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Are Alum-Based Drinking Water Treatment Residuals Safe for Land Application?[1]

Sampson Agyin-Birikorang, George A. O'Connor, and Thomas A. Obreza[2]

Introduction

Land application of aluminum-based WTRs (Al-WTR) has been shown to effectively control off-site phosphorus (P) loss to surface and ground water. Thus, amending soil with WTR could be a practical, chemical-based best management practice (BMP) to reduce off-site P movement from agricultural fields via runoff and leaching. However, recent environmental concerns about the aluminum and arsenic contents of several Al-WTRs have led to the development of guidelines for land application of WTRs in Florida (FDEP, 2006). The concern is that land application of Al-WTRs could negatively affect agricultural production and human health. This document explores possible effects of land-applying Al-WTR on the environment, and recommends ways to minimize human impacts. Target audiences include state agencies like FDEP, FDACS, water management districts trying to use Al-WTR to control P pollution, and those interested in nutrient management for environmental purposes.

Land Application of Aluminum-Based WTR and Agricultural Production

The specific concern among crop and livestock producers is that land application of Al-WTRs will result in (i) P deficiency to plants due to excessive P immobilization (ii) Al toxicity to plants, and (iii) Al toxicity to grazing animals.

(1) WTR Effects on Plant Phosphorus Deficiency

Reports of Al-WTR effects on crop yield have been contradictory. Several studies have shown decreased yield after amending soil with WTR, whereas no effects due to WTR were observed in other studies. Colorado researchers applied WTR at rates from 0 to 56 metric tons/ha (~25 tons/acre) to sorghum–sudangrass grown in two soils in a greenhouse, and observed P deficiency at the highest WTR application rate. However, doubling the P fertilizer rate in conjunction with the highest WTR rate increased sorghum–sudangrass yield by 29% (Heil and Barbarick, 1989). Similarly, other scientists in Pennsylvania found reduced P concentration in

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2. Sampson Agyin-Birikorang, postdoctoral research associate; George A. O'Connor, professor; Thomas A. Obreza, professor; Department of Soil and Water Science; Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida, Gainesville, FL 32611.

tomato and lettuce grown in WTR-amended potting media (Elliott and Singer, 1988). Application rates greater than 90-180 metric tons WTR/ha resulted in decreased wheat yields (even with P fertilizer addition), germination problems and P uptake reductions in maize, and decreases in fescue yield.

In contrast, other researchers (Bugbee and Frink, 1985, and Novak et al., 1995) observed that when Al-WTRs were applied to forests at rates ranging from 18-56 metric tons/ha (~8-25 T/A), WTR had no effect on growth or nutrient content of the plants. Application of ~22.4 metric tons/ha (10 T/A) reduced tissue P concentration, but did not induce other nutrient deficiencies or toxicities. In a 7-year field study, Naylor and Carr (1997) reported insignificant effects of WTR application (~ 22.4 metric tons/ha one-time application) on crop P nutrition. Reduction in soluble P concentration was not accompanied by plant growth limitations in soils amended with biosolids and Al-WTR.

In a similar study, we evaluated agronomic impacts of different P sources (mineral fertilizer, biosolids, and poultry manure) co-applied with Al-WTR to Florida sandy soils. Three rates of WTR (0, 22.4 and 56 metric tons/ha) and three rates of applied P [0 (control), ~ 56 kg P/ha (P-based) and ~224 kg P/ha (N-based)] were evaluated using bahiagrass and ryegrass as test crops. Although P uptake by both crops decreased with increasing WTR application rate, plant tissue P concentrations remained above critical values for the grasses, and no negative WTR effects on grass growth and dry matter yield were observed (Fig. 1).

WTR application rates in the above studies were largely based on an arbitrary WTR:soil ratio; chemical composition of the materials was not taken into account. Each drinking water treatment plant uses unique source water and site-specific treatment processes (types and amounts of chemicals), producing WTRs that differ in chemical composition and P sorption capacity. Several studies have shown a wide variation in WTR chemical characteristics that results in differing P sorption capability. Therefore, WTR application rates solely based on dry weight percentages (or fixed soil: amendment ratio) can result in excessive or inadequate immobilization of soil soluble P, depending on the amount and reactivity of Al and/or Fe added with the WTRs. Knowing the appropriate amount of WTR to land apply is critical because over-application can lead to excessive immobilization of soil P and induce plant P deficiency.

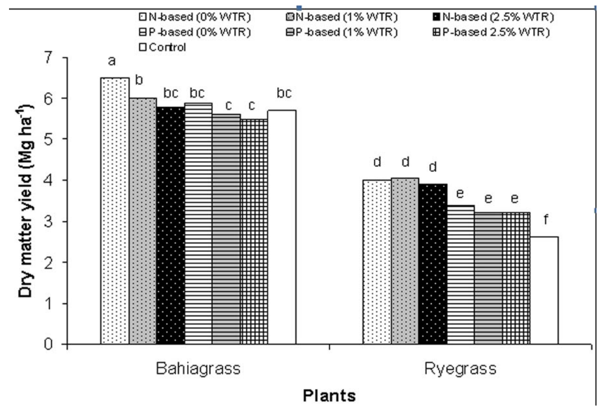

Fig. 1. Effects of Al-WTR and P fertilizer rates on dry matter yields of Bahiagrass and ryegrass. Treatments having the same letter(s) are not different by the Tukey multiple comparison at significance level (±) of 0.05. (Oladeji et al., 2006)

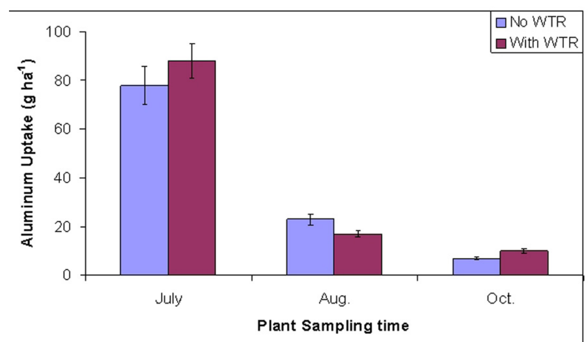

Fig. 2. Effects of Al-WTR (applied at 56 Mg/ha) and P fertilizer (224 kg/ha) on tissue aluminum uptake of Bahiagrass and ryegrass. (Oladeji et al., 2006)

(2) WTR Effects on Aluminum Toxicity to Plants

In addition to agronomic limitations involving P (e.g., excessive application of WTR causes plant P deficiency), there is a concern about potential Al toxicity to plants when Al-WTRs are land applied. Soluble Al has been implicated as the most common source of toxicity to plants in acidic soils, and is a common yield-limiting factor. We studied the impact of Al-WTR applied at 56 metric tons/ha on Al uptake and the potential for Al toxicity to bahiagrass and ryegrass cropped for four growing seasons. Al-WTR did not significantly affect plant Al uptake in any season. Plant Al uptake in treatments that received no WTR were similar to those where WTR was applied (Fig. 2). The expected antagonistic effect of increased Al uptake on the concentrations of other cations (e.g. Ca and Mg) in plants was not observed, confirming that the plant did not take up excessive Al from WTR-amended soil.

(3) WTR Effects on Grazing Animals

There is a concern that land application of WTRs high in Al (particularly Al-WTRs) to pasture could adversely affect P utilization and bone deposition in grazing livestock that inadvertently consume the WTR. When livestock graze, soil consumption can amount to as much as 10-15% of the animal's total dry matter intake. Consequently, surface application of WTR could constitute a substantial portion of the entire 10-15% of "soil" consumed by grazing cattle. Ingestion of highly-available dietary Al [e.g. aluminum chloride ($AlCl_3$)] by livestock can result in Al toxicity, which is often observed as P deficiency. For example, sheep ingestion of soluble dietary Al suppressed voluntary feed intake, plasma P, animal growth, and weight gain. Highly-bioavailable Al also negatively impacted the status of Fe, Zn, and Mg in sheep.

Effects of ingested Al-WTR (8 g Al/kg feed) on growth, feed intake, plasma P, tissue P concentration, and apparent P absorption of growing lambs were compared with effects caused by ingesting a highly available source of Al ($AlCl_3$) (Van Alstyne et al., 2007). Dietary administration of $AlCl_3$ negatively impacted average daily weight gain, body weight, feed intake, apparent absorption of P, and plasma P concentration of lambs, whereas no adverse effects were observed with Al-WTR in the diet.

In a related study, Al-WTR was applied to a pasture at a cumulative rate of 78 metric tons/ha, and researchers evaluated the effects of dietary Al from the Al-WTR on cattle over 2 years. Results showed that Al-WTR had no adverse effects on growth, development, or plasma mineral concentration of the cattle, likely due to low Al availability from Al-WTR. WTR application did not adversely affect forage mineral concentrations. The researchers concluded that Al-WTR is safe and could be applied to pastures at low to moderately high rates (<=78 metric tons/ha) to help alleviate the environmental P problem (Madison et al., 2007).

Land Application of Aluminum-based WTR and Human Health

There is a concern that land application of Al-WTRs will result in (i) soil contamination with trace elements, particularly arsenic (As), and Al that could be directly or indirectly ingested by humans, and (ii) contaminate groundwater with Al.

(1) Trace Metal Concentrations of Iron- and Aluminum-Based WTRs

Drinking-water treatment residuals are exempt from the 40 CFR Part 503 land disposal regulations for biosolids (USEPA, 1996), and are not subject to the metal limitations of the Part 503 regulation. However, Florida DEP recently issued a guidance memorandum (FDEP, 2006) advising against indiscriminate land application of Fe- and Al-WTRs in Florida due to high Al and As contents of several Fe- and Al-WTRs.

Five Al-WTRs and three Fe-WTRs (randomly selected from representative treatment plants in Florida) contained total barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), sodium (Na), and molybdenum (Mo) at concentrations well below the respective Florida groundwater guidance concentration (FGGC) and residential soil cleanup target level (SCTL) values (Table 1). Special attention has been given to Mo because a relatively small forage-Mo concentration can induce Cu deficiency (molybdenosis) in grazing animals if the forage Cu concentration is also low (< 10 mg/kg). Several Fe- and Al-WTRs tested by Elliott et al. (1990) had mean total Cr, Ni, Pb and Zn concentrations within the ranges commonly found in several soils, implying that total soil metal concentrations will remain largely unaffected by WTR application at typical loading rates (<= 56 metric tons/ha). In addition, air-dried Fe- and Al-WTRs usually contain only small numbers of coliforms (< 20 coliforms/g) because of air-drying, long-term storage, and chlorine addition during the drinking-water purification process. Thus, pathogens are not a problem in WTRs.

(2) Quantity of Arsenic and Aluminum Introduced to Soil in WTR Land Application

Typical rates of WTR application to control phosphorus in Florida range between 22 –and 56 Mg/ha (equivalent to 10-25 tons/acre, or 1-2.5 % by weight). The median As concentration in Al-WTRs is 11.3 mg/kg (11.3 ppm) and that of Aluminum is 142, 000 mg/kg (142,000 ppm) (Jain et al., 2005). Thus, when Al-WTR is surface applied, and impacts only the top 2" (5 cm) of the soil, a total of 0.9 ppm As and 7000 ppm of Al is introduced into the soil. If, on the other hand, the Al-WTR is incorporated into the soil to a depth of 6" (15 cm), the maximum amount of As and Al introduced into the soil is 0.3 ppm and 2300 ppm respectively. Such metal loads introduced into the soil due to Al-WTR application (incorporated in 6" depth) are well below the residential soil cleanup target limits of 2.1 and 72,000 ppm for As and Al, respectively. If the Al-WTR is mixed with the top 6 inches of typical FL surface soils, the Al and As hazards are negligible even at high Al-WTR rates and for multiple years of application.

Appendix A of the FDEP Guidance Memo for land application of WTRs issued in 2006 (FDEP, 2006) describes a procedure for calculating the appropriate quantity of WTR to blend with soil.

$$\text{Blend Ratio} = \frac{(A-B)}{(B-C)}$$

where A = concentration of contaminant in WTR (mg/kg),

B = target concentration in blend (mg/kg), and

C = concentration of contaminant in material blended (mg/kg)

For example, in the case of Arsenic:

A = median As concentration in Al-WTRs from Townsend et al. (2001) = 11.3 mg/kg

B = residential soil cleanup target level for As = 2.1 mg/kg.

$$\text{Blend Ratio} = \frac{(11.3-2.1)}{(2.1-0.27)} = 5$$

Thus, if the desired WTR rate is 25 tons/acre, one needs to blend a median Al-WTR with 5 X 25 T/A = 125 tons of soil. In a typical soil, 1 acre of soil 6 inches deep weighs 1000 T.

Therefore, one can calculate that 125/1000 X 6 inches = 0.75 inches of soil in which the Al-WTR would have to mixed (blended) to meet the SCTL for As. Deeper incorporation (more soil dilution) reduces the amended soil As concentrations proportionally.

In the case of Aluminum:

A = 142,000 mg/kg; B = 80,000 mg/kg (both values from the FLDEP Guidance Memo); and

C = 1300 mg/kg (from Chen et al., 2000)

$$\text{Blend} = \frac{(142{,}000 - 72{,}000)}{(72{,}000 - 1{,}300)} = 0.99$$

Thus about equal masses of soil and Al-WTR would need to be blended, and the required 25 T of soil can be calculated to be represented by only 0.15 inches of soil. Clearly, the blending calculations allow "safe" application of a median Al-WTR if mixed with <1 inch of median FL surface soil.

The FDEP Guidance Memo (Appendix A) also contains a procedure for calculating the quantity of WTR to mix with top 6 inches of soil as:

$$\text{Application Rate} = 10.89\rho_s \frac{(B-C)}{(A-B)}$$

where *Ps* = soil density = 115 lbs/ft^3, and the other terms are as defined previously.

For Arsenic:

$$\text{Application Rate} = 10.89 \times 115 \times \frac{(2.1-0.27)}{(11.3-2.1)} = 250 \text{ T/A WTR}$$

For Aluminum:

$$\text{Application Rate} = 10.89 \times 115 \times \frac{(80{,}000-1{,}300)}{(142{,}000-80{,}000)} \text{ 1589 T/A WTR}$$

The blending calculations appear to justify land application of Al-WTRs at rates needed to address off-site P loss issues without endangering human health. The Appendix A of the FDEP guidance memo calculations easily justify the 25 T/A rates shown to be effective in controlling off-site P losses as long as at least some soil mixing is performed following WTR addition.

(3) WTR as a Novel Sorbent for Arsenic

Several Al-WTRs produced in Florida have total As concentrations (8.5-16.9 mg/kg) greatly exceeding the residential (2.1 mg/kg) and industrial (3.7 mg/kg) soil cleanup target level for arsenic. Thus, surface application of Al-WTR is perceived to result in increased human exposure to As, and may result in toxicity problems.

A laboratory incubation study was conducted to determine the effect of Al-WTR on potential As availability to humans (bioaccessibility) and plants (phytoavailability) from a poorly As-sorbing soil contaminated with arsenical pesticides. Al-WTR was added to an Immokalee soil (a sandy Spodosol with minimal As-retention capacity) at rates ranging from 0 to 112 metric tons/ha (0-50 T/A). A spike of As was added using sodium arsenate at a rate of 90 mg As/kg. Bioaccessible As was determined at time 0 (immediately after spiking), and after 6 and 12 months of equilibration using an *in vitro* gastrointestinal test (IVG-AI). Arsenic phytoavailability, estimated with a 1-M potassium chloride extraction, decreased (20% availability at 112 metric tons/ha rate) immediately after spiking (at time 0) in the presence of Al-WTR relative to the untreated (no WTR) soil (Fig. 3). Arsenic bioaccessibility simulated for the stomach and intestine phases also showed that Al-WTR was effective in resisting the harsh acidic conditions of the human stomach, thus preventing As release (Fig. 4) (Sarkar et al., 2007).

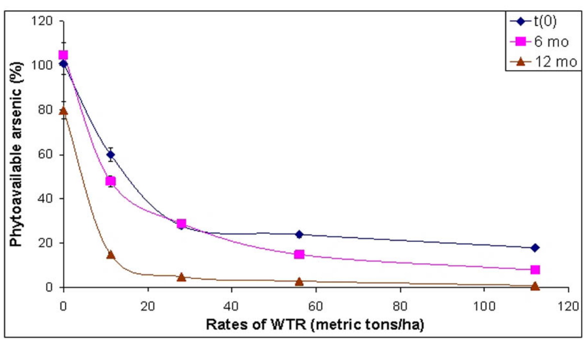

Fig. 3. Changes in arsenic phytoavailability with incubation time (months) in Immokalee soil amended with sodium arsenate, and various rates of Al-WTR. (Sarkar et al., 2007)

The study demonstrated that potential soil As availability to plants and humans decreased as Al-WTR application rate increased. Al-WTR added at

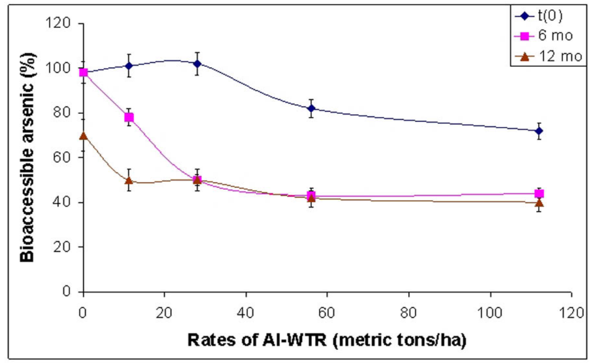

Fig. 4. Changes in arsenic bioaccessibility with incubation time (months) using an in vitro gastrointestinal test (IVG-AI) method in Immokalee soil amended with sodium arsenate, and various rates of Al-WTR. (Sarkar et al., 2007)

28 metric tons/ha (12.5 T/A) significantly decreased As phytoavailability compared with the control. However, greater WTR application rates [>56 metric tons/ha (25 T/A)] were needed to decrease soil As bioaccessibility. Thus, application of WTRs at a minimum rate of 56 metric tons/ha could be a viable and effective field remediation method for As-contaminated soils that are low in Fe and Al oxyhydroxides. Thus, the perceived threat of As toxicity following land application of WTRs is not supported by the data.

(4) WTR Effects on Groundwater Aluminum Concentrations

Jain et al. (2005) characterized Florida Al-WTRs in detail and found that several contained Al concentrations between 104 and 177 g Al /kg, which exceeded the residential soil cleanup target level of 72 g Al/ kg. Thus, potential WTR particle dissolution, particularly under acidic conditions, is a concern with respect to WTR field application in humid regions. Particle dissolution in acid soils or aqueous suspensions could release significant quantities of Al (and previously immobilized P) to the environment, which could contaminate groundwater resources.

We conducted a field study to determine if WTR could reduce P movement to shallow groundwater beneath a typical Florida Spodosol amended with P sources of different solubility. Amending the soil with an Al-WTR [~22.4 metric tons/ha (~10 T/A)] increased the oxalate-extractable Al concentration of the surface soil by several fold. The increase in soil Al content prompted us to analyze groundwater samples to determine the impact of surface-applied Al-WTR. Total dissolved Al concentrations of all groundwater samples obtained during the 20-mo study period were unaffected by Al-WTR (Fig. 5), and were similar to those in groundwater samples obtained before treatments application (Agyin-Birikorang et al., 2009). In related studies conducted in Arkansas, land application of Al-WTR at rates of 2.2 - 44.8 metric tons/ha (~0.1-20 T/A) did not increase dissolved Al concentration of surface runoff (Gallimore et al., 1999).

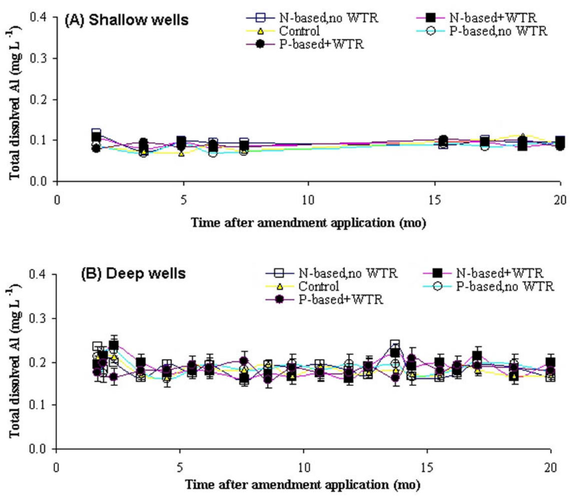

Fig. 5. Trends of total dissolved Al concentrations in groundwater samples collected from a WTR field study conducted in the Okeechobee watershed from (A) shallow and (B) deep wells in an 18-mo study period (Agyin-Birikorang et al., 2009). Various P sources (fertilizer, poultry manure, or biosolids) were applied at rates sufficient to meet the nitrogen (N-based) or phosphorus (P-based) needs of the crop.

Several studies have shown that pH control of soluble Al dominates Al ecological risks. The pH values of Al-WTRs range between 5.0 and 8.2. At these pH values, Al species are likely dominated by hydrolytes of Al and other organically-complexed Al forms, rather than free Al^{3+}. Thus, there is little concern that free Al^{3+} will leach from surface-applied Al-WTR to contaminate water, unless adverse conditions (e.g. pH < 4) that could destroy WTR particles occur.

Conclusions

The combined studies clearly demonstrate that Al-WTR should have no negative impacts on the environment and biological systems when appropriate rates (based on the chemical characteristics of WTR) are land applied. Thus, Al-WTR is a safe soil amendment to control off-site P losses to sensitive water bodies.

Further Readings

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Table 1. Selected trace metal concentrations of drinking-water treatment residuals* compared with Florida residential safe target cleanup level

Properties	Al-Based	Fe-based	***Ca-based***	***Residential STCL***
	---mg/kg-----------------------------------			
Total Arsenic	8.5-17.0	2.0-10.0	0.2-5.0	2.1
Total Cadmium	0.4-3.0	1.8-5.7	0.3-0.8	75
Total Barium	15.5-320	15.1-58.2	18.3-211	110
Total Chromium	55.2-174	17.0-152	1.0-13.0	210
Total Copper	15.0-64.0	24.0-413	1.5-31.5	110
Total lead	2.65-11.8	1.36-4.85	0.32-1.77	400
Total Molybdenum	62.5-500	55.2-166	55.2-146	390
Total Zinc	14.2-26.9	8.31-33.6	3.92-23.8	23,000
Total sodium	36.4-1100	79.3-265	66.5-4120	-
Total Aluminum	104,000-177,000	2,800-5,900	370-14,500	72,000