THESIS

REPURPOSING AGRICULTURAL AND MUNICIPAL WASTES TO SUPPLY SOIL WITH PLANT-AVAILABLE PHOSPHORUS

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ABSTRACT

REPURPOSING AGRICULTURAL AND MUNICIPAL WASTES TO SUPPLY SOIL WITH PLANT-AVAILABLE PHOSPHORUS

Inorganic phosphorus (P) is a finite resource used to develop fertilizers, heavily applied in agricultural systems, necessary to maintain global crop yields that satisfy global food security needs. In addition to concerns regarding P availability in coming decades, aquatic ecosystems surrounding agricultural lands are susceptible to environmental degradation triggered by excessive P. We tested the ability of aluminum water treatment residuals (Al-WTR), which are known to efficiently sorb inorganic P, to remove organic P from livestock wastewater and subsequently return sorb P to solution. Results that showed Al-WTR can efficiently sorb organic P and desorb P to solution. A greenhouse study was conducted to validate the effectiveness of organic P laden Al-WTR (Al/O-WTR) for its ability to supply soil with plant-available P when compared to a liquid P amendment by growing spring wheat in two differently textured soils with low P concentrations. Results demonstrated that Al/O-WTR could comparably supply coarse textured soils with plant-available P; however, results showed that liquid P amendment is a superior source of plant-available P in fine textured soils.

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DEDICATION

This work is dedicated to my parents, Bobby and Cheri Banet, who always gave me the tools to independently face challenges. To my sister, Kaela Banet, who often reminds me that greatness does not come from a single great act, but from many small acts that shape us into great people. To my fiancée, Ann Marie Kaufmann, who generates a significant portion of my daily motivation. To my grandmother, Hunora Gail Corrigan, who has always loved and supported me in ways that only a grandmother can. And to my late grandfather, James Oliver Corrigan, who inspired my career as a scientist—beam me up!

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CHAPTER I INTRODUCTORY AND BACKGROUND INFORMATION

Introduction

Freshwater is essential to life on our planet. It nourishes not only our bodies, but the crops and animals we consume for further nourishment. In centuries past, humankind built civilizations along freshwater entities, which provided easy trade routes, bountiful harvests of fish, security from invaders, and clean water for consumption. It plays a role in weather and climate patterns and determines the amount of ease with which organisms may thrive in an environment. In the modern world, water has become easily accessible and is being used more now than ever. We use it to cook meals, bathe, and dispose of waste. Freshwater can even drive the economy. For example, Aquafina, Dasani, Evian, and Nestlé are only a handful of businesses that have profited on a mass scale from the distribution and sale of bottled water. Industries utilize freshwater for manufacturing processes, and companies now design their products around water efficiency. The world in which we live continues to be shaped by freshwater availability and constituents contained within freshwater.

The United States Geological Survey (USGS) defines freshwater as "water containing less than 1,000 milligrams per liter of dissolved solids" (USGS, 2016). Less than 2.5% of all water on Earth is considered to be freshwater, and 98.8% of that freshwater is estimated to be tied up in glaciers and ice caps, or inaccessible groundwater systems (USGS, 2016). The remaining 1.2% of freshwater, or roughly 0.03% of all water on the planet, is responsible for sustaining nearly all organisms not found within oceans.

In the many parts of the world, individuals expect that they can walk to any faucet and have a clean water source. However, many locations have little to no access to clean freshwater

(UNESCO, 2015). Freshwater accessibility concerns are only expected to deepen as global population increases because the demand for water increases with population growth (Alcamo et al., 2007; Kundzewicz et al., 2008). As worldwide climate change continues to effect weather patterns, we will likely begin to observe more drastic peaks of high and low water availability, deepening our concern for freshwater supply even further. As it stands, freshwater is likely to become an increasingly inelastic good over time.

During the mid-1900's, modern countries began to realize the value of their freshwater ecosystems. Since then, for example, the United States has implemented regulations at both the state and federal levels to help protect natural waters and ensure safe drinking water (e.g. Clean Water Act, Safe Drinking Water Act, National Pollutant Discharge Elimination System, Ground Water Rule). Unfortunately, detrimental effects are still observed in freshwater due to chemical, solid, and nutrient pollutants entering these systems (Smith, 1998; Pal et al., 2010; Holt, 2000).

Phosphorus (P), a nutrient pollutant in need of mitigation, is harmful to freshwater ecosystems when in excess. Phosphorus loading is a pressing ecological concern that endangers aquatic plant and animal species, diminishes water quality, and threatens human lives. This research aims to 1) remove excess P from freshwater ecosystems, and 2) provide an alternative source for P-recovery and reuse. This research combines the effects of creating clean drinking water with potential improvements of freshwater (eco)systems by removing P from water sources, and beneficially reusing recovered P in an environmentally sound manner.

Phosphorus Background Information

Phosphorus is an element essential for most organisms to complete fundamental life processes. Plants and animals both require P as a structural component in genetic material and membranes. Phosphorus plays a major role in defining how organisms stockpile and exploit energy reserves. Animals obtain P by the consumption of other organisms, while plants obtain P from soil.

In soil, P is found in one of two chemical states, organic or inorganic. Organic P is present in organic complexes such as sugars, fats, and genetic materials (Turner et al., 2005). Organic P forms must first be mineralized into inorganic P forms prior to plant or microorganism use. Once mineralized, plants and microorganisms typically utilize one of two forms of inorganic P, $H_2PO_4^-$ or HPO_4^{2-}, depending on soil pH. Other inorganic P forms may be considered "unavailable" as P may be permanently complexed in minerals such as hydroxyapatite ($Ca_5(PO_4)_3OH$), variscite ($AlPO_4$ x $2H_2O$), or strengite ($FePO_4$ x $2H_2O$). Other inorganic P forms may also be considered greatly to slightly soluble (e.g. typical P fertilizers versus slow release P fertilizers, respectively).

When in relatively low plant-available soil concentrations, P, as with other essential nutrients, will limit plant growth. This concept was established in the mid-1800's with Justus von Liebig's Law of the Minimum, which stated that the least available nutrient essential for growth will limit the extent to which an organism may grow. For example, if P is the least plant available nutrient in relation to what the plant requires, P is considered the limiting nutrient because it then determines the extent to which the plant may physiologically and reproductively grow. Because P is an essential element for plant growth, and plays a crucial role in crop production, it is highly undesirable to raise a crop while limited by P availability. Therefore, P is often used as an agronomic fertilizer to prevent drawbacks such as stunted crop growth, underdevelopment, and lack of maturity.

The benefit of P fertilizers can be demonstrated by increased crop yield with application of P fertilizers. Mitchell et al. (1953) demonstrated increases in plant biomass and grain yield as a result of P fertilizer application. In 1961, a long-term study began at the Tribune Unit Southwest Kansas Research Center to assess the effects of Nitrogen (N) and P fertilizers. Experimental data from found there from 1992 to 2010 demonstrated that grain yields in continuously cropped irrigated corn increased 20% solely based on P fertilizer application (Schlegel & Havlin, 2017). Additionally, a study of 154 test plots concluded that wheat, barley, and canola yields increased by 10% on average due to P fertilizer application (McKenzie et al., 2003). These studies, among many others, exhibit the critical role P plays in crop productivity. Therefore, understanding P availability in relation to cycling within environmental systems is imperative to maintaining and improving future food security.

Phosphorus Cycling and Global Availability

The way in which P cycles through the environment may be considered more complicated than most essential elements. Briefly, P is naturally released to soil as rocks and minerals undergo weathering. When released into soil solution, inorganic P is absorbed relatively fast by plants or microorganisms. Plants obtain P from soil primarily through diffusion. With the assistance of P (and other essential nutrients), plants grow, die, and decompose via weathering and microorganism activity, and release P back into soil solution; organic P to inorganic P release to soil solution is called mineralization. Microorganisms utilize inorganic P in soil solution to create organic P forms such as amino acids, proteins, and genetic materials; inorganic P conversion from soil solution to organic P forms is called immobilization.

Phosphorus in soil solution may additionally form secondary mineral associations. Elements (other than P) in soil solution bond with P, and precipitate into secondary minerals. Secondary minerals associated with P precipitation can include compounds such as calcium phosphates, or Al and Fe (hydr)oxides (Ippolito et al., 2010). The majority of P found in primary and secondary minerals is not readily available to plants or microorganisms.

Because large quantities of P are found as primary or secondary rock and mineral precipitates, P must be mined in order to supply the P required for fertilizers and consequently to meet crop P demands. Furthermore, because rock phosphates finite resources, the rate of P production as a raw material has gained global attention. Peak P is the idea that there is a peak, or a maximum, point in P production. After this peak in production, it is theorized that production will only decrease until all economically viable P reserves are entirely depleted (Cordell & White, 2011). It has been estimated that peak P production may occur as early as the year 2030, or well past the year 2100 (Cordell & White, 2011; Koppelaar & Weikard 2013). While the peak P timeline is uncertain, it is best to protect against future P scarcity by constructing alternative methods to capture, recycle, and reuse P..

Phosphorus Issues in Water Bodies

Persistent mined P use for agricultural and industrial purposes has led to an increase in global P redistribution. Consequently, this may result in environmental degradation where industrial and agricultural P uses are intensive, and in excess; thereby, returning back into the environment in far greater loads of P than those released during natural P cycling. Liebig's Law of the Minimum suggests that an organism's growth is limited by the essential nutrient that is available in the lowest quantity in respect to the quantity needed. In freshwater environments this holds especially true for P, as P often acts as a limiting nutrient for various algal species (Dzialowksi et al., 2005). Eutrophication is the over-enrichment of surface waters with mineral nutrients such as P and allows algal species to reproduce at alarming rates (Correll, 1999). Therefore, when P is excessive it does longer limit the rate at which algae reproduce and thrive.

A plethora of consequences can occur via aquatic system eutrophication, including: increased phytoplankton and suspended algae biomass; shifts in phytoplankton composition towards toxic or inedible bloom forming species; decreased water column transparency; decreased aesthetic values; depleted oxygen water concentrations; and issues pertaining to taste, odor, and water filtration (Smith, 1998).

Methods of P Transport from Agricultural Settings

In agricultural settings, P is one of three primary macronutrients essential for plant growth. Phosphorus is applied to soil in various inorganic forms of fertilizer (liquid or solid) with varying concentrations. Additionally, P may be soil-applied in organic forms such as animal manures, composts, or biosolids.

After application to soil, P may then be taken up by plants. Unfortunately, not all applied P is utilized by the plants; plant P use efficiency is estimated at 10-25% (Syers et al., 2008). Reductions in plant P use efficiency may be attributed to, among other pathways, loss via transport and runoff mechanisms such as surface, subsurface, and groundwater runoff (Ryden et al., 1974). Surface runoff occurs when a precipitation event causes overland water flow. Particulate P (P attached to particles of soil) or dissolved P (P that remains in water after filtration) may be transported by overland flow. Typically, more than 90% of transported P is associated with the particulate phase (Bjorneberg et al., 2006). When dissolved P is transported offsite, it can to travel up to 18km before removal from solution (Ippolito & Nelson, 2013.) In subsurface and groundwater flow, P transport is generally thought of as occurring in the dissolved phase. This is because P must flow laterally with soil moisture, or vertically down a soil profile by means of leaching or preferential flow through macropores (Sims et al., 1998).

Subsurface and lateral P movement may also be exacerbated by artificial tile drainage systems (Gentry et al., 2007).

Wastes and Wastewaters as a P Source

Confined animal feeding operations can contribute to excess environmental P. Animals typically consume food brought to them from other locations (e.g. P redistribution issue as mentioned above), with animal manure used as a N and P source. When applied at agronomic N rates, manures can lead to a 3 to 6 fold over-application of P to soil (Carey et al., 2011). The previously mentioned mechanisms of transport also apply to manure-amended soils.

Another source of P pollution source is municipal waste. Municipal wastewater treatment systems are designed to remove contaminants that are washed/flushed down household, or commercial, drains within town or city limits. Anytime a household sink, shower, or toilet is used the fouled water is transported to a municipal waste water treatment system.

The liquid portion of the waste stream is treated after removal of large solid matter. The treatment process will vary across each facility depending on influent loads, as well as the general composition of their waste stream. Solid wastes are separated in a primary treatment stage. This consists of heavy solid particulates settling to the bottom of the waste stream while lighter solid particulates float to the top. A secondary treatment process is used to remove biological constituents from the waste stream. After secondary treatment, clean water is separated from the waste stream. As each facility treats their waste stream according to its composition (and fund capabilities), some facilities will continue to treat the "clean" water post secondary treatment by means of ultraviolet sanitization, or the addition of chlorinated compounds. The overall end goal of a waste water treatment facility is to release water back into the environment that has met standards of cleanliness set forth by municipal, state, and federal regulations.

Human waste contributes significant nutrient concentrations to the waste stream taken on by waste water treatment facilities. Wastewater treatment facilities are currently not capable of removing all nutrients in the effluent. As a result, significant P loads are released into the environment each year from waste water treatment plants (Hendriks & Langeveld, 2017). Wastewater treatment plants are not only municipal facilities. Private industries may also own wastewater treatment facilities and thus generate their own waste stream for sanitization and discharge. Phosphorus is a pollutant discharged in the waste streams from many industrial production companies that manufacture P based products such as detergents, pesticides, pharmaceuticals, food additives, and fertilizers (US EPA, 1979).

Government Regulations on Water Quality

Regardless of whether discharged effluent is from a municipal or private source, there are several regulation levels that each facility must follow. In 1948, the United States federal government passed the Water Pollution Control Act, which later expanded into The Clean Water Act of 1972 (CWA). The CWA implemented the National Pollutant Discharge Elimination System (NPDES) and set standards for acceptable levels of pollutants that can be discharged from a facility, as well as specifically which pollutants can be discharged (US EPA, 2017). The NPDES roughly defines pollutants as "any type of industrial, municipal, or agricultural waste discharged into water" (US EPA, 2017). The CWA was enacted to protect natural water sources for ecosystems to function properly, and so that future generations may have the opportunity to experience natural waters in the same way as prior generations.

In addition to the CWA, in 1974 the United States federal government enacted the Safe Drinking Water Act (SWDA), which allowed the US EPA to ascertain regulations on contaminants found in drinking water supplies (US EPA, 2017). The SWDA was amended in 1996 to ensure that the US EPA must account for "detailed cost and risk assessment, and best available peer reviewed science" for the formation, implementation, and enforcement of regulation standards (US EPA, 2017). Furthermore, individual states and territories may implement their own regulations that, while in compliance with the CWA and SDWA, promote further improvement of water quality.

The Drinking Water Treatment Process

The general human population likely does not contemplate the water source flowing from the household tap. Yet, the production of safe, clean drinking water is much more complex than simply turning on the faucet. Most households and businesses are supplied drinking water from a municipality, with that municipality treating the water prior to its distribution.

Water treatment facilities first take into consideration their source water. As facilities acquire water from rivers, lakes, reservoirs, groundwater, or other sources, they must consider the possible contaminants present in those environments. Contaminants may change geographically based on, for example, local vegetation, erosion, natural events (e.g., forest fires, mudslides, flooding, etc.), regional industrial discharge, and present microorganism communities. To eliminate contaminants, water treatment facilities must sanitize source waters before public discharge.

In many areas where surface water is used as a drinking water source (e.g. Fort Collins, Colorado), a chemical coagulant is added to begin the treatment process after water enters a water treatment facility. The chemical coagulant added bonds to particulate matter suspended in the water, and the resulting particle is called floc (Center for Disease Control and Prevention, 2015). Floc then continues to bond with other floc particles until it has acquired a mass large enough to fall out of suspension and settle at the bottom of an initial water supply basin. This settled solid phase is called water treatment residuals (WTR), which are removed from the basin and relocated to drying areas. The clean water is then forced through filters designed to remove additional materials not removed during coagulation and flocculation processes (e.g. dust, bacteria, parasites, or other chemicals; Center for Disease Control and Prevention, 2015). A final disinfection step (e.g. chlorine gas or ultraviolet light) is added to exterminate biological pests that may have survived filtration processes. After disinfection, water is then distributed to the supply area.

Water Treatment Residuals

Water treatment facilities face many issues in treating and supplying clean and safe water, yet one problematic matter often overlooked is what to do with the WTR. Once generated, WTR are typically disposed by landfilling or performing land applications (US EPA, 2011). Unfortunately, WTR landfilling imposes costs on municipalities, especially when the WTR itself has no physicochemical properties that make it desirable for direct land application.

In recent decades, research has been conducted to determine beneficial WTR uses including the recycling of WTR for the removal of elements and chemicals from the environment. Research has shown that WTR have the capacity to accumulate heavy metals such as copper (Cu^{2+}) (Castaldi et al. 2015; Elkhatib & Moharem , 2015), lead (Pb^{2+}) (Castaldi et al. 2015; Elkhatib & Moharem, 2015), nickel (Ni^{2+}) (Elkhatib & Moharem 2015), arsenic ($As^{3+}$and As^{5+}) (Makris et al., 2006), selenium ($Se^{4+}$and Se^{0}) (Ippolito et al., 2009), zinc (Zn^{2+}) (Silvetti et al. 2015), cadmium (Cd^{2+}) (Silvetti et al. 2015), mercury (Hg^{2+}) (Elkhatib et al. 2017), and perchlorate (ClO_4^-) (Makris et al., 2006).

WTR can also easily sorb P. Coagulants used in the formation of WTR are generally aluminum (Al) or iron (Fe) salts, and denotes the presence of Al and/or Fe (hydr)oxides as a portion of WTR composition (Ippolito et al., 2011). Because Al and Fe (hydr)oxides have an abundance of OH^- groups, P will replace those groups and cause the compound to restructure into a more stable form. Studies have shown P sorption onto WTR up to 37,000 mg P kg^{-1} (Makris et al., 2004; Elliot et al., 2002; Agyin-Birikorang et al., 2007; Dayton & Basta, 2005). Phosphorus typically follows a biphasic sorption process onto WTR. The first phase occurrs quickly as P sorbs onto outer particle surfaces and is followed by slower P sorption into micropores over time (Makris et al., 2005). Data presented in the aforementioned studies provides significant evidence that WTR can be used to significantly capture P, and thus potentially mitigate negative environmental implications of excess P.

Repurposing P Captured by WTR as a Fertilizer

Given numerous environmental, ecological, and economic issues associated with excess P, we propose that research be performed using aluminum-based WTR (Al-WTR) to meet three objectives: 1) utilizing Al-WTR to capture excess organic P from a wastewater source to create an organic aluminum water treatment residual composite (Al/O-WTR); 2) determination of the sorption mechanism that regulates P availability on and within Al/O-WTR; and 3) evaluate Al/O-WTR as potential plant-available P nutrient source.

Briefly, Al-WTR obtained from the City of Fort Collins Water Treatment Facility (Fort Collins, Colorado) was shaken in a liquid waste stream containing a relatively high organic P concentration to sorb the maximum amount of organic P in/onto Al-WTR. The newly formed composite, Al/O-WTR, was assessed for inorganic P and total P. The Al/O-WTR was then evaluated for P desorption over a period of time until P desorption is no longer significant. Plant root simulator (PRS) membranes were employed throughout the duration of the desorption experiment to assess the potential for Al/O-WTR to release P. The Al/O-WTR was further evaluated at the Stanford Synchrotron Radiation Lightsource to better define P sorption mechanisms. Finally, Al/O-WTR as a P fertilizer was assessed through a soil amendment greenhouse study.

By successfully capturing excess P with the creation of Al/O-WTR, and if Al/O-WTR prove to successfully supply P when enacted as a fertilizer, water treatment facilities may have the opportunity to beneficially reuse Al-WTR and no longer dispose of the material in landfills. This research also has the potential to improve freshwater ecosystems by removing excess P from waste streams that would otherwise be discharged directly into freshwater systems. Finally, a novel P fertilizer source could reduce fertilizers costs, decrease environmental impact of P mining, extending the lifespan of global P reserves and, therefore, push back the timeline for peak P production.

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CHAPTER II ALUMINUM-BASED WATER TREATMENT RESIDUALS: ORGANIC PHOSPHORUS SORPTION AND DESORPTION CHARACTERISTICS

Introduction

Water treatment residuals (WTR) are formed during the drinking water treatment process when a chemical coagulant is added to source waters. The coagulant reacts with suspended solids present in source water and forms larger heterogeneous solids known as floc. Floc falls out of suspension and settles at the bottom of settling basins. The resulting settled solids are known as WTR. WTR are removed from water treatment basins, air-dried, and then land filled (US EPA, 2011) or beneficially utilized (e.g., Ippolito et al., 2011; Ippolito, 2015).

Beneficial reuse of WTR is dependent on WTR composition, which varies based on constituents found in source waters such as sediments and nutrients. Thus, WTR composition may be affected by a number of factors including climate, soil type, land cover, hydrology, precipitation and runoff, wildlife, (non)point source runoff, and land management practices (US EPA, 2011). More importantly, the chemical coagulant used to form WTR plays a vital role in product physicochemical properties. Aluminum sulfate ($Al_2(SO_4)_3$) is a commonly implemented coagulant, and therefore the WTR generated from $Al_2(SO_4)_3$ are called aluminum-water treatment residuals (Al-WTR). Despite variations in source water composition, Al-WTR commonly have two characteristics of interest, the presence of both macro/micropores and amorphous aluminum hydroxide ($Al(OH)_3$) presence (Yang et al., 2006; Ippolito et al. 2009; Elliot et al., 2002; Makris et al., 2005). These characteristics provide Al-WTR potential for its reuse as a nutrient management tool, especially with regards to controlling oxyanion movement within the environment.

Oxyanions, such as inorganic phosphorus ($H_2PO_4^-$, HPO_4^{2-}), readily replace OH^- functional groups in $Al(OH)_3$ to form more energetically favorable molecular structures (Bohn et al., 1985). Al-WTR is abundant in amorphous $Al(OH)_3$, and therefore the material can sorb large amounts of phosphorus (P; up to 37,000 ppm; Dayton & Basta, 2005; Makris et al., 2004; Ippolito et al., 2003). Specifically, P sorption to Al-WTR is biphasic, with the first phase occurring quickly as P sorbs to outer Al-WTR surfaces, while the second phase occurs slowly as P moves into micropores (Makris et al., 2005). Based on observed sorption phenomena, both phases have shown strong inorganic P retention. Consequently, inorganic P desorption has proven difficult and may be irreversible in some cases (Makris et al., 2004; Agyin-Birikorang et al., 2007). Other P species, such as polyphosphates and organic phosphates, do not sorb as tightly to Al-WTR (Razali et al., 2007). Thus, reusing Al-WTR to sorb organic P from waste streams may prove to be a useful environmental and agronomic tool. Preemptive organic P removal from agricultural waste streams can have significant benefits by reducing the quantity of environmental P that potentially contributes to freshwater eutrophication (Correll, 1999). Because P is a non-renewable resource, reducing the need for P mining for fertilizer production may help offset concerns for peak P simply by repurposing Al-WTR to capture wastewater organic P and then return this P to soils.

Zohar et al. (2017) demonstrated that an organic aluminum water treatment residual composite (Al/O-WTR), formed by mixing dairy cattle wastewater and Al-WTR, desorbed P more readily than Al-WTR that had reacted solely with inorganic P. Based on their findings, the objective of this study was to determine if Al-WTR could similarly form Al/O-WTR capable of organic P retention by mixing swine wastewater and Al-WTR. It was hypothesized that mixing Al-WTR with swine wastewater would sorb P, and after the solid phase is removed from the waste stream, could readily desorb organic P over time. This concept could eventually lead to the potential of this composite material to act as a P fertilizer.

Materials and Methods

Phase 1: Phosphorus Sorption onto Al-WTR

Al-WTR and Swine Wastewater Characterization

Al-WTR was collected from City of Fort Collins Water Treatment Facility in Fort Collins, Colorado, air-dried, and then passed through a 2 mm sieve prior to characterization. The Al-WTR organic matter content was determined by loss on ignition and total C and N content was determined via combustion furnace (Nelson & Sommers, 1996), pH was determined by mixing Al-WTR and deionized water (DI) 1:1 (w/w) for two hours in a 50 mL centrifuge tube and measuring the slurry pH directly (Thomas, 1996), and electrical conductivity (EC) was assessed by centrifuging pH samples and decanting the supernatant into an EC meter (Rhoades, 1996). Inorganic carbon content was determined via the modified pressure calcimeter method (Sherrod et al., 2002). The Al-WTR phosphorus saturation index (PSI) and phosphorus sorption capacity (PSC) was determined by first removing $CaCO_3$ using acidified ammonium acetate (pH = 5.5) and then quantifying oxalate extractable iron (Fe_{Ox}), aluminum (Al_{Ox}), and phosphorus (P_{Ox}) via inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Loeppert & Inskeep, 1996). Total and volatile solids were assessed using EPA Methods 160.3 and 160.4, respectively, while other total elemental analyses were determined via a combination of EPA Methods 3030E and 200.7 (U.S. EPA, 1983; American Public Health Association, 1998). All analyses were performed in triplicate, with the exception of inorganic carbon content, which was assessed in duplicate. Results of Al-WTR characterization are presented in **Table 2.1**.

Table 2.1. Chemical characterization of Al-WTR and swine wastewater. PSI = Phosphorus Saturation Index, PSC = Phosphorus Sorption Capacity, BD = below detection limit, and ND = not determined.

Characteristic	Units	Al-WTR	Swine Wastewater
pH		7.57	ND
EC	dS m^{-1}	1.19	ND
Total Solids	%	87.7	0.40
Volatile Solids	%	21.2	50.0
Organic Matter	%	38.5	ND
Total C	%	11.2	72.3
Inorganic C	%	0.71	ND
Dissolved Organic C	%	ND	54.1
Total Ca	%	1.86	3.60
Total S	%	0.18	0.79
Total K	%	0.09	12.5
Total N	%	0.50	16.2
Organic N	%	0.12	15.0
NH_4-N	mg kg^{-1}	46.2	785
NO_3-N	mg kg^{-1}	22.7	432
PSI	mmol kg^{-1}	0.005	ND
PSC	mg kg^{-1}	10800	ND
Total P	mg kg^{-1}	400	6970
Total Al	mg kg^{-1}	61000	2830
Total Fe	mg kg^{-1}	7310	3730
Total Ag	mg kg^{-1}	BD	34.3
Total As	mg kg^{-1}	7.10	BD
Total Ba	mg kg^{-1}	45.9	49.3
Total Be	mg kg^{-1}	BD	2.30
Total Cd	mg kg^{-1}	0.56	ND
Total Cr	mg kg^{-1}	8.50	ND
Total Cu	mg kg^{-1}	21.6	492
Total Hg	mg kg^{-1}	BD	BD
Total Mn	mg kg^{-1}	865	242
Total Mo	mg kg^{-1}	1.10	ND
Total Ni	mg kg^{-1}	6.20	13.9
Total Pb	mg kg^{-1}	1.37	ND
Total Se	mg kg^{-1}	BD	BD
Total Zn	mg kg^{-1}	15.2	350

Wastewater was collected from a wastewater retention pond at a 1,900 feeder pig swine farm in eastern Colorado. Methods used to characterize wastewater were the same as those for Al-WTR, although dissolved organic carbon was determined by filtering wastewater through a

0.45um filter and then analyzed using EPA Method 415.1 (U.S. EPA, 1983). Results of swine wastewater characterization are presented in **Table 2.1**.

Al-WTR P Sorption Maximum Determination and Al/O-WTR Generation

Al-WTR was air-dried, passed through a 2-mm sieve, and then mixed with swine wastewater at a 1:2.5 solid to liquid ratio (Zohar et al., 2017). Twenty-five replicates of 160 g Al-WTR were mixed with 400mL swine wastewater in 500 mL Nalgene bottles. Five replicates were randomly selected and used to assess average changes in swine wastewater P content throughout the duration of the study. The remaining twenty replicates were used to generate Al/O-WTR composite for subsequent studies and evaluation (as outlined below). All bottles were placed on a reciprocal shaker for 21 days. Throughout the 21 day shaking period, 1 mL aliquots were taken from the five randomly selected shaking containers on days 1, 2, 3, 4, 5, 6, 7, 14, and 21. Aliquots were transferred into 50mL centrifuge tube and each tube was brought to a 50 mL volume with deionized water, mixed, and evaluated for total P (Standard Methods 4500-P, perchloric acid digestion, analyzed colorimetrically; Franson, 1992) and inorganic P (EPA Method 365.2, analyzed colorimetrically; USEPA, 1983). Organic P content was determined via difference between total and inorganic P. Upon completing the 21-day shaking period, all replicates were removed from the shaker, wastewater was decanted, and solids were allowed to air dry under a fume hood in their original shaking containers.

The above procedure did not properly quantify relatively quick P sorption (i.e., P sorption within 24 hours, or the first phase of biphasic sorption as described by Makris et al., 2005). Thus, 44 g Al-WTR was mixed with 110 mL of swine wastewater (1:2.5 ratio; less volume was used because less swine wastewater was available following the above shaking study) and shaken in triplicate over 16 hours. At time 1, 2, 4, 8, and 16 hours, a 1 mL aliquot was removed from each replicate, transferred into a 50 mL centrifuge tube, brought to 50 mL with deionized water, and analyzed for P as outlined above. Additionally, five post hoc blank replicates (500 mL bottles containing 160 g Al-WTR and 400 mL of 7,000 mg P L^{-1} potassium phosphate monobasic (KH_2PO_4) solution) were shaken for 24 hours following the original 21-day shaking period. Post hoc blank samples were employed to demonstrate that any P in swine wastewater was, in fact, retained by Al-WTR rather than on shaking container surfaces. After the shaking period, a 1 mL aliquot was removed, diluted 50-fold, and analyzed for P as outlined above.

Lastly, 44 g Al-WTR was shaken with 110 mL of swine wastewater for 10, 20, 30, 40, and 50 minutes. Post shaking, swine wastewater was decanted from Al-WTR samples, and solid material was air-dried. Dried materials from these shaking timepoints were saved for future x-ray absorption spectroscopy analysis.

Statistical Methods

RStudio Version 1.0.153 was used to conduct all Shapiro-Wilks, Levene, and Kruskal-Wallis statistical analyses. While Levene's test showed that variance was equal throughout both the 16-hour and 21-day shaking studies ($p = 0.2382$ and 0.1181, respectively; $\alpha = 0.05$), Shapiro-Wilks' test demonstrated that both dataset's residuals were not normally distributed ($p = 0.5701 \times 10^{-5}$ and 0.0002, respectively; $\alpha = 0.05$). Therefore, the Kruskal-Wallis test, a non-parametric alternative to ANOVA, was utilized to determine at which timepoints the shaking solution total P concentration (mg L^{-1}) mean ranks were significantly different. Kruskal-Wallis tests conducted on the 16-hour and 21-day studies demonstrated that, in fact, shaking solution total P concentration (mg L^{-1}) mean ranks were not equal across each study's sampling timepoints ($p = 0.0051$ and 2.872×10^{-7}, respectively; $\alpha = 0.05$). Finally, Tukey adjusted pairwise comparisons were utilized to highlight significantly different comparisons.

X-ray Absorption Spectroscopy: P speciation in Al/O-WTR following P sorption

Phosphorus speciation in Al/O-WTR, following the sorption experiment, was examined using bulk P *K*-edge X-ray absorption near edge structure (XANES) spectroscopy. Samples of Al/O-WTR from 0, 10, 20, 30, 40, and 50 minutes, and from 1 hour, 2, 4, 8, 16, and 24 hours, were examined using P *K*-edge XANES spectroscopy at Beamline 14-3 at the Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory, in Menlo Park, California. The Al/O-WTR samples were finely ground into a powder using a mortar and pestle. A very small quantity of each powdered sample was painted on ultra-low impurity carbon tape (Ted Pella, Inc., Redding, California, United States) using a synthetic-bristle paintbrush to avoid P contamination. A ~5 mm wide X-ray beam was directed at a portion of the sample for collection of the XANES spectrum.

During data collection, incident beam energy was selected using a Si (*1 1 1*) double crystal monochromator in the phi = 90° position, and the beam path was continuously purged with helium. Energy calibration was achieved by setting the top of the *K*-edge peak of the lazulite XANES spectrum to 2153.5 eV. Multiple spectra from the same sample were averaged using Sam's Interface for XAS Package (SIXPACK) (Webb, 2005). Averaged spectra were analyzed using the Athena software package (Ravel and Newville, 2005) to perform linear combination fits of the unknown spectra. Standard spectra for P adsorbed on Al oxides and P adsorbed on calcite, published in Giguet-Covex et al. (2013), were graciously provided by Charline Giguet-Covex, and were used in the linear combination fitting procedure.

Phase 2: Phosphorus Desorption from Al/O-WTR

Bulk Al/O-WTR generated in Phase 1 was assessed for its ability to desorb P. This was performed by mixing Al/O-WTR with 0.01 M KCl (buffered at pH 7.9 using 0.1 M Tris Buffer;

this pH was chosen to simulate pH conditions for the Al/O-WTR soil P experiment in Chapter 3) at a 1:12.5 solid to liquid ratio in 500 mL plastic Nalgene bottles (Zohar et al., 2017). Plant Root Simulator (PRS™; Western Ag Innovations, Saskatoon, SK, Canada) anion membrane probes were used to assess the P concentration desorbed from Al/O-WTR. Four replicate bottles, and three blank bottles (i.e., no Al/O-WTR) were shaken for 1, 2, 4, 7, 14, 21, 28, 60, and 90 days, followed by destructive PRS probe sampling. The solution pH was monitored immediately prior to and at the end of each shaking period. Samples shaken for 14, 21, 28, 60, and 90 days were additionally monitored for pH changes on a weekly basis. When required, solution pH was adjusted weekly using dropwise additions of 16 M NaOH.

At the end of each shaking period, the PRS™ anion membrane probes were removed, rinsed with deionized water, and scrubbed to remove Al/O-WTR particles. Each probe was individually transferred into a zip seal bag along with 17.5 mL of 0.5 M HCl. Probes remained in contact with the 0.5M HCl for one hour in order to elute all P from the probe. After one hour, eluate was collected from each zip seal bag and transferred to individual 50 mL centrifuge tubes, and then stored at 4 ^{o}C until evaluation for total P via ICP-OES. Total P desorbed from Al/O-WTR was determined by subtracting blank bottle mean total P concentrations from mean P concentrations in the Al/O-WTR - buffered 0.1 M KCl solutions.

Statistical Methods

Levene's test ($p = 0.9112$; $\alpha = 0.05$) and Shapiro-Wilks test ($p = 0.0006$; $\alpha = 0.05$) were first employed to test equality of variance and residual normality. While Levene's test demonstrated that the data maintained equal variance, the Shapiro-Wilks test demonstrated that the data residuals were not normally distributed. Therefore, the Kruskal-Wallis test was again employed to test at which timepoints the mass P desorbed (mg kg^{-1}) from Al/O-WTR mean ranks were significantly different. This analysis validated that mean ranks were not equal throughout the duration of the study ($p = 0.0014$; $\alpha = 0.05$). Lastly, Tukey adjusted pairwise comparisons were again used to highlight significantly different comparisons.

Results and Discussion

Phase 1: Phosphorus Sorption onto Al-WTR

Results from the 21-day shaking experiment demonstrated that nearly all total P was sorbed to the Al-WTR within a single day (Figure 2.1). The initial swine effluent solution total-, ortho-, and organic-P concentrations were 6970, 24, and 6950 mg L^{-1}, respectively. After only one day of shaking, the solution total-, ortho-, and organic-P concentrations were 2.12, 1.70, and 0.40 mg L^{-1}, respectively. Solution total P concentration continuously decreased until reaching an observed minimum concentration of 0.75 mg L^{-1} at day 7. However, at days 14 and 21, total P in solution was 72.8 and 74.6 mg L^{-1}, respectively. It was possible that, with continual shaking over time, physical interactions between Al-WTR particles promoted P removal and thus dissolution back into solution. Kruskal-Wallis analysis demonstrated that mean ranks between each group were significantly different ($p = 2.872 \times 10^{-7}$; $\alpha = 0.05$). Tukey adjusted pairwise comparisons demonstrated significantly different shaking solution P concentrations (mg L^{-1}) between all possible timepoint comparisons, except for comparisons between the following days: 1-2, 1-3, 2-3, 4-5, 5-6, 5-7, and 6-7.

Results from the 16-hour shaking experiment further demonstrated that P sorption to Al-WTR solids occurred very rapidly, with nearly all P removed from solution within the first hour

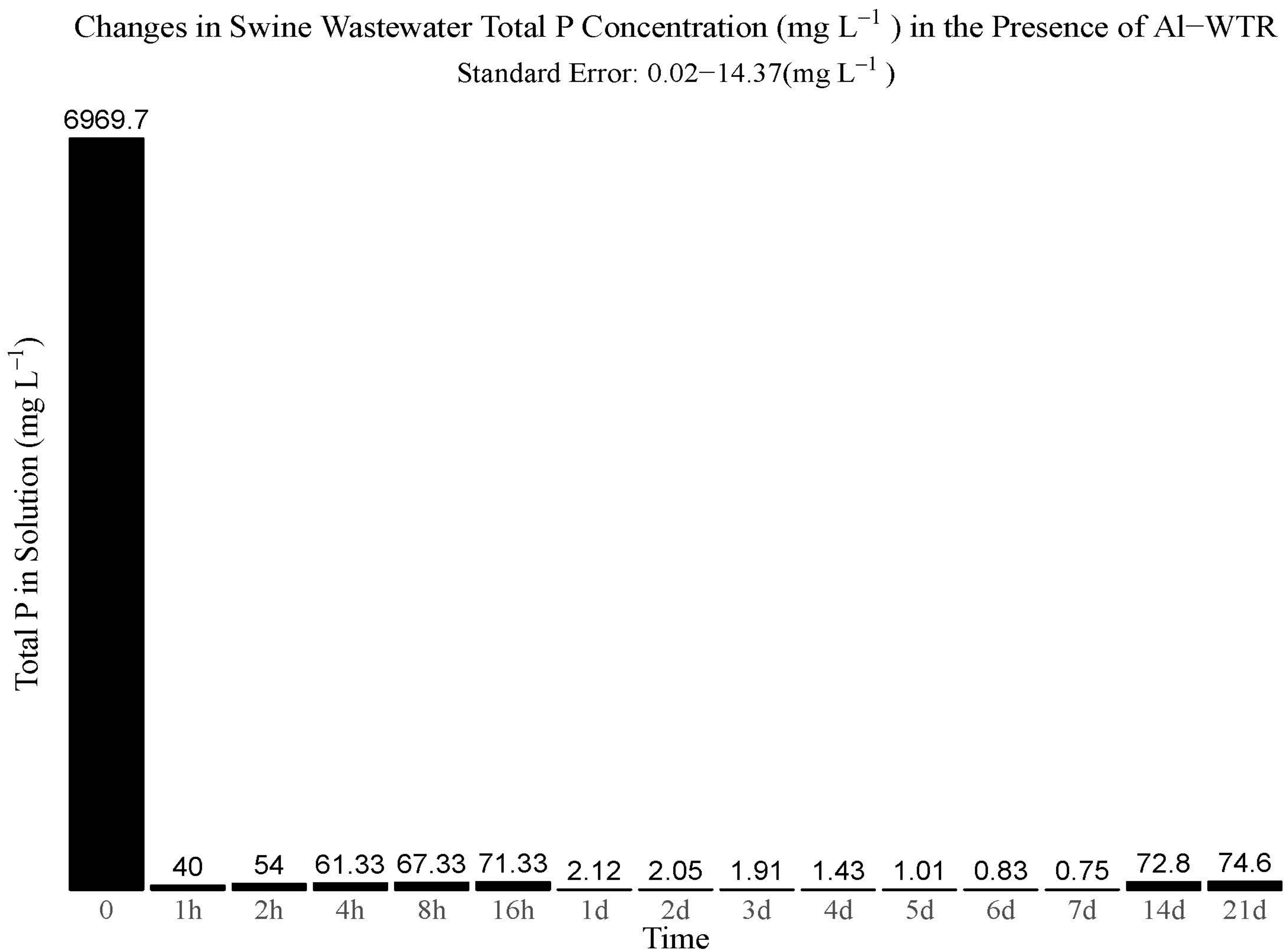


Figure 2.1. Mean (n=3 for hours 1 to 16; n=5 for days 1 to 21) total P concentration in swine wastewater solution in the presence of Al-WTR over a 21-day shaking period.

(**Figure 2.1**). The fast retention of P from solution by Al-WTR was consistent with results from previous studies (Makris et al., 2004; Makris et al., 2005; Wagner et al., 2008). Tukey adjusted pairwise comparisons demonstrated significantly different shaking solution P concentrations (mg L^{-1}) between all possible timepoint comparisons, except for comparisons between the following hours: 2-4, 4-8, and 8-16.

Based on the initial swine wastewater concentration (6970 mg L^{-1}) and the 400 mL wastewater volume used in each shaking container, the total phosphorus mass within each shaking container was approximately 2788 mg. However, based on the Al-WTR PSC (approximately 10,800 mg kg^{-1}) and the 160 g Al-WTR within each shaking container, Al-WTR within each shaking container should have been able to sorb approximately 1725 mg P. Yet results showed that Al-WTR retained ~1000 mg more P than the PSC evaluation had assessed to be possible.

To verify the differences between the calculated versus observed P sorption difference, we utilized 500 mL containers with 160 g Al-WTR shaken in 400 mL of 7000 mg L^{-1} P (as KH_2PO_4; approximately equal to total P in the swine wastewater) for 24 hours. These mixtures verified that Al-WTR had the ability to retain greater P quantities than the PSC had assessed to be possible, showing sorption to be between 2572 and 2673 mg P of the 2800 mg P present, and not equal to ~1725 mg P. Converting these values to a P per kg Al-WTR basis, on average the Al-WTR retained 16500 mg P kg^{-1} rather than 10800 mg P kg^{-1} as assessed by PSC evaluation. Ultimately, the results from containers with Al-WTR and KH_2PO_4 validated the observed sorption phenomena in containers with Al-WTR and swine wastewater. The increased P sorption was most likely due to the Al-WTR elevated Ca content (**Table 2.1**) promoting calcium phosphate precipitation from solution. Others have found elevated Ca concentrations in Al-WTR and showed Ca-P phases to be potentially present (Ippolito et al., 2003).

Phosphorus Speciation in Al/O-WTR following Sorption

The initial Al-WTR material contained about 29 atom % (±15%) Ca-associated P, and 71 atom % Al-associated P, modeled in this case with spectra of P adsorbed to calcite, and an Al oxide-humic acid P sorption complex, as shown in Giguet-Covex et al. (2013). The same model spectra were used by Massey et al. (2018) to describe P speciation in Al/O-WTR created in dairy wastewater and were found via microfocused X-ray fluorescence and microfocused P *K*-edge XANES spectroscopic analysis. During the first hour of sorption, the XANES spectra suggest that the proportion of Ca-associated P decreased, coupled with an increase in Al-associated P. These results, while somewhat speculative, suggest that P primarily adsorbed to Al oxide surfaces in the Al-WTR during the initial stages of sorption (**Table 2.2**, **Figure 2.2**). In contrast, the proportion of Ca-associated P appeared to increase from 1 hour through 24 hours of sorption (**Table 2.2**, **Figure 2.3**). One potential explanation for these varying results is that the P surface speciation did indeed shift during the sorption experiment, with P initially forming surface complexes with Al oxides, and later forming complexes or surface precipitates on Ca-rich surfaces. However, these results may be considered somewhat speculative since the trends were not consistent, the analyses were not entirely internally consistent (i.e., highly variable replicate analyses), and some of the spectra were difficult to consistently normalize (as shown by mismatches at high energy in **Figure 2.4** and **Figure 2.5**). These challenges preclude unequivocal analysis of trends in the spectra, but the proportions of P species were likely accurate to within the ±15% uncertainty in the method.

Table 2.2. Phosphorus *K*-edge XANES linear combination fitting results for the fits in Figures 2.2 through 2.5. Calcium-associated P (e.g., P adsorbed to calcite) became relatively less prevalent over the course of the adsorption experiment, though the absolute amount of both Ca-associated and Al-associated P increased substantially due to the large amount of P sorbed during the experiment. Sums of components in the linear combination fits were normalized to 100%. *R*-factor, X^2, and reduced X^2 values were calculated by the Athena software package. Uncertainty, in parentheses, is statistical uncertainty calculated by Athena; total uncertainty was approximately ±15%. Note that fits of bulk P *K*-edge XANES only capture the likely dominant P species in the WTR, and do not reflect the full diversity of P species that are actually present.

Time (min)	Replicate spectra	Ca-assoc. P (P atom %)	Ca range	Al-assoc. P (P atom %)	Al range	Example *R*-factor	Example X^2	Example Red. X^2
0	1	29% (±2%)	†	71% (±2%)	†	0.002841	1.141	0.006790
10	4	18% (±3%)	15-19%	82% (±2%)	81-85%	0.006958‡	2.581‡	0.015273‡
20	2	9% (±3%)	8-10%	91% (±2%)	90-92%	0.005532‡	2.654‡	0.015704‡
30	1	12% (±2%)	†	88% (±2%)	†	0.005632	2.662	0.015754
40	1	12% (±3%)	†	88% (±2%)	†	0.006889	2.781	0.016458
50	1	10% (±3%)	†	90% (±2%)	†	0.006798	2.731	0.016158
60	3	18% (±2%)	12-21%	82% (±2%)	79-88%	0.005849‡	2.798‡	0.016558‡
120	2	29% (±2%)	26-32%	71% (±2%)	68-74%	0.002428‡	0.710‡	0.004226‡
240	2	40% (±2%)	31-48%	60% (±2%)	52-69%	0.013633‡	3.338‡	0.019870‡
480	2	36% (±2%)	36%	64% (±2%)	64%	0.003570‡	0.974‡	0.005797‡
960	2	26% (±2%)	18-35%	74% (±2%)	65-82%	0.006279‡	1.841‡	0.010958‡
1440	2	19% (±2%)	18-20%	81% (±2%)	80-82%	0.002384‡	0.996‡	0.005893‡

† Range not listed for values with only one spectrum to fit.
‡ "Example" fit results for fit statistics were a choice of one representative set of fit statistics (calculated by the Athena software program) from fits of replicate spectra. Either a representative middle value or the worst set of fit statistics were chosen. For fits with only one spectrum, the fit statistics calculated by Athena are listed.

Phase 2: Phosphorus Desorption from Al/O-WTR

In general, P desorbed from Al/O-WTR into solution rapidly within the first day (2173 mg kg^{-1}) and continued to steadily desorb over time (e.g., 2335 mg kg^{-1} at day 2, 2350 mg kg^{-1} at day 4, and 2870 mg kg^{-1} at day 7; **Figure 2.6**). Desorption was maximized at day 14 (3440 mg kg^{-1}), at day 21 dropped to a concentration similar to the first week (2610 mg kg^{-1}) and peaked again at day 28 (3470 mg kg^{-1}). After day 28, P desorption steadily decreased and appeared to attain a new equilibrium at days 60 and 90 (1540 and 1670 mg kg^{-1}, respectively). It should be noted that data collected at days 14 and 28 contained outliers. After removing outliers, average P desorbed at 14 and 28 days was 3100 and 2930 mg kg^{-1}, respectively. Tukey adjusted pairwise comparisons showed that between days 14-60, 14-90, 28-60, and 28-90 were the only timepoints

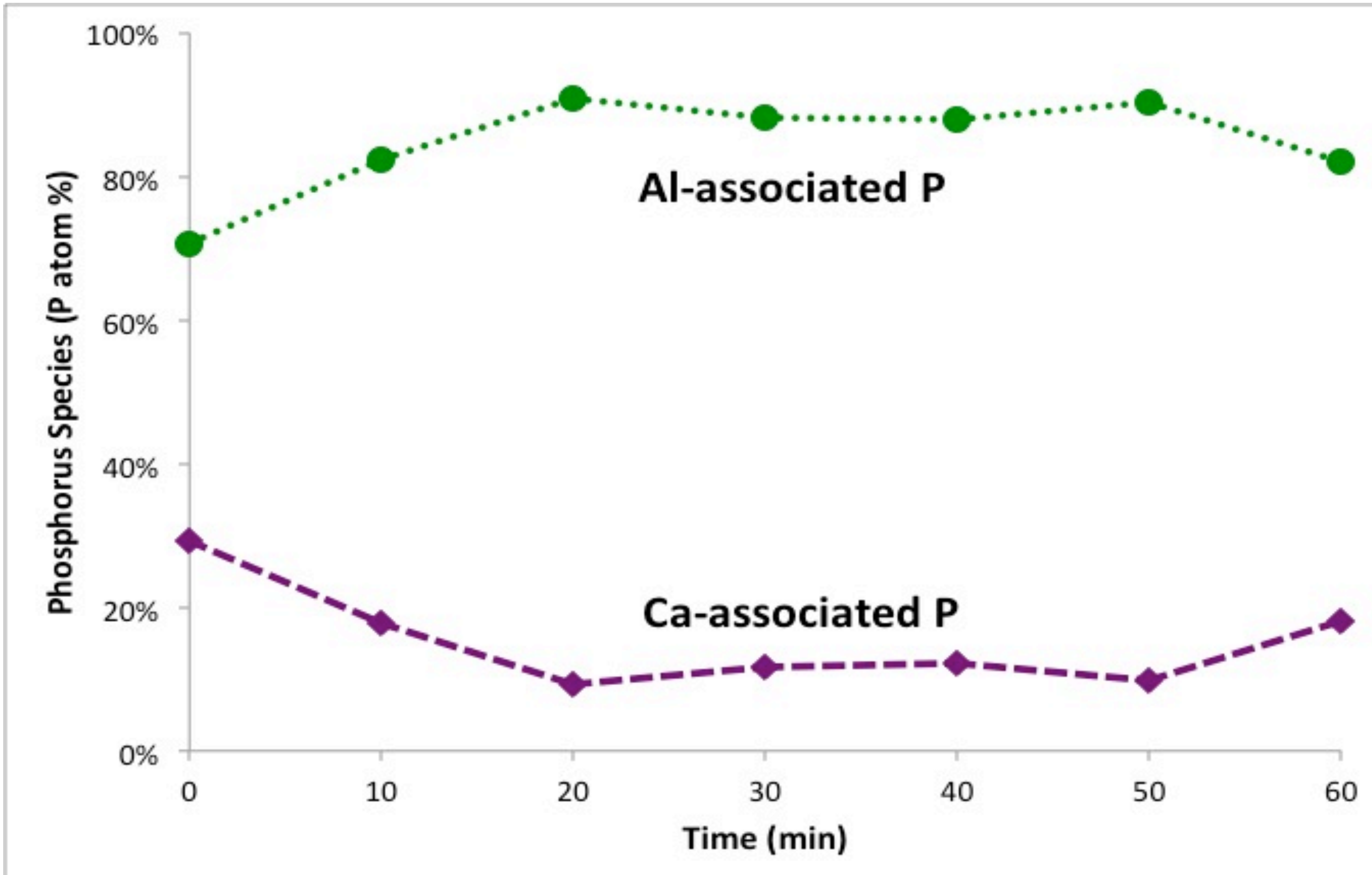


Figure 2.2. Phosphorus sorption onto calcium and aluminum phases present in Al-WTR during the first hour of shaking Al-WTR in swine wastewater.

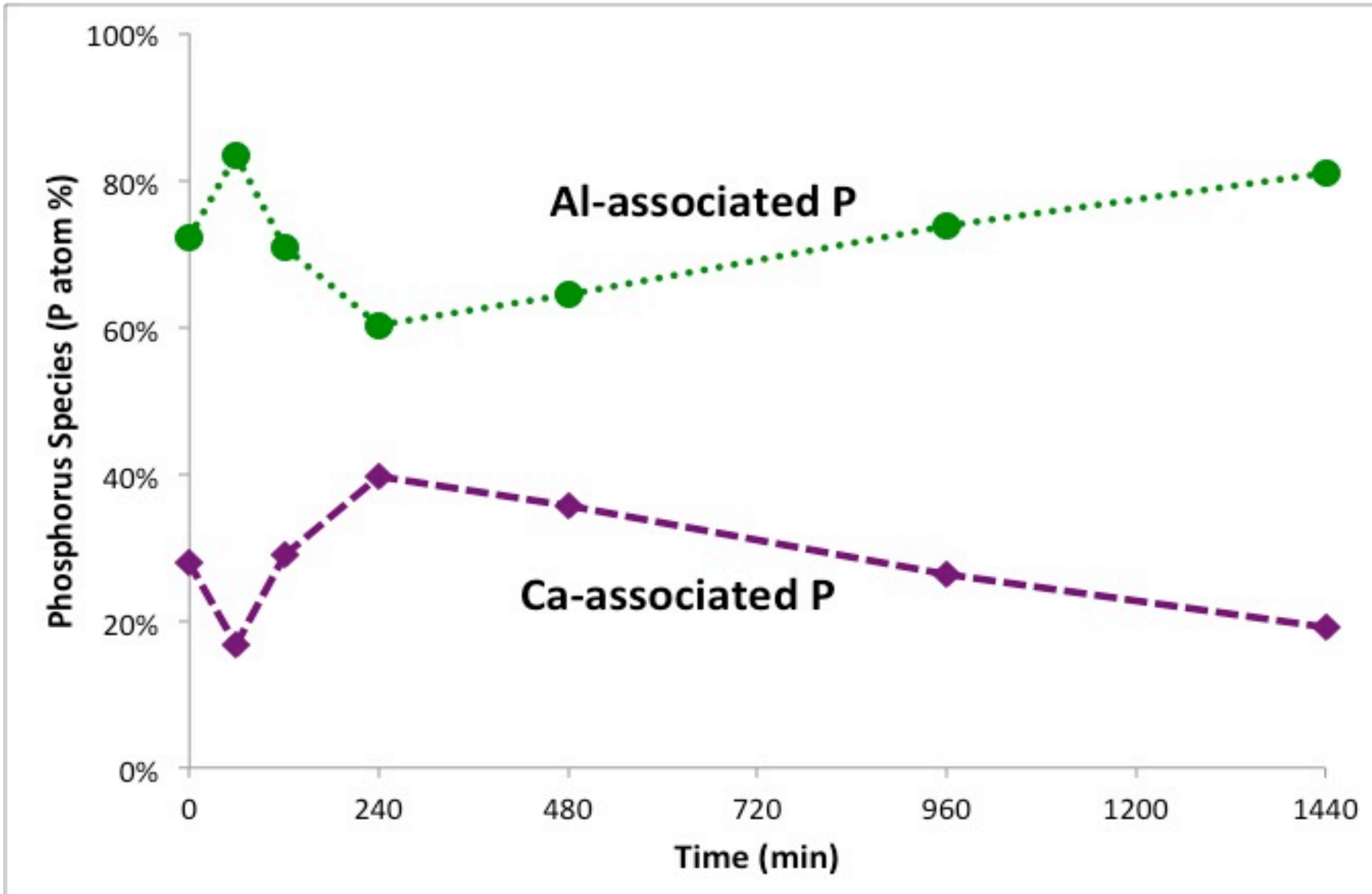
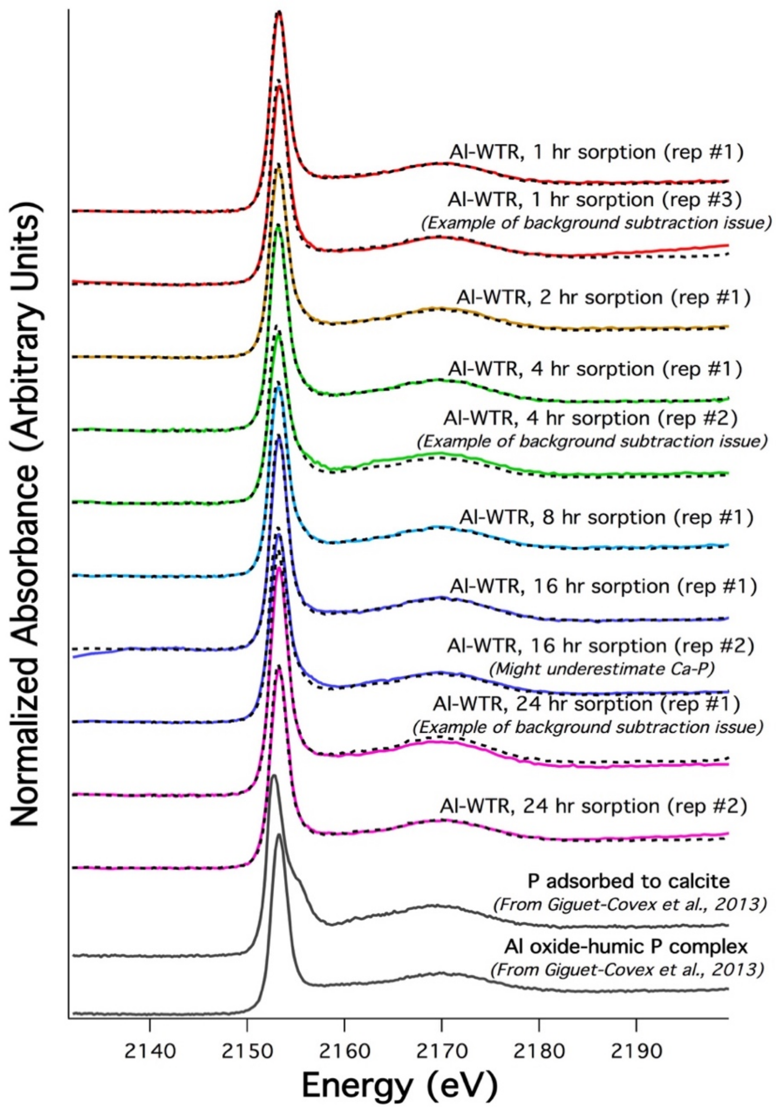


Figure 2.3. Phosphorus sorption onto calcium and aluminum phases present in Al-WTR during the first day of shaking Al-WTR in swine wastewater.



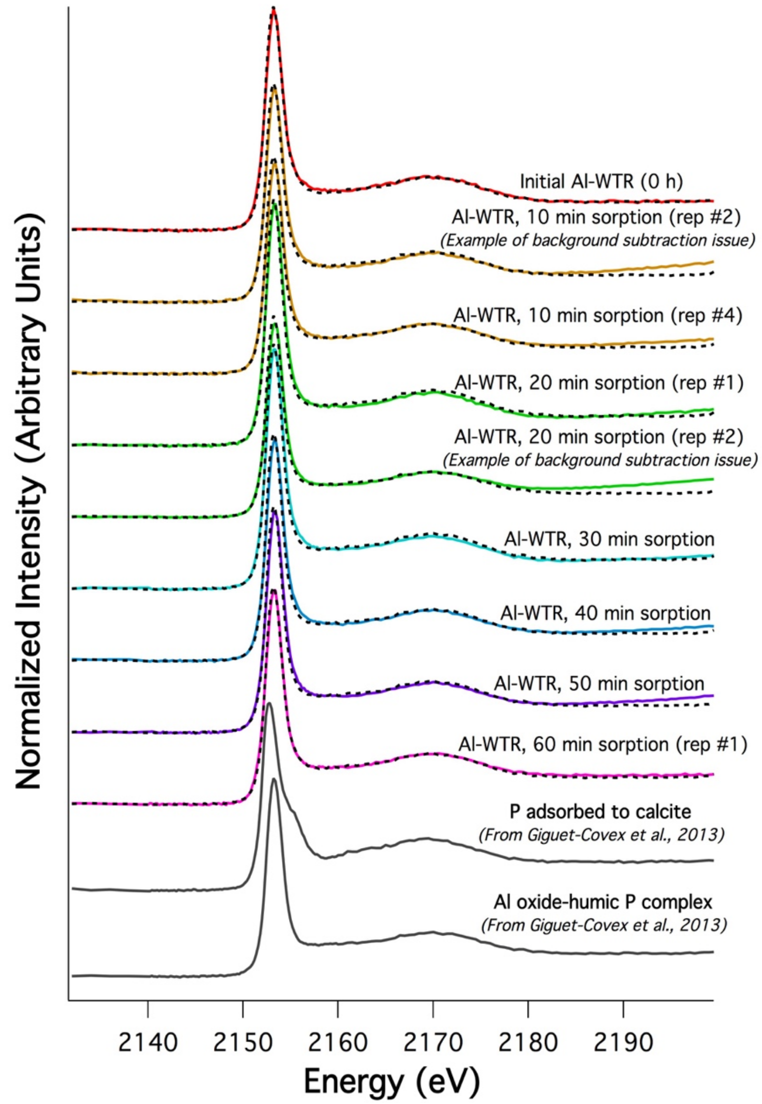


Figure 2.4 (left) and **Figure 2.5** (right). Phosphorus K-edge XANES spectra and fits for Al-WTR shaken in swine wastewater for both less than 1 hour (i.e. 10, 20, 30, 40, and 50 minutes) and between 1 hour and 24 hours (i.e. 1, 2, 4, 8, 16, and 24 hours).

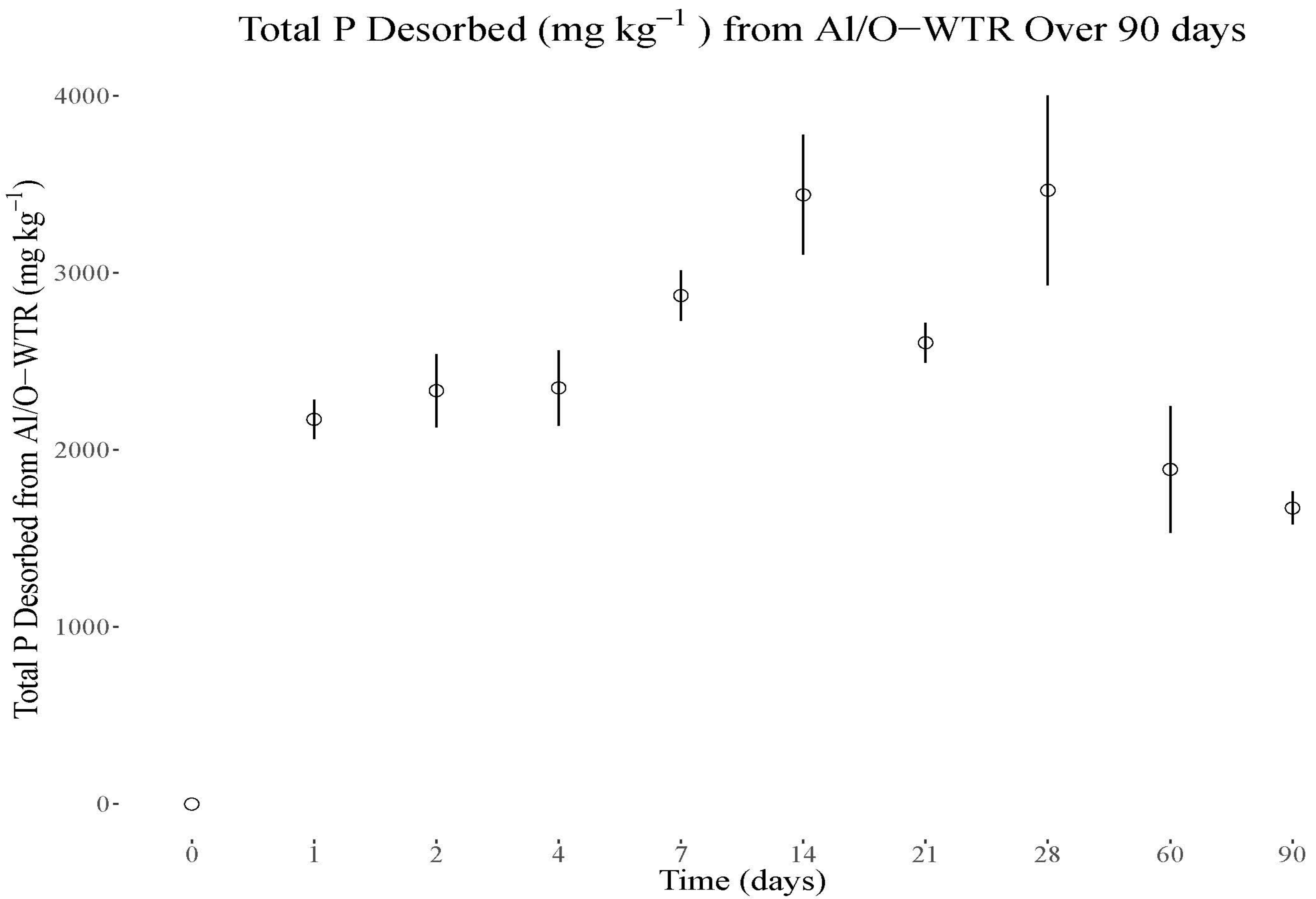


Figure 2.6. Mean (n=4) total P desorbed from Al/O-WTR over 90 days of shaking.

at which significantly different P quantities (mg kg^{-1}) were returned to solution from Al/O-WTR.

Previous research demonstrated that inorganic P is strongly retained by Al-WTR such that P desorption is nearly irreversible (Makris et al., 2004; Ippolito et al., 2003). However, results observed in this study support evidence provided by others that suggest large organic molecules containing P (e.g. polyphosphates or organic moieties rich in P) may readily return P to solution after sorbing to Al-WTR (Razali et al., 2007). Zohar et al. (2017) performed a study similar to the work outlined here, utilizing Al-WTR to sorb P from dairy wastewater. The authors showed that organic C complexes accumulated on Al-WTR particle surfaces, leading to the ability of P to be desorbed at ~ 30 mg kg^{-1}. Although P desorption in this study was two orders of magnitude greater, the findings of Zohar et al. (2017), as with ours, suggests that weak P binding onto Al-WTR surfaces occurs; thus, the potential for the material to serve as a P fertilizer source exists.

Conclusions and Implications

Results support the hypotheses that mixing Al-WTR with swine wastewater would sorb as well as readily desorb organic P over time. The data conclusively illustrate that Al-WTR has the ability to quickly and efficiently remove organic P from agricultural waste streams such as swine wastewater, and that resulting Al/O-WTR has a relatively high propensity to release organically sorbed P. In combination, these results show promise for large-scale Al/O-WTR generation, and its potential for supplying P as a soil amendment. However, it cannot be definitively stated that desorbed organic P will immediately or eventually be in a plant-available form. Thus, if added to P deficient soils, Al/O-WTR likely would contribute organic P to the total soil P pool, with the organic P pool leading to increased plant availability over time through mineralization. Further studies are required to accurately assess Al/O-WTR ability to supply P to soil P pools and to plants.

If future research findings continue to advocate Al/O-WTR for land application, Al/O-WTR land amendment could prove beneficial for numerous reasons. Municipalities could benefit by lowering their costs associated with Al-WTR management and landfill disposal. Animal producers with agricultural waste streams high in organic P could benefit from efficient P-removal from their wastewaters (e.g., P removal occurs almost immediately based on the results presented here), and crop producers could benefit from Al/O-WTR as a P fertilizer if the material can be efficiently and economically created. Lastly, removing P from agricultural waste streams to generate Al/O-WTR could reduce the risk of P transport into nearby freshwater ecosystems and improve water quality.

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CHAPTER III ASSESSING Al/O-WTR VIABILITY AS A PLANT-AVAILABLE SOIL PHOSPHORUS SOURCE

Introduction

Municipalities regularly dispose water treatment residuals (WTR), a soil-like by-product developed during drinking water sanitation, using costly disposal methods such as landfilling or deep well injection (USEPA, 2011). Aluminum water treatment residuals (Al-WTR) are created when aluminum sulfate ($Al_2(SO4)_3$) is employed as a coagulant that catalyzes flocculation of particulate matter, (e.g. soil, ash, organic matter, etc.) suspended in water. Flocculated solids settle out of solution and can be removed from municipal drinking waters. Given the significant Al-WTR quantities generated globally (10,000 tons per day; Babatunde and Zhao, 2007), municipalities bear significant financial burdens associated with on-site Al-WTR management (i.e. turning and drying the material), as well as transport and disposal costs. As it stands, municipalities have limited strategies for Al-WTR disposal or reuse. However, one strategy may be to sorb or sequester environmentally available, excess phosphorus (P).

In recent decades, Al-WTR have been investigated for their chemical properties related to inorganic, or plant-available, P retention. Studies agree that Al-WTR sorb abundant inorganic P (up to 37,000 mg kg^{-1}) to the point where P sorption is practically irreversible (Miller et al., 2011; Castaldi et al., 2014; Dayton & Basta, 2005). These properties contribute to potentially poor plant growth when Al-WTR is land applied, simply based on the material's ability to immobilize plant-available P in soil (Agyin-Birikorang et al., 2007). These same Al-WTR sorption properties, however, can be beneficial for mitigating excessive P in the environment (Haustein et al., 2000), which potentially can damage freshwater ecosystems (Dodds et al., 2011). Removing excess P from sources (e.g., wastewaters) may help mitigate damage caused by excess environmental P.

Current research has investigated the potential for Al-WTR to retain organic P, or P present within biological molecules (Zohar et al., 2017; Zohar et al., 2018). Studies have demonstrated that agricultural waste streams, such as livestock derived wastewater, often contains elevated organic P levels (Sheppard, 2018). As such, recent work has been focused on developing an organic aluminum water treatment residual composite (Al/O-WTR), or, essentially an organic P laden Al-WTR (Zohar et al., 2017). Results presented in Chapter 2 not only corroborate the previous findings that successful Al/O-WTR development is possible, but that the timeframe and efficiency in which organic P binds to Al-WTR to create Al/O-WTR holds unprecedented promise for producing a sustainable plant-available P supplement.

The research outlined below assesses the extent to which Al/O-WTR can supply plant-available P to spring wheat (*Triticum aestivum L.)* grown in two different textured, low P containing soils compared to a liquid inorganic P source (KH_2PO_4). It was hypothesized that Al/O-WTR could supply an equal amount of plant-available P in soil as compared to liquid P fertilizer when applied at equal P release rates. This research additionally aimed to provide insight as to how P supplied to soil from Al/O-WTR might influence both inorganic and organic soil P pools, other extractable nutrients, pH, and electrical conductivity (EC). It was also hypothesized that Al/O-WTR would supply significant organic P to soil, which would consequently increase organic P mineralization.

Materials and Methods

Soil Collection and Characterization

Soil was collected from two separate fields located at Colorado State University's Agricultural Research, Development and Education Center. These soils were selected due to records indicating that both fields were low (< 6 mg kg^{-1}) in Olsen extractable (i.e. plant-available) P. Additionally, soil texture was different between both fields. The upper 5 cm of soil was removed to avoid any surface accumulated P, and then soil was collected from the 5-15 cm depth and placed in 19 L buckets for the study. Soil was returned to the laboratory, air-dried, and composite samples were created by mixing soils from each bucket collected. Composite samples were used to characterize soil properties.

Soil texture was assessed via the hydrometer method (Western States Program, 1998); soils were classified as either a sandy loam or a sandy clay loam. The Web Soil Survey suggests that both soils had mixed, superactive mineralogy (Soil Survey Staff, 2019). It should also be noted that hypotheses were tested independently in each soil. Though two uniquely textured soils do not encompass the wide variety of soil textures or mineralogical properties present in agricultural systems, this study was limited to two unique soil textures due to constraints on time and resources. Plant-available P was determined via Olsen-P extraction (Olsen et al., 1954) and analyzed colorimetrically, and total P was determined via 4M HNO_3 digestion (Bradford et al., 1975) and analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Other plant-available nutrients were determined via AB-DTPA extraction (Barbarick & Workman 1987) and analyzed via ICP-OES. Soil pH and electrical conductivity (EC) were determined by shaking soil with deionized water (1:1 w/w) for two hours prior to assessment (Thomas, 1996; Rhoades, 1996). Soil inorganic carbon content was determined using the modified pressure transducer method (Sherrod et al, 2002), while total carbon and total nitrogen were assessed via combustion (Gavlak et al., 2005). Soil nitrate-N and ammonium-N content were determined using a 2M KCl extraction (Bremner, 1996) and analyzed colorimetrically. Soil field capacity was estimated by saturating ~100g soil, recording the saturated soil weight, and allowing water to freely drain for 48 hours. The percentage of moisture at field capacity was then calculated as the difference between saturated and dry soil masses divided by the dry soil mass. Soil characteristics are summarized in **Table 1**.

Table 3.1. Background soil properties prior to the greenhouse study.

Characteristic	Sandy Clay Loam	Sandy Loam	units
Sand	54.3	56.8	%
Silt	30.7	21.5	%
Clay	15.0	21.7	%
Moisture at Field Capacity	16.8	9.15	%
Inorganic C	1.06	0.90	%
Total C	1.50	1.77	%
Total N	0.06	0.10	%
NO_3-N	17.9	66.1	mg kg^{-1}
NH_4-N	1.73	0.84	mg kg^{-1}
Olsen P	2.01	3.91	mg kg^{-1}
Total P	446	446	mg kg^{-1}
AB-DTPA Extractable Al	0.00	0.00	mg kg^{-1}
AB-DTPA Extractable Fe	4.68	2.73	mg kg^{-1}
AB-DTPA Extractable K	110	692	mg kg^{-1}
AB-DTPA Extractable Mg	402	457	mg kg^{-1}
AB-DTPA Extractable Na	177	400	mg kg^{-1}
Electrical Conductivity	2.95	4.59	dS m^{-1}
pH	8.09	8.37	-

Al/O-WTR Generation

Swine wastewater was sourced from an untreated wastewater retention pond fed by approximately 1900 feeder pigs located in eastern Colorado. Al-WTR was obtained from City of

Fort Collins Water Treatment Facility in Fort Collins, Colorado. Briefly, Al/O-WTR was formed when Al-WTR and swine wastewater were mixed at a 1:2.5 ratio (w/w; solid:liquid), and were shaken for 21 days, though previous work (Chapter 2 *Results*) suggested that it required 1-hour to remove 99.9% total wastewater P to be removed by Al-WTR. Prior work also allowed us to assume that the maximum P supplied by Al/O-WTR would be 3000 mg kg^{-1} (Chapter 2 *Results*). A more detailed summary of Al/O-WTR production and P supply estimation is outlined in Chapter 2 *Materials and Methods*.

Greenhouse Experimental Setup and Design

One-liter cone-tainers, containing Polyfil in the bottom to prevent soil loss, were the experimental units used in the greenhouse trial. Both Al/O-WTR and KH_2PO_4 were applied to six replicates in both soil textures at rates 33.6, 67.3, and 134.5 kg P_2O_5 per hectare. Additionally, six control cone-tainers were used in each soil type and received no Al/O-WTR or KH_2PO_4 applications. Based on the background Olsen-P soil content (< 6 mg kg^{-1}), it was recommended that 67.5 kg P_2O_5 per hectare should be applied to soil (Davis & Westfall, 2014; Kang et al., 2011) and thus P fertilizer rates bracketed this target P application rate. For the KH_2PO_4 treatments, 800 g of air-dried field soil was placed in each cone-tainer. Then, KH_2PO_4 was applied to soil in 50 mL additions at concentrations 0.003M, 0.007M, and 0.013M, equal to 33.6, 67.3, and 134.5 kg P_2O_5 per hectare.

Using the previously mentioned assumption that Al/O-WTR supplies 3,000 mg P kg^{-1}, application rates in kg P_2O_5 were converted to kg P per hectare and then determined the masses Al/O-WTR required to meet 33.6, 67.3, and 134.5 kg P_2O_5 per hectare, or 1.75, 3.49, and 6.98 g Al/O-WTR per cone-tainer, respectively. The Al/O-WTR was mixed into replicates by first weighing 800 g soil into a plastic zip seal bag, adding the appropriate mass Al/O-WTR to each bag, and then hand working the zip seal bag until thoroughly mixed; soil was transferred to cone-tainers after mixing. After all Al/O-WTR and KH_2PO_4 cone-tainers were prepared, they were completely randomized.

Spring Wheat Planting, Watering, and Other Greenhouse Management

Soils were brought to 80% field capacity two days before planting. Five spring wheat seeds were planted in each cone-tainer, and ten days after planting the seedlings were thinned to two plants per cone-tainer. The 80% field capacity was maintained daily for three weeks after planting, yet at three weeks all plants appeared to display drought symptoms. In an effort to mitigate drought symptoms, soils were watered to 100% field capacity for the next eleven days. After this eleven-day period, it was decided that insufficient water was not the issue. Although plants did not display obvious nitrogen (N) deficiency symptoms, and the sandy clay loam soils may have benefited from N application, pre-study soil nutrient evaluations did not suggest that N application was required. Regardless, all soils received 95.3 kg hectare^{-1} N supplied by 10 mL 0.11M $Ca(NO_3)_2$ in an effort to ensure plant survival. After nitrogen application, all plant growth improved. For the remainder of the study, soil water content was maintained at 50%-80% field capacity.

Soil water content was maintained by monitoring control cone-tainer masses daily. It should be noted that the greenhouse was affected by its own spatial-temporal gradient that fluctuates on a daily basis (i.e. temperature, and therefore evapotranspiration, is not equal from one potted location to another). Because controls were randomly dispersed throughout the greenhouse among all other treatments, weighing each soil type's control replicates on a daily basis allowed us to accurately estimate each soil type's average water content on any given day.

Given this approach, it was possible to maintain soil moisture content. If the average control cone-tainer masses on any given day fell below the average control cone-tainer mass at 50% field capacity, the difference between the average control cone-tainer mass at 80% field capacity and the daily control mass average was added to all replicates for the given soil. For example, it was calculated that the control replicates for sandy loam soil averaged 887 g at 50% field capacity. It was also calculated that at 80% field capacity, the sandy loam control replicates averaged 909 g. Therefore, if the sandy loam control replicates average mass was less than 887 g, then the appropriate mass of water was added to bring the control replicate average back to 80% field capacity. Specifically, if the sandy loam control replicate average mass was 884 g then 25 mL (i.e. 25 g) water was added to all sandy loam replicates. As a whole, the sandy loam soil required greater irrigation frequency (every 2-3 days) in order to maintain the desired moisture content when compared to the irrigation frequency required in sandy clay loam soils (every 4-5 days).

Greenhouse Harvest and Plant Digestions for Phosphorus Content Analysis

Spring wheat plants were harvested 128 days after planting. Grain heads were cut from each plant by hand and were collected in paper coin envelopes. Wheat straw was then harvested by cutting straw 2 cm above the soil surface and storing in brown paper bags. Grain heads and straw were dried at 60° C for 72 hours prior to weighing. Both grain heads and straw samples were digested in concentrated nitric acid (HNO_3) and analyzed via ICP-OES for P content (Huang & Schulte, 1985). It should be noted that typically, 1g of ground plant material be digested in concentrated HNO_3. Because the grain heads and straw collected from each replicate weighed less than 1g, all unground dried plant materials were transferred to digestion tubes, weighed, and were dissolved in concentrated HNO_3 over 2 days. Plant materials dissolved in

HNO_3 were occasionally vortexed in order to ensure that any plant materials adhering to digestion tube sidewalls were dissolved in HNO_3. Elemental P concentrations assessed in the grain and straw were multiplied by the previously recorded dry weights to calculate P uptake in each tissue.

Soil Analyses Post-Harvest

Post-harvest, soil from each replicate were air-dried, passed through a 2-mm sieve, and then stored in plastic zip-seal bags. Soils were analyzed for AB-DTPA extractable nutrients, total P, pH and EC as mentioned above. Soils were also evaluated for amorphous iron (Fe_{Ox}), amorphous aluminum (Al_{Ox}), and P bound to these amorphous phases (P_{Ox}; Loeppert & Inskeep, 1996), and then using this information to determine the soil phosphorus saturation index and the soil phosphorus sorption capacity (PSC; Oladeji et al., 2007). Phosphatase enzymes (phosphomonoesterase and phosphodiesterase) were assayed using alkaline extraction procedures as outlined by Tabatabai (1994). Inorganic P fractionation was conducted using a calcareous soil procedure as outlined by Kuo (1996), whereby P bound in soluble Al/Fe phases, occluded-P, and Ca-bound P pools were determined. Organic P was calculated as the difference of total soil P minus the sum of soil inorganic P fractions (i.e. soluble Al/Fe-bound P, occluded P, and Ca-bound P).

Statistical Methods

All statistical analyses were conducted using R Version 3.5.3 and RStudio Version 1.0.153. Analysis of variance (ANOVA) was used to test the null hypothesis that means across treatments were equal. It should be noted that ANOVA assumes that data residuals are normally distributed and that variance across treatments is equal. The Shapiro-Wilks test was used to test residuals for normal distribution, and Levene's test was used test that variance was equal across treatments. In cases where Shapiro Wilk's test or Levene's test suggested that residuals were not normally distributed or that variance was not equal across treatments, the Kruskal-Wallis Rank Sum Test was employed to test the null hypothesis that mean ranks across treatments were equal. Tukey's Honestly Significant Difference pairwise comparisons test was utilized to provide further insight on where significant differences occurred between treatments. All statistical analyses were conducted at an $\alpha = 0.05$.

Results

Soil pH & Electrical Conductivity

Soil pH was not significantly different across treatments for the sandy clay loam soils ($p = 0.05$) although Tukey's post hoc test indicated that soils under the low Al/O-WTR and high KH_2PO_4 treatments both slightly increased soil pH compared to the control (**Figure 3.1)**. The Kruskal-Wallis test indicated that the sandy loam soil pH was significantly different across treatments ($p = 3.05 \times 10^{-4}$). Tukey's post hoc test showed that the sandy loam control soil pH was significantly greater than all Al/O-WTR treatment levels, and that both the target and high Al/O-WTR treatments had significantly lower soil pH than all soils under KH_2PO_4 amendment.

The Kruskal-Wallis Rank Sum test indicated that the sandy clay loam soil EC was significantly different across treatments ($p = 7.43 \times 10^{-3}$), and post hoc testing denoted that soils under high and low KH_2PO_4 applications had significantly lower EC than control soil (**Figure 3.2**). Soil EC was not significantly different across treatments in the sandy loam soil ($p = 0.06$), and post hoc analysis supported this evaluation.

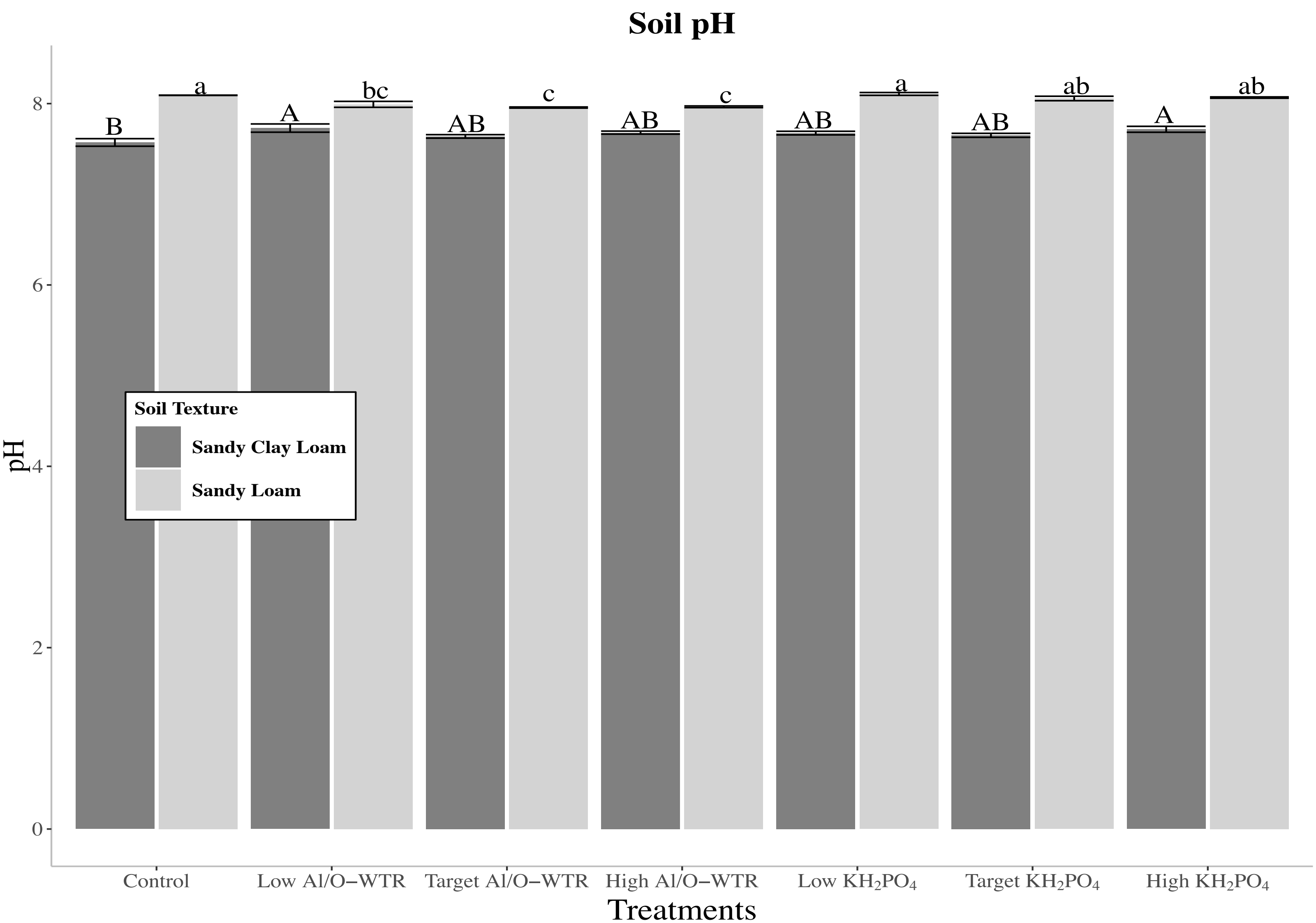

Figure 3.1. Mean (n=6) soil pH across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

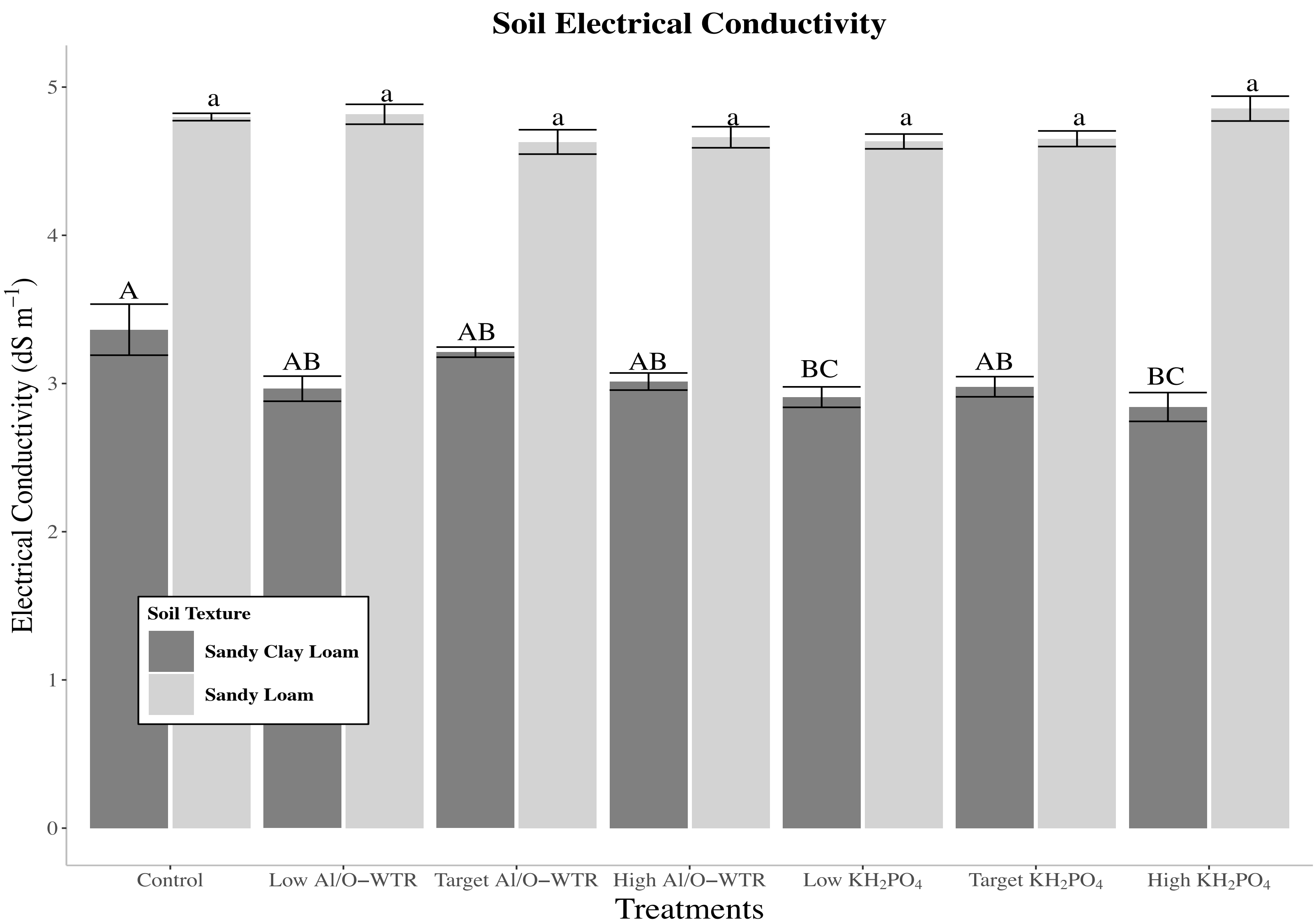

Figure 3.2. Mean (n=6) soil electrical conductivity across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

Table 3.2. Mean (n=6) AB-DTPA extractable elemental concentrations in sandy clay loam textured soils across treatments. Treatments with alike superscripts are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

Element	Control	Low Al/O-WTR	Target Al/O-WTR	High Al/O-WTR	Low KH_2PO_4	Target KH_2PO_4	High KH_2PO_4
Al	0.00^{b}	0.00^{b}	0.00^{b}	0.06^{a}	0.00^{b}	0.00^{b}	0.00^{b}
B	0.005^{c}	0.06^{bc}	0.08^{b}	0.07^{bc}	0.087^{b}	0.137^{a}	0.142^{a}
Ba	0.50^{b}	0.55^{b}	0.55^{b}	0.56^{b}	0.59^{b}	0.81^{a}	0.81^{a}
Ca	333.66^{d}	339.16^{cd}	354.17^{bc}	358.23^{bc}	360.79^{b}	461.63^{a}	458.82^{a}
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	1.83^{a}	2.19^{a}	2.81^{a}	2.69^{a}	1.89^{a}	3.95^{a}	3.17^{a}
Fe	8.53^{a}	8.74^{a}	7.70^{ab}	7.45^{ab}	6.11^{b}	8.35^{a}	7.24^{ab}
K	141.41^{bc}	146.43^{abc}	129.46^{c}	128.05^{c}	128.76^{c}	161.01^{ab}	170.00^{a}
Mg	368.76^{b}	372.15^{b}	375.90^{b}	371.14^{b}	381.63^{b}	442.22^{a}	438.02^{a}
Mn	3.50^{a}	3.51^{a}	3.87^{a}	3.48^{a}	2.80^{a}	3.96^{a}	3.38^{a}
Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	200.48^{ab}	208.12^{a}	189.68^{ab}	182.89^{ab}	172.72^{b}	196.75^{ab}	194.34^{ab}
Ni	0.67^{b}	0.71^{b}	0.72^{b}	0.70^{b}	0.72^{b}	0.87^{a}	0.84^{a}
P	0.06^{c}	0.04^{c}	0.12^{c}	0.04^{c}	0.63^{c}	2.50^{b}	6.08^{a}
Pb	1.60^{a}	1.42^{a}	1.35^{a}	1.38^{a}	1.41^{a}	1.55^{a}	1.47^{a}
V	0.31^{c}	0.31^{c}	0.33^{c}	0.33^{c}	0.38^{b}	0.57^{a}	0.59^{a}
Zn	0.67^{a}	0.77^{a}	0.87^{a}	0.88^{a}	0.78^{a}	1.28^{a}	1.31^{a}

Table 3.3. Mean (n=6) AB-DTPA extractable elemental concentrations in sandy loam textured soils across treatments. Treatments with alike superscripts are not significantly different according to Tukey's Honestly Significant Differences at an α = 0.05.

Element	Control	Low Al/O-WTR	Target Al/O-WTR	High Al/O-WTR	Low KH_2PO_4	Target KH_2PO_4	High KH_2PO_4
Al	0.00^{b}	0.03^{a}	0.03^{a}	0.03^{a}	0.00^{b}	0.00^{b}	0.00^{b}
B	0.60^{a}	0.52^{ab}	0.55^{ab}	0.53^{ab}	0.37^{b}	0.54^{ab}	0.59^{a}
Ba	0.58^{a}	0.49^{abc}	0.52^{ab}	0.4^{cd}	0.35^{d}	0.39^{cd}	0.43^{bcd}
Ca	483.14^{a}	392.91^{b}	398.06^{ab}	360.27^{bc}	287.59^{c}	330.89^{bc}	355.07^{bc}
Cd	0.01^{c}	0.01^{c}	0.02^{c}	0.05^{a}	0.03^{bc}	0.04^{ab}	0.05^{a}
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.85^{a}	0.91^{a}	1.42^{a}	1.32^{a}	1.63^{a}	1.42^{a}	1.25^{a}
Fe	5.52^{ab}	4.86^{ab}	6.12^{a}	6.215^{a}	4.66^{b}	5.15^{ab}	5.37^{ab}
K	498.66^{a}	494.52^{a}	498.53^{a}	485.35^{a}	439.50^{a}	462.83^{a}	527.69^{a}
Mg	503.14^{a}	446.17^{ab}	450.80^{ab}	404.43^{bc}	357.99^{c}	398.73^{bc}	431.16^{b}
Mn	4.44^{a}	4.51^{a}	5.39^{a}	5.20^{a}	3.64^{a}	3.86^{a}	4.50^{a}
Mo	0.02^{c}	0.03^{c}	0.03^{b}	0.07^{a}	0.04^{b}	0.06^{a}	0.08^{a}
Na	438.50^{a}	423.36^{a}	404.97^{c}	373.23^{a}	367.00^{bc}	375.48^{ab}	407.63^{a}
Ni	0.30^{a}	0.28^{a}	0.35^{a}	0.35^{a}	0.39^{a}	0.31^{a}	0.35^{a}
P	9.36^{c}	10.29^{bc}	10.71^{abc}	10.09^{bc}	8.15^{c}	13.60^{ab}	14.28^{a}
Pb	0.70^{a}	0.61^{a}	0.77^{a}	0.70^{a}	0.81^{a}	0.64^{a}	0.08^{a}
V	0.45^{bc}	0.66^{ab}	0.68^{a}	0.26^{cd}	0.19^{d}	0.28^{cd}	0.33^{cd}
Zn	0.59^{b}	0.56^{b}	0.79^{ab}	0.98^{a}	0.57^{b}	0.87^{ab}	0.89^{ab}

AB-DTPA Extractable Nutrients

Average elemental concentrations extracted by AB-DTPA in both soil textures are displayed in **Table 3.2** and **Table 3.3**, respectively. The majority of elements analyzed by AB-DTPA extraction were significantly different across treatments in both textured soils. The onlyelements not significantly different between treatments were Cu and Mn in the sandy clay loam, and Cu, K, Na, Ni, and Pb in the sandy loam. Overall, AB-DTPA extractable P concentrations were noticeably lower in the sandy clay loam soil when compared to the sandy loam.

Amorphous Al, Fe, and P

Amorphous Al (Al_{Ox}), as assessed by the Kruskal-Wallis rank sum test, was significantly different across treatments in the sandy clay loam (p = 0.03) and the sandy loam ($p = 1.88 \times 10^{-6}$; **Figure 3.3**). Tukey's post hoc test suggested that all Al/O-WTR treatment levels in the sandy clay loam contained significantly greater amorphous aluminum than all other treatments. Post hoc analysis also displayed that the target and high Al/O-WTR treatments in the sandy loam soil were significantly greater than the control soil, while low and target KH_2PO_4 treatments were significantly lower than the control.

Amorphous Fe (Fe_{Ox}) content, as evaluated by ANOVA, was significantly different in the sandy clay loam soil (p = 0.03), though post hoc analysis did not display any significantly different pairwise comparisons (**Figure 3.4**). The sandy loam soil amorphous Fe content was also significantly different across treatments ($p = 1.59 \times 10^{-8}$) with the high Al/O-WTR and low KH_2PO_4 significantly lower than all other treatments except each other. Also evaluated by ANOVA, P associated with amorphous Fe and Al phases (P_{Ox}) was not significantly different across sandy clay loam soils (p = 0.78; **Figure 3.5**). Significance was observed in the sandy loam

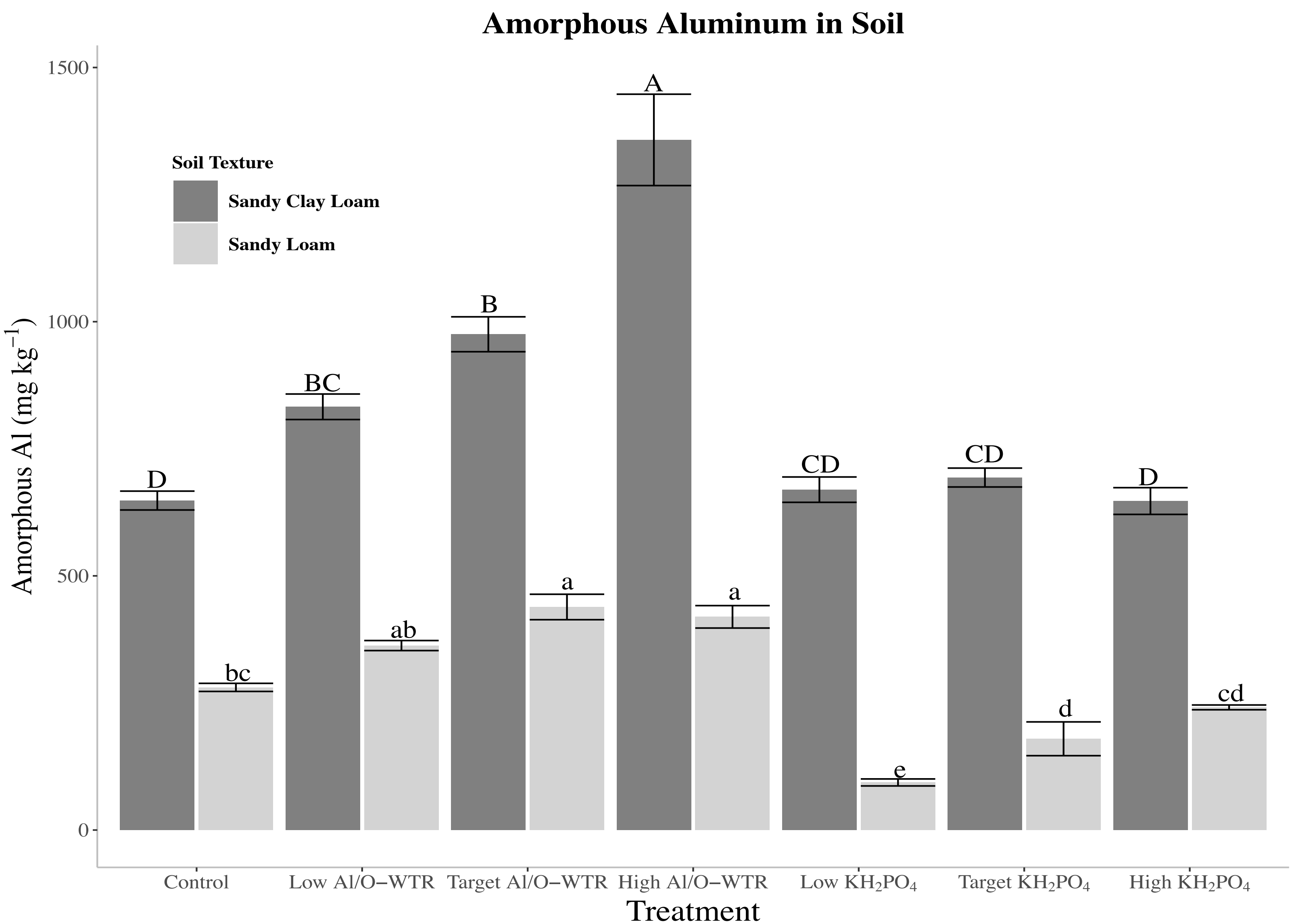

Figure 3.3. Mean (n=6) soil amorphous Al concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

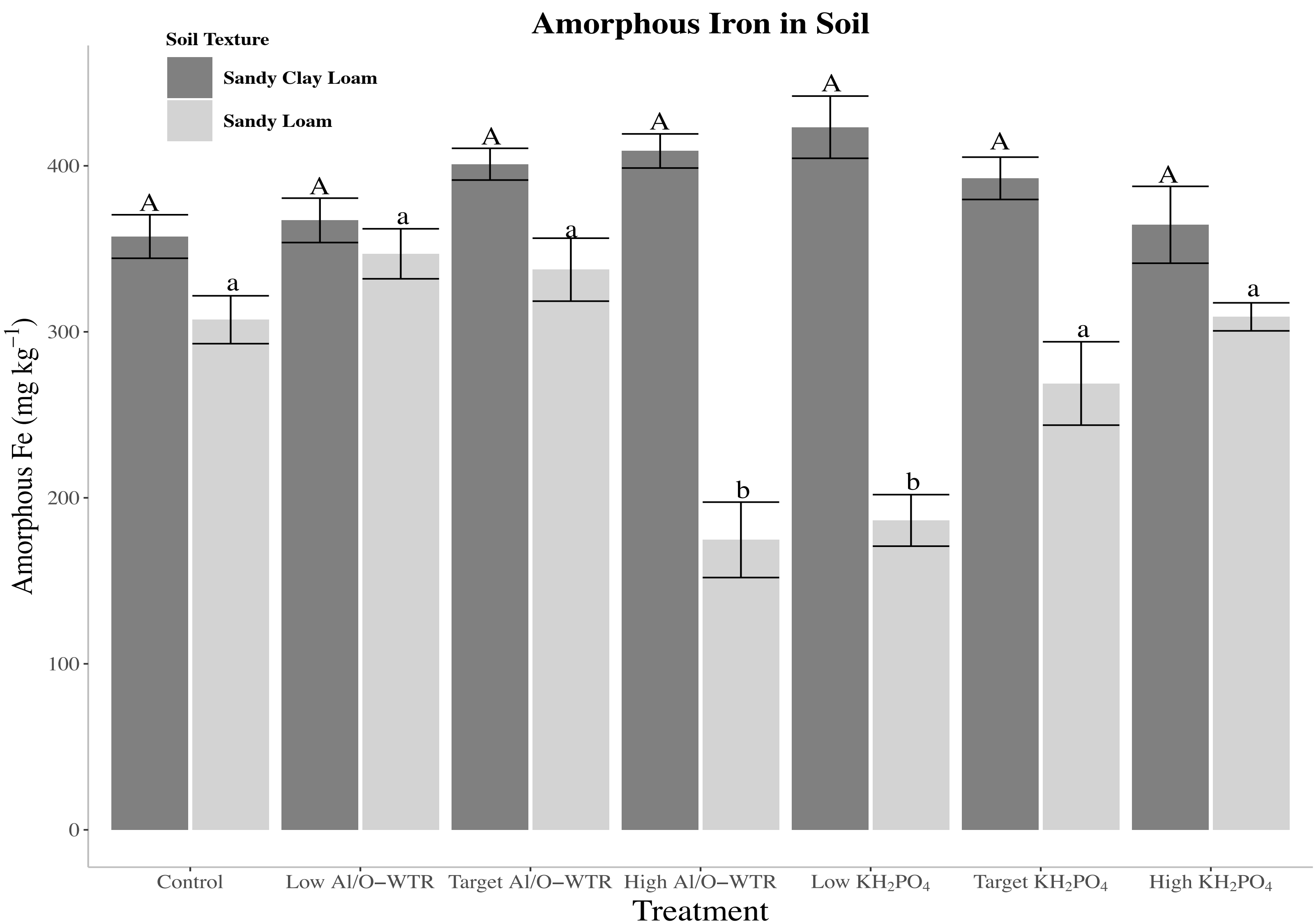

Figure 3.4. Mean (n=6) soil amorphous iron concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

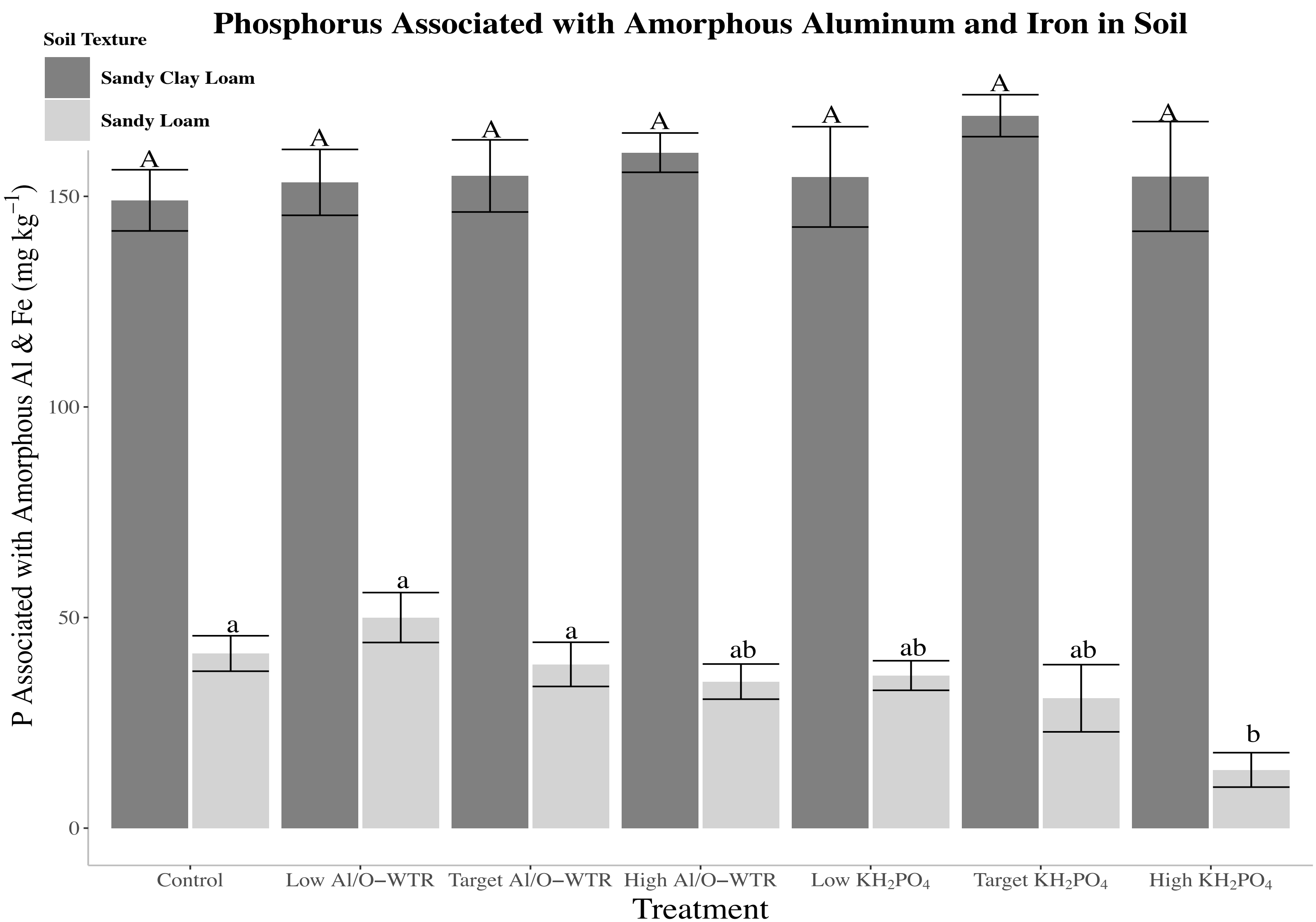

Figure 3.5. Mean (n=6) concentrations of phosphorus associated with amorphous iron across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

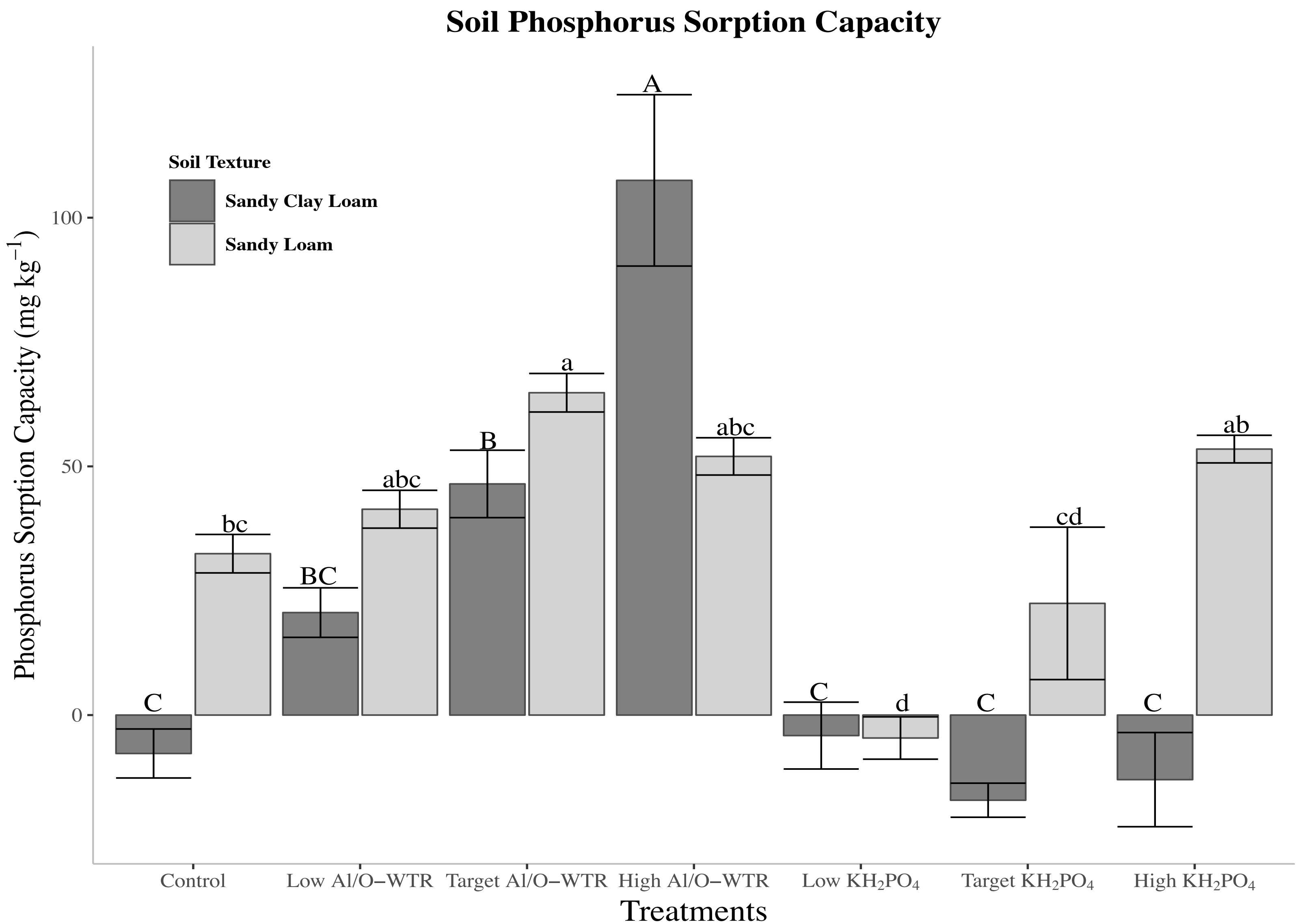

Figure 3.6. Mean (n=6) soil phosphorus sorption capacity across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

soil as the high KH_2PO_4 treatment contained significantly lower P_{Ox} than the control soil and the low and target Al/O-WTR treatments

Phosphorus Sorption Capacity

It should be mentioned that negative PSC values indicate that a soil acts as a P source, while positive PSC values indicate that a soil acts a P sink. The PSC mean rank sums across the treatments were not equal for both the sandy clay loam and sandy loam soils (p = 1.13 x 10^{-5} and p = 1.63 x 10^{-4}, respectively; **Figure 3.6**). Tukey's post hoc test showed that mean P sorption capacity was significantly greater when comparing high Al/O-WTR treated sandy clay loam soils with all other treatments. The sandy clay loam target Al/O-WTR was similar to the high Al/O-WTR, as both had significantly greater PSC than all other treatments except when compared to each other or when compared to the low Al/O-WTR treatment. Furthermore, Tukey's post hoc test indicated that sandy loam soil PSC under high KH_2PO_4 treatment was significantly greater than the low and target KH_2PO_4 treatments. Interestingly, the target Al/O-WTR amended sandy loam soil was the only treatment significantly greater than the control while the low KH_2PO_4 amended soil was the only treatment significantly lower than the control. Otherwise, pairwise comparisons across treatments were comparable.

Olsen, Organic, and Total Phosphorus

Similar to the AB-DTPA extractable P results, the Olsen P extraction results showed that the sandy clay loam soil contained lower P concentrations than the sandy loam soil. Furthermore, the sandy clay loam showed that mean Olsen P content was not equal across treatments (p = 1.34 x 10^{-3}) and suggested that the high KH_2PO_4 treatment was significantly greater than all other treatments except the target Al/O-WTR. ANOVA and post hoc analysis on the sandy loam

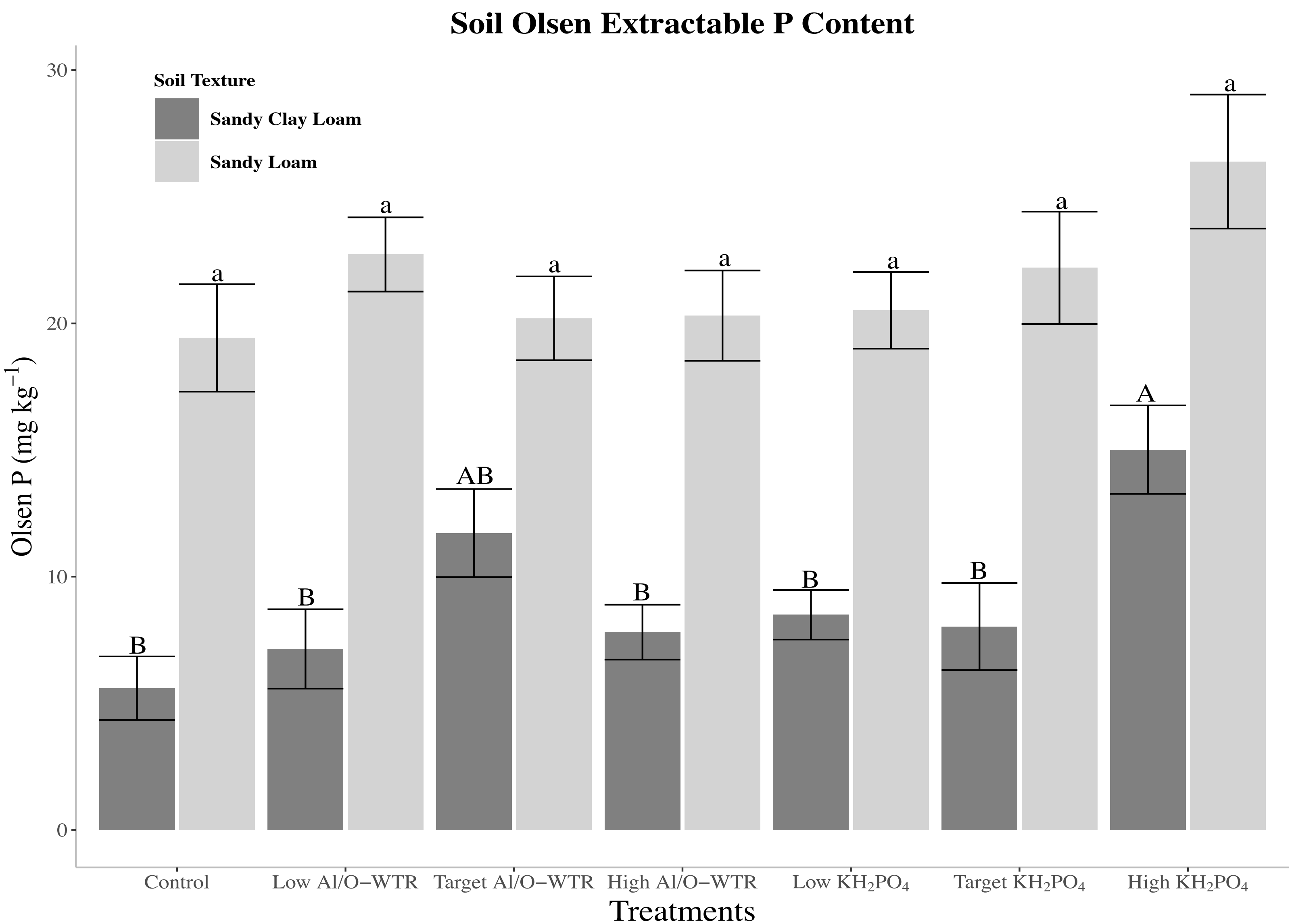

Figure 3.7. Mean (n=6) Olsen extractable P concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

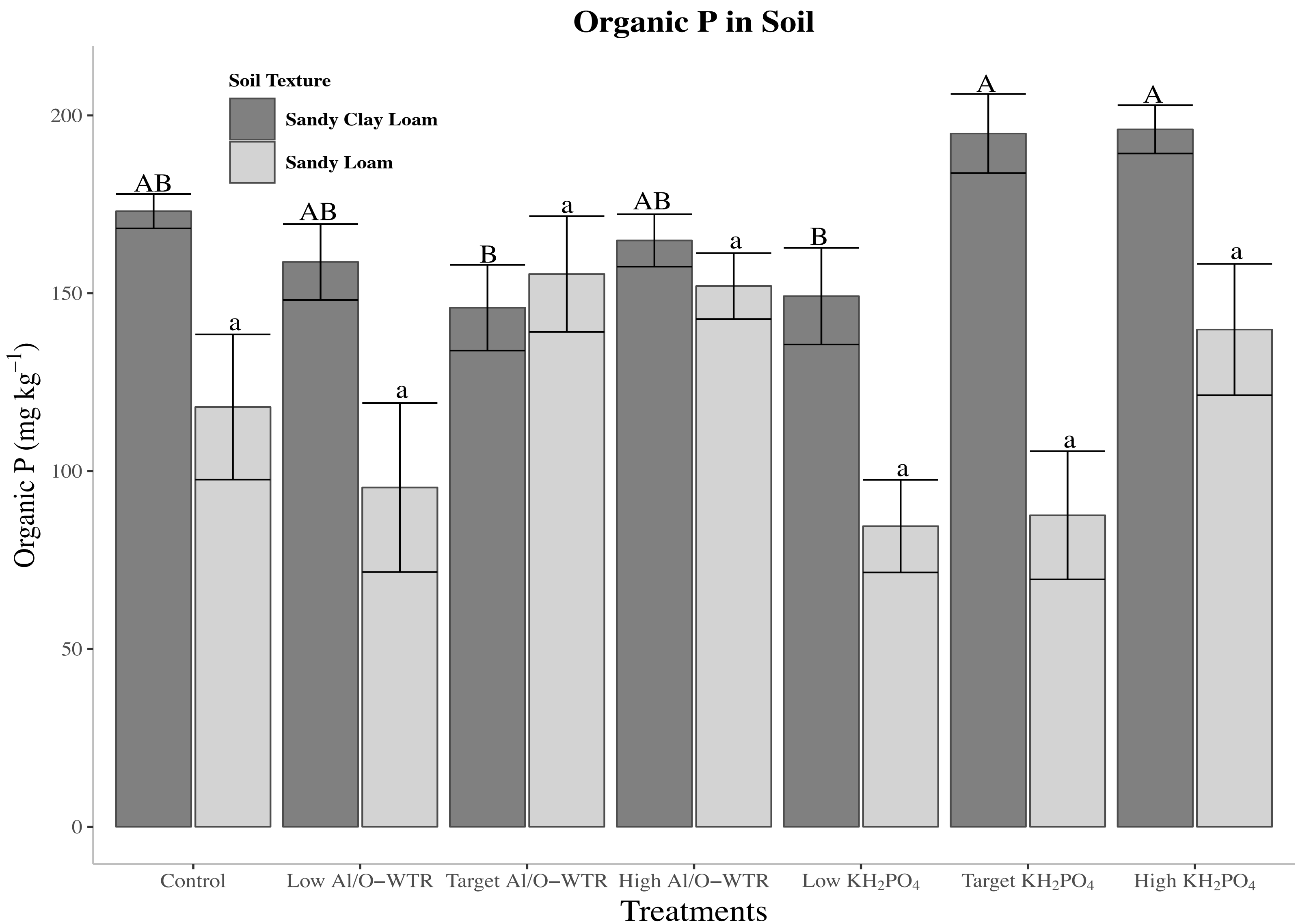

Figure 3.8. Mean (n=6) organic phosphorus concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

showed that Olsen extractable P in the sandy loam soil was not significantly different (p = 0.213) across treatments (**Figure 3.7**).

Organic phosphorus was calculated as the difference between total P and inorganic P (i.e. the sum of the inorganic P fractionation extracts). Statistical analysis showed that organic P was significantly different across treatments for the sandy clay loam (p = 2.91 x 10^{-3}**)** and the sandy loam (p = 0.02; **Figure 3.8**). Though both soil textures achieved significance according to ANOVA, Tukey's HSD indicated that significantly different pairwise comparisons were only present in the sandy clay loam textured soil. Significance observed in such pairwise comparisons showed target Al/O-WTR and low KH_2PO_4 treatments were lower than the target and high KH_2PO_4, though no treatment was significantly different from the control soil.

Total P in the sandy clay loam was significantly different (p = 1.99 x 10^{-5}) with the high Al/O-WTR amended soils having significantly lower total P than the target and high KH_2PO_4 treatments, and significantly greater total P than both the low KH_2PO_4 and target Al/O-WTR amended soils. Likewise, the sandy clay loam soil under the target Al/O-WTR and low KH_2PO_4 treatments were significantly lower than target and high KH_2PO_4 treated soils. Total P in the sandy loam was significantly different across treatments (p = 5.95 x 10^{-3}), though Tukey's post hoc test indicated that the high KH_2PO_4 treatment was only significantly greater than the control soil (**Figure 3.9**).

Inorganic P Fractionation

Inorganic P fractionation results demonstrated that P associated with the soluble/Al/Fe phase in the sandy clay loam soil was significantly different across treatments (p = 0.02), though Tukey's HSD showed no significantly different pairwise comparison (**Figure 3.10**). Soluble/Al/Fe-bound associated P in the sandy loam was not significantly different across

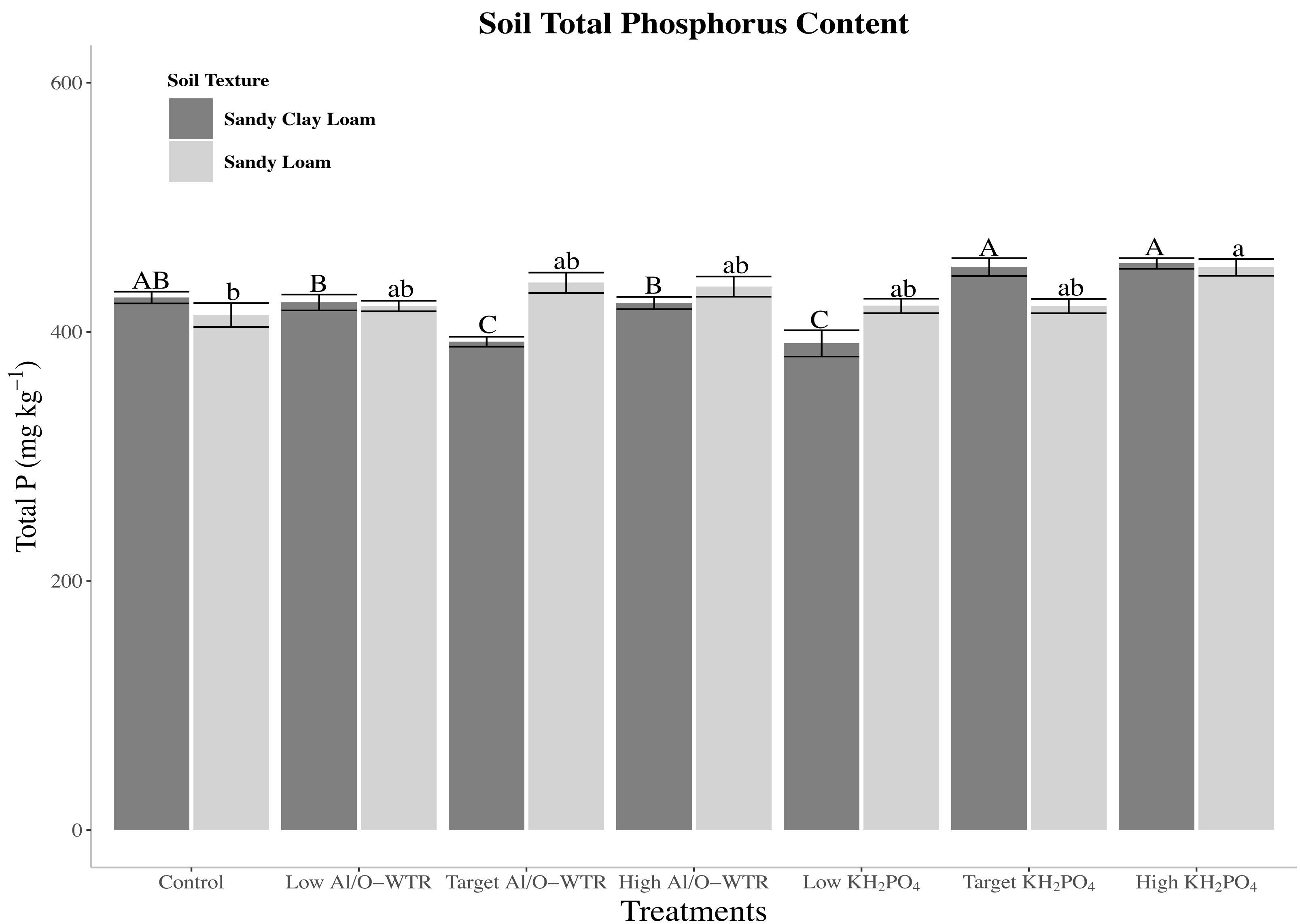

Figure 3.9. Mean (n=6) total P concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

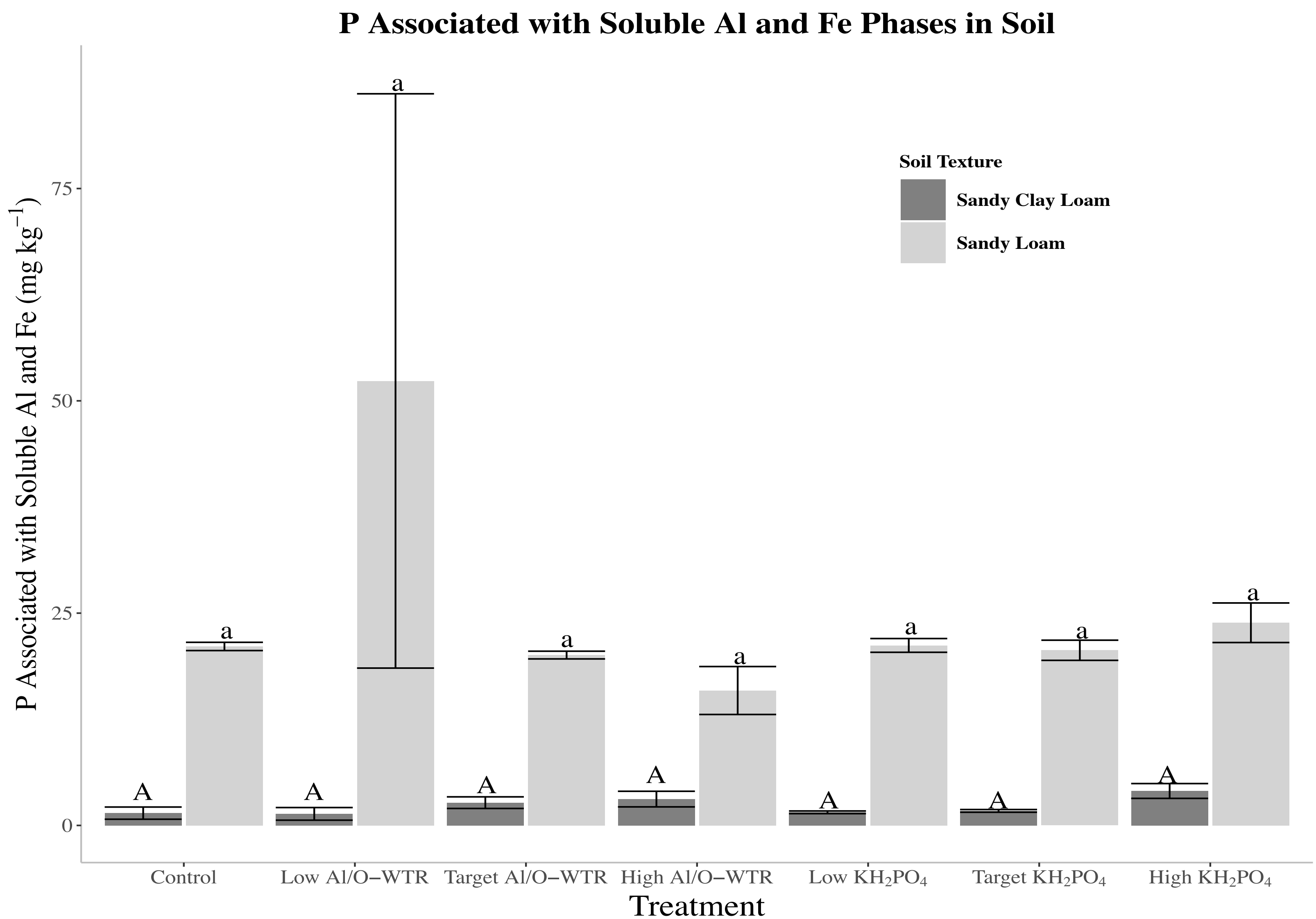

Figure 3.10. Mean (n=6) P associated with soluble Al and Fe phases concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

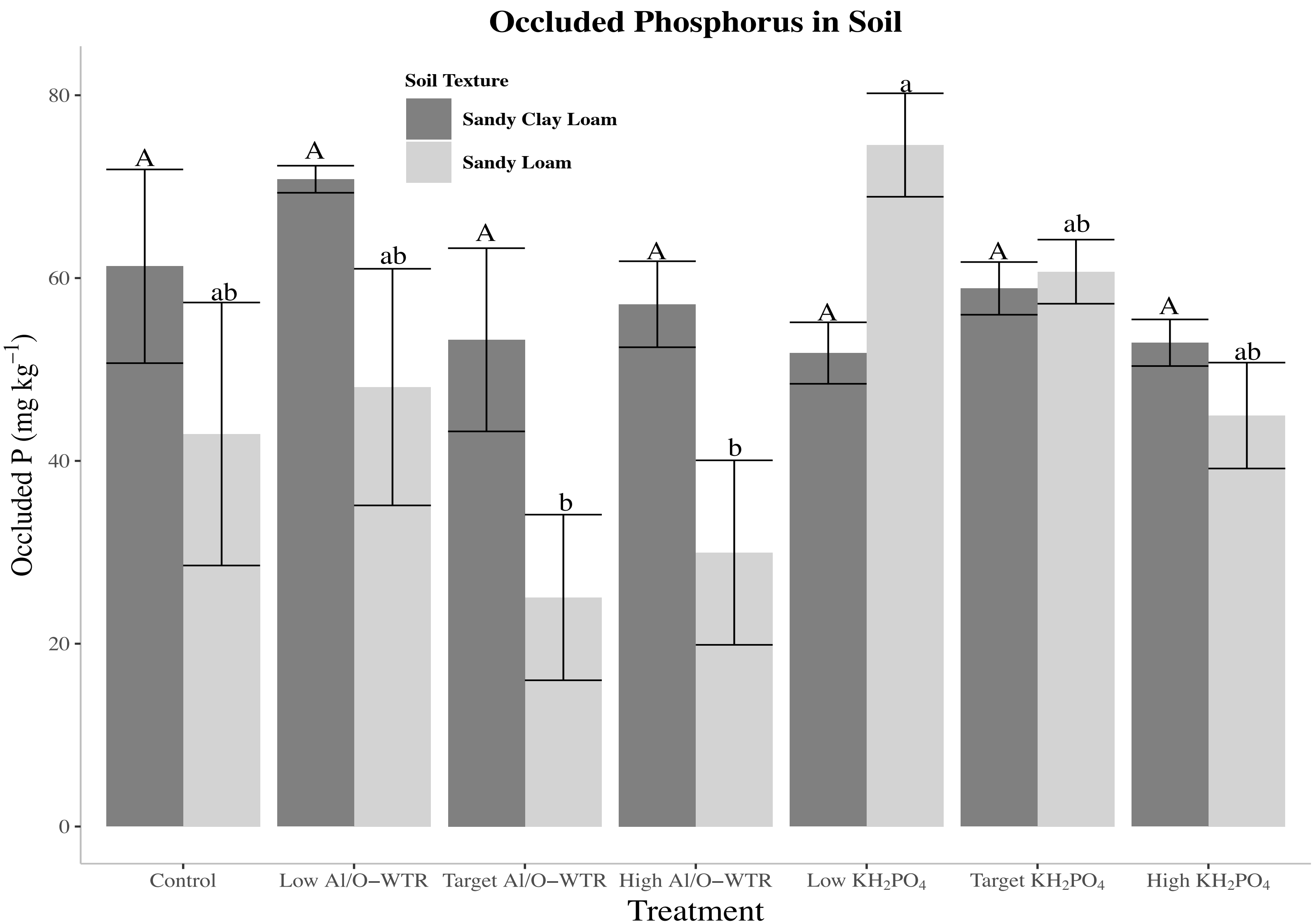

Figure 3.11. Mean (n=6) occluded P concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

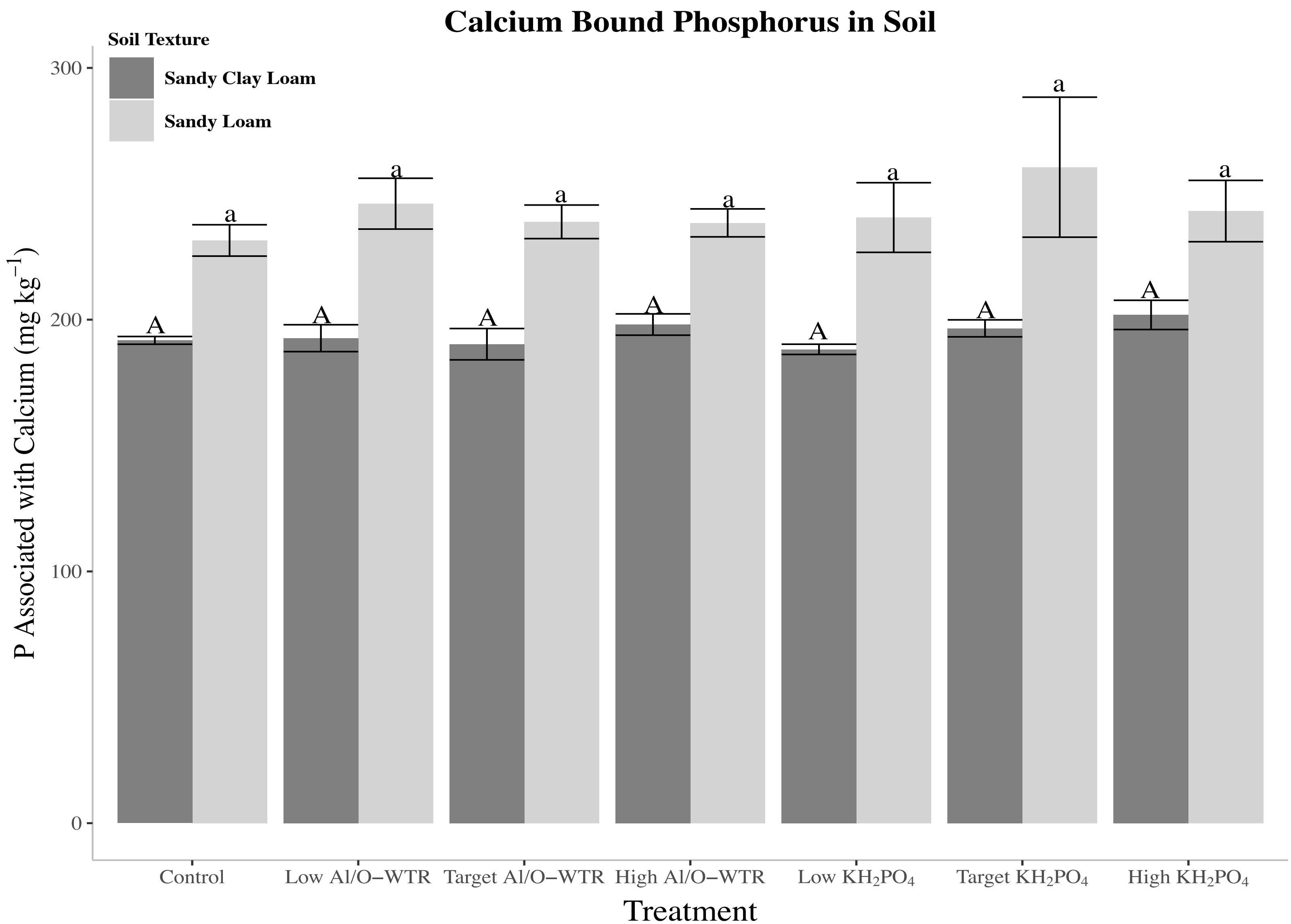

Figure 3.12. Mean (n=6) Ca associated P concentrations across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

treatments (p = 0.27). Tukey's HSD also suggested that pairwise comparisons were not significantly different. Occluded P in the sandy clay loam was significantly different across treatments (p = 0.01); however, Tukey's HSD did not indicate that any pairwise comparisons were statistically significant (**Figure 3.11**). In the sandy loam, occluded P was significantly different ($p = 7.59 \times 10^{-3}$) with Tukey's HSD, showing that the low KH_2PO_4 treatment was significantly greater than the target and high Al/O-WTR treatments. Calcium-bound P was not significantly different in the sandy clay loam (p = 0.24) or in the sandy loam (p = 0.92; **Figure 3.12**).

Phosphatase Activity

Phosphomonoesterase activity (**Figure 3.13)** in the sandy clay loam soil, as assessed by ANOVA, was not equal across treatments ($p = 9.78 \times 10^{-3}$). The low KH_2PO_4 was significantly greater than both the target and high Al/O-WTR treatments. Phosphomonoesterase activity in the sandy loam, assessed by ANOVA, also showed that enzyme activity was not equal across treatments ($p = 1.51 \times 10^{-12}$). Interestingly, the target KH_2PO_4 application was significantly lower than all other treatments, the high Al/O-WTR application was significantly greater than the low and target Al/O-WTR applications, and the target Al/O-WTR was significantly lower than the control and both the low and high KH_2PO_4 applications.

Phosphodiesterase activity (**Figure 3.14)** in the control and all Al/O-WTR amended sandy clay loam soils was significantly greater ($p = 1.10 \times 10^{-4}$), as determined by the Krukal-Wallis Rank Sum test, than both the high and target KH_2PO_4 treatments. The low KH_2PO_4 application rate was significantly greater than only the high KH_2PO_4 treatment. Sandy loam soils amended with the target and high Al/O-WTR rates had significantly greater phosphodiesterase activity ($p = 9.96 \times 10^{-5}$), as determined by ANOVA, than all KH_2PO_4 treatments.

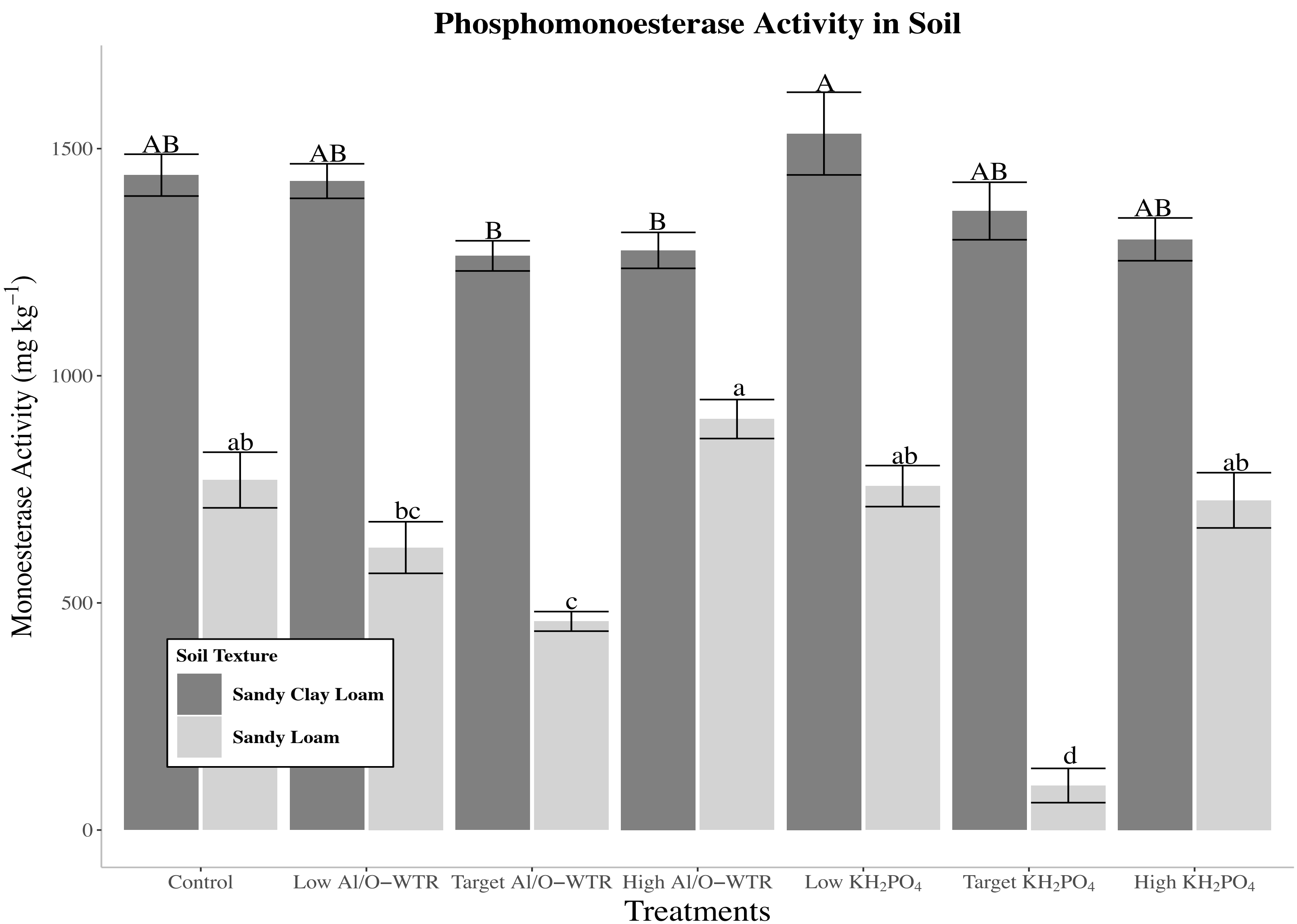

Figure 3.13. Mean (n=6) phosphomonoesterase activity across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

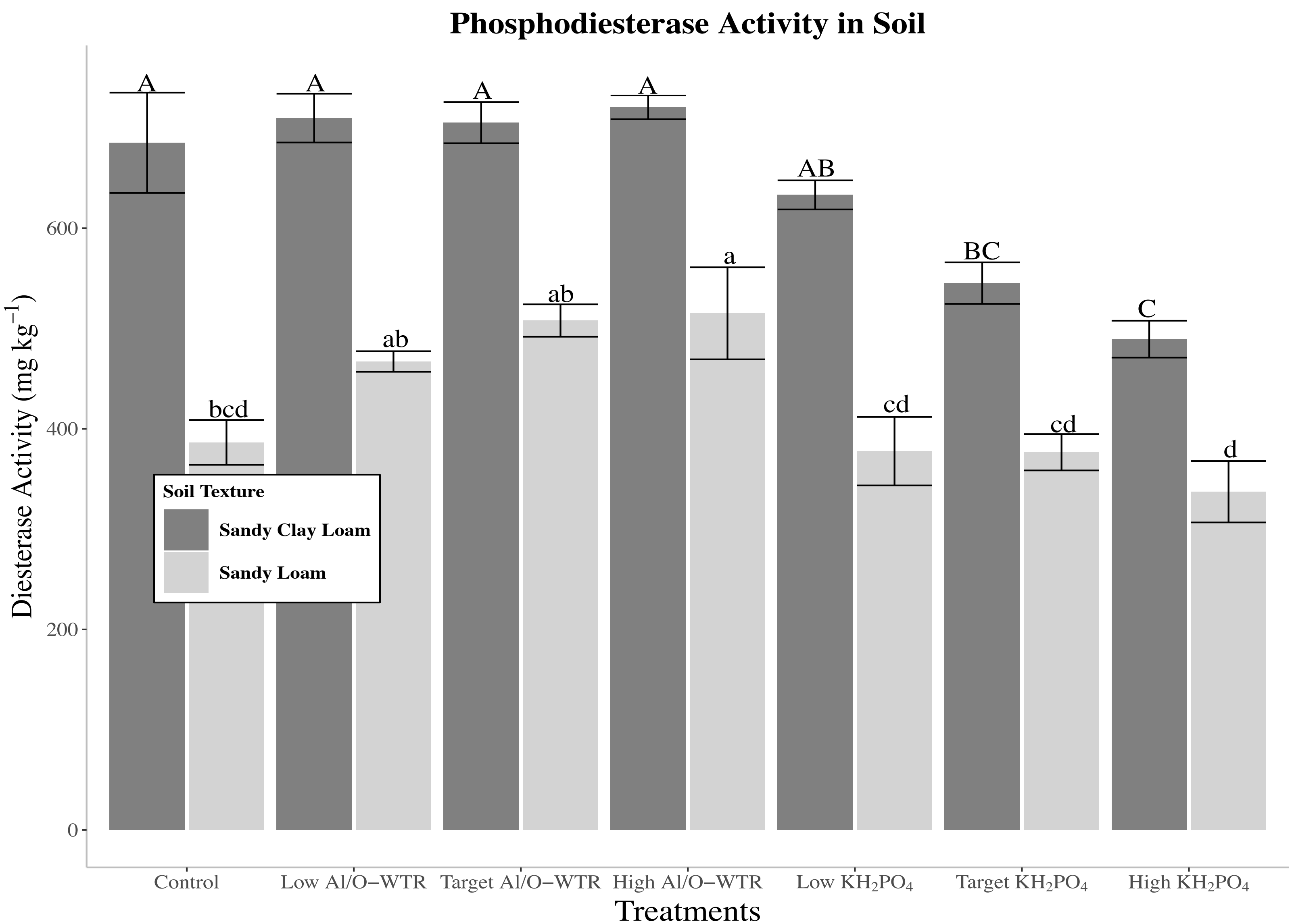

Figure 3.14. Mean (n=6) phosphodiesterase activity across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

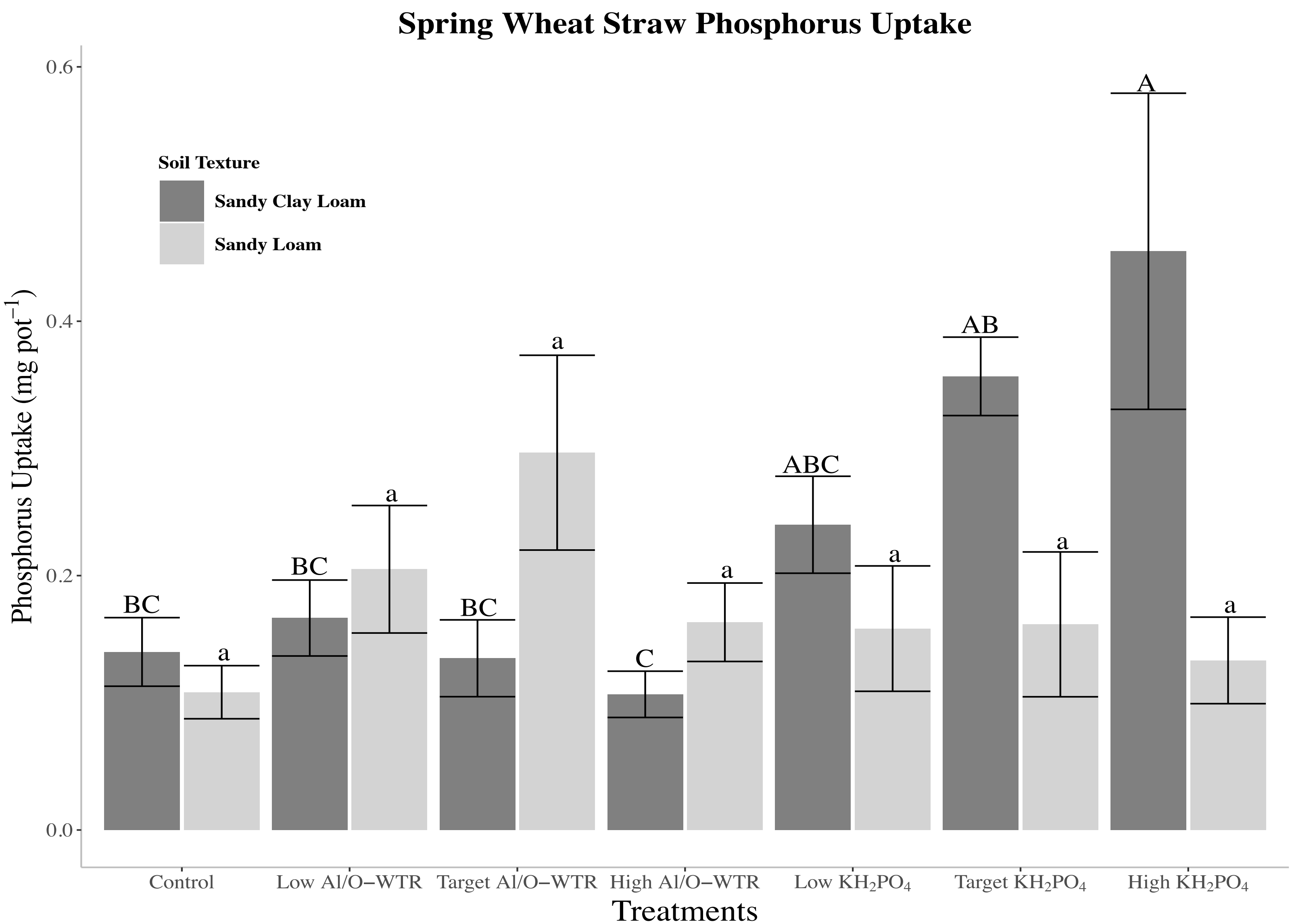

Figure 3.15. Mean (n=6) spring wheat straw P uptake across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

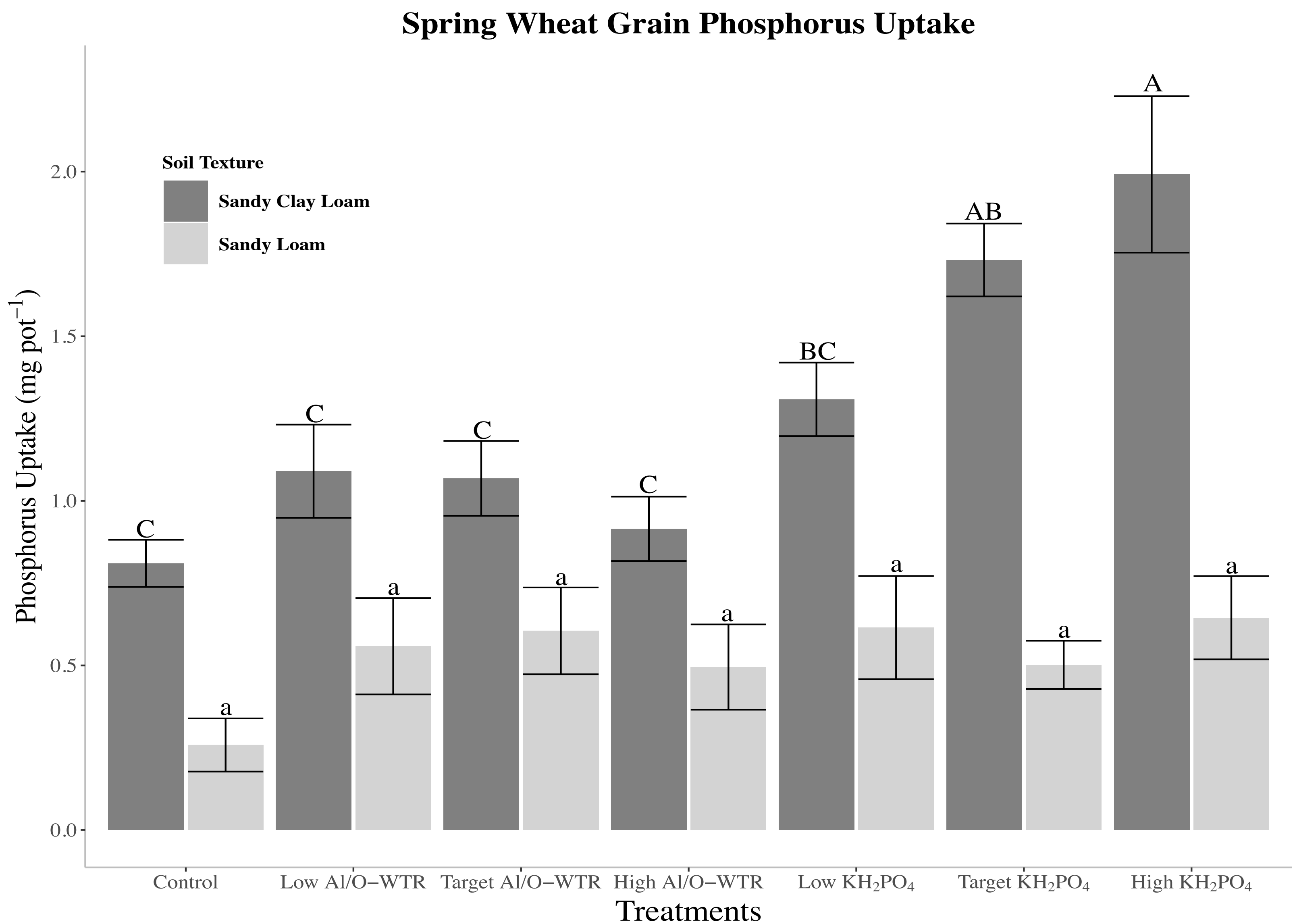

Figure 3.16. Mean (n=6) spring wheat grain P uptake across treatments and soil textures. Treatments with similar letters above bars, within a given soil texture, are not significantly different according to Tukey's Honestly Significant Differences at an $\alpha = 0.05$.

Spring Wheat Straw and Grain Phosphorus Uptake

Both straw and grain P uptake in the sandy clay loam soil, as analyzed by the Kruskal-Wallis Rank Sum test, were found to be significantly different across treatments (p = 1.74 x 10^{-4} and p = 1.35 x 10^{-6}, respectively). Tukey's HSD showed that straw P uptake (**Figure 3.15)** in sandy clay loam soils was significantly greater in the high KH_2PO_4 treatments when compared to control soil and all Al/O-WTR treatment levels. Grain P uptake (**Figure 3.16)** in sandy clay loam soil was significantly greater in the target and high KH_2PO_4 treatments when compared to control soil and all Al/O-WTR treatments. Analyzing plant digestion results with ANOVA established that neither straw, nor grain, P uptake was significantly different (p = 0.18 and p = 0.38, respectively) across treatments in the sandy loam soil.

Discussion

Soil pH and Electrical Conductivity

Concerns typically raised when applying Al-WTR to soil are Al toxicity in plants and soil acidification caused by Al hydrolysis. Contrary to these concerns, studies have shown that increasing Al-WTR application rates does not increase plant shoot Al concentrations (Ippolito et al., 1999; Oladeji et al., 2009). It is understood that Al availability decreases as soil pH increases (Sparks, 2003). Aluminum is primarily in the form $Al(OH)_3$ when soil pH is between 6.5-8.0 (Sparks, 2003). When soil pH is outside of 4.7 – 7.5, Al availability can increase (Sparks, 2003); however, Al species that become available are important outside this pH range. Below pH 4.7, Al is available as Al^{3+}, while above pH 7.5 Al is present as $Al(OH)_4^-$ (Sparks, 2003). The key difference between these two species is that Al^{3+} readily hydrolyzes water to generate soil acidity, while $Al(OH)_4^-$ does not (Sparks, 2003). In relation to the current study, soil acidification via Al hydrolysis is not a concern given the soil pH measured in this experiment.

The sandy clay loam and sandy loam soils displayed narrow pH ranges from 7.6–7.7 and 8.0–8.1, respectively. Tukey HSD shows that sandy clay loam soil pH was not influenced by Al/O-WTR application. The sandy loam soil, however, showed that all Al/O-WTR amendments significantly lowered soil pH as compared to control and KH_2PO_4 treatments. Given that soil pH was still well above 7.5, these results agree with previous research that suggested Al-WTR amendment has minimal effects on soil pH (Lombi et al., 2010; Novak & Watts, 2005).

Assessed EC values displayed similarly narrow ranges for both soils. The sandy clay loam showed a wider range of values between 2.84 –3.63 dS m^{-1} with only the low and high KH_2PO_4 treatments significantly different from the control; the sandy loam soil EC ranged between 4.65–4.85 dS m^{-1} with no significant differences across treatments. Consequently, this data suggests that Al/O-WTR application does not affect soil EC. Elevated soil EC suggests that there are abundant cationic elements present that could bind with available phosphate anions to form common mineral complexes (Lehr & Van Wesemael, 1952; Beji et al., 2017). Therefore, EC may be a parameter to consider before land applying Al/O-WTR as excessive salt concentrations could escalate competition between plant roots and cationic salt elements for available P.

AB-DTPA Extractable P and Other Nutrients

Data from AB-DTPA extraction showed that elemental salts (Ca, K, Mg, Na) are present in much greater quantities than other elements. Such relatively elevated concentrations could explain the high observed EC concentrations. Other elements were present in concentrations much lower than salts and showed numerous significant differences across treatments. Despite significant differences seen throughout the AB-DTPA extraction results, many elements assessed displayed narrow concentration ranges across treatments. For example, in both soil textures Zn was determined to be significantly different across treatments yet the largest differences in soil Zn concentrations across treatments in both soil textures were <0.7 mg kg^{-1}. Given the heterogenous nature of soils (Snakin et al., 2001), it is important to recognize that such differences, though significant, could be attributed to the way in which elements are naturally distributed in the environment rather than experimentally driven conditions.

Observed differences in extractable P concentrations were much greater than those of other extractable elements, with P concentrations that spanned a range of nearly 6 mg kg^{-1} in both soils. Most notably, AB-DTPA and Olsen extractable P concentrations were relatively greater in sandy loam textured soils, and had less variance across treatments, than sandy clay loam soils. Because P is sometimes transported to plants via mass flow, this difference might be attributed to the greater infiltration rates typically seen in low clay content soils (Brady & Weil, 2010) suggesting that soluble P is likely the most accessible form of P available for plant uptake in the sandy loam soil. Inorganic P fractionation results (discussed below) validated this contention, showing that soluble P was abundantly available, suggesting that P availability was driven by water in the sandy loam soils.

Given the organic nature of Al/O-WTR, differences in AB-DTPA and Olsen extractable P concentrations across treatments in the sandy clay loam soil were likely a due to the ability of clay textured soils to stabilize organic matter on clay surfaces and promote microbial communities (Brady & Weil, 2010; Cuadros, 2017). Elevated phosphatase activity in the sandy clay loam soils (discussed below), despite relatively low AB-DTPA and Olsen extractable P concentrations, further suggests that the majority of P made available for plant uptake was derived from organic moieties. These results imply that plant-available P is not comparably available when supplied by Al/O-WTR and ultimately favor Al/O-WTR application to low clay content soils.

Ammonium Oxalate Extractable Al, Fe, and P

Previous research has shown that Al-WTR applied to soil can act as a P sink due to its naturally abundant amorphous Al (Al_{Ox}) and Fe (Fe_{Ox}) content (i.e. ammonium oxalate extractable; Elliot et al., 2002). Consequently, it is important to monitor Al_{Ox} and Fe_{Ox} fluxes following Al/O-WTR application to ensure that land application will not reduce soil fertility in terms of P availability.

In general, Al_{Ox} and Fe_{Ox} were present at greater quantities in the sandy clay loam soil, likely due to mineralogy associated with clay particles (Sposito, 1989). While Fe_{Ox} was fairly similar across treatments and textures, soils that received Al/O-WTR amendment had noticeably greater Al_{Ox} quantities than all other treated soils across both soil textures. This suggests that Al/O-WTR application can significantly contribute Al_{Ox} to soil and, to some extent, justifies the concern that land application could immobilize P in soil.

Despite the elevated Al_{Ox} in Al/O-WTR treated soils, concentrations of P (P_{Ox}) associated with Al_{Ox} and Fe_{Ox} were essentially less than or equal to control soil concentrations. This observation brings into question the extent to which Al/O-WTR borne Al_{Ox} is available to react with the surrounding environment. It has been noted that solids containing amorphous phases typically have high specific surfaces and, consequently, great reactivity (Borgaard, 1983; Goldberg et al., 2001). This data suggests that Al_{Ox} exchange sites delivered to soil via Al/O-WTR are mostly satisfied prior to application. No observed increases in P_{Ox} in soil, despite clear increases in Al_{Ox}, suggests that P supplied to soil by Al/O-WTR does not come from P strongly complexed with Al_{Ox} and Fe_{Ox}. Rather, the data implies that P utilized by plants in Al/O-WTR treated soils is likely derived from weakly complexed organic P moieties bound to Al/O-WTR.

Organic moiety complexation to mineral surfaces is not straightforward. Kleber et al. (2007) suggested that organic compounds in soil assemble zonal structures that allow organic compounds to preferentially bind to each other. Based on this, it seems possible that organic compounds binding to Al-WTR during Al/O-WTR formation is, at least, partly preferential. Kleber et al. (2007) further cited numerous studies that indicated decomposing organic residues, such as those found in swine wastewater, are highly amphiphilic, proposing that compounds arrange into three assembly layers: a contact zone, a hydrophobic zone, and a kinetic zone. The contact zone implies direct interaction between amphiphilic compounds and mineral surfaces and additionally suggests that those compounds adhere to mineral surfaces very strongly and are protected from degradation. The hydrophobic zone is comprised of hydrophobic portions of amphiphilic compounds bound in the contact zone. For example, phospholipids can bind to mineral surfaces in the contact zone when lipid phosphate functional groups associate with Al or Fe. The phospholipid hydrocarbon chain then branches outward into the hydrophobic zone. The kinetic zone is a zone in which all remaining compounds self-assemble as a function of environmental parameters (e.g. pH, temperature, soil solution ionic strength, etc.) that influence thermodynamic kinetics.

Kleber et al. (2007) further suggested that proteins directly adsorbed to mineral surfaces in the contact zone could potentially alter the formation of the hydrophobic zone and result in zones where electrostatic interactions are the dominate mechanism responsible for binding compounds in soil solution. Given the current study and the biological nature of swine wastewater, it was plausible that P availability from Al/O-WTR is governed by multiple sorption and desorption mechanisms. Thus, it seems that plant-available P supplied by Al/O-WTR is mostly likely derived from 1) areas in which proteins interact with mineral surfaces and promote electrostatic interactions, 2) functional groups located in outer regions of the hydrophobic zone, and 3) accessible constituents found in the kinetic zone. The zonal structure and self-assemblage theory could also elucidate why Al/O-WTR desorbed approximately 3,000 mg kg^{-1} P despite having sorbed approximately 16,500 mg kg^{-1} P (Chapter 2 *Results & Discussion*).

Organic P associated with mineral surfaces in Al/O-WTR was likely bound very strongly and could be unavailable to mineralization by microorganisms. Similarly, P tied up in the inner regions of the hydrophobic zone are likely inaccessible to microorganisms that rely on water to move throughout soil and degrade organic compounds, though P found at the confluence of the hydrophobic zone and soil solution may be accessible for mineralization. Finally, areas in Al/O-WTR where proteins bind to mineral surfaces and promote electrostatic interactions are likely favored by microorganisms which can more easily cleave outer-sphere complexes and mineralize those organic moieties. Ultimately, this suggests that wastewater sources with high protein content may be best for generating Al/O-WTR that optimally contributes to plant-available P in soil.

Soil Phosphorus Sorption Capacity

As described by previous research (Sims et al, 1998; Nair & Harris, 2004; Oladeji et al. 2007), soil PSC equals $(0.15 - Phosphorus\ Saturation\ Index)\ x\ (Al_{Ox}+Fe_{Ox})\ x\ 31$ where the phosphorus saturation index (PSI) = $(P_{Ox})/(Al_{Ox} + Fe_{Ox})$ with element concentrations determined by ammonium oxalate extraction and expressed in mmol kg^{-1}. When using this equation, negative PSC values indicate that soil has essentially no exchange sites to retain P and should, theoretically, act as a P source. The opposite is also true: positive PSC values indicate that soil has some capacity to retain P and should therefore act as a P sink (Oladeji et al., 2007).

Figure 3.6 shows that the sandy clay loam soils amended with Al/O-WTR should act as a P sink, whereas other treatments of the same soil would act as P sources. This difference between treatments can be explained by significantly greater Al_{Ox} concentrations present in Al/O-WTR treatments. PSC values calculated for sandy loam treatments are more difficult to interpret. The expected result is that soils receiving KH_2PO_4 should tend to act as a P sources, as seen in the sandy clay loam textured soils, or that PSC across treatments would be comparable to that of the control. Instead, the data shows that increasing KH_2PO_4 application rate increases sandy loam soil PSC, opposite to that expected.

To expand further, spring wheat straw and grain P uptake results (discussed below) contradict PSC calculations as control and Al/O-WTR amended soils had comparable plant P uptake. This further corroborates the previously mentioned contention that exchange sites found within the extractable amorphous phases (i.e. Al_{Ox} and Fe_{Ox}) quantified to calculate PSC, while extractable, may already be satisfied when applied to soil. This stresses the distinction between extractability and availability. That is to say, an element or compound that can be extracted from a soil does not necessarily have the ability to interact with other constituents in soil. Occluded P is one such example that exemplifies this distinction. Highly insoluble Fe coatings surround soil particles and prevent P from reacting with the surrounding environment, yet it is still possible to chemically extract P within such Fe coatings. Thus, the data demonstrateds that while ammonium oxalate extraction and the PSC equation can be employed to determine a soils potential to sorb some quantity of P, such methods do not accurately account for the potential of amorphous phases to react with P in soil.

Lastly, it should be also be noted that the phosphorus sorption capacities as estimated here are likely inaccurate to some degree because the PSC equation does not account for Ca associated P. This is especially important because P is highly reactive with Ca and readily forms soil mineral precipitates in soils where Ca is readily available in high concentrations (such as the soils utilized in this study; **Table 2** and **Table 3**; Sposito, 1989). Expanding the current PSC equation to include Ca-P phases would greatly benefit the ability to accurately assess the potential for soils to act as P sources and sinks.

Inorganic Phosphorus Fractionation, Total and Organic Phosphorus

Inorganic P fractionation showed that soil inorganic P distribution was roughly equal across treatments, within soil P pools, and within respective soil textures. Inorganic P fractions were summed and then subtracted from total P concentrations to further investigate organic P distribution across treatments. While significant differences in total P did exist across treatments in both soil textures, it is difficult to say why this difference may exist when only looking at the inorganic P fractions. However, when utilizing both the inorganic fractions and organic P, some insight is gained. While organic P results show that no treatments are significantly different from the control soil, the target and high KH_2PO_4 treatments show significantly elevated organic P quantities when compared to Al/O-WTR treated soils which can explain the significant differences observed in total P. This also vaguely suggests that the organic soil P pool within Al/O-WTR treated sandy clay loam soils was degraded to a greater extent than the organic soil P pools in the target and high KH_2PO_4 amended soils.

Moreover, enzymatic activity (discussed below) suggests that Al/O-WTR application may stimulate microbial communities and increase organic P mineralization for plant uptake. Though soil carbon content and fluxes were not measured, prior research has shown that Al/O-

WTR can contribute between ~3000-5000 mg kg^{-1} dissolved organic C to solution (Zohar et al., 2017) and implies that Al/O-WTR application diminishes carbon limitations that restrict microbial community productivity (Stock et al., 2019). This may indicate that organic P was subject to less microbial degradation in the target and high KH_2PO_4 treatments, which may explain the comparatively elevated organic P quantities in those treatments. Therefore, investigating microorganism activity as a function of Al/O-WTR derived organic carbon content is a research worthy endeavor that may elucidate the mechanism by which Al/O-WTR desorbs sorbed organic P.

When combining enzymatic activity data with spring wheat and grain P uptake results (also discussed below), results suggest that organic P mineralization stimulated by Al/O-WTR amendment is a comparable plant-available P source in low clay content soils. Plants grown in soils with greater clay fractions, on the other hand, appear to not benefit from Al/O-WTR driven P mineralization to the same extent, likely due to mineralized P quickly forming associations with clay mineral surfaces.

Olsen P

Results indicated that Olsen extractable P was overall greater in the sandy loam soil, though only significantly different in the sandy clay loam soil. This further demonstrates the comparative ease at which P becomes available in low clay content soils due to the lack of reactive clay surfaces that can bind P (Brady and Weil, 2010), resulting in greater available P quantities. As a whole, this data attests that Al/O-WTR is able to supply plant-available P at rates similar to KH_2PO_4 in coarse textured soils. Olsen extractable P concentrations in sandy clay loam soils show clearly elevated plant-available P in high KH_2PO_4 and target Al/O-WTR treatments, while all other treatments remained similar to control soil. These contradictory trends do not clearly advocate for or against the ability of Al/O-WTR to comparably supply plant-available P to fine-textured soil.

Soil Phosphatase Activity

In 2008, Bayley et al. showed that acid phosphomonoesterase activity was encouraged when co-applying Al-WTR and biosolids to soil. Though authors credited increased activity to Al-WTR inflicted P deficiency in soils as previous work had demonstrated (Margesin & Schinner, 1994), results exhibit comparable phosphomonoesterase activity in soils amended with Al/O-WTR to soils amended with KH_2PO_4. This suggests that Al/O-WTR has the ability to comparably perform to liquid P fertilizers and may not inflict P deficiencies in soil as raw Al-WTR have been shown to do.

Bayley et al. (2008) also reported that Al-WTR and biosolids co-application decreased phosphodiesterase activity in soil. Results, again, show an opposite effect when comparing Al/O-WTR and KH_2PO_4 applications in soil. Instead, it was observed that phosphodiesterase activity in both soil textures was, for the most part, significantly greater in those amended with Al/O-WTR than those amended with KH_2PO_4. One explanation for this trend is the inhibitory effect that orthophosphate, the primary P form supplied to soil by KH_2PO_4, has on phosphodiesterase activity (Tabatabai, 1994). Another potential explanation for this trend could be the organic and biological nature of Al/O-WTR. As phosphodiesterase is most commonly known for its ability to degrade nucleotides (Tabatabai, 1994), Al/O-WTR application could introduce biological molecules rich in nucleic acids to soil and promote phosphodiesterase activity.

As previously mentioned, it has been shown that available carbon is the primary limiting nutrient for soil microorganisms (Stock et al., 2019). Phosphatase enzyme assays (**Figure 3.13** and **Figure 3.14**) indicate that heightened enzyme activity occurred in the sandy clay loam. This data, in combination with inorganic P fractionation data, suggest that P availability from Al/O-WTR in soils with high clay fractions is a microbially driven process. Thus, enhanced enzymatic activity in the sandy clay loam soil could be related to organic compounds from Al/O-WTR interacting with clay mineral surfaces. This serves to further supports the notion that organic C added to soil by Al/O-WTR could be responsible for increased enzymatic activity in soils that received Al/O-WTR compared to soils that received KH_2PO_4.

Spring Wheat Grain and Straw Phosphorus Uptake

Spring wheat grain and straw P uptake in the sandy loam soil were approximately equal across treatments, suggesting that P supplied by Al/O-WTR was comparably available to P supplied by KH_2PO_4. Sandy clay loam soils, on the other hand, showed that P availability from Al/O-WTR was generally lower than P supplied by KH_2PO_4. Intriguingly, plant-available P assessments (Olsen P; inorganic P fractionation soluble P; AB-DTPA extractable P) demonstrated that sandy loam soils had overall greater plant-available P when compared to sandy clay loam soils, yet overall grain and straw P uptake was markedly greater in sandy clay loam soils. This discrepancy can be explained by diffusion, the primary mechanism by which P is transported to plants (Troeh & Thompson, 1993).

As previously mentioned, sandy clay loam soils required less water to maintain the specified soil moisture contents. Fewer irrigation events is related to greater grain and straw P concentrations because diffusive gradients require water to transport ions through porous solid media such as soil. Plants utilize P near roots to create regions in soil with low P concentrations, producing a diffusive gradient that promotes P movement towards plant roots. Without soil moisture this process cannot occur. Thus, the greater extent to which clay textured soils retain moisture contributed to greater continual P plant accumulation over time compared to the sandy loam soil. Finally, AB-DTPA extraction showed that plant-available P was notably greater in the target and high KH_2PO_4 treated sandy clay loam soils and explains the comparatively lower plant and grain P uptake in the other treatments. The data ultimately suggest that applying Al/O-WTR to coarser textured soils will optimize the potential for Al/O-WTR to act as a plant-available P source.

Conclusions and Implications

The results of this work suggest that the capacity for Al/O-WTR to supply plant-available P depends on soil texture and related properties. These results presented evidence to suggest that Al/O-WTR may be an effective source of plant-available P in low clay content soils when compared to liquid P fertilizers. In soils with higher clay fractions, however, the data indicates that liquid P fertilizers will result in greater plant P uptake. It was speculated that this difference in Al/O-WTR P supply capacity was a function of wetting and drying periods that affected the rate at which P can diffuse through soil to plant roots, as influenced by soil texture. Thus, the hypothesis that Al/O-WTR can comparably supply plant-available P to soils for plant uptake was accepted in coarser textured soils, but was rejected in finer textured soils.

Increases in soil Al_{Ox} with increasing Al/O-WTR application was suggested by PSC data, suggesting that Al/O-WTR amended soils would acts as P sinks. However, P associated with Al_{Ox} and Fe_{Ox} did not change across treatments, and thus this questions the extent to which Al/O-WTR can react with nearby free P ions and compounds. Despite significant differences in soil total P concentrations across treatments, the results suggested that organic P added to soil via Al/O-WTR application does not significantly increase organic soil P. Therefore, the hypothesis that Al/O-WTR application could contribute significant masses of organic P to the organic soil P pool and would increase soil mineralization as a consequence was rejected.

Rather, we suggest that Al/O-WTR application possibly enhanced the ability of soil microorganisms to mineralize the existing organic soil P pool, firstly, because the organic soil P pools in Al/O-WTR treated soils were degraded. Though the organic soil P pool masses were not significantly affected by Al/O-WTR application, enzymatic activity results indicated that Al/O-WTR application stimulated soil microorganism communities. The heightened enzyme activity suggested that Al/O-WTR application promoted P mineralization and positively influenced the extent to which plants were capable of accessing plant-available P from Al/O-WTR. Based on other studies, it seems possible that Al/O-WTR may supply significant organic C quantities that stimulate microbial degradation of organic P and could enhance the extent to which plant roots can access P from the existing organic soil P pool. Future work should aim to characterize specific mechanisms for P release to soil solution from Al/O-WTR and characterize how repeated Al/O-WTR applications might affect soil P quantities and (in)organic P pools over time.

Supplying plant-available nutrients to agricultural soils is a requirement to maintain soil fertility and protect global food security. As such, striking a balance between fertilization practices, waste management, and environmental quality is imperative to ensuring a sustainable future. On a global basis it is currently estimated that 10,000 tons Al-WTR are produced each day (Babatunde and Zhao). Under the assumption that all Al-WTR produced can comparably retain P as the Al-WTR used in this study (i.e. ~10,000 mg kg^{-1}), it would be possible to capture 100,000 kg P per day; however with nearly 1 billion swine (271 million animal units) raised in 2018 (FAO, 2018), the P inputs from swine manure far exceed the ability of Al-WTR to retain P entering wastewater. Assuming that, on average, one animal unit produces ~34L of manure per day and that the average P concentration in swine wastewater lagoon sludge is 2498 mg L^{-1}

(Chastain et al., 2003), Al-WTR can only retain approximately 0.4% of the P produced in swine manure each day.

Therefore, future studies should investigate optimization of Al-WTR waste products for enhanced P sorption. Additional research to investigate methods, such as co-blending with municipal or other similar wastewater streams, to advance the currently known limitations could also prove useful in agronomic systems. Advancing technologies and management strategies to promote zero waste are essential to maintaining long term global sustainability and productivity.

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CHAPTER IV SUMMARY AND CONCLUSIONS

Population models predict that our planet will be home to 9-10 billion humans by the year 2050. Climate change models suggest altered weather patterns, shifts in resource availability, and human displacement will exacerbate arable land degradation. Thus, technological developments that promote sustainable resource management are crucial to maintaining global human populations, improving living standards, and enhancing quality of life. Without such developments, all life could be subjected to suboptimal living conditions.

Our ability to maintain global food security is one parameter that will significantly affect the quality of life in the face of such challenges. Generally speaking, agricultural systems that generate high quality/high quantity yields require hefty water and fertilizer inputs. Cropland irrigation demands can negatively impact water cycling, water quality, and soil health. Fertilizer production, transport, and application are costly, energy intensive processes that can similarly harm environmental quality. Research has shown that current irrigation and fertilizer management strategies could be improved to optimize fertilizer and water use efficiency. While technological advancement can certainly aid in improving efficient resource management on farm, it is imperative that we strive to develop systems that increase resource use efficiency and decrease environmental burdens.

The research we conducted aspired to advance efficient resource management and reduce environmental afflictions by combining agricultural and municipal wastes to reduce environmental phosphorus (P) contamination sources while subsequently developing a new P-supplying fertilizer. Specifically, our work aimed to further promote sustainable resource management by providing municipalities with an alternative strategy to aluminum water treatment residuals (Al-WTR) disposal, which are typically landfilled. Positive results from our work demonstrate that it could be possible to achieve these overarching goals.

Results from our initial laboratory work suggested that combining Al-WTR can efficiently remove significant quantities (>99%) of organic P from swine wastewater. Subsequent laboratory investigations further indicated that organic P removed from swine wastewater by Al-WTR could be returned to solution. This implied that the Al-WTR laden with organic P (Al/O-WTR) could possibly be used to supply soils with plant-available P. We followed these results with a greenhouse study to quantitatively assess the ability of Al/O-WTR to supply soil with plant-available P. Our results proved that applying Al/O-WTR to coarse textured soils was comparable to liquid P fertilizer application. In fine textured soils, however, Al/O-WTR application was a less effective plant-available P source than inorganic P fertilizer, likely due to the ability of clay minerals to protect organic moieties from degradation.

Completing this research also brought forth insight for future studies. Our data shows that soil microorganisms may have been stimulated by Al/O-WTR application, suggesting that soil microorganism dynamics may be influenced by Al/O-WTR derived materials, such as organic carbon. Investigating soil microorganism activity and populations dynamics as a function of Al/O-WTR added organic carbon might elucidate mechanisms by which organic P is released from Al/O-WTR and returned to soil solution in plant-available forms.

Investigating Al/O-WTR optimization for plant-available P release characteristics could expand sustainable agricultural practices and reduce environmental stresses associated with P contamination. Successful progress in this realm could lead to large-scale development of P fertilizers wholly derived from agricultural and municipal wastes, which could support farmers by providing them an efficient, cost effective alternative to traditional P fertilizers.

APPENDIX

Appendix Table 1.

P Sorption to Al-WTR Over Time						
Time Shaken	Average Total P (mg kg^{-1})	Total P Standard Error of the Mean (mg kg^{-1})	Average Ortho-P (mg kg^{-1})	Ortho-P Standard Error of the Mean (mg kg^{-1})	Average Organic P (mg kg^{-1})	Organic P Standard Error of the Mean (mg kg^{-1})
1 Hour	40.00	5.07	0.17	0.05	39.83	5.13
2 Hours	54.00	0.58	0.03	0.01	53.97	0.58
4 Hours	61.33	0.17	0.10	0.08	61.23	0.14
8 Hours	67.33	0.33	0.03	0.00	67.31	0.33
16 Hours	71.33	0.44	0.03	0.00	71.31	0.44
1 Day	2.12	0.06	1.72	0.05	0.40	0.04
2 Days	2.05	0.05	0.54	0.02	1.51	0.04
3 Days	1.91	0.05	0.30	0.02	1.61	0.05
4 Days	1.43	0.05	0.12	0.01	1.31	0.04
5 Days	1.01	0.04	0.06	0.01	0.95	0.04
6 Days	0.83	0.03	0.06	0.01	0.77	0.04
7 Days	0.75	0.02	0.00	0.00	0.75	0.02
14 Days	72.80	0.20	0.03	0.00	72.78	0.20
21 Days	74.60	0.19	0.03	0.00	74.58	0.19

Appendix Table 2.

P Desorption from Al/O-WTR Over Time		
Time Shaken	Average P Desorbed (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
1 day	2172.89	111.96
2 days	2334.93	206.18
4 days	2350.55	212.79
7 days	2872.55	142.94
14 days	3440.80	338.40
21 days	2605.90	111.47
28 days	2931.25	536.07
60 days	1543.79	358.05
90 days	1672.28	93.14

Appendix Table 3.

Sandy Clay Loam Soil AB-DTPA Extractable Elements Initial Assessment			
Soil Texture	Element	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Sandy Clay Loam	Al	0.00	0.00
Sandy Clay Loam	Ag	0.00	0.00
Sandy Clay Loam	B	0.06	0.00
Sandy Clay Loam	Ba	0.39	0.00
Sandy Clay Loam	Be	0.00	0.00
Sandy Clay Loam	Cd	0.06	0.00
Sandy Clay Loam	Cr	0.01	0.00
Sandy Clay Loam	Cu	1.49	0.00
Sandy Clay Loam	Fe	4.68	0.00
Sandy Clay Loam	K	110.35	9.55
Sandy Clay Loam	Mg	401.53	1.31
Sandy Clay Loam	Mn	0.27	0.01
Sandy Clay Loam	Mo	0.00	0.00
Sandy Clay Loam	Na	177.06	7.51
Sandy Clay Loam	Ni	0.55	0.01
Sandy Clay Loam	P	0.69	0.32
Sandy Clay Loam	Pb	1.18	0.02
Sandy Clay Loam	Sr	3.24	0.03
Sandy Clay Loam	Ti	0.03	0.00
Sandy Clay Loam	V	0.33	0.00
Sandy Clay Loam	Zn	0.62	0.02

Appendix Table 4.

Sandy Loam Soil AB-DTPA Extract Elements Initial Assessment			
Soil Texture	Element	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Sandy Loam	Ag	0.00	0.00
Sandy Loam	B	0.47	0.00
Sandy Loam	Ba	0.28	0.00
Sandy Loam	Be	0.00	0.00
Sandy Loam	Cd	0.03	0.00
Sandy Loam	Cr	0.00	0.00
Sandy Loam	Cu	0.67	0.01
Sandy Loam	Fe	2.73	0.02
Sandy Loam	K	692.47	2.86
Sandy Loam	Mg	456.66	1.82
Sandy Loam	Mn	0.25	0.01
Sandy Loam	Mo	0.00	0.00
Sandy Loam	Na	399.63	2.02
Sandy Loam	Ni	0.09	0.00
Sandy Loam	P	14.99	0.50
Sandy Loam	Pb	0.41	0.01
Sandy Loam	Sr	2.46	0.01
Sandy Loam	Ti	0.03	0.00
Sandy Loam	V	0.19	0.00
Sandy Loam	Zn	0.50	0.00

Appendix Table 5.

Sandy Clay Loam Soil AB-DTPA Extractable Elements Post Harvest			
Element	Treatment	Mean Concentration ($mg\ kg^{-1}$)	Standard Error of the Mean ($mg\ kg^{-1}$)
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.04	0.00
Ag	High KH_2PO_4	0.04	0.00
Al	Control	0.00	0.00
Al	Low Al/O-WTR	0.00	0.00
Al	Target Al/O-WTR	0.00	0.00
Al	High Al/O-WTR	0.06	0.02
Al	Low KH_2PO_4	0.00	0.00
Al	Target KH_2PO_4	0.00	0.00
Al	High KH_2PO_4	0.00	0.00
B	Control	0.06	0.00
B	Low Al/O-WTR	0.06	0.01
B	Target Al/O-WTR	0.08	0.00
B	High Al/O-WTR	0.07	0.00
B	Low KH_2PO_4	0.09	0.00
B	Target KH_2PO_4	0.14	0.01
B	High KH_2PO_4	0.14	0.01
Ba	Control	0.50	0.02
Ba	Low Al/O-WTR	0.55	0.02
Ba	Target Al/O-WTR	0.55	0.02
Ba	High Al/O-WTR	0.56	0.01
Ba	Low KH_2PO_4	0.59	0.02
Ba	Target KH_2PO_4	0.81	0.02
Ba	High KH_2PO_4	0.81	0.02
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.00	0.00

Be	High KH_2PO_4	0.00	0.00
Ca	Control	333.66	4.35
Ca	Low Al/O-WTR	339.16	6.23
Ca	Target Al/O-WTR	354.17	3.91
Ca	High Al/O-WTR	358.23	2.72
Ca	Low KH_2PO_4	360.79	2.20
Ca	Target KH_2PO_4	461.63	4.12
Ca	High KH_2PO_4	458.82	5.32
Cd	Control	0.00	0.00
Cd	Low Al/O-WTR	0.00	0.00
Cd	Target Al/O-WTR	0.00	0.00
Cd	High Al/O-WTR	0.00	0.00
Cd	Low KH_2PO_4	0.00	0.00
Cd	Target KH_2PO_4	0.00	0.00
Cd	High KH_2PO_4	0.00	0.00
Cr	Control	0.00	0.00
Cr	Low Al/O-WTR	0.00	0.00
Cr	Target Al/O-WTR	0.00	0.00
Cr	High Al/O-WTR	0.00	0.00
Cr	Low KH_2PO_4	0.00	0.00
Cr	Target KH_2PO_4	0.00	0.00
Cr	High KH_2PO_4	0.00	0.00
Cu	Control	1.83	0.54
Cu	Low Al/O-WTR	2.19	0.61
Cu	Target Al/O-WTR	2.81	1.57
Cu	High Al/O-WTR	2.69	1.20
Cu	Low KH_2PO_4	1.89	0.46
Cu	Target KH_2PO_4	3.95	0.85
Cu	High KH_2PO_4	3.17	0.43
Fe	Control	8.53	0.26
Fe	Low Al/O-WTR	8.74	0.70
Fe	Target Al/O-WTR	7.69	0.59
Fe	High Al/O-WTR	7.44	0.23
Fe	Low KH_2PO_4	6.11	0.23
Fe	Target KH_2PO_4	8.35	0.49
Fe	High KH_2PO_4	7.24	0.49
K	Control	141.41	3.07
K	Low Al/O-WTR	146.43	11.58

K	Target Al/O-WTR	129.46	5.60
K	High Al/O-WTR	128.05	2.63
K	Low KH_2PO_4	128.76	3.35
K	Target KH_2PO_4	161.01	3.36
K	High KH_2PO_4	170.00	2.22
Mg	Control	368.76	5.41
Mg	Low Al/O-WTR	372.15	6.18
Mg	Target Al/O-WTR	375.90	3.44
Mg	High Al/O-WTR	371.14	2.40
Mg	Low KH_2PO_4	381.63	2.76
Mg	Target KH_2PO_4	442.22	2.69
Mg	High KH_2PO_4	438.02	4.91
Mn	Control	3.50	0.41
Mn	Low Al/O-WTR	3.50	0.52
Mn	Target Al/O-WTR	3.87	0.70
Mn	High Al/O-WTR	3.48	0.43
Mn	Low KH_2PO_4	2.81	0.31
Mn	Target KH_2PO_4	3.96	0.58
Mn	High KH_2PO_4	3.38	0.49
Mo	Control	0.00	0.00
Mo	Low Al/O-WTR	0.00	0.00
Mo	Target Al/O-WTR	0.00	0.00
Mo	High Al/O-WTR	0.00	0.00
Mo	Low KH_2PO_4	0.00	0.00
Mo	Target KH_2PO_4	0.00	0.00
Mo	High KH_2PO_4	0.00	0.00
Na	Control	200.48	5.10
Na	Low Al/O-WTR	208.12	14.09
Na	Target Al/O-WTR	189.68	4.40
Na	High Al/O-WTR	182.89	3.02
Na	Low KH_2PO_4	172.72	3.69
Na	Target KH_2PO_4	196.75	3.48
Na	High KH_2PO_4	194.34	8.25
Ni	Control	0.67	0.02
Ni	Low Al/O-WTR	0.71	0.03
Ni	Target Al/O-WTR	0.71	0.02
Ni	High Al/O-WTR	0.70	0.01
Ni	Low KH_2PO_4	0.72	0.02

Ni	Target KH_2PO_4	0.87	0.01
Ni	High KH_2PO_4	0.84	0.01
P	Control	0.06	0.04
P	Low Al/O-WTR	0.04	0.04
P	Target Al/O-WTR	0.12	0.10
P	High Al/O-WTR	0.04	0.04
P	Low KH_2PO_4	0.63	0.10
P	Target KH_2PO_4	2.49	0.30
P	High KH_2PO_4	6.08	0.52
Pb	Control	1.60	0.22
Pb	Low Al/O-WTR	1.42	0.04
Pb	Target Al/O-WTR	1.35	0.05
Pb	High Al/O-WTR	1.38	0.03
Pb	Low KH_2PO_4	1.40	0.02
Pb	Target KH_2PO_4	1.55	0.02
Pb	High KH_2PO_4	1.47	0.04
Sr	Control	1.29	0.82
Sr	Low Al/O-WTR	0.62	0.62
Sr	Target Al/O-WTR	0.00	0.00
Sr	High Al/O-WTR	0.67	0.67
Sr	Low KH_2PO_4	0.00	0.00
Sr	Target KH_2PO_4	0.00	0.00
Sr	High KH_2PO_4	0.00	0.00
Ti	Control	0.00	0.00
Ti	Low Al/O-WTR	0.00	0.00
Ti	Target Al/O-WTR	0.00	0.00
Ti	High Al/O-WTR	0.00	0.00
Ti	Low KH_2PO_4	0.00	0.00
Ti	Target KH_2PO_4	0.02	0.00
Ti	High KH_2PO_4	0.02	0.00
V	Control	0.31	0.01
V	Low Al/O-WTR	0.31	0.01
V	Target Al/O-WTR	0.33	0.01
V	High Al/O-WTR	0.33	0.00
V	Low KH_2PO_4	0.38	0.01
V	Target KH_2PO_4	0.57	0.01
V	High KH_2PO_4	0.59	0.01
Zn	Control	0.67	0.12

Zn	Low Al/O-WTR	0.77	0.14
Zn	Target Al/O-WTR	0.87	0.33
Zn	High Al/O-WTR	0.88	0.25
Zn	Low KH_2PO_4	0.78	0.11
Zn	Target KH_2PO_4	1.28	0.19
Zn	High KH_2PO_4	1.31	0.25

Appendix Table 6.

Sandy Loam Soil AB-DTPA Extractable Elements Post Harvest			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.02	0.01
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.02	0.00
Ag	Low KH_2PO_4	0.02	0.00
Ag	Target KH_2PO_4	0.01	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	0.00	0.00
Al	Low Al/O-WTR	0.03	0.00
Al	Target Al/O-WTR	0.03	0.01
Al	High Al/O-WTR	0.03	0.01
Al	Low KH_2PO_4	0.00	0.00
Al	Target KH_2PO_4	0.00	0.00
Al	High KH_2PO_4	0.00	0.00
B	Control	0.60	0.03
B	Low Al/O-WTR	0.51	0.02
B	Target Al/O-WTR	0.55	0.02
B	High Al/O-WTR	0.52	0.02
B	Low KH_2PO_4	0.37	0.08
B	Target KH_2PO_4	0.54	0.05
B	High KH_2PO_4	0.59	0.03
Ba	Control	0.58	0.02
Ba	Low Al/O-WTR	0.49	0.02
Ba	Target Al/O-WTR	0.52	0.01
Ba	High Al/O-WTR	0.40	0.01
Ba	Low KH_2PO_4	0.35	0.04
Ba	Target KH_2PO_4	0.39	0.04
Ba	High KH_2PO_4	0.43	0.02
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.01	0.00

Be	High KH_2PO_4	0.02	0.00
Ca	Control	483.14	10.53
Ca	Low Al/O-WTR	392.91	22.58
Ca	Target Al/O-WTR	398.06	15.60
Ca	High Al/O-WTR	360.27	15.20
Ca	Low KH_2PO_4	287.58	20.64
Ca	Target KH_2PO_4	330.89	31.48
Ca	High KH_2PO_4	355.07	13.32
Cd	Control	0.01	0.01
Cd	Low Al/O-WTR	0.01	0.00
Cd	Target Al/O-WTR	0.02	0.00
Cd	High Al/O-WTR	0.04	0.00
Cd	Low KH_2PO_4	0.03	0.01
Cd	Target KH_2PO_4	0.04	0.00
Cd	High KH_2PO_4	0.05	0.00
Cr	Control	0.00	0.00
Cr	Low Al/O-WTR	0.00	0.00
Cr	Target Al/O-WTR	0.00	0.00
Cr	High Al/O-WTR	0.00	0.00
Cr	Low KH_2PO_4	0.00	0.00
Cr	Target KH_2PO_4	0.00	0.00
Cr	High KH_2PO_4	0.00	0.00
Cu	Control	0.85	0.13
Cu	Low Al/O-WTR	0.91	0.20
Cu	Target Al/O-WTR	1.42	0.25
Cu	High Al/O-WTR	1.32	0.13
Cu	Low KH_2PO_4	1.62	0.29
Cu	Target KH_2PO_4	1.42	0.13
Cu	High KH_2PO_4	1.25	0.09
Fe	Control	5.52	0.26
Fe	Low Al/O-WTR	4.86	0.17
Fe	Target Al/O-WTR	6.12	0.21
Fe	High Al/O-WTR	6.22	0.16
Fe	Low KH_2PO_4	4.66	0.47
Fe	Target KH_2PO_4	5.14	0.45
Fe	High KH_2PO_4	5.37	0.30
K	Control	498.66	18.88
K	Low Al/O-WTR	494.52	7.51

K	Target Al/O-WTR	498.53	9.26
K	High Al/O-WTR	485.35	12.33
K	Low KH_2PO_4	439.50	33.45
K	Target KH_2PO_4	462.83	29.71
K	High KH_2PO_4	527.69	27.54
Mg	Control	503.14	14.50
Mg	Low Al/O-WTR	446.17	12.45
Mg	Target Al/O-WTR	450.79	7.77
Mg	High Al/O-WTR	404.43	12.43
Mg	Low KH_2PO_4	357.99	3.82
Mg	Target KH_2PO_4	398.73	24.94
Mg	High KH_2PO_4	431.16	15.27
Mn	Control	4.44	0.19
Mn	Low Al/O-WTR	4.50	0.38
Mn	Target Al/O-WTR	5.39	0.16
Mn	High Al/O-WTR	5.19	0.43
Mn	Low KH_2PO_4	3.64	0.67
Mn	Target KH_2PO_4	3.86	0.44
Mn	High KH_2PO_4	4.50	0.32
Mo	Control	0.02	0.01
Mo	Low Al/O-WTR	0.03	0.00
Mo	Target Al/O-WTR	0.03	0.00
Mo	High Al/O-WTR	0.06	0.00
Mo	Low KH_2PO_4	0.04	0.01
Mo	Target KH_2PO_4	0.06	0.01
Mo	High KH_2PO_4	0.08	0.01
Na	Control	438.50	15.81
Na	Low Al/O-WTR	423.36	6.42
Na	Target Al/O-WTR	404.97	5.55
Na	High Al/O-WTR	373.23	13.04
Na	Low KH_2PO_4	367.00	25.49
Na	Target KH_2PO_4	375.48	23.25
Na	High KH_2PO_4	407.63	26.63
Ni	Control	0.30	0.03
Ni	Low Al/O-WTR	0.28	0.01
Ni	Target Al/O-WTR	0.34	0.01
Ni	High Al/O-WTR	0.35	0.02
Ni	Low KH_2PO_4	0.39	0.13

Ni	Target KH_2PO_4	0.31	0.03
Ni	High KH_2PO_4	0.35	0.02
P	Control	9.36	0.24
P	Low Al/O-WTR	10.29	0.53
P	Target Al/O-WTR	10.71	0.28
P	High Al/O-WTR	10.09	0.70
P	Low KH_2PO_4	8.15	0.75
P	Target KH_2PO_4	13.60	1.39
P	High KH_2PO_4	14.28	1.16
Pb	Control	0.70	0.04
Pb	Low Al/O-WTR	0.61	0.02
Pb	Target Al/O-WTR	0.77	0.07
Pb	High Al/O-WTR	0.70	0.03
Pb	Low KH_2PO_4	0.81	0.27
Pb	Target KH_2PO_4	0.64	0.06
Pb	High KH_2PO_4	0.76	0.05
Sr	Control	0.67	0.67
Sr	Low Al/O-WTR	2.40	0.76
Sr	Target Al/O-WTR	3.75	0.08
Sr	High Al/O-WTR	2.52	0.51
Sr	Low KH_2PO_4	3.17	0.44
Sr	Target KH_2PO_4	2.45	0.52
Sr	High KH_2PO_4	2.63	0.54
Ti	Control	0.05	0.01
Ti	Low Al/O-WTR	0.08	0.00
Ti	Target Al/O-WTR	0.08	0.00
Ti	High Al/O-WTR	0.04	0.00
Ti	Low KH_2PO_4	0.02	0.00
Ti	Target KH_2PO_4	0.03	0.00
Ti	High KH_2PO_4	0.03	0.00
V	Control	0.45	0.11
V	Low Al/O-WTR	0.66	0.01
V	Target Al/O-WTR	0.67	0.01
V	High Al/O-WTR	0.26	0.01
V	Low KH_2PO_4	0.19	0.01
V	Target KH_2PO_4	0.28	0.04
V	High KH_2PO_4	0.33	0.03
Zn	Control	0.59	0.07

Zn	Low Al/O-WTR	0.56	0.06
Zn	Target Al/O-WTR	0.79	0.09
Zn	High Al/O-WTR	0.98	0.07
Zn	Low KH_2PO_4	0.57	0.12
Zn	Target KH_2PO_4	0.86	0.07
Zn	High KH_2PO_4	0.90	0.03

Appendix Table 7.

Spring Wheat Straw Elemental Uptake in Sandy Clay Loam Soil			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.00	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	0.00	0.00
Al	Low Al/O-WTR	0.00	0.00
Al	Target Al/O-WTR	0.00	0.00
Al	High Al/O-WTR	0.00	0.00
Al	Low KH_2PO_4	0.00	0.00
Al	Target KH_2PO_4	0.00	0.00
Al	High KH_2PO_4	0.01	0.00
B	Control	0.01	0.00
B	Low Al/O-WTR	0.01	0.00
B	Target Al/O-WTR	0.01	0.00
B	High Al/O-WTR	0.01	0.00
B	Low KH_2PO_4	0.01	0.00
B	Target KH_2PO_4	0.02	0.00
B	High KH_2PO_4	0.02	0.00
Ba	Control	0.00	0.00
Ba	Low Al/O-WTR	0.00	0.00
Ba	Target Al/O-WTR	0.00	0.00
Ba	High Al/O-WTR	0.00	0.00
Ba	Low KH_2PO_4	0.00	0.00
Ba	Target KH_2PO_4	0.00	0.00
Ba	High KH_2PO_4	0.00	0.00
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.00	0.00

Be	High KH_2PO_4	0.00	0.00
Ca	Control	2.10	0.12
Ca	Low Al/O-WTR	2.12	0.11
Ca	Target Al/O-WTR	2.03	0.09
Ca	High Al/O-WTR	2.13	0.08
Ca	Low KH_2PO_4	3.13	0.12
Ca	Target KH_2PO_4	4.02	0.33
Ca	High KH_2PO_4	4.04	0.31
Cd	Control	0.00	0.00
Cd	Low Al/O-WTR	0.00	0.00
Cd	Target Al/O-WTR	0.00	0.00
Cd	High Al/O-WTR	0.00	0.00
Cd	Low KH_2PO_4	0.00	0.00
Cd	Target KH_2PO_4	0.00	0.00
Cd	High KH_2PO_4	0.00	0.00
Cr	Control	0.00	0.00
Cr	Low Al/O-WTR	0.00	0.00
Cr	Target Al/O-WTR	0.00	0.00
Cr	High Al/O-WTR	0.00	0.00
Cr	Low KH_2PO_4	0.00	0.00
Cr	Target KH_2PO_4	0.00	0.00
Cr	High KH_2PO_4	0.00	0.00
Cu	Control	0.00	0.00
Cu	Low Al/O-WTR	0.00	0.00
Cu	Target Al/O-WTR	0.00	0.00
Cu	High Al/O-WTR	0.00	0.00
Cu	Low KH_2PO_4	0.00	0.00
Cu	Target KH_2PO_4	0.00	0.00
Cu	High KH_2PO_4	0.00	0.00
Fe	Control	0.01	0.00
Fe	Low Al/O-WTR	0.01	0.00
Fe	Target Al/O-WTR	0.01	0.00
Fe	High Al/O-WTR	0.01	0.00
Fe	Low KH_2PO_4	0.01	0.00
Fe	Target KH_2PO_4	0.02	0.00
Fe	High KH_2PO_4	0.02	0.00
K	Control	8.23	0.74
K	Low Al/O-WTR	9.84	0.56

K	Target Al/O-WTR	9.48	0.29
K	High Al/O-WTR	9.38	0.48
K	Low KH_2PO_4	11.13	0.46
K	Target KH_2PO_4	13.39	0.93
K	High KH_2PO_4	15.23	1.43
Mg	Control	1.13	0.06
Mg	Low Al/O-WTR	1.18	0.04
Mg	Target Al/O-WTR	1.16	0.04
Mg	High Al/O-WTR	1.13	0.04
Mg	Low KH_2PO_4	1.59	0.06
Mg	Target KH_2PO_4	1.97	0.08
Mg	High KH_2PO_4	1.98	0.09
Mn	Control	0.02	0.00
Mn	Low Al/O-WTR	0.02	0.00
Mn	Target Al/O-WTR	0.02	0.00
Mn	High Al/O-WTR	0.02	0.00
Mn	Low KH_2PO_4	0.02	0.00
Mn	Target KH_2PO_4	0.03	0.00
Mn	High KH_2PO_4	0.04	0.00
Mo	Control	0.00	0.00
Mo	Low Al/O-WTR	0.00	0.00
Mo	Target Al/O-WTR	0.00	0.00
Mo	High Al/O-WTR	0.00	0.00
Mo	Low KH_2PO_4	0.00	0.00
Mo	Target KH_2PO_4	0.00	0.00
Mo	High KH_2PO_4	0.00	0.00
Na	Control	0.21	0.05
Na	Low Al/O-WTR	0.19	0.03
Na	Target Al/O-WTR	0.27	0.03
Na	High Al/O-WTR	0.30	0.05
Na	Low KH_2PO_4	0.48	0.12
Na	Target KH_2PO_4	0.43	0.09
Na	High KH_2PO_4	0.47	0.08
Ni	Control	0.00	0.00
Ni	Low Al/O-WTR	0.00	0.00
Ni	Target Al/O-WTR	0.00	0.00
Ni	High Al/O-WTR	0.00	0.00
Ni	Low KH_2PO_4	0.00	0.00

Ni	Target KH_2PO_4	0.00	0.00
Ni	High KH_2PO_4	0.00	0.00
P	Control	0.14	0.03
P	Low Al/O-WTR	0.17	0.03
P	Target Al/O-WTR	0.14	0.03
P	High Al/O-WTR	0.11	0.02
P	Low KH_2PO_4	0.24	0.04
P	Target KH_2PO_4	0.36	0.03
P	High KH_2PO_4	0.45	0.12
Pb	Control	0.00	0.00
Pb	Low Al/O-WTR	0.00	0.00
Pb	Target Al/O-WTR	0.00	0.00
Pb	High Al/O-WTR	0.00	0.00
Pb	Low KH_2PO_4	0.00	0.00
Pb	Target KH_2PO_4	0.00	0.00
Pb	High KH_2PO_4	0.00	0.00
Sr	Control	0.04	0.00
Sr	Low Al/O-WTR	0.04	0.00
Sr	Target Al/O-WTR	0.04	0.00
Sr	High Al/O-WTR	0.04	0.00
Sr	Low KH_2PO_4	0.06	0.00
Sr	Target KH_2PO_4	0.08	0.01
Sr	High KH_2PO_4	0.08	0.01
Ti	Control	0.00	0.00
Ti	Low Al/O-WTR	0.00	0.00
Ti	Target Al/O-WTR	0.00	0.00
Ti	High Al/O-WTR	0.00	0.00
Ti	Low KH_2PO_4	0.00	0.00
Ti	Target KH_2PO_4	0.00	0.00
Ti	High KH_2PO_4	0.00	0.00
V	Control	0.00	0.00
V	Low Al/O-WTR	0.00	0.00
V	Target Al/O-WTR	0.00	0.00
V	High Al/O-WTR	0.00	0.00
V	Low KH_2PO_4	0.00	0.00
V	Target KH_2PO_4	0.00	0.00
V	High KH_2PO_4	0.00	0.00
Zn	Control	0.02	0.00

Zn	Low Al/O-WTR	0.02	0.00
Zn	Target Al/O-WTR	0.02	0.00
Zn	High Al/O-WTR	0.02	0.00
Zn	Low KH_2PO_4	0.01	0.00
Zn	Target KH_2PO_4	0.01	0.00
Zn	High KH_2PO_4	0.01	0.00

Appendix Table 8.

Spring Wheat Straw Elemental Uptake in Sandy Loam Soil			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.00	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	0.00	0.00
Al	Low Al/O-WTR	0.00	0.00
Al	Target Al/O-WTR	0.00	0.00
Al	High Al/O-WTR	0.00	0.00
Al	Low KH_2PO_4	0.00	0.00
Al	Target KH_2PO_4	0.00	0.00
Al	High KH_2PO_4	0.00	0.00
B	Control	0.00	0.00
B	Low Al/O-WTR	0.01	0.00
B	Target Al/O-WTR	0.01	0.00
B	High Al/O-WTR	0.01	0.00
B	Low KH_2PO_4	0.01	0.00
B	Target KH_2PO_4	0.01	0.00
B	High KH_2PO_4	0.01	0.00
Ba	Control	0.00	0.00
Ba	Low Al/O-WTR	0.00	0.00
Ba	Target Al/O-WTR	0.00	0.00
Ba	High Al/O-WTR	0.00	0.00
Ba	Low KH_2PO_4	0.00	0.00
Ba	Target KH_2PO_4	0.00	0.00
Ba	High KH_2PO_4	0.00	0.00
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.00	0.00

Be	High KH_2PO_4	0.00	0.00
Ca	Control	1.85	0.11
Ca	Low Al/O-WTR	2.06	0.07
Ca	Target Al/O-WTR	2.15	0.23
Ca	High Al/O-WTR	1.90	0.15
Ca	Low KH_2PO_4	1.90	0.17
Ca	Target KH_2PO_4	2.20	0.25
Ca	High KH_2PO_4	2.02	0.21
Cd	Control	0.00	0.00
Cd	Low Al/O-WTR	0.00	0.00
Cd	Target Al/O-WTR	0.00	0.00
Cd	High Al/O-WTR	0.00	0.00
Cd	Low KH_2PO_4	0.00	0.00
Cd	Target KH_2PO_4	0.00	0.00
Cd	High KH_2PO_4	0.00	0.00
Cr	Control	0.00	0.00
Cr	Low Al/O-WTR	0.00	0.00
Cr	Target Al/O-WTR	0.00	0.00
Cr	High Al/O-WTR	0.00	0.00
Cr	Low KH_2PO_4	0.00	0.00
Cr	Target KH_2PO_4	0.00	0.00
Cr	High KH_2PO_4	0.00	0.00
Cu	Control	0.00	0.00
Cu	Low Al/O-WTR	0.00	0.00
Cu	Target Al/O-WTR	0.00	0.00
Cu	High Al/O-WTR	0.00	0.00
Cu	Low KH_2PO_4	0.00	0.00
Cu	Target KH_2PO_4	0.00	0.00
Cu	High KH_2PO_4	0.00	0.00
Fe	Control	0.00	0.00
Fe	Low Al/O-WTR	0.01	0.00
Fe	Target Al/O-WTR	0.00	0.00
Fe	High Al/O-WTR	0.00	0.00
Fe	Low KH_2PO_4	0.00	0.00
Fe	Target KH_2PO_4	0.01	0.00
Fe	High KH_2PO_4	0.01	0.00
K	Control	5.44	0.44
K	Low Al/O-WTR	7.48	0.48

K	Target Al/O-WTR	7.39	0.78
K	High Al/O-WTR	6.81	0.47
K	Low KH_2PO_4	7.54	0.93
K	Target KH_2PO_4	8.64	0.79
K	High KH_2PO_4	7.75	1.04
Mg	Control	1.25	0.07
Mg	Low Al/O-WTR	1.38	0.05
Mg	Target Al/O-WTR	1.48	0.12
Mg	High Al/O-WTR	1.28	0.07
Mg	Low KH_2PO_4	1.46	0.06
Mg	Target KH_2PO_4	1.59	0.12
Mg	High KH_2PO_4	1.59	0.11
Mn	Control	0.00	0.00
Mn	Low Al/O-WTR	0.01	0.00
Mn	Target Al/O-WTR	0.01	0.00
Mn	High Al/O-WTR	0.01	0.00
Mn	Low KH_2PO_4	0.01	0.00
Mn	Target KH_2PO_4	0.01	0.00
Mn	High KH_2PO_4	0.01	0.00
Mo	Control	0.00	0.00
Mo	Low Al/O-WTR	0.00	0.00
Mo	Target Al/O-WTR	0.00	0.00
Mo	High Al/O-WTR	0.00	0.00
Mo	Low KH_2PO_4	0.00	0.00
Mo	Target KH_2PO_4	0.00	0.00
Mo	High KH_2PO_4	0.00	0.00
Na	Control	1.46	0.19
Na	Low Al/O-WTR	1.29	0.17
Na	Target Al/O-WTR	1.21	0.17
Na	High Al/O-WTR	0.94	0.07
Na	Low KH_2PO_4	1.63	0.31
Na	Target KH_2PO_4	1.88	0.44
Na	High KH_2PO_4	1.92	0.59
Ni	Control	0.00	0.00
Ni	Low Al/O-WTR	0.00	0.00
Ni	Target Al/O-WTR	0.00	0.00
Ni	High Al/O-WTR	0.00	0.00
Ni	Low KH_2PO_4	0.00	0.00

Ni	Target KH_2PO_4	0.00	0.00
Ni	High KH_2PO_4	0.00	0.00
P	Control	0.11	0.02
P	Low Al/O-WTR	0.20	0.05
P	Target Al/O-WTR	0.30	0.08
P	High Al/O-WTR	0.16	0.03
P	Low KH_2PO_4	0.16	0.05
P	Target KH_2PO_4	0.16	0.06
P	High KH_2PO_4	0.13	0.03
Pb	Control	0.00	0.00
Pb	Low Al/O-WTR	0.00	0.00
Pb	Target Al/O-WTR	0.00	0.00
Pb	High Al/O-WTR	0.00	0.00
Pb	Low KH_2PO_4	0.00	0.00
Pb	Target KH_2PO_4	0.00	0.00
Pb	High KH_2PO_4	0.00	0.00
Sr	Control	0.03	0.00
Sr	Low Al/O-WTR	0.03	0.00
Sr	Target Al/O-WTR	0.03	0.00
Sr	High Al/O-WTR	0.03	0.00
Sr	Low KH_2PO_4	0.03	0.00
Sr	Target KH_2PO_4	0.03	0.00
Sr	High KH_2PO_4	0.03	0.00
Ti	Control	0.00	0.00
Ti	Low Al/O-WTR	0.00	0.00
Ti	Target Al/O-WTR	0.00	0.00
Ti	High Al/O-WTR	0.00	0.00
Ti	Low KH_2PO_4	0.00	0.00
Ti	Target KH_2PO_4	0.00	0.00
Ti	High KH_2PO_4	0.00	0.00
V	Control	0.00	0.00
V	Low Al/O-WTR	0.00	0.00
V	Target Al/O-WTR	0.00	0.00
V	High Al/O-WTR	0.00	0.00
V	Low KH_2PO_4	0.00	0.00
V	Target KH_2PO_4	0.00	0.00
V	High KH_2PO_4	0.00	0.00
Zn	Control	0.00	0.00

Zn	Low Al/O-WTR	0.00	0.00
Zn	Target Al/O-WTR	0.01	0.00
Zn	High Al/O-WTR	0.00	0.00
Zn	Low KH_2PO_4	0.00	0.00
Zn	Target KH_2PO_4	0.00	0.00
Zn	High KH_2PO_4	0.00	0.00

Appendix Table 9.

Spring Wheat Grain Elemental Uptake in Sandy Clay Loam Soil			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.00	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	0.00	0.00
Al	Low Al/O-WTR	0.00	0.00
Al	Target Al/O-WTR	0.00	0.00
Al	High Al/O-WTR	0.00	0.00
Al	Low KH_2PO_4	0.00	0.00
Al	Target KH_2PO_4	0.00	0.00
Al	High KH_2PO_4	0.00	0.00
B	Control	0.00	0.00
B	Low Al/O-WTR	0.00	0.00
B	Target Al/O-WTR	0.00	0.00
B	High Al/O-WTR	0.00	0.00
B	Low KH_2PO_4	0.00	0.00
B	Target KH_2PO_4	0.00	0.00
B	High KH_2PO_4	0.00	0.00
Ba	Control	0.00	0.00
Ba	Low Al/O-WTR	0.00	0.00
Ba	Target Al/O-WTR	0.00	0.00
Ba	High Al/O-WTR	0.00	0.00
Ba	Low KH_2PO_4	0.00	0.00
Ba	Target KH_2PO_4	0.00	0.00
Ba	High KH_2PO_4	0.00	0.00
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.00	0.00

Be	High KH_2PO_4	0.00	0.00
Ca	Control	0.00	0.00
Ca	Low Al/O-WTR	0.01	0.00
Ca	Target Al/O-WTR	0.01	0.00
Ca	High Al/O-WTR	0.01	0.00
Ca	Low KH_2PO_4	0.01	0.00
Ca	Target KH_2PO_4	0.01	0.00
Ca	High KH_2PO_4	0.01	0.00
Cd	Control	0.00	0.00
Cd	Low Al/O-WTR	0.00	0.00
Cd	Target Al/O-WTR	0.00	0.00
Cd	High Al/O-WTR	0.00	0.00
Cd	Low KH_2PO_4	0.00	0.00
Cd	Target KH_2PO_4	0.00	0.00
Cd	High KH_2PO_4	0.00	0.00
Cr	Control	0.00	0.00
Cr	Low Al/O-WTR	0.00	0.00
Cr	Target Al/O-WTR	0.00	0.00
Cr	High Al/O-WTR	0.00	0.00
Cr	Low KH_2PO_4	0.00	0.00
Cr	Target KH_2PO_4	0.00	0.00
Cr	High KH_2PO_4	0.00	0.00
Cu	Control	0.00	0.00
Cu	Low Al/O-WTR	0.00	0.00
Cu	Target Al/O-WTR	0.00	0.00
Cu	High Al/O-WTR	0.00	0.00
Cu	Low KH_2PO_4	0.00	0.00
Cu	Target KH_2PO_4	0.00	0.00
Cu	High KH_2PO_4	0.00	0.00
Fe	Control	0.00	0.00
Fe	Low Al/O-WTR	0.00	0.00
Fe	Target Al/O-WTR	0.00	0.00
Fe	High Al/O-WTR	0.00	0.00
Fe	Low KH_2PO_4	0.00	0.00
Fe	Target KH_2PO_4	0.00	0.00
Fe	High KH_2PO_4	0.00	0.00
K	Control	0.02	0.00
K	Low Al/O-WTR	0.02	0.01

K	Target Al/O-WTR	0.03	0.01
K	High Al/O-WTR	0.02	0.00
K	Low KH_2PO_4	0.02	0.01
K	Target KH_2PO_4	0.04	0.00
K	High KH_2PO_4	0.06	0.01
Mg	Control	0.01	0.00
Mg	Low Al/O-WTR	0.01	0.00
Mg	Target Al/O-WTR	0.01	0.00
Mg	High Al/O-WTR	0.01	0.00
Mg	Low KH_2PO_4	0.01	0.00
Mg	Target KH_2PO_4	0.01	0.00
Mg	High KH_2PO_4	0.02	0.00
Mn	Control	0.00	0.00
Mn	Low Al/O-WTR	0.00	0.00
Mn	Target Al/O-WTR	0.00	0.00
Mn	High Al/O-WTR	0.00	0.00
Mn	Low KH_2PO_4	0.00	0.00
Mn	Target KH_2PO_4	0.00	0.00
Mn	High KH_2PO_4	0.00	0.00
Mo	Control	0.00	0.00
Mo	Low Al/O-WTR	0.00	0.00
Mo	Target Al/O-WTR	0.00	0.00
Mo	High Al/O-WTR	0.00	0.00
Mo	Low KH_2PO_4	0.00	0.00
Mo	Target KH_2PO_4	0.00	0.00
Mo	High KH_2PO_4	0.00	0.00
Na	Control	0.00	0.00
Na	Low Al/O-WTR	0.00	0.00
Na	Target Al/O-WTR	0.00	0.00
Na	High Al/O-WTR	0.00	0.00
Na	Low KH_2PO_4	0.00	0.00
Na	Target KH_2PO_4	0.00	0.00
Na	High KH_2PO_4	0.00	0.00
Ni	Control	0.00	0.00
Ni	Low Al/O-WTR	0.00	0.00
Ni	Target Al/O-WTR	0.00	0.00
Ni	High Al/O-WTR	0.00	0.00
Ni	Low KH_2PO_4	0.00	0.00

Ni	Target KH_2PO_4	0.00	0.00
Ni	High KH_2PO_4	0.00	0.00
P	Control	0.01	0.00
P	Low Al/O-WTR	0.01	0.00
P	Target Al/O-WTR	0.01	0.00
P	High Al/O-WTR	0.01	0.00
P	Low KH_2PO_4	0.02	0.00
P	Target KH_2PO_4	0.03	0.00
P	High KH_2PO_4	0.04	0.01
Pb	Control	0.00	0.00
Pb	Low Al/O-WTR	0.00	0.00
Pb	Target Al/O-WTR	0.00	0.00
Pb	High Al/O-WTR	0.00	0.00
Pb	Low KH_2PO_4	0.00	0.00
Pb	Target KH_2PO_4	0.00	0.00
Pb	High KH_2PO_4	0.00	0.00
Sr	Control	0.00	0.00
Sr	Low Al/O-WTR	0.00	0.00
Sr	Target Al/O-WTR	0.00	0.00
Sr	High Al/O-WTR	0.00	0.00
Sr	Low KH_2PO_4	0.00	0.00
Sr	Target KH_2PO_4	0.00	0.00
Sr	High KH_2PO_4	0.00	0.00
Ti	Control	0.00	0.00
Ti	Low Al/O-WTR	0.00	0.00
Ti	Target Al/O-WTR	0.00	0.00
Ti	High Al/O-WTR	0.00	0.00
Ti	Low KH_2PO_4	0.00	0.00
Ti	Target KH_2PO_4	0.00	0.00
Ti	High KH_2PO_4	0.00	0.00
V	Control	0.00	0.00
V	Low Al/O-WTR	0.00	0.00
V	Target Al/O-WTR	0.00	0.00
V	High Al/O-WTR	0.00	0.00
V	Low KH_2PO_4	0.00	0.00
V	Target KH_2PO_4	0.00	0.00
V	High KH_2PO_4	0.00	0.00
Zn	Control	0.00	0.00

Zn	Low Al/O-WTR	0.00	0.00
Zn	Target Al/O-WTR	0.00	0.00
Zn	High Al/O-WTR	0.00	0.00
Zn	Low KH_2PO_4	0.00	0.00
Zn	Target KH_2PO_4	0.00	0.00
Zn	High KH_2PO_4	0.00	0.00

Appendix Table 10.

Spring Wheat Grain Elemental Uptake in Sandy Loam Soil			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.00	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	0.00	0.00
Al	Low Al/O-WTR	0.00	0.00
Al	Target Al/O-WTR	0.00	0.00
Al	High Al/O-WTR	0.00	0.00
Al	Low KH_2PO_4	0.00	0.00
Al	Target KH_2PO_4	0.00	0.00
Al	High KH_2PO_4	0.00	0.00
B	Control	0.00	0.00
B	Low Al/O-WTR	0.00	0.00
B	Target Al/O-WTR	0.00	0.00
B	High Al/O-WTR	0.00	0.00
B	Low KH_2PO_4	0.00	0.00
B	Target KH_2PO_4	0.00	0.00
B	High KH_2PO_4	0.00	0.00
Ba	Control	0.00	0.00
Ba	Low Al/O-WTR	0.00	0.00
Ba	Target Al/O-WTR	0.00	0.00
Ba	High Al/O-WTR	0.00	0.00
Ba	Low KH_2PO_4	0.00	0.00
Ba	Target KH_2PO_4	0.00	0.00
Ba	High KH_2PO_4	0.00	0.00
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.00	0.00

Be	High KH_2PO_4	0.00	0.00
Ca	Control	0.94	0.55
Ca	Low Al/O-WTR	1.37	0.51
Ca	Target Al/O-WTR	0.98	0.14
Ca	High Al/O-WTR	2.75	1.41
Ca	Low KH_2PO_4	1.44	0.51
Ca	Target KH_2PO_4	2.21	0.59
Ca	High KH_2PO_4	2.45	1.18
Cd	Control	0.00	0.00
Cd	Low Al/O-WTR	0.00	0.00
Cd	Target Al/O-WTR	0.00	0.00
Cd	High Al/O-WTR	0.00	0.00
Cd	Low KH_2PO_4	0.00	0.00
Cd	Target KH_2PO_4	0.00	0.00
Cd	High KH_2PO_4	0.00	0.00
Cr	Control	0.00	0.00
Cr	Low Al/O-WTR	0.00	0.00
Cr	Target Al/O-WTR	0.00	0.00
Cr	High Al/O-WTR	0.00	0.00
Cr	Low KH_2PO_4	0.00	0.00
Cr	Target KH_2PO_4	0.00	0.00
Cr	High KH_2PO_4	0.00	0.00
Cu	Control	0.00	0.00
Cu	Low Al/O-WTR	0.00	0.00
Cu	Target Al/O-WTR	0.00	0.00
Cu	High Al/O-WTR	0.00	0.00
Cu	Low KH_2PO_4	0.00	0.00
Cu	Target KH_2PO_4	0.00	0.00
Cu	High KH_2PO_4	0.00	0.00
Fe	Control	0.00	0.00
Fe	Low Al/O-WTR	0.00	0.00
Fe	Target Al/O-WTR	0.00	0.00
Fe	High Al/O-WTR	0.00	0.00
Fe	Low KH_2PO_4	0.00	0.00
Fe	Target KH_2PO_4	0.00	0.00
Fe	High KH_2PO_4	0.00	0.00
K	Control	0.00	0.00
K	Low Al/O-WTR	0.00	0.00

K	Target Al/O-WTR	0.00	0.00
K	High Al/O-WTR	0.01	0.01
K	Low KH_2PO_4	0.00	0.00
K	Target KH_2PO_4	0.01	0.00
K	High KH_2PO_4	0.01	0.01
Mg	Control	0.00	0.00
Mg	Low Al/O-WTR	0.00	0.00
Mg	Target Al/O-WTR	0.00	0.00
Mg	High Al/O-WTR	0.00	0.00
Mg	Low KH_2PO_4	0.00	0.00
Mg	Target KH_2PO_4	0.00	0.00
Mg	High KH_2PO_4	0.00	0.00
Mn	Control	0.00	0.00
Mn	Low Al/O-WTR	0.00	0.00
Mn	Target Al/O-WTR	0.00	0.00
Mn	High Al/O-WTR	0.00	0.00
Mn	Low KH_2PO_4	0.00	0.00
Mn	Target KH_2PO_4	0.00	0.00
Mn	High KH_2PO_4	0.00	0.00
Mo	Control	0.00	0.00
Mo	Low Al/O-WTR	0.00	0.00
Mo	Target Al/O-WTR	0.00	0.00
Mo	High Al/O-WTR	0.00	0.00
Mo	Low KH_2PO_4	0.00	0.00
Mo	Target KH_2PO_4	0.00	0.00
Mo	High KH_2PO_4	0.00	0.00
Na	Control	0.00	0.00
Na	Low Al/O-WTR	0.00	0.00
Na	Target Al/O-WTR	0.00	0.00
Na	High Al/O-WTR	0.00	0.00
Na	Low KH_2PO_4	0.00	0.00
Na	Target KH_2PO_4	0.00	0.00
Na	High KH_2PO_4	0.00	0.00
Ni	Control	0.00	0.00
Ni	Low Al/O-WTR	0.00	0.00
Ni	Target Al/O-WTR	0.00	0.00
Ni	High Al/O-WTR	0.00	0.00
Ni	Low KH_2PO_4	0.00	0.00

Ni	Target KH_2PO_4	0.00	0.00
Ni	High KH_2PO_4	0.00	0.00
P	Control	0.00	0.00
P	Low Al/O-WTR	0.00	0.00
P	Target Al/O-WTR	0.00	0.00
P	High Al/O-WTR	0.00	0.00
P	Low KH_2PO_4	0.00	0.00
P	Target KH_2PO_4	0.00	0.00
P	High KH_2PO_4	0.00	0.00
Pb	Control	0.00	0.00
Pb	Low Al/O-WTR	0.00	0.00
Pb	Target Al/O-WTR	0.00	0.00
Pb	High Al/O-WTR	0.00	0.00
Pb	Low KH_2PO_4	0.00	0.00
Pb	Target KH_2PO_4	0.00	0.00
Pb	High KH_2PO_4	0.00	0.00
Sr	Control	0.00	0.00
Sr	Low Al/O-WTR	0.00	0.00
Sr	Target Al/O-WTR	0.00	0.00
Sr	High Al/O-WTR	0.00	0.00
Sr	Low KH_2PO_4	0.00	0.00
Sr	Target KH_2PO_4	0.00	0.00
Sr	High KH_2PO_4	0.00	0.00
Ti	Control	0.00	0.00
Ti	Low Al/O-WTR	0.00	0.00
Ti	Target Al/O-WTR	0.00	0.00
Ti	High Al/O-WTR	0.00	0.00
Ti	Low KH_2PO_4	0.00	0.00
Ti	Target KH_2PO_4	0.00	0.00
Ti	High KH_2PO_4	0.00	0.00
V	Control	0.00	0.00
V	Low Al/O-WTR	0.00	0.00
V	Target Al/O-WTR	0.00	0.00
V	High Al/O-WTR	0.00	0.00
V	Low KH_2PO_4	0.00	0.00
V	Target KH_2PO_4	0.00	0.00
V	High KH_2PO_4	0.00	0.00
Zn	Control	0.00	0.00

Zn	Low Al/O-WTR	0.00	0.00
Zn	Target Al/O-WTR	0.00	0.00
Zn	High Al/O-WTR	0.00	0.00
Zn	Low KH_2PO_4	0.00	0.00
Zn	Target KH_2PO_4	0.00	0.00
Zn	High KH_2PO_4	0.00	0.00

Appendix Table 11.

Sandy Clay Loam Soil Total Elements			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.00	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	940.67	58.59
Al	Low Al/O-WTR	942.39	40.48
Al	Target Al/O-WTR	926.28	15.26
Al	High Al/O-WTR	922.95	47.86
Al	Low KH_2PO_4	808.18	47.08
Al	Target KH_2PO_4	830.67	14.74
Al	High KH_2PO_4	781.89	9.44
B	Control	0.00	0.00
B	Low Al/O-WTR	0.00	0.00
B	Target Al/O-WTR	0.00	0.00
B	High Al/O-WTR	0.00	0.00
B	Low KH_2PO_4	0.00	0.00
B	Target KH_2PO_4	0.00	0.00
B	High KH_2PO_4	0.00	0.00
Ba	Control	6.08	0.08
Ba	Low Al/O-WTR	5.82	0.09
Ba	Target Al/O-WTR	5.53	0.07
Ba	High Al/O-WTR	5.66	0.06
Ba	Low KH_2PO_4	5.25	0.18
Ba	Target KH_2PO_4	6.10	0.07
Ba	High KH_2PO_4	6.02	0.03
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00

Be	Target KH_2PO_4	0.00	0.00
Be	High KH_2PO_4	0.00	0.00
Ca	Control	1896.61	14.93
Ca	Low Al/O-WTR	1809.93	23.57
Ca	Target Al/O-WTR	1766.22	23.31
Ca	High Al/O-WTR	1797.11	8.76
Ca	Low KH_2PO_4	1658.06	70.14
Ca	Target KH_2PO_4	2077.20	17.18
Ca	High KH_2PO_4	2069.38	14.58
Cd	Control	0.03	0.00
Cd	Low Al/O-WTR	0.03	0.00
Cd	Target Al/O-WTR	0.03	0.00
Cd	High Al/O-WTR	0.03	0.00
Cd	Low KH_2PO_4	0.03	0.00
Cd	Target KH_2PO_4	0.03	0.00
Cd	High KH_2PO_4	0.03	0.00
Cu	Control	0.70	0.07
Cu	Low Al/O-WTR	0.74	0.08
Cu	Target Al/O-WTR	0.63	0.06
Cu	High Al/O-WTR	0.74	0.07
Cu	Low KH_2PO_4	0.63	0.05
Cu	Target KH_2PO_4	0.78	0.13
Cu	High KH_2PO_4	0.54	0.05
Fe	Control	386.84	1.06
Fe	Low Al/O-WTR	386.18	4.05
Fe	Target Al/O-WTR	365.84	6.70
Fe	High Al/O-WTR	394.77	3.23
Fe	Low KH_2PO_4	353.18	13.85
Fe	Target KH_2PO_4	356.33	1.15
Fe	High KH_2PO_4	351.75	1.98
K	Control	210.48	3.98
K	Low Al/O-WTR	202.95	5.28
K	Target Al/O-WTR	180.87	3.43
K	High Al/O-WTR	187.06	3.91
K	Low KH_2PO_4	184.22	3.53
K	Target KH_2PO_4	244.75	6.20
K	High KH_2PO_4	226.85	4.54
Mg	Control	223.42	0.73

Mg	Low Al/O-WTR	220.78	0.71
Mg	Target Al/O-WTR	217.00	0.96
Mg	High Al/O-WTR	225.70	0.53
Mg	Low KH_2PO_4	213.06	5.61
Mg	Target KH_2PO_4	214.75	0.69
Mg	High KH_2PO_4	213.29	0.29
Mn	Control	16.54	0.32
Mn	Low Al/O-WTR	16.34	0.39
Mn	Target Al/O-WTR	15.51	0.43
Mn	High Al/O-WTR	16.53	0.21
Mn	Low KH_2PO_4	14.70	0.42
Mn	Target KH_2PO_4	16.77	0.22
Mn	High KH_2PO_4	16.28	0.21
Mo	Control	0.00	0.00
Mo	Low Al/O-WTR	0.01	0.00
Mo	Target Al/O-WTR	0.01	0.00
Mo	High Al/O-WTR	0.01	0.00
Mo	Low KH_2PO_4	0.00	0.00
Mo	Target KH_2PO_4	0.00	0.00
Mo	High KH_2PO_4	0.00	0.00
Na	Control	28.63	0.59
Na	Low Al/O-WTR	27.06	0.58
Na	Target Al/O-WTR	24.13	0.51
Na	High Al/O-WTR	25.57	1.11
Na	Low KH_2PO_4	25.20	0.54
Na	Target KH_2PO_4	28.87	0.81
Na	High KH_2PO_4	27.10	0.62
Ni	Control	0.53	0.01
Ni	Low Al/O-WTR	0.52	0.01
Ni	Target Al/O-WTR	0.47	0.01
Ni	High Al/O-WTR	0.51	0.01
Ni	Low KH_2PO_4	0.47	0.01
Ni	Target KH_2PO_4	0.49	0.01
Ni	High KH_2PO_4	0.48	0.01
P	Control	34.21	0.38
P	Low Al/O-WTR	33.89	0.51
P	Target Al/O-WTR	31.37	0.32
P	High Al/O-WTR	33.85	0.39

P	Low KH_2PO_4	31.26	0.84
P	Target KH_2PO_4	36.16	0.58
P	High KH_2PO_4	36.40	0.34
Pb	Control	0.43	0.01
Pb	Low Al/O-WTR	0.43	0.01
Pb	Target Al/O-WTR	0.38	0.00
Pb	High Al/O-WTR	0.40	0.01
Pb	Low KH_2PO_4	0.38	0.01
Pb	Target KH_2PO_4	0.43	0.00
Pb	High KH_2PO_4	0.42	0.01
Sr	Control	7.23	0.43
Sr	Low Al/O-WTR	6.90	0.27
Sr	Target Al/O-WTR	6.69	0.07
Sr	High Al/O-WTR	6.16	0.31
Sr	Low KH_2PO_4	6.02	0.32
Sr	Target KH_2PO_4	7.88	0.08
Sr	High KH_2PO_4	7.62	0.07
Ti	Control	3.80	0.05
Ti	Low Al/O-WTR	3.72	0.08
Ti	Target Al/O-WTR	3.42	0.05
Ti	High Al/O-WTR	3.66	0.03
Ti	Low KH_2PO_4	3.36	0.08
Ti	Target KH_2PO_4	3.89	0.05
Ti	High KH_2PO_4	3.66	0.02
V	Control	1.03	0.02
V	Low Al/O-WTR	1.02	0.02
V	Target Al/O-WTR	0.96	0.03
V	High Al/O-WTR	1.00	0.01
V	Low KH_2PO_4	0.93	0.02
V	Target KH_2PO_4	0.98	0.01
V	High KH_2PO_4	0.95	0.01
Zn	Control	2.17	0.01
Zn	Low Al/O-WTR	2.14	0.03
Zn	Target Al/O-WTR	1.91	0.02
Zn	High Al/O-WTR	2.15	0.02
Zn	Low KH_2PO_4	1.87	0.09
Zn	Target KH_2PO_4	1.99	0.02
Zn	High KH_2PO_4	1.91	0.03

Appendix Table 12.

Sandy Loam Soil Total Elements			
Element	Treatment	Mean Concentration (mg kg^{-1})	Standard Error of the Mean (mg kg^{-1})
Ag	Control	0.00	0.00
Ag	Low Al/O-WTR	0.00	0.00
Ag	Target Al/O-WTR	0.00	0.00
Ag	High Al/O-WTR	0.00	0.00
Ag	Low KH_2PO_4	0.00	0.00
Ag	Target KH_2PO_4	0.00	0.00
Ag	High KH_2PO_4	0.00	0.00
Al	Control	453.61	14.65
Al	Low Al/O-WTR	513.34	14.25
Al	Target Al/O-WTR	550.12	9.71
Al	High Al/O-WTR	560.59	18.05
Al	Low KH_2PO_4	485.32	11.73
Al	Target KH_2PO_4	459.81	6.95
Al	High KH_2PO_4	481.91	7.55
B	Control	0.00	0.00
B	Low Al/O-WTR	0.00	0.00
B	Target Al/O-WTR	0.00	0.00
B	High Al/O-WTR	0.00	0.00
B	Low KH_2PO_4	0.00	0.00
B	Target KH_2PO_4	0.00	0.00
B	High KH_2PO_4	0.00	0.00
Ba	Control	7.76	0.15
Ba	Low Al/O-WTR	7.72	0.10
Ba	Target Al/O-WTR	7.78	0.10
Ba	High Al/O-WTR	7.63	0.17
Ba	Low KH_2PO_4	7.65	0.21
Ba	Target KH_2PO_4	7.55	0.22
Ba	High KH_2PO_4	7.80	0.11
Be	Control	0.00	0.00
Be	Low Al/O-WTR	0.00	0.00
Be	Target Al/O-WTR	0.00	0.00
Be	High Al/O-WTR	0.00	0.00
Be	Low KH_2PO_4	0.00	0.00
Be	Target KH_2PO_4	0.00	0.00
Be	High KH_2PO_4	0.00	0.00

Ca	Control	1816.60	22.30
Ca	Low Al/O-WTR	1863.86	21.04
Ca	Target Al/O-WTR	1890.61	14.25
Ca	High Al/O-WTR	1870.52	22.58
Ca	Low KH_2PO_4	1845.86	18.15
Ca	Target KH_2PO_4	1838.94	12.54
Ca	High KH_2PO_4	1889.59	13.07
Cd	Control	0.03	0.00
Cd	Low Al/O-WTR	0.04	0.00
Cd	Target Al/O-WTR	0.04	0.00
Cd	High Al/O-WTR	0.04	0.00
Cd	Low KH_2PO_4	0.03	0.00
Cd	Target KH_2PO_4	0.03	0.00
Cd	High KH_2PO_4	0.04	0.00
Cu	Control	0.22	0.04
Cu	Low Al/O-WTR	0.32	0.04
Cu	Target Al/O-WTR	0.40	0.04
Cu	High Al/O-WTR	0.29	0.04
Cu	Low KH_2PO_4	0.30	0.03
Cu	Target KH_2PO_4	0.24	0.02
Cu	High KH_2PO_4	0.27	0.02
Fe	Control	315.89	3.71
Fe	Low Al/O-WTR	325.60	2.46
Fe	Target Al/O-WTR	325.79	1.71
Fe	High Al/O-WTR	326.13	2.98
Fe	Low KH_2PO_4	323.42	2.90
Fe	Target KH_2PO_4	316.30	2.00
Fe	High KH_2PO_4	320.72	1.24
K	Control	192.00	6.58
K	Low Al/O-WTR	208.26	9.71
K	Target Al/O-WTR	220.03	5.19
K	High Al/O-WTR	208.50	9.21
K	Low KH_2PO_4	195.48	4.79
K	Target KH_2PO_4	191.90	3.53
K	High KH_2PO_4	211.43	4.89
Mg	Control	207.34	1.68
Mg	Low Al/O-WTR	211.55	1.55
Mg	Target Al/O-WTR	212.44	0.71

Mg	High Al/O-WTR	211.52	1.89
Mg	Low KH_2PO_4	209.07	1.29
Mg	Target KH_2PO_4	208.50	1.12
Mg	High KH_2PO_4	211.57	0.80
Mn	Control	14.18	0.31
Mn	Low Al/O-WTR	14.53	0.38
Mn	Target Al/O-WTR	15.51	0.26
Mn	High Al/O-WTR	15.07	0.22
Mn	Low KH_2PO_4	14.45	0.28
Mn	Target KH_2PO_4	14.14	0.21
Mn	High KH_2PO_4	14.46	0.14
Mo	Control	0.02	0.00
Mo	Low Al/O-WTR	0.02	0.00
Mo	Target Al/O-WTR	0.02	0.00
Mo	High Al/O-WTR	0.02	0.00
Mo	Low KH_2PO_4	0.02	0.00
Mo	Target KH_2PO_4	0.02	0.00
Mo	High KH_2PO_4	0.02	0.00
Na	Control	48.93	2.00
Na	Low Al/O-WTR	50.89	1.62
Na	Target Al/O-WTR	51.53	1.15
Na	High Al/O-WTR	47.48	1.68
Na	Low KH_2PO_4	49.37	1.50
Na	Target KH_2PO_4	45.99	0.84
Na	High KH_2PO_4	51.38	1.24
Ni	Control	0.39	0.01
Ni	Low Al/O-WTR	0.41	0.01
Ni	Target Al/O-WTR	0.42	0.01
Ni	High Al/O-WTR	0.42	0.01
Ni	Low KH_2PO_4	0.40	0.01
Ni	Target KH_2PO_4	0.40	0.00
Ni	High KH_2PO_4	0.41	0.00
P	Control	33.08	0.77
P	Low Al/O-WTR	33.66	0.34
P	Target Al/O-WTR	35.15	0.65
P	High Al/O-WTR	34.91	0.65
P	Low KH_2PO_4	33.67	0.46
P	Target KH_2PO_4	33.66	0.45

P	High KH_2PO_4	36.14	0.54
Pb	Control	0.31	0.01
Pb	Low Al/O-WTR	0.32	0.01
Pb	Target Al/O-WTR	0.34	0.01
Pb	High Al/O-WTR	0.32	0.01
Pb	Low KH_2PO_4	0.33	0.00
Pb	Target KH_2PO_4	0.32	0.01
Pb	High KH_2PO_4	0.33	0.01
Sr	Control	7.30	0.15
Sr	Low Al/O-WTR	7.61	0.17
Sr	Target Al/O-WTR	8.00	0.12
Sr	High Al/O-WTR	7.71	0.16
Sr	Low KH_2PO_4	7.55	0.14
Sr	Target KH_2PO_4	7.43	0.08
Sr	High KH_2PO_4	7.87	0.11
Ti	Control	2.59	0.05
Ti	Low Al/O-WTR	2.57	0.04
Ti	Target Al/O-WTR	2.76	0.04
Ti	High Al/O-WTR	2.71	0.05
Ti	Low KH_2PO_4	2.69	0.05
Ti	Target KH_2PO_4	2.71	0.04
Ti	High KH_2PO_4	2.82	0.04
V	Control	0.68	0.02
V	Low Al/O-WTR	0.71	0.01
V	Target Al/O-WTR	0.74	0.01
V	High Al/O-WTR	0.72	0.02
V	Low KH_2PO_4	0.71	0.01
V	Target KH_2PO_4	0.70	0.01
V	High KH_2PO_4	0.71	0.01
Zn	Control	1.56	0.04
Zn	Low Al/O-WTR	1.63	0.03
Zn	Target Al/O-WTR	1.67	0.02
Zn	High Al/O-WTR	1.64	0.04
Zn	Low KH_2PO_4	1.63	0.03
Zn	Target KH_2PO_4	1.55	0.02
Zn	High KH_2PO_4	1.61	0.01