403 ± 6.32
	WTR[†‡]	6.73 ± 0.20	375 ± 5.13	6.81 ± 0.19	379 ± 3.96
Site 2	CTRL	6.91 ± 0.21	386 ± 4.61	6.82 ± 0.18	382 ± 6.71
	WTR	6.88 ± 0.26	401 ± 5.21	6.74 ± 0.23	392 ± 7.34

[†] Numbers are the average of 12 replicates (4 plots run in 3 rainfall events) ± one standard deviation
[‡] No WTR amendment (Control) [†‡] Soil amended with WTR

Runoff P concentrations decreased with successive rainfall events, consistent the observation of other researchers (Kleinman et al., 2004; Elliott et al., 2005). Other studies have documented that total and dissolved P in runoff decreased with successive rainfall events following surface application of livestock manures (Sharpley, 1997) and biosolids (Rostagno and Sosebee, 2001; Penn and Sims, 2002). For biosolids amended field plots, Sims et al. (2003) found the initial event accounted for 52 to 73% of the total runoff P collected over four rainfall events. Conversely, the rate of decrease with successive rainfall events in our study was not as great as reported in the various studies mentioned above. This could be attributed to the fact that we utilized amended soils that were equilibrated for ~ 7.5 years, whereas others (Brandt and Elliott, 2003; Kleinman and Sharpley, 2003; Kleinman et al., 2004; Elliott et al., 2005) used samples equilibrated with added P for days to few weeks.

Runoff and Leachate Concentrations

Generally, there were significantly greater P losses from the soil samples collected from site 2 (both the control and the WTR amended soils) than from site 1 (Table 6-1). Results are consistent with the greater soil test P values and greater WSP values for soil at site 2 than at site 1 (Table 2-2). Many researchers have found that the P content of the surface soil directly influences the loss of P in runoff (Daniel et al., 1994; Kleinman et al., 2002; Tarkalson and Mikkelsen, 2004; Davis et al., 2005). Other researchers have shown significant relationships between STP and runoff P concentration (Sharpley, 1995; Pote et al., 1999; Cox and Hendricks, 2000). Pote et al. (1996) reported a highly significant relationship between runoff dissolved reactive phosphorus (DRP) and WSP for a Captina silt loam soil in Arkansas that received P inputs as swine and poultry manure. Edwards and Daniel (1993) reported DRP levels in runoff of 0.8, 11.9, and 29.4 mg L^{-1} from grassed plots broadcast with swine manure at rates of 0, 19, and 38 kg TP ha^{-1}, respectively. Rostagno and Sosebee (2001) and Elliott et al. (2005) found that SRP

and TDP in runoff water increased with biosolids application rates. Kleinman and Sharpley (2003) reported that the concentrations of DRP and TP in runoff increased as the total P application rate from broadcast manures increased from 0 to 150 kg P ha^{-1}.

Similarly in our study, SRP for the first rainfall event was strongly related to WSP ($r^2 \sim 0.95$, $p < 0.001$) of the soil for both the control and WTR amended plots from both sites (Figure 6-1). Our results are similar to those of McDowell and Sharpley (2001) and Fang et al. (2002) who found highly significant relationships between DRP and WSP.

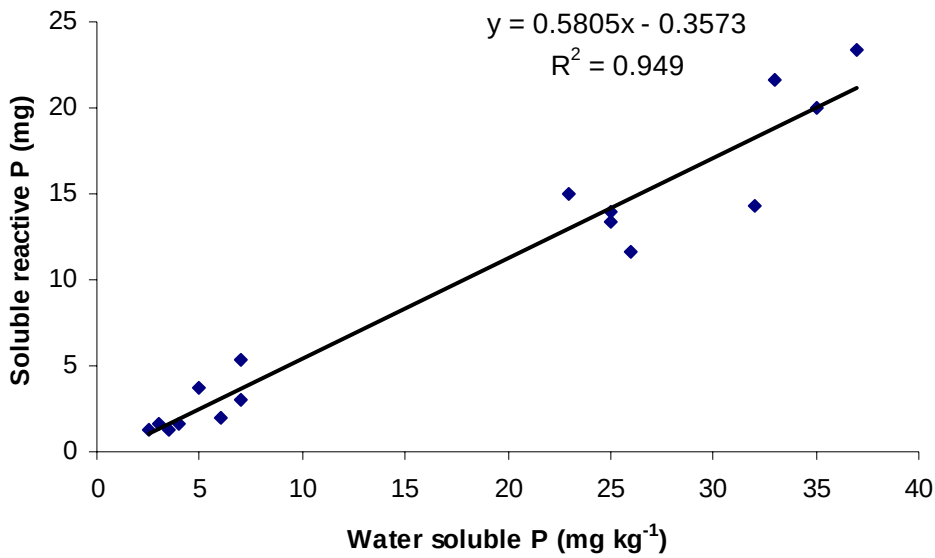


Figure 6-1. Relationship between soluble reactive P and water soluble P for the first rainfall event.

In a simulated rainfall study with a wide range of P sources, Elliott et al. (2005) reported that runoff P concentrations were linearly related ($r^2 \geq 0.83$) to the WEP levels of the various P sources. Kleinman et al. (2002) observed that dissolved reactive P losses from soils surface-amended with dairy, poultry, and swine manures (all at 100 kg P ha^{-1}) were proportional to the WEP of the applied P sources. Similar linear relationship between DRP and WSP for soil and organic P sources have been reported in several studies (Brandt and Elliott, 2003; Kleinman and Sharpley, 2003; Kleinman et al., 2004).

Most of the P loss from both sites occurred through surface runoff, rather than through leaching (Table 6-1). The total runoff P losses of the samples taken from both sites were dominated by particulate P (PP). Sieving and packing soils into boxes destroys larger soil aggregates, increasing the availability of fine particles to runoff, and possibly decreasing the stability of remaining aggregates. Kleinman et al. (2004) reported that runoff TP concentrations were strongly related to suspended solids concentrations in runoff from field plots and soil in runoff boxes, reflecting the importance of particulate P to TP concentrations in runoff. Even though the authors did not directly measure PP in their study, they hypothesized that particulate P accounted for most of the difference between TP and DRP in runoff. Tarkalson and Mikkelsen (2004b) estimated that 75–80% of the P transported in runoff from agricultural land is adsorbed to soil particles, termed particulate P (PP).

The runoff TDP at both sites was dominated by SRP, with DOP occurring in small proportions (< 10 % of TDP). Contrary to TDP in runoff, TDP in the leachate had greater absolute values of DOP than the SRP. An independent determination of the TDP was carried out on the undigested leachate samples using ICP-AES (Perkin-Elmer Plasma 3200). The values obtained from this independent determination were similar to those obtained from the digested leachate samples determined colorimetrically. We, therefore, concluded that PP loads in the leachate samples were negligible and were consequently not determined.

The high PP concentrations observed in the runoff from the soil samples, prompted estimation of BAP levels in the runoff water, using the iron-oxide impregnated paper strip method (Myers and Pierzynski, 2000). Sharpley (1993) reported that the transport of BAP in agricultural runoff can stimulate freshwater eutrophication. Total BAP loss was calculated by summing the BAP loads from the runoff and the TDP loads from the leachate. The TDP loads in

the leachate were used to represent the leachate BAP loads based on the assumption that the dissolved organic P will mineralize and eventually become bioavailable.

As expected, the total BAP loss from the soil samples taken from site 2 were significantly greater than those taken from site 1 (Table 6-1), consistent with the higher water soluble P values of the site 2 soil (Figure 5-7). For site 1, the total BAP of the control soils accounted for > 60 % of the total P loss, whereas total BAP loss from the WTR amended plots accounted for ~ 30 % of the total P loss (Table 6-1). Similar behavior was observed for the samples taken from site 2, with the total BAP accounting for > 60 % of total P loss in the control and ~ 25 % for the WTR amended soils (Table 6-1). The runoff pH and the EC values were similar for both the WTR amended and the control plots at both sites and were also similar to those observed for the leachates (Table 6-2).

Effects of WTR on Runoff and Leachate Phosphorus Losses

No significant differences were found between the flow-weighted TP mass losses from the WTR amended plots and the control plots at either site (Table 6-1). However, the flow-weighted TDP, SRP and DOP mass losses were significantly reduced at both sites in the presence of WTR (Figure 6-2). For site 1, application of WTR reduced the flow-weighted SRP masses by > 60 % and DOP by ~ 45 % (Figure 6-2). Overall, amendment with Al-WTR decreased flow-weighted dissolved P mass by ~ 60 %. Similar results were obtained for site 2. Amendment with Al-WTR reduced SRP masses by > 50 % and DOP by ~ 45 % (Figure 6-2), resulting in an overall reduction of flow-weighted dissolved P by > 50 %. The most probable explanation for the reductions in runoff P levels from the WTR amended plots is that the P adsorption capacity of the soil was increased following application of the residual and continued to remain elevated for 7.5 years following WTR application. Generally, a greater Al content equals a greater P adsorption capacity and a greater reduction in runoff dissolved P concentration (Haustein et al.,

2000). Moore et al. (2000) reported significant differences in DRP losses from pastures amended with either alum-treated compared to untreated poultry litter. They observed concomitant decreases in the water-soluble P fraction of poultry litter treated with alum and runoff DRP losses from the pasture receiving that litter.

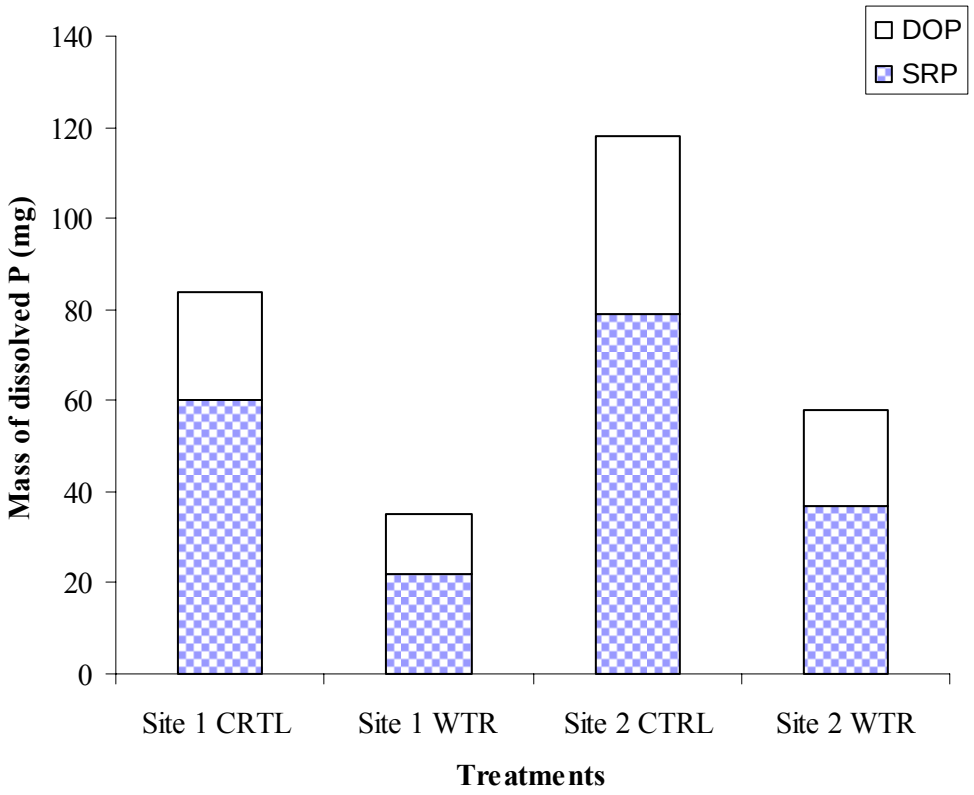


Figure 6-2. Flow-weighted total dissolved P masses of the various dissolved P forms from soil samples taken from the Michigan field study sites. Median TDP values were used to plot the graph.

Earlier studies (Figure 5-3) showed that WTR amendment increased the content of P-fixing Al and Fe concentrations in the soils at both sites. The importance of Al and Fe content in reducing soluble P levels is further illustrated in Figure 6-3, which shows that the BAP levels in the runoff were consistently lower when the oxalate extractable molar Al + Fe content of the soil was high. This is consistent with the observation of Brandt and Elliott (2003) that, as the content of P-fixing Al and Fe in soils and P sources increased, TDP concentration decreased. Elliott et al.

(2005) determined P levels in runoff from soils amended with biosolids and dairy manure under simulated rainfall, and concluded that TDP concentrations in runoff can be reduced by adding Al and Fe salts to P sources that have high concentrations of water soluble P. Dayton and Basta (2005) reported that addition of WTR as an enhanced buffer strip in a poultry litter-impacted soil greatly reduced dissolved reactive P (DRP) and the reduction was related to the P sorption capacity of the WTR.

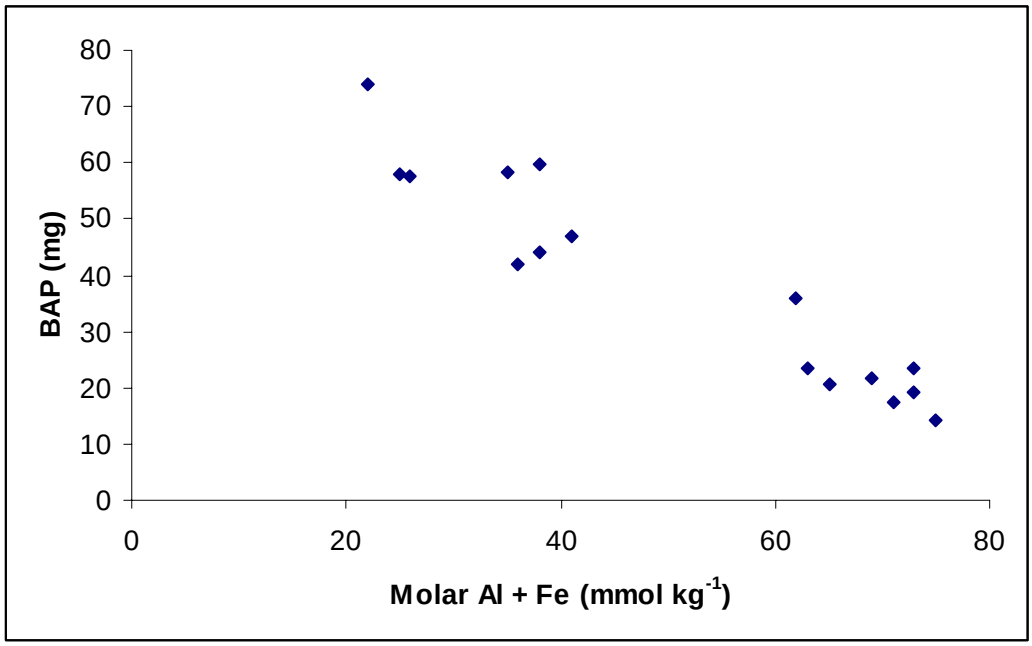


Figure 6-3. Relationship between runoff bioavailable phosphorus (BAP) and molar oxalate extractable Al + Fe content of the soil samples taken from both sites in fall 2005.

Amendment with WTR decreased the total (runoff + leachate) flow-weighted TDP concentrations from ~ 2.5 mg L^{-1} to ~ 0.86 mg L^{-1} at site 1, and from ~ 3.2 mg L^{-1} to ~ 0.94 mg L^{-1} at site 2 (Figure 6-4). The reduced values exceeded values (0.01-0.05 mg L^{-1}) usually associated with eutrophication of surface waters (USEPA, 1986b), but were below a solution concentration of 1.0 mg L^{-1} ($3.2 * 10^{-5}$ M) occasionally used as a benchmark. The 1.0 mg L^{-1} concentration is a common goal for wastewater discharges to rivers and streams and has been applied to soils on the premise that the discharge of P from soils to water should be held to the

same standard (Sims and Pierzynski, 2005). Greater single amendment rates (> 114 Mg ha^{-1}), or multiple (yearly) WTR applications are likely necessary to reduce TDP concentration to the 0.01-0.05 mg L^{-1} target concentration range. The single application of 114 Mg ha^{-1}, however, significantly reduced runoff and leachate P impacts on water quality.

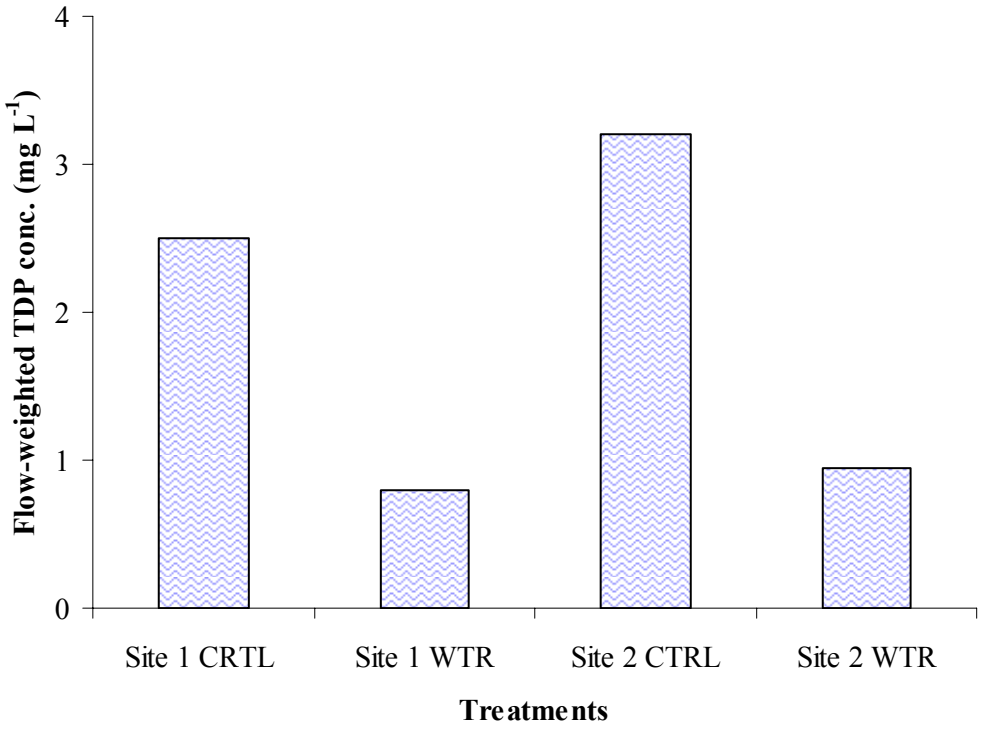


Figure 6-4. Flow-weighted TDP concentrations in runoff from soil samples from the Michigan field study. Median values were used to plot the graph.

Regressions between transformed runoff and leachate SRP values [log (SRP+1)] and soil test P (Bray-1 P) concentrations were used to derive P extraction coefficients (slope of the regression) (Sharpley, 1995). The extraction coefficient, which is an input to process-based P transport models and P site assessment indices, is the fraction of STP that can be released to overland flow for a given flow event volume (Shapley et al., 2002). A larger soil extraction coefficient represents a greater P release as dissolved P in overland flow per unit of STP increase.

In this study, the WTR amended plots and the control plots from both sites produced a variety of regressions between SRP concentration and Bray-1 P of the soil (Table 6-3). Extraction coefficients observed were in the range of those reported in literature, provided that data from the literature were transformed [log(SRP + 1)] to correspond with values from this study. Sharpley (1995) reported extraction coefficients ranging from $8 * 10^{-4}$ to $14 * 10^{-4}$ for acidic soils and $6 * 10^{-4}$ to $9 * 10^{-4}$ for alkaline soils, while Fang et al. (2002) reported an extraction coefficient of $6 * 10^{-4}$ to $18 * 10^{-4}$ for alkaline soils.

Table 6-3. Regression equations relating soluble reactive P (SRP) of runoff and leachate with Bray-1 P for the soil sample taken from the Michigan study sites.

Treatment		*Regression equation*	r^2
Site 1	Control	-0.005 + 0.0008X	0.93
	WTR amended	0.012 + 0.0003X	0.91
Site 2	Control	0.015 + 0.0013X	0.94
	WTR amended	-0.002 + 0.0004X	0.89

X = Bray-1 P (mg kg^{-1})

Statistical analysis (PROC REG, SAS Inst, 1999) showed that extraction coefficients for the control plots from the two sites were different ($p < 0.05$), but those of the WTR amended plots from both sites were not different ($p > 0.05$). The extraction coefficients of the control plots were greater than those of the WTR amended plots. The WTR amendment reduced the extraction coefficient and masked the effect of the differences in STP concentrations from both sites. Analysis of regressions generated by these studies supports the findings of the various studies in this dissertation and others (Cox et al., 1997; Ippolito et al., 1999; Elliott et al., 2002; O'Connor et al., 2002; Dayton et al., 2003; Ippolito et al., 2003; Elliott et al., 2005; Silveira et al., 2006) who reported the capability of WTR to reduce soluble P levels in soils and the threat of P loss to the environment.

A large proportion (42-75 %) of the total P load loss in runoff was PP (Figure 6-5). The flow-weighted PP masses were significantly greater in the WTR amended plots at both sites than the control plots (Figure 6-5). Possibly, the particles detached by the rain drops from the WTR amended plots had greater P enrichment due to the WTR immobilization than the soil particles detached from the control plots. Furthermore, the greater PP masses may be due to the presence of WTR contained in the eroded particles, which also contains some P.

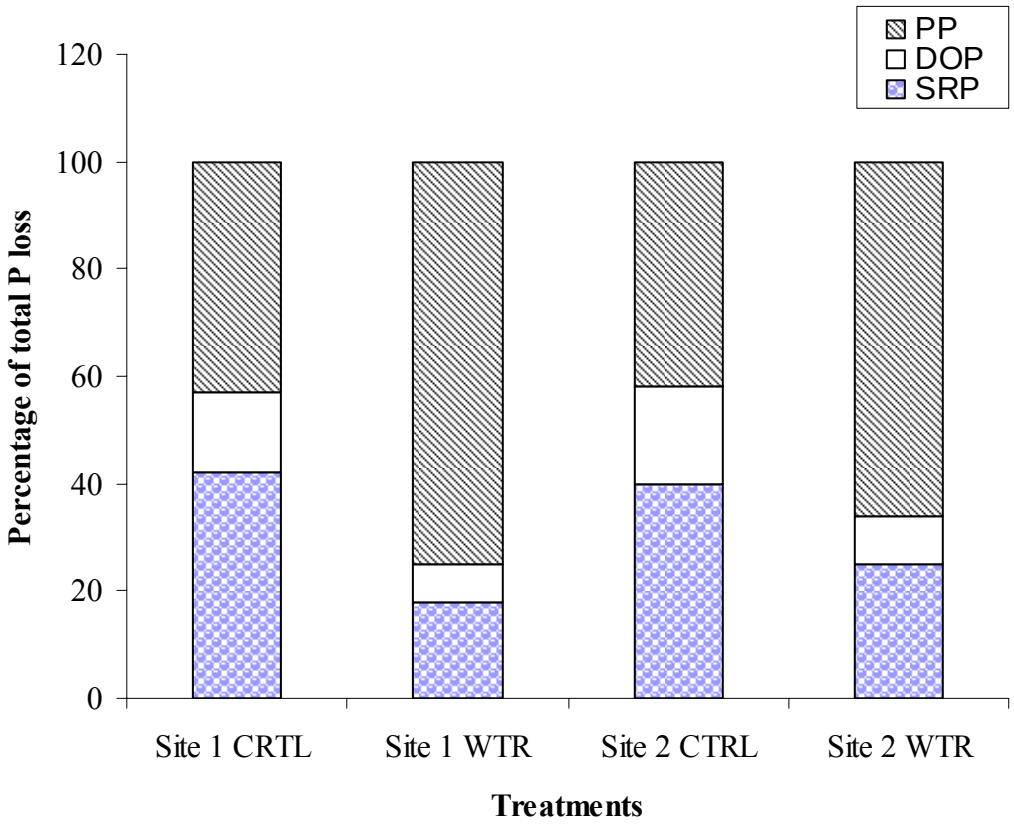


Figure 6-5. Percentages of total P mass loss represented by the various P forms from the Michigan field study. Median values of the various fractions of total P loss were used to plot the graph.

Tarkalson and Mikkelsen (2004b) reported that 11–70% of PP can become bioavailable to aquatic organisms and thus lead to eutrophication. This prompted the determination of bioavailable P (BAP) using FeO-impregnated paper strips. Unlike other extractions, which react with soil and dissolve specific P fractions, FeO paper acts as an infinite sink that adsorbs and

retains P that is mobile in the soil solution (Menon et al., 1997). Sharpley (1993) found a strong correlation between algal growth and the amount of P extracted from runoff sediment by the BAP.

Despite the greater particulate P loads in runoff from the WTR amended plots, flow-weighted BAP masses in runoff were significantly smaller than those of the control plots (Figure 6-6), suggesting that much of the particulate P was not bioavailable. Thus, even if WTR-P erodes to surface waters, there should be minimal adverse effects on water quality. The data suggest that even 7.5 years after WTR amendment of the sites, the WTR immobilized P remained non-labile. Thus, there is little justifiable fear that WTR immobilized P will dissolve into runoff and leachates to contaminate surface water and groundwater.

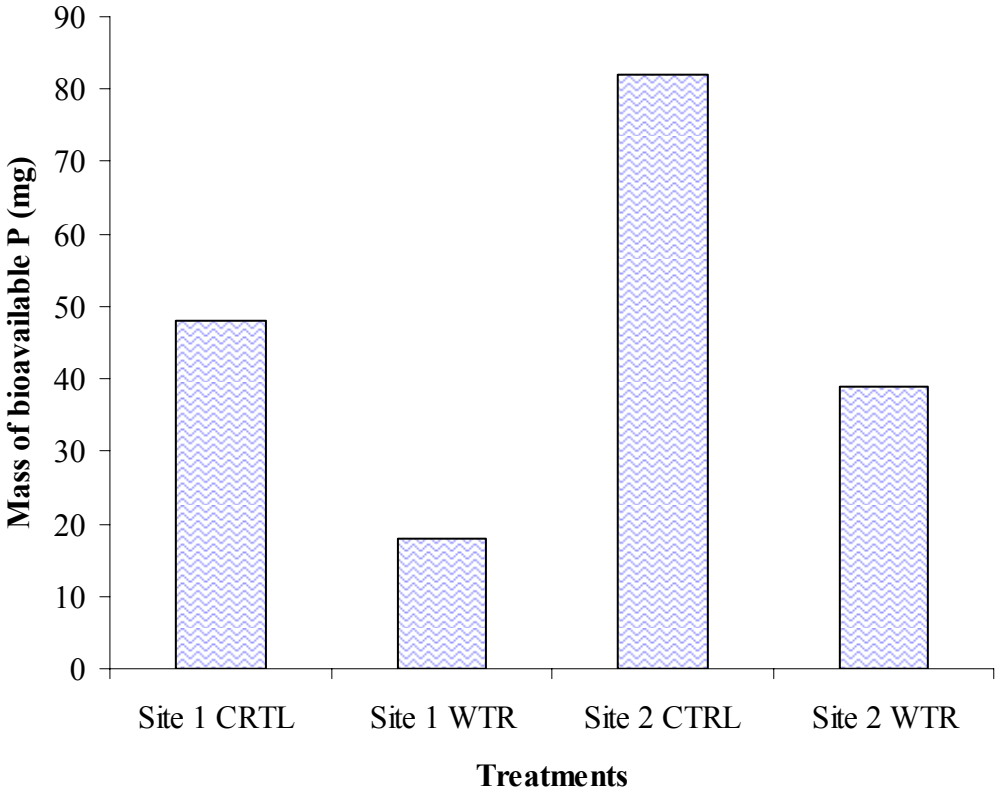


Figure 6-6. Flow-weighted bioavailable P loads in runoff from the Michigan field study. Median values of the various fractions of total P loss were used to plot the graph.

Drinking-water treatment residauls can be relied upon to control P losses in runoff and leachate. Even if WTR-P erodes to surface waters, our data suggest the bioavailability of the immobilized P is minimal. Makris et al (2004a,b) reported that P sorption by WTRs was essentially irreversible. The authors hypothesized that bottleneck-shaped micropores limited P diffusion rates; the hypothesis was consistent with time-dependent sorption and hysteretic desorption. Thus micropore-bound P likely resists desorption, which favors long-term stability of sorbed P by WTRs.

CHAPTER 7
MODELING SOLID PHASES CONTROLING SOLUBILITY OF WTR IMMOBILIZED PHOSPHORUS

Introduction

Environmental concerns have caused many states to implement laws regarding land application of P to minimize the potential for P transport in agricultural runoff. Significant amounts of P added to the soil in the form of fertilizers, biosolids and manures can pollute water supplies via surface runoff and leaching. The problem is exacerbated for poorly-P sorbing soils, such as coastal plain soils of the southeastern U.S. where P leaching occurs and polluted water is intercepted by drains (or shallow water tables) that join surface waters. However, in strongly P sorbing soils, reactions with soil constituents result in a reduction of P concentration in solution over time, following application of soluble P fertilizer to soil (Sample et al., 1980; Wolt, 1994; Folle et al., 1995). In strongly P-sorbing soils, soluble Al, Fe, Ca and Mg (depending on soil pH) quickly react with soluble P to form complexes that may precipitate from solution or be adsorbed on the surface of Fe and Al oxides or on clay particles (Lindsay et al., 1962; Martin et al., 1988).

The reactions governing the P forms and availability in soils can be described by the solubility of sparingly soluble metal-hydroxyphosphate minerals that extend pH-dependent control over soil solution phosphate activity (Lindsay, 1979; Schwab, 1989; Karathanasis, 1991; Wolt, 1994). In acid soils, Al, Fe, and other metals react with P to form new solid phases, or P is sorbed in surface complexes on Fe and Al oxides and clay particles (Wang et al., 1991; Sloan et al, 1995; Zhang and Karathanasis, 1997). If the soil pH shifts from the acid to the alkaline range, the reaction products of phosphorus fertilization will shift to calcium phosphates (Fixen et al, 1983; Hanson and Westfall, 1985). Thus, phosphate solubility is influenced by the activities of Fe and Al (in acid soils) or Ca and Mg (in alkaline soils) species in soil solutions that are largely controlled by the solid-phase solubility of Fe and Al or Ca and Mg minerals in soils (Lindsay,

1979; Sample et al., 1980). Therefore, the distribution of various forms of phosphate is related to the distribution and chemical reactions of Fe, Al, Ca and Mg fractions in soils.

In soils characterized by coarse textures and low Fe/Al or Ca hydroxide contents, P is sorbed poorly and significant amounts of applied P can be lost through runoff or leachates to contaminate fresh surface waters and/or groundwater. One suggested way to mitigate P losses is to increase the P sorption capacity of poorly P-sorbing soils with soil amendments. For example, Summers et al. (1993), Peters and Basta (1996), and Snars et al. (2003), used activated red mud (neutralized bauxite refinery residue) to improve the P sorption capacity of sandy soils. Other researchers have reported the efficacy of alum ($Al_2(SO_4)_3 \bullet 14H_2O$) in reducing P mobility in poorly P-sorbing soils (Moore et al., 1998; Haustein, 2000; Staats et al., 2004). The use of drinking-water treatment residuals (WTR) to control P mobility in poorly P sorbing soils has received increased attention recently. However, the long-term stability of the P sorbed by WTRs has only been qualitatively inferred from lab experiments (Makris et al., 2004a). Improved understanding of the P dynamics in WTR amended P-impacted soils is essential to predict the long-term stability of WTR immobilized P in the environment. We hypothesized that long-term chemical phase changes of P will be associated with WTR-Al or -Fe, as Al or Fe phosphate solid phases due to the nature of the WTR. Secondly, stable Al and Fe minerals will control P solubility of WTR immobilized P from P-impacted soils, thus ensuring that WTR immobilized P remains stable in the long-term and that the stability would vary in predictable ways.

A variety of methods have been used to distinguish between adsorption and precipitation reactions of soluble P in P sorbing soils. Pierzynski et al. (1990) used electron optical techniques to describe P-rich particles in excessively fertilized soils and found that Al and Si were the dominant elements associated with P. These amorphous, mixed Al-Si-P substances occurred as

discrete particles as well as coatings on other particles. Martin et al. (1988) used spectroscopic techniques to observe Fe-phosphate crystallites on the surface of goethite. They concluded that in an iron oxide system, phosphate retention may be due primarily to precipitation rather than adsorption. Van Riemsdijk and Lyklema (1980) found that adsorption contributed very little to total sorption at P concentrations > 1 mmol L^{-1}. Josan et al. (2005) and Silveira et al. (2006) used VISUAL MINTEQ to predict the solid phases controlling P solubility in manure-impacted soils. Alva et al. (1991) Sloan et al. (1995) 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 et al. (1995) used MINTEQA2 to determine Al speciation in acid soils amended with alkaline biosolids.

In this experiment MINTEQA2 (Allison et al., 1999) model was used to calculate the concentration of species present at equilibrium. MINTEQA2 is a program developed by USEPA and includes a geochemical equilibrium speciation model capable of computing equilibria among the dissolved, adsorbed, solid and gas phases in an environmental setting. MINTEQA2 includes an extensive database with thermodynamic data that is accessible to PRODEFA2, an interactive program designed to create the required input data file.

The objectives of this study were to investigate the influence of various species of Fe and Al on phosphate solubility and reactions, and to speculate about solid phases controlling the solubility of WTR immobilized P. The stability of the solid phases will enable the prediction of the long-term stability of WTR immobilized P.

Materials and Methods

Soil Samples Used

Field- and artificially-aged soils samples were utilized for this study. The field-aged samples were obtained from one-time WTR amended fields in Western Michigan (Jacobs and

Teppen, 2000). Two test sites in Michigan were selected in 1998 for evaluation of WTR effects on P extractability in soils having "very high" Bray-1 soil test P concentrations. Soils from both sites have a long-term (> 10 yr) history of heavy poultry manure applications. Details of the sites description and soil characterization are presented in chapters 2 and 5.

The artificially aged soil samples were prepared by amending unimpacted Immokalee A horizon soil sample with 25 g kg^{-1} of four air-dried WTRs (Bradenton, Holland, Lowell and Cocoa WTRs). Phosphorus was added to the WTR amended soils as TSP solutions at 0, low (43), or high (100) mg P kg^{-1} to roughly mimic field P-fertilization rates. The soil samples were thoroughly mixed, and aged via thermal incubation or wetting and drying to mimic long-term field effects: (see chapter 2 for the physicochemical characteristics of the soil and WTRs, and chapter 4 for detailed description of the incubation procedure).

Soil Extraction

Twenty grams (oven-dry equivalent) of each soil sample was placed in centrifuge tubes to which 20 mL of deionized water was added, giving a solid-to-solution ratio of 1:1. Two drops of toluene were added to each suspension and appropriate aliquots of diluted HCl and NaOH were added daily to the samples to provide a series of 3 pH levels (3, 5 and 7) for each treatment. The soil suspensions were equilibrated for 14 days in a reciprocating shaker at a rate of 100 strikes min^{-1} at room temperature (24 ± 2°C). The mild vigor of shaking was intended to avoid soil aggregate disruption and particle abrasion (Koopmans et al., 2004). After the equilibration period, the soil suspensions were centrifuged at a relative centrifuge force of 8000 x g for 20 min. The supernatants were collected and filtered through a 0.45-µm pore-size filter membrane for analyses. Quality assurance and quality control protocols included 5% repeats, spikes, certified samples and blanks for each procedure.

Equilibrium Modeling

The pH values and oxidation-reduction (redox) potentials (Eh) of the soils amended with Fe-WTR, and electrical conductivities (EC) of the solutions were analyzed immediately after extraction. Ionic strengths of the extracts were calculated from EC based on the following conversion (Griffin and Jurinak, 1973):

$$I = 0.0127\ EC \qquad [1]$$

where I = ion strength (mol L^{-1}).

The concentrations of aluminum (Al^{3+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), sodium (Na^{+}), and iron (Fe^{3+}) were measured using ICP-AES (Perkin-Elmer Plasma 3200). The concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^{-}), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), chloride (Cl^{-}) and fluoride (F^{-}) were analyzed using ion chromatography (Dionex Separator AS-14).

The geochemical assessment model MINTEQA2 (Allison et al., 1999) was used to calculate activities of dissolved chemical species. Total dissolved concentrations of ions measured by laboratory methods and soil solution pH were input data for MINTEQA2. Equilibrium constants were adjusted using the ionic strength calculated by MINTEQA2. Saturation indices were calculated by MINTEQA2 for all possible solids with respect to the soil solution. The saturation index (SI) is defined as:

$$SI = \log (IAP / K_{sp}) \qquad [2]$$

where IAP is the ion activity product of the appropriate chemical species and K_{sp} *is* the solubility product of the possible solid phase. Ion activity products are based solely on the speciation of the soil solution and can be used to determine whether the dissolution-precipitation reaction is actually at equilibrium (Sposito, 1989). For any specific mineral, SI > 0 indicates that

the soil solution is oversaturated and SI < 0 indicates that it is undersaturated. As the dissolution-precipitation reaction nears equilibrium, the SI value approaches zero.

Constant Capacitance Modeling

The ability of the constant capacitance model to describe phosphate adsorption on WTR (external + internal) surfaces was investigated. The constant capacitance model is based on the following assumptions (Goldberg and Sposito, 1984):

- adsorption proceeds via a ligand exchange mechanism,
- all surface complexes formed are inner-sphere complexes;
- the constant ionic medium reference state determines the activity coefficients of the aqueous species in the conditional equilibrium constants and therefore no complexes are formed with ions in the background electrolyte; and
- a linear relationship exists between surface charge (σ), [mmol L^{-1}], and the surface potential (ψ):

$$\sigma = (Cs\alpha/F)\psi \quad [3]$$

where C is the capacitance density (Fm^{-2}), s is the specific surface area ($m^2\ g^{-1}$), α is the suspension density (g L^{-1}), F is the Faraday constant (C mol^{-1}), and σ has units of mol L^{-1}.

The following equations are surface complexation reactions (Dimirkou et al., 1996; Ioannou et al., 1996) of phosphate ion on aluminum and iron hydr(oxides):

$$SOH + H^+ = SOH_2^+, \quad [4]$$

$$SOH \leftrightarrow SO^- + H^+, \quad [5]$$

$$SOH + H_3PO_4 \leftrightarrow SH_2PO_4 + H_2O \quad [6]$$

$$SOH + H_3PO_4 \leftrightarrow SHPO^- + H_2O + H^+ \quad [7]$$

$$SOH + H_3PO_4 \leftrightarrow SPO4^{-2} + H_2O + 2H^+ \quad [8]$$

where SOH in this study represents the surface functional group of Alum-and Fe-based WTRs.

The intrinsic conditional equilibrium constants (Dimirkou et al., 1996; Ioannou et al., 1996) describing these reactions are:

$$K_{+\,(int)} = ([SOH_2^+] / [SOH][H^+]) \exp(F\psi/RT) \quad [9]$$

$$K_{-\,(int)} = ([SO^-]\,[H^+] / [SOH]) \exp(-F\psi/RT) \quad [10]$$

$$K_{1\,(int)} = [SH_2PO_4] / [SOH][H_3PO_4] \quad [11]$$

$$K_{2\,(int)} = ([SHPO^-][H^+] / [SOH][H_3PO_4]) \exp(-F\psi/RT) \quad [12]$$

$$K_{3\,(int)} = ([SPO4\text{-}^2]\,[H^+]^2 / [SOH][H_3PO_4]) \exp(-2F\psi/RT) \quad [13]$$

where R is the molar gas constant (J mol^{-1} K^{-1}), T is the absolute temperature, and square brackets represent concentrations (mol L^{-1}). The intrinsic conditional equilibrium constants are obtained by extrapolating the conditional equilibrium constants to zero net surface charge (Stumm et al., 1980; Goldberg and Sposito, 1984). Goldberg (1992) defined the conditional equilibrium constants for protonation-dissociation as

$$^{c}K_{+\,(int)} = ([SOH_2^+] / [SOH][H^+]) \quad [14]$$

$$^{c}K_{-\,(int)} = ([SO^-]\,[H^+] / [SOH]) \quad [15]$$

The relationship between the intrinsic and conditional protonation constants after combining Eq. [9] with Eq. [14] and Eq. [10] with Eq. [15] is

$$K_{\pm\,(int)} = {}^{c}K \exp(F\psi/RT) \quad [16]$$

Unlike the intrinsic constants, the ordinary conditional equilibrium constants depend on surface charge (Stumm, et al., 1980). The exponential terms in Equations [9], [10], [12], and [13] represent the contribution of this mean field to the rational activity coefficients of the surface species. In practical terms, the exponential term can be considered as a solid-phase activity coefficient that corrects for the charge of a surface species (Goldberg and Sposito, 1984). With the addition of mass balance and charge balance equations, the chemical equilibrium problem

formulated above can be solved (Goldberg and Sposito, 1984). The mass balance equation for the surface functional group, SOH, is

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SH_2PO_4] + [SHPO_4^-] + [SPO_4^{-2}] \quad [17]$$

where again square brackets indicate concentrations (mol L^{-1}). The corresponding charge balance equation is

$$\sigma = [SOH_2^+] - [SO^-] - [SHPO_4^-] - 2[SPO_4^{-2}] \quad [18]$$

In order to solve the set of Equations [3], [9] - [13], [17], and [18] the computer program Ma-Za 1 (Ioannou and Dimirkou, 1994) was used. Ma-Za 1 is a computer program describing the adsorption processes for the constant capacitance model. The use of Ma-Za 1 requires values of intrinsic surface protonation-dissociation constants and intrinsic surface complexation constants. The computer program Ma-Za 2 (Ioannou and Dimirkou, 1995) was used to obtain these parameters. Ma-Za 2 employs a nonlinear, least squares method to fit equilibrium constants to experimental data. Ma-Za 2 also contains the constant capacitance model to describe surface complexation.

In this study Ma-Za 2 was used to fit the constant capacitance model to phosphate adsorption isotherm data on WTRs and to obtain optimal values of the phosphate surface complexation constants. The equilibrium constants thus obtained were employed in Ma-Za 1 to check the goodness of fit of the model at each point on the adsorption isotherms. The Ma-Za 2 program optimizes the values of adjustable parameters by changing their values until the sum of the squares (S) [$S = \sum(y_i - x_i)^2$] of the residuals between the measured adsorption data (y_i) and Ma-Za 2 calculated values (x_i) is minimized (Ioannou and Dimirkou, 1995). In general Ma-Za 2 convergence is most likely to occur when data are fitted using only two adjustable parameters. Numerical values used in this study for the intrinsic protonation-dissociation constants $K_{+\,(int)}$ and

$K_{-(int)}$ were obtained from the average values of a literature compilation of experimental data for aluminum and iron oxides (Goldberg and Sposito, 1984). The capacitance density, *C,* cannot be determined experimentally and is treated as an empirical adjustable parameter. A working value was chosen on the basis of previous applications of the constant capacitance model (Westall and Hohl, 1980; Goldberg and Sposito, 1984; Dimirkou et al., 2002). In this study, *C* was fixed at 1.06 F m^{-2}, a value which is optimal for aluminum and iron oxides (Westall and Hohl, 1980). Additional model parameters, such as specific surface area (Makris, 2004), phosphate adsorption isotherm data for WTRs, and suspension density (α), were determined experimentally. The value of the surface site density $[SOH]_T$ was determined by potentiometric titration (Kummert and Stumm, 1980; Lutzenkirchen, 1999; Goldberg, 2002; Jara et al., 2005) and was optimized to fit experimental adsorption data (Lutzenkirchen, 1999; Goldberg, 2002; Jara et al., 2005). Independent model validation was carried out using the MINTEQA2 (Allison et al., 1999) geochemical model.

Phosphorus adsorption experiments were carried out in batch systems to determine adsorption envelopes (amount of P adsorbed as a function of solution pH per fixed total P concentration) (Ioannou and Dimirkou, 1996; Dimirkou et al., 2002). Samples of adsorbent (0.1 g for the WTR samples in three repetitions) were added to 100 mL polypropylene centrifuge tubes and equilibrated with 20 ml of 0.1 *M* KC1 solution and 1 drop of toluene by shaking for 14 days on a reciprocating shaker at constant temperature (24 ± 2°C). These solutions contained 250 to 1250 mg P L^{-1} as KH_2PO_4, which had been adjusted to the desired pH values (3-7) using 1 *M* HC1 or 1 *M* KOH additions that changed the total volume by ≤ 2%. The samples were centrifuged at a relative centrifuge force of 8000 x *g* for 20 min at constant temperature (24 ± 2°C). The decantates were filtered through a 0.45 µm Whatman filter paper, and analyzed

for P using the Murphy and Riley (1962) method. The P sorbed was calculated from the difference between initial and final concentrations of P in solution. Following the P sorption experiments, the supernatants were removed and WTR samples were washed twice with anhydrous ethanol to remove residual P. The WTR-containing tubes were filled with 20 ml of 0.1 *M* KC1 solution and 1 drop of toluene and adjusted to the desired pH values as described above. The WTR suspension was then shaken for 14 days to assess P released from the P loaded WTRs. Released P was determined as described above.

Results and Discussion

Modeling results for only the soil samples taken at time zero and the final sampling of both the artificially incubated samples and the field-aged samples are presented because other sampling time data showed similar trends. We recognize that there are assumptions and uncertainties (e.g., approximation of organic speciation, non-equilibrium, kinetic effects, etc.) inherent in modeling complex solutions. We, therefore, restrict our interpretations to major trends indicated by the modeling results.

Chemical Speciation of Soil Solutions

Field-aged Samples

The samples from both the control and WTR amended MI field plots taken from both sites 1 and 2, and equilibrated at pH 5 and 7 had similar chemical P species in solution, but the relative abundance of the species was related to pH. On the other hand, the samples equilibrated at pH 3 had different chemical P species in solution.

For the samples equilibrated at pH 7 (both control and WTR amended plot at both sites), the major chemical P species in solution were HPO_4^{2-} (~ 35 % of total soluble P), $H_2PO_4^-$ (~ 30 %) and Mg-P [$MgHPO_4$ (aq) and $MgPO_4^-$] and Ca-P ($CaPO_4$) complexes (~ 20 and 12 % of total soluble P, respectively) (Tables 7-1 and 7-2). Wang et al. (1995) and Silveira et al.

(2006) predicted similar P species in solution from manure-impacted FL soils. Aluminum- and Fe-P species were not predicted to occur in the soil solutions, because of the neutral pH conditions (pH 7) and undetectable (< 0.03 mg L^{-1}) Al and Fe concentrations. Even samples from the WTR amended plots collected from both sites had soluble Al concentration < 0.03 mg L^{-1}. Samples taken at the end of the experimental period (7.5 years) had similar P chemical speciation as the samples taken at time zero from both sites in both the control and WTR amended plots. The absence of Al-P among the predicted P species was due to the fact that Al concentration was below the detection limit (< 0.03 mg L^{-1}) of the instrument. This is an indirect indication that after 7.5 years of field aging, the WTR was still stable. Silveira et al. (2006) reported that even at WTR application of 100 g kg^{-1} in a column study leached for 36 weeks, soluble Al was undetectable in the leachate and, consequently, Al-P were not predicted in chemical equilibrium modeling. Makris (2004) conducted long-term (80 days) equilibrations of Al-WTRs in unbuffered 0.01 M KCl solutions and observed that soluble Al concentrations of untreated (no P added) Al-WTRs were below the instrument's (ICP-AES) detection limit (0.03 mg Al L^{-1}). Most P-treated (10,000 mg kg^{-1} initial P load) Al-WTR suspensions released small (< 10 mg kg^{-1}) quantities of soluble Al, but one released 46 mg Al kg^{-1}. Overall, the amount of KCl-extractable Al concentrations released from Al-WTRs within 80 d was minimal (< 0.1 % of oxalate-extractable Al) (Makris, 2004).

When the samples were equilibrated at pH 5, the major chemical P species in solution were dominated by $H_2PO_4^-$ (~50 % of total soluble P) and HPO_4^{2-} accounted for only ~ 25 %. The Mg-P complex predicted was $MgHPO_4$ (~ 15 %), and Ca-P ($CaPO_4^-$) accounted for only 5 %. Similarly to the samples equilibrated at pH 7, no Fe- and/or Al-P complexes were predicted by

the model, not even from the samples taken from the WTR amended plots at the final sampling time (7.5 years after the initial WTR application).

Similarly to the samples equilibrated at pH 5, when the samples taken from both sites from the control and WTR amended plots were equilibrated at pH 3, the major solution P species in soil solutions, as indicated by solution speciation modeling, was $H_2PO_4^-$ (> 60 % of the soluble P). However, unlike the samples equilibrated at pH 7 and 5, HPO_4^-, Mg-P complexes and Ca-P complexes were not predicted in the soil solution. Instead, H_3PO_4 (~ 15 %), $AlHPO_4^+$ (~ 20 %) and $FeHPO_4^+$ (~ 5 %) were predicted (Tables 7-1 and 7-2).

Phosphorus speciation predicted by MINTEQA2 showed that soluble P species predicted from samples of both the control and the WTR amended plots equilibrated at pH 3 was distributed as $FeHPO_4^+$, $AlHPO_4^+$, $H_2PO_4^-$, and H_3PO_4.

Artificially-aged Samples

Chemical P species predicted by the model for the thermally incubated samples were similar to those predicted for the samples incubated via wetting and drying at the same P loads and pH values. Similar P species were predicted for the samples amended with the different WTR types except when the samples were equilibrated at pH 3. Thus at pH 5 and 7, the P chemical species were independent of the WTR type. In view of the similarities of the P species predicted by the model for both artificially-aged samples, the data of the thermally incubated samples are presented here to represent the artificially-aged samples.

When the control and WTR amended samples for the artificially-aged samples were equilibrated at either pH 5 or 7, the only P chemical species predicted by the model for the native Immokalee sand, without P addition, were $H_2PO_4^-$ and HPO_4^{2-} (Tables 7-3 and 7-4).

Table 7-1. Distribution of major P chemical species predicted from both the control and WTR amended plots from site 1 of the Michigan field study. Samples were equilibrated at pH 3, 5, and 7. All values are in percentages.

pH	Time	Trt	HPO_4^{2-}	$H_2PO_4^-$	H_3PO_4	$MgPO_4^-$	$MgHPO_4$	$CaPO_4^-$	$AlHPO_4^+$	$FeHPO_4^+$	SUM
3	Time zero	Control	-	61	16	-	-	-	12	5	94
		WTR amended	-	59	14	-	-	-	19	6	98
	7.5 years	Control	-	61	15	-	-	-	15	5	96
		WTR amended	-	60	13	-	-	-	21	5	99
5	Time zero	Control	26	50	-	-	12	5	-	-	93
		WTR amended	27	48	-	-	14	7	-	-	96
	7.5 years	Control	22	53	-	-	16	5	-	-	96
		WTR amended	25	51	-	-	12	6	-	-	94
7	Time zero	Control	36	30	-	12	8	12	-	-	98
		WTR amended	34	29	-	14	6	14	-	-	97
	7.5 years	Control	33	34	-	12	8	11	-	-	98
		WTR amended	37	29	-	13	7	13	-	-	99

Table 7-2. Distribution of major P chemical species predicted from both the control and WTR amended plots from site 2 of the Michigan field study. Samples were equilibrated at pH 3, 5, and 7. All values are in percentages.

pH	Time	Trt	HPO_4^{2-}	$H_2PO_4^-$	H_3PO_4	$MgPO_4^-$	$MgHPO_4$	$CaPO_4^-$	$AlHPO_4^+$	$FeHPO_4^+$	SUM
3	Time zero	Control	-	62	15	-	-	-	11	6	94
		WTR amended	-	61	15	-	-	-	17	5	98
	7.5 years	Control	-	59	16	-	-	-	13	4	92
		WTR amended	-	61	13	-	-	-	18	5	97
5	Time zero	Control	24	51	-	-	10	6	-	-	91
		WTR amended	25	53	-	-	9	7	-	-	94
	7.5 years	Control	26	51	-	-	9	9	-	-	95
		WTR amended	25	50	-	-	12	5	-	-	92
7	Time zero	Control	35	32	-	11	9	12	-	-	99
		WTR amended	34	30	-	12	7	14	-	-	97
	7.5 years	Control	36	31	-	10	8	11	-	-	96
		WTR amended	33	31	-	14	7	13	-	-	98

Table 7-3. Distribution of major P chemical species predicted from samples thermally incubated at 70 °C and equilibrated at pH 5. All values are in percentages.

	Trt.	P load	HPO_4^{2-}	$H_2PO_4^-$	$MgPO_4^-$	$MgHPO_4$	$CaPO_4^-$	SUM
Time zero	No-WTR	No P	35	62	-	-	-	97
	ABR†		30	65	-	-	-	95
	ACO‡		32	63	-	-	-	95
	AHL†‡		34	65	-	-	-	99
	ALW‡‡		31	62	-	-	-	93
	No-WTR	Low P	25	52	-	13	7	97
	ABR		22	53	-	12	9	96
	ACO		26	50	-	11	9	96
	AHL		24	50	-	10	9	93
	ALW		23	55	-	12	8	98
	No-WTR	High P	20	54	-	13	10	97
	ABR		23	49	-	14	11	97
	ACO		22	50	-	13	10	95
	AHL		24	50	-	14	9	97
	ALW		23	54	-	10	9	96
1.5 years	No-WTR	No P	36	62	-	-	-	98
	ABR		38	59	-	-	-	97
	ACO		35	61	-	-	-	96
	AHL		34	64	-	-	-	98
	ALW		32	66	-	-	-	98
	No-WTR	Low P	23	49	-	15	10	97
	ABR		25	51	-	10	11	97
	ACO		22	55	-	10	9	96
	AHL		20	54	-	12	9	95
	ALW		25	54	-	10	9	98
	No-WTR	High P	24	50	-	13	10	97
	ABR		22	55	-	12	8	97
	ACO		22	52	-	13	9	96
	AHL		25	50	-	13	10	98
	ALW		25	51	-	12	11	99

† Bradenton WTR amended soil
‡ Cocoa WTR amended soil
†‡ Holland WTR amended soil
‡‡ Lowell WTR amended soil

Table 7-4. Distribution of major P chemical species predicted from samples thermally incubated at 70 ^{o}C and equilibrated at pH 7. All values are in percentages.

	Trt	P load	HPO_4^{2-}	$H_2PO_4^-$	$MgPO_4^-$	$MgHPO_4$	$CaPO_4^-$	SUM
Time zero	No-WTR		56	42	-	-	-	98
	ABR		52	45	-	-	-	97
	ACO	No P	54	43	-	-	-	97
	AHL		51	45	-	-	-	96
	ALW		51	46	-	-	-	97
	No-WTR		42	32	-	12	8	94
	ABR		41	33	-	14	10	98
	ACO	Low P	44	32	-	12	9	97
	AHL		45	30	-	12	9	96
	ALW		43	31	-	13	10	97
	No-WTR		38	30	8	12	10	98
	ABR		34	31	10	13	9	97
	ACO	High P	35	32	9	14	9	99
	AHL		36	33	8	12	8	97
	ALW		37	32	8	12	9	98
1.5 years	No-WTR		55	41	-	-	-	96
	ABR		54	43	-	-	-	97
	ACO	No P	56	43	-	-	-	99
	AHL		54	42	-	-	-	96
	ALW		56	41	-	-	-	97
	No-WTR		43	29	-	13	9	94
	ABR		45	31	-	12	10	98
	ACO	Low P	42	33	-	10	8	93
	AHL		40	29	-	11	8	88
	ALW		41	30	-	11	10	92
	No-WTR		35	30	9	12	10	96
	ABR		36	29	11	13	8	97
	ACO	High P	36	32	12	10	7	97
	AHL		35	32	10	12	8	97
	ALW		36	31	12	11	8	98

† Bradenton WTR amended soil
‡ Cocoa WTR amended soil
†‡ Holland WTR amended soil
‡‡ Lowell WTR amended soil

No Ca-P and Mg-P complexes were predicted as was the case in the manure-impacted (Michigan) field samples. This trend may be explained by the very low SRP content (Table 2-2) and low Ca and Mg content (data not presented) of the Immokalee sand. At the low rate of P application (43 mg kg^{-1}), $CaPO_4$ and $MgHPO_4$ P forms were predicted by the model, in addition to HPO_4^{2-} and $H_2PO_4^-$ when the samples (both control and WTR amended for the artificially-aged samples) were equilibrated at pH 5 and 7. Similar P species were predicted for the highly P-impacted samples (those impacted with 100 mg P kg^{-1}) when the samples were equilibrated at pH 5. At pH 7, an additional Mg-P complex ($MgPO_4^-$) was predicted by the model to be present in soil solution (Tables 7-3 to 7-6).

Conversely, when the samples were equilibrated at pH 3, different P species were predicted by the model for the different treatment. Phosphoric acid (H_3PO_4) was predicted, in addition to $H_2PO_4^-$ for the control samples without WTR addition (Table 7-5). When the samples were amended with the Al-WTR (Bradenton, Lowell and Holland WTRs), $AlHPO_4^+$ was predicted in all cases at this pH. For the samples amended with Fe-WTR (Cocoa WTR), $FeHPO_4^+$ was predicted to occur in the soil solution (Table 7-5). This suggests that some WTR dissolved at pH 3, and that Al (or Fe) was released to form complexes with P. Similarly to the samples without P treatment, when the samples were equilibrated at pH 3, H_3PO_4, H_2PO_4 were predicted for the samples without WTR amendments. For the WTR amended samples, $AlHPO_4^+$ and $FeHPO_4^+$ species were also predicted (Table 7-5). These P chemical species were similar for both the thermally-aged samples and those aged via wetting and drying.

Solid Phase Equilibria

Saturation indices were calculated by MINTEQA2 (Allison et al., 1999) to investigate possible formation of solid phases. Tables 7-6 to 7-10 show soil solution saturation indices for phosphate minerals whose dissolution-precipitation reactions may control P activity. For any

specific mineral, saturation index (SI) > 0 indicates that the soil solution is supersaturated and SI < 0 indicates that it is undersaturated with respect to that mineral. Equilibrium with a particular solid phase is indicated by SI = 0. Phosphate solid phases in soils are rarely pure, well crystallized minerals, but can play a major role in the overall desorption/dissolution of P (Sloan et al., 1995). It is therefore insightful to investigate the WTR-P solubility behavior with respect to these minerals.

Table 7-5. Distribution of major P chemical species predicted from samples thermally incubated at 70 ^{o}C and equilibrated at pH 3.

	Trt	P load	$H_2PO_4^-$	H_3PO_4	$AlHPO_4^+$	$FeHPO_4^+$	SUM
Time zero	No-WTR		78	19	-	-	97
	ABR		74	14	10	-	98
	ACO	No P	73	15	-	8	96
	AHL		74	15	9	-	98
	ALW		74	14	9	-	97
	No-WTR		76	13	-	-	89
	ABR		75	15	9	-	99
	ACO	Low P	75	15	-	7	97
	AHL		76	14	9	-	99
	ALW		73	13	10	-	96
	No-WTR		81	16	-	-	97
	ABR		77	13	9	-	99
	ACO	High P	75	14	-	8	97
	AHL		75	15	7	-	97
	ALW		73	16	9	-	98
1.5 years	No-WTR		73	23	-	-	96
	ABR		75	14	8	-	97
	ACO	No P	74	15	-	8	97
	AHL		73	15	9	-	97
	ALW		73	16	9	-	98
	No-WTR		78	20	-	-	98
	ABR		74	15	10	-	99
	ACO	Low P	76	15	-	6	97
	AHL		74	16	9	-	99
	ALW		74	13	10	-	97
	No-WTR		76	21	-	-	97
	ABR		75	14	9	-	98
	ACO	High P	74	16	-	9	99
	AHL		73	14	10	-	97
	ALW		75	15	8	-	98

† Bradenton WTR amended soil
†‡ Holland WTR amended soil
‡ Cocoa WTR amended soil
‡‡ Lowell WTR amended soil

Field-aged Samples

Identical solid phases with similar SI values were predicted for the samples taken from the control (no WTR amendment) plots from both sites and equilibrated at pH 5 and 7 (Tables 7-6 and 7-7). Solutions were undersaturated with respect to the Mg-P minerals Farringtonite [$Mg_3(PO_4)_2$] and Newberyite ($MgHPO_4 \bullet 3H_2O$) (Tables 7-6 and 7-7). The soil solutions were supersaturated with respect to all Ca-P phases modeled, Hydroxyapatite [$Ca_5(PO_4)_3OH$], β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)] and Octacalcium phosphate [$Ca_4H(PO_4)_3 \bullet 3H_2O$], except Brushite ($CaHPO_4 \bullet 2H_2O$) and Monetite ($CaHPO_4$).

The chemical activity of solid phases can be rigorously defined if the solid solution is homogenous, but in soil systems, solid phases dissolve non-stoichiometrically, thereby creating inhomogeneity and disequilibrium between the solid's surface and interior (Bohn and Bohn, 1987). Thus, true equilibrium in soil suspensions is unlikely, and consequently, strict thermodynamics may be relaxed for element solubility calculations in soil systems. In this regard, Bohn and Bohn (1987) suggested that in soil solutions, an IAP/K_{sp} ratio between 0.1 and 1.0 ($-1 \leq SI \leq 0$) should be considered confirmation that the K_{sp} of a mineral governs the soil solution concentration of a particular ion. Based on this criterion of saturation, and using data for all soil solutions from the control plots for both sites, Mg-P (i.e., Farringtonite, and Newberryite) and Ca-P (i.e., Brushite and Monetite) minerals were within the saturation range (near equilibrium) for the soil solutions. Hence, these soluble minerals could be prospects for controlling P activity in the manure-impacted control plots (Tables 7-6 and 7-7). The most thermodynamically stable mineral modeled, Hydroxyapatite, would be stable in the control plots from both sites (if present), but would not likely be a factor in P solubility from the soils.

Table 7-6. Soil solution saturation indices for P solid phases predicted from both the control and WTR amended plots from site 1 of the Michigan field study. Samples were equilibrated at pH 3, 5, and 7

pH	Time	Trt	Predicted minerals										
			β-TCP†	OCP‡	MNT††	BST†‡	HA‡‡	FNT†††	NBT‡‡†	SGT‡††	VCT (am)‡‡‡	VCT (cr)‡‡‡†	WLT‡‡‡‡
3	Time zero	Control	-14.2	-15.0	-20.7	-25.2	-21.3	-15.9	-25.9	-16.7	-15.4	1.38	-13.1
		WTR amended	-15.9	-13.2	-22.9	-21.6	-23.4	-16.3	-26.2	-14.6	-13.2	2.13	-12.2
	7.5 years	Control	-14.7	-15.5	-25.8	-15.5	-13.2	-18.2	-22.2	-17.2	-14.7	1.12	-14.7
		WTR amended	-15.2	-12.7	-26.1	-16.0	-14.1	-13.5	-21.3	-16.9	-16.4	1.94	-10.3
5	Time zero	Control	4.06	2.56	-0.98	-0.17	13.58	-2.95	-0.48	-	-	-	-
		WTR amended	2.96	2.08	-2.42	-1.42	11.66	-3.54	-1.65	-	-	-	-
	7.5 years	Control	3.64	2.16	-0.58	-0.23	10.26	-3.65	-0.87	-	-	-	-
		WTR amended	2.77	1.96	-3.05	-1.72	6.23	-3.82	-2.04	-	-	-	-
7	Time zero	Control	3.48	2.07	-0.87	-0.18	11.66	-3.78	-0.71	-	-	-	-
		WTR amended	3.18	1.62	-2.58	-2.02	10.91	-3.94	-2.13	-	-	-	-
	7.5 years	Control	3.06	1.98	-0.89	-0.23	9.65	-4.03	-0.98	-	-	-	-
		WTR amended	2.59	1.47	-2.21	-2.13	7.28	-4.15	-1.99	-	-	-	-

† β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)] ‡ Octacalcium phosphate [$Ca_4H(PO_4)_3 \cdot 3H_2O$] †† Monetite ($CaHPO_4$)
†‡ Brushite [$CaHPO_4 \cdot 2H_2O$] ‡‡ Hydroxyapatite [$Ca_5(PO_4)_3OH$] ††† Farringtonite [$Mg_3(PO_4)_2$]
‡‡† Newberyite ($MgHPO_4 \cdot 3H_2O$) ‡††† Strengite ($FePO_4 \cdot 2H_2O$) ‡‡‡ Amorphous Variscite ($AlPO_4 \cdot 2H_2O$)
‡‡‡† crystalline Variscite ($AlPO_4 \cdot 2H_2O$) ‡‡‡‡ Wavellite [$Al_3(PO_4)_2(OH,F)_3 \cdot 5(H_2O)$]

Table 7-7. Soil solution saturation indices for P solid phases predicted from both the control and WTR amended plots from site 2 of the Michigan field study. Samples were equilibrated at pH 3, 5, and 7

pH	Time	Trt	Predicted minerals										
			β-TCP†	OCP‡	MNT††	BST†‡	HA‡‡	FNT†††	NBT‡‡†	SGT‡††	VCT (am)‡‡‡	VCT (cr)‡‡‡†	WLT‡‡‡‡
3	Time zero	Control	-13.8	-12.7	-25.1	-23.8	-16.7	-14.3	-22.3	-13.8	-23.9	2.38	-12.5
		WTR amended	-12.5	-14.0	-19.2	-24.1	-20.4	-14.6	-21.5	-19.8	-22.3	2.13	-11.7
	7.5 years	Control	-15.77	-13.4	-20.2	-15.9	-12.3	-11.5	-14.5	-15.2	-14.1	1.94	-11.3
		WTR amended	-14.46	-11.1	-21.42	-24.34	-13.0	-14.7	-24.6	-15.6	-13.2	2.22	-13.16
5	Time zero	Control	5.88	3.50	-0.74	-0.28	19.61	-2.20	-0.61	-	-	-	-
		WTR amended	4.22	2.97	-1.21	-1.69	16.24	-2.64	-1.42	-	-	-	-
	7.5 years	Control	5.19	3.08	-0.36	-0.73	14.28	-2.47	-0.55	-	-	-	-
		WTR amended	3.49	2.94	-2.30	-1.94	8.82	-2.74	-1.35	-	-	-	-
7	Time zero	Control	4.61	2.51	-0.47	-0.35	16.24	-2.44	-0.34	-	-	-	-
		WTR amended	4.53	2.31	-1.91	-1.20	15.54	-2.65	-1.03	-	-	-	-
	7.5 years	Control	4.36	2.82	-0.70	-0.73	13.78	-3.33	-0.37	-	-	-	-
		WTR amended	3.93	2.96	-1.63	-1.03	10.79	-3.23	-1.97	-	-	-	-

† β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)]
‡ Octacalcium phosphate [$Ca_4H(PO_4)_3 \cdot 3H_2O$]
†† Monetite ($CaHPO_4$)
†‡ Brushite [$CaHPO_4 \cdot 2H_2O$]
‡‡ Hydroxyapatite [$Ca_5(PO_4)_3OH$]
††† Farringtonite [$Mg_3(PO_4)_2$]
‡‡† Newberyite ($MgHPO_4 \cdot 3H_2O$)
‡†† Strengite ($FePO_4 \cdot 2H_2O$)
‡‡‡ Amorphous Variscite ($AlPO_4 \cdot 2H_2O$)
‡‡‡† crystalline Variscite ($AlPO_4 \cdot 2H_2O$)
‡‡‡‡ Wavellite [$Al_3(PO_4)_2(OH,F)_3 \cdot 5(H_2O)$]

Despite the relatively high total extractable Fe and Al contents of the soils (Table 2-2), Fe- and Al-P minerals were not predicted to occur. The circumneutral pH conditions at which the samples were equilibrated made it impossible to measure soluble Fe and Al in the soil solution (< 0.03 mg L^{-1}). However, when these two elements were assumed to be present in the soil solution even at low concentrations (0.03 mg L^{-1}), the soil solutions were predicted to be supersaturated (positive saturation indices) with respect to Strengite ($FePO_4 \bullet 2H_2O$) and Varscite ($AlPO_4 \bullet 2H_2O$) (data not presented), indicating that these minerals (if present) will not play a major role in P solubility.

Soluble Ca- and Mg-P minerals appear to control P solubility from the control samples, which is consistent with the conclusions of other studies involving manure-impacted soils (Wang et al., 1995; Hansen and Strawn, 2003; Josan et al., 2005; Silveira et al., 2006). The results indicated that phosphate solubility and activity in soil solution from the manure-impacted plots without WTR amendment were dominated mainly by the dissolution-precipitation reactions of these Ca- and Mg phosphate minerals (Brushite, Monetite, Farringtonite, and Newberryite).

Similar phosphate minerals were predicted by the model for the WTR amended soil samples from both sites equilibrated at pH 5 and 7. For this treatment, soil solutions were supersaturated (positive saturation indices) with respect to Hydroxyapatite, β-tricalcium phosphate and Octacalcium phosphate (Tables 7-6 and 7-7), indicating that those minerals are not playing a major role in P solubility. On the other hand, soil solutions were undersaturated (negative saturation indices) with respect to Brushite, Monetite, Farringtonite and Newberryite (Tables 7-6 and 7-7), and the saturation indices became more negative with time. The data are consistent with those predicted by VISUAL MINTEQ for manure-impacted soils amended with an Al-WTR (Silveira et al., 2006). No phosphate mineral appears to control P solubility from the

WTR amended samples, suggesting that mineral solubility reactions do not determine P retention/release from WTR amended soils. Makris et al. (2004a) suggested that sorption-desorption reactions determine P retention/release in WTR-treated samples, rather than precipitation-dissolution reactions. Using spectroscopic techniques, he showed that P diffuses into the micropores of the WTR and becomes irreversibly bound, which prevented P release (Makris et al., 2004a).

When the samples were equilibrated at pH 3, other Al-P and Fe-P minerals were predicted by the model for both the control and WTR amended samples from both sites of the field study (Tables 7-6 and 7-7). Together with the Ca- and Mg-P minerals mentioned above, the soil solutions were undersaturated with respect to amorphous Strengite ($FePO_4 \bullet 2H_2O$), Wavellite [$Al_3(PO_4)_2(F)_3 \bullet 5(H_2O)$] and amorphous Variscite ($AlPO_4 \bullet 2H_2O$). The soil solutions were strongly undersaturated with respect to all Mg-P minerals (Farringtonite and Newberryite) and Ca-P minerals (Brushite, Monetite, Hydroxyapatite, β-tricalcium phosphate and Octacalcium phosphate). Even Hydroxyapatite, which appeared to be the most stable P-mineral in the samples equilibrated at higher pH levels, was not stable at pH 3. The soil solutions were, however, predicted to be supersaturated with respect to crystalline Variscite. The data suggest that no P solid phase controls the solubility of P at pH 3.

Artificially-aged Samples

The solid phases predicted by the model for the thermally incubated samples were identical to those predicted for the samples incubated via wetting and drying. The values for the saturation indices were also similar for the samples incubated by the two aging methods and therefore only the data for the thermally incubated samples are presented as a representative of artificially-aged samples.

Within pH range of 5 and 7, the values of the saturation indices of the predicted minerals decreased with time, suggesting that some amount of weathering had occurred in course of the incubation. On the other hand, the values of the saturation indices for the predicted minerals for samples taken at a particular time increased with increasing rate of P application. This suggests that as the P concentration of the soil increased, some Ca-P minerals became more stable (Tables 7-8 and 7-9).

Similarly to the field-aged samples equilibrated at pH 5 and 7, the soil solution of the unamended (no WTR) samples at all P-impacted levels were supersaturated with respect to β-tricalcium phosphate, Octacalcium phosphate and Hydroxyapatite (Tables 7-8 to 7-9). The stability of these minerals appears to increase with pH (increased positive SI values). Based on the criteria of Bohn and Bohn (1987), the soil solutions of the samples with no WTR amendment appear to be at equilibrium with Ca-P minerals, Monetite and Brushite. The soil systems were, however, undersaturated with respect to Mg-P (Farringonite and Newberryite) at all P treatment levels. Thus unlike the manure-impacted (Michigan) field samples, Monetite and Brushite are the only minerals that appear to control P solubility in untreated Immokalee sand. No Mg-P solid phases seem to control P solubility in untreated Immokalee sand.

For the WTR amended samples incubated through the two methods and equilibrated at pH 5 and 7, identical P minerals with similar saturation indices were predicted for the soil systems amended with the different WTR sources (Tables 7-8 and 7-9). Soil solutions at all impacted P levels were supersaturated with respect β-tricalcium phosphate, Octacalcium phosphate and Hydroxyapatite; and undersaturated with respect to Monetite, Brushite Farringonite and Newberryite. Similarly to the field-aged WTR amended samples, the results of the model

predictions for the artificially-aged samples also suggest that P solubility from the WTR amended soils is not determined by dissolution-precipitation reactions.

Table 7-8. Soil solution saturation indices for P solid phases predicted from samples thermally incubated at 70 ^{o}C and equilibrated at pH 5.

	Trt	P load	Predicted minerals						
			β-TCP†	OCP‡	MNT††	BST†‡	HA‡‡	FNT†††	NBT‡‡†
Time zero	No-WTR	No P	2.50	1.54	-0.80	-0.91	8.21	-4.12	-1.95
	ABR	No P	2.12	1.43	-2.35	-3.25	7.58	-5.41	-2.95
	ACO	No P	2.06	1.30	-2.63	-2.72	7.27	-4.84	-2.68
	AHL	No P	1.96	1.37	-2.47	-4.78	7.04	-5.08	-2.28
	ALW	No P	1.90	1.36	-2.72	-2.75	6.11	-4.79	-2.51
	No-WTR	Low P	2.87	1.60	-0.36	-0.54	9.24	-3.43	-2.34
	ABR	Low P	2.12	1.51	-2.30	-2.43	6.97	-3.55	-3.51
	ACO	Low P	2.06	1.46	-2.42	-2.89	8.60	-3.23	-2.43
	AHL	Low P	2.12	1.52	-2.34	-2.67	7.96	-3.46	-3.05
	ALW	Low P	1.98	1.28	-2.34	-3.32	7.75	-3.65	-2.69
	No-WTR	High P	3.59	2.00	-0.27	-0.41	11.54	-2.57	-1.75
	ABR	High P	2.72	1.60	-2.06	-2.07	9.69	-2.59	-2.63
	ACO	High P	2.57	1.90	-2.12	-2.74	10.74	-2.42	-2.29
	AHL	High P	2.66	1.83	-2.08	-2.25	9.95	-2.66	-1.82
	ALW	High P	2.47	1.82	-2.01	-2.42	8.72	-2.74	-2.02
4 years	No-WTR	No P	2.22	1.48	-0.79	-0.98	7.59	-4.67	-2.20
	ABR	No P	2.03	1.28	-2.78	-3.84	7.18	-4.75	-2.43
	ACO	No P	1.98	1.32	-2.88	-3.24	7.07	-4.81	-2.38
	AHL	No P	1.86	1.52	-2.62	-3.24	6.93	-5.06	-2.51
	ALW	No P	2.11	1.31	-2.82	-4.03	6.98	-4.94	-2.80
	No-WTR	Low P	2.39	1.57	-0.63	-0.76	7.99	-3.89	-2.13
	ABR	Low P	2.12	1.51	-2.64	-3.47	7.27	-4.14	-2.30
	ACO	Low P	2.19	1.48	-2.57	-2.86	7.01	-4.39	-2.11
	AHL	Low P	2.16	1.53	-2.60	-3.15	7.71	-4.22	-2.18
	ALW	Low P	2.03	1.36	-2.56	-3.35	7.89	-4.18	-2.74
	No-WTR	High P	2.99	1.96	-0.47	-0.57	9.98	-2.92	-1.97
	ABR	High P	2.66	1.69	-2.39	-2.85	9.63	-3.13	-2.18
	ACO	High P	2.74	1.85	-2.33	-2.14	9.09	-3.29	-2.08
	AHL	High P	2.70	1.91	-1.43	-2.76	8.77	-3.17	-2.01
	ALW	High P	2.53	1.89	-2.30	-2.62	9.86	-3.11	-2.05

† β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)]
‡ Octacalcium phosphate [$Ca_4H(PO_4)_3 \cdot 3H_2O$]
†† Monetite ($CaHPO_4$)
†‡ Brushite [$CaHPO_4 \cdot 2H_2O$]
‡‡ Hydroxyapatite [$Ca_5(PO_4)_3OH$]
††† Farringtonite [$Mg_3(PO_4)_2$]
‡‡† Newberyite ($MgHPO_4 \cdot 3H_2O$)

Table 7-9. Soil solution saturation indices for P solid phases predicted from samples thermally incubated at 70 °C and equilibrated at pH 7.

	Trt	P load	Predicted minerals						
			β-TCP†	OCP‡	MNT††	BST†‡	HA‡‡	FNT†††	NBT‡‡†
Time zero	No-WTR	No P	3.01	1.75	-0.73	- 0.83	10.53	-3.43	-1.56
	ABR	No P	2.56	1.62	-2.23	-2.45	9.72	-4.51	-2.36
	ACO	No P	2.48	1.48	-2.34	-2.42	7.83	-4.23	-2.14
	AHL	No P	2.36	1.56	-2.48	-3.13	9.02	-4.03	-2.01
	ALW	No P	2.29	1.55	-2.56	-2.86	9.32	-3.99	-1.82
	No-WTR	Low P	3.46	1.82	-0.33	-0.45	11.84	-2.86	-1.87
	ABR	Low P	2.62	1.72	-2.06	-2.38	10.21	-2.96	-1.94
	ACO	Low P	2.84	1.66	-2.29	-2.56	11.02	-3.04	-2.81
	AHL	Low P	2.65	1.73	-2.22	-2.86	8.94	-2.88	-2.44
	ALW	Low P	2.38	1.45	-2.31	-2.92	9.94	-2.69	-2.15
	No-WTR	High P	4.33	2.28	-0.25	-0.34	14.80	-2.15	-1.40
	ABR	High P	3.10	2.15	-2.02	-2.04	11.18	-2.16	-1.61
	ACO	High P	3.20	1.81	-1.92	-2.17	13.78	-2.28	-2.11
	AHL	High P	3.20	2.16	-1.97	-2.44	12.76	-2.22	-1.83
	ALW	High P	2.98	2.08	-1.98	-1.89	12.43	-2.02	-1.46
4 years	No-WTR	No P	2.68	1.68	-0.72	-0.94	9.73	-3.89	-1.76
	ABR	No P	2.44	1.45	-2.62	-3.35	9.21	-3.96	-1.94
	ACO	No P	2.38	1.50	-2.47	-2.85	8.95	-4.01	-2.01
	AHL	No P	2.24	1.73	-2.71	-3.50	8.88	-4.12	-1.90
	ALW	No P	2.54	1.49	-2.65	-2.85	9.07	-4.22	-2.22
	No-WTR	Low P	2.88	1.78	-0.57	-0.63	10.24	-3.24	- 2.10
	ABR	Low P	2.56	172	-2.19	-3.04	9.32	-3.45	-2.24
	ACO	Low P	2.64	1.68	-2.11	-2.78	8.99	-3.52	-2.19
	AHL	Low P	2.60.	1.74	-2.33	-3.36	10.11	-3.66	- 2.54
	ALW	Low P	2.44	1.54	-2.58	-2.94	9.88	-3.48	- 2.33
	No-WTR	High P	3.60	2.23	-0.43	-0.47	12.80	-2.43	-1.58
	ABR	High P	3.30	2.15	-2.27	-2.53	12.64	-2.75	-1.75
	ACO	High P	3.20	1.93	-2.30	-2.34	11.24	-2.64	-1.64
	AHL	High P	3.25	2.18	-2.21	-2.46	11.65	-2.59	-1.91
	ALW	High P	3.05	2.10	-2.19	-2.77	12.35	-2.61	-1.68

† β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)]
†† Monetite ($CaHPO_4$)
‡‡ Hydroxyapatite [$Ca_5(PO_4)_3OH$]
‡‡† Newberyite ($MgHPO_4 \cdot 3H_2O$)
‡ Octacalcium phosphate [$Ca_4H(PO_4)_3 \cdot 3H_2O$]
†‡ Brushite [$CaHPO_4 \cdot 2H_2O$]
††† Farringtonite [$Mg_3(PO_4)_2$]

The artificially-aged control and WTR amended samples equilibrated at pH 3 were strongly undersaturated with respect to all Ca- and Mg-P minerals predicted by the model, similar to the field-aged samples (Tables 7-10). In addition to the Ca- and Mg-P minerals, the

system appear to be undersaturated with respect to amorphous Variscite for the samples amended with Al-WTRs (Bradenton, Holland and Lowell WTRs) and amorphous Strengite for the samples amended with Fe-WTR (Cocoa WTR).

We hypothesized that P solubility in WTR amended soils is controlled by thermodynamically stable solid phases of Al- and Fe-P. The results of the various modeling efforts compel us to reject this hypothesis and to conclude that P reactions with WTR are not through precipitation reaction. This observation is contrary to the suggestion by Butkus et al. (1998) that P is bound to WTRs through external precipitation reactions. Makris et al. (2004a) identified intraparticle diffusion into micropores as the prominent mechanism in the retention of P by WTRs, and suggested that P immobilized by WTRs should be essentially irreversibly bound. Makris et al. (2004b) reacted Fe- and Al-WTR particles with P for 80 days and then subjected the particles to an energy-dispersive X-ray spectrometer (SEM-EDS) and to electron microprobe analyses. No discrete surficial metal-P phases were detected with SEM-EDS spectroscopy, which led to the hypothesis that P diffuses into particles to reach meso- and micro-pore domains rather than precipitating on external surfaces of the WTRs. Electron microprobe analysis using wavelength-dispersive spectroscopy (EPMA-WDS) on thin-sections of P-treated WTR particles supported intraparticle P diffusion more quantitatively than SEM-EDS. Cross-sectional P distribution analysis of the P-treated WTRs showed significant ($p<0.001$) increases in the relative P concentrations in the interior of the particles (approximately 60 μm inside) with time (from 1 to 80 days) (Makris et al., 2004b). Ippolito et al. (2003) used EPMA-WDS dot maps to assess P distribution in a P-treated Al-WTR equilibrated for 211 days. Dot maps showed no evidence for P surface precipitation, but a uniform amorphous Al-P association throughout the particles (Ippolito et al., 2003). EPMA-WDS data support the notion that P moves towards

the interior of the WTR particles rather than accumulating significantly at the particle surface through precipitation.

Table 7-10. Soil solution saturation indices for P solid phases predicted from samples thermally incubated at 70 ^{o}C and equilibrated at pH 3.

	Trt	P load	Predicted minerals								
			β-TCP†	OCP‡	MNT††	BST†‡	HA‡‡	FNT†††	NBT‡‡†	SGT‡††	VCT‡‡‡
Time zero	No-WTR	No P	-23.5	-22.6	-19.2	-22.9	-11.4	-18.4	-17.5	-	-6.48
	ABR	No P	-24.2	-25.7	-21.3	-25.7	-10.6	-20.2	-18.9	-	-3.65
	ACO	No P	-22.5	-23.0	-25.1	-17.5	-12.6	-19.4	-19.7	-3.56	-
	AHL	No P	-23.6	-24.6	-24.4	-22.6	-13.8	-21.0	-21.4	-	-4.85
	ALW	No P	-21.3	-21.8	-25.5	-24.9	-10.6	-19.8	-19.3	-	-4.37
	No-WTR	Low P	-22.3	-20.5	-19.1	-26.3	-9.51	-19.4	-20.6	-	-4.83
	ABR	Low P	-24.5	-23.0	-22.7	-21.0	-11.8	-21.6	-19.8	-	-2.87
	ACO	Low P	-20.6	-20.9	-20.3	-19.3	-12.7	-20.7	-21.5	-2.37	-
	AHL	Low P	-24.9	-24.1	-25.6	-17.8	-9.90	-21.4	-14.2	-	-3.79
	ALW	Low P	-21.6	-21.8	-21.8	-22.4	-8.79	-22.4	-21.6	-	-3.30
	No-WTR	High P	-24.2	-23.1	-20.1	-16.1	-10.8	-21.7	-19.2	-	-3.32
	ABR	High P	-21.5	-24.7	-18.4	-21.0	-12.1	-24.5	-23.2	-	-2.58
	ACO	High P	-16.1	-25.6	-23.3	-23.7	-15.0	-23.4	-20.7	-2.15	-
	AHL	High P	-21.6	-22.5	-21.3	-24.6	-9.25	-21.0	-21.9	-	-2.68
	ALW	High P	-24.4	-19.9	-17.8	-24.1	-12.3	-25.5	-22.3	-	-2.84
1.5 years	No-WTR	No P	-21.0	-20.9	-21.2	-25.0	-10.7	-19.5	-18.4	-	-8.04
	ABR	No P	-19.1	-19.4	-16.4	-26.7	-12.0	-20.9	-20.1	-	-4.48
	ACO	No P	-24.5	-23.0	-19.2	-23.8	-14.8	-21.3	-19.7	-4.57	-
	AHL	No P	-25.2	-22.0	-25.4	-26.7	-10.8	-21.7	-20.5	-	-6.43
	ALW	No P	-19.3	-19.1	-21.7	-20.9	-11.9	-22.7	-22.8	-	-5.96
	No-WTR	Low P	-20.1	-21.8	-23.1	-17.4	-12.7	-19.8	-19.6	-	-6.21
	ABR	Low P	-24.5	-22.4	-18.1	-22.6	-9.05	-24.3	-21.0	-	-3.44
	ACO	Low P	-21.3	-20.2	-19.6	-21.1	-11.9	-23.3	-20.7	-3.52	-
	AHL	Low P	-19.5	-24.5	-21.8	-19.3	-12.0	-22.3	-16.0	-	-4.94
	ALW	Low P	-20.0	-19.3	-23.0	-24.2	-14.1	-21.0	-21.9	-	-4.59
	No-WTR	High P	-21.2	-21.5	-18.5	-19.3	-12.1	-23.5	-21.3	-	-4.77
	ABR	High P	-19.4	-24.4	-20.5	-22.4	-14.6	-22.9	-24.9	-	-2.65
	ACO	High P	-21.7	-20.0	-18.8	-19.5	-9.32	-20.7	-23.8	-2.70	-
	AHL	High P	-19.6	-21.0	-21.7	-20.3	-10.5	-21.4	-22.1	-	-3.80
	ALW	High P	-21.6	-19.2	-20.2	-21.9	-13.4	-19.0	-23.4	-	-3.53

† β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)]
‡ Octacalcium phosphate [$Ca_4H(PO_4)_3 \cdot 3H_2O$]
†† Monetite ($CaHPO_4$)
†‡ Brushite [$CaHPO_4 \cdot 2H_2O$]
‡‡ Hydroxyapatite [$Ca_5(PO_4)_3OH$]
††† Farringtonite [$Mg_3(PO_4)_2$]
‡‡† Newberyite ($MgHPO_4 \cdot 3H_2O$)
‡†† Strengite ($FePO_4 \cdot 2H_2O$)

Predicting P adsorption and desorption by WTRs

The inability of the chemical equilibrium modeling to predict solid phase control of WTR immobilized P solubility prompted further investigation of the phosphate adsorption mechanism on and within the WTR particles using the constant capacitance model. The model assumes a ligand exchange mechanism and considers the charge on both adsorbate and adsorbent (Goldberg and Sposito, 1984; Goldberg, 1992; Ioannou and Dimirkou, 1994; Lutzenkirchen, 1999; Dimirkou et al., 2002). The model provides a quantitative description of phosphate adsorption, including the effect of varying pH values. Unlike the empirical models, surface complexation models, such as constant capacitance model, are chemical models that attempt to give a general molecular description of the adsorption process. The driving force for the adsorption reaction is the electrostatic interaction (Goldberg and Sposito, 1984; Ioannou and Dimirkou, 1994; Lutzenkirchen, 1999). Because the models take into account the charge on both the adsorbent and the adsorbate, they have wide applicability as well as predictive power over changing conditions of soil pH, ionic strength, and phosphate ion concentration (Goldberg, 1992; Ioannou and Dimirkou, 1996; Dimirkou et al., 2002).

The computer program Ma-Za 2, a program that fits equilibrium constants to experimental data using an optimization technique, was used to obtain optimal values for the anion surface complexation constants in the WTR system, while the PC program Ma-Za 1 was used for the application of the constant capacitance model. The model could be fit to adsorption of phosphate anions well over the entire pH range studied (3-7). The main advantage of the model is its ability to represent changes in anion adsorption occurring with changes in pH.

The pH dependent sorption of P by Al-WTRs over a period of 14 days was plotted as maximum amount of P adsorbed as a function of pH (Figure. 7-1). Figure 7-1 also illustrates the model fit of data obtained for P adsorption by Al-WTRs. Similarly, the experimental data

obtained for P adsorption by Fe-WTR, and model fit of P adsorption data for the Fe-WTR are shown in Figure 7-2. Both the Al- and Fe-WTR showed similar trends in P adsorption behavior for all the initial P concentrations added to the WTRs (Figures 7-1 and 7-2). However, similar to earlier observations (chapter 2), the Al-WTRs adsorbed significantly greater ($p \leq 0.05$) P amounts than the Fe-WTR at all pH levels, for all initial P loads. Similar to previous observations (chapters 4 and 5), no significant differences ($p \geq 0.05$) were observed in the amount of P adsorbed within pH range of 4-7. P adsorbed at pH 3 was, however, significantly smaller ($p < 0.01$) than P adsorbed at the higher pH (4-7) values, for all initial P loads. With the exception of pH 3, where predicted values of adsorbed P concentration far exceeded the observed data, the model produced a close fit to experimental data obtained for the Al- and Fe-WTRs evaluated within pH 4-7 (Figures 7-1 and 7-2).

The ability of the constant capacitance model to fit adsorption isotherm data is illustrated in Figure 7-3. The model points for pH 4-7 were calculated using the corresponding set of phosphate surface complexation constants. The experimental data in these figures were obtained for P adsorption by WTRs at four pH (4-7) values. The actual data points and the corresponding model fits to these points are plotted in the form of a standard adsorption isotherm. The model is able to represent the experimental data well at all four pH values.

The degree of reversibility of the adsorption-desorption reaction determines the amount of immobilized P released by the WTRs. The relationships between P adsorption and desorption for the WTR samples equilibrated at pH 6 are presented in Figure 7-4. Figure 7-4 also illustrates the model fit of the adsorption-desorption relationship of the WTRs. Only a small fraction (≤ 2 %) of the sorbed P by the WTRs was released. The WTRs that adsorbed high proportions of applied P during adsorption reaction tended to release lower proportions during desorption reaction, and

vice versa. The data suggest a very strong hysteresis in the adsorption-desorption behavior, indicating a partial irreversibility of the adsorption-desorption reaction. Within pH values of 4-7, the model predictions mirrored experimental data reasonably well for all the WTRs (Figure 7-4). Correlation analysis, using the PROC CORR model of the SAS software (SAS Inst., 1999) showed a significant correlation ($p < 0.001$) between the predicted and the experimental data, with a coefficient of determination (r^2) value of ≥ 0.7. Similar trends were obtained for the WTRs equilibrated within the pH range of 4, 5, and 7 (data not presented).

The combined data suggest that phosphate adsorption by the WTRs can be described with the constant capacitance model. This model assumes a ligand exchange adsorption mechanism and is therefore an appropriate representation of the surface complexation behavior of specifically adsorbed phosphate ions (Ioannou and Dimirkou, 1994; Lutzenkirchen, 1999; Dimirkou et al., 2002). The good fit of the model to phosphate adsorption and desorption by the WTRs suggests that inner-sphere surface complexation could be the appropriate P retention mechanism for these materials. The charge of both the adsorptive ion and the adsorbent surface were considered by the model.

Makris (2004) showed that there is a strong hysteretic P desorption by WTRs and attributed this desorption behavior to steric limitations to P movement through “bottle-necks” consisting of complex metal-organic C assemblages (Makris, 2004). The constant capacitance modeling of P adsorption by WTRs suggests that, in addition to the bottleneck-shaped micropores of the WTRs, inner-sphere surface complexation could be the mechanism that largely limits P desorption from the WTR microsites. Thus, once immobilized by the WTR particles, the P is essentially irreversibly bound, barring destruction of the WTR particles which favors long-term stability of sorbed P by WTRs.

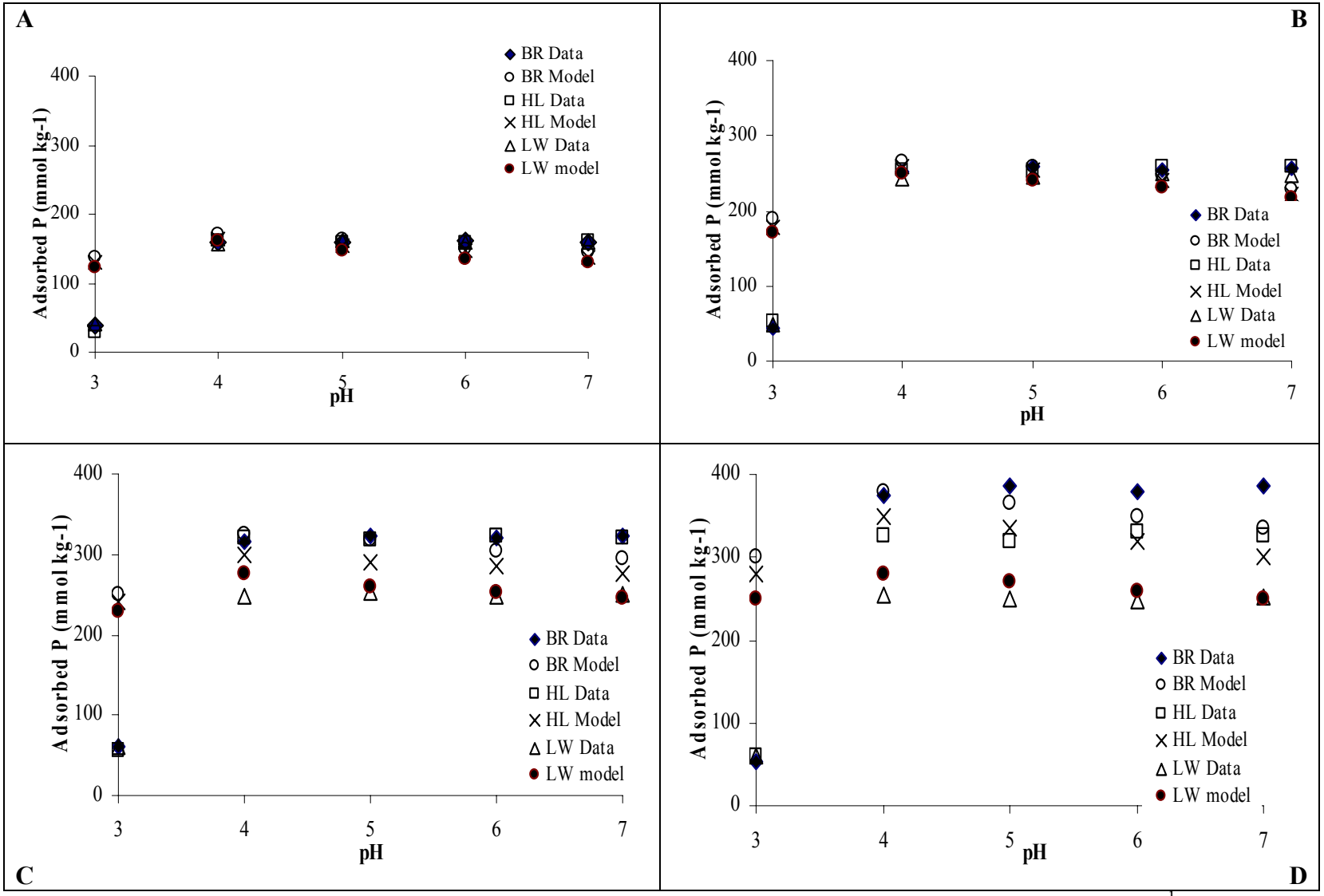


Figure 7-1 Phosphorus "adsorption envelope" on Al-WTR system at initial P concentrations (C_0) of A=0.82 mmol L^{-1}, B=1.30 mmol L^{-1}, C=1.61 mmol L^{-1}, and D=1.94 mmol L^{-1}). BR= Bradenton WTR, HL= Holland WTR, LW= Lowell WTR.

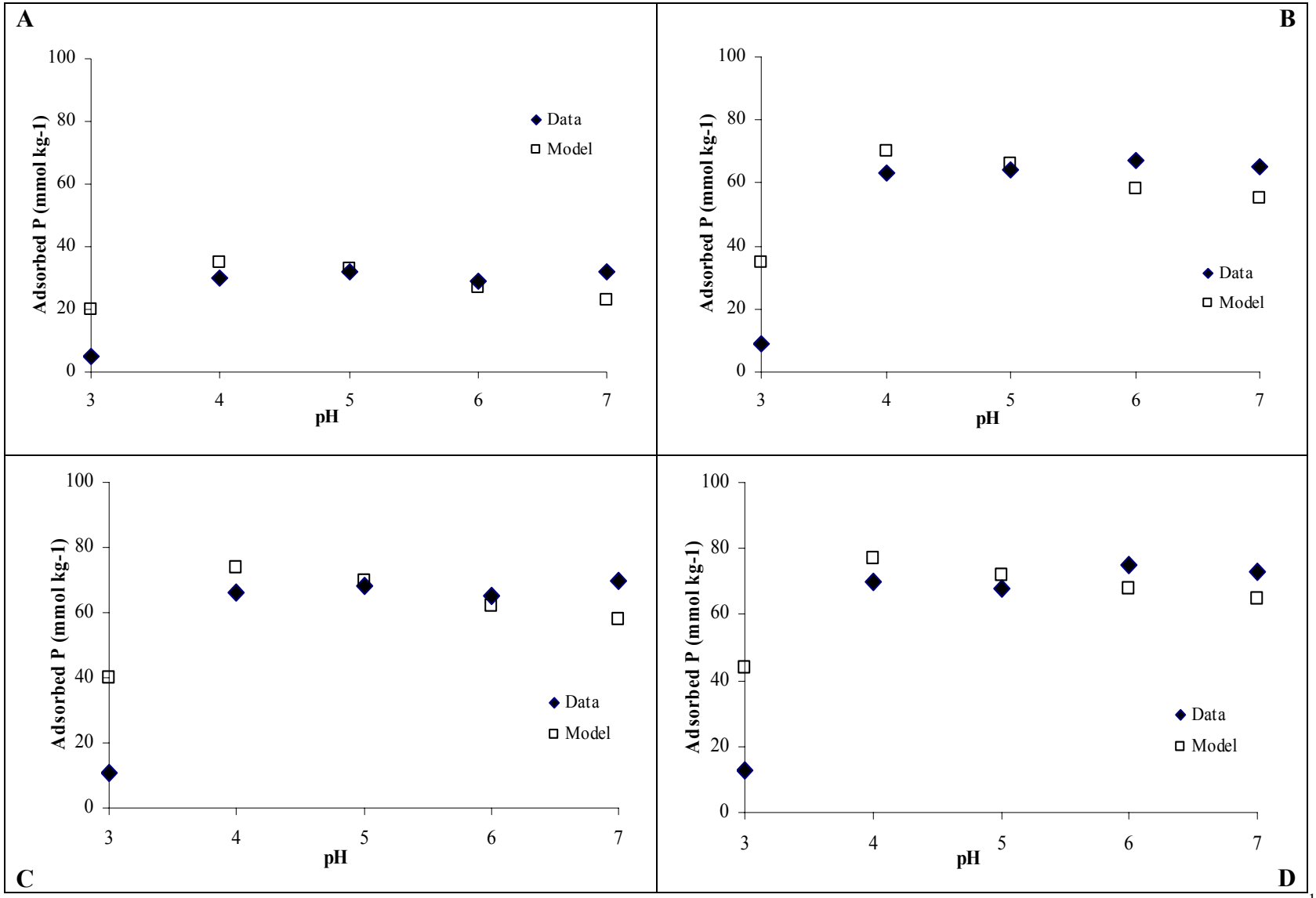


Figure 7-2. Phosphorus "adsorption envelope" on Fe-WTR (Cocoa WTR) system at initial P concentrations (C_0) of A=0.16 mmol L^{-1}, B=0.32 mmol L^{-1}, C=0.48 mmol L^{-1}, and D=0.82 mmol L^{-1}).

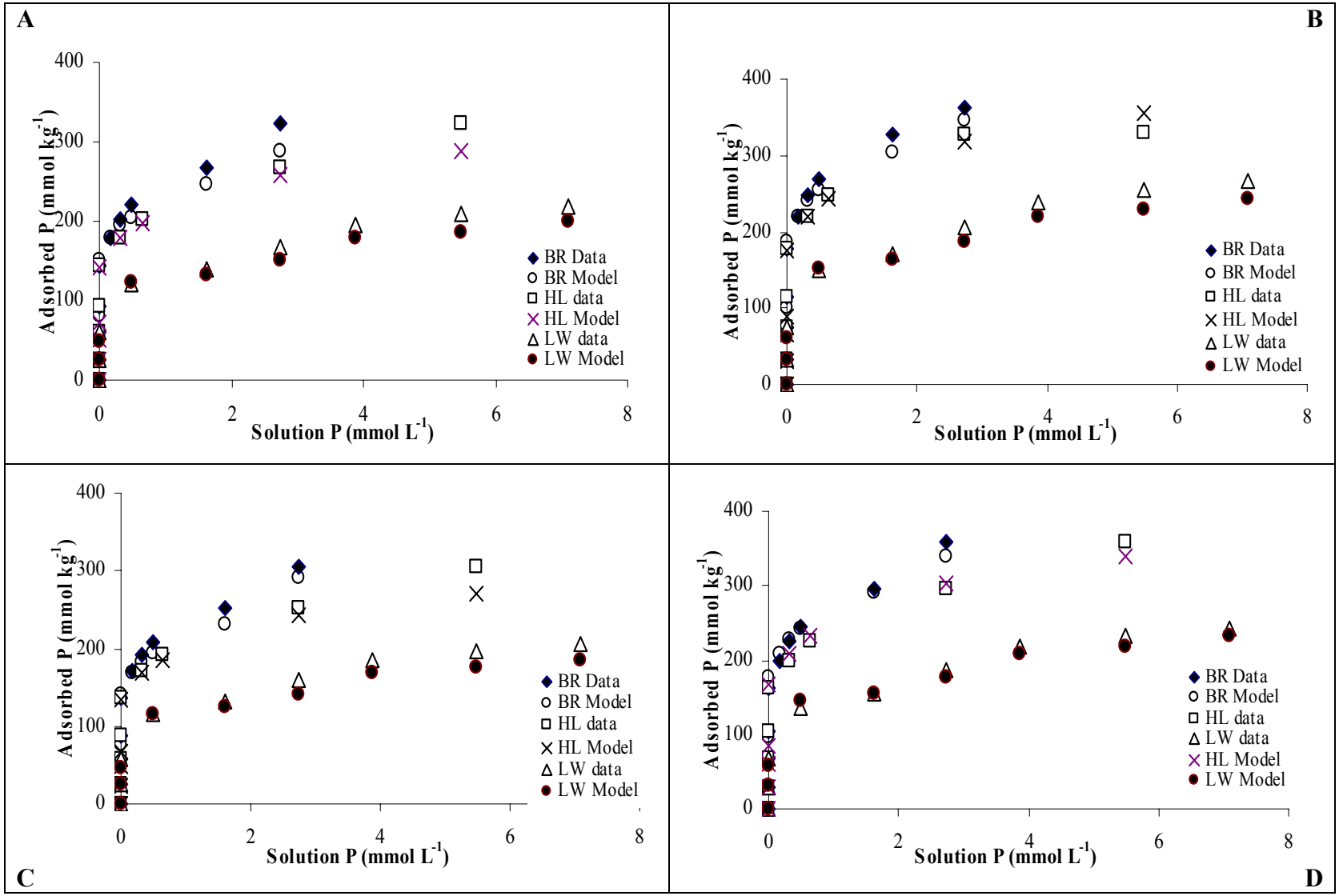


Figure 7-3. Phosphorus adsorption isotherms on Al-WTR system for the experimental data and the model prediction, at different pH values (A=4, B=5, C=6, D=7). BR= Bradenton WTR, HL= Holland WTR, LW= Lowell WTR

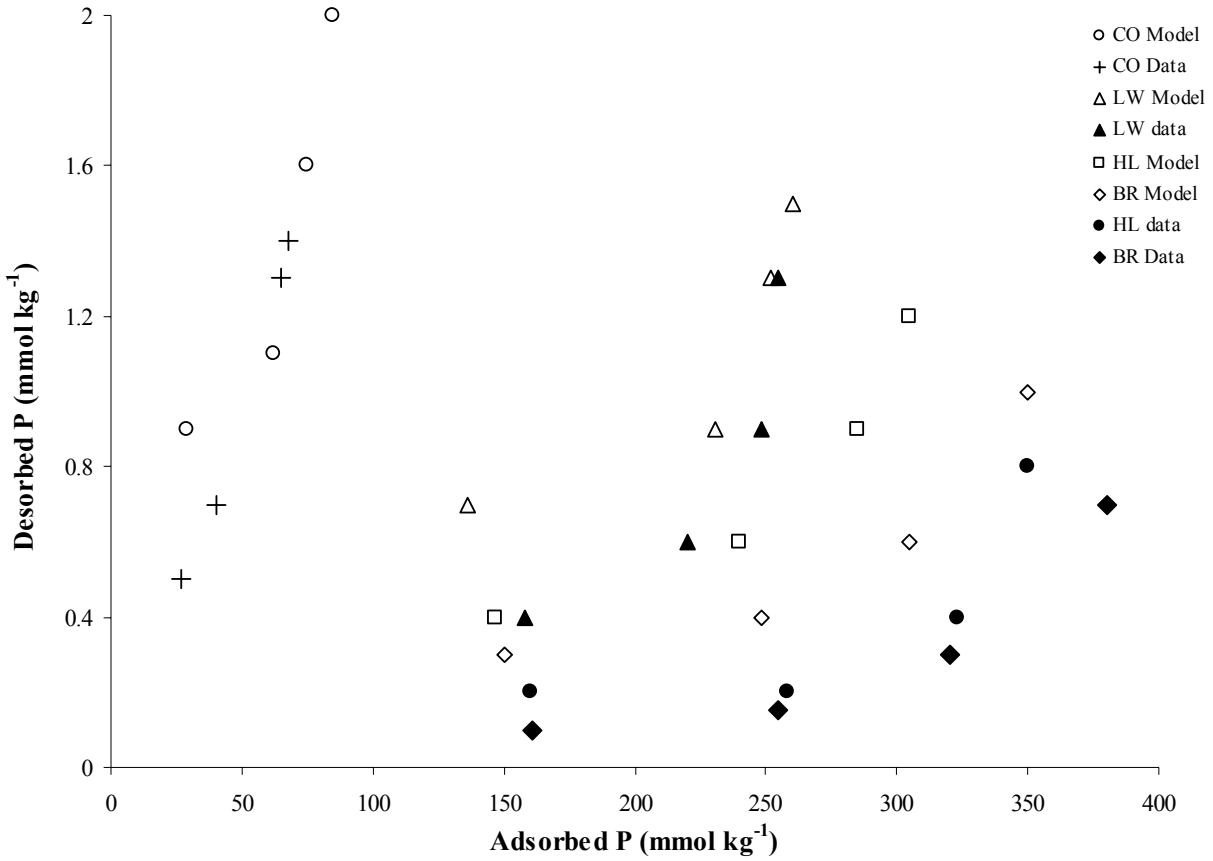


Figure 7-4. Relationship between adsorbed and desorbed phosphorus by Al- and Fe-WTRs equilibrated at pH 6. CO = Cocoa WTR (Fe-based WTR), BR= Bradenton WTR, HL= Holland WTR, LW= Lowell WTR

CHAPTER 8
LONG-TERM STABILITY OF DRINKING-WATER TREATMENT RESIDUALS (WTR) IMMOBILIZED PHOSPHORUS

Phosphorus loss from poorly P-sorbing soils is one of the major factors responsible for accelerated eutrophication of surface waters in many locations in Florida and other eastern states of USA. Excessive soluble phosphorus (P) concentrations in these soils can be controlled through the additions of drinking-water treatment residuals. Drinking-water treatment residuals are by-products of the drinking-water treatment process and are physical mixtures of Al or Fe hydr(oxides) that originate from flocculant (Al or Fe salts) additions made during the processing of drinking-water.

Short-term laboratory, greenhouse, and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P concentrations in runoff and leaching. However, the long-term stability of P sorbed by WTRs has only been qualitatively addressed in laboratory experiments. Studies have shown that adsorption of P by WTRs is strongly hysteretic and essentially independent of pH; once sorbed in the internal micropores of WTR, P release is unlikely. However, field experiments and other approaches to accurately quantify P lability are needed to test WTR efficacy in reducing soluble P concentrations and to confirm trends observed in, or inferred from, laboratory studies.

The overall objective of the study was to assess the long-term stability of WTR immobilized P. Specific objectives addressed in this dissertation were:

- to evaluate changes in lability of WTR immobilized P with time
- to determine pH effect on lability of WTR immobilized P
- to assess the stability and longevity of WTR immobilized P under field conditions
- to evaluate long-term effectiveness of WTR in improving leachate and runoff quality and

- predict solid phases controlling solubility of WTR immobilized P, and evaluate the stability of the predicted solid phases.

Appropriate hypotheses were formulated as follows:

- **H1**. Soil amendment with WTR will reduce P solubility in P impacted soils under natural (field) conditions.
- **H2**. Aging will induce changes in the nature of WTR-P binding that will prevent desorption of WTR immobilized P.
- **H3**. Sorbed P will remain unaffected by reasonably anticipated changes in important soil parameters (e.g. pH).
- **H4**. WTR application will reduce labile P concentrations in runoff and leachate, thus improving runoff and leachate quality.
- **H5**. Stable Al- and Fe-phosphate minerals will control solubility of WTR immobilized P, thus ensuring that WTR immobilized P remains stable in the long-term.

Several approaches were utilized to test these hypotheses, including artificial aging of "fresh" WTR and WTR amended soils through repeated wetting and drying, and thermal incubations at elevated temperatures (46 and 70 ^{o}C) in an attempt to hasten reactions that could take decades to occur in the field. Another approach dealt with field monitoring of the longevity of WTR immobilized P in two field sties in Western Michigan for 7.5 years after a one-time WTR application. We also evaluated WTR effectiveness in P immobilization in a field study in Kissimmee watershed, FL, where plots were amended with different P sources and at different rates of application. The next approach utilized rainfall simulation techniques to evaluate WTR effects on runoff P many years after WTR application. Lastly, we used chemical equilibrium modeling to assess the solid phases likely controlling P solubility of WTR amended soils.

The first two objectives were to evaluate aging and pH effects on the lability of WTR immobilized P using artificially-aged WTR amended soils. Artificial aging of the WTR amended samples was expected to simulate natural long-term weathering processes that could influence the stability of sorbed P. Artificial aging was achieved through incubation at elevated

temperatures and through repeated wetting and drying. The samples were either incubated via wetting and drying for 2 years or thermally incubated at elevated temperatures for up to 4.5 years. Using a modified isotopic (^{32}P) dilution technique, coupled with a stepwise acidification procedure, we monitored changes in labile P concentrations over time. This technique enabled us to evaluate the effect of pH on the lability of WTR immobilized P.

Significant reductions in labile P values of the WTR amended soil samples occurred over time with repeated wetting and drying cycles within pH range of 4 - 7. A significant decrease in labile P was observed after 5 months of incubation and the reduction of labile P continued with additional wetting and drying cycles until the system apparently reach equilibrium at 1.5 years (~ 40 wet and dry cycles). Within the pH range of 4 - 7, labile P concentrations were ultimately reduced by ≥ 75 %, relative to the no-WTR (control) samples. No reduction in labile P concentrations was observed for the WTR amended samples equilibrated at pH 3. After 4.5 years of thermal incubation, a significant decrease in labile P pools (~ 80 % relative to the samples without WTR amendment) was observed at all pH values, including pH 3. Thus, if thermal incubation truly predicts long-term aging under field conditions, not only will the WTR immobilized P remain fixed for a long time within typical soil pH values, but the destabilization of the WTR immobilized P at pH 3 will also be eliminated over time. From this experiment, we concluded that WTR application is capable of reducing labile P concentration in P impacted soils and to do so for a long time and that within the commonly encountered pH range in soils, WTR immobilized P is stable.

The next objective was to assess the stability of WTR immobilized P under field conditions. This study was conducted on a poorly P-sorbing Florida soil amended with different P sources (biosolids, manure and inorganic fertilizer) applied at P-based (56 kg ha^{-1}) and N-

based (224 kg ha^{-1}) rates. This field study was initially designed to determine WTR effects on P losses to surface and groundwater from land amended with different P sources and applied at different rates. However, the fall of 2004 was an especially busy hurricane season in south FL, and the experimental plots were heavily flooded. The flooding appeared to have compromised our treatments (moved soil and associated treatments across plots), which compelled us to terminate the experiment. Measurements taken after the flooding, however, provided a unique opportunity to assess the stability of WTR immobilized P following severe flooding of WTR amended plots. Soil samples taken from the field after the hurricanes showed that despite the flooding of the field and the resultant movement of soil and amendments across individual plots, WTR effects were still obvious. The soluble P values measured from the A (0-5 cm) horizon plots amended with WTR were significantly lower than in the plots without WTR amendments. The total- and oxalate extractable Fe+Al concentrations of the surface (0-5 cm) horizon of WTR amended plots also remained significantly greater than in plots without WTR amendment. The consistently high Al and Fe contents of the WTR amended plots suggests that those plots still possess the capacity to sorb P. The degree of P saturation (DPS) values of the WTR amended plots remained below the environmental threshold value of 25 % suggested for Florida soils. This suggests that, despite the flooding of the field, the WTR amended plots retained the capacity to retard P movement.

Measurements in the Bh horizon suggest excessive P leaching from the field during the flooding of the field. The greatest P leaching apparently occurred in the plots without WTR amendments and the control plots; very little or no P leaching occurred in the WTR amended plots. Thus, despite the extensive flooding of the fields, the WTR was able to retain the

immobilized P and prevent excessive P leaching. From this study, we concluded that WTR immobilized P is stable even under severe flooding conditions

Another objective was to assess the long-term stability of sorbed P under field conditions. Two one-time WTR amended P-impacted soils with long histories of poultry manure application in Western Michigan were utilized for the study. The WTR effects were monitored for 7.5 years (spring 1998 to fall 2005). For both sites, there was a significant increase in the concentration of total- and oxalate (200 mM)-extractable Al and Fe concentrations in the WTR amended plots over time, leading to a reduction in the P saturation ratio (PSR) values by values < 50 % of the PSR values of the control plots. The reduction in PSR suggests that the WTR amended plots have been enhanced to sorb P. Consistent with the PSR values, water soluble P (WSP) and labile P concentrations were reduced significantly in the WTR amended plots at both sites. There was no evidence of release of WTR immobilized P over time as measured by the WSP labile P values from both sites. The WSP and labile P data demonstrate delayed, but steady, reduction in soluble P with time, and ultimate reductions of ~ 60 to 70 % relative to the control soils. The results of this study led to the conclusion that WTR is not only an effective amendment to control soluble P in P-impacted soils, but WTR immobilized P is stable and will remain fixed for a long time.

Again, we evaluated long-term effectiveness of WTR in improving leachate and runoff quality using the rainfall simulation technique. We utilized P-impacted soils from the Michigan field study sites collected in fall 2005 (7.5 years after WTR amendment) for this study. Amendment with WTR reduced dissolved P (TDP) and bioavailable P (BAP) by > 50 % from both sites, and decreased the total (runoff + leachate) flow-weighted TDP concentrations from ~ 2.5 mg L^{-1} to ~ 0.86 mg L^{-1} at site 1, and from ~ 3.2 mg L^{-1} to ~ 0.94 mg L^{-1} at site 2. The reduced values exceed values (0.01-0.05 mg L^{-1}) usually associated with eutrophication of

surface waters, but are below a solution concentration of 1.0 mg L^{-1} ($3.2 * 10^{-5}$ M) occasionally used as a benchmark for wastewater discharges to rivers and streams. From this result, we concluded that, WTR is capable of reducing labile P in runoff and leachate for a long time, and eroded WTR-P should have negligible effects on water quality.

The final objective was to investigate the influence of various species of Fe and Al on phosphate solubility and reactions, and to speculate about solid phases controlling the solubility of WTR immobilized P. We utilized both artificially- and naturally (field)-aged WTR amended samples for the study, using MINTEQA2 geochemical model to do the calculations.

Similar solid phases were predicted for both artificially and field-aged samples. For both types of samples, soil solutions were supersaturated (positive saturation indices) with respect to Hydroxyapatite [$Ca_5(PO_4)_3OH$], β-tricalcium phosphate [$Ca_3(PO_4)_2$ (β)] and Octacalcium phosphate [$Ca_4H(PO_4)_3 \bullet 3H_2O$], indicating that those minerals (if present) were not playing a major role in P solubility. On the other hand, soil solutions were undersaturated (negative saturation indices) with respect to Brushite ($CaHPO_4 \bullet 2H_2O$), Monetite ($CaHPO_4$), Farringtonite [$Mg_3(PO_4)2$] and Newberyite ($MgHPO_4 \bullet 3H_2O$), suggesting that these minerals will be dissolving in the soil solution and will not control P solubility. Thus no solid phase was predicted by the model to control the solubility of WTR immobilized P.

The inability of the chemical equilibrium model to predict solid phase control of P solubility in WTR immobilization prompted further investigation of phosphate adsorption mechanism on and within the WTR particles using the constant capacitance model. The model produced a close fit to experimental data obtained for the Al- and Fe-WTRs evaluated within pH 4-7, suggesting that inner-sphere surface complexation could be the P retention mechanism for the WTRs. The constant capacitance modeling of P adsorption by WTRs suggests that, in

addition to the bottleneck-shaped micropores of the WTRs, inner-sphere surface complexation limits P desorption from WTR microsites. Thus, once immobilized by the WTR particles, the P is likely irreversibly bound, barring destruction of the WTR particles.

From the various studies, we conclude that WTR is an effective amendment to control labile P in P-impacted soils and that WTR immobilized P is stable and will remain fixed for a long time, independent of common soil pH values. Co-applying WTRs with other residuals (manures, biosolids) could effectively counter P risks associated with the residuals and allow land application of the organic P sources even in sensitive watersheds. For example, WTR could be blended with manures or biosolids (up to 25 g kg^{-1}) before application and applied at N-based rate (224 kg ha^{-1}) in the Kissimmee watershed. On the other hand, WTRs could be mixed (~ top 30 cm of the soil) with high P soils (hot spots) in the Kissimmee watershed at a rate of up to 50 Mg ha^{-1} (~25 tons $acre^{-1}$) to counter P risks associated with P-impacted soils. Future studies should focus on developing dynamic models that accurately predict the long-term fate of WTR immobilized P.

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BIOGRAPHICAL SKETCH

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