Long-Term Phosphorus Immobilization by a Drinking Water Treatment Residual

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ABSTRACT

Excessive soluble P in runoff is a common cause of eutrophication in fresh waters. Evidence indicates that drinking water treatment residuals (WTRs) can reduce soluble P concentrations in P-impacted soils in the short term (days to weeks). The long-term (years) stability of WTR-immobilized P has been inferred, but validating field data are scarce. This research was undertaken at two Michigan field sites with a history of heavy manure applications to study the longevity of alum-based WTR (Al-WTR) effects on P solubility over time (7.5 yr). At both sites, amendment with Al-WTR reduced water-soluble P (WSP) concentration by $\geq 60\%$ as compared to the control plots, and the Al-WTR-immobilized P (WTR-P) remained stable 7.5 yr after Al-WTR application. Rainfall simulation techniques were utilized to investigate P losses in runoff and leachate from surface soils of the field sites at 7.5 yr after Al-WTR application. At both sites, amendment with Al-WTR reduced dissolved P and bioavailable P (BAP) by $>50\%$ as compared to the control plots, showing that WTR-immobilized P remained nonlabile even 7.5 yr after Al-WTR amendment. Thus, WTR-immobilized P would not be expected to dissolve into runoff and leachate to contaminate surface waters or groundwater. Even if WTR-P is lost via erosion to surface waters, the bioavailability of the immobilized P should be minimal and should have negligible effects on water quality. However, if the WTR particles are destroyed by extreme conditions, P loss to water could pose a eutrophication risk.

E LEVATED phosphorus (P) concentrations in surface waters contribute to the deterioration of surface water quality. Significant amounts of P added to the soil in the form of fertilizers, biosolids, and manures can pollute water supplies via surface runoff. The problem is exacerbated in poorly P-sorbing soils, such as coastal plain soils of the southeastern United States, where P leaching occurs and polluted water is intercepted by drains (or shallow water tables) that join surface waters. These soils are characterized by coarse textures and low Fe/Al hydroxide contents. Soil amorphous Fe/Al content is well correlated with P retention (Moore, 1998; Self-Davis et al., 1998; Elliott et al., 2002b; Dayton and Basta, 2005b). Therefore soils with relatively low amorphous Fe/Al contents are expected to have low P retention capacities.

Excessive soluble P concentrations in soils can be controlled through the addition of environmentally-benign and cost-effective P-sorbing amendments, such as alum (Moore, 1998) or drinking water treatment residuals (WTRs) (Peters and Basta, 1996; Basta and Storm, 1997; Elliott et al., 2002b; Novak and Watts, 2004; Novak and Watts, 2005). Drinking water treatment residuals are byproducts of the drinking water treatment process and are physical mixtures of Al or Fe hydr(oxides) that originate from flocculant (Al or Fe salts) additions (O'Connor et al., 2002). Drinking water treatment residuals are usually disposed of in landfills and can be obtained at minimal or no cost from drinking water treatment facilities.

Short-term laboratory, greenhouse, and rainfall simulation studies have demonstrated WTR efficacy in reducing soluble P concentrations in runoff (Dayton et al., 2003; Dayton and Basta, 2005a; Elliott et al., 2005) and leachate (Elliott et al., 2002a) from areas amended with animal manure. The long-term stability of the P sorbed by WTRs has been qualitatively addressed in laboratory experiments (Ippolito et al., 2003; Makris et al., 2004). Their work suggested that intraparticle P diffusion into the WTRs, coupled with minimal P desorption, represented irreversible P sorption by the WTRs. Makris et al. (2004) observed that adsorption of P by WTRs was strongly hysteretic and essentially independent of pH. Bottleneck-shaped micropores could limit P diffusion rates, being consistent with time-dependent sorption and hysteretic desorption. Micropore-bound P likely resists desorption, which favors long-term stability of sorbed P by WTRs (Makris et al., 2004). Makris et al. (2004) and Ippolito et al. (2003) suggest that WTRs can be effective sorbents for P and that the immobilized P would be stable in the long-term. However, long-term field experiments are needed to test WTR efficacy in reducing soluble P concentrations and to confirm trends observed in, or inferred from, laboratory studies. Time constraints associated with conducting long-term field experiments are the major drawback in evaluating the long-term fate of sorbed P in WTR-amended soils, and few researchers have conducted such studies.

Some field studies (Moore, 1998; Lu and O'Connor, 2001) have monitored soluble P concentrations in high P-containing soils treated with amendments similar in chemical composition to WTRs (i.e., high in amorphous Fe or Al content, such as alum salts, or biosolids relatively high in total Al and Fe). Most Fe- or Al-WTRs resemble amorphous Fe or Al hydroxides in chemical composition, and literature pertaining to Fe/Al hydroxide effects on soluble P concentrations can be used to

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predict the long-term fate of sorbed P by WTRs (Makris et al., 2005). Self-Davis et al. (1998) studied tall fescue grass plots treated with alum-amended poultry litter for 3 yr and showed no differences in soil water-soluble P (WSP) and Mehlich III P concentrations when compared to an unfertilized control. However, WSP in the untreated (no alum) poultry litter-amended plots linearly increased each year (Self-Davis et al., 1998). Lu and O'Connor (2001) showed that biosolids (containing 27 to 109 g kg^{-1} total Fe + Al) applied to a poorly P-sorbing soil increased P sorption initially, but the effect was minimal after 4 yr.

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

MATERIALS AND METHODS

Field Layout and Amendments Application

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

A randomized, complete block design was established at each site with four replications per treatment and individual plot size of 14 m × 30 m. The Al-WTR utilized for this study was obtained from the Holland, MI water treatment plant, which was removed from lagoon storage and stockpiled for drying. The dried Al-WTR was applied (114 dry Mg ha^{-1}, based on preliminary laboratory studies) to plots using a Knight ProTwin Slinger, model 8030 V-box spreader, by making three passes on each side of the plot, or three round trips. All plots, including the untreated controls, were disked (10–15 cm) twice following Al-WTR application. Additionally, site 1 was chisel-plowed and field cultivated before planting on 5 May 1998. Site 2 was moldboard plowed (20 to 25 cm) before planting on 4 May 1998. Both sites were moldboard-plowed before planting in 1999. In April/May, 2000, both sites were rototilled before planting to promote more thorough mixing of Al-WTR, then moldboard-plowed. Moldboard-plowing was used each spring, 2001–2004, at each site before planting. Field corn (*Zea mays* L.) was planted each year at both sites. Herbicides and insecticides for weed and pest control typically used by cooperating farmers were applied at planting. Fertilizer nitrogen and potash were applied as needed. The study continued for 7 yr, but the Al-WTR amendment was applied only in 1998. Details of the field study are given in Jacobs and Teppen (2000).

Soil Sampling

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

Soil and Alum-Based Drinking Water Treatment Residual Analyses

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 Al-WTR and soil samples was determined in a 1:2 Al-WTR (or soil)/0.01 M CaCl$_2$ solution using a glass electrode (McLean, 1982). Electrical conductivity (EC) of the Al-WTR was determined in a 1:2 Al-WTR/deionized water ratio (Rhoades, 1996). Total C and N of both Al-WTR and soil samples were determined by combustion at 1010°C using a Carlo Erba NA-1500 CNS analyzer (Carlo Erba, Milan, Italy). Bray P1 concentrations were determined by reacting the soil samples with 0.025 M HCl in 0.03 M NH$_4$F solution at a ratio of 1:10 soil/solution ratio and shaken for 5 min (Brown, 1998). The WSP in soils was determined by reacting soil samples with deionized water at a 1:10 soil/solution ratio for 24 h, modified from Kuo (1996). Soluble reactive P (SRP) in the Al-WTR was measured in a 0.01 M KCl solution at a 1:10 solid/solution ratio after 40 d reaction due to the high P sorption capacity of WTRs, whereas the SRP of the soil samples was measured after reaction for 24 h. Extracts were filtered (Whatman No 42) and analyzed colorimetrically for P using the Murphy and Riley (1962) method. Following digestion according to the USEPA Method 3050A (USEPA, 1986), total recoverable P, Fe, and Al in both Al-WTR and soil samples were determined using ICP–AES (PerkinElmer Plasma 3200). Oxalate (200 mM)-extractable P, Fe, and Al of both Al-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 ratio (PSR) (Maguire et al., 2001) was calculated for the soil samples, and represents the moles of oxalate-extractable P divided by the sum of moles of oxalate-extractable (Fe + Al).

Rainfall Simulation Experiment

The rainfall simulation was performed as prescribed in the U.S. National Phosphorus Research Project indoor runoff box protocol (National Phosphorus Research Project, 2001), using soil samples from each of the four replicates of each treatment at both sites. The 100 cm long, 20 cm wide, and 7.5 cm deep wooden runoff boxes were modified to quantify P leaching in addition to P runoff by adding a second empty (waterproof) box under the first in a double-decker design. This design allowed for runoff and leachate collection simultaneously. Soil samples from each of the four replicates of each treatment at both sites were used. Boxes were packed with 5 cm (14 kg) of soil to a bulk density of 1.4 g cm^{-3} and then sloped to 3%. Soils were then prewetted to near saturation to control for antecedent moisture and to promote runoff in the subsequent rainfall simulation. Rainfall simulations were conducted three times, at 1-d intervals between rainfall events, with rainfall delivered at 7.1 cm h^{-1} from a height of 3 m above the boxes.

For each rainfall event and box, 30 min of runoff was generated by the simulated rainfall, and the volumes recorded. Simultaneously, leachate generated during the entire rainfall was collected, and the volumes recorded. Runoff subsamples were immediately filtered (0.45 μm) for SRP and total dissolved P (TDP) analysis. Representative well-mixed samples of the unfiltered runoff and leachate (~250 mL each) were also taken from each replicate for additional analysis.

Leachate and runoff (filtered and unfiltered samples) pH and EC were determined on each sample collected. Soluble reactive P was determined on the filtered runoff and the leachate samples colorimetrically (Murphy and Riley, 1962). Total dissolved phosphorus was measured on the filtered runoff and the leachate samples after digesting 10 mL of the samples with 0.5 mL 11 N H_2SO_4 and 0.15 g of potassium persulfate in an autoclave for 1 h (Pote and Daniel, 2000a, 2000b). Total P in the unfiltered runoff samples was determined by digesting 5 mL of the samples with 1 mL of 11 N H_2SO_4 and 0.3 g of potassium persulfate on a digestion block and then diluting to 10 mL with distilled deionized (DDI) water (Pote and Daniel, 2000b). All digested samples were analyzed for P colorimetrically (Murphy and Riley, 1962). The iron oxide impregnated paper strip method (Myers and Pierzynski, 2000) was used to estimate bioavailable P (BAP) in runoff waters. Particulate phosphorus (PP) was calculated by subtracting TDP from the total P (TP) of each sample. Dissolved organic P (DOP) was assumed to be the difference between SRP and TDP.

Flow-weighted P concentrations (SRP, TDP, or TP) were determined for the runoff and the leachate by summing the product of the P concentrations and volumes for the three runs (P load) and dividing the P load by the total volume of the runs. The masses of runoff and leachate P losses (mg) were calculated as the product of flow-weighted concentrations (mg L^{-1}) and the runoff and leachate volumes (L), respectively. Total labile P lost was calculated by summing the BAP loads from the runoff and the TDP loads from the leachate, on the assumption that dissolved organic P loads in the leachate will mineralize and eventually become bioavailable. Total P losses were determined by summing the masses of runoff and the leachate P loss.

Quality Control

All sample collection/handling/chemical analysis was conducted according to a standard QA/QC protocol (Kennedy et al., 1994). For each set of samples, a standard curve was constructed ($r^2 > 0.998$). Method reagent blanks, as well as certified standards from a source other than normal calibration standards, were included in the extraction process. 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 this QA/QC protocol were re-extracted and 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 Institute, 1999). The means of the various treatments were separated using a single degree of freedom orthogonal contrast procedure at a probability level of 0.05. Time series analysis was conducted using the PROC TSCSREG procedure of the SAS software (SAS Institute, 1999).

The data collected from the rainfall simulation study showed great variation about the means with coefficient of variation >60%. This prompted us to test for normal distribution of the data using the Kolmogorov-Smirnov procedure and the normal probability plots of the Statistical Analysis System (SAS Institute, 1999). The P concentration data were not normally distributed, so typical analysis of variance could not be used. Instead, the NPAR1WAY procedure of the SAS software with the Kruskal–Wallis test was used. The NPARI-WAY procedure is a nonparametric procedure that tests whether the distribution of a variable has the same location parameter across different groups. The Kruskal–Wallis procedure tests the null hypothesis that the groups are not different from each other by testing whether the rank sums are different based on a Chi-squared distribution (Hollander and Wolfe, 1999). This is a powerful and robust test that is insensitive to variation among data and the presence of outliers (Hollander and Wolfe, 1999).

RESULTS AND DISCUSSION

Chemical Properties of the Alum-Based Drinking Water Treatment Residual

The Al-WTR was analyzed for selected chemical properties (Table 1). The pH of Al-WTR was slightly alkaline (7.4), possibly as a result of pH adjustment with alkaline materials (i.e., calcium hydroxide) during water treatment. The average EC value of the Al-WTR (1.21 dS m^{-1}) was well below the critical value (4.0 dS m^{-1}) for moderately salt-sensitive crops such as corn (Brady and Weil, 2002). The Al-WTR SRP (mean of 4 mg kg^{-1}) represented only a small fraction of the total P (mean of 800 mg kg^{-1}), implying that Al-WTR would be a poor source of plant-available P in soils. The total C value (34 g kg^{-1}) agreed with the range of C values found in Al-WTRs (23 to 205 g kg^{-1}; Dayton et al., 2003; Makris, 2004). However, total C determinations may overestimate organic C content because the combustion method (temperature 1010°C) measures both organic and inorganic C. The high total C levels found in many WTRs may be attributed to either lime additions for pH adjustment during water treatment or activated carbon addition to remove taste and odor from source waters. The Al-WTR had a C/N ratio less than 25, indicating that

Table 1. Selected physicochemical properties of the unamended soils (sites 1 and 2) and the alum-based drinking water treatment residual (Al-WTR). Numbers are mean values of six replicates ± standard error of the mean.

Parameter	Al-WTR	Site 1	Site 2
pH	7.4	6.4	6.8 ± 0.2
Sand, %	nd‡	60 ± 2	76 ± 4.5
Silt, %	nd	28 ± 1.2	16 ± 2
Clay, %	nd	12 ± 1.0	8 ± 0.9
Total C, mg kg^{-1}	34 000 ± 189	nd	nd
SRP, mg kg^{-1}†	4.0 ± 0.1	22.1 ± 1.3	58.1 ± 4.2
Bray P1, mg kg^{-1}	nd	265 ± 36	655 ± 70
Oxalate P, mg kg^{-1}	570 ± 81	790 ± 5.5	970 ± 8.3
Oxalate Al, mg kg^{-1}	29 700 ± 3600	2400 ± 15.3	710 ± 8.5
Oxalate Fe, mg kg^{-1}	2300 ± 295	730 ± 5.3	290 ± 0.8
Total P, mg kg^{-1}	800 ± 62	970 ± 34.7	1100 ± 4.3
Total Al, mg kg^{-1}	39 700 ± 2510	7000 ± 28.2	3400 ± 25.5
Total Fe, mg kg^{-1}	9200 ± 342	2700 ± 88.3	1800 ± 6.7

† SRP, soluble reactive P.
‡ nd, not determined.

some plant-available N could be present. A C/N ratio of between 20 and 30 is commonly used as the range where mineralization and immobilization of an organic amendment are in balance. Total P of the Al-WTR was 800 mg P kg^{-1}, typical of Al-WTRs (300 to 4000 mg P kg^{-1}; Dayton et al., 2003, Makris, 2004). The relatively high total P content was probably due to WTR concentrating effect after removal from contaminated raw water during treatment with P becoming part of the WTR structure. Total Al was ~40 g Al kg^{-1}, within normal ranges reported by others (15 to 177 g Al kg^{-1}; Dayton et al., 2003, Makris, 2004). Aluminum (hydr)oxides are sorbents for oxyanions such as phosphate. Thus the high Al contents of WTRs suggests that they will be major sorbents for P. Oxalate-extractable P, Fe, and Al are usually associated with the amorphous phase of the particles. Oxalate-extractable Al values were close to total Al (84% of the total), suggesting an amorphous nature of the Al-WTR. Makris (2004) also found that the traditional 200 mM oxalate-extractable P, Al, and Fe concentrations in most Fe- and Al-WTRs were typically 80 to 90% of the respective total elemental concentrations. Gallimore et al. (1999) concluded that amorphous Al, rather than the total Al content, best determines WTR effectiveness in reducing runoff P.

Soil Chemical Properties

The unamended soil samples collected at both field sites had near neutral pH (Table 1). Soils from both sites had very high Bray P1 soil test P (STP) values, with site 2 soil having the greater (~2.5X) STP. The high STP values reflect the long history of poultry manure application to the fields. The SRP accounted for 3.3 and 4.2% of the total P contents at site 1 and site 2, respectively. The high SRP concentration at both sites suggests that without proper management, these soils can contribute significantly to runoff P loss. The soil from site 1 had greater total Fe and Al than at site 2, suggesting that the site 1 soil had greater potential to sorb excess soil P.

Changes in Water-Soluble Phosphorus with Time

Water-soluble P has been used to successfully characterize P phytoavailability and solubility in soils amended with Al-WTR (Di et al., 1994; Codling et al., 2000; Ippolito and Barbarick, 2006). Measured WSP levels in the control plots did not change significantly with time in the field, and were ~22 and 30 mg P kg^{-1} for site 1 (Fig. 1A) and site 2 (Fig. 1B), respectively. Site 2 had significantly (p ~0.01) greater amounts of WSP in the control plots than site 1, consistent with greater soil test P levels and coarser texture (Table 1). The high, and nearly constant WSP levels in the control plots reflect the history of heavy manure applications to these soils, and portend that soils from both sites could still supply large amounts of soluble P in runoff over many years.

Amendment with Al-WTR significantly (p = 0.015) reduced WSP concentrations at both sites. At site 1, application of Al-WTR reduced WSP values from ~22 to 15 mg P kg^{-1} 6 mo after Al-WTR application, and WSP levels continued to decline for another 2 yr. Time
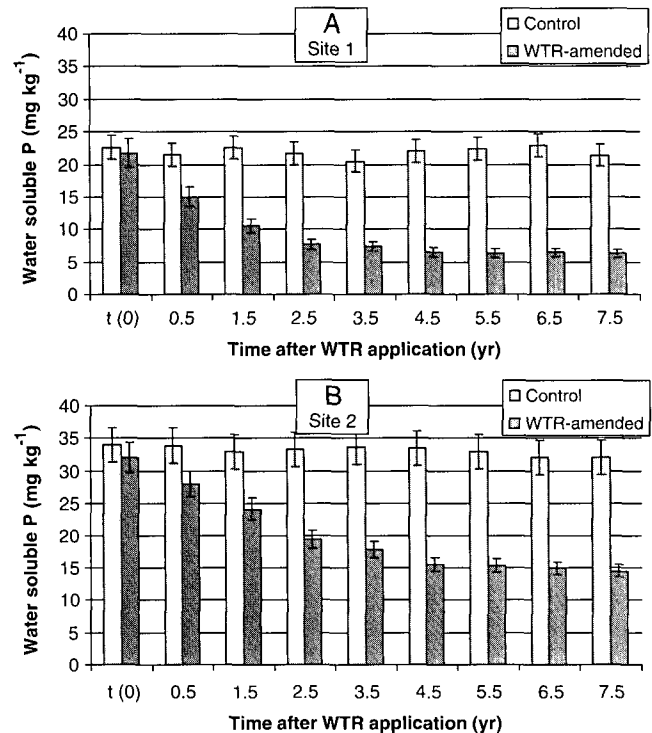

Fig. 1. Effect of alum-based drinking water treatment residual (Al-WTR) amendment on water-soluble P concentrations over the sampling period in the soils of: (A) site 1 and (B) site 2. Error bars denote one standard error of the mean.

series analysis suggests that an equilibrium WSP level (~6 mg P kg^{-1}) was reached around 2.5 yr after Al-WTR application or about a 70% reduction in WSP relative to the control. Similar Al-WTR effects were obtained for site 2 (Fig. 1B), with significant (p < 0.001) WSP reduction within 6 mo, continuing for another 4 yr. Time series analysis suggested that an equilibrium WSP level (~13 mg P kg^{-1}) was reached around 4.5 yr after Al-WTR application, which was about a 60% reduction in WSP as compared to the control. The greater WSP equilibrium time (4.5 yr) required at site 2 probably reflected the greater soil test P level as compared to site 1. The WSP reduction due to Al-WTR application is expected to reduce P loss and P pollution potential for these soils. Notable also is the longevity of the Al-WTR effect. There was no evidence of release of WTR-immobilized P over time as measured by the WSP values.

The reduction of WSP concentration due to Al-WTR amendment prompted us to assess Fe and Al concentrations changes with time. Iron and Al hydroxides, especially Al forms in Al-WTR, can be major sorbents of P. Dayton and Basta (2005b) reported that oxalate (200 mM)-extractable Al content is strongly and positively correlated (r^2 ~0.91) with the maximum P sorption capacity (P_{max}) of soils and soil amendments. Changes in the magnitude of sorbent with time are expected to influence the P sorption capacity of the amended soil. For WTR-amended plots at both sites, a significant (p ≤ 0.03) increase in oxalate-extractable soil Al and Fe concentrations was observed (Fig. 2), although the concentrations showed some variability over time. Oxalate-
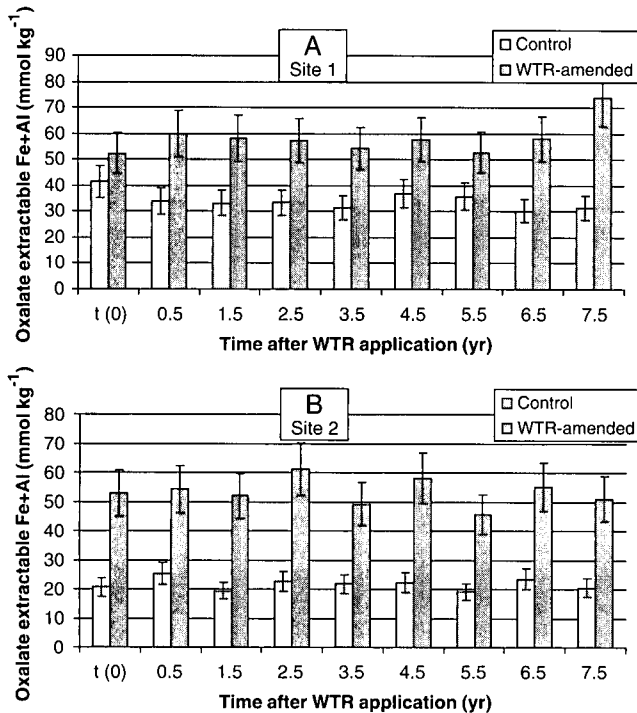
Fig. 2. Effect of alum-based drinking water treatment residual (Al-WTR) amendment on oxalate-extractable Fe and Al concentrations over the sampling period in the soils of: (A) sites 1 and (B) site 2. Error bars denote one standard error of the mean.
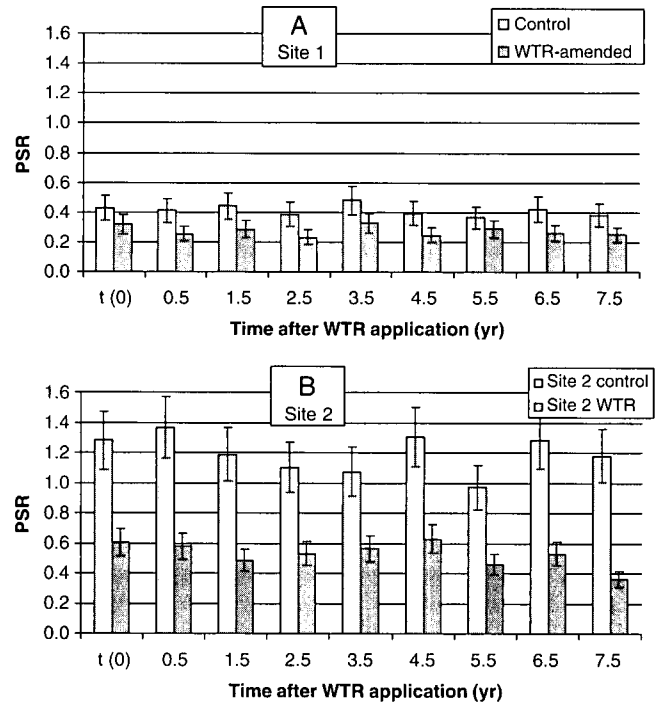

Fig. 3. Effect of alum-based drinking water treatment residual (Al-WTR) amendment on phosphorus saturation ratio (PSR) values over the sampling period in the soils of: (A) site 1 and (B) site 2. Error bars denote one standard error of the mean.

extractable Fe and Al represent noncrystalline and organically complexed Fe and Al present in the solid (McKeague et al., 1971). The WTR-amended plots of site 2 exhibited a greater increase in oxalate-extractable Al and Fe concentrations than site 1, possibly due to site 2 soil containing lower initial Al and Fe concentrations (Table 1). The variability in oxalate-extractable Al and Fe concentrations over time could be attributed to sampling variability. The variability in the oxalate-extractable Fe and Al concentrations observed with time at both sites (Fig. 2) prompted the calculation and analysis of the PSR (Maguire et al., 2001) to evaluate Al-WTR effect. The PSR is similar to the degree of P saturation (DPS) index, but omits the saturation factor, α (α = 0.3–0.5) in the ratio (Schoumans, 2000). Small PSR values (<0.1) suggest excess P sorption capacity and limited P lability. The PSR values for both sites were calculated and statistically analyzed to evaluate subtle differences between treatments over time.

For site 1, PSR values of the Al-WTR-amended plots did not significantly ($p > 0.05$) differ from the control (no WTR) plots (Fig. 3A). Aging in the field had no significant effect on the PSR values for Al-WTR-amended plots even 7.5 yr after Al-WTR application. For site 2 (Fig. 3B), PSR values were at least double those of site 1 for both control and WTR-amended plots because site 2 had about twice the STP and one-half the total Fe and Al concentrations (Table 1). Control plots of site 2 had relatively high PSR values (>1), which suggest this soil could contribute to increased P in surface runoff. Amendment with the Al-WTR significantly ($p = 0.015$) decreased PSR values 6 mo after applica-

tion, remained relatively constant thereafter, and had PSR values <50% of the control samples (Fig. 3B). Similar to the WSP findings, the lack of significant change over time suggests little potential for time-dependent P release from Al-WTR-amended plots.

Rainfall Simulation Study

The rainfall simulation study was conducted to confirm Al-WTR effects on WSP measurements. Soils from each of the four replicate plots, from the control and WTR-amended plots (7.5 yr after Al-WTR amendment), were used. The masses (mg) of the various forms of P lost in runoff and leachate from soil samples collected from both sites are given in Table 2. There was great variability within the data. As a result, the data were analyzed using a nonparametric statistical procedure, which is insensitive to data variability. Due to the high variation of the data about the mean values of the treatments, the median values were used instead to describe the central tendencies of each treatment.

There were significantly (p ~0.01) greater P losses from the soil samples collected from site 2 (both the control and the WTR-amended soils) than from site 1 (Table 2). Results were consistent with the greater STP values and greater WSP values for soil at site 2 than at site 1. Most of the P lost from both sites occurred through surface runoff rather than through leaching (Table 2).

The total runoff P losses of the samples taken from both sites were dominated by PP, and greater PP loads came from the WTR-amended plots relative to the respective control plots. The runoff TDP at both sites was

Table 2. Masses of the various P forms measured in runoff and leachate from unamended and drinking water treatment residual (WTR)-amended soils from sites 1 and 2 utilized for the rainfall simulation experiment. Numbers are flow-weighted median values. Same letters in same column denotes no significant difference ($\alpha = 0.05$).†

Treatment	Runoff						Leachate			Total P loss (runoff + leachate)‡	Total labile P loss (runoff + leachate)§
	TDP	SRP	DOP	PP	BAP	Total P	TDP	SRP	DOP		
	mg										
Site 1											
Control	48.0b	44.7b	3.31b	57.1c	62.1b	105b	31.4b	14.0b	17.9b	136b	94.0b
WTR	19.7d	17.9d	1.82c	92.5b	21.3d	112b	14.6d	6.40c	8.23d	127b	35.9d
Site 2											
Control	72.1a	66.7a	5.44a	90.0b	102a	162a	49.0a	22.4a	26.5a	211a	151a
WTR	32.8c	29.5c	3.30b	142a	39.8c	175a	20.6c	7.83c	12.7c	196a	60.4c

† TDP, total dissolved P; SRP, soluble reactive P; DOP, dissolved organic P; PP, particulate P; BAP, bioavailable P.
‡ Total P loss = runoff total P + leachate TDP.
§ Total labile P loss = runoff BAP + leachate TDP.

dominated by SRP, with DOP occurring in small proportions (<10% of TDP). Contrary to TDP in runoff, TDP in the leachate had greater absolute values of DOP than SRP. An independent determination of the TDP was performed on the undigested leachate samples using inductively coupled plasma-atomic emission spectrometry (ICP–AES) (PerkinElmer Plasma 3200; PerkinElmer, Wellesley, MA). The values obtained from this independent determination were similar to those obtained from the digested leachate samples determined colorimetrically. We therefore concluded that PP loads in the leachate samples were negligible and were consequently not determined analytically.

The high PP concentrations observed in runoff from the soil samples prompted estimation of BAP levels in the runoff water using the iron-oxide impregnated paper strip method (Myers and Pierzynski, 2000). As expected, the runoff BAP lost from the soil samples taken from site 2 were significantly greater than those taken from site 1 (Table 2), consistent with the higher STP and WSP values of the site 2 soil. For site 1, the runoff BAP of the control soils accounted for >50% of the runoff total P lost, whereas runoff BAP lost from the WTR-amended plots accounted for ~20% of the runoff total P lost (Table 2). Similar behavior was observed for the samples taken from site 2, with the runoff BAP accounting for >60% of runoff total P lost in the control and ~25% for the WTR-amended soils (Table 2).

Total labile P lost (runoff BAP plus leachate TDP) was quantified to evaluate the overall effect of the Al-WTR in improving runoff and leachate quality. For site 1, the total labile P lost from the control plots accounted for ~70% of the total P lost (from runoff + leachate), whereas total labile P lost from the WTR-amended plots accounted for ~30% of the total P lost (runoff total P plus leachate TDP) (Table 2). Similarly, for site 2, >70% of the total P lost in runoff and leachate from the control plots was labile P, whereas ~30% of the total P lost from the WTR-amended plots was accounted for by the total labile P.

Effects of Alum-Based Drinking Water Treatment Residual on Runoff and Leachate Phosphorus Losses

No significant differences were found between the flow-weighted TP mass losses from the WTR-amended

plots and the control plots at either site (Table 2). However, the flow-weighted TDP, SRP, and DOP mass losses were significantly ($p < 0.05$) reduced at both sites in the presence of Al-WTR. Conversely, the flow-weighted PP masses were significantly (p ~0.02) greater in the WTR-amended plots at both sites than the control plots (Table 2). Most likely, the particles detached by the rain drops from the WTR-amended plots contained some WTR and had greater P enrichment due to the Al-WTR immobilization than the soil particles detached from the control plots.

For site 1, application of Al-WTR reduced the flow-weighted SRP masses by ~60% and DOP by ~55% (Table 2). Overall, amendment with Al-WTR decreased flow-weighted dissolved P mass by ~60%. Similar results were obtained for site 2. Amendment with Al-WTR reduced SRP masses by >50% and DOP by ~40% (Table 2), resulting in an overall reduction of flow-weighted dissolved P by ~50%.

Field-based soil sampling (Fig. 2) showed that Al-WTR amendment increased the content of P-fixing Al and Fe concentrations in the soils at both sites. Runoff BAP concentrations were consistently lower when the oxalate extractable molar Al + Fe content of the soil was high (Fig. 4). This further emphasizes the importance of Al and Fe content in reducing soluble soil P levels. Brandt and Elliott (2003) showed that, as the content of P-fixing Al and Fe in soils and P sources in-
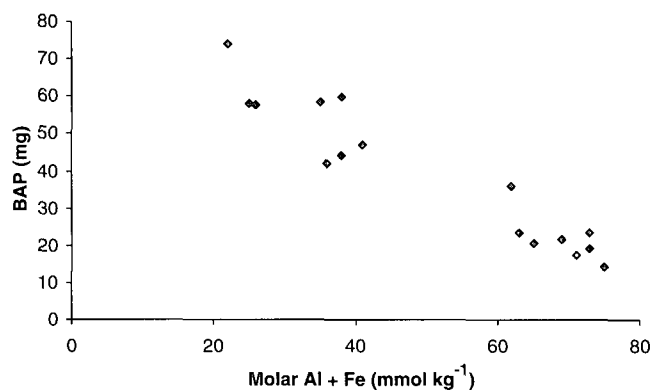

Fig. 4. Relationship between runoff bioavailable phosphorus (BAP) and molar oxalate extractable Al + Fe contents of the soil samples taken from both sites in fall 2005.

creased, TDP concentration in runoff decreased. Elliott et al. (2005) concluded that TDP concentrations in runoff can be reduced by adding Al and Fe salts to biosolids and dairy manure that had high concentrations of water-soluble P. Dayton and Basta (2005a) reported that addition of WTR as an enhanced buffer strip in a poultry litter-impacted soil greatly reduced dissolved reactive P (DRP) and the reduction was related to the WTR P sorption capacity.

Amendment with Al-WTR decreased the total (runoff + leachate) flow-weighted TDP concentrations from ~2.5 mg P L^{-1} to ~0.86 mg P L^{-1} at site 1, and from ~3.2 mg P L^{-1} to ~0.94 mg P L^{-1} at site 2 (data not presented). The reduced values exceed those (0.01 to 0.05 mg P L^{-1}) usually associated with eutrophication of surface waters (USEPA, 1986), but are below a solution concentration of 1.0 mg P L^{-1} occasionally used as a benchmark. The 1.0 mg P L^{-1} benchmark concentration is a common goal for wastewater discharges to rivers and streams and has been applied to soils on the premise that the discharge of P from soils to water should be held to the same standard (Sims and Pierzynski, 2005). Greater single amendment rates (>114 Mg WTR ha^{-1}) or multiple (yearly) WTR applications are likely to be necessary to reduce TDP concentration to the 0.01 to 0.05 mg P L^{-1} target concentration range.

A large proportion (45 to 75%) of the total P load loss in runoff was PP (Table 2). Compared to the control plots, greater PP losses occurred in the WTR-amended plots at both sites. Despite the greater particulate P loads in runoff from the WTR-amended plots, flow-weighted BAP loads in runoff were significantly smaller than those of the control plots (Table 2), suggesting that much of the particulate P was not bioavailable. Thus, even if WTR-P erodes to surface waters, there should be minimal adverse effects on water quality. However, if the WTR particles are destroyed by extreme conditions, P loss to water could pose a eutrophication risk.

After 7.5 yr, Al-WTR amendment still reduced total labile P in runoff and leachate by >60% as compared to the control plots from the two manure-impacted field sites. This suggests that WTR-immobilized P is stable and will remain fixed essentially indefinitely as long as the Al-WTR solid integrity is maintained. Co-applying Al-WTRs with other residuals (manures, biosolids) could effectively counter the P risks associated with the residuals and allow land application of the residuals even in sensitive watersheds.

CONCLUSIONS

The study was conducted to assess the longevity of Al-WTR immobilization of P from manure-impacted soils under field conditions. Amendment with Al-WTR reduced WSP concentration by ≥60% compared to the control plots, and the WTR-immobilized P remained stable for 7.5 yr. The data suggest that Al-WTR amendment should reduce P losses from soils, and do so for a long time. To confirm this, we utilized rainfall simulation techniques to investigate P losses in runoff and leachate from soils amended with a one-time application of Al-

WTR 7.5 yr earlier. Amendment with Al-WTR reduced TDP and BAP by >50% from both sites, showing that the WTR-immobilized P remained nonlabile. The data suggest that Al-WTR can be relied on to reduce P losses in runoff and leachate, and that even if WTR-P erodes to surface waters, the bioavailability of the immobilized P should be minimal. Eroded WTR should have negligible effects on the water quality, barring destruction of the WTR particles by extreme conditions.

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