

Lability of Drinking Water Treatment Residuals (WTR) Immobilized Phosphorus: Aging and pH Effects

Sampson Agyin-Birikorang* and George A. O'Connor

ABSTRACT

Time constraints associated with conducting long-term (>20 yr) field experiments to test the stability of drinking water treatment residuals (WTR) sorbed phosphorus (P) inhibit improved understanding of the fate of sorbed P in soils when important soil properties (e.g., pH) change. We used artificially aged samples to evaluate aging and pH effects on lability of WTR-immobilized P. Artificial aging was achieved through incubation at elevated temperatures (46 or 70°C) for 4.5 yr, and through repeated wetting and drying for 2 yr. Using a modified isotopic (³²P) dilution technique, coupled with a stepwise acidification procedure, we monitored changes in labile P concentrations over time. This technique enabled evaluation of the effect of pH on the lability of WTR-immobilized P. Within the pH range of 4 to 7, WTR amendment, coupled with artificial aging, ultimately reduced labile P concentrations by ≥75% relative to the control (no-WTR) samples. Soil samples with different physicochemical properties from two 7.5-yr-old, one-time WTR-amended field sites were utilized to validate the trends observed with the artificially aged samples. Despite the differences in physicochemical properties among the three (two field-aged and one artificially aged) soil samples, similar trends of aging and pH effects on lability of WTR-immobilized P were observed. Labile P concentrations of the WTR-amended field-aged samples of the two sites decreased 6 mo after WTR amendment and the reduction persisted for 7.5 yr, ultimately resulting in ≥70% reduction, compared to the control plots. We conclude that WTR application is capable of reducing labile P concentration in P-impacted soils, doing so for a long time, and that within the commonly encountered range of pH values for agricultural soils WTR-immobilized P should be stable.

THE use of drinking water treatment residuals (WTR) to control excessive soluble P concentrations in 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, 2002b; O'Connor et al., 2002; Dayton et al., 2003; Makris, 2004; Makris et al., 2004a, 2004b; Novak and Watts, 2004; Dayton and Basta, 2005; Elliott et al., 2005; Makris et al., 2005a, 2005b, 2005c; Novak and Watts, 2005; Silveria et al., 2006). One field study (Agyin-Birikorang et al., 2007) demonstrated long-term (about 7.5 yr) reduction in soluble P concentrations when WTR was applied. Time constraints associated with conducting even longer-term (>20 yr) field experiments to test the stabil-

ity 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). Martínez and McBride (1998) synthesized aged Cd, Cu, Pb, and Zn coprecipitates with amorphous iron hydroxides at 70°C thermal heating for 2 mo. 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 wk 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. Martínez et al. (1999) demonstrated that Pb initially sorbed onto soil oxides and ferrihydrite (Fe[OH]₃ × H₂O) was released into solution after thermally treating the minerals for 2 mo at 70°C. Ford et al. (1997) conducted an aging experiment (pH 6, heating at 40–70°C for 2–6 wk) 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. Martínez et al. (2001) studied Pb solubility at 70°C after prolonged aging (1.5 yr) 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.

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Abbreviations: Al-WTRs, alum-based WTR; DPS, degree of P saturation; Fe-WTRs, iron-based WTR; ICP-AES, inductively coupled plasma-atomic emissions spectroscopy; PSI, P saturation index; SAS, statistical analysis system; SSA, specific surface area; TSP, triple superphosphate; WSP, water-soluble P; WTR, drinking water treatment residuals.

The researchers dried synthetic MnO at 37°C for 24 h, and then hydrated it for 24 h, with wetting and drying cycles repeated three times over 7 d. Repeated wetting and drying resulted in a nonreversible decrease in particle size. After the 7-d incubation period, total proton binding capacities determined by acid-base titrations decreased with cyclically rewetting and drying. However, inspection by scanning electron microscopy revealed fine-grained, amorphous particles, and X-ray diffraction results indicated no crystallinity (Kennedy et al., 2004). The authors 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).

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 WTR thermally incubated at 46 and 70°C for 2 yr. We hypothesized that the structural reorganization associated with aged metal oxides contained in the WTR 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. We also evaluated the lability of P in one-time 7.5 yr WTR-amended field plots.

MATERIALS AND METHODS

Soil and Drinking Water Treatment Residuals Characterization

Native Immokalee sand (sandy, siliceous, hyperthermic Arenic Alaquods) was collected from the University of Florida Research and Education Center in Immokalee, FL, and used in the artificial aging study. The soil had no history of amendment with manure and has 'very low' soil test P and very coarse texture. Multiple random samples were collected from the A horizons (0–15 cm), and were thoroughly mixed to yield a composite sample. Four WTR samples were used in this study: three were Al-based (Al-WTR, alum-based WTR), and one was Fe-based (Fe-WTR, iron-based WTR). The Al-WTRs were obtained from one water treatment plant in Bradenton, FL, one plant in Holland, MI, and one plant in Lowell, AR. The Fe-WTR was obtained from a plant in Cocoa Beach, FL.

Samples were air-dried and passed through a 2-mm sieve before analyses. Particle size distribution of the soil 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 CaCl₂ solution using a glass electrode (McLean, 1982). Following digestion according to the USEPA Method 3050A

(USEPA, 1986), total recoverable P, Fe, and Al in the WTR and soil samples were determined using inductively coupled plasma-atomic emissions spectroscopy (ICP-AES) (PerkinElmer Plasma 3200, PerkinElmer, Wellesley, MA). Oxalate (200 mM)-extractable P, Fe, and Al of both WTR and soil samples were determined by ICP-AES after extraction at a 1:60 solid/solution ratio, following the procedures of Schoumans (2000). Phosphorus saturation index (PSI) for the WTR samples (Elliott et al., 2002a) and the degree of P saturation (DPS) for the soil samples (Nair and Graetz, 2002) were calculated as the moles of oxalate-extractable P divided by the sum of moles of oxalate-extractable Fe and Al. For the DPS calculation, a saturation factor (α) of 0.55 was incorporated in the denominator, as suggested by Nair and Graetz (2002) for Florida soils. Small PSI and DPS values (PSI < 0.1, DPS < 0.25) suggest excess P sorption capacity and limited P lability.

Sample Preparation

The air-dried soil samples were amended with 25 g kg⁻¹ of air-dried subsamples of the four WTR samples described above. Phosphorus was added as triple superphosphate (TSP) solution at three rates: 0, low, and high to roughly mimic field application rates. The "low rate" of 43 mg P kg⁻¹ (about 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 Mislav, 2001). The "high" P rate equals 100 mg P kg⁻¹ soil, and represents a highly P-impacted soil. The TSP 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 of each treatment were prepared, making a total of forty-five samples for each aging technique. The experimental design was a completely randomized design (CRD) with treatments as shown in Table 1.

Artificial Aging of Soil Samples

Artificial aging of the samples was achieved either through thermal incubation or wet and dry incubation. For the thermal incubation, subsamples of the equilibrated WTR-amended soil samples were placed in incubators and maintained at either 23, 46, or 70°C for 4.5 yr. No attempt was made to control soil moisture during incubation. Studies have shown that thermal incubation of metal oxides at elevated temperatures (>45°C) encourages structural changes that simulate long-term weathering reactions in the field (Spadini et al., 1994; Ford et al., 1997; Martínez and McBride, 1998; Makris et al., 2005a). We hypothesized that elevated temperatures would provide the necessary thermal energy for structural rearrangements with time. The changes in particle conformation, toward a lower free energy of the system, would either exclude or occlude sorbed P by the WTR. The wet and dry incubation, on the

Table 1. Treatments in the experimental design (completely randomized design).

Treatments		
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)

† Letters in parentheses are abbreviations for the four drinking water treatment residuals (WTR) samples: BR = Bradenton, HL = Holland, LW = Lowell and CO = Cocoa.

other hand, was performed by placing P-equilibrated samples of WTR-amended soil in an incubator maintained at 23°C and kept wet (about 80% of water holding capacity) for 7 d. The samples were then air-dried at 23°C in the incubator until the mass of samples became constant. The wet and dry cycles continued for 2 yr (54 cycles). Representative samples were collected periodically and analyzed for labile P concentrations using a modified isotopic dilution technique coupled with a stepwise acidification procedure.

Field-Aged Drinking Water Treatment Residuals-Amended Soil Samples

Field-Aged WTR-amended soil samples were collected from one-time WTR (Holland WTR)-amended fields (two sites) in western Michigan (Jacobs and Teppen, 2000). Soils at both sites had a long-term (>10 yr) history of heavy poultry manure applications. The field study lasted for 7.5 yr, (spring 1998 through fall 2005) but the WTR was applied (about 114 Mg ha⁻¹) only in spring 1998. Detailed description of soils and field layout are presented in Jacobs and Teppen (2000) and Agyin-Birikorang et al. (2007).

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 diam.) from the top 20-cm depth of each plot. Soil surface samples were similarly collected each fall in 1998 through 2005 for analyses to monitor changes in labile pools of P following the WTR application.

Determination of Labile Pools of Phosphorus

Two grams (oven-dry equivalent) of each soil sample were placed in centrifuge tubes to which 20 mL of deionized water was added, giving a solid/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 d in an end-over-end shaker. The samples were then spiked with 50 µL of a solution containing ³²P (500 kBq mL⁻¹) and returned to the shaker to isotopically equilibrate for 3 d. The pH of the samples was maintained at the 5 pH levels during the equilibration period. After equilibration, the samples were centrifuged at a relative centrifuge force of 8000 g for 10 min at constant temperature (24 ± 2°C), and filtered through 0.2-µm filters (Sartorius). Activities of radioactive P in the filtrates were assessed using liquid scintillation (Beckman LS 5801, Global Medical Instrumentation Inc., Ramsey, MN) counting. Phosphorus concentrations of the filtrates were 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, run in parallel with the soil suspensions (Lombi et al., 2003; Hamon et al., 2004). The labile pools (*E*) of P were determined as reported in Hamon et al. (2002):

$$E = (C_{\text{sol}}/C_{\text{sol}}^{\text{s}}) R * (V/W) \quad [1]$$

where C_{sol} is the concentration of water-extractable P in solution (µg mL⁻¹), $C_{\text{sol}}^{\text{s}}$ 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:

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

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

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

Statistical Analyses

Data from the artificially aged samples were analyzed as a factorial experiment with the CRD using the general linear model, PROC GLM, procedure of the SAS software (SAS Institute, 1999). The data from the field-aged samples, on the other hand, were statistically analyzed as a factorial experiment with a randomized complete block design (RCBD), using the PROC GLM procedure of the SAS software (SAS Institute, 1999). The means of the various treatments were separated using a single degree of freedom orthogonal contrast procedure at a significance (α) level of 0.05. Time series analyses were conducted using the PROC TSCSREG procedure of the SAS software (SAS Institute, 1999). Correlation analysis, with the PROC CORR procedure of the SAS software (SAS Institute, 1999), was used to evaluate the relationship between the two incubation (thermal and wet and dry) methods.

RESULTS AND DISCUSSION

The term ‘labile P’ as used in this paper describes the total isotopically available pool of P, and represents the sum of isotopically exchangeable P in the solid phase and soluble P (i.e., P in solution phase) (Hamon et al., 2002). The isotopic dilution technique has been widely employed for estimating the labile pool of P in soils, often termed the ‘E-value’ (e.g., Talibudeen, 1957; Tran et al., 1988; Morel and Plenchette, 1994; Tuominen et al., 1998; Bertrand et al., 2006), as well as P availability in different fertilizer sources (e.g., Hendricks and Dean, 1947; Frossard et al., 1996; Zapata and Zaharah, 2002; Mohanty et al., 2006). This technique was used to monitor the changes in lability of WTR immobilized P as affected by the aging process, and changes in soil pH.

Physicochemical Characterization of Soils and Drinking Water Treatment Residuals Samples

The Immokalee sand and the WTR samples were analyzed for selected physicochemical properties (Table 2). The pH of Al-WTRs was circumneutral (6.5–7.1), within the range of pH values reported for Al-WTRs (6.0–8.4; Makris and O’Connor, 2007), and may result from pH adjustment with alkaline materials (i.e., calcium hydroxide) during drinking water treatment. 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 WTR originates from the suspended materials removed from raw water sources treated in drinking water treatment plants and ultimately becomes a part of the WTR structure. Total Al ranged from 68 to 90 g Al kg⁻¹, within normal ranges reported by others (15–177 g Al kg⁻¹; Dayton et al., 2003; Makris, 2004). Oxalate-extractable Al values were close to total Al (80–90% of the total), suggesting an amorphous nature of the Al-WTRs. 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). Phosphorus retention is strongly related to amorphous Fe and Al concentrations. Gallimore et al. (1999), Dayton et al. (2003), and Dayton

Table 2. General physicochemical properties of soil and drinking water treatment residuals that were used in aging experiment. Numbers are mean values of six replicates \pm one standard deviation.

Property	WTR				Soil
	Bradenton Al-based	Holland Al-based	Lowell Al-based	Cocoa Fe-based	Immokalee N/A§
Source					
Form	Al-based	Al-based	Al-based	Fe-based	N/A§
Sand-size (%)	72.5	76.0	80.4	86.5	89.3
Silt-size (%)	12.7	11.8	11.5	12.4	4.60
Clay-size (%)	14.8	12.2	8.13	1.14	6.10
pH	6.5	7.1	6.8	5.1	5.6
Total P (g kg ⁻¹)	3.42 \pm 0.24	1.84 \pm 0.26	0.83 \pm 0.14	0.71 \pm 0.22	0.03
Total Al (g kg ⁻¹)	90.1 \pm 12.2	68.2 \pm 16.2	77.1 \pm 18.1	2.24 \pm 0.32	0.06
Total Fe (g kg ⁻¹)	6.24 \pm 0.63	8.71 \pm 0.42	10.7 \pm 2.61	242 \pm 362	0.11
Oxalate P (g kg ⁻¹)	2.98 \pm 0.12	1.66 \pm 0.11	0.74 \pm 0.13	0.61 \pm 0.14	0.01
Oxalate Al (g kg ⁻¹)	79.1 \pm 12.1	54.3 \pm 6.20	68.2 \pm 8.40	1.92 \pm 0.41	0.04
Oxalate Fe (g kg ⁻¹)	5.24 \pm 1.10	7.22 \pm 0.83	16.8 \pm 1.33	141 \pm 164	0.08
PSI†	0.02	0.03	0.02	<0.01	N/A
DPS‡	N/A	N/A	N/A	N/A	0.18

† P saturation index.

‡ Degree of P saturation.

§ Not applicable.

and Basta (2005) concluded that the amorphous (oxalate-extractable), rather than the total Al content of WTR, determines their effectiveness in reducing runoff P. This suggestion is consistent with the very small PSI values (about 0.02), which gives an indication that the Al-WTRs can be effective sorbents for P.

The Fe-WTR (Cocoa WTR) had acidic pH (5.1) (Table 2). Studies have shown that most Fe-WTRs are alkaline (pH values 7.2–9.2; Makris and O'Connor, 2007); however, pH values of 4 and 5.6 were reported for two Fe-WTRs investigated by Makris (2004). 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 Fe-WTRs (50 to 150 g kg⁻¹; ASCE, 1996), but within the range of values (162–260 g kg⁻¹) reported by Makris and O'Connor (2007). 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. Iron-based WTRs had reduced oxalate-extractable Fe values as a percentage (45 to 64%; Makris and O'Connor, 2007) of total Fe compared with the Al-WTRs.

The Immokalee fine sand was acidic (pH = 5.6) and contained small amounts of total Fe and Al (Table 2). Despite the low oxalate-extractable Fe and Al, the soil still had a DPS value of < 0.2, suggesting that the soil will not be a source of P supply in runoff. The low DPS value is a direct result of the low oxalate-extractable P content (<0.01 g kg⁻¹) of the soil.

Soils collected from the Michigan study sites had different physicochemical characteristics from the Immokalee soil utilized for the artificial incubation. Soil at site 1 had a fine sandy loam texture with Bray P1 test values of 265 mg P kg⁻¹. Soil at site 2, on the other hand, had loamy sand texture with Bray P1 test values of 655 mg P kg⁻¹. Details of the characteristics the Michigan soil samples utilized for the study are provided by Jacobs and Teppen (2000).

Aging and pH Effects on Phosphorus Lability

Despite the differences in the physicochemical properties of the four WTR samples used in the study (Table 2),

their effects on labile P over time and changes in pH levels followed similar trends. Therefore, only the data for the Holland WTR material are presented here. The Holland WTR was the material utilized for the Michigan field study, and showed the clearest treatment effects on P lability.

Labile Phosphorus of Thermally Incubated Drinking Water Treatment Residuals-Amended Soil

There was a significant effect of WTR amendment, aging, and pH on P lability in all the samples. Data for samples incubated at either 46 or 70°C were similar, and therefore only the 70°C data are presented. Amendment with WTR, coupled with the thermal incubation, significantly decreased labile P concentration of the WTR-amended soil 1 mo after thermal incubation at all pH levels except at pH 3 (Fig. 1). A further significant reduction was observed after 6 mo. Within the pH range of 4 to 7, reductions in labile P due to WTR amendment persisted throughout the incubation period. Measurements taken after 1 yr of thermal incubation showed that labile P concentration of the samples equilibrated at pH 3 decreased significantly, and the decrease persisted thereafter (Fig. 1). Amendment with WTR eventually decreased labile P concentrations by about 70% relative to the samples without WTR amendment. 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 soil samples incubated at room temperature (23°C) were significantly ($p \leq 0.015$) greater at all pH levels (data not presented). Similar behavior was observed for the 'low' impacted P samples and the samples without P addition (data not presented). The significant thermal aging effect is consistent with the observation of Makris et al. (2004a, 2004b) that the applied thermal energy enhances diffusion of P into the micropores of the WTR and that structural reorganization of the WTR during the aging process increases the stability of the WTR-immobilized P. Labile P concentra-

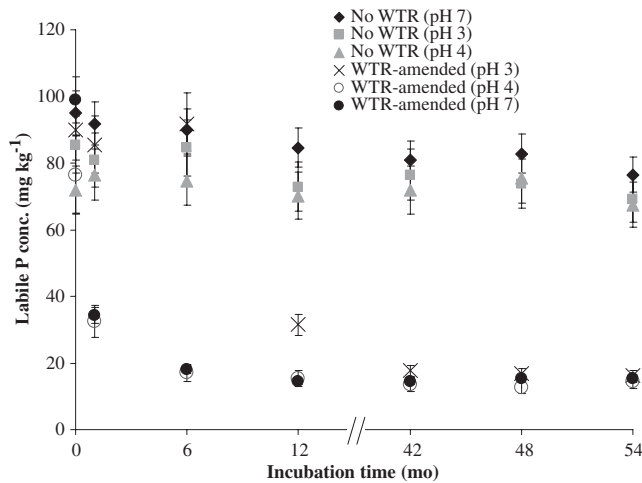


Fig. 1. Aging effects on labile P of the Immokalee soil samples spiked with 100 mg P kg^{-1} and thermally incubated at 70°C for 4.5 yr. Error bars denote one standard error of the mean.

tions measured at the various P loading rates and pH levels were similar when the samples were incubated at 46 and at 70°C , suggesting that the enhanced aging of the samples at 46°C was equally effective as the aging at 70°C .

For the Immokalee 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 (Fig. 2) and the soil samples incubated at room temperature (data not presented). The greatest labile P concentrations, on the other hand, occurred at pH 7 at all impacted P levels in both the thermally aged soil samples and the samples incubated at room temperature. 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 that P availability increases at near-neutral to neutral soil pH. However, the pH effect was eliminated by the WTR amendment. Labile P concentrations of the WTR-amended samples, equili-

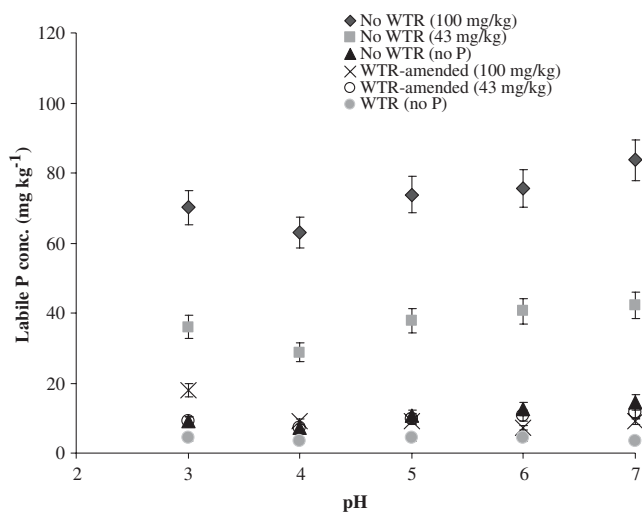


Fig. 2. pH effects on labile P of P-impacted Immokalee soil samples incubated for 4.5 yr at 70°C . Error bars denote one standard error of the mean.

brated within pH range of 4 to 7 were similar, and after 1 yr of thermal incubation, the labile P concentrations were similar at all pH levels (3–7). Thus, within the commonly encountered pH range of agricultural soils, WTR-immobilized P is stable, and reasonably anticipated changes in soil pH over time should have negligible effect on WTR-immobilized P.

Soil samples that received the greatest initial P load (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 soil samples and the samples incubated at room temperature (Fig. 2). Amendment with WTR, coupled with the aging of the samples, masked the P load effect (Fig. 2). 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, suggesting that WTR could be used to effectively counter high soluble P concentrations associated with P-impacted soils.

After 4.5 yr 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 simulates long-term aging under field conditions (Postma and Jakobsen, 1996; Ford et al., 1997; Martínez et al., 2001), 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.

Labile Phosphorus of Drinking Water Treatment Residuals-Amended Soil Aged via Wetting and Drying

Similarly to the thermally incubated samples, amendment with WTR, coupled with the aging, significantly decreased P lability at all P loads. Significant reductions in labile P of the WTR-amended soil samples were observed over time with repeated wetting and drying cycles (Fig. 3) within pH range of 4–7. Without WTR amendment, labile P concentrations of the soil samples remained high and relatively stable over time in the pH 4 to 7 range. Amendment with WTR significantly decreased labile P after 5 mo of incubation, and the decrease continued with additional wetting and drying cycles until apparent equilibrium at 1 to 1.5 yr (about 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. Within the pH range of 4 to 7, labile P concentrations were ultimately reduced by $\geq 75\%$, 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 to 7. Similar results were observed in the ‘low’ (43 mg P kg^{-1}) P-impacted and the samples without P addition (data not presented).

In the ‘high’ (100 mg P kg^{-1}) P-impacted Immokalee soil, WTR application decreased labile P concentra-

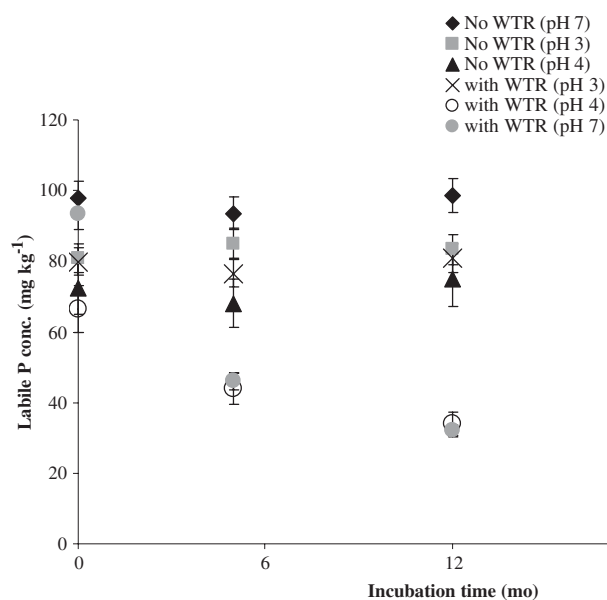


Fig. 3. Effects of drinking water treatment residuals (WTR) amendment on labile P concentrations with time of Immokalee soil samples spiked with 100 mg P kg^{-1} and artificially aged through wet and dry cycles. Error bars denote one standard error of the mean.

tions at all pH values except pH 3 (Fig. 4). This observation suggests that P immobilization by WTR is most effective within the pH range of 4 to 7, and that the WTR-immobilized P is stable within this pH range. Similar trends were observed in the 'low' (43 mg P kg^{-1}) P-impacted and the samples without P addition (data not presented). As with the thermally incubated samples and within the pH range of 4 to 7, amendment with WTR and aging through wetting and drying cycles masked the P load effect (Fig. 5), suggesting that WTR could be used to effectively counter high soluble P concentrations associated with P-impacted soils.

The incubation data for the WTR-amended Immokalee soils show that WTR effectively reduced labile P values, and suggest that within pH 4 to 7, P would remain immobilized in the long term. There was no release

of P from the WTR-amended soils on artificial aging (both thermal and wet and dry incubation). The combined data suggest that sorbed P will remain indefinitely immobilized unless particle dissolution occurs at extreme pH values < 4 . Fortunately, 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 to 7, the thermally incubated WTR-amended samples appeared to stabilize at 6 mo, whereas the samples incubated via wetting and drying apparently reached equilibrium about 1.5 yr after initiation of incubation. When the data generated from time zero until the apparent 'stabilized' times of the two aging techniques (i.e., 6 mo for thermal incubation and 1.5 yr for wet and dry incubation) were statistically analyzed, a very strong ($r \approx 0.96$) and highly significant ($p < 0.001$) correlation was observed between the two aging techniques (Fig. 6). No significant correlation ($r \approx 0.24$, $p > 0.05$) 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 (about 20 mg kg^{-1}) of the high P-impacted (100 mg kg^{-1}) WTR-amended Immokalee soil samples were achieved after about 6 mo of thermal incubation, and after about 1.5 yr 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

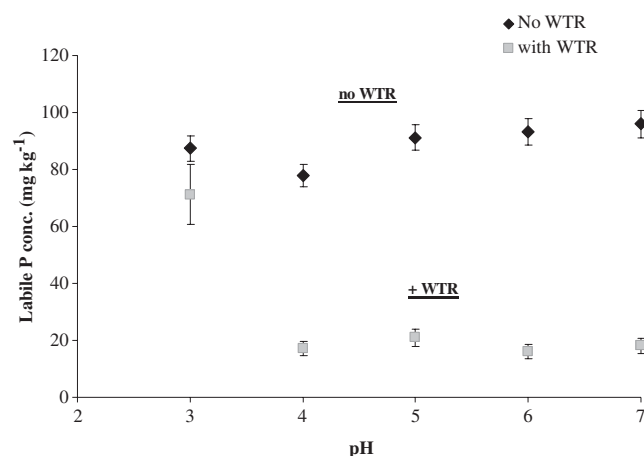


Fig. 4. Effects of drinking water treatment residuals (WTR) amendment on labile P concentrations as a function of pH for the Immokalee soil samples spiked with 100 mg P kg^{-1} and incubated via wet and dry cycles for 2 yr. Error bars denote one standard error of the mean.

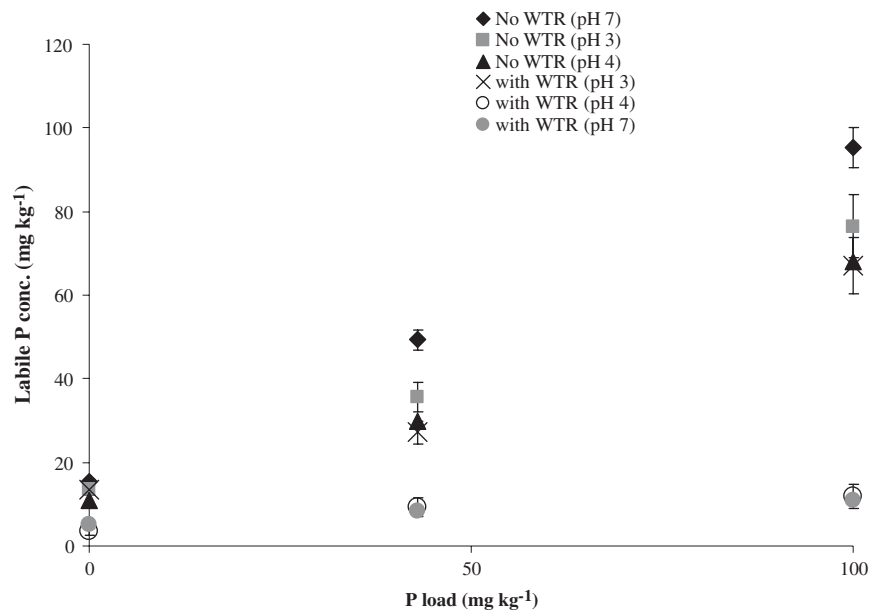


Fig. 5. Effects of drinking water treatment residuals (WTR) amendment on labile P concentrations as a function of impacted P loads for Immokalee soil samples artificially aged via wet and dry cycles for 2 yr. Error bars denote one standard error of the mean.

enhanced the diffusion of P into the micropores of the WTR (Makris et al., 2004a, 2004b). 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.

Labile Phosphorus of Drinking Water Treatment Residuals-Amended Field-Aged Samples

Field-aged soil samples with different physicochemical properties were collected from two 7.5-yr-old, one-time WTR-amended field sites to validate the trends observed with the artificially aged samples. Soils at the

field study sites had finer texture and greater soil test P content than the Immokalee soil used for the incubation study. Jacobs and Teppen (2000) and Agyin-Birikorang et al. (2007) reported that the soil at site 2 of the Michigan study site had about 2.5 times more soil test P than site 1. These differences in soil characteristics were reflected in the time required for the labile P to reach equilibrium in each case. The labile P concentration of the artificially aged (via wetting and drying) Immokalee soil reached equilibrium about 1.5 yr after initiation of the incubation, whereas the labile P of the Michigan site 1 samples reached equilibrium at 2.5 yr, and those of site 2 samples reached equilibrium between 3.5 and 4 yr. Despite the differences in time required for the labile P in soils from both sites to reach equilibrium, the trends of aging and pH effects on lability of WTR-immobilized P were similar.

The labile P concentrations were determined for all the field samples collected from both sites from 1998 to 2005, at 5 pH levels (3–7). For explanatory purposes of pH effect on P lability, data of the samples taken in 2005 are presented (Fig. 7). Similar trends of pH effects were observed in samples taken over the entire sampling period.

As in the control (without WTR amendment) treatment of the artificially aged samples, the lowest labile P concentrations in the control plots in the field study were observed at pH 4 at both sites (Fig. 7), ranging from an average of about 45 to about 85 mg P kg⁻¹ for sites 1 and 2, respectively. The greatest labile P concentrations were measured at pH 7 at both sites (about 110 and about 200 mg P kg⁻¹ at sites 1 and 2, respectively). The data suggest that more P was fixed at pH 4 than at pH 3. At pH 3, the nature of the sorbing surface of the soil could have changed due to the more acidic pH condition. Huang (1975) showed that maximum phosphate adsorption on Al oxides occurred at pH 4, and

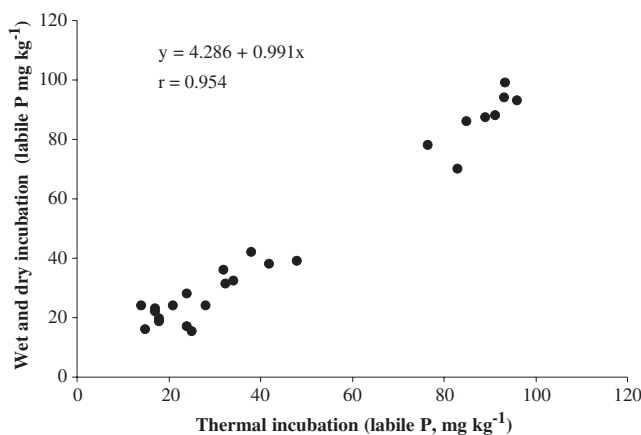


Fig. 6. Relationship between labile P concentrations of the drinking water treatment residuals (WTR)-amended P-impacted (100 mg kg⁻¹) Immokalee soil samples incubated either thermally or via wetting and drying. Measurements were taken until time to apparent equilibrium.

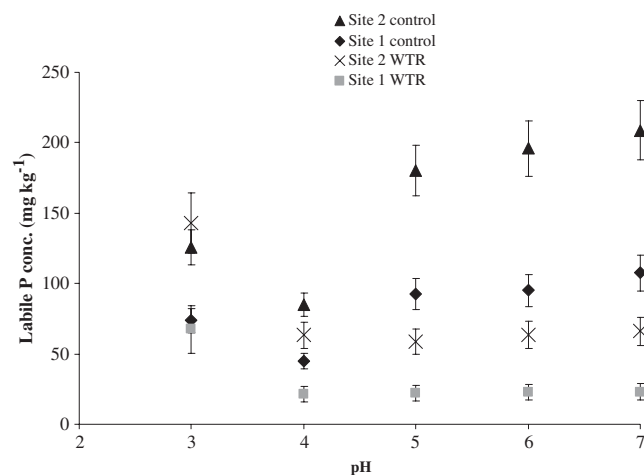


Fig. 7. pH effects on labile P concentrations of the Michigan field-aged soil samples taken in fall 2005. Error bars denote one standard error of the mean.

decreased under more acidic conditions. Lindsay (1979) also reported that at pH values < 4 , dissolution of Al-P minerals can be considerable and some sorbed P may be released via particle dissolution. A pH of 3 is rarely encountered in natural systems, and measurements at pH 3 represent a worst case scenario for release of immobilized P to solution. Similarly to the artificially aged samples, amendment with WTR significantly ($p < 0.001$) reduced labile P concentrations at both sites within pH 4 to 7 (Fig. 7). Amendment with WTR also masked the pH effect on P lability of the field-aged samples within pH 4 to 7 (Fig. 7). No differences in labile P concentrations were observed for the samples collected from the WTR-amended plots from either site and equilibrated within pH 4 to 7, showing that within this pH range, WTR-immobilized P was stable.

The labile P concentrations of the WTR-amended plots decreased with time, when the labile P concentrations were determined within the pH range of 4 to 7. For explanatory purposes, only the labile P pools measured at pH 3 and 6 are presented (Fig. 8) and discussed in terms of aging effects on lability of WTR-immobilized P. Similar trends in P lability were observed over the pH range of 4 to 7, whereas lability at pH 3 was different from the others. At site 1, labile P concentrations measured 6 mo after WTR application were significantly reduced for the samples equilibrated at pH 4 to 7 relative to the control plots, as presented in Fig. 8. The labile P concentrations continued to decline for another 2 yr, consistent with the trend observed with water-soluble P (WSP) measurements (Agyin-Birikorang et al., 2007). Within this pH range, no increases in labile P concentrations from the WTR-amended plots from either site were observed with time suggesting that the WTR-immobilized P remained intact. At pH 3, however, there was no significant ($p = 0.672$) difference between the labile P concentrations of the WTR-amended plots and the control plots over time (Fig. 8B), suggesting that the immobilized P was desorbed. The WTR structure was apparently destabilized at pH 3 and the immobilized P, as well as some P originally contained in the WTR, was released.

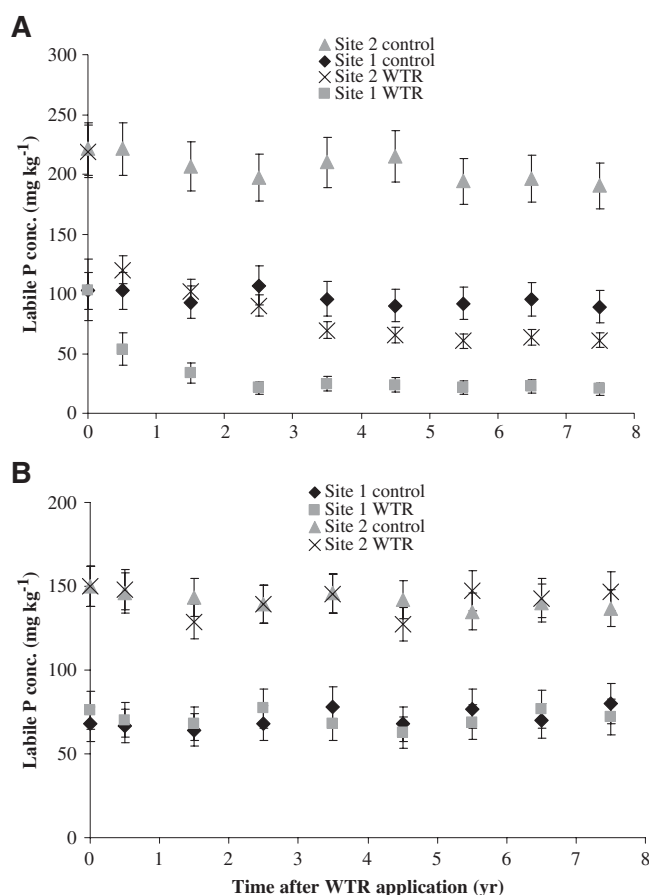


Fig. 8. Aging effects on labile P concentrations of the Michigan field-aged soil samples equilibrated at (A) pH 6 and (B) pH 3. Error bars denote one standard error of the mean.

Similar labile P behavior with time was observed for the site 2 samples (Fig. 8). Amendment with WTR reduced labile P concentrations within 6 mo (at pH 4–7), and the reductions continued for another 3 to 4 yr (Fig. 8A). Blake et al. (2002) showed that isotopically available P (labile P) concentration of about 55 mg kg^{-1} in loamy to sandy soils produces a “change point” at which the rate of P leaching and/or runoff from soil suddenly increases and poses a greater threat of eutrophication to standing waters. Thus despite the reduction in labile P concentrations by WTR amendment, the data suggest that the labile P concentrations of the WTR-amended plots of site 2 ($\sim 70 \text{ mg kg}^{-1}$) are still high enough to constitute P mobility problems at both sites. Perhaps, a greater amount ($> 114 \text{ Mg ha}^{-1}$) of WTR is needed to reduce labile P concentrations to levels that are not potentially harmful to the environment.

Data trends from the field-aged samples were consistent with data from the artificially aged soil samples. Within the pH range of 4 to 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 can be 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.

CONCLUSIONS

This study was undertaken to evaluate aging and pH effects on the lability of WTR-immobilized P using artificially and field-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 yr or thermally incubated at elevated temperatures for up to 4.5 yr. Field-aged WTR-amended samples, obtained from 7.5-yr-old one-time WTR-amended fields at two sites were used to validate trends observed with artificially aged samples. Using a modified isotopic (^{32}P) dilution technique, coupled with a stepwise acidification procedure, we monitored changes in labile P over time. This technique enabled evaluating the effect of pH on the lability of WTR-immobilized P.

Within the pH range of 4 to 7, WTR amendment, coupled with aging, ultimately reduced labile P in artificially aged samples by $\geq 75\%$, and field-aged samples by about 70% relative to the no-WTR (control) samples. No reduction in labile P was observed for the WTR-amended samples equilibrated at pH 3. However after 1 yr of thermal incubation, a significant decrease in labile P was observed at all pH values, including pH 3. Thus, if thermal incubation truly simulates 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. We conclude that WTR application is capable of reducing labile P concentration in P-impacted soils, doing so for a long time and that, within the commonly encountered pH range in agricultural soils, WTR-immobilized P is stable.

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