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Silicon Fertilization in Rice and Wheat: Dynamics with Trace Elements and Effect of Silicate Slag Granular Size on the Release Pattern of Monosilicic Acid in Soil

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SILICON FERTILIZATION IN RICE AND WHEAT: DYNAMICS WITH TRACE ELEMENTS AND EFFECT OF SILICATE SLAG GRANULAR SIZE ON THE RELEASE PATTERN OF MONOSILICIC ACID IN SOIL

A Dissertation

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by
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Table of Contents

List of Tables

List of Figures

Abstract

Studies were conducted to evaluate the impact of silicon (Si) fertilization on the uptake of harmful trace elements in Louisiana rice production system, and document the effect of silicate slag granular size on its ability to supply Si in wheat. The influence of silicate slag and lime on the uptake and translocation of harmful trace elements in rice grain was determined. Results showed that both slag and lime had similar effects on pH at five of the nine sites investigated. Soil Si was significantly (P <0.001) increased with application of silicate slag at all sites. Lime and silicate slag had no effect on the concentration of trace elements in soil. However, increasing Si rates were negatively correlated with arsenic (As) and cadmium (Cd) concentration in rice grain. The release pattern of monosilicic acid (H_4SiO_4) from wollastonite and silicate slag was compared in a wheat greenhouse study. Maximum release of Si from these materials were observed within the first 30 days after application and thereafter remained steady until 120 day after treatment application when a decline in soil Si became evident. Silicon extracted from soils treated with fine and ungraded silicate slag showed the greatest increases in soil Si when compared to wollastonite and the coarse and pellet slag materials. Wheat Si uptake was also higher for the fine silicate slag followed by ungraded silicate slag and wollastonite. But wheat yields were higher in the wollastonite treatments compared to silicate slag treatments. Among the different granular sizes of silicate slag, fine and ungraded materials resulted in higher wheat grain yield than coarse and pellet. In a field study, different granular sizes of silicate slag were applied at increasing rates to establish optimum Si application rate for wheat in Louisiana. The application of 1.8 and 3.6 Mg ha^{-1} of fine material was sufficient to increase wheat grain yield in three out of four sites studied. It is likely that application of Si in Louisiana agriculture has the potential to improve rice grain safety, by

limiting uptake of harmful trace elements and also improve grain yield in wheat cultivated on Si deficient soils.

Chapter 1. Introduction

Even with numerous studies documenting the role of silicon (Si) in higher plants, it is still not listed among the “essential nutrients” required for plant growth. The slow pace of Si research in agriculture can partially be attributed to solution culture technique research finding in the early 1860s which showed that Si is unnecessary for growth of higher plants (Epstein, 1999).

Until now, Si nutrition is only thought to be necessary for primitive plants including the diatoms, yellow-brown algae and members of the Charophyceae and Equisitaceae families (Chen and Lewin, 1969; Lewin and Reimann 1969). However, several studies suggest that certain species of plants, mostly of the Graminea or Poaceae family, perform poorly when Si is excluded from their growth medium (Datnoff et al., 2001). In field studies involving rice (*Oryza sativa*) and sugarcane (*Saccharum officinarum*) in Japan, Hawaii, Puerto Rico and Florida, (Ayres, 1966; Fox et al., 1967; Gascho, 1976; Okuda and Takahashi, 1962; Clements 1980;) reported superior performance of crops supplied with Si when compared to those without sufficient Si.

There are arguments that Si cannot be considered an essential nutrient for growth of higher plants, since they have been shown to complete their live cycles in the absence of Si. Such arguments are however difficult to sustain, because it is extremely difficult to exclude Si from growth media or cultural solutions due to its ubiquity in nature (Epstein,1994). The first Si exclusion experiment was performed by Wooley (1957), who was only able to reduce the Si content of tomato plants to 0.0006%. Finding no difference in growth between the so-called Si excluded plant and those suppled with Si, he concluded that if Si is essential for plant growth, it would be required at the molecular level or at concentration of less than 0.2µmol g^{-1} of dry weight.

1.1. Silicon as an Element in Nature

Silicon is the second most abundant element in the earth's crust and constitutes 28.8% of the earth's mass (Wedepohl, 1995). More than 370 minerals in the earth contain Si; thus, soils formed from the weathering of these minerals can often contain Si (Haynes, 2014). In soil forming minerals such as basalt and orthoquartzite, the concentration of Si often ranges between 23 – 46%; with smaller concentration also found in carbonaceous rocks such as the carbonates and limestone (Monger and Kelly, 2002).

Silicon is a highly reactive element and almost never exists in its pure form in nature, but is rather often found in combination with other elements as in silicon dioxide (SiO_2) and aluminosilicates. Silicon containing minerals are highly resistant to both physical and chemical weathering, hence the concentration of Si in soil solutions is often low (Sacala, 2009). Since the soil is mostly comprised of silicate minerals, it is often assumed that Si fertilization in agriculture is unnecessary because the earth contains an infinite supply of Si. But like any other essential plant nutrient, Si must be in a plant-available form to be taken up by plants. The plant-available form of Si found in soil solutions is the uncharged monosilicic acid (H_4SiO_4) (Lindsay, 1979; Epstein, 1994).

While large amounts of Si are often present in soils, some soils can also have low levels of Si in the plant-available form. Foy (1992), documented that soils classified as Oxisols and Ultisols, which are characterized by high weathering activities, low pH and base saturation as well as high water infiltration rates, can often be deficient in plant-available Si. Snyder et al. (1986), also reported that Histosols having high organic matter content with low levels of minerals can also have low Si content.

1.2. Role of Silicon in Plant Nutrition

For an element to be considered essential for plant growth it must be directly involved with the plant's metabolic processes; and its function must not be replaceable by other elements (Havlin et al., 2005). Despite much research documenting Si contributions to maintaining normal growth in some higher plants, its exact metabolic functions in plants are yet to be established. Since Si plays a crucial role in maintaining normal plant growth in highly Si-deficient soils, the American Association of Plant Food Control Officials recognized Si as a "plant beneficial element" (AAPFCO, 2012).

Plants grown under field conditions often encounter a wide range of stress arising from biotic (diseases and pests), and abiotic (drought, extreme temperatures, metals toxicities problems, and soil salinity among others) sources. Silicon is very essential in mitigating the harmful effects of these stressful conditions on plants, by enabling plants to maintain optimum growth and yields even in the presence of these conditions (Epstein, 2005).

1.2.1. Mitigation of Biotic Stress

Crops are often subjected to attacks from insects, nematodes, mammals and pathogenic fungi. The adoption of large-scale monoculture and sedentary agriculture has not only increased our ability to match food production with population growth, but it also serves as a breeding ground for specialized pests that compete with humans for these crops. Reducing the negative physiological impacts (which can be categorized as biotic stress) of these pests on crops is very critical to maintaining optimum growth, yield and profitability. The role of Si in mitigating biotic stress has been well documented in a wide range of crops (Datnoff et al., 1997; Cotterill et al., 2007; Torlon et al., 2016;). While the exact mechanism involved are yet not fully elucidated, there are several proposals concerning the role of Si in offering plants resistance to fungal diseases such as blast (*Magnaporthe grisea*), blight (*Phytophthora infestans*), powdery mildews (*Podosphaera xanthii)*, and root rots (*Phytophthora species*). Silicon uptake is highly associated with modification of the plant cell wall (Horst et al., 1999; Fawe et al., 2001; Lux et al., 2002). The build-up of biogenic silica in plant shoot has also resulted in improved structural integrity of plants by creating more rigid cell wall in both leaves and shoots (Rafi et al., 1997; Bélanger et al. 2003).

Nutrient management practices can also affect plant response to pathogens and diseases. For instance, nitrogen (N) fertilizer application is highly essential for maintaining high crop yields. But over application of N can cause excessive growth which can result in lodging, mutual shading and succulent plants with high susceptibility to diseases (Berry et al., 2000; Slaton, 2003). It has been demonstrated that Si application significantly reduced the occurrence of blast in rice (*Oryza sativa*) fields under high N fertilization (Ma, 2004). The suppression of blast and sheath blight (*Rhizoctonia solani)* has also been reported in rice (Datnoff et al., 1997; Seebold et al., 2001), powdery mildew (*Podosphaera xanthii)* in cucumber (*Cucumis sativus*), Arabidopsis (*Arabidopsis thaliana*), and wheat (*Triticum aestivum*) (Fauteux et al., 2005).

Heath and Stumpf (1986) and Kim et al. (2002), found that host plants treated with Si rendered greater mechanical resistance to pathogens penetration due to the accumulation and polymerization of monosilicic acid (H_4SiO_4), which provides greater rigidity to cell walls. But increased mechanical strength seems not to be the only means by which Si initiates plant resistance to pathogen and disease. Some biochemical reactions which inhibit the proliferation of plant pathogens may also be involved.

The establishment of chemical barriers which impede the progress of pathogens in host plants have been well described by several authors. For example, increased activities of enzymes responsible for triggering plants defense mechanism such as chitinases (Cruz et al., 2013), β-1,3-glucanases (Tatagiba et al., 2014), peroxidase (Mburu et al., 2016), polyphenol oxidases (PPO), phenylalanine ammonia lyase (PAL), (Zhang et al., 2013), uperoxide dismutase, ascorbate peroxidase, glutathione reductase, catalase, lipoxygenase, and glucanase (Waewthongrak et al., 2015) were reported in plants treated with Si.

Chitin and β-1, 3-glucan are the main carbohydrates found in fungi cell walls. Hence, the production of chitinases and β-1,3-glucanases enzymes, which is enhanced by Si, can result in the breakdown of fungi cell walls, making them incapacitated to mount a more aggressive attack on Si-treated plants (Keen and Yoshikawa, 1983). Cruz et al. (2013), observed an increased activity of chitinases in Si-treated plants during the early developmental stages of Asian soybean rust (*Phakopsora pachyrhizi*) symptoms relative to those plants without Si.

Peroxidase is an enzyme that triggers the production of hydrogen peroxide which is essential for plant cell wall lignification and forming cross-link with proteins in the plant cell walls (Torres et al., 2006). It has also been associated with the polymerization of phenolic compounds that enhances tissue lignification (Vidhyasekaran, 1988). In rice variety susceptible to *pyricularia grisea*, Datnoff et al. (2007), reported increased production of peroxidase transcripts, resulting in decreased severity of the disease in plants supplied with Si. Silicon-treated rice and cucumber, after been inoculated with *Bipolaris oryzae* and *podosphaera xantii* respectively, exhibited increased activities of peroxidase and chitinases (Dallagnol et al. 2011). The conversion of less toxic phenolic compounds to quinines, which is more toxic to plant pathogens, is initiated by polyphenol oxidases, which is also essential for lignin biosynthesis in plants (Song et al., 2016). The increased production of phenylalanine ammonialyase, resulting in accumulation of phenolic compounds and derivatives of lignin-thioglycolic acid in plant leaves associated with low occurrence of diseases in plants, was attributed to Si by Silva et al., 2010. It has been proposed that when plants come under attack from pathogenic fungi, Si induces rapid and extensive deployment of the plant natural defenses either by sequestering cations or by increasing the activity of some proteins (Fauteux et al., 2005).

Although reduction in plant disease incidence by Si has been widely reported, diseases are not the only biological stress that Si mitigates in plants. Reduced damage of crops by insects and grazing animals has also been reported in Si-fertilized plants. In separate experiments, Cotterill et al. (2007) and Hunt et al. (2008), demonstrated that grasses fertilized with Si were less grazed by wild rabbits (*Sylvilagus*) and locusts (*Schistocerca gregaria*), respectively, than those without Si fertilizer. They both concluded that the leaves of Si-fertilized plants were more difficult to graze by those pests due to the increased mechanical strength of leaves, which was enhanced by the high concentration of silica found in them. Similar observations have also been made for other agricultural pests such as yellow borers (*Scirpophaga incertulas*), rice chlorops (*Chlorops oryzae*), rice leafhopper (*Nephotettix bipunctatus cinticeps*), brown leafhoppers (*Nilaparvata lugens*) and weaver spider mites (*Tetranychus spp.*) (Savant et al., 1997).

In the case of aphids (*Aphidoidea*), Gomes et al. (2005), reported minimal infestation of Si-fertilized plants which they attributed to silicification of the leaves, which may offer greater resistance to penetration of aphid's stylus. However, Goussain et al. (2005), also investigated the inhibiting effect of Si on aphid stylus penetration of the leaves of infected plants. They contended that reduced infestation of aphids was not due to the creation of physical barriers induced by silicification, but chemical transformation in the plant may have caused the removal of aphids' stylus, thus making them to take up less plant sap. It has also been demonstrated by

Moraes et al. (2004), that foliar application of Si was effective against aphids' infestation, but they failed to describe the mechanism involved.

1.2.2. Mitigation of Abiotic Stress

Pests and diseases pose serious challenges for maintaining optimum crop yield, but environmental stresses are also a major cause for declining crop yield. The causes of declining crop performances not related to pests and pathogens are generally categorized as abiotic stress. An abiotic stress with the most noticeable impact on 21st century agriculture amongst others is the increasing incidence of drought and extreme temperatures which is also associated with climate change (CCSP, 2008). Prolonged crop exposure to drought can lead to damaging of cell membrane, deformed cell structure and the restriction of other important physiological processes such as cell division and photosynthesis (Hsiao, 1973; Taiz and Zeiger, 2006). Improved tolerance to drought has been recorded in Si-fertilized plants subjected to limited water regimes (Janislampi, 2012; Rizwan et al., 2012). When faced with water-stressed conditions, plants cuticle minimizes excessive water loss at stomatal closure (Riederer and Schreiber, 2001). Greater stomatal conductance, relative water contents and water potentials have been reported in Si-treated wheat compared to those without Si treatment (Pei et al., 2010).

Although the amount of water loss through cuticular transpiration only accounts for about 5 to 10% of total leave transpiration, this may become problematic when plants are exposed to high temperatures and low soil moisture conditions. Taiz and Zeiger (2006) and Ma (2004), observed that the deposition of Si beneath the cuticle of leaves can lead to formation of a Si-cuticle double layer, which facilitates a reduction in transpiration occurring through the cuticle. In drought stressed rice, Ma and Takahashi (2002), recorded Si deposition of up to 2.5 μm thick between the cuticle and endodermal cells. Ma (2004), reported that thickening of the cuticle resulted in a 30% reduction in transpiration rate in Si-treated plants. In blueberry, Morikawa and

Saigusa (2004), also reported deposits of Si in the guard cells surrounding the stomata. A decreased loss of water resulting from transpiration (Hattori et al., 2005) and reduced water uptake (Eneji et al., 2005) were associated with larger surfaces and thicker leaves of Si-treated plants, arising from higher deposition of Si in the cell walls of epidermal tissues than those without Si fertilization. In Si-fertilized *Chloris gayana* and *Sorghum sudanense* (Eneji et al., 2005) and wheat (Pei et al., 2010), greater biomass and grain yields have been reported under limited water supply.

While the accumulation of Si has been mostly reported in leaves and shoots as a major mechanism of Si-induced drought tolerance, this may not be the only way in which Si enables plants to withstand water stress. Apart from affecting physiological processes such as photosynthesis and transpiration under drought conditions, Si also enhances the development of secondary and tertiary cells of the endodermis, which facilitates faster root growth and enhances root tolerance to dry soils; enabling plant root systems to explore greater volume of soil and encouraging the uptake of more water and nutrients (Hattori et al., 2003).

Soil salinity is another abiotic factor posing serious challenges in crop production. Salinity (which is the presence of high concentration of dissolved salt in soil solution) and sodicity (the presence of high Na^+ on soil exchange sites), are most common in arid regions with limited rainfall to facilitate leaching of Na^+ below the root zone (Mavi et al., 2012). But, with increasing occurrences and intensities of tropical storms often giving rise to sea water intrusion, saline soils are also appearing along the costal belts of tropical and subtropical regions. Moreover, the sudden rise of shallow groundwater table through capillary action can also be a cause of soil salinity (Essington, 2004). In general, saline soils are not conducive for crop production, since high salt concentration reduces a plant's osmotic potential and limits water uptake (Läuchli and Grattan, 2007).

Salt stress can present extreme nutrient deficiency in plants (Gupta and Huang, 2014). The uptake of essential macro and micro plant nutrients is often impeded by saline or sodic soil conditions due to high pH and competition between Na^+ and other plant nutrients (Qadir and Schubert, 2002). It has been suggested that Si may be involved in balancing nutrient uptake, transport and distribution in drought and salt-stressed plants (Zhu and Gong, 2014; Rizwan et al., 2015). A decreased leakage in roots apoplast induced by Si in stele rice grown in a saline nutrient solution was proposed as a salt tolerance mechanism of Si (Yeo et al.,1999). The concentration of proline (a solute essential for osmotic adjustments) in plant tissue was increased in salt-stressed plants supplied with Si (Gunes et al., 2008; Crusciol et al., 2009).
In wheat plants growing in saline soil, an increase in activity of antioxidant enzymes was reportedly induced by Si (Saqib et al., 2008). A decreased permeability of plasma membrane, which permits better absorption of nutrients, was observed in Si-treated barley (*Hordeum vulgare*) (Liang et al., 1996,). In an experiment in which salt-sensitive and salt-tolerant wheat cultivars were evaluated, Tuna et al. (2008), suggested that Si could alleviate Na toxicity by blocking its translocation to the leaves.

Increasing levels of metals in agricultural lands can have grave impacts on plants health, growth and nutritional quality. While specific edaphic conditions may promote availability of metal in soils, anthropogenic causes of metal toxicity are more widespread. High levels of metals concentration can seriously alter plants physiological process and result in minimal biomass production, inhibits photosynthesis or even interferes with plant nutrient uptake. There are increasing amounts of evidence that Si plays a critical role in ameliorating metal toxicity, especially for metals which pose serious human health risks such as cadmium (Cd) (Sarwar et al., 2010) and arsenic (As) (Fleck et al., 2010). In the case of iron (Fe) toxicity, it is suggested that Si increases the oxidizing capacity of roots, which facilitates the conversion of ferric to ferrous, thus limiting the toxic effect of Fe in rice (Ma and Takahashi, 2002). Wallace (1993), hypothesized that Si limits Fe uptake in acidic soils by influencing the release of hydroxide ions in the roots of Si-fertilized plants. On the role of Si in alleviating aluminum (Al) toxicity, it has been assumed that the reaction between Si and Al in soils leads to the formation of subcolloidal and insoluble alumino-silicates, which reduces the concentration of free Al^{3+} ions in soil solutions (Liang et al., 2007). In corn (*Zea mays*), it was also assumed that Si stimulates phenolic exudation by roots which would chelate and reduce the absorption of Al by the roots (Kidd et al., 2001). Both cases mentioned above are examples of how Si reduces metal toxicity in soils. An in-planta mechanism of Si-induced reduction of Al toxicity have also been described by (Ryder et al., 2003; Wang et al., 2004), who reported that Si reduces Al toxicity in plants by forming hydroxyaluminumsilicates in the apoplast of the roots, which reduces Al translocation to shoot, or by the sequestration of phytoliths in the roots (Hodson and Sangster, 1993).

1.3. Silicon Uptake, Transport and Accumulation in Plants

While Si may be highly abundant in different forms in soils, it is only utilized by plants as H_4SiO_4. The concentration of H_4SiO_4 in soil solution mostly ranges between 0.1 to 0.6 mM in most agricultural soils (Knight and Kinrade, 2001). Plants growing in soils usually take up large amounts of Si. Three modes of Si uptake have been described in plants, which includes active, passive and rejective depending on the plant species (Cornelis et al., 2011). Based on their ability for Si uptake, different plant species have been classified as high, (e.g. rice), medium (e.g.

cucumber) and low (e.g. tomatoes) (*Solanum lycopersicum*) Si accumulators (Ma and Yamaji, 2006).

In plants with active mode of uptake, the amount of Si taken up is usually larger due to the high density of Si transporters present in their roots and shoots to facilitate the absorption of Si across cell membranes (Mitani and Ma, 2005). In rice for instance, both radial transport and uploading of Si in the xylem is facilitated by specialized transporters identified at *Lsi*l and *Lsi*2 in the roots; and *Lsi*6 in the shoot (Mitani and Ma, 2005). In medium Si accumulators such as cucumber, the uptake of Si can be a passive process driven by mass flow. Therefore, transport efficiency of Si in such plant can be limited, whereas the non-Si accumulators usually resist Si uptake as displayed by the higher concentration of Si observed in culture solution than in plants (Mitani and Ma, 2005).

Once taken up by plants, the transport of H_4SiO_4 occurs via the xylem, followed by deposition in leaves epidermal surfaces where it loses water through transpiration and becomes more condensed to form polymerized silica gel ($SiO_2 \cdot nH_2O$) or phytoliths (Yoshida et al., 1962; Jones and Handreck, 1965). These phytoliths can be found in specific cells known as silica cells, found within the vascular bundles (Raven, 1983). There is no evidence of Si mobility in plants. Hence, once deposited in plant tissues, it does not translocate within plant. Distribution of Si within plants is therefore highly contingent on soil solution concentration and plants ability for Si uptake as the main driving forces. Thus, older leaves normally contain higher levels of Si than younger ones (De Saussure, 1804; Henriet et al., 2006).

1.4. Silicon Interaction with Essential Plant Nutrients

Under certain conditions, the addition of Si to soil or nutrient solutions can influence the uptake and translocation of both macro and micro essential plant nutrients. For example, excessive phosphorus (P) fertilization can induce zinc (Zn) deficiency through the formation of Zn phosphate $Zn_3(PO_4)_2$. Si fertilization reportedly increased Zn availability under high P nutrition and suppressed the toxic effect of P in cucumber roots (Marschner, 1990), but promoted its translocation to the grains in rice and wheat (Lewin and Reimann, 1969). It has been demonstrated that Si fertilization also improved potassium (K) availability and uptake in plants (Kaya et al., 2006; Chen et al., 2016). In soybeans, the addition of Si fertilizer significantly improved the plant K status and growth (Miao et al., 2010). A recent study also revealed that Si reduced the effect of K deficiency by improving plant’s water status (Chen et al., 2016). Increased levels of Ca and Mg in soil and plant have also been associated with increasing Si fertilization (Kaya et al., 2006; Mali and Aery, 2008; Huang et al., 2011)

There has been extensive research done on the interaction between Si and micro nutrients. Chlorosis associated with Fe deficiency was reportedly corrected in soybean through the addition of Si to the nutrient solution (Gonzalo et al., 2013). In another study, an increased expression of Si transporters preceded by Si fertilization influenced the uptake and translocations of Fe, thereby improving Fe nutrition when a deficiency was present (You-Qiang et al., 2012). On the other hand, when Fe is present in toxic amounts, addition of Si can improve the root oxidizing capacity, causing the conversion of toxic ferric to ferrous, significantly reducing its absorption and translocation in plants (Ma and Takahashi, 2002). By enhancing root oxidizing capacity in rice, Si increases the manganese (Mn) oxidation quotient around the roots and facilitates its precipitation (Okuda and Takahashi, 1962). Silicon can also alleviate Mn toxicity in plants by ensuring its even distribution in the leaves, rather than allowing it to get concentrated in necrotic spots (Horst et al., 1999). Chlorosis in the leaves, as well as reduction in shoot and root biomass production in *Arabidopsis thaliana* induced by copper (Cu) toxicity, were corrected through the addition of Si to the nutrient solution (Li et al., 2008; Khandekar and Leisner, 2011).

1.5. Silicon Fertilizers

The abundance of Si in the earth crust has given rise to the notion that its application as fertilizer may not be necessary for crop production. Moreover, since the benefits of Si fertilization have mostly been reported in plants under some form of stress, more efforts are focused on mitigating those stress using other means rather than applying Si. Despite these controversies and reluctance regarding the agronomic importance of Si, the positive responses of crops to Si fertilization in deficient soils (*e.g.*, Oxisols, Ultisols, Entisols, and Histosols) continue to prove that Si fertilization is necessary (Savant et al., 1999). While it may not be listed among the essential nutrients, improved yields due to increased photosynthesis, better water use efficiency, as well as increased resistance to biotic and abiotic stresses are traceable to high Si levels in plant tissues (Epstein and Bloom, 2005). Due to these numerous benefits of Si reported globally in crop production, Si fertilizers are applied to crops such as rice and sugarcane (*Saccharum officinarum*) on a regular basis. More recently, application of Si to many horticultural crops has increased due to its role in suppressing several fungal diseases (Matichenkov and Bocharnikova, 2004).

Since crops such as rice, sugarcane and wheat take up large amounts of soluble Si from soils, cultivation of these crops can induce Si deficiency because the rate of removal often exceeds the rate of natural replenishment, thereby giving rise to the need for Si fertilization (Elawad and Green, 1979). Like any other nutrient management program, the main goal is to increase the plant-available form in soil solutions to facilitate rapid absorption and assimilation to minimize potential yield loses associated with deficiency. As such, choosing the right source of fertilizer is a critical step in correcting nutrient deficiency. Several materials have been evaluated for their potential to supply H_4SiO_4 to plants.

Residues of high Si accumulator crops are often incorporated in soil to replace some of the Si taken up. Based on the research of Ma and Takahashi (2002), it was demonstrated that the amount of Si held inside the rice straw is not immediately available upon incorporation, but over a long period of time (40 years or more), Si released by rice straw may account for over 70% of the plant utilized Si. But in the event of an acute Si deficiency, incorporation of plant residues may not be a viable solution, especially if the succeeding crop has high demand for Si. In spite of the fact that these plant residues may serve as good slow-release Si sources, increasing demand for their usage in the production of biofuel (in the case of sugarcane) and generation of steam or provision of animal feed (in the case of rice), may pose serious competition for their usages in agronomy. With this in mind, several other materials have been extensively evaluated for their ability to supply Si to crops. Sources containing high Si contents, high solubility, low cost and ease of mechanized application, and the potential to correct soil acidity, (since pH and Si availability in soil are highly correlated), are mostly desired (Korndörfer et al., 2001).

Wollastonite which is also known as calcium metasilicate ($CaSiO_3$) is the most popular source of Si for use in agriculture due to its high total Si (24.2%) and soluble Si (ranging between 2.6 to 6.5%) contents (Haynes et al., 2013; Sebastian et al., 2013). However, competition for other industrial uses of wollastonite, such as manufacture of ceramics, friction products, paint and plastics, coupled with its high cost, has made it economically unsuitable for large scale application. Its usage for agricultural purposes has therefore been restricted only to research (Haynes et al., 2013). For large scale Si fertilization, researchers have therefore focused on other sources such as silicate slag, converter slag and silico manganese slag, which are mostly industrial by-products, as well as coal fly ash, biochar from miscanthus and rice hull and straw, and silica gel among others (Savant et al., 1999; Sun and Gong, 2001; Kalapathy et al., 2002;

Haynes et al., 2013; Sebastian et al., 2013; Houben et al., 2014;). Among these materials, silicate slag is most commonly used in commercial agriculture.

Perhaps the most significant advancement in the use of silicate slag as a Si fertilizer began in the 1950s in Japan. Like most Asian countries, rice is the stable food in Japan. Intensive rice cultivation can lead to low levels of available Si in soil because rice is an Si accumulator. Several studies in Japan showed that increases in rice disease incidence was causing a dramatic decrease in yield when Si content in plant and soil were low, but the reverse was observed when soils were amended with Si. This led to the establishment of nation-wide experimental trials using silicate slag (Ma and Takahashi, 2002). Results from these experiments led to the establishment of the first nation-wide standard for Si fertilizers in 1955. In China, investigation by Zhu and Chen (1963), on different materials for their Si supplying ability to different crops, including rice, wheat, soybean, sunflower (*Helianthus*), potatoes (*Solanum tuberosum*), corn, cotton (*Gossypium hirsutum*) and beets (*Beta vulgaris*), indicated that slag application caused a 10% yield increase in rice, up to 5% yield increase in the upland crops and also improved crop quality as demonstrated by the improved oil content in sunflower, starch content of potatoes and rice, protein content of wheat, corn and cotton seeds and sugar content of beets. Slag is also widely used in rice and sugarcane production in Brazil, not only for its ability to supply Si to these crops but also as a liming material (Korndörfer et al., 2004). In the United States, the application of silicate slag to rice and sugarcane is a regular practice for producers in Florida (Avirez et al., 1988).

1.6. Silicon Status of Louisiana’s Soils

Louisiana’s agricultural soils are extremely diverse. Many formed by sediments deposited by seasonal flooding of the state’s many rivers. The high amount of organic matter incorporated into these soils during deposition of sediments can significantly enhance their fertility. High amounts of rainfall received annually across the state can also lead to leaching of plant nutrients out of root zone, thus reducing the ability of these soils to retain nutrients. Application of fertilizers containing essential plant nutrients is a regular practice in the state's agricultural production systems. Unlike most other essential plant nutrients for which extensive research has been done, little is known about the Si status in Louisiana soils. Since most of the state's soils are comprised of large proportions of clay, Si fertilization may have been grossly disregarded based on the assumption that sufficient amounts of Si already exist in these soils.

Louisiana growers produce rice, sugarcane and wheat, all of which have a high demand for Si. A survey of the Si status in rice grown in the southwestern region of the state revealed that Si content in harvested straw was consistently lower than the minimum sufficiency level of 50 mg kg^{-1} in over 60% of the fields investigated (Kraska and Breitenbreck, 2010). In a greenhouse study investigating rice response to Si fertilization in different soil series collected across the state, (Babu et al., 2016) reported significant increases in relative biomass yield of rice in five out of six soil series to which Si was applied, with the highest relative biomass yield reported in Commerce silt loam soils. These reports suggest that there is potential for Si fertilizer application to benefit the production of rice, wheat and sugarcane in Louisiana.

1.7. Economic Importance of Rice and Wheat

The current world's population of 7 billion is expected to surpass10 billion by the year 2050 (UN, 2013). The need to match food production with this increasing population is of global concern. Increased production of rice and wheat remains a global goal to meet the challenge of feeding this ever-growing population.

Rice serves as the stable food and is an important source of calories for over half of the world's population (Greenland, 1997). In developing and under developed countries in Asia, Africa and Latin America, rice remains the most significant component of the diet, providing 27 and 20% of dietary calories and protein respectively (FAO, 2004). Rice cultivation is most concentrated in regions with high population densities where it is mostly consumed. Globally, China and India both of which have the highest population densities are the highest producers and consumers of rice (FAO, 2014). In the Americas, Brazil and the United States are the leading rice producing countries with each having an estimated annual production of over 10 million metric tons (FAO, 2014).

Like rice, wheat is one of the most important crops in the world. Geographically, the cultivation of wheat exceeds all other crops (Briggle and Curtis, 1987). Wheat provides about 55% of carbohydrates and 20% of the calories in human diet on a global scale and is cultivated under a wide range of climatic conditions (Breiman and Graur, 1995). It is said that contribution of wheat to human nutrition surpasses that of all other crops (Reitz, 1967). In the United States, wheat is produced in almost every state, thus serving as the principal cereal crop of the nation. In 2016/2017, the United States was the fifth largest wheat producing country after the European Union, China, India and Russia (FAO, 2016).

1.8. Rational for Research

Rice and wheat are the two most important food crops in the world. With increasing global population, the need to intensify the cultivation of these crops to meet the imminent high demand will continue to grow. This will translate into intensive production practices which can deplete soil nutrient status. Rice is one of Louisiana's most important crops in terms of planted acreage and economic value. Its production has spread from the traditional rice producing areas of southwestern Louisiana to the northeastern region of the state.

Rice can be grown under both aerobic and anaerobic conditions. However, most of the world's rice is produced under anaerobic or flooded conduction due to the high yields associated with ease of nutrient and weed management. However, prolong submergence or flooding can lead to changes in the chemical dynamics of soils and this can impact the nutritional quality of crops grown in flooded soils. Flooding can lead to the depletion of soil oxygen levels, which also gives rise to the release of metal cations such as Al, As Fe and Mn in toxic concentrations. Once released into the soil solution, these metals cations can actively be taken up and deposited into straw, leaves and shoot of rice. In recent times, there is a growing concern in several Asian countries, including Bangladesh, Japan, India and China, where most of the world's rice is produced and consumed, over increasing levels of As and Cd reported in rice grains (Tsukahara et al., 2003; Mondal and Polya, 2008). An alternative solution to this problem would therefore be the production of aerobic rice, since high oxygen levels in non-flooded condition keeps the concentrations of these metal cations below toxic levels. But difficulties in nutrient management, especially N fertilizers as well as high weed competition which limit rice yield and profit margin, makes aerobic rice production less economical. Since consumption of high levels of trace elements especially As and Cd pose serious threat to human health, it is important to ensure that low levels of these elements are taken up by crops while simultaneously maintaining or increasing yield to meet the increasing the demand.

Wheat is another important crop in the U.S., but since the 1980s, there has been a consistent decline in wheat cultivation nationally (USDA-ERS, 2014). Cultivation of wheat in Louisiana has followed the national trend, and this could probably be due to farmers opting to grow more profitable crops. Also, extremely wet soil conditions and fluctuating temperatures during the fall and winter months, high humidity in spring and excessive rainfall during or before harvest, make wheat cultivation even more challenging for Louisiana's wheat producers. These prevailing soil and environmental conditions can increase the incidence of diseases and lodging, which can dramatically reduce crop yield.

The positive effects of Si fertilization on crop production which include improved yield and crop quality, have been well documented, but limited research has not confirmed these benefits in Louisiana's crop production system. Moreover, Si is usually applied to crops as silicate slag in large quantities usually ranging from 1 to 4 Mg per hectare (Korndörfer et al., 2001). Although slag is an industrial by-product and as such is relatively inexpensive, such high application rates can impact the cost of large-scale application depending on the location of the farmer with respect to the source of the fertilizer. It is therefore necessary to understand factors that influence the effectiveness of slag to adequately supply Si to crops. Such information will be an essential decision-making tool in determining the type and amount of fertilizer require for maximum production. The objectives of this research were to: 1) evaluate the effect of slag application on Si and trace elements content in soils and their uptake by rice grown under flooded conditions, 2) document the impact of granular size of slag on its solubility and release of monosilicic acid in soil and Si uptake by wheat, and 3) determine the optimum application rate of silicate slag and its impact on wheat grain yield using different particle sizes.

1.9. References

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Chapter 2. The Effect of Silicate Slag Fertilization on Trace Elements Content of Rice Cultivated on Flooded Louisiana Soils

2.1. Introduction

Trace element contamination of agricultural soils is an environmental problem that is raising concerns over food safety. Food and drinking water are the main source for human exposure to harmful levels of dangerous trace elements such as arsenic (As) and cadmium (Cd) (Tao and Bolger, 1999; Yu et al., 2006; Uraguchi et al., 2009;). In recent times, there have been increasing reports of high levels of As and Cd in rice (*Oryza sativa*), which is the main source of calories and stable food for over half of the world's population (Watanabe et al., 2000; Williams et al., 2005; Meharg et al., 2013). These trace metals are naturally occurring in soils and are ubiquitous as environmental contaminants; but their entry into the food chain and subsequent human exposure can be exacerbated by anthropogenic activities, such as mining, agriculture and industrialization (Alkorta et al., 2004).

In Louisiana, rice is a major crop and is cultivated mostly in the southwest and northeastern region of the state. Rice is a semiaquatic plant that is well adapted to both aerobic and anaerobic conditions. But due to ease of nutrient and weed management which often results in higher yields, a vast majority of rice produced globally is cultivated on either irrigated or flooded soils (Maclean et al., 2002). Prolong submergence of soil can however lead to a chemically reduced condition in the soil and promotes the availability of As for plant uptake (Ohtsuka et al., 2013). Epps and Sturgis (1939), accessed the impact of elevated soil As on rice cultivation in Louisiana soils and reported that As only becomes toxic to rice under water logged conditions. Ori et al. (1993), surveyed over 450 agricultural soils across Louisiana and reported As contents ranging from 0 to 73 mg kg^{-1} with a mean As level of 23.2 mg kg^{-1}. "Straight-head", a physiological disorder in rice, which inhibits grain filling and in severe cases, results in failure of panicle emergence from the flag leaf, has also been associated with elevated levels of As in flooded soils (Epps and Sturgis, 1939). Since soil redox potential influences As mobility in soil, water management has been proposed as a means of limiting As toxicity to rice as well as its uptake and translocation to rice grain. Draining the rice field at midseason reportedly reduced the severity of straight-head in flooded rice (Wells and Gilmour, 1977)

Arsenic is considered a high-level carcinogen, and has been linked to several disease conditions in humans including hypertension, diabetes mellitus, vascular disease and impaired intellectual capabilities in children (Smith et al., 1992; Wassermann et al., 2004). The intake of inorganic As through rice consumption has also been determined as a significant risk factor for cancer in a population for whom rice is a stable food (Mondal and Polya, 2008). Although drinking water is another means by which people can be exposed to As, it has been reported that the risk for human exposure to As via rice consumption far exceeds that of any other crop or drinking water (Williams et al., 2006). Due to the high human health risk posed by elevated levels of inorganic arsenic in a variety of food, standards have been set to minimize human exposure through dietary sources such as infant rice cereal. In polished rice grain intended for human consumption, the maximum level of inorganic arsenic was set at 0.2 ug g^{-1} (CODEX STAN, 1995). In 2015, the European Commission set a maximum allowable limit of 0.1 ug g^{-1} for inorganic arsenic in rice intended for infant food products (European Commission, 2015). This standard was also adopted by the United State Department of Agriculture-Food and Drug Administration in 2016 as suggested limits for U.S. rice (USDA-FDA, 2016).

Cadmium (Cd) is another potentially dangerous trace element whose accumulation in rice has been well studied. Cadmium is a highly toxic metal and its contamination of agricultural soils is considered a major environmental problem (Gallego et al., 2012; Wang and Du, 2013). Increased contamination of Cd in agricultural soils usually derives from the application of Cd containing pesticides, fertilizers, irrigating fields with ground water containing high levels of Cd, as well as other anthropogenic activities such as mining (Sandalio et al., 2001). Like As, it is well documented that rice is a significant source of human exposure to toxic levels of Cd (Yu et al., 2006; Uraguchi et al., 2009). Cadmium is absorbed from the soil solution and translocated to the shoot and grain of rice (Song et al., 2015, Wang et al., 2015) thereby enabling it to enter the food chain. Elevated levels of harmful trace elements such as As and Cd in rice pose a grave safety concern for human health, because rice is a global staple food with production exceeding 752 Mg per year (FAO 2004). It is the main source of calories in regions with high population densities.

Several management techniques have been proposed to limit the accumulation of both As and Cd in rice grain, but most have often led to conflicting results. For instance, the elevated As levels in rice grain is associated with flooded conditions where As mostly exist as arsenite (As^{3+}), the form more toxic to plants and animals (Ko et al., 2007; Xu et al., 2008). It has been demonstrated that cultivation of aerobic rice resulted in lower As levels in the grain (Arao et al., 2009; Li et al., 2009), but this practice is also associated with lower grain yields (Grassi et al., 2011). Intermittent drying and flooding of rice field has been proposed as an approach to decrease rice grain As content without compromising yield, but this can also lead to increased uptake of Cd (Arao et al., 2009).

Despite the numerous reports documenting the impact of various cultural management practices aimed at reducing As and Cd accumulation in rice grain, there is still an urgent need to develop measures that will simultaneously reduce the accumulation of these trace elements in rice without compromising the uptake of the other, or a decline in grain yield. It is reported that Si fertilization has a significant impact on the accumulation of both As and Cd in rice. Li et al. (2009), demonstrated that the application of 20 g of SiO_2 gel kg^{-1} of soil resulted in 78 and 50% reduction of As in rice straw and husk, respectively. In another study, Liu et al. (2009), reported reduced Cd accumulation in rice with foliar application of Si. Despite these reports, the effect of Si fertilization on the simultaneous decrease of these trace elements in rice has not been elucidated. The objective of this study therefore is to determine the impact of silicate slag fertilization on the availability and uptake of trace elements in rice grown in flooded Louisiana soils.

2.2. Materials and Methods

2.2.1. Field Trials Establishment

Field studies were established at nine locations in Louisiana from 2013 to 2015 under a drill-seeded, delayed-flood cultural system. The location and soil information of each site is presented in Table 2.1. Before trial establishment, composite soil samples were taken at 15 cm depth from each site and analyzed for initial pH, soil nutrients, and organic matter (OM) contents, as well as Si and trace elements content (Tables 2.2 and 2.3). Plots were than treated with varying rates of silicate slag (14% Si) applied at 1, 2, 4, 6 and 8 Mg ha^{-1} (equivalent to 140, 280, 560, 840 and 1120 Kg Si ha^{-1}, respectively), and lime (2 and 4 Mg ha^{-1}) prior to seeding. The two lime treatments were included to distinguish the effect of liming between lime and silicate slag on soil pH and the availability and uptake of metals by rice. Silicate slag does not only increase Si in soil, but can also be used to correct soil acidity. The materials were hand-broadcast applied and incorporated into the soil at a depth of 7 cm before planting. All treatments were replicated four times and arranged in randomized complete block design. In each plot measuring 1.5 x 4.9 m, rice was drill-seeded using a small-plot grain drill at a depth of 4 cm and a rate of 300 seeds m^2 with 7 cm spacing between rows. Nitrogen fertilizer was broadcast-applied as urea (46% N) when rice seedlings were around 4-leaf stage of development (about one month after germination), after which permanent flooding was established the next day and maintained until physiological maturity.

Table 2.1. Location and soil information for all experimental sites, 2013 to 2015.

Site	Year	Location	Soil Type	Soil Classification	Coordinates
1	2013	Gilbert	Sharkey Clay	Very-fine, smectitic, thermic Chromic Epiaquerts	32.0417, −91.5367
2	2013	Crowley	Crowley silt loam	Fine, smectitic, thermic Typic Albaqualfs	30.2473, −92.3488
3	2014	Gilbert	Sharkey Clay	Very-fine, smectitic, thermic Chromic Epiaquerts	32.0414, −91.5378
4	2014	Crowley	Crowley silt loam	Fine, smectitic, thermic Typic Albaqualfs	30.2462, −92.3515
5	2014	Mamou	Mowata silt loam	Fine, smectitic, thermic Typic Glossaqualfs	30.6463, −92.5055
6	2014	Lake Arthur	Kaplan silt loam	Fine, smectitic, thermic Aeric Chromic Vertic Epiaqualfs	30.0666, −92.6524
7	2014	St. Landry	Tensas Sharkey complex	Fine, smectitic, thermic Chromic Vertic Epiaqualfs	30.2462, −91.8915
8	2015	Crowley	Crowley silt loam	Fine, smectitic, thermic Typic Albaqualfs	30.2464, −92.3488
9	2015	Lake Arthur	Kaplan silt loam	Fine, smectitic, thermic Aeric Chromic Vertic Epiaqualfs	30.0675, −92.6529

Table 2.2. Initial soil organic matter and Mehlich-3 extractable nutrient contents from the experimental sites, 2013 to 2015.

			mg kg^{-1}						
Site	Site-Year	OM g kg^{-1}	P	K	Ca	Mg	S	Cu	Zn
1	2013 Gilbert	18.7	74	408	4971	1013	10.6	5.5	4.9
2	2013 Crowley	11.0	25	73	1463	271	9.0	1.9	6.7
3	2014 Gilbert	18.7	78	408	4971	1013	10.6	5.5	4.9
4	2014 Crowley	14.4	6.7	55	1595	265	9.1	1.4	4.6
5	2014 Mamou	11.0	10.5	34	557	122	1.4	0.5	2.4
6	2014 Lake Arthur	14.7	4.5	101	792	156	12.5	1.1	4.9
7	2014 St. Landry	25.9	78	228	3770	681	6.3	2.8	2.8
8	2015 Crowley	12.0	39	36	2440	347	25.0	1.4	10.0
9	2015 Lake Arthur	11.0	30	43	984	191	30.0	1.2	5.2

Table 2.3. Initial soil pH, Si and Mehlich-3 extractable trace elements content from the experimental sites, 2013 to 2015.

			mg kg^{-1}									
Site	Site-Year	pH	Si†	A l	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
1	2013 Gilbert	6.8	132	1296	0.04	0.31	5.1	481	163	2.6	2.3	3.8
2	2013 Crowley	7.3	94	698	0.20	0.26	1.5	794	242	2.2	4.3	8.2
3	2014 Gilbert	6.8	138	1401	0.35	0.10	3.0	618	87	3.2	2.0	3.7
4	2014 Crowley	7.4	26	432	0.30	0.42	2.4	706	159	4.8	3.2	8.9
5	2014 Mamou	5.3	5.5	750	0.21	0.04	0.8	449	113	5.7	0.9	5.2
6	2014 Lake Arthur	4.8	14	908	0.36	0.05	1.0	758	79	9.6	1.2	2.5
7	2014 St. Landry	7.1	151	1049	0.35	0.05	1.9	670	123	2.6	1.4	3.2
8	2015 Crowley	8.0	77	590	0.61	0.06	1.4	626	214	5.8	1.9	5.6
9	2015 Lake Arthur	5.3	40	1030	1.24	0.07	1.2	1309	105	7.5	1.3	5.4

†Soil Si was extracted using 0.5 M acetic acid solution.

2.2.2. Sampling

At harvest, rice samples were collected by harvesting two 1 m sections of the entire above ground biomass from the third row on each side of each plot and combining into one composite sample per plot. The samples were oven-dried at 55°C until a constant weight was obtained and then partitioned into grain and straw; the grain samples test weight and milling quality were also determined. After harvest, soil samples were also collected by randomly taking 12 cores at a 15 cm depth from each plot and combining into one composite sample per plot. The collected plant and soil samples were processed and analyzed for both Si and trace elements.

2.2.3. Plant Analysis

Straw and filled grains were finely ground separately; the straw was analyzed for Si content while the grains were analyzed for both Si and trace elements content. For determination of Si in plant tissues, samples were digested following the Oven-Induced Digestion (OID) procedure according to Kraska and Breitenbeck (2010) and then analyzed for Si content following the Molybdenum Blue Colorimetric (MBC) procedure as described by Hallmark et al. (1982). The trace metals content of the filled grains was determined by first subjecting the samples to the nitric acid- hydrogen peroxide (HNO_3-H_2O_2) digestion procedure, where a 0.5 g sample was weighed into a kimwipe paper measuring 5 X 5 cm. After weighing, the ends of the paper were twisted to enclose the sample and then place into a glass digestion tube. This was done to limit the amount of plant tissue that may stick to the wall of the digestion tubes. Reference samples which included a 0.25 g soybean (*Glycine max*) sample and an empty kimwipe for the blank were also included. After placing the samples into the digestion tubes, 5 mL of concentrated nitric acid (assay 67-70%) was added to each tube while ensuring that no plant tissue was left on the wall of the tube. The samples were allowed to sit in the acid for 50 minutes during which time the digestion block was adjusted to 155°C. The samples were then vigorously mixed for about 5 seconds using a Fisher Scientific vortex mixer (Volts 115VAC, Watts 150), after which they were placed into the digestion block and vigorously boiled for 5 minutes. The samples were then allowed to cool for 10 minutes, 3 mL of 30% H_2O_2 was added to each tube, covered with a glass funnel and returned to sit in the digestion block for another 2 hours and 45 minutes to complete the digestion process. After digestion, the samples were allowed to cool; the final volume was brought to 12.5 mL with deionized water and filtered using a Whatman No. 1 filter paper, and then analyzed for trace metals using the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICO-OES) procedure.

2.2.4. Soil Analysis

2.2.4. a. Soil pH Determination

The pH of soil samples collected from each plot was determined using a 1:1 (w/v) ratio of soil to water, where 10 g of dried, finely ground samples were weighed into a 50 mL screw-cap centrifuge tube, with 10 mL of deionized water, caped tightly and placed on a reciprocal shaker set at high speed for 1 hour. After shaking, the samples sat undisturbed for 1 hour to allow larger soil particles to settle; and the soil solution pH was measured using a SevenCompact^{TM} pH/ Ion S220 digital pH meter.

2.2.4. b. Soil Silicon Determination

Silicon in collected soil samples were extracted using the 0.5 M acetic acid extraction procedure with a 1:10 (w/v) ratio of soil to acetic acid solution according to Korndorfer et al. (1999), where 1 g of soil was weighed into a 50 mL centrifuge tube with 10 mL of 0.5 M acetic acid, screwed tightly and placed on a reciprocal shaker set at high speed for 1 hour. After shaking, the samples were filtered using a Whatman No. 1 filter paper and the plant-available Si in the sample extract was quantified using the MBC procedure (Korndorfer et al., 2001).

2.2.4. c. Determination of Trace Elements in Soil

Trace elements in soil samples were extracted using the Mehlich-3 solution (Mehlich 1984). Two grams of dried soil sample were weighed in 100 mL plastic bottles to with 20 mL of Mehlich-3 extractant (comprised of diluted acid-fluoride-EDTA solution adjusted to pH 2.5) and shaken on a reciprocal shaker set at high speed for 5 minutes. The samples were then filtered using a Whatman No. 42 filter paper and the extract was analyzed for trace metals using ICP-OES.

2.2.5. Data Analysis

Analysis of variance (ANOVA) was performed using the PROC MIXED procedure to determine the treatment effect (i.e., silicate slag and lime) on soil pH, Si and trace elements contents as well as Si and trace elements content in rice grain using SAS 9.4 (SAS Institute 2012). Silicate slag and lime rates were considered as fixed effects, while replications were considered as random effects. Prior to the ANOVA, a Chi-square test of homogeneity was first carried out to determine if the data could be pooled across site-years. However, results indicated a lack of homogeneity on measured variables in response to the treatments across site-years; hence ANOVA analysis was done separately for each site-year. Where significant treatment differences were observed, contrast analyses were performed to determine if there were any treatment differences between the lime and silicate slag treatments. Both linear and quadratic polynomial regressions were then used to show the relation between Si application rates and trace elements content in rice grain using Excel software. The coefficients of determination (r^2) of the regression lines and *p*-values of ANOVA were reported.

2.3. Results and Discussion

2.3.1. Effect of Silicate Slag and Lime Application on Soil pH, Si and Trace Elements Content

The effects of silicate slag and lime application on soil pH, Si and trace elements content are summarized in Table 2.4 and appendix A (Tables A.1 – A.4). The contrast analysis revealed that soil pH and Si were significantly increased by both silicate slag and lime (Table 2.4). The effect of silicate slag and lime were similar on soil pH in in five out of the nine sites investigated.

In the remaining four sites, the increase in soil pH was mostly higher in the silicate slag treated plots than the lime treated plots (Appendix A, Tables A.1 – A.4). Soil Si in the silicate slag treated plots was significantly higher across all site-years when compared to both the lime and check. The increase in soil pH and Si as affect by the application of silicate slag was expected because slag is a liming material and a good Si source for crops grown in highly Si deficient soils. Table 2.5 summarizes the relationship of silicate slag rate with soil pH, and soil Si. The relationship between silicate slag rate and soil pH were generally positive across site-years, with the highest positive relationship occurring at St. Landry 2014 (r^2 = 0.98), Lake Arthur 2014 (r^2 = 0.97), Mamou 2014 (r^2 = 0.96) and Gilbert 2013 (r^2 = 0.96). Extractable soil Si also showed positive relationships with Si application rate across all site-years; with the highest positive relationship occurring at Lake Arthur 2015 (r^2 = 0.96), Mamou 2014 (r^2 = 0.95), Crowley 2014 (r^2 = 0.93) and Gilbert 2014 (r^2 = 0.92), Unlike the Mamou 2014, and Lake Arthur 2014 sites, where the initial pH and soil Si were very low (Table 2.3), the other site-years had relatively high soil pH and plant available Si. From a survey of many different soils across diverse regions, it has been reported that a positive relationship exists between soil pH and extractable Si (Fox et al., 1967; Cheong et al., 1968; Oya and Kina, 1989; Oya et al., 1989; Miles et al., 2014). According to Korndörfer et al. (2003), the concentration of available Si in soil (initial or fertilized) decreases as soil acidity increases because lower soil pH inhibits the dissolution of Si in soil. The increases in pH across all site-years ranged only from 0.1 to 1.1 units between the least (1 Mg ha^{-1}) and highest (8 Mg ha^{-1}) application rates of silicate slag respectively. At the same application rate of 2 and 4 Mg ha^{-1}, slightly higher soil pH ranging from 0.1 – 0.6 units was observed for the silicate slag treatments over the lime treatments across site-years (Appendix A, (Tables A.1 to A.4). It has been recommended that silicate slag and lime be applied at the same rate to acid soils due to the similarity in their abilities to correct soil pH (Pereira, 1978; Korndörfer et al., 2003). However, it is important to note that these materials are different in elemental composition and surface area. Depending on the particle size, silicate slag can have greater surface area than lime. When applied to soils, this can increase its contact with soil particles and enhances its reactivity (Ramos et al., 2006). Moreover, aside from supplying calcium (Ca) and magnesium (Mg) which are also major constituents of most agricultural lime, application of silicate slag to soil also results in the release of SiO_3^{-2} which has similar H^+ neutralizing power as the CO_3^{-2} in lime (Alcarde and Rodella, 2003). Hence, it is likely that the release of SiO_3^{-2} in soil, in addition to the Ca and Mg supplied by silicate slag may have led to the slightly higher soil pH across site-years for the slag treatments than the lime.

Table 2.4. Results on analysis of variance and contrast analysis for soil pH, Si and trace elements content.

Site-Year	Sources of Variation	pH	Soil Si	As	Cd
2013 Gilbert	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	0.007	0.002	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs silicate slag	0.211	0.001	-	-
2013 Crowley	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	0.002	<0.001	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs Silicate slag	0.006	<0.001	-	-
2014 Gilbert	Treatment	0.002	<0.001	NS	NS
	Check vs Lime	0.001	0.003	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs Silicate slag	0.601	<0.001	-	-
2014 Lake Arthur	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	0.002	0.026	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs Silicate slag	0.401	<0.001	-	-
2014 Mamou	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	<0.001	0.551	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs Silicate slag	0.187	0.001	-	-
2014 Crowley	Treatment	<0.001	<0.001	0.020	NS
	Check vs Lime	<0.001	0.007	0.387	-
	Check vs Silicate slag	<0.001	<0.001	0.296	-
	Lime vs Silicate slag	<0.001	<0.001	0.009	-
2014 St. Landry	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	<0.001	0.017	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs Silicate slag	0.021	0.002	-	-
2015 Lake Arthur	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	<0.001	0.001	-	-
	Check vs Silicate slag	<0.001	<0.001	-	-
	Lime vs Silicate slag	0.204	<0.001	-	-
2015 Crowley	Treatment	<0.001	<0.001	NS	NS
	Check vs Lime	0.569	0.001	-	-
	Check vs Silicate slag	0.002	<0.001	-	-
	Lime vs Silicate slag	0.002	<0.001	-	-

Table 2.5. Model and coefficient of determination of the relationship of silicate slag rate with soil pH and Si content.

Site Year	pH		Soil Si	
	Model	r^2	Model	r^2
2013 Gilbert	y = 0.0612x + 7.0863	0.96	y = 0.06x + 148.78	0.86
2013 Crowley	y = 0.0591x + 7.8062	0.85	y = 0.0149x + 99.461	0.79
2014 Gilbert	y = 0.0528x + 6.9009	0.85	y = 0.0641x + 150.63	0.92
2014 Crowley	y = 0.0996x + 7.264	0.77	y = 0.051x + 35.297	0.93
2014 Lake Arthur	y = 0.053x + 4.824	0.97	y = 0.0128x + 16.135	0.88
2014 Mamou	y = 0.1864x + 5.6979	0.96	y = 0.0351x + 4.1179	0.95
2014 St. Landry	y = 0.1863x + 5.7179	0.98	y = 0.072x + 161.35	0.89
2015 Crowley	y = 0.0002x + 7.9593	0.84	y = 0.1138x + 43.538	0.84
2015 Lake Arthur	y = 0.0862x + 4.7513	0.89	y = 0.0647x + 47.288	0.96

While there were significant increases in soil pH and Si observed with the silicate slag and lime application across site-years, there were very few effects noted on soil aluminum (Al), As, Cd, copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Ni) content of soils across site-years (Appendix A, Tables A.1 – A.4). Nonetheless, there was an initial decrease of soil Al observed in Crowley 2014 with the application of silicate slag (Appendix A, Table A.4). In this same site, the application of 2 and 4 Mg ha^{-1} of lime also significantly (p <0.05) reduced the soil As content than equivalent application of silicate slag. In St. Landry 2014, slight decreases in soil Mn was observed with increasing application of silicate slag; but increases in soil Ni was observed in both St. Landry and Mamou in 2014 (Appendix A, Table A.3). Soil pH is considered one of the most influential factors governing the bioavailability of several micronutrients and trace elements in soils (Saunders, 1982). Generally, the bioavailability of trace elements in soils is reduced when pH is increased. Excluding molybdenum (Mo), selenium (Se) and As, the availability of most micronutrients and trace elements in soil is reduced at higher pH due to precipitation of these elements as hydroxides, carbonates or organic complexes (Olalekan et al., 2016). But these effect of pH on the bioavailability of trace elements was very minimal in the present study. Since the changes in soil pH arising from both silicate slag and lime application was also minimal, only ranging between 0.1 and 1.1 units across all site-years, it is likely that these pH increases were not sufficient to cause significant changes in the trace elements contents of these soils. These results indicate that Si-induced amelioration of trace elements or heavy metal toxicities in plant are not only derived from increases in soil pH and co-precipitation of H_4SiO_4 with trace elements as indicated by Lindsey (1979), Baylis et al. (1994) and Schulthess and Tokunda (1996), but an in-planta mechanism may also be involved as described by Richmond and Sussman (2003) and Ma et al. (2004).

2.3.2. Effect of Silicate Slag and Lime Application on Rice Si Content

The mean effect of silicate slag and lime treatments on rice Si content is reported in Table 2.6. In general, there was no effect of silicate slag treatment observed on the test weight and milling quality of rice grain (data not shown). However, the contrast analysis showed significant differences in treatment effect on rice grain, straw and total Si content across site-years. When the lime treatments were compared with the check, rice grain Si content was slightly higher in the lime treatments than the check in in all site-years accept in Lake Arthur 2014 and Crowley 2015 (Table 2.6 and Appendix B, Table B.2). The straw Si content of the lime treatments was also higher than the check except in Gilbert 2013 and Crowley 2014. The straw Si contents of silicate slag treatments were significantly (p <0.005) higher when compared to both the check and lime treated plots in all nine site-years. The increased levels of Si in rice grain and straw might be a result of increased availability of Si in the slag treated plots than the lime treated plots and checks, and this may have enhanced its uptake. Although lime is not a source of Si fertilizer, but the increases in soil pH arising from its application may have also facilitated increased levels of soil Si and enhanced its uptake in rice grain than the untreated check. Regarding total rice Si content, no difference was found between the check and lime in Lake 2014, St. Landry 2014 and

Crowley 2015. With the exception of these three sites, total rice Si content was significantly higher in the silicate slag treated plots in the remaining six sites.

2.3.3. Comparison Between Silicate Slag and Lime on Trace Elements Content in Rice Grain

The ANOVA showed no differences between the check, lime and silicate slag with respect to rice grain Al content across all nine site-years. This observation was also true for Cu, Fe, Mn, Ni, Pb and Zn with the exception of Mamou and Crowley in 2014 for Cu and Pb, respectively (data not shown). However, significant treatment effect was observed across all site-years for As and Cd contents in rice grain (Table 2.6). When the check and lime treatments were compared for grain As and Cd, the lime treatments As content was significantly lower than check in nearly all site-years, except for Gilbert 2013. Rice grain Cd was also significantly lower in the lime treated plots than the checks across site-years, except at the Gilbert 2013, Mamou and Crowley sites in 2014, and also at Lake Arthur in 2015. There was no difference in the rice grain As content in Gilbert 2014 and Lake Arthur 2014 and 2015 between lime and silicate slag, but slag application significantly reduced rice grain As content in the remaining six site-years than the lime. When lime and silicate slag were compared regarding the grain Cd content, application of the two materials only showed differences in two site-years (Lake Arthur 2015, p =0.003, and Crowley 2015, p = 0.029) out of nine where silicate slag application resulted in slight reduction in rice grain Cd content than lime (Appendix B, Tables B.2 and B.4).

Table 2.6. Results on analysis of variance and contrast analysis for plant Si and trace element content.

Site-Year	Sources of Variation	%Si Grain	%Si Straw	%Si Total	As grain	Cd grain
2013 Gilbert	Treatment	<0.001	<0.001	<0.001	<0.001	0.001
	Check vs Lime	<0.001	NS	0.012	NS	NS
	Check vs Silicate slag	<0.001	<0.001	<.0001	<0.001	0.003
	Lime vs Silicate slag	0.024	0.001	0.028	0.006	NS
2013 Crowley	Treatment	<0.001	<0.001	<0.001	<0.001	0.001
	Check vs Lime	<0.001	<0.001	0.049	<0.001	0.007
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	<0.001
	Lime vs Silicate slag	0.024	<0.001	<0.001	<0.001	NS
2014 Gilbert	Treatment	<0.001	<0.001	<0.001	<0.001	0.002
	Check vs Lime	<0.001	0.033	<0.001	<0.001	0.004
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	0.002
	Lime vs Silicate slag	<0.001	<0.001	<0.001	NS	NS
2014 Lake Arthur	Treatment	<0.001	<0.001	<0.001	<0.001	0.002
	Check vs Lime	NS	<0.001	NS	<0.001	0.009
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	0.001
	Lime vs Silicate slag	<0.001	<0.001	<0.001	NS	NS
2014 Mamou	Treatment	<0.001	<0.001	<0.001	<0.001	0.001
	Check vs Lime	<0.001	<0.001	0.003	<0.001	NS
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	0.004
	Lime vs Silicate slag	<0.001	0.006	<0.001	0.016	NS
2014 Crowley	Treatment	<0.001	<0.001	<0.001	<0.001	0.034
	Check vs Lime	<0.001	NS	0.012	0.001	NS
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	0.079
	Lime vs Silicate slag	<0.001	0.003	<0.001	<0.001	NS
2014 St. Landry	Treatment	<0.001	<0.001	<0.001	<0.001	<0.001
	Check vs Lime	<0.001	<0.001	NS	<0.001	0.043
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	0.001
	Lime vs Silicate slag	0.001	<0.001	<0.001	0.027	NS
2015 Lake Arthur	Treatment	<0.001	<0.001	<0.001	0.009	<0.001
	Check vs Lime	0.058	0.052	0.002	0.004	NS
	Check vs Silicate slag	<0.001	<0.001	<0.001	0.001	<0.001
	Lime vs Silicate slag	<0.001	0.072	<0.001	NS	0.003
2015 Crowley	Treatment	<0.001	<0.001	<0.001	<0.001	<0.001
	Check vs Lime	0.225	0.012	NS	<0.001	0.001
	Check vs Silicate slag	<0.001	<0.001	<0.001	<0.001	<0.001
	Lime vs Silicate slag	<0.001	0.001	<0.001	<0.001	0.029

2.3.4. Relationship of Si Application Rate with Rice Grain Si and Trace Elements Accumulation

The effect of Si application rate on Si accumulation in rice grain, straw and total Si content, as well as trace elements content of the grain are presented in Appendix B (Tables B.1 to B.4). The models and regression coefficients used to describe the relationship of Si application rate and rice grain, straw and total Si content are also presented in Tables 2.7 and 2.8. In general, significant positive correlations where observed between Si application rates and the Si accumulation in rice grain, straw and total Si contents across site-years (Tables 2.7 and 2.8). Rice is a Si accumulator and tends to take up more Si in the above-ground biomass as the soil supply of Si increases (Ma and Takahashi, 2002). Across site-years, the Si content of rice grain, straw and total Si contents corresponded with the soil Si content of the various sites, in that those sites with higher levels of soil Si also had higher accumulation of Si in the above ground biomass of rice (Appendix B, Tables B.1 to B4). When the relationship of Si application with trace elements content of rice grain was considered, no effect of Si application rate was found on the accumulation of Al, Cu, Fe, Mn, Ni and Zn in rice grain across all nine site-years. However, the accumulation of As and Cd in rice grain decreased with increasing application of Si across all site-years. It was interesting to see that the Pb content of rice grain was higher in the silicate slag and lime treatments than the check, but this result was only obtained in one site (Crowley 2014) out of nine site-years (Appendix B, Table B.4). There is no explanation why the Pb content in rice grain tended to be higher in the silicate slag and lime treatments as compared to the check in

Table 2.7. Model and coefficient of determination of the relationship of Si rate with total and straw Si content.

Site Year	Total Si		Straw Si	
	Model	r^2	Model	r^2
2013 Gilbert	$y = 0.0008x + 4.5354$	0.86	$y = 0.0008x + 6.2502$	0.87
2013 Crowley	$y = 0.0007x + 4.4056$	0.62	$y = 0.0009x + 6.2912$	0.72
2014 Gilbert	$y = 0.0013x + 5.0347$	0.87	$y = 0.0012x + 6.8253$	0.93
2014 Crowley	$y = 0.0016x + 4.5856$	0.88	$y = 0.0013x + 6.3053$	0.91
2014 Lake Arthur	$y = 0.001x + 1.9007$	0.83	$y = 0.0008x + 2.7761$	0.81
2014 Mamou	$y = 0.0011x + 3.3214$	0.78	$y = 0.0018x + 4.7158$	0.92
2014 St. Landry	$y = 0.001x + 4.16$	0.87	$y = 0.0009x + 5.3709$	0.91
2015 Crowley	$y = 0.0008x + 3.1298$	0.92	$y = 0.0008x + 4.0779$	0.90
2015 Lake Arthur	$y = 0.0011x + 2.1621$	0.84	$y = 0.0009x + 2.7782$	0.82

Table 2.8. Model and coefficient of determination of the relationship of Si rate with grain Si, As, and Cd.

Site Year	Grain Si		Grain As		Grain Cd	
	Model	r^2	Model	r^2	Model	r^2
2013 Gilbert	$y = 0.0005x + 2.5789$	0.73	$y = 0.0000001x^2 - 0.0003x +0 .1716$	0.97	$y = -5E-05x + 0.1117$	0.96
2013 Crowley	$y = 0.0005x + 2.0144$	0.76	$y = 1E-07x^2 - 0.0003x + 0.3265$	0.78	$y = -0.00005x + 0.1892$	0.82
2014 Gilbert	$y = 0.0015x + 2.9298$	0.87	$y = 2E-07x^2 - 0.0004x + 0.2734$	0.99	$y = -4E-05x + 0.1573$	0.96
2014 Crowley	$y = 0.0018x + 2.3418$	0.76	$y = -0.0002x + 0.4148$	0.84	$y = 1E-08x^2 - 3E-05x + 0.1826$	0.97
2014 Lake Arthur	$y = 0.0014x + 0.7498$	0.87	$y = 3E-07x^2 - 0.0006x + 0.6213$	0.92	$y = -1E-05x + 0.1853$	0.86
2014 Mamou	$y = 0.0008x + 1.4818$	0.70	$y = -0.0002x + 0.3974$	0.93	$y = -0.00005 + 0.1848$	0.93
2014 St. Landry	$y = 0.0012x + 2.6456$	0.78	$y = -0.0002x + 0.3202$	0.98	$y = -0.00001x + 0.18$	0.93
2015 Crowley	$y = 0.0008x + 2.0004$	0.90	$y = 1E-07x^2 - 0.0004x + 0.3417$	0.87	$y = 8E-09x^2 - 3E-05x + 0.1774$	0.91
2015 Lake Arthur	$y = 0.0014x + 1.4221$	0.89	$y = -0.0002x + 0.5479$	0.90	$y = 9E-09x^2 - 3E-05x + 0.1747$	0.98

this site. The bioavailability and uptake of Pb by plants has been reported to increase with decreasing soil pH and organic matter (Hassett, 1974; Zimdahl and Foster, 1976; Chaney et al., 1984;). But the Pb contents of rice grain in Crowley 2014 site does not agree with these reports because the initial pH in this site was 8, suggesting a fairly alkaline soil, and the initial organic matter content was 12 g kg^{-1}, which is also relatively high. Despite the increased Pb uptake by rice in Crowley 2014, the soil Pb content in all of the nine sites investigated in the present study were all below the reported average Pb content of 17 mg kg^{-1} naturally occurring in soils (Steinnes, 2013), and hence do not seem to pose a significant human health risk of Pb consumption from rice grown in these sites.

2.3.5. The Effect of Si Application and Soil pH on As and Cd Accumulation in Rice Grain

Specific attention was given to the accumulation of As and Cd in rice grain as affected by the application of silicate slag in the present study, because numerous studies have suggested that rice consumption is a significant source of human exposure to harmful levels of these elements (Williams et al., 2007; Ilenia et al., 2008; Arao et al., 2009). The model and r^2 of the relationship between Si rate and rice grain Si, As and Cd contents are presented in Table 2.8. Grain Si content linearly increased with increasing Si rate in Crowley 2015 (r^2 =0.90), Lake Arthur 2015 (r^2 =0.89), Lake Arthur 2014 (0.87), and Gilbert 2014 (r^2 = 87) respectively. The As in rice grain had a strong negative relationship with Si application rate in six out of nine sites (Figure 2.1). In Gilbert 2013 and 2014, and Lake Arthur 2014, there was no change in soil pH between the application rates of 140 and 280 kg Si ha^{-1}. Similarly, in Crowley 2014, soil pH did not change between the application of 560 and 840 kg Si ha^{-1}. However, it is notable that even in the absence of pH increases in these cases, rice grain As content remained declining with increasing application rate of Si (Figure 2.1). These results agree with those obtained by Bogdan and

Schenk (2008), who reported that the As concentration in rice straw and grain was negatively correlated with the soil solution Si concentration in six different soils during a two years study. Fleck et al (2013), also reported reduced accumulation of As in rice straw and husk, and also in brown and polished rice grain by 23% and 22%, respectively with increasing application of Si.

It is reported that both As and Si share similar transport pathways in rice, beginning in the roots and extending to the nodes and shoots (Ma et al., 2008; Chen et al., 2017). Since the application of silicate slag had no effect on the soil As concentration across all sites, it is likely that the reduction of As in rice grain may have resulted from better competitive advantage of Si over As being transported through the plant due to the increase concentration of soil Si arising from the application silicate slag.

Like As, the accumulation of Cd in rice grain was also decreased with Si application for all site-years. The comparison between lime and silicate slag application at equal rates showed no difference in rice grain Cd content between the two materials (Table 2.6). Therefore, the reduction of Cd accumulation in rice grain was initially thought to be a pH effect. However, the regression analysis showed that rice grain Cd decreased at higher Si application rates, even if soil pH was no longer increasing (Figure 2.2). Unlike As which shares a common transporter with Si in rice, Cd does not share a transport pathway with Si in rice. Nonetheless, two mechanisms of Cd uptake and translocation have been described in rice. First, the rice plant takes up Cd from the soil solution as Cd^{2+}. It travels through the endodermis and Casparian strips, and is translocated to the shoot where it is finally deposited in the grain (Hu et al., 2009; Miyadate et al., 2011; Song et al., 2015). It has also been suggested that Cd is absorbed through the apoplastic pathway after which it is transported across the plasma membrane with the aid of secondary cation transporters such as IRT1 (Clemens et al., 2002). In high Si accumulating crops such as rice, the uptake of Si has been described as an active process (Ma et al., 2006). Once deposited in plants, Si is strongly bounded to cell wall components where it forms a cross-link with the cell wall structures (Lukacova et al., 2013). Hence, is likely that these Si induced structural modification of the cell wall may result in blockage of these pathways and impedes the translocation Cd to the shoot.

Rice is an efficient accumulator of Si and may also take up trace elements such as As and Cd either through H_4SiO_4 transporter such as Ls1 and Ls2 which are also transporter of As (Ma et al., 2008), or through secondary cation transporter as in the case of Cd (Clemens et al., 2002). Since the application of Si had no effect on the concentration of these elements in soil, it is likely that the strong negative correlations observed between Si rate and rice grain As and Cd contents may be a result of their interaction within the plant. The high concentration of Si in rice treated with silicate slag may have suppressed the As transporting function of Ls1 and L2 in rice, thus resulting in less As been transferred to the grain. Wang et al. (2000), demonstrated that silica bound to plant cell wall has a strong affinity for Cd. Hence, it seems that the high levels of Si in rice initiated by Si fertilization may have facilitated bonding of Si with Cd either in the roots or stem, thereby limiting the translocation of Cd to the grain.

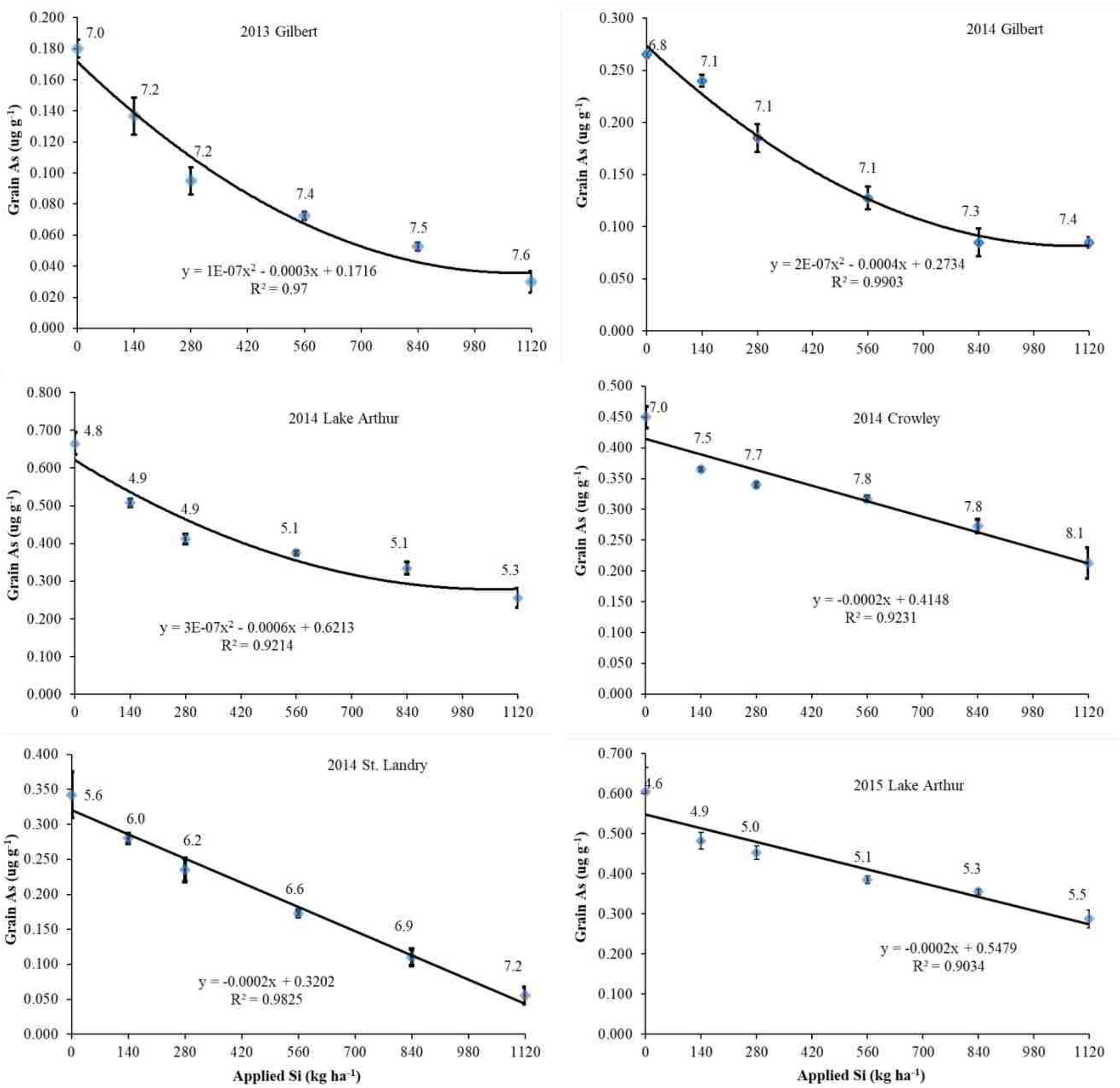

Figure 2.1. Effect of Si rate on As accumulation in rice grain. Values placed over data points on the regression lines are the corresponding soil pH level (average) for each silicate slag treatment.

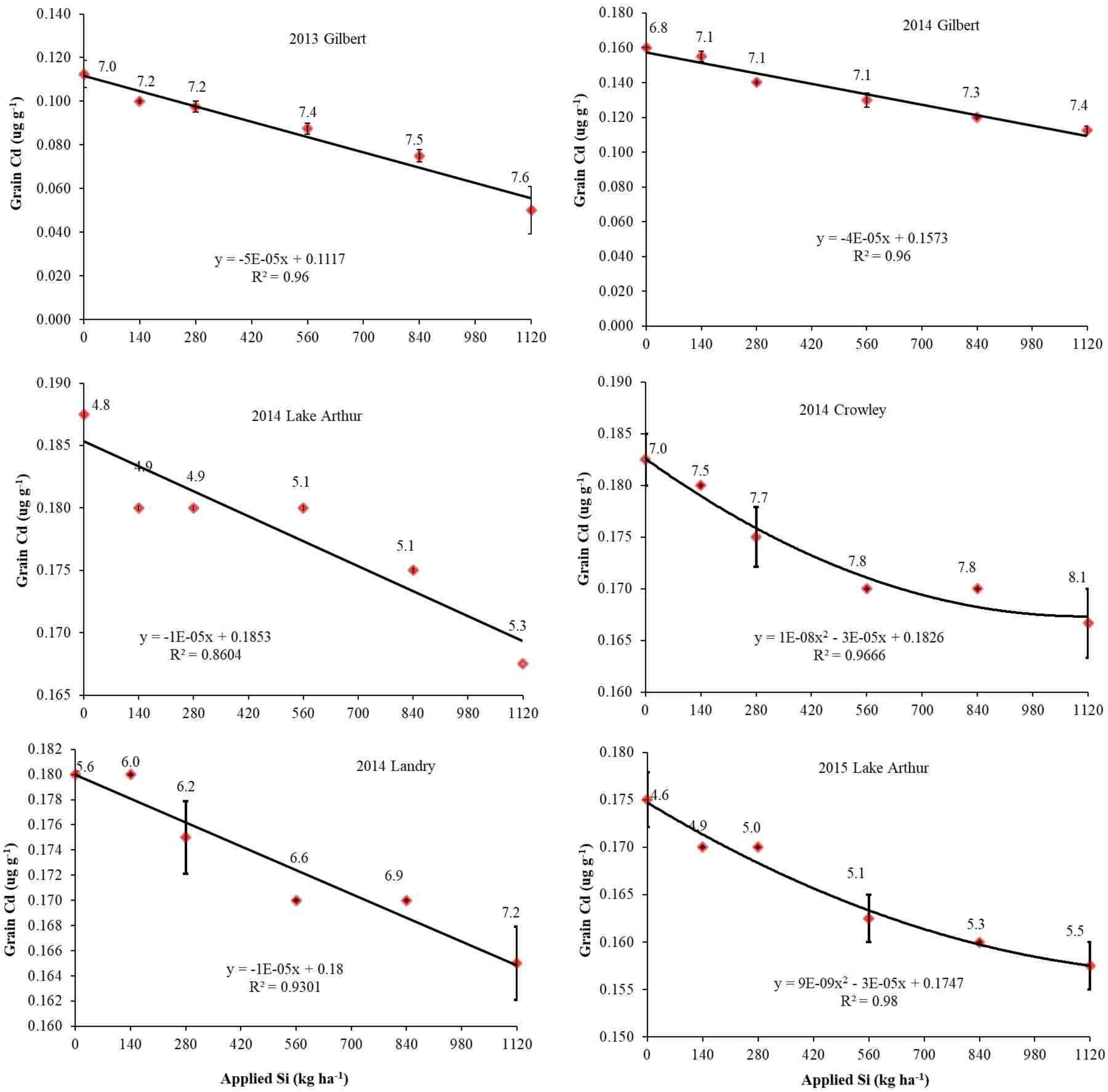

Figure 2.2. Effect of Si rate on Cd accumulation in rice grain. Values placed over data points on the regression lines are corresponding soil pH level (average) of each silicate slag treatment.

2.4. Conclusions

Silicate slag and lime were effective in raising soil pH and Si content in all the sites studied. At the rates of 2 and 4 Mg ha^{-1}, silicate slag application resulted in slightly higher soil pH than the lime in most of the sites studied. The greater effect of silicate slag on soil pH over lime could be attributed to the differences in the physical and chemical properties of these materials. The increases in soil pH initiated by silicate slag and lime were minimal, ranging only between 0.1 and 1.1 units across the nine sites investigated. Since there were limited changes in the soil Al, As, Cd, Cu, Fe, Mn, Ni, Pb and Zn content following lime and silicate slag application, it is likely that pH had limited effect on the availability and uptake of these trace elements by rice.

Soil Si content was significantly increased following silicate slag application in all the sites studied. This also resulted in enhanced Si uptake in rice. However, higher rice Si content did not affect the uptake of Al, Cu, Fe, Mn, Ni, Pb and Zn, except in Crowley 2014 where higher grain Pb was observed in rice with application of silicate slag. In general, the level of Cd present in filled rice grain across site years was below the maximum level of 0.4 ug g^{-1} for polish rice grain (CODEX STAN, 1995). While the As levels in the filled grain across site years were above the 2 ug g^{-1} maximum level, it is important to point out that this was a measure of the total As of the filled grain, and not the inorganic As which is the most toxic form of As for human. An analysis of the clean rice grain from the present study showed both As and Cd levels below detection limits (data not shown). Correlation analysis showed a strong negative relationship between Si rate and rice grain As and Cd contents. Elevated Si levels in soil which also resulted in high Si uptake by rice may have suppressed the ability of Si and As transporters to efficiently transport As to the shoot. It is also likely that Si may have inhibited the translocation of Cd to rice grain by forming a strong bond with Cd and trapping it in the roots or stem. Studies aimed at limiting the uptake of As and Cd in rice have often resulted in a compromise of either the grain yield (Grassi et al., 2011) or increased uptake of one element or the other. However, results from the present study demonstrate that application of silicate slag has the potential to simultaneously decrease the uptake of both As and Cd by rice thereby reducing the concentration of these elements in rice grown in flooded soils.

2.5. References

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Chapter 3. The Effect of Granular Size on the Solubility and Release of Monosilicic Acid from Silicate Slag and Silicon Uptake by Wheat (*Triticum aestivum*)

3.1. Introduction

The potential of silicon (Si) to improve crop yield under a wide range of stressful conditions including drought, metal toxicity, salinity and pest or disease pressure have been well-documented (Epstein, 2009; Keeping and Reynolds, 2009; Meena et al., 2014; Farooq and Dietz, 2015). In wheat *(Triticum aestivum)*, it has been reported that Si can mitigate freezing stress (Liang et al., 2008). Under water stress condition, addition of 0.89 mmol Na_2SiO_3 kg^{-1} of soil resulted in increased leaf relative water content and water potential in wheat (Gong et al., 2003). Wheat biomass production, spike weight and plant height were reportedly increased under Si fertilization (Ahmad et al., 2007). Supplying salt-stressed wheat with 0.33 mM of Si showed reduced sodium (Na) content in leaf, but had no significant effect on the leaf chlorophyll content (Ahmad et al., 1992).

Apart from improving plant resistance to biotic and abiotic stresses, application of Si fertilizers to Si-deficient soils has also been associated with either improved availability or enhanced uptake of other plant essential nutrients. For instance, Si application has been shown to have a significant interaction with phosphorus (P) in soil (Meena et al., 2014). Silicon fertilization to P-deficient soil increased the bioavailability of P and led to increase P uptake (Raleigh, 1953). The opposite of this interaction was however observed when soil P was high, where Si application led to reduced P uptake, thereby resulting in decreased accumulation of inorganic P in plants (Ma and Takahashi, 1990).

The critical soil Si levels for improving crop yield have been established by several researchers (Korndörfer et al., 2002; Narayanaswamy and Prakash, 2009; Babu et al., 2016a;

Paye et al., 2018). However, identifying the most effective Si fertilizer source for attaining maximum benefit to crops has remained a challenge. At present, several materials are under evaluation for their ability so supply Si to crops. The most desirable characteristics sought for in these materials are high soluble Si, readily available and affordable for large scale application, ease of application without need for modification of current farm machinery and minimal concern for environmental contamination regarding heavy metals (Korndörfer et al., 2002; Gascho, 2001).

Wollastonite has been used extensively as the standard source in experiments evaluating different materials for their ability to supply Si to crops (Pereira et al., 2004; Babu et al., 2016a). This is because wollastonite is a naturally formed crystalline mineral with high degree of purity and chemical stability compared to other sources of Si. However, the high cost of wollastonite arising from demand for other industrial uses makes it economically unsuitable for large scale application in agriculture (Haynes et al., 2013). Hence, many efforts to improve Si status in soil have focused on the use of industrial by-products such as steel slag that have great potential to replenish soil Si.

Unlike wollastonite which forms naturally over a long period of time, Silicate slag is formed by a reaction of limestone and silicon dioxide (SiO_2) at extremely high temperatures (Teir et al., 2007). However, these silicate materials are formed under different temperature regimes and cooling speed; thus, making their Si content highly variable from one production source to the other (Takahashi, 1981; Datnoff et al., 1992). The ability of these silcate materials to supply Si to crops may therefore vary depending on the source from which they originate and the granular size of the materials. Therefore, the present study was undertaken to evaluate the release pattern of monosilicic acid from wollastonite and four granular size fractions of two silicate slag materials and their influences on Si accumulation in wheat.

3.2. Materials and Methods

3.2.1. Trial Establishment and Experimental Design

To address the objective of this study, a pot experiment was conducted on the main campus of the Louisiana State University in Baton Rouge, Louisiana beginning in November of 2017. Two silicate slag materials of different granular sizes were obtained from two different steel producing plants and labeled as Slag-1(from a plant in Detroit) and Slag-2 (from a plant in Wisconsin). The granular sizes of the silicate slag materials were 1 x 0 mm, 2 x 1 mm and 5 x 2 mm; along with a mixture of all three granular sizes which was labelled as ungraded silicate slag material. Based on the different granular size fractions, these were graded as fine, coarse, pellet and ungraded, respectively. Each material, granular size, grading and percent Si content is presented in (Table 3.1). These materials along with wollastonite which has a higher percentage of Si (23%) were thoroughly incorporated into pots containing 5 kg of Cancienne silt loam soil (Fine-silty, mixed, superactive, nonacid, hyperthermic Fluvaquentic Epiaquepts) obtained from the LSU AgCenter Central Research Station located in Ben Hur near Baton Rouge. The Cancienne soil consists of very deep profile, level to gently undulating, somewhat poorly drained mineral soils that are moderate to slowly permeable. These soils formed in loamy and clayey alluvium deposited by the Mississippi River. The initial pH and mineralogical composition of the soil used for this experiment is summarized in Table 3.2.

Table 3.1. Source, granular size, grade and % total Si content of materials used in this experiment, 2017.

Source	Granular size (mm)	Grade	Total Si (%)
Slag 1	1 x 0	Fine	7.00
	2 x 1	Coarse	7.00
	5 x 2	Pellet	8.00
	mixed	Ungraded	7.00
Slag 2	1 x 0	Fine	5.28
	2 x 1	Coarse	5.28
	5 x 2	Pellet	5.28
	mixed	Ungraded	5.28
Wollastonite	-	-	23.00

Table 3.2. Initial soil characteristics prior to establishment of experiment.

			mg kg^{-1}						
Soil type	pH	OM† g kg^{-1}	Si	Ca	P	K	Mg	S	Zn
Silt loam	5.9	16	84	1880	25	120	297	13	1.6

†-organic matter content

The application rates of Si were 125, 250, 500, and 1000 kg Si ha^{-1} using the different granular sizes of the two silicate slag materials and wollastonite. Wollastonite contains higher percentage of Si than slag and was therefore included in the treatments to serve as a standard for monitoring the changes in soil Si as influenced by the various granular sizes of silicate slag materials. All treatments including a control (no silicate slag or wollastonite applied) were arranged in a randomized block design with four replications.

Phosphorus and potassium (K) fertilizers were applied at 71 kg ha^{-1} and incorporated along with the wollastonite and silicate slag materials prior to planting. After the treatments application, the pots were irrigated to field capacity and allowed to stand for one week. The pots were then divided into two groups. In one group, six seeds of wheat variety *Syngenta Cypress* were sowed, and the second group was left unplanted. This was done to monitor the release of monosilicic acid (H_4SiO_4) from the Si sources in a soil medium; both in the presence and absence of actively growing Si accumulating crops. The trial was set up under a hoop house with opened ends, and a transparent plastic roof. This was done to enable vernalization to occur by means of ambient temperature. One week after germination, thinning was performed by manually removing the two least vigorous seedlings from each pot, after which nitrogen (N) was applied using urea (46% N) as source at the rate of 63 kg N ha^{-1}, with another 28 kg N ha^{-1} at Feekes 5 growth stage (leaf sheaths strongly erected). After treatment application, the pots were irrigated periodically to maintain the soil moisture content at field capacity until two weeks before harvest, when irrigation was terminated.

3.2.2. Soil Sampling and Processing

Sequential soil sampling was carried out in the entire duration of the experiment. Soil sampling was done by taking three core soil samples from each pot at every sampling event beginning at 30 days after treatment application, and lasted up to 150 days with a 30-day interval between sampling. The collected soil samples were than oven dried at 55°C and processed to pass through a 2 mm sieve and then analyzed for Si.

3.2.3. Plant sampling and processing

At Feekes 10.1 growth stage (head is visible), plant biomass samples were taken by cutting the entire aboveground section of one wheat plant from each pot. These were oven dried until they reached a constant weight. Their individual weight was then obtained, after which they were finely ground using a Cyclone Sample® Mill (S/N 5117U-2; 115V 60HZ). At physiological maturity, all the remaining plants from each pot were harvested and separated into grain and straw. After drying, weights were collected and then the straw samples were processed following similar procedure used to process the biomass as described above, whereas the grain samples were processed using a Wondermill (WM2000).

3.2.4. Analysis

3.2.4a. Soil Analysis

The plant-available Si in the collected soil samples was extracted using the 0.5 M acetic acid extraction procedure, according to Korndörfer et al. (1999). After extraction, the concentration of Si in each sample extract was then quantified using the Molybdenum Blue Colorimetric (MBC) procedure (Hallmark et al., 1982) using a UV visible spectrophotometer (Hach DR 5000) set at 620 nm. Plant-essential nutrients in soil samples taken at 30 and 150 days after treatment application were extracted using Mehlich-3 solution and then analyzed by Inductively Coupled Plasma (ICP) –Optical Emission Spectroscopy (OES) for P, K, calcium (Ca), iron (Fe) magnesium (Mg), sulfur (S), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) content.

3.2.4b. Plant Analysis

Determination of Si content in harvested wheat biomass, straw and grain samples was performed by first digesting the samples following the Oven-Induced Digestion (OID) procedure (Kraska and Breitenbeck, 2010). Silicon content of the digested plant samples was then quantified based on MBC using a UV visible spectrophotometer set at 630 nm.

3.2.4c Data Analysis

All measured variables were subjected to analysis of variance (ANOVA) using the PROC MIXED procedure in SAS 9.4 to determine the significant main effects of the three Si sources on the response variables. Silicon rate using the wollastonite and the different granular sizes of silicate slag was assigned as fixed effect, and the replications was considered as random effect. Wollastonite was then removed and the program was run to determine the effect of grade and rate of the two silicate slag materials, and the interaction effects of source x rate, source x grade,

grade x rate and source x grade x rate. The difference of least square means (LSD) was then used to identify treatment differences among the three Si sources and the four granular size fractions of the two silicate slags. Control (no slag or wollastonite) treatment was not included in the ANOVA procedure for source or grade. The release pattern of H_4SiO_4 from wollastonite and the different granular sizes of the two silicate slag materials were then graphed over the 150-day sampling period for both planted and unplanted pots using Excel software. Linear and polynomial regressions were also performed using Excel for various plant variables in response to different Si rates (including the check) and for Si content of soil samples taken 30 days after treatment application.

3.3. Results and Discussions

3.3.1. Effect of Si Sources and Silicate Slag Granular Size on the Release of H_4SiO_4 in Soil

The release pattern of H_4SiO_4 within the 150-day sampling period in soil treated with wollastonite and two silicate slag sources of different granular sizes is presented in (Figure 3.1). An increase in soil Si was observed within 30 days after treatment application, and thereafter remained fairly stable within each source and granular size until 120 days after application. For both silicate slag materials, the release pattern of H_4SiO_4 was similar, with fine and ungraded materials releasing the highest Si in soil, followed by wollastonite, and then the coarse and pellet silicate slag materials. A marked decline in soil Si then occurred between 120- and 150-day sampling periods. Interestingly, the decrease in soil Si followed the same trend in both planted and unplanted pots, but with greater decrease in Si observed in the unplanted than the planted pots. This trend was similar for even the check pots to which no Si fertilizer was added (Figure 3.1).

The presence of plant roots in soil influences the chemical dynamics of the rhizosphere in that nutrient uptake by the roots causes reduction in the soil solution nutrients concentration, which promotes the solubility of nutrients from fertilizer materials and the soil exchange sites (Kato and Owa, 1997). Thus, it is likely that the uptake of Si by wheat in the planted pots may have led to decreased soil solution H_4SiO_4 concentration, resulting in higher solubility of silicate slag and wollastonite in the planted pots than the unplanted pots. It is also reported that respiration of plant roots and soil microbial community may lead to a buildup of carbon dioxide (CO_2) gas within the rhizosphere (Kimura et al., 1984). This buildup of CO_2 gas within the rhizosphere may also contribute to the solubility and dissolution of H_4SiO_4 from soil and Si fertilizers.

The mystery behind the drastic decrease in soil Si that occurred between 120 and 150-days after application is not fully understood. However, it is possible that the termination of irrigation two weeks before harvest may have caused a drastic decline in soil moisture content and facilitated increased adsorption of H_4SiO_4 by soil, thus decreasing its concentration in the soil solution. This result agrees with McKeague and Cline (1963) who observed that the concentration of H_4SiO_4 was higher in a soil suspension before drying at 100°C, but significantly reduced when the residue of the suspension was analyzed after evaporation. They concluded that the concentration of H_4SiO_4 in soil does not increase in direct response to evaporation of soil moisture, but rather decreases due to adsorption of H_4SiO_4 at soil particle exchange sites when the soil is dried. Nonetheless, Babu et al. (2016b), contended that the reduction of H_4SiO_4 from soil solution cannot only be attributed to its sorption to soil exchange sites, but also to the concept of polymerization, wherein high concentration of H_4SiO_4 in soil solution coupled with high pH, may result to its conversion to non-plant-available forms. Monosilicic acid is present in the soil in its monomeric form in both neutral and weakly acid solution, with polymerization occurring only at extremely high H_4SiO_4 concentration and solution pH in the presence of high concentration of iron and aluminum (Al) oxides (Berthelsen and Korndörfer, 2005). The reduction in soil Si observed between 120- and 150-days in this experiment however may not be attributed to polymerization because even though there was increases in soil pH resulting from Si fertilization, but the pH measured at 30 and 150 days after application (Tables 3.3- 3.6) in both planted and unplanted pots was either slightly alkaline or acidic, an ideal condition for Si to remain in solution as H_4SiO_4. Also, the concentration of H_4SiO_4 in the check pots remained unchanged until 120 days after application, and then followed the same pattern of decline as the Si treated pots (Figure 3.1). Since there was no Si added to these check pots, it is unlikely that the decline in H_4SiO_4 observed between120 and 150 days after application was due to polymerization. This is probably the reason there were minimum changes in the soil Si within treatment categories including the check, beyond 30 days after application until 120 days after application when irrigation was stopped. The termination of irrigation between 120 and 150 days after application may have caused a reduction in soil moisture content, leading to adsorption of H_4SiO_4; which reduced its concentration in solution, rather than polymerization. This conclusion is in line with Patra and Neue (2010) who reported that intermittent flooding and drying decreased the Si content compared to continuous flooding in Alfisol. The release pattern of H_4SiO_4 in soil from 30 to 120 days is also consistent with Makabe-Sasaki et al. (2013) who reported that soil Si was rapidly increased 22 days after application and then gradually leveled off with time. In another study, similar dissolution pattern of Si from silicate slag was reported by Kato and Owa (1997), who observed a gradual decline in Si in a weakly buffered acid solution over time. In another experiment where different Si sources were applied to rice (*Oryza* *sativa*), Anggria et al. (2017) reported similar observation wherein solution Si concentration was highest at the beginning of their sampling period, 7 days after transplanting and lowest at the end which was 34 days after transplanting rice.

3.3.2. Effect of Si Source, Granular Size and Application Rate on Changes in Soil Silicon

The changes in soil Si content measured at 30 days after application as influenced by Si source, silicate slag granular size and application rate are presented in Figure 3.2. For all Si sources and silicate granular size, soil Si was increased with increasing Si application rate. But the amount of acetic acid extractable soil Si varied among the different granular sizes of silicate slag (Figure- 3.2).

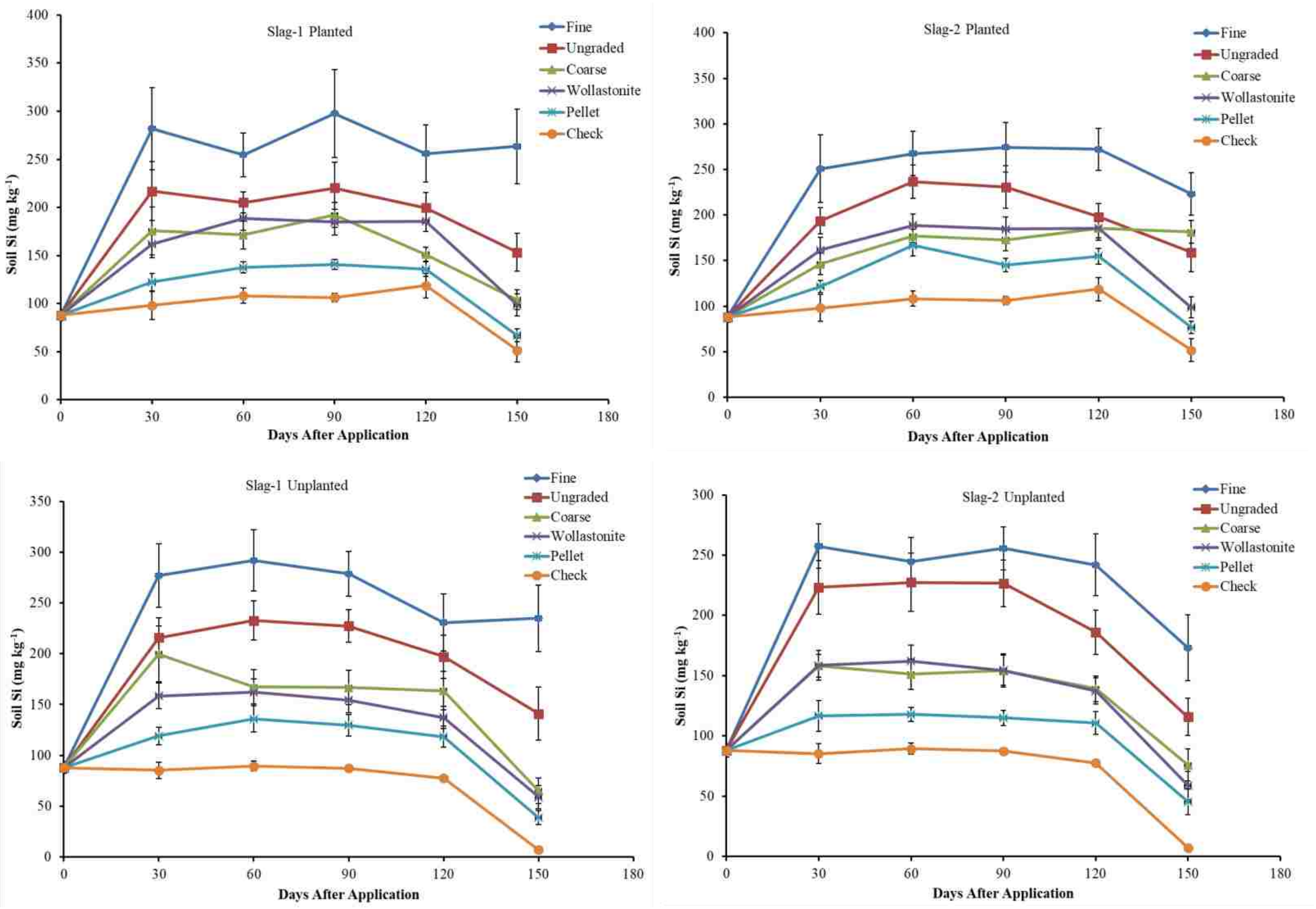

Figure 3.1. The release pattern of monosilicic acid from wollastonite and different granular sizes of two silicate slag materials over time in planted and unplanted soil.

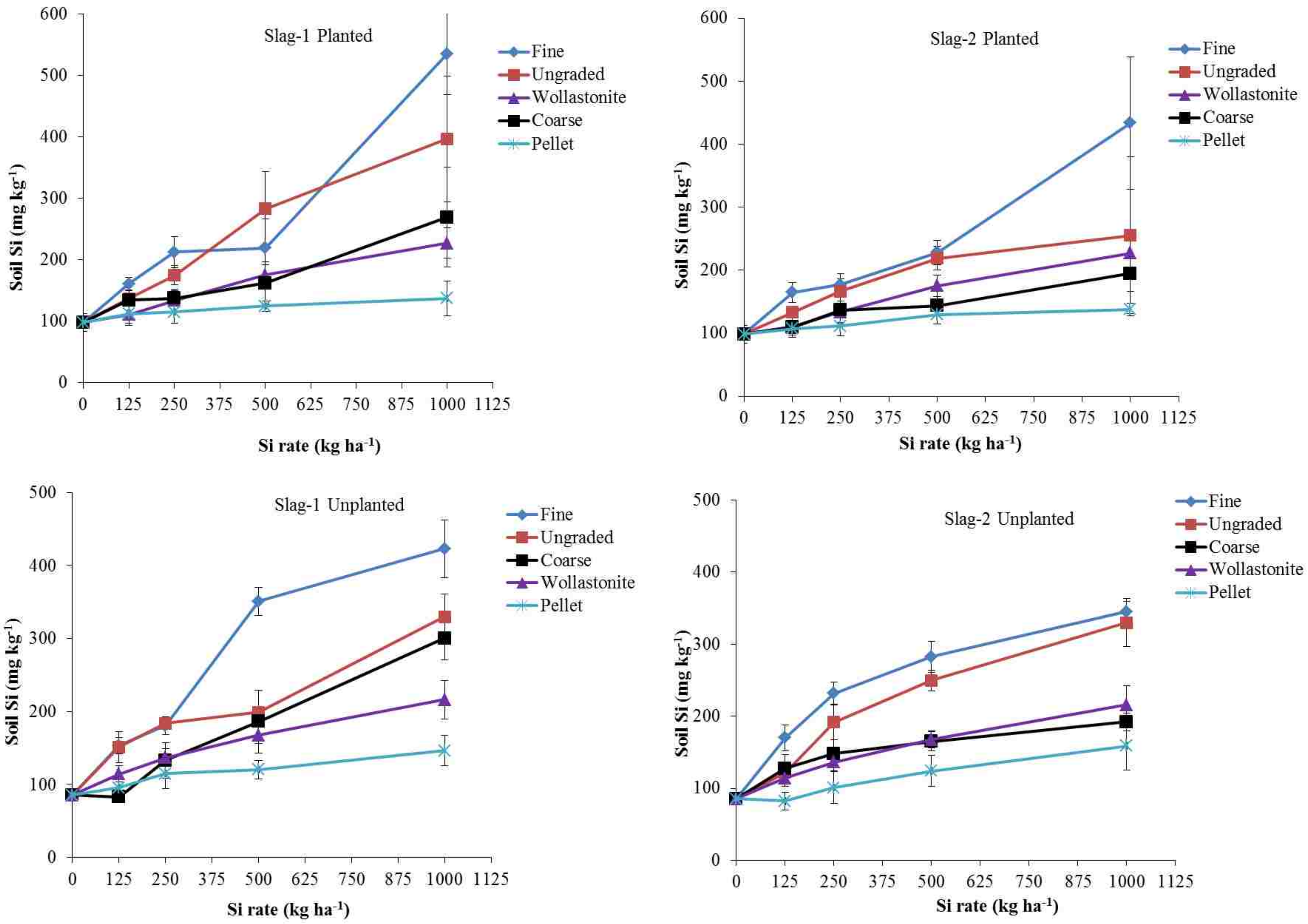

Figure 3.2. Effect of granular size and application rate of silicon on soil Si content in planted and unplanted pots as affected by slag 1, 2, and wollastonite 30 days after treatment application.

The changes in soil Si content followed the release pattern of H_4SiO_4 in that at the same Si application rate, fine and ungraded silicate slag consistently resulted in the highest amount of Si extracted from soil. These were then followed by wollastonite, coarse and then pellet silicate slag, respectively. Datnoff et al. (1992) also reported higher extractable soil Si for fine and standard grade slag material over the pelletized form while working on Si fertilization in rice in the everglades of Florida. Smaller granular size of slag improves its ability to supply Si to soil by increasing its surface area, distribution and reactivity when applied to soil (Harada, 1965; Clements et al., 1967; Datnoff et al., 1992). The higher soil Si extracted from pots treated with fine and ungraded silicate materials over wollastonite is probably because wollastonite, unlike slag is a naturally formed crystalline mineral with a higher degree of chemical stability, and therefore releases Si in soil at a slower rate and lower concentration. On the other hand, silicate slag is a recently formed non-crystalline material which is derived when limestone reacts with SiO_2 and other impurities of iron ore under higher temperature (Teir et al., 2007; Babu et al., 2016b) and is therefore chemically less stable as compared to wollastonite. Although the two silicate materials originated from different steel producing plants, they did not differ with respect to their release pattern of H_4SiO_4 and changes in soil Si content. Pereira et al (2004), also observed that steel slag materials were very similar in the amount of Si they release in soil.

3.3.3. Effect of Si Source and Granular Size on Soil pH and Nutrient Content

The release pattern of H_4SiO_4 with time indicated that the greatest increase in soil Si occurred within 30 days after treatment application, while the greatest decline in soil Si occurred between 120 and 150 days after treatment application. Hence, ANOVA was also performed for soil pH and nutrient content at 30 and 150 days after treatment application. Tables 3.3- 3.6 summarize the results of pH and Mehlich-3 extractable soil nutrients in both planted and unplanted pots. When sources were compared with regard to changes in soil pH 30 days after application in pots planted with wheat, silicate slag 1 and 2 increased the soil pH more than wollastonite (Table 3.3). However, no statistical difference was obtained among sources regarding pH in the unplanted pots at 30 days after application (Table 3.4). This is probably because the solubility of silicate slag was higher in pots planted with wheat than the unplanted pots. As stated earlier, the presence of plant roots in pots planted with wheat may have facilitated rapid dissolution of the Si fertilizers by reducing the concentration of H_4SiO_4 in soil solution through plant Si uptake, thus leading to rapid solubility of the fertilizer materials, resulting in an increase soil pH within 30 days after application. Since there was no uptake of Si in the unplanted pots, the dissolution of silicate slag or wollastonite may have been slower in these pots, thereby leading to decrease solubility of the fertilizer materials which may have resulted in minimal differences in soil pH among the sources within 30 days. At 150 days after application, no statistical difference was found in soil pH among sources in both planted and unplanted pots (Tables 3.5 and 3.6). It is possible that the termination of irrigation and subsequent dryness of the soil that followed may have prohibited further dissolution of the fertilizer materials, thereby causing minimal changes in the soil pH measured at harvest or 150 days after application among the sources.

When the different granular sizes of silicate slag were compared, fine and ungraded materials significantly ($p<0.001$) increased soil pH measured at 30 and 150 days after application in planted and unplanted pots (Tables 3.3-3.6). The order of increase in soil pH as affected by the different granular sizes of silicate slag was fine > ungraded > coarse > pellet. Silicate slag is a well-recognized liming material in regions where soil pH is low. When applied to soil, the neutralizing base SiO_3^{-2} which is contained in slag, reacts with water to release hydroxyl (OH^-) ions which neutralizes H^+ and the phytotoxic Al^{3+} ion, thus correcting both active and potential soil acidity (Alcarde and Rodella, 2003). The results from the present study suggest that using finer granular size of silicate slag does not only improve its ability to supply Si to crops, but also its potential as a liming material. The differences in soil pH as influenced by the two silicate slag materials and wollastonite may be due to differences in their solubility as well as chemical composition. Silicate slag as an industrial by-product which contains high amounts of Ca, Mg, and Si, along with traces of Mn, Al, Fe, and S, whereas wollastonite is mostly comprised of Ca and SiO_3.

When wollastonite and the two silicate slag sources regardless of granular size were compared with respect to their influences on soil nutrients, there were no differences found in the amount Ca, Cu, Fe, K, Mn, and Ni extracted from soil 30 days after treatment application in the planted pots. However, soil Mg, S and Zn were significantly ($p<0.001$) increased by silicate slag 2, whereas soil P was higher ($p = 0.031$) for wollastonite and silicate slag 1 (Table 3.3). This was also the same for the unplanted pots, except that soil Cu was increased by wollastonite and slag 2 applications (Table 3.4). An increase in soil Fe was observed for slag 1 in both planted and unplanted pots. At 150 days after application, sources did not also differ in soil Ca, Cu, K, Mn, Ni and P in the planted pots. But again, Mg, S and Zn were increased by silicate slag 2, whereas soil Fe content was high for silicate slag 1-treated pots (Table 3.5). This pattern was very similar in the unplanted pots (Table 3.6). There was a significant treatment effect of silicate slag granular size on concentration of several soil nutrients measured. Soil Ca, Mg, S and Zn decreased with increasing silicate slag granular size in both planted and unplanted pots at 30 and 150 days after application (Tables 3.3-3.6). Soil Mn was significantly ($p <0.001$) increased by the fine granular size of silicate slag in the unplanted pots at 150 days after application (Table 3.6) but Ni was increased by the coarse and pellet silicate slag materials.

There was a general increase in soil nutrients with silicate slag application rate, with the most noticeable ($p < 0.001$) increase occurring for soil Ca, Mg and S. Soil Zn was significantly increased with increasing application rate of silicate slag in the unplanted pots at 150 days after application whereas soil Fe was decreased. The increase in soil Ca and Mg arising from slag application was expected because slag contains substantial amounts of these elements. However, Zn is not a recognized constituent element of either silicate slag or wollastonite. Hence, it was interesting to find that its availability was enhanced by increasing application of these materials. Also, the bioavailability of Zn decreases with increasing soil pH (Havlin et al., 2005). Despite the increases in soil pH arising from slag and wollastonite application, Zn availability was still increased. These results are contrary to Saleh et al. (2013) and Cunha et al. (2008) who observed decreases in Zn bioavailability with increasing application of Si. Silicate slag is a by-product of steel production and as such, it contains many trace elements as impurities. It can therefore be suspected that trace amounts of Zn may have been present in these slag materials, which could explain the increase in soil Zn content arising from application.

Table 3.3. Effect of Si sources, silicate slag granular size (grade), and Si application rate on nutrient content of soil in planted pots 30 days after treatment application, 2017.

Sources of Variation	Levels	pH	mg kg^{-1}										
			Si	Ca	Cu	Fe	K	Mg	Mn	Ni	P	S	Zn
	Control	6.93	116	3846	3.33	432	385	581	104	3.5	86	20	5.4
Sources	Wollastonite	7.11B	137B	3938	3.70	384B	390	592B	110	3.1	110A	24B	5.0B
	Slag-2	7.28A	195A	4037	3.66	353B	382	729A	107	2.8	93B	34A	6.5A
	Slag-1	7.26A	176A	3754	3.45	414A	388	607B	112	2.9	106A	24B	4.8B
	p-value	0.031	0.033	0.564	0.159	0.035	0.845	<0.001	0.873	0.173	0.031	<0.001	<0.001
Grade	Ungraded	7.26 A	221 B	3896B	3.55	384B	385	668B	109	2.9	99	29B	5.7A
	Fine	7.26 A	266 A	4259A	3.68	377B	390	710A	113	2.8	102	33A	5.7AB
	Coarse	7.04 B	160 C	3318C	3.48	413A	378	577C	103	2.9	100	22C	5.1BC
	Pellet	6.98 B	122 D	3351C	3.62	398A	387	604C	113	3.1	98	24C	4.9C
	p-value	<0.001	<0.001	<0.001	0.372	0.087	0.532	<0.001	0.462	0.136	0.801	<0.001	0.003
Rate	125	7.07	132	3486	3.58	392	294	611	108	2.9	101	25	5.2
	250	7.06	153	3514	3.54	401	294	614	106	2.9	100	25	5.3
	500	7.12	189	3718	3.67	385	302	653	115	3.0	100	28	5.4
	1000	7.28	295	4107	3.53	394	304	680	109	3.0	98	30	5.3
	p-value	<0.001	<0.001	0.003	0.612	0.741	0.578	0.008	0.610	0.825	0.813	0.001	0.884
Interaction Effects†													
Sources x Grade		0.914	0.728	0.601	0.783	0.049	0.449	0.001	0.973	0.844	0.086	0.002	0.002
Sources x Rate		0.299	0.993	0.970	0.331	0.886	0.866	0.471	0.199	0.362	0.608	0.552	0.589
Grade x Rate		0.458	0.001	0.121	0.891	0.999	0.323	0.113	0.998	0.528	0.910	0.017	0.525
Sources x Grade x Rate		0.430	0.555	0.998	0.999	0.862	0.616	0.933	0.975	0.983	0.845	0.191	0.499

† Wollastonite (positive control) and control (No Si applied) were not included in the ANOVA of grade, rate, and all interaction effects. Control was not included in the ANOVA of source effect.

Means followed by the same letter are not significantly different by Fisher LSD (0.05).

Table 3.4. Effect of Si sources, silicate slag granular size (grade), and Si application rate on nutrient content of soil in unplanted pots 30 days after treatment application, 2017.

Sources of Variation	Levels	pH	mg kg^{-1}										
			Si	Ca	Cu	Fe	K	Mg	Mn	Ni	P	S	Zn
	Control	6.03	85	3316	3.30	518	377	582	82	3.1	107	27	5.1
Sources	Wollastonite	6.36	159	3685	3.45A	426B	377	544B	81	2.7	113A	24B	5.1B
	Slag-2	6.53	189	3925	3.49A	418B	383	691A	91	2.7	103B	34A	5.8A
	Slag-1	6.44	197	3646	3.30C	452A	384	576B	90	2.7	111A	25B	5.1B
	p-value	0.276	0.325	0.180	0.001	0.002	0.551	<0.001	0.260	0.870	<0.001	<0.001	<0.001
Grade	Ungraded	6.71B	219B	3990B	3.41	444	386	665B	83	2.6B	109	33B	6.0A
	Fine	6.87A	267A	4456A	3.43	419	383	714A	92	2.6B	106	40A	5.5B
	Coarse	6.28C	166C	3394C	3.45	431	387	585C	99	2.9A	103	23C	5.1B
	Pellet	6.10D	118D	3303C	3.31	445	380	668C	87	2.8A	107	22C	5.3B
	p-value	<0.001	<0.001	<0.001	0.293	0.058	0.658	<0.001	0.048	0.001	0.220	<0.001	0.003
Rate	125	6.27	123	3517	3.29	445	381	600	85	2.8	107	26	5.3
	250	6.46	161	3497	3.43	438	377	600	93	2.8	105	26	5.5
	500	6.53	210	3787	3.43	436	387	634	90	2.7	106	30	5.5
	1000	6.68	278	4341	3.45	421	389	699	93	2.7	107	35	5.6
	p-value	<0.001	<0.001	<0.001	0.162	0.162	0.213	0.006	0.383	0.141	0.925	0.004	0.660
Interaction Effects†													
Sources x Grade		0.371	0.494	0.538	0.776	0.080	0.701	0.003	0.123	0.528	0.003	0.002	<0.001
Sources x Rate		0.410	0.026	0.768	0.606	0.064	0.537	0.066	0.935	0.972	0.076	0.073	0.366
Grade x Rate		0.169	<0.001	0.003	0.757	0.444	0.663	0.064	0.909	0.695	0.487	0.094	0.075
Sources x Grade x Rate		0.755	0.004	0.999	0.807	0.990	0.865	0.964	0.587	0.932	0.531	0.804	0.155

† Wollastonite (positive control) and control (No Si applied) were not included in the ANOVA of grade, rate, and all interaction effects. Control was not included in the ANOVA of source effect.

Means followed by the same letter are not significantly different by Fisher LSD (0.05).

Table 3.5. Effect of Si sources, silicate slag granular size (grade), and Si application rate on nutrient content of soil in planted pots 150 days after treatment application, 2017.

Sources of Variation	Levels	pH	mg kg^{-1}										
			Si	Ca	Cu	Fe	K	Mg	Mn	Ni	P	S	Zn
	Control	6.71	98	3383	3.53	390	385	585	105	3.10	87	20	4.0
Sources	Wollastonite	7.11	99B	3772	3.91	395B	284	546B	111	3.21	107	24B	4.7B
	Slag-2	7.16	161A	3896	4.00	376B	302	683A	116	3.19	103	31A	5.9A
	Slag-1	7.12	147A	3916	3.88	415A	298	624B	118	3.18	111	25B	5.1B
	p-value	0.603	0.074	0.669	0.110	0.007	0.134	<0.001	0.689	0.969	0.075	0.002	<0.001
Grade	Ungraded	7.3A	156B	4067B	3.40	395	299	671B	117	3.1B	111	33A	5.7A
	Fine	7.3A	243A	4400A	3.41	397	299	717A	113	3.0B	111	34A	6.0A
	Coarse	7.0B	143B	3683C	3.46	400	305	625C	120	3.3A	104	25B	5.1B
	Pellet	7.0B	71C	3585C	3.33	392	297	621C	119	3.3A	103	23B	5.1B
	p-value	<0.001	<0.001	<0.001	0.291	0.928	0.695	<0.001	0.601	0.006	0.125	<0.001	0.002
Rate	125	7.08	101	3629	3.30	410	298	624	113	3.2	110	25	5.3
	250	7.07	116	3729	3.44	397	297	636	116	3.2	107	26	5.4
	500	7.12	164	4092	3.46	377	305	386	120	3.2	104	30	5.6
	1000	7.28	232	4286	3.47	398	300	687	119	3.1	107	34	5.8
	p-value	<0.001	<0.001	<0.001	0.167	0.076	0.702	<0.001	0.653	0.376	0.570	<0.001	0.268
Interaction Effects[†]													
Sources x Grade		0.914	0.002	0.105	0.766	0.103	0.951	0.067	0.058	0.488	0.103	0.009	0.001
Sources x Rate		0.300	0.192	0.235	0.601	0.170	0.829	0.042	0.425	0.866	0.016	0.045	0.156
Grade x Rate		0.458	<0.001	0.014	0.759	0.742	0.592	0.080	0.948	0.332	0.370	0.003	0.416
Sources x Grade x Rate		0.430	0.660	0.185	0.808	0.754	0.660	0.790	0.437	0.872	0.704	0.104	0.007

[†] Wollastonite (positive control) and control (No Si applied) were not included in the ANOVA of grade, rate, and all interaction effects. Control was not included in the ANOVA of source effect.

Means followed by the same letter are not significantly different by Fisher LSD (0.05).

Table 3.6. Effect of Si sources, silicate slag granular size (grade), and Si application rate on nutrient content of soil in unplanted pots 150 days after treatment application, 2017.

Sources of Variation	Levels	pH	Concentration mg kg^{-1}										
			Si	Ca	Cu	Fe	K	Mg	Mn	Ni	P	S	Zn
	Control	6.02	7.3	3260	3.03	502	373	557	66	3.11	132	22	5.0
Sources	Wollastonite	6.36	59B	3801	3.6A	447B	386	549C	75AB	3.1A	171A	26B	5.7B
	Slag-2	6.54	107A	3844	3.4B	450B	381	638A	73B	2.9B	142B	35A	6.3A
	Slag-1	6.44	120A	3773	3.3B	472A	389	590B	79A	3.0A	150B	27B	5.3B
	p-value	0.266	0.082	0.805	0.012	0.001	0.353	0.002	0.002	0.007	0.010	0.007	<0.001
Grade	Ungraded	6.71B	128B	3959B	3.40	463B	382	644B	76B	2.9	139B	33B	6.1B
	Fine	6.90A	204A	4429A	3.40	436C	393	722A	85A	2.9	159A	40A	6.5A
	Coarse	6.28C	72C	3544C	3.60	467B	378	562C	74BC	3.0	145B	24C	5.5C
	Pellet	6.10D	45D	3341D	3.30	477A	387	567C	72C	3.0	142B	25C	5.4C
	p-value	<0.001	<0.001	<0.001	0.269	<0.001	0.178	<0.001	<0.001	0.052	0.057	<0.001	<0.001
Rate	125	6.27	44	3405	3.30	476	384	574	73	3.0	139	25	5.3
	250	6.46	83	3577	3.40	465	381	594	77	2.9	141	26	5.4
	500	6.53	123	3926	3.40	457	385	633	78	2.9	152	33	5.6
	1000	6.68	198	4436	3.50	445	391	696	80	2.9	152	40	5.8
	p-value	<0.001	<0.001	<0.001	0.172	<0.001	0.509	<0.001	0.009	0.505	0.170	<0.001	<0.001
Interaction Effects†													
Sources x Grade		0.367	0.002	0.512	0.777	0.002	0.315	<0.001	0.005	0.607	0.033	0.086	<0.001
Sources x Rate		0.428	0.192	0.003	0.608	0.079	0.216	<0.001	0.030	0.637	0.037	0.008	<0.001
Grade x Rate		0.170	<0.001	<0.001	0.758	<0.001	0.299	<0.001	0.371	0.721	0.873	0.002	<0.001
Sources x Grade x Rate		0.785	0.307	0.720	0.806	0.106	0.747	0.181	0.789	0.736	0.051	0.916	0.002

† Wollastonite (positive control) and control (No Si applied) were not included in the ANOVA of grade, rate, and all interaction effects. Control was not included in the ANOVA of source effect.

Means followed by the same letter are not significantly different by Fisher LSD (0.05).

3.3.4. Effect of Si Source, Granular Size and Application Rate on Si Accumulation in Wheat

The results of ANOVA on Si uptake in the above-ground parts of wheat are presented in Table 3.7. When the efficiency of the sources was compared regarding Si uptake, the application of wollastonite significantly ($p < 0.001$) increased the average Si uptake in wheat biomass taken at Feekes 10.1 growth stage more than the two slag materials, even though they had the highest release of Si in soil. The application of silicate materials resulted in an average increased of Si uptake in wheat biomass by 203%, 73% and 67% for wollastonite, silicate slag 1 and 2, respectively. This result contradicts Pereira et al. (2004) who observed greater accumulation of Si in rice when silicate slag was the source compared to wollastonite, but agrees with Korndörfer and Gascho (1999), who reported higher uptake of Si in rice for wollastonite than silicate slag. Between the two silicate slag sources, there was no difference in wheat Si uptake. For straw and total Si uptake, wollastonite treated pots also had higher average Si uptake but was not significantly different from the two silicate slag sources (Table 3.7). No statistical difference was found among sources with respect to grain Si uptake. Among the granular fractions, fine silicate slag significantly ($p <0.001$) increased wheat biomass, grain and total Si uptake, as well as straw ($p < 0.05$) Si uptake. There was no significant interaction effect among source, grade and Si rate regarding Si uptake in all the measured response variables. The differences in wheat biomass Si uptake observed between wollastonite and the two silicate slag materials and also among the different granular sizes of silicate slag could due to their differences in Si content, solubility and Si supplying capacity (Haynes et al., 2013).

Silicon uptake increased with application rate irrespective of source or silicate slag granular size. Both linear and quadratic regressions were used to describe the relationship of Si source, silicate granular size and Si application rate with wheat straw, grain and total Si uptake (Figure 3.3 and 3.4). At the same Si rate, application of fine silicate slag resulted in the highest Si uptake in wheat straw, grain and total Si uptake (Figures 3.3 and 3.4). This was followed by wollastonite and ungraded silicate slag. The high Si uptake in pots treated with fine and ungraded silicate slag as well as wollastonite could be directly related to the high amounts of Si they released in soil. The rapid release of H_4SiO_4 from the fine and ungraded slag materials and the high Si content of wollastonite may have facilitated increased plant-availability and subsequent uptake of Si by wheat in pots receiving these fertilizer treatments. On the other hand, the coarse and pellet materials had the lowest Si uptake at the same application rate probably because these materials also released the least amounts of Si in soil. These results agree with Medina-Gonzales et al. (1988), who reported that Si uptake in sugarcane (*Saccharum spp*.) was highest for finely ground silicate slag material.

3.3.4. Effect of Si Source, Silicate Slag Granular Size and Application Rate on Wheat Agronomics

The application of all Si sources significantly ($p<0.001$) increased wheat biomass yield at Feekes 10.1 growth stage. The average increase in biomass yield was 67%, 28% and 40% for wollastonite, silcate slag 1 and 2, respectively compared to check pots. The application of wollastonite resulted in an average increase of 42% in head weight, while silicate slag 1 and 2 resulted in average increases of 14% and 15%, respectively. Wollastonite application also resulted in a 33% mean increase in grain yield, whereas sililcate slag 1 and 2 presented 13 and 14% increase in grain yield, respectively (Table 3.8). There was no significant effect of Si source on heads and tiller counts as well as straw yield after harvest. The effect of silicate slag granular size on tiller and heads count as well as total yield was also not significant (Table 3.8). However, biomass, grain and straw yield was significantly ($p <0.05$) increased with decreasing granular size of silicate slag.

Table 3.7. Effect of Si source, silicate slag granular size (grade), and application rate on wheat Si uptake.

Sources of Variation	Level	Biomass[†] Si uptake g m^{-2}	Straw Si uptake g m^{-2}	Grain Si uptake g m^{-2}	Total Si uptake (Grain + Straw) g m^{-2}
Sources	Control	1.65	6.85	0.57	7.50
	Wollastonite	5.00A	14.52	0.73	15.19
	Slag -2	2.76B	12.95	0.71	13.61
	Slag -1	2.85B	13.38	0.75	14.08
	p-value	<0.001	0.129	0.913	0.175
Grade	Ungraded	2.89B	13.20B	0.78B	13.91B
	Fine	3.39A	14.49A	1.04A	15.50A
	Coarse	2.54C	12.98B	0.61BC	13.59B
	Pellet	2.41C	12.02C	0.47C	12.38C
	p-value	<0.001	0.002	<0.001	<0.001
Rate	125	1.97	11.20	0.38	11.50
	250	2.58	12.58	0.49	13.13
	500	3.13	13.55	0.83	14.31
	1000	3.54	15.36	1.21	16.44
	p-value	<0.001	<0.001	<0.001	<0.001
Interaction effect[†]					
Sources x Grade		0.684	0.837	0.786	0.949
Sources x Rate		0.292	0.729	0.483	0.857
Grade x Rate		0.944	0.991	0.343	0.989
Sources x Grade x Rate		0.966	0.844	0.271	0.754

[†] Wheat biomass was taken at Feekes 10.1 when the head became visible.

Means followed by the same letter are not significantly different by Fisher LSD (0.05).

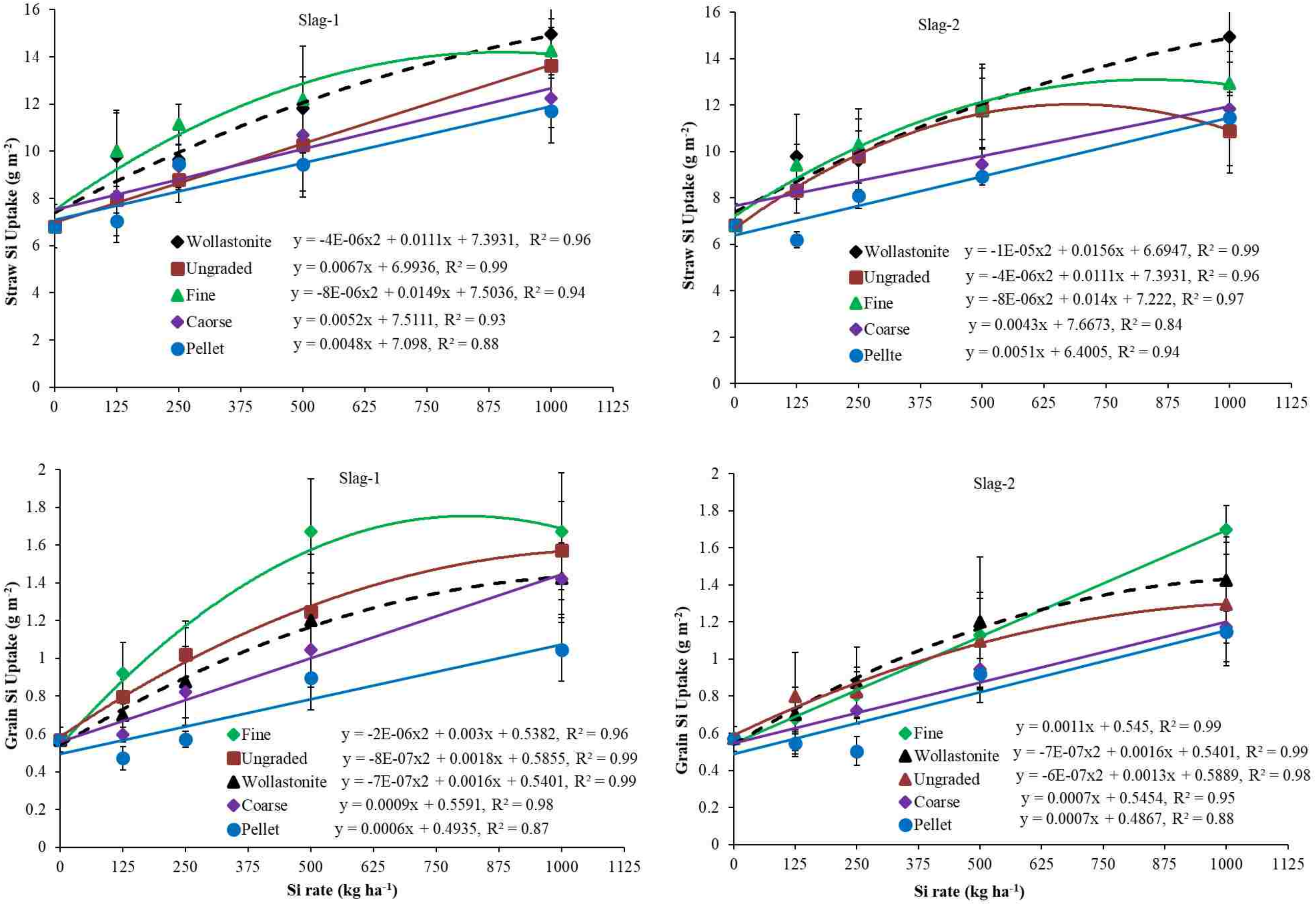

Figure 3.3. Effect of source, granular size and application rate of Si on wheat straw and grain Si uptake at harvest.

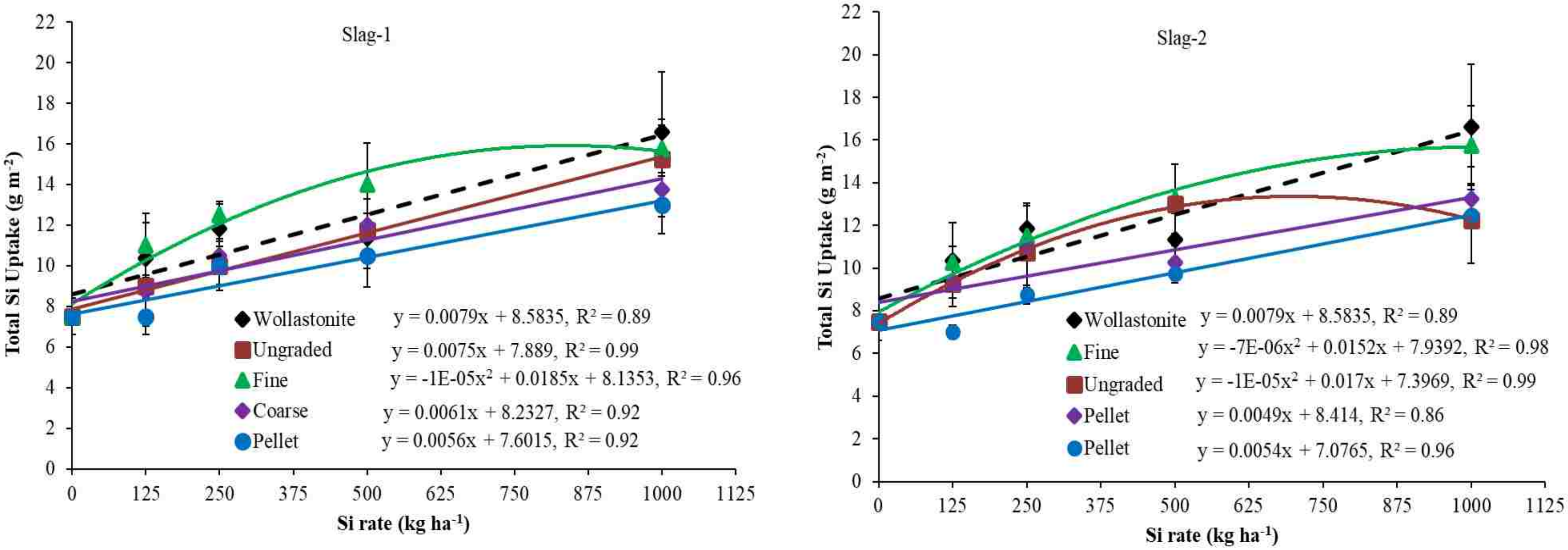

Figure 3.4. Effect of source, granular size and application rate of Si on total Si uptake in wheat at harvest.

The application of fine, ungraded, coarse and pellet silicate slag resulted in 22%, 19%, 8% and 6% increase in grain yield, respectively. These results are similar to those of Datnoff et al. (1992) who reported yield increases of 20% 18% and 4% in rice for fine, standard grade, and pellet silicate slag, respectively. Although all yield components were significantly ($p < 0.05$) increased with the application of Si, but there was no significant interaction effect of silicate slag source, rate and granular size for wheat yield components (Table 3.8). At the same Si rate, biomass, total yield (grain + straw) and grain yield of wheat were higher for wollastonite than all the silicate slag treatment regardless of granular size (Figures 3.5 and 3.6). Wollastonite had minimal effect on soil pH and nutrient content measured at 30 days after application (Table 3.3). Therefore, it is likely that its application caused minimum nutrient imbalances, thus resulting in the greater yield components in the wollastonite-treated pots than the slag treatments. On the other hand, the application of fine and ungraded silicate slag did not only increase the soil pH, but also resulted in high soil Ca, Mg and S as well as low Ni (Table 3.3). These changes in soil nutrients may have caused some level of nutrient imbalances in soil during the early growth stage, thus may have lowered the average yields for fine and ungraded silicate than wollastonite. Moreover, wollastonite unlike silicate slag, releases Si slowly over time (Babu et al. 2016b). The higher increase in yield therefore was probably because wollastonite supply adequate amount of Si for a longer time period during the growing season whereas fine and ungraded silicate slag may have supplied excess amounts of Si early in the growing season. Nonetheless, applying the fine and ungraded silicate slag materials resulted in higher wheat yield components than the coarse and pellet, thus suggesting them being better Si sources.

Table 3.8. Analysis of variance and average values of agronomic parameters as affected by source, silicate slag granular size (grade) and Si rate, 2017.

Source of Variation		Biomass[†] Yield g m^{-2}	Tiller Count m^{-2}	Heads Count m^{-2}	Heads Yield g m^{-2}	Grain Yield g m^{-2}	Straw Yield g m^{-2}	Total Yield (Head + Straw) g m^{-2}
	Control	113	427	309	420	313	581	1009
Sources	Wollastonite	189 A	478	410	598 A	415 A	620	1218A
	Slag-2	148 B	447	416	484 B	358 B	617	1102 B
	Slag-1	145 B	451	415	478 B	355 B	618	1095 B
	p-value	<0.001	0.216	0.876	0.004	0.027	0.990	0.003
Grade	Ungraded	155A	458	416	494	373A	620A	1114 A
	Fine	155A	468	421	495	381A	637A	1132 A
	Coarse	144B	428	414	477	339B	627A	1103 A
	Pellet	133C	443	413	459	332B	586B	1045 B
	p-value	0.004	0.075	0.925	0.569	0.026	0.047	0.057
Rate	125	115	421	398	439	305	586	1034
	250	139	462	407	465	344	621	1093
	500	158	463	428	496	383	626	1139
	1000	174	463	431	525	394	636	1179
	p-value	<0.001	0.009	0.020	0.027	<0.001	0.056	0.008
Interaction effect[†]								
Sources x Grade		0.944	0.766	0.978	0.994	0.994	0.999	0.996
Sources x Rate		0.996	0.987	0.978	0.997	0.999	0.996	0.998
Grade x Rate		0.892	0.422	0.999	0.999	0.991	0.578	0.984
Source x Grade x Rate		0.999	0.832	0.999	0.999	0.999	0.999	0.999

[†] Wheat biomass was taken at Feekes 10.1 when the head became visible.

Means followed by the same letter are not significantly different by Fisher LSD (0.05).

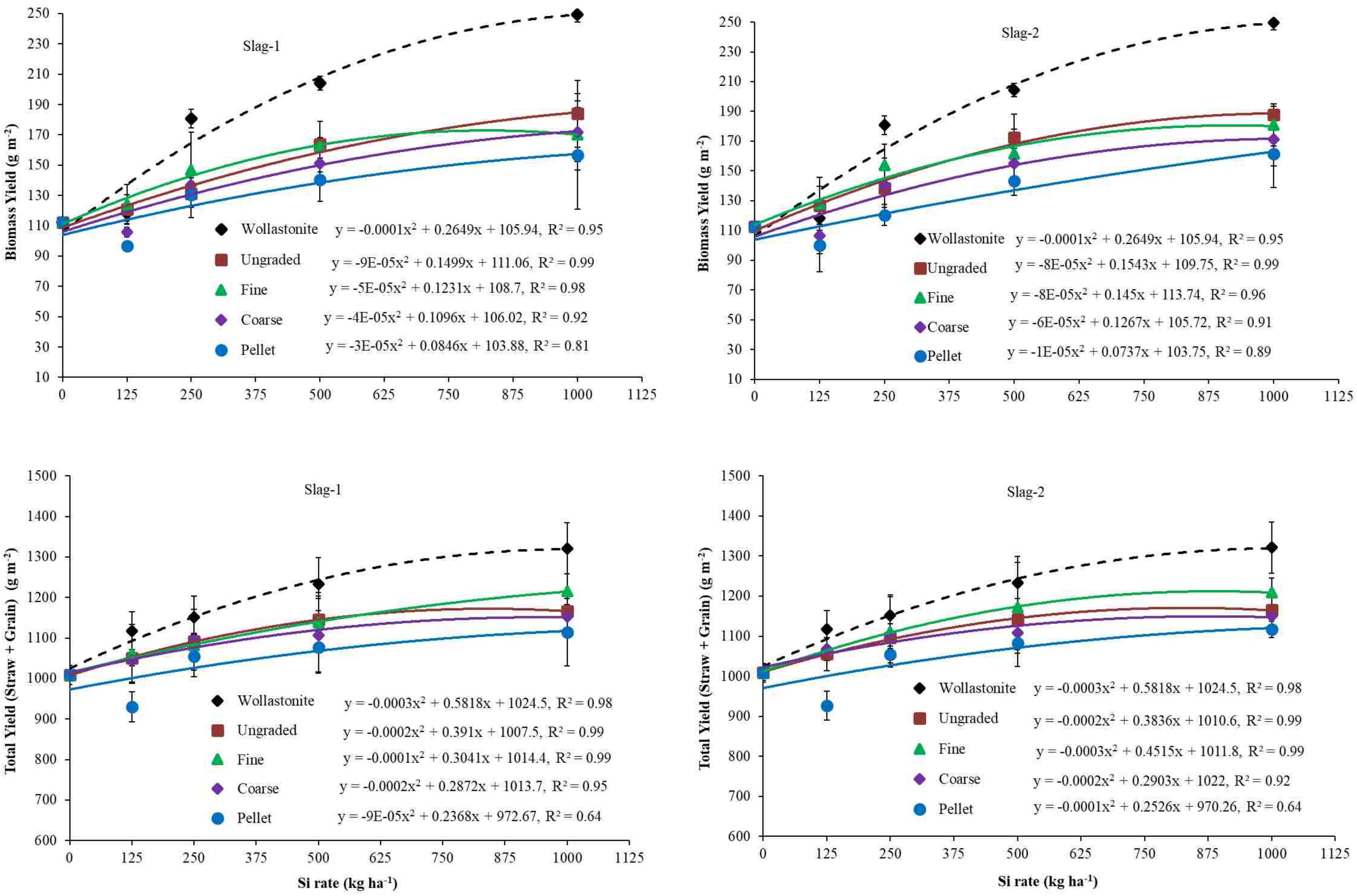

Figure 3.5. Effect of source, granular size and application rate of Si on wheat biomass taken at Feekes 10.1 and total yield at harvest.

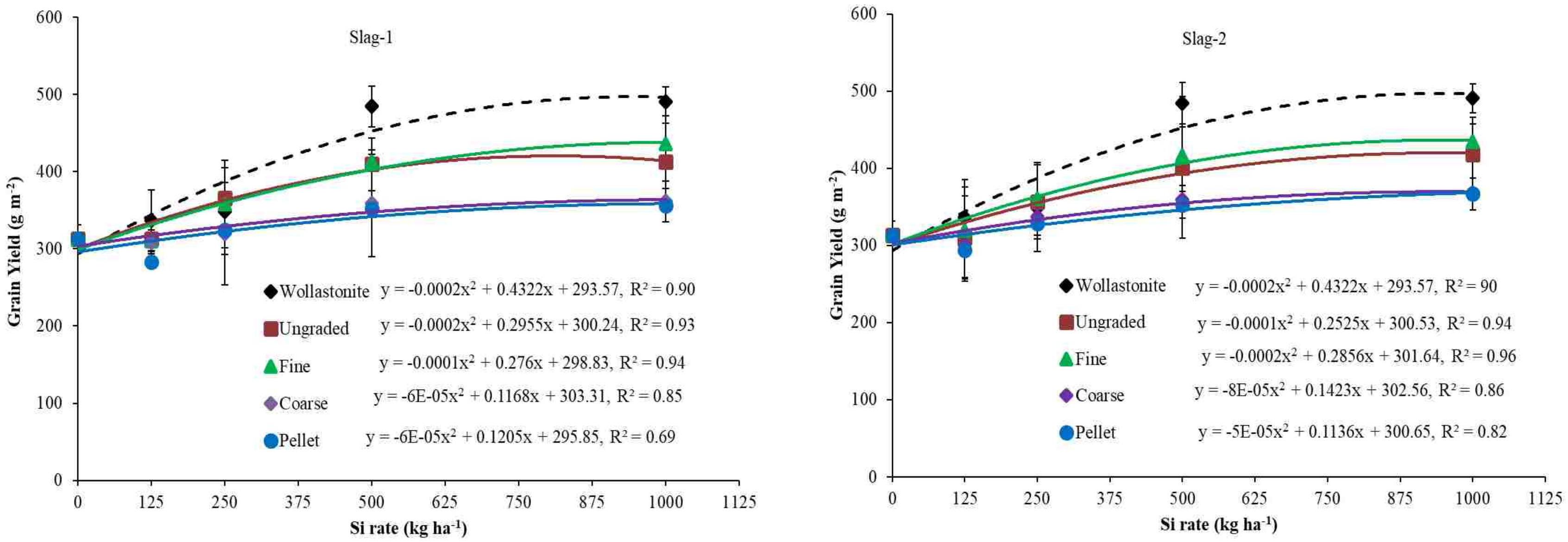

Figure 3.6. Effect of source, granular size and application rate of Si on wheat grain yield at harvest.

3.4. Conclusions

While Si is yet not considered an essential plant nutrient, remarkable crop responses have been attained from Si fertilization, especially when high Si accumulating crops such rice, sugarcane and wheat are grown in Si deficient soils. In such soils, Si is often replenished by applying high Si containing materials such as silicate slag. The data presented in the present study demonstrated that there are differences in the potential of silicate materials to supply Si to crops and the way in which they influence Si uptake and yield in wheat.

Silicate slag is an industrial by-product and contains lower amounts of soluble Si than the naturally formed wollastonite which has high Si. Nonetheless, it is evident that granular size of silicate slag is essential for improving its Si supplying power to crops. Silicate slag is highly soluble and tends to rapidly release Si in soil upon application. In this experiment, it was evident that finer granular size may further increase the amount of Si released by slag due to its high surface area, which facilitates easy distribution and solubility in soil. The maximum amount of Si released from all granular sizes of two silicate slag materials occurred within 30 days after application, leveled off until 120 days after application and then followed by drastic decline. This decline was probably related to dryness of the soil after the termination of irrigation, which may have facilitated maximum adsorption of H_4SiO_4 to soil exchange sites. The release pattern of H_4SiO_4 from silicate materials could serve as an indicator in determining the choice of material and application timing in a Si fertilization program. Fine and ungraded slag did not only show the highest increases in soil Si, but also led to substantial increase of soil Ca, Mg, S and Zn which also serves as an indicator of the potential of these granular sizes to improve soil fertility parameters when applied at optimum rates. The average grain yield was higher for wollastonite than all the granular sizes of the two silicate materials. This was probably because wollastonite with its slow release of Si may have supply optimum Si level compared to the two silicate slag sources during the growing season. However, yield components were also higher for fine and ungraded silicate slag materials than the coarse and pellet materials, thus suggesting the superiority of finer granular size of slag over the coarse or pellet form. Since the application of wollastonite in crop production is currently not economically feasible, the application of fine slag material could be an economically viable alternative for Si fertilization in Si-deficient soils.

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Chapter 4. Granule Size and Application Rate of Silicate Slag Affect Plant-Available Silicon Supply to Wheat

4.1. Introduction

Silicon (Si) is not listed among the elements considered essential for plant growth. However, several studies have shown that certain plant species especially those of the gramineae family exhibit growth abnormalities when Si is extremely low or excluded from their growth medium (Yoshida et al., 1959; Miyake and Takahashi, 1985; Datnoff et al., 2001). Despite its exclusion from the list of essential plant nutrients, considerable amounts of evidence have demonstrated that Si contributes to normal plant growth by mitigating a wide range of biotic and abiotic stresses including drought and soil salinity, nutrient imbalances, metal toxicity, plant pathogen and disease, insect attack and lodging (Ma, 2004; Liang et al., 2007; Epstein, 2009; Zhu and Gong, 2014; Adrees et al., 2015).

Silicon is highly abundant in soils, as most soil forming minerals contain Si as a basic component (Haynes, 2014). However, Si containing minerals are highly resistant to weathering. Thus, the concentration of Si in soil solution can become low if the rate of removal exceeds the rate of replenishment (Sacala, 2009).

Despite its abundance in soils, Si is usually found in combination with other minerals and may not be in the available form for plant uptake. Monosilicic acid (H_4SiO_4) is the predominant form of Si in soil solution that can be taken up by plants (Epstein, 1994). But the concentration of H_4SiO_4 in highly leached or organic soils classified as Oxisols, Ultisols and Histosols is often low; and Si fertilization of rice and sugarcane grown in these soils has often resulted in increased productivity (Elawad et al., 1982; Savant et al., 1997; Alvarez and Datnoff, 2001). These soils are usually found in regions with high rainfall and temperature which can lead to depletion of soluble soil Si and other essential plant nutrients due to high rates of water infiltration (Mckeague and Cline, 1963; Epstein, 2001). Moreover, such soils are usually acidic (pH<5.5) and contain high levels of aluminum (Al), which promotes reaction of Si with Al to form insoluble hydroxyaluminosilicates; this process eventually reduces the concentration of monosilicic acid in soil solution (Sanchez, 1976; Farmer et al., 1979; Doucet et al., 2001). In these soils, it is necessary to replenish the concentration of plant-available soil Si in order to maintain maximum productivity (Meyer and Keeping. 2001).

In natural ecosystems, the recycling of phytoliths has been recognized as a significant source for replenishing Si and this facilitates substantial Si uptake by plants even in highly weathered and Si depleted mineral soils (Lucas et al., 1993; Alexandre et al., 1997). The distribution of phytolith in soils varies with depth, with the highest concentrations usually found within the surface topsoil; and decreases as the soil depth increases (Sommer et al., 2006; Saccone et al., 2007). In cultivated soils however, the amount of plant-available Si derived from crop residue depends on whether the residues are removed or left in the field. Savant et al. (1997), noted that removing the residues of high Si accumulating crops from fields may result in depletion of the H_4SiO_4 concentration in soil and a subsequent decline in yield. It has been demonstrated by Desplanques et al. (2006), that rice field could be depleted of available Si after five years of continuous cultivation, relying on crop residue as the only source of Si for rice. Similarly, Datnoff and Rodrigues (2005), and Meunier et al. (2008), reported that the amount of Si removed from field in the form of crop residues is so substantial that it can only be supplemented through Si fertilization. Although crop residues can serve as an essential source of Si in agriculture, their effectiveness may depend on the Si demand of the succeeding crop. Based on the research of Ma and Takahashi (2002), it was demonstrated that the amount of Si held inside the rice straw is not immediately available upon incorporation. However, over a long period of time (40 years or more), Si released from the decomposition of rice straw may account for over 70% of the applied Si. In the event of an acute Si deficiency, plant residues may not be a suitable source of Si, especially if the succeeding crop has high demand for Si.

Application of Si fertilizer is therefore a common practice in many crop production systems especially in regions with intensive rice and sugarcane cultivation. Silicon fertilization of crops began in the 1950s in Japan and has also been accepted as a common agronomic practice in many countries including Korea, Taiwan, Thailand, Brazil and the United States (Liang et al., 1994; Korndörfer and Lepsch, 2001). From the onset of Si fertilization, several materials have been evaluated for their ability to supply Si. Wollastonite or calcium silicate is often used in many Si experiments due to its high soluble Si content (Maxim et al., 2008). But because it does not naturally occur in pure form (calcium silicate), its labor-intensive mining and high cost of refinery have limited its use in agriculture only to research (Park, 2001; Maxim et al., 2008). Magnesium silicate which also contains high levels of Si was evaluated for large scale agricultural application but was deemed not suitable as a Si source due to its low solubility (Weast et al., 1985). The most widely used source of Si for large scale agricultural application are those of industrial by-product such as the silicate slag, derived from steel/iron or elemental phosphorus production. The amounts of soluble Si found in these materials are highly variable due to differences in cooling speed, production temperature and granular size (Takahashi, 1981; Datnoff et al., 1992; Datnoff et al., 2001; Ma and Takahashi, 2002;). In spite of this, slag is mostly use to supply Si to crops because of its high solubility and potential to serve as a liming agent in neutralizing acid soils (Gascho, 2001, Heckman et al., 2003). Moreover, slags are relatively inexpensive compared to wollastonite, thereby making the use of slag more economical for crop production.

The rate of slag application to crops is highly variable from one region to another. This can be explained by factors such as the nutrient status of the soil, including native soil Si, availability of the material and the willingness of producers to undertake the extra investment to supply Si. In Japan for example, growers often apply 1.5 to 2 Mg ha^{-1} of steel slag prior to planting in rice fields testing low for Si; but for commercial rice production in the United Sates, growers in Florida usually apply 5 Mg ha^{-1} (Datnoff et al., 1997). Despite these established slag application rates for rice, the optimum application rate of slag to wheat (*Triticum aestivum*), which is also considered a silicon-accumulator, is yet to be established.

Wheat is one of the most important crops in the world. Geographically, the cultivation of wheat exceeds all other crops (Briggle and Curtis, 1987). Wheat provides about 55% of carbohydrates and 20% of the calories in human diet on a global scale and is cultivated under a wide range of climatic conditions (Breiman and Graur, 1995). The beneficial effect of Si is well documented in wheat. For example, shoot dry matter production was significantly increased in wheat plants under saline condition when supplied with Si, compared with those without Si treatment (Tahir et al., 2006). In a field experiment in Louisiana where the interactive effect between nitrogen (N) and Si was evaluated, White et al. (2017), reported a linear increase in wheat grain yield with increasing N and slag rates, with up to 7000 kg ha^{-1} of grain yield obtained at N and slag rates of 145 kg ha^{-1} and 9 Mg ha^{-1} respectively. However, they quickly pointed out that such a high application rate of slag may limit its economic return and serve as a potential deterrent for producer to apply Si to wheat. Datnoff et al. (1997) reported the cost of applying 5 Mg ha^{-1} of slag to rice as $84.00 in Florida where producers where reluctant to exceed this amount even though there was evidence of increased yield obtained at higher rates.

Granular size of silicate slag may affect its Si supplying ability and application rate. Several researchers have reported that smaller granular size of silicate materials is more effective in increasing plant-available Si in soils and subsequent Si uptake in plants compared with coarser materials (Medina-Gonzales et al., 1987; Datnoff et al., 1992). However, there are insufficient evidence documenting the effect of granular size of slag on application rate and wheat response to Si under field conditions. The objective of this study was to evaluate the effect of granular size of silicate slag on application rate, soil Si content and Si uptake, and grain yield of wheat in Louisiana production system.

4.2. Materials and Methods

4.2.1. Locations, Trial Establishment and Treatments

Wheat field trials were conducted at four locations in north and south Louisiana for the growing seasons 2016/2017 and 2017/2018. Prior to treatment application, 16 cores of soil samples were collected at 15 cm depth from each experimental site and analyzed for initial soil Si, pH, organic matter and other plant essential nutrients (Table 4.1). The source of Si used for this experiment was silicate slag (Plant Tuff®, 7% total Si), a by-product of steel production. The material was sieved and separated into three distinct granular sizes, which were categorized as fine (<1mm), coarse (>2mm) and whole slag (a mixture of fine and coarse).

Table 4.1. Soil type, initial pH, organic matter and nutrient composition each site year.

Site-year	Soil type	pH	OM g kg^{-1}	Extractable nutrient‡ mg kg^{-1} Si†	Ca	P	K	Mg	S	Zn
2017 Ben Hur	Silt loam	5.9	16	84	1880	25	120	297	13	1.6
2017 St. Joseph	Silt loam	5.6	19	88	2276	58	297	447	27	3.8
2018 Ben Hur	Silt loam	5.7	19	110	3576	51	329	645	18	3.5
2018Winnsboro	Silt loam	5.5	22	43	1186	51	118	195	27	2.8

† Based on 0.5 M acetic acid extraction procedure and analyzed by Molybdenum Colorimetric Blue (MBC) procedure.

‡Based on Mehlich-3 extraction procedure and analyzed by ICP-OES.

Treatments included three application rates for each granular size at 1.8, 3.6 and 7.2 Mg silicate slag ha^{-1}, which were equivalent to 125, 250, and 500 kg Si ha^{-1} respectively, along with a control (0) and 2.2 Mg ha^{-1} of wollastonite which was equivalent to 500 kg Si ha^{-1} to serve as a positive control (Table 4.2). The silicate materials were broadcast applied by hand and incorporated in the soil at a depth of 5 cm. All treatments were replicated four times and arranged in a randomized complete block design. After the treatment application, seeds of wheat variety *Syngenta Cypress* were drilled in plots measuring 1.5 x 7.6 m, with a total of seven rows per plot. One month after germination, 22 kg N ha^{-1} was applied as starter N, and then followed by 78 kg N ha^{-1} at Feekes 5 growth stage.

Table 4.2. Treatments and application rates of silicate slag and wollastonite

Treatment	Material	(Mg ha^{-1})	Si rate (kg ha^{-1})
1	Check	0	0
2	Wollastonite	2.2	500
3	Whole	1.8	125
4		3.6	250
5		7.2	500
6	Coarse	1.8	125
7		3.6	250
8		7.2	500
9	Fine	1.8	125
10		3.6	250
11		7.2	500

4.2.2. Sampling and Processing of Plant and Soil Samples

Around Feekes 10.5 growth stage and at harvest, both soil and plant biomass samples were collected to determine Si content. Plant sampling involved taking the entire above ground biomass of two 1 m sections of the third row on the opposite ends of each plot. These were combined as one composite sample for individual plots. This sampling procedure was also repeated for each plot at harvest after which the individual plots were harvested using a plot combine harvester equipped with a computerized weighing system. After harvest, the text weight for each plot was determined; the grain moisture content was adjusted to 12% and grain yields obtained in bushel per acre for each plot were then converted to kg ha^{-1}.

Plant biomass samples were oven-dried at 55°C until a constant weight was obtained. The dry matter weight for samples taken from each plot was determined, and the samples were processed by finely grinding them to pass through a 2 mm sieve using a standard Willey Mill model No.3. Plant samples taken at harvest were dried as previously discussed above and separated into spikes/heads and straw; and their individual weights were obtained. The straw samples were also processed in similar manner as the biomass samples taken at Feekes 10.5. The grains were processed by finely grinding them in a Wonder mill model No. WM2000.

Soil samples were also taken at Feekes 10.5 and at harvest and analyzed for pH, plant-available Si and a wide range of other plant essential nutrients. The soil sampling was performed by taking 12 cores at 15 cm depth from individual plots both at Feekes 10.5 and at harvest. These were dried at 55°C and processed to pass to through a 2 mm sieve, and then stored in 200 mL screw cap plastic cups until analysis.

4.2.3. Analysis

4.2.3a. Soil Analysis

The pH of collected soil samples was determined using the 1:1(w/v) soil to water ratio. Ten grams of soil samples were placed in a 50 mL centrifuge tube and 10 mL of deionized water was added. The tubes were then screwed tightly and placed on a reciprocal shaker set at high speed for one hour. After shaking, the samples were allowed to sit undisturbed for another hour to allow larger soil particles to settle and then, the pH was measured using an Oakton pH 5+ digital pH meter.

Plant-available soil Si was extracted using the 0.5 M acetic acid 1hour extraction procedure as describe by Korndorfer et al. (1999). After extraction, Si in the sample extract was quantified using the molybdenum blue colorimetric (MBC) procedure according to Korndorfer et al. (2001). Soil organic matter content was determined using the Walkley and Black wet digestion method (Walkley and Black, 1936). Other plant essential nutrients were extracted based on the Mehlich-3 extraction method (Mehlich, 1984) and then analyzed using the Inductively Couple Plasma (ICP) – Optical Emission Spectroscopy (OES).

4.2.3b. Plant Analysis

Determination of Si content in harvested wheat biomass, straw and grain samples was performed by first subjecting the samples to the oven-induced digestion procedure (Kraska and Breitenbeck, 2010). Silicon contents of the digested plant samples were then quantified by the MBC procedure (Hallmark et al., 1982), using a UV visible spectrophotometer (Hach DR 5000) set at 630 nm.

4.2.3c. Statistical Analysis

An analysis of variance (ANOVA) was performed using the PROC MIXED procedure in SAS 9.4 to determine the treatments effects on soil pH and Si, Mehlich-3 extractable plant nutrients, wheat Si content and yield components. Silicon rate was considered as fixed effect while replications were random effect. When a significant treatment effect was detected at ($p < 0.05$), a mean separation procedure was carried out using the Tukey-Kramer post-hoc test to identify the differences among treatments. Changes in soil Si with silicate slag granular size and application rate was then graphed using Microsoft® Excel 2013.

4.3. Results and Discussion

4.3.1. Effect of Slag and Wollastonite on Soil pH, and Extracted Nutrients.

The effect of granular size and application rate of silicate slag and wollastonite on soil pH, and Mehlich-3 extractable selected plant essential nutrients across all site years are summarized below. In general, there was minimal increase in soil pH with application of both silicate slag and wollastonite across site years. The most noticeable increase in soil pH was 0.7 units over the control treatment, observed at the application rate of 7.2 Mg ha^{-1} using the whole silicate slag at Winnsboro 2018 (Table 4.3). Winnsboro had the lowest initial pH and plant-available Si among the four sites (Table 4.1). However, a slight decrease in pH was observed following slag fertilization at Ben Hur 2017 (Table 4.4). Rodriguez et al. (1994) also reported slight decrease in pH over incubation time while working with silicate slag. The decrease in pH at Ben Hur 2017 may have resulted from hydrolysis of clay-ferric complexes. At St. Joseph 2017 (Table 4.5) and Ben Hur 2018 (Table 4.6), soil pH remained nearly steady, with changes only ranging between 0.1 to 0.4 units. These results are similar to those obtained by several researchers (Ali and Shahram, 2007; White et al. 1937) who also reported increase in soil pH after the application of silicate slag. Liming potential is one of the most important characteristics of silicate slag as a soil amendment. Slag contains significant quantities of calcium (Ca) and magnesium (Mg), both of which are also important ingredients found in agricultural lime. The increase in soil pH caused by silicate slag application could be due to the release of Ca and Mg in the soil after dissolution of silicate slag.

Table 4.3. Effect of granular size and application rate of silicate slag and wollastonite on soil pH, Si and nutrient content at Winnsboro, 2018.

				mg kg^{-1}							
	Silicate Slag Mg ha^{-1}	Si Kg ha^{-1}	pH	Si	Ca	P	K	Mg	S	Mn	Zn
Check	0	0	5.1	20	857	28	71	541	17	179	3.3
Wollastonite	2.2	500	5.3	36	1092	23	58	543	13	160	3.6
Whole	1.8	125	5.4	39	1014	26	64	531	14	190	3.9
	3.6	250	5.4	77	1110	25	73	495	15	202	3.5
	7.2	500	5.8	85	1497	26	68	510	16	225	3.6
Coarse	1.8	125	5.3	39	1000	28	82	534	15	182	4.1
	3.6	250	5.3	42	792	19	54	407	11	143	2.8
	7.2	500	5.5	44	1157	23	54	523	13	164	2.9
Fine	1.8	125	5.3	34	994	25	67	504	14	204	3.2
	3.6	250	5.4	43	1119	24	67	539	14	195	3.1
	7.2	500	5.6	94	1374	26	58	529	17	209	2.7
p-value			0.07	<0.001	<0.001	NS	NS	0.06	NS	NS	NS

NS= Not Significant at ($p < 0.05$)

Table 4.4. Effect of granular size and application rate of silicate slag and wollastonite soil pH, Si and nutrient content at Ben Hur, 2018.

	Silicate Slag Mg ha^{-1}	Si kg ha^{-1}	pH	mg kg^{-1} Si	Ca	P	K	Mg	S	Mn	Zn
Check	0	0	6.5	74	3175	30	183	527	19	64	3.3
Wollastonite	2.2	500	6.4	144	2905	25	184	506	18	62	3.3
Whole	1.8	125	6.4	124	3031	28	186	510	19	60	3.3
	3.6	250	6.3	102	2758	22	178	478	16	54	3.0
	7.2	500	6.3	166	2895	26	180	490	15	56	3.1
Coarse	1.8	125	6.4	123	3004	26	177	520	18	66	3.3
	3.6	250	6.3	136	2878	28	181	512	16	62	3.3
	7.2	500	6.3	158	2929	27	178	488	19	57	3.3
Fine	1.8	125	6.3	131	2885	26	179	491	15	62	3.2
	3.6	250	6.4	145	2959	25	182	502	19	59	3.2
	7.2	500	6.4	172	2968	26	184	518	19	62	3.3
p-value			NS	NS	NS	NS	NS	NS	NS	NS	NS

NS= Not Significant at ($p < 0.05$)

Table 4.5. Effect of granular size and application rate of silicate Slag and wollastonite soil pH, Si and nutrient content at St. Joseph in 2018.

	Silicate slag Mg ha^{-1}	Si kg ha^{-1}	pH	mg kg^{-1} Si	Ca	P	K	Mg	S	Mn	Zn
Check	0	0	6.1	78	2988	42	365	566	13	144	4.3
Wollastonite	2.2	500	6.2	138	2738	34	283	471	13	150	4.0
Whole	1.8	125	6.0	114	2561	37	265	484	12	163	3.7
	3.6	250	6.2	143	2803	35	287	530	13	147	3.8
	7.2	500	6.4	197	3354	59	381	596	16	145	4.9
Coarse	1.8	125	6.0	117	2733	35	284	516	12	150	3.7
	3.6	250	6.0	107	2428	34	252	462	12	151	3.5
	7.2	500	6.4	169	3177	40	350	572	12	165	4.3
Fine	1.8	125	5.9	137	2729	43	317	540	12	165	4.0
	3.6	250	6.4	142	2571	40	264	457	12	139	3.7
	7.2	500	6.5	154	2889	42	270	517	13	152	3.8
p-value			NS	<0.05	<0.05	NS	NS	NS	NS	NS	NS

NS= Not Significant at (p <0.05)

Table 4.6. Effect of granular size and application rate of silicate slag and wollastonite soil pH, Si and nutrient content at Ben Hur, 2018.

	Silicate slag Mg ha^{-1}	Si kg ha^{-1}	pH	mg kg^{-1} Si	Ca	P	K	Mg	S	Mn	Zn
Check	0	0	5.7	79	3358	34	235	672	13	59	3.5
Wollastonite	2.2	500	5.9	105	3592	45	223	629	13	69	3.6
Whole	1.8	125	5.7	93	3473	41	222	655	13	65	3.5
	3.6	250	6.0	104	3556	50	238	664	15	69	6.3
	7.2	500	6.0	117	3717	51	218	664	16	72	3.5
Coarse	1.8	125	5.9	91	3451	38	231	663	13	68	3.6
	3.6	250	5.7	93	3480	43	228	660	13	70	3.5
	7.2	500	5.8	89	3514	39	221	676	13	68	3.3
Fine	1.8	125	5.8	96	3439	35	222	685	13	62	3.3
	3.6	250	5.9	111	3569	45	223	681	16	68	5.1
	7.2	500	6.3	154	3839	45	222	687	15	73	3.4
p-value			NS	<0.001	<0.05	NS	NS	NS	<0.05	<0.05	NS

NS= Not Significant at ($p < 0.05$)

When added to soil, the Ca in slag reacts with water to form calcium hydroxide [$Ca(OH)_2$] which is effective in increasing soil pH. Calcium content was also significantly increased ($p<0.05$) at St. Joseph and Ben Hur in 2018 and ($p<0.001$), at Winnsboro in 2018, respectively following silicate slag fertilization. There were also increases in soil S and Mn, in plots which received the highest application rate of 7.2 Mg ha^{-1} of whole and fine material at Ben Hur 2018. Other measured soil nutrients remained unchanged; indicating that with the exception of Si and Ca, application of slag has minimal effects on the nutritional status of these soils. The increase in soil S and Mn could be due to trace amounts of these elements found in the material.

4.3.2. Effect of Granular Size and Silicate Slag Rate on Plant-available Soil Silicon

Figure 4.1 shows the effect of granular size and application rate of silicate slag on plant-available soil Si. There was significant increase ($p<0.001$) in 0.5 M acetic acid extractable plant-available Si in plots treated with both slag and wollastonite over the control treatments in all sites. However, fine and whole silicate slag materials were generally more effective in raising the soil Si than the coarse silicate slag and wollastonite. At Ben Hur 2017, soil Si in plots treated with coarse silicate slag with equivalent Si rate of 250 kg Si ha^{-1} was higher than Si levels of plots treated with whole material at the same application rate (Figure 4.1). However, at St. Joseph 2017, Ben Hur 2018, and Winnsboro 2018, Si extracted from soils treated with fine and whole silicate slag were consistently higher than those that received coarse silicate slag and wollastonite. Averaged across site-years, the amount of Si extracted from soil based on granular size were in the order of fine > whole > coarse; this was followed by wollastonite and then the check. Finer granular size has higher surface area, which leads to increased reactivity and faster dissolution of silicate slag in soil.

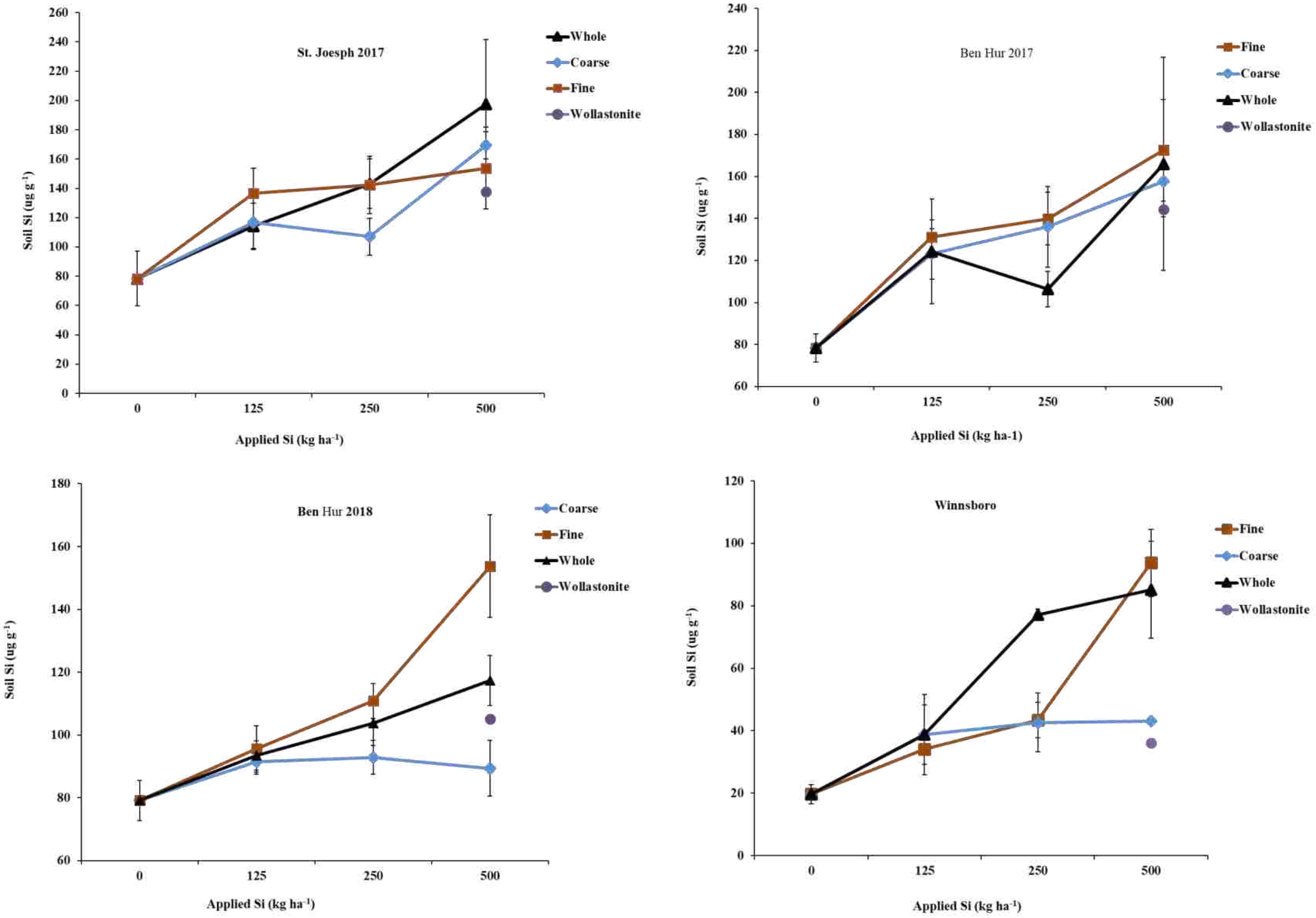

Figure 4.1. Effect of granular size and application rate of silicate slag and wollastonite on acetic acid extractable soil Si.

Medina- Gonzales et al. (1988) obtained similar results while working with two silicate materials and sugarcane in Hawaii. The application of silicate slag at 500 kg Si ha^{-1}, regardless of granular size resulted in higher increases in soil Si than wollastonite at Ben Hur and St. Joseph in 2017 and at Winnsboro 2018. However, at Ben Hur 2018, at the same application rate, soil Si level of wollastonite-treated plots was higher than those of coarse silicate slag. These results do not agree with those obtained by Babu et al (2016) and Aghostinho et al (2017) who reported consistently higher Si content in wollastonite-treated soil than silicate slag-treated soil. Results from this study indicate that while silicate slag may have less Si (7%) compared to wollastonite (23%), the high solubility of silicate slag enables it to quickly release Si to soil, making it an ideal Si fertilizer source.

4.3.3. Wheat Yield Component and Si Content as Affected by Silicate Slag and Wollastonite Application

The ANOVA revealed no significant treatment effects on measured plant variables at Ben Hur in 2017 (Table 4.7). However, the application of 7.2 Mg ha^{-1} of fine silicate slag increased wheat biomass from 290 to 387 g m^{2} (Table 4.8) at Ben Hur 2018. Silicon content in biomass taken at Feekes 10.5 was also significantly increased from 1.7% in the control plots to 2.1% in wollastonite-treated plots ($p < 0.005$). Similarly, straw Si content was also increased from 2.7% to 3.2% ($p < 0.07$). At St. Joseph 2017, the application of 1.8 Mg ha^{-1} of fine granular size of silicate slag increased wheat biomass weight from 203 in the control to 243 g m^{-2} ($p<0.05$) (Table 4.9). Grain weight was also increased from 390 to 533 g m^{-2} ($p < 0.005$) for the control plots and those that received 3.6 Mg ha^{-1} of whole silicate slag material. On the other hand, Si content of the biomass was significantly ($p<0.005$) increased only in the wollastonite-treated plots. The Si content of straw in wollastonite-treated plots was also higher than the control and silicate slag-treated plots. Similar results were obtained at Winnsboro 2018, where a significantly ($p<0.05$) higher biomass weight was obtained in plots treated with 1.8 Mg ha^{-1} of fine silicate slag material in reference to the control (Table 4.10). The highest straw Si content of 2.9% was also observed in the wollastonite-treated plots. In their research where wollastonite was among the Si sources applied to rice, Agostihno et al. (2017), also reported higher Si content in rice biomass at booting stage, and in straw and grain at harvest for wollastonite treatments than the control and other Si sources. Also, significantly higher Si content in pumpkin (*Cucurbita pepo*) tissue was reported only for wollastonite treatment than for other sources of Si in a greenhouse trial (Torlon et al., 2016). In the present study, the Si content for both biomass and straw was higher for the wollastonite-treated plots in nearly all sites, but this higher Si content did not result in production of higher biomass, straw or grain. The highest biomass, straw and grain weights were mostly observed when either whole or fine silicate slag material was the source of Si.

Regardless of the source used, there was minimal reduction in yield components at higher Si application rates observed across all site-years; but these decreases where not substantial to cause a significant reduction in grain yield. Overall, there was no significant treatment effect on the number of tillers and number of heads produced in all site-years. It has also been reported that the number of tillers and panicle in rice did not increase as a result of Si application (Tamai and Ma, 2008). However, increases in panicle number in rice (Ma et al. 1989) and number of tillers (Gholami and Falah, 2013) were observed as a result of Si application. The positive responses of crops to Si fertilization have mostly been reported when crops are under some form of stress, or when crops are grown in Si-deficient soils. The soils from these site-years were testing medium to high in soil Si, thus the reduction in some yield parameters was probably a typical crop response to over application of fertilizer.

4.3.4. Effect of Granular Size and Application Rate on Wheat Grain yield

The effect of granular size and application rate of silicate slag and wollastonite on wheat grain yield varied across site years (Figure 4.2). Results indicate that higher grain yields were obtained at lower application rates for both whole and fine silicate slag at several sites. When the effect of each treatment on wheat test weight was evaluated across site years, no effect of silicate slag or wollastonite observed (data not shown). However, at Ben Hur 2017, a 31% increase in grain yield was obtained in plots treated with 1.8 Mg ha^{-1} of fine silicate slag, whereas at Ben Hur 2018, a 16% increase in grain yield was attained with similar material. At St. Joseph 2017, the application of 3.6 Mg ha^{-1} of whole silicate slag resulted in a 17% yield increase over plot with no Si application; whereas a 20% increase in yield was obtained at Winnsboro 2018 at the application rate of 7.2 Mg ha^{-1} of fine silicate slag material.

Winnsboro had the lowest initial soil Si among the four sites. At this site, grain yield also increased slightly with increasing application of whole silicate slag and was even higher at the application of 1.8 and 3.6 Mg ha^{-1} of coarse silicate slag when compared to the control. Datnoff et al (1992), reported increases of 26, 18 and 4% in grain yield for fine, coarse and pelletized materials respectively, in rice in the Everglades Agriculture Area (EAA) of Florida. In a separate study, infection rate of brown spot (*Bipolaris oryzae*) was reduced by 21% for fine, 19% for whole and 5% for pelletized materials while rice blast (*Pyricularia grisea*) severity was reduced by 21, 19 and 11% respectively for the same categories of slag materials (Datnoff and Snyder, 1994). From these results, it seems that finer granular size of silicate slag does not only improve its effectiveness to release monosilicic acid in soil, but this could also be used to reduce the quantity of slag needed to raise the Si levels in Si deficient soils without compromising yield.

Table 4.7. Effect of granular size and application rate of silicate slag and wollastonite on wheat yield component and Si content at Ben Hur 2017.

	Silicate slag Mg ha^{-1}	Si kg ha^{-1}	Yield Component per m^2 sampling area: Biomass g	Tiller number	Head Number	Straw g	Grain g	%Si content: Biomass	Straw	Grain
Check	0	0	243	470	440	713	337	2.2	2.8	0.2
Wollastonite	2.2	500	210	433	407	703	347	2.2	2.7	0.1
Whole	1.8	125	217	396	387	723	350	2.5	3.2	0.1
	3.6	250	220	410	397	607	380	2.0	3.0	0.1
	7.2	500	210	410	403	563	363	2.1	2.9	0.2
Coarse	1.8	125	227	460	440	903	313	2.4	3.1	0.2
	3.6	250	267	453	447	777	360	2.2	3.4	0.1
	7.2	500	280	510	467	980	330	2.5	3.0	0.2
Fine	1.8	125	220	393	380	633	283	3.1	1.9	0.1
	3.6	250	196	427	423	617	430	2.4	3.4	0.1
	7.2	500	237	367	367	587	410	2.2	2.7	0.2
p-value			NS	NS	NS	NS	NS	NS	NS	NS

Table 4.8. Effect of granular size and application rate of silicate slag and wollastonite on wheat yield component and Si content at Ben Hur 2018.

			Yield Component per m^2 sampling area					% Si content		
	Silicate slag Mg ha^{-1}	Si kg ha^{-1}	Biomass g	Tiller number	Head Number	Straw g	Grain g	Biomass	Straw	Grain
Check	0	0	290	263	263	303	203	1.7	2.7	0.2
Wollastonite	2.2	500	330	283	273	306	220	2.1	3.2	0.2
Whole	1.8	125	353	253	247	270	183	1.8	2.4	0.3
	3.6	250	350	253	253	276	213	1.7	2.5	0.2
	7.2	500	347	263	260	280	220	1.7	2.7	0.2
Coarse	1.8	125	307	247	240	303	193	1.6	2.5	0.2
	3.6	250	290	240	237	253	183	1.5	2.4	0.2
	7.2	500	323	263	257	263	216	1.6	2.4	0.3
Fine	1.8	125	363	280	273	273	240	1.7	2.3	0.2
	3.6	250	343	273	287	310	213	1.7	2.5	0.2
	7.2	500	387	267	263	367	216	1.7	2.5	0.2
p-value			0.09	NS	NS	NS	NS	<0.005	0.07	NS

Table 4.9. Effect of granular size and application rate of silicate slag and wollastonite on wheat yield component and Si content at St. Joseph 2017.

			Yield Component per m^2 sampling area					% Si content		
	Silicate slag Mg ha^{-1}	Si kg ha^{-1}	Biomass g	Tiller number	Head Number	Straw g	Grain g	Biomass	Straw	Grain
Check	0	0	203	707	617	1053	390	2.6	2.6	0.2
Wollastonite	2.2	500	177	813	713	1010	460	2.9	3.0	0.2
Whole	1.8	125	213	767	723	1213	430	2.7	2.6	0.2
	3.6	250	223	810	773	1280	533	2.8	2.7	0.2
	7.2	500	196	667	660	1030	223	2.8	2.8	0.2
Coarse	1.8	125	253	733	687	1133	407	2.6	2.8	0.2
	3.6	250	203	783	680	1103	380	2.7	2.7	0.2
	7.2	500	220	633	567	1050	243	2.8	2.9	0.1
Fine	1.8	125	243	753	736	1023	477	2.8	2.8	0.3
	3.6	250	193	623	580	833	296	2.8	2.6	0.2
	7.2	500	210	743	663	1007	290	2.7	2.8	0.2
p-value			<0.05	NS	NS	NS	<0.005	<0.005	0.07	NS

Table 4.10. Effect of granular size and application rate of silicate slag and wollastonite on wheat yield component and Si content at Winnsboro 2018.

			Yield Component per m^2 sampling area					% Si content		
	Silicate slag Mg ha^{-1}	Si kg ha^{-1}	Biomass g	Tiller number	Head Number	Straw g	Grain g	Biomass	Straw	Grain
Check	0	0	497	347	343	503	443	1.4	2.0	0.2
Wollastonite	2.2	500	437	323	323	467	460	2.0	2.9	0.2
Whole	1.8	125	420	393	310	513	503	1.5	2.2	0.2
	3.6	250	427	350	350	503	497	1.5	2.2	0.2
	7.2	500	430	383	377	496	451	1.5	2.4	0.3
Coarse	1.8	125	423	357	353	467	467	1.4	2.1	0.2
	3.6	250	513	383	380	503	490	1.4	2.3	0.2
	7.2	500	460	327	323	440	430	1.5	2.0	0.2
Fine	1.8	125	543	363	359	496	496	1.6	2.4	0.2
	3.6	250	460	340	340	440	430	1.5	2.3	0.2
	7.2	500	393	387	380	567	553	1.6	2.5	0.2
p-value			<0.05	NS	NS	NS	NS	<0.005	0.07	NS

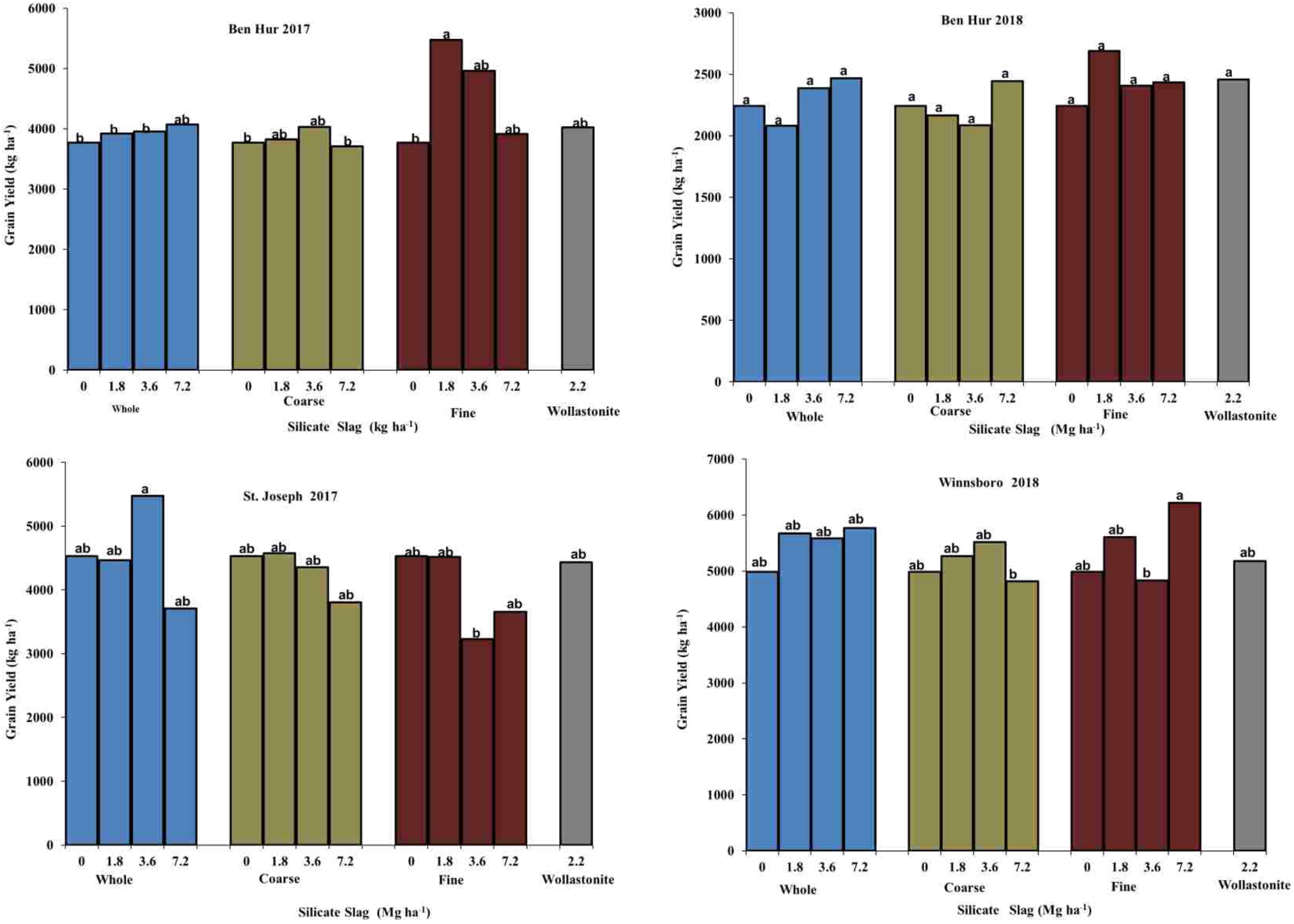

Figure 4.2. Grain yield of wheat supplied with wollastonite and different granular sizes of silicate slag at different application rate across site-years. Bars with same letters are not significantly different based on Fisher LSD (P <0.005)

4.4. Conclusions

It was found that silicate silicate slag was effective in raising the soil pH. The most noticeable increase in pH was observed in Winnsboro where soil pH was lowest among the sites investigated. At this site, the application of fine and whole granular size of silicate resulted in higher increases in soil pH than using the coarse silicate slag. Soil pH was also increased with increasing application of slag. This result confirms the effectiveness of slag as an agricultural liming material.

Plant-available Si was also increased after application of both silicate slag and wollastonite, but silicate slag was more effective in increasing the soil Si than wollastonite. Among the silicate slag treatments, plots receiving fine and whole slag had higher soil Si than the plots treated with coarse slag. This indicates that the application of finer granular size of silicate slag could be an effective way of increasing Si in Si-deficient soils. Wollastonite-treated plots had the highest Si content in biomass taken at Feekes10.5 and straw at harvest than silicate slag treated plots, but this highest plant Si content of the Wollastonite plot did not result in the highest yield.

Higher wheat grain yields were mostly observed at lower application rate of fine and whole silicate slag. At Ben Hur 2017 and 2018, the application of 1.8 Mg ha^{-1} of fine slag resulted in 31 and 16% increased grain yield over the control respectively, whereas at St. Joseph 2017 and Winnsboro 2018, 17 and 20% increase in grain yield was obtain at 3.6 and 7.2 Mg ha^{-1} of whole and fine slag respectively. Silicate slag is an industrial by-product and is relatively inexpensive due to less competition for other usage compared to wollastonite which has several industrial usages. However, the application of 5 Mg ha^{-1} of slag to rice at the cost of $84.00 as reported by (Datnoff et al. 1997) has deterred producers from applying slag even with evident increase in yield at higher application rate. This study revealed that higher grain yield can be obtained in wheat at lower application rate of fine and whole silicate slag than coarse material. In any fertilization program, the amount of fertilizer required to increase yield is often influenced by initial nutrient content of the soil. In this study, the rate of 1.8 Mg ha^{-1} of fine silicate slag material was the lowest rate at which the highest grain yield was obtained, at least at two sites, Ben Hur in 2017 and 2018, where the initial soil Si was about 80 mg kg^{-1}. In St. Joseph 2017 where the initial soil Si was 88 mg kg^{-1}, the application of 3.6 Mg ha^{-1} of whole slag material was sufficient to obtain the highest grain yield of 5475 kg ha^{-1}. However, it took the application of 7.2 Mg ha^{-1} of fine silicate slag to increase the grain yield by 20% in Winnsboro where the initial soil Si was only 43 mg kg^{-1}. While a complete cost and benefit analysis is required to ascertain the added benefits Si fertilization will bring to the Louisiana wheat industry, this study has demonstrated that finer granule of silicate slag can greatly reduce the amount of fertilizer material required to raise the soil Si and increase wheat grain yield.

4.5. References

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Chapter 5. Conclusions

The Application of silicate slag and lime resulted in increased soil pH and Si. These increases in pH however, had no influences on the concentration of trace elements in soils across the nine sites investigated. Since the concentration of these elements in the soil was not affected by slag or lime application, it is unlikely that the changes in pH resulting from their application had much influence on the uptake of trace elements in rice. Nonetheless, elevated levels of soil Si had negative correlations with As and Cd content in rice grain, thus suggesting that the Si inhibiting effect on the uptake of these elements likely occurred within the plant.

The release of H_4SiO_4 from silicate slag was highly influenced by the granular size of the material. Application of finer granular size resulted in higher release of Si in soil. The changes in soil Si as influenced by the application of silicate materials was mostly noticeable within 30 days after the treatments were applied. Wheat Si content and grain yield was also influenced by the granular size of the materials applied. Wollastonite application resulted in highest grain yield in wheat. This was followed by the application of the fine and ungraded silicate slag. At the same Si application rate, these granular sizes had higher Si contents and yield components than the coarse and pellet materials. The granular size of silicate slag also had an impact on its application rate. At Ben Hur 2017 and 2018, application of 1.8 Mg ha^{-1} resulted in 31 and 16% increase in grain over the check, and these were much higher, compared to the yield obtained by higher application rates of the coarse or pellet silicate slag materials. These results demonstrate that Si fertilization has the potential to reduce the uptake of harmful trace elements in crops and limit human exposure to As and Cd via the food chain. It also show that application of finer granular size of slag can improve the benefits it renders to producers by increasing the amount of Si released from the material especially when the soil is deficient in available Si.

Appendix A. Effect of Silicate Slag and Lime Application on Post-harvest Soil pH, Si and Trace Element Content

Table A.1. Effect of silicate slag and lime application on soil pH, Si and trace element content in post-harvest soil samples in Gilbert 2013 and 2014.

Site-Year	Silicate slag Mg ha^{-1}	pH	mg kg^{-1}									
			Si	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2013 Gilbert	0	7.0	132	1296	0.040	0.305	5.1	481	163	2.63	2.32	3.82
	1	7.2	168	1428	0.038	0.330	6.5	628	196	2.99	2.70	4.97
	2	7.2	176	1419	0.023	0.330	6.5	635	218	3.08	2.80	5.36
	4	7.4	184	1439	0.030	0.338	6.4	577	202	2.91	2.90	4.81
	6	7.5	195	1473	0.080	0.323	6.9	605	200	3.10	2.99	5.28
	8	7.6	215	1413	0.060	0.323	7.2	621	232	2.90	3.14	5.18
	0 (Lime 2 Mg ha^{-1})	7.1	158	1377	0.073	0.333	7.1	615	197	3.12	2.86	5.09
	0 (Lime 4 Mg ha^{-1})	7.4	157	1459	0.063	0.333	6.9	627	199	3.20	2.93	5.23
	P-value	<0.001	<0.001	NS	NS	NS	NS	NS	NS	NS	NS	NS
2014 Gilbert	0	6.8	138	1401	0.350	0.098	3.0	618	87	3.20	2.01	3.70
	1	7.1	170	1445	0.335	0.090	3.4	612	82	3.43	2.08	3.42
	2	7.1	175	1464	0.345	0.085	3.6	592	88	3.38	2.05	3.38
	4	7.1	185	1447	0.343	0.073	3.3	604	68	3.46	2.03	3.18
	6	7.3	200	1425	0.355	0.068	3.1	601	63	3.41	1.87	2.71
	8	7.4	223	1485	0.383	0.070	3.1	621	67	3.47	1.90	2.98
	0 (Lime 2 Mg ha^{-1})	7.0	148	1437	0.363	0.075	3.4	616	71	3.46	1.94	3.06
	0 (Lime 4 Mg ha^{-1})	7.3	160	1430	0.345	0.078	3.1	635	71	3.39	1.92	3.11
	P-value	0.002	<0.001	NS	NS	NS	NS	NS	NS	NS	NS	NS

Table A.2. Effect of silicate slag and lime application on soil pH, Si and trace metals content in post-harvest soil samples in Lake Arthur 2014 and 2015.

			mg kg^{-1}									
Site-Year	Silicate slag Mg ha^{-1}	pH	Si	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2014 Lake Arthur	0	4.8	14	908	0.360	0.048	1.0	758	77	9.66	1.16	2.46
	1	4.9	19	892	0.358	0.045	1.0	735	74	10.66	1.15	2.42
	2	4.9	23	855	0.378	0.045	1.0	741	116	24.17	1.21	2.23
	4	5.1	23	931	0.363	0.048	1.0	780	66	9.50	1.26	2.54
	6	5.1	26	937	0.395	0.043	1.1	751	73	9.65	1.32	2.62
	8	5.3	32	966	0.368	0.048	1.1	760	88	9.45	1.25	2.69
	0 (Lime 2 Mg ha^{-1})	5.0	16	891	0.403	0.043	1.0	731	59	9.54	1.14	2.34
	0 (Lime 4 Mg ha^{-1})	5.0	17	955	0.385	0.040	1.0	8.5	63	9.66	1.35	2.38
	P-value	<0.001	<0.001	NS	NS	NS	NS	NS	NS	NS	NS	NS
2015 Lake Arthur	0	4.6	40	1030	1.240	0.073	1.2	1309	105	7.50	1.30	5.36
	1	4.9	62	945	0.400	0.070	1.1	1240	92	7.52	1.28	4.82
	2	5.0	68	1038	0.418	0.075	1.2	1305	87	7.89	1.27	5.95
	4	5.1	93	1015	0.408	0.065	1.1	1189	85	7.62	1.24	5.52
	6	5.3	98	1015	0.420	0.065	1.2	1262	85	7.65	1.21	5.25
	8	5.5	114	1012	0.368	0.065	1.1	1202	107	7.37	1.29	4.95
	0 (Lime 2 Mg ha^{-1})	4.9	55	1111	0.430	0.060	1.2	1166	114	7.84	1.47	5.72
	0 (Lime 4 Mg ha^{-1})	5.1	59	1041	0.378	0.075	1.2	1207	93	7.61	1.25	5.52
	P-value	<0.001	<0.001	NS	NS	NS	NS	NS	NS	NS	NS	NS

Table A.3. Effect of silicate slag and lime application on soil pH, Si and trace metals content in post-harvest soil samples in St. Landry and Mamou 2014.

Site-Year	Silicate slag Mg ha^{-1}	pH	mg kg^{-1}									
			Si	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2014 St. Landry	0	5.6	151	1049	0.350	0.045	1.9	670	123	2.55	1.43	3.17
	1	6.0	182	1072	0.398	0.050	1.7	689	119	2.56	1.33	2.76
	2	6.2	189	1076	0.413	0.050	1.7	691	119	2.60	1.28	2.29
	4	6.6	211	996	0.405	0.046	1.7	692	114	2.55	1.27	2.12
	6	6.9	207	1096	0.423	0.048	1.8	705	122	2.58	1.28	2.62
	8	7.2	242	1159	0.415	0.043	1.7	716	102	2.74	1.62	2.55
	0 (Lime 2 Mg ha^{-1})	6.1	166	926	0.373	0.047	1.7	660	115	2.43	1.18	2.27
	0 (Lime 4 Mg ha^{-1})	6.3	174	904	0.385	0.045	1.8	658	120	2.41	1.36	2.78
	P-value	<0.001	<0.001	NS	NS	NS	NS	NS	0.042	0.083	NS	NS
2014 Mamou	0	5.6	6	750	0.205	0.035	0.8	449	113	5.65	0.92	5.16
	1	6.1	11	816	0.245	0.033	0.9	458	87	5.81	1.01	4.23
	2	6.2	13	762	0.250	0.033	0.8	463	84	5.74	0.90	5.15
	4	6.5	23	734	0.233	0.030	0.8	442	139	5.43	1.01	2.64
	6	6.9	28	791	0.273	0.033	0.7	516	114	5.38	0.94	1.98
	8	7.2	53	827	0.245	0.030	0.9	547	81	5.53	1.03	7.16
	0 (Lime 2 Mg ha^{-1})	6.0	6	748	0.268	0.030	0.8	444	65	5.96	1.00	3.29
	0 (Lime 4 Mg ha^{-1})	6.4	10	772	0.235	0.028	0.8	367	125	5.94	1.12	4.28
	P-value	<0.001	<0.001	NS	NS	NS	0.043	NS	NS	0.054	NS	NS

Table A.4. Effect of silicate slag and lime application on soil pH, Si and trace metals content in post-harvest soil samples in Crowley 2013, 2014 and 2015.

Site-Year	Silicate slag Mg ha^{-1}	pH	Mg kg $^{-1}$									
			Si	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2013 Crowley	0	7.7	94	682	0.143	0.260	1.6	818	242	2.17	4.36	8.00
	1	7.8	105	751	0.188	0.248	1.4	736	236	2.09	4.73	7.40
	2	8.0	107	628	0.185	0.258	1.6	741	228	2.15	5.68	8.60
	4	8.1	110	656	0.218	0.263	1.5	862	218	2.06	4.22	10.10
	6	8.2	110	758	0.103	0.263	1.4	829	248	2.14	4.00	9.12
	8	8.3	116	804	0.113	0.258	1.5	790	301	2.13	4.08	7.36
	0 (Lime 2 Mg ha^{-1})	7.8	101	777	0.120	0.238	0.9	840	260	1.29	2.24	9.58
	0 (Lime 4 Mg ha^{-1})	7.9	103	723	0.185	0.235	1.3	830	333	2.11	2.17	8.95
	P-value	<0.001	<0.001	NS	NS	NS	NS	NS	NS	NS	NS	NS
2014 Crowley	0	7.0	26	604	0.320	0.058	1.4	962	205	5.33	1.37	10.55
	1	7.5	48	597	0.363	0.060	1.4	924	204	5.37	1.30	9.83
	2	7.7	56	571	0.328	0.058	1.4	916	193	5.55	1.31	11.46
	4	7.8	67	597	0.370	0.058	1.4	919	213	5.66	1.32	10.01
	6	7.8	75	617	0.338	0.058	1.4	922	206	5.59	1.32	10.24
	8	8.1	96	704	0.298	0.068	1.4	1039	220	5.27	1.39	10.76
	0 (Lime 2 Mg ha^{-1})	7.4	37	557	0.293	0.060	1.4	1110	194	5.33	1.25	10.48
	0 (Lime 4 Mg ha^{-1})	7.6	46	584	0.313	0.060	1.4	1056	199	5.50	1.36	10.41
	P-value	<0.001	<0.001	0.031	0.020	NS	NS	NS	NS	NS	NS	NS
2015 Crowley	0	7.9	36	541	0.675	0.068	1.5	658	223	5.94	1.78	7.74
	1	7.9	77	606	0.633	0.068	1.4	664	227	5.73	1.79	8.07
	2	8.0	84	603	0.650	0.063	1.5	707	223	6.15	1.78	8.90
	4	8.1	110	545	0.610	0.063	1.4	653	191	5.72	1.62	7.95
	6	8.1	110	570	0.658	0.063	1.4	666	212	5.90	1.62	8.70
	8	8.1	194	623	0.613	0.063	1.5	616	245	5.71	1.89	8.12
	0 (Lime 2 Mg ha^{-1})	7.9	56	592	0.598	0.06	1.4	646	226	5.91	1.74	8.02
	0 (Lime4 Mg ha^{-1}	8.0	73	682	0.575	0.058	1.4	632	221	5.84	1.89	8.50
	P-value	<0.001	<0.001	NS	NS	NS	NS	NS	0.042	0.083	NS	NS

Appendix B. Effect of Silicate and Lime Application on Rice Grain and Trace Element Content

Table B.1 Effect of silicate slag and lime application on rice Si and trace metals content Gilbert 2013 and 2014.

Site-year	Silicate slag (Mg ha$^{-1)}$	%Si			mg kg^{-1}								
		Grain	Straw	Total	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2013 Gilbert	0	2.4	6.1	4.4	16	0.180	0.113	20	145	138	1.66	3.06	21
	1	2.8	6.5	4.8	20	0.137	0.100	16	136	138	1.60	3.13	21
	2	2.8	6.6	4.9	33	0.095	0.098	22	156	156	1.49	3.50	20
	4	2.8	6.6	4.8	23	0.073	0.088	25	146	133	1.46	3.14	22
	6	2.9	6.8	5.2	13	0.053	0.075	24	146	145	1.45	3.98	22
	8	3.1	7.2	5.5	21	0.030	0.050	28	125	152	1.66	2.82	22
	0 (Lime 2 Mg ha^{-1})	2.7	6.2	4.6	13	0.031	0.167	19	121	147	1.56	2.47	22
	0 (Lime 4 Mg ha^{-1})	2.7	6.3	4.7	24	0.027	0.167	18	118	140	1.44	2.80	21
	P-value	<0.001	<0.001	<0.001	NS	<0.001	0.001	NS	NS	NS	NS	NS	NS
2014 Gilbert	0	2.5	6.6	4.7	1.5	0.265	0.160	4.60	52	205	0.74	3.90	25
	1	3.4	7.2	5.4	8.0	0.240	0.155	5.10	63	202	0.88	3.45	28
	2	3.6	7.2	5.5	3.7	0.185	0.140	4.83	47	205	0.81	3.85	26
	4	3.8	7.5	5.9	1.7	0.128	0.130	4.68	68	199	0.81	4.38	25
	6	4.2	7.8	6.1	3.3	0.085	0.120	4.53	44	151	0.72	3.68	23
	8	4.5	8.1	6.3	2.8	0.085	0.113	5.13	48	176	0.84	3.78	26
	0 (Lime 2 Mg ha^{-1})	3.1	6.8	5.0	4.5	0.172	0.128	4.95	49	194	0.82	3.80	26
	0 (Lime 4 Mg ha^{-1})	3.3	6.8	5.2	3.3	0.135	0.125	5.10	52	183	0.91	3.85	26
	P-value	<0.001	<0.001	<0.001	NS	<0.001	0.002	NS	NS	NS	NS	NS	NS

Table B.2. Effect of silicate and lime slag application on rice Si and trace metals content Lake Arthur 2014 and 2015.

Site-year	silicate slag (Mg ha$^{-1)}$	%Si			mg kg^{-1}								
		Grain	Straw	Total	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2014 Lake Arthur	0	0.4	2.5	1.6	2.1	0.665	0.188	2.80	50	116	0.31	3.60	23
	1	1.2	3.0	2.2	2.9	0.508	0.180	2.53	53	118	0.26	3.73	22
	2	1.3	3.2	2.4	3.9	0.413	0.180	2.63	42	95	0.26	3.18	21
	4	1.6	3.3	2.5	1.4	0.375	0.180	2.65	48	111	0.35	3.25	23
	6	1.7	3.4	2.6	2.8	0.335	0.175	2.73	47	102	0.29	3.78	22
	8	2.3	3.6	3.0	2.0	0.255	0.168	2.65	56	100	0.27	3.23	23
	0 (Lime 2 Mg ha^{-1})	0.5	2.8	1.8	3.5	0.316	0.178	2.50	40	77	0.28	3.55	22
	0 (Lime 4 Mg ha^{-1})	0.8	2.9	1.8	2.1	0.410	0.175	2.71	47	94	0.28	3.28	23
	P-value	<0.001	<0.001	<0.001	NS	<0.001	0.002	NS	NS	NS	NS	NS	NS
2015 Lake Arthur	0	1.2	2.5	1.9	13.2	0.605	0.175	2.15	71	107	0.260	3.93	24
	1	1.9	3.1	2.6	4.5	0.483	0.170	2.03	39	78	0.202	2.90	25
	2	1.9	3.2	2.6	7.2	0.453	0.170	1.90	54	76	0.195	3.28	22
	4	2.1	3.3	2.7	8.8	0.385	0.163	1.98	55	74	0.228	3.98	24
	6	2.4	3.4	2.9	2.2	0.355	0.160	1.70	39	63	0.243	3.88	22
	8	3.1	3.8	3.5	1.3	0.288	0.158	1.70	38	69	0.205	2.88	23
	0 (Lime 2 Mg ha^{-1})	1.3	2.8	2.1	2.4	0.438	0.170	2.03	42	73	0.18	3.28	24
	0 (Lime 4 Mg ha^{-1})	1.6	2.9	2.4	3.5	0.376	0.176	1.85	42	79	0.15	3.93	24
	P-value	<0.001	<0.001	<0.001	NS	0.009	<0.001	NS	NS	NS	NS	NS	NS

Table B.3. Effect of silicate slag and lime application on rice Si and trace metals content St. Landry and Mamou 2014.

Site-year	silicate slag (Mg ha$^{-1)}$	%Si			mg kg^{-1}								
		Grain	Straw	Total	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2014 St. Landry	0	2.2	5.2	3.9	3.7	0.343	0.180	3.18	31	72	0.06	2.48	19
	1	3.1	5.6	4.5	2.2	0.280	0.180	3.18	30	70	0.10	2.13	18
	2	3.2	5.8	4.6	3.8	0.235	0.175	3.18	21	63	0.08	2.03	18
	4	3.4	5.8	4.7	2.8	0.173	0.170	3.30	30	85	0.08	2.33	20
	6	3.5	6.1	4.9	1.8	0.110	0.170	3.43	27	86	0.07	1.85	20
	8	3.9	6.4	5.3	2.7	0.055	0.165	3.28	27	75	0.08	1.83	20
	0 (Lime 2 Mg ha^{-1})	2.6	5.4	4.1	3.9	0.180	0.176	3.05	29	80	0.10	2.20	18
	0 (Lime 4 Mg ha^{-1})	2.9	5.5	4.3	3.1	0.120	0.165	3.23	31	81	0.14	2.23	19
	P-value	<0.001	0.002	<0.001	NS	<0.001	<0.001	NS	NS	NS	NS	NS	NS
2014 Mamou	0	1.1	4.4	2.9	2.8	0.430	0.185	1.60	44	90	0.10	3.13	25
	1	1.8	5.2	3.8	3.2	0.350	0.180	2.25	66	109	0.07	3.28	30
	2	1.9	5.5	3.8	3.8	0.318	0.178	1.80	46	103	0.03	2.95	28
	4	2.1	5.6	4.0	1.6	0.285	0.173	1.78	43	114	0.15	2.98	27
	6	2.1	6.1	4.2	2.1	0.258	0.170	1.73	53	108	0.06	2.93	27
	8	2.3	6.8	4.5	1.4	0.173	0.155	1.93	49	118	0.03	3.75	27
	0 (Lime 2 Mg ha^{-1})	1.4	4.8	3.2	2.6	0.256	0.178	1.78	46	103	0.03	3.01	28
	0 (Lime 4 Mg ha^{-1})	1.6	5.0	3.3	1.6	0.240	0.175	1.93	59	94	0.06	3.10	27
	P-value	<0.001	<0.001	<0.001	NS	<0.001	0.001	0.049	NS	NS	NS	0.105	0.365

Table B.4 Effect of silicate slag and lime application on rice Si and trace metals content Crowley 2013, 2014 and 2015.

Site-year	silicate slag (Mg ha$^{-1)}$	%Si			mg kg^{-1}								
		Grain	Straw	Total	Al	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
2013 Crowley	0	1.8	5.9	4.0	1.08	0.450	0.183	9.66	142	47	1.08	2.92	19
	1	2.2	6.6	4.8	1.04	0.365	0.180	11.10	180	50	1.16	3.44	20
	2	2.3	6.7	4.8	1.04	0.340	0.175	9.19	192	52	1.02	3.40	20
	4	2.4	7.0	4.8	1.01	0.318	0.170	9.16	184	47	1.06	3.11	19
	6	2.4	7.1	5.1	1.07	0.273	0.170	9.22	166	48	1.16	3.25	19
	8	2.6	7.1	5.1	1.12	0.213	0.148	9.66	186	50	1.26	3.14	21
	0 (Lime 2 Mg ha^{-1})	2.0	6.3	4.3	1.03	0.403	0.180	10.16	208	51	1.25	3.54	19
	0 (Lime 4 Mg ha^{-1})	2.1	6.2	4.3	1.50	0.380	0.180	9.26	185	50	1.06	3.50	20
	P-value	<0.001	<0.001	<0.001	NS	<0.001	0.033	NS	NS	NS	NS	NS	NS
2014 Crowley	0	1.6	6.1	4.2	2.58	0.450	0.183	2.80	46	96	0.09	2.93	26
	1	3.0	6.7	5.1	8.73	0.365	0.180	2.55	60	90	0.10	4.00	24
	2	3.3	6.8	5.3	12.95	0.340	0.175	2.53	54	79	0.10	4.50	24
	4	3.5	7.0	5.4	0.53	0.318	0.170	2.60	53	100	0.10	4.10	26
	6	3.8	7.2	5.8	2.03	0.273	0.170	2.53	50	88	0.11	4.33	26
	8	4.2	7.9	6.4	6.00	0.213	0.167	2.47	63	77	0.34	3.99	29
	0 (Lime 2 Mg ha^{-1})	2.2	6.2	4.5	17.00	0.340	0.178	2.58	63	102	0.85	4.28	26
	0 (Lime 4 Mg ha^{-1})	2.7	6.4	4.8	14.00	0.338	0.175	2.68	68	101	0.11	5.10	26
	P-value	<0.001	<0.001	<0.001	NS	<0.001	0.034	NS	NS	NS	NS	0.014	NS
2015 Crowley	0	1.8	3.9	3.0	3.83	0.385	0.180	3.10	46	58	0.18	4.55	21
	1	2.2	4.3	3.3	3.40	0.248	0.170	3.45	48	67	0.27	4.00	23
	2	2.4	4.4	3.5	5.25	0.220	0.170	3.33	48	69	0.15	4.43	22
	4	2.5	4.5	3.5	2.78	0.198	0.168	3.28	48	62	0.22	4.40	22
	6	2.7	4.7	3.8	3.45	0.160	0.160	3.20	45	62	0.19	4.18	23
	8	2.9	4.9	4.0	3.13	0.090	0.158	3.05	42	56	0.19	4.63	22
	0 (Lime 2 Mg ha^{-1})	1.7	3.9	2.9	2.38	0.233	0.175	3.18	47	66	0.27	0.45	22
	0 (Lime 4 Mg ha^{-1})	2.0	4.1	3.1	2.70	0.226	0.170	3.05	44	63	0.19	0.50	21
	P-value	<0.001	<0.001	<0.001	NS	<0.001	<0.001	NS	NS	NS	NS	NS	NS

Vita

Wooiklee S. Paye was born in Harbel Firestone, Liberia in February of 1984. He attended the University of Liberia and received his Bachelor of Science in General Agriculture in December of 2012. After graduation, he volunteered as a teaching assistant in the William R. Tolbert Jr. College of Agriculture and Forestry at the University of Liberia, assisting with lectures and practical demonstration for introductory agriculture courses. He then went on to work for the USAID Food and Enterprise Development (FED) project for Liberia as a Soil Analysis Technician. In January of 2014, he got accepted in the graduate program in the School of Plant, Environmental and Soil Sciences at Louisiana State University Agricultural and Mechanical College where he earned his Master of Science in Soil Science with specific focus on soil fertility, in May of 2016. After completion of his Master of Science, he went on to pursue his Ph.D. while working under the mentorship of Dr. Brenda Tubana. His Ph.D. study was focused on accessing the impact of silicate slag fertilization on the uptake of harmful trace elements in rice cultivated in flooded Louisiana soils; and developing guidelines for practicing silicon fertilization in Louisiana wheat production system. He is married to his college sweetheart Garmai Vessellee, and is currently blessed with two wonderful boys, Barnabas and Samuel.