Novel Coated Fertilizers as Multi-Nutrient Sources for Soybeans and Tomatoes

by

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ABSTRACT

Virginia's Coastal Plain region contains the majority of the state's agricultural production despite having low nutrient soils. The soils in this region are predominantly coarse-textured acid soils with low cation exchange capacities (CEC) (< 3 cmol kg^{-1}) and thus frequently exhibit nutrient deficiencies, including cationic nutrients which are not easily lost by leaching in soils with greater CEC. As a result, soils require careful nutrient management to maintain production levels. Soybean (*Glycine max*), the world's fourth largest crop, shows sensitivity to manganese availability and regularly experiences deficiency symptoms in low-CEC coastal plain soils. Tomato (*Solanum lycopersicum*) production, one of the 3 largest vegetable production systems in the world, requires careful management of various nutrients, particularly phosphorous, sulfur, and boron, for proper fruit development.

Two novel coated fertilizer products consisting of granular KCl coated in a nutrient powder and a sugar-acid chelating agent are investigated as multi-nutrient sources for soybeans and tomatoes. A comprehensive review of the chemistry, behavior, and functionality of key nutrients provided by the fertilizer (P, S, Mn, and B) in both soils and plant tissues and the current state of chelate use in agriculture is provided along with related production issues with tomatoes and soybean.

A greenhouse study investigating the ability of the first coated product (Mn + B coated KCl) to provide micronutrients to soybeans was conducted. Using both low and high organic matter (OM) soils (10 g kg^{-1}; 36 g kg^{-1}), Mn + B coated KCl increased soil Mn compared to no fertilizer and uncoated KCl. Additionally, Mn + B coated KCl increased total above ground

tissue Mn compared to control and uncoated KCl for the low OM soil but not for the high OM soil, which was likely due to OM leading to the formation of metal-ligand complexes. There were no significant results regarding B concentration in either the soil or plant tissue due to the low application rate provided by the coating.

The same fertilizer (Mn + B coated KCl) was investigated under field conditions to determine if increased soil and tissue Mn can be maintained under various environmental factors. Our results found that for all growing seasons and locations, there were no significant treatment differences between months for both Mn and B, but total monthly averages did fluctuate between months, probably reflecting changes in soil moisture and redox status. When averaged across the entire growing season, differences between treatments were inconsistent. Under field conditions, environmental conditions such as soil moisture and leaching likely masked any consistent treatment effects of the coated products.

Two potential soil amendments, P + S + B coated KCl and glucoheptonate (GH), were investigated for their ability to provide nutrients to tomatoes. Three greenhouse trials, each lasting 3 weeks, were conducted. In the first trial, P + S + B coated KCl was compared to the current agronomic recommendation rates for P, S, and B. The coated KCl significantly increased soil and plant tissue P and B compared to all but the KCl + P and KCl + B treatments. The second trial was a glucoheptonate rate trial and showed a significant positive correlation between GH rate and soil and tissue B. The third trial combined and compared the coated KCl and GH products and showed that the treatments containing the coated KCl had significantly increased P, S, and B soil and tissue concentrations, with GH application having no synergistic effect.

Novel Coated Fertilizers as Multi-Nutrient Sources for Soybeans and Tomatoes

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GENERAL AUDIENCE ABSTRACT

The majority of the Virginia's agricultural production occurs on the nutrient poor soils of the coastal plains where nutrient deficiencies are common. As a result, careful nutrient management strategies are required to maintain crop production levels, including major crops like soybean and tomato. Soybean (*Glycine max*) show sensitivity to manganese (Mn) availability and regularly experience deficiency symptoms in this region. On the other hand, tomato (*Solanum lycopersicum*) production requires careful management of nutrients such as phosphorous, sulfur, and boron for proper fruit development.

In this dissertation, two novel coated fertilizer products, granular KCl coated in a nutrient powder and a sugar-acid chelating agent, are investigated as multi-nutrient sources for soybeans and tomatoes. This dissertation starts with a comprehensive review of the chemistry, behavior, and functionality of key nutrients provided by the fertilizer in soils and plant tissues, followed by a review of the current state of sugar acid use in agriculture. The production systems for soybeans and tomatoes for VA and the USA will also be discussed.

The second component of this dissertation is a greenhouse study investigating the ability of the first coated product (Mn+B coated KCl) to provide micronutrients to soybeans. The Mn+B coated KCl significantly increased Mn compared to control and uncoated KCl treatments in the soil for both soil types and in tissue for the low OM soil. The third component of this dissertation investigates the same fertilizer under field conditions. Our results showed that for all growing seasons and locations, there were no significant treatment differences between months for both Mn and B, but monthly averaged concentrations did fluctuate over time, probably reflecting

seasonal environmental shifts. When averaged annually, inconsistent differences were seen between treatments. Under field conditions, environmental conditions like increased soil moisture and leaching likely masked any consistent treatment effects of the coated products.

The fourth component of this dissertation investigates two potential soil amendments, the second coated KCl product (P+S+B coated KCl) and glucoheptonate (GH), for their ability to provide nutrients to tomatoes. The study consists of 3 separate greenhouse trials, each lasting 3 weeks. In the first trial, P+S+B coated KCl was compared to the current agronomic recommendation rates for P, S, and B. The coated KCl significantly increased soil and plant tissue P and B compared to all but the KCl + P and KCl + B treatments. The second trial was a glucoheptonate rate trial and showed a significant positive correlation between GH rate and soil and tissue B. The third trial combined and compared the coated KCl and GH products and showed that the treatments containing the coated KCl had significantly increased P, S, and B soil and tissue concentrations, with GH application having no enhancing effect.

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Finally, the author would like to thank her family: her mother, father, and two sisters. Each and every member has provided unwavering support and encouragement over the years, and I cannot express the depth of my gratitude.

Dedication

Years ago, a similar dedication was made to my sister and me. Finally, I am able to return the favor.

The author would like to dedicate this original dissertation to her uncle, whose love and joy has filled her life with such happy memories. Thank you for showing me how to find adventure in the 'every day', whether that be sudden trips or making shapes with the pancakes. Truly, you have taught me that with passion, hard work, and an open mind, you can change your world. Thank you for everything, Rick!

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Chapter 1: Literature Review

Nutrient Forms in Soils and Plants

Manganese

Manganese and boron are essential micronutrients for all plants. For all micronutrients, there are six general forms they can exist as in nature: soluble, exchangeable, specifically adsorbed or retained, adsorbed or complexed by OM, insoluble precipitates, or as mineral constituents (Kirkby, 2012; Sparks, 1996; Sharma, 2006). Of the six general pools previously listed, Mn can be found in four broader forms within soils: as primary and secondary minerals, exchangeable Mn^{2+}, soil solution Mn^{2+}, and as Mn – OM complexes (Havlin et al., 2014; Broadley et al., 2012). Mn concentrations in rocks can range between 350 – 2000 mg kg^{-1}, with the highest concentrations occurring in mafic rocks (Kabata-Pendias, 2011). Mineral Mn is mostly found in ferromagnesian rocks and can form secondary minerals by combining with oxygen (Havlin et al., 2014). The most common Mn minerals include birnessite, pyrolusite, manganite, hausmannite, and redochrozite (Havlin et al., 2014; Kabata-Pendias, 2011). Mineral Mn can add to the adsorbed or labile Mn^{2+} pool depending on where the Mn is bound along the mineral surface and can be converted into soil solution Mn^{2+} by dissolution (Havlin et al., 2014). The major sources of Mn in soils are oxides, silicates, and carbonates (Brady and Weil, 2008; Schulte and Kelling, 1999). The most dominant form in soils is Mn^{2+} (Brady and Weil, 2008; Hawkesford and Barraclough, 2011; Havlin et al., 2014).

Boron

The major sources of B in soils are borosilicates and borates (Abat, 2014; Brady and Weil, 2008; Evan and Sparks, 1983; Havlin et al., 2014). The most dominant form in soils is

H_3BO_3 (Brady and Weil, 2008; Havlin et al., 2014; Evan and Sparks, 1983). In soils, B exists in the same four general pools as Mn (Havlin et al., 2014). Mineral B is unique in that it is the only nonmetal micronutrient. In soils, mineral B concentrations can range from 2 – 200 ppm but are more frequently found to be between 7 – 80 ppm (Havlin et al., 2014; Evan and Sparks, 1983). Of the total B content in soils, less than 5% is available to plants (Havlin et al., 2014). Of that 5%, the majority comes from the organically bound fraction (Abaye et al., 2006; Abat, 2014). Of the mineral sources, the most common B – containing mineral is Tourmaline, which is known to be insoluble and resistant to weathering. This results in the slow release of B over extensive periods of time (Havlin et al., 2014). Adsorbed B is most prevalent in alkaline soils, and most often occurs on broken Si – O and Al – O bonds along the edges of clay minerals, amorphous hydroxides, and with Fe and Al – oxide compounds (Havlin et al., 2014).

Phosphorus

Phosphorous is one of the three primary nutrients required for plants, second to only N in terms of plant demand (Brady and Weil, 2008; Marschner, 2012). Unlike N, soil P is not naturally replenished and requires outside sources in order to maintain soil levels for agricultural production (Wyngaard et al., 2016; Shen et al., 2011). The most prevalent sources of P are from primary minerals, fertilizer additions, and from organic residues or materials (Damon et al., 2014; Havlin et al., 2014). In surface soils, total P concentrations range between 0.005 – 0.15%, and tends to decrease with more intense weathering (Damon et al., 2014; Brady and Weil, 2008; Havlin et al., 2014). However, the amount of total soil P rarely correlates to the amount of plant-available P.

As was seen with Mn and B, P can be found within three major pools in soils: the soil solution pool, the inorganic pool, and the organic pool (Damon et al., 2014; Shen et al., 2011). The two plant-available forms of P, HPO_4^{2-} and $H_2PO_4^-$, are contained within the soil solution pool, but the amount of either form is heavily dependent on soil pH (Damon et al., 2014; Brady and Weil, 2008; Hinsinger, 2001). The soil solution pool consists of soluble P that is both highly extractable and available for plant uptake. The inorganic pool consists of P that has been adsorbed onto mineral surfaces or that has been precipitated out of soil solution (Damon et al., 2014; Hansen et al., 2004).

The processes of adsorption or precipitation of P in this pool is generally referred to as “P-fixation” and the rate and severity is highly dependent on various environmental factors including mineral composition, pH, cation and anion concentrations, OM content, and temporal and environmental factors (Brady and Weil, 2008; Havlin et al., 2014; Damon et al., 2014; Hansen et al., 2004; Shen et al., 2011). Of the three major soil P pools, the OM pool contains the greatest amount, representing 50 – 90% of total soil P (Wyngaard et al., 2016; Damon et al., 2014; Anderson, 1980). The OM-bound P can be released into the soil solution via microbially facilitated mineralization (Damon et al., 2014). The rate and preference of mineralization over immobilization is contingent on various soil factors but generally is increased by greater amounts of OM and is favored at C:P ratios < 200 (Damon et al., 2014; Anderson, 1980).

Sulfur

Sulfur, a secondary macronutrient, predominantly exists in four major forms within terrestrial systems: soil solution S, adsorbed S, reduced inorganic S, and organic S (Brady and Weil, 2008; Eriksen, 2009; Havlin et al., 2014; Scherer, 2001). In surface soils, solution S contains the plant-available S (SO_4^{2-}), with average sufficient concentrations ranging from 3 – 5 ppm (Havlin et al., 2014). Solution S can vary widely throughout the year, with SO_4^{2-} being susceptible to leaching losses, and is moved throughout the soil via mass flow or diffusion (Castellano and Dick, 1990; Ghani et al., 1990; Havlin et al., 2014). Adsorbed forms of S generally are found in more humid climates with highly weathered soils containing large concentrations of Fe and Al – oxides and tends to increase in the presence of anions such as phosphate (PO_4^-), nitrate (NO_3^-), and chloride (Cl^-) (Havlin et al., 2014; Scherer, 2009). Reduced inorganic S (S^{2-} and S^0) is predominately found in areas prone to regular flooding such as costal flood plains, marshes, and wetlands, and must be oxidized to become plant-available (Havlin et al., 2014; McGrath et al., 2003b). However, the process of oxidizing these reduced forms is generally very slow, with rates being dictated by factors such as microbial community composition, soil temperature, soil moisture and aeration, and soil pH (Havlin et al., 2014; Scherer, 2009; McGrath et al., 2003b).

Organic S typically contains the greatest amount of sulfur, usually in reduced forms (ex. sulfides, disulfides, thiols), redox intermediates (ex. sulfoxides, sulfonates), and oxidized forms (ex. ester sulfates) (Brady and Weil, 2008; Chapman, 2001; Scherer, 2009). Of the plant-available S within soils, 90 – 98% is contained within the OM pool. OM – bound S can be classified into three groups: HI – reducible, C – bonded, and residual S (Chapman, 2001; Havlin et al., 2014). Within the soil mineral pool, sulfates and sulfides are the most prevalent sulfur species, with sulfate being the species available for plant uptake (Brady and Weil, 2008; McGrath et al., 2003b). Atmospheric sulfur, commonly in the forms of carbonyl sulfide, hydrogen sulfide, and sulfur dioxide, can enter the soil – plant system by either wet or dry deposition (Brady and Weil, 2008).

Nutrient Availability in Soils

In general, micronutrient deficiencies are most common in leached, acid sandy soils, organic soils, soils with intense cropping, extreme pH, and eroded soils (Brady and Weil, 2008; Maathius and Diatloff, 2013). In soils, nutrient deficiency depends on a variety of conditions including nutrient concentration and behavior within soil, the mechanisms and conditions for nutrient uptake by plants, the nutrient functionality and demand within plant tissue, and the mobility of the nutrient (Hawkesford and Barraclough, 2011; Brown and Bassil, 2011). Usually, the uptake of micronutrients by plants requires the use of some H^+ - coupled transport mechanism (Maathius and Diatloff, 2013; Abaye et al., 2006). Cation micronutrients tend to show similar behaviors under various soil conditions. Under low pH conditions, cations become more plant available due to increased solubility while the opposite occurs when pH is high (Brady and Weil, 2008; Sharma, 2006). When OM content is high, cation availability decreases as they react to form water-insoluble complexes. However, these cations can be released from the OM complexes more easily than from mineral particles (Brady and Weil, 2008; Habibah et al., 2014; Havlin et al., 2014).

Nutrient interactions also play an important role in the availability and uptake of nutrients. These interactions, which occur when the presence of one nutrient (usually in greater concentrations) influences the uptake and availability of other nutrients in the system, can be broken into two categories: interactions resulting in precipitate or complex formation and interactions resulting from competition between ions with similar characteristics (Fageria, 2001). Numerous factors influence the type and degree of these interactions, including nutrient concentrations, temperature, soil aeration and moisture, soil pH, plant root development, transpiration and respiration rates (Fageria, 2001).

Manganese

The two greatest influences on Mn availability are soil pH and redox potential (Habibah et al., 2014; Hawkesford and Barraclough, 2011; Kabata-Pendias, 2011; Rivera-Becerril et al., 2013; Schulte and Kelling, 1999; Sparks, 1996). Under waterlogged or low pH conditions ($pH < 6$), plant-available forms of Mn increase. Under oxidized or high pH conditions ($pH > 6$), Mn becomes less available for plant uptake (Havlin et al., 2014; Haque et al., 2015; Sparks, 1996). Soils with excessive water content and poor aeration have increased soluble Mn^{2+} due to increased reducing conditions (Havlin et al., 2014; Haque et al., 2015). Upon being released from parent material through weathering processes, Mn is quickly converted into Mn – oxides, following similar trends seen with Fe (Kabata-Pendias, 2011). According to Chen et al. (2015), the major controls on Mn release from sediments include the following: DO, pH, temperature, bacterial community composition, and the amount of OM in the water. Mn concentrations tend to be highest in soils with mafic parent material, that are rich with Fe – oxides and hydroxides, and soils from arid or semiarid regions (Kabata-Pendias, 2011). Rivera-Becerril et al. (2013), in a study investigating the impacts of Mn mining on the surrounding environment, revealed that the presence of arbuscular mycorrhiza can also reduce plant uptake of Mn and alleviate toxicity.

Additional influences on Mn availability include the presence of certain nutrients, specifically N, P, K, Ca, Mg, Fe, Zn, and Si (Fageria, 2001; Smilde, 1973; Ramani and Kannan, 1974). Phosphorous and Zn have both show to have a positive influence on Mn availability in soils and plant tissue. Phosphorous is believed to improve soil Mn through its acidifying effect, while Zn is believed to improve the uptake and translocation of Mn in plant tissue by helping to outcompete Fe, a known enhancer of Mn – deficiency (Fageria, 2001; Smilde, 1973). The influence of N, K, Ca^{2+}, and Mg^{2+} depends on the nutrient form and concentration and can be either beneficial or antagonistic towards Mn availability (Fageria, 2001; Ramani and Kannan, 1974). When in the form of NH_4^+, N improves Mn availability by lowering the pH of the soil as it is taken up by plant. Following the same mechanism, NO_3^- lowers Mn availability by increasing the pH as it is removed from the root zone. Potassium, Ca, and Mg play regulatory roles in the uptake of Mn^{2+} and have been shown to increase Mn availability in soils when Mn concentrations are low. However, Ca^{2+} tends to be predominantly associated with antagonistic behavior with Mn due to its association with alkaline conditions (Fageria, 2001). The remaining nutrients, Fe and Si, are both known to have strongly negative impacts on Mn availability. Iron, sharing similar ionic strength, charge, and size as Mn, behaves similarly to Mn and thus is highly competitive for adsorption sites and reactivities (Fageria, 2001; Chinnery and Harding, 1980). On the other hand, Si limits Mn availability by creating an oxygenated zone around the root zone, which facilitates the formation of Mn – oxides and the potential promotion of Mn-deficiencies in plant tissue (Fageria, 2001).

Boron

Boron tends to more available in acid soils, but B deficiencies can occur in acidic sandy soils as B is easily leached (Brady and Weil, 2008; Hawkesford and Barraclough, 2011). Under high pH conditions (pH: 7 – 9), boric acid (H_3BO_3) is rapidly bound to the surfaces of clay particles and Fe – and Al – oxides through the exchange of OH – groups (Brady and Weil, 2008; Sharma, 2006). At pH < 7, boron is typically found in its plant-available form of boric acid.

Once in this form, it can be adsorbed by plant roots and transported into the xylem (Maathius and Diatloff, 2013). In soils, B distribution is heavily influenced by soil moisture status and weather, pH, soil texture, OM content, mineral composition, and tillage practices (Abaye et al., 2006; Abat, 2014; Hawkesford and Barraclough, 2011; Kashin, 2012). Plant-available B tends to decrease under cold, dry soil conditions due to reduced mineralization of OM, but can be rapidly leached out of the system under periods of heavy rainfall (Abat, 2014; Goldberg et al., 2000). Soil texture also plays a significant role in the B content, with the highest concentrations occurring in loams and the lowest in sandy soils (Kashin, 2012).

Sulfur

The major factors that influence sulfur availability in soils includes soil texture, organic matter content, temperature, moisture, and industrial deposition. Coarse textured soils with low organic matter commonly express sulfur deficiencies due to high leaching potential of sulfates and limited reservoir capacity (Scherer, 2001; McGrath et al., 2003b). Sulfur availability can also be reduced under low temperature or waterlogged soils due to constraints on microbial activity, which is fundamental in the mineralization of various forms of sulfur into plant-available sulfate (Brady and Weil, 2008; Scherer, 2009). In recent years, sulfur deficiency has become more prevalent as a result of lowered atmospheric concentrations of sulfur oxides related to higher air quality standards established through the Clean Air Act (Brady and Weil, 2008; Eriksen, 2009; McGrath et al., 2003a). Previous deposition, generally in the form of acid rain, provided sufficient levels of sulfur within terrestrial systems. As a result, less emphasis was placed on sulfur content in fertilizers, and many of today's fertilizers are thus insufficient for addressing these new deficiencies (Brady and Weil, 2008; Scherer, 2009; Eriksen, 2009)

Importance of Nutrients in Plants

Manganese

In plants, Mn is required for the activation of important enzymes such as decarboxylase, dehydrogenase, and oxidase enzymes, for the functioning of the water-splitting system of photosystem II in photosynthesis, and for the metabolism and assimilation of N (Brady and Weil, 2008; Havlin et al., 2014; Hawkesford and Barraclough, 2011; Maathius and Diatloff, 2013; Broadley et al., 2012). Plants deficient in Mn exhibit interveinal yellowing, mottled appearance, dead tissues in later stages, and lack lateral roots. Deficiency symptoms will first appear in younger tissue, and generally occurs when dry matter concentrations are less than 15 – 20 mg kg^{-1} (Brann et al., 2009; Jones, 2003). If Mn concentrations reach toxic levels (Mn > 200 mg kg^{-1}), plants may have dark green leaves with red flecks in early stages which may turn into bronze or yellow interveinal tissues later on as well as patchy green coloration (Brady and Weil, 2008; Brann et al., 2009; Jones, 2003). According to a study by Kogelmann and Sharpe (2006), the major factor responsible for the deterioration of sugar maples (*Acer saccharum*) seen in northern PA is increased Mn concentrations in the soil, foliage, sap, and xylem. The increase in Mn may have resulted in decreased photosynthesis and additional nutrient deficiencies that ultimately lowered overall yield.

Boron

While the general importance of boron in plants has been well studied, the specifics of its utilization remains poorly understood (Hawkesford and Barraclough, 2011; Marschner, 2012). Similar to Mn, B is also used by plants to activate certain dehydrogenase enzymes but that is where the similarities end. In addition to enzyme activation, B plays a role in the production and translocation of biochemical components such as sugars, nucleic acids, and plant hormones, and is fundamental for proper cell division and development (Brady and Weil, 2008; Hawkesford and Barraclough, 2011; Havlin et al., 2014; Kashin, 2012). In plants, the majority of B (~80%) is found in the cell walls as very stable organic complexes, usually polymeric sugars (Hawkesford and Barraclough, 2011; Maathius and Diatloff, 2013).

Globally, boron is considered the second most important deficiency due to its impact on reproductive growth (Hawkesford and Barraclough, 2011; Wyenandt et al., 2017). In plants experiencing B deficiencies (B < 25 mg kg^{-1} in dry matter), root and shoot dieback, reddish young leaves, malformed buds, and necrosis of internal tissues in the stems, tubers, and seed may occur (Abaye et al., 2006; Brady and Weil, 2008; Brann et al., 2009; Jones, 2003; Havlin et al., 2014; Maathius and Diatloff, 2013). Boron deficiency can also result in a condition called "brown heart" or "black heart", where the breakdown of internal tissues in root crops results in darkened spots (Havlin et al., 2014). Boron toxicity symptoms include interveinal chlorosis and marginal necrosis (Brady and Weil, 2008).

Sulfur

Sulfur is mainly involved in the formation and functioning of numerous biochemical components, particularly amino acids (cysteine and methionine) and proteins (Brady and Weil, 2008; Hitsuda et al., 2015; Marschner, 2012; Abaye et al., 2006; Eriksen, 2009). Many of these related proteins play important roles in photosynthesis and N – fixation within plant tissues (Brady and Weil, 2008; Marschner, 2012). Additionally, S is important for enzyme and vitamin production, the formation of nodules, proper seed production, and the development and functionality of chlorophyll (Marschner, 2012; Eriksen, 2009). In general, deficiency is known to be closely associated with N concentrations and occurs when plant tissue concentrations fall under 0.15%, with optimal growth occurring at 0.1 – 0.5% dry weight (Fageria, 2001; Jones, 2003; Marschner, 2012; McGrath et al., 2003b). When experiencing S deficiency, plants exhibit overall chlorosis of the leaf tissue, a reddish tint within the veins and petioles, upward leaf cupping, and reduced leaf area (Marschner, 2012; Havlin et al., 2014; Abaye et al., 2006; Eysinga and Smilde, 1981; Ward, 1976). Due to the mobile nature of the nutrient, deficiency symptoms first appear on the older, lower, portions of the plant. Due to rarity of occurrence, toxicity symptoms of S are poorly defined but may be indicated by premature leaf senescence (Jones, 2003).

Phosphorous

Like S, P primarily functions as a core component of biochemical compounds. More specifically, P is used for the formation of nucleic acids, phospholipids, ATP and ADP as well as for proper root system and seed development (Marschner, 2012; Abaye et al., 2006; Havlin et al., 2014; Peñalosa et al., 1989). For most plants, optimal growth requires P concentrations of 0.1 – 0.5% of dry weight, with critical concentrations around 2500 mg kg^{-1} (Jones, 2003; Vance, 2011). In systems where P deficiency has occurred, plants can exhibit total plant stunting, poorly developed root systems, and a dark green or purple/reddish discoloration of leaf tissue (Vance, 2011; Jones, 2003). Phosphorous toxicity tends to appear through the development of additional micronutrient deficiencies, particularly Zn and Fe, and occurs when P concentrations are greater than 1% of dry matter (Jones, 2003).

Glucoheptonate and other Chelating Agents

Chelating agents have become increasingly predominate tools in today's agricultural practices as means for addressing various nutrient deficiencies. A chelating or complexing agent, that is a molecule or ion that can bind to a metal ion to form a ring structure, helps to prevent leaching of these metal ions and can form both soluble and insoluble complexes in soils (Brady and Weil, 2008; Whitehurst, 2017; Mehltretter et al., 1953; Iyamuremye and Dick, 1996). There are two predominant types of chelates used in agriculture today: aminopolycarboxylates and hydroxycarboxylates (Clemens et al., 1990). Aminopolycarboxylates, the amino acid based organic acids, are comprised of the more prominent chelates commercially available today such as EDTA, HEEDTA, DTPA, and EEDHA (Clemens et al., 1990). Hydroxycarboxylates consist of the sugar acid chelates, such as citric acid, saccharic acids, gluconic acid, and glucoheptonic acid (Clemens et al., 1990; Iyamuremye and Dick, 1996).

Glucoheptonate ($C_7H_{13}NaO_8$), is an example of one such product that is used less frequently compared to previously mentioned options. Sugar acids are organic compounds consisting of at least a five C – chain and can be divided into three classes based on the functional group composition (Whitehurst, 2017; Ash, 2013). Aldonic sugar acids contain terminal alcohol groups (-OH), uronic acids are those with oxidized terminal C's, and saccharic acids contain an oxidized aldehyde group and/or a terminal C (Whitehurst, 2017). A seven – C sugar, glucoheptonate (GH) is produced through the hydrolysis of cyanide and exists as two isomers: α – glucoheptonic acid and β – glucoheptonic acid. Between the two isomers, the β – glucoheptonic acid is the most commercially sold at 50% concentration in the form of a liquid (Whitehurst, 2017).

Like many chelating agents, GH is predominately used for the sequestration of trace metals and cationic micronutrients within soils and has shown to be particularly useful for the adsorption of Fe^{2+} and Fe^{3+} (Whitehurst, 2017; Shaddox et al., 2006). In general, the stability of organic acid chelate – metal complexes tend to follow the same trend. This trend, referred to as the Irving and Williams Series, shows that metal stability occurs as follows: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (Essington, 2015; Norvell, 1991). Previous studies have shown that GH can bind approximately 4 molecules of Fe^{3+}, 1 – 2 molecules of Cu^{2+} (with increased binding at higher pH), and 2 molecules of Ca^{2+} under alkali conditions (Whitehurst, 2017; Hodge et al., 1963; Escander at al., 1990; Mehltretter et al., 1953). However, the adsorption of metals in the complexes are also influenced by additional factors such as the type of chelate, the type of metal, time, pH, the concentration of salts, and soil texture (Norvell, 1991). In agriculture, GH tends to be most effective as a foliar application as opposed to soil due to its tendency for rapid degradation via microbial activity (Broschat et al., 2005; Birch, 1972).

Soybeans Growth and Production

Soybeans (*Glycine max*) are one of the twelve principle food plants for humans (Johnson, et al., 2008; Jones, 2003). In addition to soybeans, there are seven main grain crops: barely, corn, grain sorghum, oats, rye, triticale, and wheat (Caffarelli et al, 2014). In Virginia, grain crops and soybeans make up the primary industry in agriculture (Caffarelli et al, 2014). Soybeans are primarily harvest for the seed oil and protein-containing meal, and the majority of production occurs on the eastern side of the state (Caffarelli et al, 2014; Johnson et al., 2008). Commonly used agricultural inputs when growing soybeans include *Rhizobia* inoculant, gypsum ($CaSO_4$) foliar Mn fertilizer, foliar insecticide, and foliar fungicide (Bluck, 2015).

Soybean are a short-day crop, with growth being predominantly driven by temperature after flowering (Holshouser, 2010). Short-day crops are plant species that initiate flowering upon sensing a shortening of daylight (aka longer nights) (Holshouser, 2010). The typical planting season for soybeans in Virginia starts in May – late June and continues through to early August. There are six identifiable stages of soybean maturity seen throughout the growing season, designated as R2 – R7 (Holshouser, 2010). Sufficient ranges of Mn and B in plants for soybean growth are 20 – 200 mg kg^{-1} and 25 – 60 mg kg^{-1}, respectively (Brann et al., 2009).

In 2007, Gordon compared the influence of Mn nutrition on glyphosate-resistant (GR) and convention soybeans. His study revealed that GR soybeans result in significantly lower Mn uptake and yields unless higher Mn-fertilizer rates (5.6 and 8.4 kg ha^{-1}) are applied compared to conventional varieties, indicating the need for specialized management practices. In a similar study performed by Loecker et al. (2010), they investigated the influence of the genetic modification of glyphosate-resistant soybeans on the Mn concentrations found in plant tissues and the plant response to fertilization. Their results showed that soybean genetics did have a significant effect on the plant's response to Mn application, but that the response of near-isoline GR-soybeans was not consistent across locations and treatments. This indicates the need for further study.

The three most prominent micronutrient deficiencies in VA are Zn, Mn, and B, with the majority of Mn deficiencies being seen with soybeans (Maguire and Heckendorn, 2018). In cases where Mn-fertilizers are required, foliar or band application are the recommended methods (Mullins and Heckendorn, 2009; Schulte and Kelling, 1999). While broadcast application can be used, it is not recommended because it does not minimize potential Mn-fixation to soil particles (Schulte and Kelling, 1999). The most commonly used Mn-fertilizers are manganese sulfate

($MnSO_4 \cdot 3H_2O$) and chelated Mn (MnEDTA) (Schulte and Kelling, 1999; Jones, 2003; Abaye et al., 2006).

According to the VA Soil Test Recommendation Handbook Soil Test Note #4 (Mullins and Heckerdorn, 2009), foliar application should supply 0.84 – 1.12 kg Mn ha^{-1} in enough water to coat the entire plant using manganese sulfate, manganese oxide, manganese chelate, or EDTA-chelates. Applications should be applied 1 – 3 times as needed prior to August 15th. Sideband application should apply 9 – 11.2 kg Mn ha^{-1} using Mn – chelates two inches below seed level at the time of planting. If broadcast application is being used, Mn sulfate or Mn-oxide should be applied 2 – 3 weeks before planting at a rate of 28 – 33.6 kg ha^{-1}.

Tomato Growth and Production

Tomato production has been steadily increasing since the 1960's, with production increasing by 300% between 1960 and 2005 (Costa and Heuvelink, 2005). In 2016, global production of tomatoes reached 177 million and accounts for 4.7 million hectares of harvest land. Global production shows an increase of 84 million tomatoes and 1.4 million hectares as compared to 1994 levels (FAOSTAT, 2018). The top producing countries include China (56 million tonnes), India (18 million tonnes), and the United States (13 million) (FAOSTAT, 2018; Minor and Bond, 2016). In the US, the top producing states include California (95%), Florida, Pennsylvania, Virginia, and Illinois (USDA NASS, 2018).

Tomatoes (*Solanum lycopersicum*) are members of the *Solanaceae* family, also known as "nightshade family", which also includes crops such as chili, bell peppers, potato, and tobacco (Costa and Heuvelink, 2005; Kemble, 2017; Brann et al, 2009). Depending on the variety, tomatoes can be either determinate, meaning all fruiting flowers occur at one time, or indeterminate, meaning fruit and flower production occurs throughout the growing season (Orzolek et al., 2006). In terms of environmental conditions, tomato plants tend to prefer full sun, moist but well-drained loamy soil (pH: 6 – 6.5), and average temperatures ranging from 21 – 32 °C (Relf et al., 2016; Hochmuth, 2015; Wyenandt et al., 2017). Field production of tomatoes can be classified as either ‘bare ground’ or ‘plasticulture’, which is used as a pest and weed management strategy (Wyenandt et al., 2017). For bare ground systems, primary nutrient recommendations range from 44.8 – 100.8 kg N ha^{-1}, 112 – 224 kg P ha^{-1}, and 112 – 336 kg K ha^{-1} (Wyenandt et al., 2017; Kemble, 2017; Maguire and Heckendorn, 2018). Along with the primary nutrients, tomatoes have also shown sensitivity to B concentrations. For VA, application recommendation rates for tomatoes is 1.12 – 2.24 kg B ha^{-1} when soil test levels are “Low” (0.0 – 0.35 mg B kg^{-1}) or “Medium” (0.36 – 0.17 mg B kg^{-1}) (Wyenandt et al., 2017; Kemble, 2017).

There are three main productions systems for tomatoes used today: process, fresh market, and greenhouse (Kemble, 2017; Abaye et al., 2006; Costa and Heuvelink, 2005). Process and fresh market are the primary production systems, but greenhouse production has become increasingly popular over the past decade. However, these production systems require intense and strictly regulated management due to the increase susceptibility to pest and disease presence (Costa and Heuvelink, 2005; Hochmuth, 2015). In VA, tomato production is almost entirely fresh market and occurs in the Coastal Plain region (Tuckey et al., 2001). For fresh market systems, the five major tomato types include the classic round, cherry or cocktail, plum or baby plum, beefsteak, and vine or truss tomatoes (Costa and Heuvelink, 2005; Tuckey et al., 2001). In general, tomatoes are highly sensitive and vulnerable to disease, pest, and nutrient conditions. For VA tomatoes, common diseases are early blight, septoria leafspot, and fusarium wilts, while common pests include whiteflies, hornworm, stink bugs, mites, fruitworm, and nematodes (Relf et al., 2016).

Conclusion

This literature review covers the current state of research on the chemistry, behavior, and availability of P, S, Mn, and B in soils and plants, the current used of chelating agents in agriculture, and the predominate production systems and practices for soybeans and tomatoes. The 4 nutrients focused on in this study (P, S, Mn, and B) predominately exist in the same 4 general pools and tend to be most heavily influenced by the same environmental conditions including soil pH, soil moisture status, soil texture, and soil OM content. In plants, P and S tend to be used as components of biochemical compound such as nucleic acids, amino acids, DNA, RNA, and proteins. Manganese plays a role in the photosynthetic processes of the plant and is an important enzyme activator while B is predominantly associated with the proper development and structure of cell walls. Glucoheptonate and similar chelating agents are most commonly used in agriculture to supply important cationic nutrients to plant tissues, generally though foliar application. However, very few studies have been conducted to investigate its influence on microbial community dynamics and its potential impact on cycles of the remaining essential nutrients. Effectively managing these nutrients is critical for successful crop production, particularly in the nutrient poor, coarse-textured soil of Coastal Plain, VA. As nutrient availability and both global and regional agronomic practices change in the face of societal and technological advances, our nutrient management practices should be continually investigated and updated to ensure maximum efficacy and sustainability of current and future food production.

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Chapter 2: Novel Fertilizer as an Alternative for Supplying Manganese and Boron to Soybeans

Abstract

Soybean (*Glycine max*) commonly experience Mn deficiencies in the coarse-textured soils of Coastal Plain Virginia, especially under high pH conditions. The objective of this study was to investigate the ability of a novel coated fertilizer to provide Mn and B to soybeans in soils where Mn deficiency is common and B deficiency, although far less common than with Mn, is possible. A 60-d greenhouse experiment was conducted with three treatments: control, uncoated KCl, and Mn + B coated KCl applied to Bojac and Dragston sandy loams. Soil and whole plant tissue samples were collected 2, 7, 14, 30, and 60 days after germination. Bojac and Dragston soils treated with the coated KCl contained 12.0 mg kg^{-1} and 15.8 mg kg^{-1} more Mehlich 1 – Mn, 21.7 mg kg^{-1} and 23.0 mg kg^{-1} more Mehlich 3 Mn, and 4.5 mg kg^{-1} and 4.6 mg kg^{-1} $CaCl_2$ – Mn than the control and uncoated KCl, respectively. Coated KCl increased above-ground tissue Mn by 42.9 mg kg^{-1} compared to the control and the uncoated KCl treatments in the Bojac soil, while the Dragston soil showed no significant differences in Mn tissue concentration between treatments. Above-ground tissue Mn was 30 – 100 mg kg^{-1} less in the Dragston soil than the Bojac, probably due to greater organic matter which chelates Mn, hence keeping it less plant available. Boron concentrations did not differ in plant tissue or soil, regardless of extraction method. Results indicate that the coated KCl product could consistently provide increased Mn concentration in acidic sandy soils despite varying levels of organic matter, but is not effective for B.

Introduction

Soybean (*Glycine max*) is the principle oilseed crop grown in Virginia (VDACS, 2013). The majority of soybean production occurs on the eastern side of the state in the Coastal Plain region, where coarse textured soils are common (Caffarelli et al., 2014; Johnson et al., 2008). Crop sensitivity to nutrient concentrations varies with crop and nutrient, with some crops impacted more by certain nutrients. Soybean is sensitive to Mn deficiency, which can cause reduced yields. Micronutrient deficiencies are typically most common in leached, sandy soils, organic soils, soils with intense cropping, higher pH soils, and eroded soils (Brady and Weil, 2008; Maathuis and Diatloff, 2013). The three most common micronutrient deficiencies in Virginia are Zn, Mn, and B, with the majority of Mn deficiencies occurring in soybean (Maguire and Heckendorn, 2018).

Soil pH and redox potential greatly affect Mn availability (Habibah et al., 2014; Hawkesford and Barraclough, 2011; Sparks, 1996; Kabata-Pendias, 2011; F. Rivera-Becerril et al., 2013; Schulte and Kelling, 1999). While the acidity of Coastal Plain soils lends to a reduction of Mn-oxides, sandy texture allows for the majority of plant-available Mn to be leached from the soil with little remaining in the root zone leading to plant deficiency. Under waterlogged or low pH conditions (pH < 6), plant available forms of Mn increase (Havlin et al., 2014; Sparks et al., 1996). Under oxidized or high pH conditions (pH > 6), Mn becomes less available for plant uptake (Havlin et al., 2014; Sparks, 1996). Soils with excessive water content and poor aeration have increased soluble Mn^{2+} due to increased reducing conditions (Havlin et al., 2014). Upon being released from parent material through weathering processes, Mn is quickly converted into Mn-oxides, following similar trends seen with Fe (Kabata-Pendias, 2011). The most readily plant available form of Mn, Mn^{2+}, rapidly binds to oxygen under oxidizing and high pH conditions which makes it less plant available and can lead to nutrient deficiencies in nearby plants (Kabata-Pendias, 2011).

Boron also tends to be more available in acid soils, and B deficiencies can occur in sandy soils as B is easily leached (Brady and Weil, 2008; Hawkesford and Barraclough, 2011). Under high pH conditions (pH: 7 – 9), boric acid is rapidly bound to the surfaces of clay particles and Fe – and Al – oxides through the exchange of OH – groups (Brady and Weil, 2008). At pH < 7, boron is typically found in its plant available form of boric acid. In soils, B – distribution is heavily influenced by physicochemical properties of the soil, the mineralogical composition of the parent material, and the migration characteristics of the various B – forms (Kashin, 2012). Soil texture also plays a role in the B-content, with the greatest concentrations occurring in loams and the least in sandy soils (Kashin, 2012).

To overcome deficiencies, inorganic sources, synthetic chelates, and natural organic complexes comprise the three main classes of micronutrient fertilizer sources (Mortvedt, 1991). The most commonly used Mn – fertilizers are manganese sulfate ($MnSO_4 \cdot 3H_2O$) and chelated Mn (e.g., Mn-EDTA and Mn-DTPA) (Martens and Westermann, 1991; Schulte and Kelling, 1999). In cases where Mn-fertilizers are required, foliar or band application are commonly recommended, with the micronutrients often mixed in with NPK fertilizers or pesticide products (Martens and Westermann, 1991; Mortvedt, 1991; Schulte and Kelling, 1999; Mullins and Heckerdorn, 2009). While broadcast application to soils can be used, potential Mn-fixation to soil particles is likely (Schulte and Kelling, 1999). Boron fertilizers are either soil applied via broadcast application or through foliar application (Martens and Westermann, 1991). The common sources for B fertilizers include boric acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$), and sodium pentaborate (B_5NaO_{15}) (Martens and Westermann, 1991; Mortvedt, 1991).

The three main methods for combining micronutrients with NPK fertilizers are incorporation, bulk blending, and coating onto granular fertilizers, with bulk blending and coatings becoming increasingly popular (Mortvedt, 1991). Additionally, using new slow-release compounds as alternative sources has increased in recent years. Bhattacharya et al. (2007) investigated the development of novel slow-releasing Fe-Mn compound and found up to 45.6% yield increases in the number of chilies (*Capsicum frutescens*) while requiring less Fe and Mn due to greater use efficiency.

If Mn and B could be coated on a common fertilizer, it would reduce farmer workload by removing the need for additional fertilizer applications throughout the season, saving both money and time. The objective of this study was therefore to investigate the ability of a novel coated fertilizer to provide Mn and B to soybean in soils where Mn deficiency is common and B deficiency can also occur. The hypothesis for this study states that the coated product will provide a noticeable increase in Mn and B concentrations in both the soil and plant tissue.

Materials and Methods

Coated fertilizer product

A 'novel' manganese coated muriate of potash was developed by Whitehurst and Associates Inc. for this research by treating muriate of potash with a proprietary water-soluble B supplying binding composition then adding manganese sulfate monohydrate ($MnSO_4.H_2O$) powder to achieve a composition of 0-0-49 with 0% S, 5.03% Mn and 0.41% B.

Soil collection and greenhouse setup

Two soils were collected from the Coastal Plain of Virginia: a Bojac sandy loam (coarse-loamy, mixed, semiactive, thermic Typic Hapludult) and a Dragston fine sandy loam (coarse-loamy, mixed, semiactive, thermic Aeric Endoqauult). They will henceforth be referred to as *Bojac* and *Dragston*. These two soils were picked based on low soil-test Mn, acidic pH, and previous observations of visible Mn – deficiency and Mn related yield reductions in soybean. Soils were collected to a depth of 15 cm. The collected soil was mixed to ensure uniformity and air-dried for 5 to 6 d prior to use for this study (Table 2.1).

Three fertility treatments (control, uncoated KCl, and Mn + B coated KCl) were implemented, with three replicates of each. All fertilizers were surface applied for each pot. The KCl fertilizers for the uncoated and coated products were applied based on the soil test recommendations of 67.25 kg ha^{-1} K_2O, which resulted in 1.36g uncoated KCl and 1.67g coated KCl applied per pot. The coated KCl applied Mn at a rate of 7.04 kg ha^{-1} and B at a rate of 0.57 kg ha^{-1}. Southern States soybean cultivar SS5711N R2 was planted in pots (15.24 cm x 16.51 cm) filled with soil to a depth of 15 to 17 cm, with 4 to 6 seeds planted at a depth of 2.5 cm. Within 2 weeks of planting, soybeans were thinned to 3 plants pot^{-1}. Each pot was lined with a coffee filter and placed over a plastic catch plate to eliminate nutrient leaching and soil loss, with any collected water being replaced within the designated pot. Pots were maintained at 70% field capacity by weight (0.147 g H_2O g^{-1}; 501.3 g H_2O pot^{-1}) and checked every 2 to 3 days. Field capacity was determined using gravitation drainage method, where the dried soils were measured to a set weight, saturated, and then allowed to drain for 2 days via holes on the bottom of a disposable cup before being weighed again (Bond, et al., 2006). Greenhouse lights were set for 14 h day^{-1} and temperature was set to 24 °C. Total above ground plant tissue, roots, and soil were collected from each pot at 2, 7, 14, 30, and 60 days after emergence, corresponding to the VC (vegetative cotyledon), V1 (first trifoliate), V2 – 3 (second or third trifoliate), V4 (fourth trifoliate), and V6 – V7 (sixth or seventh trifoliate) development stages. At each sampling period, pots were destructively sampled by hand, with aboveground tissue being cut at the soil surface followed by pots being overturned and the remaining soil and root structures being removed. Roots were then gently removed from the surrounding soil.

Soil analysis

Soil samples were air-dried for 3 to 4 days and then sieved with a No. 10 (2 mm) sieve prior to chemical analysis. Soil samples were analyzed using three different extractions: Mehlich 1, Mehlich 3, and 0.01*M* $CaCl_2$ extractions. Mehlich 1 extracted Mn and B were determined via the Mehlich I extraction method at a ratio of 5 g soil: 20 ml of extraction solution containing 0.05N HCl and 0.025N H_2SO_4 (Mehlich, 1953). The Mehlich 3 extracted Mn and B were determined via the Mehlich 3 extraction method at a ratio of 2.5 g soil: 25 ml extraction solution containing 0.2N CH_3COOH, 0.25N H_4NO_3, 0.015N NH_4F, 0.015N HNO_3, and 0.001M EDTA (Mehlich, 1984). The $CaCl_2$ extractions used methods specified by Houba et al. (2000) at a ratio of 4 g soil: 40 ml extraction solution. All extractions were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; CirOS VISION model, Spectro Analytical).

Plant tissue analysis

At harvest for the 30 and 60-day sampling periods, above ground tissue and roots were separated by hand and rinsed gently with tap water, weighed, dried in an oven at 40 °C for 3 to 4 days to constant weight, and then weighed again for total dry biomass before being ground using the Thomas Wiley® Cutting Mill. Plant tissue was digested with HNO_3 in a Chem Mars Xpress microwave digester using a 0.5 g subsample of tissue digested in 10 mL of concentrated HNO_3 following the method specified by the manufacturers for soybean meal digestion.

Statistical analysis

Statistical analysis was performed using RStudio software (version 3.2.2) (R Core Team, 2015; Mendiburu, 2016). Two-way ANOVA was conducted by soil for each greenhouse study to investigate Mn and B availability in the soil with significance indicated by p-values < 0.05. Two-way ANOVA was performed by soil type for each greenhouse study for the 30-day and 60-day sampling periods for plant tissue in order to investigate differences in Mn and B plant uptake across treatments. All treatment differences were investigated using post-hoc Tukey's honestly significance difference (HSD) at a significance level of $p < 0.05$.

Results and Discussion

Soil properties

Bojac and Dragston soils had pH values of 6.5 and 6.7, respectively, which is within the agronomic range but greater than the target pH of 6.2 for most crops in Virginia (Table 2.1; Maguire and Heckendorn, 2018). The Bojac soil had greater initial Mehlich 1 – P, greater initial Mn, and nearly identical amounts of initial B versus the Dragston soil. Soil test report values are denoted as being Low (L), Medium (M), High (H), or Very High (VH), with + or – signs being added to specify where they fall within those categories. Values reported as Low means that fertilizer application is required, while values reported as Very High indicate that additional fertilizer application is not recommended or required. According to the Soil Test Recommendations for Virginia, the Bojac soil had very high (VH) Mehlich 1 – P, medium (M) Mehlich 1 – K, Ca, and Mg. The Dragston soil had less Mehlich 1 – P (H), and greater Mehlich 1 – K (H-), Ca (H-), and Mg (VH-) than the Bojac. Additionally, both soils were sufficient for all macronutrients (crop responses are not usually seen with soil levels greater than Low ratings) and both soils showed deficiencies in Mn (Maguire and Heckendorn, 2018). Manganese recommendations for soybeans are based on the soil test Mn as well as the soil pH, as Mn becomes less plant available with increasing pH. For example, a soil test Mn of 4.7 mg kg^{-1} for the Bojac would require a pH of 6.1 or less to avoid deficiency. However, Mn was predicted to be deficient and required supplementation for proper soybean growth at a pH of 6.5. While Mn was deficient in both soils, the B soil levels were sufficient for plant growth, which is always the case for soybeans due to a lack of documentation of deficiency problems with soybean. Boron recommendations are based entirely on the crop code for all crops except alfalfa in Virginia.

The Bojac soil had 10 g kg^{-1} OM while the Dragston soil had 36 g kg^{-1} OM, which are considered Medium and Very High for Virginia soils, respectively (Table 2.1; Maguire and Heckendorn, 2018). The field where the Dragston soil was obtained has been in continuous no-till with a corn-soybean or corn-wheat-soybean rotation for over 15 years, hence a greater OM content. Organic matter is an additional component of soils that is known to influence both Mn and B availability for plant uptake (Andrade et al., 2002; Schulte and Kelling, 1999; Stevenson, 1991). Organic matter plays an important role in the cycle of many micronutrients, particularly the cations which are more readily bound by the organic matter (Stevenson, 1991). The organic fractions of Mn in soil can either be water-soluble or water-insoluble (Stevenson, 1991, Shuman, 1988; Schulte and Kelling, 1999). The application of additional OM to soils has been shown to provide a short-term increase in Mn availability in the soil, under the proper soil conditions (Fujimoto and Sherman, 1948; Shuman, 1988). However, higher levels of OM in soils with good aeration and minimal flooding and water retention can limit the rate of mineralization and lead to a deficit of the micronutrient (Andrade et al., 2002; Sanchez and Kamprath, 1959; Schulte and Kelling, 1999; Stevenson, 1999). While these bound forms are insoluble, they are more available than the inorganic forms, forms still bound to the primary minerals, and being bound helps to reduce nutrient loss due to leaching. However, to become plant available, the cations must be released during microbially-driven oxidation-reduction reactions (Stevenson, 1991).

Changes in soil manganese

Three soil extractions were used in this study and for the Bojac soil the concentration of Mn extracted followed the order Mehlich 3 > Mehlich 1 > 0.01*M* $CaCl_2$ (Fig. 2.1). The Mn concentrations extracted with Mehlich 3 would be expected to be the greatest due to Mehlich 3 being the strongest acid and containing the chelate EDTA to improve micronutrient extraction (Mehlich, 1984). However, Mehlich 1 and Mehlich 3 extracted the same amount of Mn from the Dragston soil (Fig. 2.1). This may be due to the greater amount of OM present in the Dragston soil, as both OM and EDTA have carboxyl groups. Therefore, the EDTA in Mehlich 3 would have competed with OM in the Dragston soil and resulted in the similar extractable Mn as with Mehlich 1 (Stevenson, 1991). Manganese availability is highly correlated with soil pH and is known to be the more readily available at lower pH (Brady and Weil, 2008; Havlin et al., 2014;

Kabata-Pendias, 2011; McGrath et al., 1987). The 0.01*M* $CaCl_2$ extraction resulted in the lowest Mn concentrations in both soils as it is a salt and not an acid like the Mehlich extracts. The reason the three extracts were used was that Mehlich 1 and 3 are common soil tests used in commercial labs in the U.S., while 0.01*M* $CaCl_2$ was designed to approximate soil solution salt concentration. As the 0.01*M* $CaCl_2$ extraction more accurately simulates the salt content of the soil, it may more accurately reflect the soil solution plant nutrients in the soil as opposed to the Mehlich 1 and Mehlich 3 extraction which were designed to estimate nutrient availability over a growing season.

For both soils and all three extractions, there were no differences in extractable Mn between the unfertilized control and the KCl treatment. Previous studies have reported that the use of K – based fertilizers can influence the availability and uptake of micronutrients. Szewczuk and Gudarowska (2009) found that the use of various sources of K – fertilizers had no effect on soil concentrations but did reduce the amount of Mn in the leaf tissue of apple trees (cv. Golden Delicious) when available K was increased from 120 to 200 mg kg^{-1}. Our data indicate that the addition of KCl did not affect Mn extractability by any of the three extracts used; therefore, any differences between control or KCl treatments and the coated product were due to the coating. For all extraction methods, soil treated with the coated KCl showed greater concentrations of Mn at each sampling period for both soils (Fig. 2.1).

Over the 60 days of this study, Bojac and Dragston soils treated with the coated KCl averaged 12.0 mg kg^{-1} and 15.8 mg kg^{-1} more Mehlich 1 – Mn, 21.7 mg kg^{-1} and 23.0 mg kg^{-1} more Mehlich 3 – Mn, and 4.5 mg kg^{-1} and 4.6 mg kg^{-1} more $CaCl_2$ – Mn than the control soils, respectively (Fig. 2.1). The coated KCl approximately doubled the amount of Mehlich 1 and 3 – Mn in soils at each of the five sampling periods, relative to the control and uncoated KCl, for both soils. The increase in Mn from the coated KCl moves the soils out of the deficiency range (< 18 mg kg^{-1} Mehlich 1 – Mn) at a smaller application rate than those recommended for VA (Mullins and Heckendorn, 2009). The VA recommendations are 28.0 – 33.6 kg Mn ha^{-1} for broadcast application, 8.9 – 11.2 kg Mn ha^{-1} for sideband placement, and 0.84 – 1.12 kg Mn ha^{-1} as a foliar spray (Mullins and Heckendorn, 2009). The coated KCl used in this study supplies Mn at a rate of 6.5 kg ha^{-1} and was applied via broadcast application, which well below the Mn rate recommended by Mullins and Heckendorn (2009). This may be due to the fact that recommendation rates have not been reevaluated since their original publication in 1980 or that field conditions differ from the greenhouse conditions used in this study.

While our Mehlich 1 – Mn values for these soils differed, the overall trends matched those found in a comparable study on the effect of Mn fertilizer rates on soybean yield by Alley (1975). Alley (1975) added Mn, as $MnSO_4{\cdot}H_2O$, at a rate of 5.0 mg kg^{-1} and increased Mehlich 1 – Mn from 1.4 to 17.5 mg kg^{-1} within 27 days after planting, an increase of 16.1 mg kg^{-1}. This is similar to the increase seen for our study at 30 days, where a Mn application of 7.04 kg ha^{-1} (4.9 mg kg^{-1}) increased Mehlich 1 – Mn by 11.1 mg kg^{-1} in the Bojac soil and 15.7 mg kg^{-1} in the Dragston soil. The significant difference in Mn between the added fertilizer and the soil concentrations seen in both Alley's and the current study might be a reflection of the influence of pH on Mn availability. In Alley's study, his results revealed a decrease in soil pH with increasing Mn rates, with pH levels dropping from 6.0 with the control (0 mg Mn kg^{-1}) to 5.7 at the 5 mg kg^{-1} broadcast application rate. Citing Hemstock and Low (1953), Alley suggests that the decrease in pH associated with the Mn application stems from an increase in H^+ produced by the hydrated Mn form. The decrease in pH would then limit the rapid oxidation of Mn, resulting in much greater Mn soil concentrations than can be attributed solely to the amount applied. Rich

(1959) investigated the influence of various soils factor on Mn-deficiency in peanut (*Arachis hypogaea*), which shares soybean's sensitivity to Mn availability in Coastal Plain soils of Virginia. His study found that sandy soils that produced Mn-deficient peanuts had average exchangeable Mn concentrations of 2.8 – 7.1 mg kg^{-1} Mehlich 1 – Mn and averaged 13.6 g kg^{-1} OM. The Bojac soil, which has similar OM content, had slightly greater Mn concentrations in the control and uncoated KCl treated soils. However, the increase in soil Mn by the coated KCl would still be sufficient to correct Mn deficiency in these soils (Maguire and Heckendorn, 2018).

An interaction between sampling day (time) and treatment on nutrient concentrations occurred for both soils and across all extraction types. This was because the extractable Mn for the coated KCl changed with time, while there were no significant changes in extractable Mn for the other two treatments. For both soils, changes in Mehlich 1 and Mehlich 3 – Mn with time for the coated KCl were inconsistent, relatively small, and therefore not always significant. However, Mn concentrations from the coated KCl remained significantly greater than the other treatments at each time period, despite the changes seen over time. For the coated treatment, the greatest change with time was with the 0.01*M* $CaCl_2$ extractable Mn for both soils, showing that the soil solution Mn concentration decreased as the soybean plants grew. These decreases in 0.01*M* $CaCl_2$ – Mn from Day 2 to Day 60 were substantial, dropping from 10.0 to 3.3 mg kg^{-1} (67%) in the Bojac soil and from 7.9 to 1.7 mg kg^{-1} (78%) for the Dragston soil. Although these were substantial reductions in 0.01*M* $CaCl_2$ Mn on a percentage basis, they were relatively small compared to the amount of Mn still extractable by Mehlich 1 and 3 after 60 days (Fig. 2.1).

There have been conflicting reports on the state of residual Mn in the soil. Many reports show that Mn has a short residence time lasting between 3 – 4 weeks long, which is one of the key reasons broadcast application is not usually recommended for Mn (Gettier et al., 1984;

Mullins and Heckerdorn, 2009; Sanchez and Kamprath, 1959). However, the results in this experiment show that the Mn concentrations in the sandy soils used exhibit only slight variations for the entire 60-day experiment. The lack of fluctuation in soil Mn in the study may be due to the elimination of leaching losses through the use of plastic catch-plates.

Changes in soil boron

No significant differences in B concentrations were found among treatments or over time across all extractions in the Dragston soil and for the Mehlich 1 extraction in the Bojac soil (Fig. 2.2). Average soil B concentrations for the Bojac soil were as follows: 1.24 mg kg^{-1} Mehlich 1, 0.17 mg kg^{-1} Mehlich 3, and 0.14 mg kg^{-1} $CaCl_2$. For each extraction method, Dragston soils had greater amounts of B than the Bojac, with Dragston concentration averages of 2.61 mg kg^{-1} Mehlich 1 – B, 0.37 mg kg^{-1} Mehlich 3 – B, and 2.93 mg kg^{-1} $CaCl_2$ – B. According to Mengel (1980), soybean require plant uptake of 0.11 B kg ha^{-1}, which is much less than the soil concentrations seen in this greenhouse experiment. Therefore, B sufficiency levels of soybean grown in these Bojac and Dragston soils would likely be met according to that criteria. A study performed by Touchton and Boswell (1975) investigating micronutrient application rates for correcting deficiency in soybeans found that broadcast application rates for soybean should range from 0.28 to 2.24 B kg ha^{-1}, with the optimum range being 1.12 kg ha^{-1}. The application rate from Touchton and Boswell (1975) is greater than what was used in this study because application rates for the coated KCl were based on K recommendations (67.25 kg ha^{-1} K_2O). At that application rate, the coating applied B at a rate of 0.5 kg ha^{-1}. While this rate falls within the recommended range from Touchton and Boswell's study, the lack of significance seen among treatments for soil B concentrations may be that the application rate was not the optimal rate for soybean growth and thus not enough for noticeable treatment differences to occur.

No differences between treatments were found for the Mehlich 3 extraction in the Bojac soil except for the day 60 samples, where concentrations were approximately 0.20 mg kg^{-1} to 0.12 mg kg^{-1} less than the Dragston. However, the ICP used in this analysis has a minimum detection limit equivalent to 0.2 mg kg^{-1}. In both Bojac extractions with treatment differences, the maximum concentration levels did not exceed this detection limit, and the differences may be a result of the inability of the equipment to accurately assess those concentrations. The Mehlich 1 and all extractions for both soils had minimum concentrations at least twice that of the minimum detection limit and showed no significant differences between treatments or over time.

Overall, the lack of difference seen in the soil B concentrations for either soil was likely due to the coated KCl containing only 0.41% B, which provided only 0.58 kg ha^{-1} of B. The B in the coating is a result of the binding agent that holds the Mn on the KCl and was not added for the purpose of addressing B deficiency. Furthermore, boron deficiency is far less common in eastern Virginia soils, where the majority of the state's soybean production occurs and where the soils used in this experiment were collected (Maguire and Heckendorn, 2018).

Plant tissue manganese

None of the plants displayed visible Mn deficiencies in their leaves, which are visible as yellowing of the leaf tissue and interveinal chlorosis (Brady and Weil, 2008; Sharma, 2006). There were no significant differences in total above-ground biomass between treatments, averaging 0.8 and 4.7 g $plant^{-1}$ on the Bojac soil and 3.1 and 7.9 g $plant^{-1}$ on the Dragston soil for the 30 and 60-d sampling periods, respectively. In the Bojac soil, the coated KCl treatments had significantly greater amounts of aboveground Mn at each sampling period (Fig. 2.3; Day 30 and Day 60). There was no significant difference between the control and the uncoated treatments at each sampling period, indicating that any differences in tissue Mn were due solely to the Mn coating. On average, the coated KCl increased tissue Mn by 42.9 mg kg^{-1} compared to the control and the uncoated KCl treatments in the Bojac soil. Above ground tissue Mn was much less in the Dragston soil than the Bojac, probably due to greater OM which is known to chelate Mn and keep it less plant-available (Table 2.1; Stevenson, 1991; Andrade et al., 2002). In the Dragston soil, there were no significant differences in above ground Mn between treatments within or between sampling dates, but the tissue concentrations matched those reported by Gettier et al. (1984) under Mn application rate of 60 kg ha^{-1}. The increase of 42.9 mg kg^{-1} caused by the coated product in the Bojac soil was greater than the total Mn in any tissue samples in the Dragston soil. Rich (1959) found seven factors that correlated to plant Mn content: pH, exchangeable Ca, Mg, Mn, and Na, easily reducible Mn, and cation exchange capacity (CEC).

While the influence of pH, exchangeable and easily reducible Mn and CEC on Mn availability are well documented, Rich (1959) conducted a study showing that Ca concentrations may also affect Mn availability. In his study, Rich discussed that the presence of Ca cations could cause a depression in the plant uptake of Mn due to the similar charges and ionic radii (approx. 0.80 A. for Mn^{2+} and 0.99 A. Ca^{2+}). The Dragston soil contained almost twice as much Ca as the Bojac soil, when combined with the influence of OM and pH, may have resulted in the reduced plant uptake of Mn seen in the Dragston soil. The tissue concentrations seen with the coated KCl were noticeably greater than those seen in a study conducted by Gordon (2007). Plants treated with similar rates of Mn had leaf tissue concentrations between 85 to 95 mg kg^{-1}, compared to the 105 – 126 mg kg^{-1} seen in the Bojac soils (Gordon, 2007). However, the Dragston values were much less, falling between 33.07 – 34.50 mg kg^{-1} Mn for the treated KCl.

For soybean, nutrient accumulation tends to be slowest within the early vegetative stages (approximately 30 days after germination) and faster during the mid-reproductive stages (during full bloom and early seed development) (Harper, 1971; Usherwood, 1998; Bender et al., 2015). Bender et al. (2015) conducted a field experiment investigating nutrient uptake, accumulation, and remobilization in soybeans and found that maximum Mn accumulation rates occurred at the R4 growth stage (mean = 5.28 g ha^{-1} day^{-1}) and that maximum B accumulation rates occurred between the R3 and R5 growth stages (mean = 5.18 g ha^{-1} day^{-1}). In the current study, soybeans were grown for a maximum of 60 days (to allow for adequate biomass develop and to prevent soybeans from become 'pot bound'), and early flowering (R1 and R2 growth stages) was only observed in two pots.

For both soils, all treatments provided sufficient Mn to the aboveground tissues, which is 20 mg kg^{-1} for soybeans (Donohue, 2000). While the minimum sufficiency concentration (20 mg kg^{-1}) were met by all treatments for both soils, the Bojac concentrations were 46.7 mg kg^{-1} greater in the control and uncoated KCl, and 73.8 mg kg^{-1} greater in the coated KCl treatments.

Root Mn between treatments at each sampling period were not different but decreased from Day 30 to Day 60 (69.4 to 43.0 mg kg^{-1}, respectively) in the Bojac soil. This decrease over time may correspond the movement of Mn from the roots to the aboveground tissue, which was reflected in the increase in Mn found in the aboveground tissue. In the Dragston soil, root Mn concentrations differed between treatments at the Day 30 sampling period only, with the coated KCl providing greater amounts of Mn compared to the control and the uncoated KCl (96.3, 71.7, and 64.9 mg kg^{-1} Mn, respectively).

Plant tissue boron

No differences were found between any of the treatments for any time period in the above-ground or root tissue for either soil (Fig. 2.4). Lack of significance was likely due to the high amount of variability within the data, and the relatively low application rate for B as detailed above.

Conclusions

Manganese application rates recommended for soil application range between 20 – 30 kg ha^{-1} for broadcast application and 8 – 10 kg ha^{-1} for side-banded. Based on the data from this study, the coated KCl is a viable alternative source for soil applications that required lower application rates (6.5 kg ha^{-1} Mn) and may counteract Mn deficiency under varying levels of OM. While the product can be a viable source for Mn fertilizers, the low B concentration in the binder did not affect soil or plant B; therefore, may not provide adequate B. This study determined proof of concept that the coated fertilizer can supply Mn to soybeans under greenhouse conditions, but further research to investigate the ability of this fertilizer to supply Mn to soybeans in field conditions is needed.

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Table 2.1. Mehlich 1 - extracted soil properties of the Bojac and Dragston soils used in the greenhouse study.

Name	Soil Texture	pH	P	K	Ca	Mg	Mn	Fe	B	OM
			mg kg^{-1}							g kg^{-1}
Bojac	sandy loam	6.5	70.5	55	425	50	4.7	9.9	0.3	10
Dragston	fine sandy loam	6.7	26	94.5	819	124	3.2	14.8	0.2	36

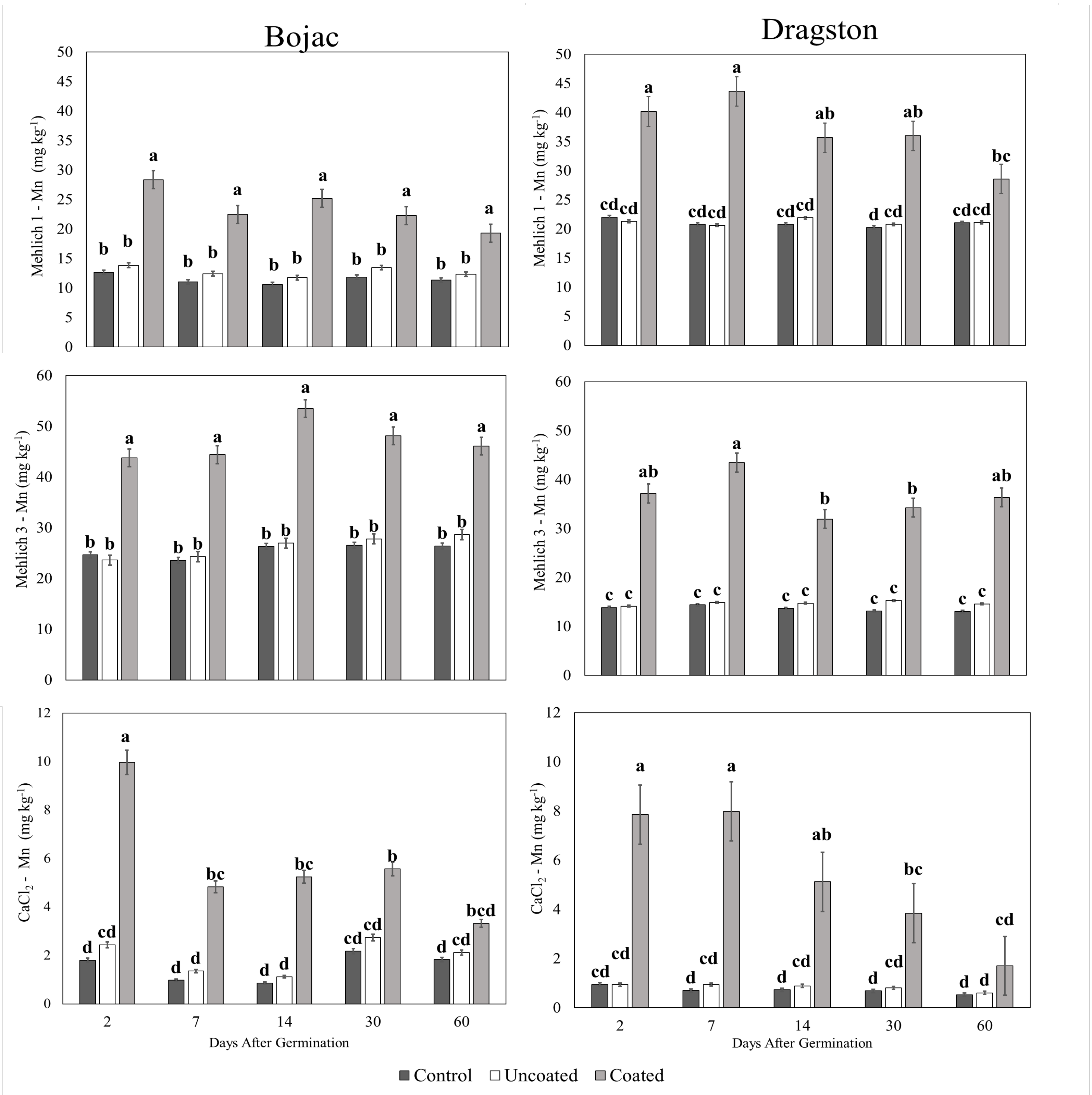

Fig 2.1. Soil manganese concentrations using three soil extraction methods for the two soils used in the greenhouse experiment. Different letters indicate significant differences ($p < 0.05$).

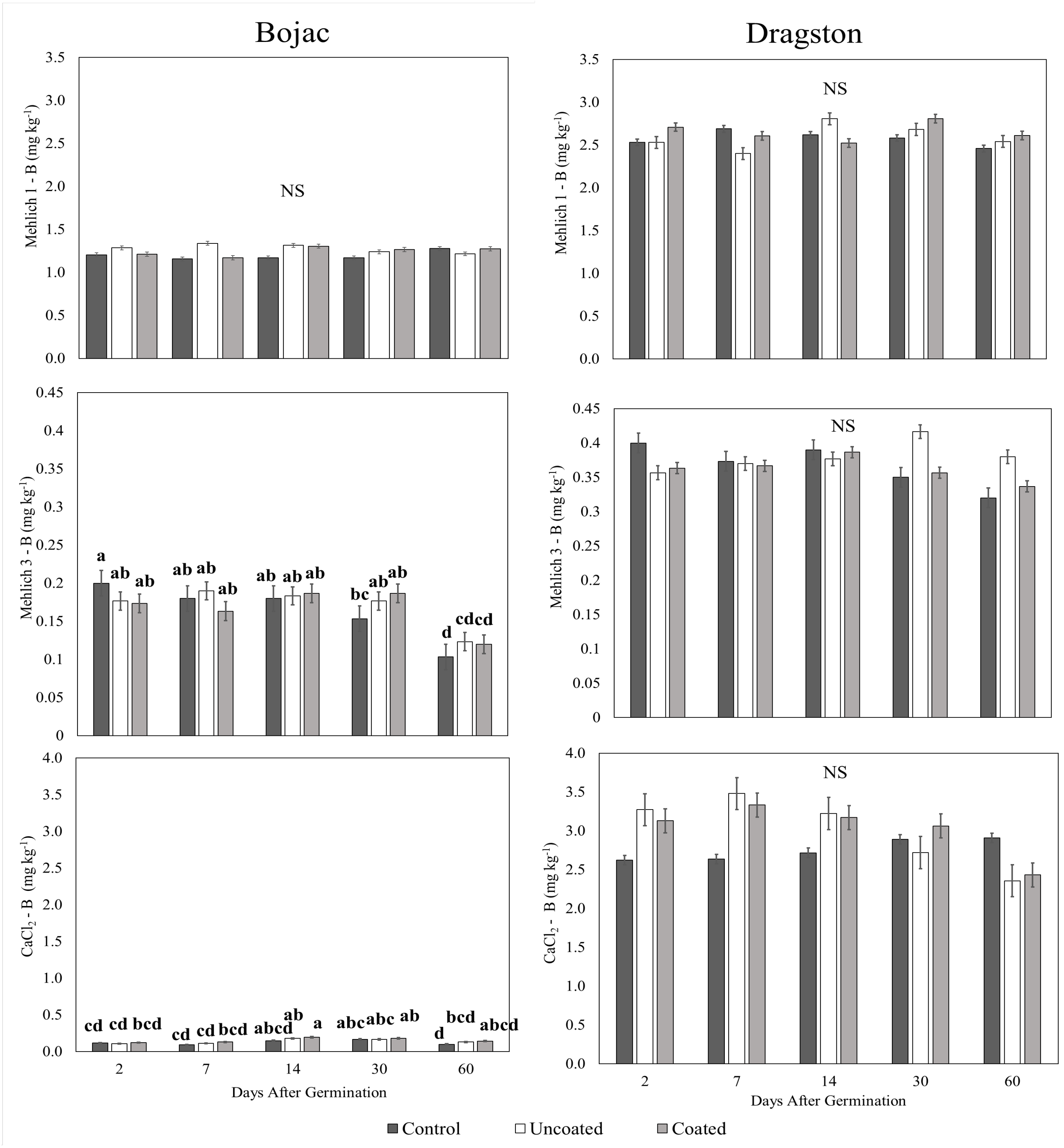

Fig 2.2. Soil boron concentrations using three soil extraction methods for the two soils used in the greenhouse experiment. Bars lacking letters indicated lack of significant difference ($p < 0.05$).

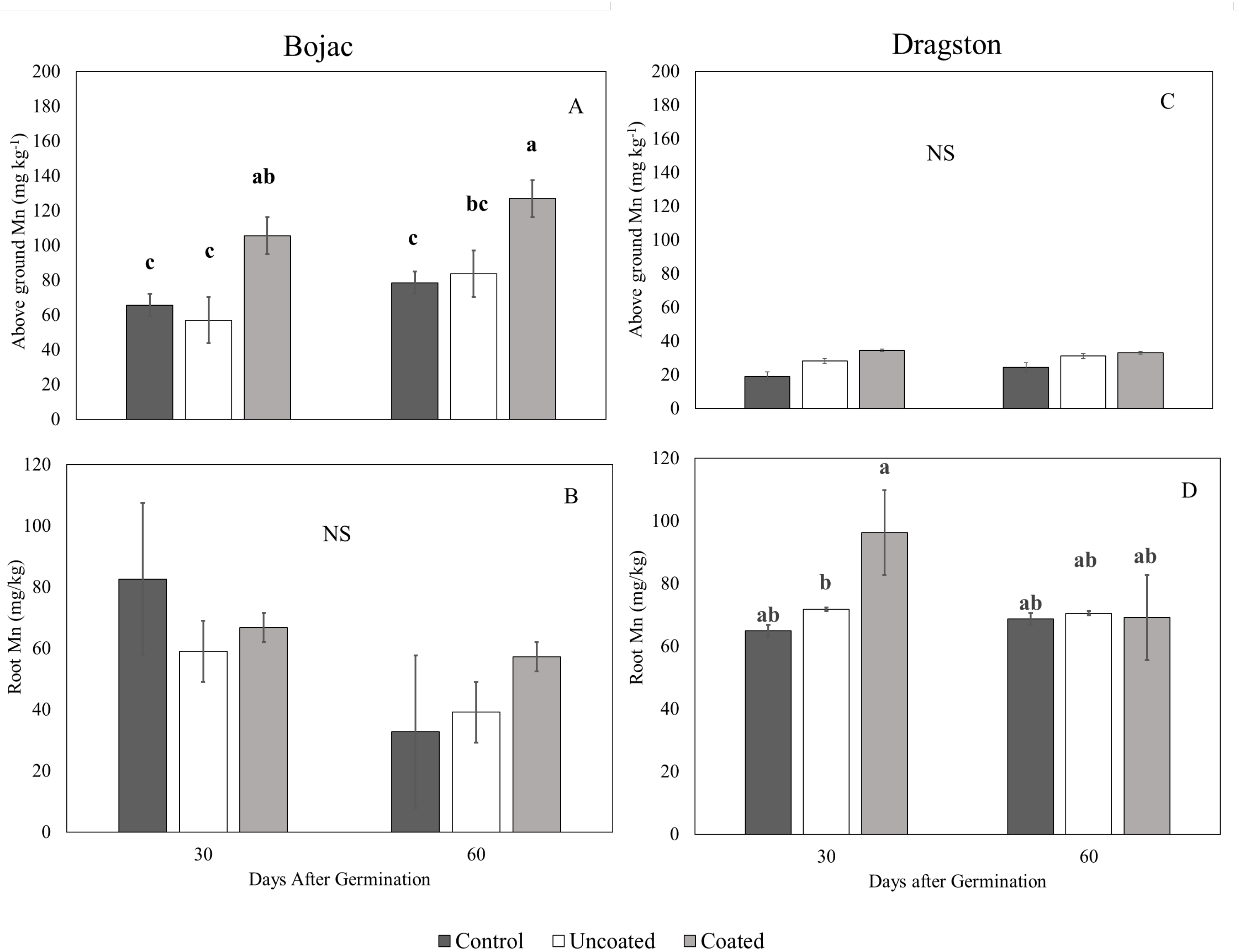

Fig 2.3. Plant tissue manganese concentrations using HNO_3 microwave digestion method. A) Above ground Tissue and (B) Roots from Bojac soil. C) Above ground Tissue and (D) Roots from Dragston soil. ($p < 0.05$). Letters above bars indicate significant differences.

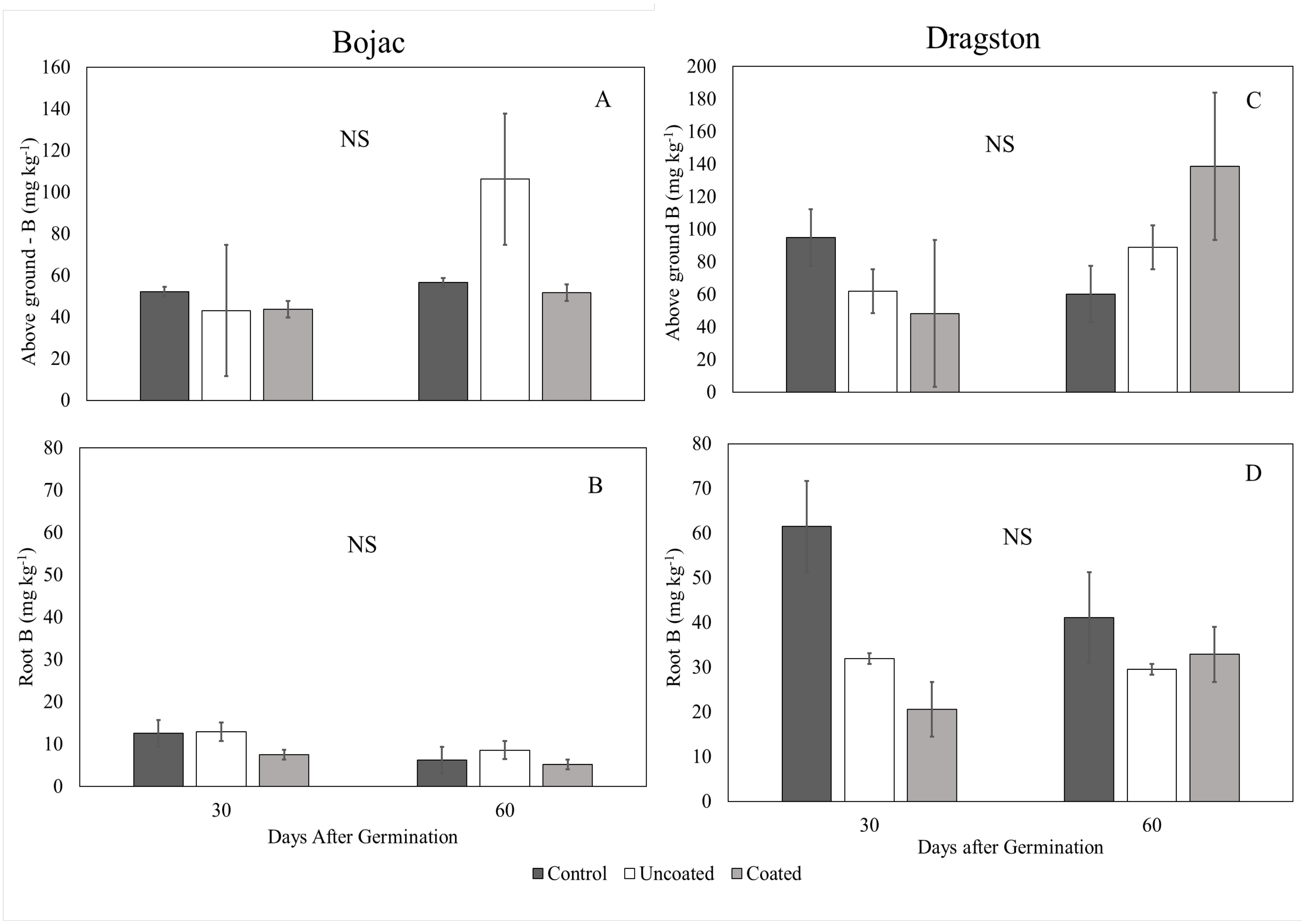

Fig 2.4. Plant tissue boron concentrations using HNO_3 microwave digestion method. A) Above ground Tissue and (B) Roots from the Bojac soil. C) Above ground Tissue and (D) Roots from the Dragston soil ($p < 0.05$). Bars lacking significant letters indicates no

Chapter 3: Field Trials for Novel Fertilizer Supplying Mn and B to Soybeans

Abstract

Virginia soybean (*Glycine max*) production occurs primarily in the coarse-textured soils of the Coastal Plain region, where Mn and B deficiencies are common. In this study, we investigated the ability the novel coated fertilizer product to supply Mn and B to soybeans under field conditions relative to foliar applications. Field studies were conducted in 2016 and 2017 at three locations in the Coastal Plain region of VA. Five treatments in 2016 (control, uncoated KCl, KCl and foliar Mn + B, 5% Mn coated KCl 5% Mn coated Grandal), and an additional 2 treatments in 2017 (8% Mn coated KCl, and 8% Mn coated Grandal) were broadcast applied by hand within 3 days of planting. Soil samples were collected every 4 weeks and tissue samples were collected at the V6 – V8 stage of plant growth. For all growing seasons and locations, there were no significant treatment differences between months for both Mn and B, but average monthly concentrations did fluctuate, possibly reflecting changes in soil moisture and redox status. When averaged across the entire growing season, differences between treatments were inconsistent. At one site, coated KCl provided an additional 37.6 mg Mn kg^{-1} in the soybean tissue compared to uncoated and foliar applications. Under field conditions, environmental conditions such as soil moisture and leaching may mask any consistent treatment effects of the coated products.

Introduction

Currently, soybean (*Glycine max*) is the fourth largest food crop in the world, with the United States being the largest global producer and exporter. Along with cottonseed (*Gossypium* spp.), sunflower seed (*Helianthus* spp.), canola (*Brassica* spp.), rapeseed (*Brassica napus*), and peanuts (*Arachis hypogaea*), soybean is one of the major oilseed crops of the US and accounts for 90% of oilseed crop production for the country (Ash, 2018). In 2017, Virginia produced 26 million bushels of soybeans (av. 2948 kg ha^{-1}), with the majority of that production occurring along the eastern side of the state in the Coastal Plain region (USDA, 2018). Soils in this region are predominately characterized as coarse-textured, acidic soils, and tend to be susceptible to numerous nutrient deficiencies.

In addition to macronutrient demands, soybeans may be highly sensitive to micronutrient deficiencies, particularly manganese. Micronutrient deficiencies are most commonly addressed via foliar application due to their low sufficiency concentrations, poor residence time in the soil, and immobile nature within plant tissue making it more efficient and economical to apply the nutrients directly to leaf tissue on an as needed basis. However, this method requires regular scouting of the affected fields to adequately identify and correct such deficiencies and prevent long-term detrimental effects on yield. While soil application recommendations do exist, they require much greater application rates (22.4 – 33.6 kg ha^{-1} Mn) to address deficiencies compared to foliar application (0.8 – 1.7 kg ha^{-1} Mn) and are not as commonly used (Maguire and Heckendorn, 2018). As an alternative method to address such deficiencies, a novel fertilizer product was investigated as a simultaneous source of K, Mn, and B for soybeans (Baxter et al., 2018 - unpublished). In a greenhouse study, the novel product, consisting of granular KCl coated in a micronutrient powder, provided significantly greater concentrations of Mn in both plant tissue and soils of various organic matter (OM) levels.

Greenhouse studies provide highly controlled environments that allow for the investigation and identification of environmental processes, patterns, and trends. However, the control level provided in greenhouse systems generates results pertaining to ideal conditions, and do not always carry over to the field. In the coarse-textured soils of the Coastal Plain region, one predominate nutrient loss pathway is leaching (Brady and Weil, 2008; Maathius and Diatloff, 2013). Coastal Plain soils are low in clay, and the clay present is mostly Kaolinite resulting in very low cation exchange capacities, generally < 3 cmol kg^{-1}. Therefore, even cationic micronutrients are susceptible to leaching and can easily be lost from the system, leading to deficiencies in crops. In the greenhouse study, soil moisture and leaching potential were controlled to meet optimal growing conditions and prevent nutrient loss from the system. While the study showed strong potential for the novel product to supply noticeably greater amounts of manganese, the results were tailored towards a system without leaching potential.

The objective of this study was to investigate how the novel fertilizer product performed to supply Mn and B to soybeans under field conditions relative to foliar applications.

Materials and Methods

Coated fertilizer product

A ‘novel’ manganese coated muriate of potash was developed by Whitehurst and Associates Inc. for this research by treating muriate of potash with a proprietary water-soluble B supplying binding composition then adding manganese sulfate monohydrate ($MnSO_4.H_2O$) powder to achieve a composition of 0 g N kg^{-1}, 0 g P_2O_5 kg^{-1}, and 490 g K_2O g kg^{-1} with 29 g S kg^{-1}, 50 g Mn kg^{-1} and 4.1 g B kg^{-1} in 2016 (Year 1). For 2017 (Year 2), an additional version of the ‘novel’ coated muriate of potash was developed following the same methodology but with a final composition of 0 g N kg^{-1}, 0 g P_2O_5 kg^{-1}, and 420 g K_2O g kg^{-1} with 46 g S kg^{-1}, 78 g Mn kg^{-1} and 6.4 g B kg^{-1}.

Field site setup

A two-year field study was conducted in the Coastal Plain region of Virginia at 3 sites per year: the Eastern Shore Agricultural Research and Extension Center (AREC), the Tidewater AREC, and a farm-based site in Prince George, VA (total: 60 plots; 0.0056 ha $plot^{-1}$; rows spaced 25.4 to 38.1 cm apart). Soil types were a Bojac sandy loam (coarse-loamy, mixed, semiactive, thermic Typic Hapludult) at the Eastern Shore AREC, a Dragston fine sandy loam (coarse-loamy, mixed, semiactive, thermic Aeric Endoqauult) at the Tidewater AREC, and a Bonneau loamy sand (loamy, siliceous, subactive, thermic Arenic Paleudults) at Prince George. The Eastern shore AREC was a tomato-soybean or corn-soybean rotation, with conventional tillage. The field at Tidewater AREC was continuously no-tilled with a corn-soybean or corn-wheat-soybean rotation for over 15 years. The field containing the Bonneau loamy sand was part of a soybean-wheat double-crop system. Planting dates differed between sites and years due to different management systems and precipitation levels. Planting did not occur until mid-late June at the Bonneau site because it was double-cropped with winter wheat. In 2017, the Bojac also experience delayed planting due to heavy rainfall in late May – early June causing the soils to be too wet.

Experiments followed a randomized complete block design consisting of 5 treatments (Control, Uncoated KCl, Coated KCl [5% Mn], KCl and Mn + B foliar application, and Grandal (filler) with Mn + B coating [5% Mn]) replicated 4 times per site. In 2017, two additional treatments were added (Coated KCl [8% Mn] and Coated Grandal [8% Mn]; 84 plots; 0.0056 ha plot^{-1}). The Grandal was the fertilizer filler used by a local fertilizer blender and was coarse limestone. To make the coated Grandal treatments, analysis was adjusted to an equivalent volume using bulk density (1563 kg m^{-3}) resulting in 1 g coated KCl: 1.4 g coated Grandal to achieve the same amount of Mn and B for each product. Fertilizer application rates were based on Virginia Cooperative Extension Soil Test Recommendations for Virginia from K soil test levels (Maguire and Heckendorn, 2018). Uncoated and coated KCl treatments were applied based on the same applications rates of 56 kg ha^{-1} K as was used in the greenhouse study, resulting in 6.8 kg Mn ha^{-1} and 0.57 kg B ha^{-1} for the 5% coated KCl and 12 kg Mn ha^{-1} and 1.02 kg B ha^{-1} for the 8% coated KCl (Baxter, 2018 – unpublished; see chapter 2). The Bonneau site received application rates of 154 kg ha^{-1} K. Foliar application rates were based on the Virginia Cooperative Extension Soil Test Recommendations for Virginia, with Mn being applied at a rate of 1.1 kg ha^{-1} and B at a rate of 0.5 kg ha^{-1} (Mullins and Heckendorn, 2009). Foliar application consisted of BRANDT Sequestar® (6% Mn) and Borax (11% B) diluted in water at a ratio of 1 pt of nutrient solution: 20 gallons of H_2O to achieve the desired application rates specified above.

Apart from the foliar application, all treatments were broadcast applied by hand near the time of planting. Prior to treatment application, soil samples were collected from each field site from 0-15 cm, 15 – 30 cm, 30 – 46 cm, and 46 – 61 cm. After planting and treatment applications, soil samples were collected to a depth of 15 cm from each plot every 4 weeks until the sites were harvested. Foliar application (once per season) occurred between the late vegetative stages (V6 – 8) and early reproductive stage (R1) using a backpack sprayer. Tissue samples were collected at the late vegetative stages (V8) following Virginia Tech sampling protocol (the uppermost trifoliate of +25 plants plot^{-1}, excluding petiole) (Abaye et al., 2000). At harvest, subsamples of seed were collected from each plot and analyzed for protein and oil.

Soil analysis

Soil samples were air-dried for 3 to 4 days and then sieved with a 2 mm sieve prior to chemical analysis. Soil samples were analyzed using three different extractions: Mehlich 1, Mehlich 3, and 0.01*M* $CaCl_2$ extractions. Mehlich 1 extracted Mn and B were determined via the Mehlich 1 extraction method at a ratio of 5g soil: 20 ml of extraction solution containing 0.05N HCl and 0.025N H_2SO_4 (Mehlich, 1953). The Mehlich 3 extracted Mn and B were determined via the Mehlich 3 extraction method at a ratio of 2.5g soil: 25 ml extraction solution containing 0.2N CH_3COOH, 0.25N H_4NO_3, 0.015N NH_4F, 0.015N HNO_3, and 0.001M EDTA (Mehlich, 1984). The 0.01*M* $CaCl_2$ extractions used methods specified by Houba et al (2000) at a ratio of 4g soil: 40ml extraction solution. All extracts were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; CirOS VISION model, Spectro Analytical) at the Soil Testing Laboratory at Virginia Tech.

Rainfall and precipitation data

Precipitation data was collected for both years at all sites using the Eastern Shore AREC weather station and Farmlogs.com. Nutrient concentrations were compared to monthly rainfall events to investigate potential correlations.

Plant tissue analysis

Upon collection, leaf tissue was weighed for wet biomass, dried in an oven at 40 °C for 3 to 4 days to constant weight, and then weighed again for dry weight before being ground using the Thomas Wiley® Cutting Mill through a 2 mm sieve/ screen. Plant tissue was digested with HNO_3 in a Chem Mars Xpress microwave digester at a ratio of 0.5g of tissue sample:10ml of concentrated HNO_3 following the method specified by the manufacturers (CHEM Mars) for soybean meal digestion. Soybean seed, adjusted for 13% moisture, was analyzed for oil and protein content by Near-Infrared Spectroscopy (NIR).

Statistical analysis

Statistical analysis was performed using JMP software (JMP Pro 13). Two-way ANOVA was conducted by soil type for each year of the field study to investigate nutrient availability in the soil and in plant tissue with significance indicated by p-values < 0.05. Two-way ANOVA was performed within each site (block effect) between months and between treatments summarized over the entire growing season. Two-way ANOVA was conducted between treatments for plant tissue within each site in order to investigate differences in tissue concentrations across treatments. All treatment differences were investigated using post-hoc Tukey's honestly significance difference (HSD) at a significance level of $p < 0.05$.

Results and Discussion

Soil properties

The Bojac, Dragston, and Bonneau soils had pH values slightly greater than the target pH of 6.2 for VA soybeans, 6.5, 6.7, and 6.2, respectively (Table 3.1; Maguire and Heckendorn, 2018). However, soil test reports still indicated that Mehlich 1 – Mn was deficient at all three locations. The Bojac soil contained more Mehlich 1 – P and Mehlich 1 – Mn and the Dragston more Mehlich 1 – K and OM. The Bojac and Bonneau soils had 10 g kg^{-1} OM, typical for coastal plain soils, but the Dragston soil contained 36 g kg^{-1}, which was likely due to continuous no-till with high-residue crops. All three soils tested deficient for Mn, while only the Bonneau tested Low for any macronutrients (K) (Maguire and Heckendorn, 2018). The plant availability of Mn for the Mehlich 1 extraction is pH dependent, with recommendations for manganese being made if the soil pH is equal to or greater than the following equation (Maguire and Heckendorn, 2018):

$$pH \geq (0.22733 \text{ x Mn ppm}) + 5.1$$

Changes in soil manganese throughout the growing season

There were no significant differences between treatments within sampling date; therefore, data were combined across treatments to show variations in extractable Mn by sampling date (the fourth week of each month) throughout the growing season (Fig. 3.1). When data for each treatment was averaged across sampling dates, significant treatment differences were revealed (Fig. 3.2). Mehlich 1 and Mehlich 3 followed similar trends, so only Mehlich 3 data is shown to reduce repetition. Between the different extraction methods, Mehlich 3 – Mn levels were the greatest followed by Mehlich 1 – Mn and then $CaCl_2$ – Mn. This would be expected as the Mehlich 3 extractant contains stronger acids than Mehlich 1 and also contains EDTA to help chelate, and hence extract, micronutrients (Mehlich, 1984; Norvell, 1991). This extraction differential also occurs for other nutrients, as Maguire and Sims (2002) reported Mehlich 3 – P was approximately double Mehlich 1 – P, and both were an order of magnitude greater than $CaCl_2$ – P.

Greater fluctuations between months were revealed with the $CaCl_2$ – Mn extraction compared to Mehlich 3 – Mn, which is to be expected due to differences in the acidity and extraction strength between the two methods. The combination of low pH and EDTA allows the Mehlich 3 extractant to access Mn that is more difficult to reduce compared to that of the $CaCl_2$ and thus, will produce greater solution concentrations upon analysis. Although extracting much lower amounts of soil Mn, the 0.01*M* $CaCl_2$ extraction is a good reflection of true nutrient availability within the soil due to having a similar ionic strength as the majority of soils and its lack of alteration to the soil's pH (Houba, 2000).

The Bojac soil had noticeably greater soil Mn across all three extractions in 2016 and for Mehlich 3 – Mn in 2017 compared to the other two sites (Fig. 3.1). In 2016, Bojac soils contained an average of 34.2 mg kg^{-1}, 6.2 mg kg^{-1}, and 1.7 mg kg^{-1} of additional Mn for the Mehlich 3, Mehlich 1, and 0.01*M* $CaCl_2$ extractions respectively. In 2017, Bojac had 9 – 24 mg kg^{-1} of Mehlich 3 – Mn greater than the other two sites (Fig. 3.1). For the remaining two soils, Mehlich 3 – Mn ranged from 8.1 – 17.6 mg kg^{-1} (Dragston) and 11.5 – 32.1 mg kg $^{-1}$ (Bonneau) (Fig. 3.1). For 2016, there were significant increases of 5.6 – 11.1 mg kg^{-1} in Mehlich 3 – Mn within two months of planting for all three sites, after which they remained stable until harvest. For both growing seasons, Mehlich 3 – Mn showed slight increases in soil concentrations within two months of planting, after which concentration levels remained relatively stable across all three locations

Similar to Mehlich 3 – Mn, the Mehlich 1 and $CaCl_2$ – Mn increased over the course of the growing season, before noticeably decreasing by the final month in 2016. All three soils saw increases of 10.7 – 13.3 mg kg^{-1} in Mehlich 1 – Mn (not shown) and of 0.3 – 3.29 mg kg^{-1} $CaCl_2$ – Mn (Fig. 3.1) over the first two months after planting. In 2017, $CaCl_2$ and Mehlich 1 – Mn concentrations were greatest at the time of planting and decreased over the following months at all three sites. For the $CaCl_2$ and Mehlich 1 extractions, soil Mn decreased by 1.5 – 4.8 mg kg^{-1} and by 5.9 – 12.1 mg kg^{-1}, respectively, throughout the course of the growing seasons (Fig. 3.1). The Dragston and Bonneau soils both showed significant increases in Mehlich 1 – Mn in September similar to what was seen in 2016, but this was not seen with the $CaCl_2$ extraction. At all three locations, $CaCl_2$ – Mn concentrations decreased from planting until August, saw slight increases in September, and then reached the lowest concentrations at the time of harvest.

The lack of significant differences between treatments seen throughout the two growing seasons may indicate that environmental factors were masking any potential increase in soil Mn provided by both the 5% and 8% coated KCl. Manganese availability is known to be closely tied to the pH and redox potential of the soil, both of which can be influenced by soil moisture (Brady and Weil, 2008; Marschner, 2012; Rich, 1959). During periods of heavy rainfall or waterlogging, oxygen levels become depleted in the soil and result in reduced conditions. Under such conditions, plant available form of Mn (Mn^{2+}) increases as increased reduction releases oxide-bound forms into soil solution (Haque et al., 2015; Schulte and Kelling, 1999). However, prolonged waterlogged conditions and periods of heavy precipitation can also result in a decrease in soil Mn as it becomes leached from the system, especially in low CEC and high-leaching potential soils as found in our studies (Haque et al., 2015; Rich, 1959).

In their 2015 greenhouse study, Haque et al. (2015) discussed the influence of soil moisture on the concentration and distribution of Mn^{2+} in flooded and non-flooded rice through PVC microcosms. Their results show that for both soil types (spodosol and vertisol), Mn^{2+} concentrations increased after flooding and saturation began and that the flooded systems showed 15 – 50% more Mn^{2+} within 4 weeks of flooding and 75 – 95% more Mn^{2+} within 34 weeks after flooding. Additionally, their study showed Mn^{2+} concentrations dropped by up to 85% during the drying period, with the rate of decline decreasing at depths greater than 7.5 cm. The significant differences in soil Mn concentrations between months seen in our study may be the result of rain events throughout the season that caused periods of saturation and flooding. For both growing seasons, the periods of greatest fluctuation in monthly rainfall occurred between July – October, which corresponds to the periods of fluctuation seen in soil Mn concentrations from the $CaCl_2$ and Mehlich 1 extractions. While regression analysis found no significant correlation between soil manganese concentrations and total rainfall (R^2 = 0.4 – 0.7; Table 3.2), the analysis was based on total monthly rainfall and does not reflect the number or length of rainfall events that may have led to prolonged periods of soil saturation or flooding.

Changes in soil manganese by treatment

While treatment responses were inconsistent throughout the field study, some differences were found. For the Bojac and Bonneau soils in 2016, the foliar application had a greater concentration of Mehlich 3 – Mn than the control or the 5% coated KCL but not the 5% coated Grandal treatment. The foliar treatments also resulted in greater soil concentration than the control for the Dragston soil. (Fig. 3.2). This may have been due to stunted soybeans at the Bojac and Bonneau sites as a result of drought stress, The foliar application during the vegetative stage resulted in much of the foliar application going straight onto the soil surface. Following the foliar treatment, the 5% coated Grandal had the second greatest Mn concentrations at each location, providing an additional 4.4, 1.6, and 2.2 mg kg^{-1} of Mehlich 3 – Mn respectively, compared to the control, uncoated, and 5% coated KCl treatments (Fig. 3.2). For the 0.01M $CaCl_2$ extraction, treatment differences were discerned for the Bonneau site in 2016 with the 5% coated Grandal providing greater concentrations of $CaCl_2$ – Mn compared to the uncoated KCl and the 5% coated KCl. No other treatment differences were determined for any site for both years.

In 2017, differences between seasonal treatment averages were only found at two of the three locations: Dragston and Bonneau. The 8% coated Grandal had the greatest concentration of Mehlich 3 – Mn (+5.91 mg kg^{-1}, Bojac; +2.57 mg kg^{-1}, Dragston; +3.37 mg kg^{-1}, Bonneau), which was greater than the control, uncoated, and 5% coated KCl treatments at the Dragston site, and the control at the Bonneau site (Fig. 3.2). No differences were seen between any of the remaining treatments, or for any of the $CaCl_2$ extractions in 2017.

In a study on similar soils, Alley (1975) investigated the established agronomic practices for correcting Mn deficiency in soybean grown on acidic sandy soils in Coastal Plain Virginia. In his field study, he investigated various application methods and rates, including broadcast (tilled-in) and foliar applications of $MnSO_4$ at rates of 11.2, 22.4, and 44.8 kg Mn ha^{-1} for broadcast and 2.2 kg ha^{-1} for foliar. According to his results, noticeable increases in Mehlich 1 – Mn and easily reducible Mn only occurred at the greatest broadcast application rates and were not seen at the 11.2 kg Mn ha^{-1} rate. In our study, a comparable application rate of 12.4 kg Mn ha^{-1} was provided by the 8% Coated KCl and Grandal products. Following the trends seen in Alley (1975), the lack of significant differences between treatments indicates that the application rates provided by the both the 5% and 8% Coated KCl and Grandal were not large enough to produce noticeable increases in soil Mn.

Previous studies have shown that potassium salts can increase extractable Mn in soils and Mn in plant tissue, which they attribute to increased ionic strength provided by the potassium amendments (York et al., 1954; Westermann et al., 1971; Krishnamurti and Huang, 1992; Tu and Racz, 1995). Although not always significant the opposite consistent trend was observed here, with a reduction in Mehlich 3 – Mn seen for the 5% Coated KCl in both years relative to the 5% coated Grandal. The reason for this effect for Mehlich 3 – Mn was not clear, but no salt effect was seen for the $CaCl_2$ extraction.

Changes in soil boron

There were no changes in soil boron between treatments within sampling date, nor were differences found over time when data were combined across treatments However, when data for each treatment was averaged across sampling dates, some treatment differences were found (Fig. 3.4)**.** Mehlich 3 – B and $CaCl_2$ – B ranged from 0.02 and 0.4 mg kg^{-1} for both years. These concentrations are close to the method detection limit of 0.2 mg kg^{-1}, so any significant differences determined between months may be the result of random error and equipment limitations. As was discussed for Mn, plant-available B depends on soil moisture and weather, soil pH, and soil texture (Abaye et al., 2006). Even more so than with Mn, soil B has shown to be heavily correlated to soil moisture and temperature and tends to be most deficient in cold, dry soils due to decreased decomposition of organic matter (Abaye et al., 2006). The changes in soil B between months seen in both growing seasons are probably a result of the changes in monthly precipitation and moisture status over time, which masked any treatment effects that might have been seen.

When averaged for the entire growing season, treatment differences did occur in 2017. 8% coated KCl and 8% coated Grandal increased Mehlich 3 and $CaCl_2$ – B compared to the uncoated KCl and control (+0.08 mg B kg^{-1}, Mehlich 3; +0.05 mg B kg^{-1} B, 0.01M $CaCl_2$) (Fig. 3.3). However, for all soils and growing seasons, soil B ranged from 0.01 to 0.36 mg kg^{-1}, which falls within the boundary of the detection limit discussed previously. Thus, true trends are difficult to determine.

Plant tissue analysis

In 2016 and 2017, all three sites had tissue Mn concentrations above the minimum sufficiency range for soybeans (20 mg kg^{-1}). This is despite the soil test showing possible Mn deficiency based on the measured Mn concentrations relative to the soil pH as discussed previously. Average tissue Mn concentrations in 2016 were 82.4 mg kg^{-1} for the Bojac, 28.3 mg kg^{-1} for the Dragston, and ranged from 73.8 – 111.9 mg kg^{-1} for the Bonneau soil (Fig. 3.4). Of the three soils, differences in tissue Mn occurred for the Bonneau soil, with the 5% coated KCl increasing tissue Mn by 36 mg kg^{-1} compared to the uncoated KCl and foliar applications. In 2017, no significant differences were seen between treatments at any of the three sites and tissue Mn averaged at 69.6 mg kg^{-1} for Bojac, 27.7 mg kg^{-1} for Dragston, and 81.8 mg kg^{-1} for Bonneau.

A similar trend in tissue concentrations was found between the low and high OM soils in the earlier greenhouse study (Baxter, 2018 - unpublished), and is thought to be the result of the OM complexation of Mn in the high OM soils. Once the OM complex has been formed, uptake of Mn is reduced and ultimately results in lower tissue concentrations (Brady and Weil, 2008; Habibah et al, 2014; Havlin et al., 2014). However, the Bojac and Bonneau sites (both low OM) had greater tissue concentration than indicated by the minimum sufficiency level, indicating a luxury uptake of Mn. Harper (1971) saw similar findings when investigating seasonal uptake and accumulation of nutrients in soybeans. Across five different application rates, his findings showed that increased nutrient uptake occurred when available, but the increased uptake did not impact soybean yield. Additionally, Alley (1975) determined that similar trends were seen in the tissue Mn concentrations, with noticeable increases only occurring at the highest application rates. Tissue concentrations in his study were similar to those found in our study and ranged from 21.9 to 32.9 mg Mn kg^{-1} at the higher OM site (Dragston).

Differences in tissue B were inconsistent between sites for both years. In 2016, significant differences were only seen at the Bonneau site with 5% coated KCl having 39.6 mg kg^{-1} more tissue B than the control and uncoated KCl treatments (data not shown). In 2017the 8% coated Grandal provided 13.4 mg kg^{-1} of tissue B compared to the control, uncoated, and foliar treatments for the Bojac soil. On the Dragston soil, the 5% coated KCl had the greatest amount of tissue B and provided an additional 10.6 mg B kg^{-1} compared to the foliar treatment. For the remaining soils, no treatment differences were seen, and tissue concentrations ranged from 44.6 to 140.1 mg kg^{-1} (2016) and from 42.5 to 55.2 mg kg^{-1} (2017). However, minimum sufficiency concentrations (25 mg kg^{-1}) were met at all sites for both growing years. While his yield values were slightly greater than those seen in this study, Freeborn et al. (2001) found a similar lack of response at boron rates ranging from 0 – 0.56 kg ha^{-1} via foliar applications with similar starting concentrations of 0.1 – 0.2 mg kg^{-1} of soil B. Freeborn argued that soil B concentrations were thus sufficient at those levels when not experiencing drought conditions and that responses to additional B amendments should not be expected. From his conclusions, the lack of significant differences seen in tissue B may be tied to sufficient concentrations in the soil.

Yield and seed quality

For both growing seasons, no differences in yield or seed quality were found between treatments at any site (Table 3.3). However, there were significant differences in yields between the sites, with Dragston soil producing 2743 and 3167 kg ha^{-1} more than the Bojac and Bonneau soil, respectively, in 2016. Differences in yield were likely due to differences in available soil moisture throughout the season. In 2017, the Bojac and Bonneau soils had noticeably better yields compared to 2016, producing an additional 1340 kg ha^{-1} and 1206 kg ha^{-1} respectively.

Soybean quality analysis showed no differences between treatments for any sites and growing seasons. In 2016, soybean oil percentages ranged from 17.6 and 18.9%, and protein percentages ranged from 35.2 to 39.0%. In 2017, oil percentages ranged from 17.4 to 18.9% while protein percentages ranged from 35.0 to 40.9% across all three sites. These values align with average protein and fat percentages for soybean seeds (Ferguson et al., 1991; Bellaloui et al., 2013). The lack of yield and tissue response to both the soil and foliar applied B matches the results seen in numerous additional studies (Freeborn et al., 2001; Reinbott and Blevins, 1995; Touchton and Boswell, 1975).

Conclusion

Despite the results seen in earlier greenhouse studies, the efficiency of the coated product was not sustained under field conditions. The potential increase in plant available Mn with the coated KCl products was mostly likely masked by prevailing environmental conditions such as soil moisture, precipitation, and leaching loss from the system. Additionally, the rate of Mn applied by the coated KCl products (7.04 – 11.26 kg Mn ha^{-1}) is below the currently established agronomic rates of 22.4 – 33.6 kg Mn ha^{-1} for broadcast application. While not the primary objective of the coated product, plant available B was still investigated but had inconsistent trends. The 8% coated KCl and Grandal did occasionally increase soil B compared to the control and uncoated KCl treatments. However, these trends were not reflected in the tissue data. While this study focused on the soybean production systems common in the Mid-Atlantic, Mn deficiency is also a common problem for soybeans grown on more alkaline and calcareous soils. Further research should be conducted to investigate the effectiveness of these novel coated products on these soils as well in order to get a more developed understanding of its potential to address manganese deficiencies.

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Table 3.1 Mehlich 1 - extracted soil properties of the Bojac, Dragston, and Bonneau soils used in the field study.

Name	Soil Texture	pH	P	K	Ca	Mg	Mn	Fe	B	OM
						mg kg^{-1}				g kg^{-1}
Bojac	sandy loam	6.5	70.5	55	425	50	4.7	9.9	0.3	10
Dragston	fine sandy loam	6.7	26	94.5	819	124	3.2	14.8	0.2	36
Bonneau	loamy sand	6.3	30.5	16.5	195.5	42	1.7	14.5	0.1	10

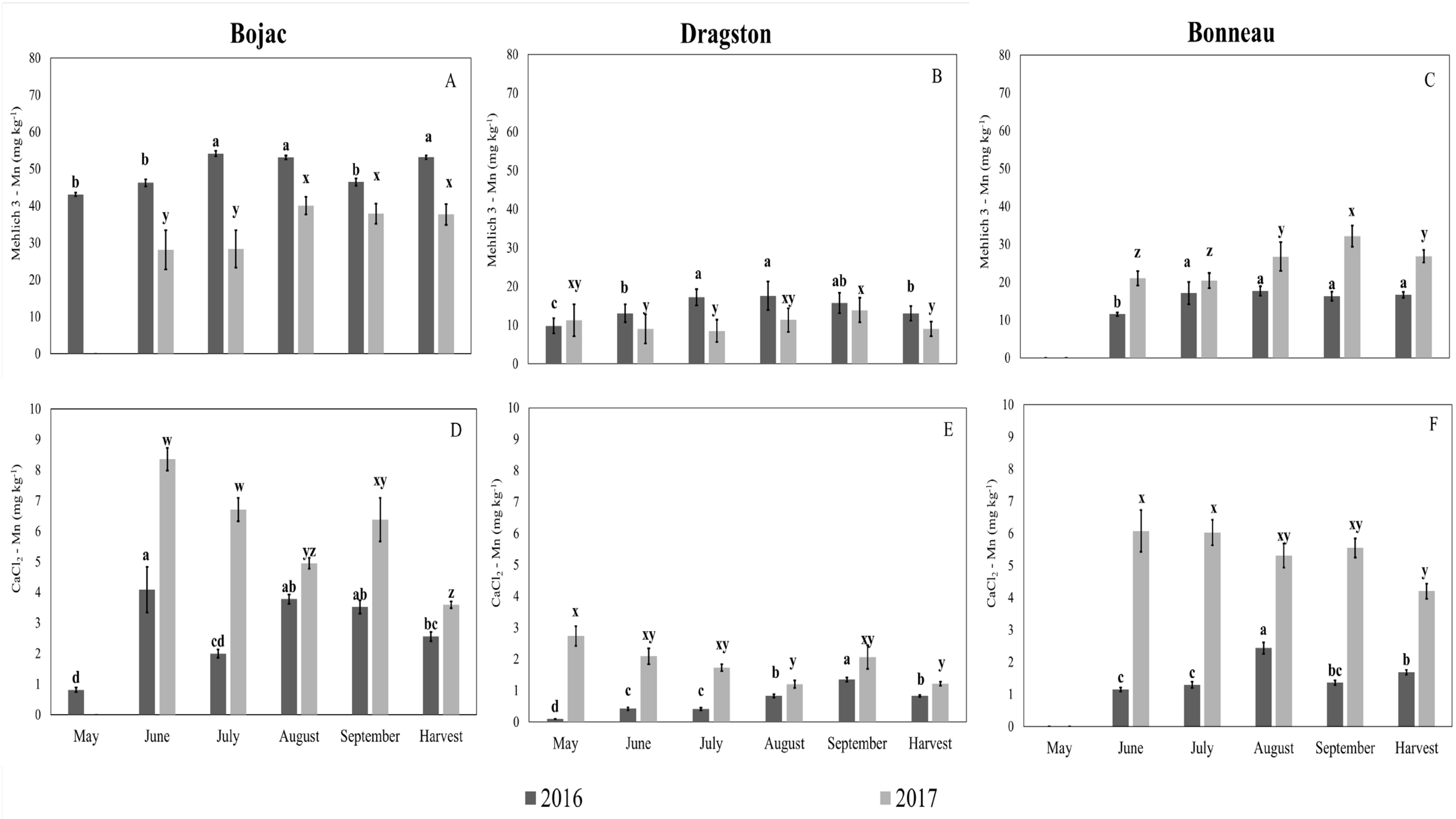

Fig 3.1. Mehlich 3 (A - C) and 0.01*M* $CaCl_2$ (D - F)– extracted manganese over time for the three soils used in the field study. Different letters indicate significant differences ($p < 0.05$). Statistical comparisons were made for letters “a, b, c” and “x, y, z”.

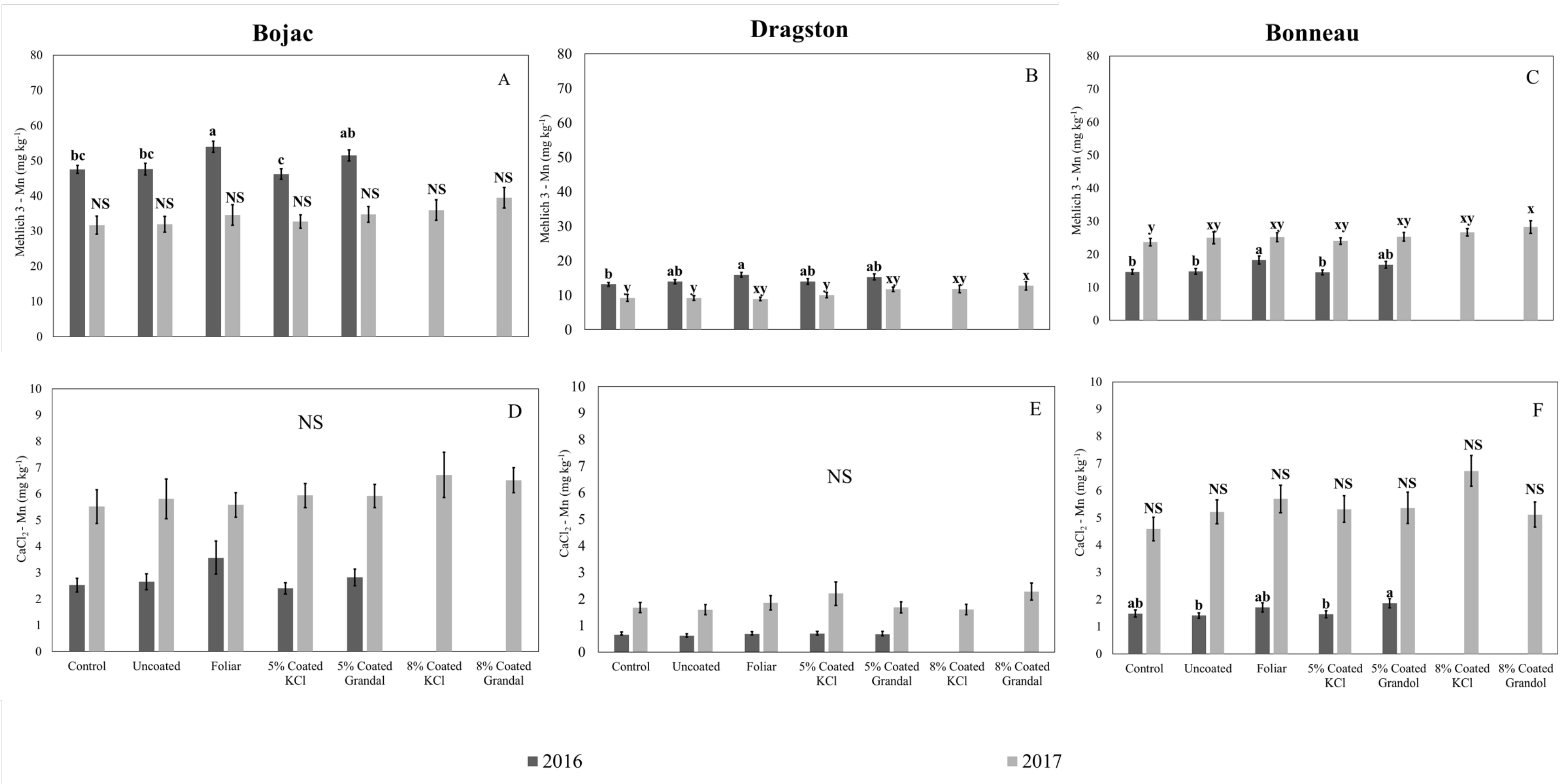

Fig 3.2. Mehlich 3 (A-C) and 0.01*M* $CaCl_2$ (D-F) – extracted manganese between treatments averaged over the entire growing season for the three soils used in the field study. Different letters indicate significant differences ($p < 0.05$). “NS” denotes lack of significant differences.

Table 3.2: Total monthly rainfall for the 3 sites for 2016 and 2017.

	2016				2017		
Month	**Bojac**	**Dragston**	**Bonneau**		**Bojac**	**Dragston**	**Bonneau**
				cm			
May	18.26	9.37	12.19		21.62	13.39	12.34
June	12.01	11.56	14.53		6.32	10.97	11.02
July	15.82	24.51	17.55		8.18	20.57	7.98
August	4.39	2.74	4.04		29.24	17.70	25.15
September	23.09	41.55	19.20		8.92	5.36	10.13
October	18.21	29.62	11.30		13.11	10.24	8.97
November	4.01	2.49	1.80		2.24	6.25	3.96
Total	95.81	121.84	80.62		89.61	90.53	83.03
Average	13.69	17.41	11.52		11.20	11.32	10.38

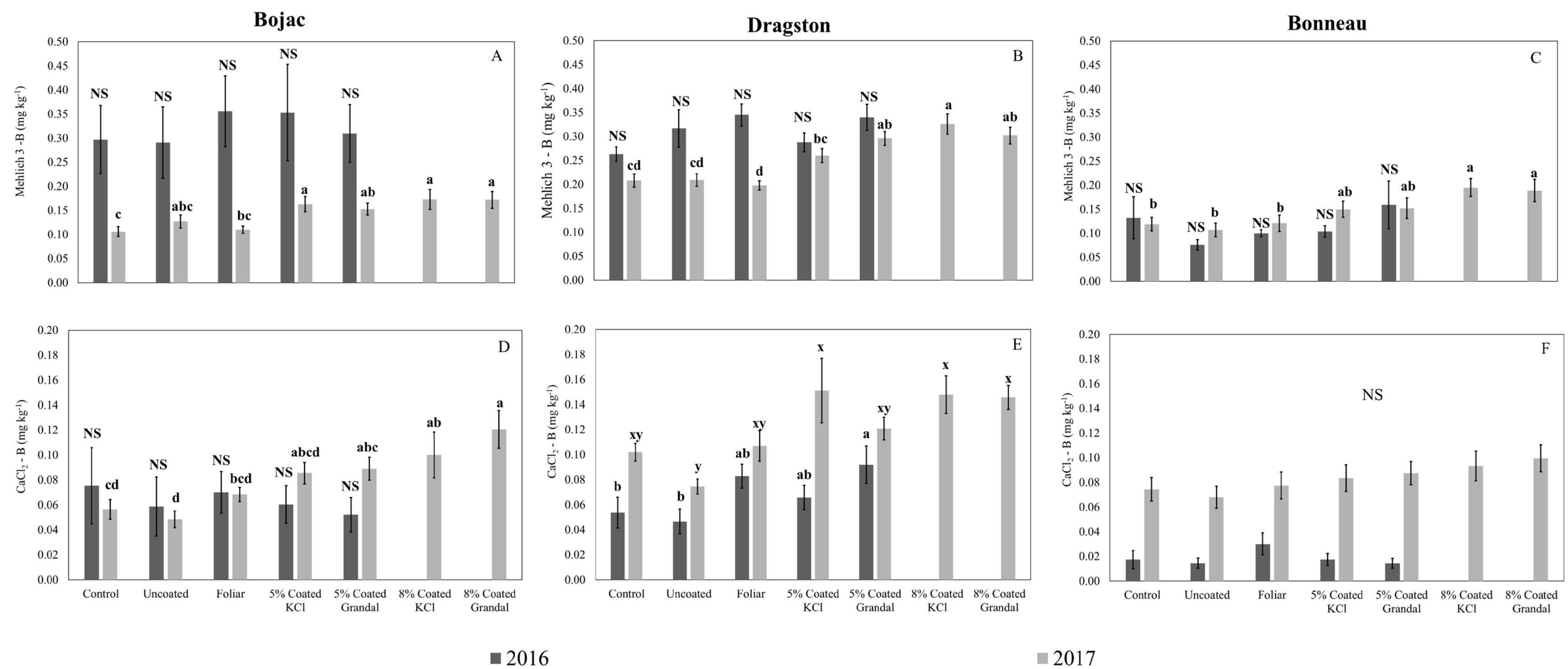

Fig 3.3. Mehlich 3 and 0.01M $CaCl_2$ – extracted boron between treatments averaged over the entire growing season for the three soils used in the field study. Different letters indicate significant differences ($p < 0.05$). “NS” denotes lack of significant differences

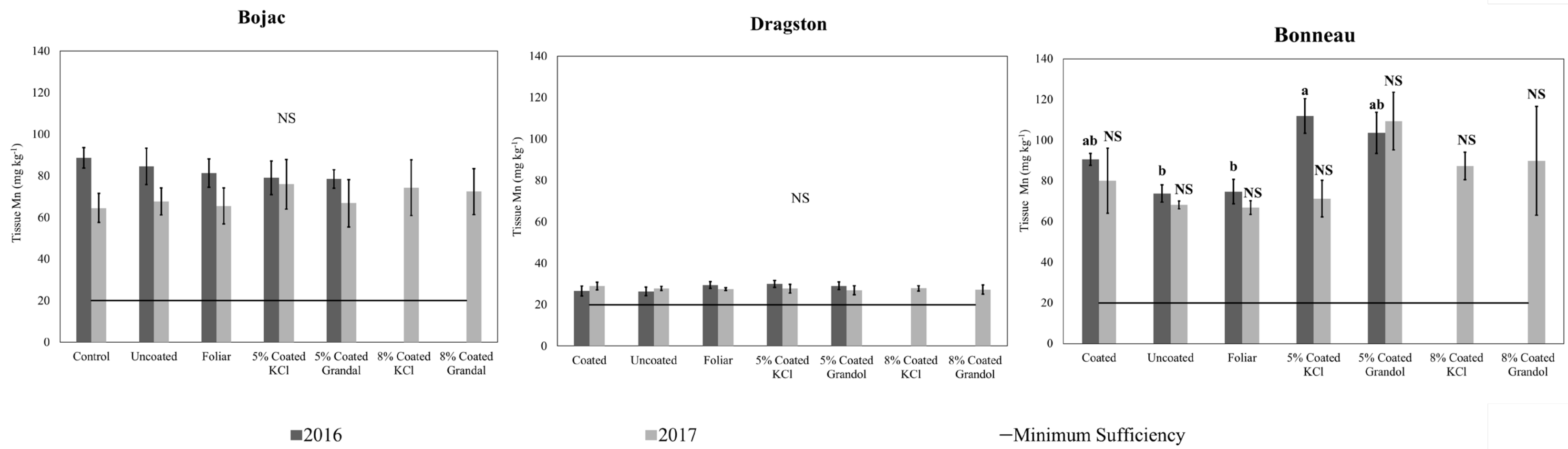

Fig 3.4. Plant tissue manganese concentrations using HNO_3 microwave digestion for the three soils used in the field study. Letters above bar indicate significant differences ($p < 0.05$). The horizontal line indicates the minimum sufficiency concentration in the uppermost trifoliate (20 mg kg^{-1}).

Table 3.3. Soybean yield and quality data for the 2016 and 2017 growing seasons.

	2016			2017		
Soil	Yield	Oil	Protein	Yield	Oil	Protein
	kg ha^{-1}	—— % ——		kg ha^{-1}	—— % ——	
Bojac	1436	18.7	38.9	2803	18.6	40.3
Dragston	4179	17.7	36	2936	18.3	35.6
Bonneau	1012	18.3	35.6	2185	17.8	35.9

Chapter 4: Greenhouse Trials Investigating Various Soil Amendments for Tomato Production

Abstract

Virginia's tomato (*Solanum lycopersicum*) production primarily occurs in the coarse-textured, nutrient poor soils of the Coastal Plain region. The objectives of this study were to investigate the ability of (1) a novel P, S and B coated KCl, (2) the sugar acid chelate glucoheptonate (GH), and (3) combinations of them to provide P, S, and B to tomatoes under varying soil conditions. Three greenhouse trials were conducted to address each objective, with each study lasting 3 weeks after tomatoes were transplanted. Trial 1 compared the coated KCl to the current agronomic rates for P, S, and B for increasing nutrient concentrations in soil and plant tissue. The coated product applied 25 – 50% P, 11.6 – 23% S, and 118 – 240% B relative to the agronomic rate. While the coated product did not increase P, S, and B to the same degree as current agronomic rates, it did significantly increase Mehlich 3 – P and B by 120 – 147 mg P kg^{-1} and 4.7 – 6.2 mg B kg^{-1} compared to the control for both soils. Trends in tissue concentration were more inconsistent, but the coated KCl generally increase tissue P and B by 408 - 1340 mg P kg^{-1} and 29 – 107 mg B kg^{-1} compared to the control for both soils. Trial 2 investigated the effect of different rates (0 – 248 kg ha^{-1}) of GH on soil and tissue nutrient concentrations. For both soil and plant tissue, the only significant differences between rates were with B, which had significant positive correlation to increasing application rates of GH for both soil types and in plant tissue (soil R^2 = 0.54 – 0.74; tissue R^2 = 0.38 – 0.47). Trial 3 combined both products (coated KCl and GH) to investigate potential interaction effects between the 2 amendments and showed that the coated KCl treatments significantly increased soil and tissue P, S, and B

compared to the control and GH. The addition of GH consistently increased soil and tissue B numerically, but not significantly. Ultimately, these trials reveal the potential for the coated KCl to be a multi-nutrient source for tomatoes, but that additional supplements may be required to address crop demands for P and S. Additionally, soil application of GH may help to increase soil and tissue B but does not equal the capacity of granular products to increase nutrient availability.

Introduction

With production on the rise since the 1960's, tomatoes (*Solanum lycopersicum*) have been one of the leading vegetable crops grown around the world. The United States is the second greatest producer of tomatoes and is the global leader in the export and production of processed tomatoes (Nag, 2017). In 2017, the US fresh market tomatoes had a 5-year average 27 million CWT, resulting in a average value of $1.03 billion USD (USDA, NASS, 2018). While farmers in CA produce the most acreage, Virginia is one of the top producers of fresh market tomatoes, with 5-year averages of 864,400 CWT ($38 million) (USDA, NASS, 2018). In VA, the vast majority of production occurs on the Eastern shore peninsula (USDA, 2018). However, sandy loam soils on Delmarva are dominated by acidic, coarse-textured soils with low CEC and high susceptibility to nutrient leaching.

Maintaining adequate nutrition and environmental conditions is critical for successful tomato production. Tomatoes are known to be particularly sensitive to soil N, P, K, S, and B nutrient concentrations as well as environmental conditions, such as soil moisture. Tomatoes are more prone to disease or pest damage if not properly managed throughout the growing season. The importance of primary macronutrient concentrations (N, P, K) has been well-established across all agronomic systems. Based on a 20 Mg ha^{-1} yield, tomatoes generally remove 134.4 kg N ha^{-1}, 44.8 kg P ha^{-1}, and 179.2 kg K ha^{-1} and thus demand thorough management of these nutrients for successful production (USDA-NRCS, 2018; Donohue, 2000; Abaye et al., 2006).

Sulfur and B have garnered increasing attention for their importance in proper tomato growth, particularly for fruit development. The majority of soil S comes from the organic matter (OM) pool and was supplemented via atmospheric deposition prior to the implementation of the Clean Air Act (Abaye et al., 2006; Brady and Weil, 2008; Havlin et al., 2014; McGrath, 2003a).

With atmospheric S deposition decreasing by 75% between 1989 - 2013, soil systems are not being replenished and are developing increasing need for S – supplements by growers (EPA, 2014). In plants, S plays a fundamental role in the production of biochemical components such as amino acids, proteins, and enzymes, and deficiencies can result in stunted and spindly growth, chlorosis, and delayed maturation and fruit development (Abaye et al., 2006; Brady and Weil, 2008; Havlin et al., 2014; Marschner, 2012).

As one of the most common micronutrient deficiencies experienced around the world, B management is also important, especially for fruiting crops like tomatoes. Boron uptake and plant availability is closely tied to soil moisture as it is taken up by plants via transpirational waterflow and can rapidly switch between sufficient and deficient concentrations based on the wetting and drying of the soil (Kemble, 2017; Marschner, 2012). While boron is believed to play a role in a wide array of plant processes, it is most prominently associated with cell division and the formation of fruiting bodies and seeds, making it particularly important for tomato production (Hawkesford and Barraclough, 2011; Kashin, 2012; Maathius and Diatloff., 2013).

Chelating agents have become more common and popular soil amendments used in agriculture today due to desires to control and focus on micronutrients. Common chelating agents used today include DTPA (diethylenetriaminepentaacetic acid), EDTA (ethylenediamine tetraacetic acid disodium salt), and sugar acid chelates such as glucoheptonate, and have shown to be effective for improving availability of cationic micronutrients within soils, especially Fe (Whitehurst, 2017 - unpublished; Shaddox et al., 2016). While numerous studies were conducted investigating DTPA and EDTA, very few studies exist that focus on glucoheptonate, and the majority that do focus solely on Fe – chelation.

In order to get a more thorough understanding of the influence of glucoheptonate on soil nutrient status and plant uptake, we investigated both application rate and potential interaction effects that may be caused by glucoheptonate in a greenhouse setting. The objectives of this study were to (1) investigate the ability of a novel fertilizer to provide P, S, and B to tomatoes under varying soil conditions, (2) investigate the influence of glucoheptonate on soil and plant nutrient status and to determine the optimal application rate across various soil types, and (3) investigate the potential interaction effects between granular fertilizer amendments and the glucoheptonate product on soil and plant nutrient concentrations.

Materials and Methods

Fertilizer products and amendments

A 'novel' coated fertilizer was developed by Whitehurst and Associates Inc. (New Bern, NC) for this study by treating muriate of potash with a proprietary water-soluble B-supplying binding agent, then adding monoammonium phosphate ($NH_4H_2PO_4$) and potassium sulfate (K_2-SO_4) to achieve a composition of 15 g N kg^{-1}, 6 g P_2O_5 kg^{-1}, 49 g K_2O kg^{-1}, 21 g S kg^{-1}, and 5 g B kg^{-1}. Glucoheptonate, CQ 70-50, was supplied by Encee Chemical Sales (Bridgeton, NC 28519).

Soil collection and greenhouse set-up

Two soils were collected from the Coastal Plain of Virginia: a Bojac sandy loam (coarse-loamy, mixed, semiactive, thermic Typic Hapludult) and a Dragston fine sandy loam (coarse-loamy, mixed, semiactive, thermic Aeric Endoqauult) (USDA Soil Survey). They will henceforth be referred to as *Bojac* and *Dragston.* Both the Bojac and Dragston soils were collected from research stations affiliated with Virginia Polytechnic Institute and State University and were picked based on their common susceptibility to nutrient leaching and deficiencies, and for their differing OM levels. Soils were collected to a depth of 15 cm and sieved with a No. 10 (2 mm) sieve prior to chemical analysis. The collected soil was mixed to ensure uniformity and air – dried for 5 to 6 d prior to use for this study (Table 4.1).

Three individual greenhouse trials were conducted between September 2017 and April 2018, with each trial being run twice ("Run 1" and "Run 2"). For each trial, tomato transplants (variety: BHN 602) were grown from seed in a Styrofoam planting tray using Promix-Bio potting media. Seedlings were grown in the greenhouse for 4 – 6 weeks before being transplanted for each trial. Once minimal height of 15 cm was reached, transplants were replanted into 15 x 16.5 cm pots, marking the beginning of each trial, after which they were grown for 3 weeks.

Fertilizer treatments for Trials 1 – 3

Trial 1 compared a nutrient coated KCl fertilizer with individual nutrient recommendation rates for meeting nutrient demands in tomatoes. Treatments will be called "coated KCl" versus "individual nutrient applications" where nutrients were added individually. Trial 1 consisted of 6 treatments (control, uncoated KCl, KCl + B [disodium octaborate tetrahydrate; $Na_2B_2O_{13}\cdot4H_2O$], KCl + S [ammonium sulfate; $(NH_4)_2SO_4$], KCl +P [monoammonium phosphate; $NH_4H_2PO_4$], and P + S + B coated KCl) replicated 3 times on 2 soil types (Bojac and Dragston) for a total of 36 pots. Trial 2 consisted of a glucoheptonate (GH) rate trial to determine the optimal application rate of the product. Trial 2 consisted of 6 application rates of glucoheptonate (0 kg ha^{-1} [control], 49.7 kg ha^{-1}, 99.6 kg ha^{-1}, 149.3 kg ha^{-1}, 199.0 kg ha^{-1}, and 248.9 kg ha^{-1}) replicated 3 times on the same Bojac and Dragston soils for a total of 36 pots. Trial 3 combined the two products in a comparison study to investigate their individual versus combined effects on overall nutrient availability in the soil and in plant tissue. Trial 3 consisted of 4 treatments (control, coated KCl, glucoheptonate (248 kg ha^{-1}), glucoheptonate + coated KCl) replicated 3 times on Bojac and Dragston soils for a total of 24 pots.

For all 3 trials, KCl applications were based on a recommendation rate of 186 kg K ha^{-1} in the Bojac soil and 93 kg K ha^{-1} in the Dragston soil. Each pot received urea applications to a total 50.4 kg N ha^{-1}, with application rates being based on the recommendation rates supplied by VA Soil Test and Recommendation Guidebook (Maguire and Heckendorn, 2018) and the Mid-Atlantic Crop Production Guidebook (2016) (Arancibia et al., 2018) (Table 4.2). Pots were maintained at 60% field capacity by weight and checked every 1 to 2 days. Field capacity was determined by saturating the dried soil and allowing gravitational draining to occur through holes made on the bottom of a disposable cup for 2 days (Bond, et al., 2006). Greenhouse temperature were maintained at 26 – 32 °C. After 3 weeks of growth, pots were destructively sampled for soil and plant tissue.

Soil analysis

Soil samples were air dried for 3 to 4 days and then sieved with a No. 10 (2 mm) sieve prior to chemical analysis. Mehlich 3 extracted nutrients were determined via the Mehlich 3 extraction method at a ratio of 2.5g soil: 25 ml extraction solution containing 0.2N CH_3COOH, 0.25N H_4NO_3, 0.015N NH_4F, 0.015N HNO_3, and 0.001M EDTA (Mehlich, 1984). The $CaCl_2$ extractions were conducted at a ratio of 4g soil: 40ml 0.01 *M* $CaCl_2$ (Houba et al., 2000). All extractions were analyzed for nutrient content (specifically focusing on P, S, and B) by

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; CirOS VISION model, Spectro Analytical).

Plant tissue analysis

Total above ground plant tissue was weighed for wet biomass, dried in an oven at 40 °C for 3 to 4 days to constant weight, and then weighed again for dry weight before being ground using a Thomas Wiley® Mini Cutting Mill. Plant tissue was digested with HNO_3 in a Chem Mars Xpress microwave digester at a ratio of 0.25g of tissue sample:10ml of concentrated HNO_3 based on the method specified by the manufacturers for plant tissue digestion where temperature was ramped to 200 °C, and digestion was maintained for 20 minutes before cool-down. The extraction ratio was modified from the original ratio of 0.5g of tissue: 10ml of concentrated HNO_3 due to biomass limitations.

Statistical analysis

Statistical analysis was performed using JMP software (JMP Pro 13). Two-way ANOVA was performed by soil type and run for each greenhouse trial in order to investigate differences in P, S, and B concentrations in soil and plant tissue among treatments. Regression analysis was run for Trial 2 to determine potential correlations between application rate and nutrient concentrations in soil and plant tissue and for potential relationships between average water loss, plant height, dry biomass, and application rate. All treatment differences were investigated using post-hoc Tukey's honestly significance difference (HSD) at a significance level of $p < 0.05$

Results and Discussion

Trial 1: Phosphorus, Sulfur, and Boron Coated KCl

Soil Nutrient Concentrations

For both the Mehlich 3 and the 0.01*M* $CaCl_2$ extractions, similar trends in soil nutrient concentrations were seen on both soil types and for each run. Since these trends were almost identical between extractions, only the Mehlich 3 will be discussed here as representation of the trends seen in this study. Although trends were the same, 0.01 *M* $CaCl_2$ only extracted 1% as much P, 72% as much S, and 62.7% as much B when compared to Mehlich 3 extracts.

The uncoated KCl treatment was added to test for any interaction effects between the KCl and the nutrient coating. Throughout the trial, there was no significant difference between the control and the uncoated KCl for both the soil and tissue nutrient concentrations, indicating that there was no interaction influencing the nutrient concentrations from the coated KCl. Thus, the uncoated KCl will not be discussed in the remaining sections.

1) **Soil Mehlich 3 – Phosphorus**

For both soil types, the KCl + P showed significantly greater Mehlich 3 – P compared to the control, uncoated KCl, KCl + S, and KCl + B treatments for both runs (Fig. 1 A - B). The KCl + P treatment increased Mehlich 3 – P by an average of 120.7 and 147.3 mg kg^{-1} compared to the control, uncoated KCl, KCl + B, and KCl + S treatments for the Bojac and Dragston soils, respectively (Figs 4.1 A – B). The coated KCl increased Mehlich 3 – P less than KCl + P, but more than all other treatments, although this was only significant for the Bojac soil where coated KCl raised Mehlich 3 – P by 65.5 mg kg^{-1} compared to all but the KCl + P treatment. For both soil types, minimum crop sufficiency concentrations were met for P (22.5 mg kg^{-1}) for all treatments (Abaye et al., 2006). Mehlich 3 – P concentrations fell within the VH test level for all treatments and soil types.

Differences between coated KCl and the KCl + P treatments for Mehlich 3 – P is likely a result of different P application rates between treatments. Based on the soil test recommendation rates for both soils, the KCl + P treatment received 49.3 kg P ha^{-1}, while coated KCl applied 24.7 (Bojac) or 12.3 kg P ha^{-1} (Dragston) when applied at the agronomic rate for KCl (Arancibia et al., 2018; Maguire and Heckendorn, 2018).

In soils, P availability is controlled by adsorption rates, which are influenced by soil mineral composition, pH, and environmental factors. Depending on pH conditions, inorganic P rapidly adsorbs to Fe/Al oxides (acidic; pH < 6.0) or form Ca phosphates (alkaline; pH > 6.5), becoming unavailable for plant uptake (Havlin, 2014; Brady and Weil, 2008; Damon et al., 2014). In addition to soil pH, P fixation is also influenced by the presence of OM, which reduces fixation by promoting more soluble organophosphate complexes, replacing H_2PO_4 with organic anions, providing additional sources of mineralizable P, and by promoting humus coatings on Fe/Al oxides and thus reducing potential adsorption sites (Havlin et al., 2014; Abaye et al, 2006). The greater increase in Mehlich 3 – P from the KCl + P treatment in Dragston compared to Bojac is likely the result of differences in OM content (36 g OM kg^{-1} Dragston; 10 g OM kg^{-1} Bojac).

2) <u>Soil Mehlich 3 – Sulfur</u>

For Mehlich 3 – S, the KCl + S treatment was significantly greater than all other treatments, increasing Mehlich 3 – S by 61.3 and 72.1 mg S kg^{-1} compared to all remaining treatments for the Bojac and Dragston soils, respectively (Figs. 4.1 C – D). The coated product was not able to increase S to show a significant increase in Mehlich 3 – S relative to the no S treatments (Figs 4.1 C – D). Currently, there is no established soil test for S in VA and therefore, will not be discussed here. Recent reports for fields containing S-deficient crops have noted Mehlich 3 concentrations ranging from 5 – 10 mg kg "critical level" of 5 mg kg^{-1} referenced in this study is based on reports relating soil S to proper onion production as well as Mehlich 3 – S concentrations in fields exhibiting S-deficiency in crops (Arancibia et al., 2018; Beegle et al., 2015).

For the coated KCl, S was applied at a rate of 5.2 kg ha^{-1} for the Bojac soil and 2.6 kg ha^{-1} for the Dragston soil which is 4.3 and 9.3 times less than the agronomic rate of 22.4 kg ha^{-1} applied with the KCl + S treatment. This is probably the reason the KCl + S treatment increased the Mehlich 3 – S relative to all other treatments, but the coated KCl did not. Despite differences in OM, S concentrations were similar between soil types throughout the trial. In soils, approximately 80% of total S comes from the organic matter pool where it becomes plant available through microbially mediated mineralization (Brady and Weil, 2008; Havlin et al., 2014; Blair, 2002; Eriksen, 2009). It was believed that the increased OM in the Dragston soil would facilitate greater concentrations of solution S as a result of this mineralization, and that this would be reflected in the Mehlich 3 concentrations. However, the lack of difference in concentrations between the two soils indicated that OM differences were not enough to result in significant differences in mineralized S.

3) Soil Mehlich 3 – Boron

For both soil types, the KCl + B and coated KCl treatments had significantly greater Mehlich 3 – B compared to all other treatments (Figs. 4.1 E – F). The KCl + B treatment increased Mehlich 3 – B by an additional 4.7 and 6.2 mg B kg^{-1} compared to the means for all other treatments, while the coated KCl increased Mehlich 3 – B by an additional 3.7 and 2.8 mg kg^{-1} for the Bojac and Dragston soils, respectively. Only the Dragston soil had significant differences between KCl + B and the coated KCl treatments, with the KCl + B treatment increasing Mehlich 3 – B by an additional 3.4 mg kg^{-1} compared to the coated KCl. For both soil types, only the KCl + B and coated KCl products had B concentrations greater than the minimum sufficiency concentration (0.35 mg kg^{-1}) (Figs 4.1 E – F) (Arancibia et al., 2018). For the remaining treatments, Mehlich 3 – B was equal to or less than the critical level for both soil types.

At the agronomic rate for K, coated KCl added B at a rate of 5.3 or 2.6 kg ha^{-1} for the Bojac and Dragston soils, respectively, since rates were based on K. The agronomic rate for B application in VA is 2.24 kg ha^{-1} for tomato (Maguire and Heckendorn, 2018). Where B was added, Mehlich 3 – B was always greater than the no B treatments. However, even though the coated KCl applied more than twice as much B as the KCl + B treatment in the Bojac soil, Mehlich 3 – B was statistically equivalent between the two. In the Dragston soil where the rate of B applied was similar between the coated KCl and KCl + B treatments, the KCl + B was significantly greater than coated KCl treatment. The discrepancy seen between application rate and soil concentrations may be the result of different dissolution rates between sources, with the coated KCl taking longer to dissolve and thus negating the increased application rate.

Plant Tissue Nutrient Concentrations

1) **Tissue Phosphorous**

The KCl + P treatment had significantly greater P concentrations compared to all other treatments for both soils, increasing tissue P by an additional 2776 – 4599 mg kg^{-1} for Bojac and

2665 mg kg^{-1} for Dragston (Figs. 4.2 A – B). For the Bojac soil, coated KCl increased tissue P by 1237 – 1340 mg P kg^{-1} compared to all but the KCl + P treatment, although treatment differences were not always significant. For the Dragston soil, coated KCl was generally statistically equivalent to all but the KCl + P treatment. While soil test concentrations for all treatments had sufficient P concentrations, minimum sufficiency (0.3% dry weight; 3000 mg kg^{-1}) was consistently met with only the KCl + P and coated KCl treatments for both soil types (Figs. 4.2 A – B). Therefore, the increase in Mehlich 3 – P for the KCl + P treatment also showed up as increased P in the plant tissue, with no other clear trends.

Tissue P concentrations in this study were similar to those seen in previous studies, falling within the average concentration range of 1000 – 5000 mg kg^{-1} (0.1 – 0.5% dry weight) (Havlin et al., 2014; Vance, 2011; Peñalosa et al., 1989; Awad et al., 1990). Peñalosa et al. (1989) investigated P effects on tomato growth and nutrition and had average tissue concentrations of 3300 – 3900 mg P kg^{-1} at application rates of 13.9 – 34.7 kg P ha^{-1}. While coated KCl application rates were slightly less, the mean tissue P ranged from 2900 – 3800 mg P kg^{-1} for the coated KCl for the Bojac and Dragston soils respectively, which falls within concentration range seen by Peñalosa et al. (1989). The differences in tissue concentrations reflects the different P application rates for the KCl + P and coated KCl. As previously discussed, the KCl + P treatment had an application rate of P that was 2 – 4 times greater than the coated KCl, and this difference was seen in both soil and tissue. While the coated KCl generally increased plant-available P enough to meet the minimum sufficiency threshold, it clearly does not match current agronomic P rates (49 kg P ha^{-1}).

2) <u>Tissue Sulfur</u>

For both soils, the KCl + P and KCl + S had the greatest tissue S concentrations followed by the coated KCl, compared to the other treatments, although this was not always statistically significant. The KCl + P and KCl + S treatments increased tissue S by 1042 – 2315 mg S kg^{-1} and 1359 – 2638 mg S kg^{-1} for the Bojac and Dragston soils, respectively (Figs. 4.2 C – D). On both soil types, the KCl + P and KCl + S consistently exceeded minimum sufficiency concentrations for tissue (3000 mg S kg^{-1}), while the coated KCl only reached sufficient concentrations on the Dragston soil (Arancibia et al., 2018). All remaining treatments did not meet minimum sufficiency concentrations.

The difference between the KCl + S and the coated KCl can again be tied to the difference in S application rates. The KCl + S applied S at a rate 10 times greater than the coated KCl, and thus had significantly greater tissue concentrations as a result. Tissue response to S applications showed varied results among studies. The tissue concentrations in this study differ from those seen by Zuchi et al. (2015) but are similar to those seen Hitsuda et al. (2005), both of which investigated S nutrition and management. Zuchi et al. (2015) investigated interactions between S and Fe in tomatoes and reported tissue concentrations from 1071 – 1263 mg S kg^{-1} when S was applied at a rate of 38.8 kg ha^{-1}. Despite the greater application rate used in their study, the tissue concentrations seen by Zuchi et al. (2015) were 372 – 2249 mg S kg^{-1} less than those seen in this study, where application rates ranged from 2.6 – 22.4 kg S ha^{-1}. However, tissue concentrations seen in our study are similar to those presented by Hitsuda et al. (2005), who reported concentrations of 2000 – 3540 mg S kg^{-1} when applied at similar application rates of 2 – 32 mg S kg^{-1}.

Increased tissue S with the KCl + P treatment may be the result of enhanced root system development. While P is predominately associated with biochemical compounds such as nucleic acids, phospholipids, and ATP, it also plays an important role in the growth and development of the root system (Abaye et al., 2006; Damon et al., 2014; Havlin et al., 2014; Marschner, 2012; Peñalosa et al., 1989). While root zone development was not measured in this study, the additional P supplied by the KCl + P treatment may have promoted root zone development and led to increased acquisition of available S. Extra P supplied by coated KCl may have also promoted increased root development and thus increased S uptake. However, the amount of P provided by the coated KCl was not enough increase tissue P and S to the same concentrations as the individual treatments.

3) **Tissue Boron**

Tissue B followed the trend KCl + B > coated KCl > remaining treatments, although this was not always significant for both soils and runs (Figs. 4.2 E – F). For the Bojac and Dragston soil, the KCl + B increased tissue B by 29.5 – 137.5 mg B kg^{-1}, respectively. The coated KCl consistently increased tissue B by 44.9 – 71.7 mg B kg^{-1} compared to all but the KCl + B treatment. Despite applying B at rate equal to or greater than the KCl + B, the coated KCl tissue concentrations were either equal to or less than the KCl + B. The coated KCl and KCl + B treatments consistently exceeded the minimum sufficiency concentration (20 mg B kg^{-1}) for both soil types (Arancibia et al., 2018).

Tissue concentrations from our study resembled those reported by Dursun et al (2010), who investigated the effect of varying B application rates on the yields and nutrient concentrations of numerous vegetable crops. According to their results, tomato shoot and leaf B concentrations were positively correlated with B application rate ($R^2 = 0.99$), with total tissue concentrations ranging from 15.7 – 142.8 mg B kg^{-1} at application rates of 0 – 4.0 kg B ha^{-1}.

Despite differences between the soils used (Entisol, pH = 7, OM = 8 – 12 kg ha^{-1}), total tomato tissue concentrations were similar to those seen in our study at application rates of 0, 2.2. 2.6, and 5.3 kg ha^{-1}. While general soil characteristics differed, both studies used soils with similar starting concentrations of B ranging between 0.1 – 0.2 mg B kg^{-1}. Plant uptake of B occurs with the transpirational uptake of water, resulting in deficiency conditions being heavily tied to soil moisture status (Abaye et al., 2006; Brady and Weil, 2008; Hawkesford and Barraclough, 2011; Kashin, 2012). The similar trends seen between the two studies, despite differences in soil type, highlights the importance of transpirational water flow on the uptake of B under increasing soil B concentrations.

Trial 2: Glucoheptonate Rate Trial

<u>*Soil Nutrient Concentrations:*</u>

1) **<u>Soil Mehlich 3 – Phosphorous</u>**

Significant differences in Mehlich 3 – P between glucoheptonate (GH) rates only occurred on the Dragston soil (Figs. 4.3 A – B). However, these differences were inconsistent, and the GH application rates had no significant effect on Mehlich 3 – P for both soil types (R^2 = 0.04 – 0.20). For both soil types and runs, Mehlich 3 – P concentrations exceeded critical levels (45 mg kg^{-1}).

While numerous studies focused on chelates as sources of transition metals such as Fe^{2+}, Cu^{2+}, and Zn^{2+}, few investigated GH specifically for its overall influence on soil and tissue nutrient concentrations. Edwards et al. (2016a; 2016b) conducted multiple studies on the influence of 4 chelates (ethylenediamine tetraacetic acid disodium salt (EDTA), hydroxyethyl ethylenediamine triacetic acid (HEEDTA), gluconic acid, and citric acid) on plant available P and experienced conflicting results. Their earlier study (2016a) showed that EDTA, HEEDTA, and citric acid significantly increased water-soluble P (WSP) and EDTA and HEEDTA application rates had significant linear correlations to WS, Mehlich 1, and Mehlich 3 – P for multiple soils and P application rates (0 and 49.3 kg P ha^{-1}). However, their following study (2016b) revealed contradictory results, with EDTA and HEEDTA inconsistently influencing WSP, Mehlich 1 – P, or Mehlich 3 – P. Of the chelates used, gluconic acid most closely resembled the GH product used in our study, with both products being sugar acid chelates with similar pKa's (3.60 and 3.66 for gluconic and GH respectively) and stability constants (LogK = 3.55 – 3.89) (Escander et al., 1990; Whitehurst, 2017). The lack of significant differences caused by the gluconic acid better matches the results seen in this study, and highlights the differences in efficacy, mode of action, and behavior between chelating agents.

2) Soil Mehlich 3 – Sulfur

As for Mehlich 3 – P, GH had no consistent effect on Mehlich 3 – S (Figs. 4.3 C – D). The Bojac soil had no significant differences between treatments, with Mehlich 3 – S ranging from 2.5 – 6.0 mg S kg^{-1}. The Dragston soil had inconsistent trends, with Mehlich 3 – S concentrations ranging from 9.1 – 12.3 mg S kg^{-1}. In general, there was no significant correlation between GH rate and Mehlich 3 – S, but regression values did vary between runs and soil types (R^2 = 0.03 – 0.45; average R^2 = 0.18). The Dragston soil consistently had greater Mehlich 3 – S compared to the Bojac soil, most likely a reflection of differences in OM.

The use of chelates in agriculture primarily focuses on micronutrient management and heavy metals, and very little attention to its potential effect on soil macronutrients such as P and S. Sugar acid chelates, such as GH, behave as organic acids and form water soluble complexes through the binding of cations onto carboxyl and hydroxyl functional groups (Clemens et al., 1990; Mehltretter et al., 1953). This allows them to be used as immediate sources of cationic nutrients. However, sugar acid chelates can be readily degraded in soils due to microbial activity, especially under acidic conditions (Whitehurst, 2017; Norvell, 1991; Birch, 1972). With most of soil S contained in OM, it was believed that the increased mineralization could release S from the OM and increase plant-available S. However, this was not seen in our study. A combination of low residual soil S along with potentially minimal increases in microbial activity may explain these results.

3) **Soil Mehlich 3 – Boron**

Unlike Mehlich 3 – P and S, significant differences between treatments were consistent for Mehlich 3 – B (Figs. 4.3 E – F). For both soil types, there was a significant positive correlation between GH application rates and Mehlich 3 – B ($R^2 = 0.54 – 0.74$), with slopes ranging from 5×10^{-4} to 7×10^{-4} (p-value < 0.001). For both soil types, 199 and 249 kg ha^{-1} rates had the greatest Mehlich 3 – B and were significantly greater than control (0 kg ha^{-1}). Compared to control, both 199 and 249 kg ha^{-1} increased Mehlich 3 – B by an average 0.16 mg B kg^{-1} for both soils.

In our study, greater GH application rates, on average, lost less water over time compared to lower application rates (Fig. 4.4). Relating back to soil trends, the 199 kg ha^{-1} and 249 kg ha^{-1} treatments had 9.9 – 17.5 g additional water on the Bojac soil and 5.7 – 11.3 g additional water on the Dragston soil when averaged across the entire greenhouse study. When average water loss was compared to GH application, regression analysis showed inconsistent results for both soil types ($R^2 = 0.09 – 0.36$; p-value = 0.009 – 0.23). Despite the inconsistent significance, there was a negative slope for all regression lines, with slopes ranging from -7.4×10^{-2} to -3.9×10^{-2}. However, average water loss does not directly correlate to overall soil moisture status as it is also influenced by factors such as plant height, biomass, and air temperatures. When regression analysis was conducted comparing GH rates with plant height and dry biomass, trends were once again inconsistent between soil types. Plant height and aboveground biomass on the Bojac soil did not have a significant negative correlation to GH rate ($R^2 = 0.008 – 0.08$; p-value = 0.72 – 0.92), but generally had a significant correlation on the Dragston soil ($R^2 = 0.26 – 0.28$; p-value = 0.025 – 0.30).

Increase in Mehlich 3 – B at greater application rates of GH may be tied to an increase in soil moisture. The movement and availability of B in soils is tied to soil moisture and water due to the dependence on transpirational water flow for plant uptake and its susceptibility to leaching, particularly in coarse-texture soils experiencing heavy rainfall (Brady and Weil, 2008; Hawkesford and Barraclough, 2011; Kashin, 2012; Abaye et al, 2006). At higher application rates, there was a visible layer on the soil surface where GH was applied. Of the three types of organic binding agents as described by Tisdall and Oades (1982), GH and other such sugar acids fall within the category of transient binding agents, which consists of polysaccharide compounds that are readily decomposed by microbial activity. Once in soils, these binding agents have shown to increase aggregate stability up to sizes of 10 μM, but breakdown within several weeks after application (Tisdall and Oades, 1982; Swincer et al, 1968; Cheshire, 1979). The addition of the GH may have increased the polysaccharide binding agents, and thus promoted microaggregate formation within the soil leading to improved water holding capacity. This may have acted as a soil crust and helped to reduce evaporative loss of soil water. However, this layer generally decreased within 7 – 12 days after planting, indicating that the GH application may also be affecting soil moisture capacity further down the soil column.

Plant Nutrient Concentrations:

1) **Tissue Phosphorous**

There were no significant differences between treatments for tissue P (Figs. 4.4 A – B). Plants had average tissue concentrations of 1660 – 2210 mg P kg^{-1} on the Bojac soil and 2255 – 3362 mg P kg^{-1} for the Dragston soil. Tissue P was generally less than the minimum sufficiency concentration (3000 mg kg^{-1}) (Arancibia et al., 2018). The Bojac plants were 790 – 1340 mg P kg^{-1} below the minimum sufficiency concentration while Dragston plants were an average of 745.4 mg P kg^{-1} below the minimum sufficiency concentration, except during the first run.

The lack of significance in tissue P between treatments matches the trends seen for Mehlich 3 – P in the soil for both soil types. Concentration ranges match those seen in the previous greenhouse trial (Baxter et al., 2018 – unpublished) with all treatments exhibiting P deficiency (Baxter et al., 2018 – unpublished). The concentrations seen in our study match those presented by Awad et al. (1990) for tomatoes grown under various levels of salt stress. The GH in our study is Na-based and may be promoting the same salt tolerance mechanisms seen by Awad et al. (1990), thus explaining the consistently deficient P concentrations.

2) <u>Tissue Sulfur</u>

For tissue S, treatment differences were insignificant except for Bojac run 1 (Figs. 4.4 C – D). Tissue concentrations ranged from 1049 – 1194 mg S kg^{-1} for Bojac and 2233 – 2160 mg S kg^{-1} for Dragston and showed no significant correlation to GH application rate (R^2 = 0.02 – 0.11). For both soils, minimum sufficiency concentrations for tissue S (3000 mg kg^{-1}) were not met, with Bojac plants have concentrations an average of 1879 mg S kg^{-1} less than sufficiency and Dragston plants having concentrations an average of 804 mg S kg^{-1} less than sufficiency (Arancibia et al., 2018).

Tissue concentrations were similar to the control treatment from Trial 1 and match reported values from previous studies where minimal or no S was applied (Ward, 1976; Hitsuda et al., 2005; Zuchi et al., 2015). The inconsistent trends with Mehlich 3 – S on the Bojac soil were repeated in the plant tissue but did not match the soil. However, tissue concentrations were similar to control and uncoated KCl concentrations seen in Trial 1, reflecting a lack of additional S provided by the GH product.

3) <u>Tissue Boron:</u>

Similar to the trends seen with Mehlich 3 – B, tissue B concentrations increased with increasing application rate of GH for both soils and runs (Figs. 4.4 E – F). For both soils, 199 kg ha^{-1} and 249 kg ha^{-1} rates increased tissue B by an additional 4.53 – 13.37 mg B kg^{-1}. However, significant differences were inconsistent between runs. Both soils had similar positive correlations between GH rates and tissue B concentrations (R^2 = 0.38 – 0.47), with slopes ranging from 2.9 x 10^{-2} to 6.3 x 10^{-2} (p-value = 0.002 – 0.01). All rates exceeded the minimum sufficiency concentration for B (20 mg kg^{-1}) for all runs (Arancibia et al., 2018).

Tissue concentrations seen in trial 2 match closely with those seen in trial 1 for all but the KCl + B and coated KCl treatments, showing that increases in tissue B provided by increased GH rates does not match those provided by conventional fertilizer sources. As was discussed for the previous trial, B concentrations and availability in soils and plant tissue is closely tied to soil moisture status and water movement within the system (Abaye et al., 2006; Kashin, 2012, add more sources). Greater GH application rates may have caused enough change in the soil moisture status to improve plant uptake of B, thus resulting in increased tissue B. However, the low concentration of starting soil B limited the amount of increased uptake provided by the GH application.

Trial 3: Coated KCl x Glucoheptonate Interactions

Soil Nutrient Concentrations:

1) **Soil Mehlich 3 – Phosphorous**

The coated KCl and the coated KCl + GH treatments significantly increased concentrations of Mehlich 3 – P by an average 65.02 and 39.76 mg P kg^{-1} compared to the control and GH treatments for the Bojac and Dragston soils respectively (Figs. 4.5 A – B).

Increased Mehlich 3 – P with coated KCl was consistent with trial 1, while the lack of response from the GH addition was consistent with the results from trial 2. The lack of significant difference between the coated KCl and coated KCl + GH treatment, along with the lack of significant difference between the control and GH treatment, indicated that GH additions did not impact Mehlich 3 – P and did not have any interaction effect with the coated KCl fertilizer. The lack of effect seen by GH treatments in early stage growth (within 4 weeks of planting) matches results seen by Edwards et al. (2017), who was investigating the influence of synthetic iron chelates on soybean growth. According to their results, the chelate addition did not have any significant effect on macronutrient concentrations or uptake. Additionally, sugar acid chelates were shown to be more effective in alkali conditions where microbial degradation is reduced (Hodge et al., 1963; Whitehurst, 2017; Escander et al., 1990).

2) **Soil Mehlich 3 – Sulfur:**

For the Bojac soil, the coated KCl and coated KCl + GH treatments increased Mehlich 3 – S by an average of 3.8 mg S kg^{-1} compared to the control and GH treatments (Figs. 4.5 C – D). For the Dragston soil, the coated KCl and coated KCl + GH treatments increased Mehlich 3 – S by an average of 3.6 mg S kg^{-1} compared to the control and the GH treatments.

The Mehlich 3 – S concentrations seen in trial 3 were similar to those seen in earlier trials for the control, coated KCl, and GH treatments, showing a consistent effect from the coated KCl and GH treatments. As was seen with Mehlich 3 – P, there was no significant difference between the coated KCl and coated KCl + GH treatments or between the control and GH treatments for Mehlich 3 – S for the Bojac and Dragston soils. This lack of difference once again highlighted the lack of influence exhibited by the addition of GH to soil nutrient concentrations.

3) <u>Soil Mehlich 3 – Boron:</u>

The coated KCl and coated KCl + GH treatments also significantly increased Mehlich 3 – B compared to the control and GH treatments for both soil types and for both runs. For the Bojac soil, the coated KCl and coated KCl + GH treatment increased Mehlich 3 – B by an average of 3.03 mg B kg^{-1} compared to the control and the GH treatments. For the Dragston soil, the coated KCl and coated KCl + GH treatments increased Mehlich 3 – B by an average 3.05 mg B kg^{-1} compared to the control and uncoated KCl. As was seen with Mehlich 3 – S, minimum sufficiency concentrations were only met by the coated KCl and coated KCl + GH treatments for both soils. As for Mehlich 3 – P and Mehlich 3 – S, there was no significant difference between the coated KCl and coated KCl + GH treatments or between the control and GH treatments for Mehlich 3 – S for the Bojac and Dragston soils. Therefore, there was no evidence for interaction between the coated product and the GH.

<u>Plant Tissue Nutrient Concentrations:</u>

1) <u>Tissue Phosphorous:</u>

Following the same trends that were seen with Mehlich 3 – P, the coated KCl and KCl + GH treatments significantly increased Mehlich 3 – P compared to the control and GH treatments for both soil types and runs (Figs. 4.6 A – B). The coated KCl and coated KCl + GH treatments had an additional 1553 – 2929 mg P kg^{-1} on the Bojac soil and 661 – 997 mg P kg^{-1} on the Dragston soil. For both soils, coated KCl and coated KCl + GH treatments had tissue P equal to or greater than the minimum sufficiency concentration (3000 mg kg^{-1}), with tissue concentrations having between 4.6 – 1762.8 mg P kg^{-1} above the minimum, while the control and GH treatments were below the minimum sufficiency concentration for both soils. As for Mehlich 3 – P, there was no interaction in tissue P between the coated KCl and coated KCl + GH treatments.

The tissue concentrations in Trial 3 are similar to Trials 1 and 2 for the control, coated KCl, GH, and coated KCl + GH treatments. However, one noticeable difference between trials is the consistent significant increase in tissue P from the coated KCl compared to the control and GH treatments on the Dragston soil.

2) <u>Tissue Sulfur:</u>

Similar to Mehlich 3 – S trends, the coated KCl and coated KCl + GH treatments significantly increased tissue S concentrations for all but one run on the Dragston soil (Figs. 4.6 C – D). As for Mehlich 3 – S, there was no interaction in tissue S between the coated KCl and coated KCl + GH treatments. For the Bojac soil, coated KCl and coated KCl + GH treatments increased tissue S by an average of 1448 mg kg^{-1} compared to control and GH treatments. For the Dragston soil, the coated KCl and coated KCl + GH treatments increased tissue concentrations by an average 1810 mg S kg^{-1} compared to the control and GH treatments. For both soils, all treatments failed to meet the minimum sufficiency concentration (3000 mg S kg^{-1}), with concentrations between 515 – 1964 mg S kg^{-1} less than the minimum.

3) **Tissue Boron:**

Consistent with the tissue P and S, the coated KCl and coated KCl + GH treatments significantly increased tissue B compared to the control and GH treatments for the all runs and for both soil types (Figs 4.6 E – F). For the Bojac soil, the coated KCl and the coated KCl + GH had an average of 254.4 mg kg^{-1} of additional B compared to the control and GH treatments. For the Dragston soil, the coated KCl and the coated KCl + GH increased tissue concentrations by an average 79.1 mg B kg^{-1} compared the control and the GH treatments. For both soil types and runs, tissue B was either equal to or greater than the minimum sufficiency concentration (20 mg B kg^{-1}) for all treatments.

Compared to the previous trials, tissue B concentrations for the control and GH treatments were not significantly different for either soil type. While the coated KCl consistently resulted in a significant increase in tissue B compared to the control treatment for both trials, the increase in concentration seen in Trial 3 was 237 – 278% greater than the increase seen in Trial 1 for the Bojac soil. However, the coated KCl product significantly increased tissue B compared to the control for both soil types.

The significant increases in tissue B seen with increasing GH application from Trial 2 were not seen in Trial 3. While significant differences were not identified in this trial, treatments containing the GH application consistently had greater tissue B concentrations compared to treatments without GH. Treatments containing the GH application had an average 32.6 and 14.5 mg kg^{-1} of additional B compared to treatments without the GH (C vs GH; coated KCl vs coated

KCl + GH). The consistent increase with GH shows that the addition of GH to soil systems can increase tissue B on various soil types. However, the lack of significant differences between the coated KCl and coated KCl + GH treatment shows that there is no significant interaction effect between the GH and KCl treatments.

Conclusion

The results from these greenhouse trials reveal the potential for coated KCl product as a multi-nutrient source for tomatoes for early growth stages, specifically for K, P and B, but would not be a sufficient source of S based on its current chemical composition. Additionally, no significant interaction effects were seen between the KCl and the nutrient coating nor with the coated KCl and the GH, indicating the P, S, and B increases from the coated KCl are from the coating itself. Differences in soil and tissue concentrations between the coated KCl and the individual treatments is most likely due to the differences in application rates, with the coated KCl applying less P and S compared to the agronomic rates. While GH did significantly increase soil and plant B, this effect was not statistically significant when compared to agronomic application rates. We propose that the main mode of influence from GH is through minor alteration of soil aggregate structure and water holding capacity, which increases soil moisture allowing for increased B availability. However, as an organic acid, GH may act as a significant energy source for the soil microbial community. Further research should be conducted to investigate GH applications influence on soil microbial dynamics to better understand the product's full effect on soil – plant systems.

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Table 4.1. Mehlich 1 - extracted soil properties of the Bojac, Dragston, and Bonneau soils used in the greenhouse study.

Name	**Soil Texture**	**pH**	**P**	**K**	**Ca**	**Mg**	**Mn**	**Fe**	**B**	**OM**
			mg kg^{-1}							g kg^{-1}
Bojac	sandy loam	6.5	70.5	55	425	50	4.7	9.9	0.3	10
Dragston	fine sandy loam	6.7	26	94.5	819	124	3.2	14.8	0.2	36

Table 4.2. Nutrient additions of Trial 1 treatments

	N	K	P	B	S
			kg ha^{-1}		
Control	50	-	-	-	-
Uncoated KCl	50	185.9 or 92.9	-	-	-
KCl + B	50	185.9 or 92.9	-	2.2	-
KCl + P	50	185.9 or 92.9	49.3	-	-
KCl + S	50	185.9 or 92.9	-	-	22.4
Coated KCl*	50	185.9 or 92.9	24.7 or 12.3	5.3 or 2.6	5.2 or 2.6

*The two rates of the K and the Coated KCl refer to the differenct application rates for the Bojac (1st) and the Dragston (2nd) based on their different recommendation rates. At the two different K rates, the different amount of P, B, and S added as a result are shown here.

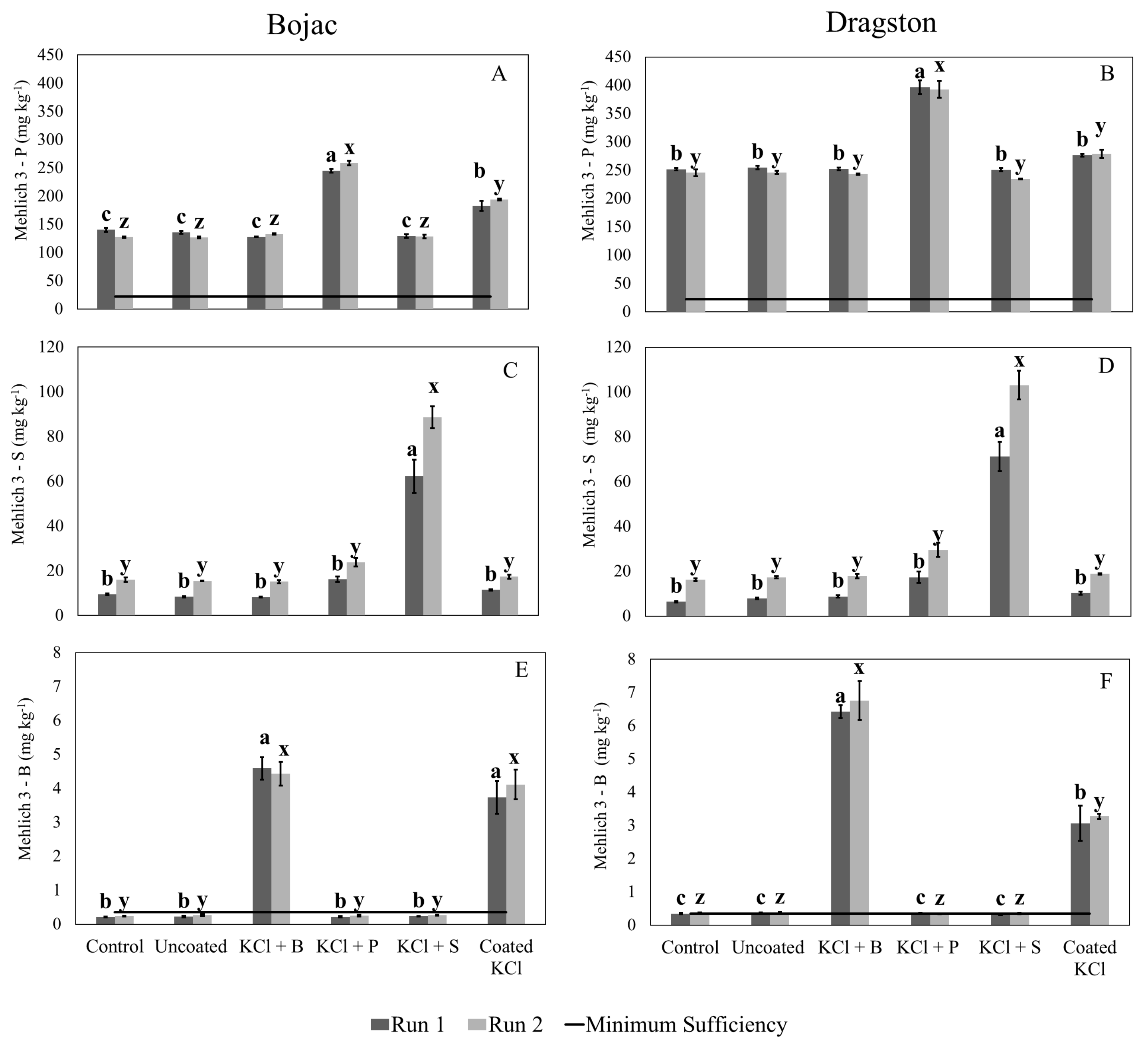

Fig 4.1. Mehlich 3 – extracted (A – B) phosphorous, (C – D) sulfur, and (E – F) boron for the Bojac and Dragston soils in Trial 1. Different letters indicate significant differences ($p < 0.05$). Statistical comparisons were made with Runs (Run 1: “a, b, c”; Run 2: “x, y, z”).

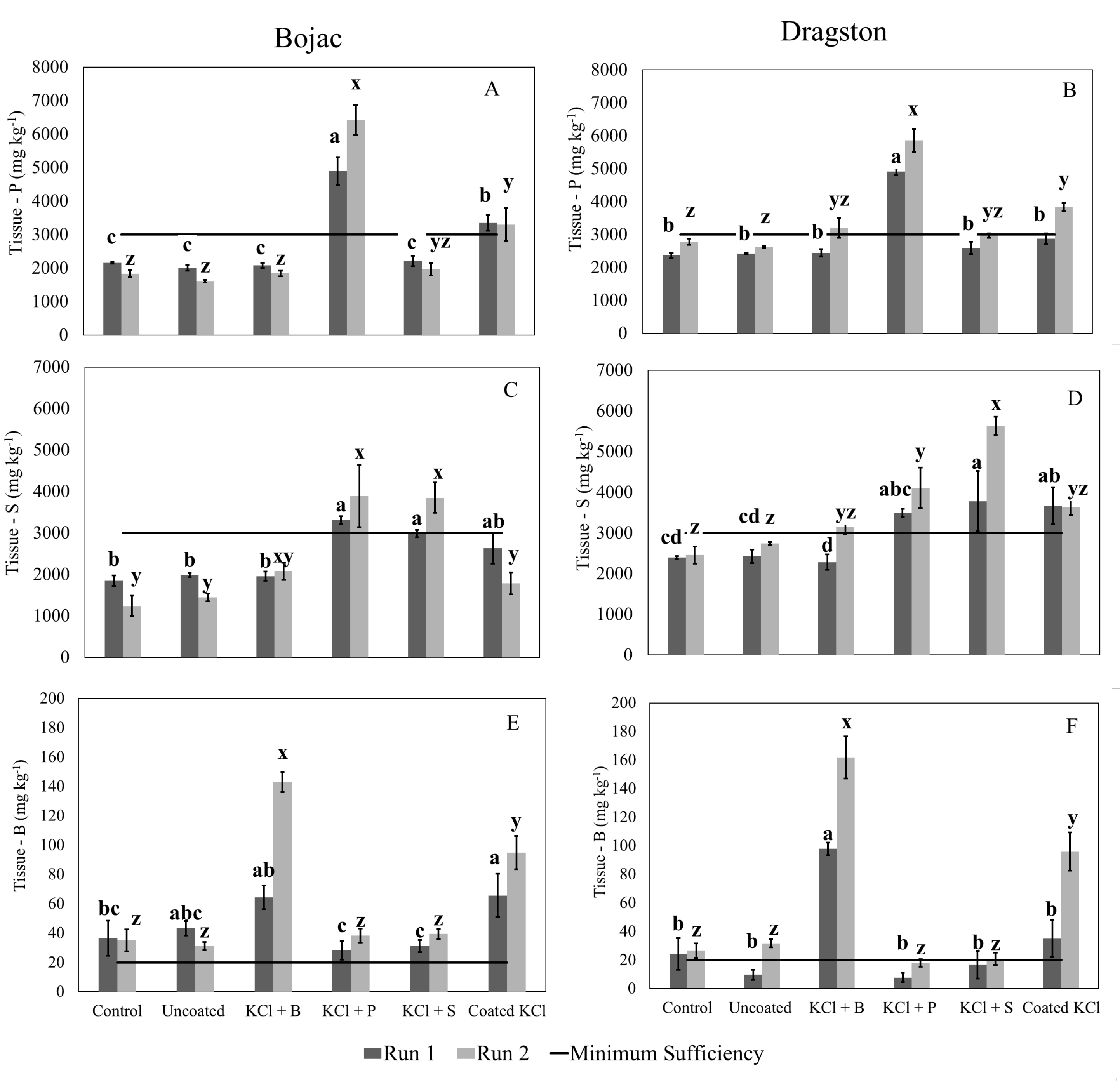

Fig 4.2. Plant tissue (A – B) phosphorous, (C – D) sulfur, and (E – F) boron using HNO_3 microwave digestion for the Bojac and Dragston soils in Trial 1. Letters above bar indicate significant differences ($p < 0.05$). Statistical comparisons were made with runs (Run 1: "a, b, c"; Run 2: "x, y, z"). The horizontal line indicates the minimum sufficiency concentration in the uppermost trifoliate (3000 mg P kg^{-1}; 3000 mg S kg^{-1}; 20 mg B kg^{-1}).

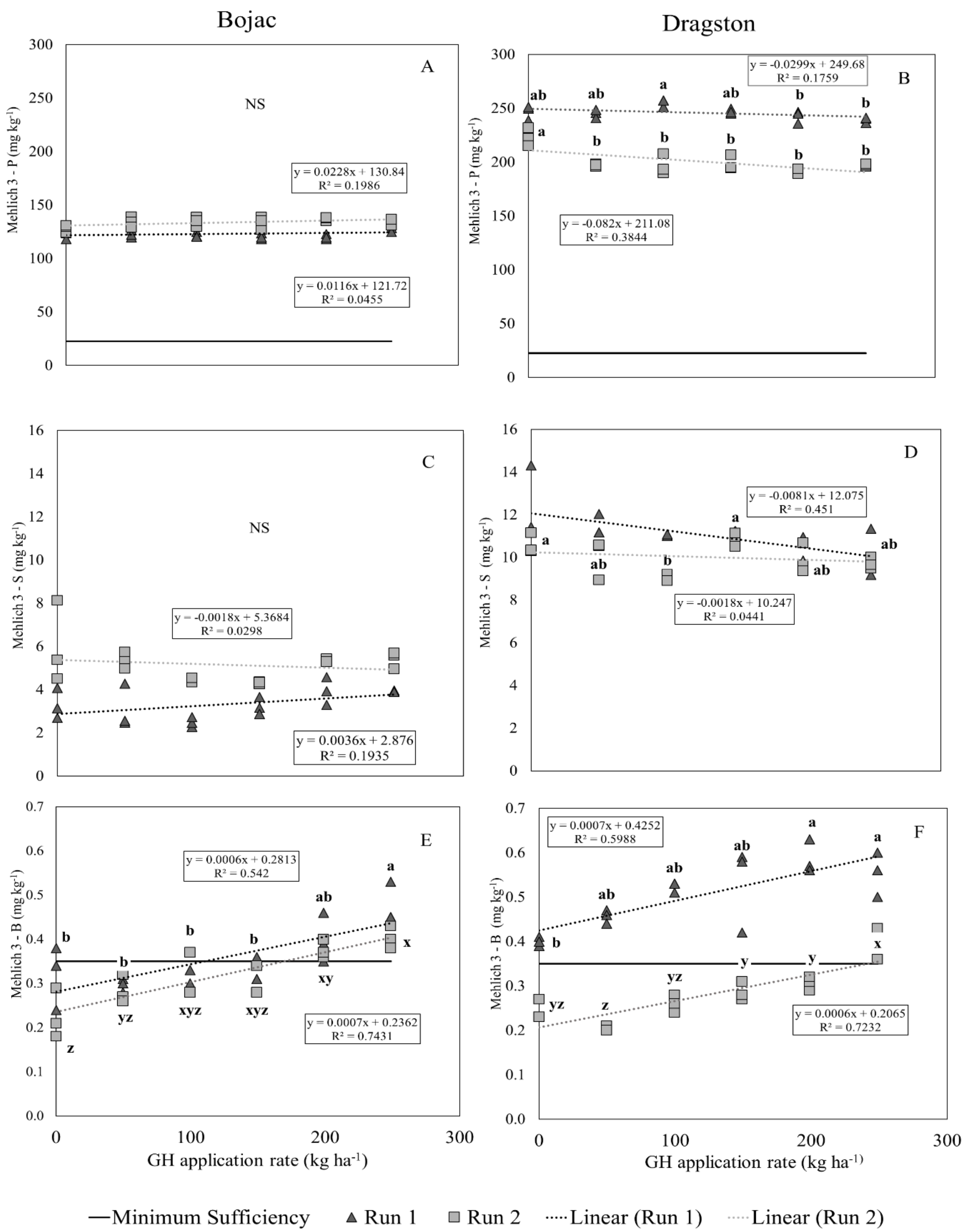

Fig 4.3. Mehlich 3 – extracted (A – B) phosphorous, (C – D) sulfur, and (E – F) boron for the Bojac and Dragston soil for Trial 2. Dotted lines represent trend lines from regression analysis comparing soil concentrations and glucoheptonate application rate ($p < 0.05$). Statistical comparisons were made for letters "a, b, c" and "x, y, z". Lack of statistical difference is denoted with "NS".

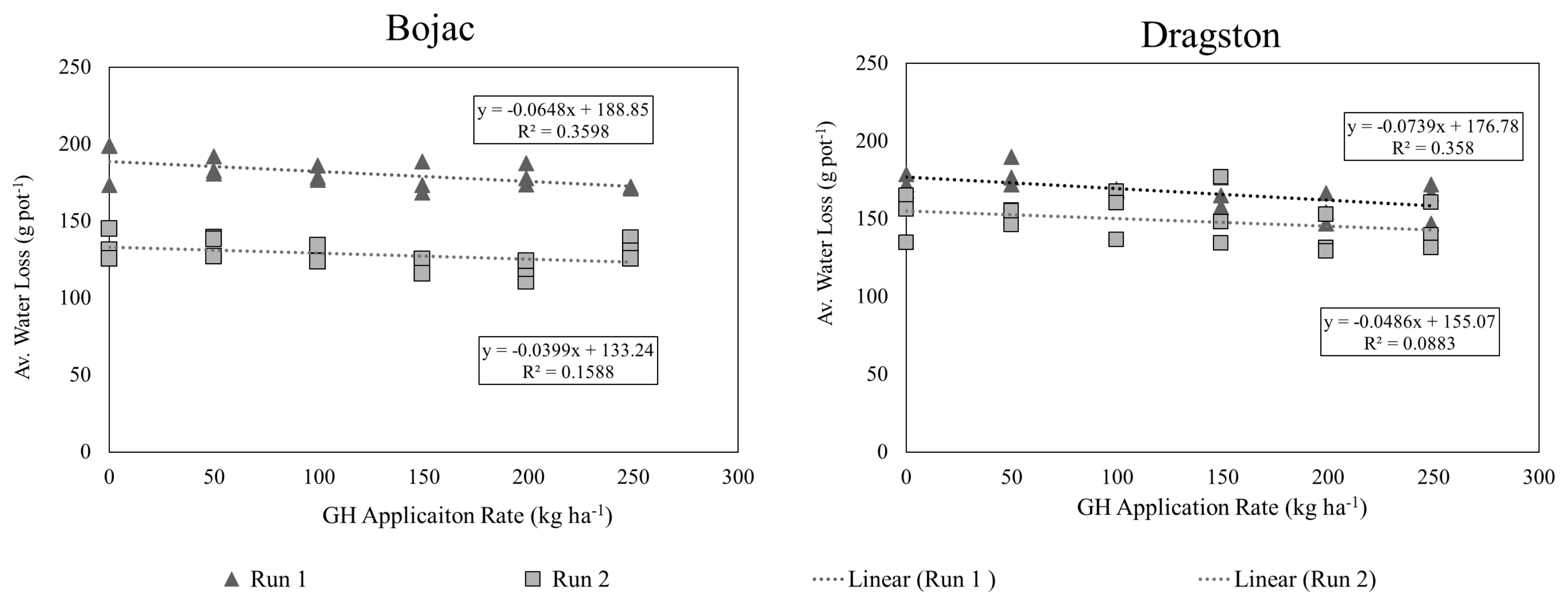

Fig. 4.4. Average water lost between watering periods (1-2 d) per pot for both soils used in Trial 2. Dotted lines represent trend lines from regression analysis comparing soil concentrations and glucoheptonate application rate ($p < 0.05$).

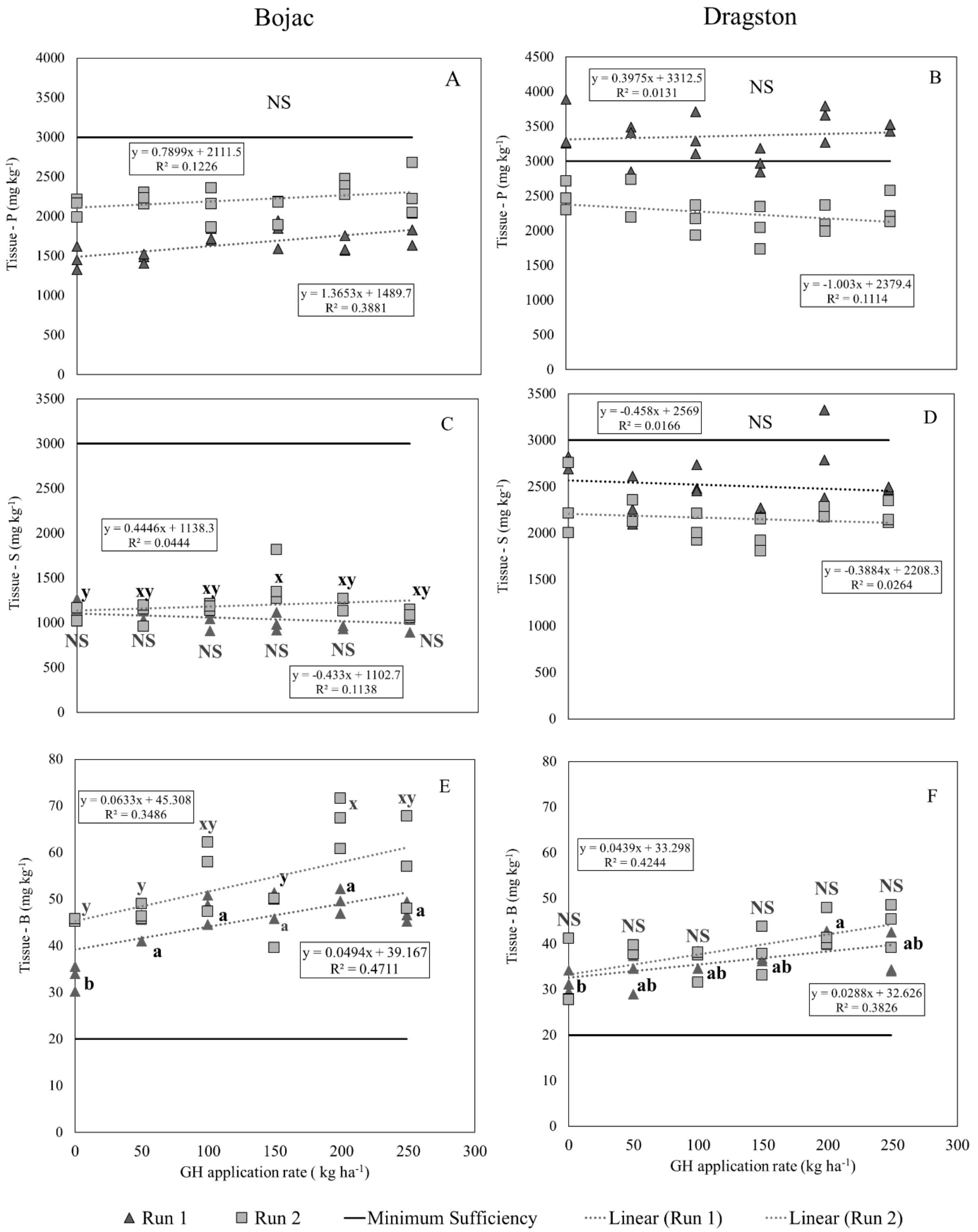

Fig 4.5. Plant tissue (A – B) phosphorous, (C – D) sulfur, and (E – F) boron using HNO_3 microwave digestion for the Bojac and Dragston soils in Trial 2. Dotted lines represent trend lines from regression analysis comparing soil concentrations and glucoheptonate application rate ($p < 0.05$). Statistical comparisons were made for letters “a, b, c” and “x, y, z". Lack of statistical difference is denoted with "NS".

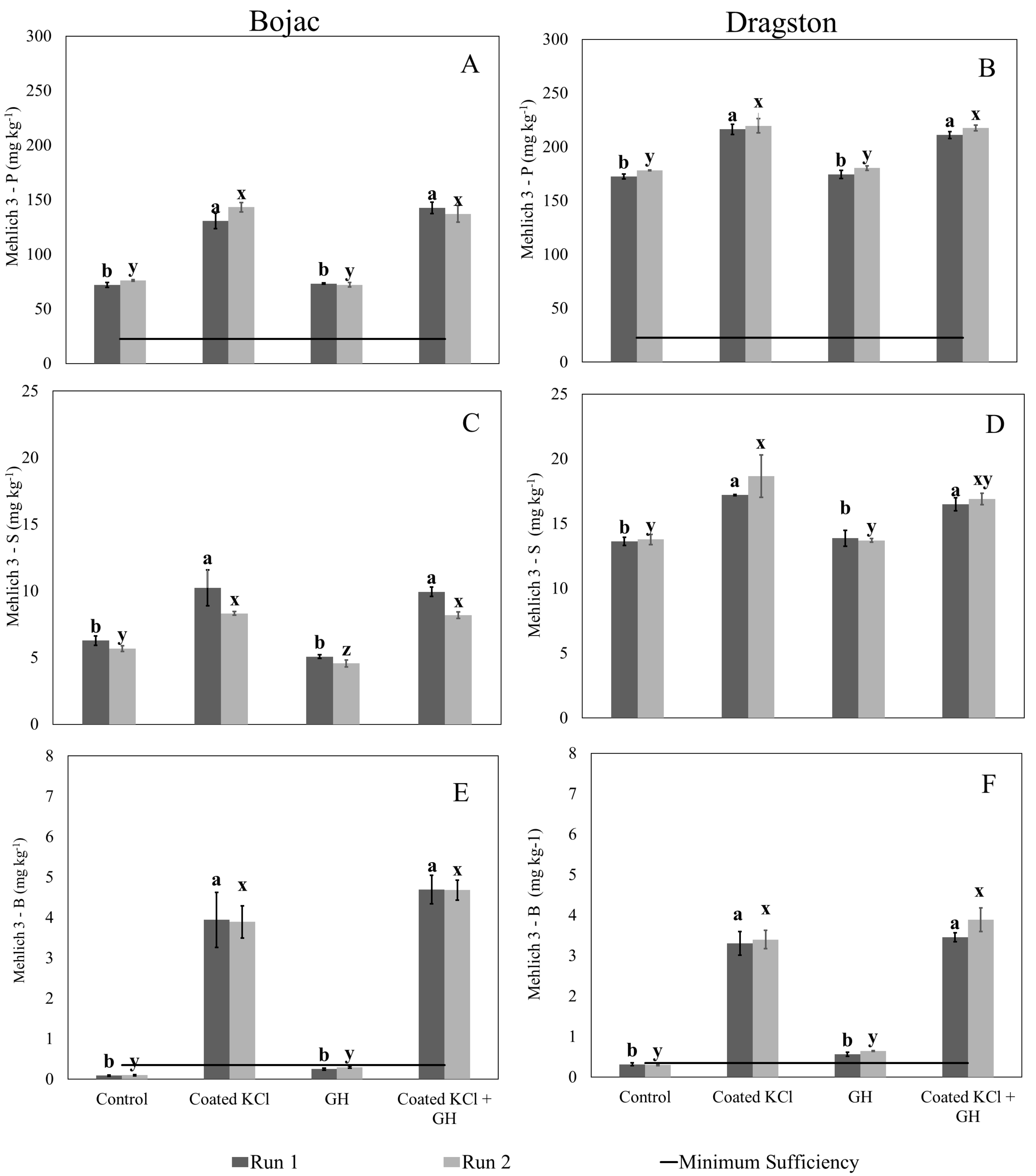

Fig 4.6. Mehlich 3 – extracted (A – B) phosphorous, (C – D) sulfur, and (E – F) boron for the Bojac and Dragston soil for Trial 3. Letters above bar indicate significant differences ($p < 0.05$). Statistical comparisons were made with Runs (Run 1: "a, b, c"; Run 2: "x, y, z"). The horizontal line indicates the minimum sufficiency concentration in the uppermost trifoliate (23 mg P kg^{-1}; 5 mg S kg^{-1}; 0.35 mg B kg^{-1}).

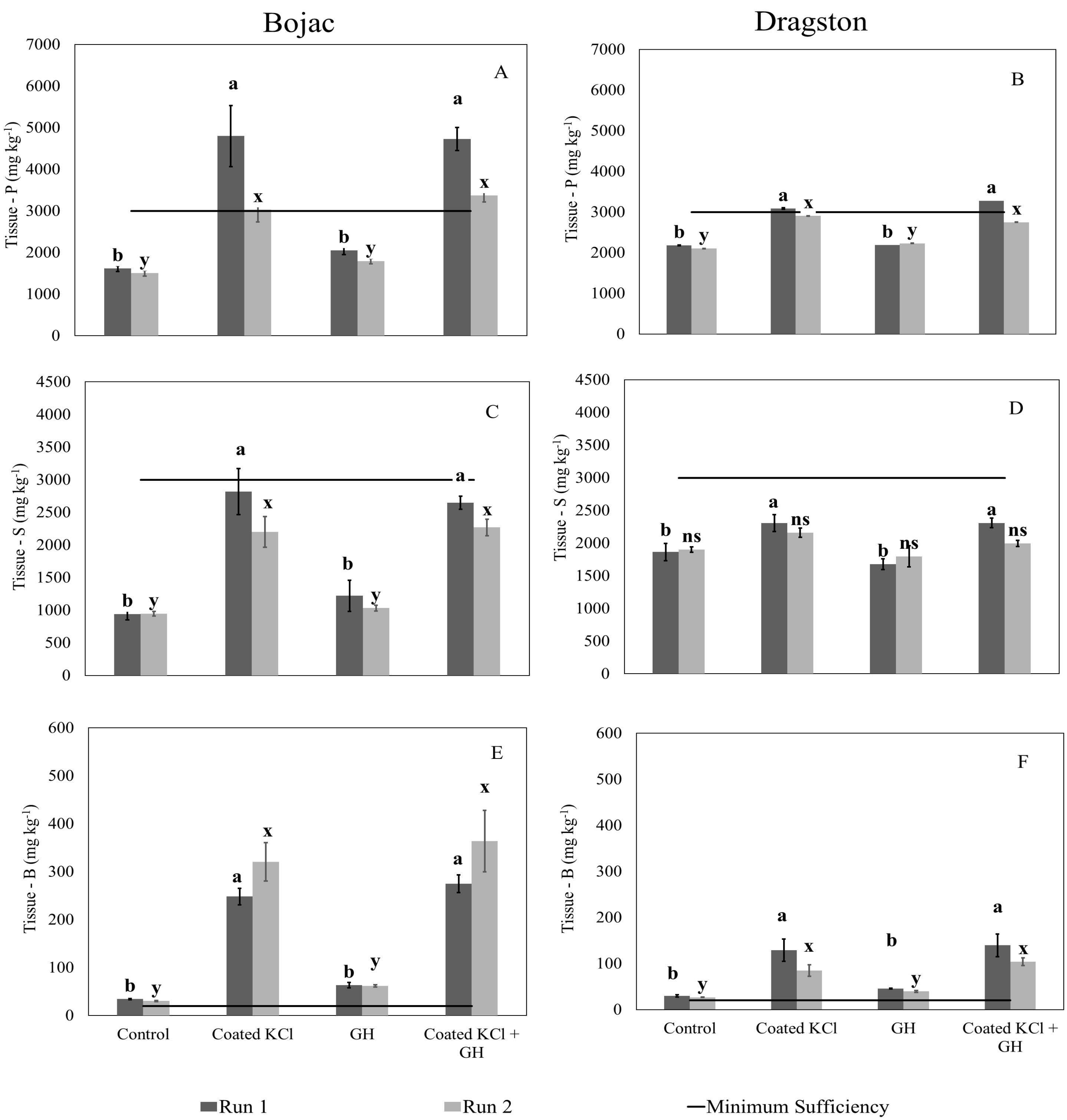

Fig 4.7. Plant tissue (A – B) phosphorous, (C – D) sulfur, and (E – F) boron using HNO_3 microwave digestion for the Bojac and Dragston soils in Trial 3. Letters above bar indicate significant differences ($p < 0.05$). Statistical comparisons were made within runs (Run 1: "a, b, c"; Run 2: "x, y, z"). The horizontal line indicates the minimum sufficiency concentration in the uppermost trifoliate (3000 mg P kg^{-1}; 3000 mg S kg^{-1}; 20 mg B kg^{-1}).

Chapter 5: Conclusion

The Mn + B coated KCl significantly increased soil and tissue Mn compared to the control and uncoated KCl on both low and high OM soils in the greenhouse. However, this increase was not replicated under field conditions, with no significant effect on either soil or tissue Mn. Environmental conditions, such as precipitation and leaching, most likely negated any potential increases provided by the Mn + B coated KCl in the field. In both cases, the coated KCl failed to increase soil or tissue B which is most likely due to the low amount of B contained within the coating. While the Mn + B coated KCl did not significantly increase Mn concentrations, it was not significantly different from the remaining treatments either, including the more commonly used foliar – application method. These results are probably due to insufficient Mn in the coated product, as recommended rates for soil applied Mn are 28.0 – 36.6 kg ha^{-1} compared to 6.86 – 11.36 kg ha^{-1} for the coated product in the field.

The tomato greenhouse trials investigated two different soil amendments: P + S + B coated KCl and glucoheptonate. Compared to the coated KCl, agronomic rates were 2 – 4 times greater for P, 4 – 10 times greater for S, and was similar for B. The P + S + B coated KCl increased soil and tissue P, S, and B compared to the control and uncoated KCl treatments but did not match the increases provided by the agronomic rates. This is most likely due to differences in application rates between the coated KCl and the current agronomic rates. While significant increases were not seen for tissue P and S, the coated KCl did significantly increase tissue B for both soil types, with concentrations that were equal to or approximately half that of the agronomic rate, and consistently above the minimum sufficiency level. The results of this study show that the coated KCl could help boost soil P, S and B, but due to insufficient P and S in the coating it would not be able to sufficiently satisfy crop demands without additional supplements, except for B.

The glucoheptonate trial revealed no significant effect on P or S across a range of application rates for both soil and tissue concentrations. However, soil and tissue B showed a significant positive correlation to GH application rate on both soil types. This is probably due to increased soil aggregate stability and water holding capacity caused by the greater application rates of GH, an organic acid chelate, based on the reduced water loss seen with greater GH application rates. However, when compared to the increases seen from fertilizer B, the increase from the GH is negligible. Additionally, no interaction effect was seen between the P + S + B coated KCl and the GH. Further studies should be conducted to investigate the impact of GH on the soil microbial community and soil water dynamics to better understand its mode of action within soil systems.

Appendix

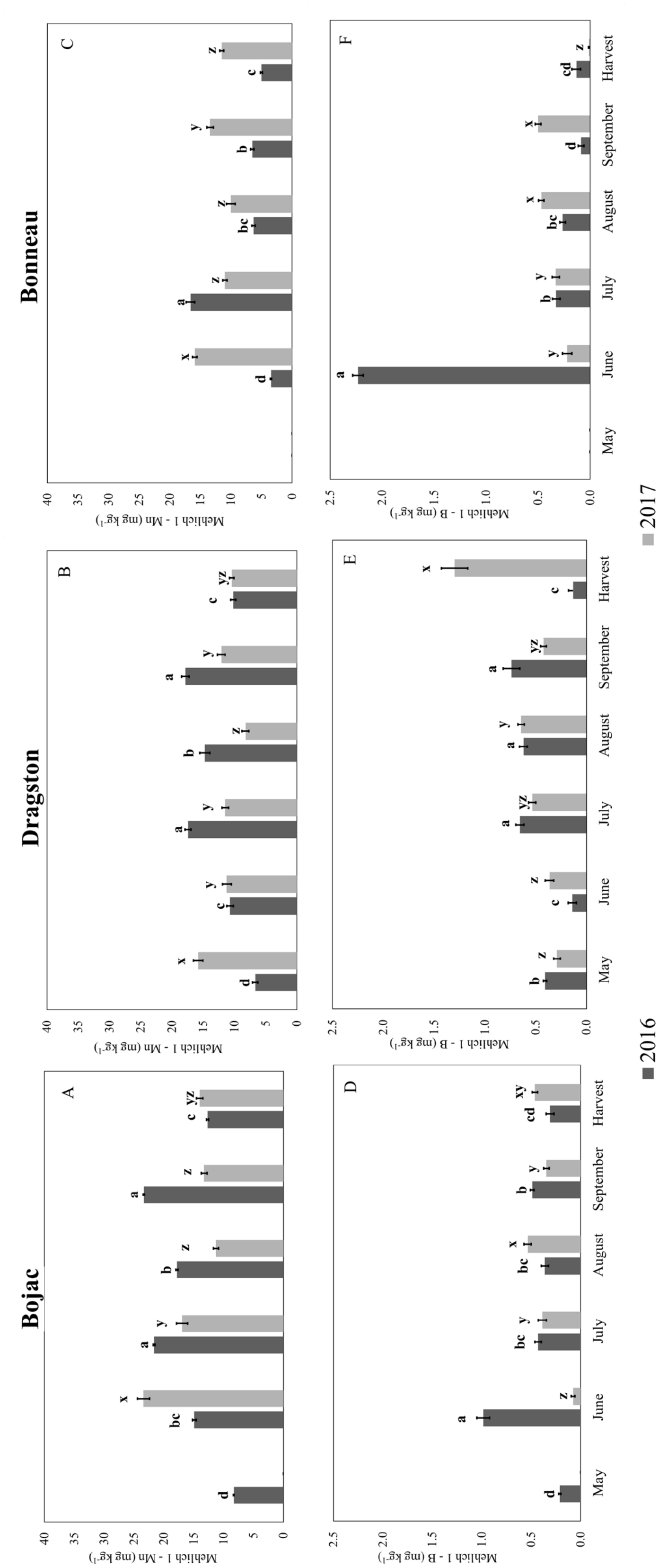

Fig A.1. Mehlich 1 - Mn (A - C) and Mehlich 1 - B (D - F) over time for the three soils used in the field study (Chapter 3). Different letters indicate significant differences ($p < 0.05$). Statistical comparisons were made for letters “a, b, c” and “x, y, z”.

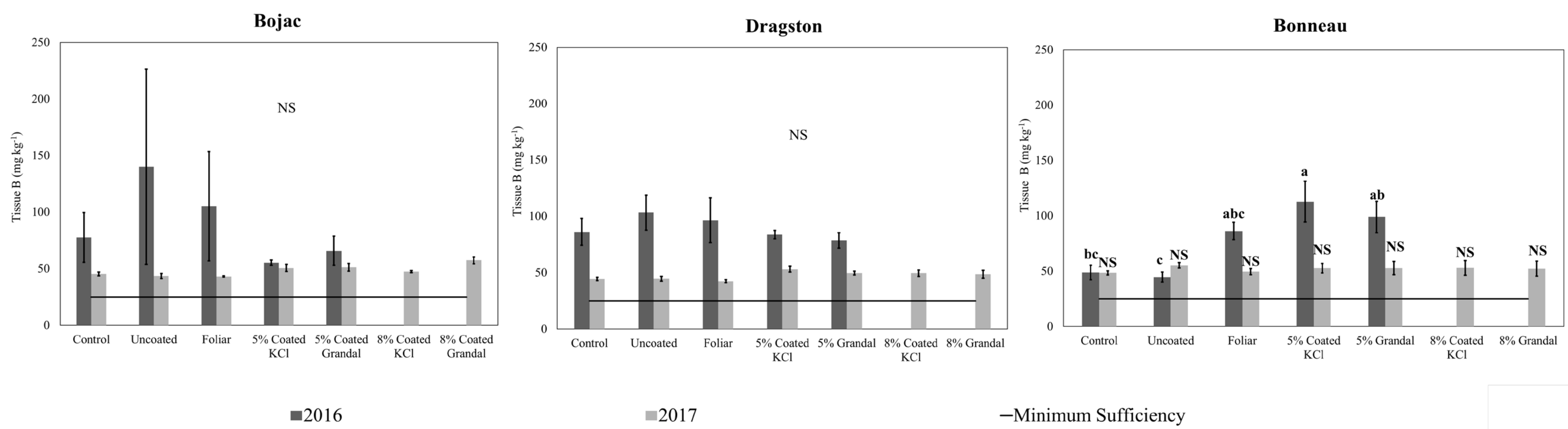

Fig A.2. Plant tissue B concentrations using HNO_3 microwave digestion for the three soils used in the field study (Chapter 3). Letters above bar indicate significant differences ($p < 0.05$). The horizontal line indicates the minimum sufficiency concentration in the uppermost trifoliate (25 mg kg^{-1}).

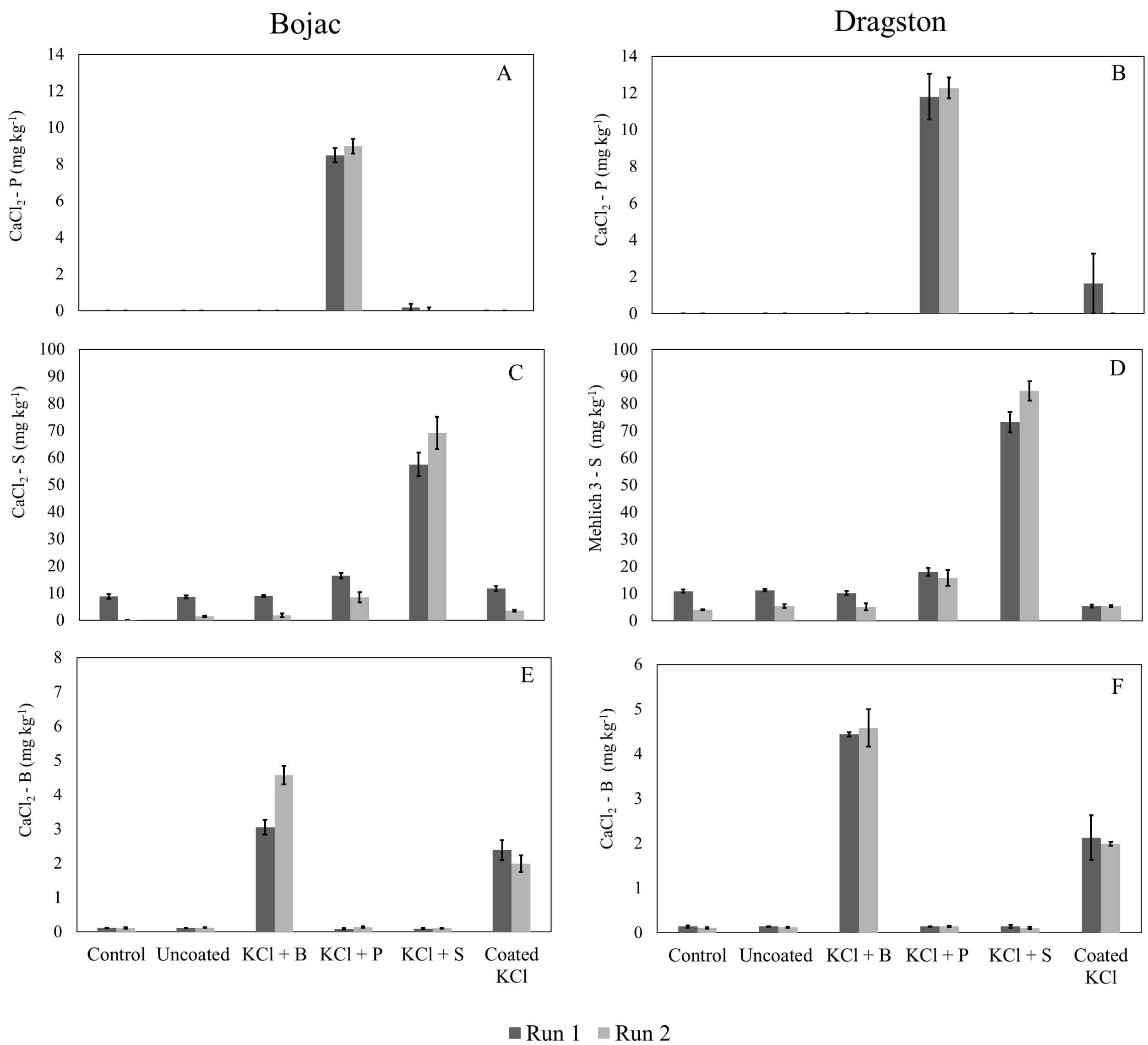

Fig A.3. $CaCl_2$ – extracted (A – B) phosphorous, (C – D) sulfur, and (E – F) boron for the Bojac and Dragston soils in Trial 1.

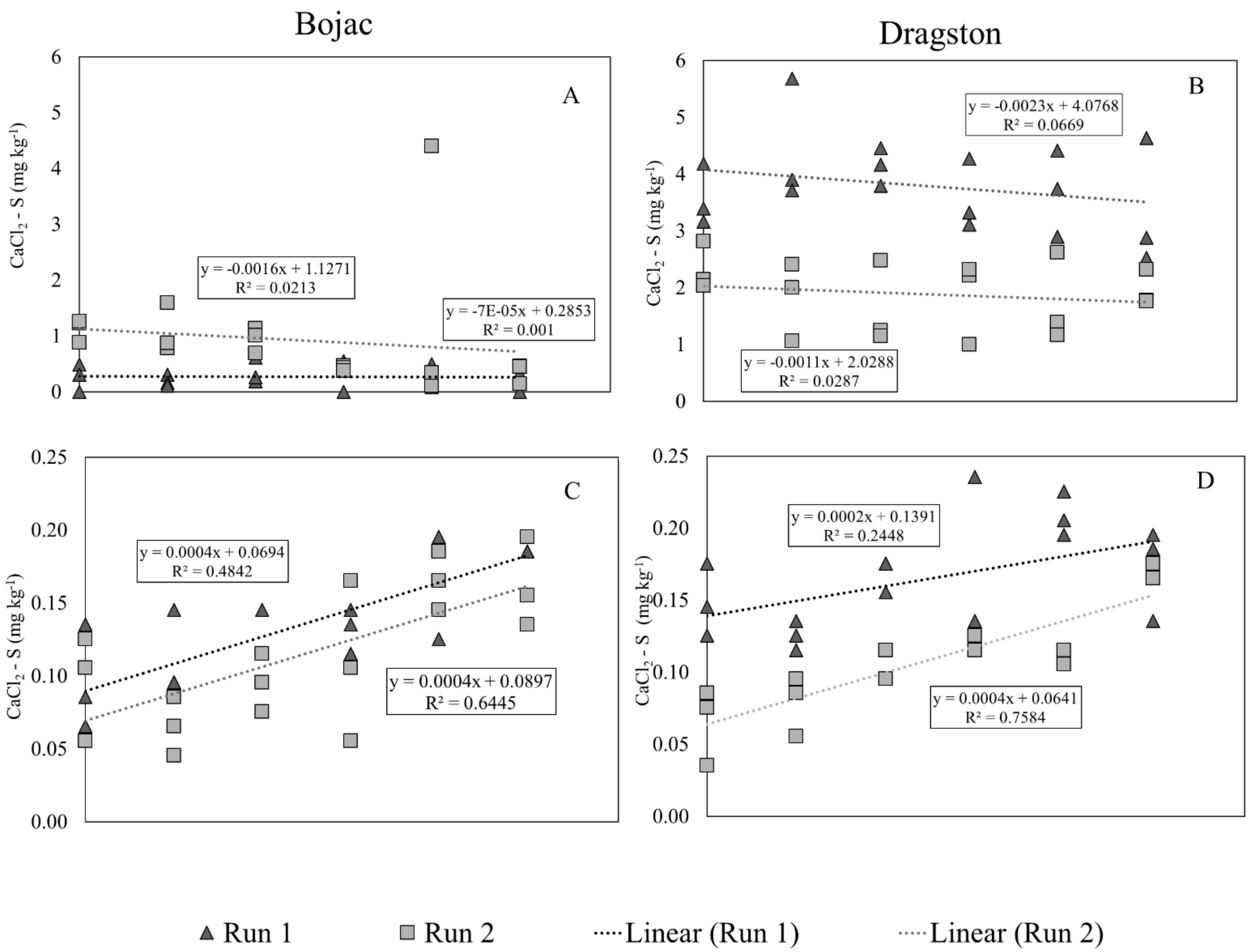

Fig A.4. *0.01M* $CaCl_2$ sulfur (A - B), and (C - D) boron for the Bojac and Dragston soil for Trial 2. Dotted lines represent trend lines from regression analysis comparing soil concentrations and glucoheptonate application rate ($p < 0.05$).

Table A.1a. Average water lost between watering periods (1 - 2 d) for both soils in Trial 2.

Soil	Run	0	49.8	99.6	149.3	199	248.9	R^2	Prob > F
		kg ha^{-1}							
Bojac	1	199.08	192.25	178.67	188.83	187.67	172.17	*0.36*	*0.0085*
	2	131.19	139.63	128.56	124.81	110.69	139.19	0.16	0.1015
Dragston	1	172.08	176.75	168.50	165.17	166.67	166.08	*0.36*	*0.0087*
	2	165.13	155.44	167.63	134.38	131.50	139.50	0.09	0.2311

Table A.1b. Average Plant Height (cm) for both soils in Trial 2.

Soil	Run	0	49.8	99.6	149.3	199	248.9	R^2	Prob > F
		kg ha^{-1}							
Bojac	1	17.63	15.87	18.53	15.60	16.27	16.90	0.008	0.7208
	2	22.10	23.37	21.73	22.93	22.60	22.47	< 0.01	0.9382
Dragston	1	24.10	23.90	22.57	20.30	17.27	21.60	*0.26*	*0.0296*
	2	35.40	31.93	31.03	32.50	29.73	30.70	*0.27*	*0.0259*

Table A.1c. Average aboveground dry biomass (g) for both soils in Trial 2.

Soil	Run	0	49.8	99.6	149.3	199	248.9	R^2	Prob > F
		kg ha^{-1}							
Bojac	1	1.81	1.79	1.79	1.32	1.51	1.47	0.08	0.2539
	2	2.89	3.76	3.10	3.43	2.84	3.31	< 0.01	0.9174
Dragston	1	2.02	2.26	1.66	1.48	1.32	1.69	*0.28*	*0.0253*
	2	4.41	3.80	4.40	4.36	3.38	3.46	0.1	0.2096

Table A.1. Regression analysis comparing average water loss per pot (a), average plant height (b), and average aboveground dry biomass (c) with GH application rates in Trial 2.

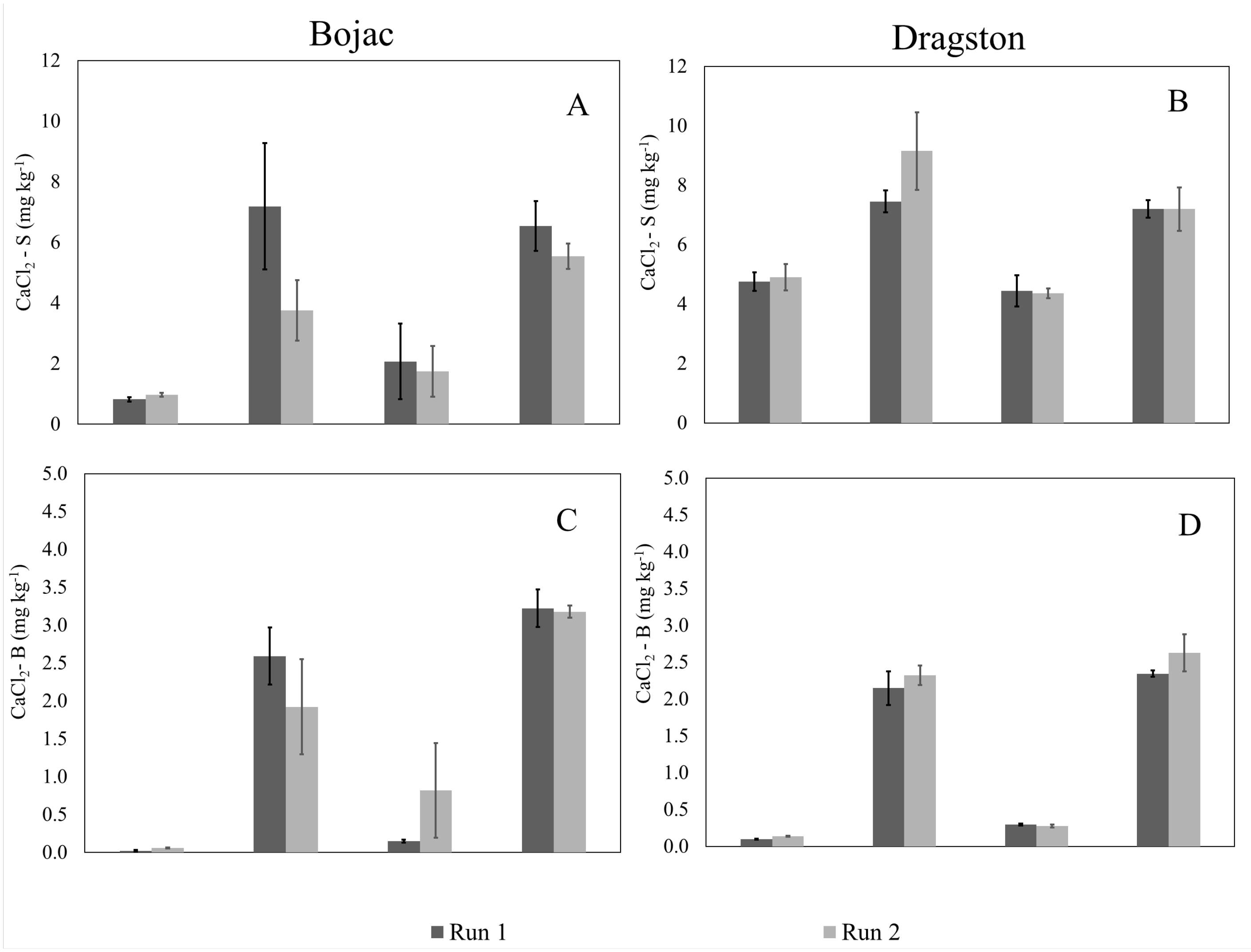

Fig A.5. $CaCl_2$ sulfur (A - B) and boron (C - D) for the Bojac and Dragston soil for Trial 3.