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Effects of Remedial Treatment on Phosphorus Availability in an Arsenical Pesticide Contaminated Soil

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Phosphorus (P) and arsenic (As) are two oxyanions with similar chemical properties that have recently received much attention due to the severe environmental problems associated with them (He et al., 1999; Matschullat, 2000). Both As and P may find their way toward surface water bodies or even to groundwater reserves from non-point sources (e.g., P-based fertilizers, As-based pesticides) and/or from specific point sources (e.g., CCA-treated wood, cattle dipping vats, poultry litter, etc.). In the late eighties and the early nineties, the USEPA banned land application of inorganic As-based pesticides (e.g., arsenic acid, lead arsenate, lead arsenite, copper arsenate, etc.), but the century-long practice had already taken its toll. Increased soil As concentrations have been detected in numerous occasions – in pesticide-treated agricultural lands and in orchards, with As concentrations typically ranging between 7 and 970 mg kg^{-1} (Matschullat, 2000). Typically, As-contaminated agricultural soils receive annual P additions as inorganic fertilizers, biosolids, animal manures, or poultry litters to increase crop yields and to maintain optimum crop growth. Phosphorus-source application is typically based on crop nitrogen requirements, which provides P in excess of the crop needs. Poorly P-sorbing soils are abundant in the southeastern states of U.S.A. These soils are primarily sandy and are often accompanied by high water tables, which make them vulnerable to vertical P losses, thereby promoting surface- and groundwater quality deterioration (Novak et al., 2000). In many cases, the gradual saturation of soil sorption sites by As due to anthropogenic As inputs may result in increased P concentrations in the aqueous phase, resulting in off-site P losses (Manning and Goldberg, 1996). Such off-site P losses may prove detrimental to downstream water quality and to the neighboring ecosystems (Edwards and Daniel, 1993). Soil literature is abundant with studies emphasizing P-As competition for similar sorption sites, often times resulting in P and/or As mobilization (Ryden et al., 1987).

Under such circumstances, appropriate measures should be taken to reduce off-site P losses in arsenical pesticide amended soils, ideally via land-application of a low-cost sorbent with the ability to offset the competitive effects of P and As by immobilizing both oxyanions. Recent studies have shown that drinking-water treatment residuals (WTRs) effectively retain P in sandy soils (Makris et al.,

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2004). The WTRs are byproducts of the drinking water treatment processes, and are typically amorphous mixtures of Fe/Al hydroxides and organic C, which can be obtained free-of-charge from the drinking-water treatment plants. Some of these WTRs are equally effective in sorbing As from contaminated water (Makris et al., 2006). Hence, it is likely that land-application of the WTRs to As-contaminated, P-enriched agricultural soils may be developed into an effective in-situ remedial treatment to immobilize both P and As. The primary objective of the reported incubation study was to assess P availability in an arsenical pesticide treated soil that is amended with a P fertilizer as a function of drinking-water treatment residual application rate and soil ageing.

MATERIALS AND METHODS

Soil samples were collected from surface horizon of the Immokalee series soil from the campus of the SW Florida Research and Education Center, Immokalee, FL. The Immokalee series is a sandy *Spodosol, Siliceous, hyperthermic, Arenic Alaquod* with low extractable Fe+Al content. The Immokalee soil has essentially no P-retention capacity (O'Connor et al., 2001). The aluminum-based WTR (Al-WTR) was obtained from the Manatee County water treatment plant in Bradenton, FL.

The soil and the Al-WTR were air-dried and passed through a 2-mm sieve. Soil samples were simultaneously spiked with 90 mg As(V) kg^{-1} (sodium arsenate as As source), and 115 mg P kg^{-1} added as triple super phosphate. The Al-WTR was applied at 5 rates (0, 0.5, 1.25, 2.5 and 5 % by wt.). Spiked soil samples were thoroughly homogenized, brought to 80 % of water holding capacity and incubated in plastic bags at room temperature. Soil samples were incubated up to a year, and bags were periodically opened to maintain aerobic conditions. All studies were conducted in triplicates. Periodically (at 0, 6 and 12 months), sub-samples were collected, and air-dried for several types of P analyses (see below).

Soil and WTR were characterized for their chemical properties. The pH of the soil and WTR suspensions was determined using a 1:4 soil to water ratio. Organic matter content was determined with the loss on ignition method (LOI) (Nelson and Sommers, 1996). Total C and N contents of the soil and the Al-WTR were determined using a PE 2400 Series II CHNS/O Analyzer. Oxalate-extractable Fe, P, and Al were determined using the acid ammonium oxalate extraction procedure (McKeague et al., 1971). The supernatant was then analyzed for Fe, P, and Al, using an PE Elan 9000 Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS). Instrumental limits of detection for P, Fe, and Al were 0.01, 0.1, and 0.1 $\mu g\ L^{-1}$, respectively. Total elemental composition (P, Fe, Al, Ca, Mg) of soils and the WTRs was determined using the USEPA method 3050B (USEPA, 2000).

Available P concentrations in soils for plant P uptake or runoff/leaching P losses were determined using three different methods. One P extraction followed the guidelines of the Mehlich 3 test for determination of plant-available P (Mehlich, 1984). The second P extraction test used a 1 M KCl solution at a 1:10 g:ml solid:solution ratio, shaken on a reciprocating shaker for 1 h at 180 rpm, centrifuged for 20 min at 6700*g*, filtered and analyzed for P to quantify the "exchangeable P". Another test employed Fe-oxide coated filter paper strips (P_i test). The Fe-oxide strips were prepared following the method described by Sarkar and O' Connor (2001). Individual Fe-oxide strips along with 1 g soil were shaken for 16 h with 50 mL of 0.001 M $CaCl_2$ solution. After shaking, the strips were removed, rinsed free of adhering solid particles with d-H_2O and air-dried. The strips were then shaken with 40 ml of 1 M HCl for 1 h to desorb P retained by the strips. The extracts were filtered and analyzed for P using the molybdenum blue method (Murphy and Riley, 1962) by a UV-Visible light spectrophotometer. All analyses were carried out in triplicates and mean values were reported. Replicates had to fall within 95-105% to be considered acceptable. Recoveries of 90-110% of spikes and external standards were considered acceptable. Analyses that did not satisfy these QA/QC protocols were reanalyzed.

Data were statistically analyzed using JMP IN version 5.1 (Sall et al., 2005). One-way analysis of variance was performed to compare the effects of WTR treatment rate and incubation time on plant-available P concentrations. Tukey-Kramer honest significant difference (HSD) test was used to statistically evaluate the differences among treatment means.

RESULTS AND DISCUSSION

Selected properties for the Immokalee soil and the Al-WTR are shown in Table 1. Both materials were acidic; the soil had a low (17 g kg^{-1}) organic matter (OM) content, but the Al-WTR had very high organic matter (OM) content (462 g kg^{-1}). Total P content of the Al-WTR (3,500 mg kg^{-1}) was greater than the median value (1,300 mg kg^{-1}) reported for a host of Al-WTRs (Dayton et al., 2003). The soil had little native P (41 mg kg^{-1}). The Al content of the WTR (87,100 mg kg^{-1}) was high compared to the soil (480 mg kg^{-1}), but it was within the typical range for WTRs (50,000 to 150,000 g kg^{-1}) (ASCE, 1996). Oxalate-extractable Al + Fe for the Al-WTR was 79 % of the total Al + Fe, indicating a prevalence of the highly reactive amorphous Al/Fe hydroxides, which makes the Al-WTR a sink for P.

Immediately after incubation, P availability (as reflected by the results of the Pi test) in the WTR-amended soil samples decreased significantly ($p<0.05$) from 100 % to 45 % at the 2.5 % Al-WTR rate, relative to the untreated control soil (Figure 1). Extractable P contents measured at the highest WTR application rate (5 %) were not statistically ($p<0.05$) different from those at the 2.5 % rate (Figure 1). After 6 or 12 months of incubation, P availability significantly ($p<0.001$) decreased for all soil samples regardless of Al-WTR application rate (Figure 1). However, the magnitude of reduction in P availability with incubation time differed between the treatments. After 6 months of incubation, the most prominent reduction in P availability with time was observed with the 2.5 and 5 % rate treatments (~ 25 % and 15 %, respectively).

Table 1. Selected properties of the Immokalee soil.

	pH	**OM***	**C**	**N**	**Total, mg kg^{-1}**					**Ox**, mg kg^{-1}**	
		-------g kg^{-1}-------			**Fe**	**Al**	**Mg**	**P**	**Ca**	**Fe**	**Al**
Soil	6.2	1.77	0.8	0.02	377	480	40	41	200	71	78

* Organic matter content

** Oxalate-extractable metal concentration

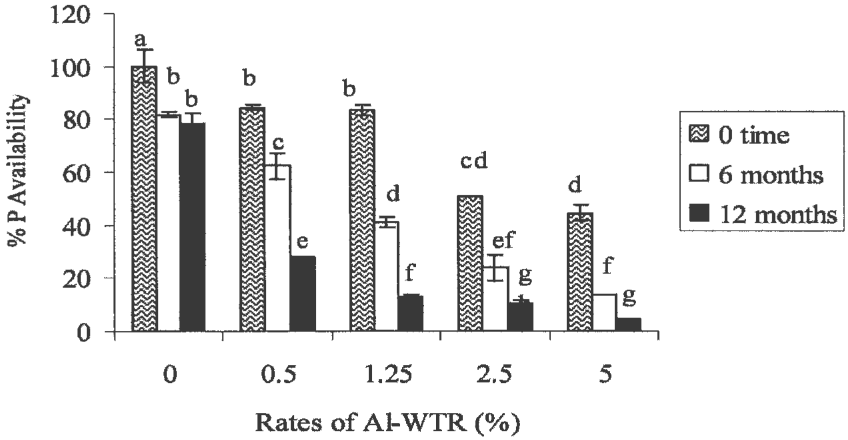

Figure 1. Effect of incubation time on P availability using the P_i extraction test (0.001 M $CaCl_2$ and Fe -strip) in Immokalee soil amended with sodium arsenate, TSP and various rates of Al-WTR. Values not labeled with the same letter are significantly different from each other.

After 12 mo, P availability was further decreased to values < 10 % for the 2.5 % and 5 % WTR rates (Figure 1), suggesting that these WTR rates effectively immobilized soluble P concentrations in arsenical-pesticide treated soils, relative to the unamended (no WTR) control soil samples (80 % after 12 months) (Figure 1). Reduction in P availability with incubation time was kinetically-controlled for the WTR-amended soil samples (Figure 1). The Pi extractable P concentrations gradually decreased ($p<0.05$) with incubation time, suggesting a slow P immobilization by the Al-WTR soil samples.

Earlier work reported that intra-particle P diffusion into Al-WTR micropores is responsible for the slow P sorption by WTRs (Makris et al., 2004). Our study shows that reduction in P availability (as expressed with the Pi test) of an Al-WTR treated is still significant despite the presence of competition induced by arsenate via application of an inorganic As-based pesticide.

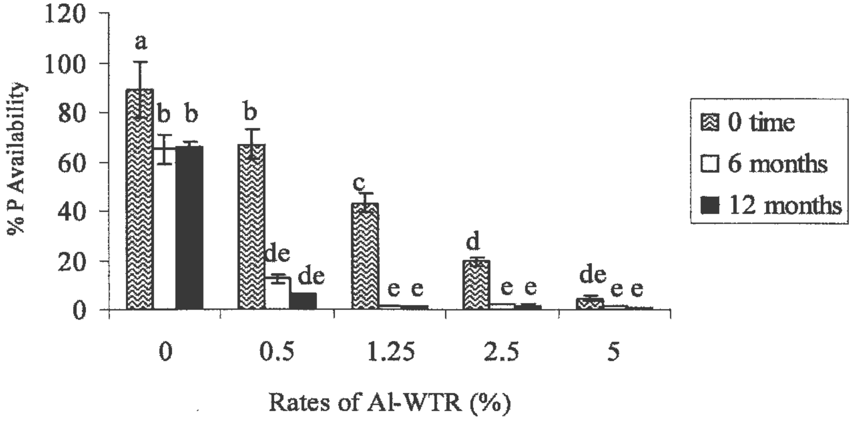

Figure 2. Effect of incubation time on P availability using 1 M KCl extraction in Immokalee soil amended with sodium arsenate, TSP and various rates of Al-WTR. Values not labeled with the same letter are significantly different from each other.

Previous studies performed by Sarkar and O'Connor (2004) showed that P extracted by KCl reflected both the phytoavailable and leachable P from three biosolids. This extraction simulates the amount of P that is relatively labile (i.e., soluble plus exchangeable), which is easily accessible by plant roots. Results from the 1 M KCl extraction test show that immediately after incubation, P availability in the control (no WTR) soil was ~ 100 %, but it was significantly ($p<0.001$) reduced for soils receiving WTR application, especially for the 2.5 % rate (20 % available P) and the 5 % rates (< 10 % available P) (Figure 2). The instantaneous decrease in P availability was further documented for samples incubated for larger time periods, where P availability decreased to almost negligible values (< 5 %) for WTR application rates ≥ 1.25 % by wt. (Figure 2). Major reductions in P availability for all WTR application rate treatments were manifested after 6 months of incubation, and remained constant thereafter (Figure 2). Similar reduction in soluble P concentrations as a function of WTR application rates were documented by Elliott et al. (2002) for soils amended with a variety of P sources (biosolids, TSP).

The Mehlich III soil P test was developed to assess the P fertility status of acidic soils (Mehlich, 1984). Phosphorus availability data as expressed by the traditional Mehlich III soil test procedure in the Al-WTR-amended soil samples treated with arsenical pesticide and TSP are shown in Figure 3. Data show that P availability in the control (no WTR) soil did not change (100 %) even after 12 months of incubation (Figure 3). Interestingly, the instantaneous decrease in P availability upon WTR addition observed for the two previous P extraction tests was not the case for the Mehlich extraction test (Figure 3). Specifically, the WTR treatment had no significant effect ($p>0.05$) on P availability at time-zero (Figure 3),

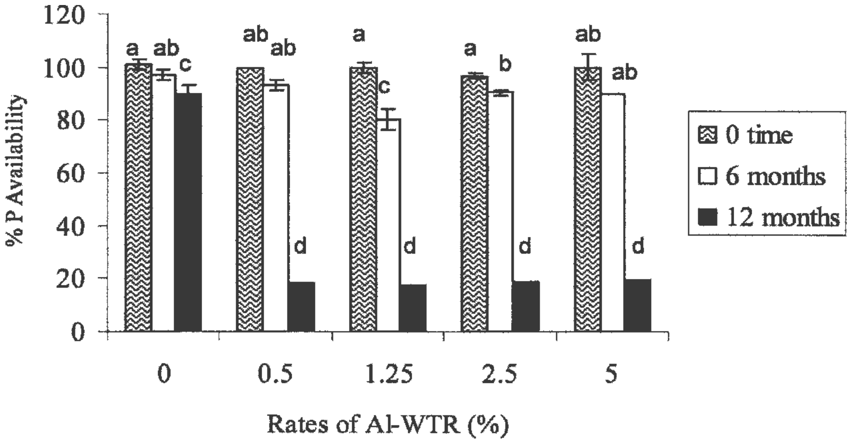

Figure 3. Effect of incubation time P availability using the Mehlich III extraction in Immokalee soil amended with sodium arsenate, TSP and various rates of Al-WTR. Values not labeled with the same letter are significantly different from each other.

suggesting that the Mehlich extractant, which is highly acidic (~ pH 3) desorbs P bound to the WTR particles. Studies have shown that acidic extractants, e.g., Mehlich III, often overestimate the plant-available P in soils with high amorphous oxide content (Gardiner and Christensen, 1991). Major reductions in P availability of the WTR-treated samples were observed after 12 months of incubation (Figure 3). However, such reductions were unaffected by the WTR application rates, reaching a constant P availability value of approximately 20 %. This slow kinetic effect, reflected by the decrease in Mehlich III-extractable P concentrations suggests that the extraction method, though acidic was unable to desorb P that diffused into the WTR pore network.

Numerous soil extractants, particularly those developed for local soils have been used by agronomists to reflect amendment effects on P extractability as well as to simultaneously infer their impacts on P phytoavailability or lability in general (Basta et al., 2000). Results have been mixed because some extractants are sufficiently rigorous to solubilize P that is otherwise unavailable for plant uptake or for contribution to leaching or surface runoff (Basta et al., 2000). Extractants supposedly designed to reflect P availability should correlate well with one another. In the unamended soils, there was a significant ($p<0.05$) correlation between the Pi test-P and the 1 M KCl test-P (across incubation time), but not with Mehlich III-P (Table 2). However, for the Al-WTR-amended soil samples, despite generating relatively low regression coefficient values, there was a significant correlation ($p<0.05$) between Mehlich III-P and the available P estimated by other soil tests (Table 2), suggesting that traditional soil tests can be used to assess long-term P availability in P-enriched soils.

Table 2. Correlation table between different available P measurements from the WTR-amended (upper graph) and unamended (lower graph) plots of Immokalee soil, including all sampling times (0 – 12 mo), in triplicates.

Available P Tests	Pi Test	1 M KCl	Mehlich III
Pi Test	1.00		
1 M KCl	**0.92***	1.00	
Mehlich III	0.18	-0.06	1.00

Available P Tests	Pi Test	1 M KCl	Mehlich III
Pi Test	1.00		
1 M KCl	**0.88***	1.00	
Mehlich III	**0.65***	**0.54***	1.00

Values denote the regression coefficients; (pooling all application rates). Values in bold are statistically significant at the 95 % confidence level.

However, soil-P availability in the presence of Al-WTR was a kinetically-controlled process and was unaffected by the presence of a high concentration (90 mg kg^{-1} soil) of a competing ion, namely, arsenate. Because of gradual intra-particle diffusion of P into the porous network of the Al-WTR structure, P availability in WTR-amended soils decreased as a function of time irrespective of the WTR application rates. Hence, results from this incubation study suggest that land application of Al-WTRs can be an efficient *in-situ* remedial treatment for P-enriched soils, and the effects of the remedial treatment on availability of soil-P can be evaluated using traditional soil extraction tests.

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