

EFFECT OF LAND APPLICATION OF LIQUID  
SULFURTRAP ON GRAIN YIELD AND  
QUALITY IN WINTER CANOLA AND  
THE IMPACT OF SOIL pH ON  
PHOSPHORUS EXTRACTION  
METHOD RESULTS

By  
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Title of Study: EFFECT OF LAND APPLICATION OF LIQUID SULFURTRAP ON GRAIN YIELD AND QUALITY IN WINTER CANOLA AND THE IMPACT OF SOIL pH ON PHOSPHORUS EXTRACTION METHOD RESULTS

Major Field: PLANT AND SOIL SCIENCES

Abstract: With rising production costs in both agriculture and oil and gas industries, developing management practices that are both cost effective and environmentally sound is challenging, but of great importance. Liquid Sulfur Trap is a newly patented material intended for use in midstream hydrocarbon gas desulfurization processes. Disposal via deep well injection is currently standard practice for similar oil & gas waste materials. However, spent Liquid Sulfur Trap (LST) may be useful in agricultural environments due to its high concentrations of potassium (K) and sulfur (S), which are essential plant nutrients. This study was conducted to determine the effects of land applied LST on grain yield and grain quality in winter canola. Treatments consist of variations in application rate and timing for two nutrient sources, LST and a K and S equivalent conventional fertilizer blend (PAS) comprised of potash (KCl) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Field trials were set up as replicated factorials in a randomized complete block design, with a check plot receiving neither LST or PAS, and three replications per treatment. Normalized difference vegetative index (NDVI) was collected periodically during the growing season, while grain data was collected at harvest. Grain quality was determined post-harvest using near infrared spectroscopy (NIR) to analyze grain oil and protein content. The calcium carbonate equivalence (CCE) of LST was evaluated using acid-base titration and a soil incubation study. LST application reduced fall NDVI in trials at LCB and Perkins, however differences in grain yield, protein, and oil content were not statistically significant. Application timing had the strongest effect, where spring applications increased NDVI by approximately 0.075 and grain yield by approximately 350 kg ha<sup>-1</sup> when compared to fall applications. The CCE of LST as determined by the soil incubation studies was 15.6%. While the CCE of LST is relatively low, soil acidity was neutralized much more rapidly than limed soils, 8 weeks and 50 weeks respectively. The effects of LST on winter canola are difficult to assess due to wildlife grazing and poor winter survival.

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## CHAPTER I

### EFFECT OF LAND APPLICATION OF LIQUID SULFURTRAP ON GRAIN YIELD AND QUALITY IN WINTER CANOLA

#### 1.1 Introduction

Air quality and emission standards have been imposed by regulatory agencies to decrease the amount of nitrogen (N) and sulfur (S) entering the atmosphere through anthropogenic activities (Office of Air Quality Planning and Standards, 1993; Wilson et al., 1972). This has led to reduction in total sulfur dioxide (SO<sub>2</sub>) emissions in the US from 31,218 Mt in 1970 to 2,457 Mt 2016 (USEPA, 2017). Decreased SO<sub>2</sub> emissions reduce smog, acid-rain, and improve air quality in general (Wilson et al., 1972). However, it has also reduced the incidental input of S to agricultural soils (National Atmospheric Deposition Program, 2016).

Sulfur is an essential plant nutrient, and S-deficiencies can reduce yield, quality, and nutrient use efficiency in crops (Karamanos et al., 2007; Ngezimana & Agenbag, 2014; Salimpour et al., 2012; Zhao et al., 1999). In general, S-deficiencies are less likely in cereal crops than in oil-seed crops. For example, an optimum winter wheat (*Triticum aestivum* L.) grain production system removes approximately 15 kg-S/ha (Zhao et al., 1999), while S-removal in a similar winter canola (*Brassica napus* L.) crop will range between 25-30 kg/ha (Zhao, 2002). Atmospheric deposition of S has exceeded crop demand in many areas since the Industrial

Revolution. As a result, the importance of S as a plant nutrient is frequently underappreciated in the soil fertility management practices of agricultural producers (Stevenson & Cole, 1999). As atmospheric deposition of S decreases, and farmers strive to increase crop yields to meet an ever increasing global demand for food, the soil's ability to supply S diminishes without S-fertilization, resulting in S-deficiencies and decreased crop yields.

Desulfurization processes are also commonly required to meet pipeline hydrogen sulfide (H<sub>2</sub>S) standards and regulations for point-source SO<sub>2</sub> emissions, increasing the costs of energy production and generating caustic and noxious waste materials. Disposal of these waste products typically requires the use of landfills or deep-well injection, both of which pose environmental concerns and increase operating costs (Bagajewicz, 2015). However, some such waste products may be suitable for disposal through land-application, also commonly referred to as land-spreading. Land application is a common practice for disposal of other oil and gas waste products, such as spent drilling mud (USEPA, 2014). If these waste materials also have some agronomic value, land application can provide agricultural producers with cost effective alternatives to conventional fertilizers while also providing oil and gas producers with an alternative disposal pathway.

This study was conducted to investigate the impact of land application of one such waste product, spent Liquid SulfurTrap™ (LST), on characteristics associated with the agronomic value of winter canola. Characteristics evaluated include normalized difference vegetative index (NDVI), grain yield, and grain quality. Due to the caustic nature of LST, its potential use as a liming agent in acidic soils was also investigated. This was accomplished through the use of both acid/base titrimetry and a soil incubation study to determine the effective calcium carbonate equivalence (CCE) of LST. Preliminary results regarding the CCE of LST were also used to guide application rates of another study investigating the impact of LST application on soil leachate.

## 1.2 Research Objectives

*Objective 1.* Evaluate the effect of LST application rate and timing on winter canola grain yield in central Oklahoma.

*Objective 2.* Evaluate the effect of LST application rate and timing on mid-season NDVI in winter canola in central Oklahoma.

*Objective 3.* Evaluate the effect of LST application rate and timing on winter canola grain quality parameters in central Oklahoma.

*Objective 4.* Evaluate the potential of LST for use as an alternative liming agent by determining the CCE of LST through acid-base titrimetry and soil incubation studies.

## 1.3 Review of Literature

### 1.3.1 Desulfurization

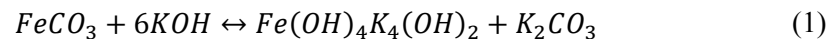
The process of removing sulfur compounds from liquid or gaseous hydrocarbon streams is commonly referred to as desulfurization, or “sweetening”, in the oil & gas industry. The oxidation of sulfur compounds, such as hydrogen sulfide ( $\text{H}_2\text{S}$ ) and thiols ( $\text{R-SH}$ ) can generate sulfuric acid ( $\text{H}_2\text{SO}_4$ ) leading to the degradation of pipelines and machinery involved in hydrocarbon transport and refining processes. Hydrogen sulfide concentrations of “pipeline” grade natural gas must be less than 4 ppm in the US, although many refineries place tariffs on material exceeding 1 ppm  $\text{H}_2\text{S}$  (Wang & Yang, 2014). Hydrogen sulfide, thiols, and their combustion products ( $\text{SO}_x$ ) have also been found to pose a risk to human health, contribute to acid rain, and increase the formation of atmospheric smog (Office of Air Quality Planning and Standards, 1993; Wilson et al., 1972). As such, the US Environmental Protection Agency (EPA) has established various regulations on the amount of  $\text{SO}_2$  that can be release by energy producers

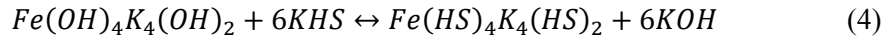
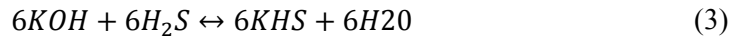
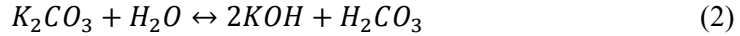
(USEPA, 2016). This combination of air-quality regulations and pipeline gas standards has led to a high demand for efficient and cost effective S-sorbing materials and desulfurization processes.

There are a variety of materials currently used as S-sorbents in desulfurization processes. The specific material used typically depends on the volumetric flow-rate, temperature, carbon dioxide (CO<sub>2</sub>), and water content of the hydrocarbon stream to be treated (Wang & Yang, 2014). Liquid amine solutions are the most common commercial sorbents as they are suitable for S extraction in high flow rate systems, such as those associated with large-reservoir conventional wells (Wang & Yang, 2014). Nanostructured sorbents are a relatively recent development, and have shown potential benefits in shale-gas wells, which are typically lower production than conventional wells (Wang & Yang, 2014). Metal oxide nanosorbents owe their high S-sorption to a combination of high particle surface area and the chemical affinity of metal cations for S (Skrzypski et al., 2011; Wang & Yang, 2014).

### 1.3.2 Liquid Sulfur Trap

Liquid Sulfur Trap (LST) is a recently developed nanosorbent material intended for use in the desulfurization of gaseous hydrocarbon streams (Farha & Irurzun, 2014). The material is predominately comprised of iron (II) hydroxides (Fe(OH)<sub>2</sub>) and oxides (FeO) (Farha & Irurzun, 2014). According to the release patent, these particles are formed most economically by the dissolution of iron (II) carbonate (FeCO<sub>3</sub>), or siderite, in a heated potassium hydroxide (KOH) solution (Farha & Irurzun, 2014). The final material has been shown to be an efficient S-scavenger, with an S-loading capacity of approximately 344% of Fe content by weight. Farha and Irurzun (2014) also thought the S-loading capacity of LST to be best explained by the following reactions:





### 1.3.3 Sulfur and its cycle in soil

Sulfur (S) is an essential element of life and is found in all living organisms as it is a key component of the amino acids cysteine and methionine (Stevenson & Cole, 1999). Sulfur occupies several oxidation states stable in the soil-water-air continuum, ranging from S<sup>-II</sup> (e.g. H<sub>2</sub>S and HS<sup>-</sup>) to S<sup>VI</sup> (e.g. SO<sub>4</sub><sup>2-</sup>), and its behavior in soils is similar to N in many regards (Essington, 2004; Stevenson & Cole, 1999). The largest S-reservoirs on Earth are the lithosphere (2.43 x 10<sup>19</sup> kg-S) and hydrosphere (1.3 x 10<sup>18</sup> kg-S), with lesser amounts sequestered in soils and the atmosphere, 2.6 x 10<sup>14</sup> and 1.3 x 10<sup>18</sup> kg-S respectively (Stevenson & Cole, 1999). Although chemical weathering of pyritic minerals can provide significant contribution to soil-S in some locations (Essington, 2004), the predominate S-input to the soil occurs via atmospheric deposition of sulfate in precipitation (Stevenson & Cole, 1999).

Due to its association with acid-rain, S-SO<sub>4</sub><sup>2-</sup> deposition has been monitored extensively across the US since the 1990 Amendments to the Clean Air Act of 1970 (Davidson & Norbeck, 2012). The amount of S deposited in this manner is highly variable with respect to space and time, and is primarily influenced by anthropogenic activities, such as the combustion of fossil fuels, and proximity to S-enriched oceanic waters (Cleavitt et al., 2015; Pardo & Duarte, 2007; Stevenson & Cole, 1999). In general, total-S deposition increases from west to east across the continental US, although deposition has decreased significantly in the last decade (National Atmospheric Deposition Program, 2016). These effects are well demonstrated by maps generated from National Trends Network (NTN) data collected by the National Atmospheric Deposition

Program (NADP), shown in Figure 1.1 and Figure 1.2. It is also important to note that the rate of S deposition from the atmosphere has historically exceeded crop requirements in many locations, resulting in little attention to S nutrient management in agriculture (Eriksen, 2009). With high demand for increased crop production and decreasing incidental S additions to soils, S management will likely become more important in the near future.

Studies have found that most soil-S in agricultural soils is present in organic forms, such as amino acids and sulfonates, rather than inorganic-S (Ghani et al., 1992; Kertesz & Mirleau, 2004). It is well understood that plants primarily uptake inorganic-S, however research has shown that organic S pools are also plant-available due to mineralization (Ghani et al., 1992; Kertesz & Mirleau, 2004). Kertesz and Mirleau (2004) found that soil microbes immobilize inorganic-S rapidly, first to sulfate esters and then to amino acids, and that immobilization can out-pace plant-uptake. It has also been shown that C and S amendments can decrease S mineralization, and that most mineralized S is from C-bonded S (Boye et al., 2010; Ghani et al., 1992). Furthermore, interactions between organic-S compounds and clay minerals can result in physical protection against microbial decomposition (Eriksen, 1997; Eriksen et al., 1995). Further studies found this to be especially true for S-esters, which explains the seeming preference for C-bonded S by microbes responsible for S-mineralization (Tanikawa et al., 2013). This would imply that the amount of S available for plant uptake is strongly dependent on microbial S-mineralization, even in S-fertilized soils. Sulfur cycling is also affected by the amount of C present, residue additions with a high C:S ratio lead to S-immobilization and lower inorganic-S than low C:S ratio residues (Boye et al., 2010; Eriksen, 1997). As S-mineralization is driven by microbial activity, rates are also strongly influenced by temperature (Nadelhoffer et al., 1991), the size of the soils organic-C pool, and the site's historic S-deposition (MacDonald et al., 1995).

There are multiple S loss pathways from the soil, leaching and volatilization being the most important. Sulfur balance studies have found that leaching is generally the most important



item affecting the S-balance in agricultural soils (Eriksen et al., 2002). Inorganic-S, typically  $\text{SO}_4^{2-}$ , is prone to leaching from soils due to the low anion exchange capacity (AEC) of most mineral soils (Stevenson & Cole, 1999). Leaching studies have shown that even in soils capable of retaining high amounts of sulfate, much of the adsorbed sulfate could be removed with a single water extraction, and nearly all sulfate could be removed with sequential water extractions (Chao et al., 1962). Desorption also increases with increasing soil-pH (Curtin & Syers, 1990) and phosphate ( $\text{PO}_4^{3-}$ ) concentrations (Chao et al., 1962). As liming, phosphate amendments, and irrigation are all common and important agricultural management practices, S-management with sulfate fertilizers proves difficult in many regards.

Similar to N, S can also be lost from the soil through the gas phase by S-volatilization. There are several volatile-S compounds that can potentially be produced in soil environments, such as hydrogen sulfide ( $\text{H}_2\text{S}$ ), dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$ ), and carbon disulfide ( $\text{CS}_2$ ) (Stevenson & Cole, 1999). The formation of these compounds from inorganic-S is nearly always the result of microbial activity in anaerobic, or reducing, soil environments (Stevenson & Cole, 1999). Soil incubation studies have shown that  $\text{H}_2\text{S}$  production was strongly influenced by oxygen levels and nitrate concentrations (Connell & Patrick, 1969).  $\text{H}_2\text{S}$  evolution is also approximately equal to the amount of ferrous iron (Fe II) produced by water-logging the soils (Connell & Patrick, 1969). Dimethyl sulfide and  $\text{CS}_2$  emissions have been observed in both aerobic and anaerobic soils when amended with amino-S (C-bonded S) (Banwart & Bremner, 1975), but  $\text{H}_2\text{S}$  was not detected. This could be explained by the presence of oxide soil surface coatings in sufficient quantity to retain any  $\text{H}_2\text{S}$  that may have been produced, as observed by Connell and Patrick (1969) and Bloomfield (1969). Volatilization is unlikely to be a significant loss pathway for S under aerobic field conditions, but could be considerable under anaerobic conditions (e.g. rice paddies).

#### 1.3.4 Behavior of Potassium in Soils

Potassium (K) is an essential plant nutrient, and is the third most common limiting nutrient for agricultural production. As an alkali earth metal, K is highly reactive and rarely found in its pure state in nature (Tan, 2000). Unlike many other plant nutrients, K remains in its ionic form ( $K^+$ ) within the plant, and is generally not assimilated into structures or organic compounds. It plays an important role in photosynthesis, metabolism, and controlling water potential within the plant. K generally receives less attention in agriculture because other nutrients are more limiting to plant growth, and K-leaching does not contribute to eutrophication (Tan, 2000).

According to Martin and Sparks (1983), the bioavailability of K in the soil is governed by equilibrium reactions between three main pools: nonexchangeable-K, exchangeable-K, and soluble-K, where the latter two are considered plant-available. The vast majority of soil-K, over 95% in most soils, is fixed in the nonexchangeable-K pool ( $K_{non}$ ), where it is either trapped between clay platelets or fixed in the crystalline structures of orthoclase and feldspars (Sparks et al., 1980). Exchangeable-K ( $K_{ex}$ ) is associated with cation exchange sites, where it is sorbed to the surface of soil particles (Sparks et al., 1980). Soluble-K ( $K_{sol}$ ) represents a small fraction of total soil-K, and exists as  $K^+$  ions in the soil solution (Sparks et al., 1980). K moves to and from  $K_{non}$  via precipitation and dissolution reactions, and the kinetic rates of which are quite slow (Martin & Sparks, 1983). As  $K^+$  is easily replaced by  $H^+$  and polyvalent cations, such as  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Al^{3+}$ , K movement between  $K_{ex}$  and  $K_{sol}$  pools is more dynamic, and strongly influenced by the presence of polyvalent cations and the pH of the soil solution (Essington, 2004; Nolan & Pritchett, 1960). Kinetic rates of sorption are fast, and generally considered to be instantaneous, although Sparks et al. (1980) and Barshad (1951) found that these rates are affected by the type of clay present, and are relatively slow in vermiculite. Most soil-K is tied up in the  $K_{non}$  pool, and will move to  $K_{ex}$  and  $K_{sol}$  pools when plant uptake or leaching remove K from the profile (Sparks, 1980). Likewise, K-fixation will occur when  $K_{ex}$  and  $K_{sol}$  increase, commonly as a result of K fertilization.

Relative to N and P, K-deficiencies are rare but have been noted in sandy soils prone to leaching, and in low-K input cropping systems (Gosling & Shepherd, 2005; Martin & Sparks, 1983; Nolan & Pritchett, 1960). Potassium is considered to be relatively immobile in the soil, due to the soil's cation exchange capacity (CEC) (Essington, 2004). However, Alfaro et al. (2004) showed that  $K_{\text{sol}}$  was actually quite mobile, and that K amendments, from both inorganic and organic K-sources, were prone to leaching in both clay and sandy soils due to preferential flow. Kolahchi and Jalali (2007) found that the presence of  $Ca^{2+}$  ions in irrigation water led to large amounts of K being leached from soils. Gosling and Shepherd (2005) found decreasing soil-K and increasing K-deficiencies in long-term organic systems because crop removal exceeded K-input.

### 1.3.5 Soil-pH and Buffering Capacity

Soil-pH is often referred to as the master chemical variable, due to the sheer number of chemical reactions involving either consumption or release of protons in the soil (Essington, 2004). The importance of soil acidity in agriculture is due more to its effect on nutrient availability than direct impediment of plant growth, which is rare. The development of acidic soils is the result of complex interactions between both chemical and physical soil properties, and can be caused by either natural processes or anthropogenic activities (Essington, 2004). According to von Uexküll and Mutert (1995) upwards of 30 percent of the world's ice-free, and otherwise arable, land area are covered by acidic soils with a pH less than 5.5.

Naturally developed acid soils are frequently caused by chemical weathering of parent material and the hydrolysis of aluminum (Al) or iron (Fe), and is most likely to occur in regions where precipitation exceeds evapotranspiration allowing base cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ) to be leached from the profile (Essington, 2004). Anthropogenic acidification in agricultural operations is generally the result of excessive N fertilization and crop biomass or grain removal. The effect

of nitrification of ammoniacal N fertilizers on soil acidity is well documented (Essington, 2004; Juo et al., 1995; Matsuyama et al., 2005; Schroder et al., 2011), and the removal of base cations through grain or biomass harvest may exacerbate the effect (Juo et al., 1995). According to Zhang and Raun (2006), most acid soils in Oklahoma are not caused by natural processes, but rather are the result of continuous crop production and nitrogen fertilization.

Crop yields in acidic soils are commonly limited by several factors. Soil acidity causes reduced root growth (Doss & Lund, 1975). Increased solubility of Al, Fe, and Mn also causes toxicity in plants (Essington, 2004). Plant availability of N, P, K, Ca and Mg is also reduced at low pH (Essington, 2004). The availability of phosphate is highly pH dependent, and precipitation of Al, Fe, and Mn phosphates is an important mechanism for decreased P availability in acid soils (Hinsinger, 2001). Yield reduction in acid soils in Oklahoma is most commonly attributed to Al toxicity and P deficiency (Boman et al., 1992; Zhang & Raun, 2006).

Remediation of acidic soils requires neutralization of the soil's total acidity (TA), and is usually achieved through the application of lime ( $\text{CaCO}_3$ ) in agricultural soils. TA can be conceptualized as two pools, active acidity and reserve acidity. Active acidity is simply the activity of  $\text{H}^+$  ions in solution. Reserve acidity is related to the size of the soil's CEC and the base cation saturation status of the CEC complex. In order to neutralize the TA of a soil, the active acidity must be neutralized and sorbed acidic cations (e.g.  $\text{Al}^{3+}$  and  $\text{H}^+$ ) must be replaced by base cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) from the CEC complex. Soil-pH measurements are effective means for determining active acidity, but some form of titration is needed to quantify the reserve acidity of the soil (Essington, 2004). Thus, soil-pH measurements are useful for determining whether lime should be applied, but cannot be used solely to determine lime application rates. Instead, these rates are usually determined using a buffer index (Zhang & Raun, 2006).

### 1.3.6 Canola Production

Canola is a member of the Brassicaceae plant family, and includes multiple species. According to Przybylki and Eskin (2011), canola is officially defined per the following:

“a seed from *B. napus* (L.) or *B. rapa* (L.) that produces an oil that must contain less than 2 percent erucic acid and solid component of the seed must contain less than 30 micromoles of any one or any mixture of 3-butenyl glucosinolate, 4-pentenyl glucosinolate, 2-hydroxy-3-butenyl glucosinolate, and 2-hydroxy-4-pentenyl glucosinolate per gram of air-dry, oil-free solid.”

Canola is the second largest oilseed crop in the world, with global production exceeding 70 Mt in 2016 (USDA Foreign Agricultural Service, 2017a). The top canola producing regions are the European Union (EU), Canada, and China, which produced 22, 18.4, 14.9 Mt respectively in 2016 (USDA Foreign Agricultural Service, 2017b). Canola production in the US is relatively low, 0.14 Mt (USDA Foreign Agricultural Service, 2017b), because it is a new crop, having only received the Generally Recognized as Safe (GRAS) status from the USDA in 1985 (Raymer, 2002). North Dakota and Oklahoma are the largest canola producing states in the US, combined they produce over 90 percent of the US crop (National Agricultural Statistics Service, 2017). In Oklahoma, canola is typically grown as a winter crop in rotation with winter wheat. It has gained attention in recent years as studies have shown canola-wheat rotations can reduce weed pressure and increase farm profitability when compared to continuous wheat cropping systems (Bushong et al., 2012).

Canola oil has a wide variety of uses, ranging from edible cooking and salad oils to feedstock for biofuel and chemical production (G. Lennox & Beckman, 2011; Przybylki & Eskin, 2011). As canola is not consumed raw, its value is dependent on the price of its major components, oil and meal, as shown in Equation 3, which was excerpted from G. Lennox and Beckman (2011).

$$\text{Canola Value} = (0.42 \times \text{Price}_{oil}) + (0.60 \times \text{Price}_{meal}) - \text{Crush} \quad (5)$$

Oil content is particularly important to the value of canola, and is strongly affected by environmental conditions the crop was grown under (Hammond, 2011). According to Hammond (2011) the most common yield limiting factors to canola are water, N, P, and S. Canola plants also require large amounts of K, however these plants are efficient K scavengers and yield responses to K are rarely documented (Hammond, 2011). Canola requires approximately 10 kg-S per ton of grain, as a result S deficiencies are more common and detrimental to yield than in cereal crops (Hammond, 2011; Mailer, 1989). Mailer (1989) found that S-fertilization increased grain protein content, but over-fertilization led to an undesirable increase in glucosinolates. It is well documented that  $\text{SO}_4^{2-}$  is the most important form of S taken up by canola (Hawkesford & De Kok, 2006; Smith, 2001). As previously discussed, sulfate ions are mobile in the soil, thus S-fertilizer recommendations should be yield based while taking soil-S into consideration. Karamanos et al. (2007) found that soil  $\text{SO}_4$ -S was not an accurate indicator of potential S-deficiency due to high spatial variability, even in fields with adequate soil-S test results. Soil-based S-recommendations are further complicated by significant variation in N and S use efficiency from one genotype to another, primarily due to differences in leaf-shedding patterns and nutrient remobilization between genotypes (Balint & Rengel, 2011).

## 1.4 Methodology

### 1.4.1 Locations and Soils

#### *1.4.1.1 Field Studies*

This study was conducted over a two-year period at three different locations in the state of Oklahoma. The first site, located at the South Central Agronomy Research Station near Chickasha, was initiated during the 2015-2016 winter canola production season in a Dale silt loam (fine-silty, mixed, superactive, thermic Pachic Haplustolls) with an initial soil-pH of 6.1, with a Sikora buffer index of 7.2. Initial Mehlich-3 K and Soil-S as sulfate were 120 ppm and 5 ppm respectively. The Chickasha study site was terminated following harvest of the 2015-2016 growing season. The second site, located approximately ten miles west of Stillwater and 2.5 miles north of Highway-51 at the Lake Carl Blackwell Agronomy Research Station (LCB), was also initiated during the 2015-2016 growing season on a Pulaski fine sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Udic Ustifluvents), with an initial soil-pH of 6.2. Initial Mehlich-3 K and Soil-S as sulfate were 145 ppm and 4.5 ppm respectively. The LCB study site was continued through the 2016-2017 growing season, however it was terminated in early March 2017 due to poor winter survival and wildlife grazing pressure. A third site, located at the Cimmaron Valley Research Station near Perkins, was initiated during the 2016-2017 growing season on a Teller fine sandy loam (Fine-loamy, mixed, active, thermic Udic Argiustolls) with an initial soil-pH of 5.5 and Sikora buffer index of 7.1. Initial Mehlich-3 K and Soil-S as sulfate were 142 ppm and 5 ppm respectively.

#### *1.4.1.2 Laboratory Studies*

Soil incubations were performed in the lab using two soils collected from two locations in Oklahoma; the Cimmaron Valley Research Station near Perkins from a Teller fine sandy loam (fine-loamy, mixed, active, thermic Udic Argiustolls), and the North Central Research Station near Lahoma from a Grant silt loam (fine-silty, mixed, superactive, thermic Udic Argiustolls).

Soils were taken from plots in a long-term study with a history of varying degrees of soil acidification (Butchee et al., 2012; Lollato, 2015). Perkins soils had an initial soil-pH of 5.9, while Lahoma soils had an initial pH of 4.75.

#### 1.4.2 Experimental Design

Studies were arranged in the field in a randomized complete block design with thirteen treatments and three replications. Treatment application rates were based on unpublished in-house studies conducted by Cegobias Jr. and Arnall (2014) to investigate the nutrient analysis of LST. Their studies reported a nutrient analysis of 50% K and 10% S. Treatments included a control plot receiving no K or S fertilization; filtered LST at three rates: Rate 1 = 46.8 L ha<sup>-1</sup>, Rate 2 = 93.5 L ha<sup>-1</sup>, and Rate 3 = 187 L ha<sup>-1</sup>; a conventional fertilizer blend (PAS) of potash (KCl) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) applied at three rates: Rate 1 = 28.1 Kg-K ha<sup>-1</sup> and 5.6 Kg-S ha<sup>-1</sup> (K and S equivalent of LST Rate 1), Rate 2 = 56.1 Kg-K ha<sup>-1</sup> and 11.2 Kg-S ha<sup>-1</sup> (K and S equivalent of LST Rate 2), and Rate 3 = 112.2 Kg-K ha<sup>-1</sup> and 22.4 Kg-S ha<sup>-1</sup> (K and S equivalent of LST Rate 3). It was necessary to balance N across all plots, as the S source used in PAS treatments also contained N. This was accomplished through the application of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) at rates equivalent to 4.9, 9.8, 19.6 Kg-N ha<sup>-1</sup> in such a way that each plot, including the control, received 19.6 Kg-N ha<sup>-1</sup> at each application event. Plots were 3 m wide by 6 m long. The variety Pioneer 46W94 was used for the experiment. Treatments were applied in either October (PP), or in late February (TD) prior to stem elongation.

#### 1.4.3 Field Methodology

All plots were sown using conservation tillage methods with a Great Plains small-plot no-till drill with a row-spacing of 37.5 cm. As previously mentioned, N was balanced across all plots, however additional N was applied in the spring to all plots at a rate of 75 kg-N ha<sup>-1</sup> to ensure grain yield was not limited by N. Plots were sown during the second week of September at



both Chickasha and LCB in the 2015-2016 growing season. Due to poor germination at Chickasha, the trial was replanted on September 27, 2015. Trials at LCB and Perkins were sown on September 28 and October 1 during the 2016-2017 growing season. Each trial was sown at a planting density of approximately 5.6 kg ha<sup>-1</sup>. Weed and insects were controlled using commercially available herbicides and insecticides as needed. Glyphosate and Prevathon were applied at 1.75 L ha<sup>-1</sup> and 1.2 L ha<sup>-1</sup>, respectively, on October 10, 2016 at Perkins. Plots were harvested with a Kincaid 8-XP self-propelled small plot combine during the first week of June at the Chickasha and LCB locations in the 2015-2016 growing season, and the last week of May at the Perkins location during the 2016-2017 growing season. The LCB location was not harvested during the 2016-2017 growing season due to poor stand caused by winter kill and heavy wildlife grazing.

#### Evaluation of Vegetative Development

Mid-season biomass development was determined from measurements of normalized difference vegetative index (NDVI) collected using a GreenSeeker sensor. NDVI measurements were collected in the fall, prior to the first hard freeze, and spring just prior to the crop entering reproductive growth stages. Percent canopy coverage was also determined, as part of another project, at the Chickasha and LCB sites during the 2015-2016 growing season using photographic images using a Cannon digital camera. These images were taken from two points along a center transect in each plot from approximately 1 m above the plant canopy, and were collected on the same day as NDVI measurements. Images were analyzed using the Canopeo desktop software package (Canopeo, 2015). Canopy cover measurements were not collected during the 2016-2017 growing season.

#### 1.4.4 Laboratory Methodology

#### 1.4.4.1 Titrimetry

The liming potential of LST was investigated using two different titration methods, as described in Method A and Method B.

##### 1.4.4.1.1 Method-A

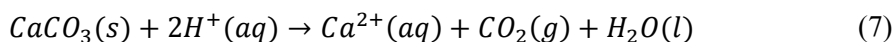
The first titration method (Method A) employed follows standard acid-base titrimetry procedures. The titration was conducted using a Metrohm 888 Titrando titrator equipped with a 20 mL exchange unit, Ecotrode Plus pH glass-electrode, and an automatic stirrer. Fifteen mL of LST was added to a Pyrex glass beaker and stirred continuously while titrated with 1.0 M hydrochloric acid (HCl). Acid was added at a mean rate of 20 mL min<sup>-1</sup>, with pH measurements automatically recorded every two seconds. The pH end-point for the titration was set to pH 2.5. Breakpoints were determined using the derivative method.

##### 1.4.4.1.2 Method-B

The second titrimetric method was adapted from Erich and Ohno (1992) in their work determining the CCE of wood ash. The solution was prepared by adding 22.0 mL of 1.0 N HCl to 4.0 mL of filtered LST. The resultant solution was then stirred for 15 minutes using a magnetic stir bar to ensure the acid neutralization capacity of LST had been exhausted, and then back-titrated using a ring-stand burette and 0.1 N sodium hydroxide (NaOH) to a pH endpoint of 8.3, which corresponds to the pKa of CaCO<sub>3</sub>. The amount of acid neutralized ( $Q$ ) by LST was calculated according to Equation 6, where the product of the volume of base required to reach the endpoint ( $V_{NaOH}$ ) and the normality of that base ( $N_{NaOH}$ ) was subtracted from the product of the volume of acid used to prepare the solution ( $V_{HCl}$ ) and the normality of that acid ( $N_{HCl}$ ).

$$Q = (V_{HCl} \times M_{HCl}) - (V_{NaOH} \times M_{NaOH}) \quad (6)$$

The CCE of LST was then determined using the moles of acid neutralized by LST, and that which would theoretically be neutralized by CaCO<sub>3</sub> according to Equation 6.



#### 1.4.4.2 Soil Incubations

The CCE of LST was also investigated using soil incubations, which were initiated on June 6, 2016. Sampling units were 1.0 L polyethylene cups containing 200 g of soil. Treatments included a control from each soil, which received neither LST nor lime (97% ECCE CaCO<sub>3</sub>); LST<sup>1</sup> at 4483.4, 8966.81, or 17933.6, 35867.2 kg ha<sup>-1</sup>; lime (CaCO<sub>3</sub>) at rates equivalent to 2241.7, 4483.4, 8966.81, or 17933.6 kg ha<sup>-1</sup> 100% ECCE lime. LST rates were double the lime rates due to significantly lower CCE determined in titration studies. Each soil was dried at 65°C for 24 hours, and ground to pass a 2 mm sieve. Samples of each soil weighing 200 g were then placed in incubation cups. Treatments were administered using an auto-pipette at the aforementioned rates, and the soils were then thoroughly mixed. Each sample was allowed to dry for approximately one week, and then rewetted with 40 mL of deionized water (17 mΩ). This wetting and drying cycle was continued until the soil-pH of the samples had stabilized, which was determined to be when the change in soil-pH was less than 0.1 pH units between cycles. All soil-pH measurements were made according to the methods discussed by EPA (2004) for 1:1 soil-water pH measurement using a Mettler Toledo™ S220 SevenCompact™ pH/Ion Benchtop Meter calibrated using a three-point calibration method with standard pH buffer solutions (pH 4, 7, and 10). Calibration slopes were deemed acceptable at 100% ± 1.5%.

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<sup>1</sup> LST rates were double that of CaCO<sub>3</sub> due to low CCE determined by preliminary titration studies.

### 1.4.5 Statistical Analyses

Data were analyzed using R Version 3.4.0 (R Core Team, 2015). Year was treated as a fixed effect, as recommended by Raun et al. (2017). Year-specific crop production factors, such as NDVI, yield, oil, and protein contents were differentiated using ANOVA methods and Tukey's Honest Significant Difference (HSD) procedures to separate the means at  $\alpha = 0.05$ . Linear regression models were used to determine the relationship of lime application rate to soil-pH, and LST application rate to soil-pH. These models were then used to estimate the CCE of LST.

## 1.5 Results and Discussion

### 1.5.1 Field Trials

#### 1.5.1.1 Chickasha

NDVI measurements at Chickasha in fall of the 2015-2016 growing season ranged from 0.45 to 0.75, with a median value of 0.58 and mean of 0.59. The effect of treatment on fall NDVI was significant at  $\alpha = 0.05$  (Table 1.2). Between-group pairwise comparisons indicate that significant treatment effects were due to application rate and nutrient source material (Figure 1.3). Fall NDVI in the control plots was not statistically different than that measured in PAS or LST plots (Figure 1.3). However, Fall NDVI in plots treated with PAS were statistically higher than plots treated with LST (Figure 1.3). Fall NDVI in plots receiving 46.8, 93.5, or 187 L ac<sup>-1</sup> were not statistically different, but were statistically higher than those measured in control plots (Figure 1.3). There were also significant differences between replications, where NDVI in Rep 1 was not significantly different than that of Rep 2, however both were greater than Rep 3 on average at  $\alpha = 0.05$  (Figure 1.3).

Spring NDVI measurements ranged from 0.51 to 0.72, with a median value of 0.61 and a mean of 0.61. There were no significant treatment effects on spring NDVI at  $\alpha = 0.05$ . There were significant differences in spring NDVI between replications (Table 1.2), where Rep 1 was

significantly greater than Rep 3 at  $\alpha = 0.05$  (Figure 1.4). Spring NDVI in Rep 1 was not statistically different than Rep 2 at  $\alpha = 0.05$ , nor was NDVI in Rep 3 statistically different from Rep 2 (Figure 1.4).

Grain yield data from Chickasha was not available from the 2015-2016 growing season, as heavy rains prevented timely field entry with harvest equipment. As a result, the pods shattered during harvest preventing accurate yield measurements. However, enough grain was collected from intact pods in each plot to conduct grain quality analyses. Grain protein contents ranged from 15.2% to 19.2%, with a median value of 17.0% and a mean of 17.1%. Grain oil content ranged from 33.9% to 46.9%, with a median value of 45.1% and a mean of 44.4%. There were no significant treatment effects on grain protein, or oil content (Table 1.2).

#### *1.5.1.2 Lake Carl Blackwell*

Fall NDVI measurements ranged between 0.62 and 0.82, with a median value of 0.74 and a mean of 0.73. Analysis of variance of the fall NDVI data indicates a significant treatment effect on NDVI at  $\alpha = 0.05$  (Table 1.3). Between-group pairwise comparisons suggest that significant treatment effects were caused by application material and rate (Figure 1.5). In general, NDVI measurements from plots treated with PAS and LST were not statistically different from those measured in control plots, however NDVI recorded from PAS treated plots were statistically higher than those measured in LST treated plots (Figure 1.5). NDVI measurements recorded from plots receiving treatment rates equivalent to 187 L ac<sup>-1</sup> were higher than those measured from plots receiving 93.5 L ha<sup>-1</sup> treatment rates, but not from plots receiving 187 L ha<sup>-1</sup> rates or the control plot (Figure 1.5).

Spring NDVI measurements ranged between 0.28 and 0.54, with a median value of 0.37 and a mean of 0.38. Analysis of variance suggested a significant treatment effect on spring NDVI at  $\alpha=0.05$  (Table 1.3). Between-group pairwise mean comparisons using Tukey's Honest

Significant Difference procedures found that the significant effects were caused by application timing (Figure 1.6). Differences in spring NDVI between control plots and those receiving treatment in either fall or spring were not statistically different at  $\alpha=0.05$  (Figure 1.6). However, spring NDVI measurements in plots receiving treatments in the spring (TD) were statistically greater than those measured in the fall treated (PP) plots at  $\alpha=0.05$  (Figure 1.6). NDVI measurements made in the spring were considerably lower than those made in the fall due to freeze damage and wildlife grazing (Table 1.3).

Grain yield in the 2015-2016 growing season ranged from 579.4 to 1803 kg ha<sup>-1</sup>, with a median value of 1232 kg ha<sup>-1</sup> and a mean of 1244 kg ha<sup>-1</sup>. There were no significant differences in grain yield between treatments at  $\alpha=0.05$ . However, between-group pairwise comparisons show that grain yield from plots receiving treatments in the spring (TD) were significantly greater than those receiving treatments in the fall (PP) (Figure 1.7).

Grain protein content ranged from 14.1% to 17.4%, with a median value of 15.8% and a mean of 15.8%. Differences in grain protein contents between treatments were not significant at  $\alpha=0.05$  (Table 1.3). Between-group pairwise comparisons show that grain protein contents of plots in Rep 1 were significantly higher than those in Rep 2 and Rep 3, while Rep 2 and Rep 3 were not significantly different at  $\alpha=0.05$  (Figure 1.8).

Grain oil content ranged from 42.8% to 47.5%, with a median value of 45.7% and a mean of 45.6%. There were no significant differences in grain oil contents (Table 1.3).

#### *1.5.1.3 Perkins*

Fall NDVI ranged from 0.50 to 0.69, with a median value of 0.58 and a mean of 0.58. There were significant treatment effects on fall NDVI at  $\alpha = 0.05$  (Table 1.4). Between-group pairwise comparisons indicate that significant effects were caused by application rate, material, and replication. Differences in NDVI in plots receiving PAS treatments were significantly higher

than plots receiving LST (Figure 1.9). NDVI in either LST or PAS treated plots were not significantly different than the control plots. Plots receiving treatment rates of 46.8 L ha<sup>-1</sup> (Rate 1) were significantly higher than the control plots and plots receiving treatment at 93.5 L ha<sup>-1</sup> rates (Rate 2) (Figure 1.9). Also, NDVI in plots located in the third replication were significantly higher than plots located in the first replication.

Spring NDVI ranged from 0.21 to 0.36, with a median value of 0.29 and a mean of 0.29 (Table 1.4). There were no significant treatment effects in spring NDVI, although the effect of replication was significant. Plots located in the third replication were significantly higher than plots located in the first replication (Figure 1.10).

Grain yield ranged from 99.2 kg ha<sup>-1</sup> to 706.4 kg ha<sup>-1</sup>, with a median value of 269.2 kg ha<sup>-1</sup> and mean of 287.3 kg ha<sup>-1</sup>. Grain protein ranged from 16.9% to 24.4%, with a median value of 19.1% and mean of 19.3%. Grain oil content ranged from 43.8% to 55.3%, with a median value of 49.4% and mean of 49.1% (Table 1.4). There were no significant treatment effects in grain yield, protein or oil content at Perkins during the 2016-2017 growing season. The lack of response is likely due severely decreased yield potential caused by poor winter survival and animal grazing pressure. A substantial number of deer tracks were found in the plots throughout the growing season, along with armadillo and geese. In the late spring some plots in the field also sustained damage caused by foraging feral hogs.

## 1.5.2 Laboratory Experiments

### 1.5.2.1 Titrimetric CCE Determination

The equivalent weight and CCE of LST as determined using acid titration was 198.17 g and 25.2% respectively. The CCE was also calculated using the second breakpoint of the titration curve shown in Figure 1.11 according to Equation 7.

$$\text{Equivalent Weight}_{LST} = \frac{\text{Mass}_{LST}}{V_{HCl} \times M_{HCl}} \quad (7)$$

The equivalent weight and CCE of LST as determined by acid-base back titration was approximately 235.3 g and 21.25% respectively. As expected, the CCE of LST was similar between Method A and B. Method B is less likely to overestimate CCE than Method A as the amount of HCl that was not neutralized, while small, is measured during back-titration with the sodium hydroxide solution and accounted for in the final calculation.

#### 1.5.2.2 Soil Incubations

The effect of application rate on soil-pH was statistically significant from both materials and in both soil types (Table 1.5, Figure 1.12). On average, soil-pH increased by 0.11 pH units per metric ton of CaCO<sub>3</sub> applied per hectare and by 0.017 pH units per ton of LST applied per hectare in the Pond Creek silt loam (Table 1.5). In the Teller fine sandy loam, soil-pH increased by 0.158 pH units per metric ton of CaCO<sub>3</sub> applied per hectare and by 0.027 pH units per metric ton of LST applied per hectare (Table 1.5). The effect of LST application rate on soil-pH can be summarized by Equation 8 for the Pond Creek silt loam and Equation 9 for the Teller fine sandy loam, where the final soil-pH ( $pH_f$ ) is equivalent to the sum of initial soil-pH ( $pH_i$ ) and the product of the mass of LST in metric tons and the regression coefficient.

$$pH_f = pH_i + 0.017 LST \quad (8)$$

$$pH_f = pH_i + 0.027 LST \quad (9)$$

The effect of CaCO<sub>3</sub> application rate on soil-pH can be summarized by Equation 10 for the Pond Creek silt loam, and Equation 11 for the Teller fine sandy loam.



$$pH_f = pH_i + 0.110 CaCO_3 \quad (10)$$

$$pH_f = pH_i + 0.158 CaCO_3 \quad (8)$$

The CCE of LST was determined by dividing the slope of the LST regression equations (Table 1.5) by the slope of the CaCO<sub>3</sub> regression equations (Table 1.5), as shown in Equation 12.

$$CCE\% = \left( \frac{m_{LST}}{m_{CaCO_3}} \right) \times \%ECCE_{CaCO_3} \quad (12)$$

Given the %ECCE of the CaCO<sub>3</sub> used in the trial was 97%, the CCE of LST was approximately 14.95% in the Pond Creek silt loam (Lahoma), and 16.3% in the Teller fine sandy loam (Perkins), yielding an average CCE of 15.6% between the two soils. Both LST and CaCO<sub>3</sub> raised soil-pH more effectively in the Teller fine sandy loam than the Pond Creek silt loam (Table 1.5). This is likely due to a lower CEC, and thus lower total acidity, in the relatively sandy Teller soil than the finer textured Pond Creek soil.

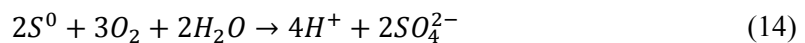
The relatively low CCE of LST could have numerous causes. As discussed by Essington (2004) raising soil-pH requires the neutralization of both active and exchangeable acidity in the soil. While the precise chemistry of LST is not well understood, active soil acidity occurs with OH<sup>-</sup>, similar to CaCO<sub>3</sub>. However, neutralization of exchangeable acidity requires displacement of Al<sup>3+</sup> from the CEC complex, this will occur with K<sup>+</sup> from LST as opposed to Ca<sup>2+</sup> from lime application. According to Coulomb's Law, the force ( $F$ ) with which hydrated cations are sorbed to CEC surfaces is directly proportional to the magnitude of the charges involved ( $q_+$ ,  $q_-$ ), and inversely related to the square of the distance ( $r$ ) separating the charges (Equation 13).

$$F = \frac{q_+q_-}{\epsilon r^2} \quad (13)$$

Le Chatelier's Principle states that when a stress is applied to a system in equilibrium, the equilibrium will change in a direction that tends to undo the effect of the stress (Essington, 2004).

Thus, while LST application can greatly increase the concentration (activity) of  $K^+$  in solution, leading to displacement of  $Al^{3+}$  from the CEC complex, the amount of  $Al^{3+}$  displaced will be less than that which would be displaced by similar amounts of  $CaCO_3$ . This results in less effective neutralization of the soil's TA, and could explain the lower CCE of LST when compared to  $CaCO_3$ . This could also explain differences in results from CCE determination using soil incubation versus that determined by the acid titration methods, as the HCl solutions used do not have any exchangeable acidity.

Another factor that may contribute to lower CCE of LST when determined by soil incubation vs acid titration is the presence of reduced S species in LST. While the soil incubations were frequently moistened, they were intentionally never saturated. Thus the reduction-oxidation (redox) potential of the soils was generally high, and the S may have been oxidized to  $SO_4^{2-}$  by soil microbes, such as Thiobacillus or Thiosprillum, in a manner similar to Equation 14.



Conversely, the discrepancy may also be due to the release of hydrogen sulfide ( $H_2S$ ) gas during the titration process, which would remove protons from the solution during titration and ultimately overestimate the CCE of LST. During acid titration (Method A), a pungent “rotten egg” odor was accompanied by profuse bubbling, which was likely indicative of the  $H_2S$  from the solution.

While the CCE of LST (15.6%) is substantially lower than that of  $CaCO_3$ , this study demonstrates that it can be used to neutralize soil acidity when applied at sufficient rates, and there may be situations where its application could be beneficial. For example, soil acidity was neutralized more rapidly in the LST soil incubations than the  $CaCO_3$  treated soil incubations, where LST treatments had stabilized after approximately six weeks, as opposed to nearly one

year for the  $\text{CaCO}_3$  treatments. Thus LST may prove particularly beneficial in situations where soil acidity must be neutralized during a small time frame.

## 1.6 Conclusions

The effect of LST on winter canola is difficult to assess given the lack of reliable grain yield data produced by the field trials. LST application reduced fall NDVI in trials at Lake Carl Blackwell and Perkins, however this did not translate to significant differences in grain yield, protein, or oil content at either location. The effect of application timing was more consistent throughout the field trials, where treatment applications made in the spring increased NDVI by approximately 0.075 and grain yield by approximately  $350 \text{ kg ha}^{-1}$  than those made in the fall.

Titration and soil incubation studies also demonstrated that LST may be used to neutralize soil acidity, with a CCE of approximately 15.6%. While its liming effect is substantially lower than  $\text{CaCO}_3$  (100% ECCE), neutralization of soil acidity occurs on a much smaller timescale. LST application may prove beneficial when producers need to make modest adjustments to soil-pH over small lengths of time. LST application would likely be most beneficial in moderately acidic soils that are also deficient in K and in S-responsive cropping systems. Determining the economic viability of LST as a liming agent or K and S fertilizer was not possible as the cost of the material was not available at the time of this study. Other potential uses of LST may include remediation of sodic soils, which are particularly detrimental to agricultural production. More studies are needed to further investigate alternative uses for this byproduct.

## 1.7 Tables

Table 1.1 Treatment structure of field trials conducted at the Chickasha, Lake Carl Blackwell, and Perkins sites. Application materials consist of Liquid Sulfur Trap (LST) and a conventional fertilizer blend of potash (KCl) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Applications were made either in the fall (PP) or spring (TD). Application rates were equivalent to 46.8 L-LST ha<sup>-1</sup> (Rate 1), 93.5 L-LST ha<sup>-1</sup> (Rate 2), 187 L-LST ha<sup>-1</sup> (Rate 3). The control plots received neither K nor S. The amount of potassium (K) and sulfur (S) applied are reported in kg ha<sup>-1</sup>.

Material	Rate	Timing	Potassium	Sulfur
Control	0	N/A	0	0
LST	1	PP	28.1	5.6
PAS	1	PP	28.1	5.6
LST	2	PP	56.1	11.2
PAS	2	PP	56.1	11.2
LST	3	PP	112.2	22.4
PAS	3	PP	112.2	22.4
LST	1	TD	28.1	5.6
PAS	1	TD	28.1	5.6
LST	2	TD	56.1	11.2
PAS	2	TD	56.1	11.2
LST	3	TD	112.2	22.4
PAS	3	TD	112.2	22.4

Table 1.2. Treatment means and ANOVA results for fall and spring NDVI, protein content (%), oil content (%) as effected by application material, rate, and timing over the 2015-2016 growing season in a Dale silt loam near Chickasha, OK. The values for protein, and oil content were corrected to 8% grain moisture. LST= Liquid Sulfur Trap, PAS = conventional K and S fertilizer blend using potash (KCl) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), PP = fall application, TD = spring application.

Material	Rate	Timing	NDVI (Fall)	NDVI (Spring)	Protein	Oil
Control	0	N/A	0.66a	0.65a	17.0a	44.5a
LST	1	PP	0.56ab	0.60a	16.8a	45.0a
PAS	1	PP	0.58ab	0.61a	17.8a	41.5a
LST	2	PP	0.52b	0.59a	16.6a	45.6a
PAS	2	PP	0.63a	0.63a	18.1a	44.5a
LST	3	PP	0.51b	0.57a	16.8a	45.6a
PAS	3	PP	0.58ab	0.60a	17.5a	40.1a
LST	1	TD	-	0.59a	17.2a	45.5a
PAS	1	TD	-	0.63a	17.1a	45.4a
LST	2	TD	-	0.61a	16.8a	40.2a
PAS	2	TD	-	0.64a	17.4a	45.3a
LST	3	TD	-	0.62a	17.2a	45.0a
PAS	3	TD	-	0.58a	16.9a	45.9a
Significance						
Rep			**	**	NS	NS
Treatment			***	NS	NS	NS
HSD†			0.104	0.109	2.91	8.21

\*, \*\*, \*\*\*, NS

Significant at p = 0.05, 0.01, 0.001, and non-significant

†

HSD values determined at a = 0.05

Table 1.3. Treatment means and ANOVA results for fall and spring normalized difference vegetative index (NDVI), grain yield (kg ha<sup>-1</sup>), protein content (%), oil content (%) as effected by application material, rate, and timing over the 2015-2016 growing season in a Pulaski fine sandy loam near Lake Carl Blackwell, OK. Application were applied at different times, either in the fall (PP) or spring (TD). The values for grain yield, protein, and oil content were corrected to 8% grain moisture.

Material	Rate	Timing	NDVI (Fall)	NDVI (Spring)	Yield	Protein	Oil
Control	0	-	0.74ab	0.36ab	996.6a	15.9a	45.7a
LST	1	PP	0.72ab	0.30b	930.3a	15.6a	45.2a
PAS	1	PP	0.78ab	0.34ab	1033.2a	16.3a	43.5a
LST	2	PP	0.70b	0.36ab	969.3a	16.1a	46.0a
PAS	2	PP	0.71ab	0.32b	1127.5a	15.2a	46.0a
LST	3	PP	0.74ab	0.33b	1223.7a	15.5a	46.7a
PAS	3	PP	0.81a	0.36ab	1202.3a	16.0a	44.9a
LST	1	TD	-	0.39ab	1203.0a	15.8a	44.9a
PAS	1	TD	-	0.39ab	1605.5a	16.0a	45.5a
LST	2	TD	-	0.41ab	1320.9a	16.2a	45.5a
PAS	2	TD	-	0.40ab	1350.6a	15.2a	46.2a
LST	3	TD	-	0.41ab	1611.2a	15.5a	45.5a
PAS	3	TD	-	0.46a	1427.3a	15.8a	46.1a
Significance							
Rep			NS	NS	*	**	NS
Treatment			*	**	NS	NS	NS
HSD†			0.096	0.13	851.7	2.20	3.98

\*, \*\*, \*\*\*, NS

†

Table 1.4. Treatment means and ANOVA results for fall and spring NDVI, grain yield (kg ha<sup>-1</sup>), protein content (%), oil content (%) as effected by application material, rate, and timing over the 2015-2016 growing season in a Pulaski fine sandy loam near Lake Carl Blackwell, OK. The values for grain yield, protein, and oil content were corrected to 8% grain moisture. LST= Liquid Sulfur Trap, PAS = conventional K and S fertilizer blend, PP = fall application, TD = spring application. Rate 5 = 46.8 L ha<sup>-1</sup>, 10 = 93.5 L ha<sup>-1</sup>, 20 = 187 L ha<sup>-1</sup>.

Material	Rate	Timing	NDVI (Fall)	NDVI (Spring)	Yield	Protein	Oil
Control	0	-	0.55bc	0.27a	260.5a	19.46	48.42
LST	1	PP	0.58abc	0.27a	258.8a	19.31	49.29
PAS	1	PP	0.64a	0.29a	250.7a	19.12	49.03
LST	2	PP	0.54c	0.31a	281.9a	18.16	49.24
PAS	2	PP	0.59abc	0.32a	305.2a	18.30	49.22
LST	3	PP	0.58abc	0.25a	178.1a	18.97	47.56
PAS	3	PP	0.62ab	0.32a	321.2a	18.62	50.69
LST	1	TD	-	0.30a	482.3a	20.45	51.98
PAS	1	TD	-	0.30a	345.7a	19.42	48.70
LST	2	TD	-	0.30aba	418.4a	19.75	48.13
PAS	2	TD	-	0.27aba	247.2a	19.92	47.66
LST	3	TD	-	0.30aba	363.0a	19.18	49.33
PAS	3	TD	-	0.28a	326.3a	20.17	48.37
Significance							
Rep			*	*	NS		
Treatment			**	NS	NS		
HSD†			0.073	0.094	404.4		

\*, \*\*, \*\*\*, NS

Table 1.4. Linear regression model parameters and statistics regarding the effect of LST and lime (CaCO<sub>3</sub>) application on a Pulaski silt loam and Teller fine sandy loam from Lahoma and Perkins, OK.

Dependent variable:				
Soil-pH				
	LST	LST	CaCO <sub>3</sub>	CaCO <sub>3</sub>
	(Pond Creek silt loam)	(Teller fine sandy loam)	(Pond Creek silt loam)	(Teller fine sandy loam)
Rate	0.01695*** (0.002)	0.02656 *** (0.003)	0.1102*** (0.004)	0.1580*** (0.023)
Constant	4.521*** (0.036)	4.861*** (0.057)	4.233*** (0.041)	4.812*** (0.209)
Observations	15	15	10	10
R2	0.853	0.852	0.987	0.859
Res. Std. Error	0.096 (df=13)	0.151 (df=13)	0.088 (df=8)	0.454 (df=8)
F Statistic	75.432*** (df=1;13)	74.551*** (df=1;13)	628.887*** (df=1;8)	48.771*** (df=1;8)
Note:	*p<0.1; **p<0.05; ***p<0.01			



## 1.8 Figures

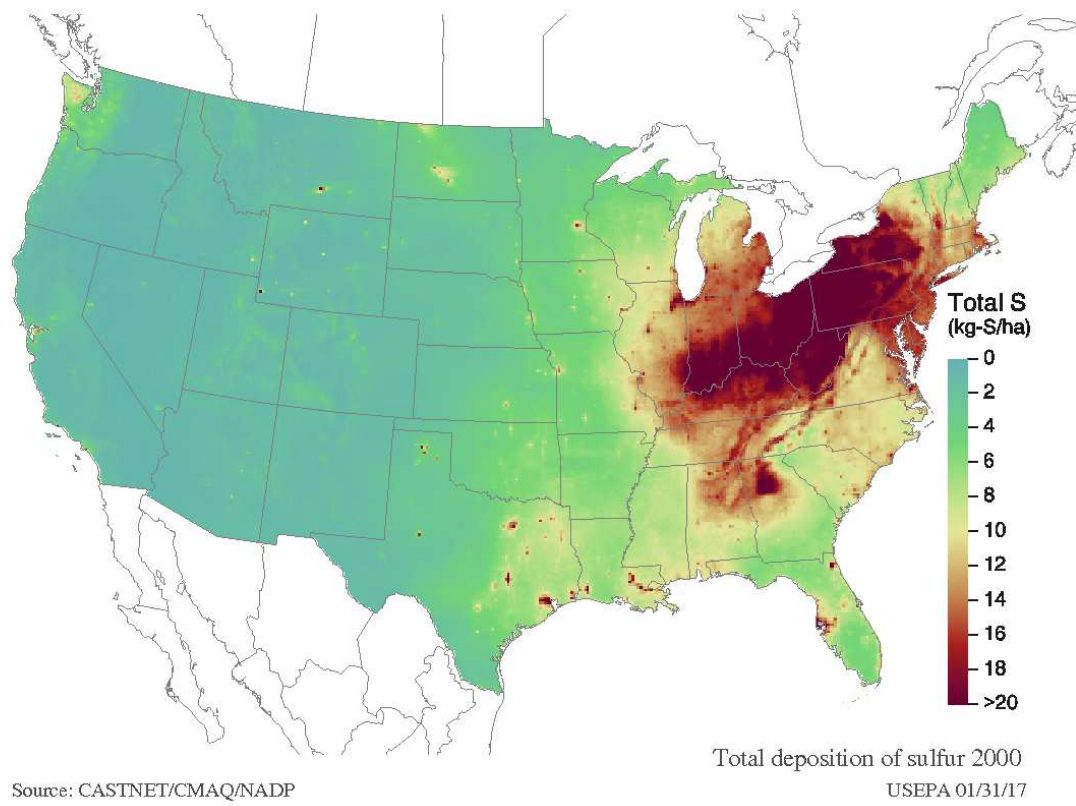


Figure 1.1. Total sulfur (S) deposition flux ( $\text{Kg-S ha}^{-1}$ ) across the continental US in 2000.

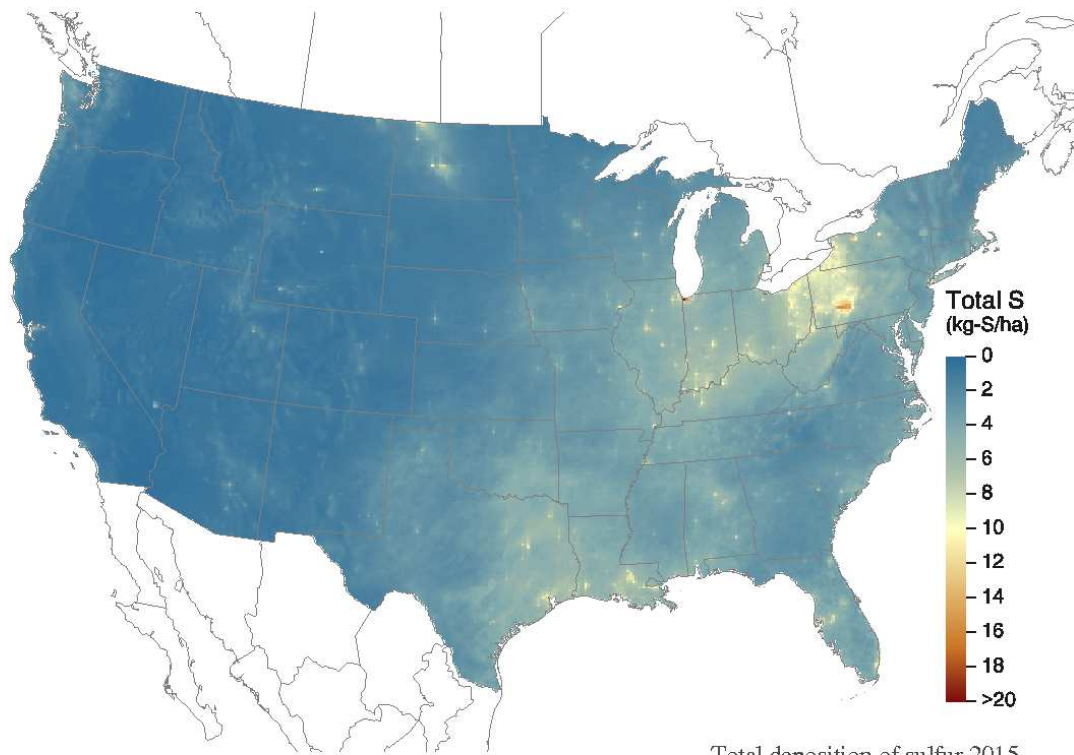


Figure 1.2. Total sulfur (S) deposition flux ( $\text{Kg-S ha}^{-1}$ ) across the continental US in 2015.

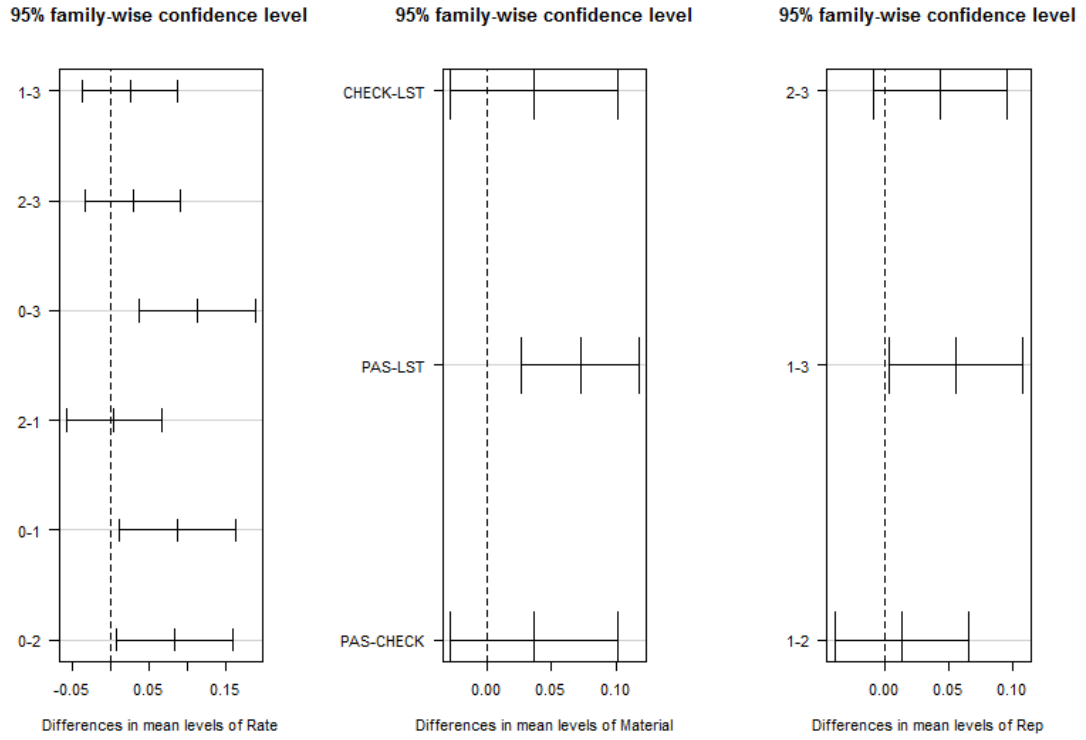


Figure 1.3. Between-groups comparisons of the effect application rate (left), application material (right), and replication (right) on fall NDVI in Chickasha (2015-2016) using Tukey's Honest Significant Difference procedures at the 95% confidence level.

**95% family-wise confidence level**

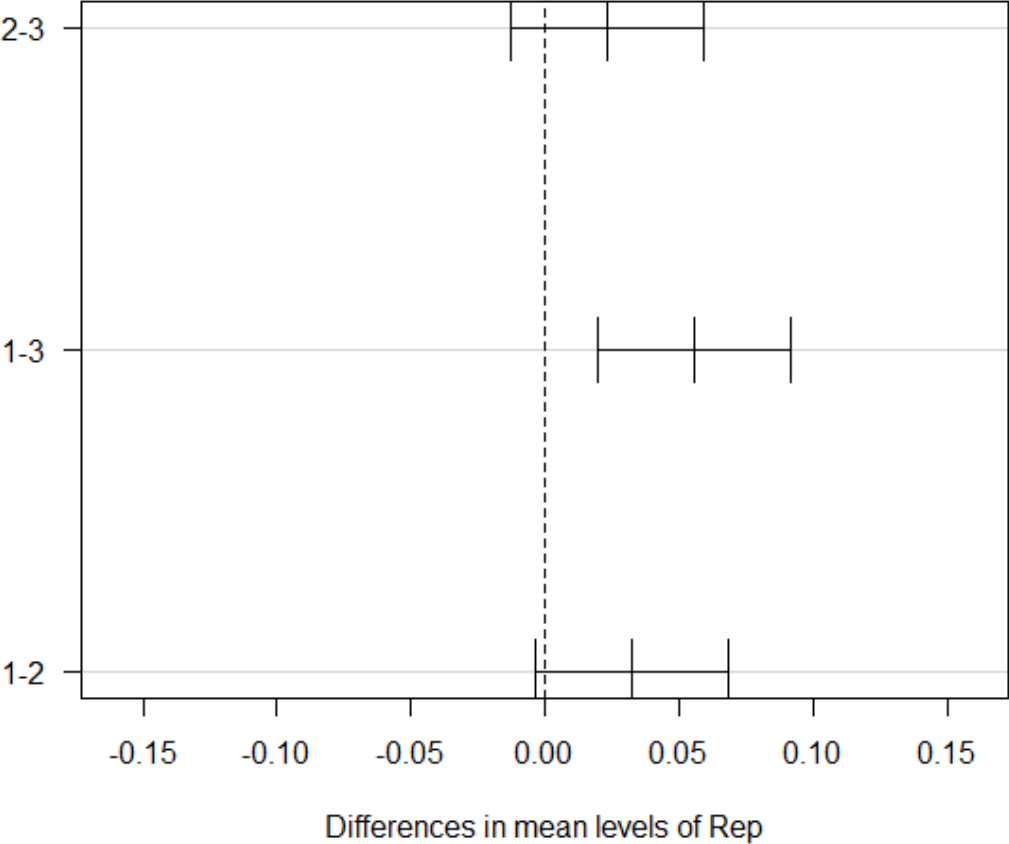
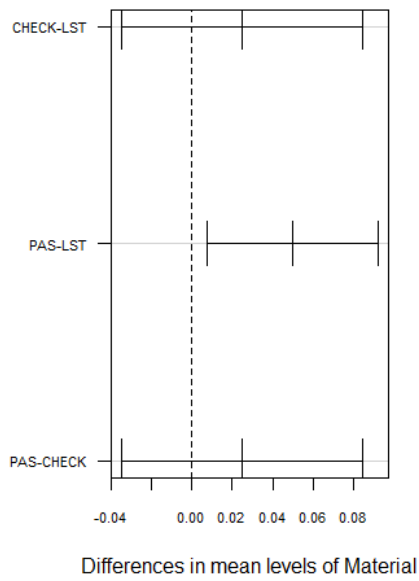


Figure 1.4. Between replication comparisons of spring NDVI at Chickasha using Tukey's Honest Significant Difference procedures at the 95% confidence level Lake Carl Blackwell.

95% family-wise confidence level



95% family-wise confidence level

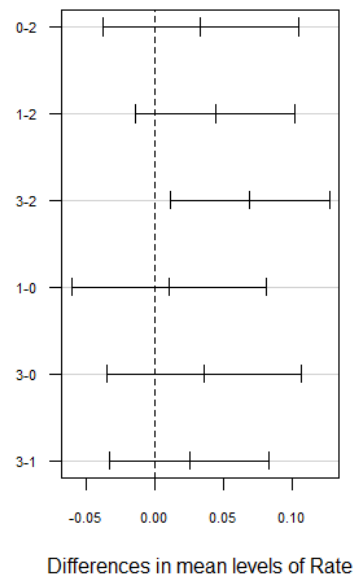


Figure 1.5. LCB mean fall NDVI between-groups comparisons of application material (left) and application rate (right) using Tukey's Honest Significant Difference procedures at the 95% confidence level. Check = control (no K or S input), LST = Liquid Sulfur Trap, PAS = conventional K and S fertilizer blend. Rate 0 = control (no K or S), Rate 1 = 46.8 L ha<sup>-1</sup>, Rate 2 = 93.5 46.8 L ha<sup>-1</sup>, Rate 3 = 187 L ha<sup>-1</sup>.

95% family-wise confidence level

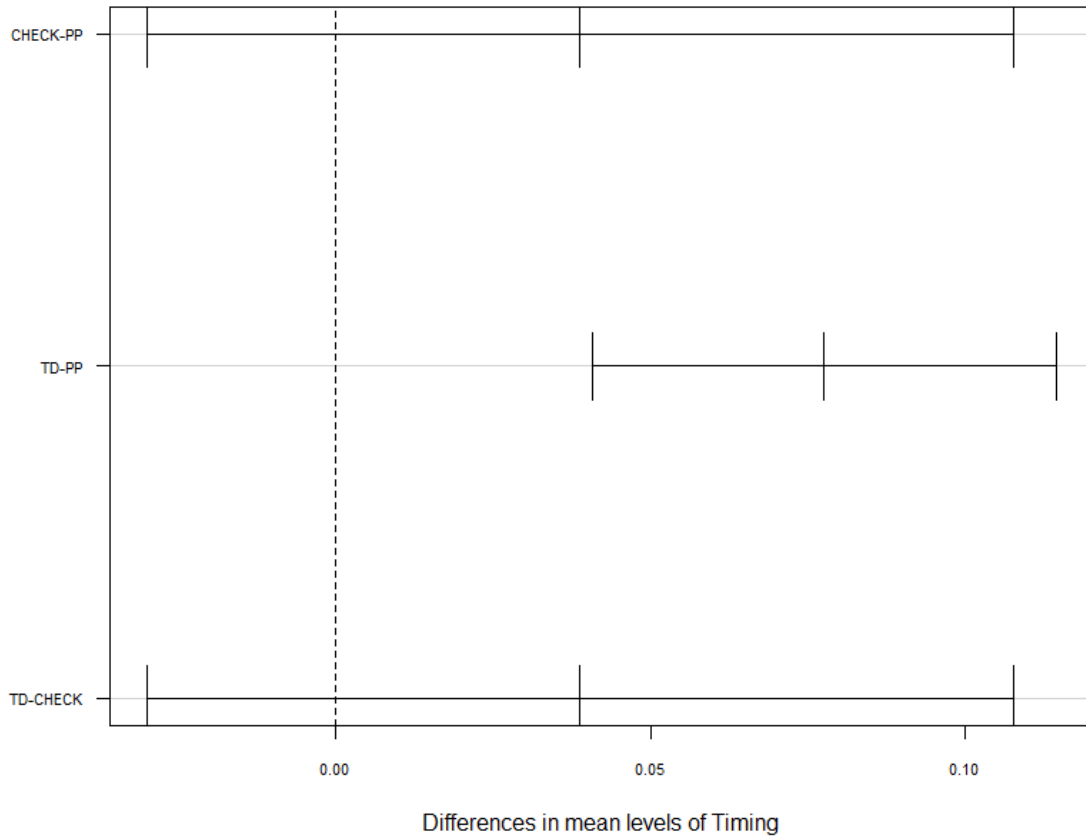


Figure 1.6. Between-group comparisons of the effects of application timing on spring NDVI at Lake Carl Blackwell during the 2015-2016 growing season. Comparisons were made using Tukey's Honest Significant Difference procedures at the 95% confidence level. Check = control (no K or S input), PP = fall application, TD = spring application.

95% family-wise confidence level

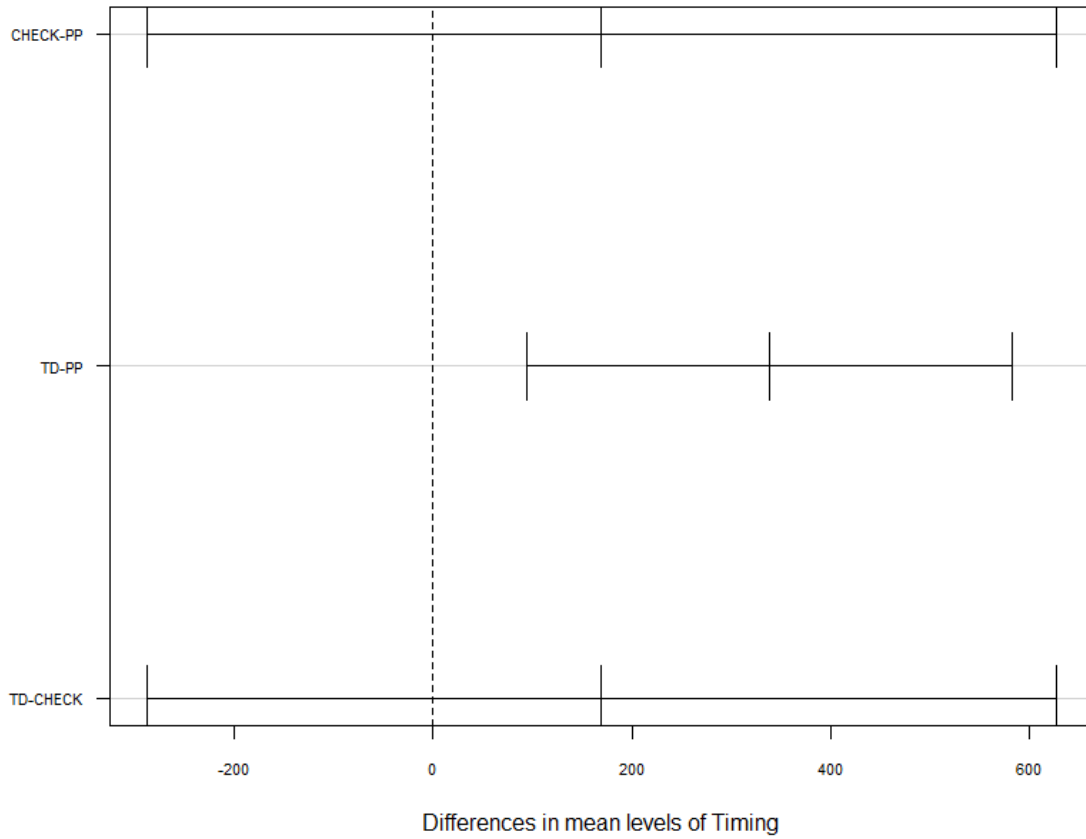


Figure 1.7. Between-groups pairwise comparison of the effect of application timing on grain yield at Lake Carl Blackwell during the 2015-2016 growing year. Comparisons made using Tukey's Honest Significant Difference procedures at  $\alpha = 0.05$ . Check = control (no K or S input), PP = fall application, TD = spring application.

95% family-wise confidence level

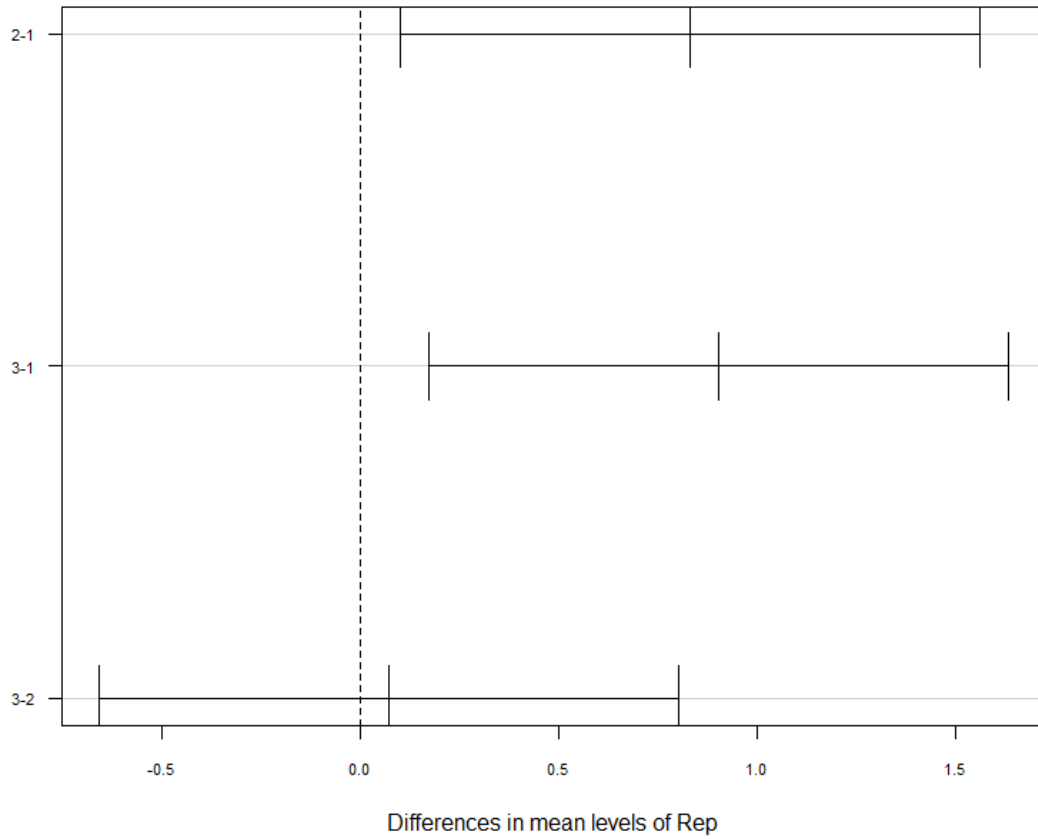


Figure 1.8. Between-groups pairwise comparison of the effect of replication on grain protein at Lake Carl Blackwell during the 2015-2016 growing year. Comparisons made using Tukey's Honest Significant Difference procedures at  $\alpha = 0.05$ .



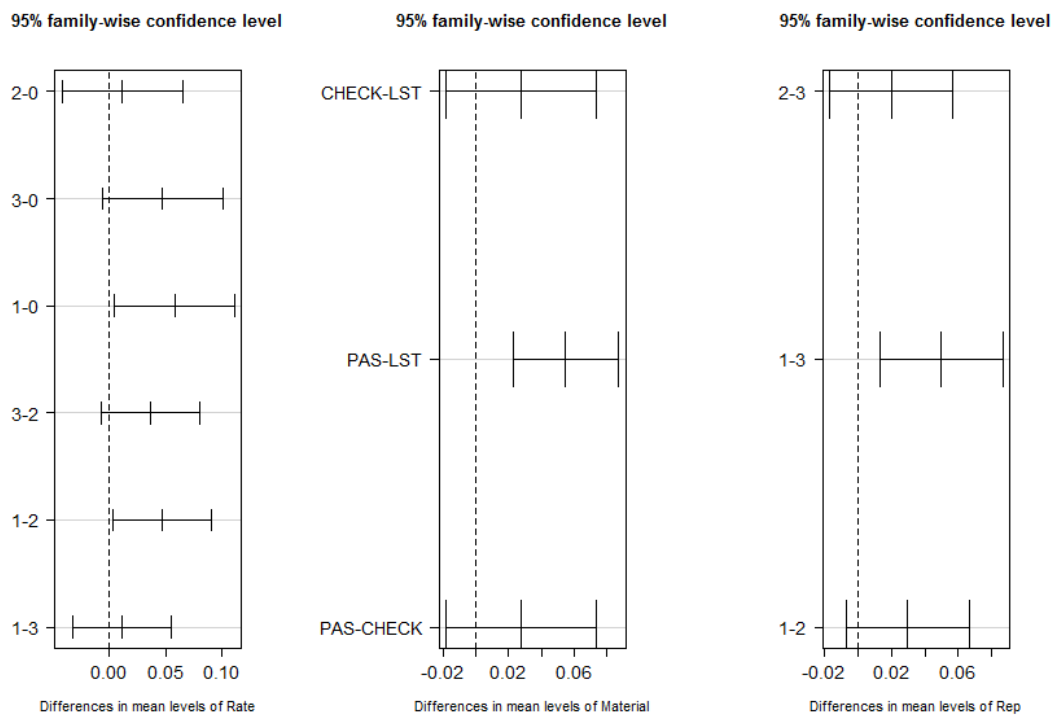


Figure 1.9. Between-groups pairwise comparisons of Fall NDVI at Perkins as affected by application rate (left), material (middle), and replication (right). Comparisons made using Tukey's Honestly Significant Difference procedures at  $\alpha = 0.05$ . Application rate 0 = 0 L ha<sup>-1</sup>, rate 1 = 46.8 L ha<sup>-1</sup>, rate 2 = 93.5 L ha<sup>-1</sup>, rate 3 = 187 L ha<sup>-1</sup>. Application material CHECK = control, LST = Liquid Sulfur Trap, PAS = conventional K and S fertilizer blend.

95% family-wise confidence level

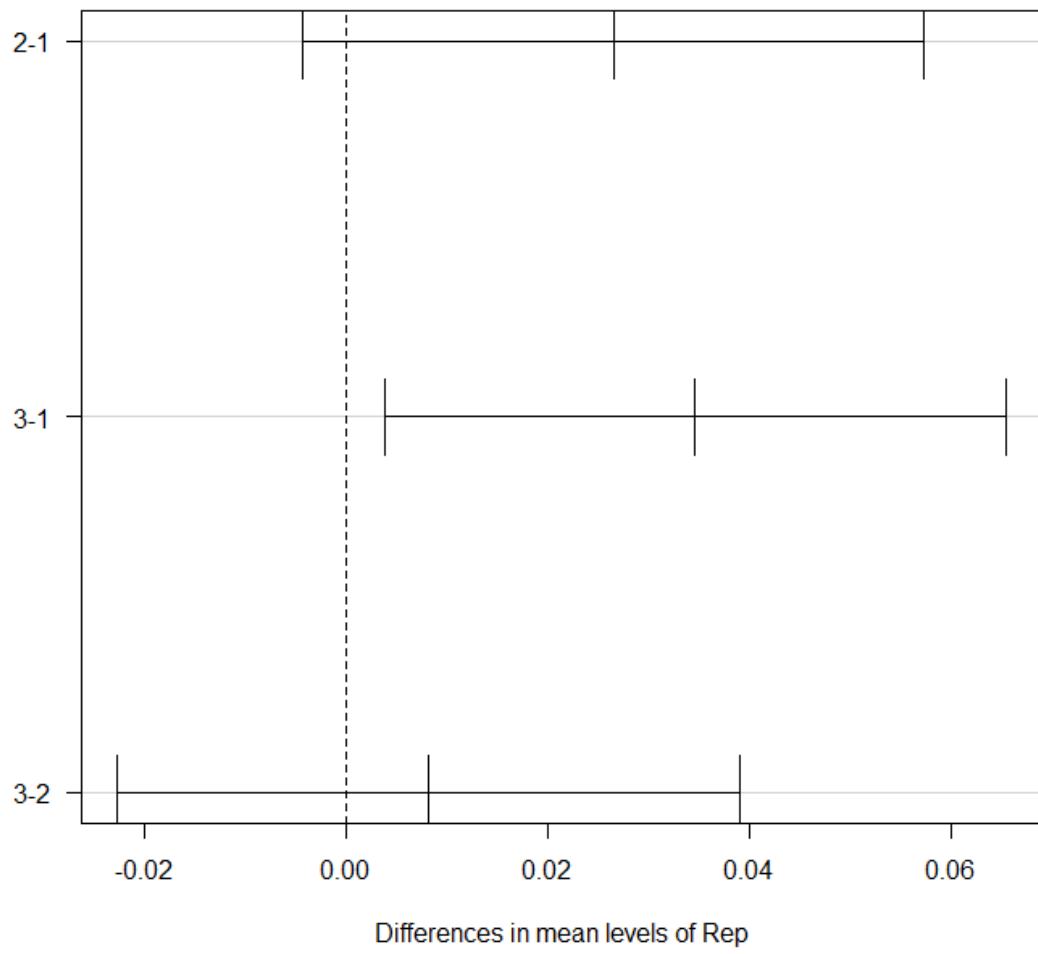


Figure 1.10. Between-groups pairwise comparisons of Spring NDVI as affected by replication at the Perkins site. Comparisons made using Tukey's Honestly Significant Difference procedures at  $\alpha = 0.05$ .

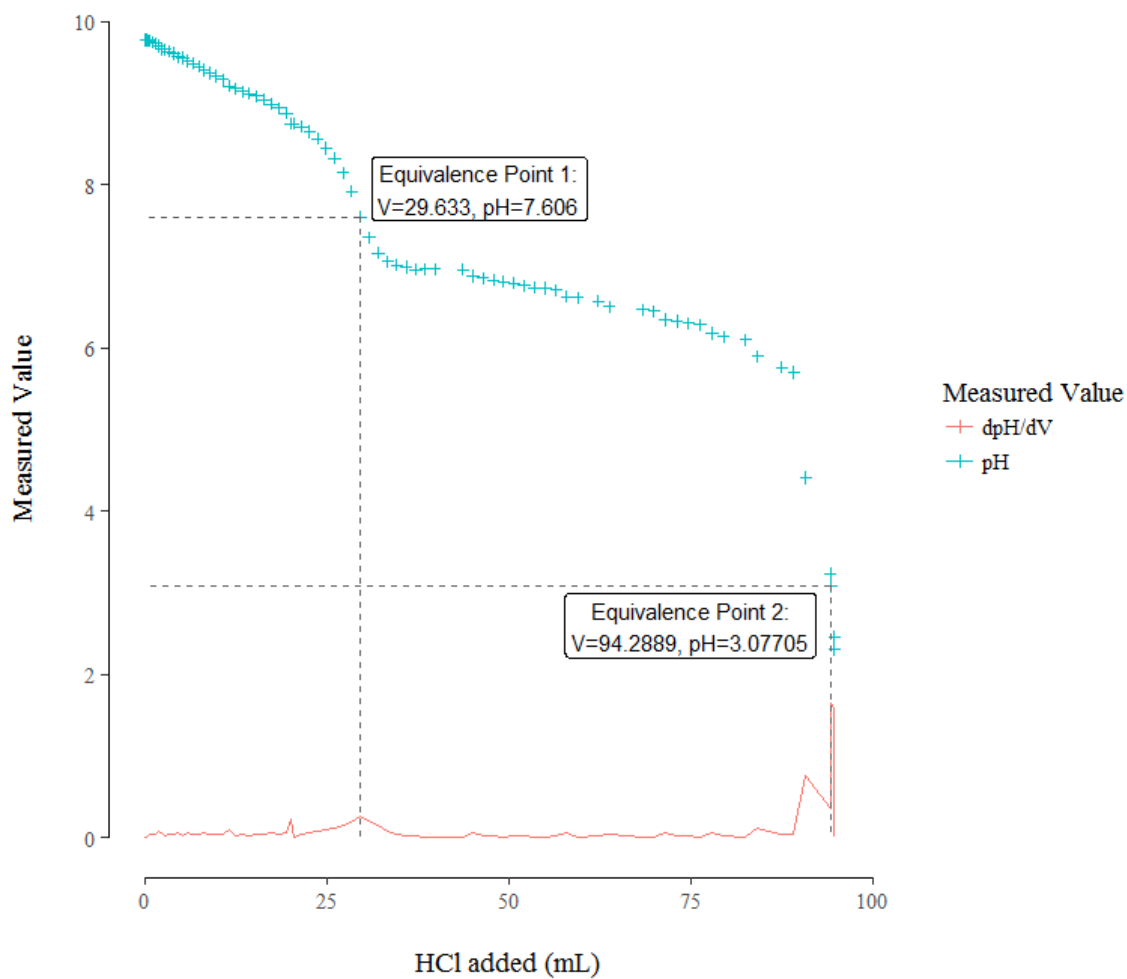


Figure 1.11. Chemical characterization of LST using acid titration 1.0 M HCl. Equivalence points were determined using the derivative method, and indicated by the intersection of dashed grey lines. Solution pH measurements are indicated by blue hashes, volumetric derivative indicated by orange line.

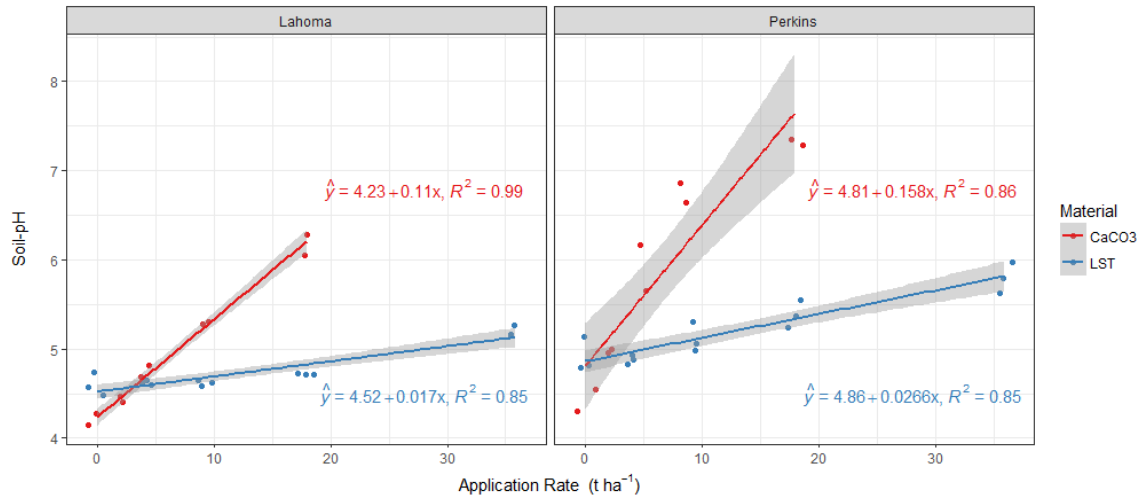


Figure 1.12. Effect of LST and lime (CaCO<sub>3</sub>) application on soil-pH in a Pulaski silt loam (left) and Teller fine sandy loam (right) from Lahoma (left) and Perkins (right), OK. Grey-shaded area indicates the 95% confidence interval for the respective linear regression equations.

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## CHAPTER II

### IMPACT OF SOIL-pH ON SOIL PHOSPHORUS EXTRACTION METHOD RESULTS

#### 2.1 Introduction

Phosphorus (P) is an essential element of life and is commonly a growth limiting factor in agricultural and natural environments. The vast majority of the earth's P is tied up in oceanic waters and marine sediments ( $8.4 \times 10^{17}$  kg), with less than one percent of the planet's P found in soils ( $1.3 \times 10^{14}$  kg) (Stevenson & Cole, 1999). Soil-P concentrations typically range from 500-1000 mg kg<sup>-1</sup>, however only a small fraction of this may be available for plant uptake (Stevenson & Cole, 1999). According to MacDonald et al. (2011) 30% of the planet's arable soils are P-deficient, and is one of the most deficient nutrients in Oklahoman soils (Zhang & Raun, 2006). Phosphorus amendment is common practice in agricultural production systems, and has been linked to eutrophication of surface waters (Bennett et al., 2001; Rabalais et al., 2010; Sharpley & Withers, 1994).

P exists as phosphate (PO<sub>4</sub><sup>3-</sup>) in soils, and is considered an immobile nutrient, as phosphate tends to form insoluble compounds in the presence of polyvalent cations (e.g. Al<sup>3+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>). Therefore, P fertilizer recommendations are frequently based on the sufficiency concept for immobile nutrients, as discussed by Bray (1953), and the degree of sufficiency is dependent on soil concentration rather than crop yield and composition (Zhang & Raun, 2006). Given that P fertilizer recommendations are dependent on soil concentration, and only a small

fraction of total soil-P is plant available, it is imperative that soil-P testing methods are accurate and well understood.

Phosphorus availability is also strongly affected by soil-pH (Essington, 2004; Stevenson & Cole, 1999; Zhang & Kovar, 2000), and maximum P-availability is expected to occur near pH 6.5 (Stevenson & Cole, 1999). Phosphate is likely to be precipitated as Al- or Fe-phosphates or sorbed to oxide surfaces in acidic soils, or as di- and tri-calcium phosphates in alkaline soils (Stevenson & Cole, 1999). Many Oklahoma soils have been acidified by continuous crop production and N-fertilization (Schroder et al., 2011).

Winter wheat P-response studies performed by Watkins (2017a) documented stratification of both soil-P and pH in no-till soil profiles, and unexpectedly low P-responses, even when Mehlich-III soil-P concentrations were below 5 mg kg<sup>-1</sup>. Given the propensity of P to form insoluble compounds at both high and low soil-pH, and the documented variability of P and pH in the field, accurate and well-understood soil-P testing methods are important to maintaining and improving P-fertilizer recommendations. The objective of this research was to investigate the relationship between soil-pH and soil-P extractability using various soil-P extraction methods. This information may help improve soil test interpretations, allowing for more accurate P-fertilizer recommendations, and conversion of soil test-P results from one method to another.

## 2.2 Research Objectives

*Objective 1:* Document the relationship between soil-pH and Bray-P1, Mehlich-III P, Total-P, and Water Soluble-P

*Objective 2:* Investigate the relationships between Bray-P1, Mehlich-III P, total-P, and Water Soluble-P across a range of soil-pH levels

*Objective 3:* Investigate the effect of soil-pH on soil-P speciation.

## 2.3 Review of Literature

Soil-pH is often referred to as the master chemical variable, due to the sheer number of chemical reactions involving either consumption or release of protons in the soil (Essington, 2004). The importance of soil acidity in agriculture is due more to its effect on nutrient and availability (solubility) than direct impediment of plant growth, which is rare. The development of acidic soils is the result of complex interactions between both chemical and physical soil properties, and can be caused by either natural processes or anthropogenic activities (Essington, 2004). According to von Uexküll and Mutert (1995) upwards of 30 percent of the world's ice-free, and otherwise arable, land area are covered by acidic soils with a pH less than 5.5.

Naturally developed acid soils are frequently caused by chemical weathering of parent material and the hydrolysis of aluminum (Al) or iron (Fe), and is most likely to occur in regions where precipitation exceeds evapotranspiration allowing base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) to be leached from the profile (Essington, 2004). Anthropogenic acidification in agricultural operations is generally the result of excessive nitrogen fertilization and crop biomass or grain removal. The effect of nitrification of ammoniacal-N fertilizers on soil acidity is well documented (Essington, 2004; Juo et al., 1995; Matsuyama et al., 2005; Schroder et al., 2011), and the removal of base cations through grain or biomass harvest may exacerbate the effect (Juo et al., 1995). According to Zhang and Raun (2006), most acid soils in Oklahoma are not caused by natural processes, but rather are the result of continuous crop production and nitrogen fertilization.

Crop yields in acidic soils are commonly limited by several factors. Soil acidity causes reduced root growth (Doss & Lund, 1975), primarily due to metal toxicity issues. Increased solubility of Al, Fe, and Mn also causes toxicity in plants (Essington, 2004). Plant availability of N, P, K, Ca and Mg is also reduced at low pH (Essington, 2004). The availability of phosphate is highly pH dependent, and precipitation of Al, Fe, and Mn phosphates is an important mechanism for decreased P availability in acid soils (Hinsinger, 2001; Lindsay, 1979). Yield reduction in acid

soils in Oklahoma is most commonly attributed to Al toxicity and P deficiency (Boman et al., 1992; Zhang & Raun, 2006).

There are numerous soil-P extraction methods currently in use by soil testing labs across the US (Pierzynski, 2000). The extraction method used varies between regions depending primarily on soil-pH. According to Elrashidi (2005) and (Pierzynski, 2000), Bray-P1, Mehlich-1, Mehlich-3, Water, and anion exchange resin (AER) are recommended for soil-P extraction in acidic to neutral soils. Olsen-P, Water, and AER are the standard methods in calcareous soils (Elrashidi, 2005; Pierzynski, 2000).

The Bray-P1 extraction method was developed by Bray and Kurtz (1945) for quantification of plant-available P in acidic soils and is currently in common use across the North Central Region of the US (Watson & Mullen, 2007). The method described by Sims (2000) calls for the suspension of 2 g of soil in 20 mL of 0.025 M HCl and 0.03 M NH<sub>4</sub>F extracting solution adjusted to a pH of  $2.6 \pm 0.05$ . The resultant suspension is shaken for 5 minutes at room temperature and filtered through Whatman No. 42 filter paper. The filtered solution is then analyzed either by colorimetry or inductively couple plasma emission spectroscopy (ICP-ES). The Bray-P1 solution extracts and prevents the resorption of P through complexation of Al and colloid surfaces with fluorine (F), and the solubility of Al-, Ca-, and Fe-bound P is enhanced by the acidic nature of the extractant (Sims, 2000). Critical Bray-P1 values vary in the literature. Beegle and Oravec (1990) determined critical values for corn to be approximately 20 mg kg<sup>-1</sup> using the Cate-Nelson procedure, while work performed by Mallarino and Blackmer (1992) indicated a critical value for 12 mg kg<sup>-1</sup> using the same crop and statistical procedures. Adeoye and Agboola (1985) identified a Bray-P1 critical range of 10 to 16 mg kg<sup>-1</sup>, as opposed to a single value for corn in South-western Nigeria.

The Olsen-P extraction method was developed by Olsen et al. (1954) for quantification of plant-available P in calcareous soils. The original method calls for the suspension of 5 g of soil in 100 mL of a 0.5 M sodium bicarbonate ( $\text{NaHCO}_3$ ) solution adjusted to a pH of 8.5. The resultant suspension was shaken for 30 minutes, and filtered through Whatman No. 40 filter paper. A 5 mL aliquot of the extracted solution is then analyzed colorimetrically using a molybdate reagent acidified with HCl to neutralize unreacted  $\text{NaHCO}_3$ . According to Olsen et al. (1954), P extraction efficiency of  $\text{NaHCO}_3$  is due to  $\text{HCO}_3^-$ ,  $\text{OH}^-$ , and  $\text{CO}_3^{2-}$ , where the activity of  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$  are reduced through the precipitation of  $\text{CaCO}_3$ , and Al and Fe hydroxides respectively. Olsen et al. (1954) also determined crop response critical values for  $\text{NaHCO}_3\text{-P}$ , where crop response to P was likely below 28 kg  $\text{P}_2\text{O}_5 \text{ ha}^{-1}$ , somewhat likely between 28-56 kg  $\text{P}_2\text{O}_5 \text{ ha}^{-1}$ , and not likely above 56 kg  $\text{P}_2\text{O}_5 \text{ ha}^{-1}$ . However, Xu et al. (2009) found that Olsen-P critical values varied with site, crop, and the model used to identify the critical point. Johnston et al. (2013) also found that Olsen-P critical values ranged from 8-36 mg  $\text{kg}^{-1}$  varying with year and site location due to varying environmental conditions and soil organic matter (SOM) content. Soils with 1.5% SOM required 2-3 times more Olsen-P to produce similar yields as soils with 2.4% SOM (Johnston et al., 2013).

The Mehlich-3 extraction procedure was modified by Mehlich (1984) by replacing chloride ions ( $\text{Cl}^-$ ) with nitrate ions ( $\text{NO}_3^-$ ), and adding ethylenediaminetetraacetic acid (EDTA) to the extracting solution. These changes increased the copper (Cu) extraction efficiency of Mehlich-3 by 170% compared to Mehlich-2, allowing Cu to be added to the list of Mehlich-3 extractable nutrients, which include Ca, Fe, K, Mg, Mn, and Zn. Mehlich-3 soil tests are popular among soil labs throughout the US because it is suited to a wide range of soils ranging from acidic to slightly basic, and allows for analysis of multiple nutrients from a single extraction (Sims, 2000). Mehlich-3 is also the standard extraction procedure for plant-available P in Oklahoma (Zhang & Raun, 2006). According to Sims (2000), the Mehlich-3 extraction procedure

calls for the suspension of 2 g of soil in 20 mL of extracting solution (0.2 M CH<sub>3</sub>COOH, 0.25 M NH<sub>4</sub>NO<sub>3</sub>, 0.015 M NH<sub>4</sub>F, 0.013 M HNO<sub>3</sub>, 0.001 M EDTA), which is adjusted to a pH of 2.5 ± 0.1, and shaken for 5 minutes. The resultant suspension is then filtered through Whatman No. 42 filter paper and analyzed by colorimetry or ICP-ES. Mehlich-3 extracts P similarly to Bray-P1, where Al activity is reduced through complexation with F, and the solubility of Al-, Ca-, and Fe-bound P is increased by the acidic nature of the extractant (Sims, 2000). The pH of Mehlich-3 is well buffered compared to the original Mehlich-1 and Bray-P1 extractants, allowing it to maintain extraction efficiency in neutral to slightly alkaline soils (Sims, 2000; Tran et al., 1990). While many studies have found strong relationships between Mehlich-3 P and crop response, a study performed by Slaton et al. (2006) found improved prediction of crop response combining both soil-pH and Mehlich-3 P. The critical value used for Mehlich-3 P in Oklahoma is 32.5 mg kg<sup>-1</sup> determined colorimetrically (Zhang & Raun, 2006), although other states recognize higher values, such as 50 mg kg<sup>-1</sup> in Delaware (Sims et al., 2002).

Numerous studies have been performed investigating the correlation between Mehlich-3 and Bray-P1 (Michaelson et al., 1987; Tran et al., 1990). Tran et al. (1990) found the correlation between Mehlich-3 P and Bray-P1 to be 0.98 and highly significant. Regression analysis performed by Michaelson et al. (1987) on Mehlich-3 P and Bray P indicated a significant relationship between the two with slopes ranging from 1.01 to 1.88, with Mehlich-3 extracting substantially more P in volcanic ash soils than Bray-P1 and slightly more in loess derived soils.

Water soluble P (WSP) is not commonly used in the US to predict crop P-response, but is often used as an environmental indicator to determine risk of soil-P loss and water contamination, especially in regions with a history of manure application (Fox et al., 2016; Parvage et al., 2015). Water soluble P is particularly useful when eutrophication is of concern, as orthophosphates (e.g. HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) are the primary form of P utilized by aquatic microorganisms (Fox et al., 2016). A WSP extraction protocol is described in detail by Self-Davis et al. (2000). Briefly, 2 g of soil



are suspended in 20 mL distilled water, shaken for 1 hour, centrifuged for 10 minutes, and then filtered through Whatman No. 42 filter paper. The filtrate is then analyzed using colorimetry or ICP-ES. Water soluble P typically decreases in acidic soils, as aluminum and iron phosphates have very low solubility in water (Essington, 2004; Lindsay, 1979). Water soluble P is similarly limited in calcareous soils due to low solubility of Ca phosphates in water (Essington, 2004; Lindsay, 1979). While WSP is a useful indicator for bioavailable P (Fox et al., 2016), several workers have suggested correlations between Mehlich-3 P and WSP and the use of M3P in place of WSP to determine the risk of water quality degradation (Bond et al., 2006; Sims et al., 2002).

There are numerous soil P extraction methods, and the method used often varies from one soil testing lab to another. Mehlich-3 is the dominant extraction method used for phosphorus recommendations in Oklahoma. Recent studies have found a lack of crop response to applied P in soils with STP as low as 2 mg kg<sup>-1</sup> (Watkins, 2017b). Such discrepancies reduce fertilizer use efficiency and farm profitability. More information regarding the relationship between Mehlich-3 P, and other commonly used extraction methods, and important soil characteristics, such as soil pH, may improve their respective interpretations and ultimately improve P fertilizer recommendations and fertilizer use efficiency.

## 2.4 Methodology

### 2.4.1 Locations and soils

The effect of soil-pH on soil test phosphorus was investigated using soils from four field trials established during previous studies. Soils investigated include a Grant silt loam (fine-silty, mixed, superactive, thermic Udic Argiustolls) collected from the North Central Agronomy Research Station near Lahoma, OK; an Easpur silt loam (fine-loamy, mixed, superactive, thermic Fluventic Haplustolls) collected from the Stillwater-Efaw Agronomy Research Station in Stillwater, OK; a Dale silt loam (fine-silty, mixed, superactive, thermic Pachic Haplustolls)

collected from the South Central Agronomy Research Station in Chickasha, OK; a Teller fine sandy loam (Fine-loamy, mixed, active, thermic Udic Argiustolls). Site environment and soil information is summarized in Table 2.1.

#### 2.4.2 Experimental Design

Trials were initiated in the field by other students during previous studies. A detailed description of the original experimental design and treatment structure for Chickasha and Efaw sites can be found in Lollato (2015), and for Lahoma and Perkins in Butchee et al. (2012).

The Chickasha and Efaw trials were initiated in 2012 by Lollato (2015). Plots were arranged in the field as a six by four treatment structure in a randomized complete block design. Plots were 7.6 m wide by 7.6 m long and separated by a 1.5 m alley. Treatments consisted of target soil-pH, ranging from 4.0 to 7.0 (e.g. 4.0, 4.5, 5.0, 5.5, 6.0, and 7.0). Mean initial soil-pH at Chickasha and Efaw for the 0-15 cm soil layer were 6.2 and 5.2 respectively. Soil-pH was adjusted in the plots through the application of various rates of hydrated lime ( $\text{Ca}(\text{OH})_2$ ) and aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) (Lollato, 2015).

The Lahoma and Perkins trials were initiated in 2009 by Butchee et al. (2012). Plots were arranged in a six by four treatment structure in randomized complete block design with four replications. Plots were 6 m long by 3 m wide and replications were separated by 4.6 m alleys. Soils in each plot were adjusted to the target soil-pH, which ranged from 4.0-7.0 (e.g. 4.0, 4.5, 5.0, 5.5, 6.0, 7.0). Mean initial soil-pH at Lahoma and Perkins for the 0-15 cm soil layers were 4.86 and 5.5 respectively. Soil-pH was adjusted in the plots through the application of various rates of hydrated lime and aluminum sulfate. Application rates were calibrated using linear regression equations fit to data from a soil incubation study to determine the response of soil-pH to alum and hydrated lime application. A detailed description of this calibration process can be found in the Butchee et al. (2012) paper.

### 2.4.3 Field Methodology

The soils used in this study from Chickasha and Efav were collected over multiple growing seasons, as described by Lollato (2015). Soils from Lahoma and Perkins were collected in June, after the 2015-2016 winter wheat growing season. Soils were sampled by collecting twenty soil cores from each plot to a depth of 15 cm. Plot samples were thoroughly mixed in buckets and placed in cloth soil sample bags, with a separate bag for each plot. Samples were then oven dried at 60°C for 48 hr and ground to pass a 2 mm sieve. The dried and ground samples were stored in a climate controlled environment on the Oklahoma State University-Stillwater campus at Agricultural Hall until extraction.

### 2.4.4 Laboratory Methodology

#### 2.4.4.1 *Soil-pH*

Soil-pH data was collected in the manner similar to that described by EPA (2004) using a Metler Toledo SevenCompact pH/Ion meter equipped with an Expert Pro-ISM glass membrane pH electrode. Measurements were collected from each sample using a 1:1 soil-water ratio, with  $10 \pm 0.01$  g of soil and  $10 \pm 0.1$  mL of 17 M $\Omega$  deionized (DI) water. Slurries were shaken for 30 minutes and then allowed to settle for an additional 30 minutes prior to measurement.

#### 2.4.4.2 *Total-P*

Total-P was determined according to the EPA-3050B acid digestion method (EPA (1996). Digestions were not performed on every sample due to the high-maintenance and time consuming nature of the process. Nine samples were selected for digestion from each location based on soil-pH. Three samples were collected from “low”, “mid”, and “high” pH range of each location. A blank and control sample of known Total-P was also included in each run.

#### 2.4.4.3 *Water Soluble P*

Water soluble P data were collected from each sample using a 1:10 soil-water ratio in a manner similar to that described by Self-Davis et al. (2000).  $2.0 \pm 0.01$  g of soil was suspended in  $20.0 \pm 0.1$  mL DI water and shaken for 1 hr. The resultant suspension was centrifuged at 2000 rpm for 30 minutes and filtered through Whatman No. 42 filter paper and analyzed for orthophosphate using colorimetry with a Lachat QuickChem 8500 Flow Injection Auto-analyzer at 880 nm.

#### 2.4.4.4 *Bray-P1*

Bray-P1 data were collected from each sample using a 1:10 soil-water dilution ratio in a manner similar to that described by Sims (2000).  $2.0 \pm 0.01$  g of soil was suspended in  $20.0 \pm 0.1$  mL of Bray-P1 extracting solution (0.025 M HCl, 0.03 M  $\text{NH}_4\text{F}$ ). Suspensions were shaken for five minutes at 200 rpm and filtered through Whatman No. 42 filter paper and analyzed for orthophosphate using colorimetry with a Lachat QuickChem 8500 Flow Injection Auto-analyzer at 880 nm.

#### 2.4.4.5 *Mehlich-3*

Multi-elemental Mehlich-3 data were collected from each sample using a 1:10 soil-water ratio as described by Provin (2010).  $2 \pm 0.01$  g of soil was suspended in  $20 \pm 0.1$  mL of Mehlich-3 extracting solution (0.2 N acetic acid, 0.25 N  $\text{NH}_4\text{NO}_3$ , 0.015 N  $\text{NH}_4\text{F}$ , 0.013 N  $\text{HNO}_3$ , 0.001 M EDTA). Suspensions were shaken at 200 rpm for five minutes and filtered through Whatman No. 2 filter paper. The resultant solution was then analyzed using an ICP-ES for Al, Ca, Fe, K, Mn, Mg, and P.

#### 2.4.4.6 *Chang-Jackson P Fractionation*

Phosphorus fractionation data were collected from selected samples in a manner similar to that described by Watkins (2017a); Zhang and Kovar (2000). Due to the time consuming and

intensive nature of the procedure it was only performed on the same samples as Total-P ( $n = 36$ ). Samples were analyzed following the Murphy-Riley method (Murphy & Riley, 1962) using a spectrophotometer at 880 nm. The instrument used for colorimetric analysis was a Milton Roy SPECTRONIC 21D spectrophotometer. The method entails five sequential extractions, where Extraction A, B, C, D, and E. Extraction A = soluble and loosely bound P; Extraction B = Al bound P; Extraction C = Fe bound P; Extraction D = reductant soluble P; Extraction E = Ca bound P.

Extraction A:  $1 \pm 0.01$  g of soil was suspended in  $50 \pm 0.1$  mL of 1.0 M  $\text{NH}_4\text{Cl}$  and shaken at 200 rpm for 30 minutes. Samples were centrifuged for 15 minutes at 2000 rpm, and the supernatant solution was decanted and brought to a 50 mL volume. Extraction A samples are interpreted as soluble and loosely bound P.

Extraction B: 50 mL of 0.5 M  $\text{NH}_4\text{F}$  (adjusted to pH 8.2) was added to the residue from Extraction A. Samples were shaken for one hour and centrifuged for 30 minutes at 2000 rpm. The supernatant solution was decanted and stored in a 100 mL volumetric flask. Soil samples were then washed two times with 25 mL aliquots of saturated NaCl solution, centrifuged for 15 minutes at 2000 rpm and decanted into the Extraction B flasks. Extraction B samples were then brought to a final volume of 100 mL with DI water. Extraction B extractions are interpreted as Al bound P.

Extraction C: 50 mL of 0.1 M NaOH solution was added to the residue left from Extraction B and shaken for 17 hours. Samples were then centrifuged for 30 minutes at 2000 rpm and decanted into 100 mL volumetric flasks. The residues were then washed twice with 25 mL aliquots of saturated NaCl, centrifuged for 30 minutes at 2000 rpm, and decanted to the Extraction C flasks, and brought to a final volume of 100 mL. Extraction C extractions are interpreted as Fe bound P.

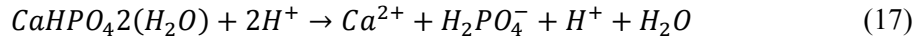
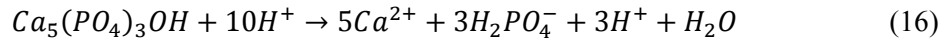
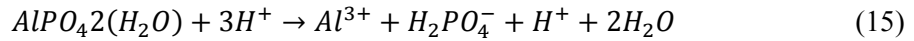
Extraction D: 40 mL of 0.3 M sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) solution was added to the soil residue left from Extraction C and heated to 85 °C. 1.0 g of sodium dithionate ( $\text{Na}_2\text{S}_2\text{O}_4$ ) was added to the samples, stirred rapidly, and allowed to heat for 15 minutes longer, and then centrifuged at 2000 rpm for 30 minutes. The supernatant solution was then decanted into 100 mL volumetric flasks. Soil residues were washed twice with 25 mL aliquots of saturated NaCl and centrifuged for 30 minutes at 2000 rpm. This solution was decanted into the Extraction D flasks. Flasks were left opened to oxidize the sodium dithionite, as recommended by Zhang and Kovar (2000). Extraction D extractions are interpreted as reductant soluble P.

During sample preparation for colorimetric analysis, using the Murphy-Riley method, Extraction D samples became extremely cloudy causing an interference in the measurements. Samples were further oxidized using an air pump and manifold built in-house to bubble air through samples for 8 hrs (Figure 2.1). Air was bubbled through DI water to increase its relative humidity and decrease sample volume loss through evaporation. Samples were weighed before and after aeration to determine the volume of water lost in each sample, and lost water was added in the form of DI water. Air hoses were also rinsed in DI water and shaken dry prior to aerating new samples.

Extraction E: 50 mL of 0.25 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was added to the residue left from Extraction D and shaken for one hour at 200 rpm. The suspension was centrifuged for 30 minutes at 2000 rpm and decanted into a 100 mL volumetric flask. Residues were then washed twice more with 25 mL aliquots of saturated NaCl solution and centrifuged for 15 minutes at 2000 rpm. The supernatant solution was decanted into Extract E flasks and brought to a final volume of 100 mL. Extraction E extractions are interpreted as Ca bound P.

#### 2.4.4.7 Soil Phosphorus Chemical Equilibrium Diagrams

Double function parameters were used to investigate the solubility equilibrium between Al and P, and Ca and P. Functions were constructed using the phosphate potential ( $\log H_2PO_4^- - pH$ ),  $Al^{3+}$  potential ( $\log[Al^{3+}] + 3pH$ ), and  $Ca^{2+}$  potential ( $\log[Ca^{2+}] + 2pH$ ) of the soils based on data collected from samples representing the range of soil-pH across each site. Samples were extracted with water following the previously described WSP method and analyzed using ICP. These values were then related to the solubility of Al- and Ca-P minerals thought to be important factors controlling P solubility. According to Lindsay (1979), the solubility of variscite is governed by chemical reaction described in Equation 15, with an equilibrium constant  $\log K^\circ = -2.50$ . Similarly, the solubility of hydroxyapatite and brushite are governed by Equations 16 and 17, with equilibrium constants equal to 14.46 and 0.63 respectively.



The equilibrium reactions (Equations 15-17) were then rearranged to their respective solubility product equations (Equation 18, 19, 20) and solved for the  $Al^{3+}$  and  $Ca^{2+}$  potentials respectively (Equations 21, 22, 23).

$$\frac{[Al^{3+}][H_2PO_4^-][H^+]}{[H^+]^3} = 10^{-2.5} \quad (18)$$

$$\frac{[Ca^{2+}]^5[H_2PO_4^-]^3[H^+]^3}{[H^+]^{10}} = 10^{14.46} \quad (19)$$

$$\frac{[Ca^{2+}][H_2PO_4^-][H^+]}{[H^+]^2} = 10^{0.63} \quad (20)$$

$$\log Al^{3+} + 3pH = -1(H_2PO_4^- - pH + 2.5) \quad (21)$$

$$\log Ca^{2+} + 2pH = -0.6(\log H_2PO_4^- - pH) + 2.89 \quad (22)$$

$$\log Ca^{2+} + 2pH = -1((\log H_2PO_4^- - pH) - 0.63) \quad (23)$$

Double function diagrams were created by plotting the phosphate potential and  $Al^{3+}$  or  $Ca^{2+}$  potential of the soils, as well as the solubility equilibrium for the various minerals according to Equations 21, 22, 23. For example the line representing variscite equilibrium is plotted as:

$$y = -1(x + 2.5)$$

Where:

$$y = \log[H_2PO_4^-] - \text{soil pH}$$

$$x = \log[Al^{3+}] + 3(\text{soil pH})$$

#### 2.4.5 Statistical Analyses

Data were analyzed using R Version 3.4.0 (R Core Team, 2015). In general, samples were analyzed by location, soil-pH was treated as an independent variable and extracted nutrients were treated as dependent variables. Linear regression models were used to investigate the relationship between soil-pH and M3-P, soil-pH and M3-Al, soil-pH and M3-Fe, soil-pH and M3-Ca, soil-pH and M3-Mn, soil-pH and Bray-P1, and soil-pH and WSP. Multiple linear regression was also employed with Mehlich-3 multi-nutrient data. Pearson's product-moment correlation procedures were used to determine the relationship between Total-P and soil-pH within each location, as well



as relationships between Mehlich-3 and WSP, Mehlich-3 and Bray-P1, Mehlich-3 and Total-P, Bray-P1 and WSP, Bray-P1 and Total-P, WSP and Total-P. Analysis of variance, with Total-P as the dependent variable and Location as the independent variable, was used to investigate differences in Total-P between location. Comparisons of mean Total-P were made using Tukey's Honest Significant Difference procedures at  $\alpha = 0.05$ .

## 2.5 Results and Discussion

### 2.5.1 Soil-pH

Soil-pH data and their distribution are summarized in Table 2.2 and Figure 2.2. Soil-pH in the Dale silt loam (Chickasha) ranged from 4.56 to 7.61, with a median value of 6.03 and mean of 5.96. Soil-pH in the Easpur silt loam (Efaw) ranged from 4.34 to 7.59, with a median value of 5.48 and mean of 5.71. Soil-pH in the Grant silt loam from Lahoma ranged from 4.79 to 7.14, with a median value of 5.34 and mean of 5.58. Soil-pH in the Teller fine sandy loam from Perkins ranged from 4.58 to 7.1, with a median of 5.14 and mean of 5.28.

### 2.5.2 Total Phosphorus

Differences in Total-P concentrations were significant between locations according to one-way ANOVA procedures (Table 2.3). Total-P at Chickasha was significantly higher than all other locations, Lahoma was significantly higher than either Efaw or Perkins, and Efaw was significantly higher than Perkins ( $\alpha=0.05$ ). Total-P in the Dale silt loam from Chickasha ranged from 282.9 mg kg<sup>-1</sup> to 335.6 mg kg<sup>-1</sup>, with a median value of 324.3 and a mean of 319.8 mg kg<sup>-1</sup>. Total-P in the Easpur silt loam from Efaw ranged from 173.8 mg kg<sup>-1</sup> to 210.3 mg kg<sup>-1</sup>, with a median value of 186.3 mg kg<sup>-1</sup> and mean of 181.5 mg kg<sup>-1</sup>. Total-P in the Grant silt loam collected from Lahoma ranged from 245.6 mg kg<sup>-1</sup> to 301.6 mg kg<sup>-1</sup>, with a median value of 280.9 mg kg<sup>-1</sup> and a mean of 277.8 mg kg<sup>-1</sup>. Total-P in the Teller fine sandy loam collected from

Perkins ranged from 138.9 mg kg<sup>-1</sup> to 183.0 mg kg<sup>-1</sup>, with a median value of 164.0 mg kg<sup>-1</sup> and a mean of 163.0 mg kg<sup>-1</sup>.

As expected, correlations between Total-P and soil-pH were not significant at any location ( $\alpha = 0.05$ ) (Table 2.3). Since Total-P was not measured for all plots, and there is no significant relationship with soil-pH, the assumption was made that Total-P was equal to the mean in all plots (Figure 2.3). Constant Total-P is an important assumption for this study, as it reduces the likelihood that any relationships between Mehlich-3 P, Bray-P1, and WSP and soil-pH are actually caused by variations in total soil P.

### 2.5.3 Water Soluble Phosphorus

WSP in the Dale silt loam collected from Chickasha ranged from 0.46 mg kg<sup>-1</sup> to 3.85 mg kg<sup>-1</sup>, with a median value of 2.41 mg kg<sup>-1</sup> and a mean of 2.29 mg kg<sup>-1</sup>. WSP in the Easpur silt loam collected from Efav ranged from 0.27 mg kg<sup>-1</sup> to 6.91 mg kg<sup>-1</sup>, with a median value of 3.39 mg kg<sup>-1</sup> and a mean of 3.48 mg kg<sup>-1</sup>. WSP in the Grant silt loam collected from Lahoma ranged from 0.35 mg kg<sup>-1</sup> to 3.38 mg kg<sup>-1</sup>, with a median value of 1.24 mg kg<sup>-1</sup> and mean of 1.31 mg kg<sup>-1</sup>. WSP in the Teller fine sandy loam ranged from 0.68 mg kg<sup>-1</sup> to 2.22 mg kg<sup>-1</sup>, with a median value of 1.24 mg kg<sup>-1</sup> and mean of 1.31 mg kg<sup>-1</sup> (Table 2.4).

Using analysis of variance techniques, significant differences in WSP were found between sites (Table 2.4). According to comparisons made with Tukey's HSD procedures, WSP at the Efav site was significantly greater than Chickasha, Lahoma, and Perkins. Differences in WSP between Chickasha and Lahoma were not significant at  $\alpha = 0.05$ , while WSP at Chickasha was significantly greater than Perkins. Differences in WSP between Lahoma and Perkins were not statistically different at  $\alpha = 0.05$ . As none of the sites have a history of P fertilizer or manure

application, differences in mean WSP across sites are likely due to differences in soil type and environment. As expected, total soil P is not a good indicator of WSP, and vice versa, as illustrated by the Chickasha soils, where significantly higher Total-P did not correspond to high WSP.

The relationship between soil-pH and WSP within each location were investigated using ordinary least squares (OLS) regression techniques (Table 2.5, Figure 2.4). Quadratic models were significant at Chickasha, Efaw, and Lahoma, but were not significant at Perkins (Equation 14, 15, 16, 17; Table 2.5).

$$\text{Chickasha} \quad WSP = 7.309pH - 0.567pH^2 - 20.839 \quad (9)$$

$$\text{Efaw} \quad WSP = 13.334pH - 1.113pH^2 - 35.404 \quad (10)$$

$$\text{Lahoma} \quad WSP = 11.485pH - 0.911 - 33.469 \quad (10)$$

Given the interpretation of WSP as bioavailable P (Fox et al., 2016), and the significance of the regression models, the soil-pH corresponding to the highest bioavailability can be calculated for each site by setting the first derivative with respect to soil pH  $\left(\frac{dWSP}{dpH}\right)$  of the regression equations to zero and solving for pH, if the second derivative is less than zero. Therefore, P has the highest bioavailability at a soil-pH of 6.4 at Chickasha, 6.0 at Efaw, and 6.3 at Lahoma (Equation 12, 13, 14). These findings agree with P availability theory common in texts and literature on the subject, where P is believed to be the most available at a pH range between 6 and 7 (Essington, 2004; Stevenson & Cole, 1999).

$$\text{Chickasha} \quad \frac{dWSP}{dpH} = 7.309 - 1.134pH \quad (11)$$

$$\text{Efaw} \quad \frac{dWSP}{dpH} = 13.334 - 2.224pH \quad (12)$$

$$\text{Lahoma} \quad \frac{dWSP}{dpH} = 11.485 - 1.822pH \quad (13)$$

#### 2.5.4 Bray-P1 Extractable Phosphorus

Differences in Bray-P1 between locations were statistically significant at  $\alpha = 0.05$  (Table 2.6). Bray-P1 extracted from the Dale silt loam from the Chickasha site ranged from 4.46 mg kg<sup>-1</sup> to 26.35 mg kg<sup>-1</sup>, with a median value of 11.4 mg kg<sup>-1</sup> and mean of 12.10 mg kg<sup>-1</sup>. Bray-P1 extracted from the Easpur silt loam at the Efaw site ranged from 9.06 mg kg<sup>-1</sup> to 70.76 mg kg<sup>-1</sup>, with a median value of 29.68 mg kg<sup>-1</sup> and mean of 31.15 mg kg<sup>-1</sup>. Bray-P1 extracted from the Grant silt loam from the Lahoma site ranged from 17.18 mg kg<sup>-1</sup> to 52.81 mg kg<sup>-1</sup>, and a median value of 35.00 mg kg<sup>-1</sup> and mean of 35.63 mg kg<sup>-1</sup>. Bray-P1 extracted from the Teller fine sandy loam at Perkins ranged from 14.02 mg kg<sup>-1</sup> to 32.59 mg kg<sup>-1</sup>, with a median value of 23.55 mg kg<sup>-1</sup> and mean of 23.79 mg kg<sup>-1</sup>. Bray-P1 at Lahoma was statistically higher than at Chickasha, Efaw, and Perkins at  $\alpha=0.05$ . Bray-P1 at Efaw was greater than at Perkins, and both were higher than Chickasha (Table 2.6).

The relationship between Bray-P1 and soil-pH was significant at all locations (Table 2.7; Figure 2.5). In general, Bray-P1 was highest in the acidic range and lowest between a pH 6 and 7 (Figure 2.5). Correlations between Bray-P1 and WSP were not significant in the soils from the Efaw or Lahoma sites at  $\alpha=0.05$  (Table 2.7). These results are surprising given that Bray-P1 is interpreted as plant-available P, and P is thought to be most available between a pH of 6 and 7 (Essington, 2004; Stevenson & Cole, 1999; Zhang & Raun, 2006). In fact, P-deficiency is a

common problem in acidic soils, if the interpretation of Bray-P1 holds true for these soils, then P availability to plants is actually increasing with a decrease in soil-pH. Based on these results Bray-P1 is not a good predictor of WSP (Table 2.8).

#### 2.5.5 Mehlich-3 Extractable Phosphorus

Mehlich-3 P (M3P) varied significantly between locations, where M3P in soils from the Lahoma and Efaw sites were significantly greater than that from Perkins and Chickasha sites at  $\alpha = 0.05$ . Differences in M3P between Lahoma and Efaw were not statistically significant at  $\alpha = 0.05$ . M3P site means were separated using Tukey HSD procedures at  $\alpha = 0.05$  (Table 2.9).

M3-P extracted from the Dale silt loam at the Chickasha site ranged from 14.77 mg kg<sup>-1</sup> to 33.63 mg kg<sup>-1</sup>, with a median value of 21.66 mg kg<sup>-1</sup> and mean of 21.66 mg kg<sup>-1</sup>. M3-P extracted from the Easpor silt loam at the Efaw site ranged from 16.13 mg kg<sup>-1</sup> to 57.53 mg kg<sup>-1</sup>, with a median value of 40.70 mg kg<sup>-1</sup> and mean of 40.30 mg kg<sup>-1</sup>. M3-P extracted from the Grant silt loam at the Lahoma site ranged from 26.22 mg kg<sup>-1</sup> to 64.11, with a median value of 46.28 mg kg<sup>-1</sup> and mean of 47.59 mg kg<sup>-1</sup>. M3-P extracted from the Teller fine sandy loam at the Perkins site ranged from 23.04 mg kg<sup>-1</sup> to 50.65 mg kg<sup>-1</sup>, with a median value of 34.54 mg kg<sup>-1</sup> and mean of 35.91 mg kg<sup>-1</sup>.

The relationship between M3-P and soil-pH was significant at all locations (Table 2.10). Similar to the Bray-P1 extractions, M3P was significantly higher in the acidic pH range than the neutral pH range for all soils. Quadratic models provided the best fit at Chickasha and Efaw (Table 2.10, Figure 2.6). The second order terms for Lahoma and Perkins were not significant, these terms were removed and linear models were fit to the data (Table 2.10, Figure 2.7). Statistical models describing the relationship between soil-pH and M3P for Chickasha, Efaw, Lahoma, and Perkins are shown in Equations 14, 15, 16, and 17.

The relationship between M3-P and WSP was investigated using Pearson product moment correlations at  $\alpha = 0.05$  (Table 2.11). The correlation between M3-P and WSP was significant at Chickasha and Perkins, but not significant at Efaw or Lahoma (Table 2.11). Some workers have reported a positive correlation between M3P and WSP, and suggest that M3P may be used to predict WSP. Soils from Perkins showed a significant positive correlation of moderate strength ( $r = 0.49$ ), however the correlation from Chickasha soils was negative ( $r = -0.32$ ) (Table 2.11). Mehlich-3 P was generally not a good predictor of WSP in these soils (Figure 2.12)

The relationship between M3-P and Bray-P1 was investigated using Pearson product moment correlations evaluated at  $\alpha = 0.05$  (Table 2.12; Figure 21). As expected, correlations were highly significant at all sites (Table 2.12). Correlations at Chickasha, Efaw, and Lahoma were strong ( $r \geq 0.9$ ), while the correlation at Perkins was moderately strong,  $r = 0.79$  (Table 2.12). A strong relationship is expected as the extractants are both acidic and use F to reduce  $Al^{3+}$  activity. Similar correlations have been found by others, and M3-P fertilizer recommendations are often based on Bray-P1 yield response curves and converted to M3-P. On average M3-P was approximately 9% greater than Bray-P1 (Figure 2.8).

$$\text{Chickasha} \quad M3P = 1.852pH^2 - 26.665pH + 114.735 \quad (14)$$

$$\text{Efaw} \quad M3P = 3.663pH^2 - 49.287pH + 198.663 \quad (12)$$

$$\text{Lahoma} \quad M3P = 116.987 - 12.645pH \quad (13)$$

$$\text{Perkins} \quad M3P = 60.210 - 4.662pH \quad (14)$$

## 2.5.6 Factors controlling P Solubility

Double function diagrams were used to investigate the soil P chemical equilibrium in soils from Chickasha, Efaw, Lahoma and Perkins. The  $\text{Al}^{3+}$  potential and phosphate potential were plotted with variscite solubility lines using water soluble data analyzed with ICP (Figure 2.9). Most soils were supersaturated with respect to variscite, suggesting there is more Al and P in solution than is necessary to precipitate variscite (Figure 2.9). This is likely due to other, more soluble, forms of P controlling solubility, except at the lowest pH levels in soils from Chickasha and Efaw, where variscite seems to be in equilibrium with the solution. Soils at Lahoma and Perkins were supersaturated with respect to variscite over the investigated range of soil pH (Figure 2.9). Amorphous Al-P forms are considerably more soluble than variscite (Lindsay, 1979), and may be controlling P solubility in some of these soils. Unfortunately, these materials were unable to be modeled in this study.

The  $\text{Ca}^{2+}$  potential and solubility products of brushite and hydroxyapatite were also determined for selected soils from Chickasha, Efaw, Lahoma, and Perkins. As expected, models displayed in the double function diagrams indicate that soils from all locations have the potential to form Ca-P minerals at higher pH ranges (Figure 2.10). Soils were under-saturated with respect to both hydroxyapatite and brushite at low to mid pH ranges at all locations, indicating that other compounds are likely controlling solubility (Figure 2.10).

The chemical equilibrium of soil P was also investigated using MINTEQA2 geochemical speciation models (Table 2.13; Figure 2.11). Based on these models it seems likely that P solubility is largely controlled by variscite in the lowest pH soils, and Ca-P minerals in the highest pH soils. It is interesting to note that manganese phosphates (e.g.  $\text{MnHPO}_3$ ,  $\text{MnHPO}_4$ , etc.) appear to play an important role in P solubility over the entire range of soil pH. While these results are merely predictions, and do not take amorphous P materials into consideration, they may provide useful insight regarding the true soil-P equilibrium in these soils, and illustrate the important role Mn may play in P solubility.

## 2.6 Conclusions

The relationships between soil-pH and extractable soil-P was investigated using various extraction procedures. Relationships between WSP and soil-pH were as expected, where WSP was generally highest between a soil-pH of 6 and 7, and decreased at both lower and higher pH. These results confirm the results of previous studies, and follow current theory regarding the relationship between P-bioavailability and soil-pH. Based on the literature, WSP is likely reduced by Al- and Fe-P in acidic soils, and Ca-P in higher pH soils. Geochemical speciation models suggest that Mn may be an important factor controlling P solubility, particularly in soils with a pH between 5 and 7. These are interesting results, and may help explain the unexpected relationship between Bray-P1 and soil-pH, and Mehlich-3 P and soil-pH. Based on the chemical equilibrium model predictions and the relationship between M3-P/Bray-P1 and soil-pH, it appears that both Bray-P1 and Mehlich-3 extract Al-P efficiently, but may extract Mn-P less effectively in these soils.

Relationships between soil-pH and Bray-P1 and soil-pH and M3-P were surprising in that their highest values generally occurred in the range of soil-pH where P is believed to be least available. As M3-P and Bray-P1 are both commonly used to quantify plant available P in soils, and are used for P fertilizer recommendations, it follows that they would have also been highest between soil pH 6 to 7. P-deficiency is a common problem in acidic soils, yet Bray-P1 and M3-P were highest in the acidic pH range at all locations, and P fertilizer recommendations for these soils would have been higher in the neutral pH soils than the acidic soils. Since there were no crops used in this study, true plant availability of P cannot be established. Determining the true availability of P in the acidic soils would be challenging with crops due to Al toxicity issues. The cause of the anomaly could not be determined, however speciation models predicted a surprisingly strong effect of Mn on P-availability at mid-range pH soils from all locations. The anomaly may also be related to the historic alum and lime applications used to manipulate soil-



pH in previous trials. While alum application, or soil acidification, aluminum is an important driver of soil acidification in natural systems, as is Ca in alkaline soils. Unlike alum, lime application is commonly used in agriculture to alleviate the Al toxicity and P deficiency symptoms commonly associated with acidic soils. However, lime application appears to have decreased P-extractability according to both the Bray-P1 and Mehlich-3 data collected from soils used in this study.

The relationship between Mehlich-3 P and WSP was also surprising. Some previous studies have found significant correlations between WSP and M3-P, and proposed the use of M3-P to predict WSP and bioavailable P. The soils used in this study likely differ from those of previous studies in that total soil P was constant across a range of soil-pH. These results indicate that Mehlich-3 P may not be an appropriate predictor of WSP in some circumstances. More work is needed regarding Mehlich-3 extractable P pools, and the influence of Mn on P availability, extractability, and solubility.

## 2.7 Tables

Table 2.1. Soil and site description for field sampling locations. Mean annual precipitation and temperature are based on Mesonet data from 2004-2016 and are reported in  $\text{cm yr}^{-1}$  and  $^{\circ}\text{C}$  respectively

Location	Soil Type	Precipitation	Temperature
Chickasha	Dale silt loam	87.4	16.1
Efaw	Easpur silt loam	85.7	15.6
Lahoma	Grant silt loam	76.6	15
Perkins	Teller fine sandy loam	85.7	15.6

Table 2.2. Soil-pH (1:1 soil-water) summarized by location and soil type for long term trials initiated in 2009 in Lahoma and Perkins, or 2012 in Chickasha and Efaw. Initial soil pH refers to the native soil pH at sites prior to initial treatment application. Median soil pH and soil pH range reflect values measured in 2015.

Location	Year Initiated	Initial soil pH	Median soil pH	Soil pH Range
Chickasha	2012	6.2	6.03	4.56-7.61
Efaw	2012	5.2	5.48	4.34-7.59
Lahoma	2009	4.9	5.34	4.79-7.14
Perkins	2009	5.5	5.14	4.58-7.10

Table 2.3. Total-P varied significantly across locations ( $\alpha=0.05$ ). Total-P determined by the EPA-3050B digestion method. Location means were separated using Tukey's Honest Significant Difference procedures. Means and standard errors are reported in  $\text{mg kg}^{-1}$ .

Location	Soil Type	Mean Total-P	Std. Error
Chickasha	Dale silt loam	319.8a	15.56
Efaw	Easpur silt loam	186.3c	12.76
Lahoma	Grant silt loam	277.8b	21.75
Perkins	Teller fine sandy loam	163.0d	15.6

Table 2.4. Data summary and significance for WSP in soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Mean WSP are reported in mg kg<sup>-1</sup> and comparisons were made using Tukey's Honest Significant Difference procedures. Means with the same letter are not significantly different at  $\alpha=0.05$ .

Location	Soil Type	WSP	Std. Error
Chickasha	Dale silt loam	2.29b	0.70
Efaw	Easpur silt loam	3.48a	1.57
Lahoma	Grant silt loam	1.95bc	0.89
Perkins	Teller fine sandy loam	1.31c	0.47

Table 2.5. Regression table for water soluble P (WSP) extracted from soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Significant relationships were best explained by second-order polynomial models at Chickasha, Efaw, and Lahoma, but were not significant at Perkins.

	Dependent variable:			
	WSP			
	Chickasha	Efaw	Lahoma	Perkins
Soil-pH (1)	7.309***	13.334***	11.485**	0.283
Soil-pH (2)	-0.567***	-1.112***	-0.911**	-0.019
Constant	-20.839***	-35.404***	-33.469**	0.348
Observations	59	51	34	35
R <sup>2</sup>	0.611	0.365	0.450	0.010
Adj. R <sup>2</sup>	0.597	0.338	0.414	-0.052
Res. Std. Error	0.445 (df=56)	1.274	0.683 (df=31)	0.481 (df=32)
F Statistic	43.992*** (df=2; 56)	13.788*** (df=2;48)	12.664*** (df=2;31)	0.158 (df=2; 32)
Note:	*p<0.1; **p<0.05; ***p<0.01			

Table 2.6. Bray-P1 data summary and significance for soil collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Means separated using Tukey HSD procedures and means with the same letter are not statistically different. Mean Bray-P1 and standard errors reported in mg kg<sup>-1</sup>.

Location	Soil Type	Bray-P1	Std. Error
Chickasha	Dale silt loam	12.1d	4.03
Efaw	Easpur silt loam	31.15b	8.77
Lahoma	Grant silt loam	35.63a	8.48
Perkins	Teller fine sandy loam	23.79c	5.31

Table 2.7. Regression table for Bray-P1 extracted from soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Significant relationships were best explained by second-order polynomial models at Chickasha, Efaw, Lahoma, and Perkins.

	Dependent variable:			
	Bray-P1			
	Chickasha	Efaw	Lahoma	Perkins
Soil-pH (1)	-22.926***	-44.579***	-62.019**	-56.088***
Soil-pH (2)	1.652***	3.413***	4.352*	4.560***
Constant	90.711***	172.168***	244.728**	190.550***
Observations	57	48	36	36
R <sup>2</sup>	0.597	0.546	0.586	0.483
Adj. R <sup>2</sup>	0.582	0.526	0.561	0.451
Res. Std. Error	2.096 (df=54)	4.639 (df=45)	5.615 (df=33)	3.93 (df=33)
F Statistic	39.965*** (df=2; 54)	27.079*** (df=2;45)	23.383*** (df=2;33)	15.400*** (df=2; 33)

Note: \*p<0.1; \*\*p<0.05; \*\*\*p<0.01



Table 2.8. Pearson's product moment correlation between Bray-P1 and water soluble P (WSP) for soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Correlation coefficient estimates (r) and significance of the relationship (p) determined at  $\alpha=0.05$ . NS = not significant.

Location	Soil Type	r	p
Chickasha	Dale silt loam	-0.36	0.005
Efaw	Easpur silt loam	NS	0.353
Lahoma	Grant silt loam	NS	0.121
Perkins	Teller fine sandy loam	0.41	0.013

Table 2.9. Mehlich 3-P (M3P) data summary and significance for soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Means were separated using Tukey HSD procedures, and means with the same letter are not statistically different at  $\alpha=0.05$ . Mean M3P and standard errors reported in  $\text{mg kg}^{-1}$ .

Location	Soil Type	M3P	Std. Error
Chickasha	Dale silt loam	20.70c	5.82
Efaw	Easpur silt loam	44.11a	11.95
Lahoma	Grant silt loam	47.59a	9.66
Perkins	Teller fine sandy loam	35.91b	6.84

Table 2.10. Regression table for Mehlich-3 P extracted from soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Significant relationships were best explained by second-order polynomial models at Chickasha and Efaw. The second order term was not significant at Lahoma or Perkins.

	Dependent variable:			
	M3P			
	Chickasha	Efaw	Lahoma	Perkins
Soil-pH (1)	-26.665***	-49.287***	-12.465***	-4.662**
Soil-pH (2)	1.852***	3.663***	--	--
Constant	114.735***	198.663***	116.987***	60.210***
Observations	59	65	36	36
R <sup>2</sup>	0.634	0.566	0.514	0.178
Adj. R <sup>2</sup>	0.621	0.552	0.500	0.154
Res. Std. Error	2.711 (df=54)	5.637 (df=45)	6.827 (df=33)	6.295 (df=33)
F Statistic	48.477*** (df=2; 56)	40.363*** (df=2;62)	36.010*** (df=1;34)	7.357*** (df=1; 34)

Note: \*p<0.1; \*\*p<0.05; \*\*\*p<0.01

Table 2.11. Pearson's product moment correlation between Mehlich-3 P (M3P) and water soluble P (WSP) for soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. Correlation coefficient estimates (r) and significance of the relationship (p) determined at  $\alpha=0.05$ . NS = not significant.

Location	Soil Type	r	p
Chickasha	Dale silt loam	-0.32	0.015
Efaw	Easpor silt loam	NS	0.451
Lahoma	Grant silt loam	NS	0.440
Perkins	Teller fine sandy loam	0.49	0.002

Table 2.12. Pearson's product moment correlation between Mehlich-3 P (M3P) and Bray-P1 for soils collected from the Chickasha, Efaw, Lahoma, Perkins, and all sites combined (All). Correlation coefficient estimates (r) and significance of the relationship (p) determined at  $\alpha=0.05$ .

Location	Soil Type	r	p
Chickasha	Dale silt loam	0.94	0.000
Efaw	Easpor silt loam	0.90	0.000
Lahoma	Grant silt loam	0.97	0.000
Perkins	Teller fine sandy loam	0.79	0.000
All	---	0.97	0.000

Table 2.13. MINTEQA2 geochemical speciation model predictions based on water soluble nutrient data collected from soils located at the Chickasha, Efaw, Lahoma, and Perkins sites. Elemental data reported as % precipitated. Minerals included in the MINTEQA2 models include variscite (Var), hematite (Hem), gibbsite (Gibb), and hydroxyapatite (HAP). Amorphous Al-, Fe-, Mn-P, etc. are not taken into consideration.

Site	Soil pH	Al	Ca	Fe	Mn	PO4	Mg	Minerals
Chickasha	4.56	0	0	100	2.1	70.1	0	Hem, MnHPO4
Chickasha	4.62	16.3	0	100	1.5	66.9	0	Hem, Var, MnHPO4
Chickasha	4.67	0	0	100	2.8	64.4	0	Hem, MnHPO4
Chickasha	5.93	100	0	100	94.6	63	0	Gib, Hem, MnHPO4
Chickasha	5.99	100	0	100	94.5	67.6	0	Gib, Hem, MnHPO4
Chickasha	6.03	100	0	100	95.4	61.9	0	Gib, Hem, MnHPO4
Chickasha	7.25	100	1.7	100	99	48.1	0	Hem, Gibb MnHPO8, HAP
Chickasha	7.45	100	4.8	100	95.9	83.3	0	Hem, Gibb MnHPO8, HAP
Chickasha	7.61	100	5.4	100	89.9	92.3	0	Hem, Gibb MnHPO8, HAP
Efaw	4.40	13	0	100	4.4	65.3	0	Hem, Var, MnHPO4
Efaw	4.45	97.1	0	100	0	96.2	0	Var, Hem, Gibb
Efaw	4.47	95.6	0	100	0	94.8	0	Var, Hem, Gibb
Efaw	5.82	100	0	100	96.5	36.4	0	Var, Hem, Gib, MnHPO4
Efaw	5.99	100	0	100	98.4	36.4	0	Hem, Gib, MnHPO2
Efaw	6.08	100	0	100	97.4	39.5	0	Hem, Gib, MnHPO3
Efaw	7.49	98.2	0	100	8.2	99.9	0	Hem, Gib, MnHPO4
Efaw	7.48	100	6.5	100	95.8	93.9	0	Hem, Gib, MnHPO4, HAP
Efaw	7.59	100	4.5	100	87	97.1	0	Hem, Gib, MnHPO4, HAP
Lahoma	4.79	99.6	0	100	0	92.2	0	Var, Hem, Gibb
Lahoma	4.81	99.6	0	100	0	90.5	0	Var, Hem, Gibb
Lahoma	4.96	99.8	0	100	0	86.9	0	Var, Hem, Gibb
Lahoma	5.27	100	0	100	39.8	82.9	0	Var, Hem, Gibb MnHPO3
Lahoma	5.29	100	0	100	55.1	85	0	Var, Hem, Gibb MnHPO4
Lahoma	5.47	100	0	100	75.1	70.3	0	Var, Hem, Gibb MnHPO5
Lahoma	6.33	100	0	100	94.1	24.9	0	Hem, Gibb MnHPO6
Lahoma	6.87	100	0	100	99.2	18.4	0	Hem, Gibb MnHPO7
Lahoma	7.14	100	1.5	100	97.3	39.4	0	Hem, Gibb MnHPO8, HAP
Perkins	4.79	99.9	0	100	0	93.7	0	Var, Hem, Gibb
Perkins	4.81	99.9	0	100	0	93.7	0	Var, Hem, Gibb
Perkins	4.96	99.9	0	100	0	88	0	Var, Hem, Gibb
Perkins	5.27	100	0	100	43.9	79.1	0	Var, Hem, Gibb MnHPO3
Perkins	5.29	100	0	100	48.3	81.7	0	Var, Hem, Gibb MnHPO4
Perkins	5.47	100	0	100	72.5	71.3	0	Var, Hem, Gibb MnHPO5
Perkins	6.33	100	0	100	98.9	16.5	0	Hem, Gibb MnHPO6
Perkins	6.87	100	0	100	99.4	21.1	0	Hem, Gibb MnHPO7
Perkins	7.14	100	7.6	100	98.5	72.4	0	Hem, Gibb MnHPO8, HAP

## 2.8 Figures



Figure 2.1. Picture of air pump and manifold built in house to aerate Extraction D samples and oxidize residual sodium dithionate. During operation, air was bubbled through a large flask with water to reduce evaporation in the samples.

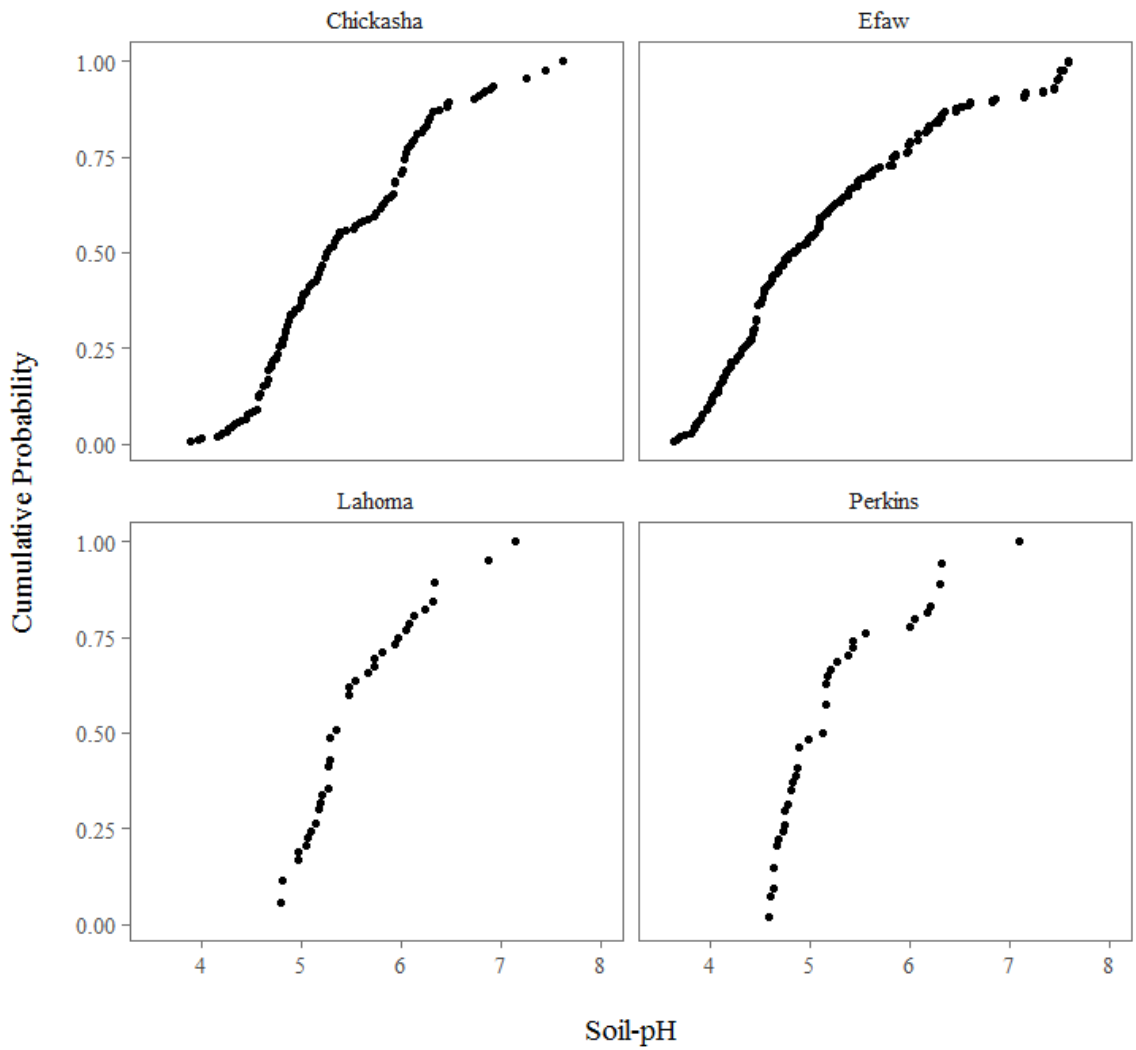


Figure 2.2. Empirical cumulative distribution plots displaying the distribution of soil-pH data collected from a Dale silt loam (top left), Easpur silt loam (top right), Grant silt loam (bottom left), and a Teller fine sandy loam (bottom right). Soil-pH was manipulated using aluminum sulfate or hydrated lime at various to achieve target soil-pH.



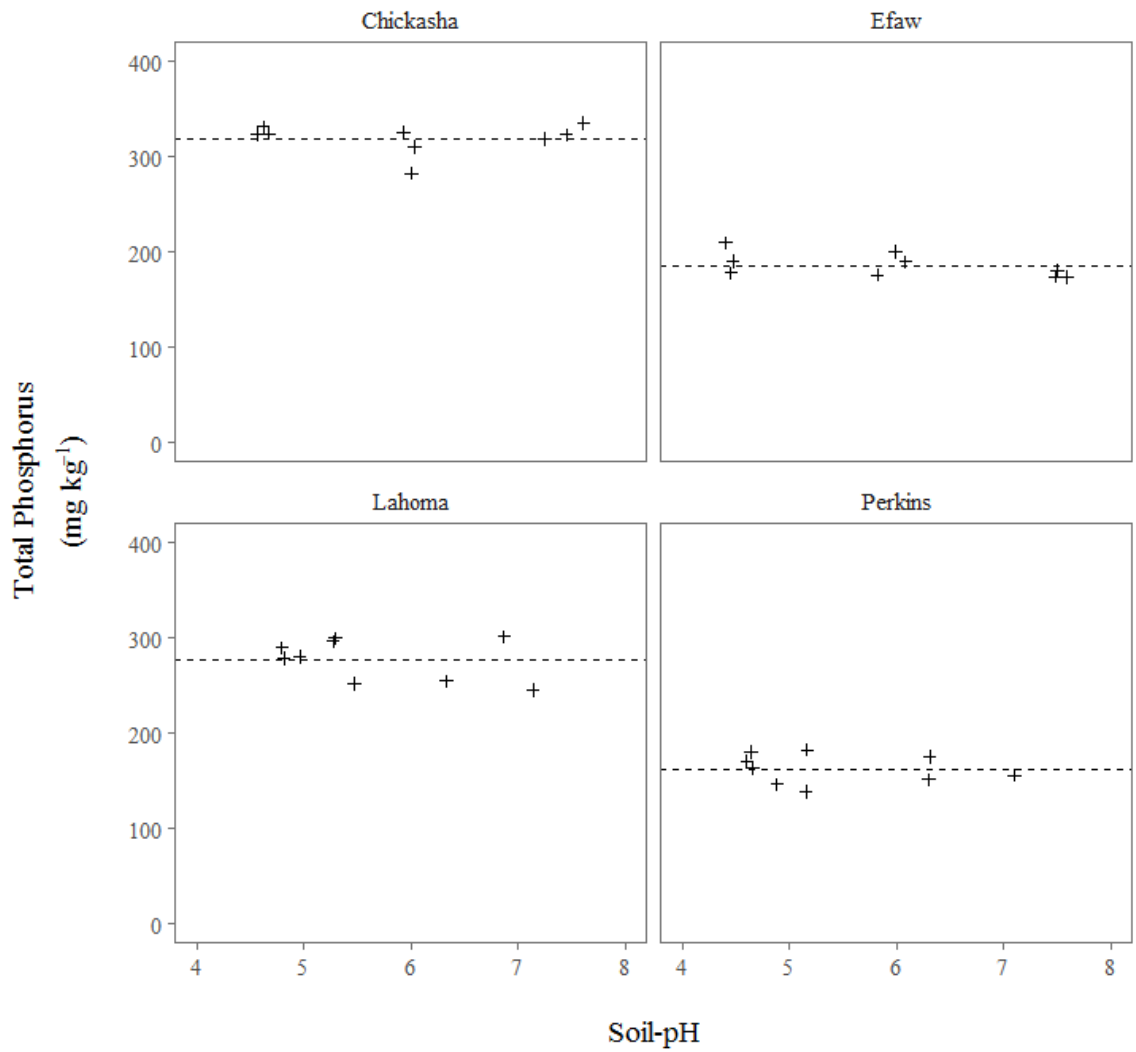


Figure 2.3. Total soil P as a function of soil-pH in soils collected from Chickasha, Efaw, Lahoma, and Perkins. Total-P was determined using an EPA-3050B acid digestion and is reported in mg kg<sup>-1</sup>. Dashed lines represent mean Total-P for each location.

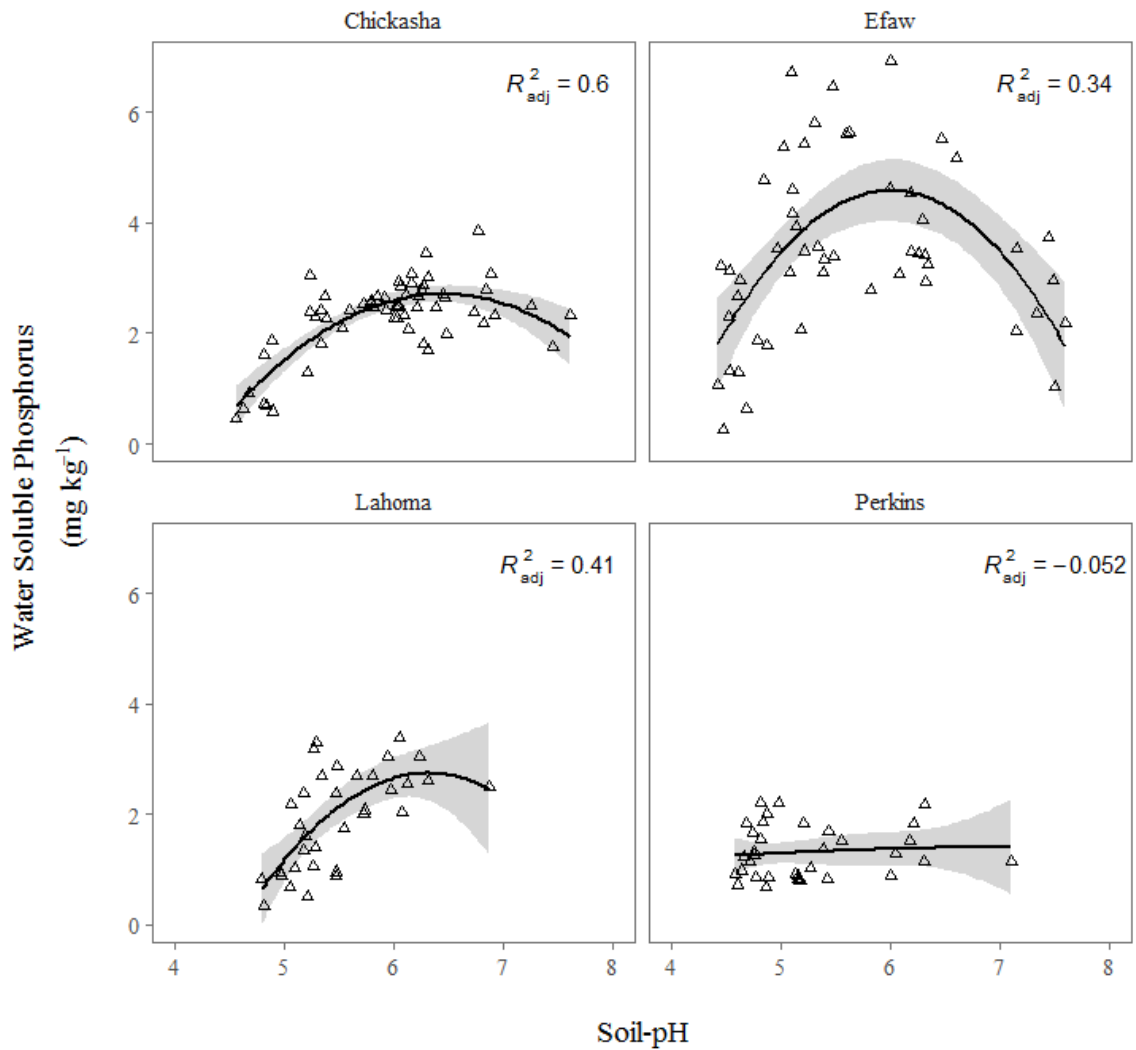


Figure 2.4. Water soluble phosphorus (WSP) as a function of soil-pH in soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. WSP reported as  $\text{mg kg}^{-1}$ , solid black lines indicate the respective quadratic regression models detailed in Table 2.4, and the shaded grey regions indicate 95% confidence interval for the model estimates.

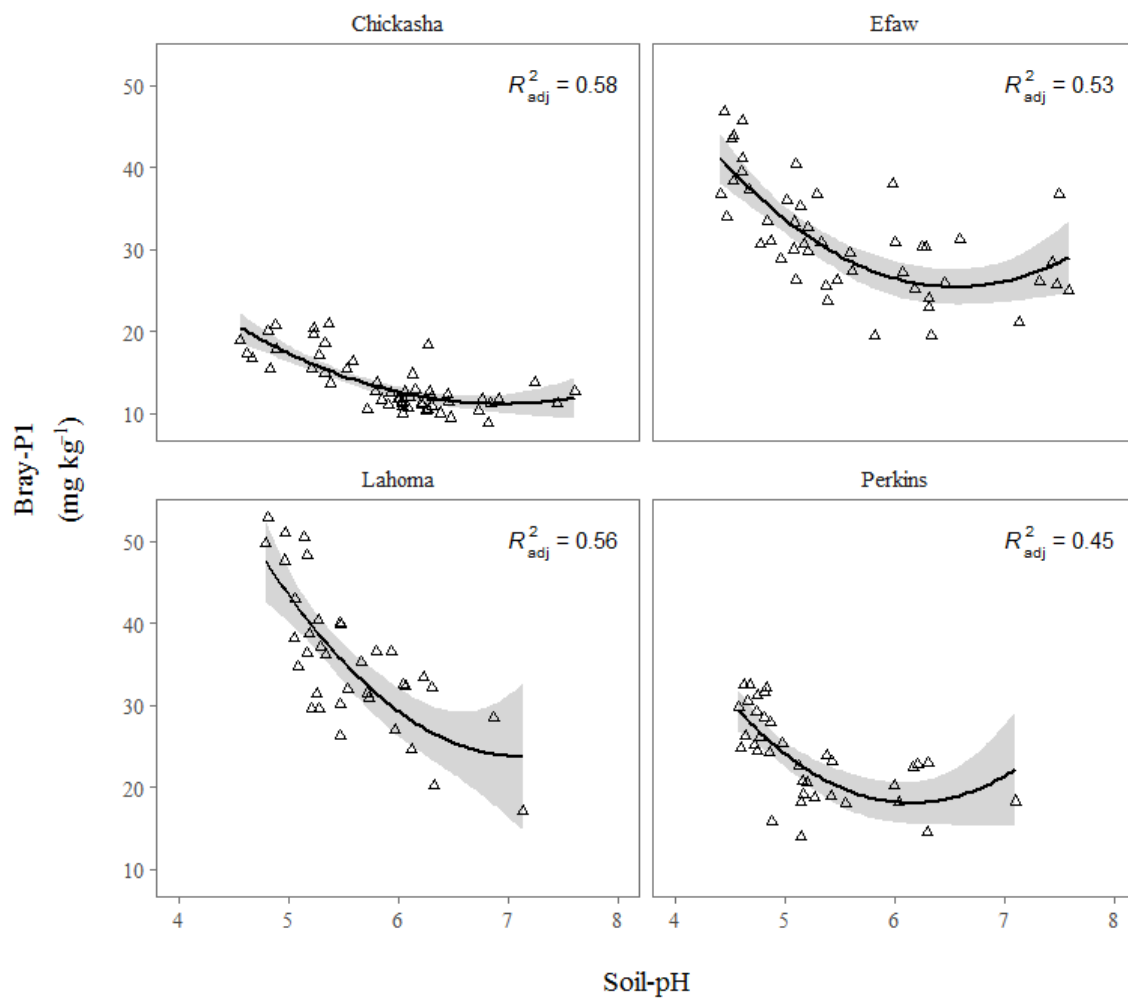


Figure 2.5. Bray-P1 as a function of soil-pH in soils collected from the Chickasha, Efaw, Lahoma, and Perkins sites. WSP reported as mg kg<sup>-1</sup>, solid black lines indicate the respective quadratic regression models detailed in Table 2.4, and the shaded grey regions indicate 95% confidence interval for the model estimates.

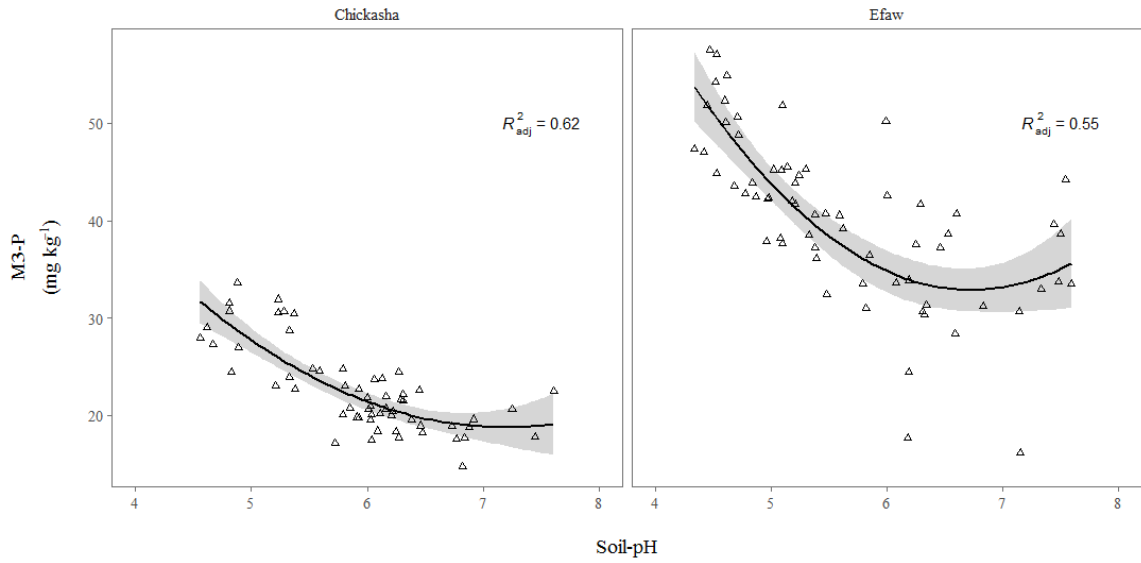


Figure 2.6. Mehlich-3 extractable phosphorus (M3-P) as a function of soil-pH in soils from Chickasha and Efav. Regression equations using first and second order terms were significant at  $\alpha=0.05$ . M3-P is expressed as  $\text{mg kg}^{-1}$

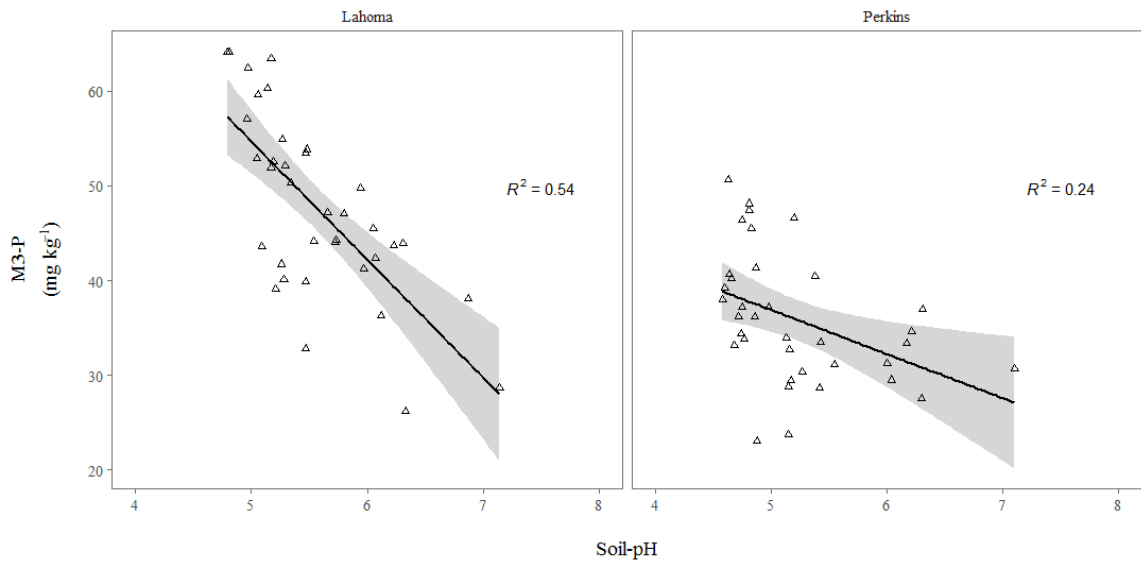


Figure 2.7. Mehlich-3 extractable phosphorus (M3-P) as a function of soil-pH in soils from Lahoma and Perkins. Regression equations using the second order terms were not significant at  $\alpha=0.05$  and were removed from the model. M3-P is expressed as  $\text{mg kg}^{-1}$ .

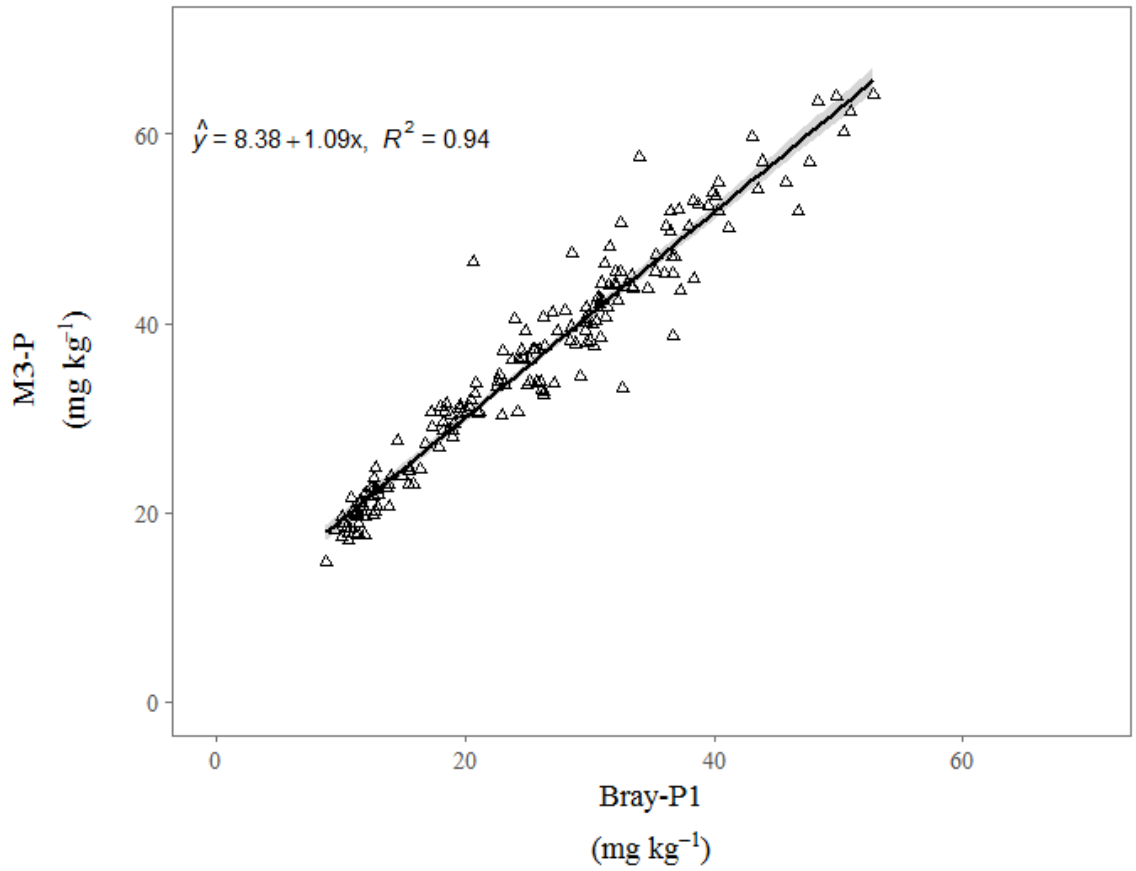


Figure 2.8. Mehlich-3 phosphorus (M3-P) as a function of Bray extractable phosphorus (Bray-P1) using combined data from the Chickasha, Efaw, Lahoma, and Perkins sites. The first order linear regression coefficient and intercept were significant at  $\alpha=0.05$ .

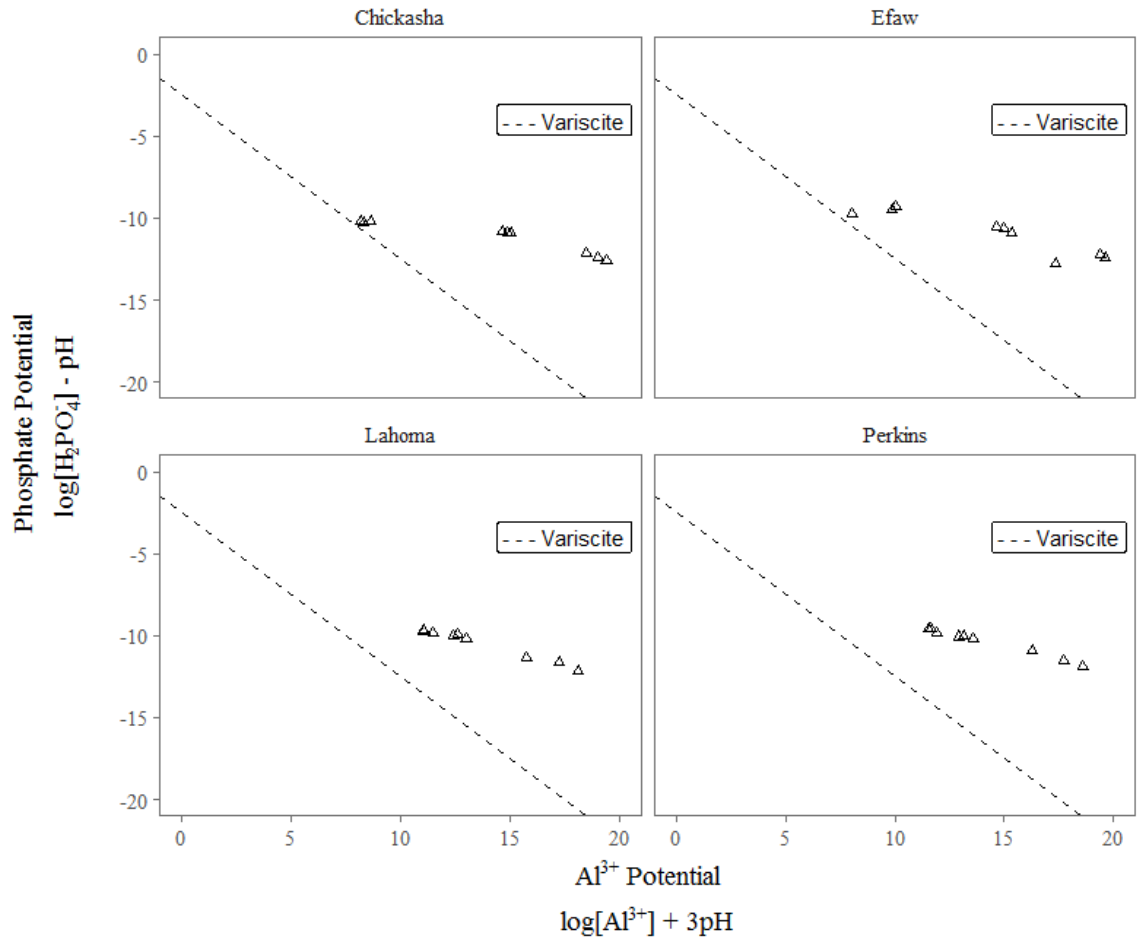


Figure 2.9. Aluminum and phosphate double function diagram. Phosphate potential is calculated as  $\log(\text{H}_2\text{PO}_4^-) - \text{pH}$  based on water soluble P data; Aluminum potential is calculated as  $\log[\text{Al}^{3+}] + 3\text{pH}$  based on water soluble Al data. The dashed line represents the solubility of variscite. Points above the line are saturated with respect to variscite.

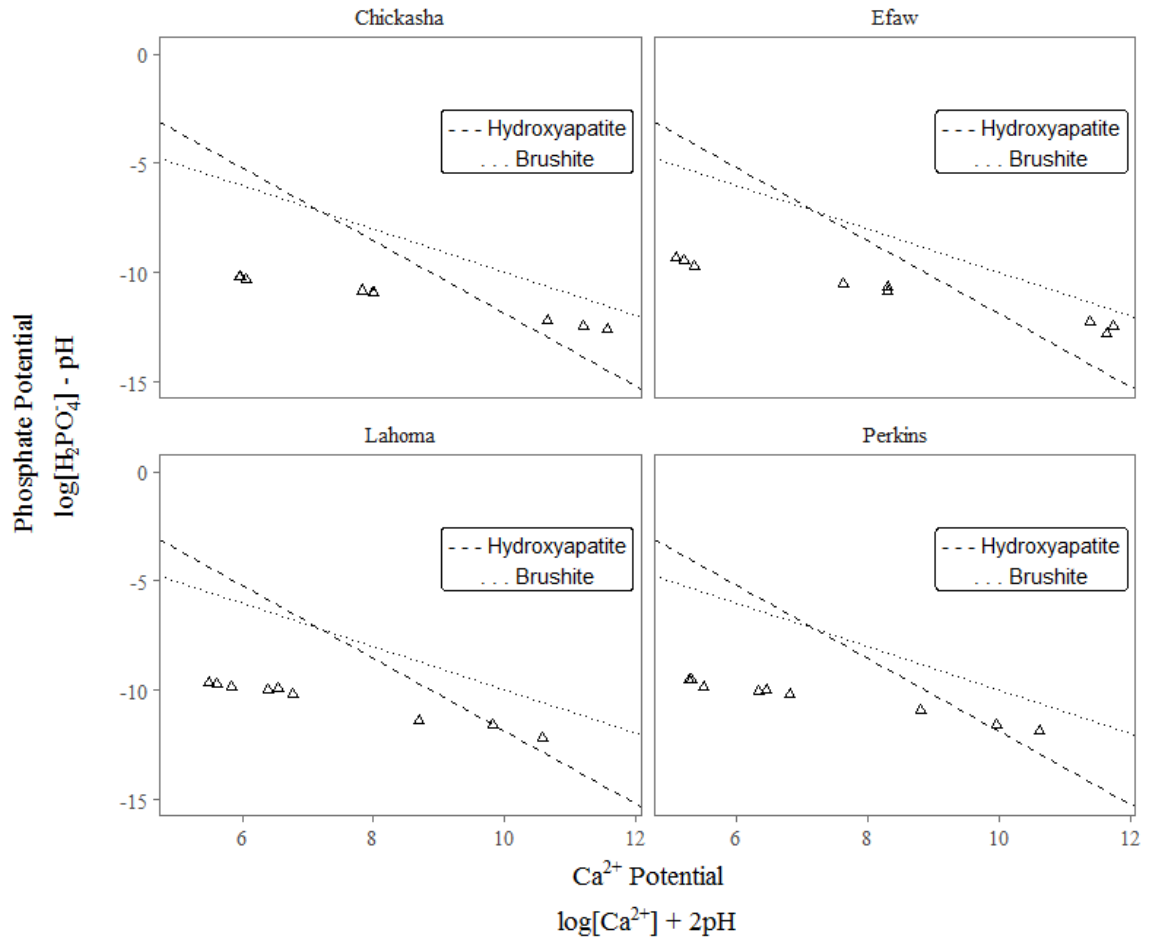


Figure 2.10. Calcium and phosphate double function diagram. Phosphate potential is calculated as  $\log(\text{H}_2\text{PO}_4^-) - \text{pH}$  from water soluble P data; calcium potential is calculated as  $\log[\text{Ca}^{2+}] + 2\text{pH}$  from water soluble Ca data. The dashed line represents the solubility of hydroxyapatite while the dotted line represents brushite. Points above the lines are saturated with respect to the minerals.

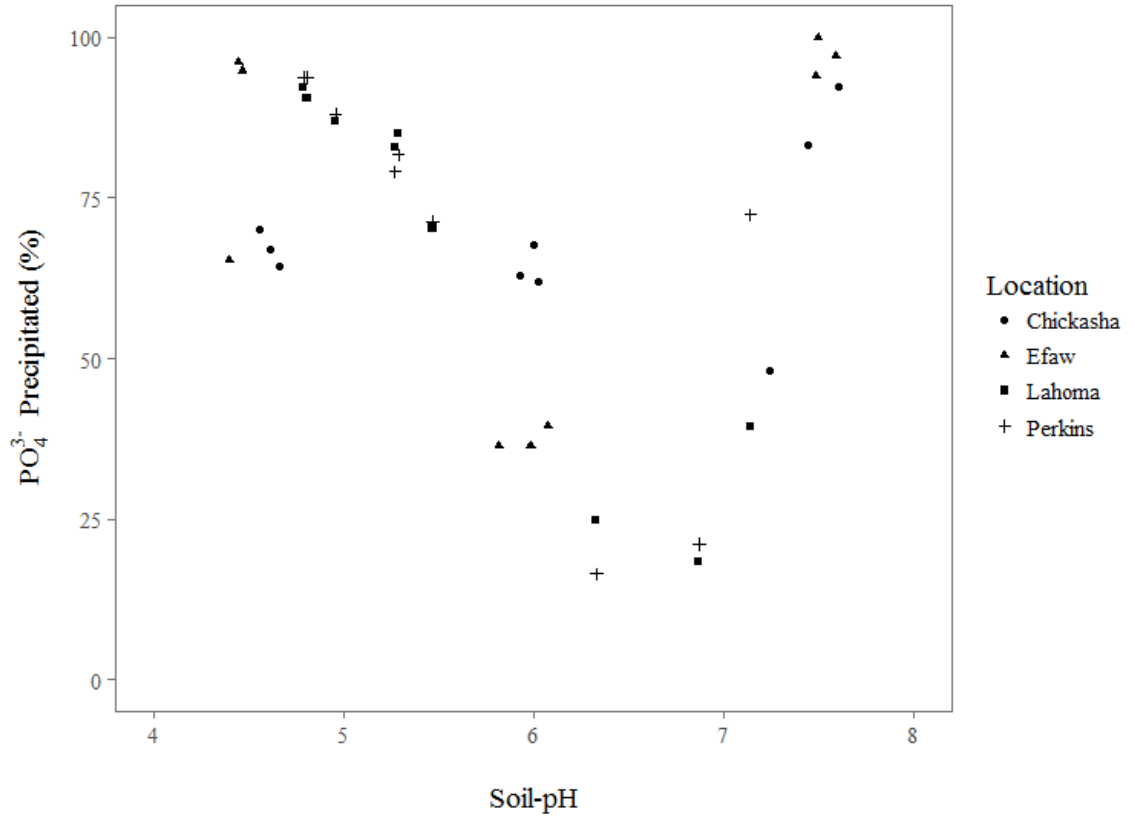


Figure 2.11. Geochemical speciation model predictions phosphate precipitation (%) as a function of soil-pH from selected soils from the Chickasha, Efaw, Lahoma, and Perkins sites. Predicted values generated using the MINTEQA2 chemical speciation model with water soluble ICP input parameters.



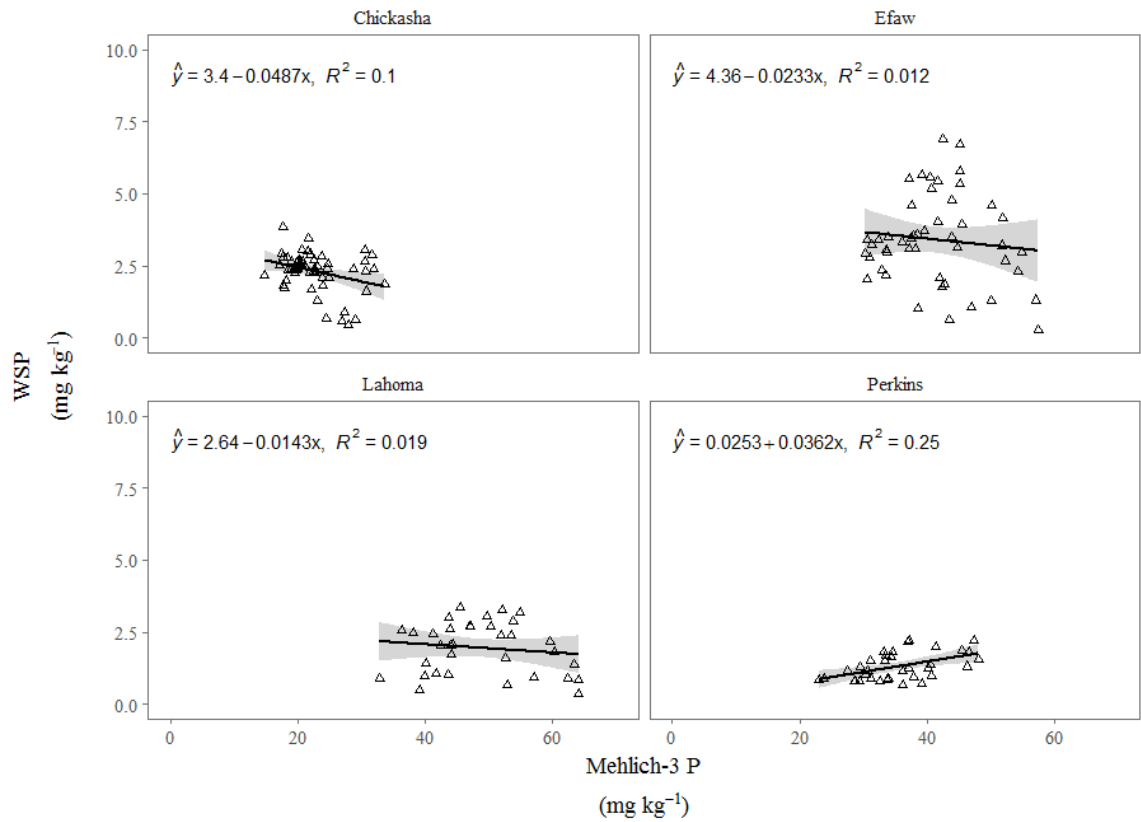


Figure 2.12. Water soluble phosphorus (WSP) as a function of Mehlich-3 phosphorus (M3-P) in soils collected from Chickasha, Efaw, Lahoma, and Perkins. WSP and M3P values are reported in mg kg<sup>-1</sup>.

## 2.9 References

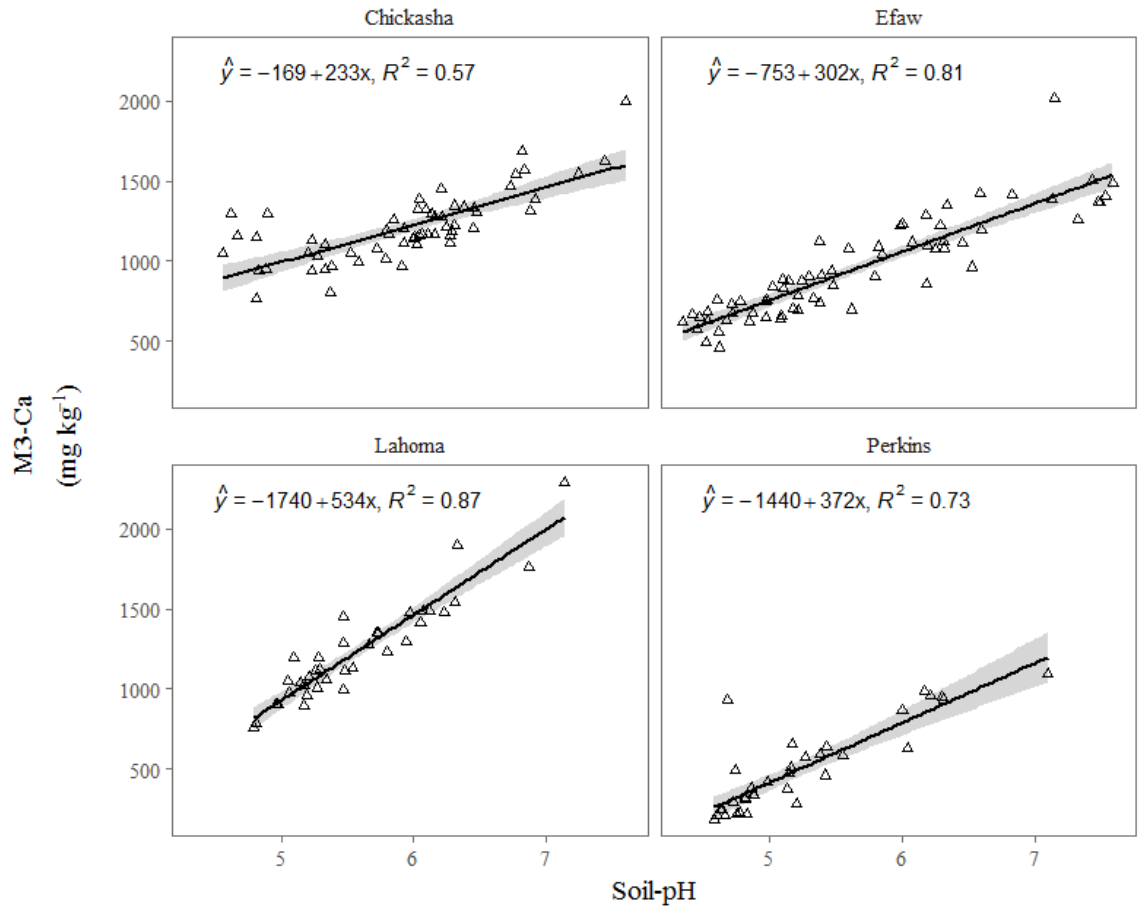
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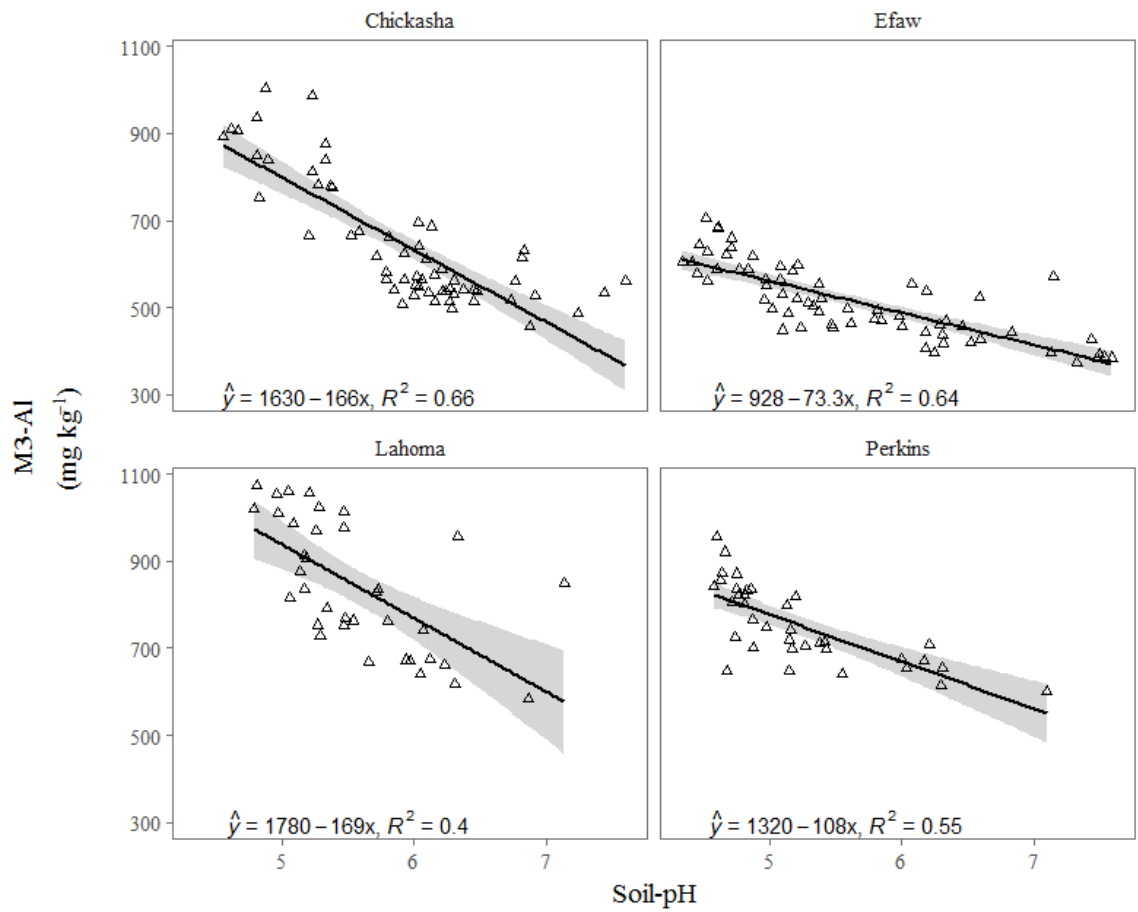
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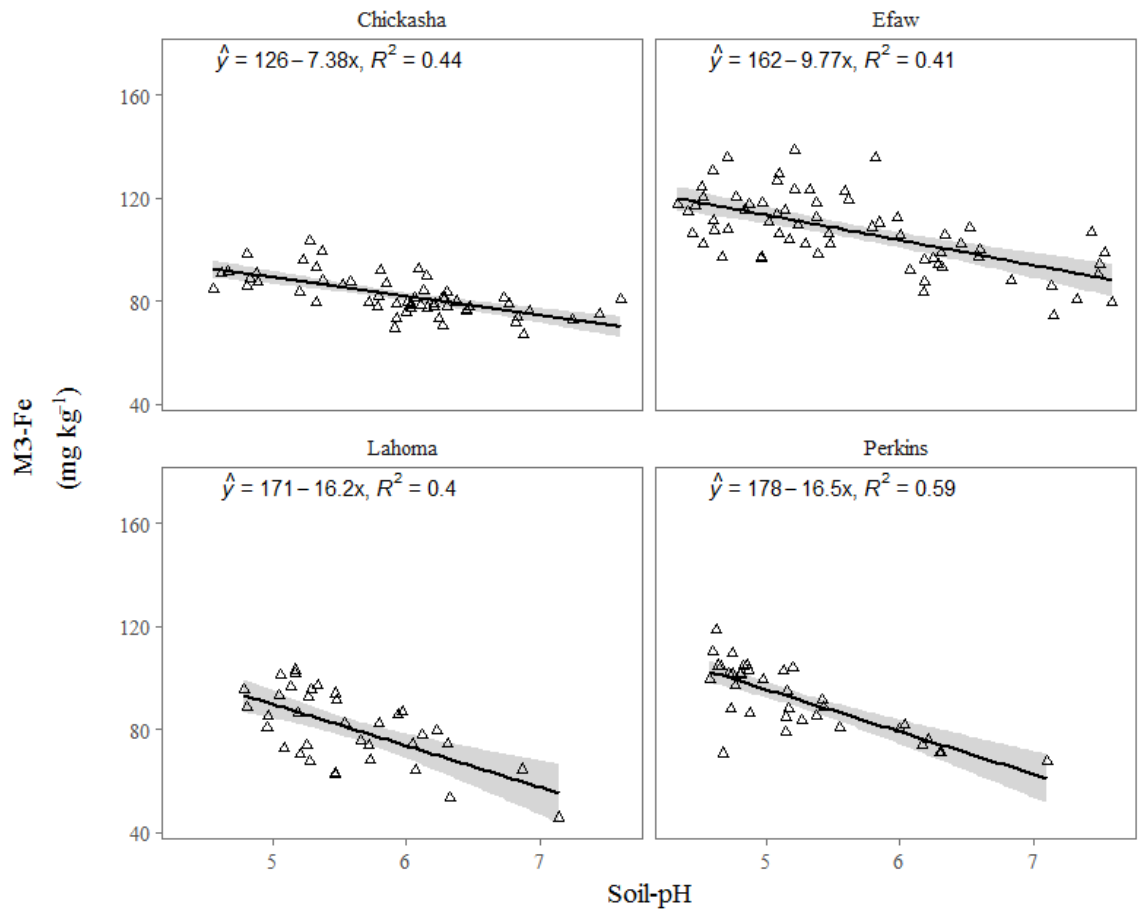
## APPENDICES



Appendix A. Mehlich-3 extractable calcium (M3-Ca) as a function of soil-pH for soils collected from Chickasha, Efaw, Lahoma, and Perkins. Linear regression models were significant at all locations at  $\alpha=0.05$ .

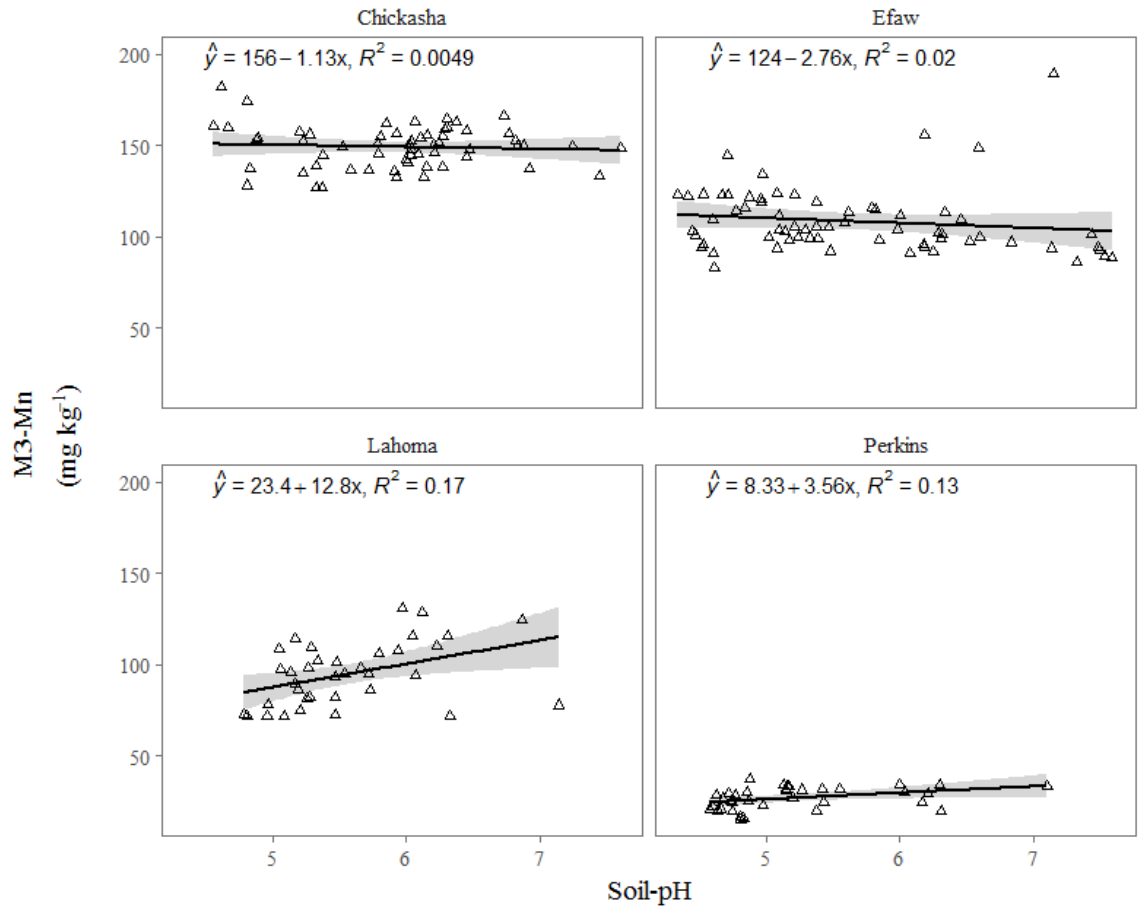


Appendix B. Mehlich-3 extractable aluminum (M3-Al) as a function of soil-pH for soils collected from Chickasha, Efaw, Lahoma, and Perkins. Linear regression models were significant at all locations at  $\alpha=0.05$ .

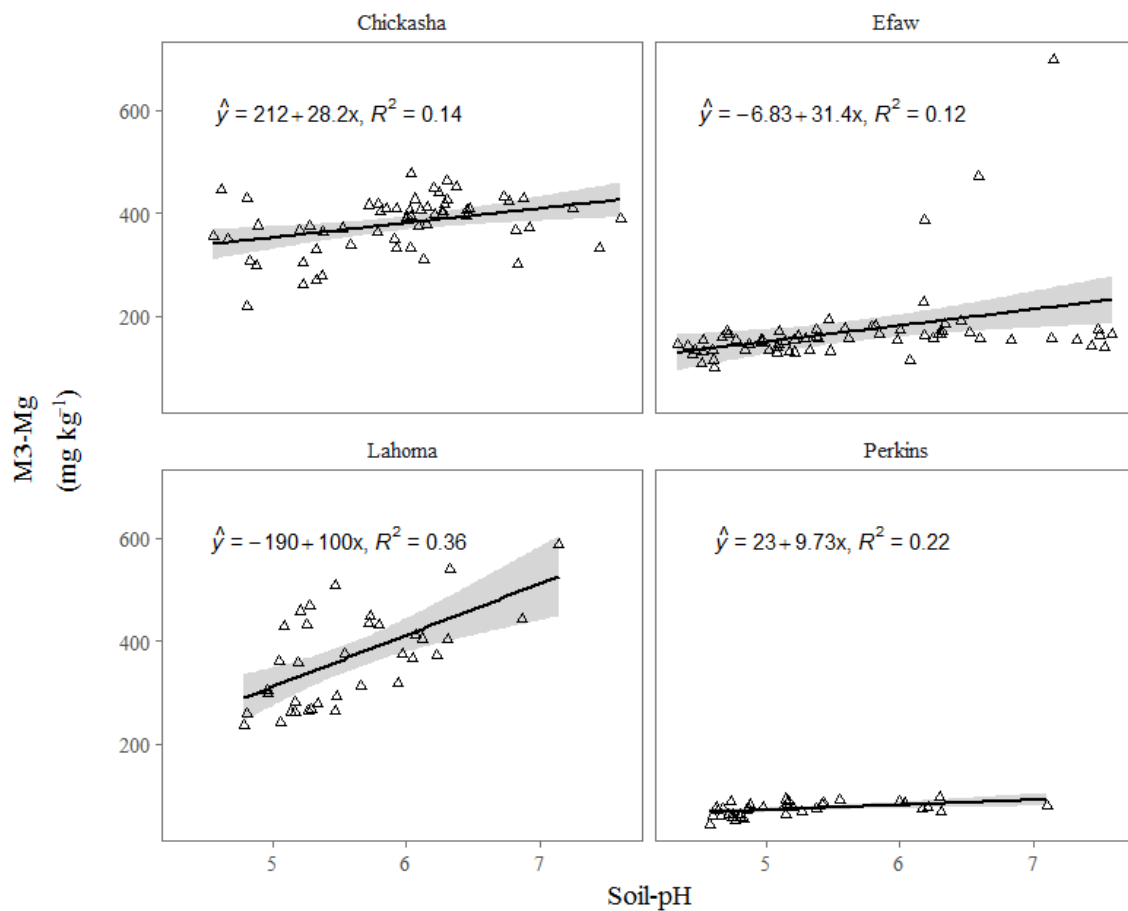


Appendix C. Mehlich-3 extractable iron (M3-Fe) as a function of soil-pH for soils collected from Chickasha, Efaw, Lahoma, and Perkins. Linear regression models were significant at all locations at  $\alpha=0.05$ .

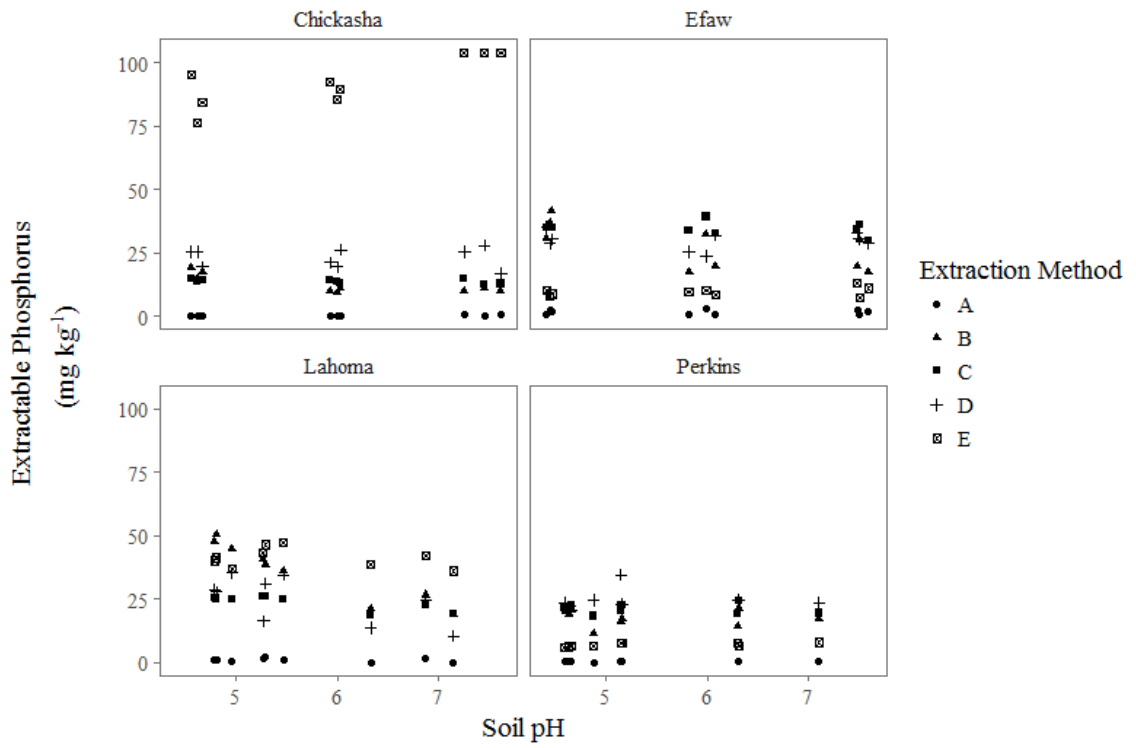




Appendix D. Mehlich-3 extractable manganese (M3-Mn) as a function of soil-pH for soils collected from Chickasha, Efaw, Lahoma, and Perkins. Linear regression models were significant at  $\alpha=0.05$  at all locations, with the exception of Perkins ( $p=0.40$ ).



Appendix E. Mehlich-3 extractable magnesium (M3-Mg) as a function of soil-pH for soils collected from Chickasha, Efaw, Lahoma, and Perkins. Linear regression models were significant at all locations at  $\alpha=0.05$ .



Appendix F. Chang-Jackson soil phosphorus (P) fractionations. Extractable P reported in mg kg<sup>-1</sup> for each extraction, where A = soluble and loosely bound P; B = aluminum bound P; C = Iron bound P; D = reductant soluble P; E = calcium bound P.

Appendix G. Mehlich-3 extractable nutrients for soils from Chickasha, Efaw, Lahoma, and Perkins. Data for all nutrients reported in mg kg<sup>-1</sup>.

<b>Location</b>	<b>pH</b>	<b>P</b>	<b>Al</b>	<b>Fe</b>	<b>Mn</b>	<b>Ca</b>	<b>Mg</b>
Chickasha	5.79	24.77	582.59	77.93	151.03	1009.36	364.75
Chickasha	5.91	19.82	506.84	69.58	135.78	964.98	350.52
Chickasha	6.03	21	570.92	78.56	150.51	1103.36	406.81
Chickasha	6.25	18.37	537.28	73.41	152.11	1214.15	441.12
Chickasha	6.38	19.56	540.52	79.79	162.79	1336.24	451.69
Chickasha	6.73	18.9	518.2	81.28	166.15	1464.33	431.02
Chickasha	6.00	21.84	528.24	75.37	142.49	1138.24	390.02
Chickasha	6.04	20.13	549.13	78.21	148.34	1156.23	395.02
Chickasha	6.48	18.19	538.53	77.71	148.26	1306.31	408.04
Chickasha	6.27	17.75	513.84	70.37	138.59	1156.26	403.7
Chickasha	6.31	21.52	562.6	83.38	164.69	1345.32	462.34
Chickasha	6.11	20.16	534.6	78.37	154.24	1171.24	407.65
Chickasha	6.22	20.44	538.25	79.08	146.63	1272.86	398.19
Chickasha	6.46	18.95	512.74	75.93	144.04	1327.9	394.51
Chickasha	6.06	23.73	563.3	81.34	163.17	1169.83	427.75
Chickasha	5.93	22.67	563.7	78.76	156.52	1108.68	408.38
Chickasha	6.16	21.94	513.94	77.5	155.73	1165.34	411.56
Chickasha	6.29	21.66	496.24	81.07	158.78	1182.67	418.79
Chickasha	5.85	20.76	539.85	86.94	162.23	1260.41	408.06
Chickasha	6.31	22.15	531.64	77.86	159.97	1218.53	425.44
Chickasha	6.45	22.56	540.46	76.6	158.05	1200.5	405.79
Chickasha	5.72	17.12	619.25	79.34	136.38	1080.35	416.30
Chickasha	5.38	22.70	775.02	87.82	144.65	969.79	362.82
Chickasha	6.82	14.77	613.56	71.47	152.45	1683.94	365.80
Chickasha	5.33	23.95	877.31	79.47	139.33	1102.07	331.06
Chickasha	6.04	17.43	642.23	78.76	153.02	1385.83	477.67
Chickasha	4.88	33.63	1001.66	90.63	153.26	949.13	298.83
Chickasha	5.33	28.73	837.94	93.23	127.34	952.4	271.13
Chickasha	6.84	17.67	632.55	74.08	150.43	1572.16	300.64
Chickasha	6.03	19.52	695.72	77.06	144.54	1321.49	333.93
Chickasha	4.81	30.73	936.26	85.72	128.31	762.15	218.11
Chickasha	5.59	24.59	674.12	87.37	136.73	998.21	338.01
Chickasha	5.81	23.03	661.2	92.21	154.77	1171	403.76
Chickasha	6.09	18.4	611.23	92.77	145.66	1319.89	376.52
Chickasha	5.37	30.5	779.51	99.29	127.38	805.19	279.7
Chickasha	5.23	30.55	813.5	95.81	135.06	938.08	305.48
Chickasha	6.13	23.84	686.64	83.95	132.66	1297.24	310.76
Chickasha	5.23	31.93	987.24	95.77	153.03	1128.41	261.28
Chickasha	6.77	17.61	561.09	78.77	156.56	1540.12	423.91
Chickasha	6.01	20.61	550.4	79.69	140.73	1147.21	391.75

Chickasha	4.83	24.45	752.02	88.57	137.85	936.51	307.64
Chickasha	7.45	17.83	534.76	75.06	133.67	1623.34	333.32
Chickasha	5.93	19.8	623.12	73.31	132.58	1203.55	331.9
Chickasha	6.21	19.94	587.09	77.88	150.12	1452.59	447.89
Chickasha	4.62	29.03	908.9	90.67	181.99	1291.83	447.35
Chickasha	4.67	27.3	906.03	91.23	159.75	1160.49	350.96
Chickasha	7.61	22.48	560.39	80.83	148.66	1997.51	388.67
Chickasha	6.92	19.6	528.31	76.2	137.42	1386.42	373.3
Chickasha	4.56	27.94	893.13	84.38	160.97	1046.7	355.61
Chickasha	5.21	23.07	664.43	83.58	157.2	1047.67	367.82
Chickasha	5.79	20.14	564.63	81.63	145.28	1194.43	417.48
Chickasha	6.16	20.69	575.47	89.53	138.15	1276.06	378.51
Chickasha	5.28	30.65	783.01	103.39	156.29	1033.03	375.08
Chickasha	4.81	31.59	849.52	98.51	174.29	1152.35	428.69
Chickasha	6.27	24.44	543.57	81.03	155.17	1113.05	399.48
Chickasha	5.53	24.83	665.12	86.47	149.33	1047.4	370.97
Chickasha	4.89	26.97	838.55	87.36	154.38	1291.5	376.56
Chickasha	7.25	20.59	485.88	72.61	149.38	1546.14	410.1
Chickasha	6.88	18.82	458.41	67.24	150.67	1315.16	429.28
Efaw	6.59	28.4	525.14	97.1	148.52	1423.33	470.84
Efaw	7.15	16.13	570.53	74.48	189.55	2016.53	698.99
Efaw	5.47	40.73	462	106.44	105.31	938.09	193.05
Efaw	6.18	17.68	444.01	83.49	95.69	1283.67	228.62
Efaw	4.72	48.78	638.01	107.92	122.86	677.24	165.66
Efaw	5.85	36.51	471.84	110.47	98.49	1035.74	164
Efaw	6.83	31.22	443.04	88.13	97.06	1415.34	154.13
Efaw	6.19	24.46	536.62	87.6	156.08	1093.68	386.42
Efaw	4.42	47	605.86	114.66	122.2	663.78	141.29
Efaw	4.84	43.88	588.07	115.21	116.01	622.28	134.83
Efaw	5.09	45.18	594.4	126.6	123.75	657.17	139.03
Efaw	5.62	39.22	464.18	119.46	113.19	697.6	155.49
Efaw	7.48	33.78	384.65	90.51	94.06	1368.31	173.41
Efaw	5.21	41.7	520.52	123.03	122.93	695.79	154.59
Efaw	7.50	38.66	393.9	94.22	92.44	1367.89	163.03
Efaw	6.46	37.25	457.76	102	109.47	1112.36	189.53
Efaw	5.10	37.64	448.79	106.21	112.18	833.09	172.07
Efaw	4.87	42.43	618.65	117.75	121.91	673.05	146.63
Efaw	6.19	33.9	405.72	95.79	93.96	858.7	161.66
Efaw	7.59	33.56	385.26	79.76	88.33	1488.33	165.4
Efaw	4.96	37.88	517.46	96.73	120.92	747.91	152.34
Efaw	6.32	30.36	418.75	93.2	101.17	1080.65	170.46
Efaw	7.33	32.96	373.36	80.7	86	1261.23	152.91
Efaw	4.68	43.54	620.73	97.07	122.81	632.33	159.17

Efaw	4.52	54.28	704.23	124.61	94.38	491.86	108.8
Efaw	5.48	32.45	454.29	102.23	92.26	847.62	132.65
Efaw	5.33	38.53	504.87	123.08	99.5	769.3	133.13
Efaw	5.21	43.92	596.4	138.5	105.46	785.41	129.76
Efaw	7.44	39.67	426.56	107.03	101.44	1505.02	141.64
Efaw	6.31	30.65	438.47	98.92	99.14	1123.64	164.74
Efaw	5.38	37.22	554.14	112.72	105.81	1125.56	173.24
Efaw	5.08	38.21	565.51	113.51	93.86	634.78	129.7
Efaw	6.08	33.66	553.08	92.03	91.34	1117.41	113.1
Efaw	4.61	50.11	681.7	111.58	91.32	553.88	115.51
Efaw	5.39	36.12	520.1	98	98.72	909.64	155.69
Efaw	6.34	31.3	471.78	105.44	113.25	1353.4	186.01
Efaw	5.82	31.01	494.84	135.9	115.3	1089.77	183
Efaw	7.14	30.68	396.33	85.58	93.9	1384.26	156.7
Efaw	4.62	54.92	684.45	107.58	82.87	460.85	99.88
Efaw	5.18	41.99	584.08	103.79	97.93	701.09	130.29
Efaw	7.54	44.24	386.71	98.99	89.33	1406.59	139.66
Efaw	4.53	57.14	627.56	120.18	123.47	680.68	154.91
Efaw	5.14	45.55	486.11	115.09	103.11	872.54	150.9
Efaw	5.10	51.88	530.22	129.74	104.19	883.83	144.4
Efaw	4.60	52.34	586.65	130.7	109.27	753.08	133.04
Efaw	5.99	50.25	481.1	112.29	104.28	1225.17	154.82
Efaw	6.25	37.55	397.36	96.56	91.98	1077.59	156.95
Efaw	5.02	45.25	498.27	110.83	99.72	841.91	133.22
Efaw	4.78	42.8	588.17	120.43	114.08	746.61	154.18
Efaw	5.24	44.6	453.37	109.75	99.89	874.62	161.56
Efaw	4.47	57.53	644.1	116.88	101.09	646.4	135.04
Efaw	6.29	41.71	460.98	94.05	102.31	1224.56	165.01
Efaw	5.30	45.26	509.8	102.46	103.96	904.62	157.26
Efaw	6.00	42.54	458.17	105.41	112.17	1235.13	174.98
Efaw	5.59	40.56	498.18	122.46	107.91	1076.36	177.11
Efaw	6.60	40.7	425.88	99.86	99.83	1198.15	155.41
Efaw	4.45	51.86	576.24	106.27	103.02	573.6	126.75
Efaw	4.53	44.82	559.78	102.06	95.71	626.45	130.07
Efaw	4.97	42.23	563.04	96.94	118.84	645.64	149.66
Efaw	5.79	33.52	472.5	108.77	115.55	902.1	180.33
Efaw	4.98	42.35	551.05	118.37	134.12	757.39	154.35
Efaw	4.71	50.61	659.79	135.94	145.01	730.97	169.69
Efaw	5.38	40.64	490.03	117.98	118.91	738.29	158.32
Efaw	4.34	47.39	606.05	117.47	123.28	623.11	145.69
Efaw	6.53	38.63	419.15	108.4	97.72	962.39	167.3
Lahoma	6.87	38.12	585.33	64.44	124.32	1762.17	442.69
Lahoma	6.31	43.97	618.42	74.22	115.63	1545.14	403.19

Lahoma	5.94	49.76	673.11	85.63	107.66	1295.25	317.5
Lahoma	5.47	53.48	751.73	93.98	93.2	993.59	264.32
Lahoma	5.17	63.41	911.4	101.45	89.44	889.65	260.7
Lahoma	4.79	64.07	1019.88	95.52	72.5	761.66	235.37
Lahoma	4.81	64.11	1073.72	88.73	71.49	788.02	257.88
Lahoma	4.96	57.09	1053.73	80.72	72.14	899.07	303.64
Lahoma	5.09	43.61	987.04	72.52	72	1192.77	428.25
Lahoma	5.47	32.86	977.07	62.27	72.43	1453.14	509.14
Lahoma	6.33	26.22	955.31	53.25	72.09	1898.77	540.53
Lahoma	7.14	28.69	848.95	45.69	77.85	2289.73	588.07
Lahoma	5.8	47.05	762.34	82.55	105.91	1232.8	432.87
Lahoma	6.23	43.74	661.33	79.4	110.34	1476.26	373.45
Lahoma	5.14	60.31	877.11	96.61	95.98	1035.91	262.39
Lahoma	5.29	52.13	729.52	95.34	109.27	1122.23	267.04
Lahoma	5.06	59.66	815.88	101.26	97.64	978.7	243.05
Lahoma	5.27	54.92	753.57	92.44	98.56	1007.51	264.23
Lahoma	5.66	47.17	667.46	75.69	98.29	1275.64	313.35
Lahoma	4.97	62.39	1011.17	85.19	78.57	900.03	299.34
Lahoma	6.07	42.39	742.82	63.94	94.46	1484.77	412.29
Lahoma	5.73	44.3	836.46	68.17	86.6	1348.6	449.75
Lahoma	5.28	40.13	1022.26	67.69	82.54	1191.36	468.42
Lahoma	5.47	39.94	1014.53	62.78	82.44	1283.59	507.4
Lahoma	5.34	50.35	792.07	97.27	102.09	1057.02	278.84
Lahoma	6.12	36.29	673.58	77.69	128.77	1483.87	405.03
Lahoma	5.97	41.24	671.46	86.98	131.03	1473.95	375.34
Lahoma	5.17	51.91	835.82	103.09	114.56	1024.42	281.25
Lahoma	5.05	52.92	1060.55	93.31	108.72	1049.71	359.84
Lahoma	5.48	53.85	768.44	91.57	101.47	1115.97	293.53
Lahoma	6.05	45.51	640.38	74.47	116.11	1410.28	367.63
Lahoma	5.54	44.15	763.62	82.48	95.22	1131.1	375.54
Lahoma	5.19	52.61	907.03	86.43	86.11	960.97	357.3
Lahoma	5.72	44.04	829.32	73.88	94.88	1350.93	435.97
Lahoma	5.26	41.74	969.55	74.02	81.45	1116.67	432.8
Lahoma	5.21	39.16	1055.6	70.44	74.76	1076.89	458.91
Perkins	7.1	30.75	602.33	67.77	33.70	1098.61	79.37
Perkins	6.04	29.52	656.09	81.84	30.10	631.53	86.50
Perkins	5.42	28.66	715.00	91.26	32.04	460.40	82.21
Perkins	5.13	33.96	799.78	102.62	34.48	374.93	77.53
Perkins	4.75	37.16	870.87	101.83	24.57	222.64	62.17
Perkins	4.66	40.27	920.99	104.73	21.00	213.55	61.69
Perkins	4.6	39.26	954.79	109.92	22.40	213.92	60.86
Perkins	4.64	40.71	872.35	104.76	20.24	244.26	70.85
Perkins	4.86	36.24	836.64	104.93	30.58	383.30	72.77

Perkins	5.16	32.67	742.70	94.98	33.70	511.77	84.20
Perkins	5.17	29.48	697.57	87.79	33.12	657.65	87.27
Perkins	6	31.23	673.37	79.87	34.59	863.98	87.94
Perkins	4.77	33.80	821.45	97.03	28.49	227.16	52.07
Perkins	5.27	30.37	705.03	83.46	31.45	576.26	67.51
Perkins	5.15	28.77	720.17	84.91	30.67	472.22	64.03
Perkins	4.58	37.94	842.68	99.27	20.46	183.45	43.41
Perkins	4.72	36.22	806.73	101.78	29.53	290.46	62.99
Perkins	6.21	34.66	708.41	76.20	29.72	958.33	76.92
Perkins	4.68	33.21	649.05	70.69	26.62	932.15	74.19
Perkins	6.17	33.40	672.48	74.09	24.38	980.82	74.19
Perkins	4.83	45.52	833.54	104.59	15.49	216.63	54.43
Perkins	5.43	33.49	697.12	88.38	24.41	641.65	86.61
Perkins	4.98	37.24	748.43	99.52	23.32	420.69	77.73
Perkins	4.87	41.39	765.98	103.07	25.37	341.94	74.86
Perkins	4.88	23.04	702.49	86.45	37.25	341.23	83.96
Perkins	5.15	23.80	648.82	78.68	31.48	475.92	92.88
Perkins	6.3	27.57	613.28	71.20	34.55	946.86	96.77
Perkins	5.55	31.17	642.08	80.71	32.19	586.85	91.33
Perkins	4.75	46.37	834.81	109.56	19.60	222.50	56.99
Perkins	4.81	48.13	823.08	101.42	16.78	317.04	58.43
Perkins	6.31	37.01	655.90	71.01	19.58	935.16	68.29
Perkins	4.81	47.40	802.92	101.03	15.10	308.59	64.19
Perkins	5.38	40.50	713.10	84.96	19.86	592.56	75.15
Perkins	5.2	46.60	818.62	104.13	26.90	281.20	77.08
Perkins	4.74	34.43	726.16	88.19	25.24	494.07	89.36
Perkins	4.63	50.65	855.50	118.62	28.93	245.34	76.45



Appendix H. Phosphorus (P) extraction data for all soils and locations. P data for all extraction methods are reported in mg kg<sup>-1</sup>. Extraction methods used include Bray-P1, (bray1), Chang-Jackson P fractionation (A, B, C, D, E), Mehlich-3 P (m3), water soluble P (WSP), total soil P (EPA-3050B).

Location	Extraction Method	pH	P
Chickasha	A	6.03	0.274188
Chickasha	A	6	0.343675
Chickasha	A	5.93	0.343675
Chickasha	A	7.45	0.274188
Chickasha	A	4.62	0.274188
Chickasha	A	4.67	0.274188
Chickasha	A	7.61	0.691113
Chickasha	A	4.56	0.274188
Chickasha	A	7.25	0.691113
Efaw	A	4.42	1.108038
Efaw	A	7.48	2.358813
Efaw	A	7.5	0.830088
Efaw	A	7.59	1.8724
Efaw	A	6.08	1.108038
Efaw	A	5.82	0.7606
Efaw	A	5.99	3.26215
Efaw	A	4.47	2.15035
Efaw	A	4.45	2.567275
Lahoma	A	6.87	1.733425
Lahoma	A	5.47	1.247013
Lahoma	A	4.79	1.108038
Lahoma	A	4.81	1.177525
Lahoma	A	4.96	0.830088
Lahoma	A	6.33	0.274188
Lahoma	A	7.14	0.274188
Lahoma	A	5.29	2.080863
Lahoma	A	5.27	1.663938
Perkins	A	7.1	0.7606
Perkins	A	4.66	0.7606
Perkins	A	4.6	0.691113
Perkins	A	4.64	0.830088
Perkins	A	5.16	0.7606
Perkins	A	5.15	0.48265
Perkins	A	4.88	0.274188
Perkins	A	6.3	0.48265
Perkins	A	6.31	0.830088
Chickasha	B	6.03	11.00844
Chickasha	B	6	9.46638
Chickasha	B	5.93	9.9804

Chickasha	B	7.45	11.26545
Chickasha	B	4.62	15.37761
Chickasha	B	4.67	17.6907
Chickasha	B	7.61	10.0832
Chickasha	B	4.56	18.97575
Chickasha	B	7.25	9.9804
Efaw	B	4.42	30.79821
Efaw	B	7.48	19.74678
Efaw	B	7.5	30.28419
Efaw	B	7.59	17.6907
Efaw	B	6.08	19.74678
Efaw	B	5.82	17.6907
Efaw	B	5.99	32.34027
Efaw	B	4.47	41.84964
Efaw	B	4.45	37.22346
Lahoma	B	6.87	26.68605
Lahoma	B	5.47	35.93841
Lahoma	B	4.79	47.50386
Lahoma	B	4.81	50.33097
Lahoma	B	4.96	44.93376
Lahoma	B	6.33	21.03183
Lahoma	B	7.14	18.97575
Lahoma	B	5.29	38.76552
Lahoma	B	5.27	40.56459
Perkins	B	7.1	17.43369
Perkins	B	4.66	20.51781
Perkins	B	4.6	20.2608
Perkins	B	4.64	19.23276
Perkins	B	5.16	17.43369
Perkins	B	5.15	15.89163
Perkins	B	4.88	11.52246
Perkins	B	6.3	14.34957
Perkins	B	6.31	21.54585
Chickasha	bray1	5.85	4.46
Chickasha	bray1	5.15	9.35
Chickasha	bray1	4.83	10.35
Chickasha	bray1	4.31	19.49
Chickasha	bray1	4.33	18.88
Chickasha	bray1	4.78	10.72
Chickasha	bray1	4.52	15.46
Chickasha	bray1	4.82	11.17
Chickasha	bray1	4.97	9.7
Chickasha	bray1	4	26.35

Chickasha	brayl	4.84	9.15
Chickasha	brayl	3.88	22.35
Chickasha	brayl	5.09	6.92
Chickasha	brayl	4.66	10.57
Chickasha	brayl	5.15	7.26
Chickasha	brayl	4.78	8.88
Chickasha	brayl	5.44	6.11
Chickasha	brayl	4.55	13.22
Chickasha	brayl	4.49	15.59
Chickasha	brayl	4.75	9.81
Chickasha	brayl	5.31	7.56
Chickasha	brayl	5.23	7.21
Chickasha	brayl	5.35	8.6
Chickasha	brayl	5.74	8.14
Chickasha	brayl	5.01	7.62
Chickasha	brayl	4.71	8.54
Chickasha	brayl	4.76	10.34
Chickasha	brayl	5.19	7.06
Chickasha	brayl	5.02	7.23
Chickasha	brayl	5.08	7.74
Chickasha	brayl	4.44	13.01
Chickasha	brayl	4.92	9.66
Chickasha	brayl	4.25	13.44
Chickasha	brayl	5.19	6.78
Chickasha	brayl	5.25	6.44
Chickasha	brayl	5.89	5.66
Chickasha	brayl	5.28	7.23
Chickasha	brayl	4.99	9.84
Chickasha	brayl	4.87	9.42
Chickasha	brayl	4.68	11.78
Chickasha	brayl	4.85	10.2
Chickasha	brayl	4.69	10.8
Chickasha	brayl	4.45	14.62
Chickasha	brayl	4.85	10.21
Chickasha	brayl	4.93	7.69
Chickasha	brayl	5.14	7.61
Chickasha	brayl	4.4	16.22
Chickasha	brayl	4.66	12.71
Chickasha	brayl	4.15	15.62
Chickasha	brayl	4.56	13.29
Chickasha	brayl	3.96	23.28
Chickasha	brayl	4.76	10.22
Chickasha	brayl	5.19	8.53

Chickasha	brayl	5.66	5.48
Chickasha	brayl	5.83	5.68
Chickasha	brayl	5.74	7.55
Chickasha	brayl	4.99	12.32
Chickasha	brayl	5.35	7.13
Chickasha	brayl	4.74	11.72
Chickasha	brayl	4.57	11.24
Chickasha	brayl	4.21	17.84
Chickasha	brayl	4.7	11.28
Chickasha	brayl	4.83	10.62
Chickasha	brayl	4.19	21.33
Chickasha	brayl	5.1	9.51
Chickasha	brayl	4.56	15.1
Chickasha	brayl	4.98	9.63
Chickasha	brayl	4.58	14.48
Chickasha	brayl	5	10.71
Chickasha	brayl	5.17	8.97
Chickasha	brayl	5.17	9.47
Chickasha	brayl	5.08	11.52
Chickasha	brayl	5.52	6.81
Chickasha	brayl	5.23	6.8
Chickasha	brayl	4.99	9.77
Chickasha	brayl	5.25	13.08
Chickasha	brayl	4.87	10.8
Chickasha	brayl	4.27	19.07
Chickasha	brayl	4.67	12.82
Chickasha	brayl	4.3	19.52
Chickasha	brayl	4.7	12.82
Chickasha	brayl	4.36	16
Chickasha	brayl	4.8	12.52
Chickasha	brayl	4.65	11.7
Chickasha	brayl	5.08	10.09
Chickasha	brayl	5.04	10.89
Chickasha	brayl	4.85	11.64
Chickasha	brayl	4.45	19.5
Chickasha	brayl	4.78	12.16
Chickasha	brayl	4.78	12.39
Chickasha	brayl	5.01	12.82
Chickasha	brayl	4.88	13.15
Chickasha	brayl	5.94	7.22
Chickasha	brayl	6.04	7.53
Chickasha	brayl	6.06	6.34
Chickasha	brayl	5.61	9.07

Efaw	brayl	3.63	70.76
Efaw	brayl	3.68	50.94
Efaw	brayl	3.75	51.73
Efaw	brayl	3.69	41.68
Efaw	brayl	3.96	33.45
Efaw	brayl	3.96	35.64
Efaw	brayl	3.9	32.12
Efaw	brayl	4.09	33.66
Efaw	brayl	3.8	40.5
Efaw	brayl	4.09	29.32
Efaw	brayl	3.83	33.44
Efaw	brayl	7.152	9.06
Efaw	brayl	4.21	37.58
Efaw	brayl	4.3	37.16
Efaw	brayl	4.68	29.63
Efaw	brayl	4.07	32.62
Efaw	brayl	4	32.5
Efaw	brayl	4.09	46.02
Efaw	brayl	4.03	34.05
Efaw	brayl	4.17	40.08
Efaw	brayl	5.25	28.87
Efaw	brayl	5.469	27.74
Efaw	brayl	6.51	30.46
Efaw	brayl	5.66	25.73
Efaw	brayl	6.85	29.48
Efaw	brayl	3.83	49.81
Efaw	brayl	3.66	48.78
Efaw	brayl	3.86	35.45
Efaw	brayl	3.84	55.93
Efaw	brayl	4.26	23.77
Efaw	brayl	4.15	22.86
Efaw	brayl	4.47	23.99
Efaw	brayl	4.31	23.49
Efaw	brayl	3.91	32.28
Efaw	brayl	4.12	27.94
Efaw	brayl	4.21	23.49
Efaw	brayl	4.47	24.97
Efaw	brayl	4.25	30.07
Efaw	brayl	4.13	29.62
Efaw	brayl	4.03	30.9
Efaw	brayl	4.14	28.18
Efaw	brayl	5.86	22.1
Efaw	brayl	5.43	21.76

Efaw	brayl	5.7	23.04
Efaw	brayl	6.15	19.92
Efaw	brayl	4.4	21.64
Efaw	brayl	5.08	19.83
Efaw	brayl	4.88	20.03
Efaw	brayl	4.74	21.5
Efaw	brayl	4.31	37.77
Efaw	brayl	4.29	26.22
Efaw	brayl	4.93	29.05
Efaw	brayl	4.57	23.33
Efaw	brayl	4.55	19.43
Efaw	brayl	4.44	18.77
Efaw	brayl	4.54	22.99
Efaw	brayl	4.5	30.49
Efaw	brayl	4.37	28.81
Efaw	brayl	4.2	35.38
Efaw	brayl	4.15	35.48
Efaw	brayl	4.02	30.95
Efaw	brayl	4.75	30
Efaw	brayl	5.37	38.7
Efaw	brayl	5.09	29.48
Efaw	brayl	5.04	22.73
Efaw	brayl	4.05	47.41
Efaw	brayl	4.01	44.92
Efaw	brayl	3.91	51.46
Efaw	brayl	4.11	37.8
Efaw	brayl	5.96	22.07
Efaw	brayl	5.08	20.4
Efaw	brayl	5.64	26.61
Efaw	brayl	4.37	31.02
Efaw	brayl	4.21	32.64
Efaw	brayl	4.47	24.73
Efaw	brayl	4.46	24.03
Efaw	brayl	4.66	20.59
Efaw	brayl	4.71	21.31
Efaw	brayl	4.79	20.63
Efaw	brayl	4.64	28.47
Efaw	brayl	4.51	24.98
Efaw	brayl	4.34	24.3
Efaw	brayl	4.43	26.02
Efaw	brayl	4.53	24.78
Efaw	brayl	4.98	23.13
Efaw	brayl	5.52	24

Efaw	brayl	5.49	20.41
Efaw	brayl	4.74	28.35
Efaw	brayl	3.88	45.37
Efaw	brayl	3.97	45.89
Efaw	brayl	3.91	46.78
Efaw	brayl	4	43.14
Efaw	brayl	3.85	30.7
Efaw	brayl	4.16	26.23
Efaw	brayl	4.08	28.01
Efaw	brayl	4	33.54
Chickasha	brayl	5.79	12.77
Chickasha	brayl	5.91	11.06
Chickasha	brayl	6.03	11.49
Chickasha	brayl	6.25	10.4
Chickasha	brayl	6.38	10.09
Chickasha	brayl	6.73	10.3
Chickasha	brayl	6	11.85
Chickasha	brayl	6.04	10.88
Chickasha	brayl	6.48	9.54
Chickasha	brayl	6.27	10.52
Chickasha	brayl	6.31	10.84
Chickasha	brayl	6.11	12.07
Chickasha	brayl	6.22	11.1
Chickasha	brayl	6.46	11.4
Chickasha	brayl	6.06	12.65
Chickasha	brayl	5.93	12.64
Chickasha	brayl	6.16	12.99
Chickasha	brayl	6.29	12.68
Chickasha	brayl	5.85	11.74
Chickasha	brayl		12.82
Chickasha	brayl		12.51
Chickasha	brayl	6.31	11.98
Chickasha	brayl	6.45	12.4
Chickasha	brayl		11
Chickasha	brayl	5.72	10.6
Chickasha	brayl	5.38	13.76
Chickasha	brayl	6.82	8.82
Chickasha	brayl	5.33	14.9
Chickasha	brayl	6.04	10.09
Chickasha	brayl	4.88	20.85
Chickasha	brayl	5.33	18.66
Chickasha	brayl	6.84	11.21
Chickasha	brayl	6.03	11.33

Chickasha	brayl	4.81	20.07
Chickasha	brayl	5.59	16.39
Chickasha	brayl	5.81	13.83
Chickasha	brayl	6.09	10.68
Chickasha	brayl	5.37	21.06
Chickasha	brayl	5.23	19.76
Chickasha	brayl	6.13	14.85
Chickasha	brayl	5.23	20.42
Chickasha	brayl	6.77	11.87
Chickasha	brayl	6.01	11.76
Chickasha	brayl	4.83	15.48
Chickasha	brayl	7.45	11.36
Chickasha	brayl	5.93	12.6
Chickasha	brayl	6.21	11.24
Chickasha	brayl	4.62	17.29
Chickasha	brayl	4.67	16.81
Chickasha	brayl	7.61	12.82
Chickasha	brayl	6.92	11.87
Chickasha	brayl	4.56	18.95
Chickasha	brayl	5.21	15.42
Chickasha	brayl	5.79	12.81
Chickasha	brayl	6.16	12.92
Chickasha	brayl	5.28	17.22
Chickasha	brayl	6.27	18.47
Chickasha	brayl	5.53	15.46
Chickasha	brayl	4.89	17.84
Chickasha	brayl	7.25	13.9
Efaw	brayl	4.415	36.81
Efaw	brayl	4.842	33.43
Efaw	brayl	5.085	33.37
Efaw	brayl	5.616	27.4
Efaw	brayl		28.88
Efaw	brayl	7.483	25.74
Efaw	brayl		37.18
Efaw	brayl		27.4
Efaw	brayl	5.212	29.71
Efaw	brayl	7.498	36.67
Efaw	brayl		29.13
Efaw	brayl	6.457	25.91
Efaw	brayl	5.101	26.38
Efaw	brayl		31.39
Efaw	brayl	4.873	31.02
Efaw	brayl	6.185	25.16



Efaw	brayl		39.07
Efaw	brayl		24.28
Efaw	brayl	7.591	24.96
Efaw	brayl	4.963	28.83
Efaw	brayl	6.317	22.94
Efaw	brayl		23.19
Efaw	brayl	7.325	26.11
Efaw	brayl	4.675	37.29
Efaw	brayl		33.84
Efaw	brayl	4.52	43.54
Efaw	brayl	5.48	26.23
Efaw	brayl	5.33	30.84
Efaw	brayl	5.213	32.8
Efaw	brayl	7.438	28.49
Efaw	brayl	6.311	24.19
Efaw	brayl		26.8
Efaw	brayl	5.375	25.6
Efaw	brayl	5.081	30.06
Efaw	brayl	6.076	27.14
Efaw	brayl	4.61	41.15
Efaw	brayl		23.83
Efaw	brayl	5.39	23.74
Efaw	brayl	6.338	19.54
Efaw	brayl	5.818	19.58
Efaw	brayl	7.135	21.1
Efaw	brayl	4.615	45.73
Efaw	brayl	5.175	30.76
Efaw	brayl	4.53	43.85
Efaw	brayl	5.141	35.24
Efaw	brayl	5.1	40.35
Efaw	brayl	4.603	39.52
Efaw	brayl	5.985	37.97
Efaw	brayl	6.25	30.3
Efaw	brayl	5.021	36.02
Efaw	brayl	4.775	30.64
Efaw	brayl		34.89
Efaw	brayl	4.47	33.96
Efaw	brayl	6.287	30.32
Efaw	brayl	5.295	36.67
Efaw	brayl	6.003	30.83
Efaw	brayl	5.592	29.64
Efaw	brayl	6.598	31.25
Efaw	brayl	4.45	46.75

Efaw	brayl	4.531	38.38
Lahoma	brayl	6.87	28.45
Lahoma	brayl	6.31	32.16
Lahoma	brayl	5.94	36.48
Lahoma	brayl	5.47	40.11
Lahoma	brayl	5.17	48.31
Lahoma	brayl	4.79	49.83
Lahoma	brayl	4.81	52.81
Lahoma	brayl	4.96	47.64
Lahoma	brayl	5.09	34.67
Lahoma	brayl	5.47	26.33
Lahoma	brayl	6.33	20.19
Lahoma	brayl	7.14	17.18
Lahoma	brayl	5.8	36.61
Lahoma	brayl	6.23	33.4
Lahoma	brayl	5.14	50.44
Lahoma	brayl	5.29	37.17
Lahoma	brayl	5.06	43.05
Lahoma	brayl	5.27	40.35
Lahoma	brayl	5.66	35.33
Lahoma	brayl	4.97	50.99
Lahoma	brayl	6.07	32.28
Lahoma	brayl	5.73	30.94
Lahoma	brayl	5.28	29.66
Lahoma	brayl	5.47	30.2
Lahoma	brayl	5.34	36.13
Lahoma	brayl	6.12	24.65
Lahoma	brayl	5.97	27.03
Lahoma	brayl	5.17	36.45
Lahoma	brayl	5.05	38.29
Lahoma	brayl	5.48	39.85
Lahoma	brayl	6.05	32.48
Lahoma	brayl	5.54	32.02
Lahoma	brayl	5.19	38.74
Lahoma	brayl	5.72	31.52
Lahoma	brayl	5.26	31.42
Lahoma	brayl	5.21	29.63
Perkins	brayl	7.1	18.32
Perkins	brayl	6.04	18.21
Perkins	brayl	5.42	18.93
Perkins	brayl	5.13	22.62
Perkins	brayl	4.75	24.48
Perkins	brayl	4.66	30.55

Perkins	brayl	4.6	24.82
Perkins	brayl	4.64	26.26
Perkins	brayl	4.86	24.26
Perkins	brayl	5.16	20.76
Perkins	brayl	5.17	19.09
Perkins	brayl	6	20.3
Perkins	brayl	4.77	26.08
Perkins	brayl	5.27	18.81
Perkins	brayl	5.15	18.18
Perkins	brayl	4.58	29.78
Perkins	brayl	4.72	25.2
Perkins	brayl	6.21	22.73
Perkins	brayl	4.68	32.59
Perkins	brayl	6.17	22.5
Perkins	brayl	4.83	32.11
Perkins	brayl	5.43	23.15
Perkins	brayl	4.98	25.46
Perkins	brayl	4.87	28.02
Perkins	brayl	4.88	15.85
Perkins	brayl	5.15	14.02
Perkins	brayl	6.3	14.54
Perkins	brayl	5.55	18
Perkins	brayl	4.75	31.2
Perkins	brayl	4.81	31.63
Perkins	brayl	6.31	23.01
Perkins	brayl	4.81	28.54
Perkins	brayl	5.38	23.95
Perkins	brayl	5.2	20.66
Perkins	brayl	4.74	29.24
Perkins	brayl	4.63	32.49
Chickasha	C	6.03	13.37609
Chickasha	C	6	13.80543
Chickasha	C	5.93	14.52101
Chickasha	C	7.45	12.66051
Chickasha	C	4.62	14.09166
Chickasha	C	4.67	14.52101
Chickasha	C	7.61	12.94674
Chickasha	C	4.56	14.95035
Chickasha	C	7.25	14.95035
Efaw	C	4.42	34.84334
Efaw	C	7.48	34.55711
Efaw	C	7.5	35.98826
Efaw	C	7.59	29.83431

Efaw	C	6.08	32.5535
Efaw	C	5.82	33.69842
Efaw	C	5.99	39.2799
Efaw	C	4.47	34.98645
Efaw	C	4.45	35.27268
Lahoma	C	6.87	22.67856
Lahoma	C	5.47	24.82529
Lahoma	C	4.79	25.54086
Lahoma	C	4.81	25.25463
Lahoma	C	4.96	24.82529
Lahoma	C	6.33	18.81446
Lahoma	C	7.14	19.38692
Lahoma	C	5.29	26.11332
Lahoma	C	5.27	25.97021
Perkins	C	7.1	19.53003
Perkins	C	4.66	22.39233
Perkins	C	4.6	21.53364
Perkins	C	4.64	20.96118
Perkins	C	5.16	22.53545
Perkins	C	5.15	20.38872
Perkins	C	4.88	18.38511
Perkins	C	6.3	19.10069
Perkins	C	6.31	24.39594
Chickasha	D	6.03	26.30021
Chickasha	D	6	19.67749
Chickasha	D	5.93	21.33317
Chickasha	D	7.45	27.95589
Chickasha	D	4.62	25.47237
Chickasha	D	4.67	19.67749
Chickasha	D	7.61	17.19397
Chickasha	D	4.56	25.47237
Chickasha	D	7.25	25.47237
Efaw	D	4.42	35.40645
Efaw	D	7.48	32.92293
Efaw	D	7.5	30.43941
Efaw	D	7.59	28.78373
Efaw	D	6.08	32.09509
Efaw	D	5.82	25.47237
Efaw	D	5.99	23.81669
Efaw	D	4.47	30.43941
Efaw	D	4.45	28.78373
Lahoma	D	6.87	24.64453
Lahoma	D	5.47	34.57861

Lahoma	D	4.79	28.78373
Lahoma	D	4.81	27.95589
Lahoma	D	4.96	35.40645
Lahoma	D	6.33	13.88261
Lahoma	D	7.14	10.57125
Lahoma	D	5.29	31.26725
Lahoma	D	5.27	16.36613
Perkins	D	7.1	23.81669
Perkins	D	4.66	20.50533
Perkins	D	4.6	23.81669
Perkins	D	4.64	22.16101
Perkins	D	5.16	22.98885
Perkins	D	5.15	34.57861
Perkins	D	4.88	24.64453
Perkins	D	6.3	24.64453
Perkins	D	6.31	24.64453
Chickasha	E	6.03	89.75
Chickasha	E	6	85.55
Chickasha	E	5.93	92.3
Chickasha	E	7.45	104
Chickasha	E	4.62	76.4
Chickasha	E	4.67	84.5
Chickasha	E	7.61	104
Chickasha	E	4.56	95.3
Chickasha	E	7.25	104
Efaw	E	4.42	10.25
Efaw	E	7.48	13.25
Efaw	E	7.5	7.25
Efaw	E	7.59	11.15
Efaw	E	6.08	8.45
Efaw	E	5.82	9.8
Efaw	E	5.99	10.25
Efaw	E	4.47	8.9
Efaw	E	4.45	7.85
Lahoma	E	6.87	42.35
Lahoma	E	5.47	47.3
Lahoma	E	4.79	40.25
Lahoma	E	4.81	41.3
Lahoma	E	4.96	37.25
Lahoma	E	6.33	38.6
Lahoma	E	7.14	36.2
Lahoma	E	5.29	46.55
Lahoma	E	5.27	43.55

Perkins	E	7.1	8
Perkins	E	4.66	6.5
Perkins	E	4.6	6.05
Perkins	E	4.64	6.35
Perkins	E	5.16	7.55
Perkins	E	5.15	7.7
Perkins	E	4.88	6.65
Perkins	E	6.3	7.55
Perkins	E	6.31	6.8
Chickasha	EPA_3050B	6.03	310.68
Chickasha	EPA_3050B	6	282.86
Chickasha	EPA_3050B	5.93	325.59
Chickasha	EPA_3050B	7.45	323.4
Chickasha	EPA_3050B	4.62	332.01
Chickasha	EPA_3050B	4.67	324.55
Chickasha	EPA_3050B	7.61	335.6
Chickasha	EPA_3050B	4.56	324.3
Chickasha	EPA_3050B	7.25	319.25
Efaw	EPA_3050B	4.4	210.32
Efaw	EPA_3050B	7.48	174.4
Efaw	EPA_3050B	7.5	181.5
Efaw	EPA_3050B	7.59	173.85
Efaw	EPA_3050B	6.08	190.25
Efaw	EPA_3050B	5.82	176.5
Efaw	EPA_3050B	5.99	200.77
Efaw	EPA_3050B	4.47	190.9
Efaw	EPA_3050B	4.45	178.36
Lahoma	EPA_3050B	6.87	301.65
Lahoma	EPA_3050B	5.47	252.22
Lahoma	EPA_3050B	4.79	290.15
Lahoma	EPA_3050B	4.81	278.6
Lahoma	EPA_3050B	4.96	280.88
Lahoma	EPA_3050B	6.33	254.97
Lahoma	EPA_3050B	7.14	245.64
Lahoma	EPA_3050B	5.29	299.98
Lahoma	EPA_3050B	5.27	296.53
Perkins	EPA_3050B	7.1	155.96
Perkins	EPA_3050B	4.66	164.03
Perkins	EPA_3050B	4.6	170.68
Perkins	EPA_3050B	4.64	180.42
Perkins	EPA_3050B	5.16	182.95
Perkins	EPA_3050B	5.15	138.93
Perkins	EPA_3050B	4.88	146.68

Perkins	EPA_3050B	6.3	151.5
Perkins	EPA_3050B	6.31	175.87
Chickasha	m3	5.85	9.93
Chickasha	m3	5.15	18.42
Chickasha	m3	4.83	19
Chickasha	m3	4.31	31.05
Chickasha	m3	4.33	29.12
Chickasha	m3	4.78	22.16
Chickasha	m3	4.52	25.99
Chickasha	m3	4.82	18.5
Chickasha	m3	4.97	15.61
Chickasha	m3	4	35.77
Chickasha	m3	4.84	14.58
Chickasha	m3	3.88	37.3
Chickasha	m3	5.09	12.31
Chickasha	m3	4.66	18.75
Chickasha	m3	5.15	16.1
Chickasha	m3	4.78	17.94
Chickasha	m3	5.44	10.59
Chickasha	m3	4.55	21.18
Chickasha	m3	4.49	28.4
Chickasha	m3	4.75	19.18
Chickasha	m3	5.31	14.86
Chickasha	m3	5.23	14.63
Chickasha	m3	5.35	16.47
Chickasha	m3	5.74	13.88
Chickasha	m3	5.01	14.89
Chickasha	m3	4.71	13.8
Chickasha	m3	4.76	16.98
Chickasha	m3	5.19	16.12
Chickasha	m3	5.02	13.66
Chickasha	m3	5.08	14.16
Chickasha	m3	4.44	25.6
Chickasha	m3	4.92	17.22
Chickasha	m3	4.25	23.03
Chickasha	m3	5.19	12.96
Chickasha	m3	5.25	14.62
Chickasha	m3	5.89	10.86
Chickasha	m3	5.28	14.43
Chickasha	m3	4.99	15.45
Chickasha	m3	4.87	15.94
Chickasha	m3	4.68	19.57
Chickasha	m3	4.85	19.42

Chickasha	m3	4.69	18.22
Chickasha	m3	4.45	25.59
Chickasha	m3	4.85	17.41
Chickasha	m3	4.93	14.44
Chickasha	m3	5.14	13.71
Chickasha	m3	4.4	25.4
Chickasha	m3	4.66	20.69
Chickasha	m3	4.15	27.08
Chickasha	m3	4.56	20.31
Chickasha	m3	3.96	35.2
Chickasha	m3	4.76	17.62
Chickasha	m3	5.19	13.9
Chickasha	m3	5.66	9.95
Chickasha	m3	5.83	10.34
Chickasha	m3	5.74	15.82
Chickasha	m3	4.99	22.52
Chickasha	m3	5.35	12.82
Chickasha	m3	4.74	21.56
Chickasha	m3	4.57	19.76
Chickasha	m3	4.21	33.08
Chickasha	m3	4.7	21.13
Chickasha	m3	4.83	18.95
Chickasha	m3	4.19	33.2
Chickasha	m3	5.1	16.03
Chickasha	m3	4.56	25.64
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Chickasha	m3	4.58	26.07
Chickasha	m3	5	18.82
Chickasha	m3	5.17	15.78
Chickasha	m3	5.17	16.56
Chickasha	m3	5.08	18.69
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Chickasha	m3	5.23	15.1
Chickasha	m3	4.99	18.29
Chickasha	m3	5.25	13.43
Chickasha	m3	4.87	18.55
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Chickasha	m3	4.67	24.64
Chickasha	m3	4.3	32.78
Chickasha	m3	4.7	24.44
Chickasha	m3	4.36	25.65
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Chickasha	m3	4.65	22.52



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Chickasha	m3	4.78	20.24
Chickasha	m3	5.01	20.53
Chickasha	m3	4.88	21.8
Chickasha	m3	5.94	12.79
Chickasha	m3	6.04	12.16
Chickasha	m3	6.06	11.73
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Efaw	m3	3.69	60.91
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Efaw	m3	3.8	62.57
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Chickasha	m3	6.06	23.73
Chickasha	m3	5.93	22.67
Chickasha	m3	6.16	21.94
Chickasha	m3	6.29	21.66
Chickasha	m3	5.85	20.76
Chickasha	m3	6.31	22.15
Chickasha	m3	6.45	22.56

Chickasha	m3	5.72	17.12
Chickasha	m3	5.38	22.7
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Chickasha	m3	6.04	17.43
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Chickasha	m3	5.33	28.73
Chickasha	m3	6.84	17.67
Chickasha	m3	6.03	19.52
Chickasha	m3	4.81	30.73
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Chickasha	m3	5.81	23.03
Chickasha	m3	6.09	18.4
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Chickasha	m3	5.23	30.55
Chickasha	m3	6.13	23.84
Chickasha	m3	5.23	31.93
Chickasha	m3	6.77	17.61
Chickasha	m3	6.01	20.61
Chickasha	m3	4.83	24.45
Chickasha	m3	7.45	17.83
Chickasha	m3	5.93	19.8
Chickasha	m3	6.21	19.94
Chickasha	m3	4.62	29.03
Chickasha	m3	4.67	27.3
Chickasha	m3	7.61	22.48
Chickasha	m3	6.92	19.6
Chickasha	m3	4.56	27.94
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Chickasha	m3	5.79	20.14
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Chickasha	m3	5.28	30.65
Chickasha	m3	4.81	31.59
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Efaw	m3	6.59	28.4
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Efaw	m3	4.6	52.34
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Efaw	m3	4.78	42.8
Efaw	m3	5.24	44.6
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Efaw	m3	5.3	45.26
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Efaw	m3	4.45	51.86
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Efaw	m3	4.97	42.23
Efaw	m3	5.79	33.52
Efaw	m3	4.98	42.35
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Efaw	m3	4.34	47.39
Efaw	m3	6.53	38.63
Lahoma	m3	6.87	38.12
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Lahoma	m3	5.05	52.92
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Perkins	m3	4.75	46.37
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Perkins	m3	6.31	37.01
Perkins	m3	4.81	47.4
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Perkins	m3	5.2	46.6
Perkins	m3	4.74	34.43
Perkins	m3	4.63	50.65
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Chickasha	water	5.91	2.63
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Chickasha	water	6.25	2.79
Chickasha	water	6.38	2.46
Chickasha	water	6.73	2.38
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Chickasha	water	6.04	2.5
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Chickasha	water	6.27	1.8
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Chickasha	water	6.29	3.44
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Chickasha	water	6.45	2.69
Chickasha	water	5.72	2.53
Chickasha	water	5.38	2.26
Chickasha	water	6.82	2.18
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Chickasha	water	6.04	2.93
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Chickasha	water	5.59	2.41
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Chickasha	water	5.23	3.05
Chickasha	water	6.13	2.08
Chickasha	water	5.23	2.39
Chickasha	water	6.77	3.85
Chickasha	water	6.01	2.48



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Chickasha	water	7.45	1.75
Chickasha	water	5.93	2.41
Chickasha	water	6.21	2.46
Chickasha	water	4.62	0.62
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Chickasha	water	7.61	2.32
Chickasha	water	6.92	2.33
Chickasha	water	4.56	0.46
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Chickasha	water	5.79	2.56
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Chickasha	water	5.28	2.3
Chickasha	water	6.27	2.88
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Chickasha	water	7.25	2.5
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Efaw	water	6.18	4.55
Efaw	water	4.42	1.07
Efaw	water	4.84	4.76
Efaw	water	5.09	6.72
Efaw	water	5.62	5.64
Efaw	water	7.48	2.97
Efaw	water	5.21	5.42
Efaw	water	7.5	1.03
Efaw	water	6.46	5.51
Efaw	water	5.1	4.59
Efaw	water	4.87	1.79
Efaw	water	6.19	3.48
Efaw	water	7.59	2.17
Efaw	water	4.96	3.53
Efaw	water	6.32	2.94
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Efaw	water	5.48	3.39
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Efaw	water	5.21	3.49
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Efaw	water	5.08	3.11
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Efaw	water	4.6	2.68
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Lahoma	water	6.87	2.49
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Perkins	water	4.75	1.26
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Perkins	water	4.86	0.68
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Perkins	water	5.17	0.8
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Perkins	water	4.72	1.16
Perkins	water	6.21	1.83
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Perkins	water	4.83	1.86
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Perkins	water	4.98	2.2
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Perkins	water	5.15	0.89

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Perkins	water	5.55	1.51
Perkins	water	4.75	1.31
Perkins	water	4.81	1.56
Perkins	water	6.31	2.18
Perkins	water	4.81	2.22
Perkins	water	5.38	1.37
Perkins	water	5.2	1.83
Perkins	water	4.74	1.66
Perkins	water	4.63	

VITA

Edmond Bryan Rutter

Candidate for the Degree of

Master of Science

Thesis: EFFECT OF LAND APPLICATION OF LIQUID SULFURTRAP ON GRAIN  
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OF SOIL pH ON PHOSPHORUS EXTRACTION METHOD RESULTS

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