



Drinking Water Treatment Residuals to Control Phosphorus in Soils¹

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Introduction

The use of drinking-water treatment residuals (WTR) to control excess phosphorus (P) in soils with limited P adsorption capacity has received increased attention in recent times. The target audience for this publication includes state agencies, like the Florida Department of Environmental Protection (FLDEP), and water management districts trying to control P pollution, and those interested in nutrient management for agricultural and environmental purposes.

Phosphorus Problem in Florida

Many agricultural soils in Florida contain excess soil phosphorus (P) concentrations as a result of repeated fertilizer, manure or biosolids applications. Accumulation of P in soil does not damage soil fertility or harm plants, but can promote off-site losses of P to surface water bodies. Water pollution due to excessive P is a major concern receiving much attention. Phosphorus moves from agricultural fields either dissolved in water that drains away or as particulate matter (attached to soil particles) that travels with eroding soil. Increased P in water bodies

is recognized as one of the major factors responsible for eutrophication-related decrease in water quality. "Eutrophication" is a term used to describe the process whereby a water body becomes rich in nutrients, particularly phosphate and nitrate, which promote the growth of algae. The decomposition of dead algae depletes the water body of oxygen that impedes the survival of other species.

Worldwide, most soils have a moderate to high capacity to retain P, which reduces P movement with drainage water. The term that describes the process by which a soil retains P is "sorption." In contrast to other areas, Florida has abundant soils that retain P poorly. Many of these soils are also very poorly drained, i.e. they flood during periods of heavy rainfall. Low P sorbing capacity, in conjunction with a high water table, makes Florida soils vulnerable to P losses. Off-site P transport can also readily occur by leaching, which is the downward movement of P through the soil to the water table. Leached P can then move to surface waters via lateral subsurface flow as the soil drains internally.

The potential for a soil to lose P can be decreased if its P sorption capacity is increased through

1. This document is SL 300, one of a series of the Soil and Water Science Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida. Original publication date July 2009. Visit the EDIS Web Site at <http://edis.ifas.ufl.edu>.

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application of certain soil amendments. A municipal byproduct proven to be an effective amendment in controlling off-site P transport from poorly P-sorbing soils is drinking-water treatment residual (WTR), a byproduct of drinking water purification. WTR naturally has a very high P sorption capacity, so researchers have proposed using it to reduce P loading into surface or ground water. Several best management practices (BMPs) using WTR to reduce nonpoint source pollution by P have been proposed. One approach is to surface-apply WTR to reduce transport of P in runoff water. Another approach is to incorporate WTR into soil to reduce the solubility of P accumulated from previous applications, preventing P leaching.

What Are WTRs And How Are They Generated?

Drinking-water treatment residuals are primarily sediment, metal (aluminum, iron or calcium) oxide/hydroxides, activated carbon, and lime removed from raw water during the water purification process. Polymers are sometimes added to aide the dewatering process. The relative effectiveness of WTRs in reducing soluble P depends on several factors, including source water characteristics, water treatment methods, and length of residual storage time prior to land application. Each water treatment facility uses unique source water and different treatment chemicals and processes, producing WTR with different physical and chemical compositions and P sorption capability (Table 1).

Coagulation, flocculation, and sedimentation (or coagulation and filtration) are processes used in water treatment to remove turbidity, color, taste, and odor from raw water, and to speed particulate matter removal. The purpose of coagulation and flocculation is to promote small particle combination and formation of larger aggregates. Typically, metal salts such as ferric chloride (FeCl_3) or alum [$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$] are used during the coagulation process to accomplish these steps. The residuals resulting from the use of iron or aluminum salts as coagulants are herein referred to as aluminum-based WTR (Al-WTR) and iron-based WTR (Fe-WTR). The other major residual type, calcium-based WTR

(Ca-WTR), is produced in water-softening facilities where lime is used to decrease hardness.

How Are WTRs Disposed?

A consequence of the global expansion and proliferation of water treatment facilities is the increased generation of WTRs that require appropriate methods of disposal. There are thousands of drinking-water treatment plants in the United States that use metal salts as coagulants for efficient removal of particulate solids and colloids from surface water, generating more than 2 million metric tons of WTR daily. Drinking-water treatment residuals can be disposed: a) directly to a receiving stream; b) to sanitary sewers; c) to a landfill, assuming that the residual contains no free-draining water and does not have toxic characteristics as defined by the toxicity characteristic leaching procedure (TCLP) test; and d) by land application. A 1991 national survey of 612 utilities serving populations of >50,000 showed that landfilling was the predominant disposal method, followed by land application, sanitary sewer disposal, direct stream discharge, and lagooning (Kawczyinski and Achtermann, 1991). In Florida, the most acceptable long-term disposal methods for WTRs are landfilling and land application (O'Connor et al., 2002). The disposal (via landfill) cost of non-hazardous materials, including WTRs, is ~ \$50 per metric ton, which can substantially increase the cost of treated drinking water. Furthermore, landfill space for WTR disposal will be limited in the near future. Land application of WTR is therefore an attractive and less expensive alternative means of WTR disposal and may have the added benefit of immobilizing P in poorly sorbing soils.

Using WTR to Control Off-Site Phosphorus Losses

Land application of WTR has been shown to be cost-effective for effectively sorbing excess levels of labile P in soils. The high amorphous Al or Fe contents of the WTR increase soil P sorption capacity. Laboratory studies have shown that Al-WTRs adsorb large amounts of P and increase the P-sorbing capacity of poorly P-sorbing soils, thereby decreasing P losses in runoff and leaching. We

reacted Al- and Fe-WTRs with inorganic P solutions at P loads up to 10,000 mg P/kg and observed that almost all the added P was sorbed by most WTRs, although some WTRs sorbed little P (Table 1).

Surface application of WTR has successfully reduced dissolved P concentrations in runoff water. In a rainfall simulation study, we amended P-impacted Immokalee fine sand with Al-WTR at rates up to 56 metric tons/ha and observed ~88% reduction in runoff + leachate dissolved P, relative to the control soil without WTR amendment (Fig. 1). We also evaluated WTR effectiveness in a typical Florida Spodosol (Immokalee fine sand) amended with different P sources (manure, biosolids and inorganic fertilizer) in a field study and observed decreases in soluble P concentrations of the P-source amended soil. Treatments without WTR amendments had greater water extractable P (WEP) concentrations (>10 mg/kg) than the WTR amended treatments (Fig. 2). In the absence of WTR, there were differences in WEP concentrations between different P-source treatments. However, with WTR amendment, not only were the WEP values significantly decreased, but the differences in the WEP concentrations arising from the differences among the P sources were no longer obvious (Fig. 2).

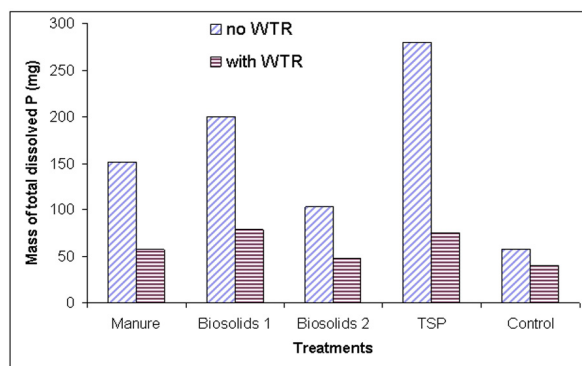


Fig. 1. Effect of WTR (10 tons/acre) amendment on masses of total dissolved phosphorus lost from Immokalee fine sand treated with P (100 lbs/acre) sources of different solubilities in a rainfall simulation experiment.

Beneficial use of WTR has also been expanded to reduce the solubility of P in organic soil amendments like manure or biosolids. Co-blending WTR with manure or biosolids before land application reduces P solubility and allows farmers to take advantage of the nitrogen, micronutrients, and

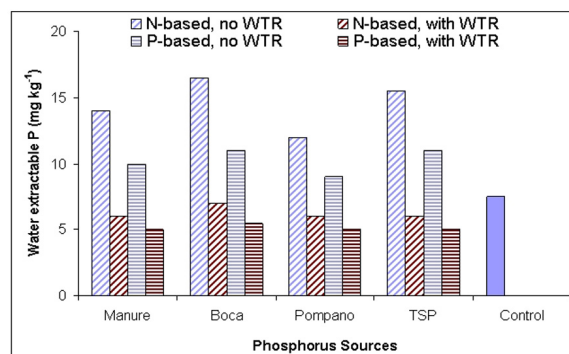


Fig. 2. Effect of phosphorus sources (applied at N-based, and P-based rates) and WTR amendment (10 tons/acre) on water extractable phosphorus saturation (WEP) of the A horizon (0-5 cm depth) of the soil samples in a field study.

organic carbon content of the manure or biosolids without increasing the P loss risk.

Land-application of WTRs can also reduce P leaching, but the maximum benefit occurs when full contact of soil soluble P with the WTR particles is ensured. Either Fe- or Al-based WTRs reduced P leaching in a low P-sorbing Florida sand amended with dewatered biosolids and triple superphosphate (TSP) fertilizer. Amendment with WTRs reduced P leaching to 3.5% (Ca-WTR), 2.5% (Fe-WTR) and <1% (Al-WTR) of applied P from TSP. For the biosolids treatments, all WTRs retarded P leaching to the extent that leachate P concentration did not differ from the unamended control soil. In a similar study, we evaluated WTR effectiveness in reducing P loss to groundwater (under natural field conditions) from a typical Florida Spodosol surface-amended with P sources of different solubility. Surface-applied WTR reduced P leaching into shallow groundwater. In the presence of WTR, groundwater P concentrations were significantly lower than in plots without WTR (Fig. 3).

Applying WTRs to poorly P-sorbing soil increases the P sorption capacity of the soils, and reduces off-site P movement from fields via runoff and leaching. However, the magnitude of the increase in P sorption capacity of the soil depends on the P binding effectiveness of the WTRs. Reducing off-site P transport reduces P loads into surface water, which in turn can minimize eutrophication and protect water quality.

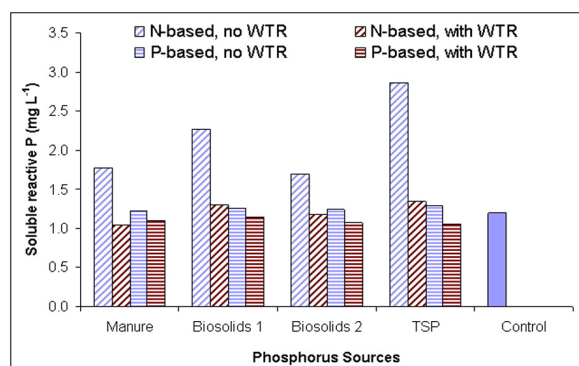


Fig. 3. Effects of P sources (applied at N-based-, and P-based rates) and WTR amendment (10 tons/acre) on the soluble phosphorus concentrations of shallow (~0.9 m) groundwater samples obtained from a field study.

Can Aluminum-Based WTR Retain P for a Long Time?

Concerns have been raised about the long-term stability of P that has been sorbed by a WTR soil amendment. We used methods such as spectroscopic and solid-state characterization of P-loaded WTR particles to better understand the long-term stability of sorbed P. The results suggest that P sorption by Al-WTRs is practically irreversible. Once P reaches the WTR microsites, the adsorption is very strong, and little or no desorption is likely. Thus, once immobilized by the WTR particles, P is likely irreversibly bound, barring destruction of the WTR particles associated with extremely low soil pH values.

We evaluated aging and pH effects on the lability of WTR-immobilized P using artificially-aged WTR-amended Immokalee soil and field-aged Granby loamy sand. Within the pH range of commonly occurring agricultural soils (4 to 7), WTR amendment, coupled with aging, ultimately reduced labile P in artificially aged samples by ~75%, and field-aged samples by about ~70% relative to the control (no-WTR) samples (Fig. 4). The results suggest that WTR application can reduce the labile P concentration in P-impacted soils for a long time within the pH range commonly encountered in agricultural soils (Agyin-Birikorang and O'Connor, 2007).

In a related field study in Michigan, we assessed the longevity of an Al-WTR immobilization of P in two fields with long histories of poultry manure

applications (Agyin-Birikorang et al., 2007). We utilized rainfall simulation techniques to investigate P losses in runoff and leachate from soils amended with a one-time application of an Al-based WTR 7.5 yr earlier. Amendment with Al-WTR reduced soluble P concentration in the soils by >60% compared with control plots, and the WTR-immobilized P remained stable for at least 7.5 years. Amendment with Al-based WTR reduced total dissolved P and biologically available P by >50%, showing that the WTR-immobilized P indeed remained nonlabile (Agyin-Birikorang et al., 2007).

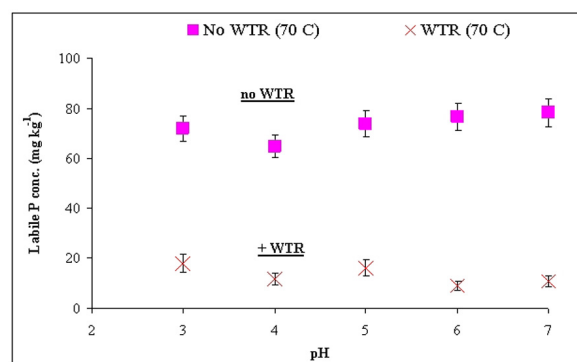


Fig. 4. pH effects on labile P of P impacted Immokalee soil samples incubated for 4.5 yr at 70°C. Error bars denote one standard error of the mean.

How Much WTR Must Be Applied?

Different WTRs can have different chemical characteristics (including different P sorption capacities), and application of different WTRs at the same rate can result in different agronomic and/or environmental impacts. Hausteine et al. (2000) compared the potential of two Al-rich materials to reduce runoff P from excessively P-impacted fields. The material with greater total Al concentration (46.7 g/kg), applied at both 9 and 18 metric tons/hectare, decreased runoff P below that measured in control plots throughout the 4-month experiment. At the same WTR application rates, the material with a lower total Al concentration (15.9 g/kg) decreased the runoff P for only 1 month (Hausteine et al., 2000).

Determining the appropriate application rate of WTR is complicated due to variation in chemical properties influenced by the source of water, treatment chemicals and processing used by drinking-water treatment plants. Soils, and P-sources

co-applied with WTR, can also vary in physical and chemical properties. Thus, the compositional variability of soils, P-sources (if co-applied with WTR), and WTRs need to be considered when determining WTR application rate. A quantitative approach using WTRs to reduce P flux from P-amended soils should be based on ensuring sufficient reactive Al + Fe in the WTR to immobilize labile P in the soil.

Nair and Harris (2004) developed a technique [soil phosphorus storage capacity (SPSC)] to predict the amount of P a soil can sorb before exceeding a threshold soil equilibrium concentration. The SPSC values are calculated from oxalate-extractable P, Fe, and Al concentrations of a soil as:

$$SPSC (mgP/kg) = (0.15 - PSR) * (Al_{ox} + Fe_{ox}) * 3I$$

$$\text{where } PSR = \text{Phosphorus sorption ratio} = \frac{(P_{ox})}{(Al_{ox} + Fe_{ox})}$$

P_{ox} , Al_{ox} , and Fe_{ox} are 0.2 M oxalate-extractable P, Al, and Fe concentrations of the soil respectively (expressed in mmoles). The SPSC values can indicate the risk arising from P loading as well as the inherent P sorption capacity of the soil. The SPSC values range from negative values (for highly P-impacted soils with no remaining P retention capacity) to positive values (for less P-impacted soils, excess P retention capacity). Oladeji et al. (2007) identified zero SPSC as an agronomic threshold above which yields and P concentrations of plants may decline and below which there is little or no yield response to increased plant P concentrations. The consensus among researchers is that soils can be managed to maintain soil test P for optimal economic crop yields while minimizing the risk of offsite P loss. Applying P sources at any rate, along with sufficient WTR to give a SPSC value of 0 mg/kg, enhances environmental benefits (reduced P loss potential) without negative agronomic impact.

An application of WTR based on the SPSC threshold targets only the excess P that poses environmental threats, and is not expected to negatively impact plant-available soil P needed to meet the plant requirement. Therefore P storage capacity should be determined for WTRs and P sources (if any) prior to land application. The P

storage capacity of the WTR and the P sources can be determined by modifying the SPSC equation (above) by substituting PSR with the phosphorus saturation index (PSI). (The PSI is similar to PSR but PSI is used to describe P binding/release potential of organic sources whereas PSR is used for soils). Thus, the P storage capacity of the P sources ($APSC_{source}$) and WTR ($APSC_{WTR}$) can be calculated as:

$$APSC (mg P/kg) = [(0.15 - PSI) * (Al_{ox} + Fe_{ox})] * 3I$$

where APSC = amendment P storage capacity, and

$$PSI = \text{Phosphorus sorption index} = \frac{(P_{ox})}{(Al_{ox} + Fe_{ox})}$$

The P storage capacity of the soils and amendments can then be combined to determine the amount of WTR to apply to a P impacted soil or to be co-applied with other P sources.

The amount of WTR to be added can then be determined as:

$$SPSC_{soil} * Mass_{soil} + APSC_{source} * Mass_{source} + APSC_{WTR} * Mass_{WTR} = 0$$

The SPSC value of the soil and the APSC values of P-source and the WTR can be determined from the chemical compositions of the soil and amendments. The quantity of the P-sources is known from the application rate, and the mass of soil could be determined from the land area to depth of impact (depending on application method; 15 cm depth if incorporated, or 5 cm when surface applied) and the soil bulk density. The only unknown in the equation would be the mass of WTR, which can be determined by substituting the known values into the equation.

The SPSC-based WTR application rate will not only account for the P, Al, and Fe concentrations in the residuals and the soil, but the threshold soil P value as well. Thus, the WTR rate required to attain a desired SPSC value can be calculated to ensure a soil P concentration below the environmental threshold, while at the same time supplying sufficient P to meet plant needs.

Further Readings

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Table 1. Selected chemical properties of Drinking-Water Treatment Residuals. Numbers are average values of six replicates for Al-WTR, eight for Fe-WTR, and two for Ca-WTR

Properties	Al-Based	Fe-based	Ca-based
pH	5.03 - 8.24	4.10 - 9.22	8.43 - 11.4
KCl-P (mg/kg)	2.24 – 5.61	6.25 – 6.31	0.82-1.63
Total C (g/kg)	8.51 - 225	94.0 - 206	114-201
Total N (g/kg)	3.04 – 10.0	5.0 1– 11.0	0.32-1.26
Total Al (g/kg)	15.1 - 300	2.23 – 10.0	0.34-14.1
Total Fe (g/kg)	5.02 – 66.0	109 – 251	0.44-1.46
Total Ca (g/kg)	3.02 – 50.0	16.4-17.5	310 - 520
Total P (g/kg)	0.26 – 4.42	0.34 – 3.20	0.04 - 0.20
Oxalate Al (g/kg)	1.34- 91.0	0.20 – 9.80	0.03-0.64
Oxalate Fe (g/kg)	2.30 – 5.82	108 - 195	0.35-0.53
Oxalate P (g/kg)	0.05 – 3.00	0.15 – 2.64	0.05-0.93
P sorption capacity (g/kg)	10.5-18.0	5.04-10.5	3.40-7.45