2015

Calibration and Categorization of Plant Available Silicon in Louisiana Soils

Tapasya Babu
Louisiana State University and Agricultural and Mechanical College, tbabu1@lsu.edu

Recommended Citation

Babu, Tapasya, "Calibration and Categorization of Plant Available Silicon in Louisiana Soils" (2015). *LSU Doctoral Dissertations*. 2353.
https://digitalcommons.lsu.edu/gradschool_dissertations/2353

CALIBRATION AND CATEGORIZATION OF PLANT AVAILABLE SILICON IN LOUISIANA SOILS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The School of Plant, Environmental, and Soil Sciences

by
Tapasya Babu
B.S., Kerala Agricultural University 2010
M.S., University of Agricultural Sciences, GKVK 2012
December 2015

To Mo, who kicked out the walls in my heart.

Acknowledgements

Thank you to my family especially my husband Vinay Bhaskar Iyer, mother Latha Joseph, father Babu Francis and sister Nisitha Jeffry for all your love, support and help, even when I didn't realize it, and particularly when I brought you sufferings that no family member should have to experience by staying far away from you all for too long.

Thank you to all my teachers and especially my advisor Dr Brenda Tubana, who continues to be an inspiration and my greatest strength. Thank you for seeing the potential and believing in me. Thank you for your wisdom, advice, encouragement and compassion as you helped me during this entire journey.

Thank you to my soil fertility family, where I met some incredible people who will always be close to my heart. Thank you all for your time, support and valuable inputs. Thank you for lifting me up and praying for me.

Thank you, God, for your never-ending love and guidance to find my way throughout my life's journey and fully embrace it.

Table of contents

Acknowledgements iii

List of tables vii

List of figures viii

Abstract xi

Chapter 1. Introduction 1
- 1.1 Direct influence on the plants 2
  - 1.1.1 Increased growth and yields 2
  - 1.1.2 Biotic stress resistance 4
  - 1.1.2.a. Plant diseases 4
  - 1.1.2.b. Agricultural pests 5
  - 1.1.3 Abiotic stress resistance 7
  - 1.1.3.a. Silicon remediation of heavy metal toxicity in soil and plants 7
  - 1.1.3.b. Silicon and salt tolerance 8
  - 1.1.4 Physical stress resistance 9
- 1.2 Indirect influence through soil fertility 9
  - 1.2.1 Effect of Si on the uptake of other nutrients 9
  - 1.2.2 Silicon and soil physicochemical properties 10
- 1.3 Silicon accumulation in plants 11
  - 1.3.1 Benefits of Si in rice 13
  - 1.3.2 Silicon accumulation and uptake in rice 16
- 1.4 Source and status of Si in soil 17
- 1.5 Soils of Louisiana 19
- 1.6 Silicon fertilization in soil 21
- 1.7 Rationale for Research 22
- 1.8 References 23

Chapter 2. Survey of the plant-available silicon status of agricultural soils in Louisiana 32
- 2.1 Introduction 32
- 2.2 Materials and Methods 34
  - 2.2.1 Survey strategy 34
  - 2.2.2 Sampling 35
  - 2.2.3 Soil silicon analysis 35
  - 2.2.4 Determining Soil pH, extractable P, K, Ca, Mg, S, Cu and Zn 37
  - 2.2.4.a. Soil pH (1:1 water) 37
  - 2.2.4.b. Soil texture 37
  - 2.2.4.c. Statistical Analysis 37
  - 2.2.4.d. Extractable Nutrients by Mehlich-3 Procedure (Mehlich 1984) 38
- 2.3 Results and Discussion 38
- 2.4 Conclusions 56

2.5 References 57

Chapter 3. Release and adsorption pattern of monosilicic acid in different soils of Louisiana treated with silicon fertilizer: A laboratory incubation study.......................... 60
3.1 Introduction 60
3.2 Materials and Methods 62
3.2.1 Silicon analysis 62
3.2.2 Sorption study of H_4SiO_4 64
3.2.3 Effect of time on H_4SiO_4 release from Si fertilizer 65
3.2.4 Effect of Si concentration on release of H_4SiO_4 from Si fertilizer 65
3.2.5 Estimation of polymerized and sorbed quantity of H_4SiO_4 in different soils of Louisiana treated with slag and wollastonite... 66
3.3 Results and Discussion 68
3.3.1 Sorption study of H_4SiO_4 68
3.3.1.a. Effect of H_4SiO_4 concentration on sorption 68
3.3.1.b. Effect of incubation time on sorption 73
3.3.2 Effect of time on H_4SiO_4 release from Si fertilizer 77
3.3.3 Effect of Si concentration on release of H_4SiO_4 from Si fertilizer 82
3.3.4 Estimation of polymerized and sorbed quantity of H_4SiO_4 in different soils of Louisiana treated with slag and wollastonite... 87
3.4 Conclusions 97
3.5 References 98

Chapter 4. Establishing soil silicon test procedure and critical silicon level for rice in Louisiana soils 103
4.1 Introduction 103
4.2 Materials and methods 105
4.2.1 Bulk sampling and green house study 105
4.2.2 Extraction and estimation of Si in soil and plants 106
4.2.2.a. Soil Si analysis 106
4.2.2.b. Plant Si analysis 106
4.2.2.c. Correlation analysis 107
4.2.3 Calibration of Si in soils 107
4.3 Results and Discussions 111
4.3.1 Plant available Si determined by different extractants 111
4.3.2 Effect of Si application on the rice dry matter yield 120
4.3.3 Effect of Si application on Si content and uptake by rice plants 127
4.3.4 Correlation of soil available Si with plant Si and yield response to Si fertilization.. 130
4.3.5 Critical limits of plant available soil silicon as determined by different extraction procedures 131
4.4 Conclusions 142
4.5 References 143

Chapter 5. Conclusions 148

Appendix A. Soil silicon concentration based on different extractants 149

Appendix B The change in pH 152

Appendix C The critical level of silicon in soil estimated by different methods in Louisiana soils 153

Vita... 159

List of tables

Table 2.1 Different extractants and procedures used for evaluating available Si in different soils 37

Table 2.2 Number of fields in each parish and range of soil-test silicon content based on different extraction methods 41

Table 3.1 Selected properties of the six different soil series used in the study 63

Table 3.2 Mean concentration of metal ions in the supernatant solution of different soils studied analyzed in ICP-OEM 73

Table 3.3 Mean concentration of metal ions ($P< 0.05$) in the supernatant solution of two different silicon fertilizers studied with increasing quantities of added fertilizers .. 84

Table 4.1 The elemental composition of the two sources of Si.................................... 109

Table 4.2 Properties of soil series used in greenhouse study during the summer of 2014 and 2015.. 109

Table 4.3 Different extractants and procedures used for evaluating plant available silicon in select Louisiana soils 110

Table 4.4 Initial soil silicon extracted from different soils before planting using different extraction procedures 110

Table 4.5 The soil silicon extracted from different soils with different extraction procedures after harvest.. 114

Table 4.6 Relative biomass yield in different soils with different rates of silicon as wollastonite and slag 123

Table 4.7 The dry matter yield of rice at harvest in different soils with two sources of Si applied at different rates 125

Table 4.8 The total yield and silicon uptake of rice grown on different soil series........ 126

Table 4.9 The silicon content and uptake in rice panicle and straw with different rates of silicon in different soils 128

Table 4.10 Coefficient of determination (r^2) between extractable soil silicon based on different extraction procedures and different plant response variables 133

List of figures

Figure 2.1 The different parishes of Louisiana with major crops grown surveyed for determining soil silicon status 36

Figure 2.2 Average soil silicon within different soil textural classes using different extraction procedures in Louisiana soils. Number of soil samples with very fine silty loam, fine silty loam, silty loam and clay loam were 27, 7, 113 and 65 respectively 43

Figure 2.3 Relationship between soil silicon extracted using different procedures and soil pH in Louisiana soils 46

Figure 2.4 Relationship of soil silicon levels determined by deionized water and calcium chloride extraction procedures across all soil samples 47

Figure 2.5 Comparison of soil silicon levels based on acetic acid-2 and citric acid extraction procedures for all soil samples 51

Figure 2.6 Average soil silicon distribution using 0.5 M acetic acid-2 (a), 0.01 Calcium chloride (b), 0.01 M Citric acid (c), 0.5 M ammonium acetate (d), 1 M Sodium acetate (e), 0.5 M acetic acid-1 (f), and deionized water (g) extraction procedures in Louisiana soils 52

Figure 3.1 Major land resource areas and locations where the soil samples were collected in Louisiana.. 63

Figure 3.2 Amount of H_4SiO_4 adsorption in six different soils after seven days of incubation in 0.1 M NaCl with varying concentrations of monosilicic acid.................. 70

Figure 3.3 Amount of H_4SiO_4 sorbed in Caushatta silt loam soil (a), Clovelly muck (b), Crowley silt loam (c), Sharkey clay (d), Commerce silt loam (e) and Perry clay (f) after 4, 7 and 30 days of incubation in 0.1 M NaCl with varying concentrations of monosilicic acid 74

Figure 3.4 Concentration of H_4SiO_4 in solution of sharkey clay (a), Caushatta silt loam (b), Clovelly muck (c), Perry clay (d), Crowley silt loam (e) and Commerce silt loam (f) soils treated with 23 mg Si g^{-1} as wollastonite and slag within a period of 200 days.. 78

Figure 3.5 Concentration of H_4SiO_4 in 0.1 M NaCl solution with 23 mg Si g^{-1} as wollastonite and slag within a period of 200 days... 82

Figure 3.6 Concentration of H_4SiO_4 in Caushatta silt loam, commerce silt loam and Crowley silt loam (a) and Perry clay, Clovelly muck and Sharkey clay (b) soils after 7 days of incubation in 0.1 M NaCl treated with varying rates of Si as slag 85

Figure 3.7 Concentration of H_4SiO_4 in Perry clay, Sharkey clay and Clovelly muck (a) and Caushatta silt loam, commerce silt loam and Crowley silt loam (b) soils after 7 days of incubation in 0.1 M NaCl treated with varying rates of Si as wollastonite 86

Figure 3.8 Silicon (polymerized and sorbed) measured as H_4SiO_4 in 0.5 M acetic acid solution on six different soils, with slag and wollastonite as the source of Si after 200 days of incubation in 0.1 M NaCl solution... 89

Figure 3.9 Quantity of H_4SiO_4, adsorbed, polymerized and that present in solutions of six different soils treated with 23 mg Si g^{-1} as wollastonite (a) and slag (b) after 200 days of incubation in 0.1 M NaCl solution.* H_4SiO_4 in ug g^{-1} for percent adsorbed, ug ml^{-1} for percent polymerized and in solution... 90

Figure 3.10 Total silicon from 23 mg g^{-1} Si added as slag and wollastonite measured as H_4SiO_4 concentration in 0.5 M acetic acid within 10, 30, 60, and 120 minutes of incubation 92

Figure 3.11 Pattern of X-Ray diffraction analyses for slag (a) and wollastonite (b)...... 93

Figure 3.12 Scanning electron microscopy images of wollastonite (a) and slag (b) 94

Figure 3.13 Elemental compositions of slag (a) and wollastonite (b) from Electron Dispersive X-ray analyses 95

Figure 4.1 The $CaCl_2$ extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag (each point is an average of 30 observations).. 117

Figure 4.2 The deionized water extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag 117

Figure 4.3 Acetic acid-2 (0.5 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag 118

Figure 4.4 Acetic acid-1 (0.5 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag 118

Figure 4.5 Citric acid (0.1 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag 119

Figure 4.6 Sodium acetate (1 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag 119

Figure 4.7 Ammonium acetate (0.5 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag 120

Figure 4.8 The linear plateau model fitting to determine the soil critical level of Si in Sharkey clay 135

Figure 4.9 The linear plateau model fitting to determine the soil critical level of Si in Perry clay 135

Figure 4.10 The linear plateau model fitting to determine the soil critical level of Si in Commerce silt loam 136

Figure 4.11 The linear plateau model fitting to determine the soil critical level of Si in Caushatta silt loam 136

Figure 4.12 The quadratic model fitting on Perry clay to determine the critical level of soil Si 137

Figure 4.13 The quadratic model fitting on Commerce silt loam to determine the critical level of soil Si 138

Figure 4.14 The quadratic model fitting on Crowley silt loam to determine the critical level of soil Si 139

Figure 4.15 Critical level of soil Si determined by Cate and Nelsons' graphical method in Perry clay 140

Abstract

A survey was conducted to document the silicon (Si) content of soils from 27 (selected) agrarian parishes of Louisiana using different extraction procedures. For 0.01 M calcium chloride ($CaCl_2$) extraction procedure, all surveyed soils (n=212) fell below 56 mg Si kg^{-1}. For five of the procedures, about 50% of surveyed soils in Louisiana had Si level below the critical Si level that thus far established in other regions. Calcium silicate slag and wollastonite were compared through chemical extractions after laboratory incubation with six different soil types, and then an assessment of quantity of monosilicic acid (H_4SiO_4) sorbed and the quantity in solution was made. It was concluded that the addition of large quantities of slag or any Si rich fertilizer with high rate of dissolution will lead to the greater polymerization of the H_4SiO_4. A greenhouse study was also conducted with six soil series of Louisiana with distinct physico-chemical properties, to evaluate different soil test methods and estimate the critical soil Si level for rice. At harvest, dry matter yield and Si uptake by straw and panicles, and soil Si levels using seven different extractants were evaluated. The soil Si extracted by 0.5 M acetic acid (24 hours rest, 2 hours shaking) and 0.01 M $CaCl_2$ showed maximum linear positive correlation ($r^2>0.45$) with shoot biomass yield, and Si uptake. The soil Si critical level determined using quadratic regression model ($P<0.03$) for Sharkey clay soil was 110 mg kg^{-1} but for Crowley silt loam and Commerce silt loam were 37 and 43 mg kg^{-1} . It is very likely that certain regions in Louisiana would benefit from Si fertilization in rice and sugarcane production. Also, there is a need to establish the soil or site specific extraction procedure because it is unlikely that there is a single universal extraction procedure for all soils.

Chapter 1. Introduction

Crops grown in the field are subjected to a large number of stresses. The significance of silicon (Si) is most clearly apparent in plants that are under some environmental stress, whether biotic or abiotic (Epstein 2005). These stressful features include diseases and pests, gravity (the cause of lodging of cereals), and excessively high or low temperatures, metal toxicities, salinity, and others.

Moreover, rapid progress is needed in agriculture. The world population is now 6.3 billion and will reach about 8.3 or 10.9 billion by 2050 (UN 2013). More food will have to be grown. Most good land is already farmed, so that higher yields have to be wrung from existing crop land, and marginal land will have to be pressed into service. Additional challenges will come from global climate change, pollution, salinization, and still other adversities. Therefore the plant world, which is our life support system, will increasingly come under stress, and as stated above, it is plants under stress that respond most markedly to Si (Epstein 2005).

Silicon is not an essential nutrient because most plants can complete their reproductive cycle when grown in nutrient solutions lacking Si in their formulation. This conclusion may not be valid because of the ubiquity of Si as a contaminant (Epstein 1994). Nutrient culture studies show that plants accumulate some Si even in carefully controlled studies to exclude its presence in growth solutions (Epstein 1994). Of all the “non-essential” elements assimilated by plants, Si alone is consistently present at concentrations similar to those of the macro- and secondary nutrients. Silicon concentrations range from 0.1% (similar to that of phosphorus, P and sulphur, S) to more than 10% of whole plant dry matter (Epstein 1999). Silicon has been considered to be a ‘‘quasi-essential element for plant growth’’ (Epstein and Bloom 2005). In February 2012, Si was approved by The Association of American Plant Food Control Officials (AAPFCO) as a

“Plant Beneficial Substance” (AAPFCO, 2012). Numerous laboratory, greenhouse and field experiments have shown the benefits of Si fertilizers for agricultural crops and the importance of Si fertilizers as a component in sustainable agriculture (Matichenkov and Calvert 1999).

Different effects on plants due to Si fertilizers may be classified as direct influences on the plants or indirect influences through soil fertility.

1.1 Direct influence on the plants

The benefits of Si on plants include (Ma et al. 2006 and Savant et al. 1999) increased growth and fruit yields in some species, biotic stress resistance (*e.g.,* insects and pest infection), abiotic stress resistance (*e.g.,* frost, drought and salinity, toxicity by aluminum (Al), manganese (Mn) and other heavy metals) and resistance to physical stress (*e.g.,* lodging).

1.1.1 Increased growth and yields

It has been reported that Si has many positive effects on the growth and yield as well as physiology and metabolism of different crops. Gong et al. (2003) observed that Si increased plant height, leaf area and dry mass of wheat (*Triticum aestivum*) even under drought. Ma et al. (2002) reported that more than 80% of total Si in the barley *(Hordeum vulgare L.)* grain was localized in the hull. High Si concentration of barley hull have beneficial effect on high barley yield as percentage of ripening panicles markedly increased with addition of silicic acid. This can be attributed to Si accumulating on the hull, may prevent excessive water loss from the grains.

Interaction between Si and nitrogen (N) was positive and had significant effect in obtaining higher grain and straw yield, reduced percent blank spikelet and incidence of pest and diseases (Deren et al. 1994). Increased growth was reported in crops including cotton (*Gossypium hirsutum*), Boston fern (*Nephrolepis exaltata)*, pumpkin (*Cucurbita pepo)*, barley, rye (*Secale cereal*), oats (*Avena sativa*), and watermelon (*Citrullus lanatus*) by Datnoff et al. (2001). Increase in sugar yield in sugarcane (*Saccharum officinarum*) was reported by Berthelsen et al. (2001). Field and greenhouse experiments conducted in Florida, Hawaii and Mauritius demonstrated that application of Si fertilizers increased productivity from 17 to 30% and the production of sugar rose from 23 to 58% (Matichenkov and Calvert 2002). Economic analysis of the use of calcium silicate in Florida indicates that grower revenues can be increased if applied at 3 t ha^{-1} to soils with insufficient soluble Si (less than 10 ug g^{-1} Si) (Morgan et al. 2009). Histosol soils in Florida amended with 5 t ha^{-1} of silicate slag resulted in a 73-86% and 58-75% reduction in blast *(Pyricularia grisea)* and brown spot (*Helminthosporium oryzae*) in rice with concurrent yield increases between 56-88% (Datnoff and Snyder 2001).

Abro et al. (2009) tested different levels of silicic acid in a pot experiment to assess their effects on improvement of growth and yield in wheat. The silicic acid concentrations affected crop positively as well as negatively as all the varieties produced highest plant growth and yield at 0.25% and 0.50% silicic acid application while the lowest plant growth and yield was found under 0.75% silicic acid.

Mali and Aery (2009) studied the effect of different levels of Si on growth performance, biochemical constituents, and nutritional status of cowpea (*Vigna unguiculata (L.) Walp*). Lower applications of Si resulted in an enhancement in relative yield, leaf area, chlorophyll, and iron (Fe) contents and a reduction in proline contents. A significant dependence of tissue Si concentration on soil Si concentration was observed. The results indicate a beneficial effect of Si on cowpea plants.

1.1.2 Biotic stress resistance

1.1.2.a. Plant diseases

Application of N fertilizers is an important practice for increasing yield. But excess N causes succulence, lodging, mutual shading and susceptibility to pest and diseases (Berry et al. 2000; Slaton 2003). The occurrence of blast disease is significantly inhibited by Si application in the field, especially when N application is heavy (Ma 2004). There are numerous reports of Si suppressing plant disease and pest, such as blast and sheath blight (*Rhizoctonia solani*) in rice (Datnoff et al. 1997; Seebold et al. 2001), powdery mildew (*Podosphaera xanthii)* in cucumber (*Cucumis sativus*), Arabidopsis (*Arabidopsis thaliana*), and wheat (Fauteux et al. 2005) and rust (*Phakopsora pachyrhizi*) in cowpea (Heath and Stumpf 1986). There are several hypotheses concerning the role of Si in imparting resistance in plants to fungal diseases such as blast, blight, powdery mildews, and root rots. The Si-treated host plants had a greater resistance to pathogen penetration of host tissue due to the specific accumulation and polymerization of monosilicic acid [$Si(OH)_4$] in cell walls (Heath and Stumpf 1986; Kim et al. 2002). Recent work, however, contended that Si may act by stimulating the natural defense mechanisms of the plant (Bélanger et al. 1995).

Cherif et al. (1994) reported a marked stimulation of chitinase activity and intense and rapid activation of peroxidases and polyphenoloxidases in cucumber plants amended with soluble Si after the infection with *Pythium spp*. Increased β- glucosidase activity was detected in protein extracts of infected Si amended plants. Studies have shown that plants treated with Si produce increased amounts of phytoalexins in the form of inactive glycosylated precursors (Fawe et al. 1998). Silicon is involved in the increased resistance of cucumber to powdery mildew by enhancing the antifungal activity of infected leaves. This antifungal activity was attributable to the presence of low-molecular-weight metabolites. One of these metabolites, described here as a phytoalexin, was identified as a flavonol aglycone rhamnetin. Subsequent infection of these Si pre-treated plants by powdery mildew then caused these compounds to be activated, thereby inducing fungal cell death (Currie and Perry 2007).

Experiments performed on cucumber leaves following fungal infection showed that further resistance to infection is acquired by expression of a proline-rich protein together with the presence of silica at the site of attempted penetration. The C-terminus of this protein contained a high density of lysine and arginine residues proposed to catalyze the localized deposition of silica at the site of vulnerability (Kauss et al. 2003). These results associated with Si with specific plant defense reactions appear to be multi- component, and resistance is contingent on the activation of a cascade of associated biochemical changes (Currie and Perry 2007). Further investigation of these defense mechanisms by Bélanger et al. (2003) and Rodrigues et al. (2003), studying wheat and rice blast, respectively, indicated that these species were also capable of inducing similar biologically active defense agents, including increased production of glycosylated phenolics and antimicrobial products such as diterpenoid phytoalexins in the presence of silica.

1.1.2.b. Agricultural pests

The application of Si to crops is a viable component of an integrated management program for insect pests and diseases because it leaves no pesticide residue in food or the environment, is relatively cheap and could easily be integrated with other pest management practices (Laing et al. 2006). It has been reported that Si suppresses insect pests such as stem-borers (*Chilo auricilius),* brown plant-hopper (*Nilaparvata lugens*), green leaf-hopper (*Cicadella viridis*), white-backed plant- hopper (*Sogatella furcifera*), and non-insect pests such as spider mites (*Tetranychidae*) (Savant et al. 1997, Ma and Takahashi 2002). Improved Si nutrition in sugarcane has been shown to increase resistance to stem borer (*Diatracea saccharalis F.*) (Anderson and Sosa 2001), and increase resistance to stalkborer (*E.saccharina*) (Elawad et al. 1982; Keeping and Meyer 2003).

Laing et al. (2006) reported that Si controls red spider mite on dicotyledonous crops such as green beans (*Phaseolus vulgaris*), brinjal (*Solanum melongena*), tomato (*Solanum lycopersicum*) and cucumber. Furthermore, Si deposits in plant organs were reported in most crops, including the mono and dicotyledonous families (Jones and Handreck 1967; Nishimura et al. 1989). This implies that Si plays a role in pest resistance in most, if not all, cultivated crops. Several mechanisms have been proposed to explain the tolerance and resistance of plants to insect pests. According to Bernays and Barbehenn (1987) most of the plant Si occurs in the epidermis, which might dislodge young larvae before they can establish in the stem. Various studies have demonstrated that Si increases the hardness of plant tissue, which negatively impacts insect larval boring and feeding ability. Djamin and Pathak (1967) showed that increased Si content in rice plants resulted in mandibular teeth loss of stem borer larvae. Recently, a parallel mechanism as that seen in the resistance of plants to diseases via an activation of the plant's own defense mechanisms by soluble Si has been observed for insect pests. Sieburth et al. (1990) reported such a mode of action against insects such as the noctuid (*Trichoplusia ni)*, the coccinellid (*Epilachna varivestis)*, the aphid (*Acyrthosiphon pisum)*, and the cockroach (*Periplaneta americana)*. Similarly, Keeping and Meyer (2005) reported the resistance of sugarcane to *E.saccharina*.

1.1.3 Abiotic stress resistance

1.1.3.a. Silicon remediation of heavy metal toxicity in soil and plants

Silicon can improve plant growth and tolerance to biotic and abiotic stresses (Epstein 1999; Liang et al. 2007; Newmann 2001). In the case of heavy-metal stress, the presence of Si in the growth medium is helpful for reducing uptake and accumulation of heavy metals like cadmium (Cd) in rice (*Oryza sativa*) (Shi et al. 2005), wheat (Nowakowski et al. 1997), and maize (*Zea mays*) (Liang et al. 2005) seedlings.

When exposed to Al no differences in pH values of the bulk nutrient solution were detectable in Si- treated plants over Si- untreated plants. Therefore, it seems likely that apoplastic Si buffers the H^+ concentration so that Si- treated plants may have higher pH values at the root surface and in the apoplast of the outer cortex. This leads to the precipitation and lower uptake of Al. Another possibility would be the formation of insoluble aluminium phosphate at the root surface. Also, the roots of Si- treated plants had considerably higher P concentrations than those of Si- untreated plants (Corrales et al. 1997).

Song et al. (2011) concluded that Si mediated alleviation of zinc (Zn) toxicity in plants is mainly attributed to Si-mediated antioxidant defense capacity, membrane integrity and the reduction of root-to-shoot translocation of Zn. He conducted a study in which the rice plants treated with Si presented not only biomass increase but also lower Zn toxicity. The lower lipid peroxidation and higher antioxidant defense activity in roots of both cultivars were also observed as a result of Si application.

The role of Si application in reducing Cd accumulation in edible plant parts has been well documented (Liang et al. 2005, Chen et al. 2000). Increasing amount of evidence has shown that Si significantly interferes with root uptake and translocation of Cd from roots to shoots in plants.

The relationship between Si application and reduced Cd uptake has been extensively studied. As stated by Liang et al. (2007) and Wang et al. (2000), the possible mechanisms responsible for low Cd accumulation in edible parts of plants are: (1) lower mobility of Cd towards roots due to silicate induced pH rise in soils; (2) Si induced co-precipitation of Cd and Si in soil; (3) co-precipitation of Si and Cd at root surfaces; (4) decreased transport of Cd from roots to xylem; (5) reduced translocation of Cd from roots to shoots due to decreased evapotranspiration associated with Si deposition in cell walls, and as a double layer of polymerized Si in the cuticle; and (6) increased uptake of calcium (Ca) with the application of Si, which decreased Cd uptake due to competition for uptake.

1.1.3.b. Silicon and salt tolerance

Silicon has been reported to reduce the shoot and leaf Ca content in rice and alfalfa (*Medicago sativa L.*) plants under salt stress, which suggests that Si resulted in a low transpiration rate (Ma and Takahashi 1993). Gunes et al. (2007) investigated the effect of Si on the growth, uptake of sodium (Na), chloride (Cl), and boron (B) in spinach (*Spinacia oleracea***)** and tomato grown in sodic- B toxic soil. Silicon applied to the sodic- B toxic soil at 2.5 and 5.0 mM concentrations significantly increased the Si concentration in the plant species and counteracted the deleterious effects of high concentrations of Na, Cl and B on root and shoot growth by lowering the accumulation of these elements in the plants. He deduced that Si alleviates sodicity and B toxicity by preventing both oxidative membrane damage and also translocation of Na, Cl and B from root to shoots and/or soil to plant, and lowering the phytotoxic effects of Na, Cl and B within plant tissues.

Liang and Ding (2002) investigated the micro- distribution of ions in roots as affected by Si with respect to salt tolerance. The results showed that Si depressed the uptake of Na but enhanced the uptake of potassium (K) by salt-stressed barley. The addition of Si significantly enhanced leaf photosynthesis and stimulated the uptake of K but depressed the uptake of Na by plants, thereby increasing the selectivity ratio (K: Na). The likely mechanism involved was the increased H^+-ATPase activity in salt-stressed plants in the presence of Si. However, no significant difference was observed in P content between the salt treatment with and without added Si.

1.1.4 Physical stress resistance

Silicon is accumulated primarily in the epidermal tissues of both roots and leaves in the form of a silica-gel (phytoliths). This thickened epidermal Si-cellulose layer supports the mechanical stability of plants, thereby resisting lodging and also a greater retention of seed, especially in grasses (Savant et al. 1999). The increased mechanical strength also increases the light receiving posture of the plant. Leaves were reported to be darker green, stiffer and slower to senesce, increasing their potential for photosynthesis and growth (Epstein 1994). The deposition of Si in the culms, leaves and hulls also decreases transpiration from the cuticle and this increases resistance to lodging, low and high temperature, radiation, UV and drought stress (Ma and Yamaji 2006).

1.2 Indirect influence through soil fertility

1.2.1 Effect of Si on the uptake of other nutrients

The presence of Si in nutrient solutions affects the absorption and translocation of several macro and micro-nutrients (Epstein 1994). Increased Si fertilization increases Zn uptake if deficient, especially if P is excessive (Marschner et al. 1990). Silicon fertilization retards the toxic uptake of P by roots, such as in cucumbers (Marschner 1990), while promoting its translocation to grain in rice and wheat (Lewin and Reimann 1969). Cultivated plants can use only about 30% of applied phosphate fertilizer, if leaching is low. The mixture of active Si with P fertilizer can increase the efficiency of P fertilization by 40-60% (Matichenkov et al. 1997). Importantly, Si-rich amendments are recommended for the reduction in leaching of N, P and K based fertilizers (Matichenkov and Bocharnikova 2010).

1.2.2 Silicon and soil physicochemical properties

In the soil solution, or liquid phase, Si is present as H_4SiO_4 [$Si(OH)_4$], referred to as plant-available Si and polysilicic acid (the polymer of plant-available Si) as well as complexes with organic and inorganic compounds such as Al oxides and hydroxides (Berthelsen et al. 2003). While it is the plant-available Si that is taken up by the plants and has a direct influence on crop growth, the polysilicic acid and inorganic and organic complexes are important sources/sinks that replenish the plant-available Si following crop use. They also have an important and significant effect on the soil properties such as improving soil aggregation and increasing soil water holding capacity as well as increasing the exchange and buffering capacity of the soil (Berthelsen et al. 2003). Silicon controls the chemical and biological properties of soil with the benefits like reduced leaching of P and K (Sadgrove 2006), reduced Al, iron (Fe), Mn and heavy metal mobility (Matichenkov and Calvert 2002), increased stability of soil organic matter (Matichenkov and Calvert 2002), improved microbial activity (Matichenkov and Calvert 2002), soil texture (Sadgrove 2006), water holding capacity (Sadgrove 2006), increased stability against soil erosion (Sadgrove 2006), and cationic exchange capacity (CEC) (Camberato 2001). Therefore even if a plant is a low Si-accumulator, it will benefit from the improved soil properties resulting from the application of Si.

1.3 Silicon accumulation in plants

Silicon is taken up in the form of an uncharged molecule, silicic acid. Recent reviews reported that Si accumulation is, in general, higher in monocot than in non-monocot species (Epstein 1999; Richmond and Sussman 2003).The difference in Si accumulation has been attributed to the ability of the roots to take up Si.Three different modes of Si uptake have been proposed for plants having different degrees of Si accumulation, that is, active, passive, and rejective uptake. Plants with an active mode of uptake take up Si faster than water, resulting in a depletion of Si in the uptake solution. Plants with a passive mode of uptake take up Si at a rate that is similar to the uptake rate of water; thus, no significant changes in the concentration of Si in the uptake solution are observed. By contrast, plants with a rejective mode of uptake tend to exclude Si, which is demonstrated by the increasing concentration of Si in the uptake solution (Takahashi et al. 1990).

Liang et al. (2006) characterized Si uptake and xylem loading in rice, maize, sunflower (*Helianthus annuus*) and ash gourd *(Benincase hispida)* in a series of hydroponic experiments. Both active and passive Si-uptake components co-exist in all the plants tested. The active component is the major mechanism responsible for Si uptake in rice and maize. By contrast, passive uptake prevails in sunflower and ash gourd at a higher external Si concentration (0.85 mM), while the active component constantly exists and contributes to the total Si uptake, especially at a lower external Si concentration (0.085 mM). Silicon accumulation into various plant organs varies among rice genotypes (Winslow et al. 1997). Different parts of the same plant can show large differences in Si accumulation. In rice, this variation can be seen from 0.5 g kg^{-1} in polished rice, 50 g kg^{-1} in rice bran, 130 g kg^{-1} in rice straw, 230 g kg^{-1} in rice hulls to 350 g kg^{-1} in rice joints (found at the base of the grain) (Van Hoest 2006).

Maize shows a high accumulation of Si. Mitani et al. (2009) isolated two genes (*ZmLsi1 and ZmLsi6*) in maize which are homologous to rice Si transporter. Immuno staining showed that *ZmLsi1* was localized on the plasma membrane of the distal side of root epidermal and hypodermal cells in the seminal and crown roots, and also in cortex cells in lateral roots. *ZmLsi6* was found in the xylem parenchyma cells that are adjacent to the vessels in both leaf sheaths and leaf blades.

Hodson and Sangster (1988) observed that in the case of wheat, Si compounds predominantly deposited in the epidermal cells of the abaxial side of the leaves, while in older leaves incorporated Si compounds are on the adaxial side as well. Mecfel et al. (2007) reported that significant Si contents in the cell walls suggesting that the enrichment with Si compounds is due to an accumulation of Si within regions that are rich in matrix materials like hemicelluloses and pectins.

Despite an abundance of studies on the site and shape of silica depositions within plants, no molecular mechanism for this deposition has been characterized. Depositions of opal occur throughout the plant in cell walls, cell lumens, tricombs, intracellular spaces, roots, leaves, and reproductive organs. Silica depositions primarily occur through evapotranspiration (Motomura 2002), a hypothesis based on the fact that the common locations of opal coincide with major evapotranspiration sites. There is, however, some evidence that plant macromolecules participate in forming an organic matrix for silica deposition (Inanaga et al. 1995). Such molecules have already been identified in other organisms that deposit silica (Kroger et al. 2002).

Neumann and Figueiredo (2002) studied the components of some silica deposits which showed to be precipitates of Si and Zn, or Si and Al. It is thought that this co-precipitation of heavy metals and Si is part of the mechanism that allows plants to ameliorate heavy metal toxicity. Silicon may have additional roles in increasing tolerance of Al. Silicon-treated maize plants release fifteen times more phenolics than untreated maize plants (Kidd et al. 2001). These flavonoid- phenolics (i.e. catechin and quercetin) have a strong Al-chelating ability and may provide heavy-metal tolerance in plants.

Phytoliths are silica deposits that retain genus or species specific morphological characteristics in higher plants. Recently, phytoliths have received increased attention because of the application of phytolith analysis in archeological research. Unique and specific deposits have been noted in Equisitaceae (horsetails), Coniferophyta (gymnosperms), and Magnoliophyta (angiosperms; including monocots and dicots) (Sangster et al. 2001).

Work by Piperno et al. (2002) and Dorweiler and Doebley (1997) examined the genetic basis of silica deposition. In the dicot Cucurbita, phytolith deposition was correlated with the presence of a mutant locus called Hard rind (Hr); whereas in the monocot maize, phytolith deposition appeared to be linked to the teosinte glume architecture1 (tga1) locus. In both plant species, silification appeared to be linked to loci that are involved in lignification. However, silicic acid has a strong affinity to the organic polyhydroxyl compounds, which participate in the synthesis of lignin.

1.3.1 Benefits of Si in rice

When accumulated Si typically represents more than 1% of dry mass, a species is considered a Si-accumulator (Epstein 1994). Many species of wetland grasses, notably rice, accumulate 5% Si or more in their leaf tissue. Singh et al. (2006) suggested an increased dry matter and yield in rice with Si application. In rice, about 66% of the Si in the whole plant and 70-75% in the leaf blades were absorbed during the reproductive stage and 75% Si in the panicle was absorbed during ripening stage. During vegetative phase about 50% of absorbed Si was present in leaf blades. The application of Si, hardly influenced the 1000- grain weight, but there was an increase in filled spikelets and grain yield. Dry weight of straw increased about 30-200% when Si was applied at reproductive stage (Ma et al. 1989).

In upland rice of humid tropics, where the soil is low in available Si, an increase in grain yield was observed by an average of 34% by the application of Si and magnesium (Mg). Application of Mg improved the uptake of Si and increased the Si content in rice plants. Silicon increased the percentage of filled spikelet and 1000- grain weight and markedly reduced panicle damage and grain discoloration (Yamauchi and Winslow 1989).

In rice, Si has been demonstrated to be necessary for the growth and production. Islam and Saha (1969) reported that Si application to the nutrient solution promoted the uptake of P, Ca and Mg and decreased the uptake of K by rice plants. A retarding effect on the uptake of P was also reported by Okuda and Takahashi (1965). By means of Electron probe micro-analyzer (EPMA), Soni et al. (1972) examined the effect of the accumulation of Si on the accumulation of various elements in silica cells of rice leaves. They reported that smaller or no amount of K and P was detected in silica cells in the adaxial epidermis of leaf blade compared with the adjoining cells, while the amount of Mg was slightly greater in silica cells than the abaxial surface of leaf sheath.

Ma and Takahashi (1990) conducted an experiment to measure the effect of Si on P uptake and on the growth of rice plant at different P levels. Shoot dry weight increased with increased application of P when Si was applied suggesting Si application raised the optimum P level in rice. The beneficial effect of Si on the growth of rice was clearly shown when P was low or high. This effect may have resulted from decreased Mn and Fe uptake.

Gong et al. (2006) carried out research using sodium Chloride salt (50 mM NaCl) that reduced the growth of shoots and roots; and after adding silicate (3 mM) to the saline culture solution he reported improved growth of the shoots, but not roots. The improvement of shoot growth in the presence of silicate was correlated with reduced sodium concentration in the shoot. The net transport rate of Na from the root to shoot was also decreased by added silicate. There was, however, no effect of silicate on the net transport of K. The K: Na in the shoot was greater in silicate treated seedlings than plants grown without additional Si. From these results, he suggested that Si deposition in the exodermis and endodermis reduced Na uptake in rice seedlings under NaCl stress through a reduction in apoplastic transport across the root.

Savant et al. (1997) reviewed the accumulated Si in the cuticle. Silicon double layer of the rice plant tissues helps the plant to maintain erect leaves, increase mechanical strength against fungal disease and minimize transpiration. To control rice blast effectively at the nursery stage, the absolute SiO_2 (silicon dioxide) content necessary for rice plants to resist blast disease was investigated using various rice cultivars and soils (Hayasaka et al. 2005). In all the rice cultivars studied, the number of lesions was significantly reduced when SiO_2 content increased in the rice seedling; lesions were reduced to 5% – 20% when the seedling SiO_2 content reached 5%. These results suggest that SiO_2 content of at least 5% in the rice plant can control this disease at the nursery stage under any conditions. Rodrigues et al. (2001) measured levels of sheath blight, caused by *Rhizoctonia solani* in six rice cultivars grown with and without Si. The treatment with Si increased the concentration of Si in plant tissue by 80%. Overall Si treatment, significantly reduced the severity of sheath blight, and the total area under the vertical lesion in moderately susceptible and susceptible cultivars compared to those cultivars high in partial resistance without Si. In the absence of disease, Si enhanced dry matter accumulation by 15% over the control, whereas Si application, more than doubled the mean dry matter accumulation in infected plants. Rodrigues et al. (2003) indicated that rice cultivars were capable of inducing similar biologically active defense agents, including increased production of glycosylated phenolics and antimicrobial products such as diterpenoid phytoalexins in the presence of silica.

Voleti et al. (2008), investigated promoter or carrier-induced Si transportation into rice in relation to blast disease resistance. The results showed simple amino acids, such as histidine, imidazole, glutamic acid, glycine and glutamine significantly enhanced the levels of H_4SiO_4 in the stem and 14-18% Si transport into the leaf surface. The work identified a novel class of bio-compatible molecules, which exhibit remarkable resistance to blast infections and generate higher dry matter and increased yields.

1.3.2 Silicon accumulation and uptake in rice

The uptake of Si by rice and other plants is not well understood, but appears to be influenced by a number of soil and climatic factors. Growth chamber studies comparing the effects of low (4°C) and high (25°C) temperatures showed that low temperatures substantially suppressed assimilation of Si by rice and corn as did chemical inhibitors of metabolism (Liang et al. 2006). They also observed that increasing solution concentrations of Si, however, increased Si uptake even at low temperatures, suggesting that uptake is a combination of both metabolic rate and Si availability.

The uptake system of Si was investigated by Mitani and Ma (2005) in terms of the radial transport from the external solution to the root cortical cells and the release of Si from the cortical cells to the xylem in rice, cucumber, and tomato, which differ greatly in shoot Si concentration. The concentrations of Si in the root-cell symplast in rice were 3 and 5 fold higher than that in cucumber and tomato, respectively. These results indicate that a higher density of transporter for radial transport and the presence of a transporter for xylem loading are responsible for the high Si accumulation in rice.

Recently, three transporters *Lsi1*, *Lsi2* and *Lsi6* responsible for the high capacity of rice for Si uptake have been identified. *Lsi1* is an influx transporter of silicic acid, while *Lsi2* is an active efflux transporter of silicic acid. *Lsi6* is the transporter responsible for the transport of Si out of the xylem and subsequently affects the distribution of Si in the leaf. *Lsi2* actively transports Si into the stele and thereby maintains a low Si concentration in exodermis and endodermis cells. The resulting concentration gradient between endodermis and exodermis on the one hand and cortex and soil solution on the other hand drives Si influx through *Lsi1*, which is involved in the distribution of Si in the shoots (Ma et al. 2006, 2007a, 2007 b; Yamaji et al. 2007). The translocation and deposition of Si in rice are closely related to cuticular transpiration, and Si is localized along the transpiration stream. Silicon is predominantly deposited in the epidermis of all tissues of rice. In rice leaves, Si is deposited in the epidermis, vascular bundles plus bundle sheath, and sclerenchyma. The Si layer forms in epidermal cell walls beneath the cuticle, which has been referred to as the cuticle-silica double layer (Yoshida et al. 1962).

1.4 Source and status of Si in soil

Although Si is the second most abundant element after oxygen in the earth's crust, certain soils tend to be low in plant-available Si (Datnoff et al. 1997). Low-Si soils are typically highly weathered, leached, acidic, and low in base saturation. Thus Oxisols and Ultisols can be quite low in soluble Si (Foy 1992). Histosols with an organic matter content greater than 80%, and thus low in mineral content, are also deficient in plant-available Si (Snyder et al. 1986). Soils comprised mainly of quartz sand (SiO2), such as sandy Entisols, are also very low in plant-available Si (Datnoff et al. 1997). Repeated cropping of rice can also reduce the level of plant-available Si to the point that supplemental Si application is required for maximum production (Elawad and Green 1979). These soils may be found in some golf courses, athletic fields, and home lawns where perennial ryegrass is cultivated. In addition, repeated cropping of perennial ryegrass and removal of grass clippings may reduce the level of plant-available Si in these soils.

Mineral soils develop from rocks or sediments and are mainly composed of primary crystalline silicates such as quartz, feldspars, mica and secondary silicates, especially clay minerals (Iler 1979). Moreover, they contain Si of biogenic origin (Jones and Hendreck 1969) and pedogenic amorphous silica (Drees et al. 1989). Silicon also occurs in soil as complexes with Fe, Al, heavy metals and organic matter (Farmer et al. 2005). Silicic acid dissolved in soil solution has some part of it adsorbed to soil minerals, particularly oxides and hydroxides of Fe and Al (Hansen et al. 1994; Dietzel 2002). Dissolved silicic acid in soil solutions primarily occurs as monomeric or oligomeric silicic acid (Iler 1979). Knight and Kinrade (2001) reported that monomeric silicic acid ($Si(OH)_4$) dissociates into H^+ + $H_3SiO_4^-$ above pH 9 and into $2H^+$ + $H_2SiO_4^{2-}$ above pH 11. Oligomeric silicic acid is only stable at high concentration of silicic acid at pH > 9. In most of soils and natural waters only undissociated monomeric silicic acid occurs (Dietzel 2000).

Silicon compounds in the soils are classified into soil solution and adsorbed Si forms (monosilicic and polysilicic acids), amorphous forms (phytoliths and silica nodules), poorly crystalline and microcrystalline forms (allophane, immogolite and secondary quartz), and crystalline forms (primary silicates: quartz, feldspars, secondary silicates: clay minerals) (Saur et al. 2006; Cornelis et al. 2011). Wang et al. (2004) also suggested that the seven extractants used in their study characterized different pools of Si-supplying capacity of the soil: extractable by water, extractable by any of HCl, citric acid, acetic acid, acetate buffer, and NH_4OAc, and extractable by Mehlich-3. The dissolution of Si in paddy soils is influenced by soil temperature, soil redox potential, soil pH and Si concentration in soil solution (Sumida 1991). Plant-available Si is only present in solution at less than pH 9 and has a solubility of 65 mg L^{-1}, which is constant between pH 2 to 8.5 (Jones and Handreck 1967). There is a polymerization of plant-available Si to form a silica-gel if it exceeds a concentration of 65 mg L^{-1} or if there is dehydration of the soil, which is reversible on dilution (Savant et al. 1999). Silicon can be added via irrigation water and fertilization but it is lost through plant absorption and leaching. Therefore solubility of Si in the soil is affected by a number of factors occurring in the soil including the particle size of the Si fertilizer, the soil pH, organic complexes, presence of Al, Fe and phosphate ions, temperature, exchangeable or dissolution reactions and soil moisture (Berthelsen et al. 2003).

1.5 Soils of Louisiana

The high concentrations of soluble silicate in soil water and large reserves of silicate minerals might be the reasons to dismiss silica deficiency in most mineral soils, especially in soils containing appreciable amounts of 2:1 clay minerals such as those that occupy much of Louisiana’s landscape. Sufficient reports of improved crop yields and other benefits to Si applications have been documented in the scientific literature to suggest that Si fertilization merits consideration in all regions used for commercial production of rice, sugarcane, wheat and other crops that accumulate high amounts Si in their tissues and harvested components (Savant et al. 1999; Berthelsen et al. 2001; Datnoff et al. 2001).

The benefits of Si fertilization on crop yields and quality has been studied extensively in Asia, Africa, South America and most other regions where rice, sugarcane and other Si-accumulating crops are commercially grown (Snyder et al. 1986). The most common form of silicate fertilizer applied to soils is slag, a by-product of steel manufacturing. In addition to calcium silicate, slag typically contains calcium hydroxide and calcium oxide as well as calcium carbonate and numerous micronutrients. Because slag application causes an increase in soil pH and exchangeable Ca, it may be considered an alternative to Ag-lime (calcium carbonate) application for soils rendered acidic by cropping and fertilization.

Recent investigations into the cause of localized decline (Breitenbeck et al. 2006), a malady of unknown cause affecting flooded rice in southwestern Louisiana; suggest that Si deficiency may be a contributor, if not a primary cause of this disorder. Tissue analyses have confirmed that toxic levels of Fe and Al in young rice plants are a diagnostic characteristic of this disorder even though soil pH and other soil properties in afflicted fields are not consistent with Fe and Al toxicity. This inconsistency prompted a study that confirmed the possibility of silica deficiency contributing to the onset of localized decline. Numerous studies have shown that Si uptake mitigates Al and Fe toxicity as well as a range of other abiotic and biotic stresses in rice and other crops (Ma and Takahashi 2002; Epstein 1999). The specific mechanisms responsible for benefits of silica are not completely understood, but it is clear that Si influences the solubility of Fe and Al in flooded soils, the uptake of these potentially toxic metals by roots, and the ability of plants to tolerate elevated tissue concentrations (Ma and Takahashi 2002).

After their review of extensive field studies in Asia, Lian (1976) concluded no significant increase in yield occurred when mature straw contained greater than 61 g Si kg^{-1} (Japan and Korea) and 51 g Si kg^{-1} (Taiwan). Indian rice varieties growing in tropical regions of Sri Lanka and India appear to respond to Si fertilization at straw concentrations less than 37 g Si kg^{-1}. This latter value is similar to value of 34 g Si kg^{-1} established by Korndorfer et al. (2001) as the economic response to Si fertilization in the Everglades Agricultural Area of Florida. Studies to establish early or late season critical Si values for other rice growing regions of the US have not been reported.

Compared to the impacts of other nutrients on rice production, the economic importance of Si is poorly understood in the south central US. While a number of soil test have been proposed to assess Si availability, none of these tests has found widespread acceptance. A more complete understanding of the Si status of agricultural soils in the south Central US is needed to characterize the potential for Si deficiency and the merits of additional Si research in our region.

1.6 Silicon fertilization in soil

Silicon deficiency in crops has been recognized since the 1970s. The optimization of Si nutrition has been shown to have positive effects on plants. In particular, substantial research on rice and sugarcane has shown that Si application can significantly enhance insect pest and disease resistance with consequent yield increases. Plants differ in their ability to accumulate Si (Ma and Yamaji 2006) but in order for any plant to benefit from Si it must be able to acquire this element in high concentrations. The concentration of plant-available Si in the soil is dynamic and influenced by soil pH, temperature, composition of the soil and moisture, amongst others. Silicon fertilizer is necessary to improve soils deficient in Si and replace Si removed by cropping and leaching. The composition of soils in terms of the level of Si is an important parameter to measure in order to determine its Si-deficiency. For example, Queensland sugarcane soils are considered deficient in Si if the concentration is less than 10-15 mg Si kg^{-1} dry soil following extraction with 0.01 M $CaCl_2$ (Muir et al. 2001). Berthelsen et al. (2003) analyzed three different Australian soils: Bundaberg (Hydrosol soil), Mossman (Tennosol) and Innisfail (Ferrosol). These soils varied in their levels of plant-available Si in the order: Hydrosol > Tennesol > Ferrosol. Areas of high rainfall and temperature undergo significant weathering where important nutrients

(Ca^{2+}, Mg^{2+}, K^+ and Na^+) are stripped from the soil resulting in acidification of the soil, which in turn dissolves aluminosilicate clay minerals with the concomitant leaching of Si. Matichenkov and Calvert (2002) report that 210-224 million tons of plant-available Si is removed from arable soils globally on an annual basis, assuming 700-800 kg ha^{-1} of plant-available silica is removed with the harvesting of crops. Harvesting cultivated plants usually results in Si being removed from the soil. In most cases much more Si is removed than other macronutrients (Savant et al. 1997). In continuous cropping with high Si-accumulator species such as sugarcane and rice, the removal of plant-available Si can be greater than the supply via natural processes releasing it into the soil unless fertilized with Si (Savant et al. 1997).

While other plant-available elements are restored by standard fertilization, Si is not. The Green Revolution experienced since the 1960’s was borne of high-yielding rice varieties in irrigated areas with high fertilizer and insecticide usage. This intensive rice production was also supported by reducing the crop fallow periods, which would have been insufficient to allow regeneration of plant-available Si (Savant et al. 1997). With the likely removal of large amounts of plant nutrients, including Si, from the soil, attempts were made to replace these nutrients using conventional fertilizers (Savant et al. 1997). However, the potential beneficial role of Si was overlooked. Silicon-depleted soils have been associated with lower resistance to insect pests and fungal diseases as well as crop lodging (Savant et al. 1997; Flinn and DeDatta 1984). Japanese rice farmers have sustained high yields under intensive cultivation due probably in part by the application of silicate slag (Savant et al. 1997).

1.7 Rationale for Research

Silicon has become widely accepted as an important element in considering soil condition and plant nutrient programs. Over the past few decades a significant body of knowledge has developed regarding the role of Si in soil health and increased crop yield and productivity. Studies from the rice industry in Japan to the sugar cane industry in North America have shown the importance of Si as an element in the nutrition programs of key economic crops and beyond that the ability of Si to enhance the efficacy of delivering other elements in broader fertilization programs. This is of particular importance for the agricultural soils of Louisiana subjected to repeated cropping and heavy rainfall throughout the year.

There is a need for a systematic approach for determining soil Si status that can become the basis of soil analysis and fertilizer recommendations. Thus this research consisted of three major objectives; 1) to document the plant available Si status using different extraction procedures in agricultural soils of Louisiana; 2) to study the sorption and changes in concentration of plant-available Si in solutions of six different soils with two different Si fertilizers, and 3) to evaluate the soil test methods to determine the soil critical level of plant available Si based on different soil test methods, by assessing the effect of soil Si concentrations on Si uptake and biomass yield in rice.

1.8 References

AAPFCO (Association of American Plant Food Control Officials). 2012. http://www.aapfco.org/index.html (accessed Sept 9, 2015).

Abro, S. A., Qureshi, R., Soomro, F. M., Mirbahar, A. A., and Jakhar, G. 2009. Effects of silicon levels on growth and yield of wheat in silty loam soil. *Pakistan Journal of Botany* 41:1385-1390.

Anderson, D. L., and Sosa Jr., O. 2001. Effect of silicon on expression of resistance to sugarcane borer (*Diatraea saccharalis*). *Journal of the American Society of Sugar Cane Technologists* 21:43-50.

Belanger, R. R. 1995. Soluble silicon: Its role in crop and disease management of greenhouse crops. *Plant Diseases* 79:329-336.

Bélanger, R. R., Benhamou, N., and Menzies, J.G. 2003. Cytological evidence of an active role of silicon in wheat resistance to powdery mildew (*Blumeria graminis* f. sp *tritici*) *Phytopathology* 93:402-412.

Bernays, E., and Barbehenn, R. 1987. Nutritional ecology of grass foliage-chewing insects. *Nutritional Ecology of Insects, Mites, Spiders and Related Invertebrates* 147-175.

Berthelsen, S., Hurney, A., Noble, A., Rudd, A., Garside, A., Henderson, A., and Hogarth, D. 2001. An assessment of current silicon status of sugar cane production soils from Tully to Mossman. In *The Proceedings of the Conference of the Australian Society of Sugar Cane Technologists*, 289-296. Mackay, Queensland, Australia.

Berthelsen, S., Noble, A., Kingston, G., Hurney, A., Rudd, A., and Garside, A. 2003. Improving yield and CCS in sugarcane through the application of Si based amendments. *Final Report on SRDC Project CLW009.* http://elibrary.sugarresearch.com.au/ (accessed Sept 9, 2015).

Berry, P.M., Griffin, J.M., Sylvester-Bradley, R., Scott, R.K., Spink, J.H., Baker, C.J., and Clare, R.W. 2000. Controlling plant form through husbandry to minimize lodging in wheat. *Field Crops Research* 67:59-81.

Breitenbeck, G., Saichuk, J., and Kraska, J. 2006. Unraveling mystery malady in south Louisiana rice. *Louisiana Agriculture* 49:11.

Camberato, J. J. 2007. Cation exchange Capacity–Everything you want to know and much more. *Magnesium* 2:240.

Chen, H., Zheng, C., Tu, C., and Shen, Z. 2000. Chemical methods and phytoremediation of soil contaminated with heavy metals. *Chemosphere* 41:229-234.

Chérif, M., Asselin, A., and Bélanger, R. 1994. Defense responses induced by soluble silicon in cucumber roots infected by *Pythium spp. Phytopathology* 84:236-242.

Currie H. A. and Perry C. C. 2007. Silica in plants: biological, biochemical and chemical studies. *Annals of Botany* 100:1383–1389.

Datnoff, L., Raid, R., Snyder, G., and Jones, D. 1991. Effect of calcium silicate on blast and brown spot intensities and yields of rice. *Plant Diseases* 75:729-732.

Datnoff, L., Deren, C., and Snyder, G. 1997. Silicon fertilization for disease management of rice in Florida. *Crop Protection* 16:525-531.

Datnoff, L. E., G. H. Snyder, and G.H. Kornodörfer (eds). 2001. *Silicon in agriculture.* The Netherlands: Elsevier Science.

Deren, C. W., Datnoff, L. E., Snyder, G. H., and Martin, F. G. 1994. Silicon concentration, disease response, and yield components of rice genotypes grown on flooded organic Histosols. *Crop Science* 34: 733-737

Dietzel, M. 2000. Dissolution of silicates and the stability of polysilicic acid. *Geochimica Et Cosmochimica Acta* 64:3275-3281.

Dietzel, M. 2002. Interaction of polysilicic and monosilicic acid with mineral surfaces. In *Water-rock interaction*, ed. V.P. Singh, 207-235 Netherlands: Springer.

Djamin, A., and Pathak, M. 1967. Role of silica in resistance to asiatic rice borer, (*chilo suppressalis*) (walker), in rice varieties1. *Journal of Economic Entomology* 60:347-351.

Dorweiler, J., and Doebley, J. 1997. Developmental analysis of *teosinte* glume architecture1: A key locus in the evolution of maize (poaceae). *American Journal of Botany* 84:1313.

Drees, L. R., Wilding, L. P., Smeck, N. E., and Senkayi, A. L. 1989. Dixon, J. P. (Ed.) Silica in soils: Quartz and disordered silica polymorphs. In *Minerals in Soil Environments* 913-974.

Elawad, S., and Green, Jr. V. 1979. Si and the rice plant environment: A review of recent research. *Riso* 28:235-253.

Elawad, S., Gascho, G., and Street, J. 1982. Response of sugarcane to silicate source and rate. I. growth and yield. *Agronomy Journal* 74:481-484.

Epstein, E. 1994. The anomaly of silicon in plant biology. In *Proceedings of the National Academy of Sciences of the United States of America* 91:11-17.

Epstein, E. 1999. Silicon. *Annual Review of Plant Biology* 50:641-664.

Epstein, E. 2005. Silicon in agriculture: A historical review. In *The proceedings of the Third Silicon in Agriculture Conference*, eds. L. E. Datnoff, G. H. Korndorfer, and G. H. Snyder, 15–18. Federal University of Uberlandia, Uberlandia, Brazil.

Epstein, E. and A.J. Bloom (ed). 2005. *Mineral nutrition of plants: principles and perspectives.* Second edition. Sunderland, Massachusetts: Sinauer Associates, Inc.

Farmer, V., Delbos, E., and Miller, J. 2005. The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. *Geoderma* 127:71-79.

Fauteux, F., Rémus-Borel, W., Menzies, J. G., and Bélanger, R. R. 2005. Silicon and plant disease resistance against pathogenic fungi. *FEMS Microbiology Letters* 249:1-6.

Fawe, A., Abou-Zaid, M., Menzies, J., and Bélanger, R. 1998. Silicon mediated accumulation of flavonoid phytoalexins in cucumber. *Phytopathology* 88:396-401.

Flinn, J. C., and De Datta, S. 1984. Trends in irrigated-rice yields under intensive cropping at philippine research stations. *Field Crops Research* 9:1-15.

Foy, C. D. 1992. Soil chemical factors limiting plant root growth, Limitations to plant root growth, eds. Hatfield J.L, and Stewart B.A. In *Advances in Soil Science* 19: 97–149.

Hansen, H. B., Raben-Lange, B., Raulund-Rasmussen, K., and Borggaard, O. K. 1994. Monosilicate adsorption by ferrihydrite and goethite at ph 3-6. *Soil Science* 158:40-46.

Hayasaka, T., Fujii, H., and Namai, T. 2005. Silicon content in rice seedlings to protect rice blast fungus at the nursery stage. *Journal of General Plant Pathology* 71:169-173.

Heath, M. C., and Stumpf, M. A. 1986. Ultrastructural observations of penetration sites of the cowpea rust fungus in untreated and Si-depleted french bean cells. *Physiological and Molecular Plant Pathology* 29:27-39.

Hodson, M., and Sangster, A. 1988. Silica deposition in the inflorescence bracts of wheat (*Triticum aestivum*) I: scanning electron microscopy and light microscopy. *Canadian Journal of Botany* 66:829-838.

Iler, R. K. 1979. *The chemistry of silica: Solubility, polymerization, colloid and surface properties, and biochemistry*. Canada: John Wiley and Sons Inc.

Inanaga, S., Okasaka, A., and Tanaka, S. 1995. Does silicon exist in association with organic compounds in rice plant? *Soil Science and Plant Nutrition* 41:111-117.

Islam, A., and Saha, R. 1969. Effects of silicon on the chemical composition of rice plants. *Plant and Soil* 30:446-458.

Jones, L., and Handreck, K. 1967. Silica in soils, plants, and animals. *Advances in Agronomy 19*:107-149.

Jones, L., and Handreck, K. 1969. Uptake of silica by *Trifolium incarnatum* in relation to the concentration in the external solution and to transpiration. *Plant and Soil* 30:71-80.

Kauss, H., Seehaus, K., Franke, R., Gilbert, S., Dietrich, R. A., and Kröger, N. 2003. Silica deposition by a strongly cationic proline-rich protein from systemically resistant cucumber plants. *The Plant Journal* 33:87-95.

Keeping, M., and Meyer, J. 2003. Effect of four sources of silicon on resistance of sugarcane varieties to *Eldana saccharina* (lepidoptera: Pyralidae). *Proceedings of South African Sugar Technologists Association* 77:99-103.

Kidd, P. S., Llugany, M., Poschenrieder, C., Gunse, B., and Barcelo, J. 2001. The role of root exudates in aluminium resistance and Si-induced amelioration of aluminium toxicity in three varieties of maize (*Zea mays L.*). *Journal of Experimental Botany* 52:1339-1352.

Kim, S. G., Kim, K. W., Park, E. W., and Choi, D. 2002. Silicon-induced cell wall fortification of rice leaves: A possible cellular mechanism of enhanced host resistance to blast. *Phytopathology* 92:1095-1103.

Knight, C. T., and Kinrade, S. D. 2001. A primer on the aqueous chemistry of silicon. *Studies in Plant Science* 8:57-84.

Kroger, N., Lorenz, S., Brunner, E., and Sumper, M. 2002. Self-assembly of highly phosphorylated silaffins and their function in biosilica morphogenesis. *Science* 298:584-586.

Laing, M., Gatarayiha, M., and Adandonon, A. 2006. Silicon use for pest control in agriculture: A review. *Proceedings of the South African Sugar Technologists' Association* 80:278-286.

Lewin, J., and Reimann, B. E. 1969. Silicon and plant growth. *Annual Review of Plant Physiology* 20:289-304.

Liang, Y., Sun, W., Si, J., and Römheld, V. 2005. Effects of foliar-and root-applied silicon on the enhancement of induced resistance to powdery mildew in *Cucumis sativus*. *Plant Pathology* 54:678-685.

Liang, Y., Wong, J., and Wei, L. 2005. Silicon-mediated enhancement of cadmium tolerance in maize (*Zea mays L.)* grown in cadmium contaminated soil. *Chemosphere* 58:475-483.

Liang, Y., Hua, H., Zhu, Y., Zhang, J., Cheng, C., and Römheld, V. 2006. Importance of plant species and external Si concentration to active Si uptake and transport. *New Phytologist* 172:63-72.

Liang, Y., Sun, W., Zhu, Y., and Christie, P. 2007. Mechanisms of silicon-mediated alleviation of abiotic stresses in higher plants: A review. *Environmental Pollution* 147:422-428.

Liang, Y., Zhu, J., Li, Z., Chu, G., Ding, Y., Zhang, J., and Sun, W. 2008. Role of silicon in enhancing resistance to freezing stress in two contrasting winter wheat cultivars. *Environmental and Experimental Botany* 64:286-294.

Ma, J., Nishimura, K., and Takahashi, E. 1989. Effect of silicon on the growth of rice plant at different growth stages. *Soil Science and Plant Nutrition* 35:347-356.

Ma, J., and Takahashi, E. 1990. Effect of silicon on the growth and phosphorus uptake of rice. *Plant and Soil* 126:115-119.

Ma, J. F., and Takahashi, E. 1993. Interaction between calcium and silicon in water-cultured rice plants. *Plant and Soil* 148:107-113.

Ma, J. F., and Takahashi, E. 2002. *Soil, fertilizer, and plant Si research in japan.* Amsterdam: Elsevier.

Ma, J. F. 2004. Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses. *Soil Science and Plant Nutrition* 50:11-18.

Ma, J. F., Tamai, K., Yamaji, N., Mitani, N., Konishi, S., Katsuhara, M., and Yano, M. 2006. A silicon transporter in rice. *Nature* 440:688-691.

Ma, J. F., and Yamaji, N. 2006. Silicon uptake and accumulation in higher plants. *Trends in Plant Science* 11:392-397.

Ma, J. F., Yamaji, N., Mitani, N., Tamai, K., Konishi, S., Fujiwara, T., and Yano, M. 2007a. An efflux transporter of silicon in rice. *Nature* 448: 209-212.

Ma, J. F., Yamaji, N., Tamai, K., and Mitani, N. 2007b. Genotypic difference in silicon uptake and expression of Si transporter genes in rice. *Plant Physiology* 145:919-924.

Mali, M., and Aery, N. 2009. Effect of silicon on growth, biochemical constituents, and mineral nutrition of cowpea. *Communications in Soil Science and Plant Analysis* 40:1041-1052.

Marschner, H., Oberle, H., Cakmak, I., and Römheld, V. 1990. Growth enhancement by silicon in cucumber (*Cucumis sativus*) plants depends on imbalance in phosphorus and zinc supply. *Plant and Soil* 124:211-219.

Matichenkov, V., Calvert, D., and Snyder, G. 1999. Silicon fertilizers for citrus in Florida. *Proceedings-Florida State Horticultural Society* 112:5-8.

Matichenkov, V., Bocharnikova, E., Ande, B., Ande, P., and Calvert, D. 2002. Effect of silicon - rich slag and lime on P leaching in sandy soils. *Journal American Society of Sugarcane Technologists* 22:9-20.

Matichenkov, V., and Calvert, D. 2002. Silicon as a beneficial element for sugarcane. *Journal American Society of Sugarcane Technologists* 22:21-30.

Matichenkov, V.V., and Bocharnikova, E.A. 2010. Technology for natural water protection against pollution from cultivated areas, In Proceedings of *15th Annual Australian Agronomy Conference*. Lincoln, New Zealand. http://www.regional.org.au/au/asa/2010/farming-systems/nutrients-water/7052_matichenkovvl.htm#TopOfPage (accessed Sept 9, 2015).

Mecfel, J., Hinke, S., Goedel, W. A., Marx, G., Fehlhaber, R., Bäucker, E., and Wienhaus, O. 2007. Effect of silicon fertilizers on Si accumulation in wheat. *Journal of Plant Nutrition and Soil Science* 170:769-772.

Mitani, N., and Ma, J. F. 2005. Uptake system of silicon in different plant species. *Journal of Experimental Botany* 56:1255-1261.

Mitani, N., Yamaji, N., and Ma, J. F. 2009. Identification of maize silicon influx transporters. *Plant and Cell Physiology* 50:5-12.

Morgan, K., McCray, J., Rice, R., Gilbert, R., and Baucum, L. 2009. Review of current sugarcane fertilizer recommendations: A report from the UF/IFAS sugarcane fertilizer standards task force. https://edis.ifas.ufl.edu/ss508 (accessed Sept 9, 2015).

Motomura, H., Mita, N., and Suzuki, M. 2002. Silica accumulation in long-lived leaves of *Sasa veitchii* (carriere) *Rehder* (poaceae-bambusoideae). *Annals of Botany* 90:149-152.

Neumann, D., and Zur Nieden, U. 2001. Silicon and heavy metal tolerance of higher plants. *Phytochemistry* 56:685-692.

Neumann, D., and De Figueiredo, C. 2002. A novel mechanism of silicon uptake. *Protoplasma* 220:0059-0067.

Nishimura, K., Miyake, Y., and Takahashi, E. 1989. On silicon, aluminium, and zinc accumulators discriminated from 147 species of angiospermae. *Memoirs of the College of Agriculture-Kyoto University (Japan)* 133: 23-43.

Nowakowski, W., and Nowakowska, J. 1997. Silicon and copper interaction in the growth of spring wheat seedlings. *Biologia Plantarum* 39:463-466.

Okuda, A., and Takahashi, E. 1965. The role of silicon. In *The Mineral Nutrition of the Rice*. Symposium of the International Rice Research Institute, 123-146. Baltimore, Maryland: The John Hopkins Press.

Piperno, D. R., Holst, I., Wessel-Beaver, L., and Andres, T. C. 2002. Evidence for the control of phytolith formation in cucurbita fruits by the hard rind (hr) genetic locus: Archaeological and ecological implications. *Proceedings of the National Academy of Sciences of the United States of America* 99:10923-10928.

Richmond, K. E., and Sussman, M. 2003. Got Silicon? The non-essential beneficial plant nutrient. *Current Opinion in Plant Biology* 6:268-272.

Rodrigues, F., Vale, F., Korndörfer, G., Prabhu, A., Datnoff, L., Oliveira, A., and Zambolim, L. 2003. Influence of silicon on sheath blight of rice in Brazil. *Crop Protection* 22:23-29.

Rodrigues, F.A., Benhamou, N., Datnoff, L.E., Jones, J.B., and Bélanger, R.R. 2003. Ultrastructural and cytochemical aspects of silicon-mediated rice blast resistance. *Phytopathology* 93:535–546.

Sadgrove, N. 2006. Nutrient and moisture economics in diatomaceous earth amended growth media. *Southern Cross University.*

Sangster, A., Hodson, M., and Tubb, H. 2001. Silicon deposition in higher plants. *Studies in Plant Science* 8:85-113.

Sauer, D., Saccone, L., Conley, D. J., Herrmann, L., and Sommer, M. 2006. Review of methodologies for extracting plant-available and amorphous silicon from soils and aquatic sediments. *Biogeochemistry* 80:89-108.

Slaton, N. A., R. D. Cartwright, J. Meng, E. E. Gbur, and R. J. Norman. 2003. Sheath blight severity and rice yield as affected by nitrogen fertilizer rate, application method, and fungicide. *Agronomy Journal* 95: 1489–1496.

Savant, N., Snyder, G., and Datnoff, L. 1997. Silicon management and sustainable rice production. *Advances in Agronomy* 58:151-199.

Savant, N. K., Korndörfer, G. H., Datnoff, L. E., and Snyder, G. H. 1999. Silicon nutrition and sugarcane production: A review 1. *Journal of Plant Nutrition* 22:1853-1903.

Seebold, K., Kucharek, T., Datnoff, L. a., Correa-Victoria, F. J., and Marchetti, M. A. 2001. The influence of silicon on components of resistance to blast in susceptible, partially resistant, and resistant cultivars of rice. *Phytopathology* 91:63-69.

Shi, Q., Bao, Z., Zhu, Z., He, Y., Qian, Q., and Yu, J. 2005. Silicon-mediated alleviation of mn toxicity in *Cucumis sativus* in relation to activities of superoxide dismutase and ascorbate peroxidase. *Phytochemistry* 66:1551-1559.

Shi, X., Zhang, C., Wang, H., and Zhang, F. 2005. Effect of silicon on the distribution of cd in rice seedlings. *Plant and Soil* 272:53-60.

Sieburth, S. M., Manly, C. J., and Gammon, D. W. 1990. Organosilane insecticides. part I: Biological and physical effects of isosteric replacement of Si for carbon in etofenprox and MTI-800. *Pesticide Science* 28:289-307.

Singh, K., Singh, R., Singh, J., Singh, Y., and Singh, K. 2006. Effect of level and time of silicon application on growth, yield and its uptake by rice (*Oryza sativa*). *Indian Journal of Agricultural Science* 76:410-413.

Snyder, G., Jones, D., and Gascho, G. 1986. Silicon fertilization of rice on everglades histosols. *Soil Science Society of America Journal* 50:1259-1263.

Song, A., Li, P., Li, Z., Fan, F., Nikolic, M., and Liang, Y. 2011. The alleviation of zinc toxicity by silicon is related to zinc transport and antioxidative reactions in rice. *Plant and Soil* 344:319-333.

Soni, S. L., Kaufman, P. B., and Bigelow, W. C. 1972. Electron probe analysis of silicon and other elements in leaf epidermal cells of the rice plant (*Oryza sativa L.*). *American Journal of Botany* 59:38-42.

Sumida, H. 1991. Characteristics of silica dissolution and absorption in paddy soils: Application to soil test for available silica. *Japanese Journal of Soil Science and Plant Nutrition (Japan).*

Takahashi, E., Ma, J., and Miyake, Y. 1990. The possibility of silicon as an essential element for higher plants. *Comments on Agricultural and Food Chemistry* 2:99-102.

Van Soest, P. 2006. Rice straw, the role of silica and treatments to improve quality. *Animal Feed Science and Technology* 130:137-171.

UN News Centre. June 14, 2013. "World population projected to reach 9.6 billion by 2050 – UN report". Retrieved Sept 9, 2015.

Voleti, S., Padmakumari, A., Raju, V., Babu, S. M., and Ranganathan, S. 2008. Effect of silicon solubilizers on silica transportation, induced pest and disease resistance in rice (*Oryza sativa L.). Crop Protection* 27:1398-1402.

Wang, L., Wang, Y., Chen, Q., Cao, W., Li, M., and Zhang, F. 2000. Silicon induced cadmium tolerance of rice seedlings. *Journal of Plant Nutrition 23*:1397-1406.

Wang, J.J., Dodla, S.K., and Henderson, R.E. 2004. Soil silicon extractability with seven selected extractants in relation to colorimetric and ICP determination. *Soil Science* 169: 861-870.

Winslow, M. D., Okada, K., and Correa-Victoria, F. 1997. Silicon deficiency and the adaptation of tropical rice ecotypes. *Plant and Soil* 188:239-248.

Yamaji, N., and Ma, J. F. 2007. Spatial distribution and temporal variation of the rice Si transporter *Lsi1*. *Plant Physiology* 143:1306-1313.

Yamauchi, M., and Winslow, M. 1989. Effect of silica and magnesium on yield of upland rice in the humid tropics. *Plant and Soil* 113:265-269.

Yongchao, L., and Ruixing, D. 2002. Influence of silicon on microdistribution of mineral ions in roots of salt-stressed barley as associated with salt tolerance in plants. *Science in China Series C: Life Sciences* 45:298-308.

Yoshida, S., Ohnishi, Y., and Kitagishi, K. 1962. Histochemistry of silicon in rice plant: II. localization of silicon within rice tissues. *Soil Science and Plant Nutrition* 8:36-41.

Chapter 2. Survey of the plant-available silicon status of agricultural soils in Louisiana

2.1 Introduction

Today, it is universally acknowledged that silicon (Si) is crucial to the healthy growth of many crops, especially Si-accumulators such as rice (Meyer and Keeping 2001; Savant et al. 1997, 1999). The main role of Si in rice has been its role against plant disease (Miyake and Takahashi 1983). Six states now account for over 99% of all rice (*Oryza sativa*) grown in the US. These are Arkansas, California, Louisiana, Mississippi, Missouri and Texas. In 2013/14, US rice crop was projected, by at 185.1 million cwt (hundredweight, rough basis), 7% below with previous year and 24 percent below the record 2010/11 crop (USDA, NASS 2013). Maintaining sufficient level of nitrogen (N), phosphorus (P) and potassium (K) without considering other nutrients such as Si and micro elements can result in an imbalance in plant nutrition. Moreover, rice cultivation (generally 2-3 times a year) without sufficient nutrient replenishment could also be responsible for the degradation in soil productivity. Uptake of Si in rice plants ranges from 230 to 470 kg Si ha^{-1}, which is two times higher than N uptake (Savant et al. 1997). While Si fertilization is routine in many countries, it is not widely practiced in the United States. The Everglades Agricultural Area (EAA) of south Florida is a notable exception. As the organic mucks and sandy soils offer very low Si availability, many rice and sugarcane (*Saccharum officinarum*) fields are treated with slag to increase Si availability (Snyder 2003). Silicon fertilization has largely been overlooked in Louisiana and other rice growing regions of the US where most soils contain appreciable amounts of 2:1 layered silicate clay minerals, and therefore are presumed to supply adequate amounts of silicates to crops (Kraska and Breitenbeck 2010). There is little evidence, however, to support the assumption that these mineral soils supply sufficient Si to meet fully, the needs of rice, sugarcane and other Si accumulating crops. A preliminary survey of Louisiana rice at mid-tiller showed that plants affected with a mysterious early season disorder labeled "localized decline" also contained low levels of Si (12-36 mg kg^{-1}), suggesting that Si deficiency may be a contributing factor to localized decline (Breitenbeck et al. 2006).

A study conducted by Narayanaswamy and Prakash (2009) showed that the application of calcium silicate resulted in significant increase in Si content of rice plants as compared to the control plants. In a study conducted by Jaspreet et al. (2013) in Louisiana, soil Si amendment led to lower relative growth rates and helped in significantly reducing the intensity of stem borer (*Diatraea saccharalis*) larvae that plague the sugarcane plants vis-a-vis control plants. Further, these results suggest that soil Si amendment has the potential to fit into the IPM (Integrated Pest Management) program for stem borers as it is feasible, environment friendly and compatible with other control tactics.

Soils of Louisiana vary significantly. One reason for this high variation is the deposition process associated with many Louisiana soils. The fluvial process of soil deposition, where sediment originated from various weathered parent materials across the upper portion of the Mississippi River drainage basin, brings about highly diverse soils that can be deposited in a very small area. This high variability can influence many physicochemical properties, which include texture, soil pH, and essential plant nutrients (Hodges 1997; Stanturf and Schoenholtz 1998). The climate of Louisiana is humid and subtropical, with average annual temperatures from 17°C in the northern part of the state to 22°C in coastal areas. Average annual rainfall ranges from 119 cm in the northwestern part of the state to 180 cm in isolated southeastern areas (Soil Survey Staff 2012). A major consequence of the chemical weathering of primary silicate minerals is desilication. The severe and frequent soil erosion and sediment transportation in these areas owing to high rainfall and coarse texture of soil could lead to desilication and relatively low soil Si (White 1995). Weathering releases highly mobile basic cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}), moderately mobile monosilicic acid [$Si(OH)_4$], and relatively immobile Al and Fe into soil solution (White 1995; Karathanasis 2006). Part of the Si released from the mineral structure reacts with Al (and to a lesser extent Fe and Mg) to form secondary clay minerals, while the remainder is subjected to leaching. As a consequence, most soils experience a loss of Si and basic cations during weathering (White 1995). Desilication is most pronounced in humid tropical environments and occurs to a lesser extent in temperate regions (Karathanasis 2006).

Silicon can exist both as monosilicic acid [$Si(OH)_4$] and polysilicic acid [$Si(OH)_4$]$_x$ in soil solutions and soil extracts. The plant available form is [$Si(OH)_4$], and the molybdenum blue colorimetry (MBC) procedure reacts only with [$Si(OH)_4$]. Therefore, does not determine Si in the [$Si(OH)_4$]$_x$ form. Atomic absorption spectroscopy and Inductively Couple Plasma (ICP) measure total Si, including [$Si(OH)_4$], [$Si(OH)_4$]$_x$, and soluble organosilicon compounds (Snyder, 2001). Thus, in this study evaluation of different procedures for estimating plant-available Si was done by measuring the [$Si(OH)_4$] brought into solution using the MBC.

The main objectives of this study were to: 1) survey the extractable Si in the agricultural soils of different parishes of Louisiana, 2) relate extractable Si with soil texture and pH, and 3) categorize soil Si levels in Louisiana based on established critical levels.

2.2 Materials and Methods

2.2.1 Survey strategy

With the help of LSU AgCenter Extension Agents, 212 representative agricultural fields of 27 parishes of Louisiana were included in the survey. Sampling sites included agricultural fields in different parishes presently under the cultivation of different crops to represent the principal cropping systems and soils in Louisiana. The survey was conducted from 2012 to 2015.

2.2.2 Sampling

A uniform area within a production field that had not received any prior Si amendments was sampled. Soil samples were obtained from 27 parishes (Figure 2.1). Each field sample represents a composite of 20 separate cores. On receipt, the soils were oven dried and stored until the analysis was started. Soils were uniformly ground and sieved through a 2-mm stainless-steel mesh. Sampling locations were geo-located using the global positioning system (GPS) receiver.

2.2.3 Soil silicon analysis

Silicon was extracted from soils using seven extractants as outlined by different researchers (Table 2.1). Silicon concentration in soil extracts was determined using Molybdenum Blue Colorimetry (Korndorfer et al. 2001). A known volume of filtrate was transferred into a plastic centrifuge tube and then 10 mL of deionized water, plus 0.5 mL of 1:1 hydrochloric acid (HCl), and 1 mL of 10% ammonium molybdate [$(NH_4)_6Mo_7O_2$] solution (pH 7.5) was added. After 5 minutes, 1 mL of 20% tartaric acid solution was added and after two minutes, 1 mL of the reducing agent amino napthol n-sulphonic acid (ANSA) was added. After five, but not later than 30 minutes following addition of the reducing agent**,** absorbance was measured at 630 nm using UV visible spectrophotometer (Hach DR 5000). Simultaneously, Si standards (0.2, 0.4, 0.8 and 1.2 mg L^{-1}) prepared in the same matrix were also measured using UV visible spectrophotometer.

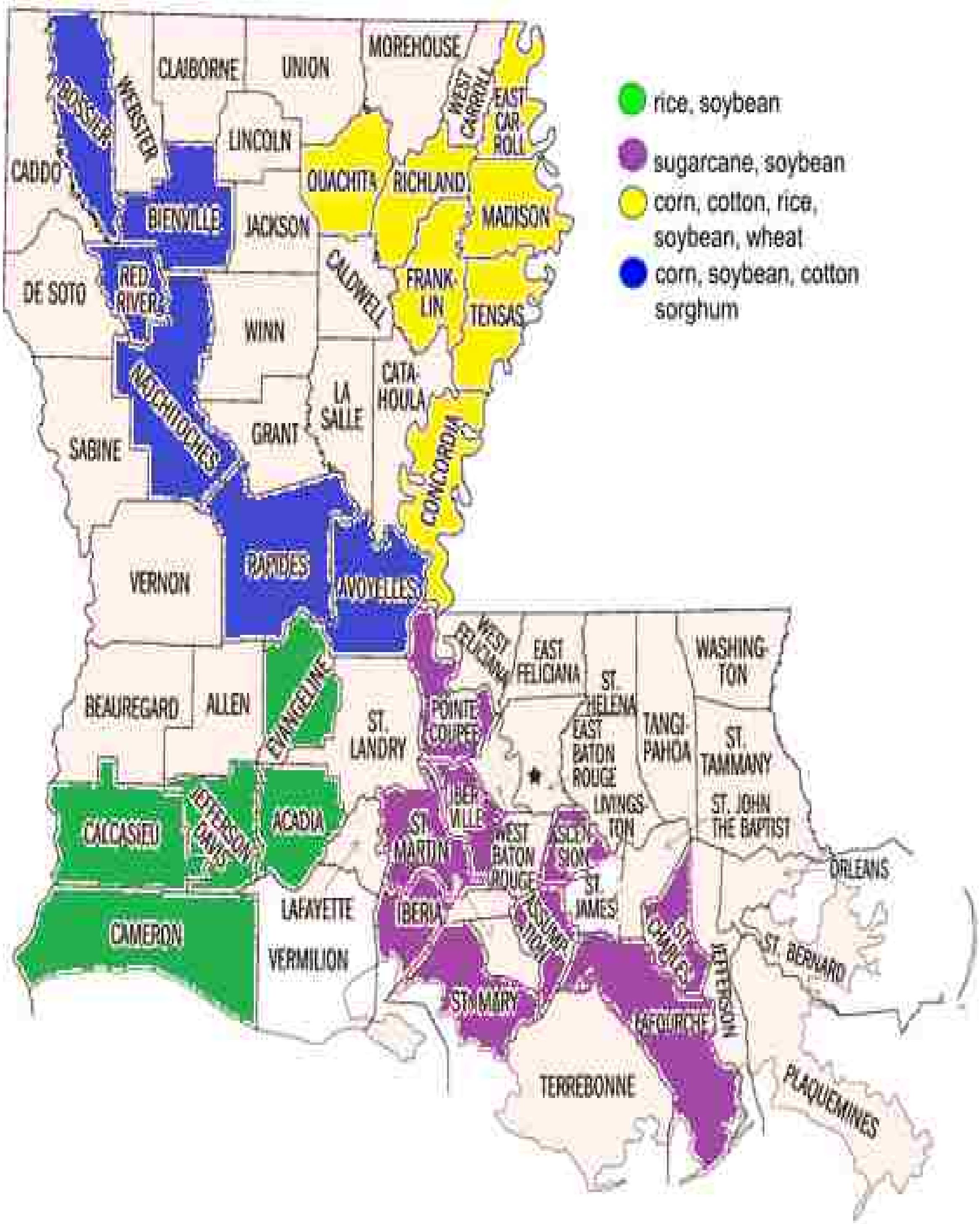


Figure 2.1 The different parishes of Louisiana with major crops grown surveyed for determining soil silicon status

Table 2.1 Different extractants and procedures used for evaluating available Si in different soils

Extractants	Soil: solution ratio	Procedures	Reference
0.5 M Acetic Acid-1	1:10	1hr	Korndorfer et al. 1999
0.01 M Calcium Chloride ($CaCl_2$)	1:10	1hr	Korndorfer et al. 1999
1 M Sodium Acetate (NaOAc)	1:10	1hr	Fox et al. 1967
Deionized water	1:10	1hr	Korndorfer et al. 1999
0.5 M Ammonium Acetate (NH_4OAc)	1:10	1hr	Korndorfer et al. 1999
0.1 M Citric Acid	1:50	2 hrs; 24hrs rest; 1hr	Acquaye and Tinsley 1965
0.5 M Acetic Acid-2	1:2.5	24hrs rest; 2hr	Snyder 2001

2.2.4 Determining Soil pH, extractable P, K, Ca, Mg, S, Cu and Zn

2.2.4.a. Soil pH (1:1 water)

Ten (10) grams soil sample was weighed and added with 10 mL distilled water. Samples were shaken for 1 hour in a reciprocal shaker and set undisturbed for 1 hour. The soil pH was measured using pH electrode meter.

2.2.4.b. Soil texture

Soil textural class was determined by the Feel method (Thien 1979). For each soil textural class, the average soil Si was determined using different extraction procedures.

2.2.4.c. Statistical Analysis

The relationship between soil pH, Mehlich-3 extractable nutrients and extractable soil Si based on different procedures was evaluated using regression analysis using PROC REG in SAS

9.4 (SAS Institute, 2012). PROC REG was also used to find the correlation between soil Si extracted by different procedures. The coefficient of determination (r^2) and P-value was used as a criterion to determine the significance of their relationship.

2.2.4.d. Extractable Nutrients by Mehlich-3 Procedure (Mehlich 1984)

A two (2) gram soil sample was weighed out into 100 mL plastic bottles followed by the addition of 20 mL of Mehlich-3 solution (dilute acid-fluoride-EDTA solution, pH 2.5). The samples were shaken on a reciprocal shaker set at high speed for 5 minutes and then filtered using Whatman No. 42 filter paper. The extract was then analyzed using ICP– Optical Emission Spectroscopy (OEM) for P, K, Ca, Mg, S, Cu and Zn.

2.3 Results and Discussion

The Si extracted by different extractants viz., 0.5 M acetic acid-1, 0.5 M acetic acid-2, 0.01 M $CaCl_2$, deionized water, 0.5 M NH_4OAc, 1 M NaOAc and 0.1 M citric acid ranged from 10 to 562 ug g^{-1}, 3 to 208 ug g^{-1}, 0 to 56 ug g^{-1}, 0.51 to 66 ug g^{-1}, 3 to 208 ug g^{-1}, 11 to 241 ug g^{-1} and 63 to 3323 ug g^{-1}, respectively (Table 2.2). The average Si extracted by various extractants used for the study was in the order of high to low: 0.1 M citric acid > 0.5 M acetic acid-2 > 0.5 M acetic acid-1 > 1 M NaOAc > 0.5 M NH_4Oac > deionized water> 0.01 M $CaCl_2$. This trend observed was in agreement with the results of Narayanswamy and Prakash (2009) and Wang et al. (2004). Narayanswamy and Prakash (2009) attributed this variation to dissolution of soluble, exchangeable, and specifically adsorbed Si; dissolution of some unavailable forms of Si present in the soils such as polymerized and precipitated Si; kind and nature of the extractant used; soil to solution ratio; pH of the extractant used; and shaking period. Wang et al. (2004) also suggested that the seven extractants used in their study characterized different pools of Si-supplying capacity of the soil: extractable by water, extractable by any of HCl, citric acid, acetic acid, acetate buffer, and NH_4OAc, and extractable by Mehlich-3. Nayar et al. (1977) reported similar extracting power for Si among different extractants as 0.2 N HCl > 0.025 M citric acid >1 N acetate buffer > water.

The measured pH in the pure extractants used in this study followed the order 0.1 M citric acid (2.2) < 0.5 M acetic acid (2.6) < 1.0 M NaOAc (4.0) < 0.5 M NH_4OAc (4.8) < deionized water (6.8, unbuffered) < 0.01 M $CaCl_2$ (7.2). All the acidic extractants extracted greater quantity of Si when compared with $CaCl_2$ and deionized water. Fox et al. (1967) also noticed a greater extraction potential of Si from soils with acetic acid, sulfuric acid (H_2SO_4) and calcium dihydrogen phosphates than with water and $CaCl_2$. The NH_4OAc , acetic acid, and phosphate buffer extracted 1, 1.5, and 3 times more Si from sugarcane soils of South Africa than distilled water and $CaCl_2$ (Berthelsen et al. 2001). They suggested that $CaCl_2$ and distilled water extracted more easily soluble Si while NaOAc, acetic acid, and phosphate buffer dissolved some exchangeable Si also, while citric acid and H_2SO_4 provided an estimate of the potential pool of Si by measuring soluble, exchangeable and specifically adsorbed Si. According to Brown and Mahler (1987), acidity and anions could additively impact Si release from soils. Wang et al. (2004) also pointed out that the combined effect of acidity and anions may explain the quantity of Si extracted by different procedures. Fluoride ions increased the solubility of silicate minerals substantially, especially under acid conditions (Iler, 1979). Citrate, along with phosphate, replaced strongly adsorbed Si through ligand exchange reactions (Brown and Mahler, 1987). Therefore, the maximum quantity of Si extracted by 0.1 M citric acid could be attributed not only to the low pH of this extractant but also to the fact that the citrate ions can bring even the strongly adsorbed forms of Si into solution.

Evidently, citric acid and acetic acid-2 extracted highest extractable Si among all extractants irrespective of the soils tested in this study. This could also be due to the fact that these two extractants, besides being acidic in nature, were also the two extractants that were in contact with the soil samples for the longest period of time. Also, when 0.5 M acetic acid-1 was compared with 0.5 M acetic acid -2, the former extracted lower quantities of Si. These results were in agreement with Hurney (1973) who also stated that the longer the contact times of the soil in the extractant, the higher the recovery of extractable Si. This happens because, with a continuous shaking of 16 hrs, silicate clay minerals are affected both chemically and mechanically, and thereby resulting in an overestimation of available Si by citric acid and acetic acid-2 (Hurney 1973).

The soils with high clay content showed the highest range of Si removed by all extractants, whereas the remaining light textured soil showed the least quantity removed (Figure 2.2). In a survey of the Si status of soils in the South African Sugar industry, the 0.01 M H_2SO_4 + $(NH_4)_2SO_4$ extractant was considered by Meyer and Keeping (2000) as the best Si extraction method for plant available Si because it was better correlated with the soil clay content. In the present study, the Si concentrations removed by all extractants were seen to be increasing with clay content which was very evident in 0.5 M acetic acid-1 as shown in Figure 2.2. This result was in agreement with the findings of Meyer (2001) who reported that extractable Si values increased with soil clay contents which could be attributed to the dissolution of high content of native Si present in the clay soils. Gontijo (2000) studied soils from different locations and with different textures, and observed that soil Si values decreased as sand values increased. Most of these soils of Louisiana having high Si content were present along the Mississippi river flood line where there is high deposition of silt and organic matter.

Table 2.2 Number of fields in each parish and range of soil-test silicon content based on different extraction methods

Parish†	Total Area†† (ha)	0.5 M Acetic Acid - 1†††	0.01 M Calcium Chloride	1 M Sodium Acetate	Deionized Water	0.5 M Ammonium Acetate	0.1 M Citric Acid	0.5 M Acetic Acid-2††††
		………………………………………………				…ug g^{-1}…………………………………………		
Acadia(10)	950	34-158	9-24	29-108	14-34	13-64	256-735	57-151
Ascension(11)	840	10-125	5-42	13-104	5-47	6-53	351-1474	40-165
Assumption(12)	200	41-338	16-49	45-233	14-55	13-118	682-2352	78-240
Avoyelles(7)	400	16-252	3-32	33-206	7-28	5-96	188-1837	21-224
Bienville(10)	600	22-90	2-4	12-31	3-16	7-13	61-158	12-29
Bossier(8)	450	16-61	4-29	19-68	7-35	6-31	154-587	36-175
Calcasieu(14)	850	15-78	2-26	19-72	10-21	3-36	102-562	16-141
Cameron(10)	530	22-44	4-15	19-57	9-20	6-23	189-510	27-64
Concordia(10)	500	45-204	16-51	19-172	20-59	17-103	490-1746	69-216
East Carroll(6)	450	84-319	20-39	64-224	37-52	37-130	957-2173	124-228
Evangeline(11)	600	16-43	6-16	19-51	12-26	9-19	233-546	48-80
Franklin(2)	100	81-96	14-21	79-106	30-31	19-38	338-365	128-132
Iberia(2)	100	50-92	22-26	19-57	24-32	21-32	730-760	103-165
Iberville(1)	40	72	22	19	27	26	1030	102
Jefferson Davis(10)	600	14-54	4-20	21-69	12-23	10-25	226-77	36-82

†Values in parentheses are number of fields surveyed. †† Combined area of all fields surveyed †††1 hour shaking. ††††24 hours shaking and 2 hours rest.

(Table 2.2 continued)

Parish†	Total Area†† (ha)	0.5 M Acetic Acid - 1†††	0.01 M Calcium Chloride	1 M Sodium Acetate	Deionized Water	0.5 M Ammonium Acetate	0.1 M Citric Acid	0.5 M Acetic Acid-2††††
	………………………………………………ug g^{-1}……………………………………………							
Lafourche(10)	580	44-177	12-37	19-155	21-58	11-92	319-1726	58-201
Madison(6)	450	53-231	25-52	55-186	20-50	27-91	837-1726	107-221
Natchitoches(6)	500	29-87	5-17	19-65	10-21	8-27	242-701	29-132
Ouachita(10)	800	10-229	0-50	15-185	7-47	3-97	190-1542	20-202
Pointe Coupee(10)	950	25-184	11-34	19-119	14-37	10-48	655-2118	53-232
Rapides(1)	40	16	24	19	0.5	32	610	100
Red River(10)	845	12-173-	5-36	21-156	10-26	3-83	295-1479	36-231
Richland(7)	920	20-109	9-34	19-84	12-42	11-44	258-946	46-147
St Martin(12)	520	28-171	12-41	41-157	15-47	15-95	397-1447	60-174
St. Charles(8)	725	57-563	10-56	32-241	13-66	13-208	503-3323	51-159
St. Mary(2)	50	134-138	23-24	90-122	28-29	60-77	1014-1034	148-181
Tensas(6)	300	18-77	0-22	20-94	11-28	8-32	390-1014	42-126
Range	10-200	10-563	0-56	11-241	0.51-66	3-208	63-3323	12-240
Average		77	19	64	23	33	734	97

†Values in parentheses are number of fields surveyed. †† Combined area of all fields surveyed †††1 hour shaking. ††††24 hours shaking and 2 hours rest.

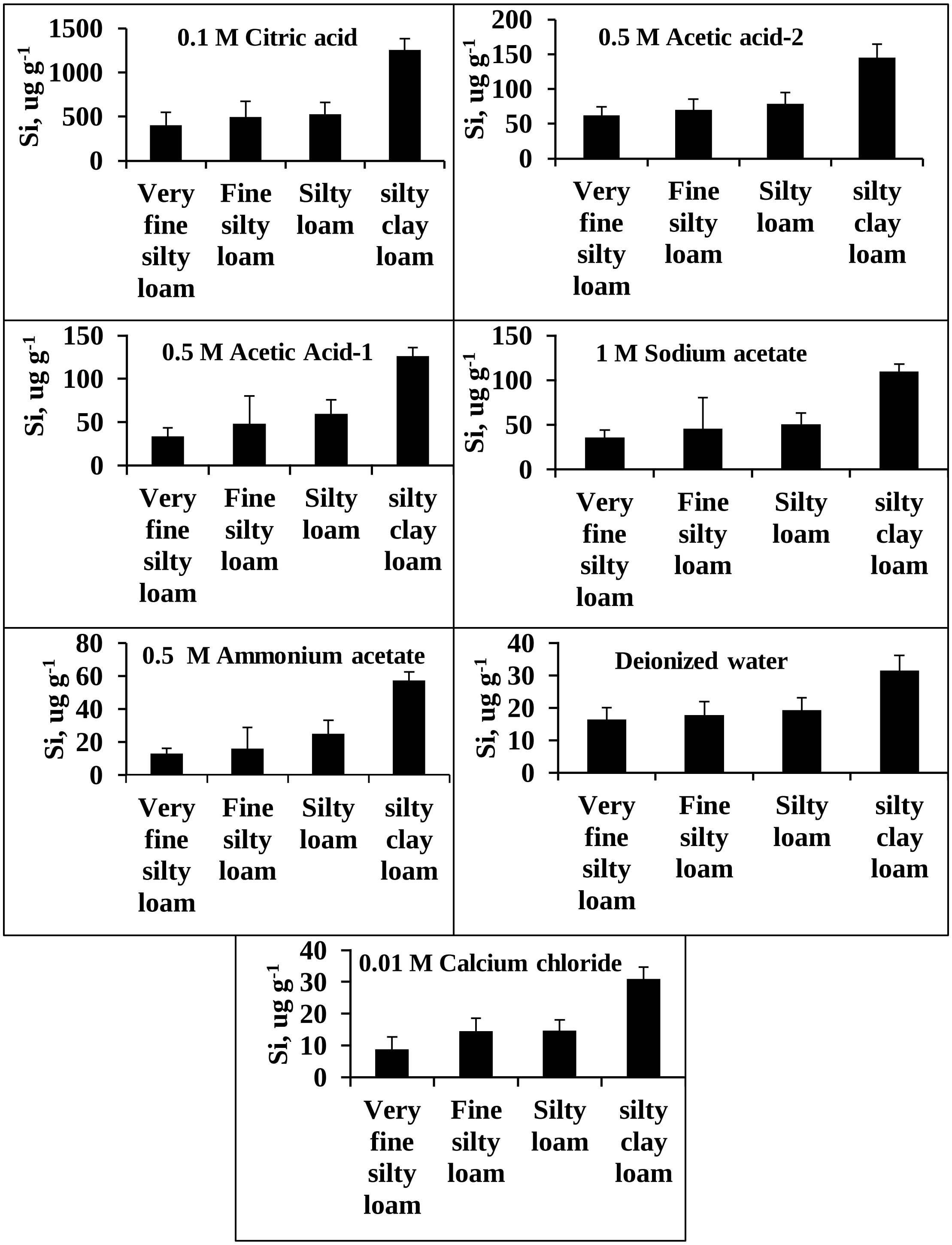


Figure 2.2 Average soil silicon within different soil textural classes using different extraction procedures in Louisiana soils (Number of soil samples with very fine silty loam, fine silty loam, silty loam and clay loam were 27, 7, 113 and 65, respectively)

These high concentrations of Si in these soils with high clay and organic matter might not be sufficient with plant available Si because soluble Si is adsorbed by clay and organic matter and is not available in soil solution for plant uptake.

The soil pH and Si concentrations in these soils showed a weak relationship ($r^2 < 0.31$, $P<0.0001$) using different extraction procedures (Figure 2.3) Where a large group of soils in a region of a country is surveyed, there is generally a positive relationship between pH and Si solubility or extractability (Fox et al. 1967; Cheong et al. 1968; Oya and Kina 1989; Oya et al. 1989; Miles et al. 2014). Oliveira et al. (2007), Korndörfer et al. (2005) and de Camargo et al. (2007) further explained that the concentration of available soil Si (whether native Si or added as an amendment) decreases with increasing soil acidity due to the decrease in dissolution of Si in soil (Korndörfer et al. 2005). According to Oliveira (2004) increases in soil pH from 4.5 to 6.0 promoted the release of colloid-adsorbed Si to the soil solution and there was an increase in available Si. There are also studies reporting that a high concentration of H^+ dissolved aluminosilicates and released Si into solution (Beckwith and Reeve 1964; Lindsay 1979; Brown and Mahler 1987). However, such a relationship was not very evident in this study. This could be because the solubility of crystalline or amorphous Si was essentially constant at solution pH 2-8.5 (Iler, 1979). The pH of the soils used in this study also fell in this range of constant solubility.

Calcium chloride and deionized water extracted the least amount of Si from all soils ranging from 0 to 56 and 0.51 to 66 ug g^{-1}, respectively. However deionized water was poorly (r^2=0.35, P<0.0001) correlated with 0.5 M acetic acid-1 extraction method while 0.01 M $CaCl_2$ extractable Si values were fairly correlated (r^2=0.56, P<0.0001) to the same (Appendix A, Table A.1). It is possible that the Si form extracted by deionized water and $CaCl_2$ extractants is different from that extracted by acetic acid. Whereas, a good correlation (r^2=0.52, P<0.0001) was observed between deionized water and the 0.01 M $CaCl_2$ extracted Si values as shown in the figure 2.4. Wang et al. (2004) reported that the correlations between deionized water and other extractants were low (r^2 <= 0.430) and that the, unbuffered deionized water extraction, reflects primarily a transient pool of soluble Si for a specific soil condition. They also suggested that the Si removed by different extractants could basically be classified into three categories: (i) water-extractable, (ii) extractable by HCl, citric acid, acetic acid, acetate buffer, and NH_4OAc, and (iii) Mehlich-3 extractable Si.

Also, extracting with water dilutes the ionic strength of the soil solution greatly so that the amounts extracted will differ from those present in soil solution. Silicon adsorption onto metal hydrous oxides increases with decreasing ionic strength of the extractant. In addition, the low ionic strength results in dispersion of soil particles (Berthelsen and Korndorfer 2005) meaning that the extracted solution may require filtering through a micropore filter (after centrifugation) prior to analysis. Therefore, unbuffered salt solutions such as 0.01 M $CaCl_2$ are favored (Berthelsen et al. 2003; Hohn et al. 2008; Miles et al. 2014) since they have an ionic strength similar to that of the soil solution and the dominant cation is Ca^{2+} as is the case in most soil solutions. Their ionic strength also prevents dispersion and facilitates easy extraction and analysis. Deionized water has been used by some workers to estimate readily soluble Si (Fox et al. 1967; Elawad et al. 1982). This extraction, especially on a moist sample basis, has been used by some to characterize mobile forms of Si, with $Si(OH)_4$ being the dominant form along with $[Si(OH)_4]x$ and inorganic and organic Si complexes (Matichenkov et al. 2000; Ma and Takahashi 2002).

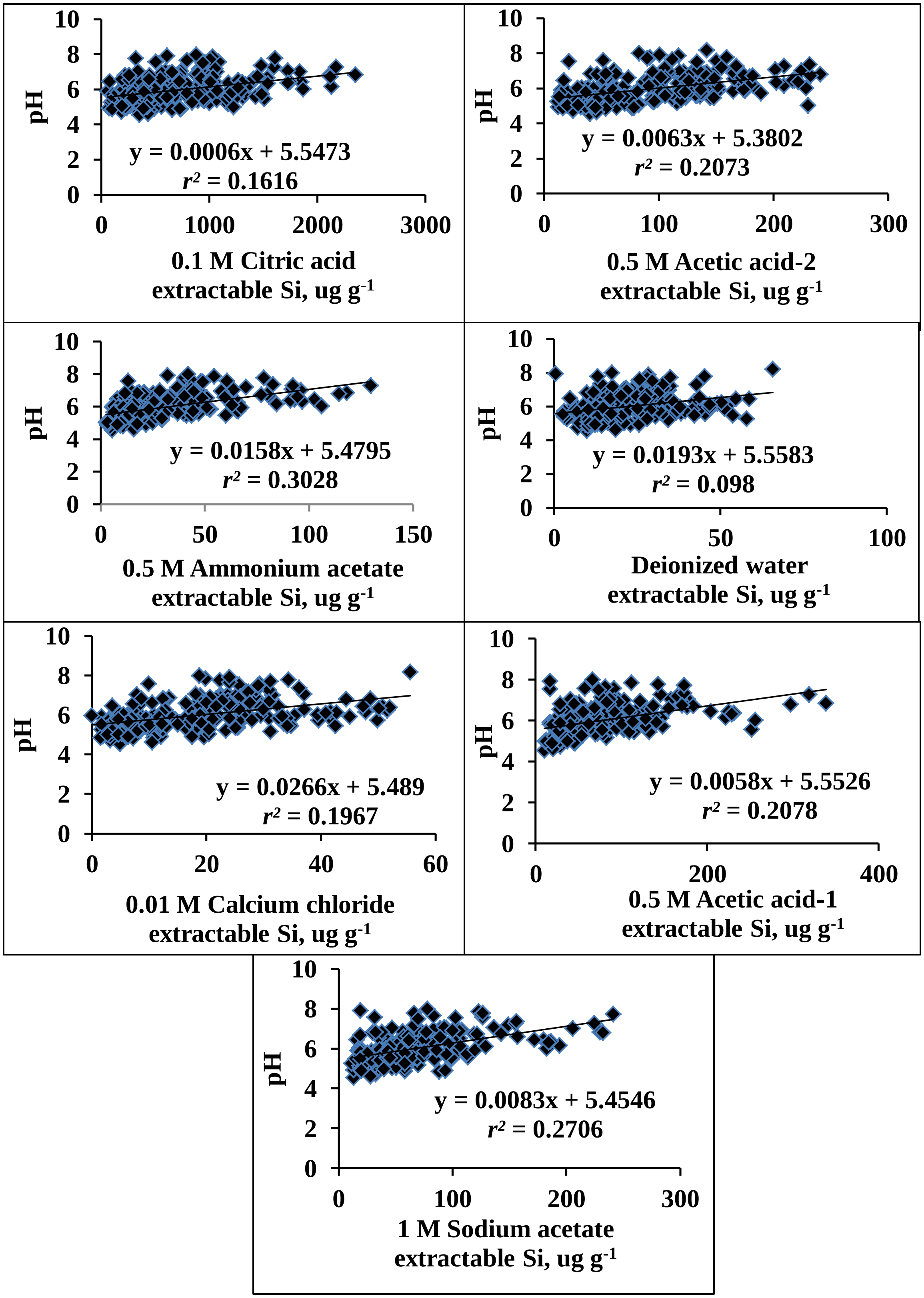


Figure 2.3 Relationship between soil silicon extracted using different procedures and soil pH in Louisiana soils (*P*<0.0001)

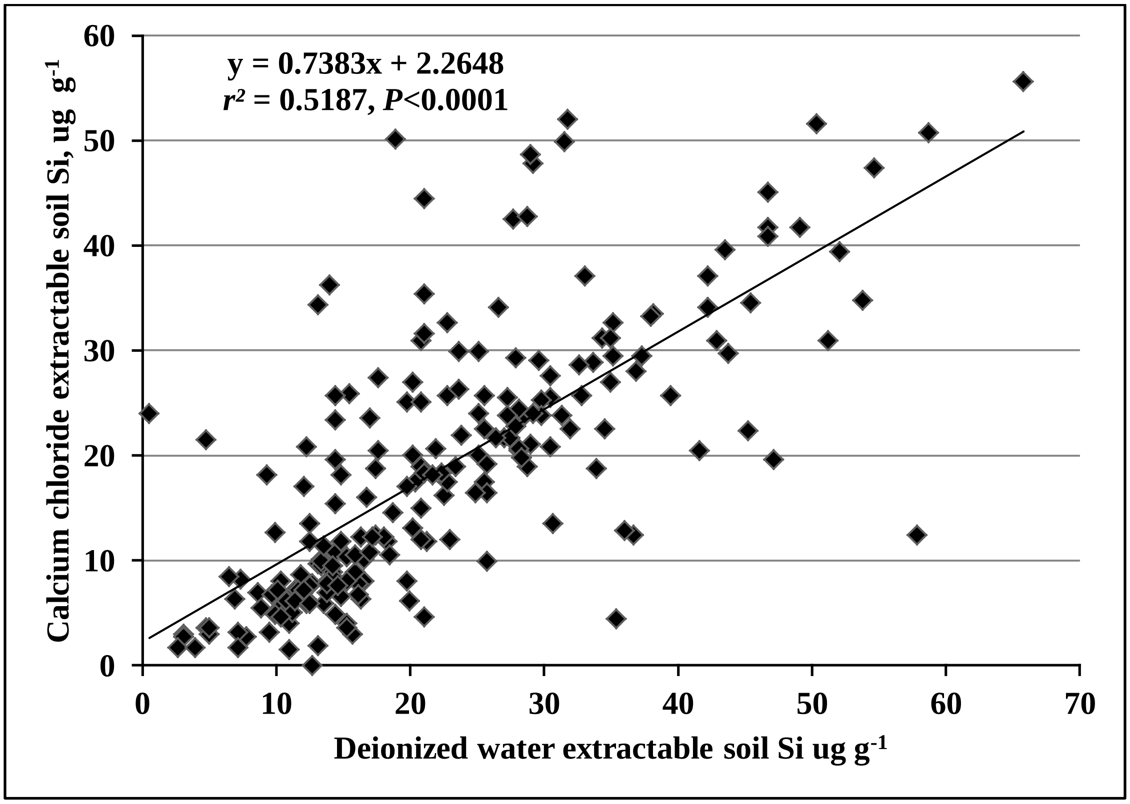


Figure 2.4 Relationship of soil silicon levels determined by deionized water and calcium chloride extraction procedures across all soil samples

Since polymerization and depolymerization of soluble Si is very much controlled by soil pH, salt concentration, and dry-wet cycles (Iler, 1979), it is doubtful that this method can provide a reasonable Si nutritional status for the soil for an entire growing season (Wang et al. 2004). This could also be true for 0.01 M $CaCl_2$ extraction procedure because the good correlation between these two extractants (Figure 2.4) suggests that they could be extracting Si from the same pools in soil.

Ammonium- and Na-acetates (buffered at low pH with acetic acid) as well as acetic acid itself have been extensively used as extractants for soil Si (Sauer et al., 2006). The acid extraction would result in dissolution of amorphous Al and Fe oxides and hydroxides with release of adsorbed Si (Sauer et al. 2006; Hohn et al. 2008) and leads to dissolution of amorphous aluminosilicates and any highly soluble crystalline aluminosilicates material, while the presence of the acetate anion might also favor desorption of adsorbed silicate. The Si values from both NH_4OAc and NaOAc extractants had very good correlation with near equal values (r^2=0.78 and 0.72 respectively with P<0.0001) with acetic acid-1 (Appendix A, Table A.2) method suggesting that these extractants may remove the same form of Si from soil. Earlier reports suggest that these extractants removes Si that is either mobile or loosely bound and some fractions of amorphous forms (Matichenkov et al. 2000; Wang et al. 2004).

Citric acid has been used by other researchers (Acquaye and Tinsley 1965), and the modes of extraction are likely to include solubilization of Al and Fe hydrous oxides and aluminosilicates, displacement of adsorbed silicate by citrate and complexation of Fe and Al by citrate, thus, preventing formation of Al and Fe complexes with Si during extraction (Sauer et al. 2006). In general, acids such as H_4SO_4 and citric acid extract more Si than the Na- and NH_4-acetate-based extractants, which in turn extract more Si than water and $CaCl_2$ (Fox et al. 1967; Berthelsen et al. 2003; Barbosa Filho et al. 2004; Wang et al. 2004; Kanamugire et al. 2006; Haynes et al. 2013). This was observed in this study as well, with citric acid extracting up to 3323 ug Si g^{-1} soil. Although acetic acid-1 and acetic acid-2 method used the same reagent, the correlation between them was only fair with r^2=0.46 with P<0.0001 (Appendix A, Table A.3).

Interestingly, a good correlation with near equal values was observed between citric acid extractable Si values and that of acetic acid-2 extractable Si values with r^2=0.72 (P<0.0001) as shown in Figure 2.5. This suggests that the form of Si extracted by citric acid and acetic acid-2 extraction method are possibly the same. Therefore the same reagent when used in two different extraction procedures (acetic acid-1 and acetic acid -2), extracted different forms of Si from soil. This is further proof of the fact that contact time and dilution also decides the form of soil Si extracted although the reagent used might be the same as pointed out by Narayanswamy and Prakash (2009). Wang et al. (2004) also reported relatively large amounts of citric acid extractable Si than acetic acid-1, NH_4Oac, and acetate buffer and noted significant correlations between citric acid and HCl suggesting that citric acid and HCl extractions reflect a certain fraction of slowly releasable Si, a capacity factor that is proportional to the soluble Si of soil. Wang et al (2004) further suggested that any one of these extractants except for deionized water is likely to predict a similar pool of labile Si for plant uptake even though citric acid might be predicting a portion of capacity factor as well as intensity factor of soil Si status. They also attributed the low concentration of Si extracted by deionized water to be the measure of (readily available) a transient status of soil Si which did not account for the polymerization-depolymerization and adsorption-desorption happening with the changes in temperature and moisture content in soil during a growing season. Poor correlations between 0.01 M $CaCl_2$, deionized water, citric acid, acetic acid-2 with other extractants suggest that acetic acid-2 like citric acid may extract a certain fraction of capacity factor (slowly releasable Si) that is proportional to the soluble Si of soil, unlike the other five extractants. Also, the unbuffered 0.01 M $CaCl_2$ may reflect only a transient status of soil soluble Si, similar to deionized water extraction. All of the seven extractants used in this study have been found to correlate with plant uptake of Si at various locations. The greenhouse study discussed in Chapter 4 showed the best correlation of soil Si extracted and plant response variables to be in 0.01 M $CaCl_2$ and acetic acid-2 procedures.

From these results, it is possible that no single measure is adequate to determine plant available Si. However, it is clear that a number of extractants can be successfully used to estimate soil Si. The choice of extractant will often be based on its ease of adoption for a particular laboratory and its suitability for specific soil characteristics, which will in turn be reflected in its ability to correlate with plant uptake of Si. As 0.01 M $CaCl_2$ extractable Si represents the Si readily plant available in the soil solution and this fact was evident with its good correlation with plant uptake. But its near equal values with deionized water suggests that it could reflect only a transient status of soil soluble Si. However, 0.5 M acetic acid-2 may reflect the net effects of the sorption/desorption reactions by extracting the readily as well as the slowly releasable Si (a capacity factor that is proportional to the soluble Si of soil) that control solubility, thus giving a true measure of current availability. Additionally, it also showed good correlation with plant uptake in different soils as discussed in Chapter 4. Therefore, it might be suggested that these two extraction procedures (0.01 M $CaCl_2$ and 0.5 M acetic acid-2) may be used either together or as a single measure of plant available Si.

Besides trying to find the best extractant for determining the plant available soil Si status, the distribution of Si-deficient soils by parish was also of interest in this study, since all soil samples represent native soils under agricultural production with no prior history of Si fertilization. The Si status of Louisiana soils distributed into three ranges (low, medium and high) based on the critical levels of soil Si established previously by scientists like Snyder (1991), Korndorfer et al. (2001), Narayanaswamy and Prakash (2009), Liang et al. (1994), and Xu et al. (2001) are depicted in maps as shown in Figures 2.6. The critical level determined in Louisiana soils in the greenhouse studies conducted during the years 2014 and 2015 as discussed in Chapter 4 was also taken as a basis for the categorization of the surveyed soils into high, medium and low Si soils. None of the soils deemed as low in Si were above the critical levels established in other parts of the world as well as that determined in Louisiana irrespective of the extractant used.

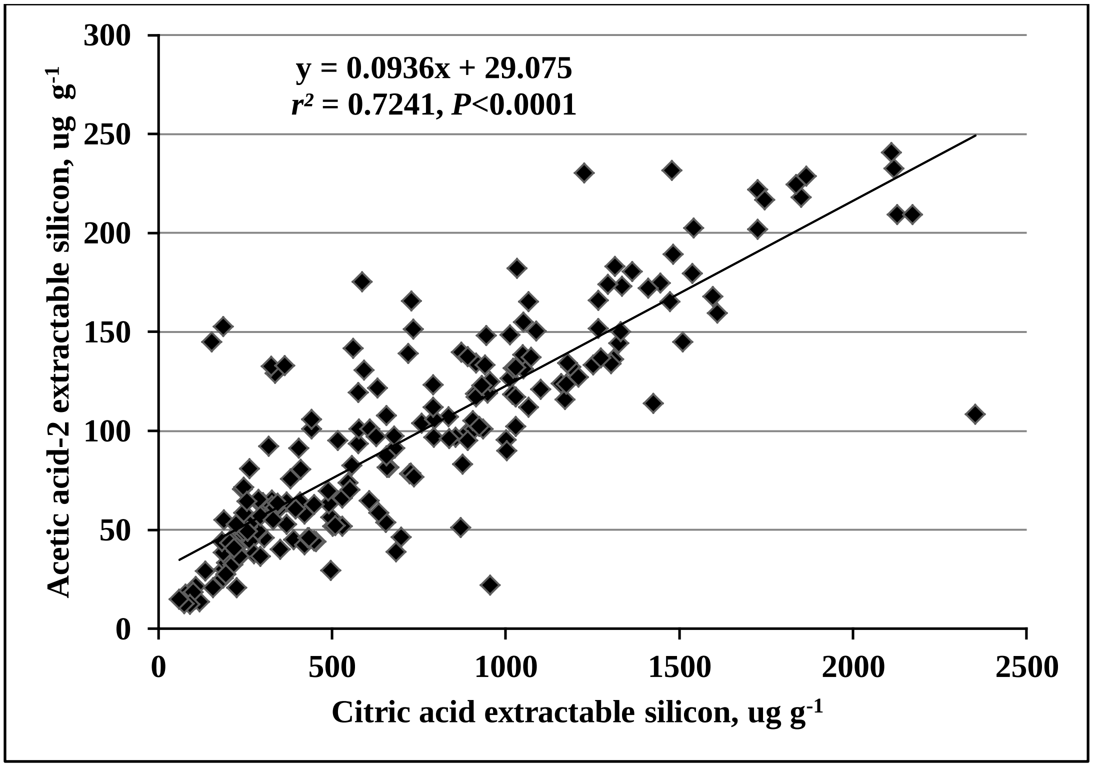
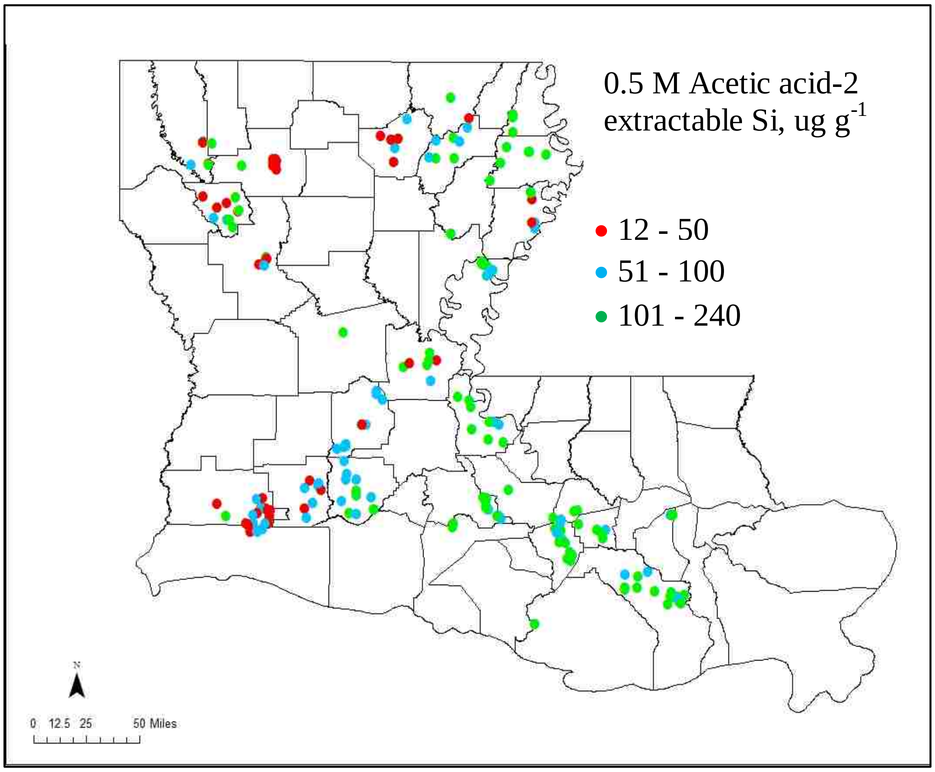


Figure 2.5 Comparison of soil silicon levels based on acetic acid-2 and citric acid extraction procedures for all soil samples

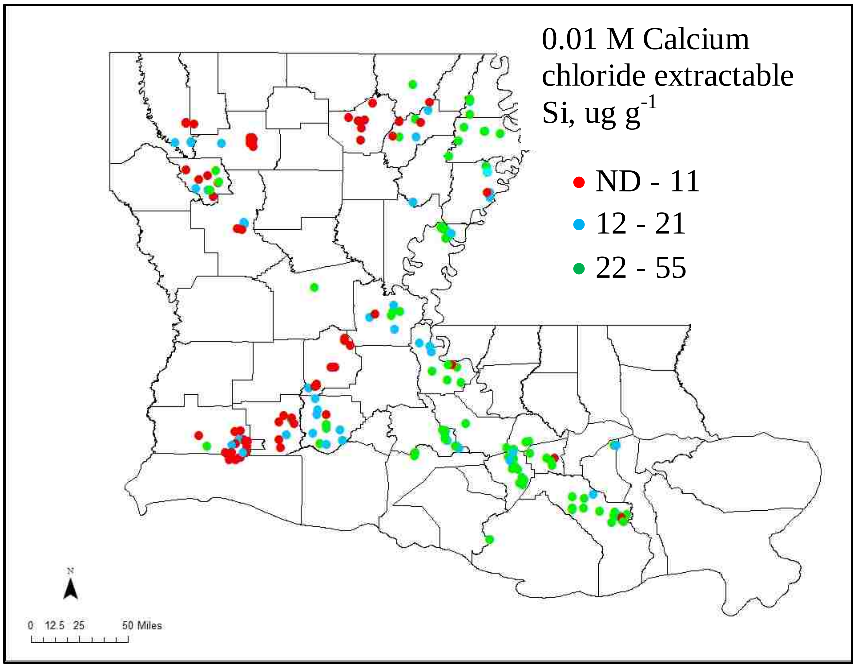
Interestingly, soils along the floodplains of Mississippi river were seen to be relatively higher in soil Si irrespective of the extractant used. Organic matter, which in high amounts in flooded soil, may induce a higher Si mobility due to the reduction of Fe hydrous oxides that release adsorbed $Si(OH)_4$ (Kabata-Pendias and Barbara 2001). Considering, the critical level of soil Si for 0.01 M $CaCl_2$ extraction method as 43 mg kg^{-1} for rice production established by Narayanaswamy and Prakash (2009), 93% of these soils could be categorized as low in soil Si. Haysom and Chapman (1975) suggested that the critical soil Si value using the 0.01 M $CaCl_2$ extraction was roughly 20 mg kg^{-1} soil, which when taken into account could make 54% of these soils low in soil Si for rice and sugarcane production. Nevertheless, the $CaCl_2$ extractant would bring almost half of these fields (out of 212) surveyed in Louisiana under the low Si category. Although , a relatively, lower range of 0-11 ug g^{-1} for 0.01 M $CaCl_2$ extractable Si which was identified to be well below the critical level of Si established using the same extractant across different soils, was set to the data generated, numerous soils low in Si were identified in this survey, as shown in Figure 2.6.

The critical value of available Si identified by Imaizumi and Yoshida (1958) and Lian (1976) utilizing the sodium acetate buffer method was 60 mg kg^{-1} soil and by this standard, 58% of the soils evaluated in this study are low in Si. Coincidentally, almost the same percent (60%) of these soils are low in Si t using the critical limit (32 mg kg $^{-1}$) for ammonium acetate determined by Narayanaswamy and Prakash (2009).

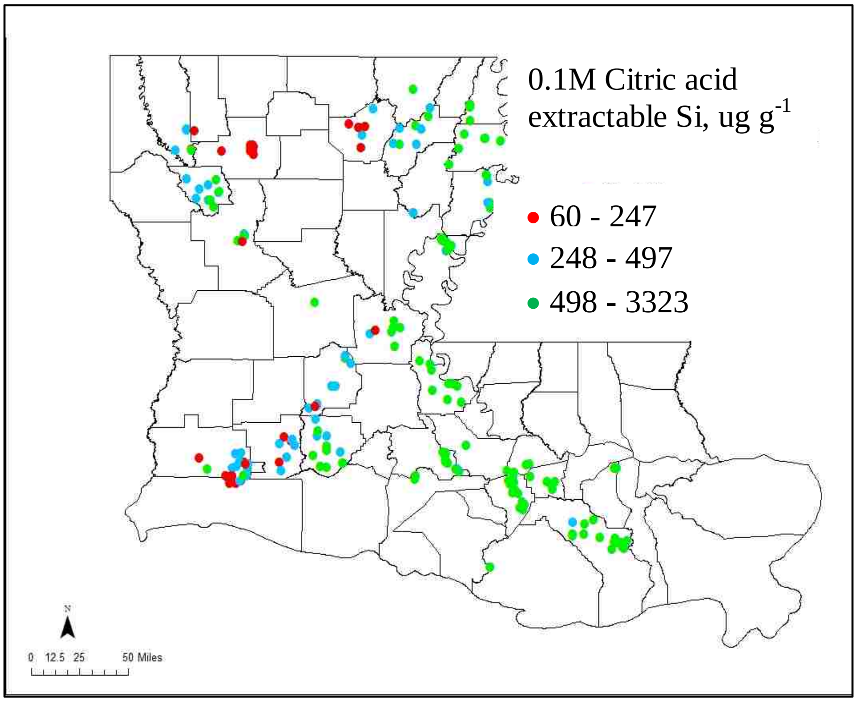


a.

Figure 2.6 Average soil silicon distribution using 0.5 M acetic acid-2 (a), 0.01 Calcium chloride (b), 0.01 M Citric acid (c), 0.5 M ammonium acetate (d), 1 M Sodium acetate (e), 0.5 M acetic acid-1 (f), and deionized water (g) extraction procedures in Louisiana soils. € ND =Non-detectable levels

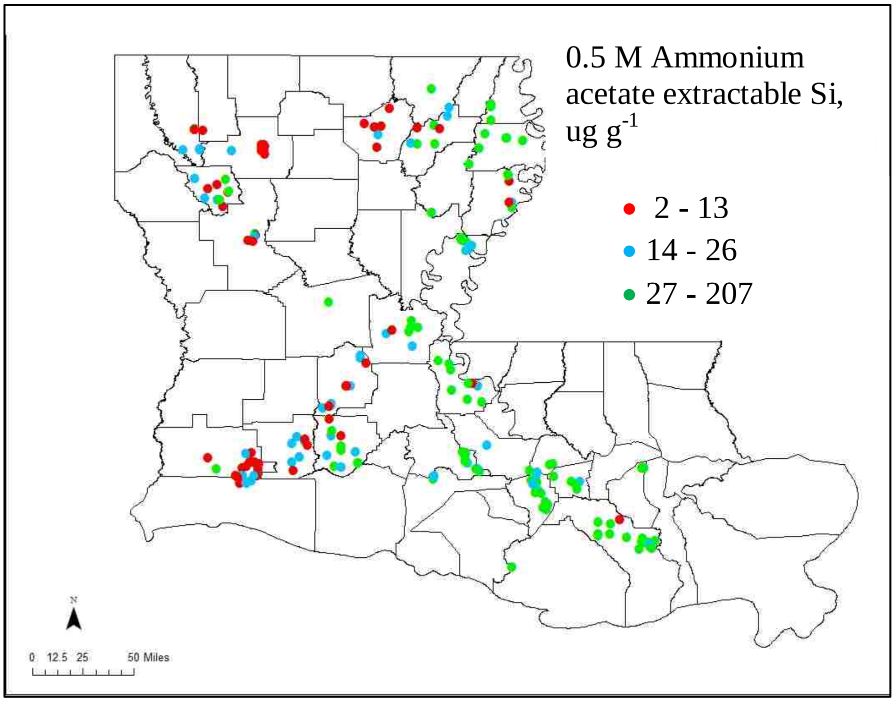


b.

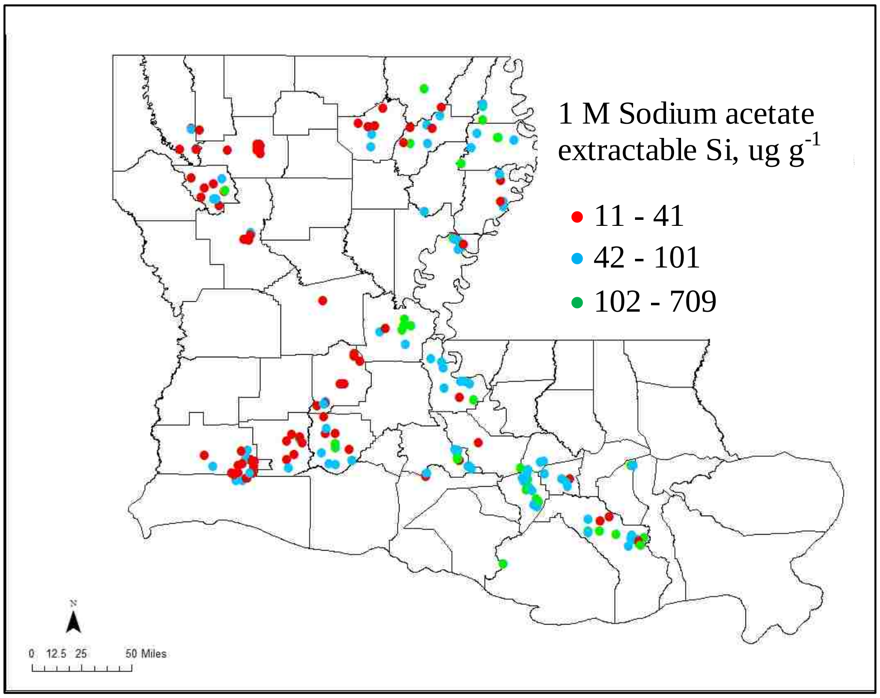


c.

(Figure 2.6 continued)

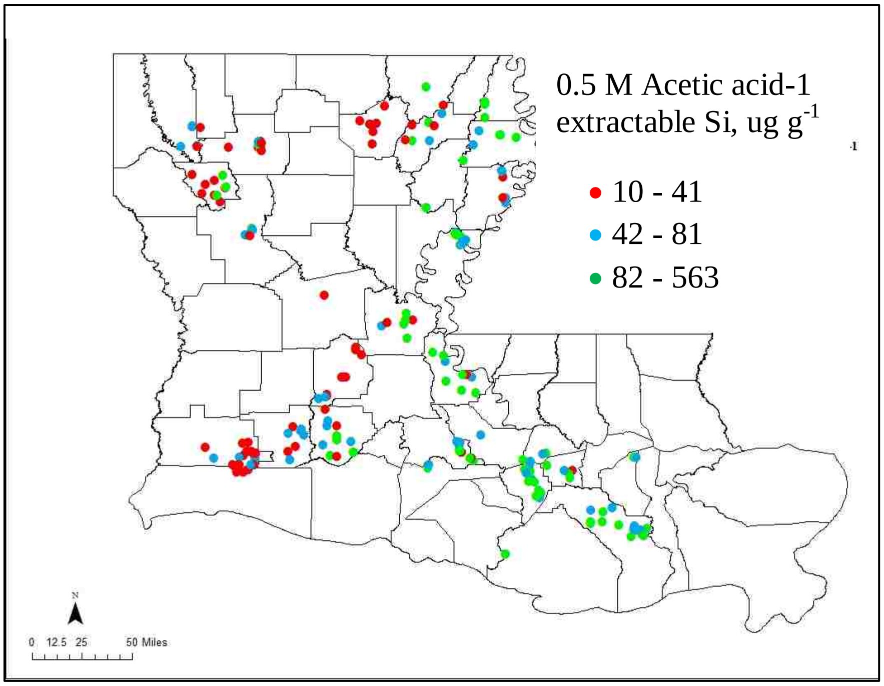


d.

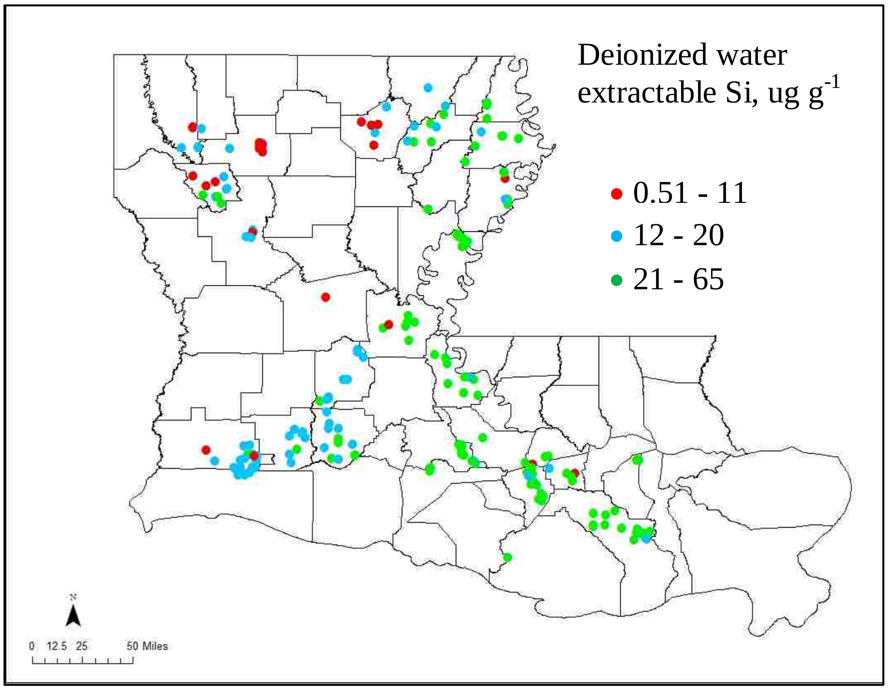


e.

(Figure 2.6 continued)



f.



g.

(Figure 2.6 continued)

When the Si values generated in this study were further compared with the published critical soil-test Si values of 24 and 54 mg kg $^{-1}$ with 0.5 M acetic acid-1 determined by Korndorfer (2001) and Narayanaswamy and Prakash (2009) respectively, about 13 and 50% of these soils were low in Si for rice and sugarcane production. The 0.5 M acetic acid-2 method could produce up to 48% of the investigated soils of the current study in the region of low soil Si when compared with an established critical value of 87 mg kg^{-1} for Si in rice generated by Narayanaswamy and Prakash 2009. However, the citric acid method could categorize only 7.6% of these soils as low in Si as per the established critical level of 185 mg kg^{-1} by Narayanaswamy and Prakash (2009).

2.4 Conclusions

Soils which have Si values equal to or below the critical soil-test value for each respective extraction procedure would likely require Si fertilization. Comparison of Si concentrations measured in this survey with critical values established for other rice and sugarcane growing areas indicate that soil Si might not be adequate in most agricultural fields of Louisiana. On the basis of these data, it is very likely that certain regions in Louisiana would benefit from Si fertilization in rice and sugarcane production. This study suggests that any one of the tested extractants is likely to predict a pool of readily available and labile Si for plant uptake. Poor correlations between deionized water, 0.01 M $CaCl_2$, and other extractants suggest that the unbuffered 0.01 M $CaCl_2$ extraction may reflect only a transient status of soil soluble Si similar to deionized water extraction procedure. There is a need to test and develop either a single or a combination of these extraction procedures. It is unlikely that there is a single universal extraction procedure for Si for all types of soil.

2.5 References

Berthelsen, S., A. D. Noble., and A. L. Garside. 2001. Silicon research down under: Past, present, and future. In *Silicon in agriculture: Silicon deposition in higher plants*, eds. L. E. Datnoff, G. H. Snyder, and G. H. Korndorfer, 244–255, The Netherlands: Elsevier Science.

Beckwith, R.S., and R. Reeve. 1964. Studies on soluble silica in soils. II. The release of monosilicic acid from soils. *Australian Journal Soil Research* 2:33-45.

Brown, T.H., and Mahler, R.L. 1987. Effects of phosphorus and acidity levels on levels of silica extracted from a Palouse silt loam. *Soil Science Society of America Journal* 59:39-45.

Breitenbeck, G., Saichuk, J., and Kraska, J. 2006. Unraveling mystery malady in south Louisiana rice. *Louisiana Agriculture* 49:11.

Cheong, W. Y., Ross, L., and Cavalot, P. C. 1968. Silicon Status of Mauritius Soils. *Annual report of the Mauritius Sugarcane Industry Research Institute 1967*, Mauritius 78–81.

Fox, R. L., Silva, J. A., Younge, O. R., Plucknett, D. L., and Sherman, G. D. 1967. Soil and plant silicon response by sugarcane. *Soil Science Society of America Journal* 31: 775–779.

Gontijo, I. Características físicas e químicas dos solos determinantes da disponibilidade do silício para as plantas. 2000. Monografia – Instituto de Ciências Agrárias da Universidade Federal de Uberlândia, 2000.

Haysom, M.B.C., and Chapman, L.S. 1975. Some aspects of the calcium silicate trials at Mackay. *Proceedings of Queensland Society of Sugar Cane Technologists* 42: 117–122.

Hodges, J.D. 1997. Development and ecology of bottomland hardwood sites. *Forest Ecology and Management* 90:117-125.

Hurney, A. P. 1973. A progress report on the calcium silicate investigations. *Proceedings of Australian Sugarcane Technology* 40: 109–113.

Iler, R.K. 1955. *The Colloid Chemistry of Silica and Silicates*. Ithaca, New York, Cornell University Press.

Iler, R. K. 1979. *The chemistry of silica: Solubility, polymerization, colloid and surface properties, and biochemistry*. Canada: John Wiley and Sons Inc.

Imaizumi, K., and Yoshida, S. 1958. Edaphological studies on silicon supplying power of paddy soils. *Bulletin of the National Institute of Agricultural Sciences (Japan)* B 8: 261–304.

J.K. Sidhu, M.J. Stout, D.C. Blouin, and L.E. Datnoff. 2013. Effect of silicon soil amendment on performance of sugarcane borer, *Diatraea saccharalis* (Lepidoptera:*Crambidae*) on rice. *Bulletin of Entomological Research* 103:656-664.

Kabata- Pendias, A., and Barbera. S. 2015. Trace elements in Soils and Plants. Boca Raton, London, CRC Press.

Kanamugire, A., Meyer, J. H., Haynes, R. J., Naidoo, G., and Keeping, M. G. 2006. An assessment of soil extraction methods for predicting the silicon requirement of sugarcane. *Proceedings of South African Sugar Technologists Association* 80: 287–290.

Karathanasis, A. D. 2006. Clay Minerals: Weathering and Alteration. In *Encyclopedia of Soil Science*, ed. Lal, R, 2: 281–286 Boca Raton, CRC Press.

Korndorfer, G.H., Snyder, G.H., Ulloa, M., Powell, G., and Datnoff, L.E. 2001. Calibration of soil and plant Silicon analysis for rice production. *Journal of Plant Nutrition* 24: 1071–108.

Kraska, J.E. and G.A. Breitenbeck. 2010. Survey the silicon status of flooded rice in Louisiana. *Agronomy Journal* 102:523–529

Lian, S. 1976. Silica Fertilization of Rice: The Fertility of Paddy Soils and Fertilizer Application for Rice, *Food and Fertilizer Technology Center*, 197–221, Taipei, Taiwan.

Ma, J. F., and E. Takahashi. 2002. *Soil, Fertilizer and Plant Silicon Research in Japan*. Boston, Massachusetts**:** Elsevier.

Matichenkov, V. V., E. A. Bocharnikova, D. V. Calvert, and G. H. Snyder. 2000. Comparison study of soil silicon status in sandy soils of south Florida. *Soil and Crop Science Society of Florida Proceedings* 59:132-137.

Meyer, J.H, and Keeping, M.G. 2001. Past, present and future research of the role of silicon for sugarcane in southern Africa. In *Silicon in agriculture: Silicon deposition in higher plants*, eds. L. E. Datnoff, G. H. Snyder, and G. H. Korndorfer, 257–276, The Netherlands: Elsevier Science.

Mehlich, A.1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis* 15:1409-1416.

Mengel, K., and Kirkby, E.A. 2001. *Principles of Plant Nutrition*, Fifth Edition, Dordrecht, Netherlands, Kluwer Academic Publishers.

Miles, N., Manson, A. D., Rhodes, R., van Antwerpen, R., and Weigel, A. 2014. Extractable silicon in soils of the South African sugar industry and relationships with crop uptake. *Communications in Soil Science and Plant Analysis* (in press).

Miyake,Y., and Takahashi, E. 1983. Effect of silicon on the growth of -cultured cucumber plant. *Soil Science and Plant Nutrition* 29: 71-83.

Nayar, P. K., A. K. Misra, and S. Patnaik. 1977. Evaluation of silica supplying power of soils for growing rice. *Plant and Soil* 47:487–494.

Oliveira L.A. 2004. Acumulação de silício em arroz e soja influenciada por diferentes condições de pH rizosferico. Uberlândia 2004. 105f. Dissertação (mestrado em agronomia) – Instituto de Ciências Agrárias da Universidade Federal de Uberlândia.

Oya, K., and Kina, K. 1989. Fertility studies on soils of Okinawa in relation to sugarcane production: pH and soluble silica in dark red soils. *Science bulletin of the College of Agriculture, University of the Ryukyus* 36: 25–31.

Oya, K., Kuroshio, K., and Hokama, Y. 1989. Fertility studies on soils of Okinawa in relation to sugarcane production. 2. Soil pH and soluble silica. *Science bulletin of the College of Agriculture, University of the Ryukyus* 36: 19–23.

Savante, N. K., Snyder, G. H., and Datnoff, L. E. 1997. Silicon management and sustainable rice production. *Advances in Agronomy* 58: 151–199.

Savante, N. K., Korndorfer, G. H., Datnoff, L. E., and Snyder, G. H. 1999. Silicon nutrition and sugarcane production: a review. *Journal of Plant Nutrition* 22: 1853–1903.

Snyder, G. H. 2001.Methods for silicon analysis in plants, soils and fertilizers. In *Silicon in agriculture: Silicon deposition in higher plants*, eds. L. E. Datnoff, G. H. Snyder, and G. H. Korndorfer, 185–196, The Netherlands: Elsevier Science.

Soil Survey Staff. 2004. Official Soil Series Descriptions. USDA NRCS. Available online at http://soils.usda.gov/technical/classification/osd/index.html. (accessed Dec 10, 2013)

Stanturf, J.A., and S.H. Schoenholtz. 1998. Soils and landforms. In *Southern forested wetlands: ecology and management*, eds. M.G. Messina and W.H. Conner, 123-147. Boca Raton, FL. Lewis Publishers/CRC Press.

Thien, S. J. 1979. A flow diagram for teaching texture by-feel analysis. *Journal of Agronomic Education* 8:54-55.

United States Department of Agriculture National Agricultural Statistics Service. Retrieved 25 June 2014.

Wang, J.J., Dodla, S.K., and Henderson, R.E. 2004. Soil silicon extractability with seven selected extractants in relation to colorimetric and ICP determination. *Soil Science* 169: 861-870.

White, A. F. 1995. Chemical weathering rates of silicate minerals in soils. *Reviews in Mineralogy and Geochemistry* 31:407–461.

Chapter 3. Release and adsorption pattern of monosilicic acid in different soils of Louisiana treated with silicon fertilizer: A laboratory incubation study

3.1 Introduction

Due to the increasing demand for food as a, consequence of exponential growth in population, crop productivity has increased with liberal scientific inputs, and little increase in the available cultivable land area. Subsequently, the plant world, which is our life support system, has been subjected to marked stress and it is plants under stress that respond most positively to silicon (Si) (Epstein 2005). Silicon is a beneficial element best known for its significant role in alleviating biotic and abiotic stress in various crops during the formative period (Epstein 2005; Datnoff et al. 2001). There is a large body of evidence from scientists around the world about the utility of this element in improving yields of crops like rice (*Oryza sativa*), sugarcane (*Saccharum officinarum*), wheat (*Triticum aestivum*), sorghum *(Sorghum bicolor),* corn (*Zea mays*) and millets (*e.g.,Eleusine coracana)* especially when subjected to stressful growing conditions like drought, salinity, pests and diseases (Datnoff et al. 2001). Today, Si fertilization has become an agronomic practice in the Histosols of Florida (USA) and the Oxisols of Brazil (Datnoff et al. 2001, 1997). Silicon absorption by plants occurs as monosilicic acid (H_4SiO_4), being proportional to the Si concentration in soil solution (Jones and Handreck 1967; Fox et al. 1967). Most H_4SiO_4 in the soil is weakly adsorbed (Matichenkov 1990). Monosilicic acid migrates very slowly in the soil profile (Khalid Silva 1980) and forms complexes with heavy metals and organic compounds in soil solution (Datnoff et al. 2001). Monosilicic acid will remain in solution in the monomeric state in neutral and weakly acidic solutions. However, an analytically important fact is that at the appropriate pH and concentration, H_4SiO_4 released from these fertilizers, such as slag and wollastonite, will in course of time polymerize (Berthelson and

Korndorfer 2005). The total Si content of soils has an insignificant relationship to the concentration of soluble Si in soils, which is the component vital for plant growth. In other words, the concentration of soluble Si in soils is dynamic. Therefore, the exact value of the total H_4SiO_4 concentration available for plant uptake with time, from these fertilizers cannot be obtained directly from the Molybdenum blue Colorimetry (MBC) or spectrophotometric methods.

Given the paucity of information and procedures to compare the sources of Si (slag and wollastonite) used today with respect to solubility, soil property interferences, H_4SiO_4 released for plant uptake, further research is imperative to evaluate their potential as fertilizers. Even today, we are yet to determine the best source and also the rate of distributive application of these fertilizers in different soils of Louisiana. Often times, there is a decrease in biomass yield when these fertilizers are applied at a higher rate. Haynes et al. (2013) observed a similar scenario and reported that this growth reduction is attributable to the combined effect of the very high pH (possibly also inducing deficiencies of Zn and Mn for steel slag) and electrical conductivity (EC) (and high Na for processing mud) in soils from these treatments at the high Si rate. This decline could also be attributed to a decrease in H_4SiO_4 due to polymerization (Iller 1979). The purpose of this study was to document the potential release of H_4SiO_4 from Si fertilizers and its relationship with properties including clay content, organic matter content and pH of soils from six different soil series. This study was undertaken based on the hypothesis that the concentration of H_4SiO_4 in soil solution after the addition of high quantities of Si fertilizers in soil is influenced by polymerization and adsorption (a process controlled by the soil physico-chemical properties including presence of metal oxides and hydroxides, clay and organic matter content and soil pH). For the purpose of this study, the term sorption is defined as transfer of ions from the solution phase to the solid phase via various mechanisms such as physical and chemical adsorption, surface precipitation and absorption (fixation) as given by Apak (2002). The objectives were to: 1) quantify the adsorbed fraction of added H_4SiO_4 in soil solution with time; 2) document the effect of addition of wollastonite and slag on the concentration of H_4SiO_4 in soil solution within a 200-day period; and 3) evaluate the relationship between quantity of sorbed H_4SiO_4 and polymerized H_4SiO_4 with the addition of wollastonite and slag in different Louisiana soils.

3.2 Materials and Methods

Monosilicic acid sorption was investigated using six soil series of Louisiana (Figure 3.1). Total clay percent, acetic acid extractable Si, organic matter content, oxyhydroxides of iron (Fe) and aluminum (Al); and pH of different soil series are provided in Table 3.1.

3.2.1 Silicon analysis

Silicon concentration in soil extracts was determined using Molybdenum Blue Colorimetry (Korndorfer et al. 2001). Known volume of filtrate was transferred into a plastic centrifuge tube and then 10 mL of deionized water, plus 0.5 mL of 1:1 hydrochloric acid (HCl), and 1 mL of 10% ammonium molybdate [$(NH_4)_6Mo_7O_2$] solution (pH 7.5) were added. After 5 minutes, 1 mL of 20% tartaric acid solution was added and after two minutes, 1 mL of the reducing agent amino napthol n-sulphonic acid (ANSA) was added. After five, but not later than 30 minutes following addition of the reducing agent**,** absorbance was measured at 630 nm using UV visible spectrophotometer (Hach DR 5000). Simultaneously, Si standards (0.2, 0.4, 0.8 and 1.2 mg L^{-1}) prepared in the same matrix were also measured using UV visible spectrophotometer.

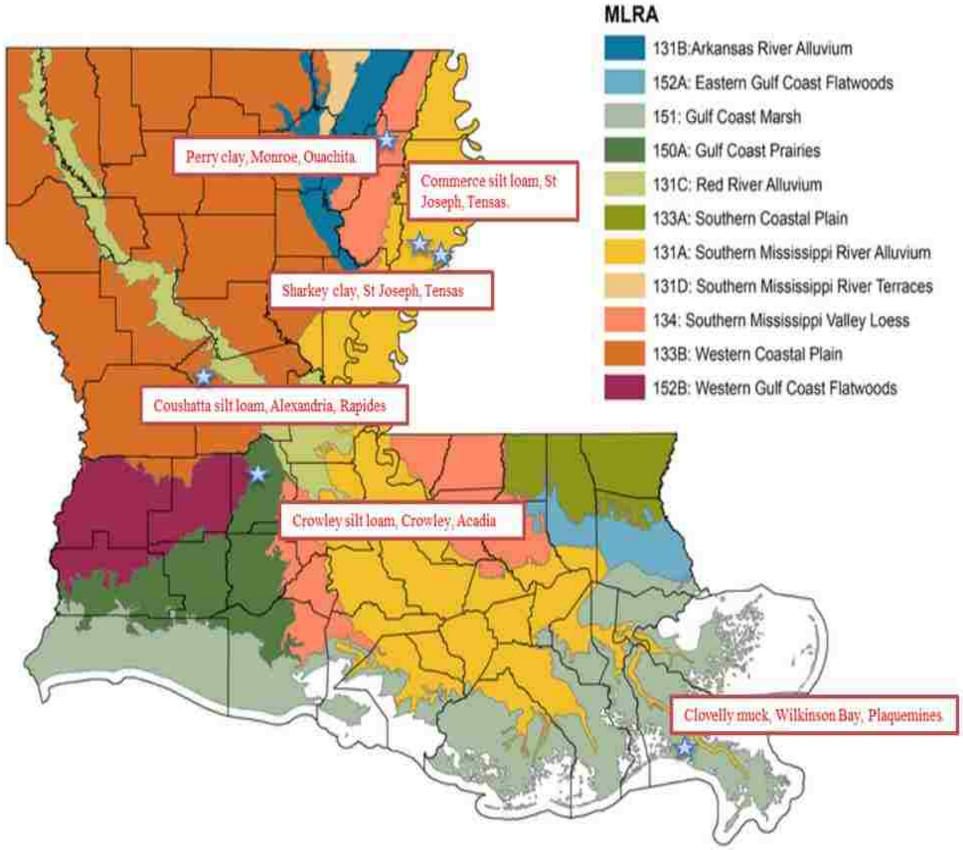


Figure 3.1 Major land resource areas and locations in Louisiana where the bulk soil samples were collected for the greenhouse studies conducted during the years 2014 and 2015.

Table 3.1 Selected properties of the six different soil series used in the study

Soil type	pH (1:1 soil : water)	Si* (ug g^{-1})	Fe** (ug g^{-1})	Al** (ug g^{-1})	Total clay*** (%)	Organic matter**** (%)
Caushatta silt loam	7.8	77	634	51	18	3.41
Clovelly muck	5.6	53	515	390	26	8.08
Sharkey clay	5.7	82	645	90	32	2.24
Perry clay	5.3	41	1373	128	32	2.71
Crowley silt loam	5.0	8	829	76	4	1.26
Commerce silt loam	5.6	32	444	49	7	1.79

* Si determined by 0.5 M acetic acid extraction and Molybdenum Blue Colorimetry. **The dithionite–citrate–bicarbonate (DCB) extraction was applied to quantify crystalline and non-crystalline Fe and Al oxyhydroxides (Mehra and Jackson 1960). ***X-Ray Diffraction***Walkley and Black (1934).

3.2.2 Sorption study of H_4SiO_4

A standard solution of H_4SiO_4 was prepared by passing an aqueous solution of sodium orthosilicate (0.5 g in 1 L of deionized water) through a column of strongly acidic cation exchange resin at the rate of 1 L in 30 minutes through a column packed with 10 g resin (Wickramasinghe and Rowell 2005). The resulting solution was checked for the concentration of H_4SiO_4 and diluted to obtain the required standard solutions with concentrations up to 50 ug Si ml^{-1} in 0.1 M sodium chloride (NaCl). These solutions were used for the sorption experiments. According to Obihara and Russell (1972) and McKeague and Cline (1963) sorption isotherm for silicate was the same whether the supporting electrolyte was 0.1 M NaCl or 0.01 M or 0.02 M $CaCl_2$. Additionally, results from our preliminary experiments showed that polymerization was minimal or absent when the concentration was below 50 ug ml^{-1} and when prepared in 0.1 M NaCl, which was also in agreement with results reported by Wickramasinghe and Rowell (2005).

Samples of soil (1 g) were weighed into 50 mL polypropylene centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl solution for 4, 7 and 30 days on an orbital shaker. The 0.1 M NaCl solutions consisted of 0, 10, 20, 40 and 50 ug ml^{-1} Si added as H_4SiO_4. The soils were shaken at 50 rpm in an orbital shaker at 25°C in the presence of few drops of toluene to inhibit microbial growth. After the equilibration period, the samples were centrifuged; aliquots of the supernatant were removed, analyzed for pH and for Si concentrations using UV- VIS Spectrophotometer (Hach DR 5000) according to the method given by Korndorfer et al. (2001). The equilibrium period (the duration after which there was no change in adsorbed quantity) was estimated by plotting sorbed quantity against time. The sorption isotherms were then plotted (solution Si concentration against Si sorbed).At equilibrium period, the concentration of Al, Fe, manganese (Mn) and magnesium (Mg) ions in the supernatant solutions of all six soils with no added Si was determined using ICP-OEM (Inductively Coupled Plasma- Optical Emission Spectroscopy). The pH of the supernatant solution was also measured at the end of 4, 7 and 30 days of incubation.

3.2.3 Effect of time on H_4SiO_4 release from Si fertilizer

Incubation experiments were carried out on all six soils to investigate Si dissolution from soils and fertilizers. One gram of soil in duplicate was shaken gently with 25 mL of 0.1 M NaCl at 25°C in polypropylene bottles. The following treatments were imposed on each of the soil series: soil alone, soil +100 mg of wollastonite (equivalent to 23 mg Si), and soil +135 mg of slag (equivalent to 23 mg Si). Also, wollastonite and slag were incubated with no soil added during the same time period. The solution mixtures were homogenized and incubated at 25°C. This procedure was done by maintaining samples separately for each time interval. The bottles were kept standing at 25°C and were shaken by hand daily for 30 seconds. Subsamples were removed at fixed intervals within the 200 days incubation period (after 10 and 30 minutes, 4 and 24 hours, 7th, 15th, 30th, 60th, 90th, 120th, 150th, 180th and 200th day). Before each sampling, the bottles were shaken continuously for 2 hours in an orbital shaker at 25°C. They were then centrifuged at 1500 rpm for 20 minutes and then filtered using Whatman 42 filter paper. The concentration of H_4SiO_4 in the supernatant solution was measured using UV- VIS Spectrophotometer (Hach DR 5000) according to the method given by Korndorfer et al. (2001). Altering the pH of the soils was not attempted, but rather pH values in 0.1 M NaCl solution at the end of every incubation period were measured.

3.2.4 Effect of Si concentration on release of H_4SiO_4 from Si fertilizer

Soil samples (1 g) were added to 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl solution for 7 days. The soil samples consisted of 0, 4.25, 8.5, 17 and 34 mg of slag and 0, 3.12, 6.25, 12.5 and 25 mg of wollastonite.. The soils were maintained at 25°C in the presence of few drops of toluene to inhibit microbial growth. After the equilibration period, the samples were shaken at 50 rpm in an orbital shaker at 25°C, centrifuged; aliquots of the supernatant removed, and analyzed for pH and Si concentrations using UV- VIS Spectrophotometer according to the method given by Korndorfer et al. (2001). Another set consisted of 4.25, 8.5, 17 and 34 mg of slag and 3.12, 6.25, 12.5 and 25 mg of wollastonite in 0.1 M NaCl solution with no added soil. The concentrations of H_4SiO_4 in the supernatant solution were plotted against the increasing concentration of Si added (with increasing increments of slag and wollastonite). Analysis of variance (ANOVA) was performed using PROC MIXED in SAS 9.4 (SAS Institute, 2012) to determine significant effects of treatments on soil. For understanding the treatment effect ($P<0.05$), mean comparison was done by contrast and the best model describing the data was identified as quadratic. Quadratic regression (Microsoft® Excel 2013) was performed to determine the trend of change in concentration of H_4SiO_4 in supernatant solution with increasing concentration of Si added. The metal cations in the supernatant solution at the end of 7 days of incubation were determined using ICP-OEM. Analysis of variance (ANOVA) was performed using PROC MIXED in SAS 9.4 (SAS Institute, 2012) to determine significant effects of treatments. For significant treatment effect ($P<0.05$), mean separation was done by Tukey–Kramer post-hoc test to identify treatment differences and this data is presented in Table 3.3.

3.2.5 Estimation of polymerized and sorbed quantity of H_4SiO_4 in different soils of Louisiana treated with slag and wollastonite

Acetic acid (0.5 M) extraction procedure after 0.1 M NaCl incubation and extraction was used to estimate the concentration of H_4SiO_4 polymerized, sorbed and that remaining in solution. Analysis of variance (ANOVA) was performed using PROC MIXED in SAS 9.4 (SAS Institute,

2012) to determine significant effects of treatments on quantities of Si released into 0.5 M acetic acid in different soils at the end of 200 days of incubation in 0.1 M NaCl. For significant treatment effect ($P<0.05$), mean separation was done by Tukey–Kramer post-hoc test to identify treatment differences and this data is presented in Figure 3.8.

Dilute salt solutions like 0.1 M NaCl provided a measure of the readily available Si present in the soil solution, while results obtained using 0.5 M acetic acid gave an account of total silicon by solubilizing polymerized forms of Si. After analyzing for the concentration of H_4SiO_4 in 0.1 M NaCl solution on the 200th day, ten mL of 0.5 M acetic acid was used to replace the 0.1 M NaCl solution in all treatments (six replicates) and shaken for 1 hour at 50 rpm in an orbital shaker at 25°C before centrifuging and filtering using Whatman No. 42 filter paper. The acetic acid extraction procedure brought the polymerized (heavy molecules formed and settled at the soil surface during the 200 days of incubation) forms of Si back into solution as H_4SiO_4. Thus, the total Si, T_1 (H_4SiO_4 + polysilicic acid) released from the fertilizer sources into the solution (0.5 M acetic acid and that in 0.1 M NaCl) at the end of 200 days of incubation period was calculated as the sum of concentration of H_4SiO_4 in 0.5 M acetic acid and that in 0.1 M NaCl with only added fertilizers (without soil sorption). The total Si, T_2 (H_4SiO_4 + polysilicic acid) released from fertilizer + soil mixtures into the supernatant solutions of different soils was calculated as the sum of H_4SiO_4 released from fertilizers with added soil in 0.5 M acetic acid and in 0.1 M NaCl solution. The sorbed quantity of H_4SiO_4 on different soils was calculated as the difference between the concentration of H_4SiO_4 in solutions (0.5 M acetic acid and 0.1 M NaCl) from fertilizer materials (slag or wollastonite) without and with soils (sorption surface) which is equal to S_1 (T_1-T_2). Finally, the polymerized quantity in each soil was estimated as T_2- S_1. The relationship between the quantities that was polymerized, sorbed, and remained in solution was shown graphically among the six soils with slag and wollastonite.

In a different experiment, centrifuge tubes with slag or wollastonite added at a rate equivalent to 23 mg Si were shaken in an end to end shaker with 10 ml of 0.5 M acetic acid (allowing no polymerization) to determine the total Si released from the fertilizers into an acidic solution at fixed time intervals without the effect of polymerization. Total concentration of H_4SiO_4 in the filtered solution was determined after 10 minutes, 30 minutes, 1 hours and 2 hours using UV- VIS Spectrophotometer according to the method given by Korndorfer et al. (2001). The X-Ray diffraction (XRD) patterns of slag and wollastonite were obtained using picker powder diffractometer with a graphite crystal in which diffracted beam monochrometer was used to run the X-ray diffraction scans. The percent clay content was also determined in the 6 different soils using the XRD patterns of the soils (Cook et al. 1975). Digital images were taken of two fertilizers (slag and wollastonite) and elemental composition was determined using a SEM equipped with EDX capabilities (FEI Quanta 3D FEG FIB/SEM with EDAX TEAM™ PEGASUS EDS) to look into the differences in the elemental composition of these fertilizers.

3.3 Results and Discussion

3.3.1 Sorption study of H_4SiO_4

3.3.1.a. Effect of H_4SiO_4 concentration on sorption

The sorbed quantity increased with increasing equilibrium concentration of H_4SiO_4 for all of the tested soil samples (Figure 3.2). The net sorption was zero when no H_4SiO_4 was added to the soil. There were only small increases at lower levels of equilibrium concentration in all soils with greater sorption taking place at higher levels of equilibrium concentration. However, at the two highest levels of equilibrium concentrations, all soils tend to attain a saturation point in sorption with little or no increases observed. Therefore, the shape of these sorption isotherms fell into the S−type isotherms (Evangelou 1998; Huang et al. 2006). Huang et al. (2006) explained the initial slow increase in sorbed silicate was probably due to the strong competition of other anions with the added silicate ion for the available sorption sites in the soils. They further stated that, after the equilibrium concentration reached a certain level the rapid increase in sorption indicated that the silicate ion replaced some of the exchangeable anions with an increase in soluble silicate concentration. After this the increase in sorption slowed down again as equilibrium concentration reached higher levels, which could be attributed to the added silicate approaching saturation of anion exchange sites. Sorbed quantity of H_4SiO_4 in the selected soils followed the order Caushatta silt loam > Clovelly muck> Sharkey clay > Perry clay > Crowley silt loam > Commerce silt loam. Yu and Li (1999) also found similar results and stated that silicate sorption increased rapidly with increasing equilibrium concentration at low levels and slowly at the high levels, resulting in curves that were concave downwards. In contrast, Gao et al. (1998) found silicate sorption increased slowly at low levels, and rapidly at the high levels, resulting in curves that were concave upwards. Differences among the results of these groups might be due to different physicochemical properties of the soils, different reaction times, water: soil ratios or initial silicate concentrations. Further studies should be undertaken to address the relative importance of the possible reasons for the differences in isotherm shapes that different researchers reported. Caushatta silt loam had an initial soil pH of 7.8, which went up to 8.2 after 7 days of incubation in 0.1 M NaCl. Whereas the soil pH of the other 5 soils used in this study was below 7.5 (Appendix B).The quantity of sorbed H_4SiO_4 was maximum in Caushatta silt loam. This could be attributed to the fact that there is an increase in concentration of silicate ions when the soil pH reaches as high as 8 (Sheikholeslami and Tan 1999). Iller (1978) stated that at pH 7 and higher, there is an increasing degree of ionization of H_4SiO_4 to silicate ions, and these are adsorbed and can form a silicate-type bond with a variety of hydroxides that are in a highly dispersed state in the soil solution. The data obtained showed that a pH-dependent sorption reaction is involved in controlling the concentration of silica in soil solutions as has been proven in a study conducted by McKeague and Cline (1963).

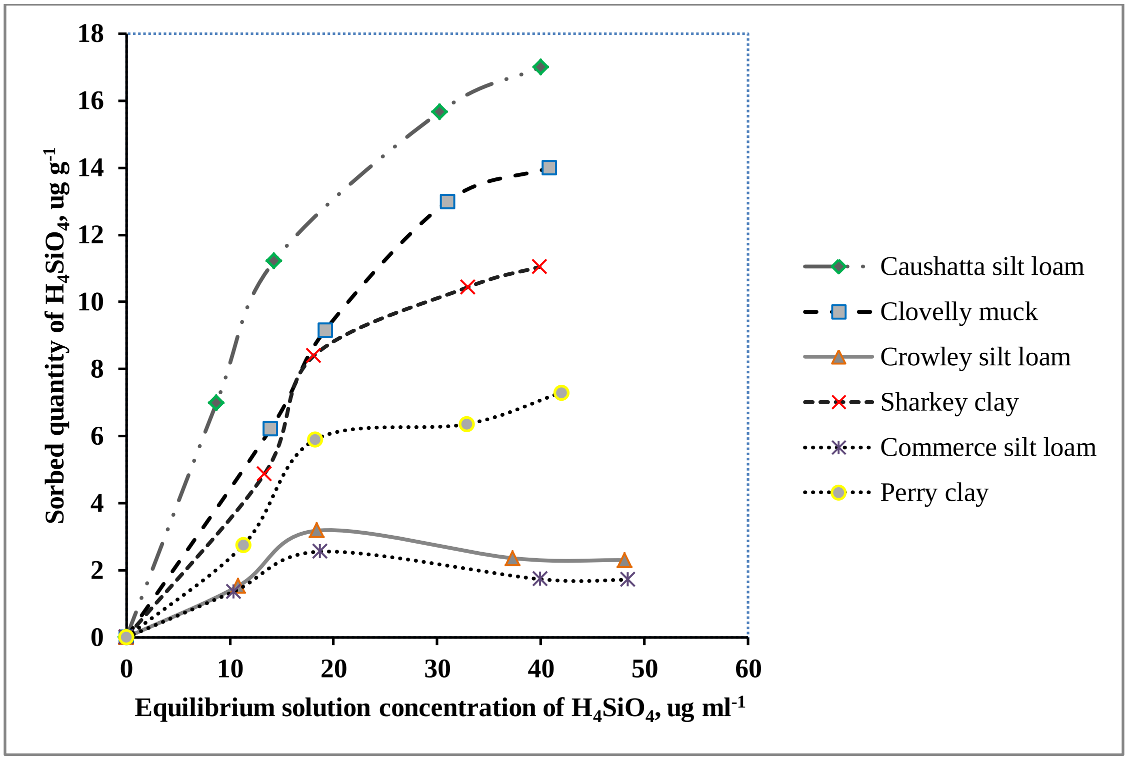


Figure 3.2 Amount of H_4SiO_4 sorption in six different soils after seven days of incubation in 0.1 M NaCl with varying concentrations of monosilicic acid

As shown in Figure 3.2, although the total sorbed quantity of H_4SiO_4 in Clovelly muck, which is the soil with highest organic matter content, was lower than Caushatta silt loam, this soil had a sorbed quantity of 14 ug g^{-1} of H_4SiO_4, which was greater than the two clay soils used in this study. The dithionate-citrate-bicarbonate (DCB) extraction measured 390 and 515 ug g^{-1} of Al and Fe oxyhydroxides respectively in this soil. In a previous study conducted by Harder (1965), silica was adsorbed and precipitated by hydroxides of Al, Fe, manganese (Mn), and magnesium (Mg) .Sesquioxides and phyllosilicates are a significant component of most soil systems, and many investigators believe that these minerals play a major role in determining the concentration of silica in soils (McKeague and Cline 1963; Beckwith and Reeve 1963, 1964;

Jones and Handreck 1963). Additionally, the highest quantity (390 ug g^{-1}) of Al oxyhydroxides was measured in Clovelly muck among all the other soils used in the study. Both Fe and Al oxides adsorb H_4SiO_4 but among oxides of similar crystallinity, Al oxide is more effective than ferric oxide (Jones and Handreck 1965). This was also evident in the clay soils (Sharkey clay and Perry clay) and organic soil (Clovelly muck) recording the highest quantity of sorbed H_4SiO_4 among the soils with near neutral pH having the highest quantity of Al-oxyhydroxides in the current study (Table 3.1).

It was also observed that organic matter content magnified the sorption more than the total clay content (Figure 3.2). This could be ascribed to three main reasons. First one being that the Mg^{2+} ions brought into the solution from the organic soil was 175 ug g^{-1} compared with 81 and 45 ug g^{-1} from Perry clay and Sharkey clay soils, respectively (Table 3.3). These Mg^{2+} ions could have directly or indirectly reduced the H_4SiO_4 in solution by co-precipitation or sorption of H_4SiO_4 on freshly formed metal hydroxides. Negatively charged surfaces are not receptive to the sorption of H_4SiO_4 but can be made so by the well-known methods used for preparing surfaces for the deposition of metals such as treatment with polybasic metal salts of Fe or Al which are known to reverse the charge on negative surfaces (Iller 1978). As shown in Table 3.3 the reduction of Fe and Al in the soils under anaerobic condition brought free Fe^{2+}, Mn^{2+} and most importantly Mg^{2+}ions into solution and made them available to reverse the surface charges on mineral surfaces and H_4SiO_4 could have been sorbed on these surfaces forming the siloxane bridges described by Chadwik et al. (1987). Also, H_4SiO_4 can react with Al, Fe, and Mn, forming slightly soluble silicate substances in solution (Horigushi, 1988; Lumsdon and Farmer, 1995). Bien et al. (1958) showed that sorption on suspended particles in the presence of electrolytes is also effective in removing dissolved silica from very dilute solutions. Iller (1978) also brought into light the fact that silica, both soluble and colloidal can be removed from water to varying low levels in neutral or slightly alkaline solution by co-precipitation with insoluble metal hydroxides *in situ* or by sorption upon freshly formed hydroxides added to the water. Wohlberg and Bucholz (1975) reviewed the literature on the reduced solubility of silica in the presence of metal salts and hydroxides. The second reason for the greater quantity of sorption in Clovelly muck would be that, the higher organic matter content in this soil, increased the total surface area available for sorption reactions. The relationship between surface area of solid and removal of H_4SiO_4 from solution is consistent with the results of McKeague and Cline (1962) who proved that a sorption reaction involving H_4SiO_4 increases with surface area of the substrate. Likewise, minimum sorption of H_4SiO_4 was recorded in the soils with soils of comparatively lower surface area (due to the textural difference), namely Crowley silt loam and Commerce silt loam soils and also with minimum free Mg^{2+} ions in solution after 7 days of submergence. The third reason, as discussed earlier, the presence of Al and Fe oxyhydroxides decreased the H_4SiO_4 in solution with Al having greater effect (Jones and Handreck 1965).

Further, an increase in the sorbed quantity of H_4SiO_4 with an increase in its solution concentration was observed. This was in agreement with the results discussed by Iller (1978) who concluded that silica will be deposited from supersaturated solution onto a solid surface at a rate that increases with degree of supersaturation. In this study, we observed that although Perry clay had the highest quantity of Fe and Al oxyhydroxides, the quantity sorbed was highest in Sharkey clay irrespective of added concentration of H_4SiO_4. This difference between the two clay soils could be attributed to the initial Si content in these soils with Sharkey clay having 82 ug g^{-1} Si which was greater than Perry clay with 41 ug g^{-1} Si

Table 3.2 Mean concentration of metal ions in the supernatant solution of different soils studied analyzed in ICP-OEM

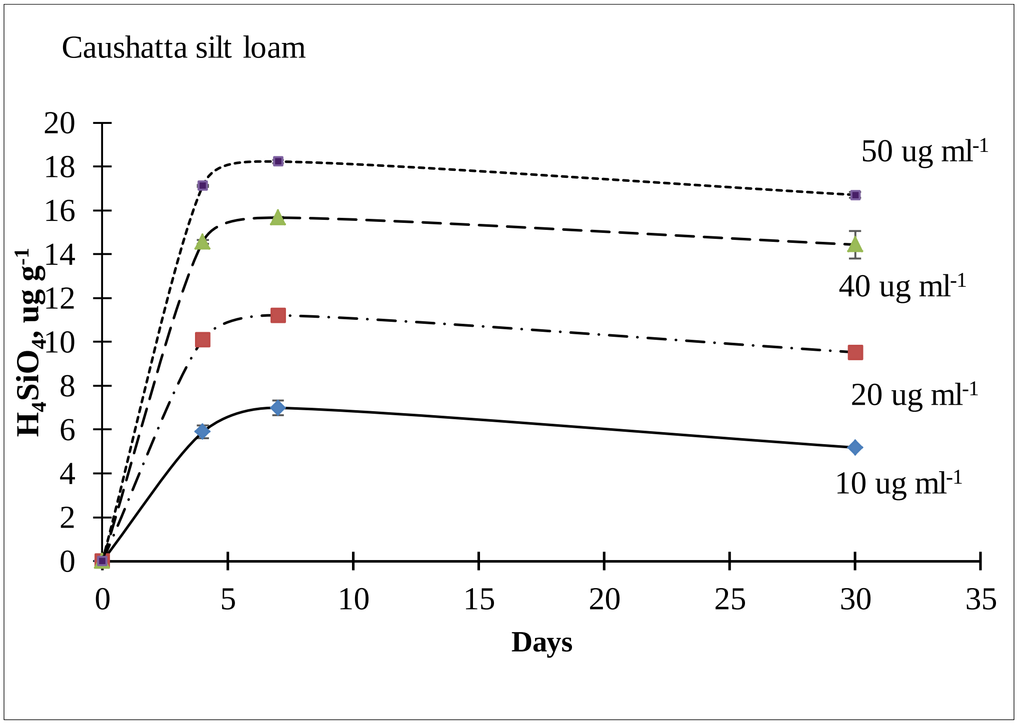
Soil type	[1]Al	Fe	Mn	Mg
	………..…………………ug ml^{-1}	……………………………		
Clovelly muck	[2]ND	0.006	1.73	175
Caushatta silt loam	ND	0.086	0.39	19
Sharkey clay	ND	0.141	6.64	45
Perry clay	ND	0.270	3.90	81
Commerce silt loam	0.024	0.023	2.21	12
Crowley silt loam	ND	0.230	4.30	7

[1]concentration of Al, Fe, Mn and Mg detected in the supernatant solution of 0.1 M NaCl. [2]ND = non-detectable concentrations

3.3.1.b. Effect of incubation time on sorption

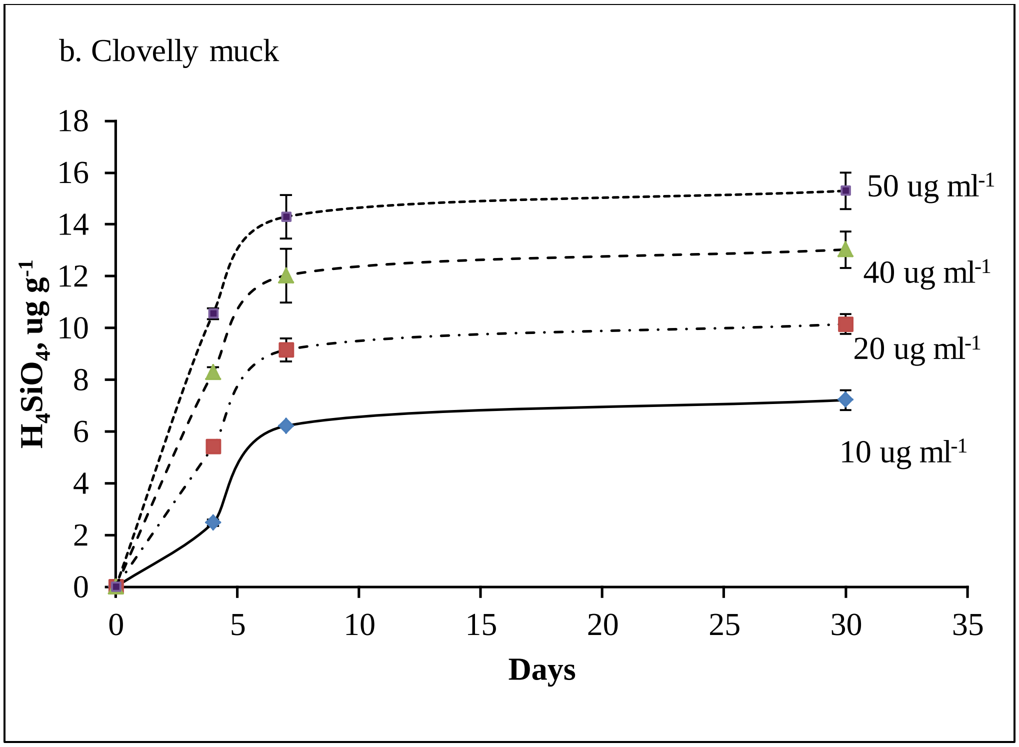
There was no net sorption of H_4SiO_4 before 24 hours of incubation. Clovelly muck had the highest sorption within 7 days of incubation, followed by the clay soils with sorption greater than silt loam soils (Figure 3.3a, 3.3b, 3.3c, 3.3d, 3.3e and 3.3f). All soils showed an increase in sorption with time up to 7 days during the 30 days of incubation period. There was no further increase in sorption after 7 days in this study. Therefore, the estimated equilibration time for these soils was around 7 days after incubation. The change in total sorption recorded between 4 and 7 days of incubation, in the high pH soil (Caushatta silt loam) was lower than clay soils (Sharkey clay and Perry clay) and organic soil (Clovelly muck) and similar to what was observed in silt loam soils (Commerce silt loam and Crowley silt loam).

From these results, one can infer that, in a soil with near neutral pH, combined effects of organic matter content, oxyhydroxides of metal cations and clay content would have more influence on total sorption of H_4SiO_4 from solution than the sole effect of soil pH. Also, among the soils with acidic to near neutral pH, soils with particles of greater surface area determined by the total clay content and organic matter content (Table 3.1), continued to show greater sorption during the entire duration of incubation over the others. Similar relationship between sorption and the particle size (specific surface area) was established by McKeague and Cline (1962). Results of studies of the removal of H_4SiO_4 from solution in the presence of soils support the hypothesis, suggested by studies of the dissolution of silica from soils, that sorption of dissolved silica on soil particle surfaces plays a significant role in controlling the concentration of H_4SiO_4 in soil solutions (McKeague and Cline 1963) although leaching of silica from the soil and quantity taken up by crops are also important in determining silica concentrations in soils (Kittrick 1969).

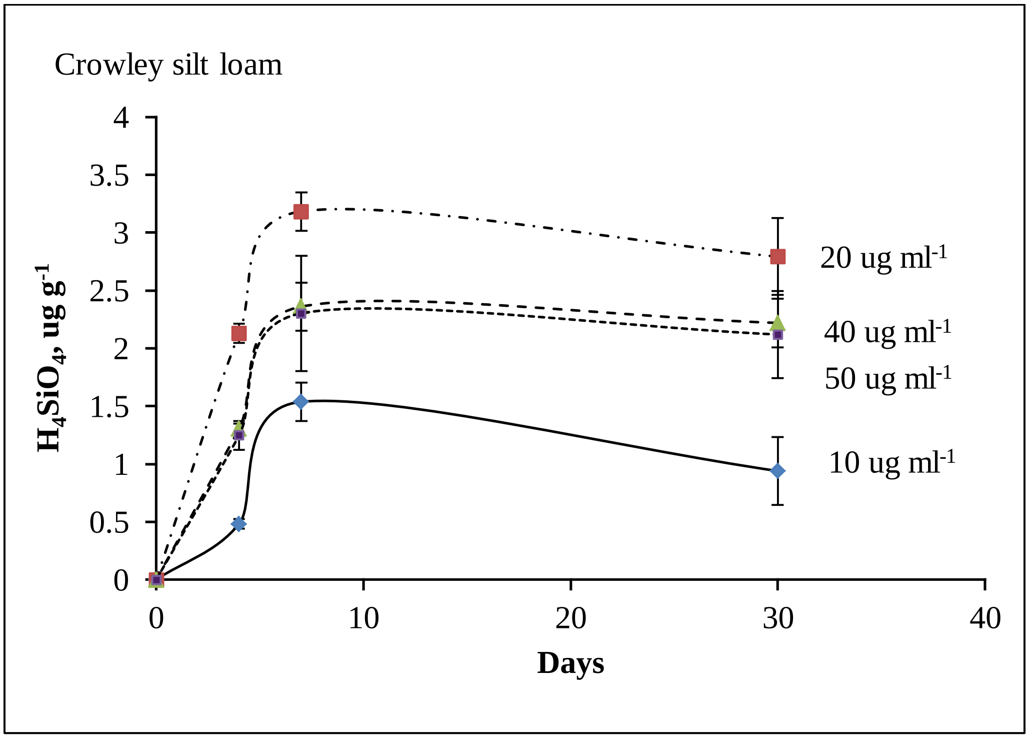


a.

Figure 3.3 Amount of H_4SiO_4 sorbed in Caushatta silt loam soil (a), Clovelly muck (b), Crowley silt loam (c), Sharkey clay (d), Commerce silt loam (e) and Perry clay (f) after 4, 7 and 30 days of incubation in 0.1 M NaCl with varying concentrations of monosilicic acid

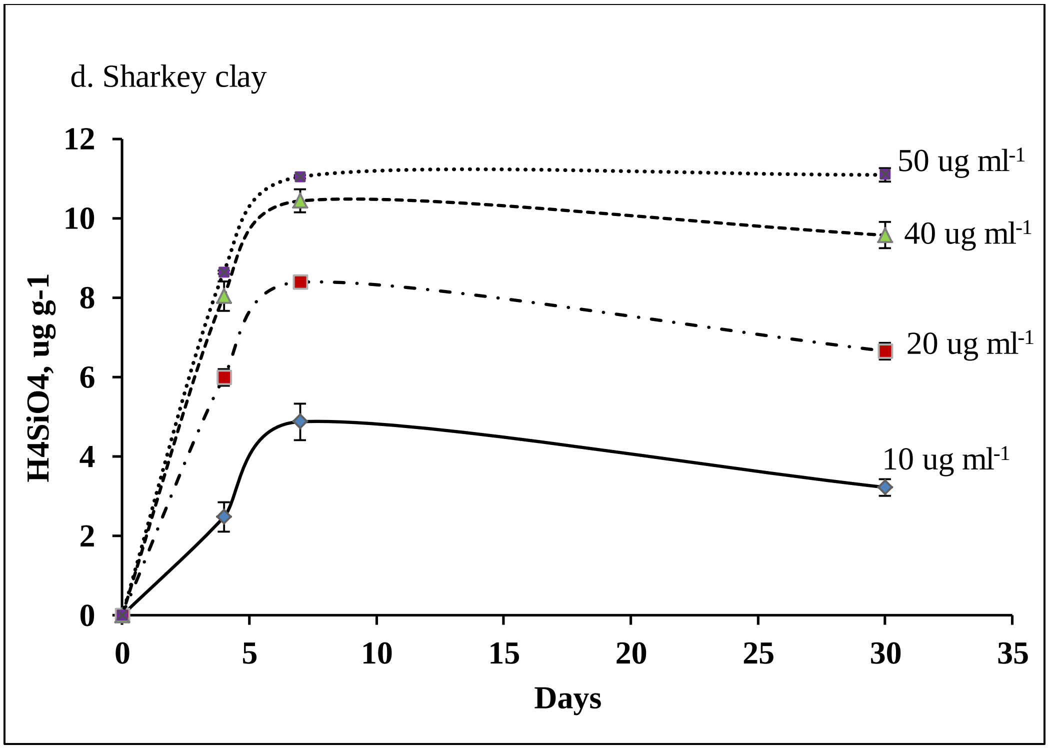


b.

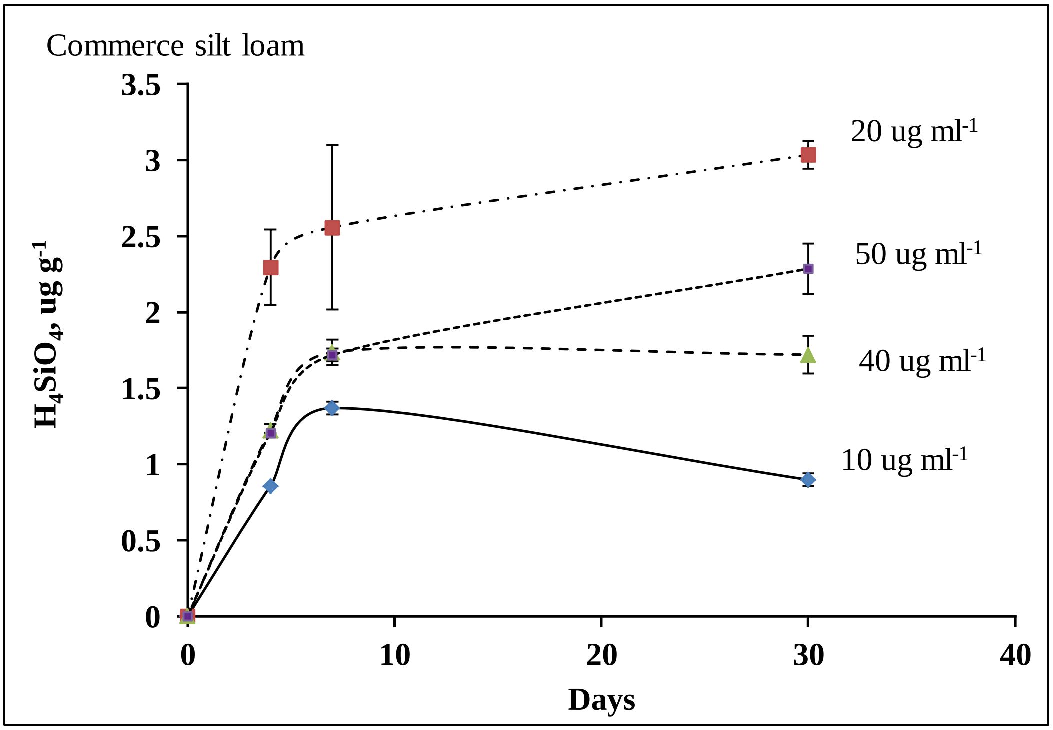


c.

(Figure 3.3 continued)

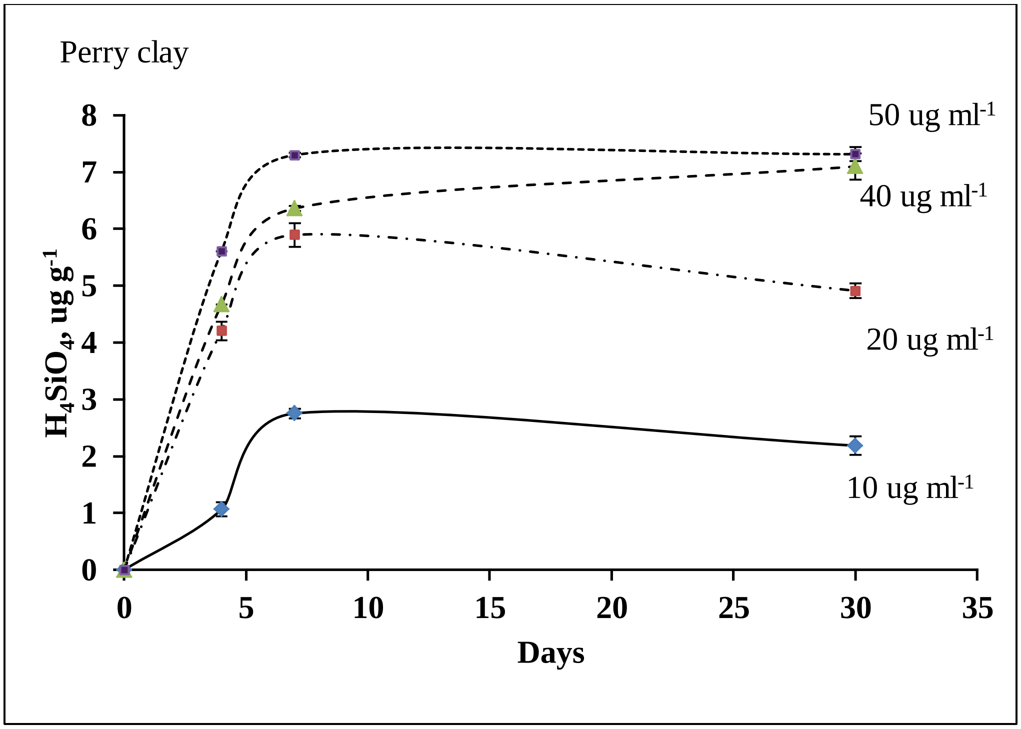


d.



e.

(Figure 3.3 continued)

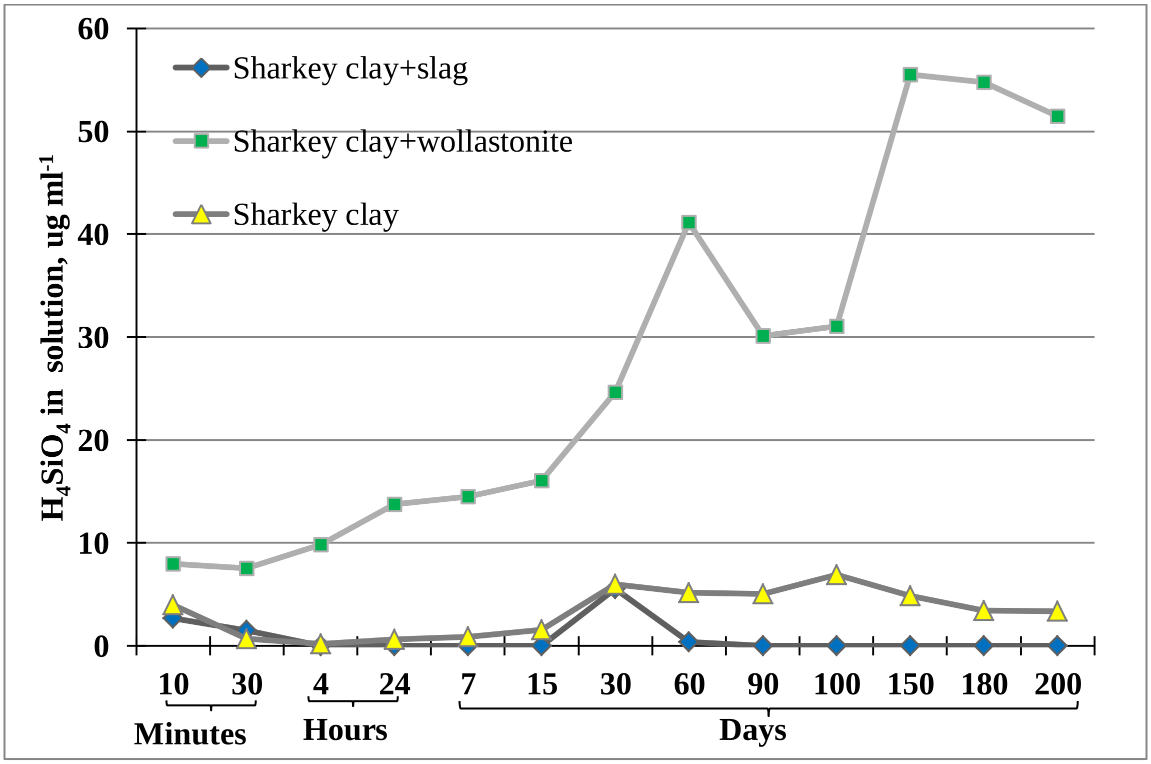


f.

(Figure 3.3 continued)

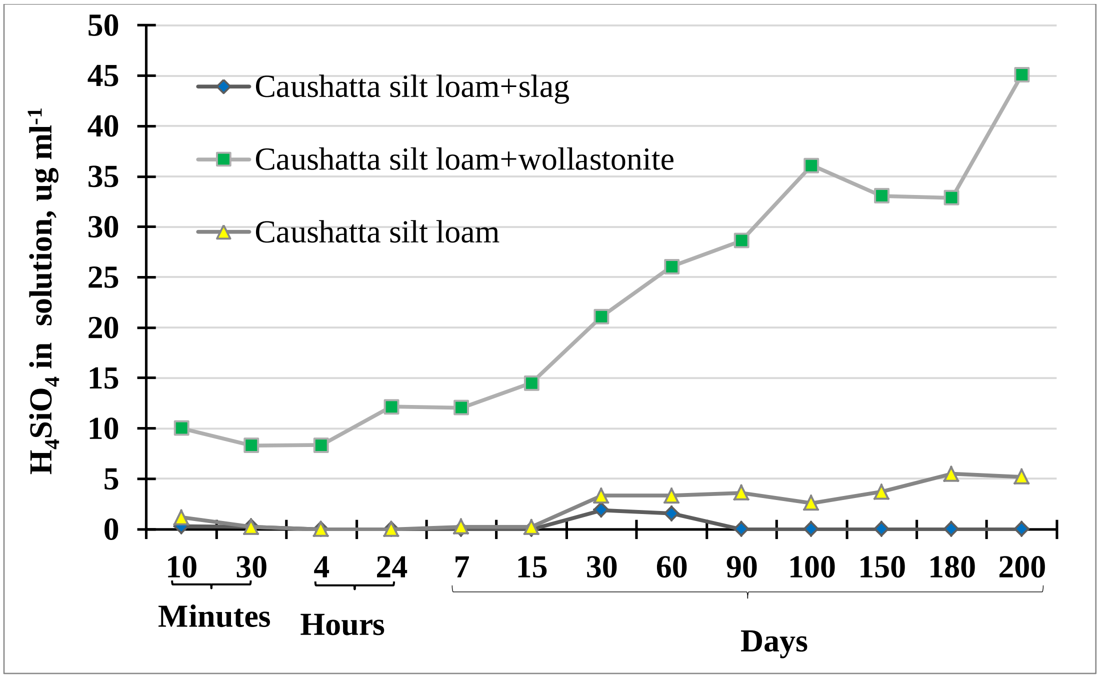
3.3.2 Effect of time on H_4SiO_4 release from Si fertilizer

An increase in the concentration of H_4SiO_4 in the supernatant solution of all the soils was recorded, when the source of Si added was wollastonite (Figure 3.4). Interestingly, on the other hand, there was no detectable concentration of H_4SiO_4 in the supernatant solutions of all soils when slag was the source of added Si. This trend of decreasing concentration of H_4SiO_4, monitored throughout the incubation period of 200 days was gradual in the case of wollastonite whereas there was a sudden decline to below detection levels within 7 days of incubation, in the case of slag. This reduction in concentration was much greater than the sorbed quantities of H_4SiO_4 measured in different soils (Table 3.3). Therefore, this reduction of H_4SiO_4 from solution could not be attributed to soil sorption alone, but also could be attributed to the phenomenon of polymerization of H_4SiO_4 at high concentrations. The decrease in concentration of molybdate-reactive silica was monitored over time by Icopini et al. (2005) to determine the extent of oligomerization. They found this decrease in concentration of molybdate-reactive silica is accompanied by the appearance of a transient population of nanocolloidal particles with diameter 3 nm, as determined by atomic force microscopy (AFM). This could have been the polymerized species of Si. Monosilicic acid will remain in solution in the monomeric state in neutral and weakly acid solutions. However, rapid polymerization occurs at high solution concentrations, with increasing soil pH and in the presence of oxides and hydroxides of Al and Fe (Berthelsen and Korndorfer 2005). This could be a reason for the rice and wheat yield depression observed at higher rates of slag applications (Haynes et al. 2013; Abro et al. 2009) concurrent with the decline in 0.01 M Calcium chloride extractable Si in soils.

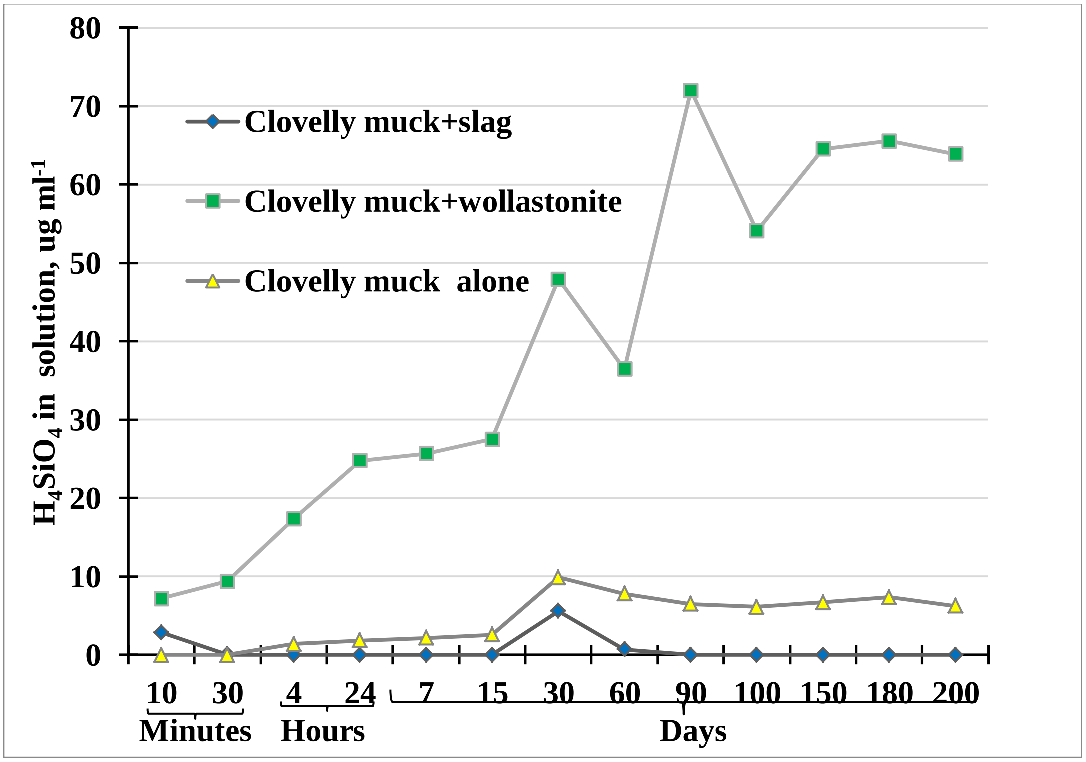


a.

Figure 3.4 Concentration of H_4SiO_4 in solution of sharkey clay (a), Caushatta silt loam (b), Clovelly muck (c), Perry clay (d), Crowley silt loam (e) and Commerce silt loam (f) soils treated with 23 mg Si g^{-1} as wollastonite and slag within a period of 200 days.

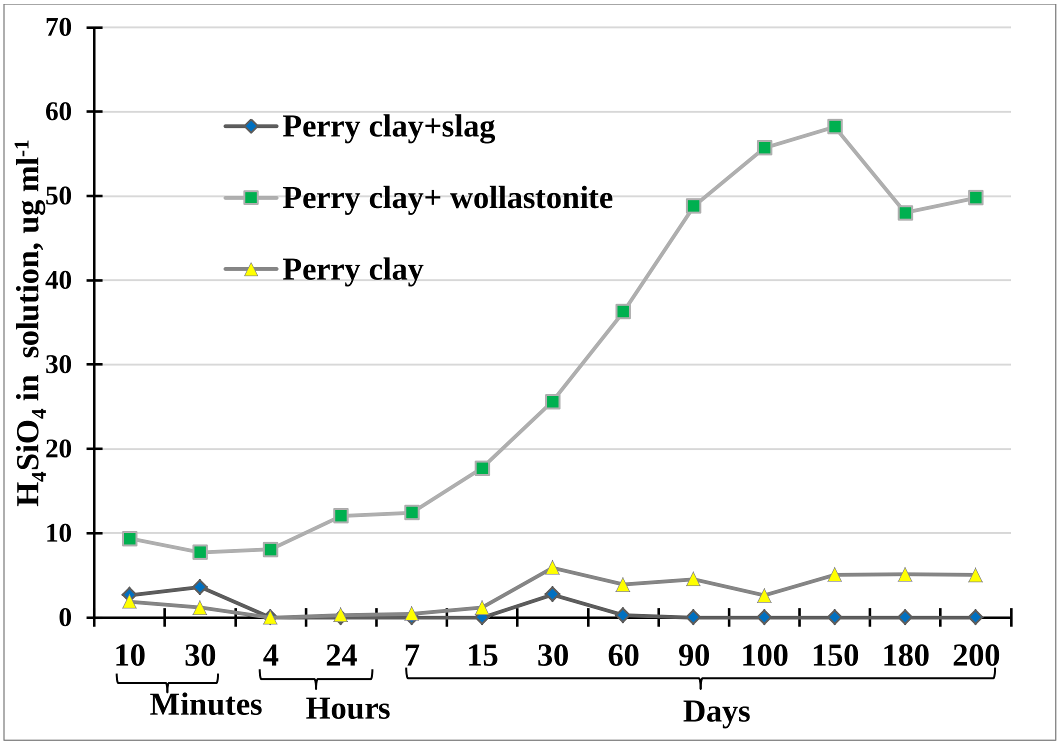


b.

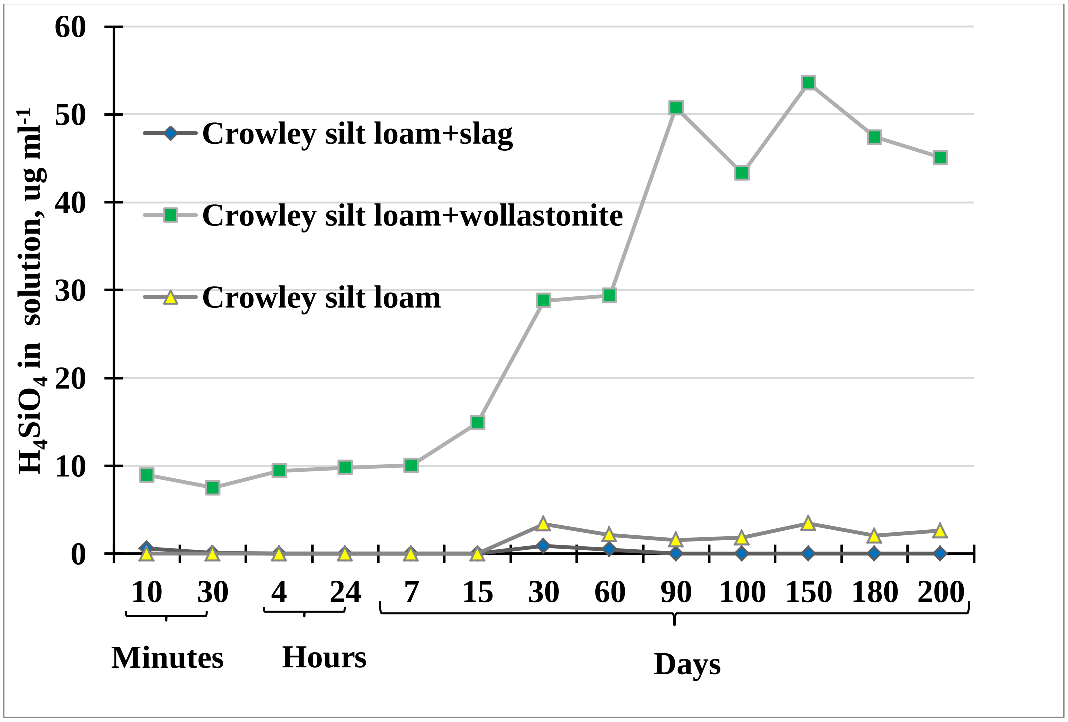


c.

(Figure 3.4 continued)

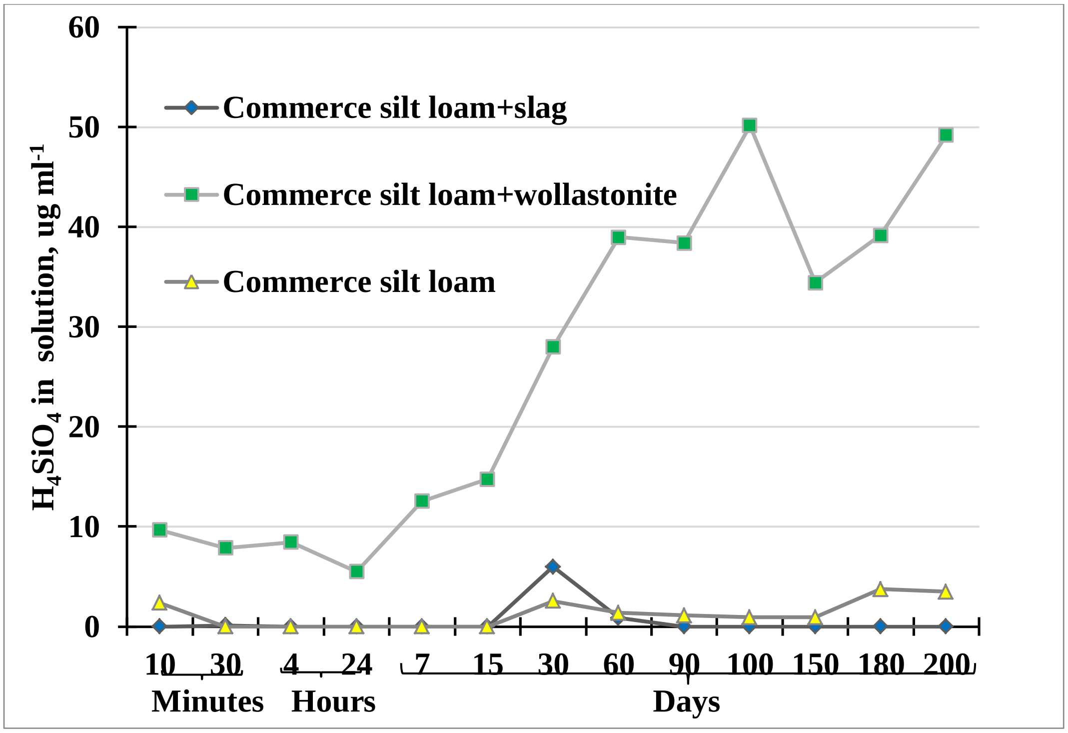


d.



e.

(Figure 3.4 continued)



f.

(Figure 3.4 continued)

The concentration of H_4SiO_4 in 0.1 M NaCl solution with wollastonite (without soil) (Figure 3.5), increased from 10 to 35 ug ml^{-1}, within the 200 day incubation time. However, no detectable concentration of H_4SiO_4 was present in the 0.1 M NaCl with slag. This confirmed that the difference observed between the treatments with slag and wollastonite in different soil suspensions was to a great extend due to the differences in chemical and physical properties of these two sources of Si (wollastonite and slag) than the influence of soil properties alone. The major questions arrived at, after this experiment was if there was any release of H_4SiO_4 from slag in the soil suspensions. Also, it was important to know if there was any influence of soil property on the release of Si from these fertilizers. The influence of the chemical and physical properties of two Si fertilizers and the soils is discussed further in the following sections.

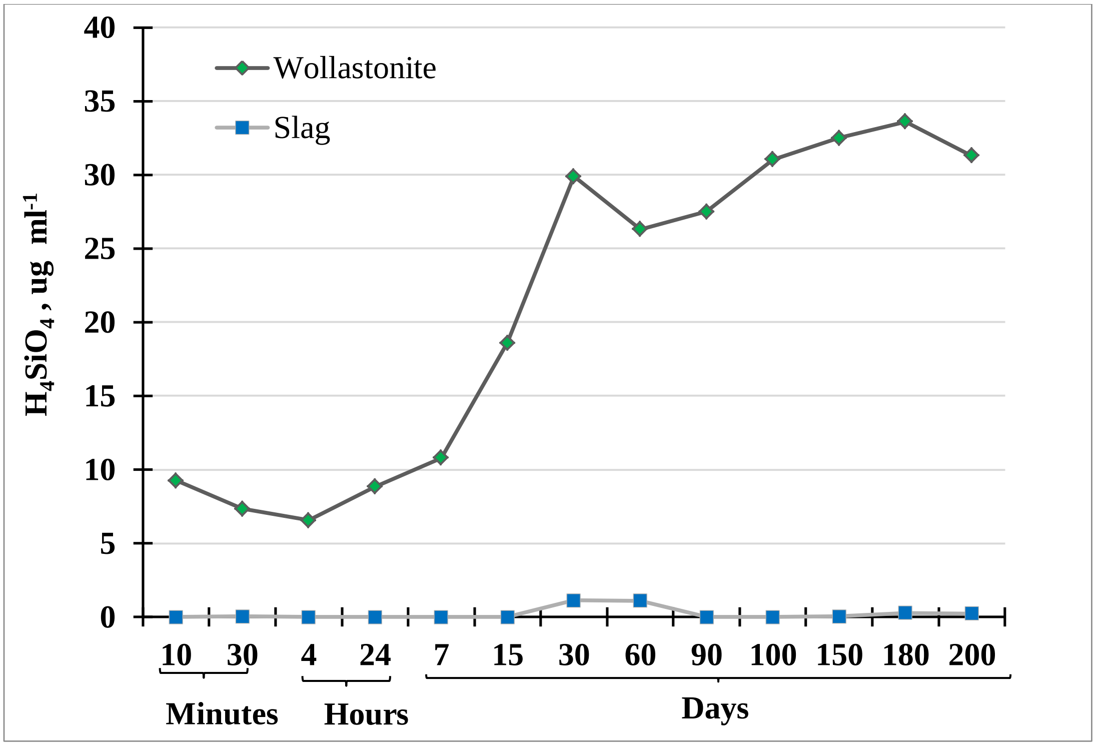


Figure 3.5 Concentration of H_4SiO_4 in 0.1 M NaCl solution with 23 mg Si g^{-1}as wollastonite and slag within a period of 200 days.

3.3.3 Effect of Si concentration on release of H_4SiO_4 from Si fertilizer

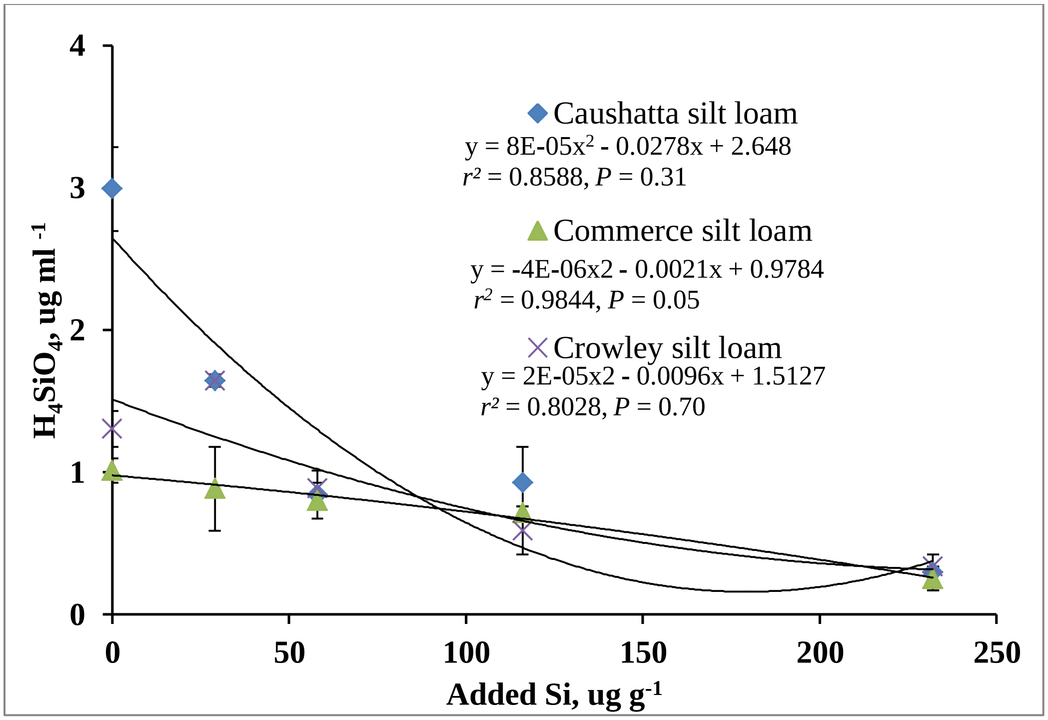
The PROC MIXED analysis in SAS showed differences in treatments in all soils tested ($P < 0.0001$) and it was also seen that quadratic model can best characterize the relationship between added Si and concentrations in soil solutions ($P < 0.05$), except for Caushatta silt loam and Crowley silt loam when slag was the added source of Si and for Perry clay when wollastonite was the source of added Si, which gave *P*-values larger than 0.05. These results indicated that the higher the added quantities of slag in soils, the lower the capabilities of soils to maintain Si in solution. This change was drastic in the case of slag which showed a decline in solution concentration even at lower levels of added Si. It appears based on the results that the change in solution concentration of H_4SiO_4 took place only slowly in the case of wollastonite which showed steady increase in solution concentrations at lower levels of added Si, but with small or no changes at higher levels of added Si (Figure 3.6). Although, there was a decrease in concentration of H_4SiO_4 in the supernatant solution with increase in quantity of added slag, this experiment confirmed that the release of H_4SiO_4 from slag was not zero and this released concentration of H_4SiO_4 was being negatively affected by the quantity of added slag. The increase in quantity of wollastonite did not decrease the solution concentration of H_4SiO_4 as much as slag. An interesting difference in the concentration of Al^{3+} ions was discovered, when the solution concentration of free metal ions with different increments of slag and wollastonite was measured. With increasing added slag, the concentration of Al^{3+} ions rose from 9 to 44 ug ml^{-1} in solution. On the contrary, there was no change detected in solution concentration of Al^{3+} ions when wollastonite was the source of Si added (Table 3.3). This finding further explained the difference in supernatant concentration of H_4SiO_4 between two Si sources. Clearly, there is an indirect relationship between the concentration of Al^{3+} ions and the quantity of H_4SiO_4 in the solution. As shown by Willey (1975) and by Iler (1973) the presence of traces of Al reduces the equilibrium solubility of silica because alumina can also be co-deposited with silica as aluminosilicate ions in a silica matrix. As stated by Wohlberg and *Bucholz* (1975) that the presence of metal salts and hydroxides reduced solubility of silica and it was concluded by them that alumina is the best adsorbent. Over a long period of time monomeric silica, or $Si(OH)_4$ reacts with Al^{3+} ion at 25°C to form colloidal Al silicate of the halloysite composition. Monomeric silica is strongly sorbed onto the surface of hydrous Al oxides (Iller, 1978).

It was noticed that the organic and clay soils had higher concentration of H_4SiO_4 in the solution in all soils at all treatments than the silt loam soils (Figure 3.6 and 3.7). This means when there was a substrate with higher sorption capacity (organic and clay soils), proportional to the rate of dissolution of Si from a fertilizer source, resulted, in a higher concentration of H_4SiO_4 maintained in the solution. Clearly, sorption capacity of soils showed a positive relationship with concentration of H_4SiO_4 maintained in solution. Therefore sorption could not be concluded as the sole reason for such a drastic decline of the concentration of H_4SiO_4 observed in this experiment due to two main reasons. Firstly, the maximum adsorbed quantity observed in all soils tested could not account for the total reductions in H_4SiO_4. Secondly, as discussed above, the soils with higher sorption capacity including the organic and clay soils had higher concentration of H_4SiO_4 maintained in solution.

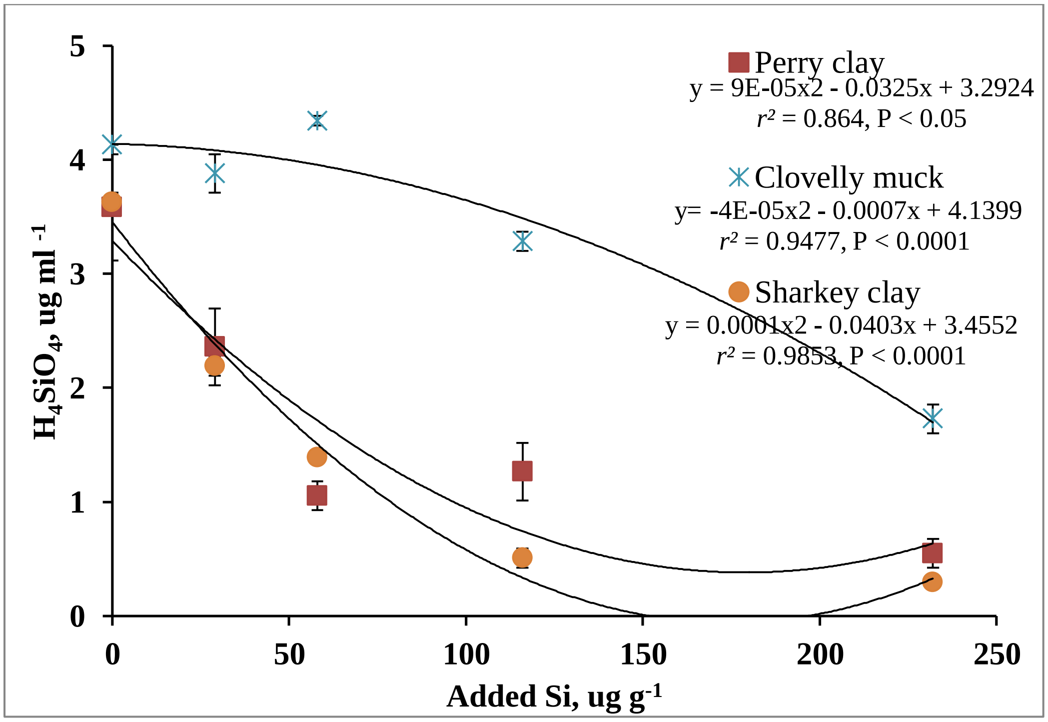
Table 3.3 Mean concentration of metal ions ($P< 0.05$) in the supernatant solution of two different silicon fertilizers studied with increasing quantities of added fertilizers

Fertilizer	Rate of Si added.	Al	Fe	Mn	Mg
	…………………………..ug ml^{-1}……………………………..				
Slag	0.7	9d	0.1a	0.02a	0.46a
	1.4	18c	0.11a	0.02a	0.43b
	2.8	33b	0.11a	0.02a	0.43b
	5.8	44a	0.11a	0.02a	0.39c
Wollastonite	0.7	0.16a	0.11a	0.02b	0.50a
	1.4	0.16a	0.11a	0.03a	0.53b
	2.8	0.16a	0.11a	0.03a	0.45c
	5.8	0.13b	0.09b	0.02b	0.41d

The next main possibility that could decrease the concentration of H_4SiO_4 in solution is polymerization of H_4SiO_4 to form polysilicic acid. Sorbed H_4SiO_4 may constitute a part of soil coatings; it may go into solution when water is added to soil or it may react with other constituents of such coatings to form secondary substances. Sorption of H_4SiO_4 as the soil solution is concentrated by evaporation may be one of the steps involved in the accretion of amorphous coatings at mineral particle surfaces in soil. (McKeague and Cline 1962).

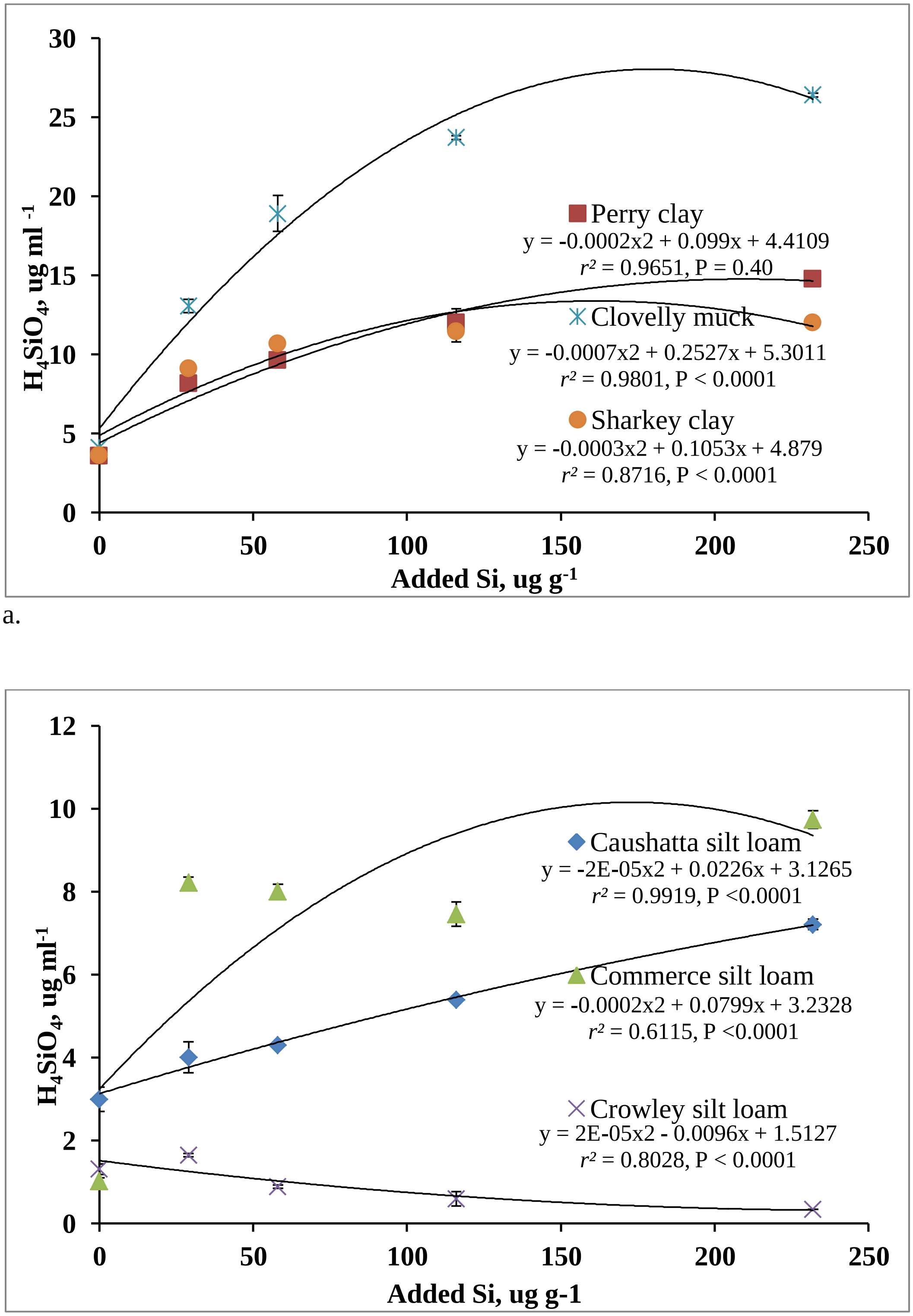


a.



b.

Figure 3.6 Concentration of $H_4 SiO_4$ in Caushatta silt loam, commerce silt loam and Crowley silt loam (a) and Perry clay, Clovelly muck and Sharkey clay (b) soils after 7 days of incubation in 0.1 M NaCl treated with varying rates of Si as slag.



a.

b.

Figure 3.7 Concentration of $H_4 SiO_4$ in Perry clay, Sharkey clay and Clovelly muck (a) and Caushatta silt loam, commerce silt loam and Crowley silt loam (b) soils after 7 days of incubation in 0.1 M NaCl treated with varying rates of Si as wollastonite.

Similarly, one may postulate that as the concentration of H_4SiO_4 increases in soil solution, there is an accumulation of the same in the solution unless the rate of sorption of H_4SiO_4 is slightly greater or equal to the rate of dissolution of Si from fertilizer material. If there is a decline in the rate of sorption and an overall increase in the rate of dissolution, polymerization of H_4SiO_4 occurs to form polysilicic acid molecules in the solution. Iller (1978) explained this phenomenon in detail and quoted that when silicic acid/silicate ions condense and polymerize, they form a plethora of structural motifs, including rings of various sizes, cross-linked polymeric chains of different molecular weights, oligomeric structures, etc. The resulting polymeric Si is a complex and amorphous product (colloidal silica)—a complicated mixture of the above components.

3.3.4 Estimation of polymerized and sorbed quantity of H_4SiO_4 in different soils of Louisiana treated with slag and wollastonite

At the end of 200 days of incubation, the 0.1 M NaCl solution was replaced with 0.5 M acetic acid (10 ml) in all the treatments with six replicates to dissolve or depolymerize the polysilicic acid into H_4SiO_4 and to bring them back into supernatant solution. This when added to what was released into 0.1 M NaCl gave a measure of the total quantity of Si released from the soil + fertilizer mixtures. The H_4SiO_4 measured in 0.5 M acetic acid + 0.1 M NaCl solution of fertilizers with no soil (therefore; no sorption on soils) added was taken as the total quantity (polysilicic acid + H_4SiO_4) released from these fertilizers. The total Si in 0.1 M NaCl alone before adding acetic acid will not take into account the polymerized and sorbed Si that has settled at the bottom on the solid phases. Dilute salt solutions like 0.1 M NaCl provided a measure of the readily available Si present in the soil solution, while results obtained using ammonium acetate (NH_4OAc) and acetic acid indicated that the Si solubilized was likely to be the more simple polymers (Berthelsen and Korndorfer 2005). Once in solution, H_4SiO_4 can be measured by the silicomolybdate blue colour method (Iler, 1979). Kraut (1931) prepared H_4SiO_4 by dissolving sodium metasilicate hexahydrate in various acidic solutions at low temperature. He reported that H_4SiO_4 is most stable at around pH 2-3. Weitz et al. (1950) also demonstrated that when $Na_2SiO_3 \cdot 9H_2O$ was reacted with acetic acid it liberated H_4SiO_4. There was significant difference in the quantities of Si released into 0.5 M acetic acid all between treatments (soil alone, soil+slag and soil+wollastonite) irrespective of the soil series ($P < 0.0001$). The differences in the quantities of Si released at the end of 200 days into 0.5 M acetic acid were also present within different soil series treated with slag or wollastonite ($P < 0.0001$). Quantification and evaluation of polymerized, sorbed and that present in solution as H_4SiO_4 in different soils with slag or wollastonite as added fertilizers enabled further analysis of the observed differences. The polymerized quantities of H_4SiO_4 in all soils treated with slag were considerably higher than when treated with wollastonite ($P < 0.0001$) as shown in Figure 3.8.

This greater concentration of polysilicic acid in the soil solutions with slag as the added source of Si was seen concomitant with a drastic reduction of H_4SiO_4 in solution (Figure 3.9). Baumann (1959) found that the polymerization rate increased rapidly with increasing dissolved silica concentration, and also that it increased with increasing pH. Savant et al. (1999) also reported that there is polymerization of plant-available Si to form a silica-gel if it exceeds a concentration of 65 mg L^{-1} or if there is dehydration of the soil, which is reversible on dilution. The minimum concentration of Si released into 0.5 M acetic acid ($P < 0.0001$) and thereafter, the minimum calculated polysilicic acid was in the supernatant solution of the organic soil (Clovelly muck) with wollastonite as the source of Si (Figure 3.8 and 3.9). Among the different soils, the silt loam soils with minimum clay content of 9% (Crowley silt loam,) had the maximum concentration of Si released into 0.5 M acetic acid ($P < 0.0001$) which in turn measured the maximum polysilicic acid in solution. This could be due to the fact that there was minimum sorption in this soil (also observed in the sorption experiment).

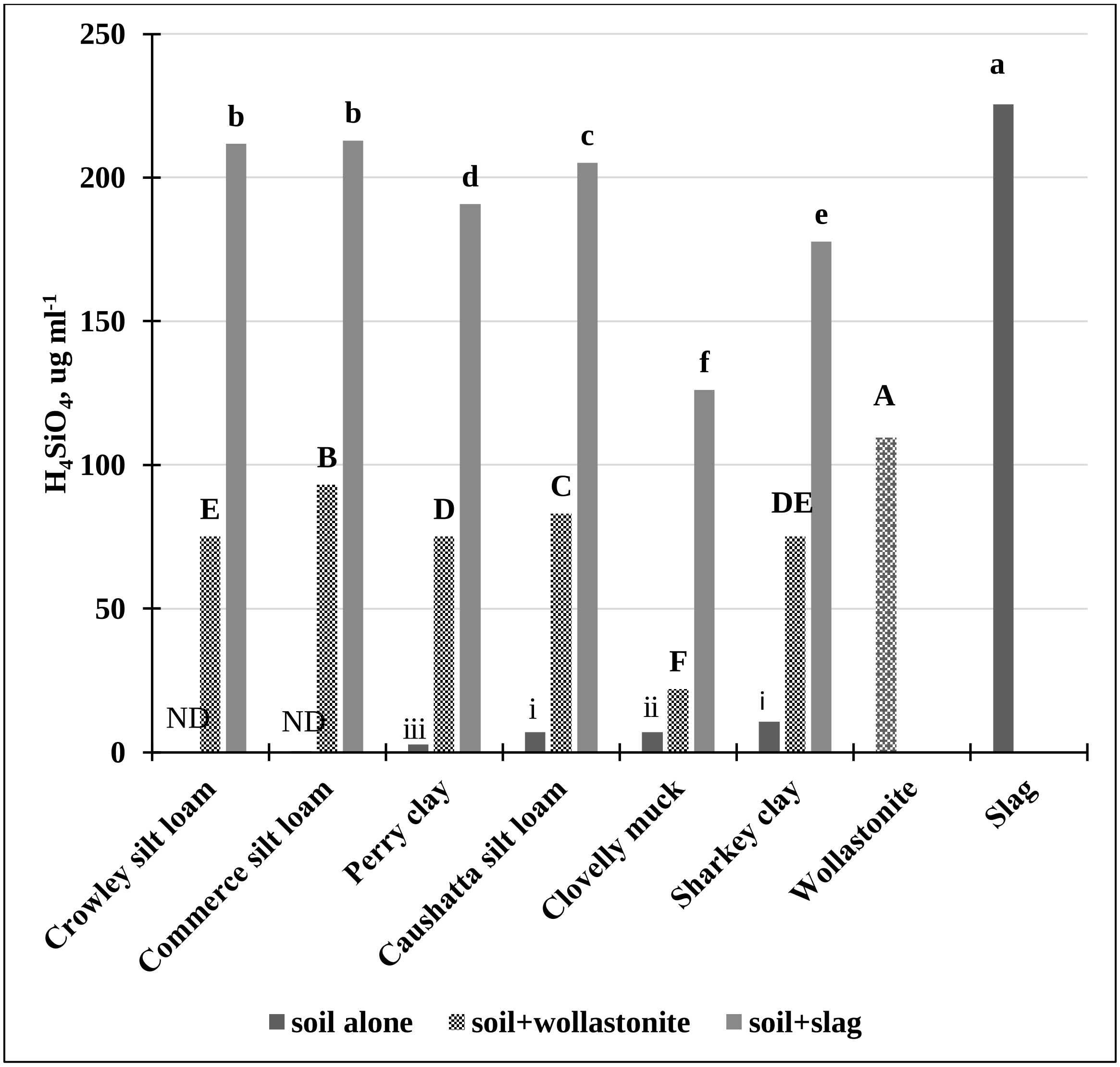
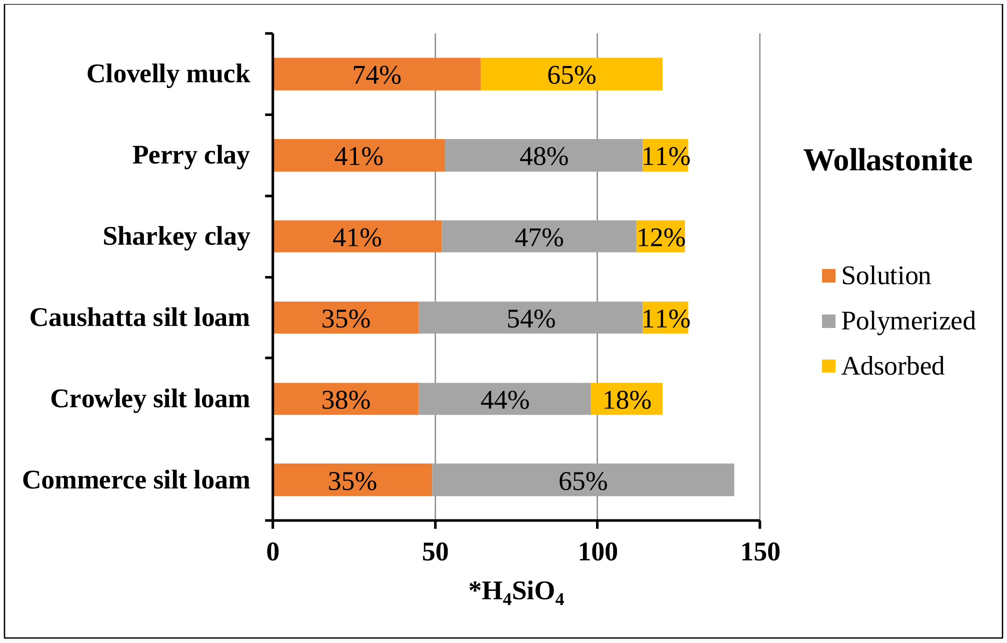
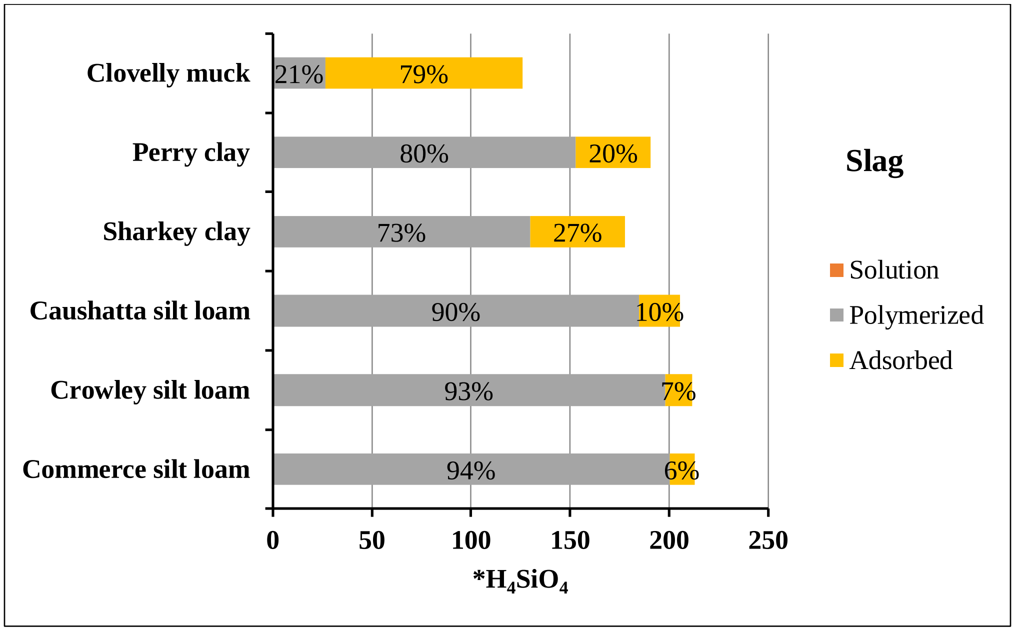


Figure 3.8 Silicon measured as H_4SiO_4 in 0.5 M acetic acid solution on six different soils, with slag and wollastonite as the source of Si after 200 days of incubation in 0.1 M NaCl solution. Bars with the same lower case letter represent H_4SiO_4 values measured from soil+slag and slag alone that are not statistically different. Bars with same upper case letters represent H_4SiO_4 values measured from soil+wollastonite and wollastonite alone that are not statistically different. Bars with roman numerals represent H_4SiO_4 values measured from soil alone. ND= Not detected.



a.



b.

Figure 3.9 Quantity of H_4SiO_4, adsorbed, polymerized and that present in solutions of six different soils treated with 23 mg Si g^{-1} as wollastonite (a) and slag (b) after 200 days of incubation in 0.1 M NaCl solution.* H_4SiO_4 in ug g^{-1} for percent adsorbed, ug ml^{-1} for percent polymerized and in solution

The rate of polymerization increases when the rate of dissolution is greater than the rate of sorption because polymerization takes place when the concentration of H_4SiO_4 is high. This was studied and explained by Iller (1978) who stated that H_4SiO_4 is soluble and stable in water at 25°C for long periods of time if the concentration is less than about 100 ug ml^{-1} as SiO_2 but when a solution of monomer, $Si(OH)_4$., is formed at a concentration greater than about 100-200 ug ml^{-1} as SiO_2, and in the absence of solid phase on which the soluble silica might be deposited, then the monomer polymerizes by condensation to form dimer and higher molecular weight species of silicic acid.

Clays in the soil may adsorb excess silica, thus inhibiting the formation of silica polymorph from soluble silica (Williams and Crerar, 1985). A similar scenario was perceived in this study as well. Evidently, with an increase in sorption, there was a decrease in polymerized quantity of H_4SiO_4 (Figure 3.9). The greatest adsorbed quantity of H_4SiO_4 was found in Clovelly muck which also had the minimum polymerized quantity of H_4SiO_4 at the end of 200 days of incubation. The adsorbed quantity was minimum in the case of silt loam soils wherein a greater polymerization of H_4SiO_4 was also recorded. The process of sorption of H_4SiO_4 on the solid phases decreases its concentration in the solution. When there was a decrease in the available surface area for sorption on the solid phases, there was a marked increase in the quantity of polymerized Si in solution. A greater quantity of polysilicic acid in the supernatant solutions of slag was observed compared with wollastonite supporting the findings about the role of Al^{3+} ions released from slag into solution in accelerating the process of polymerization and decreasing the concentration of H_4SiO_4 to almost zero with an increase in quantity of slag added.

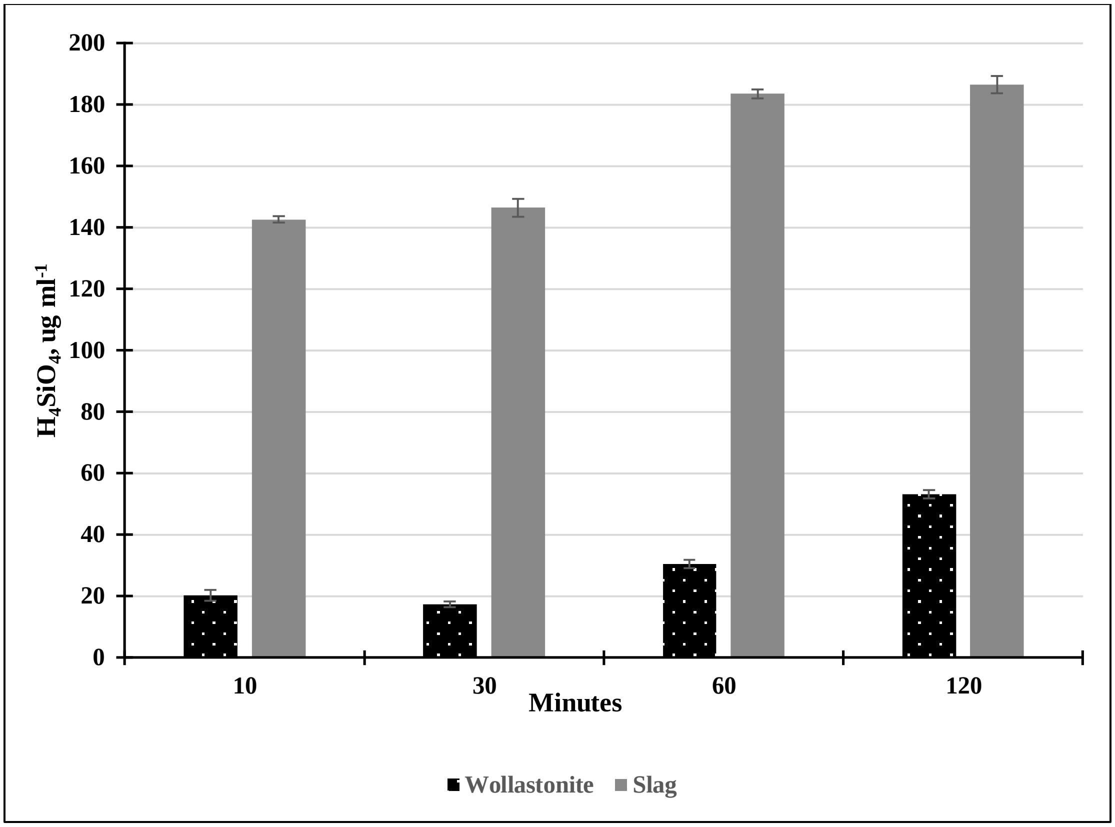


Figure 3.10 Total silicon from 23 mg g $^{-1}$ Si added as slag and wollastonite measured as H_4SiO_4 concentration in 0.5 M acetic acid within 10, 30, 60, and 120 minutes of incubation

The laboratory experiment conducted between 10 minutes to 120 minutes of incubation in 0.5 M acetic acid (depolymerizing reagent) proved that there existed a great difference between the dissolution rates of Si from slag and wollastonite. The total concentration of H_4SiO_4 (including the H_4SiO_4 from depolymerization of polysilicic acid) with Slag added was 143 ug ml^{-1} but with wollastonite, the concentration reached only 21.44 ug ml^{-1} within 10 minutes of incubation in 0.5 M Acetic acid (Figure 3.10). This faster dissolution rate of Si from slag is yet another reason for the accumulation of H_4SiO_4 in solution leading to an increased rate of polymerization in neutral solutions like 0.1 M NaCl, when slag is added as the Si source. This could be a direct effect of the physical structure of the slag particles.

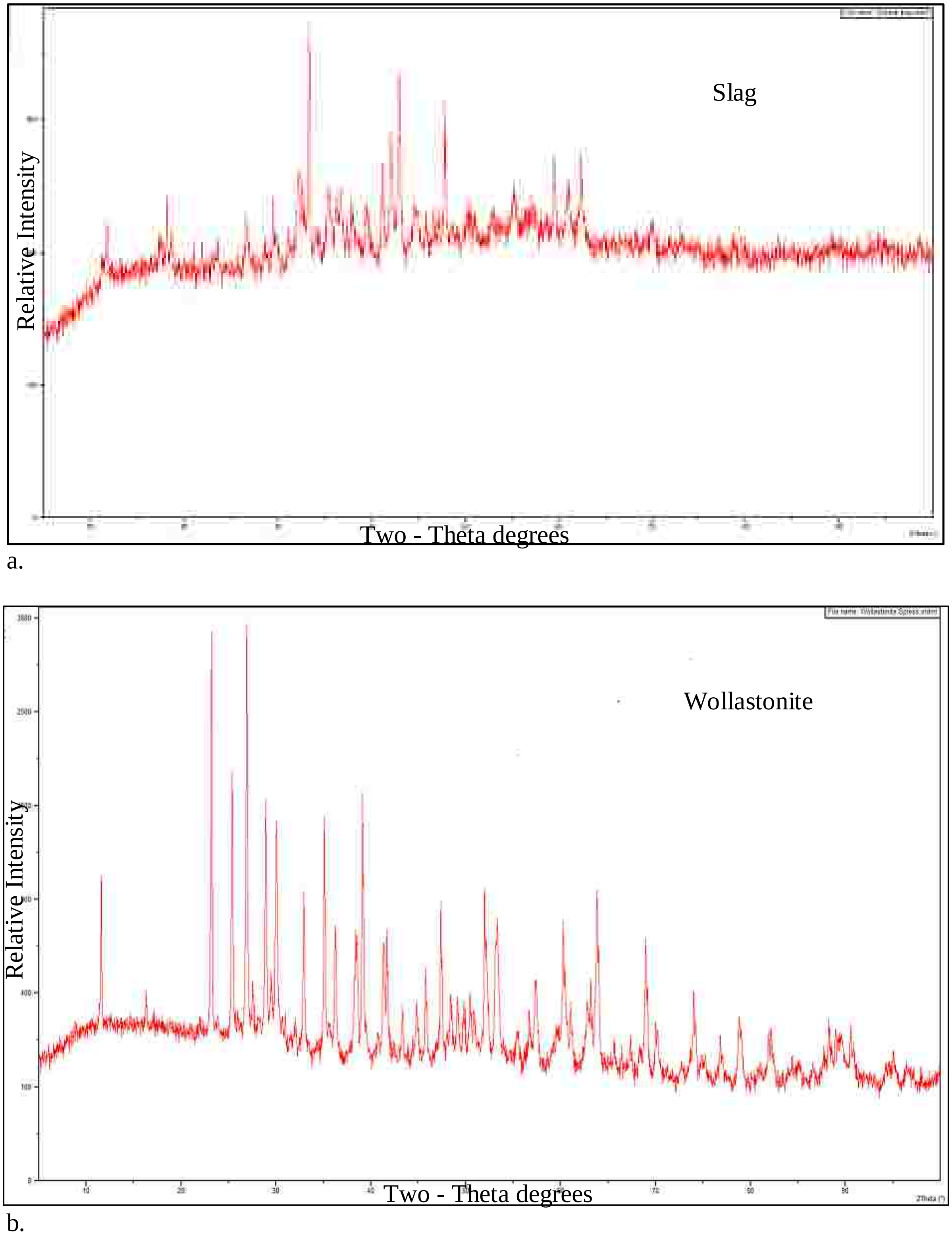
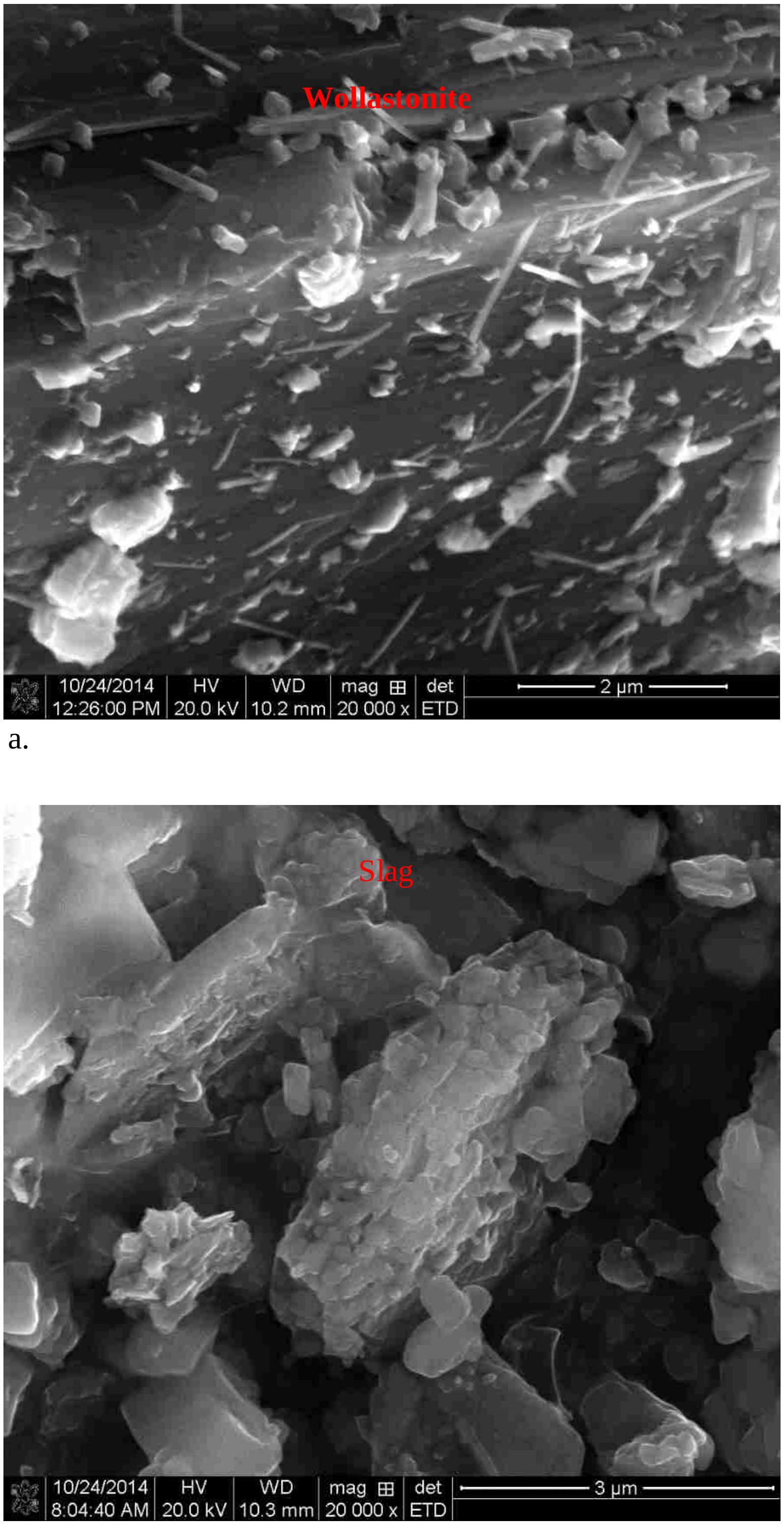


Figure 3.11 Pattern of X-Ray diffraction analyses for slag (a) and wollastonite (b)



a.

b.

Figure 3.12 Scanning electron microscopy images of wollastonite (a) and slag (b)

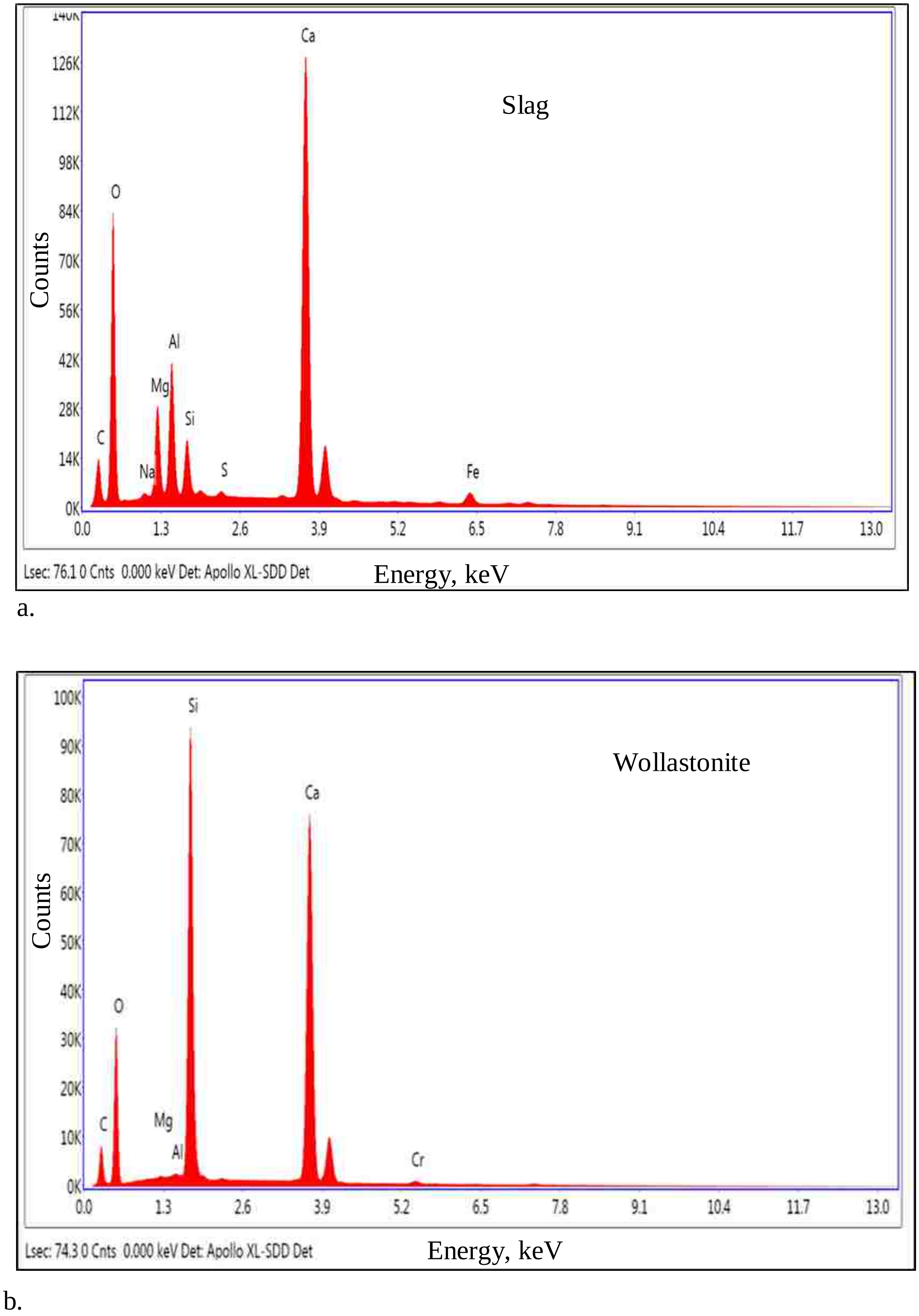


Figure 3.13 Elemental compositions of slag (a) and wollastonite (b) from Electron Dispersive X-ray analyses

The XRD patterns were obtained to further confirm the difference observed between the rates of dissolution of H_4SiO_4 from slag and wollastonite. The XRD patterns show more intense and narrow peaks with increasing crystallinity (Lee 2007). A distinguished pure crystalline pattern was seen for wollastonite, which differed from the XRD pattern of slag confirming its polycrystalline nature with more amorphous phases (Figure 3.11). The amorphous nature of slag would make it a fertilizer material with greater rate of dissolution than the crystalline wollastonite because polycrystalline substance is always more soluble than crystalline substance due to their amplified surface energy which in turn is a direct result of their less-ordered structures. Freshly ground or agitated suspensions of quartz commonly show abnormally high solubility levels (37 mg Si L^{-1}, Morey et al. 1962). This has been attributed to the formation of a disrupted surface layer, which is believed to be amorphous (Nagelschmidt et al. 1952; Liberti and Devito Francesco 1963; Siffert 1967; Ribault 1971) or microcrystalline (Lidstrom 1968; Moore and Rose 1975). Slag is a material that is a byproduct of iron and steel industry and therefore a slag material has been relatively newly formed compared with the wollastonite which is a pure mineral. Thus the surface layers of this slag material will surely have a far less crystalline nature. Since the solubility of the disrupted surface layer, whether amorphous or polycrystalline is considerably greater than that of wollastonite, the apparently high solubility of slag that has been observed in this study may, in fact, reflect the solubility of the disrupted surface layer. Secondly, EDX-SEM images showed the presence of Al^{3+} ions on slag particles at a concentration greater than that on wollastonite (Figure 3.11). These ions act as catalysts and accelerate the process of polymerization. Certain impurities such as Al^{3+} in minute amounts not only reduce the rate of dissolution of silica, but by chemisorption on the surface of silica, even in amounts less than a monomolecular layer reduce the solubility of silica at equilibrium.(Iller

1978). In particular, Okamoto et al. (1957) have shown that $A1^{3+}$ has a strong effect on the solubility of silica. Therefore the second reason would be that a relatively low content of Al ion greatly reduces the concentration of monosilicic acid, thus explaining why slag had a greater decline in H_4SiO_4 concentration due to greater polymerization. This observation emphasizes the point that, it may be very difficult to obtain an accurate measure of solubility unless traces of Al and other metals forming insoluble silicates are rigidly excluded from the system.

3.4 Conclusions

Rate of polymerization has a negative effect on the concentration of H_4SiO_4 in solution. The lower the soil sorption capacity, the higher will be the quantity polymerized. Higher rate of dissolution of fertilizer material and concentration of ions like Al and Mg in the fertilizer material as well as in the soil solution can also increase the rate of polymerization. If the soil characteristically has low silica concentration value, large additions of silica from other sources might not result in favorable results since the H_4SiO_4 released from these fertilizers will not remain long in solution in simple forms due to greater sorption and polymerization losses. Greater polymerization of the H_4SiO_4 released from these fertilizers could be a possible explanation in addition to losses due to sorption mechanisms (sorption, precipitation and absorption/fixation) that can make Si unavailable in soil solution.. The Si deficient soils high in organic matter and clay content might respond to greater quantity of Si fertilizers since these soils were shown to have maximum sorption capacity and, therefore minimum polymerization. The absence of alumina is undoubtedly of critical importance because Al^{3+} ions can accelerate the process of polymerization and reduce the availability of H_4SiO_4 from fertilizer materials especially when applied in large quantities on light textured soils. Changes in moisture content related to alternating wetting-drying cycles in the soil may influence the silica concentration in solution more readily than the other processes. Of greater significance may be the microenvironment surrounding individual fertilizer particles, and the specific chemical environment at particle to particle contacts of these fertilizers when applied in soil. The chemical equilibrium and kinetic reactions at fertilizer particle contacts may not be reflected in bulk solution chemistry, but may be part of the driving force determining reaction rates.

3.5 References

Abro, S. A., Qureshi, R., Soomro, F. M., Mirbahar, A. A., Jakhar, G. 2009. Effects of silicon levels on growth and yield of wheat in silty loam soil. *Pakistan Journal of Botany* 41:1385-1390.

Apak, R. 2002. Adsorption of heavy metal ions on soil surfaces and similar substances. *Encyclopedia of surface and colloid science* ed. A. T. Hubbard, 385-417. New York: Marcel Dekker.

Alexander G. B. 1954. The polymerization of monosilicic acid. *Journal of the American Chemical Society* 76: 2094–2096.

Baumann, H. 1959. *Kolloid-Zeitschrift* 1:162: 28.

Beckwith, R. S., and Reeve, R. 1963. Studies on soluble silica in soils- The sorption of Si acid by soils and minerals. *Australian Journal Soil Research* 1:157-168.

Beckwith, R.S., and R. Reeve. 1964. Studies on soluble silica in soils. II. The release of monosilicic acid from soils. *Australian Journal Soil Research* 2:33-45.

Berthelsen, S., and Korndorfer, G. H. 2005. Methods for silicon analysis in plant, soil and fertilizers. *Proceedings of the third International Conference on Silicon in Agriculture* 82-89. Uberlandia, Brazil.

Bergna, H.E. 1994. The Colloid Chemistry of Silica, American Chemical Society,Washington DC.

Bien, G. S., Contois, D. E., and Thomas, W. H.1958. Removal of soluble silica from fresh water entering the sea. *Geochimica et Cosmochimica Acta* 14: 35-54

Chadwick O.A., Hendriks D.M., and Nettleton, W.D., 1987. Silica in durick soil. *Soil Science Society of America. Journal* 51: 4: 975-982

Cheong, B.T. 1982. Some significant functions of silicon to higher plants. *Journal Plant Nutrition* 5:1345-1353.

Cook, H. E., Johnson, P. D., Matti, J. C., Zemmels I. 1975. Methods of sample preparation and X-ray diffraction data analysis, X-ray mineralogy laboratory, Deep Sea Drilling Project, University of California. In *Riverside: Initial Reports, DSDP* 28: 999-1007.

Datnoff, L. E., G. H. Snyder, and G.H. Kornodörfer (ed). 2001. *Silicon in Agriculture.* The Netherlands, Elsevier Science.

Datnoff, L., Deren, C., and Snyder, G. 1997. Silicon fertilization for disease management of rice in Florida. *Crop Protection* 16:525-531.

Epstein, E. 2005. Silicon in Agriculture: A historical review. In Proceedings of *Third Silicon in Agriculture Conference,* eds. L. E. Datnoff, G. H. Korndorfer, and G. H. Snyder, 15–18. Uberlandia, Brazil.

Evangelou, V.P. 1998. *Environmental Soil and Water Chemistry - Principles and Applications*, JohnWiley and Sons Inc., New York.

Fox, R. L., Leva, J. A., Young, O. P., Pluncknett, U.L., Hermaw, G. D. 1967. Soil and plant silicon and silicate response by sugarcane. *Soil Science Society of America Proceedings* 31: 775-779.

Freitas, L. C., Costa, Filho, J. F., Aloisi, R. R., Melo, W.J. 1977. Contribuição ao estudo da sílica solúvel em alguns perfis de solos. *Científica* 5:296-305.

Harder, H. 1965. *Geochimica et Cosmochimica Acta* 29:429.

Horiguchi T. 1988. Mechanism of manganese toxicity and tolerance of plant. IV. Effect of silicon on alleviation of manganese toxicity of rice plants. *Soil Science and Plant Nutrition* 34: 65-73.

Huang L, Li H, Zhang X, Lu W, Liu Y. 2006. Silicate adsorption in paddy soils of Guangdong Province, China. *Pedosphere* 16: 654–659.

Icopini, G. A., Brantley, S. L. and Heaney, P. J. 2004. Kinetics of silica oligomerization and nanocolloid formation as a function of pH and ionic strength at 25°C. *Geochimica et Cosmochimica Acta* 69: 2: 293–303.

Iler, R. K. 1979. *The chemistry of silica: Solubility, polymerization, colloid and surface properties, and biochemistry*. Canada: John Wiley and Sons Inc.

lIer. R. K. 1973. Effect of adsorbed alumina on the solubility of amorphous silica in water. *Journal of Colloid and Interface Science* 43:399-408.

Jones, L. H. P., and Handreck, K. A. 1965. The relation between the silica content of the diet and the excretion of silica by sheep. *The Journal of Agricultural Science* 65:129-134.

Jones, L. H. P., and Handreck, K. A. 1967. Silica in soils, plants, and animals. *Advances in Agronomy* 19: 107–149.

Jones, L. H., and Handreck, K. A. 1969. Uptake of silica by Trifoliumincarnatum in relation to the concentration in the external solution and to transpiration. *Plant and Soil* 30: 71-80.

Khalid R.A., and Silva J.A. 1980. Residual effect of calcium silicate on pH, phosphorus and aluminium in tropical soil profile. *Soil Science and Plant Nutrition* 26: 87-98.

Kittrick, J.A. 1969. Soil minerals in the Al_2O_3-SiO_2-H_2O system and a theory of their formation. *Clays and Clay Mineralogy* 17:157-167

Koo, T., Lee, Y. and Sheikholeslami, R. 2001. Silica fouling and cleaning of reverse osmosis membranes. *Desalination* 139: 43-56.

Korndörfer, G.H., Snyder, G.H., Ulloa, M., Powell, G., and Datnoff, L.E. 2001. Calibration of soil and plant silicon analysis for rice production. *Journal of Plant Nutrition* 24:1071-1084.

Kraut, H. 1931. *Berichte der Deutschen Chemischen Gesellschaft 64B:* 1709.

Lee, D. R. 2007. Characterization and the diagenetic transformation of non- and microcrystalline silica minerals. (*http://www.geos.ed.ac.uk/homes/s0789516/microsilica. pdf, 20 pp.).*Retrieved on 20 September 2014.

Liberti, A., and G. Devitofrancesco. 1963. The nature of ground quartz particles. *Chemistry and Industry* 51:1983-1984.

Lidstrom, L. 1968. Surface and bond-forming properties of quartz and silicate minerals and their application in mineral processing techniques. *Acta Polytechnica Scandinavica: Chemistry of Metallurgy series* 75:1-50.

Lumsdon D.G., and Farmer V.C., 1995. Solubility characteristics of proto-imogolite sols: how silicic acid can de-toxify aluminium solutions. *European Journal of Soil Science* 46: 179-186.

Ma, J.F., and Takahashi, E. 1990. The effect of silicic acid on rice in a P deficient soil. *Plant and Soil* 126: 121- 125.

Matichenkov V.V. 1990. Amorphous oxide of silicon in soddy podzolic soil and it influence on plants. Canadian Dissertation, Moscow State University, 26.

McKeague, J.A., and Cline, M.G. 1963. Silica in soil solutions. II. The adsorption of monosilicic acid by soil and by other substances. *Canadian Journal of Soil Science* 43:83–96.

Mehra, O.P., and Jackson, M.L. 1960. Iron oxides removed from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*7:317.

Moore, G.S.M., and H.E. Rose. 1975. The dissolution of powdered quartz. *Nature* 253:525-527.

Morey, G.W., R.O. Fournier, and J.J. Rowe. 1962. The solubility of quartz in water in the temperature interval from 25 to 300°C. *Geochimica et Cosmochimica Acta* 26: 1029-1043.

Nagelschmidt, G.R., L. Gordon, and O.G. Griffin. 1952. Surface of finely ground silica. *Nature* 169:539-540.

Obihara, C. H and Russell, E. W. 1972. Specific adsorption of silicate and phosphate by soils. *Journal of soil science* 23:105-117.

Okamoto, G., Okura, T., and Goto, K., 1957. Properties of silica in water: *Geochimica et Cosmochimica Acta* 12: 123-132.

Raij, B. V, and Camargo, O.A. 1973. Sílica solúvel em solos. *Bragantia* 32:223-236

Raven, J. A. 1983. The transport and function of Si in plants. *Biological Review*5 8:179-207.

Ribault, L.L. 1971. Presence d'une pellicule de silice amorphe a la surface den cristaux de quartz des formations sableuses. *CR Hebd Seances Acad Sci Ser D Sci Nat* 272: 1933-1936.

Savant, N. K., Korndörfer, G. H., Datnoff, L. E., and Snyder, G. H. 1999. Silicon nutrition and sugarcane production: A review. *Journal of Plant Nutrition* 22:1853-1903.

Siffert, B. 1967. Some reactions of silica in solution. Formation of clay. Israel program for scientific translations Ltd., Jerusalem. Translation of Memoires du service de la carte geologique d' Alsace et de Lorraine. Rep. no21 (1962).

Sheikholeslamia, R., Al-Mutaz, I., Tan, S., and Tan, S, D. 2002. Some aspects of silica polymerization and fouling and its pretreatment by sodium aluminate, lime and soda ash. *Desalination* 150: 85-92.

Walkley, A. and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid filtration method. *Soil Science* 37: 29-38.

Wickramasinghe, D. B., and Rowell, D.L. 2006. The release of silicon from amorphous silica and rice straw in Sri Lankan soils *Biology and Fertility of Soils* 42:231–240.

Weitz, E., H, Franck., and M, Schuchard. 1950. *Chemiker Zeitung* 74: 250-25.

Willey, J. D. 1975. *Marine. Chemistry* 3:241.

Williams, L.A. and D.A. Crerar. 1985. Silica diagenesis, II. General mechanisms. *Journal of sedimentary petrology*.55:312-321.

Wohlberg. C and J. R. Bucholz, 1975. Silica in water in relation to cooling tower operation. In *International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials*, Toronto, Ontario, Canada. Los Alamos Scientific Laboratories, LA-UR-74-1895. http://permalink.lanl.gov/object/tr?what=info:lanl-repo/lareport/LA-UR-74-1895. Retrieved on 20 September 2015.

Yu, Q. Y and Li, X. L. 1999. Study on adsorption and desorption of silicon in soils. Journal of Anhui Agrotechnicaz Teachers College (in Chinese) 13:1-6.

Chapter 4. Establishing soil silicon test procedure and critical silicon level for rice in Louisiana soils

4.1 Introduction

Silicon (Si) is absorbed by plants as monosilicic acid (H_4SiO_4) (Jones and Handreck, 1967). Silicon can be supplied to rice (*Oryza sativa*) in the form of calcium silicate (wollastonite and slag) which is incorporated into the soil before planting. Rice is a Si accumulator (Yamaji and Ma 2007). Depletion of plant-available Si in soils where rice is grown could be a possible limiting factor contributing to declining or stagnating yields in many rice growing countries (Savant et al. 1997). During the past decade, in a study conducted by Breitenbeck et al. (2006) documented numerous rice fields in southwestern Louisiana have begun to display symptoms similar to the devastating nutritional disorder 'Akagare' that occasionally occurs in Japanese rice fields. Symptoms of “localized decline” are invariably associated with uptake of excessive levels of iron (Fe) and aluminum (Al) by young rice plants. Affected plants are often low in zinc and potassium, but applications of these nutrients has failed to offset the onset of this disorder. A preliminary survey of Louisiana rice at mid-tillering stage showed that affected plants also contained low levels of Si (12-36 mg kg^{-1}), suggesting that Si deficiency may be a contributing factor to “localized decline”. Several studies in the past few years suggest that increasing Si uptake mitigates Al and Fe toxicity as well as a range of other abiotic stresses in rice and other crops (Ma and Takahashi 2002). Silicon fertilization increases the number of tillers and grains (Liang et al. 1994). Snyder et al. (1986) demonstrated that application of calcium silicate increased rice yields in Histosols mainly due to the supply of available Si and not due to supply of other nutrients. The effect of Si on reducing diseases unquestionably contributes to increased yields, but Si has also been shown to increase yield in the absence of disease (Datnoff et al.

1992). Before a fertilizer recommendation is made, the critical limits for a particular nutrient in the soil for plant growth and development must be determined. The information obtained will indicate the degree of nutrient deficiency and the amount of nutrient to be applied as a fertilizer to correct the deficiency (Korndorfer et al. 2001).

Identifying the most appropriate extraction method is another essential aspect to be considered when recommending fertilizers. To develop recommendations for field applications of silicate materials, knowledge of soil Si status and availability of Si in the amendment is essential. Predicting crop responses to application of Si requires calibration of soil Si status and plant uptake. The challenge for routine testing of soils and amendment materials is the development of a simple, dependable, and robust method that correlates well with changes in soil Si status and corresponding plant tissue levels. A number of chemical extraction procedures have been developed to determine the plant-available soil Si status, and have been compared on various soil types (Elliott and Snyder 1991; Matichenkov et al. 2000; Korndörfer et al. 2001; Ma and Takahashi 2002; Pereira et al. 2003; Wang et al. 2004; Berthelsen and Korndörfer 2005). The relationships between different extraction methods have not been well documented (Savant et al. 1999; Ma and Takahashi 2002).

Although critical limits for many nutrient elements are available for Louisiana soils, there is no information with respect to Si for Louisiana rice soils. The pH of the extractant is also fundamental for H_4SiO_4 solubility, just as soil pH is important for soil solution concentration and Si absorption by plants. Not enough silicate and lime comparative studies are available to prove if just the pH increase is able to provide this element to rice growing in soils with low Si concentration, causing doubts about the effectiveness of silicate fertilizations. This study was conducted with the following objectives: 1) to determine the effect of Si fertilization on Si tissue concentrations, plant biomass, and yield; 2) to evaluate the relationship between plant Si uptake and soil Si based on different extraction procedures; and 3) to establish a critical Si level for soil using different extraction procedures.

4.2 Materials and methods

4.2.1 Bulk sampling and green house study

Six bulk soil samples: Perry Clay, Sharkey Clay, Commerce silt loam, Crowley Silt Loam, Coushatta Silt Loam and Mowata silt loam from the locations viz., Ouachita, Tensas, Evangeline, Rapides and Calcasieu parish were collected from 0 to 6^+ cm depths. A greenhouse pot culture study was conducted with 4 graded levels of Si (0, 170, 340, and 680 kg ha^{-1}) applied as slag (Plant Tuff®) and wollastonite (Table 4.1) with five replications. Each plastic pot was filled with 7 kg of soil and a calculated quantity of slag or wollastonite was applied, mixed properly, before sowing seeds of rice. Seeds of rice variety, CL 111 were sown at the rate of 6 seeds per pot. Thinning was performed ten days after germination, leaving two plants per pot and nitrogen (N), potassium (K) and phosphorus (P) in the form of urea, muriate of potash and Triple super phosphate were applied at the rate of 134: 90: 90 (NPK) kg ha^{-1}. One third of nitrogen and potassium was applied 45 days after planting and the rest was applied before planting. The pots were maintained under flooded condition after 20 days of germination until 7 days before harvest. Regular plant protection practices were used throughout the crop growing period. The details of the bulk samples collected and initial soil properties are presented in Table 4.2. At maturity, panicles were separated from tillers. All tillers from each pot were cut as close to the soil surface. The panicles and straw samples were oven dried at 65°C for 72 hours. The grain and straw yield was then calculated as dry weight (g) per pot. Silicon uptake by rice and availability in soil in each pot were recorded at harvest using different extraction procedures (Table 4.3).

4.2.2 Extraction and estimation of Si in soil and plants

4.2.2.a. Soil Si analysis

Silicon was extracted from soils using seven extractants as outlined by different researchers (Table 4.3). The Si in the extracting solution was determined by Molybdenum Blue Colorimetry (Korndorfer et al. 2001). Fixed quantity of filtrate was transferred into a plastic centrifuge tube and then 10 mL of deionized water, plus 0.5 mL of 1:1 hydrochloric acid (HCl), and 1 mL of 10% ammonium molybdate [$(NH4)_6Mo_7O_2$] solution (pH 7.5) were added. After 5 minutes, 1 mL of 20% tartaric acid solution was added and after two minutes, 1 mL of the reducing agent Amino napthol n-sulphonic acid (ANSA) was added. After five, but not later than 30, minutes following addition of the reducing agent**,** absorbance was measured at 630 nm using UV visible spectrophotometer (Hach DR 5000). Simultaneously, Si standards (0.2, 0.4, 0.8, 1.2, 1.6 and 2.0 mg L^{-1}) prepared in the same matrix were also measured using UV visible spectrophotometer.

4.2.2.b. Plant Si analysis

Plant Si content was determined using Oven-induced Digestion Procedure (Kraska and Breitenbeck 2010). Dry, ground tissue samples (100 mg) were weighed into 50-mL polyethylene screw-cap centrifuge tubes. To reduce foaming, 5 drops of octyl-alcohol were added prior to adding H_2O_2 and NaOH. Samples were wetted with 2 mL of 30% H_2O_2, washing the sides of the tube free of sample. The tube was tightly capped and placed in a convection oven at 95°C. After 30 min, the tubes were removed and 4 mL of 50% NaOH added to the hot samples. The sample tubes were then gently vortexed, capped loosely, and returned to the oven (95°C) every 15 minutes. After 4 hours, samples were removed and 1 mL of 5 mM NH_4F was added to facilitate the formation of H_4SiO_4 prior to the final dilution to make up the volume to 50-mL with deionized water.

The Si in the digested solution was determined by Molybdenum Blue Colorimetry (Hallmark et al. 1982). A 2-mL aliquot of digested sample solution was added to a 50 mL polyethylene screw-cap centrifuge tube. Ten mL of 20% acetic acid was then added to each tube, followed by 2 mL of 0.3 M ammonium molybdate. After 5 minutes, 2 mL of 20% tartaric acid solution was added and after two minutes, 2 mL of the reducing agent Amino napthol n-sulphonic acid (ANSA) was added. The samples were diluted to a final volume of 30 mL with 20% acetic acid, capped and shaken. After 30 minutes, tubes were shaken vigorously to mix prior to determining absorbance using a spectrophotometer (Hach DR 5000) calibrated at 630 nm. Simultaneously, Si standards (0.4, 0.8, 1.6, 3.2, 4.8 and 6.4 mg L^{-1}) were prepared in the same matrix were also measured using UV visible spectrophotometer.

4.2.2.c. Correlation analysis

The relationship between extractable soil Si based on different procedures and different plant response variables was evaluated using regression analysis with PROC REG in SAS 9.4 (SAS Institute, 2012). The relationship between extractable soil Si based on different procedures and soil Si rates was also evaluated using regression analysis with PROC REG. The coefficient of determination (r^2) and P-value were used as criteria to determine the significance of their relationship.

4.2.3 Calibration of Si in soils

The critical limits of soil for relative maximum yields were estimated using three methods, namely graphical Cate and Nelson method, quadratic regression and linear plateau model. The critical limit of Si in soil may be defined as optimum Si concentration in soil beyond which a positive response in terms of yield is highly unlikely and below which the plant fail to attain the maximum potential yield. The graphical method of Cate and Nelson entails plotting the plant available soil Si extracted by different extractants on X-axis and relative yield on the Y-axis. A transparent overlay with a vertical line and an intersecting horizontal line maximized the number of points in the first and third quadrants. Afterwards, the soil test value corresponding to the intersection was taken as the critical value for Si (Cate and Nelson 1965; 1971).

The optimum Si concentration which is equal to the minimum Si concentration in soil that corresponded to the maximum yield (Waugh et al. 1973) was also determined using quadratic model. Quadratic model was used with parameter estimates derived separately for each soil type by plotting relative biomass yield to soil nutrient level with the REG procedure in SAS (version 9.4, SAS Institute, 2012). The critical level for Si response was the value associated with highest yield level (peak) of the projected yield, which was calculated using the quadratic formula.

Bouqet et al. (2009) stated that the linear-plateau model asserts that yield beyond an optimum nutrient concentration, the joint of the linear and plateau regions, remains constant. The plateau region corresponds to maximum yield. Yield data points anywhere in the plateau region are statistically the same. And the response to added fertilizers is highly unlikely after this point of soil concentration from where the plateau begins. Also, there are high chances of yield decline below the maximum potential yield below this level of soil Si concentration in soil and the likelihood of response to added Si fertilizers is significantly higher below this estimated critical concentration of Si in soil.

Table 4.1 The elemental composition of the two sources of Si

Elements	Si	Al	Ca	Fe	Mg	S	B	Cu	Zn
	……………..……………………..%	....							
Wollastonite	23	5.3	31	14	13.9	0	0	0	0
Slag (Plant Tuff®)	17	4.8	23	14	7	1.71	0.01	0.0004	1.09

Table 4.2 Properties of soil series used in greenhouse study during the summer of 2014 and 2015

Soil series with taxonomic class	[3]OM %	pH 1:1 Water	[2]Si	[1]P	[1] K	[1] Ca	[1] Mg	[1] S	[1] Zn
			------------------------ mg kg^{-1} ---------------------						
Crowley silt loam (Fine, smectitic, thermic Typic Albaqualfs)	1.6	5.0	53	11	73	669	101	12	1.4
Sharkey clay (Very-fine, smectitic, thermic Chromic Epiaquerts)	3.0	5.7	83	65	466	3,112	565	42	4.0
Perry Clay (Very-fine, smectitic, thermic Chromic Epiaquerts)	3.6	5.3	79	17	236	1,731	628	33	3.8
Commerce silt loam (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts)	1.9	6.0	25	16	198	1,158	203	18	2.4
Caushatta silt loam (Fine-silty, mixed, superactive, thermic Fluventic Eutrudepts)	2.1	8.0	98	22	206	3,702	416	43	2.9
Mowata silt loam (Fine, smectitic, thermic Typic Glossaqualfs)	2.5	7.4	47	81	257	2,064	104	33	1.4

[1] Extractable nutrients determined by Mehlich- 3 extraction procedure followed by ICP analysis. [2] Si determined by 0.5 M acetic acid extraction procedure and Molybdenum Blue Colorimetry. [3] Organic matter determined by Walkley and Black method, colorimetrically (Walkley and Black 1934).

Table 4.3 Different extractants and procedures used for evaluating plant available silicon in select Louisiana soils

Extracting solution	Soil: solution ratio	Shaking period	Reference
0.5 M Acetic acid-1	1:10	Continuous shaking for 1 hour	Korndorfer et al. (1999)
0.01M Calcium chloride ($CaCl_2$)	1:10	Continuous shaking for 1 hour	Korndorfer et al. (1999)
1 M Sodium acetate (NaOAc)	1:10	Continuous shaking for 1 hour	Korndorfer et al. (1999)
Deionized water	1:10	Continuous shaking for 1 hour	Korndorfer et al. (1999)
0.5 M Ammonium acetate (NH_4OAc)	1:10	Continuous shaking for 1 hour	Fox et al. (1967)
0.1M Citric acid	0.5:25	Shaking for 2 hours, resting for 24 hours and then shaking for 1 hour	Acquaye and Tinsley (1965)
0.5 M Acetic acid-2	4:10	24 hours rest and then continuous shaking for 2 hours	Snyder (2001)

Table 4.4 Initial soil silicon extracted from different soils before planting using different extraction procedures

Soil type	0.5M Acetic acid-1	1 M NaOAc	0.01 M $CaCl_2$	0.5 M NH_4OAc	Deionized water	0.1 M Citric acid	0.5 M Acetic acid-2	Mean
	………………………………..….ug g^{-1}………………………………………………							
Crowley silt loam	53	24	25	24	31	144	67	53
Sharkey clay	83	67	22	65	22	1309	240	258
Perry Clay	79	37	37	37	40	404	137	110
Commerce silt loam	25	17	17	22	25	349	82	77
Caushatta silt loam	98	62	30	63	50	492	144	134
Mowata silt loam	47	30	22	47	47	414	132	112

The optimal Si concentration estimated by the linear plateau model thus does not only consider the Si concentration that results in the highest yield, it identifies the point (optimum Si concentration) at which further increases in soil Si concentration would not result in significant increases in relative biomass yield. Statistical analysis of Si data using linear-plateau regression of soil Si concentration on rice relative biomass yield was done with the NLIN procedure available in SAS. The lower limit of the plateau portion of the function was considered to be the critical level (Cate and Nelson 1971). If there was no projected critical level within the range of our data, linear plateau model (NLIN procedure) was not used to determine a critical level. All regression models were statistically evaluated using the coefficient of determination (r^2) and p-value.

Analysis of variance (ANOVA) was performed using PROC MIXED in SAS 9.4 (SAS Institute, 2012) to determine significant effects of treatments on soil and plant Si level and biomass yield. For any significant treatment effect ($P<0.05$), mean separation was done by Tukey–Kramer post-hoc test to identify treatment differences.

4.3 Results and Discussions

4.3.1 Plant available Si determined by different extractants

A significant difference was observed between the soils, when the initial Si content was analyzed using different extractants. The mean Si level, over the range of seven extractants in Sharkey clay soil was the greatest with 258 ug g^{-1} and the minimum was noted in Crowley silt loam with 53 ug g^{-1} (Table 4.4). The clay soils had higher soil Si than the silt loam soils. A positive correlation existed between soil pH and mean soil Si among the soils with same texture. Caushatta silt loam had the maximum mean soil Si of 135 ug g^{-1} and a pH of 8 among the light textured soils and in the case of heavy textured soils, Sharkey clay had higher Si content and pH than Perry clay.

The results from the composite Si-treated soil samples analyzed after the harvest of rice by different extractants clearly showed changes in Si availability in relation to the rates of Si sources across the six soil series investigated (Table 4.5). The amount of Si extracted by all extractants was not always proportional to the rate of Si applied. However, the acid extractants extracted greater Si from soil than $CaCl_2$ and deionized water. The available Si extracted by different extractants viz., 0.5 M acetic acid-1, 0.5 M acetic acid-2, 0.01 M $CaCl_2$, deionized water, 0.5 M NH_4OAc, 1 N NaOAc and 0.1 M citric acid ranged from 42 to 383 ug g^{-1}, 72 to 470 ug g^{-1}, 6 to 107 ug g^{-1}, 8 to 130 ug g^{-1}, 14 to 181 ug g^{-1}, 21 to 334 ug g^{-1} and 306 to 2154 ug g^{-1} respectively (Table 4.5). The available Si extracted by various extractants irrespective of the soils used for the study was in the order of high to low: 0.1 M citric acid >0.5 M acetic acid-2 >0.5 M acetic acid-1 > 1 M NaOAc-1 > 0.5 M NH_4OAc > deionized water > 0.01 M $CaCl_2$.

In general it can be stated that 0.1 M citric acid, 0.5 M acetic acid, 0.5 M NH_4OAc and 1 M NaOAc extracted more Si than 0.01 M $CaCl_2$, and deionized water. Similar results were reported by scientists who interpreted that extraction solutions containing sulfuric acid, sulfurous acid, sulfate, citric acid, and citrate, extract adsorbed Si, with the different extractants desorbing various amounts of the specifically adsorbed Si fraction (Fox et al. 1967; Korndorfer et al. 1999; Berthelsen et al. 2000). The acetic acid is able to extract non available Si present in some materials such as Ca and Mg silicate, but it is not true for wollastonite (Pereira et al. 2004). Xu et al. (2001) attributed to calcium silicate dissolution the high Si extracted with acid extracting solution (pH 4) in calcareous soils.

According to Brown and Mahler (1987), acidity and anions could additively impact Si release from soils, as showed by Wang et al. (2004). This was in agreement with the data from the second chapter.

The soluble Si concentration extracted by 0.01 M $CaCl_2$ increased in soils treated with wollastonite. Slag did not increase Si concentration extracted by 0.01 M $CaCl_2$ in the soil (Figure 4.1). This trend also existed with deionized water extractable soil Si (Figure 4.2) but with an increased Si concentration in soil which could be attributed to greater solubility of fertilizer slag in deionized water than the 0.01 M $CaCl_2$. However, the 0.5 M acetic acid, 0.1 M citric acid and acetate (1 M NaOAc-1 and 0.5 M NH_4OAc) extractable Si in all soils increased with increasing rates of wollastonite and slag (Figure 4.3 to 4.7). This was expected as the acid extractants dissolve slag material better than wollastonite which is insoluble in weak acids. It has also been pointed out by Haynes et al. (2013) that acid extractants can remove very large amounts of Si from soils treated with slags since these materials are acid-soluble. Some of the Si extracted originates from residual unreacted slag present in the soil. Similar observations have been made regarding the Na-acetate buffer (pH 4.0) method (Imaizumi and Yoshida 1958) by both Sumida (2002) and Wang et al. (2001). These strongly acidic extractants should therefore be avoided on Si-fertilized soils.

Also, the Si source content coupled with its solubility was likely to influence yield response and plant Si uptake. Wollastonite with Si content higher than slag, is often added in lesser quantities than slag to meet the same Si requirements in soil. These larger quantities of slag coupled with its fast dissolution than wollastonite might lead to the conversion of monosilicic acid released into the soil into unavailable forms due to the processes of polymerization and adsorption.

Table 4.5 The soil silicon extracted from different soils with different extraction procedures after harvest

Source	Rate kg Si ha^{-1}	0.5M Acetic acid-1	1M NaOAc	0.01M $CaCl_2$	0.5M NH_4OAc	Deionized water	0.1M Citric acid	0.5M Acetic acid-2
		……………………….Caushatta silt loam, ug g^{-1}…………………………………………….						
Control	-	132d	70	28b	66d	15c	929ab	120d
Check lime	†	134d	137	22b	68cd	19c	809b	140d
Wollastonite	170	170cd	219	33b	66d	25c	1076ab	202bc
	340	203 c	50	49ab	91bc	62ab	1206a	222ab
	680	362a	80	76a	86bcd	81a	1239a	244a
Slag	170	188c	83	29b	78bcd	34c	885ab	177c
	340	273b	128	21b	101b	38bc	1004ab	198bc
	680	320ab	174	24b	130a	21c	1110ab	213b
P-value		*<0.0001*	*(NS)*	*<0.0001*	*<0.0001*	*<0.0001*	*0.0052*	*<0.0001*
		……………………….Commerce silt loam, ug g^{-1}…………………………………………….						
Control	-	78e	26c	6d	29d	15c	401c	99de
Check lime	†	79e	27c	16cd	40cd	20c	478c	71e
Wollastonite	170	125de	36bc	24bc	50bc	25c	740b	198b
	340	174d	81b	43a	59b	51b	755b	228ab
	680	229c	69bc	52a	58bc	75a	1090a	259a
Slag	170	169d	46bc	30b	39cd	22c	570bc	125d
	340	304b	155a	15cd	50bc	13c	529bc	160c
	680	383a	171a	13d	123a	18c	654bc	209b
P-value		*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*

(P < 0.05= significant; NS=Non-significant). † - application rate was 1 ton material ha^{-1}

(Table 4.5 continued)

Source	Rate kg Si ha^{-1}	0.5M Acetic acid-1	1M NaOAc	0.01M $CaCl_2$	0.5M NH_4OAc	Deionized water	0.1M Citric acid	0.5M Acetic acid-2
		…………………………Crowley silt loam, ug g^{-1}…………………………………………						
Control	-	42b	21f	16d	14e	14c	315e	94e
Check lime	†	45b	40ef	18d	25d	19c	339e	110e
Wollastonite	170	61b	37ef	25bc	30cd	20c	353de	157d
	340	124ab	65cd	30b	39c	26b	540b	205bc
	680	205a	103b	55a	62b	39a	826a	335a
Slag	170	86b	52de	20cd	34cd	18c	405d	175cd
	340	83b	79c	21cd	54b	17c	469c	218b
	680	206a	125a	19d	96a	19c	575b	362a
P-value		*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*
		………………………Mowata silt loam, ug g^{-1}………………………………………………..						
Control	-	53d	26c	16c	33c	22 abc	306c	112ef
Check lime	†	145c	52c	13c	37c	8c	367c	82f
Wollastonite	170	219b	36c	19bc	44c	24ab	545bc	148de
	340	358a	65bc	30ab	56bc	29a	766ab	267ab
	680	221b	59bc	38a	78ab	37a	938a	294a
Slag	170	188bc	61bc	19c	56bc	9bc	532bc	190cd
	340	237b	129ab	17c	73ab	24ab	553bc	195cd
	680	330a	146a	16c	96a	21abc	516bc	236bc
P-value		*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*

(P < 0.05= significant; NS=Non-significant). †- application rate was 1 ton material ha^{-1}

(Table 4.5 continued)

Source	Rate kg Si ha^{-1}	0.5M Acetic acid-1	1M NaOAc	0.01M $CaCl_2$	0.5M NH_4OAc	Deionized water	0.1M Citric acid	0.5M Acetic acid-2
		……………………………Perry clay, ug g^{-1}……………………………………………						
Control	-	215c	162d	50bc	93c	60a	1366bc	328b
Check lime	†	230bc	188cd	37cd	105bc	20e	1376bc	310b
	170	260bc	187cd	52cd	112bc	50bc	1372bc	380ab
Wollastonite	340	329a	227b	60b	129ab	48ab	1734ab	439a
	680	331a	231b	68b	146a	48ab	1972a	443a
	170	256bc	196c	45c	104bc	45abc	1325bc	352ab
Slag	340	287ab	198c	37c	128ab	26de	1407bc	378ab
	680	329a	280a	32a	147a	30cde	1465bc	376ab
P-value		*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*0.0026*
		……………………………Sharkey clay, ug g^{-1}……………………………………………						
Control	-	156d	113e	52d	81e	72cd	1371f	333e
Check lime	†	205cd	166d	53d	109d	77c	1407f	334e
	170	206cd	165d	64c	109d	81bc	1576e	392cd
Wollastonite	340	256bc	179cd	92b	113cd	93b	1812c	437ab
	680	284ab	203bc	107a	143b	130a	2154a	470a
	170	239bc	167d	58cd	112cd	58de	1661d	363de
Slag	340	308a	226b	58cd	129bc	76bc	1837c	423bc
	680	313a	334a	51d	181a	45e	2004b	467a
P-value		*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*

(*P* < 0.05= significant; NS=Non-significant). † - application rate was 1 ton material ha^{-1}

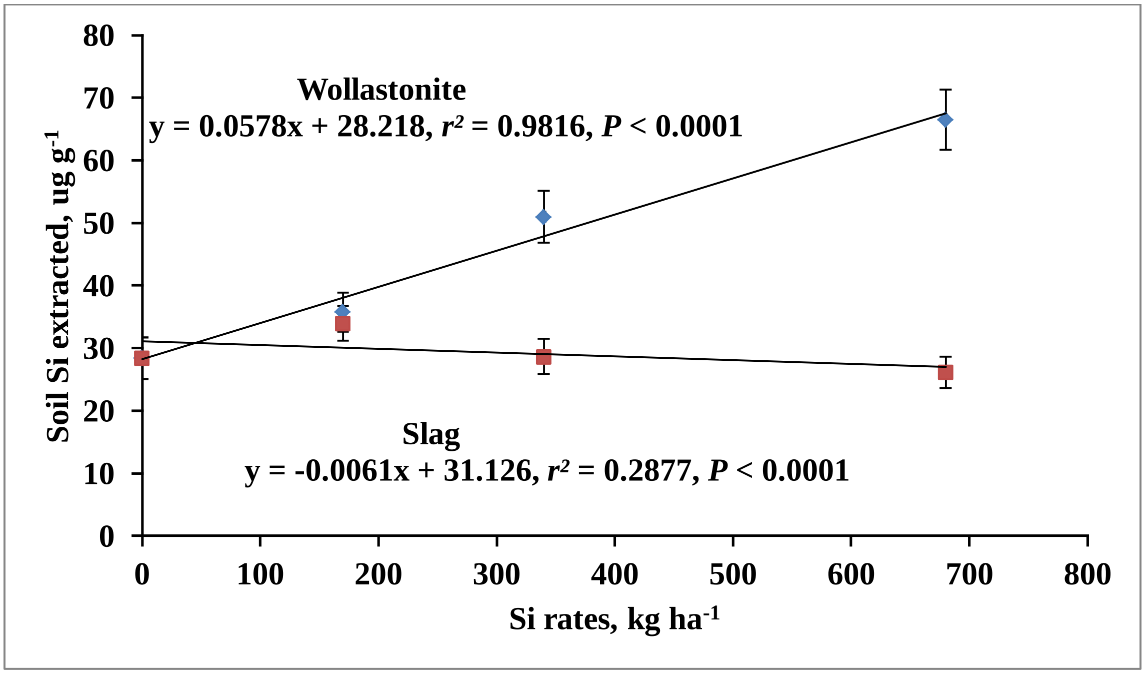


Figure 4.1 The $CaCl_2$ extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag (each point is an average of 30 observations)

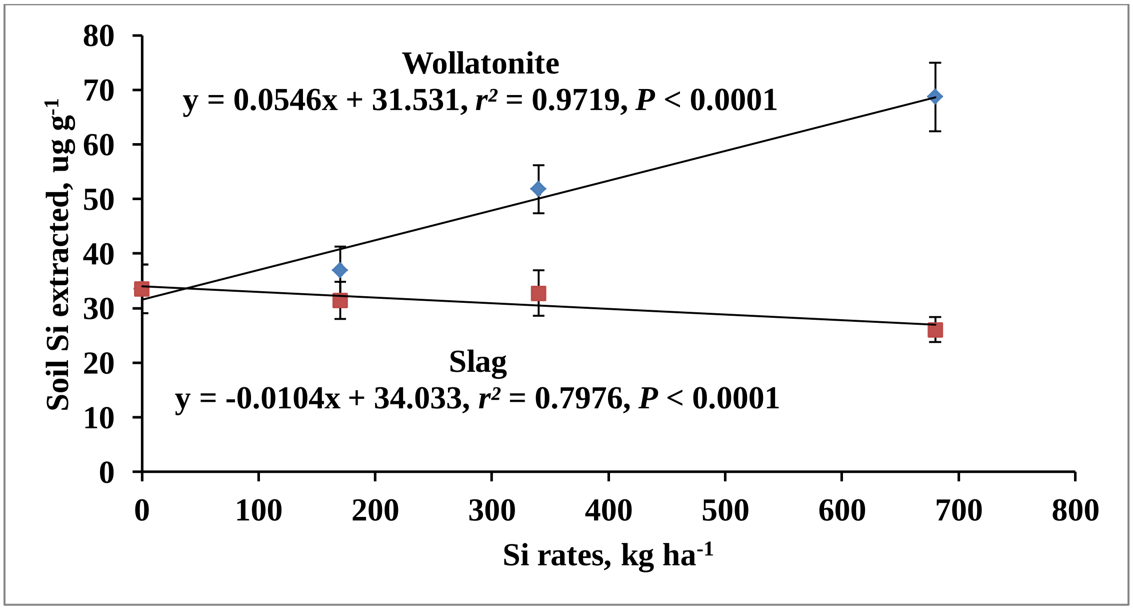


Figure 4.2 The deionized water extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag

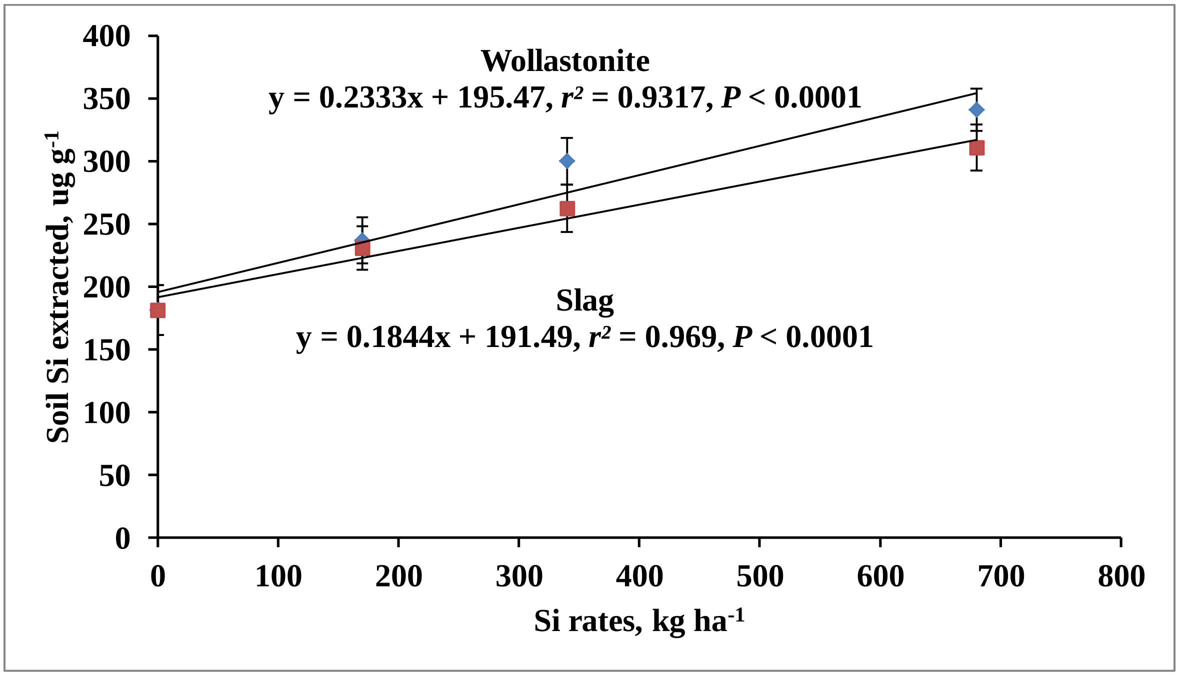


Figure 4.3 Acetic acid-2 (0.5 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag

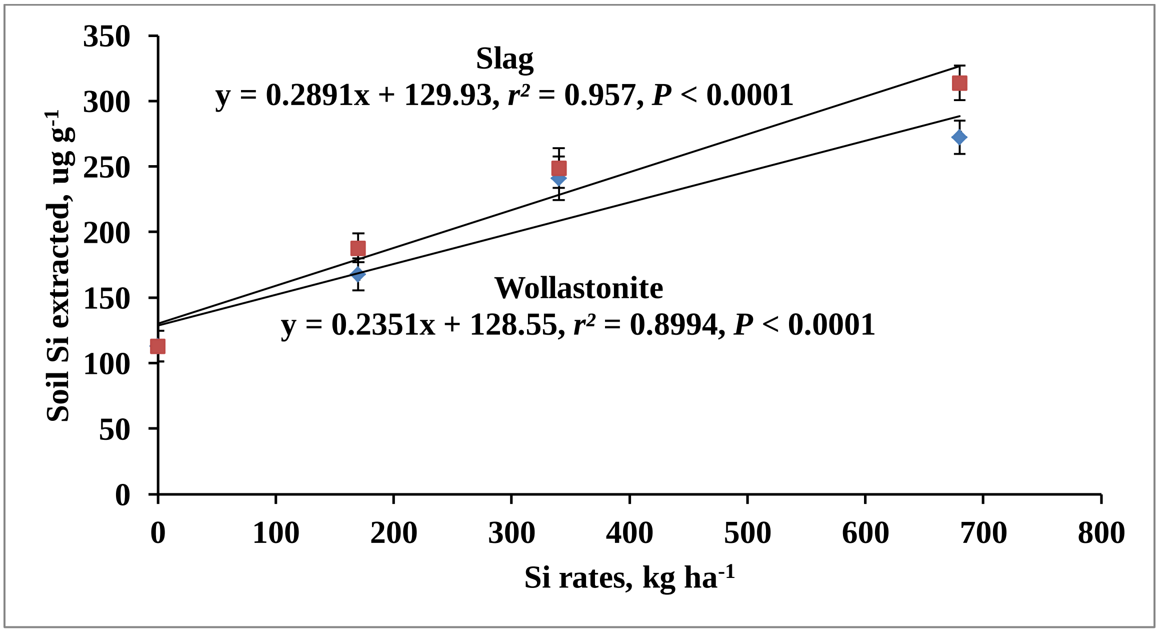


Figure 4.4 Acetic acid-1 (0.5 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag

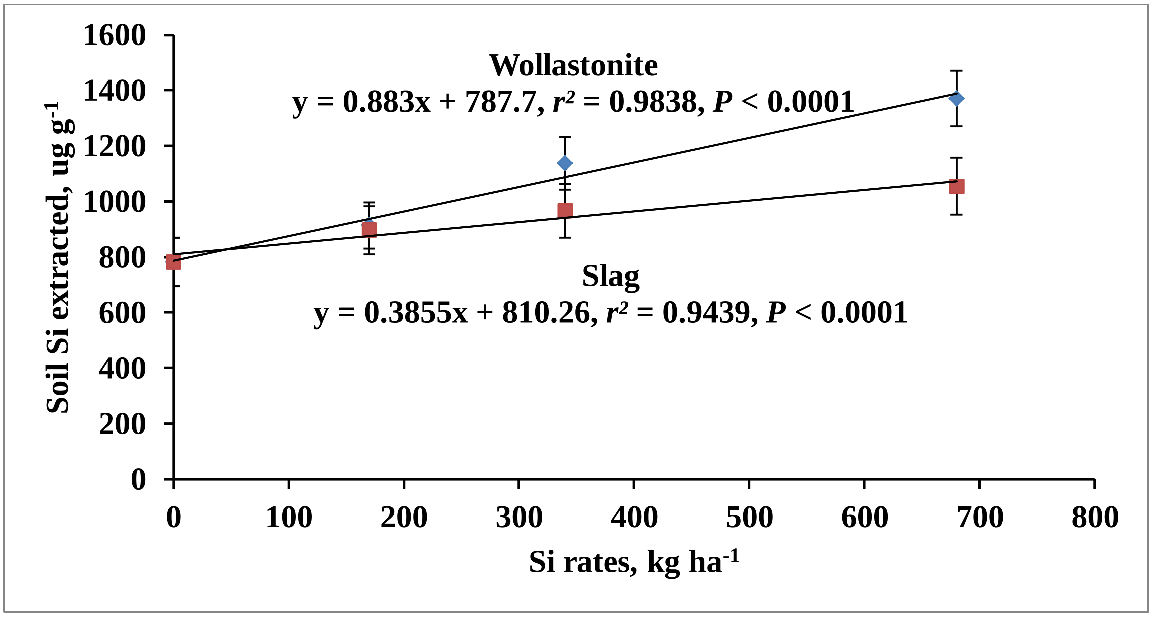


Figure 4.5 Citric acid (0.1 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag

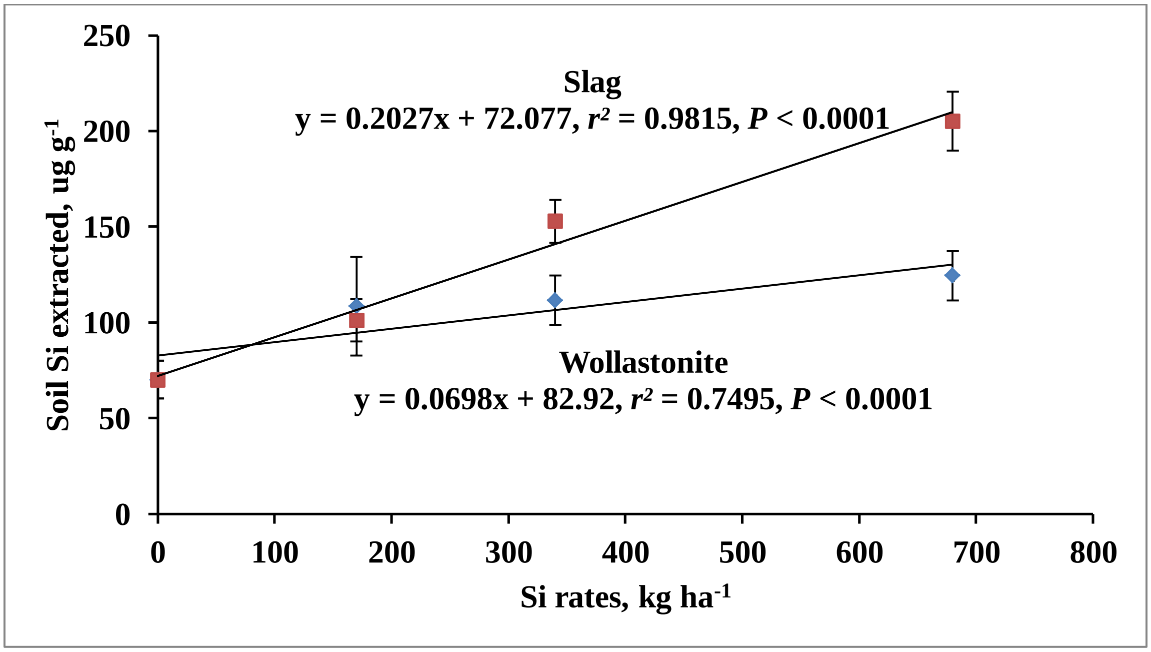


Figure 4.6 Sodium acetate (1 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag

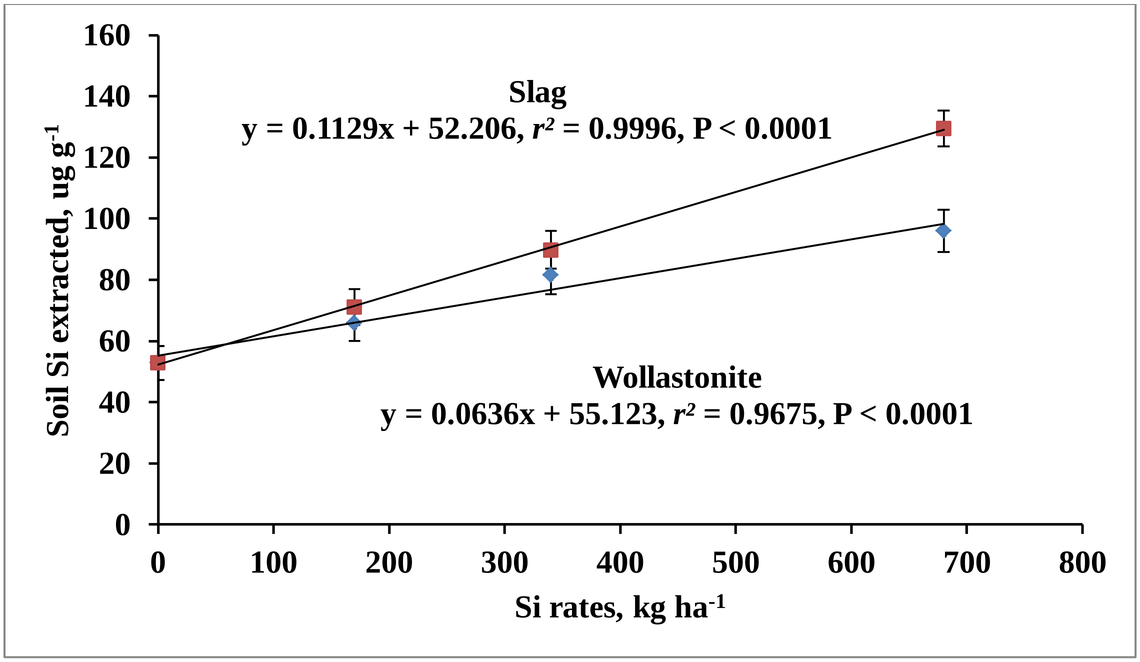


Figure 4.7 Ammonium acetate (0.5 M) extractable soil silicon with different rates of silicon applied in soil in the form of wollastonite and silicate slag

4.3.2 Effect of Si application on the rice dry matter yield

Relative biomass yield (%) is often used effectively in soil testing calibration to eliminate the experiment site influences (Evans 1987). The relative biomass yield (RBY) used in the present experiments was defined as the percentage of total yield (grain and straw) of rice without Si to that with Si application. The relative yield in this study ranged from 57 to 94% (Table 4.6). The addition of Si has increased the relative yield in all soils (with the exception of Perry clay) at some level although it was very pronounced in the case of Commerce silt loam soil ($P<0.05$). It was interesting to note that Commerce silt loam and Perry clay were the soils with lowest and highest extractable Si, respectively when 0.01 M $CaCl_2$ was used to determine the native Si concentration (Table 4.4). These varied responses of soil to applied Si may be attributed to variation in native plant available Si content of these soils. Narayanaswamy and Prakash (2009) reported that soils having low to medium in available Si responded to applied Si fertilizers to greater extent than the soils having higher levels of available Si. Similar results were also observed for organic soils of Florida (Korndorfer et al. 2001). The addition of lime was not sufficient to meet the maximum relative yield attained in all soils. This further supports that Si is essential for rice growth (Epstein 1999). It also seems likely that the wollastonite was more effective on all types of soil with the higher relative biomass yield as presented in the Table 4.6. Also, the scenario of yield depression at the higher Si rates appears in all soils except for clay soils. This becomes very evident in Caushatta silt loam ($P<0.0001$) where slag showed an increased relative yield (compared to control and check lime treatments) of 80% at 170 kg Si ha^{-1} and thereby decreased to 57% at 680 kg Si ha^{-1}. Similar trend was observed in Commerce silt loam as well ($P<0.0001$). Therefore, it is likely that the slag, with a high Si content, coupled with its high rate of release, leading to increase in polymerized form of Si, seemed to have caused a nutrient imbalance especially at the higher Si rates. However, it was interesting to note that this scenario of yield depression was not documented in the case of clay soils. The adsorption capacity of clay soils could have prevented this and made Si more available for plant uptake. Williams and Crerar (1985) stated that clays in the soil may adsorb excess silica, thus inhibiting the formation of silica polymorph from soluble silica.

Grain yields increased with the application of Si in all soils with the exception of Mowata silt loam (Table 4.7). No significant yield increases were observed with the application of lime ($CaCO_3$) and most were similar to the control (Table 4.7). The highest grain yield was observed in soils treated with wollastonite. The decline in yield at higher rates of Si was noted in most of the soils studied, with the exception of Sharkey clay. Haynes et al. (2013) observed a similar scenario and reported that this growth depression is attributable to the combined effect of the very high pH (possibly also inducing deficiencies of Zn and Mn for steel slag) and EC (and high

Na for processing mud) in soils from these treatments at the high Si rate. The high pH, of silicate slag is exacerbated by the fact that it has relatively low Si contents (12-17%) and therefore has to be applied at a higher rate than wollastonite to give the same rate of Si application.

Among all soils, grain yield increased up to 16.5% at 680 kg Si ha^{-1} as wollastonite in Sharkey clay. An increase in rice yield under flooded conditions was also noticed with Si fertilization in Sri Lanka (Takijima et al. 1970) and India (Singh et al. 2006). Snyder et al. (1986) showed that the application of calcium silicate increased rice yields in Histosols, mainly due to the supply of plant-available Si and not of any other nutrients. The effect of Si on decreasing disease incidence unquestionably contributes to increased yields, but Si has also been shown to increase yield in the absence of a disease (Datnoff et al. 1992). The increase in grain yield might be due to more efficient use of solar radiation, moisture, and nutrients since Si makes the rice plant more erect (Rani et al. 1997).With the application of Si as wollastonite and slag, an increase in straw yield was observed only at 170 kg Si ha^{-1} as slag and as wollastonite in Commerce silt loam and at 340 kg Si ha^{-1} Si as wollastonite in Caushatta silt loam. The total biomass yield increased in all soils with the application of Si as wollastonite. Total yield increased up to 22%, with application of slag in Caushatta silt loam and Commerce silt loam at the lowest rate of 170 kg Si ha^{-1}. This increase in total yield with the application of slag was evident only in these two soils. The greater rate of slag application has not shown any favorable responses in these soils. Slag is a recently formed polycrystalline material as opposed to wollastonite a naturally formed pure crystalline mineral. Therefore, slag release monosilicic acid at faster rates and higher concentrations when compared to wollastonite and this leads to the conversion of soluble Si released by slag into adsorbed forms which are unavailable for plant uptake.

Table 4.6 Relative biomass yield in different soils with different rates of silicon as wollastonite and slag

Treatments	Rate kg Si ha^{-1}	Caushatta silt loam	Commerce silt loam	Crowley silt loam	Mowata silt loam	Perry clay	Sharkey clay
		……………………………%………………………………………………					
Control	-	62bc	63c	76b	84bc	57	73b
Check lime	†	62bc	66c	77b	85abc	60	82ab
	170	75ab	93a	82ab	94a	69	81ab
Wollastonite	340	88a	82b	87a	81c	73	87a
	680	76ab	82b	79ab	82c	70	88a
	170	80a	81b	83ab	93ab	64	84ab
Slag	340	79ab	70c	81ab	77c	66	82ab
	680	57c	64c	80ab	79c	67	79ab
P-value		*<0.0001*	*<0.0001*	*0.0399*	*<0.0001*	*(NS)*	*0.0402*
Mean		72.4	75.2	80.5	84.1	65.6	82.0

The yield depression observed could be due to high pH, which in turn induces deficiencies of Zn and Mn with slag addition as noted by Haynes et al. (2013). This could also be attributed to the greater release of Si from slag and low soil adsorption capacity in light textured soils which in turn makes the Si unavailable for plant uptake. This was studied and explained by Iller (1979) who stated that H_4SiO_4 is soluble and stable in water at 25°C for long periods of time if the concentration is less than about 100 ug g^{-1} as SiO_2 but when a solution of monomer, $Si(OH)_4$, is formed at a concentration greater than about 100-200 ug g^{-1} as SiO_2, and in the absence of solid phase on which the soluble silica might be deposited, then the monomer polymerizes by condensation to form dimer and higher molecular weight species of silicic acid.

Further, there was no increase in total yield with increased rates of Si in clay soils, these soils did not show total yield depression at higher levels. The clay soils with a greater solid surface area also showed higher availability of soil Si than silt loam soils at all treatment levels (Table 4.5). This could be due to lower rate of polymerization as explained by Iller (1979) in these soils than the silt loam soils and therefore, higher availability of Si for plant uptake creating no negative if not, a positive impact on total yield. These studies demonstrate the importance of Si in maximizing the yield potential of rice. Agarie et al. (1992) also reported that maintenance of photosynthetic activity due to Si fertilization could be one of the reasons for increased dry matter production. Overall, addition of Si resulted in a significant increase in total yield over the control treatment (NPK only) and over treatments that applied $CaCO_3$ in these soils of Louisiana. This would mean that lime alone was not sufficient to maintain the maximum potential yield in these soils. Silicon fertilization showed a positive effect on maintaining greater yield stability in rice.

Table 4.7 The dry matter yield of rice at harvest in different soils with two sources of Si applied at different rates

Source	Rate kg Si ha^{-1}	Caushatta silt loam	Commerce silt loam	Crowley silt loam	Mowata silt loam	Perry clay	Sharkey clay
……………………………..Straw Yield (g pot^{-1})……………………………							
Control	-	29bc	22d	35	26bc	30	48
Check lime	†	29bc	23cd	35	26abc	33	54
Wollastonite	170	34abc	34a	36	30a	46	54
	340	40a	28b	42	27abc	39	56
	680	31bc	28b	37	27abc	36	57
Slag	170	36abc	32ab	38	29ab	35	54
	340	35abc	28b	39	25c	37	54
	680	27c	28bc	39	25bc	38	52
P-value		*0.0002*	*<0.0001*	*NS*	*0.0014*	*NS*	*NS*
……………..……………………..Grain Yield (g pot^{-1})……………………							
Control	-	32bc	22cd	40	41ab	36b	54b
Check lime	†	33bc	23c	41	42ab	37b	59ab
Wollastonite	170	41ab	32a	45	45a	55a	59ab
	340	47a	29ab	44	38b	47ab	65ab
	680	45a	29ab	41	39b	46ab	65a
Slag	170	44ab	24bc	44	46a	40ab	62ab
	340	43ab	21cd	41	37b	40ab	60ab
	680	29c	17d	40	39b	41ab	58ab
P-value		*<0.0001*	*<0.0001*	*NS*	*<0.0001*	*0.0098*	*0.0397*

Table 4.8 The total yield and silicon uptake of rice grown on different soil series

Source	Rate kg Si ha^{-1}	Caushatta silt loam	Commerce silt loam	Crowley silt loam	Mowata silt loam	Perry clay	Sharkey clay
	…………………………………………….Total Yield (g pot^{-1})…………………………………………….						
Control	-	62bc	44c	75b	67bc	67b	102b
Check lime	†	62bc	46c	76b	68abc	70ab	113ab
Wollastonite	170	75ab	65a	81ab	75a	81ab	113ab
	340	88a	57b	86a	65c	86a	121a
	680	76ab	57b	78ab	66c	82ab	122a
Slag	170	80a	57b	82ab	75ab	75ab	116ab
	340	78ab	49c	80ab	62c	77ab	114ab
	680	56c	45c	79ab	64c	79ab	110ab
**P-value*		*<0.0001*	*<0.0001*	*0.0399*	*<0.0001*	*0.0514*	*0.0402*
	……………………………………………..Total uptake (g pot^{-1})…………………………………………….						
Control	-	1.20e	0.52e	1.96d	1.66bc	2.03	2.90b
Check lime	†	1.37de	0.53e	2.12cd	1.58bc	2.21	3.61ab
	170	2.09bc	1.50b	2.65abc	2.55a	2.60	3.97a
Wollastonite	340	3.07a	1.67ab	2.83a	2.34a	2.95	4.14a
	680	2.23b	1.78a	2.71ab	2.55a	3.09	4.27a
	170	1.80bcd	0.91c	2.21bcd	1.88b	2.68	3.89a
Slag	340	1.68ede	0.82cd	2.46abcd	1.64bc	2.97	3.66ab
	680	1.21e	0.59de	2.25bcd	1.39c	2.48	3.70ab
P-value		*<0.0001*	*<0.0001*	*<0.0001*	*<0.0001*	*NS*	*0.0008*

4.3.3 Effect of Si application on Si content and uptake by rice plants

The greater effectiveness of the Si treatments might be associated, as stated by Meyer and Keeping (2000), with an increase of Si concentration in the plant. Detailed uptake data by rice plants in terms of the respective; Si source, application rates and soil types are given in Table 4.9. It was observed that increasing rates of Si applied to the soil as wollastonite had a direct effect on rice Si content in all the soil types *($P<0.05$)* with the exception of Crowley silt loam as indicated by the concentration of Si (%) in the rice straw. Averaged across all the soil types, plant Si levels in treatments receiving Si as wollastonite were generally more than those in plants from untreated pots (Table 4.8). However, the straw content of Si did not increase with addition of slag.

The panicle content of Si was also seen to increase in three (Caushatta silt loam, Commerce silt loam and Mowata silt loam) out of the six soils tested. Again this increase was evident only when wollastonite was the source of Si. Also, Si uptake in rice straw and grain was significant *($P<0.05$)* when wollastonite was the source of Si in five out of the six soils studied. With regard to total Si uptake, wollastonite-treated rice showed maximum increases (Table 4.9). The difference in efficacy of the two Si sources might be due to their differences in silicon content and solubility (Haynes et al. 2013). When the efficiency of the slag with regard to total Si uptake was considered in comparison to the standard wollastonite, slag showed almost equivalent rates of uptake in Sharkey clay, Crowley silt loam, and Caushatta silt loam as the standard wollastonite at their lowest rates of application *($P<0.001$).* Plant Si uptake (Table 4.9) was increased by both sources in Caushatta silt loam, Commerce silt loam and Sharkey clay when compared with control *($P<0.001$).*

Table 4.9 The silicon content and uptake in rice panicle and straw with different rates of silicon in different soils

Source	Rate kg Si ha^{-1}	Caushatta silt loam	Commerce silt loam	Crowley silt loam	Mowata silt loam	Perry clay	Sharkey clay	Mean
		……………………………Straw Content (%)……………………………						
Control	-	2.97c	1.54c	3.74b	4.29b	4.37c	4.22b	3.52
Check lime	†	3.42c	1.54c	4.17b	3.77b	4.49c	4.63ab	3.67
	170	4.70b	2.91b	4.87ab	5.96a	4.92bc	5.27a	4.77
Wollastonite	340	4.96ab	4.28a	4.78ab	6.15a	5.21abc	5.06ab	5.08
	680	5.44a	4.83a	5.28a	6.42a	5.94a	5.01ab	5.49
	170	3.47c	1.85c	3.80b	3.97b	5.30abc	5.05ab	3.91
Slag	340	3.50c	1.85c	4.50ab	4.33b	5.63ab	4.89ab	4.13
	680	3.43c	1.68c	3.98b	4.26b	4.51c	5.23a	3.85
P-value		*<0.0001*	*<0.0001*	*NS*	*<0.0001*	*<0.0001*	*0.0356*	
		……………………………………………Panicle Content (%)……………………………………..........						
Control	-	1.03b	0.82b	1.64	1.33d	1.91	1.67	1.40
Check lime	†	1.16b	0.77b	1.66	1.40cd	1.91	1.86	1.46
	170	1.22b	1.66a	1.96	1.64bc	2.20	1.92	1.77
Wollastonite	340	2.25a	1.59a	1.95	1.83ab	1.99	1.98	1.93
	680	1.28b	1.53a	1.96	2.07a	2.03	2.21	1.85
	170	1.29b	1.31a	1.75	1.61bcd	2.08	1.82	1.64
Slag	340	1.05b	1.41a	1.70	1.54bcd	2.21	1.72	1.61
	680	0.97b	0.74b	1.77	0.83e	1.92	1.79	1.34
P-value		*<0.0001*	*<0.0001*	*NS*	*<0.0001*	*NS*	*NS*	

(Table 4.9 continued)

Source	Rate kg Si ha^{-1}	Caushatta silt loam	Commerce silt loam	Crowley silt loam	Mowata silt loam	Perry clay	Sharkey clay	Mean
……………………………………..Straw Uptake (g pot^{-1})……………………………………								
Control	-	0.87d	0.34d	1.31c	1.11b	1.34	2.00b	1.16
Check lime	†	0.99d	0.35d	1.44bc	1.00b	1.49	2.51ab	1.30
	170	1.58bc	0.97b	1.77abc	1.81a	2.31	2.85a	1.88
Wollastonite	340	2.00a	1.21a	1.97a	1.65a	2.01	2.85a	1.95
	680	1.65ab	1.33a	1.92ab	1.76a	2.16	2.83a	1.94
	170	1.24cd	0.60c	1.44bc	1.15b	1.86	2.75ab	1.51
Slag	340	1.23cd	0.52cd	1.76abc	1.07b	2.09	2.62ab	1.55
	680	0.93d	0.46cd	1.55abc	1.07b	1.70	2.66ab	1.40
P-value		*<0.0001*	*<0.0001*	*0.009*	*<0.0001*	*NS*	*0.0207*	
………………………………………Panicle Uptake (g pot^{-1})…………………………………..								
Control	-	0.33cd	0.18c	0.65b	0.55b	0.69b	0.90b	0.55
Check lime	†	0.38bcd	0.18c	0.68ab	0.59b	0.72b	1.10ab	0.61
	170	0.51bc	0.52a	0.88a	0.74a	1.22a	1.12ab	0.83
Wollastonite	340	1.06a	0.46a	0.86a	0.69ab	0.93ab	1.29ab	0.88
	680	0.58b	0.45a	0.79ab	0.80ab	0.93ab	1.44a	0.83
	170	0.56b	0.32b	0.77ab	0.74ab	0.82ab	1.14ab	0.72
Slag	340	0.45bcd	0.29b	0.70ab	0.57b	0.88ab	1.03ab	0.65
	680	0.29d	0.13c	0.70ab	0.32c	0.78b	1.04ab	0.54
P-value		*<0.0001*	*<0.0001*	*0.0083*	*<0.0001*	*0.0026*	*0.0084*	

At harvest, with the exception of two clay soils, total Si uptake was substantially lowered for both these sources applied at the rates higher than 170 kg Si ha^{-1}. This could be due to lower plant available Si (monomeric form) concentration in soil at higher rates of fertilizer application as a result of higher dissolution of the fertilizer materials in silt loam soils having low adsorption capacity that leads polymerization as shown by Iller (1979).

4.3.4 Correlation of soil available Si with plant Si and yield response to Si fertilization

In the present study, the amount of soil Si extracted by all extractants was linearly correlated with both the Si content and uptake in panicle and straw and with total Si uptake by rice (above ground biomass) (Table 4.9). In general, soil test method for evaluating nutrient availability must be correlated with crop response to the fertilizer application (Allen et al. 1994). The common statistical techniques used to predict yield responses are the linear plateau model and Cate and Nelson (graphical) method. The RBY was not linear proportional to the soil available Si level in this study, to fit the linear equation. However, the RBY data showed a good fit with quadratic equation (Appendix C, Table C.1- C.6). Therefore, besides the linear plateau model and Cate and Nelson method to determine the critical level, quadratic regression model was also used. The significant test of linear fit between the plant Si (content and uptake) and soil Si extracted respectively by the seven procedures showed greater positive correlations with four extraction methods (0.01 M $CaCl_2$, Deionized water, 0.1 M Citric acid and 0.5 M Acetic acid-2) out of the seven and could be suggested as being the most suitable for evaluating the soil Si availability (Table 4.10). However, the extracted soil solution by the deionized water has deeper color of soil organic and other pigments. Repeated filtering is needed to clear the extracting solution which complicates the routine molybdenum blue colorimetric process (Xu et al. 1996). Furthermore, the $CaCl_2$ extraction method has been widely used as the conventional method for evaluating available Si status in acid and neutral soils (Savant et al. 1997). As already discussed, highest yields were recorded for wollastonite at the lower rate of Si addition. Nevertheless, for both materials, yields were depressed at the higher Si rate. Also, because of the low measured extractability of wollastonite in soils, the higher acid extractability of slag and the yield depressions induced by the high rates of slag, correlations between extractable soil Si and RBY were very poor and generally not significant when all the experimental data was used. Generally, the 0.01 M $CaCl_2$ and 0.5 M acetic acid-2 extractants gave the highest correlations (Table 4.10) with both yield and total Si uptake and therefore seemed most appropriate for use. Such conclusions are similar to those of others. Berthelsen et al. (2001) considered that if a single measure is required for available Si, then 0.01 M $CaCl_2$ is the most suitable.

4.3.5 Critical limits of plant available soil silicon as determined by different extraction procedures

The critical level (level below which response to the added Si fertilizer is expected) for Si in the soil calculated as given by Cate and Nelson (1965; 1971) procedure varied by different extractants. The critical limits for soil Si as extracted by seven extractants in six soils are presented in Appendix C in Tables C.1 to C.6. In general, improved r^2 values were obtained for individual soils than for all soils combined. Table 4.2 summarizes the properties of the six soils. As can be seen, texture, organic matter content, and pH varied at wide ranges. On average, the soils were light-textured to heavy textured, moderately acidic to moderately basic, and relatively moderate to high in organic carbon. The wide range in initial Si concentration could be a result of differences in soil texture and parent material. Many studies have shown that soils with light or sandy texture are usually deficient in available Si and thus have low Si-supplying power, while those with heavy or clayey texture are Si sufficient (Kawaguchi and Kyuma 1977; He 1993; Liang et al. 1994; Zhang et al. 1996, 2003). Soil-available Si content is positively correlated with clay content in soils (Wan et al. 1993; Zhang et al. 1996; Dai et al. 2004) as soil clay minerals with high specific surface have a high capacity to adsorb silicates. Also, there is an increase in release of colloid - adsorbed silicon into soil solution when soil pH rises from 4 to 6 (Oliveira 2004). Therefore the soils differed considerably in Si sorption and buffering capacity as a result of differences in clay content and pH. The highest critical limit was observed for 0.1 M Citric acid and 0.5 M Acetic acid-2 and the least was noticed in 0.01 M $CaCl_2$ and deionized water. This trend was also observed by Narayanswamy and Prakash (2009) among the seven extractants. There was wide variation in critical levels of soil Si determined by different extractants and this variation was probably due to the extracting power of extractants, pH of the extracting solution, shaking period, soil to solution ratio as well as nature of different extractants used as reported by Narayanswamy and Prakash (2009). Similar results were also noticed for organic soils of Florida by Korndorfer et al. (2001). Fox et al. (1967) also reported greater extracting power for extractants such as calcium phosphate, acetic acid and sulphuric acid extractants than neutral extractants. The extractant measuring the readily available or soluble forms of Si were the neutral extractants and estimating the critical levels using these neutral extractants might give only the estimate of plant available Si required for a certain growth stage of a crop. Whereas, the extractant measuring the exchangeable and adsorbed forms of Si (acidic extractants) in addition to soluble forms of Si might give the plant available Si required for the entire crop growth period. Therefore, either a combination of neutral and acidic extraction procedures can be used to determine the critical level of soil Si or the 0.5 M acetic acid-2 procedure which gave the highest correlation (Table 4.10) between soil Si and plant response variables may be used to determine the soil critical level of Si.

Table 4.10 Coefficient of determination (r^2) between extractable soil silicon based on different extraction procedures and different plant response variables

Plant response Variables	……………………………………Soil Si Extraction Procedures……………………………………………						
	0.5M Acetic acid-1	1M Sodium acetate	0.01M Calcium chloride	0.5M Ammonium acetate	Deionized water	0.1M Citric acid	0.5M Acetic acid-2
Straw content	0.095**	0.084**	0.304***	0.121***	0.193***	0.232***	0.363***
Straw uptake	0.074**	0.251***	0.592***	0.304***	0.490***	0.540***	0.638***
Grain content	0.012^{ns}	0.074**	0.312***	0.087***	0.186***	0.233***	0.415***
Grain uptake	0.026**	0.157***	0.528***	0.209***	0.427***	0.433***	0.541***
Total uptake	0.054**	0.216***	0.584***	0.272***	0.485***	0.514***	0.608***
Total Yield	0.020*	0.189***	0.492***	0.235***	0.473***	0.449***	0.458***
Straw yield	0.022*	0.241***	0.479***	0.270***	0.464***	0.472***	0.494***
Grain yield	0.019*	0.145***	0.449***	0.194***	0.418***	0.387***	0.401***

*P < 0.05, ** P < 0.001, ***P < 0.0001 and ns = non-significant

When correlations are done with potted plant studies, the overall relative yields are usually lower (greater response) than those measured in field trials. Logically, then, the horizontal split on relative yield may not be so much a separation between soils which give large response vs. those which give little or no response, but rather a distinction between degrees of responsiveness. Since potted plant studies are not designed to provide economic interpretation of response, the exact position of the horizontal line should not be counted as having much importance in correlation work (Cate and Nelson, 1971).

The critical limit of 0.1 M NaoAc extractable soil Si in Sharkey clay was estimated as 150 ug g^{-1} ($P = 0.012$) using the linear plateau model (Figure 4.8). The critical limit of 0.5 M acetic acid-1 extractable soil Si was estimated as 272 ug g^{-1} ($P < 0.001$) in Perry clay with linear plateau model (Figure 4.9). The only other soils for which the model gave a good fit was commerce silt loam and Caushatta silt loam as 156 ($P = 0.007$) and 174 ug g^{-1} ($P = 0.02$) respectively using 0.5 M acetic acid-2 extraction procedure as shown in Figures 4.10 and 4.11. Perhaps more study sites should be selected with soil test Si levels less than 25 ug g^{-1}. The critical levels estimated by this model are much higher than the established critical levels in other parts of the world by different scientists. This could be because of high native Si in clay soils and also due to the extended time of (24 hours) soaking of soil in the procedure with 0.5 M Acetic acid-2. But these high Si critical values cannot be ignored because in spite of higher Si content (71–181ug g^{-1}) in calcareous soils of China, as extracted by sodium acetate buffer, rice yields continued to respond to applications of Si fertilizers (Liang et al. 1994). Although the model gave a good fit with $CaCl_2$ and deionized water extractable soil Si in Commerce silt loam, and deionized water extractable Si in Caushatta silt loam, the values were not considered to be significant because it was outside the range of data collected.

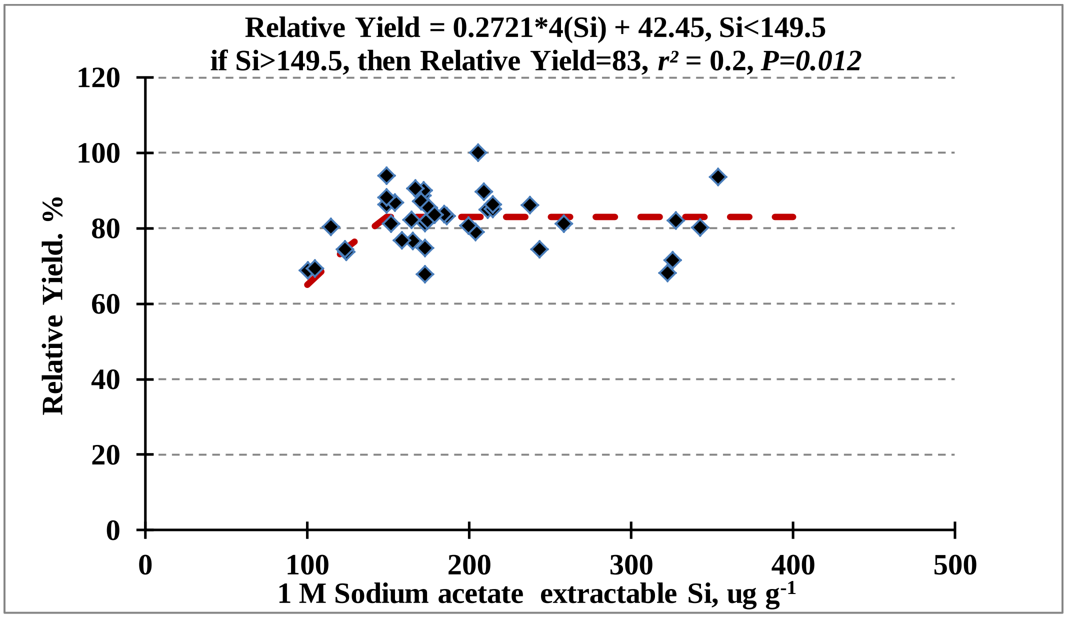


Figure 4.8 The linear plateau model fitting to determine the soil critical level of Si in Sharkey clay

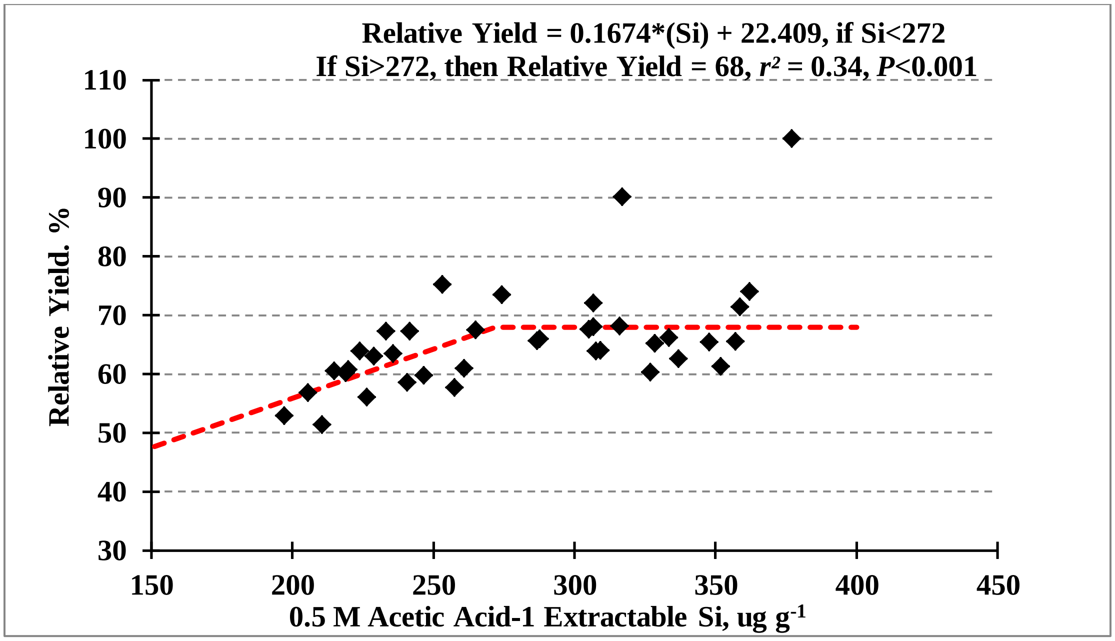


Figure 4.9 The linear plateau model fitting to determine the soil critical level of Si in Perry clay

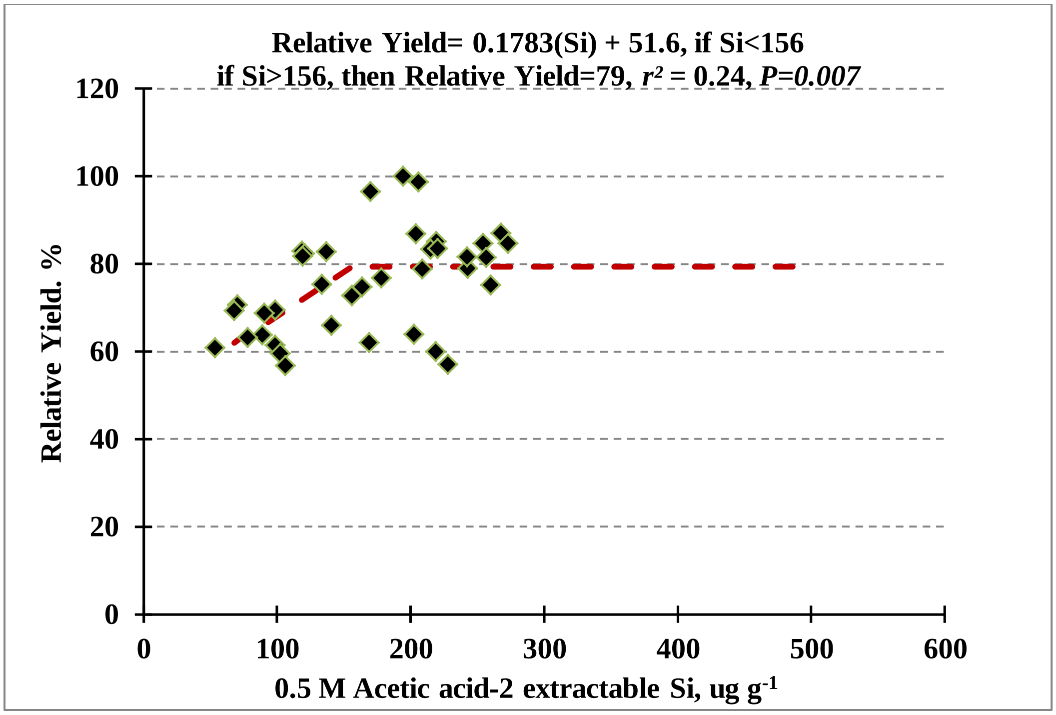


Figure 4.10 The linear plateau model fitting to determine the soil critical level of Si in Commerce silt loam

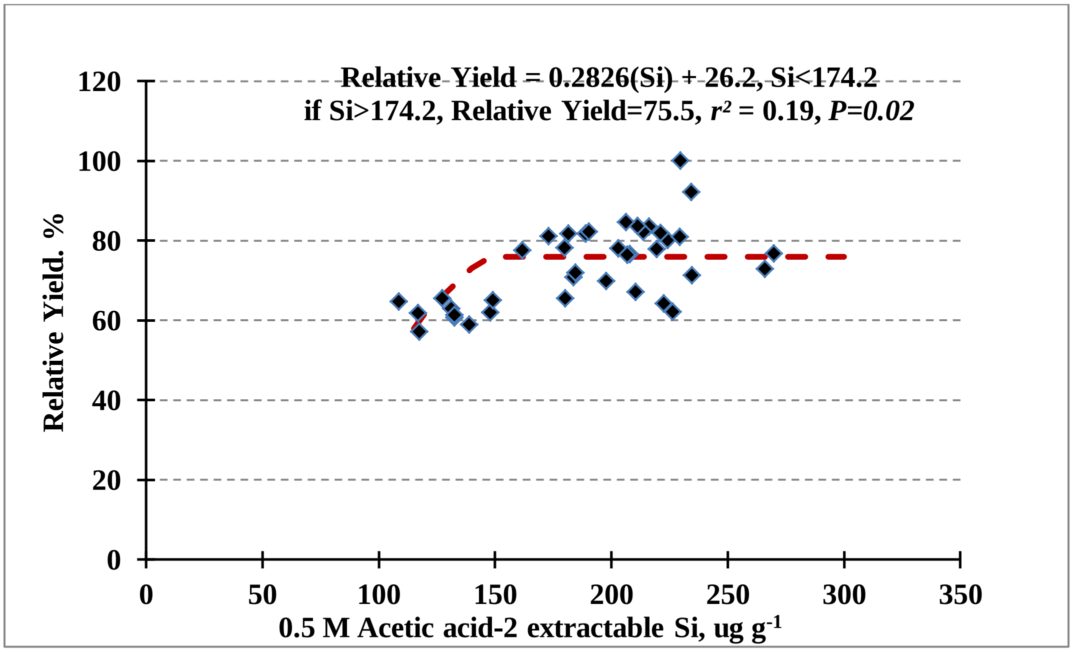


Figure 4.11 The linear plateau model fitting to determine the soil critical level of Si in Caushatta silt loam

Although, the quadratic regression model was able to produce a critical level for Perry clay as 296 ug g^{-1} as shown in Figure 4.12 ($P < 0.001$), this was considerably higher than critical levels established previously. The quadratic regression model gave significant values for critical levels in Commerce silt loam across all extractants. Whereas in other soils, this model was able to produce critical values using only one or few of the extractants. Traditionally, fertilization recommendations are devised from calibration of relative yield with soil test or tissue analysis, and fertilizer applied. However, the Si soil test and tissue can be unrelated to yield due to the influence of soil type.

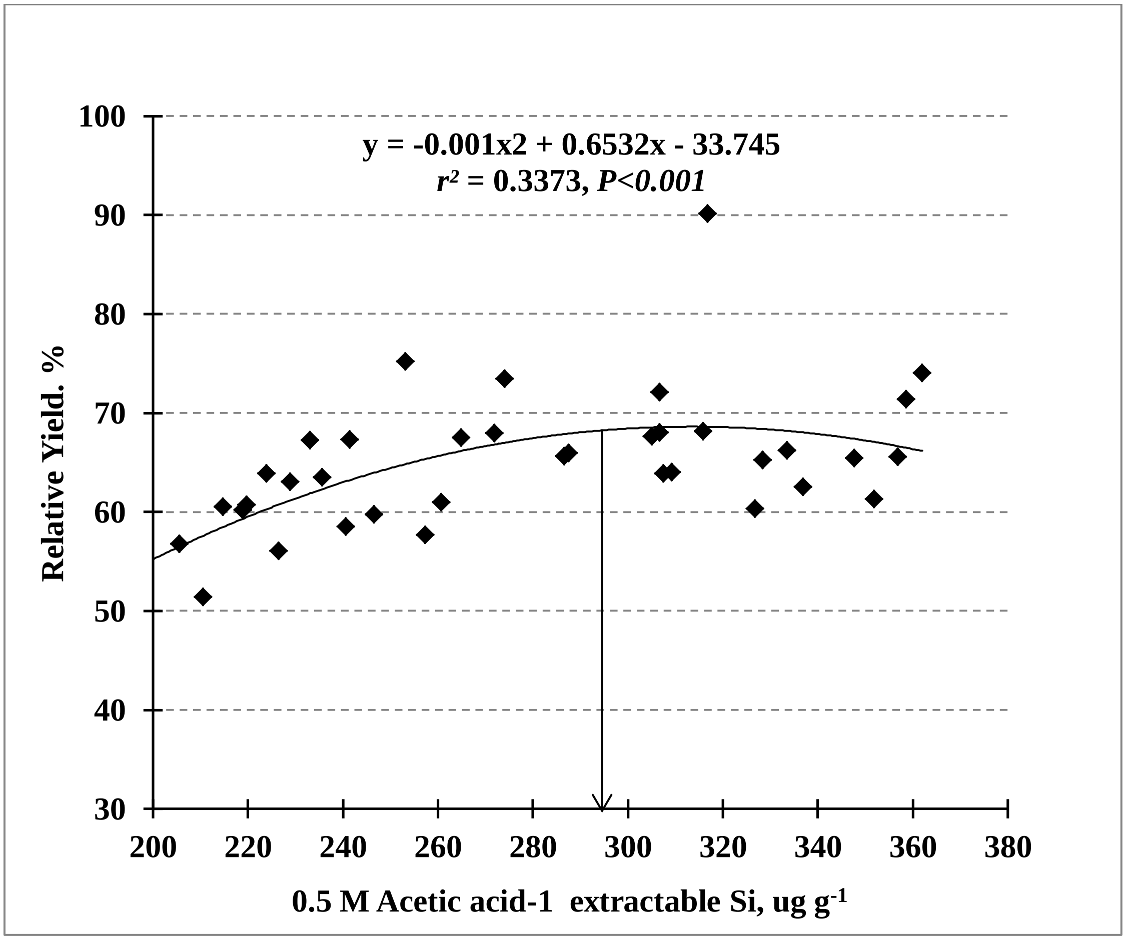


Figure 4.12 The quadratic model fitting on Perry clay to determine the critical level of soil Si

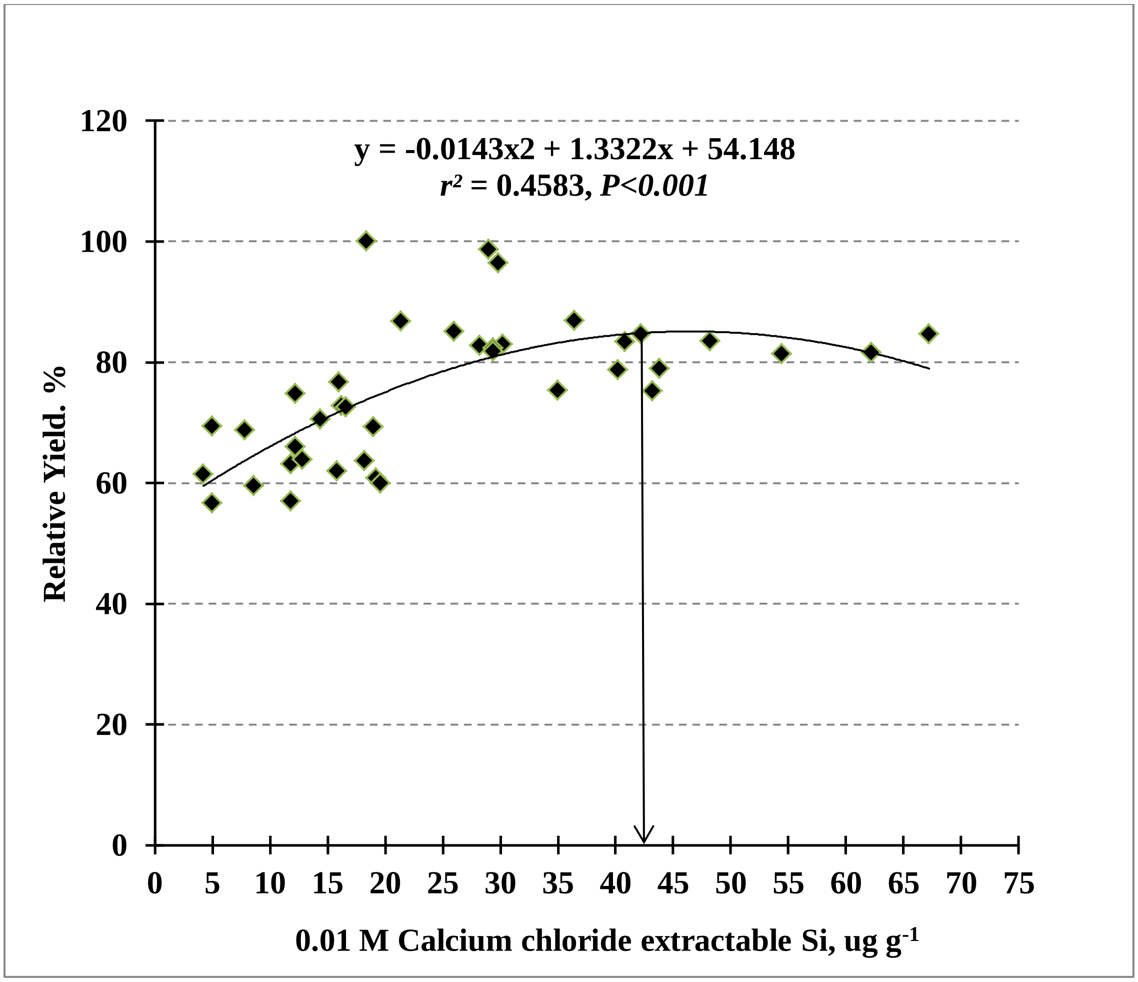


Figure 4.13 The quadratic model fitting on Commerce silt loam to determine the critical level of soil Si

The critical value for Commerce silt loam (Figure 4.12) and Crowley silt loam (Figure 4.13), using 0.01 M $CaCl_2$ method was 43 ug g^{-1} (*P <0.001*) and 37 ug g^{-1} (*P =0.009*). This value was in good agreement with the value (43 ug g^{-1}) generated by Narayanswamy and Prakash (2009) in rice soils of south India. Pereira and Cabral (2005) considered that for BF slag amended soils, 0.01 M $CaCl_2$ was the most suitable extractant followed by 0.5 M NH_4OAc. Our estimates of critical Si levels are compared with published levels reported from earlier studies. In the Caushatta silt loam, critical soil Si level estimated by quadratic regression was 250 (r^2=0.19, *P=0.019*), was much higher than the value of 87 mg kg^{-1}

(using 0.5 M acetic acid-2) reported by Narayanaswamy and Prakash(2009). A critical level of 928 ug g^{-1}(r^2=0.43,$P < 0.001$) was estimated using 0.1 M citric acid in Commerce silt loam which was also considerably higher than the value reported by Narayanaswamy and Prakash (2009).

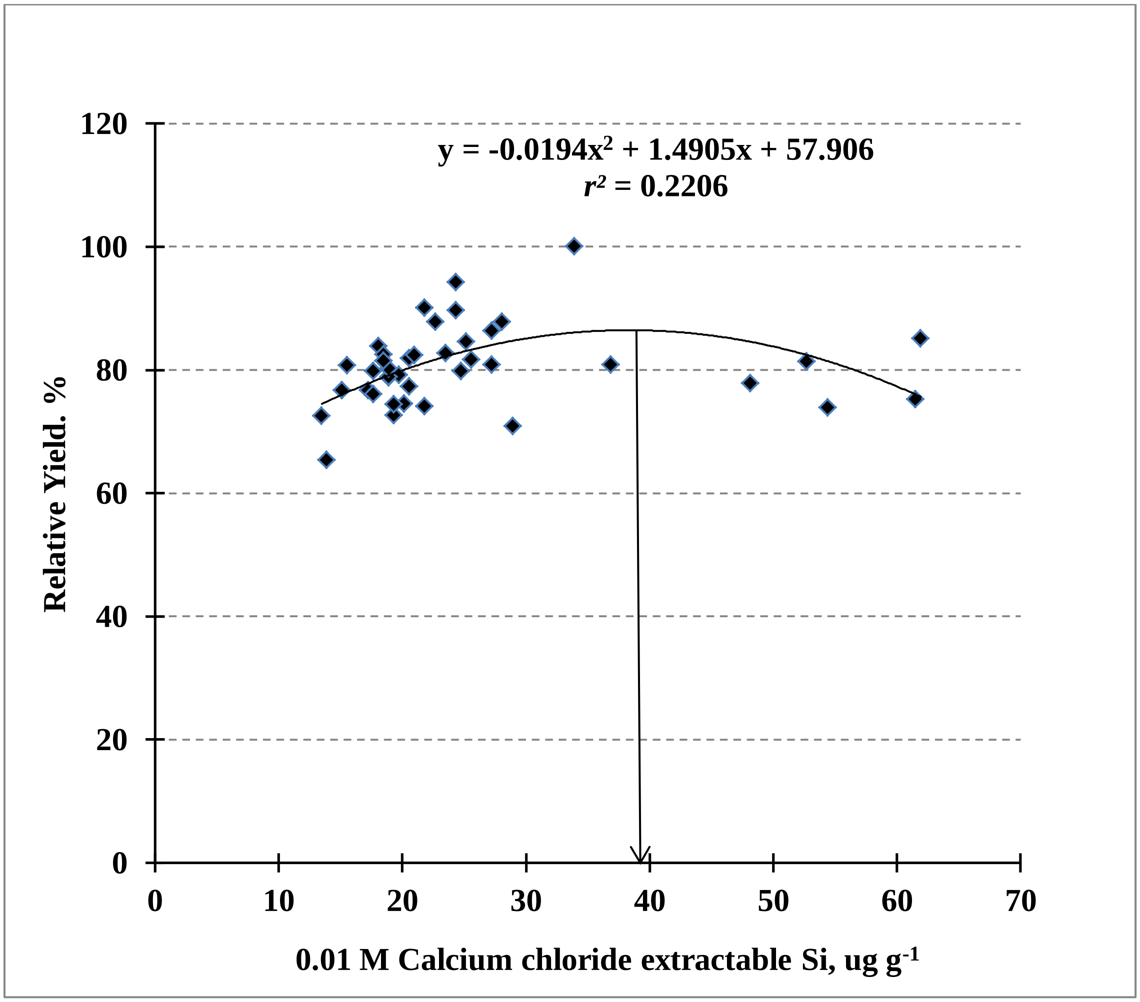


Figure 4.14 The quadratic model fitting on Crowley silt loam to determine the critical level of soil Si

The Cate-Nelson correlation method was performed on data from all soils to evaluate the visual indication of a soil test critical level for Si utilizing different soil test extraction procedures (Appendix C, Table C.1- C.6). The critical limits for all soil types could be derived from Cate and Nelson method. This shows an advantage that the visual Cate-Nelson approach has to linear-plateau models. However it also can be potentially miss-used to imply significance when the trends may be due to random error.

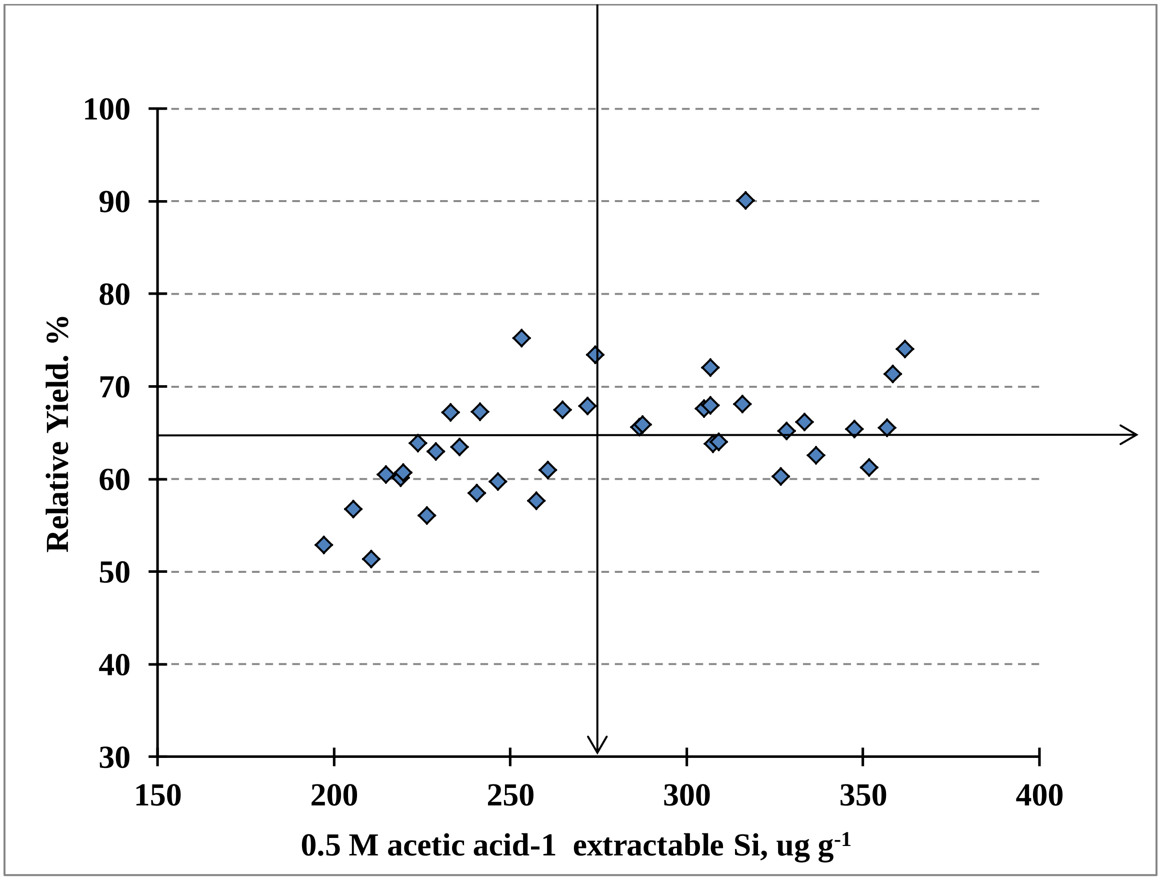


Figure 4.15 Critical level of soil Si determined by Cate and Nelsons' graphical method in Perry clay

Data collected from this study, using seven extractants show Cate-Nelson, linear–plateau and quadratic regression derived critical Si values around 3 to 1352, 149 to 272 and 37 to 928 ug g^{-1} (Appendix C, Table C.1- C.6), respectively. This wide range may be attributed to the initial soil Si variability observed from the sites. The critical value observed from the historic data and current data suggest that some soils have very high critical values. The confidence interval also stresses that the critical value is not an exact number and may change depending on factors described by Fixen and Grove (1990) of soil nutrient mineralization, and rainfall. It is important to note that any appropriate mathematical model may be used to estimate the critical value. Dodd and Mallarino (2005) examined Cate-Nelson, linear-plateau, quadratic, and exponential models, each with different results in a P calibration study. The Cate-Nelson and linear plateau models were used in this study because Dodd and Mallarino (2005) found the Cate-Nelson to be most economical and the linear plateau to give the lowest critical value of the other mathematical models. The use of a mathematical method takes out user bias as compared to the Cate-Nelson, and also prevents critical levels being established that may be due to random error. Quadratic models giving higher Si critical value estimations are not preferred from an economical and environmental perspective. To be profitable one wants to apply the least amount of fertilizer needed to obtain an economically optimum yield. Applications of Si when they are not needed may increase Si polymerization and unavailability to plant uptake.

No significant linear relationship between relative yield and Si fertilizer applied was found using the response data. However, a significant linear relationship between total yield and Si applied was found on the current data. Reasons for why a statistically significant critical level could not be found using the entire range of data across the soil types may be due to the wide variations among the soil types studied. This data was from six soil types which could be identified as six major groups of soils in a calibration study. Usually the calibration studies are comprised of replications of similar soil types, and for more than two years, which may help to tease out environmental differences in blocks such as moisture availability. Another reason for this poor response in these soils may be because they are inherently sufficient Si. The Si fertilizer studies are in their infancy and lack of data for critical soil Si level makes it difficult to set a benchmark for defining soils inherently low in Si. Additionally, sometimes, soils high in initial Si respond to Si fertilization which makes this process all the more challenging. Thus, there is a need, to look beyond the initial Si level in soil for establishing critical levels specific to soil type. Therefore at this point, conducting more number of these calibration studies, for a number of years, across different soil types is crucial. The scarcity of published calibration data for Si, in peer reviewed papers, research reports or extension bulletins, makes comparison of these results to other studies also difficult.

4.4 Conclusions

In general, it was observed that not only soils low to medium in available Si have a high response to applied Si in achieving higher grain yields, but also soils containing higher levels of Si responding moderately to Si applications. Among the soils studied, Sharkey clay and Perry clay soils have a high response to applications, with higher total yield followed by Commerce silt loam and Caushatta silt loam. Compared with other extractants, the soil Si extracted by 0.5 M acetic acid-2 and 0.01 M $CaCl_2$ had relatively higher positive correlation (r^2>0.45) with shoot biomass yield, straw and grain Si uptake and increasing rates of applied Si. The soil Si critical level determined with the respective best extractant and quadratic regression model *($P<0.05$)* for Caushatta silt loam, Crowley silt loam, Commerce silt loam, Sharkey clay, Perry clay, and Mowata vidrine silt loam were 71 with deionized water, 37, 43, 110 with 0.01 M calcium chloride , 272 and 221 ug g^{-1} with 0.5 M acetic acid-1, respectively.

This correlation study suggests that the soil Si critical level in Louisiana may be well above 50 mg kg^{-1}. The lack of a response on soils may be due to high initial Si content. Fertilizer applications to rice were rarely observed to be responsive in this study. It is important to understand that while it may not be profitable to apply fertilizer to rice, they do remove Si at harvest, which if not replaced will lower a soil's Si content. Thus this presents opportunities to focus Si fertilizer applications to more responsive crops in the rotation, and to make multi-year applications to these responsive crops, contrary to current recommendations and dogma. However, ignoring the Si removing effect of producing rice would result in declines in Si levels over time, eventually dropping Si levels and triggering a response to direct fertilization of Si.

4.5 References

Acquaye, D., and J. Tinsley. 1965. Soluble silica in soils. In: *Experimental Pedology*, eds. E. G. Hallworth, and D. V. Crawford, pp. 126–148. London: Butterworth's.

Agarie, S., Dgata, W., Kubota, H., and Kaufmann, P. S. 1992. Physiological role of Si in photosynthetic and dry matter production in rice plant. *Journal of Crop Science.* 61:200-208.

Allen, E.R.; Johnson, G.V., and Unruh, L.G. 1994. Current Approaches to Soil Testing Methods: Problems and Solutions. In *Soil Testing: Prospects for Improving Nutrient Recommendations,* Havlin, J.L., Jacobsen, J.S., Eds.; Special Publications No. 40., Soil Science Society of America, Madison, WI, 40: 203–220.

Berthelsen, S. 2000. An assessment of the Si status of soils in north Queensland, and the impact of sub-optimal plant available soil Si on sugarcane production systems. MSc thesis, Tropical plant Sciences within the School of Tropical Biology, James Cook University, Townsville.

Berthelsen, S., and Korndörfer, G. 2005. Methods for silicon analysis in plant, soil and fertilizers In *The proceedings of the Third Silicon in Agriculture Conference*, eds. L. E. Datnoff, G. H. Korndorfer, and G. H. Snyder, 85-91. Federal University of Uberlandia, Uberlandia, Brazil.

Boquet, D.J., B. S. Tubaña, H. J. Mascagni Jr., M. Holman, and S. Hague. 2009. Cotton yield responses to fertilizer nitrogen rates in a cotton-corn rotation. *Agronomy Journal* 101: 400–407

Breitenbeck G.A., J.K. Saichuk, and J.K.,Kraska. 2006. Unraveling the mystery malady in South Louisiana rice. *Louisiana Agriculture* 49:3.

Brown, T.H.; Mahler, R.L. 1987. Effects of phosphorus and acidity levels on levels of silica extracted from a Palouse silt loam. *Soil Science Society of America Journal* 59:39-45.

Cate, Jr., R. B., and L. A. Nelson. 1965. A rapid method for correlation of soil test analysis with plant response data. *International Soil Testing Series Technical Bulletin,* No. 1. Raleigh, NC: North Carolina Agricultural Experiment Station.

Cate, R.B. Jr., and L.A. Nelson. 1971. A simple statistical procedure for partitioning soil test correlation data into two classes. *Soil Science Society of America Proceedings* 35:658-660.

Dai, G. L., Duanmu, H. S., Wang, Z., Zhao, Y. B., Zhu, G., Zhou, J. 2004. Study on characteristics of available silicon content in Shaanxi province. *Journal of Soil and Water Conservation* 18:51–3 (In Chinese with English abstract).

Datnoff, L. E., G.H. Snyder, and C. W. Deren. 1992. Influence of Si fertilizer grades on blast and brown spot development on rice yields. *Plant Diseases* 76:1011-1013.

Dodd, J.R., and A.P. Mallarino. 2005. Soil-test phosphorus and crop grain yield responses to long-term phosphorus fertilization for corn-soybean rotations. *Soil Science Society of America Journal* 69:1118-1128.

Elliott, C. L. and G. H. Snyder. 1991. Autoclave-induced digestion for the colorimetric determination of Si in rice straw. *Journal of Agricultural and Food Chemistry*. 39:1118-1119.

Epstein, E.1999. Silicon. *Annual Review of Plant Physiology and Plant Molecular Biology 50:*641–664.

Evans, C.E. 1987. Soil Test Calibration. In *Soil Testing: Sampling, Correlation,Calibration, and Interpretation*; ed., Brown, J.R., Soil Science Society of America: Madison, WI; SSSA Special Publication 21: 23–30.

Fixen, P.E., and J.H. Grove. 1990. Testing soil for phosphorus. In *Soil testing and plant analysis,* ed.,R.L. Westerman. 141–180. Third edition. SSSA Book Series 3. SSSA, Madison, WI.

Fox, R. L., J. A. Silva, O. R. Younge, D. L. Plunkett., and G. D. Sherman. 1967. Soil and plant silicate response by sugarcane. *Journal of Soil Science Society of America Proceedings* 6:775–779.

Haynes, R. J., Belyaeva, O. N., and Kingston, G. 2013. Evaluation of industrial wastes as sources of fertilizer Si using chemical extractions and plant uptake. *Journal of Plant Nutrition and Soil Science* 176:238–248.

He, D. Y. 1993. Form, content and availability of silicon in main farmland of Hunan province and research on furnace slag fertilizer. *Research in modern agriculture* (Chinese) 14:43–7.

Iler, R. K. 1979. The Chemistry of Silica. Wiley, New York.

Imaizumi, K., and Yoshida, S.1958. Edaphological studies on Si supplying power of paddy soils. *Bulletin of the National Institute of Agricultural Sciences (Japan)* B8, 261–304.

Jones, L. H. P. and Handreck, K. A. 1967. Silica in soils, plants and animals. *Advances in Agronomy* 19:107-149.

Jones, L. H. P., and K. A. Handreck. 1967. Silica in soils, plants and animals. *Advances in Agronomy* 19: 107–149.

Kawaguchi K., and Kyuma K. 1977. *Paddy soils in tropical Asia, their material nature and fertility*. Honolulu: University Press of Hawaii.

Korndorfer, G. H., M. N. Coelho, G. H. Snyder., and C. T. Mizutani. 1999. An evaluation of soil extractants for Si availability in upland rice. *Journal of Plant Nutrition* 23:101–106.

Korndorfer, G. H., Snyder, G. H., Ulloa, M., and Datnoff, L. E., 2001, Calibration of soil and plant Si for rice production. *Journal of Plant Nutrition* 24:1071-1084.

Kraska, J.E. and Breitenbeck, G.A.2010. Simple, robust method for quantifying Si in Plant tissue. *Communications in Soil Science and Plant* Analysis 41: 2075–2085.

Liang, Y.C., Ma, T.S., Li, F.J., and Feng, Y.J. 1994. Silicon availability and response of rice and wheat to Si in calcareous soils. *Communications in Soil Science and Plant Analysis* 25:2285–2297.

Ma, J.F. and Takahashi, E. 2002. Silicon uptake and accumulation in higher plants. *Soil, Fertiliser and Plant Si Research* 11:8.

Matichenkov, V.V., Bocharnikova, E.A., Calvert, D.V., and Snyder, G.H. 2000. Comparison study of soil Si status in sandy soils of south Florida. *Proceedings - Soil & Crop Science Society of Florida* 59:132-137.

Meyer J. H and Keeping M. G. 2000. Review of research into the role of silicon for sugarcane production . *Proceedings of the South African Sugar Technologists' Association*. 74:29-40.

Oliveira L.A. 2004. Acumulação de silício em arroz e soja influenciada por diferentes condições de pH rizosferico. Uberlândia 2004. 105f . Dissertação (mestrado em agronomia) – Instituto de Ciências Agrárias da Universidade Federal de Uberlândia.

Pereira, H.S., Korndorfer, G.H., Moura, W.F., and Correa, G.F. 2003.Extratores de silício disponível em escórias e fertilizantes. *Revista Brasileira de Ciência do Solo*. 27:265-274.

Pereira, H.S., Korndörfer, G.H., Vidal, A.A., and Camargo, M.S. 2004. Silicon sources for the rice plants *Scientia Agricola* 61:522-528.

Pereira, H. S., and Cabral, N. B. 2005. Slag as a silicon source: application criterion. *Proceedings of the 3rd International Conference 'Silicon in Agriculture'*, 22–26 October 2005, Uberlkander, Brazil, pp. 90–101.

Rani, Y. A., Narayanan, A., Devi, V., and Subbaramamma, P. 1997. The effect of Si application on growth and yield of rice plants. *Annals of Plant Physiology* 11:125-128.

SAS Institute. 2012. SAS for Windows v. 9.4, SAS Inst., Cary, NC.

Savant, N.K., Snyder, G.H. and Datnoff, L.E. 1999. Silicon management and sustainable rice Production. *Advances in Agronomy* 58:151-199.

Singh, K. K., Singh, K., Ragevendra, S., Yogeshwar, S., and Singh, C. S. 2006. Response of nitrogen and Si levels on growth, yield attributes, and nutrient uptake of rice (*Oryza sativa L.). Oryza* 43:220-223.

Snyder, G.H., D.B. Jones, and G.J. Gascho. 1986. Silicon fertilization of rice on Everglades Histosols. *Soil Science Society of America Journal* 50: 1259-63.

Snyder, G. H. 2001. Methods for Si analysis in plants, soils and fertilizers. In: *Si in Agriculture*, eds. L. E. Datnoff, G. H. Snyder, and G. H. Korndorfer, pp. 185–207. New York: Elsevier Science.

Sumida, H. 2002: Plant available silicon in paddy soils. *Proceedings of the 2nd International Conference 'Silicon in Agriculture'*, 22–27 August 2002, Tsuruoka, Japan, pp. 43–49.

Takijima, Y, Wijayaratna, H. M. S., and Seneviratne, C. J. 1970. Nutrient deficiency and physiological disease of lowland rice in Ceylon. III. Effect of silicate fertilizers and dolomite for increasing yields. *Journal of Soil Science and Plant Nutrition* 16:11-16.

Walkley, A. and I.A. Black. 1934. An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science* 63:251-263.

Wan, X. S., He, D. Y., and Liao, X. L. 1993. Silicon forms of soils in Hunan province in relation to soil properties. *Soils* 25:146–51 (In Chinese).

Wang, H., Li, C., and Liang, Y. 2001. Agricultural Utilization of Silicon in China, In *Silicon in Agriculture*: *Studies in Plant Science*, eds. Datnoff, L. E., Snyder, G. H., Korndo¨rfer, G, 8: 343–358, Elsevier, Amsterdam, The Netherland.

Wang, J. J., Dodla, S. K., and Henderson, R. E. 2004. Soil silicon extractability with seven selected extractants in relation to colorimetric and ICP determination. *Soil Science* 169:861-870.

Waugh, D.L., R.B. Cate, and L.A. Nelson. 1973. Discontinuous models for rapid correlation, interpretation, and utilization of soil analysis and fertilizer response data. Technical Bulletin 7. International Soil Fertility Evaluation and Improvement Program. North Carolina State Univ., Raleigh

Williams, L. A. and Crerar, D. A. 1985. Silica diagenesis, II. General mechanisms. *Journal of Sedimentary Petrology* 55:312 - 321.

Xu, G., Zhan, X., Chunhua, L., Bao, S., Liu, X., and Chu, T. 2001. Assessing methods of available Si in calcareous soils. *Communication in Soil Science and Plant Analysis* 32:787-801.

Xu, G.H., Zhen, W.J., Liu, Y.K., Zhan, X.H., and Bao, S.D. 1996. Some critical factors in the colorimetric determination of silicon in calcareous soil extracts for available silicon. *Pedosphere 6*:279–284.

N. Yamaji, J.F. Ma. 2007. Spatial distribution and temporal variation of the rice silicon transporter Lsi1. *Plant Physiology*143:1306–1313.

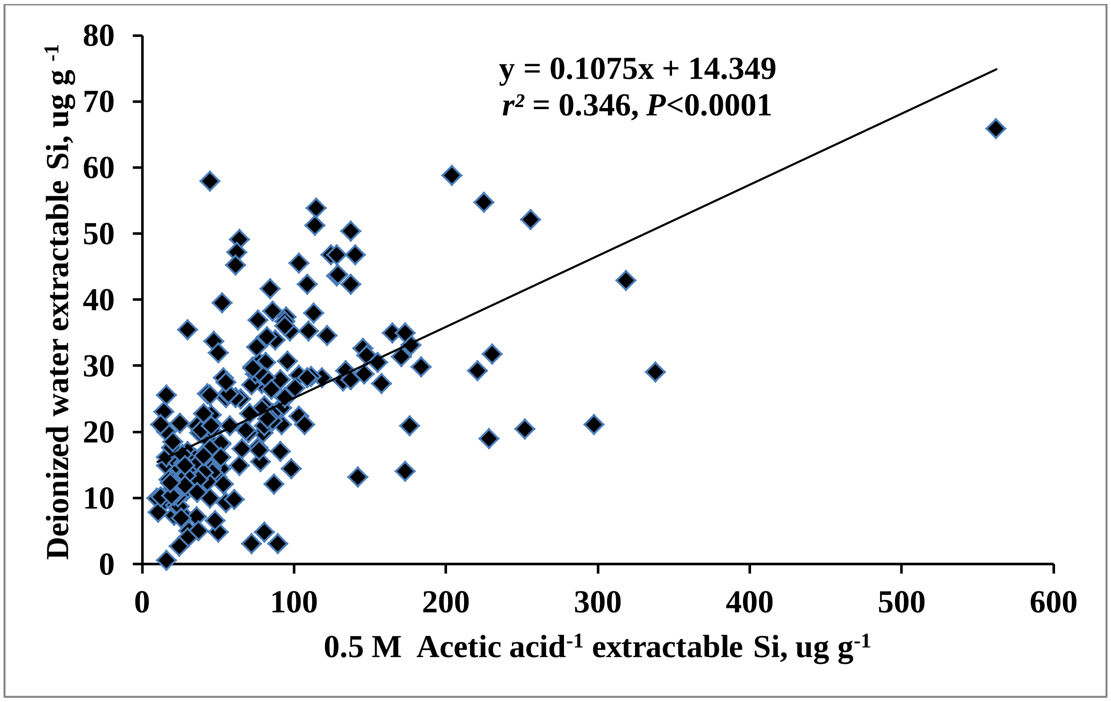
Zhang, X. M., Zhang, Z. Y., Yin, K. S., Li, G. L., Qiu, Z. X., and Liu, Y. Q. 1996. Study on the available silicon content and its relationship with soil physico-chemical properties. *Journal of Heilongjiang August First Land Reclamation University* 8:42–5 (In Chinese with English abstract).

Zhang, Y. L., Li, J., Liu, M. D., and Huang, Y. 2003. A preliminary study of soil silicon status of paddy soils in Liaoning province. *Chinese Journal of Soil Science* 34:543–7 (In Chinese with English abstract).

Chapter 5. Conclusions

For five of the procedures about 50% of surveyed soils in Louisiana had Si level below the critical Si level that thus far established in other regions. For 0.01 M calcium chloride ($CaCl_2$) extraction procedure, all surveyed soils (n=212) fell below 56 mg Si kg^{-1}. Also, it was seen that high rate of polymerization has a negative effect on the concentration of H_4SiO_4 in solution. The lower the soil sorption capacity, the higher will be the quantity polymerized. Higher rate of dissolution of fertilizer material and concentration of ions like aluminum and magnesium in the fertilizer material as well as in the soil solution will also increase the rate of polymerization. The 0.01 M $CaCl_2$, extractable Si increased in the soil only with wollastonite. Silicon absorption by the above-ground part of the rice plants was highly correlated with rates of wollastonite, and fairly to that of by silicate slag. The effect of soil pH increase with lime application did not prove to be equivalent to application of Si fertilizers. The soil Si extracted by 0.5 M acetic acid-2 and 0.01 M $CaCl_2$ was significantly correlated with shoot biomass yield, straw and grain Si uptake and increasing rates of applied Si ($r^2 > 0.45$). The soil Si critical level determined using quadratic regression model ($P<0.03$) for Sharkey clay soil was 110 mg kg^{-1} but for Crowley silt loam and Commerce silt loam were 37 and 43 mg kg^{-1} and was in good agreement with established critical level for rice in Ultisols. It is very likely that certain regions in Louisiana would benefit from Si fertilization in rice and sugarcane production. Also, there is a need to evaluate and establish the soil or site specific extraction procedure because it is unlikely that there is a single universal extraction procedure for all soils.

Appendix A. Soil silicon concentration based on different extractants



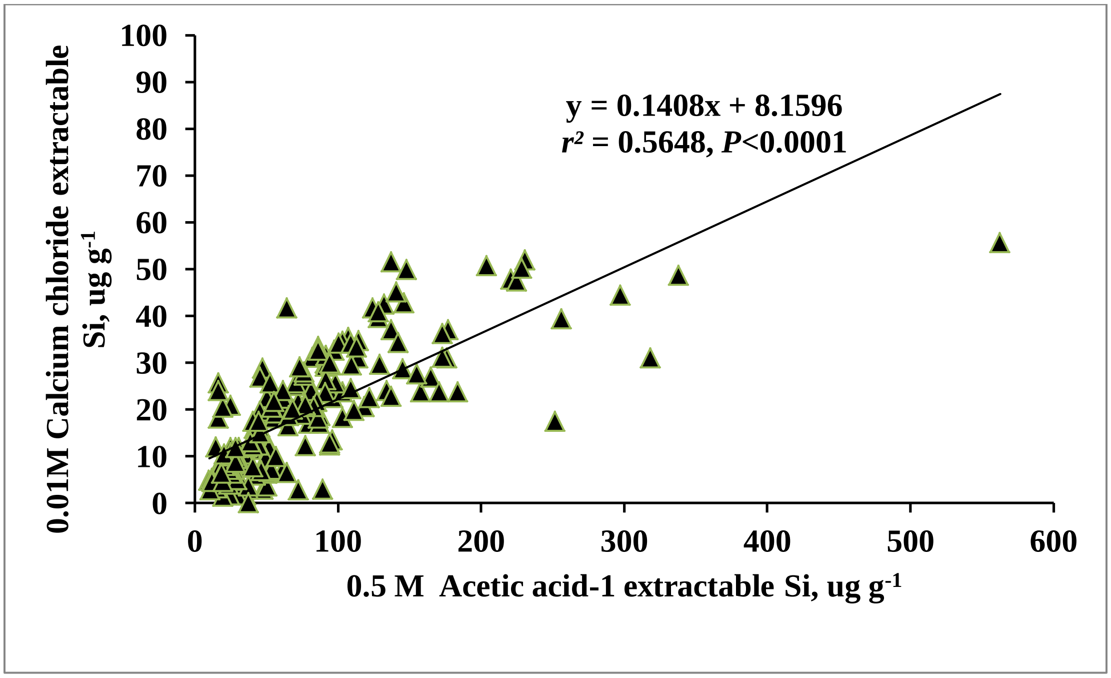


Figure A.1 The correlation between the 0.5 M acetic acid-1 extractable Si with 0.01 M calcium chloride and deionized water extractable Si

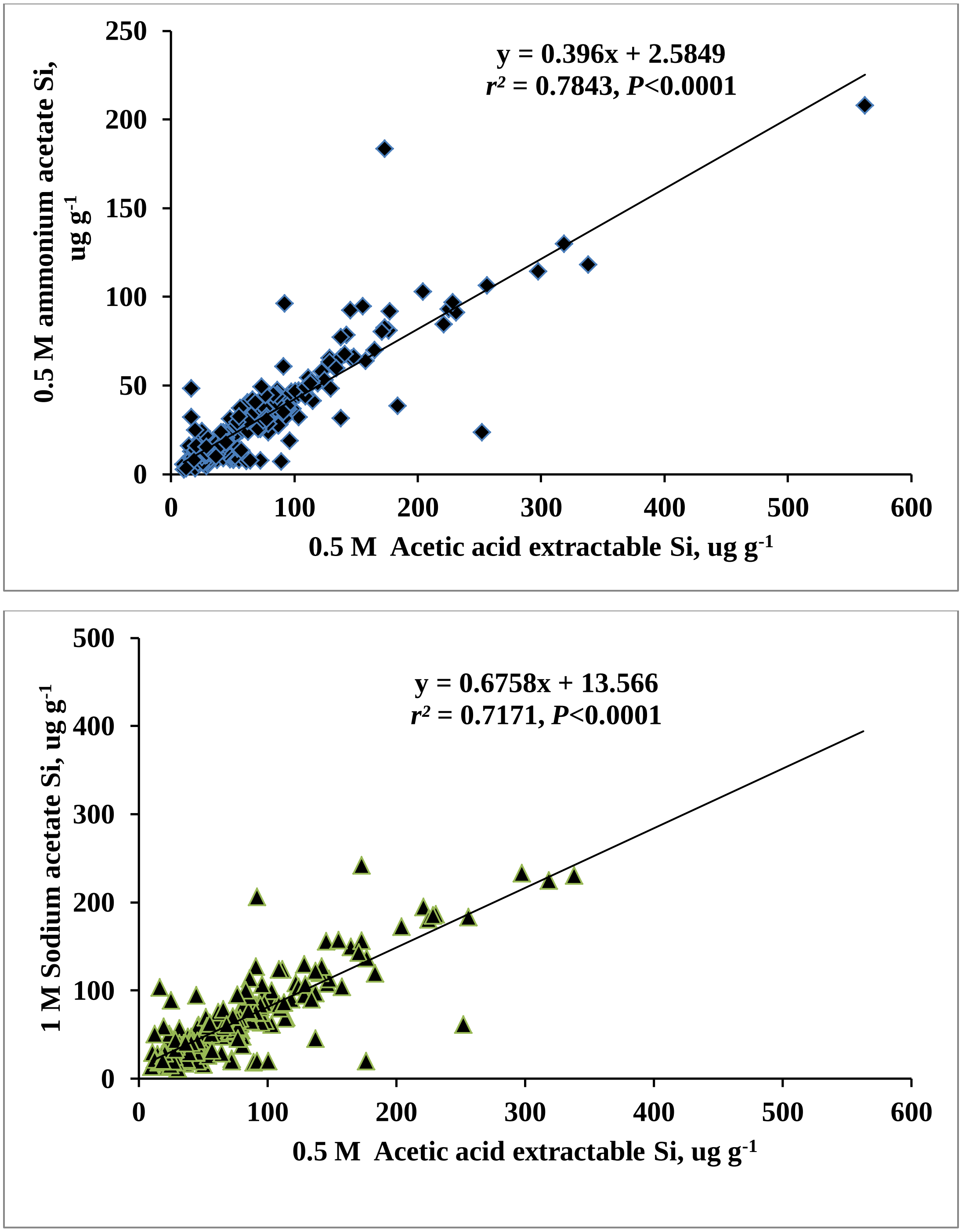


Figure A.2 The correlation between the 0.5 M Ammonium acetate and1 M Sodium acetate extractable Si with 0.5 M acetic acid-1 extractable Si

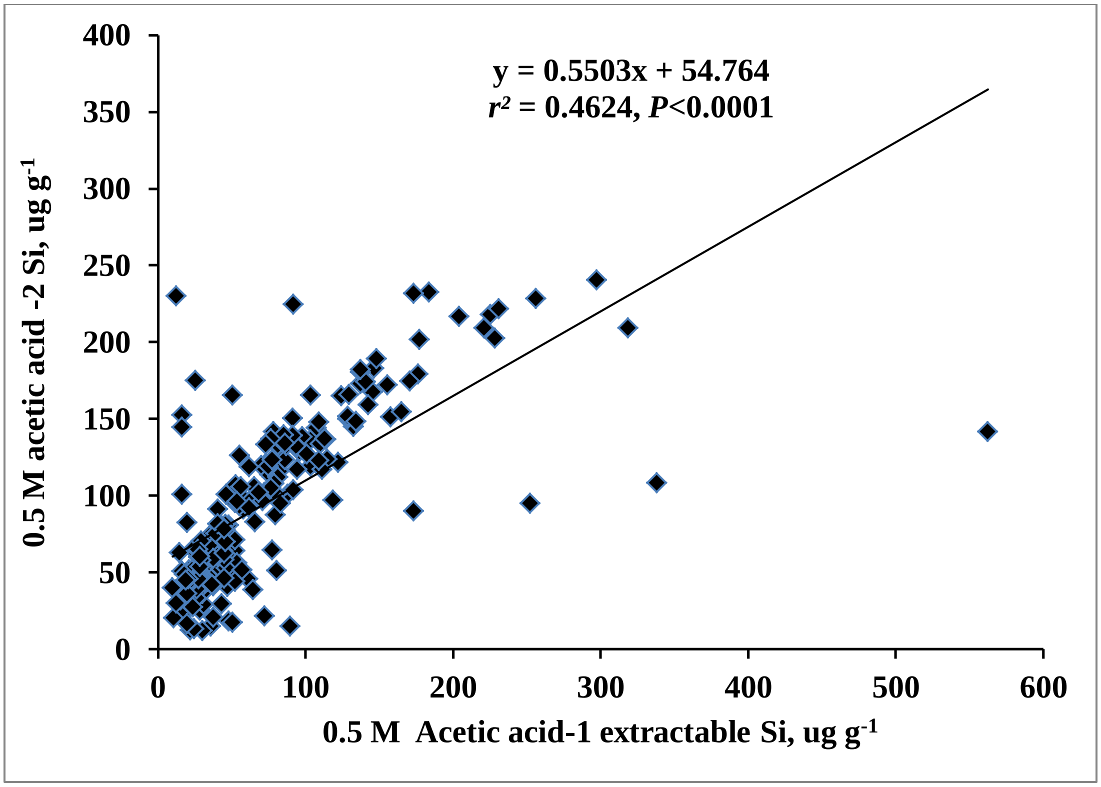


Figure A.3 The correlation between the 0.5 M Acetic acid-1 extractable Si with 0.5 M Acetic acid-2 extractable Si

Appendix B The change in pH

Table B The average soil pH after 7 days of incubation in 0.1 M NaCl

Monosilicic acid, ug ml^{-1}	Caushatta silt loam	Commerce silt loam	Crowley silt loam	Clovelly muck	Perry clay	Sharkey clay
0	8.2	6.5	6.2	6.8	6.5	6.5
10	7.8	6.6	6.3	7.0	6.4	6.8
20	7.8	6.2	6.5	7.0	6.2	6.6
40	7.8	6.2	6.3	7.1	6.3	6.8
50	8.0	6.3	6.4	7.1	6.3	6.7
Initial pH	7.8	5.6	5.0	5.6	5.3	5.7

Appendix C The critical level of silicon in soil estimated by different methods in Louisiana soils

Table C.1 The critical level estimated by different methods in Caushatta silt loam

Extraction Procedure	Linear Plateau			Quadratic Regression			Cate and Nelson
	Critical Limit	r^2	*P*-value	Critical Limit	r^2	*P*-value	Critical Limit
0.5M Acetic acid-1	185	0.14	0.063	†	0.11	0.108	96
1M Sodium acetate	†	0.03	0.544	†	0.06	0.327	32
0.01M Calcium chloride	†	0.03	0.582	†	0.045	0.419	17
0.5M Ammonium acetate	†	0.02	0.712	†	0.11	0.104	51
Deionized water	200	0.22	0.009	71	0.31	0.001	5
0.1M Citric acid	†	<0.001	1	†	0.01	0.798	734
0.5M Acetic acid-2	174	0.19	0.018	250	0.19	0.019	108

† The model was not able to estimate a critical level.

Table C.2 The critical level estimated by different methods in Crowley silt loam

Extraction Procedure	Linear Plateau			Quadratic Regression			Cate and Nelson
	Critical Limit	r^2	*P*-value	Critical Limit	r^2	*P*-value	Critical Limit
0.5M Acetic acid-1	†	0.03	0.540	†	0.04	0.475	38
1M Sodium acetate	†	0.01	0.860	†	0.09	0.166	15
0.01M Calcium chloride	†	0.01	0.814	37	0.22	0.009	13
0.5M Ammonium acetate	†	0.001	0.969	†	0.05	0.380	11
Deionized water	†	0.010	0.826	†	0.06	0.300	11
0.1M Citric acid	†	<0.001	1	596	0.14	0.058	293
0.5M Acetic acid-2	140	0.14	0.067	250	0.16	0.037	79

† The model was not able to estimate a critical level.

Table C.3 The critical level estimated by different methods in Commerce silt loam

Extraction Procedure	Linear Plateau			Quadratic Regression			Cate and Nelson
	Critical Limit	r^2	*P*-value	Critical Limit	r^2	*P*-value	Critical Limit
0.5M Acetic acid-1	†	0.003	1	202	0.25	0.005	64
1M Sodium acetate	†	0.035	0.526	92	0.13	0.082	17
0.01M Calcium chloride	200	0.32	<0.001	43	0.45	<0.001	4
0.5M Ammonium acetate	†	0.013	0.789	75	0.34	0.006	26
Deionized water	†	0.175	0.031	63	0.20	0.020	3
0.1M Citric acid	†	<0.001	1	928	0.43	<0.001	323
0.5M Acetic acid-2	156	0.24	0.007	256	0.25	0.006	54

† The model was not able to estimate a critical level.

Table C.4 The critical level estimated by different methods in Sharkey clay

Extraction Procedure	Linear Plateau			Quadratic Regression			Cate and Nelson
	Critical Limit	r^2	*P*-value	Critical Limit	r^2	*P*-value	Critical Limit
0.5M Acetic acid-1	†	0.12	0.101	†	0.11	0.121	98
1M Sodium acetate	149	0.21	0.011	258	0.13	0.070	101
0.01M Calcium chloride	200	0.18	0.03	110	0.18	0.026	44
0.5M Ammonium acetate	†	0.02	0.659	†	0.10	0.133	69
Deionized water	†	0.10	0.155	†	0.12	0.081	33
0.1M Citric acid	†	<0.001	1	†	0.14	0.062	1352
0.5M Acetic acid-2	†	<0.001	1	†	0.07	0.274	305

† The model was not able to estimate a critical level.

Table C.5 The critical level estimated by different methods in Perry clay

Extraction Procedure	Linear Plateau			Quadratic Regression			Cate and Nelson
	Critical Limit	r^2	*P*-value	Critical Limit	r^2	*P*-value	Critical Limit
0.5M Acetic acid-1	272	0.34	<0.001	296	0.34	<0.001	265
1M Sodium acetate	223	0.20	0.024	223	0.17	0.040	151
0.01M Calcium chloride	†	0.003	0.95	†	0.005	0.919	28
0.5M Ammonium acetate	200	0.16	0.073	150	0.25	0.012	78
Deionized water	†	0.003	0.994	37	0.26	0.99	18
0.1M Citric acid	†	<0.001	1	†	0.036	0.20	1078
0.5M Acetic acid-2	†	<0.001	1	†	<0.001	1	303

† The model was not able to estimate a critical level.

Table C.6 The critical level estimated by different methods in Mowata silt loam

Extraction Procedure	Linear Plateau			Quadratic Regression			Cate and Nelson
	Critical Limit	r^2	*P*-value	Critical Limit	r^2	*P*-value	Critical Limit
0.5M Acetic acid-1	†	0.005	0.90	221	0.16	0.043	27
1M Sodium acetate	†	0.09	0.163	†	0.098	0.147	17
0.01M Calcium chloride	†	0.02	0.687	†	0.099	0.144	10
0.5M Ammonium acetate	200	0.14	0.061	†	0.16	0.042	23
Deionized water	200	0.14	0.061	†	0.15	0.054	21
0.1M Citric acid	†	<0.001	1	†	0.01	0.830	230
0.5M Acetic acid-2	†	<0.001	1	†	0.10	0.131	74

† The model was not able to estimate a critical level.

Vita

Tapasya Babu was born in Kerala, India in March of 1987. She attended Kerala Agricultural University and received her Bachelor of Science in Agriculture in June of 2010. After graduating she was accepted into the University of Agricultural Science (GKVK) Bengaluru, India, with a Junior Research Fellowship from Indian Council of Agricultural Research where she received her Master of Science in Soil Science and Agricultural Chemistry in July 2012. During the same year, she was accepted into the Soil Fertility program at LSU to pursue her Ph.D. and worked under the guidance of Dr Brenda Tubana on the development of silicon fertilization guidelines in different crop production systems of Louisiana. She married Vinay Bhaskar in the spring of 2015.