IMPACT OF IN-FURROW STARTER FERTILIZERS IN SOYBEAN PRODUCTION IN OKLAHOMA AND EFFECT OF THE USE OF A NOVEL BYPRODUCT FROM THE DESULFURIZATION OF HYDROCARBON STREAMS IN AGRICULTURAL SOILS

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CHAPTER I

IMPACT OF IN-FURROW STARTER FERTILIZERS IN SOYBEAN PRODUCTION IN OKLAHOMA

ABSTRACT

Soybean [*Glycine max* (L.) Merrill] is an important oilseed worldwide due its high protein content and level of oil in the seed, which makes it valuable for human consumption, livestock feed, and bioenergy. Soybean ranks second as the most planted crop in the US in terms of acreage. As the acreage of soybeans in Oklahoma increases, so does the need for improved fertilizer management in no-till soybean systems. The use of starter fertilizers provides readily available nutrients where undeveloped root system of the seedling can easily access. This study evaluated the effects of multiple starter fertilizer sources on soybean production in Oklahoma. Commonly used, commercially new, and experimental starter fertilizers were applied to soybean at planting either in-furrow or broadcast application at Stillwater and Perkins in 2015, and at Stillwater, Lahoma, and Lamont in 2016. Soybean germination, canopy coverage, and NDVI measurements were significantly reduced due to stressed induced by high temperatures and drought experienced during the growing season. Yield was not positively affected by any starter fertilizer applied. Timely precipitation was likely to be the most important limiting factor for soybean production in this study, masking any starter fertilizers improvement and making the use of starter fertilizer not indicated in Oklahoma.

INTRODUCTION

Soybean [*Glycine max* (L.) Merrill] is an important oilseed crop due to its high protein content (35-50%) (Hwang et al. 2014) and level of oil (12-30%) (Liu, 1997) in the seed, which makes it valuable for human consumption, livestock feed, and bioenergy (Goldsmith, 2008). In the 2015/2016 season, worldwide soybean production was 313 million metric tons (MMT), which comprised 60% of the world oilseed production. The U.S. is the largest soybean producer with 107 MMT, followed by Brazil at 96 MMT, Argentina at 57 MMT, and China at 12 MMT [United States Department of Agriculture (USDA), 2017]. The acreage of soybean in the US has increased by 65% in the last 20 years (NASS, 2017). As the acreage of soybeans in Oklahoma increases, so does the need for improved fertilizer management in soybean systems to improve yield. The use of starter fertilizers provides readily available nutrients where undeveloped root system of the seedling can easily access. Moreover, early season soil nutrient availability for summer crops often is lower than later in the season because mineralization is depressed. Positive influence of starter fertilizer in many crop productions is well documented (Guthrie, 1991; Grubinger et al., 1993; Mullins and Burmester, 1997; Vetsch and Randall, 2000; Vetsch and Randall, 2002). However, previous work has been somewhat inconsistent on whether or not it increases early growth and grain yield in soybeans. Touchton and Rickerl (1986) stated that phosphorus (P), potassium (K), nitrogen (N)-K, and P-K starter fertilizers increased yields by 46% compared to the control when residual P and K were low, and 26% on sandy soils, even when residual P and K were high. On the other hand, Clapp and Small (1970) found that in loam, fine sandy loam, and sandy loam soils, liquid fertilizer applied with the seed as low as 35.5 liters ha^{-1} of 5-8.8-4.2 (N-P-K) decreased seedling stand and yield in North Carolina. They also found that granular fertilizer rates as low as 11.2 kg ha^{-1} of 10-15-5 (N-P-K) decrease stand, but not grain yield. Furthermore, little information for soybean production in Oklahoma requires produces to use data from other states that may, or may not, be comparable due to the specific conditions of Oklahoma soybean production (D.B. Arnall, personal communication, July 7, 2016). The purpose of this study is to evaluate the effect of various starter fertilizer sources in Oklahoma to determine if it is an effective way to maximize plant health and vigor, and grain yield in soybean.

REVIEW OF LITERATURE

Soybean

Soybean is an oilseed native to East Asia that belongs to the family *Fabacea*, genus *Glycine* and subgenus *Soja* (Moench), which includes the cultivated soybean, *Glycine max* (L.) Merrill, and the wild soybean, *Glycine soja* Sieb.& Zucc. The cultivated species has an erect structure, bushy and annual life cycle (Kumudini, 2010). Soybeans varieties present either determinate or indeterminate growth habit. Determinate varieties stop vegetative growth as soon as anthesis starts, while indeterminate varieties continue producing nodes on the main stem until the beginning of seed fill (Purcell et al., 2014). The growth stage identification system in use today was first reported by Fehr and Caviness (1977). It was created to establish a pattern, regardless any other factor, such as the variation in plant development cause by growth habit (Fehr and Caviness, 1977). The system is divided into vegetative and reproductive development. Soybean vegetative phenology is typically described with an incremental ordinal numbers (Vn) assigned to consecutive main stem nodes, beginning with the cotyledonary (VC = V0) stage, until the topmost node in the main stem. Nodes are used for determination because they are permanent, while leafs can be broken or cut off. Reproductive phenology is also described with incremental ordinal numbers assigned to the beginning and end of the floral, pod, seed, and maturity phases (Rn). Planting date, photoperiod, temperature, location and variety, as well as, soil fertility and moisture affect soybean growth (Ruiz-Vega, 1984; Purcell et al., 2014).

Soybean is globally important due to its high protein content (35-50%) (Hwang et al. 2014) and significant level of oil (12-30%) (Liu, 1997) in the seed, which makes it valuable for human consumption, livestock feed, and bioenergy (Goldsmith, 2008). The oil is used for several purposes, such as cooking oil, ingredients for food formulations, such as margarine, and industrial uses, such as plastic, solvents, and biodiesel [U.S. Soybean Export Council (USSEC), 2006]. The protein rich meal, which is left after the oil has been removed from the seed, is used as a protein source in feed for livestock farming (98%), while a minor part (2%) is used directly in the human consumption (Goldsmith, 2008; Liu, 1997). Soybeans comprise 60 percent of the world's oilseed production with 313 MMT produced in 2016. The United States is the largest producer with 107 MMT, followed by Brazil (96 MMT), Argentina (57 MMT), and China (12 MMT) (USDA, 2017). In the last 50 years, soybean production, harvested hectares, and yields in the US have increased by 323, 123, and 87%, respectively (USDA, 2016). Soybean production ranks second as most planted agronomic crop in the US, behind corn, with 33 million hectares planted in 2016 (USDA, 2017). In Oklahoma, soybean is the third most planted crop after wheat and sorghum (NASS, 2016). According Barreiro (2011), the increase of soybean production in the state was due high demand and prices of the crop worldwide. The price of soybean in the US has increased by 45% in the last 20 years. Most of the production in Oklahoma has been concentrated in the north central and north east region due to more favorable weather conditions for soybean production.

Oklahoma has a high temperature and low precipitation in the summer, which hinders flower development and pod filling of soybeans.

Mineralization

Mineralization is a natural process carried out by microorganisms that convert organic compounds from the organic matter to inorganic compounds, and releases them into soil solution as readily available ions for plants (Brady and Weil, 1996). It is an important process in crop production, since it is responsible for the nutrient cycling in the soil (Curtin et al. 1997).

Environmental factors, such as soil aeration, moisture, pH, and temperature are directly related to mineralization. Well-aerated soil has a high rate of mineralization, since well aerated soil increases the activity of aerobic organisms, which are responsible for the breakdown of organic matter. Anaerobic organisms present in poorly aerated soil will still breakdown residues, however it occurs at a slow rate. Also, released oxidized products from poorly aerated soil can be toxic to plants when present in high concentration (Brady and Weil, 1996). In turn, water is inversely proportional to air content in the pores of the soil. The optimum moisture content required for mineralization is between 80% and 100% of field capacity (Guntiñas et al. 2012) as water is positively linked to growth and nutrition of the microorganisms (Del Pino Machado, 2005), which are located in the soil water and on soil particle surface (Crohn, 2004). Soil acidity is also an important factor associated to the decomposition of organic matter, since pH affects the microbial community responsible for mineralization (Rousk et al., 2009). The value of soil pH to optimum microbial development ranges from 6 to 8 (Brady and Weil, 1996), considering that the pH of microbial cell is about 7 (Miller and Gardiner, 2001). It is important because soybean production in Oklahoma is concentrated in regions of

Oklahoma that are well documented at being acidic (Zhang and Raun, 2006) Another important factor in mineralization is soil temperature. According to Davidson and Janssens (2006), temperature boosts mineralization because the chemical and enzymatic reactions for decomposition of organic matter are temperature-dependent. The extreme temperatures for the activity of most of soil microorganisms range from 0ºC to 40ºC, with optimal temperature between 25º C and 37ºC (Miller and Gardiner, 2001). Brady and Weil (1996) stated that microbial activity is insignificant below 10ºC. Many farmers in Oklahoma are planting summer crops earlier in the spring to avoid the development of critical developmental growth stages during the hottest part of the season (Hedges, 2012). However as noted earlier the cooler soil conditions may have slower soil mineralization rates and hence the potential need of external inputs to provide essential nutrients to the plants.

Fertilizers

There are 16 essential elements for the life cycle of the plants. Oxygen (O), hydrogen (H) and carbon (C) are supplied by air and water (Flynn, 2013). N, P, K, calcium (Ca), sulfur (S), magnesium (Mg), boron (B), chlorine (Cl), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo) are found in the soil and absorbed by diffusion, mass flow or root interception. The establishment of agriculture results in a constant decrease of nutrient in the soil due to removal of the elements by the harvested crop (Beegle, 1995). In order to ensure adequate level of nutrient needed to reach maximum yield, supplemental sources of nutrients are applied, such as chemical fertilizers, animal manures, green manures, and legumes (Beegle, 1995).

Fertilizers are any material containing one or more nutrients (organic or inorganic, natural or synthetic) that are applied on or into the soil or directly to the plants, in order to suppress fertility deficiencies that reduce potential growth and crop yield (McKenzie, 1998). Manufactured fertilizers are the most commonly source used for crop production. The percentage of nitrogen, as N; P, as P_2O_5; and K, as K_2O, are labeled (N-P-K) in all fertilizers, because of the high importance of these nutrients for crop production. Therefore, 100kg of a 10-20-10 fertilizer has 10 kg of N, 20 kg of P_2O_5, and 10 kg of K_2O. Fertilizers can be sold as solid, liquid, or gaseous forms (Savoy, 2016). Each physical form has its own singularity, limitations and uses (Beegle, 1995). Methods such as pre-plant (broadcast or incorporated), starter fertilizer at planting, sidedress during early growth, and fertirrigation, are used to the fertilizer application.

The term starter fertilizer means the application of nutrients with or close to the seed at planting. The main objective of this application is to supply emerging seedlings with essential nutrients within its rooting zone. Crops can respond to starter fertilizers independently to the soil fertility levels (Havlin et al., 1993). Under low nutrient availability in cold soils during early growing season, starter fertilizers may promote better plant and root vigor, as well as, yield increases (Touchton and Rickerl, 1986; Hedges, 2012).

The positive influence of starter fertilizer in many crop production systems is well documented. According to Guthrie (1991), application of ammonium polyphosphate at the rate of 17 and 25 kg ha^{-1} of N and P, respectively, as starter fertilizer in cotton resulted in more plant vigor, which resulted in increased flowering and increased lint yield by 9% in loamy sand and sandy loam soils in North Carolina. Mullins and Burmester (1997) had similar results in a silt loam soil in Alabama. They found that the addition of 15-15-0 (N-P-K) as liquid fertilizer at rate of 140 L ha^{-1}at planting increased cotton yield by an average of 8.1%. Grubinger et al. (1993) stated that the application of 10-15-0 (N-P-K) as starter fertilizer in a loam soil in New York increased tomato yield by 11t ha^{-1} when soil P was low and without any other P fertilization. Vetsch and Randall (2000) found that in a clay loam soil in Minnesota the use of starter fertilizer with anhydrous ammonia as N source increased corn yield by 0.5 t ha^{-1}. Vetsch and Randall (2002) concluded that the use of 9-10-24 (N-P-K) as starter fertilizer at the rate of 168 kg ha^{-1} increased corn yield by 0.5 t ha^{-1} in a silt loam soil.

However, the results of previous work evaluating the use of starter fertilizers is inconsistent and inconclusive, especially on the effect on early growth and grain yield of soybean. Touchton and Rickerl (1986) stated that the addition of P, K, N-K, and P-K starter fertilizers increase soybean yields by 46% compared to the control when residual P and K were low, and 26% when the residual P and K were high in a sandy loam soil. Osborne and Riedell (2006) concluded that starter N fertilizer applied in band increased soybean yield by 6% compared to the unfertilized treatment in a clay loam soil in South Dakota. On the other hand, Clapp and Small (1970) found that application of liquid fertilizer with the seed as low as 35.5 L ha^{-1} of 5-8.8-4.2 (N-P-K) decreased seedling stand and yield in loam, fine sandy loam, and sandy loam soils in North Carolina. They also found that granular fertilizer rates at 11.2 kg ha^{-1} of 10-15-5 (N-P-K) decreased stand but not grain yield. Ham et al. (1973) stated that broadcast application of 0-26-25 to 0-44-125 (N-P-K) and 5 x 5 cm placement of 10-20-10 to 16-40-53 (N-P-K) increased yield in soybean, while in-furrow placement of 4-8-1 to 4-8-12 (N-P-K) affected stand.

Fertilizer placement is an important consideration when applying starter fertilizers. Several placements methods are used for, such as banded (e.g. 5 cm below the seed; 5 cm to the side; 5 x 5 cm - 5 centimeters beside by 5 centimeters below the seed; or 5x10 cm - 5 centimeters beside by 10 centimeters below the seed), dribble band (surface banding off the row), and in-furrow (fertilizer in contact with the seed), Armstrong (1991) stated that surface placement is broadly preferred for soybean. Miller (2016) found that the use of 2-6-16, 3-10-13, 7-12-11(N-P-K) at the rate of 19 L ha^{-1} significantly reduced plant stand but not yield when applied with the seed. Hedges (2012) concluded that the use of 6 kg ha^{-1} of N and 13 kg ha^{-1} in furrow at planting reduced stand but not yield. He also found that the application of 11, 22, and 33 kg ha^{-1} of N with S and Zn banded 5 cm below and 5 cm to the side of the seeds did not affect stand or yield. These results corroborated to results found by Sij et al. (1979), where the application of 16.8 and 50.4 kg ha^{-1} of nitrogen banded did not affect soybean production. Salt index of the fertilizer, soil texture, soil moisture and crop are factors that must be considered for choosing the fertilizer placement.

Salt Index

The concept of salt index (SI) proposed by Rader et al. (1943) is defined as the potential for increasing salt concentration in the soil solution caused by the use of fertilizers (Follett et al., 1981). The SI is given as the variation of osmotic pressure of the soil solution, based on the osmotic pressure (relative value of 100) of the same weight of sodium nitrate (Mortvedt, 2001). High salt concentration may have detrimental effects on roots and germinating seeds, such as plasmolysis of cells caused by osmosis (Eash et al., 2015). Fertilizers are separated as high-analysis and low-analysis fertilizers, which relate to the percentage of nutrient in their formulations. Fertilizers with 30% or less of nutrient are classified as low-analysis, while fertilizers with more than 30% are classified as high-analysis (McKenzie, 1998). This concept is important due to the relative nature of the salt index measurement. For example, urea (46-0-0) has a higher salt index than UAN (28-0-0); however, urea has a lower salt index per unit of plant nutrient than the latter. This is because in order to supply 10 kg of N, 35 kg of UAN is required, while only 22 kg is required with urea. Hence, the lower rate needed by higher-analysis fertilizer exposes the germination seeds to a low probability of salt injury (Havlin et al., 1993). A popular method used to determine the safe fertilizer rate is to calculate the amount of N and K_2O applied. For minimal salt injury in soybean, a range of 1 to 6 kg ha^{-1} (N + K_2O) is suggested depending on soil texture, row space, and moisture (Gelderman, 2008).

A concern with the use of starter fertilizers in soybean is related to the high salt sensitivity of the crop, thus the placement and rate must be carefully calculated. In a study conducted in Wisconsin by Hoeft et al. (1975) on the effect of four fertilizer sources (ammonium nitrate, monoammonium phosphate, concentrated superphosphate, and potassium chloride) combined to provide all possible combinations of N-P-K at three rates with the seed on soybean emergence, they found a decrease on seedling stand by as much as 50% when the salt index reached 2.32 and concluded that salt index and stand are inversely proportional. In Minnesota, Rehm and Lamb (2010) found that the application of 16 and 28 L ha^{-1} of fluid fertilizers (10-15-0 and 4-4.4-8.3; N-P-K) in-furrow did not have negative effect on emergence, but higher rates (32 and 56 L ha^{-1}) of the same fluid fertilizers and 3-8-15 did reduce emergence although soybean yield was not affected.

OBJECTIVE

The objective of this study is to measure the effect of various starter fertilizer sources in Oklahoma on plant stand, biomass production, and grain yield in soybean.

METHODOLOGY

Locations

The study was conducted over a two-year period (2015-2016) at five locations in north central and north east Oklahoma. In 2015, the study was located at the Lake Carl

Blackwell Research Farm near Stillwater, OK (36° 9'6.80"N, 97°17'23.79"W), on a Pulaski fine sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Udic Ustifluvents), and the Canadian Valley Research Station near Perkins, OK (35°59'44.19"N, 97° 2'38.55"W), on a Konawa (fine-loamy, mixed, active, thermic Ultic Haplustalfs) and Teller (fine-loamy, mixed, active, Udic Argiustolls) loam soils. In 2016, the study was conducted at the Lake Carl Blackwell Research Farm near Stillwater, OK (same location as in the previous year), at the North Central Research Station near Lahoma, OK (36°23'13.49"N, 98° 6'36.92"W), on a Grant silt loam (fine-silty, mixed, superactive, thermic Udic Argiustolls), and on a producer's field near Lamont, OK (36°41'33.00"N, 97°35'21.33"W), on a McLain silt loam (fine, mixed, superactive, thermic Pachic Argiustolls) soils. All five site-years were conducted under no till dryland cropping system except in 2016 at Stillwater site where it was conducted under limited irrigation system due to mechanical problem in the pivot during the season.

Soil Sampling and Analysis

A composite soil sample composed of 20 soil cores at 15 cm depth was collected per location. Soil samples were analyzed for soil pH (1:1 water), buffer index using Sikora buffer test, extractible P, K, Ca, and Mg by Mehlich 3, N and S using 0.008M of Calcium Phosphate, and Fe, Cl, Zn, Cu, and B using DTPA- Sorbitol. Soil test results for all sites are presented in Table 1.1. Analysis was performed at the Oklahoma State University Soil, Water and Forage Analytical Laboratory (SWFAL).

Planting and Treatment Establishment

Soybean variety 'P49T24SR' was planted at both locations in 2015 and varieties 'P39T64R' and '4806R2' were planted at Lahoma site and at Stillwater and Lamont sites, respectively in 2016 (Table 1.2). Soybean varieties were based upon company recommendations and planted at a depth of approximately 3.8 cm with a John Deere MaxEmerge two row planter. Planting rate was calibrated at 325,000 seeds ha^{-1}. Experimental plots were maintained weed free using glyphosate and hand weeding as needed. Prior planting glyphosate and Valor XLT was applied at Stillwater 2015, Stillwater 2016, and Lahoma 2016

A randomized complete block design was used in all site-years. In 2015, the study consisted of 13 treatments replicated three times. In 2016, two more treatments were added from the previous year (total of 15 treatments) with three replications at Stillwater site and four replications at Lahoma and Lamont sites. For comparison, an unfertilized plot (check) was included (Table 1.3). Fertilizers were applied at planting either through in-furrow (for liquid fertilizers) or broadcast (for dry fertilizers).

Commonly used, commercially new and experimental starter fertilizers were used in this study. An untreated check (treatment 1) was established to analyze the effect of starter fertilizers on the crop. Ammonium polyphosphate (APP), a liquid source of nitrogen (ammoniacal) and phosphorus (polyphosphate) was applied at 23L ha^{1} as pure solution (treatment 2), diluted with water at ratio 1:1 (treatment 3), mixed with Accomplish (Loveland. Greeley, CO), a microbial solution for improving the conversion of fertilizers into plant-available forms (treatment 4), and mixed with MicroBolt Zn (Nachurs. Marion, OH), liquid source of chelated zinc (treatment 5). Liquid fertilizer 9-18-9 source of nitrogen (ammoniacal and urea), phosphorus (orthophosphate) and potassium (salt), was applied at rate 23L ha^{-1} and diluted with water at ratio 1:1 (treatment 6), and diluted with water and mixed with Soygrow (Nachurs. Marion, OH), liquid fertilizer source of chelated iron, chelated magnesium, chelated manganese, and chelated zinc (treatment 7). K-leaf (ENC-Helena. Collierville, TN), a liquid source of potassium (salt) was applied at rate 23L ha^{-1} and diluted with water at ratio 1:1 (treatment 8). Pro-germinator (Agro-Culture. St. Johns, MI), a liquid source of nitrogen (ammoniacal, nitrate and urea), phosphorus (polyphosphate), potassium (salt), and iron (salt) was applied at rate 23L ha^{-1} as pure solution (treatment 9). Treatments 10, 11, and 12 were dry fertilizers broadcast applied; Diammonium phosphate (DAP), a nitrogen (ammoniacal) and phosphorus (orthophosphate) at rate 112 kg ha^{-1} (treatment 10), Potash, a potassium (salt) source at rate 112 kg ha^{-1} (treatment 11), and MESZ (Mosaic. Plymouth, MN), a nitrogen (ammoniacal), phosphorous (orthophosphate), sulfur (salt and elemental), and zinc (elemental) source at rate 129 kg ha^{-1} (treatment 12). SulfurTrap is an experimental fertilizer. It is a source of potassium and sulfur. Its properties and uses are still being currently studied. SulfurTrap was applied at rate 14 L ha^{-1} and diluted at ratio 1:2.3 (treatment 13). In 2016, two new fertilizers were established in the study due the high use by farmers in Oklahoma. Rhyzo-Link (Nachurs. Marion, OH) is a source of nitrogen (ammoniacal and urea), phosphorus (orthophosphate), potassium (salt), sulfur (salt), and chelated zinc. It was applied at rate 14 L ha^{-1} and diluted at ratio 1:2.3 (treatment 14). Triple Option (Nachurs. Marion, OH) is a nitrogen (ammoniacal and urea), phosphorus (orthophosphate), potassium (salt), and sulfur (salt) source. It was applied at rate 14 L ha^{-1} and diluted at ratio 1:2.3 (treatment 15).

Table 1.3 lists the treatment structure and analysis for all fertilizers used in this study. Attached to the planter was a CO_2-powered liquid sprayer system attached to a Schaffert Seed Rebounder™ Seed Firmer that was used for in-furrow (direct contact to the seed), liquid fertilizer applications (Figure 1.1).

Growth and Development Evaluations

Soybean stand counts were taken when the crop was at V1 to V3 growth stages by counting the number of soybean plants that emerged within the 30.5 cm stick placed in four count points randomly chosen along the two middle rows of each plot. To determine crop health and vigor at late vegetative and reproductive stages, normalized-difference vegetative index (NDVI) measurements were obtained using a GreenSeeker^{TM} sensor at growth stages R1 and R5 approximately 70 to 100 cm directly above the canopy. The NDVI index is calculated as the ratio between the subtraction of Red reflected from near infrared reflected (NIR) and the sum of NIR reflected and Red reflected. The NDVI readings were taken at both R1 and R5 in order to observe crop health and vigor at late vegetative and reproductive stages. The measurements were taken in the two inner rows along the entire length of the plot. Canopy closure was measured using Canopeo. Canapeo is a tool, developed by Oklahoma State University, which analyzes fractional green canopy cover (FGCC) from a digital image. The analysis is based on the selection of pixels according to ratios of color bands in the image, resulting in a new black and white image, where black and white correspond to “not green canopy” and “green canopy”, respectively (Patrignani and Ochsner, 2015). Two images were taken per plot using a photographic camera with the lens pointing down and encompassing the two inside rows in an area of approximately 1 m^2.

Grain Yield Evaluations

A Massey Ferguson 8XP combine equipped with a Harvest Master Grain (for grain yield per plot determination) was used to harvest the two middle rows of each plot at all sites. In 2015, grain yield was only obtained in Stillwater because of crop being grazed by deer at Perkins during pod fill, most plots experience leaf removal of 65% or greater. In 2016, Lamont site was not harvested due to severe pigweed (*Amaranthus* spp.) pressure, despite multiple applications of glyphosate and attempts to remove the weeds via hand hoeing. Lahoma experienced green stink bug, *Acrosternum hilare* infestations in mid-season that likely decreased potential yield on average. All grain yields were adjusted to 13% moisture content. Subsamples were collected and analyzed for grain protein and oil content using near-infrared (NIR) spectroscopy by Perten Instruments DA 7000 NIR analysis system (Baianu et al., 2012). This method is based on absorption of NIR energy, which occurs because of the vibration and rotation of chemical bonds within molecules that generates series of energy levels.

Statistical Analysis

Stand count, NDVI, canopy closure, grain yield, and protein and oil concentrations in the grain were analyzed using PROC GLIMMIX of SAS version 9.4. Site, years and their interactions were considered as fixed effects and replications were considered as random effect. LSmeans were used to find specific differences among treatments at the 5% probability level of significance. Slice options were used to investigate simple effects when interactions occur. Correlation coefficient analysis between NDVI measurements vs Canopeo readings was done by using PROC CORR of SAS 9.4.

RESULTS and DISCUSSION

Climatic Conditions

Average maximum and minimum temperatures in Oklahoma were similar to each other between 2015 and 2016; however, total precipitation varied between years (Appendices 1 and 2). The 2015 growing season was a wetter year compared to 2016.

Total amount of rainfall from January to December 2015 was 600 mm more than the total amount of rainfall in 2016. Despite the large difference in annual precipitation, there was adequate moisture in all locations during crop establishment until early flowering stage of soybean. As the crop reached its reproductive stage, however, low rainfall and high temperatures occurred which may have decreased fertilization response and yield potential at all locations. Soil temperature at planting (Table 1.4) was lower than the optimum condition for mineralization and soybean germination (25ºC), but higher than the minimum required for microorganism activity (10ºC).

Stand count

In 2015, Stillwater and Perkins sites had lower seed count compared to the 2016 sites. Soybeans at these sites were planted in a no-till planter that was not properly calibrated for the targeted rate of 325,000 seeds ha^{-1}, which may have caused the reduction on the number of seeds planted per hectare. Moreover, stand counts at Stillwater site were lower than at Perkins site possibly because of the high amount of rainfall (58 mm) that Stillwater site received a day after planting and 52 mm more in the next five days. High amount of rainfall causes saturation and flooding of fields which could result to poor germination and emergence of soybeans (Elmore and Mueller, 2015).

Stand count loss ranged from 2 to 45% depending on treatments. In general, low and non-statistically significant losses were observed in plots with dry fertilizers applied broadcast compared to the untreated check. According to Kleijan and Bly (2015) soybeans are very sensitive to salts. Even small amounts of fertilizers in the furrow with the seed can reduce stands by 20% or more. Sij et al. (1979) stated that the application of 16.8 and 50.4 kg ha^{-1} of N banded did not affect soybean production. Hedges (2012) concluded that the use 6 kg ha^{-1} of N and 13 kg ha^{-1} in furrow at planting reduced soybean stand but not yield, and the application of variable rates of N with sulfur and zinc banded 5 cm below and 5 cm to the side of the seeds did not affect both stand and yield. Schatz (2017) found that any amount of starter fertilizer applied with the seed resulted in significant reductions in stand establishment.

Significant differences in stand count among treatments were noted at Perkins and Lamont sites (Table 1.5). Specific environmental conditions at locations may play an important role to the variability among treatments as well. Perkins soil has a low clay content, which increases cation availability and potential damages to the seeds (Verbeten, 2015). Soybeans applied with APP plus water, APP plus Zn, and 9-18-9 with or without additive had lower stand counts than the untreated check at Perkins. At Lamont, 7 of 11 in-furrow treatments resulted to low stand count compared to the untreated check. Differences in stand count among treatments may have been intensified by the high pigweed (*Amaranthus* spp.) infestation at emergence, since soybeans establishment is sensitive to high weed pressure (Vollmann, 2010; ASGROW, 2015). The Lamont site did not get further evaluations due to a high weed pressure. Figure 1.2 shows the relative stand count of treatments in the five experimental sites compared to the check.

NDVI Measurements

NDVI readings were measured at R1 (NDVI1) and R5 (NDVI2) growth stages, except at Perkins 2015 and Stillwater 2016, where measurements were taken only at R1 and at R5, respectively (Table 1.6). The NDVI measurement in R5 and further evaluations in Perkins was disregarded due to damages caused by deer feeding, while NDVI was measured only in R5 in Stillwater 2016 due to unexpected early development. Measurements of NDVI were taken at these stages in order to analyze vigor and healthy in late vegetative stage (R1) and completely developed plants (R5).

Significant differences among treatments were found at Stillwater 2015 and Perkins sites for NDVI1 measurements. At both locations, plants applied with APP and 9-18-9 fertilizers generally had lower NDVI measurements compared to the unfertilized check and the broadcast applied treatments. The pattern of NDVI results observed at both locations are similar to that of the stand count results. Plots with low stand count had low NDVI readings while plots with higher stand count had higher NDVI readings (Table 1.7). This could be explained by the sparse stand canopy and greater reflectance of soil, which showed lower values of NDVI than a denser canopy. These results conform to the previous findings of Carlson and Ripley (1997) about sensitivity of NDVI to fractional cover of a canopy until a full coverage is reached. However, the effects on canopy cover may vary field-to-field due to soybeans compensation capacity (Barnhart and Lenssen, 2012). In Perkins, besides the effect of soil texture on potential plant damages, it was also caused by environmental condition during the season, such as low pH, that is detrimental to plant development, since it reduces nutrient availability in the soil to the plants, as well as, herbicide efficiency (Arnall, 2016). According to Hunt (2016), a favorable environmental condition is required for a greater capacity of plant compensation. In Stillwater 2015, the results may be highly variable because the poor stand and inconsistencies caused by the high soil saturation after planting.

Soybeans typically respond to P and K fertilization when soil levels are low (Kleinjan and Bly, 2015). Interestingly, soybean plants in plots treated with SulfurTrap (0-0-60-12S) showed no clear response to the addition of K. Lower NDVI values than the unfertilized check were observed in soybeans applied with this treatment.

As opposed to NDVI1, the NDVI2 values were more statistically similar among treatments (Table 1.6). No difference among treatments may be due to saturation issue of the sensor which is one of the known limitations of NDVI at crop canopy closure (Arnall et al., 2016). Lower NDVI values at Lahoma site were most likely because sensing was delayed (due to unfavorable weather condition) and leaves of the crop were starting to become chlorotic. Similar results were observed by Abit et al. (2016) when sensing was delayed in canola.

Canopy cover measurements using Canopeo

Canopeo analyzes plant images to determine fractional green canopy cover (Patrigini and Oschner, 2015). This information is a valuable indicator of crop development and light interception. Because of this information, Canopeo can be used to assess canopy closure.

Canopy closure measurements were taken at R1 (Canopeo1) and R5 (Canopeo2) growth stages. The results were similar to NDVI measurements. There was a significant difference among treatments in Canopeo 1 at Perkins and Stillwater 2015. No statistical differences were found at Stillwater 2016 and Lahoma (Table 1.8). As NDVI readings, Canopeo presented correlation with stand count results (Table 1.9). The check and solid fertilizers in broadcast application resulted in the highest canopy closure measurements at the locations with significant response on treatments.

Correlation coefficient analysis indicated that Canopeo values were well correlated with NDVI readings in all site-years (Table 1.10), suggesting that the observed Canopeo values, regardless of growth stage, could be used to determine NDVI parameters (Appendix 1.3). This analysis is a result of an initial study to look at the relationship of Canopeo and GreenSeeker values. Further research, however, is necessary to extract strong conclusions about the correlation of each method.

Grain Yield

Soybean grains yield ranged from 1148 to 1702, 1978 to 2587, and 780 to 1459 kg ha^{-1} at Stillwater 2015, Stillwater 2016 and Lahoma sites, respectively. There were no significant differences among treatments on yield at all locations despite the fact that soil test analysis from these sites recommended application of P and K. Based on Snyder (2000) and the soil test results, relative yield in Stillwater 2015, Stillwater 2016 and Lahoma 2016 were 90, 74 and 75%, respectively. Therefore, it would be expected that the addition of P and K containing fertilizers would increase yield in the locations with soil test values below optimum, Stillwater 2016 and Lahoma 2016. The lack of significant effect between treatments in yield may been caused by the environmental conditions, such as low rainfall and high temperature experienced during the vegetative and early reproductive stages. A tool called Irrigation Planner, developed by Mesonet, was used to obtain the evapotranspiration and rainfall per location and calculate the water balance during the crop cycle, in order to understand the effect of water deficit on soybean production. The results are shown on Figure 1.3. According to the graphs, plants in Lahoma were exposed to water deficit from R2 to harvest time and Stillwater 2015, from R3 to harvest time. Stillwater 2016 was exposed to water stress even under irrigation due to mechanical problems in the linear pivot during the season. However, plants at Stillwater 2016 were exposed to a less severe water stress (-93.7 mm), from R5 to harvest time. Germination and reproductive stages are the most susceptible stages for yield losses caused by water stress (Lenssen, 2012). According to the results, yield average may be correlated to length and severity of water stress in reproductive stages, since water is likely to be the most limiting factor for soybean production in Oklahoma.

Oil and Protein Content

Soybeans are primarily grown for its oil and protein content. Thus, oil and protein are important parameters when assessing soybean quality as this significant information will determine value or end use preference. Seeds in Lahoma site presented more oil content (19.5 to 20.9%) on average compared to Stillwater (2015 and 2016) sites (16.3 to 17.3% and 17.1 to 19.2%, respectively). In turn, protein content was higher on average at Stillwater 2015 and 2016 sites (36.0-36.6% and 33.0 – 34.3%, respectively) than at Lahoma site (31.1 – 33.3%). Protein content notably increased with a concomitant decrease in oil. These results are in agreement with the study of Bennett (2015, unpublished) on soybean seed components. Differences in oil and protein content seen among sites are likely attributed to varietal differences and geographic/environmental factors (Table 3).

No differences in seed protein or oil contents (Table 10) were noted among treatments. Oil and protein content of all treatments were within the typical commodity-range of 16 to 20% and 30 to 40%, respectively (USSEC, 2016).

CONCLUSION

Results from this study showed that soybean stand count were negatively affected by in-furrow placement of starter fertilizers. In the plots with reduced stands, soybean plants were able to compensate from stand count losses through additional branching. This would indicate that the initial negative impact of in-furrow starter fertilizers could be overcome during the growing season. GreenSeeker and Canopeo values presented significant and high correlation; however, further studies should be conducted to establish a solid relation between the two methods. Regardless of site-years, oil and protein contents were similar among treatments, thus application of starter fertilizer did not affect the seed quality soybean. Based upon preplant soil test results a yield response to added phosphorus was expected at all locations. However, the lack of response indicated that in this study nutrients were not the most liming yield factor. Drought and heat stress during the reproductive stages is not uncommon the central Great Plains under rainfed production system. The results of this study indicate that the use of starter fertilizers was not beneficial in rainfed soybean production in Oklahoma. Further work is needed to identify the impact of irrigation on the response to starter fertilizers.

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TABLES

Table 1.1 Results of pH, buffer index, and nitrogen, phosphorus, potassium, sulfur, calcium, magnesium, iron, zinc, boron, and copper concentrations t 0-15 cm at Stillwater and Perkins, 2015 and at Stillwater, Lahoma and Lamont, 2016

Location	Year	pH	Buffer Index	N	P	K	S	Ca	Mg	Fe	Zn	B	Cu
				----------	----------	----------	----------	ppm	----------	----------	----------	----------	----------
Stillwater	2015	5.9	7.1	19	22	109	2	851	218	25.1	0.98	0.17	1.08
	2016	6.0	7.3	6	13	95	0.7	760	204	18.2	0.40	0.10	0.90
Perkins	2015	4.9	6.6	2	24	163	2.8	443	127	45.3	0.52	0.19	2.21
Lahoma	2016	6.2		111	10	134	4.3	1214	581	8.1	0.3	0.2	0.3
Lamont	2016	5.3	6.9	12	24	157	1.7	726	177	41	0.8	0.1	0.7

Table 1.2 Year, locations, planting date, seed varieties and seeding rate used for this study.

Year	Location	Planting Date	Variety	Population (seed ha^{-1})
2015	Stillwater	5-May	Pioneer P49T24SR	325,000
2015	Perkins	12-May	Pioneer P49T24SR	325,000
2016	Lahoma	5-May	Pioneer P39T67R	325,000
2016	Stillwater	6-May	Channel 4806R2	325,000
2016	Lamont	11-May	Channel 4806R2	325,000

Table 1.3 Treatment structure to evaluate the impact of broadcast and starter fertilizer treatments on soybean production evaluated over 5 site years from 2015-2016. Treatments 14 and 15 not evaluated in 2015. Treatments 10, 11, 12 broadcast preplant while all over treatments applied in-furrow

Treatment	Name	Source†	Rate ($L\ ha^{-1}$)	Additive	Rate ($L\ ha^{-1}$)	N	P	K	S	Mg	Mn	Fe	Zn
						---- $kg\ ha^{-1}$ ----							
1		Check											
2	APP	10 - 14.8 - 0	23			3.3	4.9						
3	APP	10 - 14.8 - 0	23	H_2O	23	3.3	4.9						
4	APP	10 - 14.8 - 0	23	Accomplish	2.3	3.3	4.9						
5	APP	10 - 14.8 - 0	23	MicroBolt Zn	2.3	3.3	4.9						0.27
6	9-18-9	9 - 7.8 - 7.5	23	H_2O	2.3	2.8	2.4	2.3					
7	9-18-9	9 - 7.8 - 7.5	23	H_2O / Soygrow	23 / 2.3	2.8	2.4	2.3		0.014	0.074	0.011	0.044
8	K-Leaf	0 - 0 - 24.9	23	H_2O	23			7.8					
9	Pro-Germinator	9 - 10.5 - 2.5 - 0.1Fe	23			2.8	3.3	0.75				0.001	
10	DAP	18 - 20 - 0	112‡			20.2	22.5						
11	Potash	0 - 0 - 49.8	112‡					55.9					
12	MESZ	12 - 20 - 0 - 6.7 S - 1Zn	129‡			15.5	22.5		8.64				1.3
13	SulfurTrap	0 - 0 - 49.8 - 12S	14	H_2O	33			8.4	2				
14	Rhyzo-Link	3 - 4.4 - 10.8 - 1S - 0.1Zn	14	H_2O	33	0.5	0.78	1.9	0.18				0.018
15	Triple Option	4-5.7-14.1-1S	14	H_2O	33	0.8	1.1	2.7	0.18				

† Sources represented by the concentration (%) of nitrogen, phosphorus and potassium in the formulation. The concentration (%) of other nutrients are shown according to its symbol at periodic table of elements.

‡ Dry fertilizers broadcast applied. Rate in kilogram per hectare.

Table 1.4 Soil temperature at planting collected at five cm depth at Perkins, Lake Carl Blackwell, Lahoma, and Lamont sites in 2015 and 2016.

Year	Location	Planting Date	Soil Temperature (^oC)
2015	Stillwater	5-May	20
2015	Perkins	12-May	18
2016	Lahoma	5-May	17
2016	Stillwater	6-May	21
2016	Lamont	11-May	24

Table 1.5 Soybean stand count (x1000 plants ha-1) as affected by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015, and at Stillwater, Lahoma, and Lamont in 2016. Treatments 10, 11, and 12 were dry products applied broadcast while all over treatments were liquid fertilizers applied in-furrow.

Treatment	Source	Stillwater 2015	Perkins 2015	Stillwater 2016	Lahoma 2016	Lamont 2016
		------------------ x1,000 plants ha^{-1} ------------------				
1	Check	133	266[ab†]	327	277	320[a]
2	APP	83	248[abc]	342	240	258[bcde]
3	APP + H_2O	111	183[cd]	319	296	275[abcd]
4	APP + Accomplish	79	212[bcd]	309	307	199[e]
5	APP + Zn	97	147[d]	298	237	253[bcde]
6	9-18-9	100	162[d]	352	274	215[de]
7	9-18-9 + Soygrow	93	151[d]	319	291	283[abc]
8	K-Leaf	129	201[bcd]	323	261	240[cde]
9	Pro-Germinator	122	194[bcd]	341	250	245[bcde]
10	DAP	126	291[a]	312	266	291[abc]
11	Potash	93	255[abc]	327	320	301[ab]
12	MESZ	136	240[abc]	334	240	277[abc]
13	SulfurTrap	104	237[abc]	337	258	288[abc]
14	Rhyzo-Link	-	-	327	258	293[abc]
15	Triple Option	-	-	395	288	248[bcde]
		NS[*]	P = 0.0052	NS	NS	P = 0.0144

[†] Within columns, means followed by the same letter are not significantly different according to LSD (0.05).
[*] NS, nonsignificant.

Table 1.6 Normalized difference vegetation index (NDVI) measurements at growth stages: R1 (NDVI1) and R5 (NDVI2) as influenced by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015, and Stillwater and Lahoma in 2016.

Treatment	Source	Stillwater 2015		Perkins 2015	Stillwater 2016	Lahoma 2016	
		NDVI1	NDVI2	NDVI1	NDVI2	NDVI1	NDVI2
1	Check	0.77[a†]	0.86	0.83[a]	0.90	0.71	0.56
2	APP	0.66[de]	0.83	0.81[abc]	0.90	0.71	0.55
3	APP + H_2O	0.68[bcde]	0.83	0.78[bcde]	0.90	0.73	0.61
4	APP + Accomplish	0.70[bcde]	0.84	0.75[e]	0.91	0.74	0.57
5	APP + Zn	0.73[abcd]	0.83	0.7[f]	0.90	0.70	0.54
6	9-18-9	0.68[bcde]	0.86	0.77[cde]	0.90	0.69	0.55
7	9-18-9 + Soygrow	0.64[e]	0.81	0.76[e]	0.90	0.67	0.51
8	K-Leaf	0.72[abcd]	0.84	0.78[cde]	0.91	0.70	0.59
9	Pro-Germinator	0.72[abcd]	0.86	0.76[e]	0.90	0.77	0.61
10	DAP	0.72[abcd]	0.84	0.82[ab]	0.91	0.71	0.54
11	Potash	0.75[ab]	0.87	0.8[abcd]	0.90	0.73	0.56
12	MESZ	0.73[abc]	0.86	0.80[abc]	0.91	0.73	0.55
13	SulfurTrap	0.66[cde]	0.83	0.76[de]	0.90	0.67	0.57
14	Rhyzo-Link	-	-	-	0.89	0.71	0.54
15	Triple Option	-	-	-	0.91	0.73	0.59
		P = 0.022	NS[*]	P= 0.012	NS	NS	NS

[†] Within columns, means followed by the same letter are not significantly different according to LSD (0.05).
[*] NS, nonsignificant.

Table 1.7 Correlation coefficient analysis between stand count and GreenSeeker measurements at beginning of bloom (R1) as influenced by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015, and Lahoma in 2016.

Stillwater 2015	Perkins 2015	Lahoma 2016
$p<0.0001$	$p<0.0001$	$p=0.1649$
$R^2=0.77$	$R^2=0.64$	

Table 1.8 Fraction green canopy cover measurements at growth stages: R1 (Canopeo1) and R5 (Canopeo2) as influenced by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015 and Stillwater and Lahoma in 2016

Treatment	Source	Stillwater 2015		Perkins 2015	Stillwater 2016	Lahoma 2016	
		Canopeo1	Canopeo2	Canopeo1	Canopeo2	Canopeo1	Canopeo2
1	Check	$0.455^{abc\dagger}$	0.814	0.411^{ab}	0.855	0.351	0.395
2	APP	0.365^{cde}	0.786	0.377^{abcd}	0.842	0.422	0.402
3	APP + H_2O	0.481^{abc}	0.845	0.328^{de}	0.823	0.366	0.444
4	APP + Accomplish	0.419^{abcde}	0.801	0.341^{de}	0.817	0.372	0.412
5	APP + Zn	0.436^{abcd}	0.755	0.267^{fg}	0.836	0.397	0.373
6	9-18-9	0.378^{bcde}	0.827	0.348^{cd}	0.845	0.391	0.387
7	9-18-9 + Soygrow	0.316^{e}	0.814	0.289^{efg}	0.833	0.364	0.369
8	K-Leaf	0.422^{abcde}	0.811	0.324^{def}	0.881	0.366	0.408
9	Pro-Germinator	0.433^{abcde}	0.822	0.345^{cde}	0.839	0.399	0.438
10	DAP	0.468^{abc}	0.791	0.418^{a}	0.852	0.408	0.380
11	Potash	0.496^{ab}	0.839	0.357^{bcd}	0.858	0.393	0.448
12	MESZ	0.519^{a}	0.856	0.4^{abc}	0.857	0.388	0.430
13	SulfurTrap	0.330^{de}	0.798	0.263^{g}	0.848	0.336	0.421
14	Rhyzo-Link	-	-	-	0.845	0.384	0.395
15	Triple Option	-	-	-	0.867	0.365	0.432
		P= 0.023	NS*	P= 0.025	NS	NS	NS

† Within columns, means followed by the same letter are not significantly different according to LSD (0.05).
* NS, nonsignificant.

Table 1.9 Correlation coefficient analysis between stand count and Canopeo measurements at beginning of bloom (R1) as influenced by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015, and Lahoma in 2016.

Stillwater 2015	Perkins 2015	Lahoma 2016
$p<0.0001$	$p<0.0001$	$p=0.1071$
$R^2=0.69$	$R^2=0.59$	

Table 1.10 Correlation coefficient analysis between GreenSeeker and Canopeo measurements at beginning of bloom (R1) and full seed (R5) as influenced by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015, and Stillwater and Lahoma in 2016.

Stillwater 2015		Perkins 2015	Stillwater 2016	Lahoma 2016	
R1	R5	R1	R5	R1	R5
$p<0.0001$ $R^2=0.82$	$p<0.0001$ $R^2=0.67$	$p<0.0001$ $R^2=0.69$	$p<0.0001$ $R^2=0.69$	$p<0.0001$ $R^2=0.81$	$p<0.0001$ $R^2=0.95$

Table 1.11 Soybean grain yield as influenced by broadcast and starter fertilizer treatments at Stillwater 2015, Stillwater 2016 and Lahoma in 2016.

Treatment	Source	Stillwater 2015	Stillwater 2016	Lahoma 2016
		---------------------	kg ha^{-1} ---------------------	
1	Check	1688	2088	979
2	APP	1310	2165	866
3	APP + H_2O	1265	2520	1026
4	APP + Accomplish	1243	1978	1067
5	APP + Zn	1260	2465	1459
6	9-18-9	1411	2221	1374
7	9-18-9 + Soygrow	1477	2136	912
8	K-Leaf	1148	2318	1071
9	Pro-Germinator	1316	2371	1269
10	DAP	1415	1935	780
11	Potash	1599	2417	1079
12	MESZ	1702	2142	1071
13	SulfurTrap	1339	2926	840
14	Rhyzo-Link	-	2473	1092
15	Triple Option	-	2587	1053
		NS*	NS	NS
Yield on Average		*1398*	*2316*	*1062*

* NS, nonsignificant.

Table 1.12 Protein and oil content in the seeds in soybean as influenced by broadcast and starter fertilizer treatments at Stillwater 2015, Stillwater 2016, and Lahoma 2016.

Treatments	Source	Stillwater 2015		Stillwater 2016		Lahoma 2016	
		Protein	Oil	Protein	Oil	Protein	Oil
		-------------------------- % --------------------------					
1	Check	36.5	16.9	33.5	17.5	31.3	20.5
2	APP	36.0	17.0	33.5	17.4	32.6	19.5
3	APP + H_2O	36.3	16.8	33.7	18.6	32.5	20.5
4	APP + Accomplish	36.3	16.7	34.0	17.8	32.6	20.0
5	APP + Zn	36.2	16.6	34.1	17.9	32.6	20.1
6	9-18-9	36.0	17.0	34.2	17.9	32.0	20.6
7	9-18-9 + Soygrow	36.4	17.3	33.8	17.7	31.1	20.9
8	K-Leaf	36.0	16.5	34.0	17.8	32.3	20.3
9	Pro-Germinator	36.6	16.3	34.1	17.9	32.6	20.3
10	DAP	36.3	16.8	33.4	17.1	32.4	19.9
11	Potash	36.3	17.0	33.0	18.6	32.5	20.6
12	MESZ	36.8	17.0	33.8	17.7	31.6	20.4
13	SulfurTrap	36.1	16.7	33.5	19.2	32.0	20.5
14	Rhyzo-Link	-	-	33.5	17.8	32.4	19.9
15	Triple Option	-	-	34.3	18.1	33.3	20.3
		NS*	NS	NS	NS	NS	NS

* NS, nonsignificant.

Figure 1.1 John Deere MaxEmerge two rows planter with a CO_2 system. Schaffert Seed Rebounder™ Seed Firmer was used for in-furrow liquid fertilizer applications.

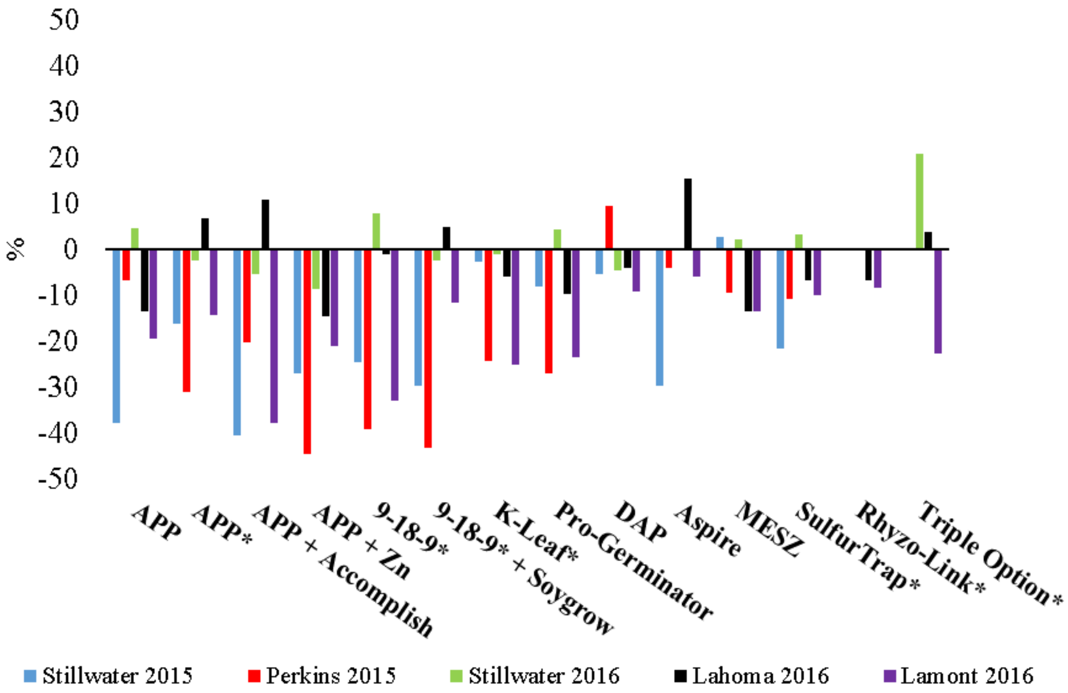


Figure 1.2 Relative stand count (%) of treatments compared to the check at Stillwater and Perkins in 2015, and at Stillwater, Lahoma, and Lamont in 2016.

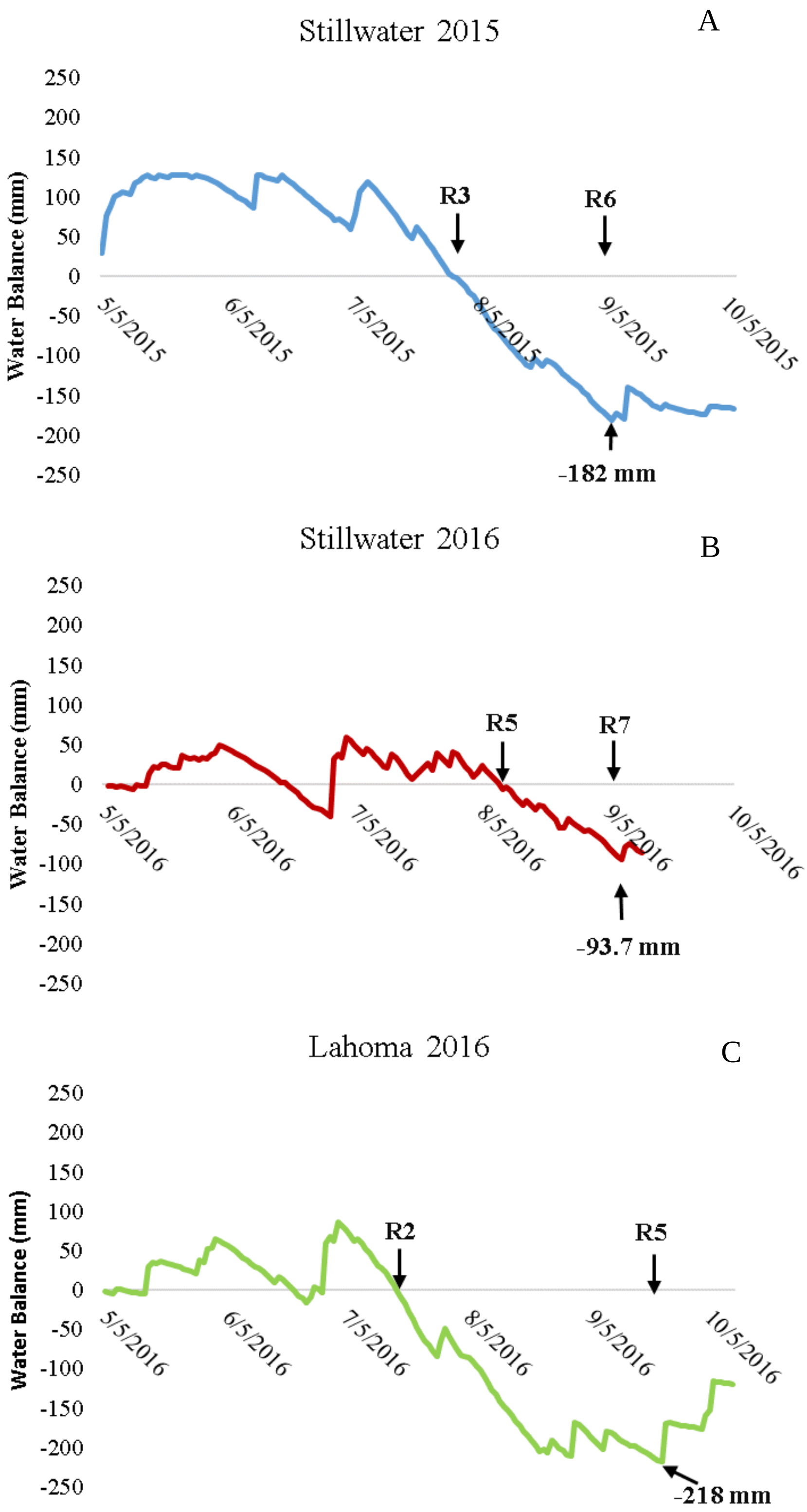
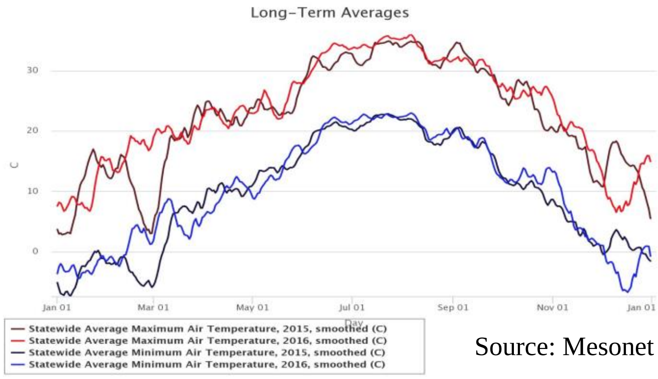


Figure 1.3 Water balance (mm) at Stillwater 2015(A), Stillwater 2016 (B), and Lahoma 2016 (C) as influenced by broadcast and starter fertilizer treatments. First arrow indicates the crop stage at which water deficit first occurred at reproductive stage. Second arrow indicates maximum water deficit (mm).

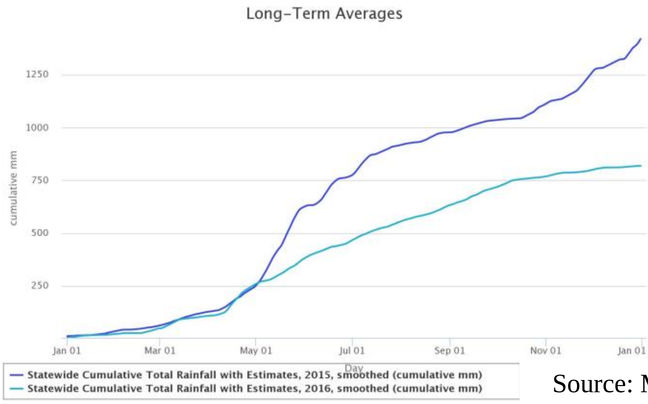
APPENDICES

Appendix 1.1 Average of maximum and minimum temperatures in Oklahoma in 2015 and 2016.



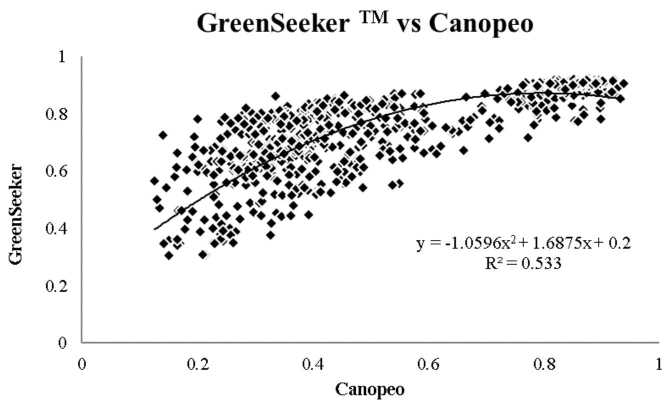
Source: Mesonet

Appendix 1.2 Cumulative total rainfall in Oklahoma in 2015 and 2016.



Source: Mesonet

Appendix 1.3 Correlation between NDVI (GreenSeeker) and Canopy Cover % (Canopeo) measurements at beginning of bloom (R1) and full seed (R5) as influenced by broadcast and starter fertilizer treatments at Stillwater and Perkins in 2015, and Stillwater and Lahoma in 2016



CHAPTER II

EFFECT OF THE USE OF A NOVEL BYPRODUCT FROM THE DESULFURIZATION OF HYDROCARBON STREAMS IN AGRICULTURAL SOILS

ABSTRACT

Liquid SulfurTrap (LST) may be a potential source of potassium and sulfur for agricultural purposes or to reduce soil acidity. However, it must be tested in order to confirm its characteristics, as well as, its effect in soil and plants. A greenhouse study was established with 32 columns filled with two soils and four rates of LST (0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}). Water was applied weekly and the leachate was collected. After the series of leaching events, soil was separated by depth in order to analyze movement of the nutrient through the profile. Our results showed that, in a sandy loam soil with high pH, LST significantly increased potassium concentration in the soil, as well as, increased leaching of potassium, calcium and magnesium at 15.2 x1,000 L ha^{-1}. LST can increase pH of an alkaline soil at 7.6 and 15.2 x1,000 L ha^{-1}. Based on the results, 7.6 x 1,000 L $ha^{-1}$is the highest rate indicated in use in agricultural soils. Further studies should be done in order to analyze the effect of LST in other soil types, the effect of sulfur oxidation when Liquid SulfurTrap is applied in an established crop, as well as, the effect of very high potassium concentration as regard to magnesium uptake by the plants.

INTRODUCTION

LST is a hydrogen sulfide (H_2S) scavenger used to remove H_2S from several hydrocarbon streams (e.g. natural gas) because of the detrimental effects of sulfur (S) for health. Initial evaluation of LST documented that the product has a density of 1.2 g ml^{-1}, initial pH 14, high concentration of potassium (K) and sulfur (60 and 12%, respectively), as well as, an effective calcium carbonate equivalent (ECCE) of 25%. As an experimental product, LST must be analyzed for its effect in the soil and plants. For example, in order to supply the equivalent of LST to 1 metric ton of $CaCO_3$ per hectare 5,900 kg of potassium and 1,200 kg of sulfur are loaded into the soil, increasing the probability of leaching of ions, as K can replace cation in the exchangeable sites and sulfur compounds can decrease pH and increase the concentration of several cations in the soil solution. Clay type, solution pH, and relative concentration of cation in the soil solution may affect the adsorption of one nutrient over another (Brady and Weil, 1996). In acid soils, hydrogen (H^+) and aluminum (Al^{+3}) remove cation from the exchangeable sites due to their high strength of adsorption. When an acid soil is neutralized, H^+ and Al^{+3} concentration decreases, increasing calcium and magnesium concentration in the exchangeable sites. Monovalent cations, such as potassium, can also replace exchangeable cation by mass action, since it is in sufficient concentration in soil solution (Havlin et al., 2016). Thus, the objective of this study was to analyze the capacity of LST to provide K and S for agricultural purposes, as well as, the effect of the application of high LST rates on soil pH, EC, as well as, on N, P, K, S, Ca, Mg, Na, Fe, Zn, B, Cu concentrations in the soil.

REVIEW OF LITERATURE

Ion Exchange

Soil is defined as "…a natural body comprised of solids (mineral and organic matter), liquid, and gases that occurs on the land surface…" (Soil Survey Staff, 2014). Formed by weathering of rocks and minerals, soil provides support, water, and nutrients for plant growth. The characteristics of each soil are unique and based on parent material, climate, biota, topography and time (Miller and Gardiner, 2001). The physical and chemical weathering of parent material results in the inorganic constituents of soil, which basically consists in sand, silt, and clay particles (Havlin et al., 2016). These minerals vary in size and proportion in the soil. Sand, silt, and clay diameters range from 2 to 0.05 mm, 0.05 to 0.002 mm, and <0.002 mm, respectively (Brady and Weil. 1996). Clay particles play an important role on plant nutrition due to high surface to mass ratio. With organic matter, clay particles act directly on the soil capacity to retain and exchange nutrients, since they exhibit positive and negative charges in their surface area that attract nutrients and water, which are taken up by plants (Brady and Weil, 1996). The soil capacity of hold and exchange cation and anions is referred to as cation exchange capacity (CEC) and anion exchange capacity (AEC), respectively. CEC is commonly predominant in most soils due to a higher concentration of negative charges on soil particles in (Havlin et al., 2016). There are several methods to quantify the CEC in the soil, such as direct displacement of the saturating salt and radioactive tracer method (Bache, 1976). However, the most common method used is the summation of exchangeable cation. This method is based on the sum of exchangeable calcium, magnesium, potassium, and an estimate of exchangeable acidity obtained from the buffer pH (Mengel, 1914). In turn, Bache (1976) states that sodium should also be account for this method.

Some cations and soil characteristics affect the relative proportion of cation adsorbed by exchangeable sites. Each cation has a specific valence and radius; therefore, the strength of adsorption is proportional to valence to hydrated radius ratio. The order of strength of cation adsorption (in equivalent quantities) is described by lyotropic series, represented by:

$Al^{3+} \geq H^{+} > Ca^{2+} \geq Mg^{2+} > K^{+}$ = ammonium (NH_4^{+}) > Na^{+} (Arnall, 2016 a)

However, clay type, solution pH, and relative concentration of cation in the soil solution may affect the adsorption of one nutrient over another (Brady and Weil, 1996; Havlin et al., 2016). For example, H^{+} and Al^{3+} are highly concentrated in the soil solution of acid soils, removing cation from the exchangeable sites. In turn, when an acid soil is neutralized, calcium and magnesium dominate the exchangeable sites and concentration of H^{+} and Al^{+3} decreases. The replacement of exchangeable cation may occur by mass action of monovalent cations, since in sufficient concentration in soil solution (Havlin et al., 2016).

Potassium

Potassium is a macronutrient essential for plant life cycle (Kaiser et al. 2016). Unlike other essential nutrients, K is not incorporated into biochemical compounds in the plant, being associated to enzyme activation, photosynthesis, transport of sugar (Armstrong, 1998), as well as, water and nutrient transport and stomatal activity, which is correlated to the mobility of K in the plant (Havlin et al., 2016). Plants uptake K as K^{+} by mass flow (10%) and diffusion (90%) (Arnall, 2016 b).

Immobile in most soils, mineral K represents up to 98% of total K, which is not available for plant uptake, since it is in a crystalline-insoluble form (Kaiser et al., 2016).

The small portion of available K is concentrated in the clay or in the soil solution. It is divided in nonexchangeable (fixed in the clay), exchangeable and soil solution. Potassium in soil solution and exchangeable sites are readily available for plant uptake, while fixed K is slowly available (Brady and Weil, 1996). According McLean and Watson (1985), soil solution represents only 5% of total crop demand at a time, or 0.1- 0.2% of the total soil K. Soil solution is in equilibrium with exchangeable K (1-2% of the total soil K) and fixed K (1-10% of the total soil K). When K is removed from the solution, K is rapidly replenished by exchangeable sites, which is slowly replenished by the K fixed in the clays. In turn, K replenishment from the mineral K to nonexchangeable K or soil solution pools during the process of weathering is very slow (Bar Tal, 2011). This processes may, or may not, supply the total K needed for plant growth, based on sufficiency levels of potassium required by each crop (Brady and Weil, 1996). However, other factors can affect the K availability, such as clay type, CEC, and environment condition (Havlin et al., 2016). Neutral or alkaline soil increases the K fixation in soil and decrease K levels in soil solution (Varbanova and Bache, 1975; Brady and Weil, 1996).

The interaction among K and other nutrients can also affect nutrients availability. Interaction among K and Mg is well documented (Kabu and Toop, 1970; Kresge et al., 1988; Brady and Weil, 1996; Armstrong, 1998; Kaiser et al., 2016). Armstrong (1988) states that high K concentration can reduce Mg concentrations, particularly when Mg is low in the soil. Kabu and Toop (1970) stated that tomato decreased Mg uptake even growing in a substrate with high concentration of magnesium due to high concentration of K in the substrate. In turn, high concentration of Mg and Ca in soil solution may reduce K uptake due to competition among them for uptake by roots (Brady and Weil, 1996).

Sulfur

Sulfur is an essential macronutrient secondary, such as calcium and magnesium. Sulfur is constituent of amino acids essentials for protein, vitamins and enzymes related to photosynthesis and nitrogen (N) fixation (Brady and Weil, 1996). The amount of S removed is directly related to crop-to-crop (Stevenson and Cole, 1999). For example, grains, such as corn and wheat, remove 9-13 kg ha^{-1}, while vegetable, such onion and cabbage, remove 20-43 kg ha^{-1}(Tabatabai, 1986). Plants uptake S as SO_4^{2-} by mass flow and diffusion (Oliveira et al. 2010). Unlike the other macronutrients, the importance of sulfur was neglected for decades due to the indirect addition of S by fertilizer and pesticides that contain S in the composition, as well as, by atmospheric deposition caused by industry pollution, releasing SO_2 to atmosphere through burning of fossil fuels (Miller and Gardiner, 2001). However, many crops have been exhibited S deficiency due to the use of high analyzes fertilizers, use of an effective emission-control system by industry, and increase of potential yield (Stevenson and Cole, 1999).

Sulfur is naturally found in the organic matter, soil minerals and gases in the atmosphere (Brady and Weil, 1996). Organic matter represents 90-98% of total S in the soil. The mineralization of organic matter by microorganisms release mainly SO_4^{2-}, which can be uptake by plant, immobilized by microorganisms, reduced to sulfides and elemental S, or lost by leaching because it is negatively charged and not be held tightly by clay particles (Brady and Weil, 1996). In humid region with weathered soils and $pH < 6$, SO_4^{2-} may be also adsorbed by Fe and Al oxides (Havlin et al, 2016).

The oxidation process of sulfur is important for agricultural land, because it increases soil acidity. The oxidation is a biochemical process executed by autotrophic bacteria, mainly by genus *Thiobacillus*, which oxides sulfur compounds and releases sulfate and H^+ in the soil solution (Brady and Weil, 1996). Environmental condition plays an important role in the process. Favorable conditions for a readily oxidation are soil temperature from 27 to 40ºC and soil moisture near to field capacity. Oxidation may occur over a wide soil pH range, however, oxidation increases as pH increase (Stevenson and Cole, 1999). The oxidation of the mineral pyrite (FeS_2) may result in pH as low as 3.5, due to release of sulfuric acid to soil solution (Stevenson and Cole, 1999). That low pH increases Al and Fe toxicity and decreases nutrients availability, making crop production not feasible.

Liquid SulfurTrap

Liquid SulfurTrap is a hydrogen sulfide (H_2S) scavenger used to remove H_2S from several hydrocarbon streams, such as natural gas and natural gas liquid (US Patent No. 9023237, 2014). LST is composed of iron (II) oxides and/or hydroxides, which is formed from the reaction of ferrous carbonate (synthetized or naturally find in siderite) suspended in an alkaline solution of potassium hydroxide (KOH) at 40-50ºC. The solution has a KOH to iron molar ratio of 4:1 to 6:1 (US Patent No. 9023237, 2014). LST is loaded into vessels and reacts with sulfur compounds present in the hydrocarbon streams. According to Chemical Products (2014), LST has a capacity to remove H_2S at levels greater than 35% by weight. The desulfurization is necessary as sulfur compounds can be extremely harmful for health, corrosive for the oil pipelines, and an air pollutant. The reaction results in a stable and non-hazardous byproduct, which is proposed to be disposed in landfills and injection wells, if cannot be used in agriculture or safely land applied. Due to the experimental nature of this byproduct, most of the specific data about the composition of LST is nonpublished. LST has a density of 1.2 g ml^{-1}, initial pH 14, as well as, high concentration of potassium (60%) and sulfur (12%) According studies performed by Rutter (personal communication, January 7, 2016), LST has an effective calcium carbonate equivalent (ECCE) of 25%, which represents the neutralizing power per weight of material relative to pure $CaCO_3$. Therefore, LST may potentially be used as source of potassium and sulfur, as well as, used to increase soil pH. However, as an experimental product, it must be tested regards as to its effect in the soil and plants. The use of LST in order to neutralize soil acidity may add up to 5,900 kg of potassium and 1,200 kg of sulfur, when applied as equivalent of 1 metric ton of $CaCO_3$ per hectare, increasing the probability of leaching of ions.

OBJECTIVE

The objective of this study was to evaluate the impact of LST on soil and leachate pH, as well as, the effect of high volumes of LST on N, P, K, S, Ca, Mg, Na, Fe, Zn, B, Cu, concentrations and soil and leachate EC.

METHODOLOGY

Soil Collection

The study was conducted in 2016 in a temperature controlled greenhouse (32ºC) in Stillwater, OK. The study was composed of four rates of LST applied in two different soils types. Soil type A was collected from the Lake Carl Blackwell Research Farm near Stillwater, OK (36° 9'6.80"N, 97°17'23.79"W), while Soil type B was collected from South Central Experimental Station near Chickasha, OK (35°02'43.4"N 97°54'06.0"W). A composite soil sample of each soil type was collected at the upper 20 cm depth and were submitted to Soil, Water and Forage Analytical Laboratory (SWFAL) and analyzed for soil pH (1:1 water), buffer index using Sikora buffer test, extractible P, K, Ca, and Mg by Mehlich 3, N and S using 0.008M of Calcium Phosphate, and Fe, Zn, Cu, and B using DTPA- Sorbitol (Table 2.1), as well as, for soil organic matter (by combustion) and percentage of sand, silt, and clay using Hydrometer method (Table 2.2). Soil A was a Konawa fine loamy soil, with soil organic matter content of 0.97%, initial soil pH 5.9, and soil bulk density 1.62 g cm^{-3}. The particle size distribution was 50, 33.8, and 16.3% sand, silt, and clay, respectively. Soil B is a Yahola fine sandy loam with soil organic matter content of 1.38%, initial soil of pH 8.1, and soil bulk density of 1.4 g cm^{-3}. The particle size distribution was 62.5, 27, and 10.6% sand, silt, and clay, respectively.

Columns Establishment

Each experimental unit was composed of a polyvinyl chloride column (70 cm in length and 10 cm in diameter) filled with either soil A or soil B. Soil bulk density was used to determine the amount of soil that was needed to fill the column, based on the volume of the columns. The 70-cm length column was divided into six layers. The first layer was 15 cm in length: 10 cm as headspace for water application and 5 cm for the 0-5 cm soil depth. Second to fifth layers were 5 cm in length (each) and represented the 5-10, 10-15, 15-20, 20-25 cm depths. The sixth layer was 35 cm in length and represented the 25 to 60 cm depth of the soil column. The layers were stacked together using a plastic tape. At the bottom of the soil-filled section, a cotton cloth and plastic screen with a 10 cm hose clamp were placed to prevent soil loss. The columns were placed on top of a funnel and leachates were collected using a plastic container.

Liquid SulfurTrap and Water Application

After the column establishment, LST was applied on the soil surface of each column using a single channel manual pipette. The LST-water solution was prepared at a 1:9 ratio due to small rates of LST needed per column. The LST rates were based on the correlation between common agricultural liming rates and the 25% of effective calcium carbonate equivalent of LST. Each column was applied with LST at 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1} which corresponds to 0, 1.12, 2.24 and 4.48 metric tons of calcium carbonate per hectare, respectively (Table 2.3). Each column was added with 1000 ml of water two days after LST application, and five more water applications at 700 ml weekly to saturate the soil and produce leachate. The total amount of water added in each column over the study period was equivalent to 573 mm of precipitation, approximately 60% of the average annual precipitation in Stillwater, OK.

Leachate and Soil Analysis

For the duration of the study, there were six leaching events that occurred (based on the number of times water was added to the column). Each leaching event was monitored daily until no more leachate was collected from the columns. A single leaching event ranges from 1 to 7 days in duration. To account for the potential leachate evaporation during these days, the final leachate volume (last day of collection) was adjusted based on the initial volume of leachate collected (first day with no more leaching). Evaporation of LST or water on the soil surface, however, was not measured. In every leaching event, a 50 ml of leachate per column was collected in a plastic bottle for further analysis. Leachate samples were filtered using a Whatman paper filters #40 and submitted to SWFAL. Samples were analyzed for soil pH using a pH meter, electrical conductivity (EC) using an EC meter, extractible P, K, S, Ca, Mg, B, Fe, Zn, Cu, sodium (Na), and manganese (Mn) by ICP-AES analysis. Concentration of each nutrient was summed per treatment to analyze the effect of the treatments on the total concentration of nutrients in the leachate. The concentrations were converted from ppm to mg L^{-1} based on the total volume of leachate per week.

Two weeks after the last leaching event, all the soils in each layer (0-5, 5-10, 10-15, 15-20, 20-25 cm depths) of the column were separately collected and submitted to SWFAL for analysis except for the 25-60 cm depth. At the 25-60 cm depth, the soil was thoroughly mixed and a subsample was collected for analysis. The samples were analyzed for soil pH, EC, N, P, K, S, Ca, Mg, B, Fe, Zn, Na, and Cu. The concentrations of nutrients were converted to mg cm^{-3} based on the volume of the columns to determine the total nutrient concentration in the soil per treatment.

Experimental Design and Statistical Analysis

A randomized complete block design with factorial structure was used in this study. Factorial structure was formed by two soil types and four rates of Liquid SulfurTrap. There were four replications of each treatment. Soil samples were analyzed with depth as repeated measures. The leachates were analyzed with time (week) as repeated measures.

Statistical analysis software (SAS) version 9.4 (SAS Institute, Cary, NC, 2001) was used to analyze the main effects of LST rate. PROC GLIMMIX (SAS® Institute Inc., 2001) was used to analyze soil pH, electrical conductivity, and nutrients concentration. The LS means adjusted by Tukey-Kramer was used to find specific differences among treatments. Main effects were analyzed using analysis of variances at the α=0.05

RESULTS AND DISCUSSION

Preferential flow and leakage of LST and water in between the layers were observed in columns filled with soil A. This may be attributed to the texture of soil A (loam soil) which may have induced higher water pressure on the walls of the columns. Therefore, results shown below are related to soil B only. Potassium, phosphorus, sodium, calcium, magnesium, and electrical conductivity presented unexpected trend on week six when compared to previous weeks in the leachate, which is believed to be caused by water contamination. In the results and discussion, the check (no LST), the lowest LST rate (3.8 x1000 L ha^1), the medium LST rate (7.6 x1000 L ha^1), and the highest LST rate (15.2 x1000 L ha^1) are referred to LST 0, LST 400, LST 800, and LST 1600, respectively.

SOIL

Potassium

Significant interaction between treatments and depths was found for concentration of K in the soil (Table 2.4). LST 0 did not vary K concentration over layers, which was expected since K is immobile in the soil. LST 400 significantly increased K concentration in the layers 0-5, 5-10, and 10-15 cm compared to the check. LST 800 and LST 1600 significantly increased K concentration in the layers 0-5, 5-10, 10-15, 15-20, and 20-25 cm compared to the check. LST 800 also increased K concentration in the soil in the layers 5-10, 10-15, and 15-20 cm compared to LST 400, while LST 1600 increased K concentration in the layers 5-10, 10-15, 15-20, and 20-25 cm when compared to LST 400 and LST 800 (Figure 2.1). Total mass of K in the soil was 0.088, 0.138, 0.197, and 0.346 mg cm^{-3} for LST 0, 400, 800, and 1600, respectively, with significant effect of treatments on K concentration (Table 2.12). The results showed a linear increased of K in the soil as LST rate increased (Figure 2.2).

Sulfur (as sulfate)

Only depth presented significant effect on SO_4 concentration in the soil (Table 2.5). SO_4 was significantly concentrated at top 5 cm (0-5 cm), decreasing to the minimum concentration in the layers 5-10 and 10-15cm when compared to 25-60 cm (Figure 2.3). The favorable environmental conditions may have oxidized S compounds added from LST, releasing SO_4 to soil solution. The high concentration on top layer, as well as, no differences among treatments are caused by the high mobility of SO_4 in the soil. The SO_4 is concentrated in the soil solution; therefore, the water saturation in the soil results in leaching, pushing S-SO_4 down. In turn, the water evaporation in the soil after the last leaching event carried sulfate, which was not leached, to the top layer.

Other nutrients

Significant interaction between treatments and depths was found for concentration of Ca, Mg, and Na in the soil (Table 2.6). LST 0 and 400 did not vary the concentration of Ca over layers. LST 800 had lower concentration in the layer 5-10 cm compared to 20-25 cm, and LST 1600 had lower Ca concentration in the layers 5-10, 10-15, and 15-20 cm compared to 25-60 cm (Figure 2.4). LST 400, 800 and 1600 did not affect Ca concentration in the soil compared to the check. Total mass of Ca in the soil (2.54, 2.49, 2.39, and 2.46 mg cm^{-3} for LST 0, 400, 800, and 1600, respectively) did not vary among treatments, confirming the lack of effect of treatments on Ca concentration in the soil (Table 2.7). Magnesium was significantly concentrated in the top 5 cm (0-5 cm) in all treatments. LST 400 was not significantly different compared to LST 0. LST 800 had decreased Mg concentration in the layers 5-10 and 10-15 cm compared to LST 0, while LST 1600 had decreased Mg concentration in the layers 5-10, 10-15, 15-20, and 20-25 cm compared to LST 0, as well as, in the layer 5-10 cm when compared to LST 400 (Figure 2.5). Total mass of Mg in the soil was 0.184, 0.179, 0.171, and 0.162 mg cm^{-3} for LST 0, 400, 800, 1600, respectively. LST 1600 decreased by 12% total Mg in the soil compared to LST 0 (Table 2.7). Sodium was concentrated in the top 5 cm (0-5 cm) in all treatments. LST 400 and 800 treatments did not differ to LST 0. LST 1600 had increased Na concentration in the layer 5-10 cm compared to LST 0 and LST 400 (Figure 2.6). Total mass of Na in the soil was 0.045, 0.041, 0.04, and 0.046 mg cm^{-3} for LST 0, 400, 800, 1600, respectively. There was no difference among treatments on total mass of Na in the soil (Table 2.7). Only depth had significant effect on nitrogen, zinc, boron, and copper concentration, being all concentrated in the top layer. No treatments effects were observed for the other nutrients analyzed.

Soil pH and Electrical conductivity (EC)

The check (LST 0) pH did not vary over depth, while the treatments with LST application showed increased pH from the layer 5-10 to 10-15 cm, with the exception of LST 1600, which have increased pH from 5-10 to 20-25 cm. LST 400 had increased pH from 5-10 cm to 15-20 cm, but pH did not vary when compared to LST 0. LST 800 had an increase in pH from 5-10 cm to 10-15 cm compared to LST 0. LST 1600 had an increase in pH in the layers 0-5, 5-10, 10-15, 15-20, 20-25cm compared to LST 0, as well as, had an increase in pH in the layers 5-10, 10-15, 15-20 cm compared to LST 400 (Figure 2.7).

EC is significantly higher at top 5 cm than at 5-10, 10-15, 15-20, 20-25, 25-60cm for all treatments. LST 400 and 800 did not differ when compared to LST 0, while LST 1600 increased the electrical conductivity of the soil compared the LST 0 and 400 (Figure 2.8). The variations of EC by depth, as well as, among treatments are caused by the high concentration of salt in the top layers.

LEACHATE

Potassium Concentration

Significant interaction between treatments and weeks was found for K concentration in the leachate (Table 2.8). LST 0 and LST 400 did not show significant effect in K concentration in all collection timings except in week six. LST 800 had higher amounts of potassium leached on week two and three compared to week one, while LST 1600 generally increased the concentration of K in the leachate after week one (Figure 2.9). Potassium concentration of LST 1600 was significant at $\alpha=0.05$ compared to LST 0, LST 400, and LST 800 on week three.

Total mass of potassium on leachate was 20.8, 20.5, 19.7, and 32.9 mg for LST 0, 400, 800, and 1600, respectively. LST 1600 significantly increased total K concentration in the leachate compared to LST 0, LST 400, and LST 800 (Table 2.11). We hypothesize that soil have reached a saturation point between 800 and 1600 GPA due to the high concentration of potassium applied, start leaching the nutrient at this point. However, the increase of concentration of K leached at 1600 GPA represent only 0.14% of total mass of K applied (8.6g), due to a low mobility of potassium in the soil.

Sulfur

Significant interaction between treatments and weeks was found for concentration of SO_4 in the leachate (Table 2.9). On average, variation over time and among treatments occurred in the weeks 2 and 3, increasing SO_4 concentration in the leachate as increased LST rate and decreasing to initial concentration on week 4. LST 0 did not vary SO_4 concentration over time. LST 400 increased the leaching of SO_4 on week 2 compared to the LST 0. LST 800 increased the leaching of SO_4 on week 2 and 3 compared to the LST 0. LST 1600 increased the leaching of SO_4 on week 2 and 3 compared to the check, as well as, when compared to LST 400. Significant difference was also found on week 2 compared to LST 800 (Figure 2.10). Total mass of SO_4 on leachate was 40, 140, 266, and 396 mg L^{-1} for LST 0, 400, 800, and 1600, respectively, with significant effect of treatments on SO_4 concentration in the leachate (Table 2.11). The results showed a linear increase of SO_4 leaching as LST rate increases (Figure 2.11).

Other Nutrients

Calcium and Magnesium presented similar trend as regard to LST application. Significant interaction between treatments and weeks was found for concentration of Ca and Mg in the leachate (Table 2.10). The variation of concentration among treatments was concentrated in the weeks 2 and 3 (Figure 2.12 and 2.13). Total mass of Ca on leachate was 82, 146, 237, and 324 mg L^{-1} for LST 0, 400, 800, and 1600, respectively. Calcium concentration in the leachate was higher in LST 1600 than LST 0, 400, and 800. LST 400 and 800 did not differ, but both presented more Ca in the leachate than LST 0 (Table 2.11). Total mass of Mg on leachate was 23, 27, 36, and 48 mg L^{-1} for LST 0, 400, 800, and 1600, respectively. Magnesium concentration in the leachate was higher in LST 1600 than LST 0, 400, and 800 (Table 2.11). The results showed a linear increase of both Ca and Mg leaching as LST rate increases (Figure 2.14 and 2.15). We hypothesize that the variations were caused by the high concentration of potassium added to soil, as well as, the decrease of pH on weeks 2 and 3, caused by the oxidation of sulfur to sulfate, moving these base cations from the CEC to soil solution, increasing the likelihood of leaching. Sodium presented a similar trend as Ca and Mg about the variation of leaching over time, but not significant at $\alpha=0.05$, as well as, no differences were find among treatments on total Na concentration (Table 2.11). The other nutrients were analyzed, but there were no evidences of effect of treatments on the leaching of these elements.

pH and Electrical Conductivity (EC)

Treatments had significant effect on week 2, decreasing pH as increased LST rate compared to LST 0 (Figure 2.16). We hypothesize that it is related to increase of sulfur on the leachate, decreasing pH while sulfur is oxidized to sulfate. EC variation was concentrated in the weeks 2 and 3 (Figure 2.17). LST 400 did not differ from LST 0, while LST 800 and LST 1600 presented higher EC than LST 0 in the weeks 2 and 3, and higher EC than LST 400 in the week 3. The variability of EC among treatments over time is related to increase of salts on the leachate in the same period.

CONCLUSION

According to the results at this study conditions, Liquid SulfurTrap (LST) increased K concentration in the soil compared to the check, reaching up to 294% in the highest rate compared to the check. The high initial pH increased the adsorption of K in the exchangeable site; however, soil reached a saturation point between 7.6 and 15.2 x 1,000 L ha^{-1}, increasing K in the soil solution and leaching K at this point. We hypothesize that S concentration in the soil was not affected by treatments, because S compounds from LST were oxidized to SO_4^{2-} from week two to week four, leaching due its high mobility in an alkaline soil with high moisture. The increase of SO_4^{2-} in the leachate in the same period, as well as, the linear increase in total mass of S in the leachate as LST rate increased, confirm the hypothesis. The S oxidation increased the concentration of H^+, which explain the significant decrease of pH from week two to week four among treatment in the leachate. We hypothesize that the same trend of pH occurred in the soil over time. It may have affected the behavior of Ca and Mg. The highest LST rate increased the concentration of Ca and Mg in the leachate the same period that pH decreased. Mg presented the same results in the soil, while Ca concentration in the soil was not affected by treatment due to the high Ca concentration in the soil. LST increases pH even with an initial pH of 8.1. Our results showed that LST can increase the leaching of base cation and should not be applied at rate over 7.6 x 1,000 L ha^{-1}. Unfortunately, Soil A which had a lower initial pH was lost and a better understanding of LST impact on soil pH could not be better tested. Further studies should be done in order to analyze the effect of S oxidation when Liquid SulfurTrap is applied in an established crop or pasture, as well as, the effect of very high K concentration as regard to Mg uptake by the plants.

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TABLES

Table 2.1 Soil pH, buffer index, and nutrient concentrations at soil collected from Lake Carl Blackwell and Chickasha, OK, 2016.

Location	pH	BI	P	K	SO_4	Ca	Mg	Fe	Zn	B	Cu
			ppm								
LCB	5.9	7.1	12.5	151	9	751	232	14	3.8	0.144	0.465
Chickasha	8.1		22	109	4	2911	189	5.2	0.30	0.189	0.245

Table 2.2 Soil texture, particle size distribution, and organic matter content at soil collected from Lake Carl Blackwell and Chickasha, OK, 2016.

Location	Texture	Sand	Silt	Clay	OM
		%			
LCB	Loam	50	33.8	16.3	0.97
Chickasha	Sandy Loam	62.5	26.9	10.6	1.31

Table 2.3 Treatment structure to evaluate the impact of Liquid SulfurTrap rates in the nutrients, pH, and electrical conductivity of the soil. Rates were based on calcium carbonate equivalent of 25% of LST.

Treatment	**Soil**	**Liquid SulfurTrap**	**Equivalent $CaCO_3$**
		(x1000) L ha^{-1}	t ha^{-1}
1	LCB	0	0
2	LCB	3.8	1.12
3	LCB	7.6	2.24
4	LCB	15.2	4.48
5	Chickasha	0	0
6	Chickasha	3.8	1.12
7	Chickasha	7.6	2.24
8	Chickasha	15.2	4.48

Table 2.4 Type III tests of fixed effects for potassium concentration in the soil.

	K	
Effect	*F value*	*Pr > F*
Treatment	409.26	<.0001
Depth	88.31	<.0001
Treatment*Depth	18.98	<.0001

Table 2.5 Type III tests of fixed effects for sulfate concentration in the soil.

	SO_4	
Effect	*F value*	*Pr > F*
Treatment	1.04	0.3806
Depth	57.96	<.0001
Treatment*Depth	0.45	0.9534

Table 2.6 Type III tests of fixed effects for calcium, magnesium and sodium concentration in the soil.

	Ca		Mg		Na	
Effect	*F value*	*Pr > F*	*F value*	*Pr > F*	*F value*	*Pr > F*
Treatment	0.58	0.6289	14.26	<.0001	11.86	<.0001
Depth	7.31	<.0001	221.07	<.0001	84.19	<.0001
Treatment*Depth	1.86	0.0468	5.15	<.0001	3.09	0.001

Table 2.7 Total mass (mg cm-3) of potassium, sulfate, calcium, magnesium, and sodium in the soil (0-60cm deep) by treatment.

Treatment	K	S-SO_4	Ca	Mg	Na
	mg cm^{-3}				
LST 0	0.088[d]*	0.004[a]	2.54[a]	0.184[a]	0.045[a]
LST400	0.138[c]	0.004[a]	2.49[a]	0.179[ab]	0.041[a]
LST 800	0.197[b]	0.004[a]	2.39[a]	0.171[ab]	0.040[a]
LST 1600	0.346[a]	0.005[a]	2.46[a]	0.162[b]	0.046[a]

*The same letter within the same column are not significant at *P* = 0.05

Table 2.8 Type III tests of fixed effects for potassium concentration in the leachate. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

	K	
Effect	*F value*	*Pr > F*
Treatment	8.98	<.0001
Time	56.42	<.0001
Treatment*Time	2.66	0.0038

Table 2.9 Type III tests of fixed effects for sulfate concentration in the leachate. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

	SO_4	
Effect	F value	Pr > F
Treatment	261.45	<.0001
Time	31.98	<.0001
Treatment*Time	6.26	<.0001

Table 2.10 Type III tests of fixed effects for calcium and magnesium concentration in the leachate. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

	Ca		Mg	
Effect	*F value*	*Pr > F*	*F value*	*Pr > F*
Treatment	51.88	<.0001	20.1	<.0001
Time	31.46	<.0001	28.78	<.0001
Treatment*Time	7.22	<.0001	6.42	<.0001

Table 2.11 Total mass (mg L^{-1}) of potassium, sulfate, calcium, magnesium, and sodium leached by treatment. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

Treatment	K	SO_4	Ca	Mg	Na
	mg L^{-1}				
LST 0	11.9^{b}*	39.7^{d}	82.3^{c}	23.3^{b}	47.9^{a}
LST400	10.6^{b}	138.4^{c}	144.0^{b}	26.6^{b}	47.5^{a}
LST 800	11.9^{b}	261.7^{b}	231.9^{b}	35.5^{b}	51.5^{a}
LST 1600	17.2^{a}	395.7^{a}	323.6^{a}	48.4^{a}	54.9^{a}

*The same letter within the same column are not significant at $P = 0.05$

FIGURES

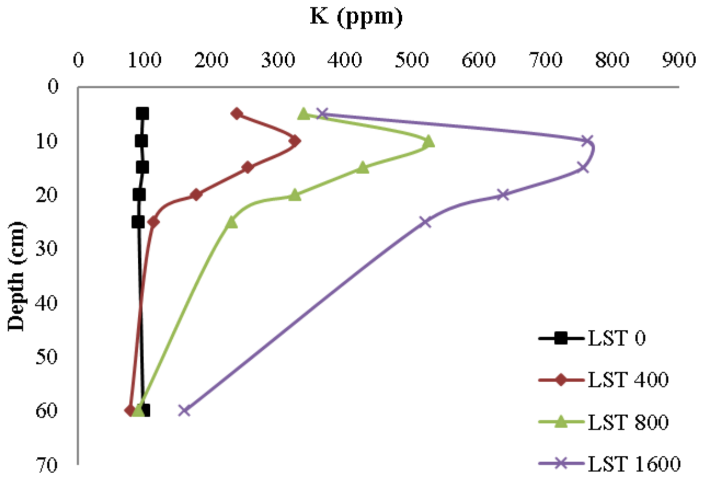

Figure 2.1. Effect of four Liquid SulfurTrap (LST) rates on potassium concentration (ppm) in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

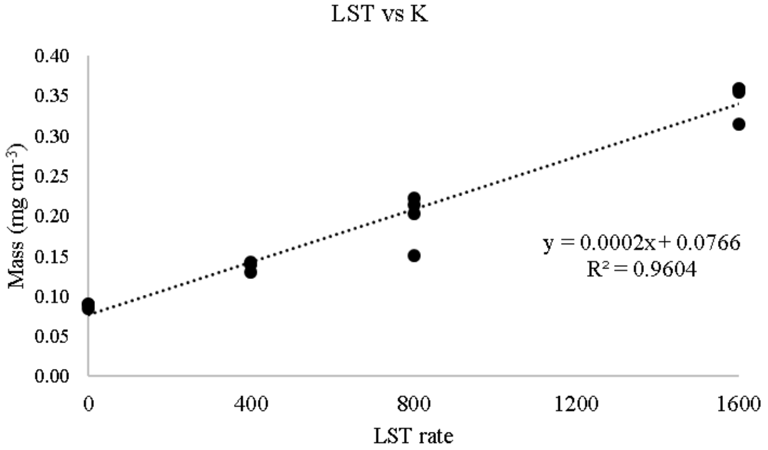

Figure 2.2. Correlation between Liquid SulfurTrap (LST) and total potassium concentration (mg cm^{-3}) in the soil after leaching by treatment. LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

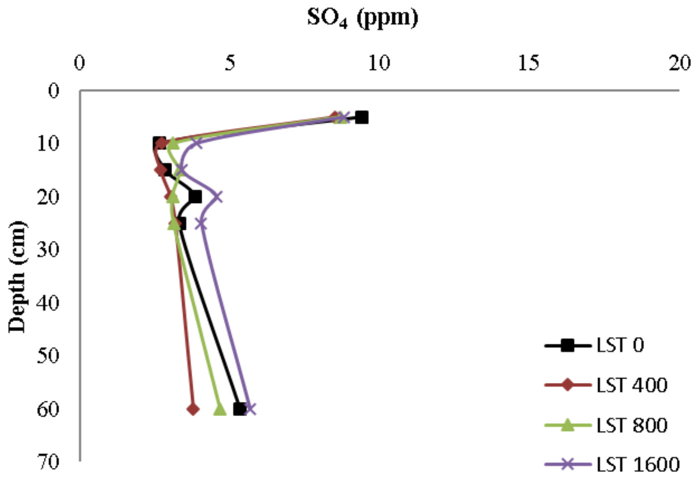

Figure 2.3. Effect of four Liquid SulfurTrap (LST) rates on sulfate concentration (ppm) in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

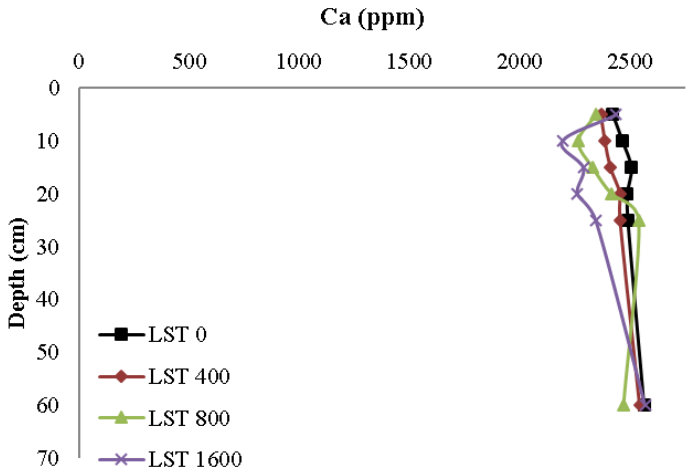

Figure 2.4. Effect of four Liquid SulfurTrap (LST) rates on calcium concentration (ppm) in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

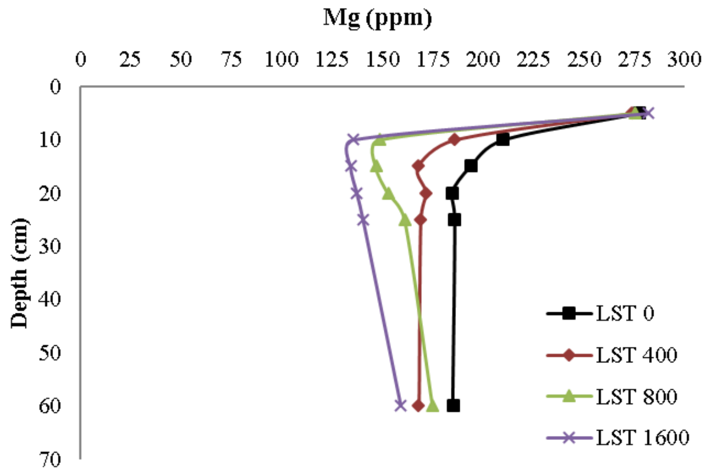

Figure 2.5. Effect of four Liquid SulfurTrap (LST) rates on magnesium concentration (ppm) in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

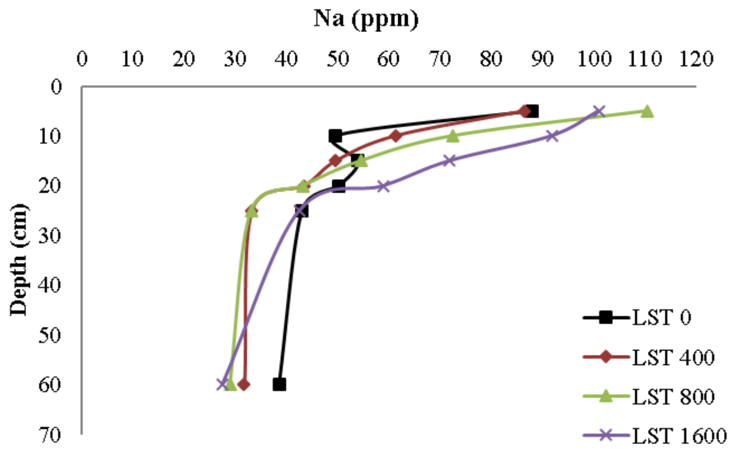

Figure 2.6. Effect of four Liquid SulfurTrap (LST) rates) on sodium concentration (ppm) in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

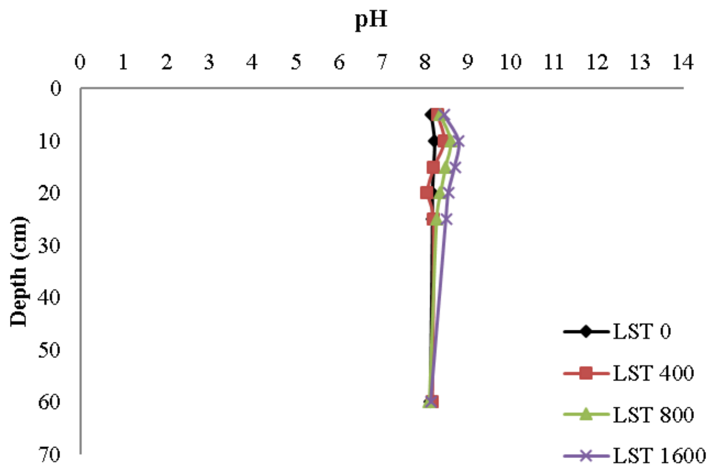

Figure 2.7. Effect of four Liquid SulfurTrap (LST) rates on pH in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

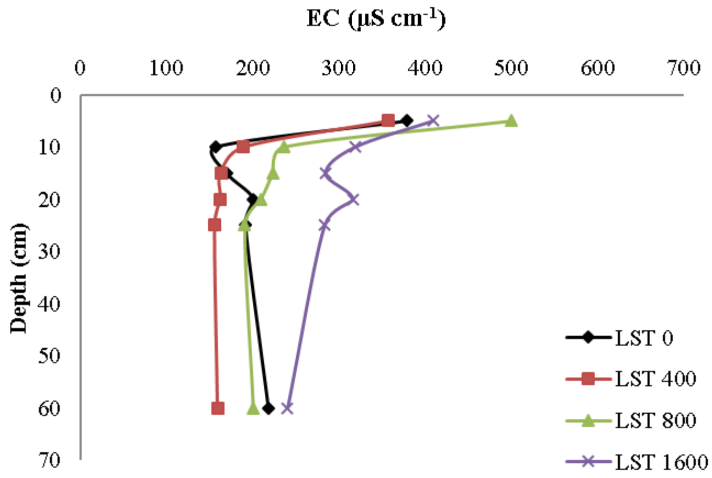

Figure 2.8. Effect of four Liquid SulfurTrap (LST) rates on electrical conductivity (µS cm^{-1}) in the soil by depth (0-5, 5-10, 10-15, 15-20, 20-25, 25-60 cm). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

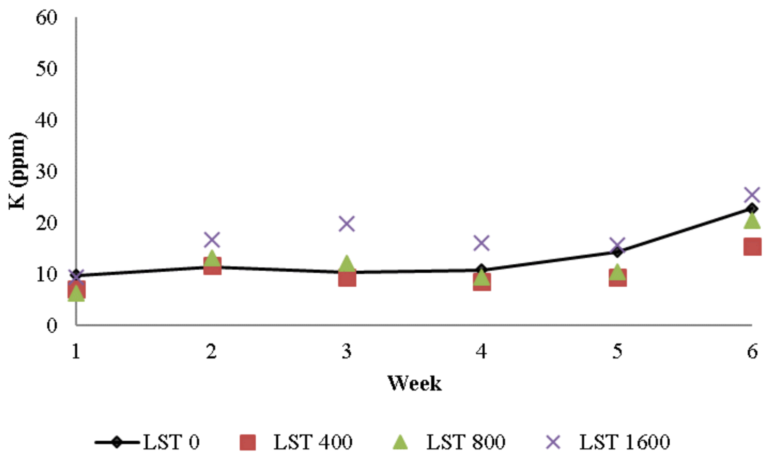

Figure 2.9. Effect of four Liquid SulfurTrap (LST) rates on potassium concentration (ppm) in the leachate over time (week 1-6). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

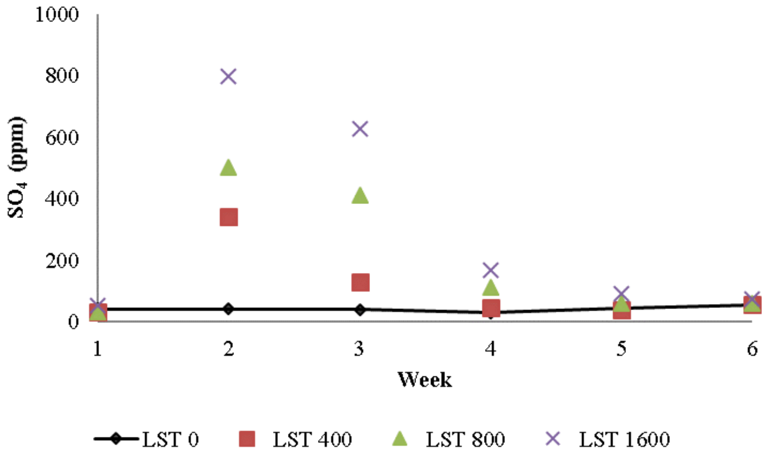

Figure 2.10. Effect of four Liquid SulfurTrap (LST) rates on sulfate concentration (ppm) in the leachate over time (week 1-6). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

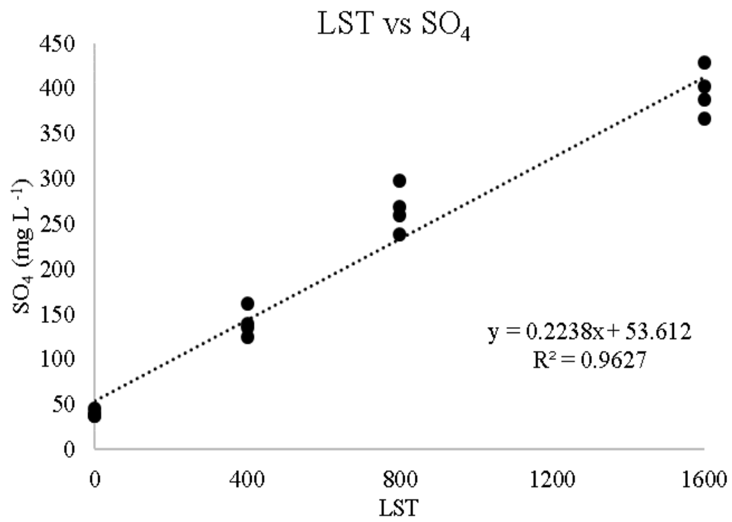

Figure 2.11. Correlation between Liquid SulfurTrap (LST) and total sulfate concentration (mg L^{-1}) in the leachate by treatment. LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

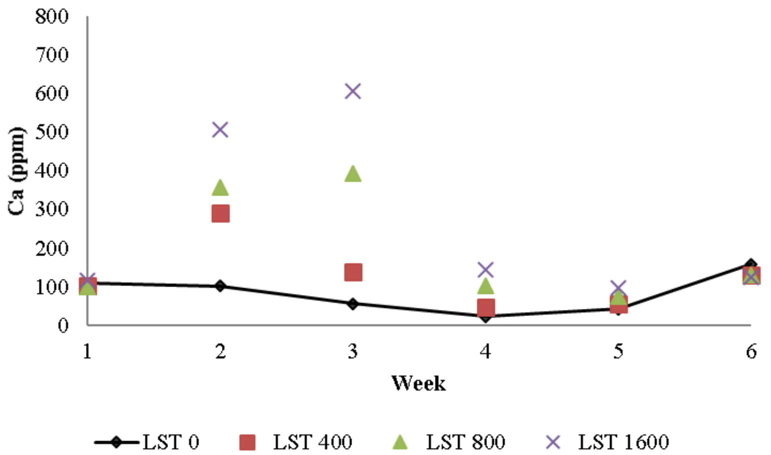

Figure 2.12. Effect of four Liquid SulfurTrap (LST) rates on calcium concentration (ppm) in the leachate over time (week 1-6). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

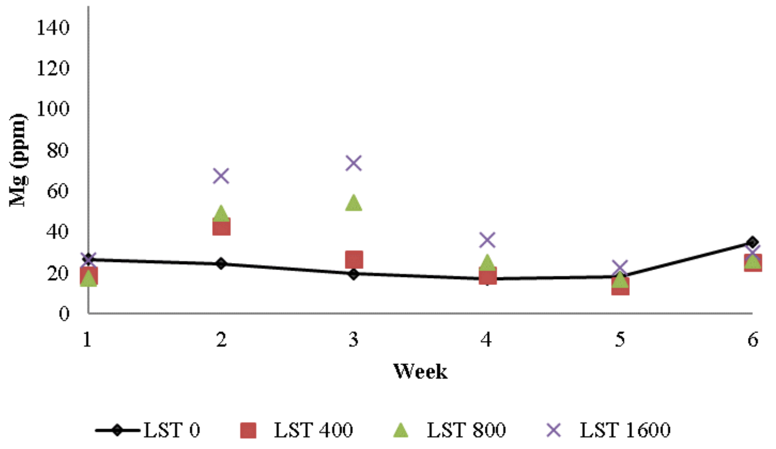

Figure 2.13. Effect of four Liquid SulfurTrap (LST) rates on magnesium concentration (ppm) in the leachate over time (week 1-6). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

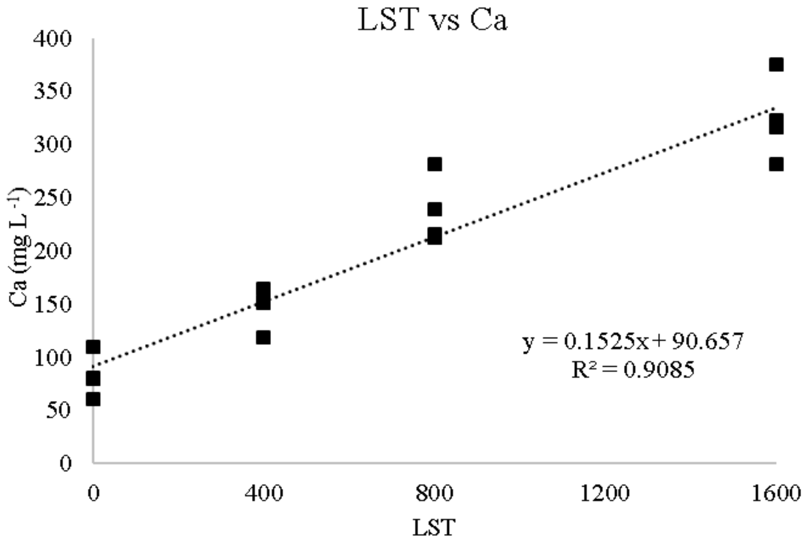

Figure 2.14. Correlation between Liquid SulfurTrap (LST) and total calcium concentration (mg L^{-1}) in the leachate by treatment. LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

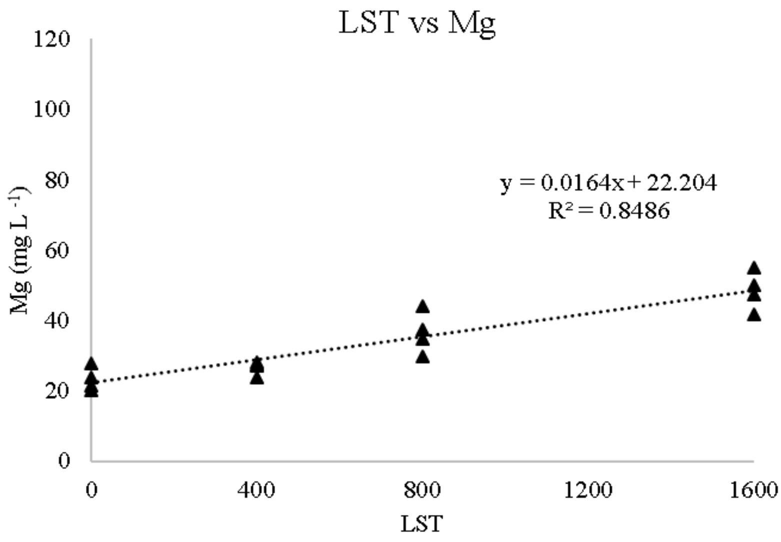

Figure 2.15. Correlation between Liquid SulfurTrap (LST) and total magnesium concentration (mg L^{-1}) in the leachate by treatment. LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively.

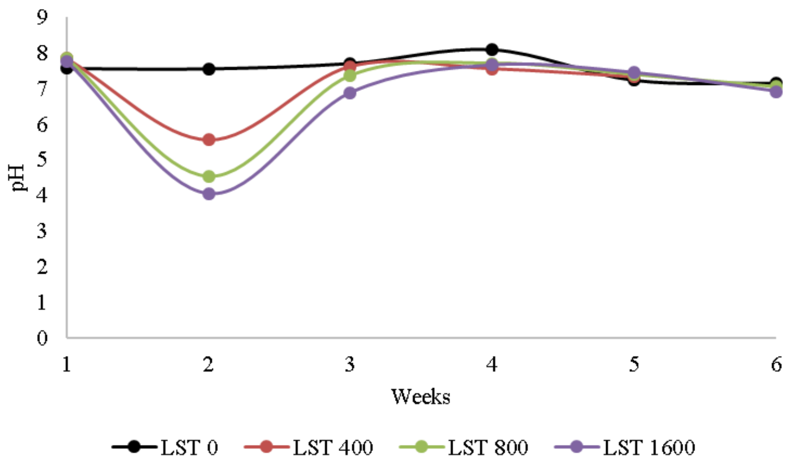

Figure 2.16. Effect of four Liquid SulfurTrap (LST) rates on pH in the leachate over time (weeks 1-6). LST 0, 400, 800, and 1600 are referred to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

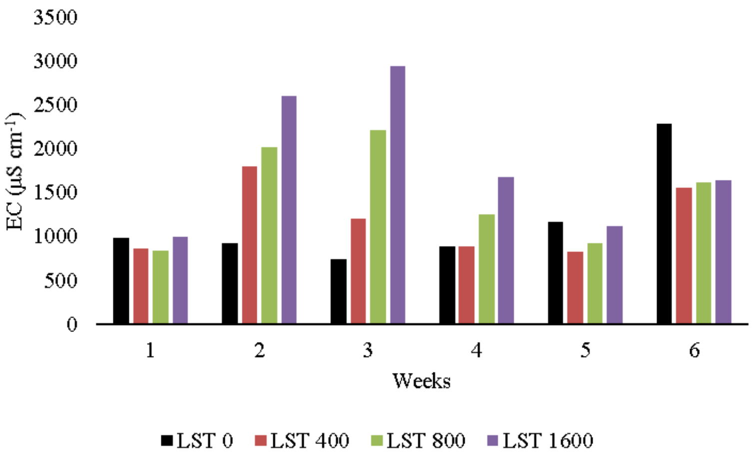

Figure 2.17. Effect of four Liquid SulfurTrap (LST) rates on electrical conductivity (µS cm^{-1}) in the leachate over time (weeks 1-6). LST 0, 400, 800, and 1600 are referred to to 0, 3.8, 7.6, and 15.2 x1,000 L ha^{-1}, respectively. Columns received 573 mm of water after having four rates of a potassium and sulfur containing material was added at four rates.

VITA

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