

ALUMINUM WATER TREATMENT RESIDUALS FOR REDUCING PHOSPHORUS  
LOSS FROM MANURE-IMPACTED, HIGH-WATERTABLE SOILS

By

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by

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To my Granddad, my partner in crime, for all the summers he encouraged my passion for agriculture, the environment, and life

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Abstract of Thesis Presented to the Graduate School  
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Dairy and beef operations in the Lake Okeechobee watershed in Florida and across the nation are receiving attention as a result of their contribution of phosphorus (P) to surficial water bodies. Numerous efforts are being made to support the agricultural industry by reducing P losses from the soil. One such effort involves the addition of water treatment residuals (WTRs) to the soil. Prior research has shown that Al-WTRs are capable of binding P and therefore reducing P loss through runoff and leaching. The objective of this research was to evaluate the effect of Al-WTR on P loss from a manure-impacted soil obtained from a dairy sprayfield using a rainfall simulation protocol. Soil was removed from the field site as 0–10 and 10–20 cm depths. Both depths contained high concentrations of water-soluble P and Mehlich-1 P; approximately 18 and 950 mg P kg<sup>-1</sup>, respectively. After air drying and sieving, the soil was placed in rainfall simulation boxes (100 cm x 30 cm x 20 cm) designed to collect runoff, subsurface flow, and leachate. An Al-WTR was either surface applied or incorporated to 10 or 20 cm depths

at a rate of 2.5% of soil dry weight. The soil was then sprigged with stargrass (*Cynodon nlemfuensis*). Rainfall simulations were run six times at 3 wk intervals. Runoff was collected for 30 min after initial runoff began. Subsurface flow and leachate were collected (depths of 10 and 20 cm, respectively) after runoff ceased.

When Al-WTR was surface-applied, the SP concentration in runoff was reduced by approximately 75% compared to untreated soil; however, SP concentrations in subsurface flow and leachate did not decrease. When Al-WTR was incorporated into the soil at depths of 0–10 or 0–20 cm, runoff SP concentrations were reduced by approximately 45%. Incorporation of Al-WTR to a depth of 10 cm decreased SP concentrations in subsurface flow and leachate by 37 and 11%, respectively. However, with incorporation of Al-WTR to a depth of 20 cm, both subsurface flow and leachate SP concentrations were reduced by approximately 90%. The incorporated Al-WTR reduced soil water-extractable P (WEP) by approximately 70%. However, Mehlich-1 P concentrations were not affected by the incorporation of Al-WTR in the soil. Care must be taken to ensure complete incorporation of Al-WTR throughout the P-impacted layer, as Al-WTR is only effective in reducing SP concentrations when it is in contact with the impacted soil. Shoot and root growth of stargrass were not adversely affected by the Al-WTR applied at a rate of 2.5% of soil weight.

## CHAPTER 1 INTRODUCTION

Over the past 5,000 yr, the Lake Okeechobee watershed has developed an ecosystem to thrive under oligotrophic conditions. The watershed is approximately 12,000 km<sup>2</sup> and flows roughly from Orlando to the Everglades (SFWMD, 1997). On average, the watershed receives 120 cm of rain annually (McCaffery et al., 1976). The elevation in the watershed is predominately flat, with a range from 3.1 to 22.9 m above mean sea level (Soil Survey, 2003). As a result, the watertable is naturally close to the surface for much of the year. Prior to development and utilization of the land, much of the watershed was completely saturated for one to two months a year (Gatewood and Bedient, 1975).

The watershed is divided into six regions. The two most important regions are the Lower Kissimmee River (LKR) and Taylor Creek/Nubbin Slough (TCNS) because they contribute approximately 57% of the total phosphorus (P) load to Lake Okeechobee (Fluck et al., 1992). Phosphorus discharge to surficial water bodies has recently become a major concern in the watershed. One of the current major contributors to the situation is waste from livestock which contains high amounts of P. As Florida has continued to develop, land has become more valuable and farmers and ranchers have intensified their operations by increasing the concentration of animals per acre. The resulting effect has been increased discharge of P into the watershed.

Because of the warm climate and abundance of water, the agricultural community has flourished, and land use practices in the LKR and the TCNS have intensified to

maximize production. In particular, the beef and dairy industries have, respectively, amassed herds of 133,000 and 32,000 animals in Okeechobee County (Florida Agriculture Statistical Directory, 2004). To support these herds, 31% of the land in the LKR and 62% of the land area in the TCNS has been drained and converted to improved pastures. Improved pasture area increased by 500% between 1950 and 1970. Currently, improved pastures comprise approximately 87,000 ha in the LKR and the TCNS (Flaig and Havens, 1995). Inorganic fertilizer used on improved pastures account for 34% of all P imports to the watershed (Boggess et al., 1995). Additional P imports come from mineral supplements and winter feed. The most intensive land use in the watershed is dairy farming. From 1960 to 1990, dairies increased their imports of P in cattle feed from 360 t P yr<sup>-1</sup> to 1200 t P yr<sup>-1</sup> (Flaig and Havens, 1995; Boggess et al., 1995). Dairy feeds constituent 35% of P imports into the watershed, but P impacts have been decreasing since 1990 as a result of the dairy buyout program which closed 19 of 49 dairies in the basin (Flaig and Reddy, 1995).

Phosphorus is a vital nutrient in both natural and agricultural environments and is often imported to foster agricultural operations. Traditionally, P has been considered relatively immobile in soils, primarily only subject to loss by erosion. However, P can also move vertically or horizontally within some soil profiles and can be transported into the surface water of canals, streams, and lakes. Graetz and Nair (1995) found residual P from manure has the potential to leach laterally because of the surface horizon's low P-retention capacity in a Spodosol. The resulting soluble P in surface water often causes detrimental impacts on native ecosystems.

Phosphorus occurs in soluble and insoluble compounds in both organic and inorganic forms in the soil environment (Faulkner and Richardson, 1989). Organic forms exist as both living plant tissue and in deposits of detrital material. Inorganic P is found as insoluble phosphate and minerals adsorbed to clay particles, organic matter, and Fe and Al hydroxides (Mitsch and Gosselink, 1993). Nevertheless, the majority of P is unavailable to biota. Unlike nitrogen, P does not have any significant losses to the atmosphere. Therefore, P remains in the soil or is transported by another mechanism besides volatilization.

Soils in the watershed consist predominately of Spodosols, Entisols, and Histosols. The Histosols occur primarily as small deposits in wetlands, where as Spodosols dominate the northern portion of the watershed. The surface horizons are typically between 0.08 and 0.20 m thick and are underlain by a spodic horizon at 0.5 to greater than 2 m depth (USDA, 1990). The closer the spodic horizon is to the surface, the more poorly drained the soil. Spodosols are characterized by high infiltration rates because of the greater than 90% sand content. However, they have poor internal drainage because of the low permeability of the spodic horizon. The Spodosols, Myakka (32%), Immokalee (30%), and Pomello (2%) cover 64% of Okeechobee County (Soil Survey Staff, 2003). The concern regarding the high watertable and high infiltration rates is that surface horizons of Entisols and Spodosols have a limited capacity to retain P and, thus, are susceptible to P loss.

The Bh (spodic horizon) in South Florida Spodosols contains Al and/or Fe and organic material accumulated from the stripping of the E horizon. Spodosols in general are naturally deficient in P (Hodges et al., 1967). Nevertheless, as a result of the

accumulation of material, the spodic has the ability to retain downward moving P onto Fe and Al oxides (Nair et al., 1995). These eluvial materials enable the possible retention of excess P from agricultural operations. Depth to Bh has an impact on the P leaching potential of the soil. As the depth of the Bh increases the potential for P loss via subsurface drainage increases. Moreover, as the depth of the spodic increases its P adsorption capacity decreases (Nair et al., 1999).

Despite the sorption of P in the soil, it can still be highly mobile. The combination of the fluctuating and perched watertable allows lateral movement of P through the soil and into the surface water (Graetz and Nair, 1995). In fact P can move so readily, that between 1973 and 1988, the concentration of P in Lake Okeechobee increased approximately 250% (Neganban, 1993).

In an effort to reduce eutrophication and restore the Everglades to a system resembling the past, larger releases of water to the Everglades and reductions in P loading are mandatory. Therefore, to meet the requirements of the Comprehensive Everglades Restoration Plan, the South Florida Water Management District, U.S. Army Corps of Engineers, and other state agencies created massive water treatment areas, instituted use of Best Management Practices (BMPs), and increased water flow to the Everglades (SFWM, 1997). Representative BMPs include fencing off canals, adding water troughs to pastures, and reducing P concentrations in feed.

These measures alone are not adequate to meet the acceptable P levels within the watershed due to residual P levels remaining in soils highly impacted by manure. Recent studies have suggested that the addition of soil amendments has the potential to reduce P loss from soil. Investigations have included numerous amendments from differing

sources. One promising area of investigation is the land application of water treatment residuals (WTRs). WTRs are the waste product from drinking water purification, and typically contain Al, Ca, or Fe compounds used to remove nutrients and particulate matter from source water. Land application of WTRs has the potential to help reduce water soluble P (WSP) concentrations in P-impacted soils. Previous research has shown that WTRs containing Al are the most efficient in reducing WSP in soils. Therefore, a study was developed to evaluate the effect of an Al-WTR on soil P dynamics in a sandy soil with a fluctuating watertable. The study had two main objectives:

1. To determine the effect of surface application, partial mixing, and complete mixing of Al-WTR with soil on P loss in runoff, subsurface flow, and leachate.
2. To determine the Al-WTR's effect on forage growth.

## CHAPTER 2 LITERATURE REVIEW

### **Forms of Phosphorus in Soil**

Phosphorus (P) is commonly found in soils in small total quantities (Lindsay, 1989). Forms of P in soils can be either inorganic or organic. Phosphate minerals, organometallic complexes, and P bound to metals and hydroxides are all inorganic forms of P that may be present in the soils. Microbes, humus, and undecomposed litter make up the organic P fraction (Gale et al., 1994). Reddy et al. (1996) identified five major pools of P in soils: a) labile inorganic P, b) P bound to Fe and Al minerals, c) P bound to Ca and Mg minerals, d) P bound in labile organic forms, and e) residual organic P.

The labile pool of P is of particular environmental concern because labile P can potentially move laterally or vertically in the soil profile as a result of precipitation. The *Glossary of Soil Science Terms* (SSSA, 2006) defines the labile pool of P as “that portion which is readily solubilized or exchanged when the soil is equilibrated with a salt solution,” and the available pool as “the amount of soil P in chemical forms accessible to plant roots or compounds likely to be convertible to such forms during the growing season.”

Oxalate-extractable Al and Fe dominate P retention in many soils and provide strong sorption of P (Ballard and Fiskell, 1974). The retention of P by Fe/Al or Ca/Mg depends on the soil's pH. In acid and neutral soils, P retention is dominated by Fe and Al compounds because P binds with protonated surfaces of hydroxides of Fe and Al (Olila and Reddy, 1995). In alkaline soils, Ca and Mg compounds are more dominant in

retaining P because P sorption decreases due to competition between  $\text{PO}_4^{3-}$  and  $\text{OH}^-$  anions. Anion exchange binds phosphates with Fe and Al hydroxides (Olila and Reddy, 1995). Because amorphous Al and Fe hydroxides have a larger number of singly coordinated surface hydroxyl ions, they have a higher P sorption capacity than crystalline oxides (Reddy and Smith, 1987). In reduced conditions, Fe stability is affected. As a result of the reduced stability, P associated with  $\text{Fe}^{3+}$  maybe solubilized and released into the soil solution. However, Al compounds associated with P are not affected by changing oxidation and reduction conditions in the soil (Miner, 2001).

Labile organics represent the short term storage of P as living tissue in plants. This P is quickly returned to the soil either through manure or decomposition, whereas, residual organics represent long term storage of P as detrital tissue that is resistant to decomposition (Reddy et al., 1996). Because of the P storage ability of plant tissue, phytoremediation of warm-season perennial grasses has been examined. Warm-season perennials have the ability to extract more P than warm-season annuals and cool-season grasses because the potential dry matter yield of perennials is greater. Howard (2006) estimates that adding nitrogen (N) to increase forage yields in hay production could decrease soil P concentration 4 to 13  $\text{mg kg}^{-1}$  annually.

The soil's ability to retain P determines the risk of environmental consequences related to P leaching. Therefore, the continued assessment of a soil's capacity to retain P remains a vital tool in environmental sustainability. Soluble forms of P react and form less soluble compounds with soil components. The amount of P available to be removed from solution depends on the quantity of P-reactive colloidal surfaces within the soil (Holford et al., 1997). The sorption and desorption capacity of soils between horizons

has the potential to influence the movement of P within the profile (He et al., 1999). Variations of P sorption are attributed to surface area variability based on particle size (Atalay, 2001). Soil sorption and desorption mechanisms control the solution phase P (Frossard et al., 1995).

Determining the movement and availability of P in soils and groundwater is paramount in the preservation of natural resources. By using the Langmuir adsorption isotherm equation, an estimate of P sorption capacity and strength can be determined in the soil. Soil extractable P can be related to the P-sorbing capacity of a soil by using the degree of P saturation test (DPS);  $DPS = (\text{extractable soil P} / \text{P sorption maximum}) * 100$  (Breeuwsma and Silva, 1992). Degree of P saturation may also be expressed as a percentage of double-acid extractable P (Mehlich-1) to the P sorption capacity of a soil (Nair and Graetz, 2002).

When sorption equals desorption a system is at equilibrium. Therefore, if the concentration of P in soil water decreases, desorption will occur until equilibrium is reached. Likewise, if the P in soil water increases, sorption will occur until equilibrium is attained (Froelich, 1988). The occurrence of no net sorption or desorption is known as the equilibrium P concentration (EPC). Sharpley and Menzel (1987) found sorption properties of the soil control the conversion from dissolved P to particulate P and back to dissolved P. Therefore, the concentration of P controls the direction of exchange. A prediction of loss or gain of P from solution can be determined using the EPC; soils with low EPC values tend to sorb soluble P.

Graetz and Nair (1995) found that the A and E horizons of a manure-impacted Spodosol had higher EPC values than the Bh horizon. Therefore, A and E horizons are

inferred to have a lower retention capacity than the Bh horizon. In manure-impacted soils, high EPC values reflect high P loading. Graetz and Nair (1995) also found that oxalate-extractable Al and total organic carbon accounted for approximately 69% of the variability in the P retention maximum in the A, E, and Bh horizons forage, pasture, and intensive areas. Maximum P retention capacity increases with depth. In fact, the Bh was found to have a P retention capacity three to four times greater than the A and E horizons (Reddy et al., 1996).

The high cost of inorganic N fertilization has prompted agriculture to better utilize waste products through the application of biosolids and animal manures. These amendments are typically applied to meet a crop's N requirement. The result of this common practice is an excessive accumulation of P in the soil. Soils with low P sorption capacities, such as sandy soils, are more susceptible to P loss through runoff and subsurface water movement. Kleinman and Sharpley (2003) evaluated P runoff from two soils amended with three types of manure (applied at 6 rates ranging from 0–150 kg TP ha<sup>-1</sup>) following the National P Protocol for rainfall simulation studies. Dissolved reactive P (DRP) in runoff increased with increased manure application rate. Water-extractable P (WEP) concentrations in the manures were directly related to DRP runoff concentrations. Repeated rainfall events diminished DRP concentrations in runoff with all manure types and application rates. This trend was attributed to both the translocation of manure P into the profile and the loss of previous applied P by runoff.

A close association between soluble P (SP) concentration in land-applied manures and P concentrations in runoff has been shown in recent studies. Moore et al. (1994) and Withers et al. (2001) indicated that DRP loss from amended soils was proportional to the

soluble P content of the source. In addition, Kleinman et al. (2002) found the WSP concentration of surface applied manure (dairy, swine, and poultry) was highly correlated with DRP in runoff from three soils.

### **Water Treatment Residuals as Soil Amendments**

Efforts to reduce P loss in agricultural sandy soils include several strategies: reducing P loading, increasing the ambient P storage, and maximizing P retention. Many soils with high P concentrations currently discharge P into surficial water bodies. Phosphorus retention in highly impacted sandy soils could be improved with the addition of amendments such as water treatment residuals (WTRs) derived from the treatment of drinking water to remove color, taste, turbidity, and odor. The chemical composition of WTRs depends on the metal salts used to clarify the water. The typical salts used are Al (alum), Fe (ferric chloride), or Ca ( $\text{CaCO}_3$ ). The by-product of this water purification process is solid material commonly referred to as WTR. The WTR is often considered a waste product because it is currently being disposed in landfills, sanitary sewers, or in lagoons (Ippolito et al., 2002). Water treatment residuals have historically had little success as a soil substitute or soil amendment compared to their counterpart, biosolids (Cornell and Westerhoff, 1981). However, recently WTRs have been considered as soil amendments because of the P-sorbing characteristics.

Recently WTRs have been evaluated for use as both a soil substitute and a soil amendment because their properties are similar to fine textured soils (Elliott et al., 1990). These fine textured substances are comprised of sand, silt, and clay particles as well as activated carbon, polymers, Al, Fe oxides, and calcium carbonate derived from the raw water (Elliott and Dempsey, 1991). The WTRs have improved soil conditions in numerous studies by increasing organic matter content, water holding capacity, and pH.

However, because of the high relative surface area of the amorphous Al and Fe compounds, Al- and Fe-WTRs can cause P deficiencies in soils and reduce crop yields (Bugsbee and Frink, 1985).

Dayton and Basta (2001) tested the beneficial properties of WTRs by evaluating 17 WTRs for use as a soil substitute by comparing their nutritive, physical, and chemical properties with soil. The WTRs contained the full spectrum of available nutrients, except P. A bioassay was performed with tomato seedlings (*Lycopersicon esculentum*) to validate the results of soil tests used to measure P adequacy in the WTRs. All plants had low tissue P (561–1840 mg kg<sup>-1</sup>; median 923 mg kg<sup>-1</sup>); 1000 mg kg<sup>-1</sup> is considered deficient. Vegetative yield was limited primarily because of P deficiencies and in some cases, phytotoxic levels of NO<sub>2</sub>-N (>10 mg kg<sup>-1</sup>).

In an effort to utilize the positive aspects of organic wastes and minimize detrimental effects, Gallimore et al. (1999) examined four surface application treatments of Al-WTR (0, 11.2, 44.9 Mg ha<sup>-1</sup> and 44.8 Mg ha<sup>-1</sup> in a buffer strip at the end of the plot) on bermudagrass plots receiving 6.72 Mg ha<sup>-1</sup> of poultry litter. The plots received simulated rainfall for 75 mins at 6.3 cm hr<sup>-1</sup> within 24 hr of the application of the litter and Al-WTR. Surficial runoff was collected and analyzed for TN, NH<sub>4</sub>-N, TP, SP, dissolved Al, and dissolved solids. No reductions in SP concentrations were observed with the 11.2 Mg ha<sup>-1</sup> rate. Soluble P concentration was reduced from 15.0 mg L<sup>-1</sup> in the control to 8.6 mg L<sup>-1</sup> in the 44.9 Mg ha<sup>-1</sup> application rate. Similar results were obtained when the WTR was applied just in the buffer strip. These reductions were attributed to the amorphous Al in the Al-WTR. In addition, dissolved solids and Al content did not increase in surface runoff with the application of the Al-WTR.

The potential P-sorption and precipitation capability of Al-, Ca-, and Fe-WTRs has generated interest in their use as an amendment in highly P-impacted soils. O'Connor et al. (2002) found that WTRs reduced P solubility and leaching in manure-amended soils. Brown and Sartain (2000) reported that Fe-WTR was able to significantly reduce P leaching on a simulated golf course using 2.5% by weight of the Fe-WTR. Al-WTRs reduced P and  $\text{NH}_4^+$  by 75% in surface runoff from land treated with poultry manure (Basta and Sloan, 1999). All soluble P was adsorbed in an 8:1 mixture of Al-WTR and biosolids (Fort Collins, CO). Increasing this ratio has the potential to adsorb all available P in the biosolids and the soil P (Ippolito et al., 2002).

A rainfall simulation runoff study by Haustein et al. (2000) evaluated both Al-WTR and HiClay Alumina (HCA-a byproduct of commercial alum production) to test P adsorption capabilities in a soil highly impacted by P. The HCA P-adsorption capacity was 20 times less than the Al-WTR P-adsorption capacity (86 vs. 1750  $\text{mmol kg}^{-1}$ ). In addition, the Al-WTR increased the total recoverable Al in the soil, while HCA did not affect the recoverable Al concentration. These differences were attributed to the greater total Al content of the Al-WTR compared to the HCA (159 vs. 46.7  $\text{g kg}^{-1}$ ).

The effect of WTR composition on P solubility and leaching was tested by Elliott et al. (2002) in a sandy soil (Immokalee-Spodosol) after additions of biosolids and triple superphosphate (TSP) to increase P concentrations in the soil. The study evaluated the ability of Al-WTR, Fe-WTR, Ca-WTR, and pure hematite to reduce P loss from the soil. Soluble P concentrations in the leachate decreased in the order: Al-WTR > Ca-WTR  $\approx$  Fe-WTR >> hematite.

The retention mechanisms of an Al-WTR were studied by Ippolito et al. (2003). The research involved shaking an Al-WTR for 1–211 d and analyzing the solution for pH, Ca, Al, and P. The pH increased from 7.2 to 8.2 after shaking. Change in pH beyond 84 d of shaking was not significant. In addition, the shaking increased Ca and Al concentration and decreased P concentration. The average maximum pH of 8.15 and Ca desorption suggest that the Al-WTR's Ca source was the raw water used at the treatment plant (South Platte River pH~7.5–8 and Ca = 41.9 g kg<sup>-1</sup>). Removal of P was attributed primarily to chemisorption on the amorphous Al mineral phase.

Novak and Watts (2004) evaluated the impact of incorporating two Al-WTRs on two Ultisols in a laboratory setting. The Al-WTRs were added at the following rates: 2.5, 5.0, 7.5, and 10.5% by weight. The P<sub>max</sub> values for both amended soils (175 and 85 mg P g<sup>-1</sup>) were significantly higher than P<sub>max</sub> values without the addition of Al-WTRs (<1.0 mg P g<sup>-1</sup>). The results demonstrate the usability of Al-WTRs to increase P adsorption in sandy soils. In addition, the findings suggest off-site P-transport could be reduced by the implementation of this new chemical based BMP.

Application rate of an Al-WTR (0, 2.5, 5.0, and 10.0% by weight), the degree of mixing of the Al-WTR with the soil, and the mixing of an un-impacted E-horizon with an impacted A-horizon on P leaching was examined by Miyittah-Kporgbe (2004). Runoff and leaching rates were determined via rainfall simulations and columns, respectively (leachate was also collected from rainfall simulation.). Phosphorus leaching was reduced by 87 to 99.7% when the Al-WTR was mixed completely with 15 cm of soil, compared to partial mixing (7.5 cm of soil), which only reduced P leaching from 40 to 58%. Improved P retention was attributed to increased contact of the Al-WTR with soil P. The

runoff results found that soluble P concentrations met the critical threshold of  $<0.03 \text{ mg L}^{-1}$  when Al-WTR was surface applied. However, due to limited contact between the amendment and soluble P, the leachate soluble P concentrations exceeded the critical value. Combining the impacted A-horizon with the un-impacted E-horizon increased the Al-WTR efficiency. This increase in efficiency was attributed to the dilution of soluble organic material, which can block P adsorption sites on the Al-WTR. Conclusions from the data suggest Al-WTR must be in direct contact with soluble P to prevent loss by leaching. In addition, an increase in surface application (10%) can be as effective as mixing lower quantities (2.5%) of Al-WTR. Application and distribution of Al-WTR in the soil must be made in accordance with anticipated P losses; surface application with runoff or mixing with leaching.

### **Aluminum Toxicity**

Aluminum toxicity to plants is a primary concern when Al-WTR is applied to soil. In acidic soils, Al toxicity has been shown to be one of the primary growth-limiting factors (Foy et al., 1978). Mobility and phytotoxicity of Al in the soil solution as a result of soil acidification (Taylor et al., 1989) is a potential problem. Soil acidity impacts approximately 40% of the arable soil in the world (Haug, 1984). As a result, Al phytotoxicity presents a serious agricultural concern (Van Wambeke, 1976). Symptoms of Al toxicity, such as reduced root and shoot growth, mimic phosphate, Ca, and Fe deficiencies (Foy, 1984). Extensive Al research has been conducted which indicates Al toxicity primarily affects the roots: a) the observable symptoms of Al toxicity are the reductions in root elongation (Osborne et al., 1981; Jarvis and Hatch, 1986); b) the production of root biomass compared to shoot biomass is typically more sensitive to Al

(Buss et al., 1975; Zhang and Taylor 1988); c) in Al-stressed plants there is no correlation between an accumulation of Al in the shoots and the supply of Al (Foy et al., 1972); and d) the Al tolerance of a cultivar has been shown to be determined by the rootstock in grafting experiments (Klimashe, 1970).

The visual appearance of mature roots is not the exclusive determination of Al toxicity or tolerance. At the cellular level, Al influences leaf tissue metabolism (Ohki, 1986; Hoddinott and Richler, 1987; Sarkunan et al., 1984). Taylor et al. (1989) suggested potential mechanisms of Al disruption on cell functions to be: a) disruption of membrane structure and functions; b) inhibition of DNA synthesis and mitosis; c) inhibition of cell elongation; d) disruption of mineral nutrition; and e) disruption of phosphate and Ca metabolism. Taylor also suggested several possible immediate toxic effects of Al. The membrane structure and/or function at the soil root interface maybe altered. Membrane-bound enzymes will be affected. Aluminum may also reduce cell elongation by affecting cell wall components or assembly. Phosphate in the DNA appears to bind with Al in the cytosol. As a result, DNA synthesis will be inhibited because of repressed template activity. Finally, toxic effects of enzyme-mediated reactions in phosphate metabolism seem probable.

Aluminum occupies approximately 7% of the of earth's crust. Based on the toxicity issues described previously, it is fortunate the availability of Al is reduced by ligands or the Al occurs in other nonphytotoxic forms (i.e., aluminosilicates and precipitates) (Delhaize and Ryan, 1995). However, the solubilization of Al is enhanced by low pH. Trivalent Al ( $\text{Al}^{3+}$ ) dominates in acidic conditions ( $\text{pH} < 5$ ), compared to  $\text{Al}(\text{OH})^{2+}$  and  $\text{Al}(\text{OH})_2^+$  that form as pH increases. Near neutral pH, the solid phase

gibbsite occurs ( $\text{Al}(\text{OH})_3$ ) while in alkaline conditions, aluminate ( $\text{Al}(\text{OH})_4^-$ ) forms. Many of the monomeric Al cations have the ability to bind with organic and inorganic ligands, including:  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ , organic acids, proteins, and lipids (Delhaize and Ryan, 1995).

Since  $\text{Al}^{3+}$  is predominately restricted to acidic conditions and many trivalent cations are toxic to plants, it is typically assumed to be the major phytotoxic species. However, based on the complex nature of Al, this has been difficult to prove conclusively (Delhaize, 1995). In addition, most of the monomeric Al species previously listed have been considered toxic in one or more studies (Kinraide, 1991). To combat toxicity, numerous strategies have been utilized. The method preferred in North America and Europe has been the application of calcium carbonate (lime) to raise soil pH. As the pH rises, the Al is converted to less toxic forms (Samac, 2003).

Aluminum toxicity and heavy metal contamination concerns have been raised regarding the land application of Al-WTRs. Dayton and Basta (2001) tested 17 WTRs (14 were alum based) for heavy metals and nutrients according to the U.S. Environmental Protection Agency's (EPA) toxicity characteristic leaching procedure (TCLP), a test designed to determine the mobility of organic and inorganic analytes in liquids, solids, and multiphasic wastes (U.S. EPA, 1988). The results of the test found that all of the WTRs contained significantly lower than regulatory levels of the EPA's TCLP and the residuals were therefore, classified as nonhazardous wastes. Total N ranged 1.3 to 18.4  $\text{g kg}^{-1}$  with an average value of 7  $\text{g kg}^{-1}$ . Typical soil levels of soil total N range from 0.2 to 5.0  $\text{g kg}^{-1}$  (Dayton and Basta, 2001). The sources of higher N levels in the WTRs are the algae, detritus, etc. removed from raw water. Mineralization of organic N in the WTRs

may pose potential problems related to  $\text{NO}_2^-$  concentration in WTRs containing higher than  $10 \text{ g kg}^{-1}$  total N. Most significantly, Dayton and Basta (2001) found soluble Al levels at a median concentration of  $0.054 \text{ mg L}^{-1}$ , with a range from 0.02 to  $0.92 \text{ mg L}^{-1}$ . Therefore, problems stemming from both Al toxicity and heavy metals are not expected with WTR use. Elliot and Depsey (1991) found that unless the raw water source is contaminated, the nutrient content of WTRs is generally low. As a result, the WTRs pose only a minor threat to the environment.

### **Rainfall Simulation**

Rainfall simulation studies over the past 40 yr have become popular because irregular distribution of rainfall hampers the possibility of reasonable time periods for study (Neff, 1979). Simulators were first used for erosion studies. The two primary issues were raindrop size distribution and energy (Esteves, 2000). Through a variety of research, two types of rainfall simulators have emerged: (i) drip formers (Farmer, 1973; Romkens et al., 1975; Munn and Huntington, 1976) and (ii) nozzles (Meyer and McCune, 1958; Swanson, 1965; Miller, 1987; Riley and Hancock, 1997). Pressurized nozzle systems have become the preferred method for large area field studies ( $10$  to  $500 \text{ m}^2$ ) (Esteves et al., 2000). Simplicity and speed are the basic requirements for the movement and assembly of a rainfall simulator from one research location to another. As a result, compromises have been made between technical constraints and the reproduction of natural rainfall characteristics (Esteves et al., 2000).

A critical factor for experiments using rainfall simulators is the estimation of rainfall at the ground level (Yu et al., 2003). As rain gauge's catchment area is elevated above the ground's surface, the pressure of simulated rain from the nozzle decreases as greater distances are reached. The elevated catchment area has the possibility to

overestimate rainfall volume. Overestimation without adjustment could range from six to 29 percent depending on catchment height (Yu et al., 2003). Additional variability can occur due to water pressure differences, nozzle aging, and imperfect nozzle spray overlap. Wind can also cause non-uniform spatial variation. Measures to avoid variability include better pressure control, stainless steel nozzles, and the use of a windbreak (Yu et al., 2003; Esteves et al., 2000).

An additional challenge for research is the comparability of experimental results from different researchers. The potential for human error is enhanced by differing sampling techniques, recording methods, measurements, and setup. To avoid differences in results, the National Phosphate Research Project (NPRP, 2001) adapted a specific design for rainfall simulators. The establishment of a single design for a simulator expedites data collection, promotes comparable results, and attempts to maintain field relevancy (Sharpley and Kleinman, 2003). The designs of Shelton et al. (1985) and Miller (1987) are the basis of the portable rainfall simulator used by the NPRP (Humphry et al., 2002).

Numerous studies across the nation have used the NPRP protocol for rainfall simulations both for field and box studies to evaluate P loss under differing soils and amendment treatments. Kleinman et al. (2003), Moore et al. (2000), and Withers et al. (2001) have used rainfall simulators to demonstrate P loss in runoff. As our knowledge base has increased with these studies so has the need with the design of the rainfall boxes. Miyittah-Kporgbe (2004) has used NPRP's runoff box design and added a false bottom to collect leachate and examine WTR's effect on both runoff and leachate. Further studies

are needed to investigate the impact on soluble P with the mixing of WTRs at differing depths and the impacts on plant growth and chemical composition.

## CHAPTER 3 MATERIALS AND METHODS

### **Project Description**

#### **Site Description and Soil Collection**

Soil for this study was obtained from a tile-drained sprayfield at Larson Dairy Barn 5 near Okeechobee, Florida (N 27°16.088', W 80°46.460'). The field had received applications of dairy manure for several years. In addition, effluent from the farm's lagoon was applied to the field periodically as needed to maintain lagoon capacity. The soil was an Immokalee fine sand (sandy, siliceous, hyperthermic Arenic Alaquods) brought into agricultural production as a pasture. The site was planted with stargrass (*Cynodon nlemfuensis*) for silage production in 1990. A series of surface soil samples was taken over the entire field to select a sample site with relatively high P levels. These samples were analyzed for water-soluble P using a HACH Orthophosphate Test Kit and areas of high P levels were identified. Based on these results, an area within the field was selected and a more intensive grid sampling was conducted to identify the final sampling site. These samples were then analyzed for water soluble P (WSP) using a 1:10 soil to solution ratio and Mehlich-1 extractant (Mehlich, 1953) to determine P concentration.

Bulk soil samples were obtained from 0–10 cm and 10–20 cm depths at the selected site in a 6.5 x 1.5 m area after removal of above-ground vegetation. The soil was transported to Gainesville, FL, air dried, and sieved (0.64 cm mesh) to remove debris and to homogenize the soil. Five samples from the bulk dried and sieved soil were randomly

collected per depth (10 in total) and analyzed for WSP and Mehlich-1 P to evaluate uniformity of the soils prior to packing the rainfall simulator boxes.

### **Aluminum Water Treatment Residual Collection**

The aluminum water treatment residual (Al-WTR) for the study was obtained from the Manatee County water treatment plant in Bradenton, FL. Slurry ponds were used to hold the Al-WTR until it was dry enough to be moved with a front-end loader. The solid material was then moved to spoil piles to continue to dry before it was disposed of at a landfill. The Al-WTR samples used for this study were collected from the spoil piles. Size distribution of the Al-WTR particles varied widely. Material ranged from clay sized particles to 10 cm fragments. The Al-WTR was air dried for 2 wk under an open-sided greenhouse, because of its high moisture content, before sieving to pass a 0.64 cm mesh. Even after the material was dried and sieved, the moisture content was 29% because of the high organic content of the Al-WTR. Five samples were randomly collected from the bulk Al-WTR and analyzed for WSP, Mehlich-1 P, and TP.

### **Construction of Runoff Boxes**

Runoff boxes (100 cm long by 30 cm wide and 20 cm deep) were constructed using pine lumber (Fig. 3-1). A 4 cm rail was added to raise the bottom of the runoff box. A 2 cm lip surrounded the box on three sides to prevent loss of water through runoff and/or splashing. One end of the box was 2 cm lower to allow runoff to be collected. The box corners and sampling ports were sealed using latex caulk, and the entire box was covered with a gel coat to make the box watertight. Ports used to collect subsurface flow and leachate were covered with a double layer of garden weed screen to prevent blockage of the ports with debris. Thirty-nine kg of the sieved 10–20 cm depth and then 39 kg of 0–10 cm depth were added to replicate field soil depths.

A slit PVC pipe (5.6 cm ID by 40.6 cm length) with end caps was attached to one end of the box to collect runoff. Gravity allowed the runoff water to be collected through a port in the center of the pipe. Six drainage ports with attached Tygon tubing were installed on the bottom of the boxes to monitor the watertable and to collect leachate (Fig. 3-1). The ports were located in pairs: 77.0, 38.5, and 5.6 cm from the runoff collection end and 5.6 cm from the side walls. In addition, two ports with attached Tygon tubing were placed at the end of the box between the two soil layers to collect subsurface flow.

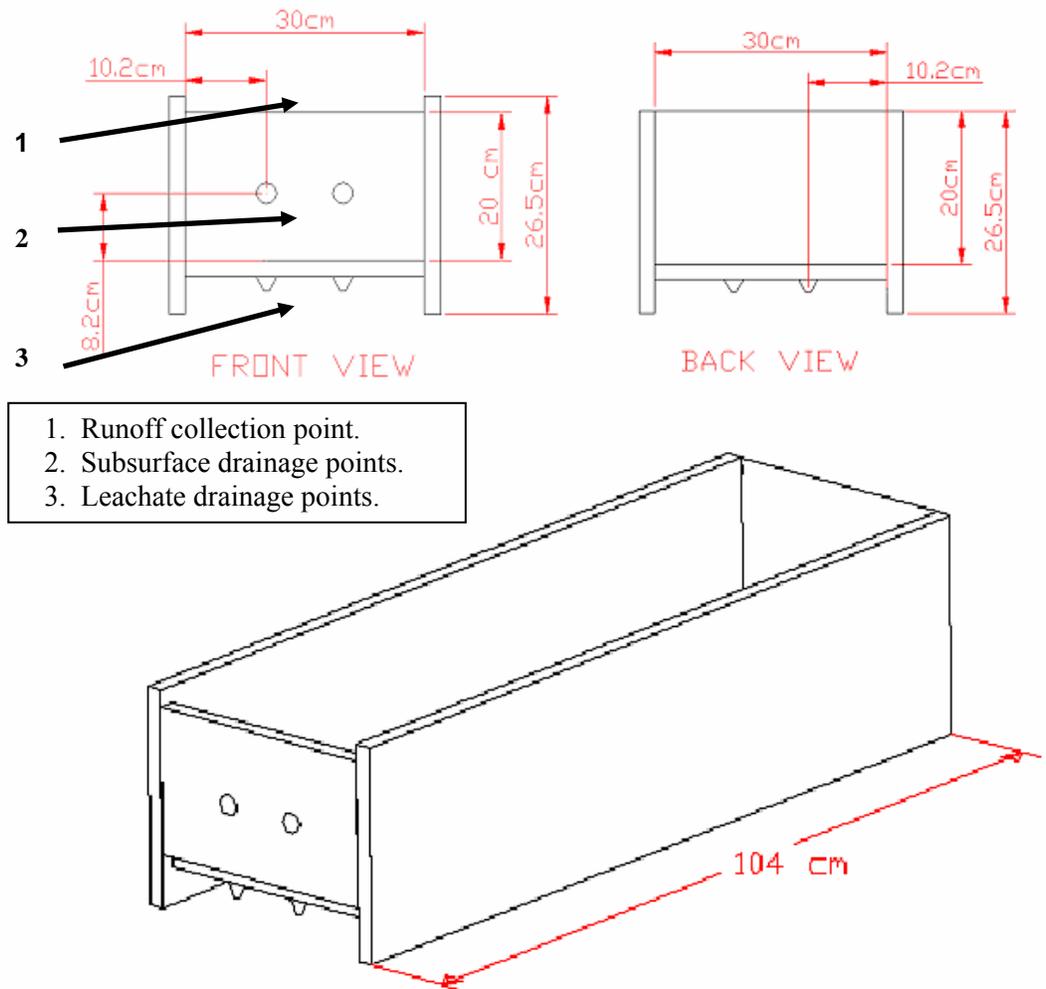


Figure 3-1. Runoff box design.

Soil was placed in the boxes either as discrete 0–10 cm (39.5 kg) and 10–20 cm (39.5 kg) depths or as a mixed layer at approximately  $1.3 \text{ g cm}^{-3}$  to mimic field conditions as noted in the experimental design section below. Al-WTR from Manatee County was applied to the appropriate treatments at a rate of 2.5% of dry soil weight (0.975 kg of Al-WTR dry weight per 10 cm of soil treated). The Al-WTR and soil were mixed using a cement mixer to evenly distribute the Al-WTR and/or soil in the appropriate boxes. After establishing the appropriate treatments, stargrass cuttings obtained from an area adjacent to the sampling site in the sprayfield were sprigged at 30 per box to simulate field density of grass. Simulation boxes were kept in an open-sided greenhouse during the study to protect them from rainfall.

### **Rainfall Simulation**

Rainfall simulation was conducted according to a protocol developed by the National Phosphorus Research Project (NPRP) to quantify soil P-runoff relationships (NPRP, 2001). Rainfall intensity was uniformly applied at  $7.1 \text{ cm h}^{-1}$  (approximately  $210 \text{ cm sec}^{-1}$ ) from a height of 3 m above the soil surface. This is equivalent to a 10 yr, 24 hr rain. Gainesville municipal water was adjusted from a pH of approximately 8.5 to 5 using 3 M HCl to mimic rainfall pH in South Florida. Rainfall was dispersed uniformly using a TeeJet™ HH-SS50WSQ nozzle centered under a 3 x 3 x 3 meter frame protected from wind (Fig. 3-2). Thirty cups were distributed in a grid to test rainfall distribution uniformity. There were no significant differences in volume within the grid. Rainfall simulations were repeated every 3 wk, for a total of 6 rainfall simulation events.

Analysis of the source water and rainfall (pH adjusted source water) was conducted by inductively coupled plasma atomic emission spectroscopy; total Fe and Al were approximately  $0.15$  and  $0.45 \text{ mg L}^{-1}$  respectively. Source water and rainfall also

contained Ca ( $14 \text{ mg L}^{-1}$ ) and Mg ( $8 \text{ mg L}^{-1}$ ). These Ca and Mg levels were expected based on the municipality's well field pumping water from the Floridan aquifer which passes through both limestone and the Hawthorne formation. In addition, the municipality treats the water with lime. Soluble P, TP,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  were below detectable limits ( $0.03$ ,  $0.03$ , and  $0.02$ , and  $0.06 \text{ mg L}^{-1}$ , respectively).

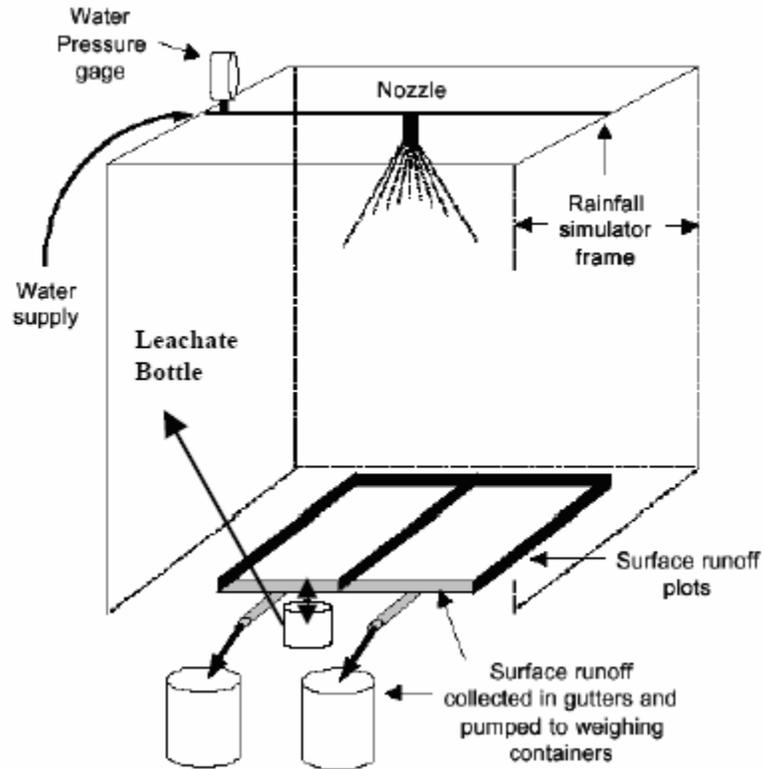


Figure 3-2. Schematic diagram of rainfall simulator (NPRP, 2001).

Rainfall boxes were placed five at a time, under the simulator at a 1 to 2% slope (See Figure 3-3). Thirty minutes of runoff (collection point out side of simulator) was collected from the boxes via Tygon tubing connected to the runoff port. Runoff did not start at the same time for each box; therefore each box was covered after 30 min of runoff had been collected. The boxes were left in place under the simulator for approximately half an hour while subsurface flow and leachate were collected. This was done by

draining the two side and two front leachate ports, respectively. All collected samples were weighed and then sub-sampled. A 1 L sub-sample was taken from runoff, and 250 mL sub-samples were taken from subsurface flow and leachate. Two filtered (0.45  $\mu\text{m}$ ) sub-samples (20 mL) were taken from each sub-sample, using a vacuum pump to obtain approximately 40 mL aliquot for analysis. The sub-samples were refrigerated until P analysis was performed, usually the following day. One 20 mL filtered sample was acidified and refrigerated until  $\text{NO}_3^-$  and  $\text{NH}_4^+$  could be measured.



Figure 3-3. Box placement under simulator.

During the 3 wk intervals between the first six simulations, the soil was watered with pH-adjusted water to saturation and the watertable was allowed to drop to the bottom of the boxes before watering again. A seventh simulation was run to evaluate the effect of maintaining the soil in a saturated condition during a 4 wk period after the sixth simulation was run. After the sixth simulation, vegetation was cut to the soil surface and the watertable was raised to cover the surface. Water was added as needed over 4 wk to maintain soil saturation. A plastic cover was added to reduce evaporation from the boxes. The watertable was allowed to subside approximately 5 cm during the 2 d prior to

the 7<sup>th</sup> simulation to facilitate moving the boxes to the simulator. The variation to the study was made as a result of recent research at the MacArthur Agro-ecology Research Center indicating that longer saturation times may elevate SP losses (Res. Comm., P.J. Bohlen, MacArthur Agro-ecology Research Center).

### Experimental Design

Five treatments, with four replications each were used (Fig. 3-4). Soil was placed in the simulation boxes either as discrete layers (treatments C1, T1, and T2) or with the two depths mixed (treatments C2 and T3). The Al-WTR was applied on the soil surface (T1), mixed with the 0-10 cm soil depth (T2), or mixed with the combined soil depths to a depth of 20 cm (T3).

<b>C1*</b>	No Al-WTR applied.	
<b>T1*</b>	Al-WTR surface applied.	
<b>T2*</b>	Al-WTR incorporated into 0-10 cm soil depth.	
<b>T3**</b>	Al-WTR incorporated into 0-20 cm soil depth.	
<b>C2**</b>	No Al-WTR applied.	

\*0-10 and 10-20 cm soil depths placed in box in sequence.

\*\*0-10 and 10-20 cm soil depths mixed prior to placement in box.



Figure 3-4. Treatment descriptions

### **Soil Sampling and Forage Harvest**

A soil core from each packed box from both depths (0–10 and 10–20 cm) was taken prior to the start of rainfall simulations (refilled based on soil depth) and after the sixth (5 boxes) or seventh rainfall simulations (16 boxes). Before each rainfall simulation, the forage was harvested to a height of approximately 15 cm. The cuttings were dried, weighed, ground to 1 mm, and stored. Upon completion of the sixth simulation, the roots were harvested, dried, weighed, and ground from replicate 4. After the seventh simulation, all other roots were harvested, dried, weighed, and ground. All vegetation (initial sprigs, grass cuttings, and roots) were analyzed for total P, N, and Al.

### **Analytical Methods**

#### **Soil**

The soil samples were dried and analyzed for WEP, TP, Mehlich-1 P, and pH. Water extractable P in the soil was determined on air dried soil. Three grams of soil were weighed into 50 mL centrifuge tubes and 30 mL of DDI water was added to obtain a soil to water ratio of 1:10. The suspension was then continuously shaken on a mechanical shaker for 1 hr and vacuum filtered (0.45  $\mu\text{m}$ ). Analysis was identical to the water samples.

Soil TP was determined by the ignition method (Anderson, 1976). One gram of soil was weighed into a 50 mL beaker and ashed in a muffle furnace. The furnace temperature was raised to 250°C and maintained for 30 min before ramping to 550°C for 4 hr. After ashing, the samples were brought to room temperature in a desiccator and weighed. The cooled ash was moistened with distilled dionized water (DDI) before adding and evaporating 20 mL of 6.0 M HCl slowly on a hotplate at approximately 120°C. Once digested, the ash was resolublized with 2.25 mL of 6.0 M HCl and

quantitatively transferred and filtered into 50 mL volumetric flasks using Whatman #41 paper. The beaker and the filter paper were each rinsed three times before bringing the flask to volume (Anderson, 1976). Twenty milliliter sub-samples were taken and stored in scintillation vials at room temperature. The Murphy-Riley method was used to determine TP in solution using a Technicon™ Autoanalyzer, EPA Method 365.1 (EPA, 1993a).

Mehlich-1 extractable P, Fe, Al, Ca, and Mg were determined on air dried soil samples from both depths (0–10 cm and 10–20 cm) of each box prior to simulations and after simulation 7. Four grams of soil were weighed into 50 mL centrifuge tubes and 16 mL of Mehlich-1 solution (0.025 M HCl and 0.0125 M H<sub>2</sub>SO<sub>4</sub>) was added and shaken continuously on a mechanical shaker for 5 min (Mehlich, 1953). The samples were then vacuum filtered through a 0.45 µm filter and analyzed on a Technicon™ Autoanalyzer. The pH of the soil was measured on the supernatant of a 1:2 soil to solution ratio (DDI). The samples were stirred and allowed to equilibrate for 30 min before determining the pH using an Orion pH electrode.

### **Aluminum Water Treatment Residuals**

Total P (TP) in the Al-WTR was determined via the ignition (ashing) method (Anderson, 1976) and analyzed for P following the Murphy and Riley (1962) method. The Al-WTR samples were digested following the EPA method 3050A and analyzed for Al, Fe, Ca, and Mg by inductively coupled plasma atomic emission spectroscopy (ICP) (USEPA, 1993b). Standard methods were used to determine pH (1:2 soil to solution) and percent solids (Page, 1982).

The pH of the Al-WTR samples was measured on the supernatant 1:2 soil to solution ratio (DDI). The samples were stirred and allowed to equilibrate for 30 min

before the pH was taken by the Orion pH electrode. Percent solids were determined for the AI-WTR by taking the oven dried weight over the air dried weight. This is a critical factor in determining the air dried application rate of the AI-WTR. In addition, percent solids were determined for all water samples during the TP procedure by taking the evaporated beaker weight over the known volume, assuming 1 mL equals 1 g.

### **Forage**

All forage samples were digested using a modification of the standard Kjeldahl procedure at the Forage Evaluation Support Laboratory (FESL) at the University of Florida. Ground samples (0.25 g) were weighed into 75 mL digestion tubes and 1.5 g of the 9:1 catalyst ( $K_2SO_4$ : $CuSO_4$ ) was added. Using 4.5 mL of  $H_2SO_4$  and 2 mL of  $H_2O_2$ , the forage was digested for at least 4 hr at 375° C (Gallaher et al., 1975). Upon completion of the digestion, the samples were brought to volume and filtered using Fisher screening column paper. A 20 mL sub-sample taken and was stored at room temperature until it could be analyzed for total N (TN) by semiautomated colorimetry (Hambleton, 1977).

### **Runoff, Subsurface Flow, Leachate**

All water samples (runoff, subsurface flow, and leachate) were vacuum filtered through a 0.45  $\mu$ m filter within 5 hr of collection and stored in 20 mL scintillation vials at 4° C. Soluble P (SP) was analyzed using the filtered runoff samples. Total P (TP) by digestion (see 'Soils') and pH analysis were performed on the unfiltered sample. In addition, the runoff, subsurface flow, and leachate were analyzed for total Al using unfiltered samples. The data were used to determine particulate P (PP) in the runoff by subtracting soluble P (SP) from TP ( $TP-SP=PP$ ). Water soluble P was determined by

EPA Method 365.1 using a Technicon™ Autoanalyzer, (USEPA, 1993a). Analyses was performed within 48 hr of sample collection.

Water total P (TP) was determined based on a variation of the ignition (ashing) method (Anderson, 1976). Approximately 20 to 30 mL of water was poured into a 50 mL beaker and evaporated at 100°C. The samples were then placed in a muffle furnace and digested and sub-sampled identical to the soil samples. The Murphy-Riley method was used to determine TP in sub-sample solution using a Technicon™ Autoanalyzer (EPA Method 365.1, 1993a).

Total Al concentration of the water samples was determined by a nitric acid digestion procedure (Clesceri et al., 1989). One hundred milliliters of runoff or 50 mL of subsurface and leachate were measured into a 125 mL erlenmeyer flask with two or three glass beads. Ten milliliters of 12 M HNO<sub>3</sub> acid were added to the flask. The solution was evaporated on a hot plate until approximately 10 to 20 mL remained. The flask was then brought up to approximately 75 mL of solution using DDI water and 10 mL of 12 M HNO<sub>3</sub> acid was added again and allowed to evaporate to 10 to 20 mL of solution. The solution was then filtered using Whatman #42 paper. Samples were then stored at room temperature until analyzed for Al by atomic absorption spectroscopy.

All water samples were stored at 4°C until the pH could be measured using an Orion pH electrode (Orion Research Inc. Boston, MA), usually within a week of collection. The duplicate filtered water samples in 20 mL scintillation vials were acidified using H<sub>2</sub>SO<sub>4</sub> and stored at 4° C until analysis for ammonium and nitrate. Ammonium was analyzed on a Technicon™ Autoanalyzer following EPA method 350.1 (USEPA,

1993c). Nitrate was analyzed on an Alpkem Corp. Rapid Flow Analyzer following method A303-S170 (Alpkem, 1990).

### **Quality Assurance and Quality Control**

Quality assurance and quality control (QA/QC) were met through 10% repeats, spikes, and blanks for each procedure. Certified external standards were used for quality control, in addition to, standard calibration curves. A 10% relative standard deviation was required for all repeats. Less than 5% of the total samples required re-runs because few were out-of-range values. All spike values and quality control checks fell within 90-110% acceptance levels.

### **Statistical Analysis**

Statistical analysis was performed using SAS version 8.2 1999–2001 (SAS Institute Inc., Cary, North Carolina, USA). A repeated measures model was explored to estimate and examine time (simulation) effects as well as expected correlations between treatments and their respective control for a given simulation. Normality was checked, and log-transformation was performed on the data (variables) to achieve normal distribution. The General Linear Model procedure was used in order to analyze the changes (variables) over time (simulation), between treatments, and between type. The means values for (variables) were compared by treatment/type/simulation using the Waller-Duncan procedure. A paired-t test was conducted in order to compare the “pre” and “post” values for the response variables measured.

CHAPTER 4  
RESULTS AND DISCUSSION

**Initial Soil P Concentrations and pH**

The initial soil was highly impacted with animal manure as indicated by the high concentrations of water extractable P (WEP), Mehlich-1 extractable P, and total P (TP) (Table 4-1). Mehlich-1 extractable P concentrations above 60 mg kg<sup>-1</sup> would require no further addition of P from an agronomic standpoint. An un-impacted Immokalee fine sand (A horizon) would likely have WEP concentrations of less than 1 mg kg<sup>-1</sup> and Mehlich-1 extractable P in the range of 3 to 8 mg kg<sup>-1</sup> (Graetz and Nair, 1995). Water extractable P concentrations and pH were similar between the 0–10 and 10–20 cm depths; however, Mehlich-1 P and TP concentrations were greater in the 10–20 cm depth than in the 0–10 cm depth.

Table 4-1. Initial soil mean values of P concentrations and pH of the Immokalee fine sand used in the study.

Depth (cm)	WEP (mg kg <sup>-1</sup> )	Mehlich-1 P (mg kg <sup>-1</sup> )	TP (mg kg <sup>-1</sup> )	pH
0–10	18	879	1301	6.7
10–20	17	1034	1427	7.0

**Aluminum Water Treatment Residual Characteristics**

The applied Al-WTR had a moisture content of approximately 30%, a pH of 5.9, and was dominated by Al (51,000 mg Al kg<sup>-1</sup>) (Table 4-2). Miyittah-Kporgbe (2004) reported approximately 80% of the Al was amorphous in a similar material. Concentrations of Fe, Ca, and Mg were low compared to Al (Table 4-2). The TP concentration was approximately 1300 mg kg<sup>-1</sup>. This relatively high TP concentration is

not expected to affect the P dynamics in the soil because of its low availability. Makris (2004) reported desorption of P by Al-WTR was less than 1%. A Hillsborough Al-WTR as reported by O'Connor et al. (2002) had a low degree of P saturation (DPS:  $\approx 0.032$ ), which suggests active Fe and Al for P retention.

Table 4-2. Selected characteristics of the Manatee County Al-WTR.

% Solids	pH	Fe mg kg <sup>-1</sup>	Al mg kg <sup>-1</sup>	Ca mg kg <sup>-1</sup>	Mg mg kg <sup>-1</sup>	TP mg kg <sup>-1</sup>	WEP mg kg <sup>-1</sup>
71	5.9	1,790	51,000	580	120	1,300	BDL <sup>†</sup>

<sup>†</sup> Below detectable limit: 0.02 mg L<sup>-1</sup>.

### Runoff, Subsurface Flow, and Leachate Characteristics

#### Volume

Runoff, subsurface flow, and leachate volumes were measured for each simulation event to provide the basis for loading calculations (Table 4-3). Runoff volumes averaged 13.9 L per event with no differences in runoff volumes between treatments. Subsurface flow volumes were considerably smaller than runoff volumes (1.2 L average) and were uniform as well, except for treatment C2 which was greater than the other treatments. The higher volume in C2 was attributed to slight differences in box construction<sup>1</sup> and soil packing, which resulted in slightly more standing water remaining in the C2 treatment boxes after runoff ceased. Leachate from the bottom ports was collected only for simulations 5 through 7. Leachate volume was smaller than subsurface flow volume but was uniform between treatments. The uniformity of the runoff, subsurface flow, and leachate indicate the Al-WTR does not significantly influence the soil's water holding capacity at the rate applied.

<sup>1</sup> Treatment C2 was added to the study after boxes were already constructed for all other treatments. The boxes for treatment C2 were slightly taller than the other boxes, resulting in an increase of water held on the soil surface after runoff ceased. This was reflected in increased subsurface flow.

Table 4-3. Average runoff, subsurface flow, and leachate volumes as influenced by treatment from six simulations of runoff, five simulations of subsurface flow, and two simulations of leachate.

Collection Point	Treatments <sup>†</sup>					Average
	C1	T1	T2	T3	C2	
Runoff	13.97a‡	13.95a	13.76a	13.88a	13.79a	13.87
Subsurface Flow	1.18b	1.13b	1.12b	1.02b	1.54a	1.20
Leachate	0.40b	0.54b	0.39b	0.63a	0.63a	0.52

<sup>†</sup>C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

‡ Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

## pH

Runoff pH decreased from 6.76 for the first simulation to 6.02 in the sixth simulation (Fig. 4-1A). In contrast, subsurface flow pH increased from 7.05 to 7.66 during the same period. Leachate pH, measured for the final two simulations, was slightly greater, but similar to, subsurface flow pH. Averaged over the six simulations, there were no differences in pH among treatments for any of the measured components ( $p < 0.05$ ; Fig. 4-1B). Results showed pH was significantly different between collection points during each simulation and averaged over all simulations.

## Phosphorus

Soluble P concentrations in surface runoff were smaller than corresponding concentrations in subsurface flow and leachate for all treatments (Table 4-4). Soluble P concentrations in the subsurface flow and leachate were at least 10-fold greater than in the runoff. This can be attributed to greater volumes of rainfall appearing as runoff (diluting the SP) than appearing as subsurface flow and leachate and less interaction with the P-impacted soil. Runoff SP concentration was reduced by 77% by the addition of Al-WTR to the soil surface (T1). An approximately 45% reduction in runoff SP

concentration was observed when the Al-WTR was mixed with the 0–10 cm soil depth (T2) and 0–20 cm soil depth (T3).

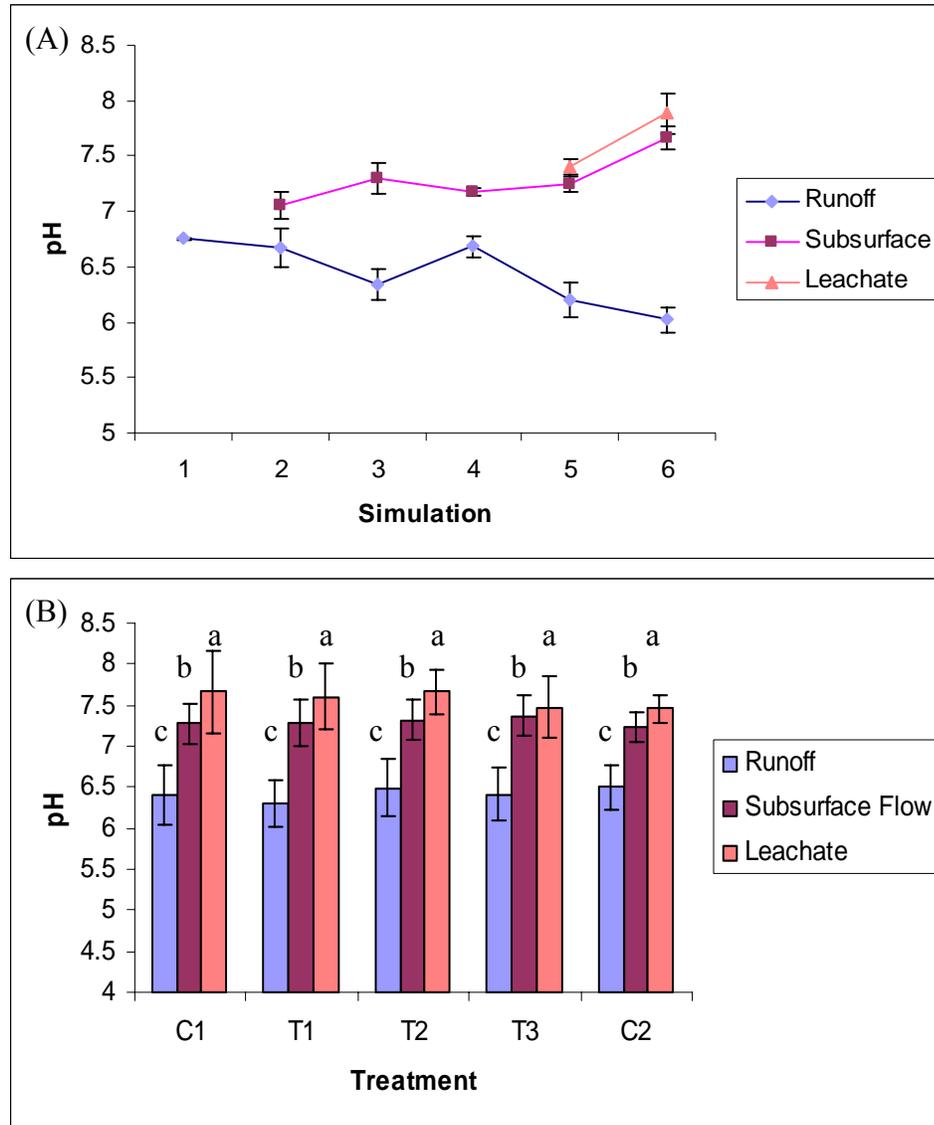


Figure 4-1. Runoff, subsurface flow, and leachate pH values from six, five, and two simulations, respectively. (A) Average treatment pH per. (B) Simulation averages for each treatment. C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm. Error bars represent the standard deviation of 4 replicates. Mean pH value within a treatment followed by the same letter are not significantly different using the Waller-Duncan method ( $p < 0.05$ ).

Surface application of Al-WTR (T1) did not reduce SP concentrations in subsurface drainage or leachate (Table 4-4). Phosphorus concentrations for subsurface flow were reduced 37% by mixing the Al-WTR in the top 10 cm of soil (T2) and 90% by mixing the Al-WTR with the whole soil depth (T3). This difference between T2 and T3 was unexpected because the subsurface flow was collected at a depth of 10 cm and it was anticipated that SP concentrations in the subsurface flow would be influenced primarily by SP concentration reductions in the 0-10 cm depth. However, it appears that the SP concentration of the subsurface flow was influenced by both the 0-10 and 10-20 cm soil depths. This may be explained by the fact that the watertable was moving upward through the 10-20 cm depth during part of the simulation event allowing water from the 0-10 cm depth containing Al-WTR to mix with water from the untreated 10-20 cm depth. The SP concentration in subsurface flow and leachate in T1 increased slightly (11%) for some unexplained reason. Treatments C1, T1, and T2 had similar leachate SP concentrations, whereas C2 and T3 SP concentrations were significantly different. Al-WTR treatment of the complete profile (T3) had the greatest effect on subsurface drainage and leachate SP concentrations with reductions of 90 and 95%, respectively.

Table 4-4. Average soluble P concentrations by treatment in runoff (six events), subsurface flow (five events), and leachate (two events).

Collection Point	Treatments <sup>†</sup>				
	C1	T1	T2	T3	C2
Runoff	0.34a	0.08d	0.18c	0.16c	0.29b
Subsurface Flow	4.13b	4.57a	2.60c	0.41d	4.16b
Leachate	4.52b	4.63b	4.02b	0.36c	6.85a

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>‡</sup> Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

Soluble P concentrations in runoff, subsurface flow, and leachate for each simulation event are shown in Fig. 4-2 A, B, and C, respectively. Concentrations were greatest and most variable in the first two simulations in runoff, subsurface flow, and leachate. These greater concentrations may be attributed to the presence of highly-labile soil P that interacted with the rainfall during the first two simulation events. In addition, disturbance of the soil during sampling and repacking of the simulator boxes likely accounted for the variability observed during the first two simulations. After the first two simulation events, concentrations of all treatments remained relatively stable for surface runoff, subsurface flow. This consistency reinforces results from treatment averages described previously.

Runoff SP concentrations (Figure 4-2A) were the greatest in the first two simulations when compared to the following four simulations. In simulations 3 through 6, runoff SP concentrations in all treatments were stable and did not significantly differ between treatments. After simulation 2, the control SP concentrations were not significantly different and stabilized at approximately  $0.3 \text{ mg L}^{-1}$ . When AI-WTR was mixed with soil (T2 and T3), runoff SP concentration stabilized after two simulations at approximately  $0.15 \text{ mg L}^{-1}$ . When AI-WTR was surface-applied (T1), SP concentration was less than  $0.1 \text{ mg L}^{-1}$  and was significantly lower than all other treatments for all simulations.

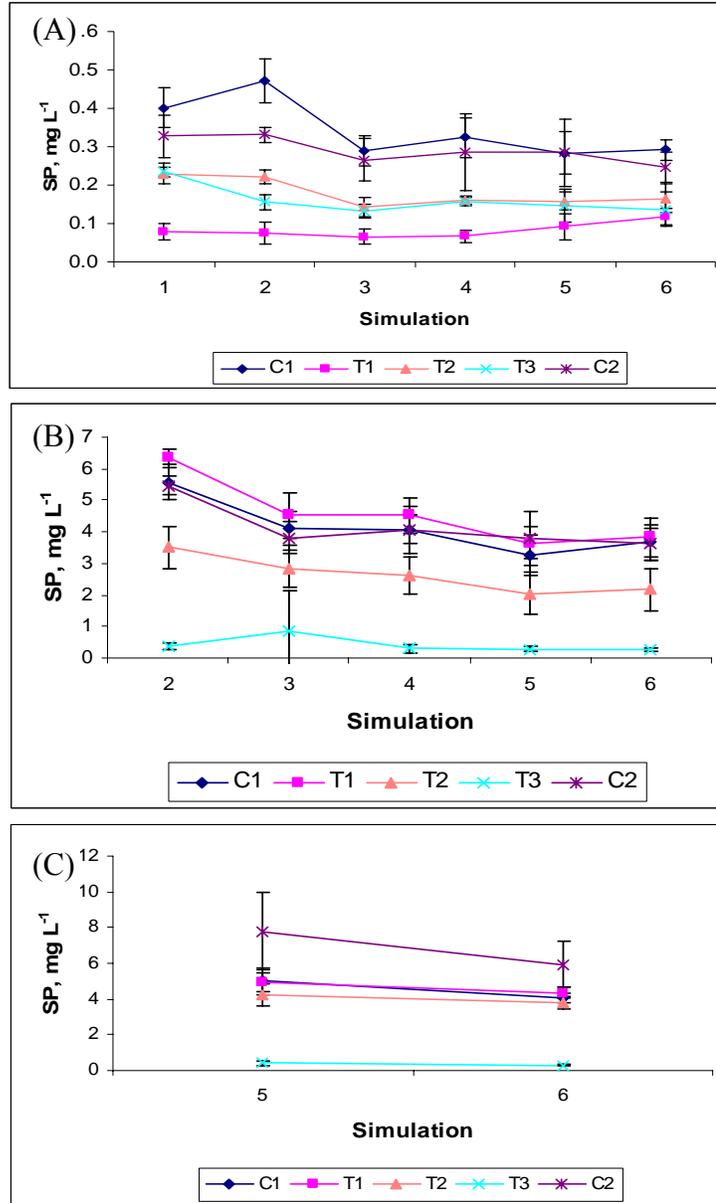


Figure 4-2. Average treatment SP concentrations and standard deviations from the three collection points. (A) Runoff: six simulations. (B) Subsurface flow: five simulations. (C) Leachate: two simulations. C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

Similar stabilization occurred with SP concentrations in subsurface flow after simulation 2 (Figure 4-2B) for all treatments. Soluble P concentrations stabilized at approximately 4 mg L<sup>-1</sup> after simulation 2 for the surface-applied Al-WTR (T1) and for the controls (C1 and C2). When the Al-WTR was incorporated in to the soil (T2 and T3),

SP concentrations stabilized at 2.5 and 0.4 mg L<sup>-1</sup>, respectively. The decision to collect leachate after simulation 4 limits interpretation of the leachate data. However, with the exception of C2, the leachate SP concentrations were relatively consistent between simulations 5 and 6. Soluble P concentrations for C2 were expected to be similar to C1, but instead were higher. The reason for this is not obvious, but this difference might be attributed to the higher water extractable P (WEP) and Mehlich-1 concentrations found in C2 (Tables 4-11 and 4-12).

After simulation six, the soil was maintained in a flooded condition for 4 wk prior to simulation seven. Contrary to expectations, flooding the soil reduced runoff SP concentration by approximately 65% (Table 4-5) compared to the first six simulations (Table 4-4). This effect was believed to be a result of longer interaction time with soil/AI-WTR sorption sites. Starting the rainfall event with the soil flooded likely minimized the rainfall interaction with the soil solution which resulted in lower P concentrations in the runoff. Flooding of the soil also slightly reduced subsurface SP concentrations compared to the previous six simulations. No impact of flooding on SP concentrations was observed for the leachate.

Table 4-5. Average soluble P concentrations in runoff, subsurface flow, and leachate after 4 wk of flooded conditions (Simulation 7).

Collection Point	Treatments <sup>†</sup>				
	C1	T1	T2	T3	C2
	-----mg P L <sup>-1</sup> -----				
Runoff	0.13a <sup>‡</sup>	0.04b	0.04b	0.03b	0.15a
Subsurface	3.53a	3.43a	1.61b	0.20c	2.69a
Leachate	3.96b	4.20b	3.49bc	0.23c	7.95a

<sup>†</sup> C1, no AI-WTR, not mixed; T1, surface applied AI-WTR, not mixed; T2, AI-WTR mixed in 0–10 cm; T3, AI-WTR mixed in 0–20 cm; C2, no AI-WTR, mixed 0–20 cm.

<sup>‡</sup>Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

Runoff, subsurface flow, and leachate volumes for simulation 7 followed the same trend of consistency between treatments as was observed for the first 6 simulations (Table 4-6A). Flooding the soil lowered the average runoff pH from 6.8 (simulations 1-6) to 6.3 (simulation 7) (Table 4-6B). Average subsurface flow and leachate pH values decreased from approximately 7.6 to 7.3.

Table 4-6. Runoff, subsurface flow, and leachate collected during simulation 7. (A) Volume. (B) pH.

(A)	Treatments <sup>†</sup>				
	C1	T1	T2	T3	C2
Collection Point	-----L-----				
Runoff	15.81b <sup>‡</sup>	16.78b	15.23c	15.83b	16.63b
Subsurface	0.77a	0.86a	1.07b	1.11ab	1.22b
Leachate	0.42a	0.73a	0.36a	0.63a	0.57a

(B)	Treatments <sup>†</sup>				
	C1	T1	T2	T3	C2
Collection Point	-----pH-----				
Runoff	6.34a <sup>‡</sup>	6.10a	6.44a	6.30a	6.38a
Subsurface	7.37b	7.42b	7.39b	7.31b	7.19b
Leachate	7.44c	7.44c	7.59c	7.35c	7.34c

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>‡</sup> Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

Soluble P loss per box from each treatment per rainfall event was calculated by multiplying volume by concentration (Table 4-7). The same trend was observed as with SP concentrations, which was expected based on volume similarities among treatments (Table 4-6A). These results emphasize the importance of treating P-impacted soils to reduce risk of P loss. Mixing 2.5% Al-WTR with the P-impacted soil can reduce field loss of SP by approximately 80% compared to 30% by surface applied Al-WTR. Surface application and partial mixing of the impacted zone (T1 and T2, respectively) had less impact compared to total mixing of Al-WTR with the P-impacted soil (T3). The relatively lower volumes of subsurface and leachate pose an equal risk of SP loss to that

of runoff because what is lacking in volume is compensated by concentration. A rough estimate of SP loss on a hectare basis can be calculated, assuming that similar P losses would be encountered over larger areas (Table 4-7). The expected loss per rainfall event in an untreated field would be 350 to 500 g ha<sup>-1</sup>. Partial treatment of the impacted zone could reduce P loss approximately 200 to 300 g ha<sup>-1</sup>. Soluble P loss could be reduced to less than 100 g ha<sup>-1</sup> if AI-WTR was incorporated throughout the P-impacted layer.

Soil mixing in C2 did not reduce P loss as was found by Miyittah (2004), because both the 0–10 and 10–20 cm depths were highly P-impacted. Miyittah (2004) mixed a P-impacted soil with an un-impacted E horizon, which in effect, diluted the P-impacted soil.

Table 4-7. Soluble P mass loss (SP concentration \* volume) averaged over six rainfall events and estimated SP loss per hectare per rainfall event.

Collection Point	Treatments <sup>†</sup>				
	C1	T1	T2	T3	C2
Runoff (mg P box <sup>-1</sup> )	4.36a <sup>‡</sup>	1.07d	2.22c	1.96c	3.68b
Subsurface (mg P box <sup>-1</sup> )	4.75b	4.92b	2.76c	0.45d	6.07a
Leachate (mg P box <sup>-1</sup> )	1.69b	2.37b	1.50b	0.20c	4.61a
Total SP loss (mg P box <sup>-1</sup> )	10.80	8.36	6.48	2.61	14.36
SP loss (g P ha <sup>-1</sup> )	360	279	216	87	479

<sup>†</sup> C1, no AI-WTR, not mixed; T1, surface applied AI-WTR, not mixed; T2, AI-WTR mixed in 0–10 cm; T3, AI-WTR mixed in 0–20 cm; C2, no AI-WTR, mixed 0–20 cm.

<sup>‡</sup>Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

Particulate P (PP) concentration was calculated in runoff, subsurface flow, and leachate by subtracting SP from TP (Table 4-8). Runoff PP concentrations ranged from 0.1 to 0.3 mg L<sup>-1</sup>. On average, PP accounted for approximately 20 and 60% of TP in the controls and the AI-WTR treatments, respectively. Therefore, PP should also be a concern on minimally sloped landscapes, particularly if AI-WTR has been applied. Particulate P concentrations in the subsurface flow and leachate were below detectable limits. Although PP concentrations in runoff showed marked trends among treatments, the differences were not significant because of the high standard deviations among

treatments. This is believed to be a result of small variations in soil surface levels compared to the box edge rather than treatment effects. This would affect the amount of particulate matter leaving, or conversely, retained, at the box edge where runoff was collected.

Table 4-8. Total, soluble, and particulate P concentrations in runoff for each treatment averaged over six rainfall events.

	Treatments <sup>†</sup>				
	C1	T1	T2	T3	C2
	-----mg P L <sup>-1</sup> -----				
Total P	0.47a <sup>‡</sup>	0.21b	0.38ab	0.47a	0.34ab
Soluble P	0.34a	0.08d	0.18c	0.16c	0.29b
Particulate P	0.13a	0.13a	0.20a	0.31a	0.05a

<sup>†</sup> C1, no AI-WTR, not mixed; T1, surface applied AI-WTR, not mixed; T2, AI-WTR mixed in 0–10 cm; T3, AI-WTR mixed in 0–20 cm; C2, no AI-WTR, mixed 0–20 cm.

<sup>‡</sup>Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

### Nitrate- and Ammonium-Nitrogen

Ammonium-N concentrations in runoff, subsurface flow, and leachate averaged less than 1 mg L<sup>-1</sup> and there were no differences among treatments (Table 4-9A). Nitrate-N concentrations (Table 4-9B) were also below 1 mg L<sup>-1</sup> and showed no differences between treatments with two exceptions. The exceptions were greater NO<sub>3</sub>-N concentrations in subsurface flow and leachate in T1 compared to all other treatments. There are no obvious explanations for these differences at this time. Under typical production conditions, N fertilizer would be added to maintain production and forage nutritive value. However, to simplify this experiment, no additional fertilization was used.

Table 4-9. Average N concentrations in runoff, subsurface flow, and leachate from six, five, and two simulations, respectively. (A) NH<sub>4</sub>-N. (B) NO<sub>3</sub>-N.

(A)	Treatments <sup>†</sup>				
	C1 <sup>†</sup>	T1	T2	T3	C2
Collection Point	-----mg NH <sub>4</sub> -N L <sup>-1</sup> -----				
Runoff	0.19a <sup>‡</sup>	0.19a	0.18a	0.23a	0.19a
Subsurface	0.38a	0.38a	0.35a	0.30a	0.33a
Leachate	0.35a	0.36a	0.42a	0.47a	0.44a

(B)	Treatments <sup>†</sup>				
	C1 <sup>†</sup>	T1	T2	T3	C2
Collection Point	-----mg NO <sub>3</sub> -N L <sup>-1</sup> -----				
Runoff	0.15a <sup>‡</sup>	0.14a	0.14a	0.13a	0.12a
Subsurface	0.23b	0.77a	0.10b	0.14b	0.13b
Leachate	0.12b	0.74a	0.11b	0.10b	0.08b

<sup>†</sup> C1, no AI-WTR, not mixed; T1, surface applied AI-WTR, not mixed; T2, AI-WTR mixed in 0–10 cm; T3, AI-WTR mixed in 0–20 cm; C2, no AI-WTR, mixed 0–20 cm.

<sup>‡</sup>Means within a row and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

### Total Calcium, Magnesium, Iron, and Aluminum Concentrations

Calcium and Mg concentrations were in the order of runoff < subsurface flow < leachate (Table 4-10). There were no significant differences in Ca and Mg concentrations in runoff among treatments. Calcium and Mg concentrations were different among treatments for subsurface flow and leachate. Aluminum-WTR treatments had higher concentrations of Ca in subsurface flow and leachate which is likely due to the Ca contained in the AI-WTR (580 mg L<sup>-1</sup>). Iron concentrations were similar in runoff, subsurface flow, and leachate, and did not vary between treatments. Total Al concentrations were highly variable and showed no meaningful differences among treatments. However, a trend of higher Al concentrations was observed in leachate from treatments where AI-WTR was incorporated into the soil (T2 and T3). Random samples were tested for soluble Al from all collection points, treatments, and simulations and all concentrations were below detection limits (0.3 mg L<sup>-1</sup>). This suggests that essentially all of the Al was in particulate form.

Table 4-10. Average total Ca, Mg, Fe, and Al concentrations in runoff, subsurface flow, and leachate from six, five, and two simulations, respectively. (A) Runoff. (B) Subsurface flow. (C) Leachate.

(A)		Runoff			
	Ca	Mg	Fe	Al	
Treatments <sup>†</sup>	-----mg L <sup>-1</sup> -----				
C1	15.8	8.83	0.27	0.66	
T1	16.3	8.90	0.53	1.06	
T2	16.4	8.44	0.43	1.62	
T3	17.6	8.68	0.51	2.68	
C2	15.7	8.36	0.23	2.71	

(B)		Subsurface Flow			
	Ca	Mg	Fe	Al	
Treatments <sup>†</sup>	-----mg L <sup>-1</sup> -----				
C1	64.3c <sup>‡</sup>	22.1b	0.23	0.00b	
T1	80.2b	26.8ab	0.42	1.22a	
T2	91.1ab	30.6a	0.34	0.00b	
T3	95.9a	31.6a	0.38	0.00b	
C2	49.0d	16.4c	0.54	0.76a	

(C)		Leachate			
	Ca	Mg	Fe	Al	
Treatments <sup>†</sup>	-----mg L <sup>-1</sup> -----				
C1	95.2b <sup>‡</sup>	45.8b	0.19	0.00a	
T1	94.4b	48.7b	0.09	0.00a	
T2	138.8ab	67.9a	0.15	1.94b	
T3	199.3a	63.0a	1.14	5.67b	
C2	87.7b	28.1c	0.12	3.70b	

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>‡</sup>Means within a column and followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

### Pre- and Post-simulation Comparisons

#### Soil Phosphorus

When Al-WTR was incorporated into the soil, WEP decreased by approximately 70% i.e., T2 (0–10 cm depth) and both depths in T3, compared to the respective controls (Table 4-11). There was no change in soil WEP concentrations in any of the treatments prior to or after the study (paired T Test;  $p < 0.05$ ).

Table 4-11. Pre- and post-simulation water extractable P concentrations in the 0-10 and 10-20 cm soil depths.

Treatments <sup>†</sup>	0–10 cm depth		10–20 cm depth	
	Pre-simulation <sup>‡§</sup>	Post-simulation	Pre-simulation	Post-simulation
	-----mg P kg <sup>-1</sup> -----			
C1	21 a	20 a	24 a	26 a
T1	14 c	14 b	24 a	23 ab
T2	7 d	7 c	19 b	18 b
T3	6 d	7 c	7 c	6 c
C2	25 a	24 a	24 a	25 a

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>§</sup> Means within a column followed by the same letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

Application of Al-WTR had essentially no effect on Mehlich-1 extractable P (Table 4-12). Apparently, Mehlich-1 extractant removes P adsorbed to the soil as well as that adsorbed to Al-WTR. There were few differences in pre- and post-simulation concentrations statistically compared using the paired T Test ( $p < 0.05$ ).

Table 4-12. Pre- and post-simulation Mehlich-1 P concentrations in the 0-10 and 10-20 cm soil depths.

Treatments <sup>†</sup>	0–10 cm depth		10–20 cm depth	
	Pre-simulation <sup>‡§</sup>	Post-simulation	Pre-simulation	Post-simulation
	-----mg P kg <sup>-1</sup> -----			
C1	679 AB	785 B	882 A	882 BC
T1	635 AB	774 B	825 AB	1017 A
T2	614 B	709 B	760b AB	954a AB
T3	779 A	770 B	720 B	795 C
C2	777a A	958b A	823 AB	903 B

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>‡</sup> Means for each soil depth within a row followed by the same lower case letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

<sup>§</sup> Means for each soil depth within a column followed by the same upper case letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

## Soil pH

Soil pH decreased slightly by the end of the study (Table 4-13). However, application of Al-WTR had essentially no effect on soil pH before or after simulation

events. It appears the soil was well-buffered due to the Ca and Mg accumulated from the manure applications.

Table 4-13. Pre- and post-simulation soil pH values in the 0-10 and 10-20 cm soil depths.

Treatments <sup>†</sup>	0–10 cm depth		10–20 cm depth	
	Pre-simulation <sup>‡§</sup>	Post-simulation	Pre-simulation	Post-simulation
C1	6.9a A	6.6b A	7.0a AB	6.7b A
T1	6.7 AB	6.6 A	7.0a A	6.6b A
T2	6.9 B	6.6 A	6.9a ABC	6.6b A
T3	7.0a A	6.6b A	6.8 C	6.6 A
C2	6.9a A	6.6b A	6.8a BC	6.6b A

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>‡</sup> Means for each soil depth within a row followed by the same lower case letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

<sup>§</sup> Means for each soil depth within a column followed by the same upper case letter are not significantly different by Waller-Duncan ( $p < 0.05$ ).

### Forage

Shoot yields were smaller for the surface-applied Al-WTR (T1) than for incorporated Al-WTR (T2 and T3) treatments for the initial three harvests (Table 4-14). This might suggest that surface-applied Al-WTR was detrimental to stargrass growth. However, this same trend occurred for control C2. This suggests that the differences may be due to initial stand establishment rather than toxicity effects. After the first two simulations (63 d of growth), the stargrass became well-established. For simulations 4-6, shoot yields were similar between treatments. There was no visual evidence of adverse effects on stargrass shoot growth. In addition, root mass of all treatments was approximately 30 g box<sup>-1</sup> during the experiment (Figure 4-3). Root biomass was not significantly different among treatments; therefore Al-WTR does not appear to adversely affect stargrass roots.

Table 4-14. Stargrass shoot biomass harvested prior to each simulation.

Treatments <sup>†</sup>	Sim 1	Sim 2	Sim 3	Sim 4	Sim 5	Sim 6 <sup>‡</sup>	Avg
	-----g box <sup>-1</sup> -----						
C1	35a <sup>§</sup>	17a	38a	16a	8a	57a	23
T1	17b	8b	24b	19a	4b	41a	14
T2	35a	21a	35ab	18a	7a	50a	23
T3	31a	14a	30ab	17a	7a	56a	20
C2	14b	6b	28ab	21a	9a	47a	15

<sup>†</sup> C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm.

<sup>‡</sup>Simulation 6 data includes all above-ground biomass. Simulation 1–5 data are shoot biomass above 15 cm height.

<sup>§</sup>Shoot biomass was compared (column) between treatments using a log transformation followed by Waller-Duncan method. Treatments with the same letter are not significantly different ( $p < 0.05$ ).

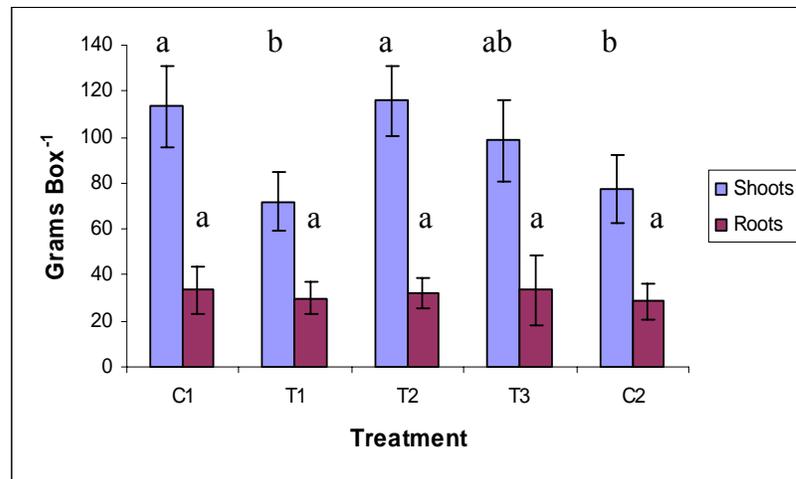


Figure 4-3. Total shoot and root growth per treatment averaged over six simulations. C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm. Error bars represent the standard deviation of 4 replicates. Treatments means within a plant fraction and followed by the same letter are not significantly different using the Waller-Duncan method ( $p < 0.05$ ).

Shoot and root P concentrations among all treatments averaged over the six simulations were not different ( $p < 0.05$ ; Figure 4-4A). During the first two simulations, the stargrass contained approximately 3 mg of P g<sup>-1</sup> of forage and declined by approximately 0.5 mg uniformly across all treatments by the end of the experiment (Figure 4-4B). The original planting material contained approximately 3.2 mg g<sup>-1</sup>. The decline was expected based on seasonal change in growth (August to January).

Simulation 1 began in August and simulation 6 ended in December. Root P concentrations were approximately  $1.7 \text{ mg g}^{-1}$  and did not significantly vary among treatments (Figure 4-4A).

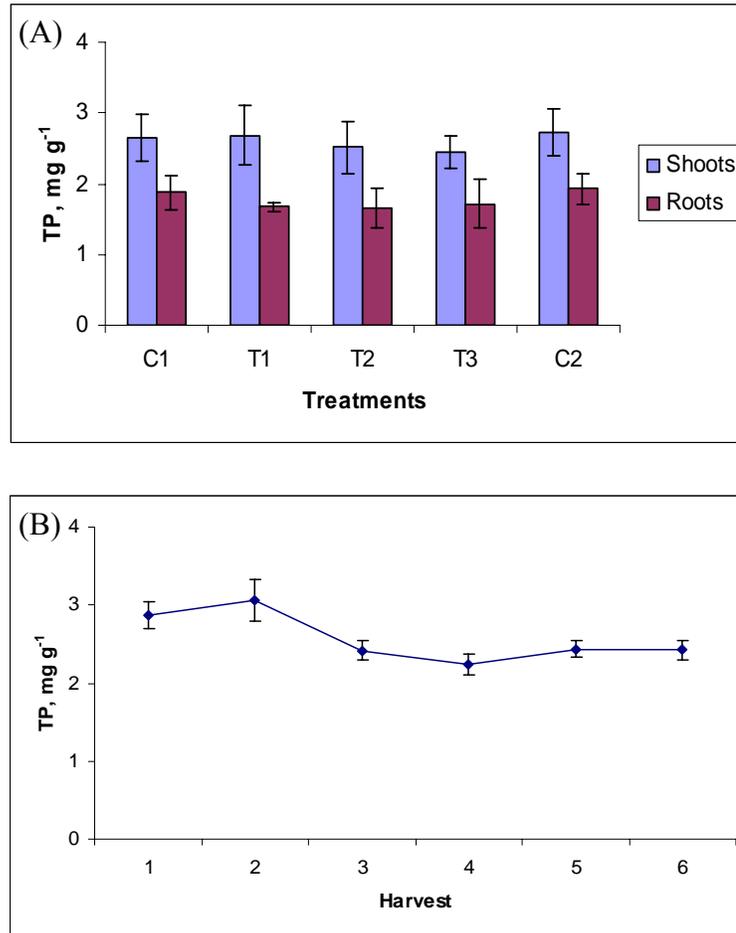


Figure 4-4. Average stargrass TP concentrations per treatment averaged over all simulations (A) and per simulation averaged over all treatments (B). C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm. Error bars represent the standard deviation of 4 replicates.

Shoot and root TN concentrations also were not affected by treatment ( $p < 0.05$ ; Figure 4-5A). Shoot TN concentration was approximately  $25 \text{ mg N g}^{-1}$  in the planting material and for the first two simulations (Figure 4-5B). However, with no additional N input, the N concentration declined to approximately  $10 \text{ mg N g}^{-1}$ . Root TN concentrations at the end of the study were similar for all treatments (Figure 4-5A).

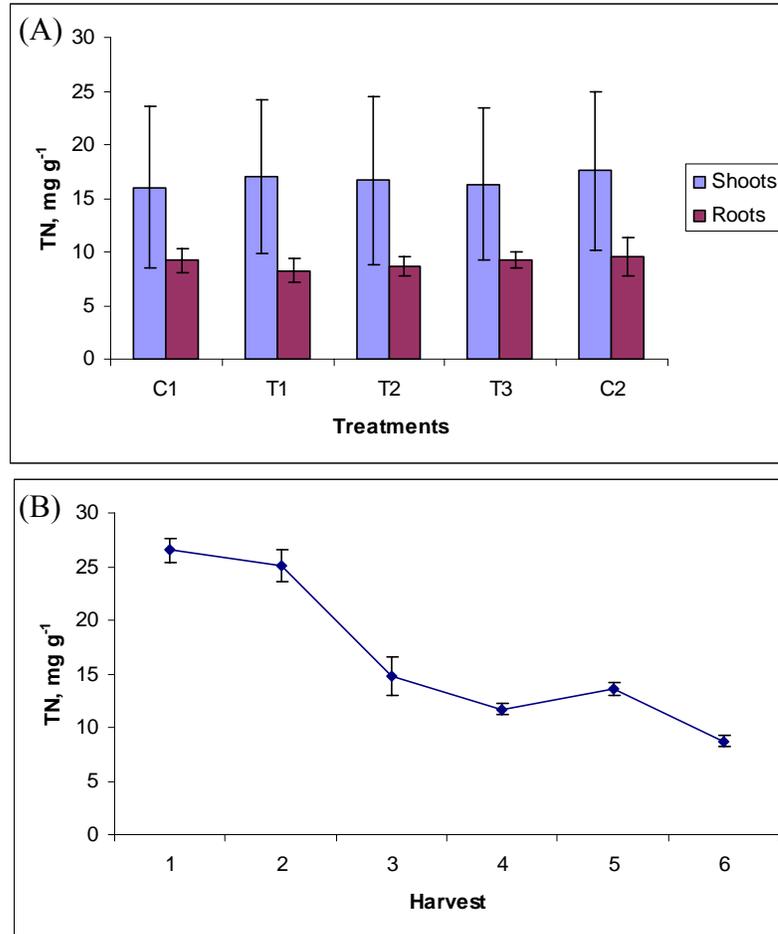


Figure 4-5. Average stargrass TN concentrations per treatment averaged over all simulations (A) and per simulation averaged over all treatments (B). C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm. Error bars represent the standard deviation of 4 replicates

Shoot Al concentrations fluctuated slightly between treatments and simulations, but typically remained below 40  $\mu\text{g g}^{-1}$  (Figure 4-6A, B). These concentrations were at the low end of the typical range (60–14,500 ppm) for grasses (Pendias and Pendias, 2001). Root Al concentrations ranged from 970 to 310  $\mu\text{g g}^{-1}$  of forage. These values also fall within the typical range for forage plants. Because of the high standard deviation, there were no significant differences among treatments ( $p < 0.05$ ). Contamination is believed to be a factor even though roots were washed multiple times to remove soil and Al-WTR

particles. No stunted roots were observed. Aluminum concentration (Figure 4-6B) exhibited a decline that was similar to P and N concentrations in simulations 3 through 5. The increase in concentration in simulation 6 is attributed to shoot contamination when cutting shoots close to the soil surface; which is supported by the large standard deviation.

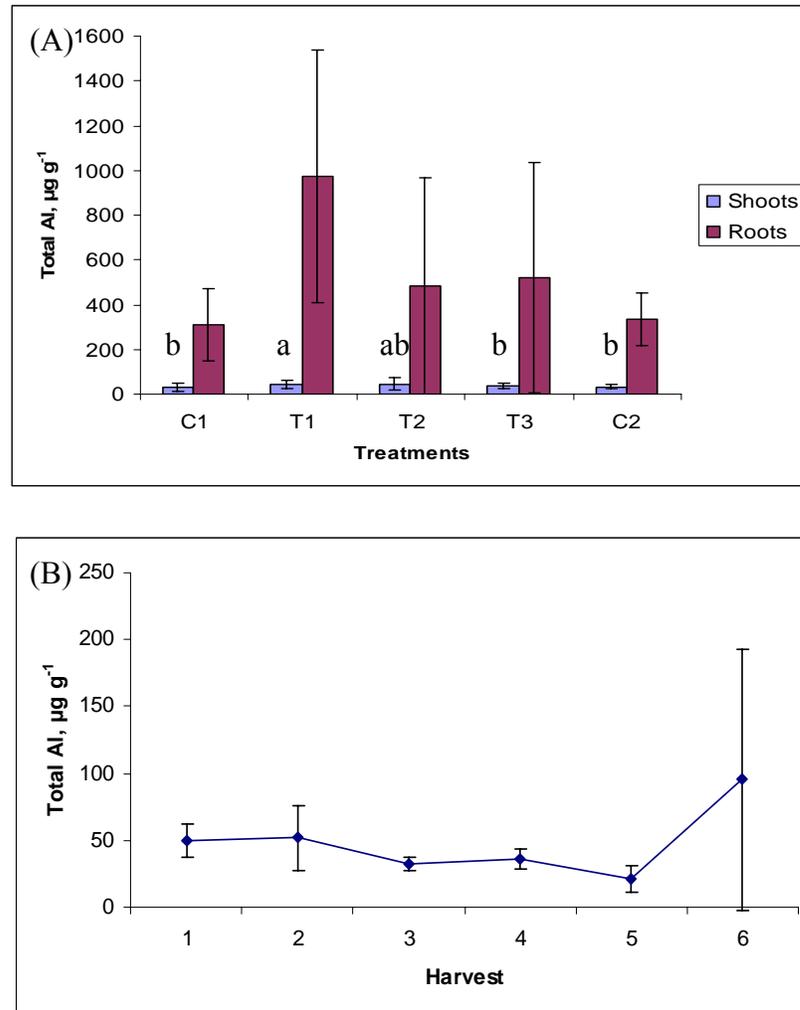


Figure 4-6. Average stargrass Al concentrations per treatment averaged over all simulations (A) and per simulation averaged over all treatments (B). C1, no Al-WTR, not mixed; T1, surface applied Al-WTR, not mixed; T2, Al-WTR mixed in 0–10 cm; T3, Al-WTR mixed in 0–20 cm; C2, no Al-WTR, mixed 0–20 cm. Error bars represent the standard deviation of 4 replicates. Treatments means within the root fraction and followed by the same letter are not significantly different using the Waller-Duncan method ( $p < 0.05$ ).

## CHAPTER 5 CONCLUSIONS

Previous research has shown that land applying Al-WTR is effective in reducing soluble P loss from agricultural fields. This study was developed to provide Al-WTR management information on manure-impacted sandy soils with a fluctuating high watertable. The research evaluated different methods of applying Al-WTR (surface and incorporated) as well as different incorporation depths, P loss over time, and potential effects on forage productivity and chemical composition. Runoff boxes were filled with a P-impacted sandy soil and the respective Al-WTR application treatments. The rate of Al-WTR application (2.5% of dry weight of soil) was selected based on Miyittah's (2004) recommendation for a practical field application rate that would significantly reduce soluble P concentrations in the soil solution. Boxes were placed under a rainfall simulator to create uniform rainfall distribution at known intervals and duration. Phosphorus loss was examined from the three collection points (runoff, subsurface flow, and leachate) because of potential water movement above a restricting layer (spodic). Concerns about P deficiency and Al toxicity in stargrass were addressed throughout the duration of the study.

The application of Al-WTR, whether surface applied or mixed within the profile, impacted SP loss. Surface applied Al-WTR was more effective in reducing SP in runoff than when incorporated. However, incorporated Al-WTR was more effective in reducing SP in subsurface flow and leachate than was surface Al-WTR application. Care must be taken to ensure complete incorporation of Al-WTR throughout the P-impacted layer, as

Al-WTR is only effective in reducing SP concentrations when it is in contact with the impacted soil. To achieve the best results for reducing P loss in both surface runoff and subsurface flow/leachate from highly impacted soils, Al-WTR should be first mixed with the impacted soil depth to reduce subsurface flow/leachate P loss AND then added to the soil surface to minimize P loss in runoff. For an un-impacted area with low initial soil P concentration intended for manure application, surface application of Al-WTR would likely suffice to minimize P loss.

Application of Al-WTR at 2.5% of soil weight did not adversely affect forage yield or quality of stargrass, based on the uniform values of yield and P, N, and Al concentrations between treatments. Field scale forage studies are needed to validate box-scale results.

Effective P control on intensively managed agricultural land is imperative. The use of Al-WTRs is not a single source solution. Rather, it is an effective management tool in an intricate comprehensive management plan. This study attempted to mimic field conditions to provide realistic results. However, short- and long -term field studies are needed before Al-WTR application can be included in best management practices.

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## BIOGRAPHICAL SKETCH

Thomas J. Rew (“TJ”) was born on August 15, 1981. He is the first child of Tom and Diana Rew. TJ grew up in a military family and attended eight schools before earning his undergraduate degree from the University of Florida in Environmental Management in Agriculture with a Land and Water Specialization (August 2003). While a high school and undergraduate student, TJ spent his summers and holidays working on the family cattle ranch, Hayman’s 711 Ranch. It was here he developed a love of the outdoors. This experience led TJ to develop an interest in the interdependency of the environment, agriculture, and the world’s growing population. In August of 2003, TJ began his master’s work in soil and water science, focusing on phosphorus loss from manure impacted soils, at the University of Florida.