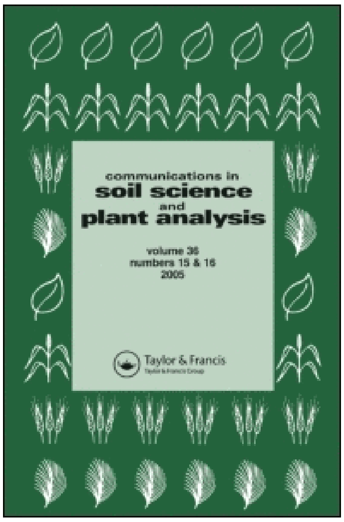

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Drinking-Water Treatment Residual Effects on the Phosphorus Status of Field Soils Amended with Biosolids, Manure, and Fertilizer

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Abstract: Concerns about surface water pollution with phosphorus (P) from biosolids and manures are prompting land application guidelines that limit residual application rates to those based on crop-P removals (typically, no more than 2 Mg ha^{-1}). Such rates are so low that the beneficial recycling of residuals is seriously threatened. Greater application rates [i.e., nitrogen (N) based] require judicious selection of residuals (low soluble P contents) and/or soil amendments, such as drinking-water treatment residuals (WTRs) to control soluble P concentration. Although in the short term, WTR is effective in reducing soluble P levels, field studies to evaluate the stability of WTR-immobilized P are scarce. The initial objective of this study was to determine the effects of WTR on P losses to surface and groundwater from Florida sand 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 because of severe flooding of the field 17 months after amendment application. The flooding appears to have compromised the treatments (moved soil and associated amendments across plots), which forced early termination of the experiment. Measurements taken after the flooding, however, provided a unique opportunity to assess the usefulness of WTR in controlling P solubility following severe flooding of WTR-amended plots. Soluble P values measured from WTR-amended A horizon plots were significantly lower than the plots without WTR

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amendment throughout the study. Phosphorus-specific measurements in the Bh horizon suggest that excessive P leaching apparently occurred in the plots without WTR amendment and the control plots, whereas very little or no P leaching occurred in the WTR-amended plots. Thus, despite extensive hurricane-induced flooding of the fields, the WTR was able immobilize P and prevent excessive P leaching. We conclude that WTR could reduce offsite P transport, which will lower P loads into nutrient-sensitive surface water systems, and that WTR-immobilized P is stable even under severe flooding conditions.

Keywords: Degree of P saturation, drinking-water treatment residuals, iron strip–extractable P, P saturation index, water-extractable P

INTRODUCTION

Phosphorus (P) 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, Sharpley, and Lemunyon 1998; Sims, Simard, and Joern 1998; Sims et al. 2000; Maguire et al. 2001). The Kissimmee River, one of the major aquatic resources for water storage, wildlife, and recreation in south Florida, is threatened by cultural eutrophication from excessive P loading in the surrounding basins (Whalen et al. 2002). 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 (residual) sources of P are typically based on crop nitrogen (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 buildup 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, O'connor, and Brinton 2002; 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, O'Connor, and Brinton 2002; O'Connor, Elliott, and Lu 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,no more than 2 Mg ha^{-1}). Such rates are so low (uneconomical and impractical) that the beneficial recycling of biosolids and manure 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

(Shreve et al. 1995; Moore et al. 1998; Smith et al. 2004) or drinking-water treatment residuals (WTRs) (Elliott et al. 2002; Dayton et al. 2003; Ippolito et al. 2003; Novak and Watts 2004; O'Connor, Brinton, and Silveira, 2005; Silveira Miyittah, and O'Connor 2006; Agyin-Birikorang et al. 2007). Numerous P sorption desorption studies and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P from P-impacted soils (Elliott, O'Connor, and Brinton 2002; Dayton et al. 2003; Makris 2004; Makris et al. 2004a, 2004b; Novak and Watts 2004, 2005). Although in the short term, WTR is effective in reducing soluble P levels, field studies to ascertain the stability of WTR-immobilized P are scarce. The stability of sorbed P by WTRs has been qualitatively addressed in laboratory experiments (Makris et al. 2004a, 2004b; Ippolito et al. 2003). The laboratory 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, laboratory 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 because of an act of nature. The fall of 2004 was an especially busy hurricane season in southern Florida, and the experimental plots were heavily flooded and berms separating the plots were breached. The flooding appears to have compromised the treatments (moved soil and associated amendments 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 after severe flooding.

MATERIALS AND METHODS

Field Layout and Amendment Application

The study was carried out at a cattle pasture (Kirton Ranch) located in the Kissimmee watershed, on the eastern border of Okeechobee County, 11.5 km ($\sim$7 miles) northeast of Okeechobee and north of Lake Okeechobee. The soil at the experimental site is 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: (i) two biosolids: a "moderate-soluble P" source from Pompano

Beach, Fl., and a "high-soluble P" source from Boca Raton, Fl.; (ii) poultry manure from Indiantown, Fl.; and (iii) triple superphosphate (TSP), an inorganic fertilizer. 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, and individual plots were bermed to avoid cross-contamination. 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 Institute of Food and Agricultural Sciences (IFAS) recommended rate for bahiagrass (*Paspalum notatum)* (Hanlon 1995) and are identified as P-based rate treatments. Similarly, the 179 kg N ha^{-1} rate represents the recommended (Hanlon 1995) N-based rate. The triple superphosphate (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 percentage of solids of the biosolids and the poultry manure were used to calculate the quantities of materials to be applied. Plant-available – was estimated based on the assumption of an N mineralization rate of 40% annually. The WTR was applied at a rate of 22.4 Mg ha^{-1} (oven-dry equivalent), based on preliminary laboratory studies, to selected plots. Ammonium nitrate was applied 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 continued for 19 months (terminated in Dec. 2004), but amendments were applied only in May 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, iron (Fe), and aluminum (Al) by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) (Perkin-Elmer Plasma 3200, Perkin-Elmer, Wellesley, Mass.) following digestion according to the EPA Method 3050A (USEPA 1986). Oxalate (200 mM)–extractable P, Fe, and Al were determined by ICP-AES after extraction at a 1:60 solid:solution ratio, following the procedures of Schoumans (2000). Total carbon (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 the materials (1:2 solid or soil–solution ratio). Percentages of solids were determined by drying materials at 105°C (Sparks 1996).

Periodic Soil Sampling and Analysis

Composite soil samples (formed by mixing 20 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 ($\sim$45–55cm from the surface), and the top 10 cm of the Bh horizon. The impact of the amendments on the P chemistry in the entire A horizon (0–15 cm) was determined in another sampling in March 2004. A final sampling was done in December 2004, following the termination of the field study. Samples were taken from the A horizon (0–5 cm and 0–15 cm), the middle of the E horizon ($\sim$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 previously. The degree of phosphorus (P) saturation (DPS) was calculated for the soil samples and represents the moles of oxalate (200 mM)–extractable P divided by the sum of moles of oxalate (200 mM)–extractable (Fe + Al), assuming a saturation factor (α) value of 0.55 as suggested by Nair and Graetz (2002) 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 Fe-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 1 h (Kuo 1996). The P concentration was analyzed colorimetrically with the Murphy and Riley method (1962). The Fe-strip P was determined by reacting the soil samples with Fe-impregnated [0.65 M iron chloride ($FeCl_3$) in 0.6 M hydrochloric acid (HCl)] filter paper and then extracting the P adsorbed with 0.1 M sulfuric acid (H_2SO_4) (Van der Zee, Fokkink, and Van Riemsdijk 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 quality assurance/quality control (QA/QC) protocol (Kennedy, Rowland, and Parrington 1994). 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. Percentage recovery ranged from 97 to 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 to 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 these 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–Mar. 2004 (before the occurrence of the hurricanes) enabled us to evaluate the effectiveness of the applied WTR in reducing soluble P levels in soils amended with different P sources and applied at different rates under field conditions. Although the hurricanes precluded continuing the study, sufficient data were collected to evaluate the stability of WTR-immobilized P after severe flooding of the field. The P-specific measurements of the samples collected from the field (Kirton Ranch) study site before the hurricanes followed similar trends. Therefore, for explanatory purposes, only the measurements taken from the June 2003 samples are discussed to represent the prehurricane field situation.

Soil and Amendment Characteristics

The surface soil at the experimental site (Immokalee sand; sandy, siliceous, hyperthermic Arenic Alaquods) was acidic (pH = 5.5) and contained small amounts of soluble P and total and oxalate-extractable Fe and Al (Table 1). Despite the low oxalate-extractable Fe and Al, the soil still had a degree of P saturation (DPS) value of 0.1, suggesting that the soil should not be source of P supply in runoff. The low DPS value is a direct result of the low oxalate-extractable P content ($\sim$10 mg kg^{-1}) of the soil. The measured values obtained for the lower horizons (E and Bh) (Table 1) were similar to those observed for another Spodosol (Myakka; sandy, siliceous, hyperthermic Aeric Alaquods) located in the Okeechobee and Kissimmee watersheds (Nair, Graetz, and Portier 1995). However, the data generated for the three horizons showed that the soil of the project site was very heterogeneous, which was reflected in the large variability (CV $\geq$ 30%) among chemical measurements of the same treatments.

Table 1. Selected P-specific characteristics of the Immokalee soil used in the field study

Chemical characteristics	Horizons		
	A (0–10 cm)	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
WEP[a]	4.07 ± 0.78	0.77 ± 0.32	3.31 ± 0.54
Fe-strip P	9.6 ± 0.11	1.36 ± 0.12	16.4 ± 3.29
DPS[b]	0.10	0.14	0.02

[a]Water extractable P.

[b]Degree of phosphorus saturation.

Notes. Units for all measurements (except pH and DPS) are expressed in mg kg^{-1}. Numbers are mean values of six replicates ± one standard deviation.

The pH values of the P sources ranged from 6.8 for the poultry manure to 8.2 for the Boca Raton biosolids (Table 2). 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, O'Connor, and Brinton, 2002; Elliott et al. 2002; 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- and Fe strip–extractable P) value, consistent with the total P content of the P sources (Table 2). However, unlike the trends in total P values, poultry manure had greater available P than the Pompano biosolids. The P saturation index (PSI) qualitatively identified the Boca Raton material as a good labile P source. The Pompano material, on the other hand, was qualitatively identified as a poor labile P source.

The pH of the WTR used was 5.6 (Table 2), slightly below the range of pH values reported for Al-WTRs (6.0–8.4; Makris and O'Connor 2007). Total P values were typical of Al-WTRs (0.3 to 4.0 g P kg^{-1}; Dayton et al. 2003; Makris 2004). Total Al value of 107 g Al kg^{-1} was within normal ranges reported by others (15–177 g Al kg^{-1}; Dayton et al. 2003; Makris 2004). Oxalate-extractable Al value was ∼80% of the total, suggesting

Table 2. Selected chemical properties of amendments (oven-dry basis) utilized in the Kirton Ranch field study

	Source			
Parameter	Indiantown	Boca Raton	Pompano	Bradenton
Form	Manure	Biosolids	Biosolids	Al-WTR
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
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
Fe strip P	1.34 ± 0.3	6.42 ± 1.2	1.05 ± 0.2	nd[d]
WEP[a]	0.85 ± 0.1	2.59 ± 0.6	0.34 ± 0.1	nd[d]
PSI[b]	NA[c]	1.44	0.7	0.02

[a]Water-extractable P.
[b]Phosphorus saturation index.
[c]Not applicable.
[d]Not determined.
Notes. 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.

an amorphous nature of the WTR. 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 WTR determines their effectiveness in reducing runoff P. This suggestion is consistent with the very small PSI value (~0.02), which indicates that the Al-WTR can be effective sorbent for P.

Effects of WTR on Phosphorus Solubility

Amendment with WTR significantly ($p < 0.001$) reduced the DPS values in surface soils amended with any of the P sources applied at the two rates (Figure 1), suggesting that the capacity of the soil to sorb P was enhanced by WTR amendment. Degree of P saturation 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

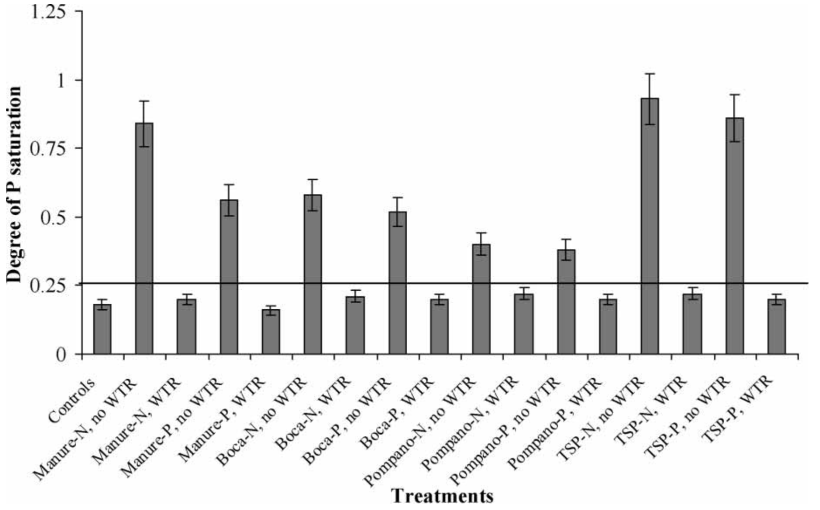

Figure 1. Effect of WTR amendment on degree of P saturation (DPS) of the A horizon (0–5 cm deep) of the Kirton Ranch soil samples taken in Jan. 2004. Error bars denote one standard deviation. NS: WTR amended vs. control is not significant; *** Plots without WTR vs. control is highly significant; ***Plots without WTR vs. WTR amended is highly significant; NS: WTR amended N rate vs. P rate is not significant; $n = 51$; ***indicates significance ($p < 0.001$); NS indicates non-significant ($p > 0.05$).

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 Flsoils is suggested to be 0.25 (25%) (Nair et al. 2004); soils with DPS values greater than 25% are expected to release significant amounts of P to surface runoff or leaching, whereas soils with DPS values less than 25% are not.

The plots treated with poultry manure (N-based) and TSP, without WTR amendment, had DPS values of 0.84 and 0.93, respectively, which suggest that these treatments could contribute significant amounts of P in runoff and/or leaching. Amendment with WTR decreased the DPS values of the TSP-treated plots 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 ($p \leq 0.013$). For the plots treated with Boca Raton biosolids, the reduction in the DPS values ranged between 49% (N-based) and 60% (P-based) relative to the respective treatment without WTR amendment. For the Pompano biosolids–treated plots, the reduction in DPS values ranged from 48% (N-based) to 53% (P-based) relative to the same treatments without WTR amendment. 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 2). For all P sources and rates of application, WTR amendment decreased the DPS values to values well less than the environmental critical threshold values (25%) suggested for Fl soils. In the presence of WTR amendment, no significant differences in DPS values were observed among the P sources and between the two rates of P application. The lower DPS values of the WTR-amended plots indicate the potential of WTR amendment to immobilize soluble P and to reduce P-source impacts on water quality.

Consistent with the DPS values, plots amended with WTR also had significantly lower water-extractable P (WEP) concentrations than the plots without WTR amendment (Figure 2). 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 2). As with the DPS data, immobilization of P by WTR also masked differences in WEP values among the P sources and the two rates of P application. In the absence of WTR, there were significant ($p \leq 0.011$) differences among the WEP values of the plots having different P sources and between the two rates of P application. However, with WTR amendment, theses differences were eliminated

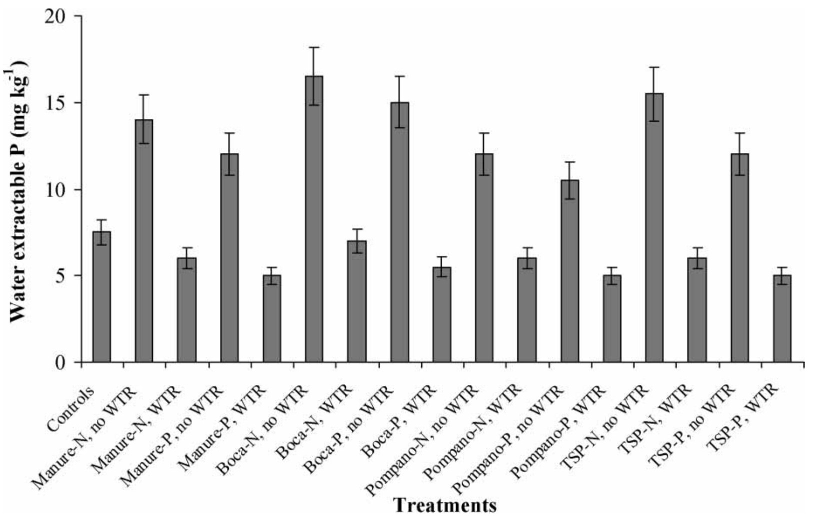

Figure 2. Effect of WTR amendment on water-extractable P of the A horizon (0–5 cm deep) of the Kirton Ranch soil samples taken in Jan. 2004. Error bars denote one standard deviation. NS: WTR amended vs. control is not significant; ***Plots without WTR vs. control is highly significant; ***Plots without WTR vs. WTR amended is highly significant; NS: WTR amended N rate vs. P rate is not significant; n = 51; ***indicates significance ($p < 0.001$); NS indicates non-significant ($p > 0.05$).

(Figure 2). Similar trends were observed for the Fe strip–extractable P (ISP) concentrations (data not presented).

As expected, oxalate-extractable Fe + Al concentrations of the samples were significantly ($p \leq 0.004$) greater in the WTR-amended plots than in the plots not amended with the WTR (Figure 3). Iron and Al hydroxides are major sorbents for oxyanions in soil. An increase in the sorbent content of the WTR-amended plots is expected to increase the P sorption capacity of these plots. Dayton et al. (2003) found a significant relationship ($r^2 = 0.69$, $p = 0.013$) between oxalate-extractable Al concentration (Al_{ox}) and the maximum P sorption capacity (P_{max}). Elliott et al. (2002) 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 h, soil P desorption from 44 German soils was inversely related to the oxalate-extractable Fe and Al content of the soil. The increased Fe and Al concentrations observed in the samples taken from the WTR-amended plots of our study were reflected in the DPS calculations, which showed significantly ($p < 0.001$) lower DPS values for the WTR-amended plots than for the plots without WTR amendment (Figure 1).

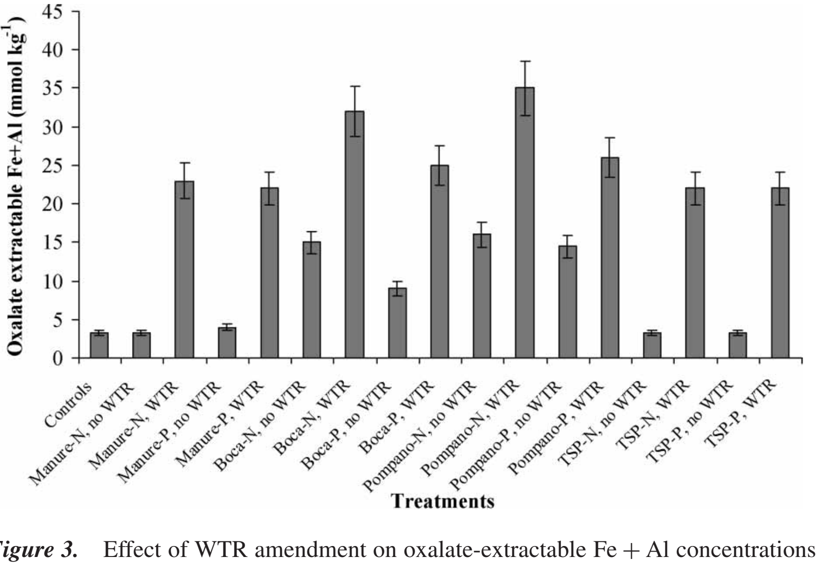

Figure 3. Effect of WTR amendment on oxalate-extractable Fe + Al concentrations of the A horizon (0–5 cm deep) of the Kirton Ranch soil samples taken in Jan. 2004. Error bars denote one standard deviation. NS: WTR amended vs. control is not significant; ***Plots without WTR vs. control is highly significant; ***Plots without WTR vs. WTR amended is highly significant; NS: WTR amended N rate vs. P rate is not significant; n = 51; ***indicates significance ($p < 0.001$); NS indicates non-significant ($p > 0.05$).

The data from the Kissimmee watershed (Kirton Ranch) field study is consistent with that of other studies (Elliott et al. 2002; Dayton et al. 2003; Ippolito et al. 2003; Makris et al. 2004a, 2004b, 2005a, 2005b, 2005c; Dayton and Basta 2005, Novak and Watts 2004, 2005; O'Connor, Brinton, and Silveira 2005; Silveira, Miyittah, and O'Connor 2006; Agyin-Birikorang et al. 2007) 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 best management practice (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 (Dayton and Basta 2005). However, the magnitude of the soil P sorption increase will depend on the P binding effectiveness of the WTR. Different WTRs have widely different characteristics, therefore for such field studies it is imperative to identify effective WTRs through preliminary laboratory studies.

Effects of Hurricane-Induced Flooding on Treatments

The soil P-specific measurements for 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 ($p = 0.021$) than those taken in June 2003 and Jan. 2004 (Figure 4a). Similar trends were observed in the ISP and WEP values (data not presented). 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 in the WTR-amended plots of A horizon (0–5 cm) soil samples (Figure 4b). Oxalate-extractable Fe + Al concentrations mirrored the trends observed in the totals (data not presented). Conversely, total P concentrations increased in the control plots and the plots not amended with WTR (Figure 4a). 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 amendment 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 of the WTR-amended plots can only result from physical movement of the soil and soil amendments from the WTR-amended plots to the plots without WTR amendment, and vice versa, due to the flooding of the field by the hurricanes.

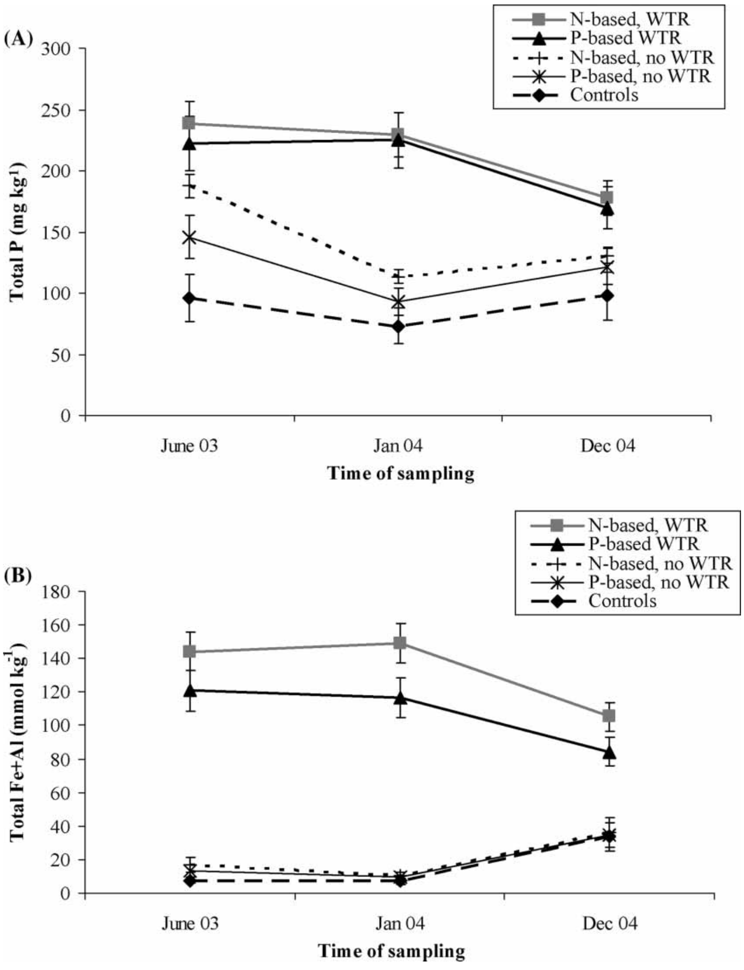

Figure 4. Effect of hurricane-induced flooding on (A) total P and (B) total Al + Fe concentrations of the A horizon (0–5 cm deep) of the Kirton Ranch soil samples. Error bars denote one standard deviation.

Stability of WTR-Immobilized Phosphorus

Despite the hurricane-induced flooding of the field that resulted in the movement of soil and amendments to and from individual plots, measured P values of the samples collected after the hurricanes continued to reflect the effectiveness of WTR in reducing soluble P levels. The WEP values measured from the A (0–5 cm) horizon plots amended with WTR were significantly lower ($p = 0.012$) than values from the plots without WTR amendment (Figure 5). Similar behavior was observed in the A (0–15 cm)

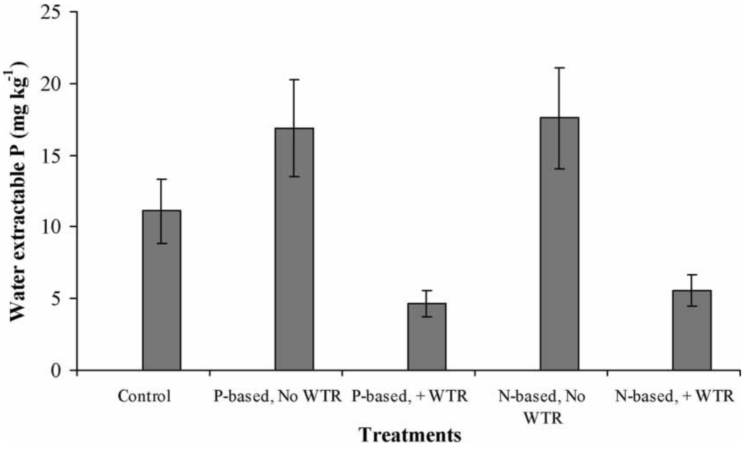

Figure 5. Effect of WTR amendment on water-extractable P of the A horizon (0–5 cm deep) of the Kirton Ranch soil samples after the hurricane-induced flooding. Error bars denote one standard deviation.

soil samples (data not presented). The ISP concentrations mirrored the trends observed in the WEP values (data not presented). The WEP and ISP data suggest that, despite the flooding of the field, most of the WTR-immobilized P remained stable.

Consistent with the WEP values, the DPS values of the WTR-amended plots sampled in Dec. 2004 were significantly ($p \leq 0.013$) smaller than those of the plots without WTR amendment (Figure 6). 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 values for the WTR-amended plots treated with biosolids was also significant ($p = 0.022$). For the plots treated with Boca Raton biosolids, the reduction in the DPS values ranged between 53% (N-based) and 46% (P-based). For the Pompano biosolids–treated plots, the reduction ranged from 55% (N-based) and 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 plots without WTR amendment, compared to the DPS values for the samples taken before the hurricanes (Figure 1). Nevertheless, the DPS values of the WTR-amended plots remained less than the threshold value of 25%, suggesting that, despite the flooding of the field, the WTR-amended plots retained the capacity to retard P movement.

Comparing the WEP values in the Bh horizon of the Dec. 2004 samples with those observed previously (June 2003 and Jan. 2004), a significant

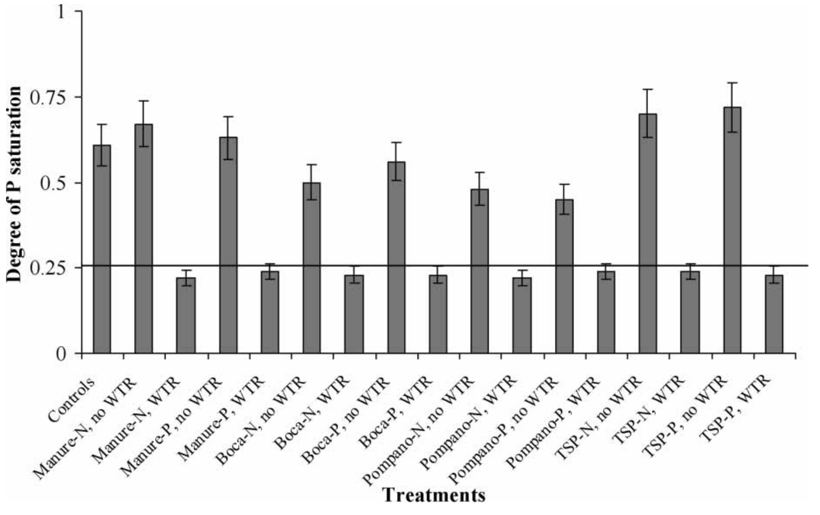

Figure 6. Effect of WTR amendment on the degree of P saturation (DPS) of the A horizon (0–5 cm deep) of the Kirton Ranch soil samples after hurricane-induced flooding. Error bars denote one standard deviation. NS: WTR amended vs. control is not significant; ***Plots without WTR vs. control is highly significant; ***Plots without WTR vs. WTR amended is highly significant; NS: WTR amended N rate vs. P rate is not significant; n = 51; ***indicates significance ($p < 0.001$); NS indicates non-significant ($p > 0.05$).

($p = 0.031$) increase in the WEP values was observed in the control plots and the plots without WTR amendment (Figure 7). 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 ISP, total, and oxalate-extractable P data (data not presented). 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 amendment and the control plots, whereas little or no P leaching occurred in the WTR-amended plots.

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 plots treated with P sources and P rates, with and without WTR amendment 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 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,

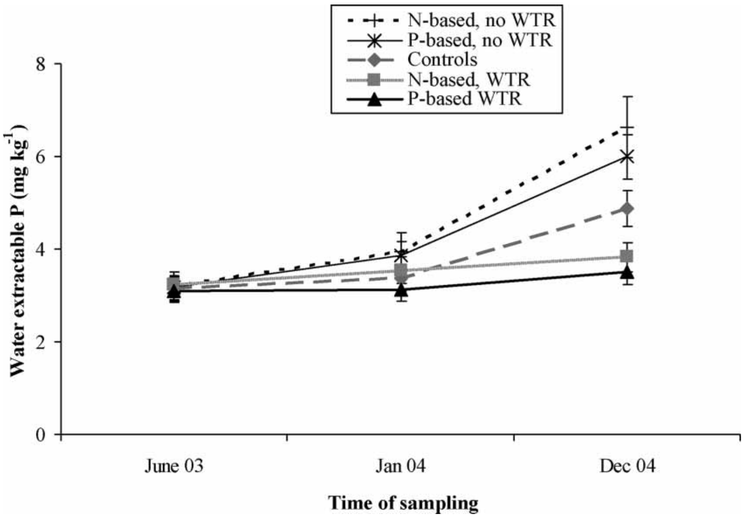

Figure 7. Effect of WTR amendment and hurricane-induced flooding on water-extractable P of the Bh horizon of the Kirton Ranch soil samples. Error bars denote one standard deviation.

rather than the WTR-immobilized P. 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 amendment 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 prevented excessive P leaching.

The combined data from this field study strongly suggest that Al-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, Miyattah, and O'Connor (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 (2007) concluded that once P diffuses to WTR micro-sites, very strong adsorption and highly hysteretic desorption occur. 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 (e.g., $pH < 4$).

CONCLUSIONS

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 and N-based rates. The 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 Florida, and the experimental plots were heavily flooded. The flooding appeared to have compromised the treatments (moved soil and associated treatments across plots), which compelled termination of 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 WTR effects were still obvious, despite the flooding of the field and the resultant movement of soil and amendments across individual plots. The soluble P values measured from the A (0–5 cm) horizon of plots amended with WTR were significantly lower than in the plots without WTR amendment. The degree of P saturation (DPS) values of the WTR-amended plots remained less than the environmental threshold value of 25% suggested for Florida soils. Phosphorus-specific 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 amendment and the control plots, whereas 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 prevented excessive P leaching. We conclude that WTR could reduce offsite P transport, which will lower P loads into nutrient-sensitive surface water systems, and that WTR immobilized P is stable even under severe flooding conditions.

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