

Chapter 1 Introduction

1.1 Background

Silicon (Si) is not generally regarded as an essential element for higher plants, yet it is the second most abundant (28 - 31%) element, after oxygen (46-49%), in the Earth's crust (Greenland and Mott, 1978; Sposito, 1989). The beneficial role of Si in stimulating the growth and development of many plant species has been generally recognized. Silicon is known to effectively mitigate various abiotic stresses, such as manganese (Mn), aluminium (Al) and heavy metal toxicities, as well as salinity and climate stresses, and to improve resistance and/or tolerance to biotic stresses, such as fungal diseases and insect pests (Savant *et al.*, 1997a; Savant *et al.*, 1999; Ma *et al.*, 2001; Mengel and Kirkby, 2001). In soils, the beneficial effect of Si has also been well documented in increasing cation exchange capacity (CEC) (Noble *et al.*, 2001; Berthelsen *et al.*, 2003; Noble *et al.*, 2003) and decreasing phosphorus (P) sorption (Smyth and Sanchez, 1980; Exley *et al.*, 1993; Guadalix and Pardo, 1994; Owino-Gerroh and Gascho, 2004).

Most soils contain mixtures of both constant- (or permanent) and variable (or pH-dependent) surface charge minerals (Uehara and Keng, 1975). Variable charge soils (VCS) are considered to be soils that have developed under intensive weathering and leaching conditions in tropical and subtropical regions, and have been strongly subjected to the process of desilication (Theng, 1980). These soils predominantly contain minerals with variable surface charge density, such as kaolinite, gibbsite, goethite, hematite, and amorphous minerals. These clay minerals carry both variable negative and positive charge on their surfaces (Uehara and Keng, 1975; Qafoku *et al.*, 2004). For instance, Oxisols are the most highly weathered soils in the tropics as indicated by their clay mineralogy being dominated by kaolinite and sesquioxides (i.e. gibbsite, hematite and goethite) (Herbillon, 1980; Sposito, 1989; Melo *et al.*, 2001). Within a soil profile, it is generally found that the topsoil possesses net negative charge whereas the subsoil may have net positive surface charge (Gillman, 1984; Phan *et al.*, 2005; Moody and Phan, 2008). This difference in the sign of net charge is due to less organic matter and more Fe/Al hydrous oxides in the B horizon relative to the A horizon (Gillman, 1985; Gillman and Sumpter, 1986; Gillman and Sumner, 1987). Variable charge soils are rich in constituents of surface reactive groups with amphoteric properties which can be protonated or deprotonated to create variable positive or negative charge on their surfaces, respectively (Uehara and Gillman, 1981; Barrow, 1986; McBride, 1994; Zhang and Zhao, 1997).

Therefore, the magnitude and sign of their surface charge changes with alteration of soil pH and ionic strength (Sumner, 1995). In addition, the point of zero charge (PZC) or pH_0 is important in the characterisation of VCS because at this pH, net variable charge is zero, so that any residual charge is net permanent charge (Gillman, 1985). If soil pH values are below pH_0 , the variable charge sites will carry net positive charge; in contrast, if soil pH is above pH_0 , they will carry net negative charge.

Variable charge soils, in their natural state, often maintain highly productive and diverse ecosystems. They, however, pose a particular challenge to sustainable management in terms of low values of CEC at soil pH, rapid reduction in CEC, particularly basic cation exchange capacity (CEC_B), as soil acidity increases, and their ability to adsorb anionic species (Gillman and Sumpter, 1986). On the other hand, these soils (particularly in the subsoil or B horizon) develop appreciable anion exchange capacity (AEC) under acidic conditions, and can retain leachable anions such as nitrate and sulfate (Qafoku *et al.*, 2004). Soil acidity, Al toxicity and high P fixation are other major constraints that often occur in VCS (Qafoku *et al.*, 2004). Thus, basic cations are easily leached out of the soil profile and the soils have low nutrient supplying capacity.

Options for management of VCS include liming, organic matter addition, P and Si amendment (Uehara and Gillman, 1981; Bolan *et al.*, 1999; Qafoku *et al.*, 2004). All these management strategies aim to manipulate the surface charge characteristics of VCS in order to control the retention of cations and anions. Because variable charge characteristics largely depend on the pH of the soil solution, soil treatments with pH amendments have usually been applied to control the reactions of nutrient ions and to reduce the toxicity of heavy metals (Bolan *et al.*, 1999), and thus the manipulation of soil pH is important to the proper management of such soils (Uehara and Gillman, 1981). In addition, application of specifically adsorbed anions, such as P and Si (Noble *et al.*, 2003), and organic matter (Gillman, 1985; Zhang and Zhao, 1997; Phan, 2000; Nkhalamba *et al.*, 2003) can increase CEC of the soils.

Lime application is the most common practice used for neutralizing acidity and increasing pH, thereby influencing the surface charge characteristics of variable charged components in the soil (Mora and Barrow, 1996). In addition, an increase in soil pH has been shown to reduce phytotoxic Al (Al^{3+}), decrease the retention of anions such as SO_4^{2-} and HPO_4^{2-} (Marsh *et al.*, 1987; Bolan *et al.*, 1988; Naidu *et al.*, 1990) and increase the ability of soils to retain nutrient ions and potential toxic heavy metals (Adams, 1984; Helmke and Naidu, 1996).

However, large amounts of lime need to be applied to VCS to increase pH above a certain level (e.g., pH 5.5) because of the high buffering capacity in these soils. This is due to hydroxyl ions formed by the hydrolysis of the carbonate ion creating charge by deprotonation of surface hydroxyls (Uehara and Gillman, 1981). This could be very costly and may result in pH-induced micronutrient deficiencies. Another adverse effect of lime associated with changes to surface charge is the adsorption of Ca^{2+} into the Stern layer, causing charge reversal (Wann and Uehara, 1978a, b). This is due to specifically adsorbed Ca^{2+} shifting the pH_0 to a higher value (Uehara and Keng, 1975).

Another option to increase the CEC of VCS is to lower pH_0 of the soils. Organic matter, Si and P application can shift pH_0 of VCS to a lower value. The pH_0 values of organic matter and of silanol surfaces (Si-OH) are around pH 2.0 (Sposito, 1984), so overall lowering of the soil pH_0 can be achieved by sorption of organic anions or silanol groups onto particle surfaces, thereby masking some positive charges of variable charge components of VCS. On the other hand, P and Si anions can be specifically adsorbed and increase CEC of the soils (Hingston *et al.*, 1967; Hingston *et al.*, 1968; Parfitt, 1978; Mott, 1981). Another beneficial effect of Si is that Si can compete with P on the adsorbed sites of VCS, thus reducing P sorption capacity of the soils (Smyth and Sanchez, 1980; Guadalix and Pardo, 1994; Owino-Gerroh and Gascho, 2004; Lee and Kim, 2007). In addition, many researchers have reported that Si-induced amelioration of Al toxicity can be attributed to both external (nutrient solution) (Baylis *et al.*, 1994; Ma *et al.*, 1997; Hiradate *et al.*, 1998; Liang *et al.*, 2007) and internal mechanisms (within plant) (Cocker *et al.*, 1998a, b; Liang *et al.*, 2001; Wang *et al.*, 2004) related to the formation Al-Si complexes.

Most studies investigating the amelioration potential of Si have usually involved alkaline Si sources such as sodium- (Na), calcium (Ca) silicate and other silicate slags; as a result, the beneficial effects on the above major constraints of VCS have been mainly attributed to the effect of increased pH rather than that of Si (Baylis *et al.*, 1994; Morikawa and Saigusa, 2002). Thus, the role of Si (both alkaline and acidulated Si sources) in surface charge characteristics, P sorption capacity and Al toxicity of selected VCS with different mineralogical compositions was studied in this current project using various Si amendments. The investigated soils are a Redoxic Hydrosol, an Aquic Grey Vertisol (from north Queensland) and Red Ferrosols (from both north Queensland and New South Wales). The Red Ferrosol from north Queensland used in this study has similar physico-chemical characteristics to Vietnamese Ferralsols, one of the major upland soil types in Vietnam (Ton

et al., 1996; Nguyen and Thai, 1999). These soils are characterised by high desilication, excessive soil acidity and high P fixation and are intensively cultivated with minimal fertiliser input (Nguyen and Thai, 1999). Their surface charge is often characterised by net positive charge, a 'geric property', especially in the subsoil layer (Moody and Phan, 2008). Silicon amendments were both inorganic silicate and organic amendments. In addition to monosilicic acid, calcium silicate, acidulated calcium silicate, magnesium silicate, acidulated magnesium silicate and mulched sugarcane trash amendments, fused magnesium phosphate (FMP), a product of Vietnam, and *Tithonia diversifolia*, a green manure, were also used in this study. Fused magnesium phosphate is high in Ca, Mg, P and Si content, and has been commonly used in farming systems of Vietnam as a P fertiliser. This material has recently been imported to Australia and is currently used as a P source and liming material (information from TNN Industries Pty Ltd). Although the benefit of FMP is well known in association with its liming effect and P content, the effect of Si contained in this product has not been investigated and the beneficial effect of Si on surface charge characteristics is still unknown. *Tithonia diversifolia* has been widely applied as a green manure (Phan, 2000; Phan *et al.*, 2005). It grows in the wild, is highly productive and is easily collected, particularly in the central highlands of Vietnam where VCS (Ferrosols) dominate. It not only contains Si, but also high amounts of Ca, Mg and P compared to other sources of green manure. Lime (CaCO_3) and P ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) amendments were also used in this study in order to separate the Si effect from the pH and P effects associated with FMP, sugarcane trash or *Tithonia* amendment.

1.2 Project objectives

The overall objective of the project was to study the role of Si in the amelioration/amendment of major constraints of VCS from north Queensland and NSW, which have similar properties to VCS in the uplands of Vietnam, particularly the Red Ferrosol. Specific objectives were to:

- Evaluate native surface charge characteristics and P sorption capacities of selected VCS from both north Queensland and NSW.
- Investigate the effect of Si derived from both inorganic silicates and organic amendments on surface charge characteristics and P sorption capacities of these VCS.
- Examine Si-induced amelioration of Al toxicity in a Red Ferrosol from NSW.
- Apply the project results to guide further research on relevant VCS in Vietnam.

1.3 Thesis outline

Silicon content and chemistry in soils, surface charge chemistry and management of VCS, beneficial effects of Si on major soil constraints (particularly P availability, Al and Mn toxicity), and the Si budget in Vietnamese farming systems are reviewed in Chapter 2. Comprehensive reviews on acidic VCS associated with soil pH and soluble Si reactions and surface charge characteristics, mechanisms by which soils develop their charge surfaces, and the interaction between Si and P in the soils are assessed and discussed. Chapters 3, 4, 5 and 6 present results from incubation experiments. Native surface charge characteristics and P sorption capacity of selected VCS with different mineralogical compositions from north Queensland and New South Wales are described in Chapter 3. Surface charge characteristics and P sorption capacities of selected VCS from north Queensland affected by the application of inorganic silicate and organic amendments are investigated in Chapter 4. Chapter 5 describes changes in surface charge characteristics and the P sorption capacity of a Red Ferrosol from New South Wales following the application of different rates and different inorganic silicate and organic amendments at different incubation periods. A short-term bioassay using mungbean seedlings grown in extracted soil solution from the incubation experiment of Chapter 5 to investigate Si-induced amelioration of Al toxicity is presented in Chapter 6. Within each chapter, experimental procedures are described, results are given, analyses are discussed and conclusions are drawn. General conclusions of the research and suggestions for further research are given in Chapter 7. To complete the thesis, Appendices are included to present surface charge characteristic curves of different soils and different Si treatments.

Chapter 2 Literature review

Silicon pools and Si chemistry in soils are reviewed in this chapter, together with properties of variable charge soils (VCS) and soil management in relation to the interaction between Si and phosphorus (P), aluminium (Al) and manganese (Mn) for improving soil fertility and crop production. In addition, the Si budget in farming systems in Vietnam, including the Si input as fertilisation and the output as crop removal, is described in order to highlight the importance of Si fertilisation for rectifying soil constraints, improving soil fertility and enhancing crop production in Vietnam.

2.1 Silicon pools in soils

Silicon commonly comprises from 5 to 40% of total soil weight, mainly in the forms of silicon dioxide (SiO_2) and various aluminosilicates (Matichenkov and Bocharnikova, 2001; Matichenkov and Calvert, 2002). Soil Si can be divided into two phases, solid and liquid, as shown in Figure 2.1. Quartz, crystalline silicates (feldspar and mica), secondary minerals and amorphous silica are the essential sources providing Si to the soil solution through numerous processes during soil formation (McKeague and Cline, 1963c; Drees *et al.*, 1989; Matichenkov and Bocharnikova, 2001; Sommer *et al.*, 2006).

The crystalline forms that are available as potential sources of Si in soils, and their proportions, vary with the mineralogical composition of parent materials (McKeague and Cline, 1963c). For example, the approximate proportions of Si minerals in various rocks are: for igneous rocks: feldspars 60.0 per cent, quartz 12.0 per cent and micas 4.0 per cent; for sandstone: quartz 65.0 per cent and feldspars 10.0 per cent; for shale: feldspars 30.0 percent and quartz 20.0 percent (McKeague and Cline, 1963c; Juo and Franzluebbers, 2003).

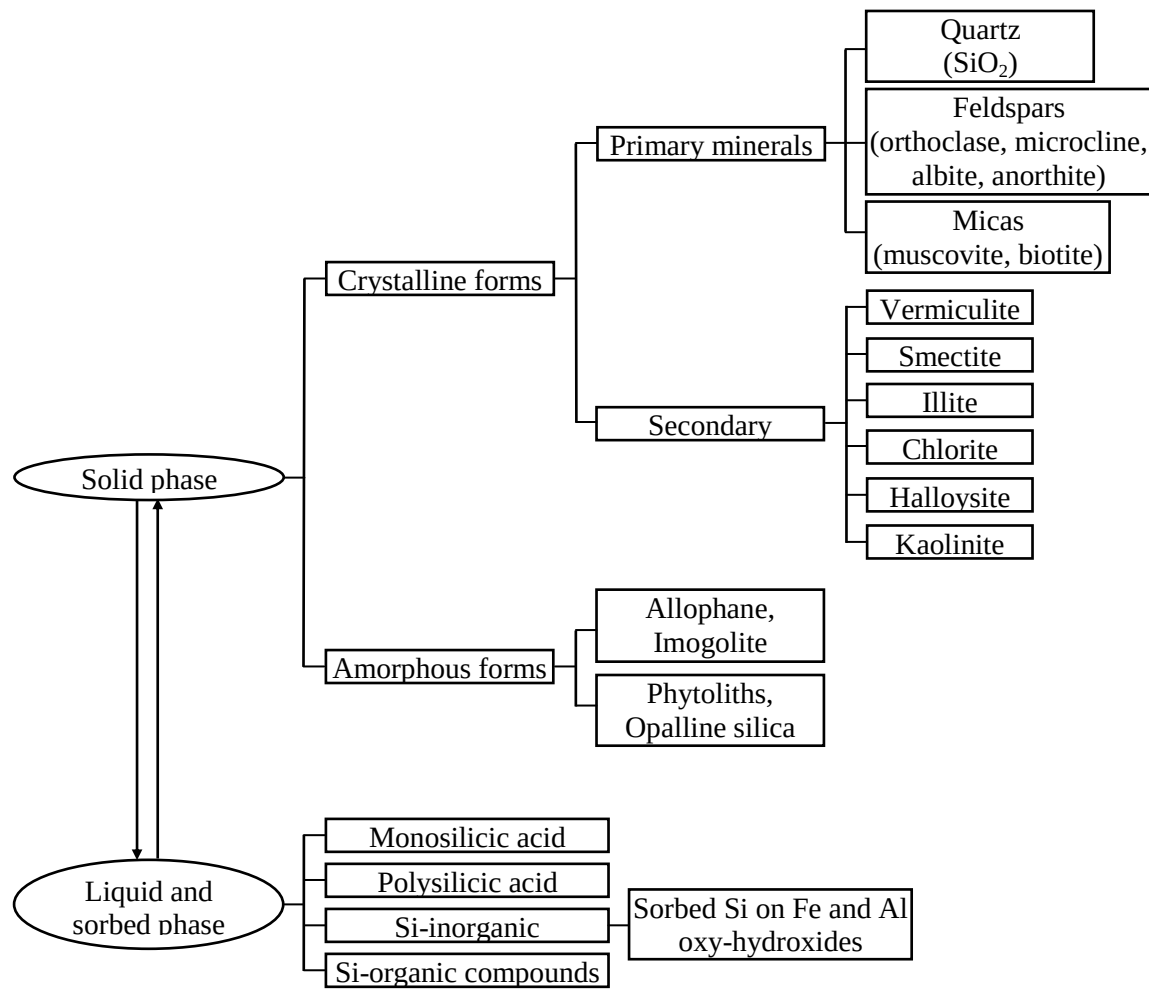


Figure 2.1 The various forms of silicon in soils (adapted from Tan, 2000; Matichenkov and Bocharnikova, 2001)

Quartz (SiO_2) is a stable crystalline mineral. It is resistant to weathering and comprises a major portion of the sand and silt fractions in soils (Juo and Franzluebbers, 2003). Depending on the parent material and degree of weathering the quartz content of the clay fraction of soils generally ranges from 0 to 25% (Tedrow, 1954; Le Roux, 1973; Juo and Franzluebbers, 2003). The solubility of quartz is commonly very low, from 0.08 to 0.25 mM SiO_2 (Rimstidt, 1997; Savant *et al.*, 1999), whereas that of amorphous Si forms varies from approximately 1.67 to 2.17 mM SiO_2 at neutral pH (Alexander *et al.*, 1954; McKeague and Cline, 1963a, b; Iler, 1979). Thus, there is evidence that amorphous Si is more soluble and provides more Si to solution than crystalline Si forms such as quartz. Alexander *et al.* (1954) have also demonstrated that the different forms of amorphous Si, such as finely divided powder, wet Si gel and colloidal particles in the form of a sol, are soluble to a similar extent. According to Lindsay (1979), the solubility of silica minerals in terms of H_4SiO_4 (calculated from the equilibrium reactions for silica species at 25°C) is expected to range from 0.10 mM (quartz) to 1.82 mM (amorphous silica) (Figure 2.2).

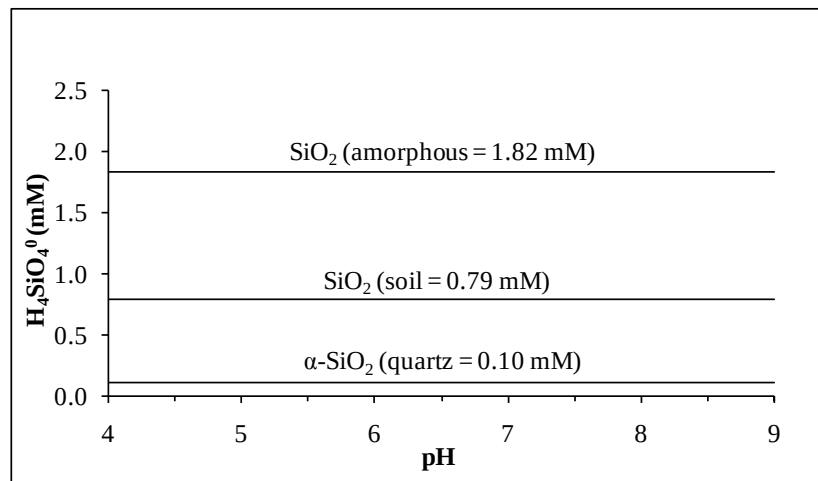


Figure 2.2 The activity of H_4SiO_4 maintained by different forms of silica (adapted from Lindsay, 1979)

Under the influence of climate and biological activity, primary minerals are broken down and altered into secondary minerals (Tan, 2000). Also, the processes of rock weathering leave parent materials that range widely in the amounts and kinds of Si-containing material, including both secondary Si materials and amorphous Si forms (McKeague and Cline, 1963c; Sommer *et al.*, 2006). The formation of secondary Si-containing minerals in the soil environment is influenced by many factors such as pH, temperature, and the presence of cations and organic compounds in solution (Drees *et al.*, 1989). These products continue to segregate and change their structures during soil development, contributing Si to the soil solution (McKeague and Cline, 1963c; Savant *et al.*, 1999; Sommer *et al.*, 2006). This phenomenon is pronounced in very acid soil and is termed desilication when this production of soluble Si is combined with leaching to remove Si from the soil profile (Sommer *et al.*, 2006).

Amorphous silicates include allophanes and imogolite. These are hydrated Al silicates (Demumbrum and Chesters, 1964) and occur as a major constituent of young soils formed from volcanic ash. According to Cresser *et al.* (1993) allophane can be described as both amorphous silica and amorphous Al hydroxide. Although allophane is generally grouped with the clay minerals, its structure is highly variable and poorly defined. Unlike allophane, imogolite is now accepted to be a crystalline mineral with a definite structural form (Cresser *et al.*, 1993).

Opalline silica occurs in most soils and may be of either organic or inorganic origin and contains significant amounts of occluded, chemisorbed or solid-solution impurities, including

Al, Fe, Ti, Mn and C (McLaren and Cameron, 1996). Inorganic opal is formed in soils only when soil environmental conditions favour supersaturated soluble Si levels, and serves as primary cement for indurated soil horizons (duripans), particularly in arid and semiarid environments. Biogenic opal is formed from the silicification of grasses and parts of deciduous trees (Tan, 2000) and in the tissues of plants when silicic acid which has been taken up from soil solution is precipitated at cell walls, lumens and in intercellular voids (Jones and Handreck, 1967; Ma *et al.*, 2001).

Amorphous silica deposits around root channels in soil are thought to be due to evaporation of silica-bearing solutions (McKeague and Cline, 1963c) or from plants (Sommer *et al.*, 2006). When plant material decomposes in the soil, the opal accumulates in the soil in the form of small structures known as phytoliths (McLaren and Cameron, 1996). Phytoliths generally comprise the major component of the biogenic silica pool in soils followed by diatoms and sponge spicules (Clarke, 2003). In soils, phytoliths range from 0.01 to 50 per cent w/w of the clay fraction (Jones and Beavers, 1964; Clarke, 2003). However, most soil horizons show phytoliths content in the range between 0.1 and 3.0 per cent w/w (Sommer *et al.*, 2006).

The liquid phase of Si in soils is complex, and agronomically important (Savant *et al.*, 1999). There are a variety of Si forms and species in the liquid phase, such as monosilicic acid, polysilicic acid, Si-inorganic and Si-organic compounds (Figure 2.1). Numerous studies during the 1960s and 1970s have shown that monosilicic acid [$\text{Si}(\text{OH})_4$ or H_4SiO_4] is the main component of soil solutions at pH values below 9.0 and may range from 0.04 to 1.43 mM Si (Alexander *et al.*, 1954; Beckwith and Reeve, 1963; McKeague and Cline, 1963a, b; Beckwith and Reeve, 1964; Davies, 1964; Jones and Handreck, 1965, 1967).

As monosilicic acid loses water, it transforms into polysilicic acid under strongly alkaline conditions (Dietzel, 2000, 2002). In addition, when the dissolved Si in soil solution exceeds 2.32 mM Si, polymerisation of Si usually occurs and a mixture of monosilicic and polysilicic acid, and Si-organic compounds may be found (Tan, 1994; Matichenkov and Ammosova, 1996). The results of dissolution experiments from various minerals show solutions contain both monosilicic and polysilicic acid, but polysilicic acid decomposes into monosilicic acid over time (Dietzel, 2000).

For Si-inorganic compounds, several studies in the past concluded that Si is chemically adsorbed on surfaces of soil constituents, such as Al hydroxides, Fe oxides and carbonates (Beckwith and Reeve, 1963; Iler, 1979; Dietzel, 2002). The interaction between the sorbed

and liquid Si phases in soils is mainly determined by Fe and Al oxy-hydroxides, particularly the latter (Jones and Handreck, 1963; Beckwith and Reeve, 1964; Hingston and Raupach, 1967). Sorption of Si onto mineral surfaces is associated with the amount, type, size and crystallinity of the oxy-hydroxides (Sommer *et al.*, 2006). Dissolved Si might also combine chemically with certain organic substances in soils, but there is no clear evidence that this occurs (McKeague and Cline, 1963c). The reviews of both McKeague and Cline (1963c) and Savant *et al.* (1999) question whether or not Si in soils interacts with organic compounds.

The solubility of primary and secondary Si compounds determines the concentration of Si in soil solution through the processes of rock weathering and soil formation (Sommer *et al.*, 2006). The dissolution kinetics of soil Si are affected not only by the characteristics of the Si polymorphs, such as particle size, structure and composition, and mineral stability (McKeague and Cline, 1963c), but also by a variety of factors in the soil, such as organic matter, redox potential, metallic ions, phyllosilicates, sesquioxides, surface coatings, and overall soil solution dynamics (Drees *et al.*, 1989). The behavior of soil Si can be summarised in Figure 2.3, which illustrates the complex relationships between Si-containing substances and the Si in the soil solution. The factors and the processes that influence the concentration of Si in the soil solution will be discussed in the following sections.

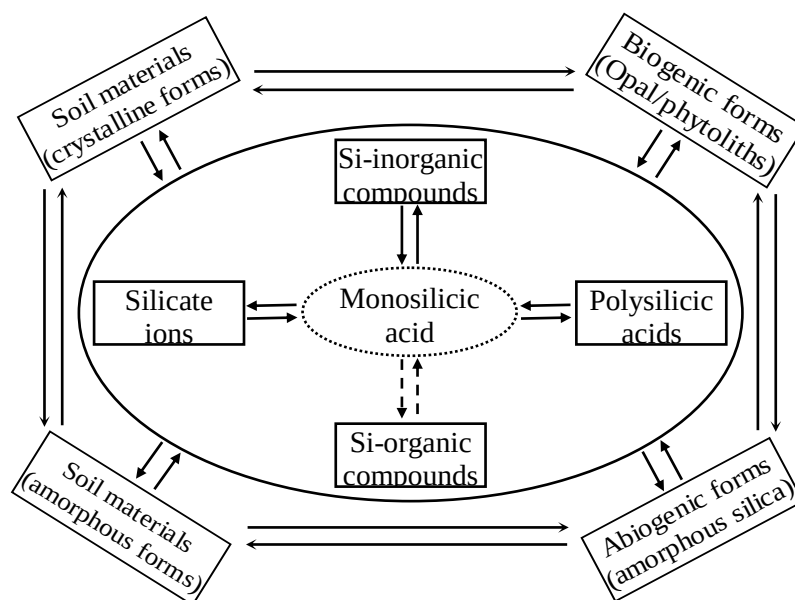


Figure 2.3 Interactions between and within Si-liquid and Si-solid phases

2.2 Silicon chemistry in soils

2.2.1 Soil pH and reactions of soluble silicon

Many authors have asserted that monosilicic acid is the main form of Si in soil solutions. For example, Alexander *et al.* (1954) showed that silica in solution is mostly present as monosilicic acid, H_4SiO_4 , at pH below 9.0. The concentration of monosilicic acid in a saturated solution of pure amorphous silica ranges from 2.0 to 2.33 mM SiO_2 at 25°C and at pH values below 9.0. According to Alexander *et al.* (1954), the solubility of natural silica is independent of pH in the range 2.0 to 9.0, but it increases markedly above pH 9.0 because of the formation of silicate ions, as shown in Figure 2.4.

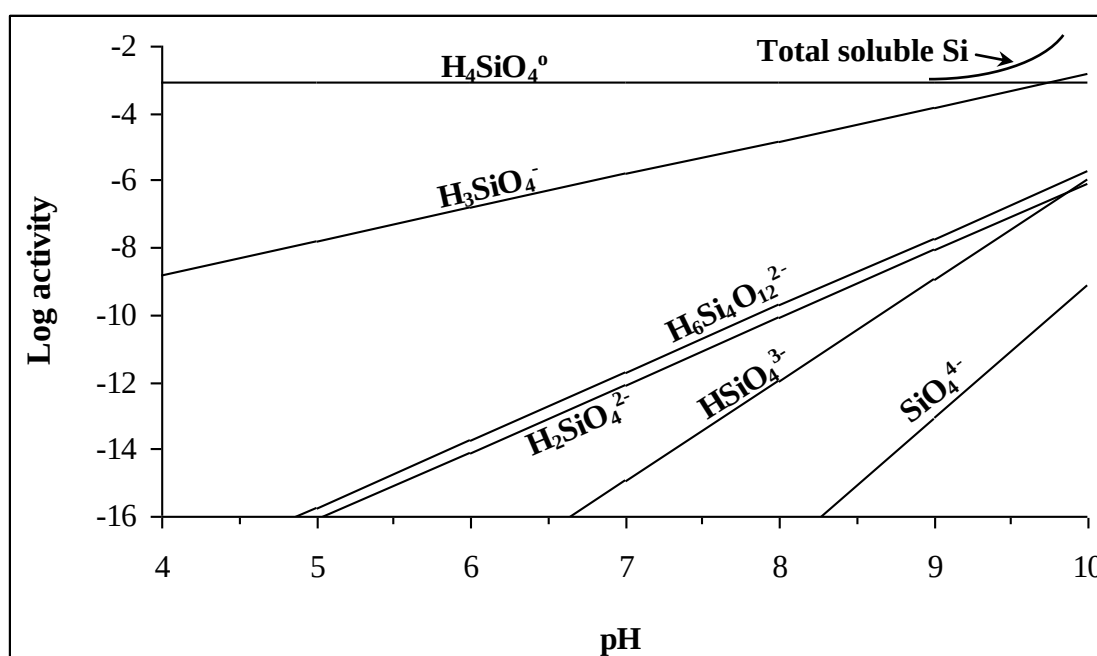
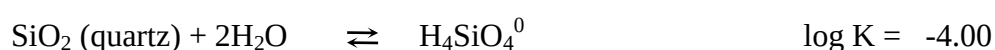
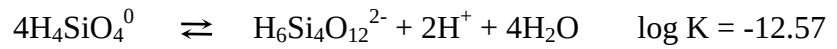
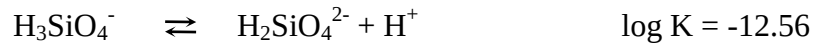
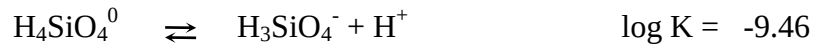


Figure 2.4 Solubility of silicate species in equilibrium with amorphous silica (values calculated from equilibrium solubility reactions at 25°C) (adapted from Lindsay, 1979)

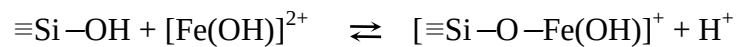
The following equilibria can be used to explain the formation of monosilicic acid and the increase in the solubility of natural silica at high pH (Stumm and Morgan, 1970; Lindsay, 1979).





In natural solutions, the concentration of monosilicic acid at the same pH value varies with soil types, and is usually in the range of 0.10 to 1.33 mM SiO₂ (Beckwith and Reeve, 1963; Davies, 1964; Jones and Handreck, 1965, 1967; Epstein, 1994; Ma and Takahashi, 2002).

Soil acidification increases the concentration of monosilicic acid (Beckwith and Reeve, 1963; McKeague and Cline, 1963a; Beckwith and Reeve, 1964; Jones and Handreck, 1967). In their study on the sorption of silicic acid by soils and minerals, Beckwith and Reeve (1963) stated that the residual concentration of monosilicic acid under near equilibrium conditions depends on the pH of the soil suspension, and is controlled by an adsorption equilibrium which is dependent on pH. Specifically, the residual concentration of monosilicic acid in soil suspensions increases with acidification. For example, when pH decreases from 6.4 to 4.8 the concentrations increase from 0.67 to 1.25 mM SiO₂ (Beckwith and Reeve, 1963); on the other hand, when pH increases from 5.4 to 7.2 the concentrations decrease from 1.17 to 0.38 mM SiO₂ (Jones and Handreck, 1965). When studying the release of monosilicic acid from soils, Beckwith and Reeve (1964) also concluded that the release was minimal at pH 7-9 and increased continuously with acidity. The following reaction of silicic acid occurs at oxide surfaces and it is considered that silicic acid only reacts with metal ions which have at least one hydroxyl group attached (Iler, 1955).



Beckwith and Reeve (1964) explained the effect of increasing acidity on monosilicic acid concentration by the following mechanisms; as pH decreases extra H⁺ ions compete more strongly with Al or Fe ions for oxygens linked to Si ions, and when the pH is lowered still further the number of metal ions with hydroxyl groups attached steadily decreases and opportunities for the formation of Si-O-M bonds are correspondingly diminished. Also, under sufficiently acid conditions, dissolution of active metal ions from the hydroxide surface may occur (Beckwith and Reeve, 1963).

As mentioned above, Si in soil solution is mainly present in the form of monosilicic acid, an uncharged monomeric molecule, at pH values below 9.0. The solubility and forms of Si existing in soil solution are influenced by soil pH and silica concentration (Figure 2.5). According to Alexander *et al.* (1954), Jones and Handreck (1965), Ma *et al.* (2001) and Savant *et al.* (1999), monosilicic acid dissociates into the silicate ion $[(OH)_3SiO^{-1}]$ as soil pH increases above 9.0.

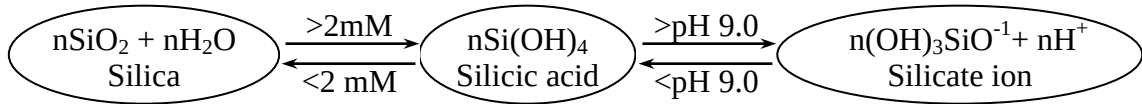
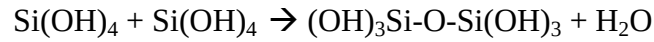
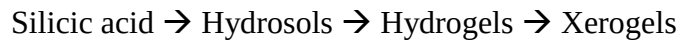


Figure 2.5 Solubility and various forms of silicon as a function of pH and silicon concentration (after Ma *et al.*, 2001)

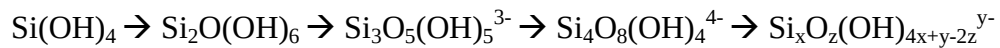
Polymerisation of Si usually occurs when the soluble Si exceeds 2.00 mM SiO₂ in soil solution (Tan, 1994; Matichenkov and Ammosova, 1996; Ma *et al.*, 2001). Soluble Si forms polysilicic acids with dissociation of H₂O (Mengel and Kirkby, 2001) by the following equation:



According to Drees *et al.* (1989) there is a gradual transition from monosilicic acid to larger molecules following the sequence:



Also, Dietzel (2002) has recently stated that polymerisation of silica may build up dimeric, trimeric, tetrameric and higher order polymeric silica through silicon-oxygen-silicon bonds, which usually exists at high pH and high concentrations of dissolved silica, as illustrated below.



The formation of polysilicic acids results in a decrease of the solubility of Si which, in turn, lowers its concentration in soil solution (Mengel and Kirkby, 2001). However, Betz *et al.* (1941) and McKeague and Cline (1963a) found that although dissolved silica is

supersaturated with respect to amorphous silica at concentrations ranging from 2.93 to 4.00 mM SiO₂, the polymerisation of monosilicic acid is very low at pH values below 4.0.

The rate of depolymerisation of polysilicic acids to monosilicic acid depends on pH, temperature, initial concentrations of polysilicic and monosilicic acid, and concentrations of dissolved components (Dietzel, 2002). At the pH value of 3.0, decomposition of polysilicic acids is very low and polymerisation of monosilicic acid does not occur (Dietzel, 1998). Polysilicic acids are also stable at low temperature and at high concentrations of heavy metal ions (Dietzel, 1998, 2000). Hydroxyl ions catalyse the depolymerisation rather than hydrogen ions (Dietzel, 1998). In addition, polysilicic acids decompose to monosilicic acid as a function of time. The decomposition time ranges from a few hours to days and polysilicic acids may exist as a metastable component over several months in acid solutions which are rich in bivalent cations (Dietzel, 2000). Dietzel (1998, 2000) concluded that in most natural aqueous solutions, conditions of pH, temperature and dissolved components provide high depolymerisation capacities.

2.2.2 Dissolution and precipitation of monosilicic acid

The concentration of silica in soil solution increases with increasing soil:water ratio and with increasing temperature (McKeague and Cline, 1963a). Soil moisture dynamics appear to play an important role in determining the concentration of Si in soil solution. When water evaporates from soils, deposition of amorphous Si coatings may occur, reducing the total amount of silica in solution, and concentrations do not reach those required for a saturated solution of amorphous silica. The concentration of Si in solution almost doubles with temperature increasing from 25°C to 43°C at the rate of about $3 \text{ to } 5 \times 10^{-3} \text{ mM SiO}_2$ per one degree centigrade (McKeague and Cline, 1963a).

Many kinds of soluble salts such as NaCl, NH₄Cl, MgCl₂, CaCl₂, BaCl₂ and MgSO₄ at different concentrations (0.001, 0.01 and 0.1 M) have little effect on the concentration of silica in solution (Beckwith and Reeve, 1963; McKeague and Cline, 1963a). However, the concentration of monosilicic acid in 0.1 M citrate solution increases with acidity. This might be due to citrate ions preferentially blocking Si sorption sites and also forming complexes with metal atoms which are responsible for Si sorption (Beckwith and Reeve, 1963).

Much of the monosilicic acid in the soil solution is derived from desorption from adsorbing surfaces rather than from dissolution of amorphous silica or crystalline silicate mineral

structures (Beckwith and Reeve, 1963). Under strongly acid conditions, different soils can release different concentrations of monosilicic acid into solution even though the initial concentration is near the saturation value of amorphous silica (Beckwith and Reeve, 1963).

Redox processes are important for the dissolution of Si when Fe oxides are present (Jones and Handreck, 1967; Ma and Takahashi, 2002; Sommer *et al.*, 2006). Jones and Handreck (1967) suggest that the increase in soluble Si is a result of the release of silica from Fe-Si complexes, under reducing conditions, through the conversion of ferric to ferrous complexes of higher solubility or through the removal of ferric iron from the silica complexes by organic anions.

Conversely, excess monosilicic acid in soil solution may enhance the capacity of Fe and Al oxides to adsorb silicate (Huang *et al.*, 2006) and could result in polymerisation and precipitate formation on Fe and Al oxide surfaces (Jones and Handreck, 1963).

2.2.3 Adsorption of silicon in soils

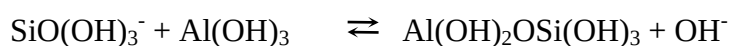
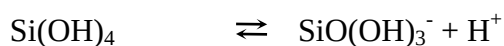
Silica adsorption onto oxide and hydroxide surfaces depends mostly on specific surface area, surface charge, and functional groups of the solid phase as well as on the pH and the chemical composition of the solution (Hingston *et al.*, 1972). Freshly precipitated hydroxides of polyvalent metal ions, such as Fe, Al, and Mg are most effective, whereas crystalline Fe oxides and bauxite are moderately effective in adsorption of silica from solution (McKeague and Cline, 1963b). The effectiveness of freshly precipitated hydroxides of polyvalent metal ions is not only related to their chemical composition, but also to the high specific surface due to their amorphous nature (McKeague and Cline, 1963b). For instance, goethite with particle size less than 75 microns adsorbs more silica from solution than that with particle size from 75 to 250 microns (McKeague and Cline, 1963b).

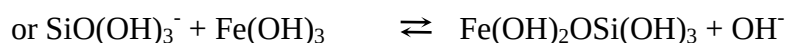
The concentration of silica in soil solution is partially controlled by adsorption reactions (McKeague and Cline, 1963a), but also by dissolution of amorphous Si deposited on the surfaces of soil particles (Brown and Mahler, 1987). The adsorption of silicate increases with increasing equilibrium silicate concentration (Huang *et al.*, 2006) and with increasing temperature (McKeague and Cline, 1963b). When concentrations of dissolved silica are greater than 0.67 mM, adsorption of silica increases with increasing temperature between 5, 25, 50 and 70°C; however, there is no consistent relationship between temperature and adsorption of silica at lower concentrations (McKeague and Cline, 1963b). Monosilicic acid adsorption on soil particle surfaces is also a function of time. As water infiltrates a soil, the

concentration of dissolved silica increases quickly only during the first few minutes. It then changes very slowly with time and the rate decreases after one or two days (McKeague and Cline, 1963a).

Although silica is adsorbed on the surfaces of numerous inorganic compounds in soils, sesquioxides play the most important role in sorption of monosilicic acid (Beckwith and Reeve, 1963; McKeague and Cline, 1963b; Jones and Handreck, 1967). The adsorption onto mineral surfaces is related to the amount, type, size and crystallinity of Fe and Al oxy-hydroxides (Sommer *et al.*, 2006). Many studies of Si adsorption indicate that sesquioxides, especially Al oxides, are mainly responsible for the capacity of soils to sorb Si and the maximum adsorption capacity is between pH 8.0 and 10.0 (Jones and Handreck, 1963; Beckwith and Reeve, 1964; Drees *et al.*, 1989). According to Wada and Inoue (1974) the effect of pH on Si adsorption is primarily associated with the total number of available sites for Si sorption at a given pH. Thus, the solubility of Si in soils at the same pH varies with differences in concentrations of the free sesquioxides present. Jones and Handreck (1967) state that the degree of crystallinity of Al oxides has more effect on their adsorptive capacity than is the case with Fe oxides, and the least crystalline Al oxide adsorbs three times as much as the most crystalline.

Monosilicic acid and polysilicic acid are both adsorbed on the mineral surface of Fe oxides and gibbsite, but the adsorption of monosilicic acid is lower than that of polysilicic acid (Dietzel, 2002). The adsorption of polysilicic acid on the mineral surfaces of gibbsite and goethite increases with decreasing pH, whereas the adsorption of monosilicic acid shows the opposite trend (Dietzel, 2002). This is partly due to the formation of polysilicic acids from monosilicic acid on Fe oxide surfaces (Dietzel, 2002), the latter being the dominant species in soil solutions with pH below 9.0. The pH-dependent sorption-desorption of Si by sesquioxides and clays reaches faster equilibrium between solid and liquid phases of Si in soil than dissolution-precipitation phenomena (Jones and Handreck, 1963; McKeague and Cline, 1963a; Beckwith and Reeve, 1964). McKeague and Cline (1963b) also assert that adsorption of silica by soils is strongly dependent on pH and increases with increasing pH over the range of 4.0 and 9.0, but decreases at pH values above 10. A typical pH-dependent adsorption of Si(OH)_4 by sesquioxides can be explained by the following reactions (Savant *et al.*, 1999):





In paddy soil, amorphous oxides of Al and Mn, rather than Fe, play the most important role in adsorption of silica (Huang *et al.*, 2006). When the concentration of silica increases above 0.2 mM, Al oxides are more effective in adsorption of silica than Mn oxides.

Under acid conditions, silicate minerals and carbonates have little or no effect on the adsorption of silica from solution (McKeague and Cline, 1963b). Kaolinite, bentonite and carbonates, however, are able to sorb monosilicic acid from soil solution at pH greater than 7.0 (Beckwith and Reeve, 1963). In addition, soluble salts at low concentrations (up to 0.3 M) have little effect on the adsorption of silica from solution if the addition of salts does not cause an appreciable pH change (McKeague and Cline, 1963b). Exceptions to this are citrate and phosphate ions, which can partially obstruct the sorption of monosilicic acid by soils (Beckwith and Reeve, 1963).

2.3 Chemistry and management of surface charge of variable charge soils

2.3.1 Variable charge soils

Variable charge soils (VCS) belong to the soil orders (US soil taxonomy) of Oxisols, Ultisols, Alfisols, Spodosols and Andisols (Qafoku *et al.*, 2004). These soil orders are rich in constituents with amphoteric surface reactive groups such as kaolinite, goethite, hematite, and amorphous minerals (mostly allophane, imogolite or ferrihydrite) (Theng, 1980; Uehara and Gillman, 1981; Qafoku *et al.*, 2004). Variable charge soils have mainly developed either under intensive weathering and leaching, or are derived from volcanic ash parent material. They are also more common in the tropics than in temperate regions because their formation requires desilication, as illustrated in Figure 2.6, which proceeds faster in warm and moist climates (Sollins *et al.*, 1988).

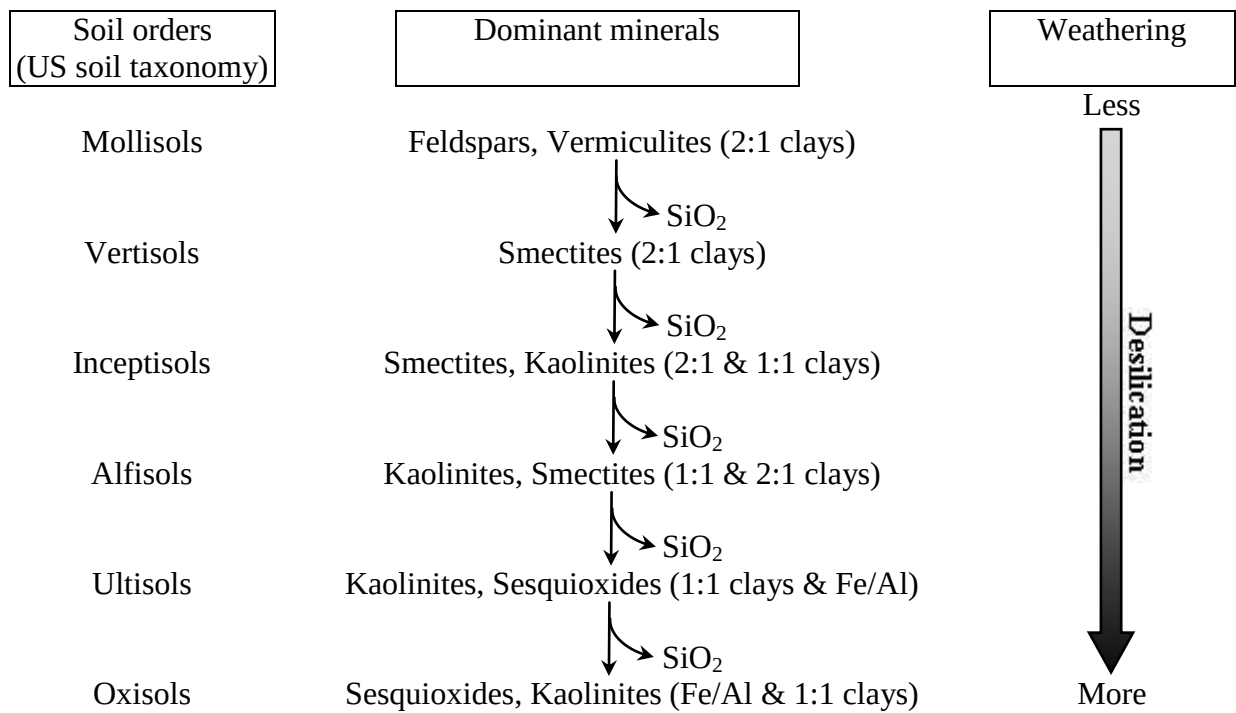


Figure 2.6 Desilication in soils affected by weathering sequence (adapted from Savant *et al.*, 1999)

Large areas of the world are occupied by VCS (Table 2.1). The mineralogy of the sand, silt and clay fractions of Alfisols, Oxisols, and Spodosols is characterized by the presence of thermodynamically stable primary and secondary minerals (Qafoku *et al.*, 2004). Although the common 2:1 silicate minerals (namely mica, vermiculite, smectite and muscovite) are found in the clay fraction of VCS with argillic horizons (Murali *et al.*, 1974; Gallez *et al.*, 1975), the dominant clay mineral is kaolinite (Fripiat, 1959 cited by Yu, 1997; Qafoku *et al.*, 2004), and goethite and hematite are the most commonly occurring minerals (Segalen, 1971; Yu, 1997).

Table 2.1 Global areas and percentages of variable charge soils*

Order	Suborder	Area (10 ³ km ²)	Proportion (%)
Alfisols	Aqualfs	836	0.64
	Cryalfs	2518	1.94
	Udalfs	2706	2.09
	Ustalfs	5664	4.37
	Xeralfs	897	0.69
Subtotal		12621	9.74
Andisols	Cryands	255	0.20
	Torrands	2	0.00
	Udands	279	0.22
	Ustands	63	0.05
	Vitrands	281	0.22
	Xerands	32	0.02
Subtotal		912	0.70
Oxisols	Aquox	320	0.25
	Perox	1162	0.90
	Torrox	31	0.02
	Udox	5201	4.01
	Ustox	3096	2.39
Subtotal		9810	7.57
Spodosols	Aquods	169	0.13
	Cryods	2460	1.90
	Humods	58	0.04
	Orthods	667	0.51
Subtotal		3354	2.59
Ultisols	Aqualts	1281	0.99
	Humults	344	0.27
	Udults	5540	4.27
	Ustults	3870	2.99
	Xerults	19	0.01
Subtotal		11054	8.53
Total		37751	29.12

* Data from USDA-NRCS, Soil Survey Division, World Soil Resources, 1998 (modified from Wilding, 2000)

The mineralogy of Andisols and Ultisols comprises free Fe oxy-hydroxides, secondary 2:1 phyllosilicates containing basic cations both in the lattice and in the interlayer spaces, and Al-bearing constituents which are characterized by short range order minerals, namely allophane and imogolite (Yoshinaga and Aomine, 1962a, b; Parfitt *et al.*, 1983; 1984; Wada, 1987). Gibbsite, kaolinite, halloysite and free Al constituents with crystalline structure such as gibbsite-boehmite (Wada, 1980, 1985, 1987; Van Ranst *et al.*, 1990; Dahlgren *et al.*, 1993) also occur. However, if the surface horizon of Andisols is rich in OM, the formation of allophane and imogolite can be hindered because of the formation of Al complexes with OM leading to a decline in Al activity in the soil solution (Dahlgren and Ugolini, 1989). Thus, the rate of co-precipitation with Si to form allophane and imogolite decreases and may promote Si precipitation in the form opalline silica (Wada, 1980).

Despite VCS having a wide spectrum of morphological, mineralogical, chemical, physical, biological, and genetic characteristics (Qafoku *et al.*, 2004), they have one property in common; the magnitude and sign of their amphoteric surface charge is dependent on the chemistry of the ambient solution, i.e., pH, ionic composition and ionic concentration (Uehara and Gillman, 1980; Sumner, 1995). This will be discussed in more detail in the following section.

2.3.2 Surface charge chemistry of variable charge soils

Soil chemical properties are influenced by soil surface charge characteristics through both the quantity of electric charge and the surface charge density (Zhang and Zhao, 1997). The quantity of surface charge determines the quantity of ions adsorbed, while the surface charge density determines the strength of adsorption. Furthermore, the negative and positive signs of surface charge sites determine the adsorption of cations and anions, respectively. Surface charge properties affect the movement of ions in soil, the formation of organo-mineral complexes, and dispersion, flocculation, swelling, and shrinkage characteristics (Zhang and Zhao, 1997). Consequently, surface charge properties have a significant influence on soil structure and plant nutrition.

Variable charge soils are not only characterized by large amounts of Fe and Al oxides, but their clay mineralogical composition is also dominated by 1:1-type clay minerals, namely kaolinite (Yu, 1997). In addition to these constituents, 2:1-type clay minerals, such as vermiculite and smectite are also generally present. However, because Fe and Al oxides often occur as colloidal coatings on the surfaces of clay minerals, the surface charge characteristics

of these clay minerals are often not exhibited (Yu, 1997). As a result, surface charge comprises a mix of both variable (or pH-dependent) charge and permanent (or constant) charge. Variable charges originate from preferential adsorption of certain ions on particle surfaces and are pH dependent, whereas permanent charges result from structural imperfections, such as isomorphous substitution in mineral structures, and are unaffected by external factors, such as pH changes. This mixture of variable and constant charge minerals results in the surface charge of VCS exhibiting unique and complex properties, which set them apart from other soils dominated by permanent charge (van Raij and Peech, 1972b; Parfitt, 1980; Zhang and Zhao, 1997).

The typical surface charge characteristics of VCS are: points of zero charge at pH values where plant roots normally develop (van Raij and Peech, 1972b); a relatively large anion adsorption capacity (Hingston *et al.*, 1967; Kinjo and Pratt, 1971; Hingston *et al.*, 1972; Hingston *et al.*, 1974; Charlet and Sposito, 1987, 1989; Bellini *et al.*, 1996; Qafoku *et al.*, 2000; Qafoku and Sumner, 2002); high pH buffering capacity, i.e., high lime requirement to achieve neutral pH (Sumner, 1993); and considerable sorption affinity for cations, such as Ca and other metal ions, which may form both inner- and outer-sphere surface complexes (Charlet and Sposito, 1987). Inner-sphere complexes can be described as the formation of one or more direct bonds between the adsorbate molecule and the adsorbent surface functional group with no water molecules interposed; outer-sphere complexes involve hydration water interposed between the adsorbate and the adsorbent surface (Isbell, 1996).

The variable charge component chiefly derives from surfaces of organic soil constituents, such as carboxyl, phenolic and amino reactive groups, and surfaces of inorganic soil constituents, such as hydroxyl reactive groups (Parfitt, 1980; Qafoku *et al.*, 2004). Variable charge soils are heterogeneously charged soil systems. The coexistence and interactions of soil particles and colloids with net opposite surface charges give much more complex patterns of soil chemical behavior than typical in permanent charge soils (PCS) (Thomas, 1977; Theng, 1980; Uehara and Gillman, 1981; Sposito, 1989; Zhang and Zhao, 1997; Sposito, 2008). In terms of the dynamics of nutrient mobility and nutrient cycling processes, VCS differ essentially from PCS (Sollins *et al.*, 1988). For example, as the pH of VCS decreases, decreases in cation exchange capacity (CEC) and increases in anion exchange capacity (AEC) occur (Figure 2.7). When AEC exceeds CEC, cations such as ammonium and potassium will be more mobile than anions such as nitrate. This contrasts with the situation in PCS. Variable charge surfaces also adsorb P, causing plant nutritional problems with respect to P deficiency.

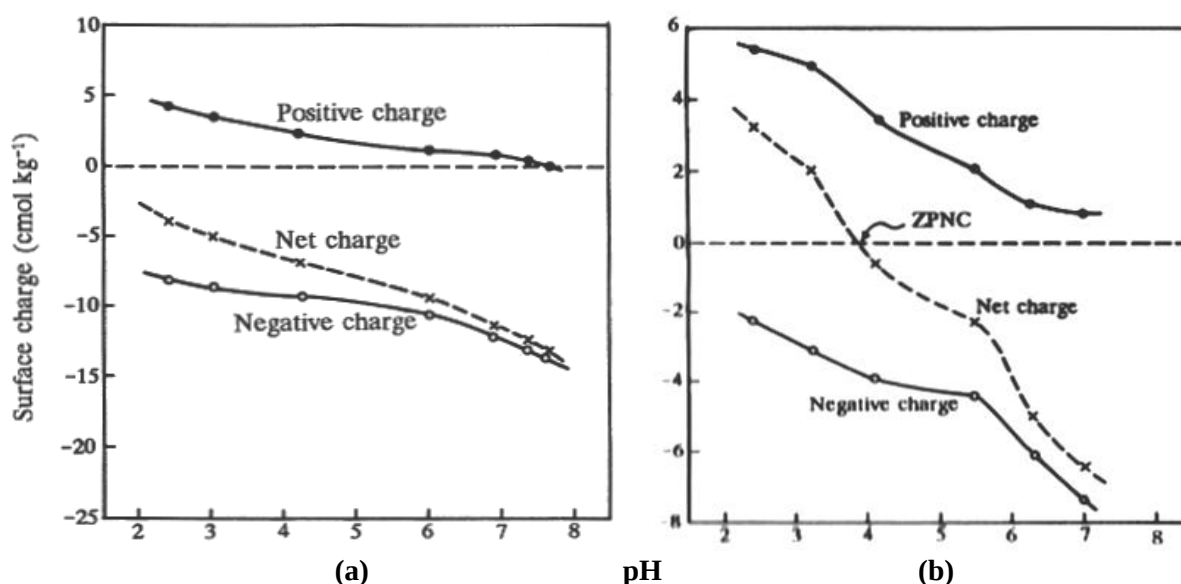


Figure 2.7 Changes in surface charge with pH of an Ultisol (a) and an Oxisol (b) (adapted from Zhang and Zhao, 1997)

Humus usually contains large amounts of dissociated organic acid groups which produce variable negative charge. Zhang and Zhao (1997) indicate that the quantity of negative charge carried by humus is within the range of 200 – 500 cmol_c kg⁻¹. These negative charges originate chiefly from carboxyl groups with a pK_a value of 4 – 5. Hydroxyl groups, such as phenolic, quinonic and enolic hydroxyls can also significantly contribute to negative charge, but the pK_a value of these hydroxyl groups is usually higher than that of carboxyl groups. Generally, these two functional groups control the electrochemical behavior of humic matter. According to Tan (2009) the carboxyl groups start to dissociate protons at pH = 3.0, resulting in the humic molecule becoming negatively charged, and with the charge increasing with increasing pH; hydroxyl groups start to dissociate protons at pH = 9.0. In addition, at high pH, amino groups can also contribute to negative charge. However, VCS often occur in tropical and subtropical climates of high weathering, intensive rainfall and leaching (Qafoku *et al.*, 2004), accompanied by warm, moist conditions and regular cultivation (Uehara and Gillman, 1981). As a result, the humus content is usually low to very low and the principal sources of variable charge are Fe and Al oxy-hydroxides and edge faces of clay minerals (Zhang and Zhao, 1997).

Oxides and hydrated oxides of Fe, Al, Mn, Ti and Si often occur in weathered soils (Mitchell *et al.*, 1964; Parfitt, 1978; Barrow, 1986; Tan, 1994; Barrow, 1996; Zhang and Zhao, 1997; Bolan *et al.*, 2000; Tan, 2000). These oxides, such as hematite (α -Fe₂O₃), corundum (α -Al₂O₃), and silicon oxide (SiO₂), can be hydrated under moist conditions, changing to those of hydrated oxides such as goethite (α -FeOOH), gibbsite [Al(OH)₃], and silica gel (SiO₂nH₂O).

The surface of all these oxides and hydrated oxides contain hydroxyl groups that can bond directly with Fe, Al and Si ions; they can also bond with adsorbed water molecules through hydrogen bonding (forming so called ferrol, aluminol and silanol groups, respectively). As a result of the dissociation of H^+ ions from hydroxyl groups on surfaces and the combination of these hydroxyl groups with H^+ ions from the ambient solution, electrochemical charges are produced on the surfaces of hydrated oxides (Figure 2.8).

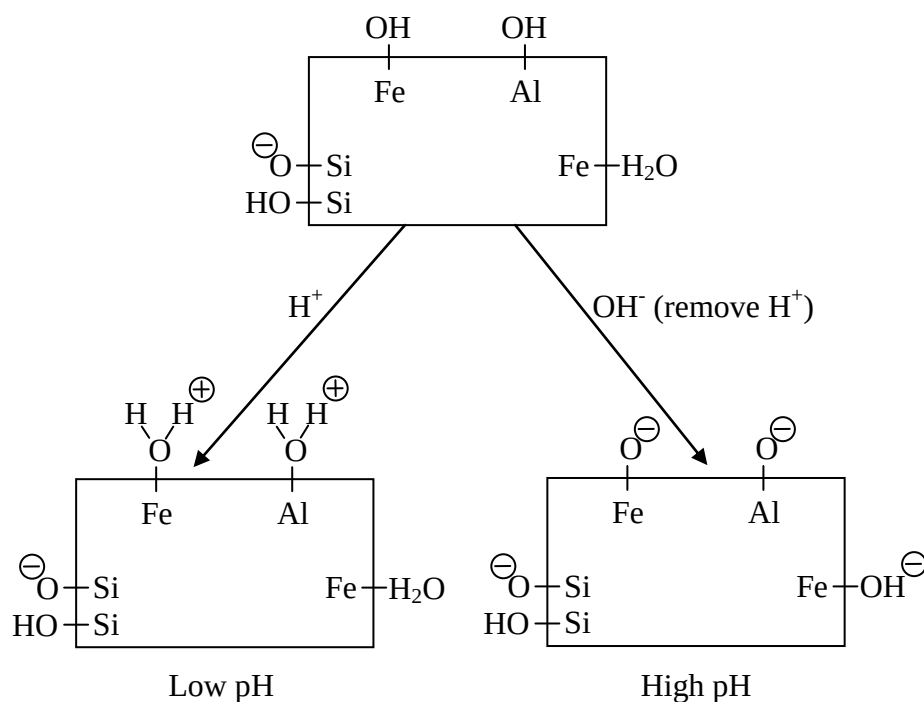


Figure 2.8 The development of positively and negatively charged sites on surfaces of soil constituents at low and high pH (reproduced from Parfitt, 1980)

A surface will carry negative charge when the hydroxyl groups lose H^+ ions at high pH; conversely, it will carry positive charge when the hydroxyl groups adsorb H^+ ions under low pH conditions (Figure 2.8). One example of this in VCS is allophane (Zhang and Zhao, 1997). Allophane is a group of hydrated Al silicates with different Si:Al ratios which possess Si-O-Al bonds. Allophane carries negative charges on the surface at high pH through the dissociation of H^+ ions from the silanol group ($\equiv Si-OH$), and it carries positive charges on the surface at low pH owing to the acceptance of H^+ ions by the aluminol group ($Al-OH_2^+$).

Kaolinite is the most typical layer silicate in VCS and the edge face of kaolinite contributes to the variable charge surfaces of VCS (Uehara and Gillman, 1980; Schroth and Sposito, 1997; Zhang and Zhao, 1997; Qafoku *et al.*, 2004). The development of electric charge of the edge face of kaolinite is illustrated in Figure 2.9. The edges of kaolinitic particles have single

coordinated aluminol and silanol variable charge groups with unsatisfied charge (Wieland and Stumm, 1992; Qafoku *et al.*, 2004). According to Zhang and Zhao (1997), under nearly neutral conditions each of the two oxygens in an aluminium-oxygen octahedron bond with one proton, and each oxygen also connects to Al by one half of the bond at the same time. Since one of the two oxygens also connects to Si, this oxygen carries a half positive charge. Similarly, the other oxygen only connected to Al carries a half negative charge (Figure 2.9). Therefore, the net charge on the edge surface is zero in this case. If under acid conditions, the oxygen bonded with Al and carrying a half negative charge accepts one proton the result is a half positive charge. This results in one unit of edge surface carrying one positive charge. Under alkaline conditions, one unit of edge surface carries two negative charges because of the dissociation of two H^+ ions from two OH groups connected to Si.

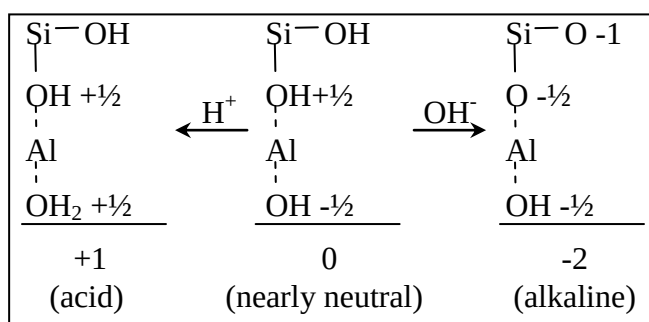


Figure 2.9 The change in electric charge on the edge face of kaolinite by protonation and deprotonation (adapted from Zhang and Zhao, 1997)

In addition to the pH effect, ionic strength and ionic composition also affect surface charge characteristics of VCS (Zhang and Zhao, 1997; Qafoku *et al.*, 2004). According to the diffuse double layer theory, there are two mechanisms that explain the effect of ionic strength on the surface of variable charge minerals. The principal cause of the effect of ionic strength on the quantity of surface charge of variable charge colloids is that the surface charge density is proportional to the square root of ion concentration of the solution and therefore surface charge decreases as EC decreases (van Olphen, 1977; Uehara and Gillman, 1981; Zhang and Zhao, 1997). However there is another possible cause for a decrease in surface charge density; positive and negative charge sites co-exist independently on the surface of variable charge colloids. These sites are compensated by oppositely charged ions in their diffuse double layer (Uehara and Gillman, 1981; Qafoku *et al.*, 2004). Because the thickness of the diffuse double layer is inversely proportional to the square root of the ion concentration, oppositely charged double layers may expand when the soil solution is dilute. Two adjacent diffuse double layers

may partly overlap, causing mutual compensation between positive and negative charge. This would lead to a decrease in adsorption of anions and cations.

As previously discussed, VCS usually consist of both variable charge and permanent charge minerals. In such a mixed system, the permanent charge is likely to remain constant in magnitude, and be negative, zero, or positive, whereas the variable charge will vary with pH and electrolyte concentration. Based on these notions, two zero points of charge, namely zero point of net charge (ZPNC) and zero point of charge (ZPC) or pH_0 , are involved in VCS. According to Gillman and Uehara (1980), ZPNC is the pH value at which the total net surface charge of mixed systems is zero or where the adsorption of cations from an indifferent electrolyte equals that of anions; ZPC or pH_0 is the pH value at which variable net surface charge resulting from the adsorption of potential determining ions H^+ and OH^- is zero (Gillman and Uehara, 1980). At this pH, the adsorption of H^+ and OH^- are equal and it is the point of intersection of potentiometric titration curves at different electrolyte concentrations.

Figure 2.10 and the following equation show the relationships between ZPNC, pH_0 , permanent surface charge density, and electrolyte concentration. The pH_0 is independent of either the quantity of permanent surface charge (σ_p) or the concentration of electrolyte (C), whereas ZPNC varies with the change in electrolyte concentration. When soil colloids carry permanent negative surface charges, ZPNC is lower than pH_0 ; conversely, when soil colloids carry permanent positive surface charges, ZPNC is higher than pH_0 (Gillman and Uehara, 1980; Uehara and Gillman, 1980). When the electrolyte concentration increases in mixed systems, ZPNC usually decreases and the quantity of surface charge increases.

Although the quantity of surface charge increases with the increase in electrolyte concentration, in some cases the ZPNC remains unchanged or is even slightly increased (Zhang and Zhao, 1997). A typical example is shown in Table 2.2. These results can be explained by the pH_0 of this soil (Hyper-Rhodic Ferralsol) being close to the ZPNC (approximately pH 4.80) because this soil carries only a negligible quantity of permanent surface charge (Zhang *et al.*, 1989).

$$\text{ZPNC} = \text{pH}_0 + \frac{\sigma_p}{\text{constant} \times C^{1/2}}$$

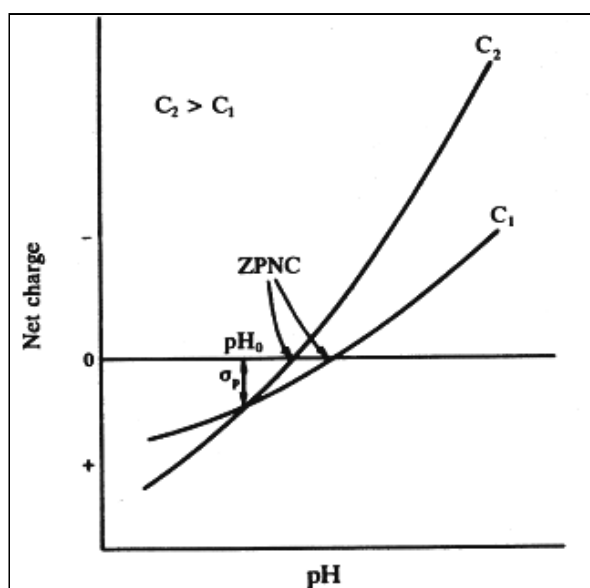


Figure 2.10 The relationships of ZPNC, pH_0 and permanent surface charge (σ_p) with respect to electrolyte concentration C (adapted from Uehara and Gillman, 1981; Zhang and Zhao, 1997)

Table 2.2 Influence of electrolyte concentration (KCl) on ZPNC and surface charges of a Rhodic Ferralsol and a Hyper-Rhodic Ferralsol (data from Zhang and Zhao, 1997)

Electrolyte concentration (M)	Rhodic Ferralsol		Hyper-Rhodic Ferralsol	
	ZPNC	Charge ($\text{cmol}_c \text{ kg}^{-1}$)	ZPNC	Charge ($\text{cmol}_c \text{ kg}^{-1}$)
0.005	4.3	0.6	4.7	1.3
0.010	4.1	1.1	4.8	1.6
0.050	3.9	1.6	4.8	2.2
0.100	3.6	2.3	4.9	2.2

Another important characteristic of VCS is specific ion adsorption which can be classified into low-affinity and high-affinity specific adsorption (Uehara and Gillman, 1981). The former refers to adsorption in the Stern layer (or compact layer) and the latter refers to chemical coordination to the surface metal ion, so called chemisorption. Low-affinity and high-affinity specific adsorption of ions such as SO_4^{2-} and Ca^{2+} cause a change in pH_0 and surface charge properties of VCS (Gillman and Uehara, 1980; Uehara and Gillman, 1981; Zhang and Zhao, 1997).

According to Uehara and Gillman (1981) low-affinity specific adsorption of a cation induces additional negative charge on the oxide surface because of proton desorption. The pH must be lowered to cause proton adsorption in order to establish a new pH value of zero net charge, pH_0 . Conversely, the low-affinity specific adsorption of an anion results in additional positive charge on the oxide surface and raises the pH_0 value (Figure 2.11). These effects have been observed with Ca^{2+} and SO_4^{2-} for hematite (Breeuwsma and Lyklema, 1971) and soil materials (Keng and Uehara, 1973).

On the other hand, if the adsorbed ion becomes part of the surface and transfers its charge to the solid, this is referred to as high-affinity specific adsorption. Adsorption of a cation on an oxide surface at zero net charge causes a net positive charge, and raises pH_0 and the isoelectric point (IEP), the pH value at which the plane between the compact and diffuse layer has zero net charge. However, high-affinity specific adsorption of an anion causes a net negative charge and lowers both pH_0 and the IEP (Uehara and Gillman, 1981). For example, applications of silicate and phosphate lowered pH_0 of goethite (Hingston *et al.*, 1967) and of an Oxisol, respectively (Wann and Uehara, 1978a).

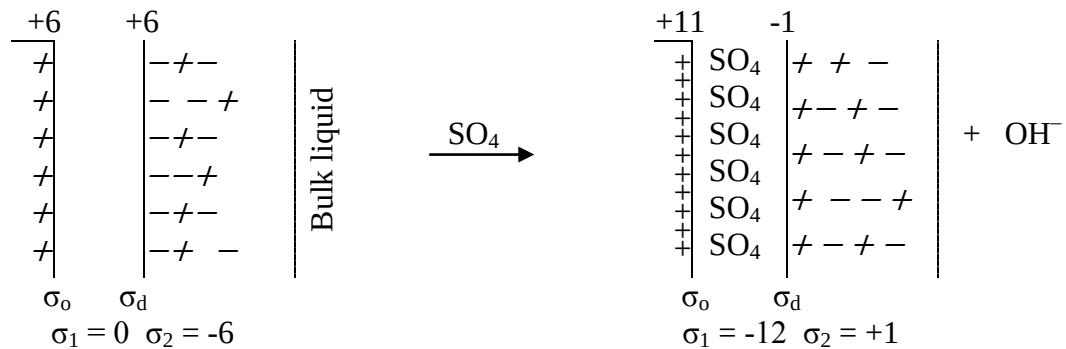


Figure 2.11 Surface charge (σ_o) reversal in the diffuse layer (σ_2) due to the adsorption of SO_4^{2-} in the Stern layer (σ_1) [additional positive charge onto the surface (protonation) results in a higher value of pH_0 , but the pH where $\sigma_d = 0$ (IEP) is lowered] (reproduced from Uehara and Gillman, 1981)

Previous studies have proved that the phosphate anion coordinates with the surface metal ion and replaces HOH and OH^- ions bonded to the metal ions (Parfitt *et al.*, 1975; Rajan, 1976), as illustrated in Figure 2.12. If the phosphate ion replaces one water molecule, a decrease in positive charge or an increase in net negative charge occurs, whereas the replacement of hydroxyl by phosphate does not change the charge.

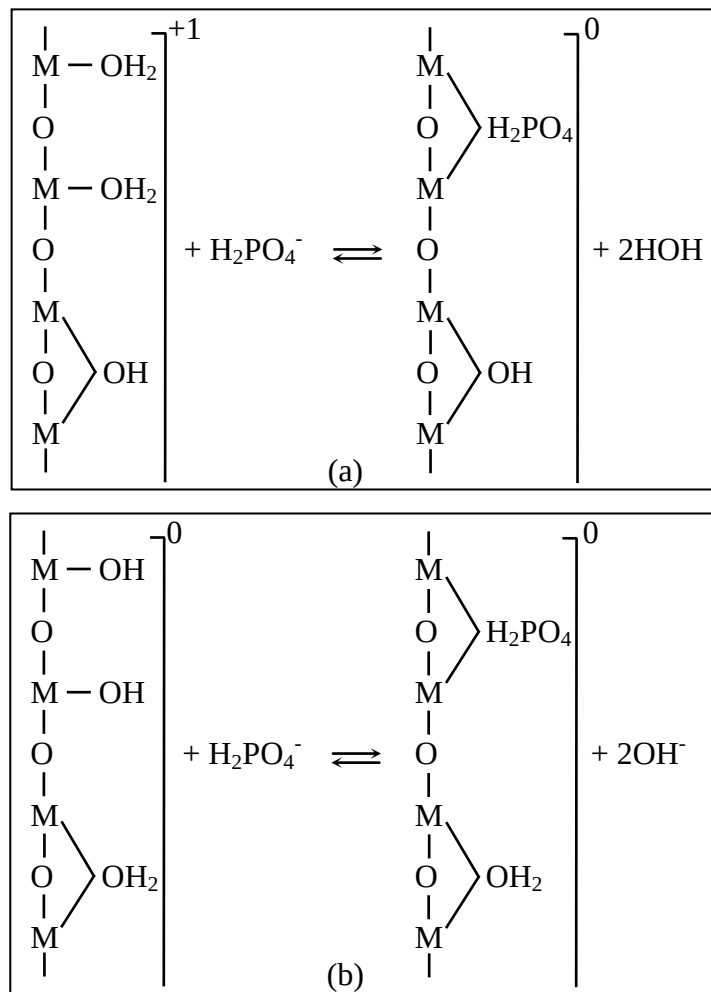


Figure 2.12 Displacement of water (a) and hydroxyl (b) group from a metal oxy-hydroxide surface by phosphate ion (reproduced from Uehara and Gillman, 1981)

Many authors suggest that the mechanisms of phosphate, sulfate and silicate adsorption are similar and that these ions compete for the same sorption sites, although sulfate and silicate do not compete strongly with phosphate (Zhang and Zhao, 1997; Chorover, 2005). The influence of specific adsorption of anions on surface charges of VCS is also associated with the quantity of the anions (Zhang *et al.*, 1989). For example, sulfate and phosphate application to an Oxisol causes a decrease in positive charge and an increase in negative charge. However, the amount of sulfate adsorbed by an Andisol is much lower than that of phosphate and decreases strongly with increasing pH (Chorover, 2005). Also, in comparing specific adsorption of silicate and phosphate, Obihara and Russell (1972) concluded that phosphate is adsorbed by soils in the pH range 4.0 – 6.0 much more strongly than silicate. In addition, the effect of specific adsorption of anions on the surface charge of VCS is closely related to pH. Studies on three VCSs found the net negative charge surfaces increased to different extents after the

adsorption of phosphate at different pH; the higher the pH, the larger the increase of net negative surface charge especially when pH was higher than 5.0 (Zhang and Zhao, 1997).

2.3.3 Management of variable charge soils

Highly weathered VCS are characterized by low values of exchangeable basic cations, acidic reaction and their ability to adsorb anions (Gillman and Sumpter, 1986). Soil organic matter (SOM) can be considered as an effective slow release nutrient source that mediates the cycling of nutrients and chemical attributes of soils. However, when these soils are disturbed through continuous cultivation, productivity often declines rapidly due to a loss in SOM, accelerated soil acidification and a decrease in the CEC (Qafoku *et al.*, 2004). This reduces the ability of the soil to hold nutrients such as Ca^{2+} , Mg^{2+} , and K^{+} which are rapidly lost through leaching. On the other hand, VCS can develop appreciable AEC under acidic conditions. Consequently, managing surface charge properties is the key to the sustainable management of VCS.

Zero point of charge, pH_0 , is one of the most important parameters to determine in VCS because it indicates the sign of the net surface charge. When the actual soil pH is lower than pH_0 , the surface carries net positive charge; conversely, the surface is net negatively charged if the soil pH is higher than pH_0 . The colloidal fraction of VCS is usually dominated by Fe and Al oxides that possess relatively high pH_0 values, ranging between pH 7.0 and 9.0 depending on their composition and degree of crystallinity. As a consequence, subsoils of low OM content in VCS usually exhibit an anion exchange capacity. Conversely, silicate and organic matter have low pH_0 values and therefore increase the CEC of VCS (Uehara and Gillman, 1981). Previous studies on VCS have provided many management options in order to manipulate the surface charge characteristics. These options are comprised of managing soil pH, OM management and the application of specifically adsorbed anions such as HPO_4^{2-} and SiO_4^{2-} (Uehara and Gillman, 1981; Zhang and Zhao, 1997; Qafoku *et al.*, 2004).

As mentioned above, soil pH determines the magnitude of net charge because of its relationship to pH_0 . Thus raising soil pH by application of lime is commonly practiced to increase the soil's CEC by increasing soil pH above the pH_0 (Barrow, 1984; Mora and Barrow, 1996). Increasing soil pH reduces phytotoxic levels of exchangeable acidity (H^{+} and Al^{3+}), decreases the retention of anions such as SO_4^{2-} and HPO_4^{2-} (Marsh *et al.*, 1987; Bolan *et al.*, 1988; Naidu *et al.*, 1990) and increases the ability of soils to retain positively charged nutrient ions (Adams, 1984).

Despite this common practice, it is usually difficult to raise the pH of VCS above pH 6.0 because of the high buffering capacity associated with the high specific area of variable charge surfaces. For example, a material such as calcium carbonate releases hydroxyl ions into the system by hydrolysis of the carbonate ion, and a hydroxylated variable charge surface will release protons to neutralize OH⁻, thus buffering the soil against pH change. Therefore, a large input of lime is required which is ineffective and uneconomic and may also induce micronutrient deficiencies (Uehara and Gillman, 1981). Furthermore, when applying management practices that focus on changing soil pH, an increase in CEC may result in increased agricultural production, but a decrease in AEC decreases the capacity of soils, especially subsoils, to retain contaminant anions such as nitrate (Qafoku *et al.*, 2004). Consequently, reducing the value of pH₀ rather than raising the soil pH is another option that can be considered in order to achieve sustainable management of VCS.

The CEC and reserves of plant nutrients in highly weathered and variable charge soils are chiefly associated with the SOM content (Qafoku *et al.*, 2004). Also, OM has a low pH₀, so lowering pH₀ can be achieved by increasing OM content of the soil (Uehara and Gillman, 1981). Low SOM content reduces the ability of the soil to supply nutrients such as nitrogen, P and sulfur to plants and to retain cations in exchangeable form (Van Ranst, 1995 cited by Qafoku *et al.*, 2004). Therefore, agricultural management practices focused on increasing SOM content such as zero tillage and accompanied by decreasing SOM removal through erosion control and crop residue management are important. However, SOM decreases gradually with time in these soils due to erosion and/or OM oxidation during regular cropping, and under humid tropical conditions maintaining and increasing SOM is problematic (Qafoku *et al.*, 2004).

Many studies have asserted that application of specifically adsorbed anions such as HPO₄²⁻ and SiO₄²⁻ reduce the pH₀ value (Uehara and Gillman, 1981; Zhang and Zhao, 1997; Fiantis *et al.*, 2002; Qafoku *et al.*, 2004) and consequently increase the CEC (Silva, 1971; Zhang and Zhao, 1997; Fiantis *et al.*, 2002; Noble *et al.*, 2003) of VCS. The specific adsorption of these individual anions also causes interactions between them. For example, the application of SiO₄²⁻ reduced HPO₄²⁻ sorption in a Typic Gibbshumox (Fox, 1978), in an actual acid sulfate soil (Tran *et al.*, 2005a), and several strongly phosphate-fixing soils (Obihara and Russell, 1972). Other researchers (Wann and Uehara, 1978a) have shown that P fertilisers added to VCS not only increase the P status, but also increase the CEC. This is associated with a shift

in the PZC to a lower pH value (Hingston *et al.*, 1972; Wann and Uehara, 1978a) and neutralisation of positive charge (Hingston *et al.*, 1972).

Application of silicate to an Oxisol resulted in the decrease of pH_0 from 3.8 to 3.5 whereas application of phosphate led to a change of pH_0 from 3.8 to 3.2 and decreased the ZPNC from 3.7 to 3.4 (Zhang and Zhao, 1997). Similarly, Fiantis *et al.* (2002) have stated that superphosphate has a greater effect on lowering the pH_0 of volcanic soils than calcium silicate, and adsorption of phosphate by a Hydrandept soil increased the CEC more than adsorption of silicate (Mekaru, 1969 cited by Silva, 1971). These results can be explained by the following possible mechanisms: a) changes in the surface charge would produce changes in zeta potential, which is the potential at the slipping plane between the Stern layer and the diffuse layer. For example, Zhang and Zhao (1997) found that the IEP of an Oxisol decreased to 3.75 and 4.20 from an original value of 4.40 after treatment with phosphate and silicate, respectively (Figure 2.13); b) calcium silicate dissolution produces Ca^{2+} and SiO_3^{2-} ions; Ca^{2+} may specifically adsorb onto negative surface charges, causing an increase in pH_0 whereas the silicate ion can be polymerized when present in soil solution. Therefore, the silicate ion does not undergo specific adsorption as would occur with the phosphate ion, and the calcium ion masks the effect of the silicate ion on lowering the pH_0 value (Fiantis *et al.*, 2002); and c) the more specifically an anion is adsorbed, the lower the pH_0 (Gillman and Uehara, 1980); the amounts of phosphate adsorbed in soils are greater than those of silicate at pH values of 4.0 – 6.0, which normally occur in VCS (Obihara and Russell, 1972).

As a consequence of results such as those above, P fertiliser application has been proposed as a management approach to increase negative surfaces of VCS (Probert, 1983) thereby increasing CEC. However, because of the very high P fixing ability of VCS large amounts of P are required to cause a substantial increase in CEC (Bolan *et al.*, 1999) and improve plant growth (Uehara and Gillman, 1981). Another option that can be used to rectify problems of VCS is the application of silicate. The ZPC of SiO_2 is approximately 2.0 and so a silicate-dominated system carries negative charge under ordinary soil pH conditions (Zhang and Zhao, 1997). In addition, silicate anions are able to specifically adsorb onto oxide surfaces through the replacement of hydroxylate and hydroxyl groups bonded to metal ions (Uehara and Gillman, 1981). Consequently, masking a portion of the positive charge, lowering pH_0 , increasing negative surface charge and consequently raising the CEC of VCS can be achieved by the application of silicate (Qafoku *et al.*, 2004).

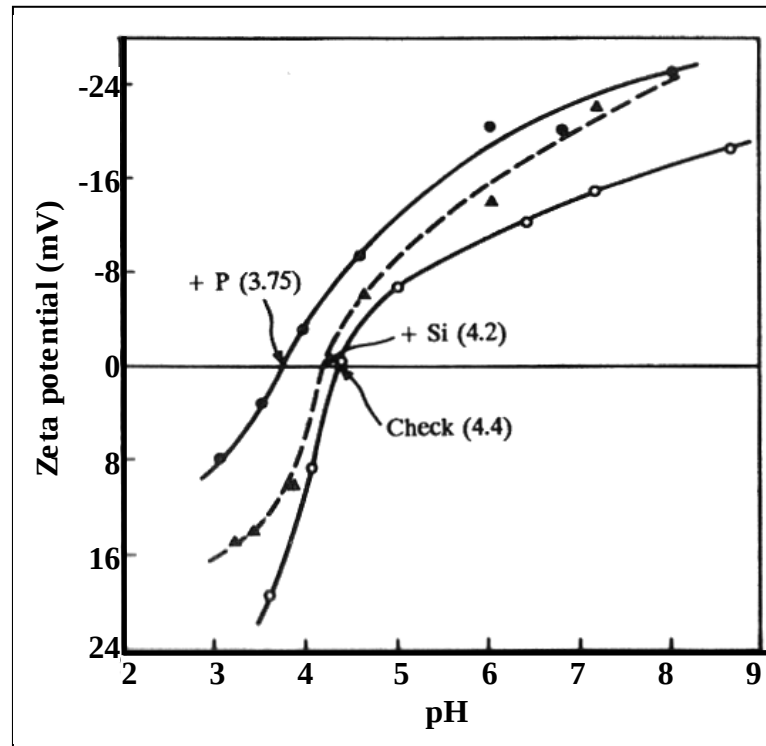


Figure 2.13 Influence of phosphate and silicate on IEP of the colloid fraction of an Oxisol (adapted after Zhang and Zhao, 1997)

Although the effect of the silicate ion on the surface charge of soil colloids is potentially less than that of the phosphate ion, it may play a key role in the correction of the constraints of VCS. Crop responses to, and the beneficial effects of, the application of Si or silicate materials are generally obtained in VCS where Si content has been reduced by leaching or desilication (Silva, 1971; Uehara and Gillman, 1981). Therefore, Si repletion is an important practice for not only improving surface charge characteristics, but is also associated with interactions with P availability and Al toxicity (Silva, 1971).

2.4 Effects of silicon on phosphorus availability, aluminium and manganese toxicity

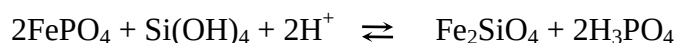
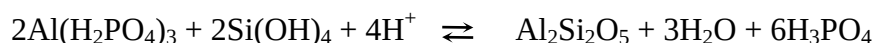
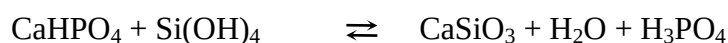
2.4.1 Interaction between silicon and phosphorus in soils

Although P deficiency is a worldwide issue, it is the most commonly confronted agronomic problem and appears to be more severe in the humid tropics particularly where there are acid, heavy-textured soils high in oxy-hydroxide mineral content (Arai and Parks, 2007). For instance, the highly weathered soils that have been derived from volcanic ash and soils containing variable charge minerals present the most serious P deficiency problems (Uehara and Gillman, 1981). According to Uehara and Gillman (1981) there are a number of reasons

for the differences in P adsorption among soils, such as differences in surface reactivity, differences in specific surface, differences in capacity to occlude P, and the presence of competitive species at P adsorption sites.

Many studies have shown that some organic and inorganic ions are adsorbed onto oxy-hydroxide surfaces (Wada and Harward, 1974; Bowden *et al.*, 1980; Fox, 1980; Parfitt, 1980; Tate and Theng, 1980; Uehara and Gillman, 1981; Yu, 1997; Zhang and Zhao, 1997; Qafoku *et al.*, 2004). Although P seems to be the most competitive adsorbate at least among the inorganic species, the presence of other anionic species can reduce phosphate sorption capacity (Uehara and Gillman, 1981). For example, Roy *et al.* (1971) found that Hawaiian soils adsorbed less P when silicate was applied as calcium silicate slag, and the possible mechanism for this is calcium silicate, which hydrolyzes to monosilicic acid in solution, partially adsorbs onto the surface and thus reduces the number of sites available for phosphate sorption (Uehara and Gillman, 1981).

Most investigations of monosilicic acid effects on soil properties are associated with their interaction with soil phosphates (Matichenkov and Ammosova, 1996; Matichenkov and Bocharnikova, 2001). Several studies have shown that applied Si amendments, such as amorphous SiO₂, CaSiO₃ and silicate slags (industrial by-products), increase plant-available P and decrease P leaching from the soil (Gladkova, 1982; Matichenkov and Ammosova, 1996; Matichenkov and Bocharnikova, 2001, 2002; Matichenkov and Calvert, 2002). These effects involve several processes. First, Si amendments added to the soil increase concentrations of monosilicic acid in the soil solution, which is adsorbed on phosphates of Ca, Al, Fe and Mg, releasing P into solution as shown in the following reactions:



On the other hand, Si amendments adsorb P, thereby decreasing P leaching from the soil and keeping it in a plant available form (Tables 2.3 and 2.4) (Matichenkov and Bocharnikova, 2001). Thus, Si amendments may regulate the solubility of P in soils and provide an increase in P fertiliser efficiency.

Table 2.3 The effect of Si amendments on P adsorption by a Spodosol pre-treated with various Si amendments (data from Matichenkov and Bocharnikova, 2001)

Treatment	P in supernatant (mg L ⁻¹)		
Original solution	0.500	2.000	10.000
Amorphous SiO ₂	0.482	1.920	4.820
CaSiO ₃	0.342	0.485	0.940
Slag	0.390	0.430	0.670
Recmix slag	0.025	0.018	0.110
LSD _{0.05}	0.060	0.080	0.100

Table 2.4 Phosphorus concentration in a cultivated Spodosol pre-treated with various Si amendments before and after irrigation with a P-bearing solution of 10 mg P L⁻¹ (data from Matichenkov and Bocharnikova, 2001)

Treatments	Before irrigation		After irrigation	
	¹ P _w	² P _a	P _w	P _a
	(mg P L ⁻¹)			
Control	5.9	51.1	8.6	84.3
SiO ₂	6.1	52.3	9.4	87.3
CaSiO ₃	6.0	51.4	8.4	94.2
Slag	5.8	54.2	9.7	99.7
Recmix slag	5.7	51.6	9.8	104.5
LSD _{0.05}	0.8	6.1	0.8	6.1

¹P_w: water extractable P; ²P_a: acid extractable P

Previous studies on the specific adsorption of anions, particular phosphate and silicate, have shown that the adsorption depends on the pK values of the anion acids, and this confers a negative charge on the surface and shifts the ZPC to lower pH values (Hingston *et al.*, 1967). Weak acid anions show maximum adsorption close to the pK value because at this pH the anion is ionized and hydroxyls are displaced by anion adsorption. Silicate adsorption increases with increasing pH and exhibits a maximum adsorption at about pH 9.2, a little below the pK of silicic acid (9.7). Similarly, phosphate adsorption decreases with increasing pH and the adsorption envelopes are at about pH 6.4 and 11.6, a little below the two relevant pKs of phosphate ion (7.2 and 12.7). The adsorption curves of phosphate and silicate intersect at about pH 6.5 (Hingston *et al.*, 1967; Obihara and Russell, 1972). This can be explained by

the adsorption of phosphate by soils being much stronger than silicate in the pH range 4.0 – 6.0. However, if the adsorbed phosphate in the soil is very low, the ability of a certain concentration of silicate in solution to displace phosphate increases as the pH of the soil increases. Thus silicate applied to low phosphate soils would be expected to release phosphate and the effect is more pronounced for neutral or calcareous soils than for acid soils (Obihara and Russell, 1972).

Although silicate adsorption is much less than that of phosphate at ordinary soil pH and is highly pH-dependent, the ability of the silicate anion (H_3SiO_4^-) to compete with phosphate anions for sorption sites has been assessed in many studies. Working with six soils from different regions of Brazil, Lopes (1977) (cited in Savant *et al.*, 1999) reported that, in general, Si adsorption increased with increasing soil pH and the adsorption of Si by soils decreased P adsorption, especially around pH 7.0. Despite the fact that the pH of the soil increased as the rate of applied silicate increased, the water-soluble P in the soil also increased. This suggests that the Si effect is to reduce the adsorption of P by the freshly precipitated Fe and Al hydroxides (Savant *et al.*, 1999). Also, McKeague and Cline (1963b, c) found that freshly precipitated hydroxides of polyvalent metals such as Al and Fe are highly effective in Si sorption. This can lower the activity of Al ion in solution and so prevent it from precipitating with P. Silicic acid also competes with phosphate for sorption sites on the surface of hydrated sesquioxides (Jones and Handreck, 1967).

Shariatmadari and Mermut (1999) studied the effect of dissolved Si on sorption of P by calcite and showed that an addition of 0.36 mM Si to a calcite and several mixtures of mineral clay and calcite systems markedly reduced the P sorption of calcite and caused around a 20% reduction in P sorption by the mixtures. The authors found that the application of Si to the system increased total soluble Ca concentration. Therefore, the solubility of both calcite and newly formed Ca-P compounds in the system can be enhanced by Si addition, which results in a higher P concentration remaining in the solution. In addition, Koski-Vahala *et al.* (2001) showed that the application of Si to an aerobic sediment of high P retention capacity resulted in an increased P concentration in the solution because of the competition between Si and P for sorption sites. The authors also indicated that a combination of added Si and elevated pH released more P to the solution by desorption of P from Fe oxides. A similar study of the effect of Si on P desorption from a silty loam and a loam from Korea showed that P desorption increased with increasing Si concentration and temperature (Lee *et al.*, 2004).

In addition to liming of VCS in tropical and subtropical regions, the application of Si containing materials, such as calcium silicate and/or silicate slags, have also been used to rectify the problem of soil acidity and P fixation. In comparing the effect of CaCO_3 and CaSiO_3 on P availability and other soil properties, many studies have confirmed that calcium silicate has more effectiveness than does CaCO_3 (Fox, 1980; Smyth and Sanchez, 1980; Violante *et al.*, 2002; Tran *et al.*, 2005a). This can be explained by one or more of the following mechanisms: a) CaCO_3 may induce K deficiency (Fox, 1980); b) calcium silicate not only increases pH and supplies Ca and soluble silica to the soil, but can also lower the ZPC through anion adsorption effects (Violante *et al.*, 2002); and c) the presence of CaCO_3 may not have any effect on P solubility or may even lower the level of P in solution compared to that in the absence of CaCO_3 , whereas calcium silicate decreases P sorption which results in an increase of P concentration in solution (Tran *et al.*, 2005a).

In addition to the above, application of both phosphate and silicate to the soil causes either or both to move deeper into the subsoil. Gillman and Fox (1980) (cited by Uehara and Gillman, 1981) showed that liming a Gibbshumox with calcium silicate increased CEC to a greater depth than the depth of incorporation. An increase in subsoil CEC and subsoil acidity correction would allow a greater retention of calcium, which in turn would enable plant roots to extract water and nutrients from a larger soil volume. This may be a relatively simple approach to addressing subsoil acidity without deep lime incorporation (Uehara and Gillman, 1981).

2.4.2 Effect of silicon on phosphorus availability and crop growth

As discussed in the previous section, Si is able to improve soil phosphate status through several processes, particularly by reducing P sorption and enhancing P desorption. These effects provide increased P mobility and availability in the soil solution leading to a greater amount of available P for plant uptake and growth, which will be discussed in this section.

Ma and Takahashi (1990b) studied the effect of Si as silicic acid (1.66 mM Si) on P uptake and the growth of rice in solution culture at three P concentrations of low (0.014 mM), medium (0.21 mM) and high (0.70 mM). They found that shoot dry weight with Si application increased at the low and high P level more than that at the medium level, whereas that without Si application was maximum at the medium P concentration level. However, the application of Si decreased P uptake at the medium and high P level treatments from 27 to 30 percent compared to those without Si application, respectively. These results show that Si

regulated P uptake by rice, reducing P uptake when P was high and increasing P availability within deficient plants when P was low. Therefore, Si optimized P levels for the plant leading to greater shoot weight increases at low or high P levels than at the medium P level. Similarly, working with an actual acid sulfate soil from Vietnam, Tran *et al.* (2005b) showed a significant increase of Si, P and N uptake by rice 25 days after sowing with sodium silicate application compared to those without sodium silicate treatment. A similar result was also found by Ma and Takahashi (1991) for rice grown on a P-deficient soil.

Cooke (1956) carried out glasshouse and field experiments on a P-deficient soil to investigate the effect of some silicate slags on P uptake by barley, sugar-beet and swedes in comparison with ground limestone both in the presence and absence of superphosphate. He found that the crops contained considerably more P following the addition of steel-furnace slags than the addition of ground limestone both in the presence and absence of P fertiliser. Likewise, Owino-Gerroh and Gascho (2004) found that when calcium silicate was added with P to a low pH soil, P uptake by maize was promoted and a higher total biomass was obtained in comparison with P addition alone (Owino-Gerroh and Gascho, 2004). Similar effects were obtained in experiments on a Spodosol and an Entisol to investigate the growth of Bahiagrass (Matichenkov and Bocharnikova, 2002), and on Latosols from Hawaii used for the growth of sugarcane (Roy *et al.*, 1971). These effects have been attributed to several potential factors including the increase in soil pH due to the accompanying carbonate anion added as Na_2CO_3 , a reduction of P sorption (Ma and Takahashi, 1991) and the increase in concentration of Si in the soil solution leading to specifically adsorbed Si anion releasing hydroxyl ions (Smyth and Sanchez, 1980), and the maintenance of P concentration in the soil solution during P depletion (Roy *et al.*, 1971).

2.4.3 Effects of silicon on aluminium and manganese toxicity

Silicon has been shown to ameliorate toxicities of Al and Mn. Possible mechanisms have been examined most extensively for Al (Liang *et al.*, 2007). Ameliorative effects vary with plant species, probably due to differences in Al tolerance and/or differences in the mechanisms involved (Ma, 2004). Hodson and Evans (1998) reported that sorghum (*Sorghum bicolor* L.), barley (*Hordeum vulgare* L.), teosinte (*Zea mays* L. ssp. *Mexicana*), and soybean (*Glycine max* L. Merr.) showed significant alleviation of Al toxicity by Si, while rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), cotton (*Gossypium hirsutum*) and pea (*Pisum sativum* L.) exhibited little or no such effect. Other studies have also suggested Si application as an

alternative approach to detoxifying Al in tomato (*Lycopersicum esculentum* L.) (Ma *et al.*, 1997), sorghum (Cocker *et al.*, 1998a), and barley (*Hordeum vulgare* L.) (Barceló *et al.*, 1993; Corrales *et al.*, 1997). With respect to barley, as much as 80% amelioration of the decrease in root length was achieved using 2.8 mM Si in the presence of 50 μ M Al, and the addition of Si also reduced Al uptake into the roots (Barceló *et al.*, 1993).

The interaction between Si and Al reducing the activity of toxic Al ion species in the medium can be considered as one possible external mechanism for the detoxification of Al by Si (IRRI, 1965; Hiradate *et al.*, 1998). The amelioration may result from the formation of hydroxyl-aluminosilicate species which mitigate Al toxicity in plants (Epstein, 1999). In experiments with maize in which Si afforded protection against the inhibition of root elongation by Al, Ma *et al.* (1997) also concluded that the formation of Al-Si complexes was responsible.

Another interaction of Si and Al is co-deposition that seems to occur not only in the growth media but also within plants (Corrales *et al.*, 1997). Cocker *et al.* (1998b) suggested that co-deposition of Si with Al in cell walls requires a relatively high pH as well as the presence of organic anions, particularly malate. Based on the experiments with teosinte (*Zea mays* L. ssp. *Mexicana*) in nutrient solution culture, Barceló *et al.* (1993) concluded that Si has a significant effect on both Al speciation in the solution and Al uptake by the plants. They also noticed that Si in the solution caused a substantial increase in malic acid concentration in the plant roots, and postulated that chelation of Al by malic acid is another mechanism of Si-induced Al tolerance. It is notable that significantly higher concentrations of malic and formic acids were observed in plants grown in the presence of added Si and Al (Liang *et al.*, 2007). Furthermore, Liang *et al.* (1997) found a very small change in the concentration of Al and Si in culture solution. They believed that co-deposition of Al and Si in solution was negligible because silicic acid rather than alkaline Na_2SiO_3 was used in the experiment. However, co-deposition of Al and Si in the growth media using alkaline Na_2SiO_3 as the Si source and within the plant is likely. This may be the mechanism for amelioration of Al toxicity by Si in plants grown with toxic levels of Al. Working with an Al-sensitive variety of corn (*Zea mays* var. BR 201 F), Corrales *et al.* (1986) found that Si pre-treatment is effective in counteracting the inhibition of root elongation by Al and diminished the absorption of Al by the plants, suggesting a reaction in the soil solution between the two elements. In addition, Si may have additional roles in increasing tolerance of Al by mediating the metabolism of phenolic compounds as it has been reported that Si-treated maize plants release fifteen times more

phenolics than untreated maize plants (Horst *et al.*, 1999). These flavenoid-phenolics (i.e., catechin and quercetin) have a strong Al-chelating ability and may provide metal tolerance in plants.

Stimulation of plant growth by Si can be caused by the prevention or amelioration of Mn and Fe toxicity (Williams and Vlamis, 1957a; Vlamis and Williams, 1967). In an experiment with rice grown in nutrient solution culture in which Si was applied as silicic acid (1.66 mM Si), Ma and Takahashi (1990b) found that in the presence of Si, the uptake of Fe and Mn by rice decreased by 20 and 50 percent, respectively. Application of Si slag (2 tonnes ha⁻¹) to soil with high exchangeable Fe and Mn reduced Mn concentration in rice plants without producing any Mn toxicity symptoms (Iwasaki *et al.*, 2002a). Horiguchi (1988) confirmed that the alleviation of Mn toxicity in rice seedlings is due to the decreased uptake of Mn by the Si-treated plants. Horst and Marschner (1978) studied the effect of Si on Mn tolerance of bean plants (*Phaseolus Vulgaris* L. var. 'Red Kidney') grown in water culture at different levels of Mn supply. They found that growth depression and toxicity symptoms on the plants occurred at a low Mn level (0.5 µM) in the nutrient solution without Si. However, the plants tolerated a higher Mn level (5 µM) after the application of 0.75 µM Si and at a higher Si supply of 40 µM, tolerated as much as 10 µM Mn in the nutrient solution without any growth depression. The authors asserted that the increase in Mn tolerance in bean plants was not only due to lower Mn uptake, but also to an increase in the tolerance of leaf tissue to high Mn levels. For species that have low tissue tolerance to high Mn levels, such as barley and bean, the application of Si can redistribute Mn evenly within the leaf tissue (Peaslee and Frink, 1969). On the other hand, in the absence of Si the distribution of Mn is heterogeneous and characterized by spot-like accumulations. Horst and Marschner (1978) consider these spots to resemble typical visible symptoms of Mn toxicity, namely, brown spots of Mn oxides surrounded by chlorotic or/and necrotic areas. Although the effect of Si on Mn distribution is not fully understood, Si prevents this accumulation thereby increasing tissue tolerance to high Mn levels (Hodson and Evans, 1995). For example in sugarcane, the main effect of Si on alleviating Mn toxicity is to distribute Mn more evenly through the leaves, thereby preventing it from collecting into localized areas which become necrotic (Jones and Handreck, 1965, 1967; Vlamis and Williams, 1967). Horst *et al.* (1999) observed that Si lowered the apoplastic Mn concentration in cowpea, suggesting that Si may modify the cation binding capacity of the cell wall. Iwasaki *et al.* (2002a, b) stated that Si supply alleviates Mn toxicity not only by decreasing the concentration of soluble apoplastic Mn through enhanced adsorption of Mn on

the cell walls, but a role of soluble Si in the apoplast in the detoxification of apoplastic Mn is also indicated.

The effect of Si on increased tolerance to excessive levels of Mn and Fe in the root medium of paddy rice is also due to depressed rates of Fe and Mn uptake (Ma and Takahashi, 1990b). This could be due to Si increasing the ‘oxidizing power’ of the paddy rice roots by increasing the proportion of air-filled spaces in shoots and roots, thereby enhancing oxygen transport from the shoots to the submerged root system exposed to toxic concentrations of reduced Mn and Fe (Okuda and Takahashi, 1961; Fleck *et al.*, 2011). Furthermore, in Si-treated plants less Mn is located in the symplast (< 10%) and more Mn is bound to the cell wall (> 90%) compared with non-Si-treated plants (about 50% in each compartment) (Iwasaki *et al.*, 2002b). Manganese present in Si-treated plants is therefore less available and for this reason less toxic than in plants not treated with Si.

2.5 Silicon budget in farming systems in Vietnam

The Si budget of a farming system can be considered to comprise the relationship between Si in soil, Si removal by crop production, and the application of Si bearing amendments and crop residues. In Vietnam, upland soils cover an area of about 72 percent of the total land surface of 33 million ha with the major soil groups of the uplands being Acrisols and Ferralsols (FAO-UNESCO classification) that account for 71.1% and 23.8% of the total area, respectively (Ton *et al.*, 1996; Nguyen and Thai, 1999). These soils are characterized by a history of intensive weathering processes. These soils are mostly located on steep slopes (from 8 to 25 percent or more) that are strongly affected by erosion, and are generally intensively cultivated with low fertiliser input (Nguyen and Thai, 1999). Thus, these soils have low nutrient fertility and can be rapidly degraded. Soil surface charge is sometimes characterized by net positive charge (Phan *et al.*, 2005) especially in the subsoil layer of Ferralsols (Moody and Phan, 2008), which is the major upland soil type in the eastern region and the central highlands of southern Vietnam (Nguyen and Thai, 1999).

Vietnam has 7 million ha of agricultural land with rice occupying about 4.2 million ha as the predominant crop in most of the ecological regions of the country (Table 2.5). Cropping intensity has reached approximately 170 percent and the national average rice grain yield is about 5.0 tonnes ha⁻¹. Thus, the actual sown area is 7.2 million ha producing approximately 36 million tonnes of paddy rice grain annually. Rice is grown in three major ecosystems: a) irrigated and intensive (lowland); b) rainfed and flood prone (coastal land); and c) upland. The

lowland ecosystem comprises 60 percent of the rice land, while the coastal land and the upland ecosystems account for 32 and 8 percent, respectively (Bui, 1998). Maize and sugarcane are the two main annual crops cultivated in the uplands, particularly in the central highlands and the eastern region of southern Vietnam.

Table 2.5 Area and yield of major crops in Vietnam (2007)*

Crops	Area planted (x 10 ³ ha)	Yield (tonnes ha ⁻¹)	Production (x 10 ³ tonnes)
Rice	7200	4.98	35867
Maize	1068	3.87	4134
Sugarcane	291	59.74	17378
Groundnut	254	1.99	505
Cassava	497	16.07	7985
Sweet potato	178	8.20	1457
Soybean	190	1.45	275
Rubber	550	1.61	602
Coffee	506	1.97	961
Cashew	437	1.03	323
Pepper	48	2.21	90

*Statistics and food security online database 2007, Ministry of Agriculture and Rural Development (MARD)

As indicated in many investigations, rice and sugarcane are known as Si-accumulating crops. These crops absorb Si, as Si(OH)₄, from the soil far more than any other mineral nutrients (IFA, 1992; Savant *et al.*, 1997a; Savant *et al.*, 1997b; Savant *et al.*, 1999). It is estimated that rice normally removes from 230 to 470 kg Si ha⁻¹ for a grain yield of 5.0 tonnes ha⁻¹ (Amarasiri and Perera, 1975; IFA, 1992). Likewise, from 380 to 400 kg Si ha⁻¹ is removed from soil by a crop of 74 tonnes ha⁻¹ of sugarcane (tops and millable cane) (Savant *et al.*, 1999). Assuming an annual production estimate of 36 million tonnes of rice and 17 million tonnes of sugarcane in Vietnam (Table 2.5) and no Si-bearing amendment application, annual rates of removal of Si will be from 1.66 to 3.38 million tonnes and from 0.87 to 0.92 million tonnes from soils of rice and sugarcane cultivation, respectively. As described previously, Si application not only improves soil fertility in terms of CEC and nutrient supply, but also protects plants from biotic and abiotic stresses, such as disease and pests, ameliorates Al, Mn and Fe toxicities, and increases P availability. Savant *et al.* (1997a; 1999) also state that the depletion of plant available Si is one of the factors associated with overall decline of crop

yields. In Vietnam, however, the practice of integrated nutrient management for sustainable crop production has not addressed the application of Si but concentrated on application of N, P, K, lime, micronutrients and organic amendments. In fact, Si is generally only added incidentally through the application of fused magnesium phosphate (FMP) (namely Van Dien and Ninh Binh thermo-phosphate fertilisers) which is used as a P source and liming agent. Silicon is a constituent of the mineral apatite used to produce these fertilisers and their SiO₂ contents range from 15 to 20 percent.

According to the list of fertilisers used in Vietnam (MARD's online database, 2004 - 2008), there are various Si-bearing fertilisers, such as NPK compounds, micro-nutrient mixtures, organic composts and foliar fertilisers that are produced in Vietnam or imported. Depending on fertiliser sources and types, these fertilisers have a wide range of SiO₂ contents from 1 to 35 percent.

Although the significant role of Si in agriculture has been studied since the last century, research on the role of Si in farming systems in Vietnam is negligible. There are only some investigations on the effect of Si on P adsorption and nutrient uptake by rice grown on an actual acid sulfate soil (Tran *et al.*, 2005a, b). There is a large gap in knowledge about the relationship of Si to farming systems in Vietnam, particularly with respect to the management of VCS in the uplands where a variety of crops are intensively cultivated. Therefore, to develop sustainable farming systems in Vietnam, it is necessary to investigate the influence of Si on soil fertility improvement, particularly in terms of the increasing negative surface charge and ameliorating widespread Al toxicity.

2.6 Conclusions

Although total Si content in soils by far exceeds the contents of other nutrient elements, soluble Si in VCS, which is not only a beneficial nutrient for crop growth but also may rectify some or all of the major constraints of VCS, is usually low in VCS due mainly to desilication during soil development under tropical conditions. Silicon repletion may help to overcome the core problem of soils with very low surface negative charge.

Variable charge soils are important agricultural soils in Vietnam. These soils are often P deficient and Al toxic, have high P sorption capacities and low CECs, and maintaining the productivity of these soils presents a challenge to the smallhold farmer. Silicon application to VCS has been shown to increase CEC, ameliorate Al toxicity and decrease P fixation and so represents a management strategy that might provide long-lasting benefits. The effects of locally available silicate materials such as fused magnesium phosphate (FMP) and Si-rich organic amendments (such as *Tithonia diversifolia*) on the properties of VCS needs to be investigated to assess whether the use of such materials is likely to be of benefit in Vietnamese cropping systems.

Chapter 3 Surface charge characteristics and phosphorus sorption capacity of variable charge soils

3.1 Introduction

Most soils contain mixtures of minerals that can be categorized into two distinct groups: those minerals in which surface charge density is a constant or permanent quantity, and those whose surface charge density and the sign of the surface charge are variable or pH-dependent. In general, soils of the temperate regions contain minerals with constant surface charge density, such as smectite, vermiculite, illite, and chlorite, and these clay minerals possess permanent negative charge surfaces. For these soils there are well-established soil management parameters, based on surface charge, and ion exchange, that have been developed and applied successfully (Uehara and Keng, 1975). However, soils that have developed under intensive weathering and leaching conditions in tropical and subtropical regions predominantly contain minerals with variable surface charge density, such as kaolinite, gibbsite, goethite, hematite, and amorphous minerals, and these clay minerals carry variable negative and positive charge on their surfaces (Uehara and Keng, 1975; Qafoku *et al.*, 2004). Such soils are considered variable charge soils (VCS). However, although VCS soils have been recognized as a general group, they are located in different regions and affected by different degrees of weathering, and this results in differences in their clay mineralogy and thus their charge characteristics (Qafoku *et al.*, 2000). For instance, Oxisols are the most highly weathered soils in the tropics as indicated by their clay mineralogy being dominated by kaolinite and sesquioxides (i.e. gibbsite, hematite and goethite) (Herbillon, 1980; Sposito, 1989; Melo *et al.*, 2001). These minerals are known to generate mainly variable charge on their surfaces (Bolland *et al.*, 1976; Schwertman and Taylor, 1989; Zhang and Yu, 1997). As the soil development processes reach an advanced stage of weathering, the variable charge becomes dominant over permanent charge (Hendershot and Lavkulich, 1978), and the end products of the weathering processes, Fe/Al hydrous oxides, usually possess a net positive surface charge under acidic conditions (Qafoku *et al.*, 2004). In addition, even if within a soil type the charge characteristics differ between profile horizons, it is generally found that the surface charge of the topsoil possesses net negative charge whereas the subsoil may have net positive surface charge, the so-called ‘geric property’ (Phan *et al.*, 2005; Moody and Phan, 2008). This difference in the sign of net charge is due to less organic matter and more Fe/Al hydrous

oxides in the B horizon relative to the A horizon (Gillman, 1985; Gillman and Sumpter, 1986; Gillman and Sumner, 1987).

As previously reviewed in Chapter 2, VCS are rich in constituents of surface reactive groups with amphoteric properties which can be protonated or deprotonated to create variable positive or negative charge on their surfaces, respectively. Therefore, the magnitude and sign of their surface charge changes with alteration of soil pH and ionic strength. It is well known that the point of zero charge (PZC) or pH_0 (the pH value at which the number of H^+ and OH^- ions adsorbed on the amphoteric surfaces are equal) is of fundamental significance to the characterisation of VCS because at this pH, net variable charge is zero, so that any residual charge is net permanent charge (Gillman, 1985). If soil pH values are below pH_0 , the variable charge sites will carry net positive charge; in contrast, if soil pH is above pH_0 , they will carry net negative charge. Actually, the pH_0 value reflects the overall contribution to protonation/deprotonation reactions from a variety of soil components, all of which have particular pH_0 values. Thus, the oxides of Al and Fe have high pH_0 values (pH 7-9), while silica (SiO_2) and organic matter have low pH_0 values (pH 2-3) (Uehara and Gillman, 1981). The value of the soil pH_0 therefore yields important information about the surface charge characteristics of a soil containing significant quantities of variable charge.

Another important physicochemical characteristic of VCS is the pH buffering capacity (pHBC) (Oorts *et al.*, 2004). The pHBC of a soil is defined as the amount of acid or base needed to change the pH of the soil by one unit. In the tropics, many VCS have pH values lower than 5.5 and have relatively high concentrations of exchangeable Al (Fox, 1980). Because the charge characteristics of VCS are largely dependent on soil pH, soil acidification often has severe consequences for overall fertility of these soils (e.g., the decrease in CEC as a consequence of acidification results in lower retention capacity for base cations, and the possibility of Al and/or Mn toxicities). Liming, therefore, is often required not only for better crop production, but also for restoration of soil fertility. Thus, it is essential to know the sensitivity of the soil to pH changes to establish appropriate soil pH management schemes for these soils. The pHBC depends on both mineral dissolution and protonation/deprotonation reactions of the functional groups on variable charge surfaces such as OM and clay minerals (Oorts *et al.*, 2004). Good correlations have been found between pHBC and CEC across a wide range of Australian soils (Moody *et al.*, 1997; Conyers *et al.*, 2000), and pHBC has been shown to increase with increasing ionic strength and variable charge (Aitken and Moody, 1994).

Although VCS, in their natural state, often maintain highly productive and diverse ecosystems, they pose a particular challenge to sustainable management in terms of low values of CEC at soil pH, rapid reduction in CEC, particularly CEC_B , as soil acidity increases, and their ability to adsorb anionic species (Gillman and Sumpter, 1986). On the other hand, these soils (particularly in the subsoil or B horizon) develop appreciable AEC under acidic conditions, and can retain leachable anions such as nitrate and sulfate (Qafoku *et al.*, 2004). Due to these intrinsic characteristics, surface charge properties are of central importance to the management of VCS. The majority of the reactions that control nutrient availability and also many physical properties of these soils are dependent on the physicochemical processes that occur at soil particle surfaces. Therefore, it is essential to determine the charge characteristics of VCS, with a correct determination of the *in situ* CEC and a full understanding of the variation of charge with pH, before establishing strategies for sustainable management of these soils.

Some VCS, namely Red Ferrosols from north Queensland (Pin Gin series from the Palmerston site) and New South Wales (Dorrigo site), were used in this study to investigate the extent and distribution of charge characteristics at different soil depths (horizons). In addition, in order to compare the different characteristics of charge between soil types, another two soil types, a Redoxic Hydrosol and an Aquic Grey Vertisol, which were considered to be less weathered than the Ferrosols but considered to be VCS, were also collected for determination of their charge characteristics. The correlations between the charge characteristics of these soils and their physicochemical properties will be presented in this chapter.

3.2 Materials and methods

3.2.1 Soil collection and preparation

A range of soils were collected from high rainfall areas of Eastern Australia with contrasting VCS properties intended to reflect soil types dominant in geric upland soils in Vietnam as quarantine precludes bringing soil into Australia. Four soil types were collected from New South Wales (NSW) and north Queensland. An acidic Red Ferrosol soil (Isbell, 1996) or Tropeptic Eutrustox in the USDA Soil Taxonomy (Soil Survey Staff, 2003) was collected from pasture land about 5 km south-east of the town of Dorrigo, northern NSW (hereafter referred to as Dorrigo Ferrosol) at the depths of 5 - 20 cm; 20 - 40 cm and over 50 cm; these depths were sampled to remove interference from organic matter in determining charge

characteristics. Another Ferrosol was sampled from sugarcane land at Palmerston, north Queensland. This soil is an acidic Red Ferrosol of the Pin Gin series (hereafter referred to as Palmerston Ferrosol) (Isbell, 1996) and samples were taken from depths of 0 - 20 and 20 - 40 cm. This soil type has similar characteristics, i.e. geric properties, to many upland soils in Vietnam (Moody and Phan, 2008). The other two soil samples were collected from a Redoxic Hydrosol (Sandy Clay series) (hereafter referred to as Hydrosol) and an Aquic Grey Vertosol (Heavy Clay series) (hereafter referred to as Vertosol) (Isbell, 1996) under sugarcane cultivation in the Herbert district, Ingham, north Queensland. In order to minimise the interference of organic matter on charge determinations of these soils, samples were collected at a depth of 20 - 40 cm.

The soil samples were air-dried and passed through a 2 mm-sieve before taking representative samples for determining charge characteristics and analysing the physicochemical properties of the soils. The results from mid-infrared reflectance (MIR) scans of the soils compared to the scans of pure clay minerals showed that the Hydrosol and Vertosol have clay mineralogy dominated by smectite and kaolinite, the Dorrigo Ferrosol is dominated by kaolinite, hematite and goethite; while the Palmerston Ferrosol is dominated by kaolinite, hematite, goethite and gibbsite. The clay contents and some chemical properties of these soils are given in Table 3.1.

Table 3.1 Clay contents and some chemical properties of the studied soils

Soils	Depths (cm)	Clay	¹ TOC	² Al _{Ox}	³ Fe _{Ox}	⁴ Si _{Ox}	⁵ Al _{Cryst.}	⁶ Fe _{Cryst.}
		(%)						
New South Wales								
Dorrigo Ferrosol	5 - 20	56	4.58	0.40	0.6	0.01	0.6	5.4
	20 - 40	65	2.50	0.40	0.4	0.01	0.7	6.0
	> 50	68	1.39	0.50	0.4	0.03	0.5	6.1
North Queensland								
Palmerston Ferrosol	0 - 20	62	2.50	0.30	0.4	0.01	2.0	14.6
	20 - 40	65	1.55	0.30	0.3	0.01	1.8	14.1
Hydrosol	20 - 40	23	0.72	0.05	0.2	0.02	0.0	0.7
Vertosol	20 - 40	61	0.88	0.10	0.2	0.03	0.2	1.8

¹ total organic carbon; ² oxalate extractable Al; ³ oxalate extractable Fe; ⁴ oxalate extractable Si; ⁵ crystalline Al; and ⁶ crystalline Fe, which are derived from the differences between citrate bicarbonate dithionite extractable Al/Fe and oxalate extractable Al/Fe, respectively

3.2.2 Analytical determinations

Chemical properties

The following methodologies were used to determine the properties of the soils: particle size analysis on dispersed samples as described by Thorburn and Shaw (1987); total organic carbon (TOC) by the 6B2B method (Rayment and Lyons, 2011); oxalate extractable Fe, Al and Si (Fe_{Ox} , Al_{Ox} and Si_{Ox} , respectively) by the 13A1 method (Rayment and Lyons, 2011); citrate bicarbonate dithionite Fe and Al (Fe_{CBD} and Al_{CBD} , respectively) by the 13C1 method (Rayment and Lyons, 2011).

Phosphorus buffer index (PBI) was determined using the method described by Burkitt *et al.* (2002). The PBI is briefly described as follows: the amount of freshly sorbed P (Ps) in the soil ($mg\ P\ kg^{-1}$) is calculated as the difference between the initial amount of P added ($1000\ mg\ P\ kg^{-1}$ at the specified soil:solution ratio of 1:10) and the amount of P left in the equilibrating solution (expressed as c , $mg\ P\ L^{-1}$). Because PBI is derived from the Freundlich equation for describing the relationship between total P sorbed and final solution P concentration (i.e. P sorption curve), the total amount of P sorbed by the soil is calculated as the amount of previously sorbed P, plus the amount of freshly sorbed P. The previously sorbed P is estimated as the Colwell extractable P (Colwell, 1963). The total P sorbed for use in calculating PBI is therefore the addition of the Colwell-P to the amount of freshly sorbed P. The PBI is calculated according to the following equation:

$$PBI_{Colwell} = \frac{[Ps\ (mg\ P\ kg^{-1}) + Colwell.P\ (mg\ kg^{-1})]}{c(mg\ P\ L^{-1})^{0.41}}$$

Charge characteristics

Charge fingerprints, which are curves describing the charge characteristics of soils such as the total cation exchange capacity (CEC_T), base cation exchange capacity (CEC_B) and anion exchange capacity (AEC), at solution ionic strength approximating field conditions, were determined using methodology described by Gillman (2007), as shown in Figure 3.1. The charge fingerprint can also determine the soil pH, the pH buffering capacity (pHBC), the

point of zero charge (pH_0) and the point of zero net charge (PZNC). This procedure can be briefly described as follows:

- For each soil sample, 2 g of soil and 20 mL of 0.1 M CaCl_2 were added into six pre-weighed 50 mL centrifuge tubes, and the tubes agitated in an end-over-end shaker (12 rpm) for two hours in order to saturate exchange sites with Ca^{2+} and Cl^- . The samples were then centrifuged at 3000 rpm (relative centrifugal force, $\text{RCF} = 1814$) for 10 min and the supernatant solution discarded.
- To begin the process of lowering the ionic strength, 20 mL of 0.002 M CaCl_2 [ionic strength (IS) = 0.006; this is considered to be the typical IS of weathered tropical soils] were added to each subsample, the soil/solution re-suspended with a vortex stirrer, centrifuged, and the supernatant discarded. This step was repeated two more times.
- The soil pH was measured after adding another 20 mL of 0.002 M CaCl_2 and re-suspending with a vortex stirrer.
- The pHs of the six suspensions of each soil sample were then adjusted over the pH range of 4.0 to 7.0, i.e. 4.0, 4.6, 5.2, 5.8, 6.4 and 7.0, using 0.1 M HCl and 0.02 M $\text{Ca}(\text{OH})_2$, and equilibrated overnight in the end-over-end shaker.
- The pHs of the suspensions were read on the next day, and the pH values re-adjusted as above for three more times. After each re-adjustment, the samples were equilibrated in the end-over-end shaker for two hours. Once pH values were close to the required range, the samples were again equilibrated in the end-over-end shaker overnight.
- The pH of diluted suspensions (pH_{dil}) was recorded on the next day. After adding 0.5 mL of 2 M CaCl_2 and placing in the end-over-end shaker for one hour, the pHs of the concentrated suspensions (pH_{conc}) were recorded, and suspensions then washed with 20 mL of 0.002 M CaCl_2 (as described in the previous steps). The samples were again adjusted over the required pH range and placed in the shaker overnight.
- The pHs of suspensions were read on the next day, and pH values re-adjusted as above for three more times. After each re-adjustment, the samples were equilibrated in the end-over-end shaker for two hours. Once pH values were close to the required range, the samples were again equilibrated in the end-over-end shaker overnight.

- After overnight equilibration, the pH of suspensions was recorded and designated as equilibrium pH (pH_{equil}). The suspensions were centrifuged and the supernatants were retained for the first Ca, Al and Cl analysis. The entire tubes with lids were weighed to estimate the volume of entrained solution. Thus, the remaining amounts of Ca, Al and Cl in solution could be calculated. Twenty millilitres of 1 M NH_4NO_3 were added to the soil samples and equilibrated in the over-end-over shaker for two hours. The suspensions were then centrifuged and the supernatant retained for the second Ca, Al and Cl analysis. Calcium and Al were analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES) (Vista MPX-radial model, Varian, Australia), and Cl was analysed by the Skalar method M239-541 on a Continuous Flow Analyzer (Skalar Analytical B.V., The Netherlands). Finally, the amounts of cations (Ca^{2+} and Al^{3+}) and anion (Cl^-) adsorbed were calculated by the difference between the amounts of Ca, Al and Cl in the first and second supernatants. These amounts were equated with total negative and positive charge, respectively.
- The charge fingerprint curves were obtained by plotting Ca^{2+} adsorbed (CEC_B), Ca^{2+} and Al^{3+} adsorbed (CEC_T) and Cl^- adsorbed (AEC) against the pH_{equil} (Figure 3.1).
- $\Delta\text{CEC}_{4.5-5.5}$ was computed from the difference between CEC_T at soil pH 5.5 and 4.5 and expressed as the variation of CEC_T for 1 unit pH change.
- The point of zero variable charge (pH_0) was determined by plotting the change in pH of each subsample between low and high ionic strengths, i.e. the difference between pH_{conc} and pH_{dil} (delta pH), against suspension pH (pH_{dil}).
- The point of zero net charge (PZNC) was determined at the point where $\text{CEC}_T = \text{AEC}$ (Figure 3.1).
- The pHBC was determined by plotting the total amount of acid and alkali added against the pH_{equil} . The relationship between pH and H^+ and OH^- added was linear within the pH_{equil} range and a linear regression was fitted. The reciprocal of the slope of the regression line was designated as the pHBC. Buffering capacity was expressed as the amount (cmol_c) of H^+ or OH^- required to change the pH of one kilogram of soil by one pH unit.

- Total net charge of the soil was computed from the regression curve of the net charge, at the soil pH value, which is derived from the difference between cation adsorption (Ca^{2+} and Al^{3+}) and anion adsorption (Cl^-) (Figure 3.1). Similarly, the net permanent charge was calculated from the regression curve of the net charge, but at the pH_0 of the soil. Thus, the net variable charge was obtained from the difference between total net charge and net permanent charge.

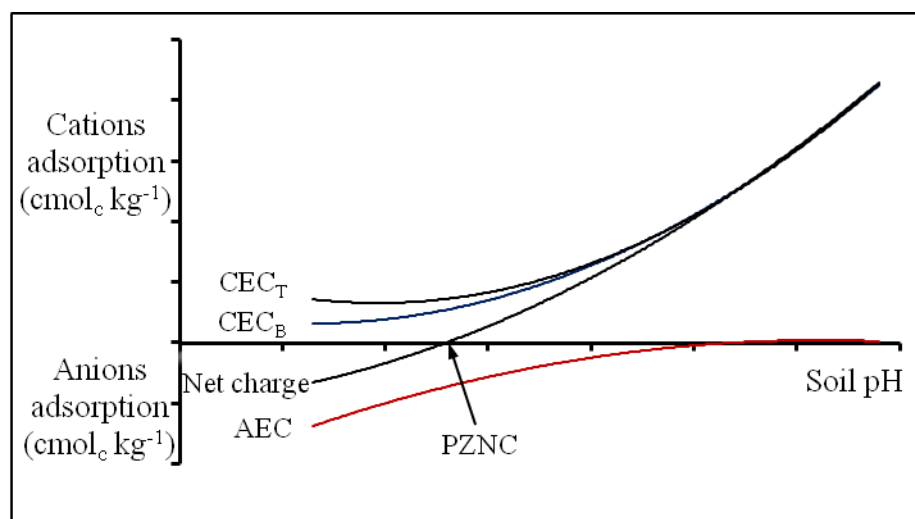


Figure 3.1 The charge fingerprint for charge characteristics, consisting of the total cation exchange capacity (CEC_T) (adsorbed Ca^{2+} and Al^{3+}), the base cation exchange capacity (CEC_B) (adsorbed Ca only) and anion exchange capacity (AEC) (adsorbed Cl^-)

3.2.3 Data analysis

Charge fingerprint curves were plotted using Microsoft Office Excel 2007 for Windows XP Professional 2002. Charge characteristic values were calculated using regression equations derived from charge fingerprint curves. General analysis of variance (ANOVA), standard error of means and least significant differences of means ($\text{LSD}_{0.05}$) were used to compare differences between the means of the soil layers in a given soil and of the soil types with the same soil layer. Linear correlation coefficient (r) matrices were also computed for the various analyses of all soils to express the relationships of surface charge characteristics and P sorption capacity with soil properties. All analyses were undertaken in the GenStat Discovery Edition 3 (seventh edition, version - 7.2.2.222) Copyright 2008 for Windows XP.

3.3 Results

3.3.1 Soil pH and surface charge characteristics of the Dorrigo Ferrosol and Palmerston Ferrosol at different soil depths

The Dorrigo Ferrosol

Soil pH, pH₀ and pHBC of the Dorrigo Ferrosol at different soil depths (5 - 20, 20 - 40 and > 50 cm) are presented in Table 3.2. The pH values of the soil were very low (4.54 – 4.70) through the soil profile and decreased with soil depth. Although this change was only 0.16 unit from the topsoil to the subsoil (> 50 cm), the pHBC was significantly lower in the subsoil than in the topsoil (more than 2 cmol_c H⁺ or OH⁻ kg⁻¹ for a change of 1 pH unit). The pH₀ increased with soil depth and the increase was more than 0.2 unit in the subsoil compared to the topsoil (Table 3.2). Note that the pH₀ of the topsoil (5 - 20 cm) was not directly determined from the titrated curve (Figure 3.2a) within the adjusted pH range of 4.0 to 7.0. Therefore, this pH₀ value was estimated by extrapolation using the regression equation shown in Figure 3.2a.

Table 3.2 Means and standard error of means (in brackets) for soil pH, pH₀ and pHBC of the Dorrigo Ferrosol at different soil depths

Soil depth (cm)	Soil pH _{0.002M CaCl2} (1:10)	pH ₀	pHBC (cmol _c kg ⁻¹ .pH ⁻¹)
5 - 20	4.70 (± 0.00)	3.74 (± 0.05)	6.78 (± 0.16)
20 - 40	4.62 (± 0.00)	3.99 (± 0.04)	6.51 (±0.06)
> 50	4.54 (± 0.00)	3.94 (± 0.03)	4.71 (±0.04)

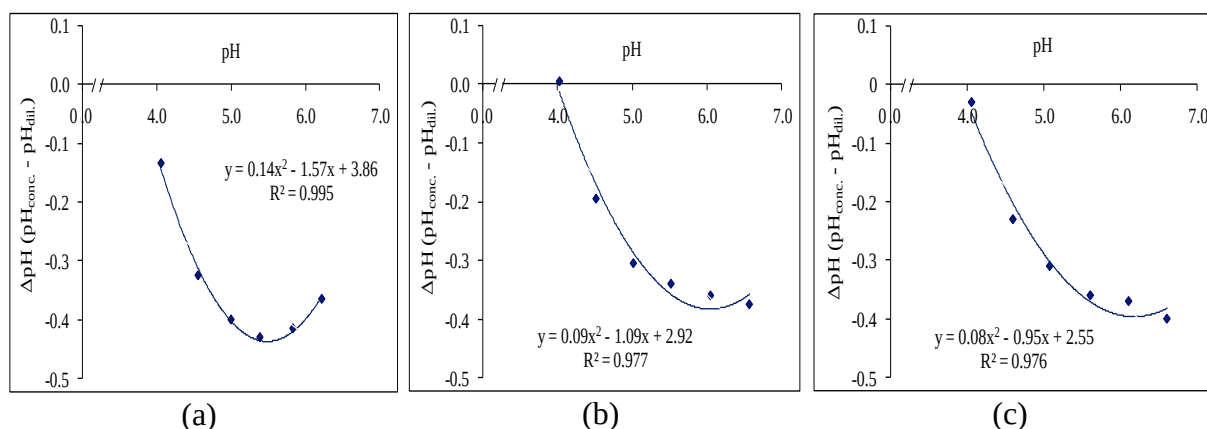


Figure 3.2 Point of zero charge (pH_0) of the Dorrigo Ferrosol at different soil depths: (a) 5 - 20 cm; (b) 20 - 40 cm and (c) > 50 cm

As shown in Table 3.3, both base cation exchange capacity (CEC_B) and total cation exchange capacity (CEC_T) of the soil were very low at soil pH ($< 2 \text{ cmol}_c \text{ kg}^{-1}$). The values of CEC_B and CEC_T decreased with soil depth, and the differences between CEC_T and CEC_B also increased with soil depth, being 0.13, 0.16 and $0.19 \text{ cmol}_c \text{ kg}^{-1}$ for 5 - 20 cm, 20 - 40 cm and > 50 cm layers, respectively (Table 3.3). It can be seen from the charge curves of different soil depths in Figures 3.3a, b and c, that the differences between CEC_T and CEC_B for all soil depths started at pH around 5.0 and greater differences were found at lower pH values. Although AEC of the topsoil (5 - 20 cm) did not develop at the existing soil pH, some small values were found in the subsoil layers (Table 3.3). The point of zero net charge (PZNC), which is defined as equal amounts of adsorbed cations (Ca^{2+} and Al^{3+}) and adsorbed anion (Cl^-), was not identified in this soil within the pH range of 4.0 to 7.0 (Figures 3.3a, b and c). Therefore, the soil exhibited total net negative charge at existing soil pH in all depths (presented as positive values in Table 3.4), and the charge decreased with soil depth. Total net charge comprises permanent and variable charge components. The former is calculated as the net charge at the pH_0 of the soil (Figure 3.3). Table 3.4 shows that the amounts of variable charge at all depths were lower than those of permanent charge and contributed less than 40% to the total net charge.

Table 3.3 Means and standard error of means (in brackets) for CEC_B CEC_T and AEC at soil pH of the Dorrigo Ferrosol at different soil depths

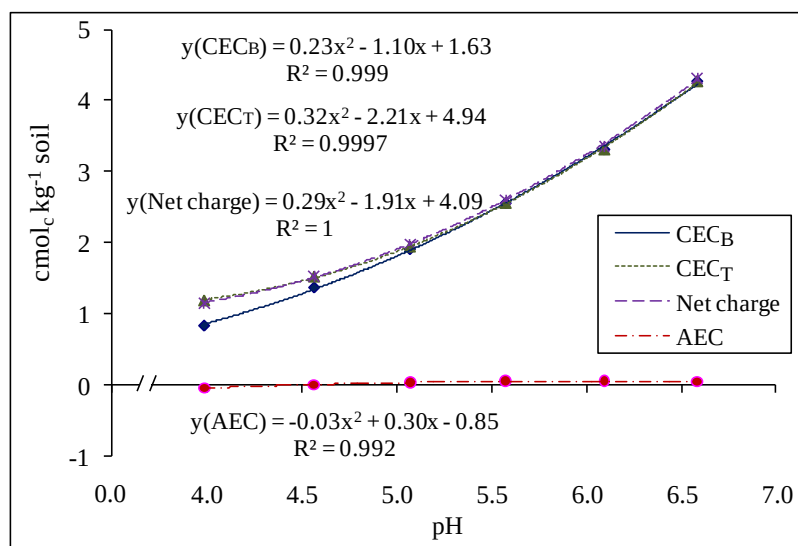
Soil depth (cm)	CEC _B	CEC _T	AEC
	(cmol _c kg ⁻¹)		
5 - 20	1.48 (± 0.07)	1.61 (± 0.06)	0.02 (± 0.00)
20 - 40	1.08 (± 0.07)	1.24 (± 0.06)	-0.07 (± 0.01)
> 50	0.98 (± 0.03)	1.17 (± 0.04)	-0.06 (± 0.00)

Table 3.4 Means and standard error of means (in brackets) for total net charge, net permanent- and net variable charge of the Dorrigo Ferrosol at different soil depths

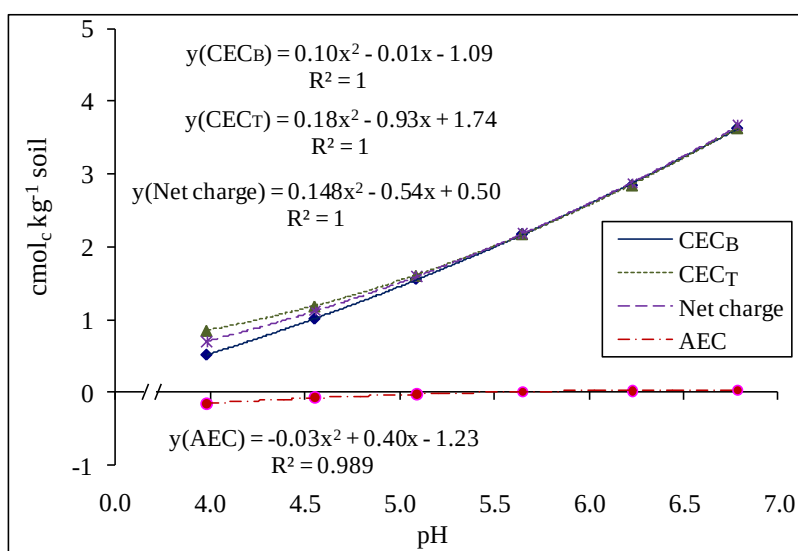
Soil depth (cm)	Total net charge	Net permanent charge	Net variable charge	Percentage of variable charge
	(cmol _c kg ⁻¹)			(%)
5 - 20	1.62 (± 0.07)	1.06 (± 0.02)	0.56 (± 0.08)	34.6
20 - 40	1.17 (± 0.08)	0.71 (± 0.01)	0.46 (± 0.07)	39.3
> 50	1.11 (± 0.04)	0.76 (± 0.01)	0.35 (± 0.03)	31.5

The Palmerston Ferrosol

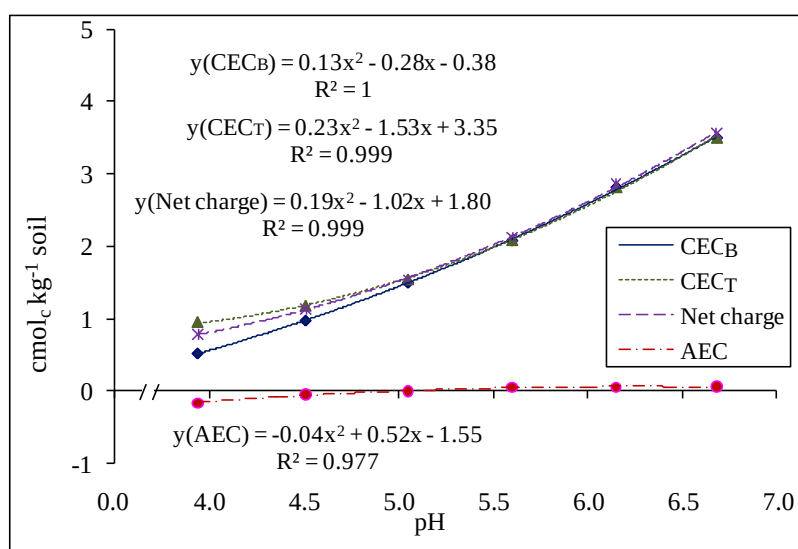
Soil pH of the Palmerston Ferrosol was also very low, being pH 4.40 and 4.26 in the topsoil (0 - 20 cm) and the subsoil (20 - 40 cm), respectively (Table 3.5). Buffering capacity was high in the topsoil, 5.81 cmol_c kg⁻¹.pH⁻¹, and reduced to 4.21 cmol_c kg⁻¹.pH⁻¹ in the subsoil (Table 3.5). Similar to the Dorrigo Ferrosol, the pH₀ and PZNC in the top layer of this soil were not captured by the titration curve (Figure 3.4a) and the net charge curve (Figure 3.5a) within the pH range of 4.0 to 7.0. Therefore, the pH₀ value of the topsoil (3.81) shown in Table 3.5 was estimated by extrapolation of the regression equation of the curve (Figure 3.4a). The pH₀ in the subsoil was 4.63 and markedly higher than that in the topsoil; this value was also higher than the existing soil pH (4.26) at this depth. In addition, the PZNC was identified in this layer as 4.88 which is higher than the pH₀ (Table 3.5).



(a)



(b)



(c)

Figure 3.3 Charge characteristics of the Dorrigio Ferrosol at different soil depths [(a) 5 - 20 cm; (b) 20 - 40 cm and (c) > 50 cm]

Both CEC_B and CEC_T were very low at the existing soil pHs [approximately $0.50 \text{ cmol}_c \text{ kg}^{-1}$ for the topsoil and $0.25 \text{ cmol}_c \text{ kg}^{-1}$ for the subsoil (Table 3.6)]. There is no large difference between CEC_B and CEC_T , particularly in the case of the subsoil over the entire pH range (Figure 3.5). The soil had positive charges (AEC) in both layers. At soil pH, AEC was $-0.62 \text{ cmol}_c \text{ kg}^{-1}$ in the subsoil and this was higher than that of the topsoil ($-0.08 \text{ cmol}_c \text{ kg}^{-1}$) (Table 3.6).

Surface charge characteristics of the soil are presented in Table 3.7. The total net charge was very low in the topsoil, being $< 0.5 \text{ cmol}_c \text{ kg}^{-1}$. Although net negative charge was found in the topsoil, the subsoil exhibited net positive charge, i.e., net AEC. The soil was dominated by variable charge surfaces in both soil layers, with variable charge accounting for more than 50% of the total net charge (Table 3.7).

Table 3.5 Means and standard error of means (in brackets) for soil pH, pH_0 , PZNC and pHBC of the Palmerston Ferrosol at different soil depths

Soil depth (cm)	Soil $pH_{0.002M \text{ CaCl}_2}$ (1:10)	pH_0	PZNC	pHBC ($\text{cmol}_c \text{ kg}^{-1} \cdot \text{pH}$)
0 - 20	4.40 (± 0.00)	3.81 (± 0.07)	¹ n.e.	5.81 (± 0.27)
20 - 40	4.26 (± 0.00)	4.63 (± 0.00)	4.88	4.21 (± 0.19)

¹ not estimated

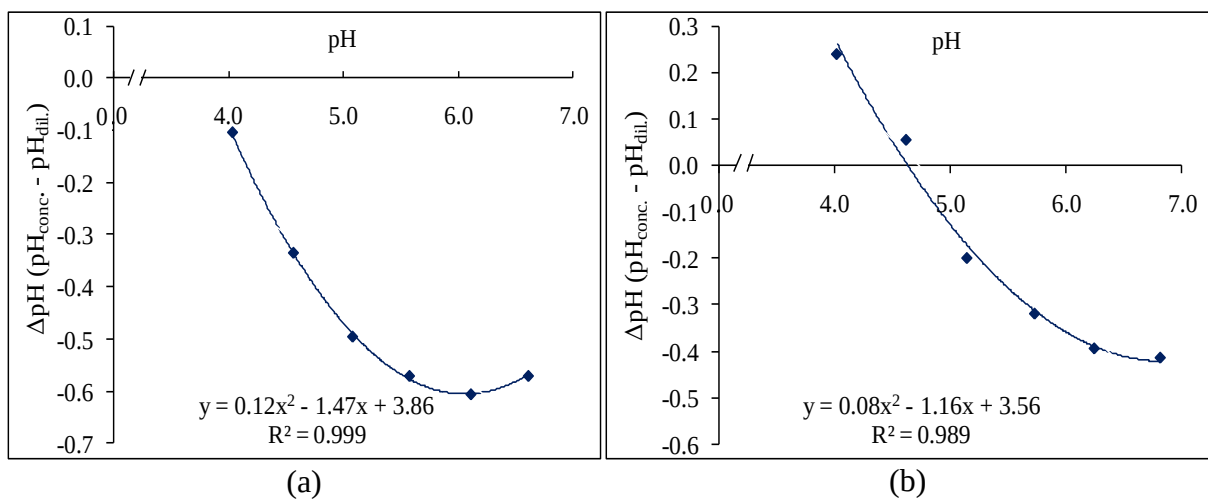
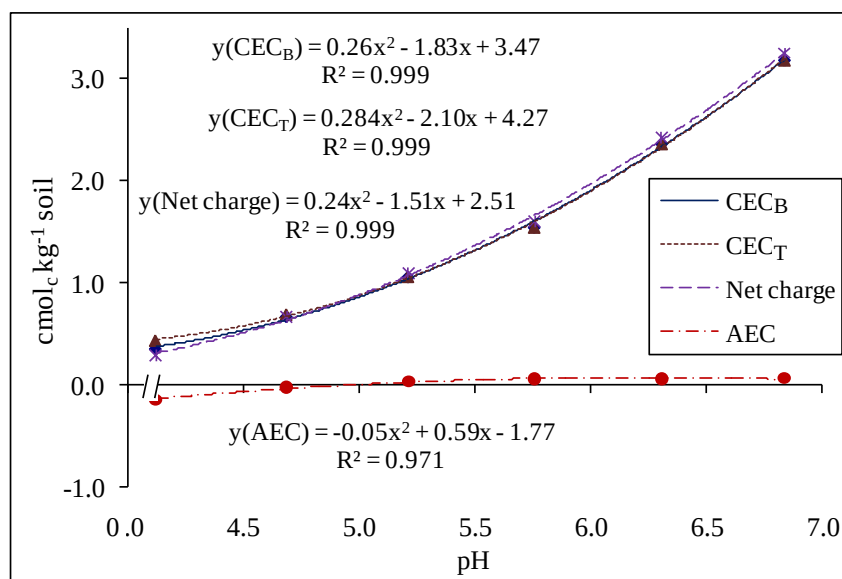


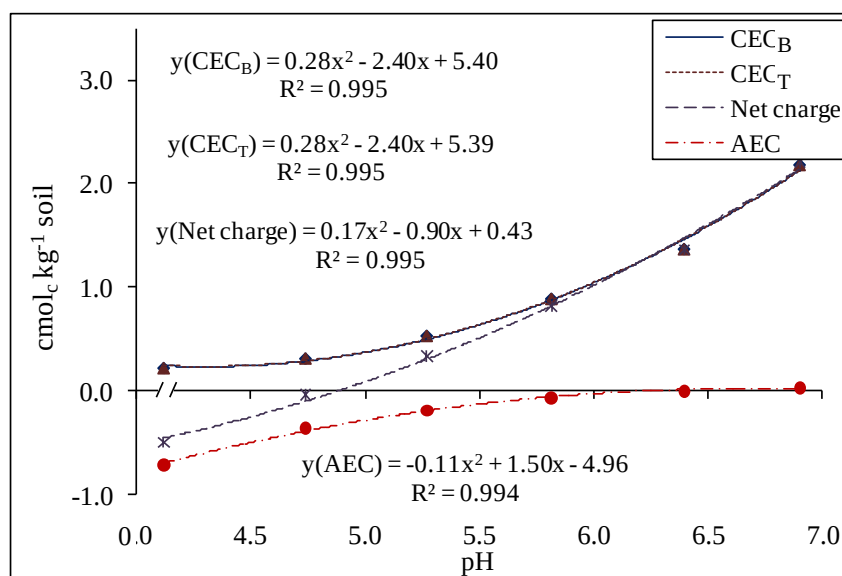
Figure 3.4 Point of zero charge (pH_0) of the Palmerston Ferrosol at different soil depths [(a) 0 - 20 cm and (b) 20 - 40 cm]

Table 3.6 Means and standard error of means (in brackets) for CEC_B CEC_T and AEC at soil pH of the Palmerston Ferrosol at different soil depths

Soil depth (cm)	CEC_B	CEC_T	AEC
	(cmol _c kg ⁻¹)		
0 - 20	0.49 (± 0.03)	0.54 (± 0.03)	-0.08 (± 0.00)
20 - 40	0.23 (± 0.01)	0.24 (± 0.01)	-0.62 (± 0.05)



(a)



(b)

Figure 3.5 Charge characteristics of the Palmerston Ferrosol at different soil depths [(a) 0 - 20 cm and (b) 20 - 40 cm]

Table 3.7 Means and standard error of means (in brackets) for total net charge, net permanent- and net variable charge of the Palmerston Ferrosol at different soil depths

Soil depth (cm)	Total net charge	Net permanent charge	Net variable charge	Percentage of variable charge
	(cmol _c kg ⁻¹)			(%)
0 - 20	0.46 (± 0.02)	0.20 (± 0.09)	0.26 (± 0.11)	56.5
20 - 40	-0.39 (± 0.05)	-0.18 (± 0.03)	-0.21 (± 0.02)	53.8

3.3.2 Differences of soil pH, pH buffer capacity and surface charge characteristics in the subsoil layer of variable charge soils

Soil pH, pH₀ and pHBC of the subsoil (20 - 40 cm) of the Dorriggo Ferrosol, the Palmerston Ferrosol, the Hydrosol and the Vertosol are displayed in Table 3.8. Existing soil pH values of the Hydrosol and Vertosol were significantly higher than those of both Ferrosols. The highest pH value, 5.15, was shown in the Vertosol. In contrast, pHBC of the Hydrosol and Vertosol were lower than those of the two Ferrosols. The lowest pHBC value, 2.49 cmol_c kg⁻¹.pH⁻¹, was found in the Hydrosol. The pH₀ values of both the Hydrosol and Vertosol were significantly lower than those of the Ferrosols. However, these values were estimated by extrapolation from the regression equations for the titration curves of these soils, as shown in Figures 3.6a and 3.6b for the Hydrosol and Vertosol, respectively. Therefore, the accuracy of these estimated pH₀ values is questionable, particularly in the case of the Vertosol (Table 3.8).

The CEC_B and CEC_T of the Hydrosol and Vertosol were substantially higher than those of the two Ferrosols (Table 3.9). Since the Vertosol had the highest soil pH, it also exhibited the highest CEC values, being 4.30 cmol_c kg⁻¹ for CEC_B and 4.34 cmol_c kg⁻¹ for CEC_T. Conversely, the Palmerston Ferrosol had the lowest soil pH, accompanied by the lowest CECs of 0.23 and 0.24 cmol_c kg⁻¹ for CEC_B and CEC_T, respectively. Most of the studied soils had only a small difference between CEC_B and CEC_T, with the Dorriggo Ferrosol being the exception. It should be noted that although the CEC of the Vertosol was not as high as is typical of alkaline Vertosols (Stace *et al.*, 1968), it is still approximately 20-fold higher than the CECs of the two Ferrosols (Table 3.9). As previously shown, the Palmerston Ferrosol exhibited a significant amount of AEC at soil pH, whereas the other three soils had negligible AECs at their soil pH values (Table 3.9).

Table 3.8 Comparison of soil pH, pH₀, and pHBC between the subsoils (20 - 40 cm) of the Dorrigo Ferrosol, Palmerston Ferrosol, Hydrosol and Vertosol

Soil	Soil pH _{0.002M CaCl2} (1:10)	pH ₀	pHBC (cmol _c kg ⁻¹ .pH ⁻¹)
Dorrigo Ferrosol	4.62 c	3.99 b	6.51 a
Palmerston Ferrosol	4.26 d	4.63 a	4.21 b
Hydrosol	4.88 b	3.50 c	2.49 c
Vertosol	5.15 a	*1.26 d	3.93 b
Prob.	< 0.001	< 0.001	< 0.001
LSD _(0.05)	0.02	0.17	0.44
CV(%)	0.1	1.8	3.7

Means in the same column followed by different letters are significantly different at $P < 0.05$.

* This value is estimated from the regression curve in Figure 3.6b and is questionable.

Table 3.9 Comparison of CEC_B, CEC_T, and AEC at soil pH between the subsoils (20 - 40 cm) of the Dorrigo Ferrosol, Palmerston Ferrosol, Hydrosol and Vertosol

Soil	CEC _B	CEC _T	AEC
	(cmol _c kg ⁻¹)		
Dorrigo Ferrosol	1.08 c	1.24 d	-0.07 b
Palmerston Ferrosol	0.23 d	0.24 c	-0.62 c
Hydrosol	1.42 b	1.46 b	0.04 a
Vertosol	4.30 a	4.34 a	0.05 a
Prob.	< 0.001	< 0.001	< 0.001
LSD _(0.05)	0.16	0.15	0.10
CV(%)	3.2	3.0	24.5

Means in the same column followed by different letters are significantly different at $P < 0.05$.

The total net charge of the four studied soils ranged from -0.39 to 4.34 cmol_c kg⁻¹, in which the Hydrosol and the Vertosol were significantly higher than the two Ferrosols, and with the Palmerston Ferrosol exhibiting a net positive charge (Table 3.10). According to the proportions of permanent and variable charges, it is suggested that the Hydrosol and the Dorrigo Ferrosol are dominated by permanent charge surfaces, since their net variable charges accounted for 30.8 and 39.3% of the total net charge, respectively; however the other two soils have more than 50% of variable charge contributing to the total net charge (Table 3.10).

In the case of the Vertosol, however, the extremely low soil pH_0 calculated from the titration curves is considered to be an artifact (as previously discussed). As indicated in Section III.2.1, this Vertosol had similar mineralogical characteristics to the Hydrosol and the Dorrigo Ferrosol, inferring that this soil should be considered to have more permanent charge surfaces than variable charge surfaces. Thus, only the Palmerston Ferrosol has more variable than permanent charge surfaces.

Table 3.10 Comparison of total net charge, net permanent-, and net variable charge between the subsoils (20 - 40 cm) of the Dorrigo Ferrosol, Palmerston Ferrosol, Hydrosol and Vertosol

Soil	Total net charge	Net permanent charge	Net variable charge	Percentage of variable charge
		(cmol _c kg ⁻¹)		(%)
Dorrigo Ferrosol	1.17 c	0.71 b	0.46 b	39.3
Palmerston Ferrosol	-0.39 d	-0.18 c	-0.21 c	53.8
Hydrosol	1.46 b	1.01 a	0.45 b	30.8
Vertosol	4.34 a	*1.16 a	*3.18 a	*73.3
Prob.	< 0.001	< 0.001	< 0.001	
LSD _(0.05)	0.19	0.25	0.27	
CV(%)	4.2	13.2	9.9	

Means in the same column followed by different letters are significantly different at $P < 0.05$.

* Values are estimated and calculated from the pH_0 of the soil, and are questionable

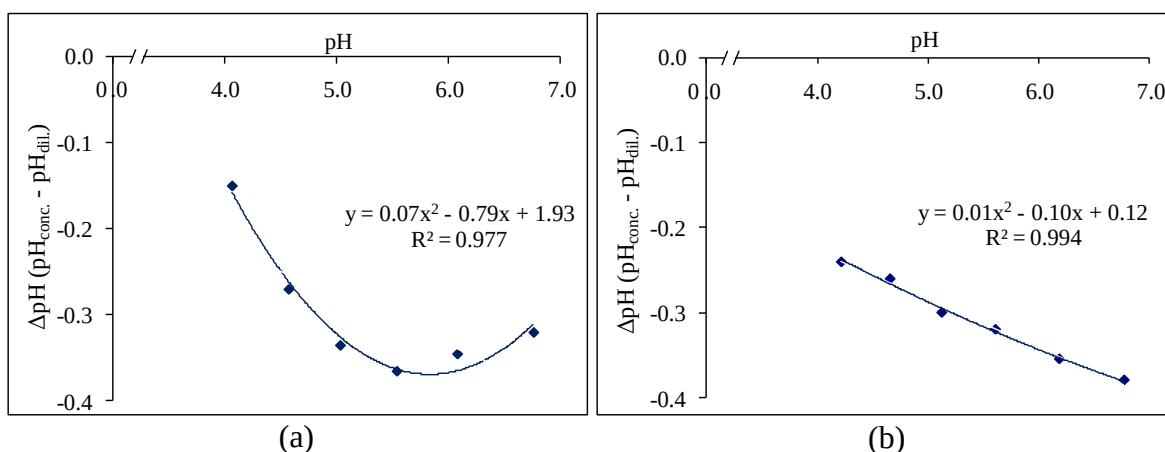
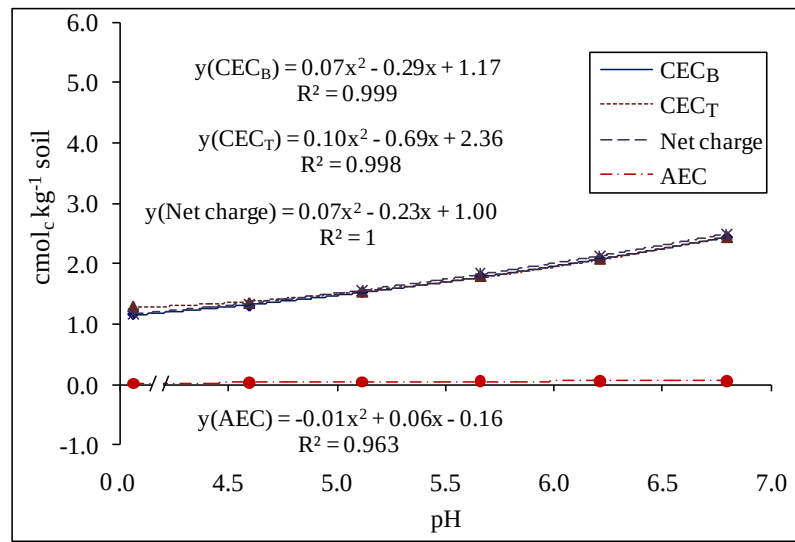
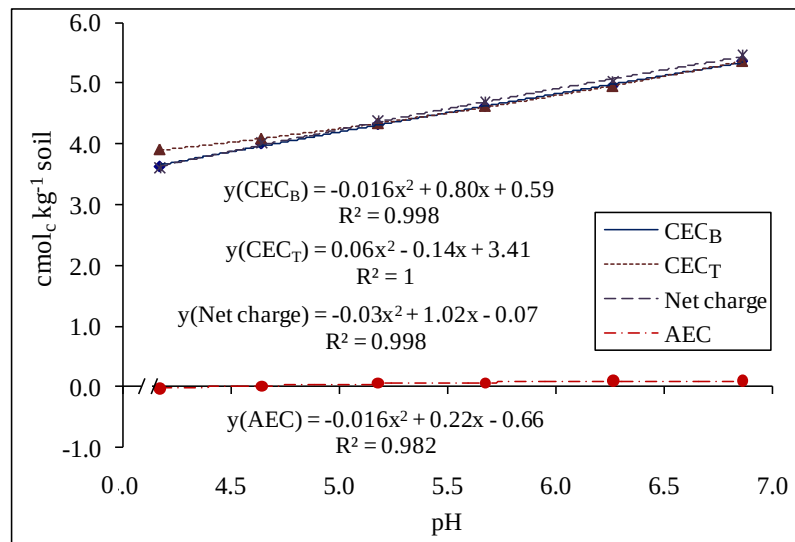


Figure 3.6 Point of zero charge (pH_0) of (a) the Hydrosol and (b) the Vertosol at the soil depth of 20 - 40 cm



(a)



(b)

Figure 3.7 Charge characteristics of (a) the Hydrosol and (b) the Vertosol at the soil depth of 20 - 40 cm

3.3.3 Phosphorus sorption capacity

Phosphorus (P) fixation is a commonly occurring constraint in VCS, and this issue is exacerbated under acidic conditions. A single-point P buffering index (PBI) has been developed (Burkitt *et al.* 2002) to characterise soil P sorption capacity and the higher the value of PBI, the greater the P sorption capacity of a soil. The results in Fig. 3.8 show the PBI of the two Ferrosols at different soil depths. The PBI values in both soils increased markedly with soil depth. The topsoil (0 - 20 cm) of the Palmerston Ferrosol had a similar PBI to the subsoil (20 - 40 cm) of the Dorrigo Ferrosol, whereas the PBI of its subsoil (20 - 40 cm) was more than double that of the subsoil of the Dorrigo Ferrosol (Figure 3.8). The Hydrosol and

Vertosol exhibited very low PBIs in comparison to the two Ferrosols, with the Hydrosol having the lowest PBI value (Figure 3.9).

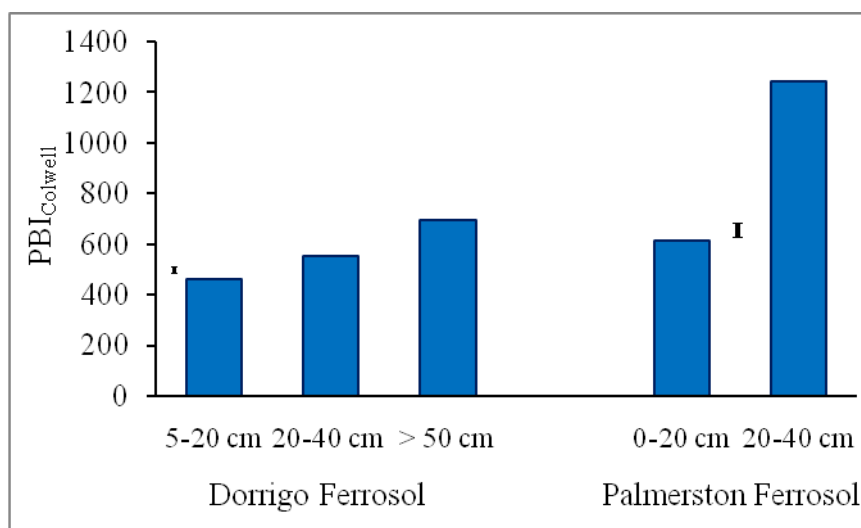


Figure 3.8 Phosphorus buffering index (PBI_{Colwell}) of the Dorrigio Ferrosol and the Palmerston Ferrosol at different soil depths. Vertical bars are the least significant differences of means at $P = 0.05$

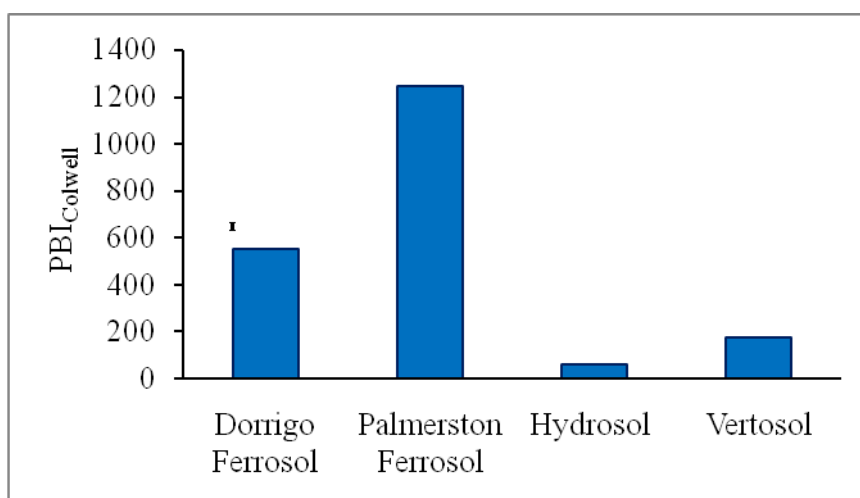


Figure 3.9 Differences of phosphorus buffering index (PBI_{Colwell}) between the subsoil (20 - 40 cm) of the Dorrigio Ferrosol, Palmerston Ferrosol, Hydrosol and Vertosol. The vertical bar is the least significant differences of means at $P = 0.05$

3.4 Discussion

Variations in soil pH and pH buffering capacity

Soil pH is the most important factor influencing the surface charge of VCS. The quantity of variable charge on a surface is determined by both the dissociation of H^+ ions from, and the adsorption of H^+ ions by the hydroxylated surface as a function of the pH of the medium. Therefore, in determining the surface charge of a given soil, the existing pH of that soil should be taken into account. In the present study, surface charge characteristics of the soils were determined using the charge fingerprint method (Gillman, 2007).

The $pH_{0.002M\ CaCl_2}$ (1:10) of the soils in this study range from 4.26 to 5.15, classifying the soils as very acidic (Hydrosol and Vertosol) or extremely acidic (the Ferrosols), and within the pH range typical of highly weathered soils in the tropical regions (Uehara and Gillman, 1981; Anda *et al.*, 2008), particularly within the same soil orders (Gillman and Murtha, 1983; Gillman, 1984; Gillman and Sumpter, 1986; Aitken *et al.*, 1998; Noble *et al.*, 2001). Perhaps because of the lower pHBC of the Ferrosol subsoils relative to the surface layers, subsoil pH values are lower than in the topsoil (Tables 3.2 and 3.5) in response to a given proton sink from weathering processes and land use (Rowell and Wild, 1985; Aweto *et al.*, 1992) although the through leaching of alkalinising base cations deposited at the surface in litter that normally redistributes the charge can't accumulate in geric subsoils.

Many researchers have found that organic matter (OM) and clay content are the two most important factors influencing pHBC (Kamprath, 1970; Uehara and Keng, 1975; Bache, 1988; Aitken *et al.*, 1990b; Aitken *et al.*, 1998). Buffering capacity is also associated with the oxide content (Uehara and Keng, 1975) and the amount of variable charge (Uehara and Keng, 1975; Gillman and Sumpter, 1986; Oorts *et al.*, 2004). All these authors indicated that pHBC increased with increasing of OM, clay and sesquioxide content, and with greater amounts of variable charge. Our pHBC results can be interpreted in the light of these findings. Table 3.11 indicates that pHBC is highly correlated ($P < 0.01$) with TOC and Fe_{Ox} . The pHBC values of the two Ferrosols decreased with increasing soil depth (Tables 3.2 and 3.5) and this is attributed to the smaller amounts of TOC contained in the subsoil layers. The data shown in Table 3.8 also indicate that the different pHBC values of the subsoils are affected by the different TOC and Fe_{Ox} contents of these soils (Table 3.1). The lowest subsoil pHBC value is found in the Hydrosol which also has the lowest clay content (Table 3.1). The effect of OM on pHBC is clearly demonstrated by comparing the subsoils of the two Ferrosols; both

subsoils have the same clay content (65%), but the Dorrigo Ferrosol has higher OM content resulting in greater buffering capacity (Table 3.8). Slattery *et al.* (1995) also attributed the greater pHBC of soils in north-eastern Victoria to a higher TOC content, whereas Gillman and Sumpter (1986) stated that the lower lime requirement of developed soils in high rainfall tropical Queensland reflected the decreases in OM following clearing and cultivation. Additionally, in studies on 40 acidic surface soils from Queensland, Aitken *et al.* (1990b) found that buffering capacity was significantly ($P < 0.001$) correlated with TOC and clay content ($R^2=0.88$), with TOC being the most important factor. From the results in the present study, it can be concluded that OM is an important factor responsible for pHBC.

Table 3.11 Linear correlation coefficient (r) for the relationships between soil properties and pH buffering capacity, phosphorus sorption, and surface charge characteristics

	¹ TOC	Clay	² Al _{Ox}	³ Fe _{Ox}	⁴ Si _{Ox}	⁵ Al _{Cryst.}	⁶ Fe _{Cryst.}
pH ₀ ^A	0.09	0.81 [*]	0.32	-0.03	-0.30	0.54	0.60
ΔCEC _{4.5-5.5}	0.69	0.09	0.73 [*]	0.84 ^{**}	-0.20	0.11	-0.01
pHBC	0.96 ^{***}	0.23	0.75 [*]	0.95 ^{***}	-0.62	0.57	0.39
PBI	0.34	0.85 ^{**}	0.56	0.36	-0.30	0.71	0.89 ^{***}

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$ ¹total organic carbon; ²oxalate extractable Al; ³oxalate extractable Fe; ⁴oxalate extractable Si; ⁵crystalline Al; and ⁶crystalline Fe, which are derived from the differences between citrate bicarbonate dithionite extractable Al/Fe and oxalate extractable Al/Fe, respectively;

^A Vertosol pH₀ omitted from correlations

Variations in surface charge characteristics

The point of zero charge of the variable charge components (pH₀) of VCS is considered to be of essential significance because its position relative to the existing soil pH determines the cation exchange capacity (CEC) and anion exchange capacity (AEC) of such soils. In addition, pH₀ can be used to estimate the net permanent charge of the soil if it is located within the pH range of the charge fingerprint curves (Uehara and Gillman, 1980; Gillman, 2007).

Generally, pH₀ decreases with increasing OM and increasing amounts of minerals having substantial isomorphous substitution (i.e. negatively charged materials); it tends to increase with increasing amounts of Fe and Al hydrous oxides (Parfitt, 1980) as these materials carry some positive charge at low pH (Sumner, 1963). In the present study, the pH₀ values of the two Ferrosols are lower in the topsoil than the subsoil layers (Tables 3.2 and 3.5). This is

attributed to the higher TOC in the topsoil than the subsoil layers in both soils, although the correlation between pH_0 and TOC is not significant ($P > 0.05$) (Table 3.11). Similarly, due to low TOC (1.55 – 2.50 %) and very high Fe oxide contents (14.1 – 14.6 %) in the Palmerston Ferrosol compared to those in the Dorrigo Ferrosol (2.50 – 4.58 % and 5.4 – 6.0 % for TOC and $Fe_{Cryst.}$, respectively) (Table 3.1), the pH_0 values for both soil depths of the Palmerston Ferrosol are higher than those of the Dorrigo Ferrosol (Tables 3.2 and 3.5). These results are consistent with the work of Gillman (1985) for oxidic soils from north Queensland and Anda *et al.* (2008) for Malaysian Oxisols which suggested that OM together with iron oxides influenced pH_0 by masking mineral surfaces. All these authors concluded that pH_0 was reduced by about one pH unit for each one percent increase in organic carbon. Likewise Jiang *et al.* (2010) studied four Ultisols in China and found differences in charge characteristics were mainly associated with soil OM content. The relationships between pH_0 and some soil properties (Table 3.11) indicate that the correlations between pH_0 and Fe/Al hydrous oxides and the clay fraction are positive, but in the case of amorphous Si, negative (although not significant; $P > 0.05$). This suggests that pH_0 tends to increase with increasing Fe/Al hydrous oxides and clay content, but decrease with increasing Si content in the soils. It is suggested that the significant ($P < 0.05$) correlation between pH_0 and clay content occurs because clay content is an integrating property that reflects the content of Fe and Al hydrous oxides plus clay minerals such as kaolinite (Table 3.11).

The amount of the positive surface charge in the subsoil of the Palmerston Ferrosol is greater than that of the other three soils (Table 3.9). Note that there is no positive surface charge in the subsoil of the Hydrosol and Vertisol, and that of the Dorrigo Ferrosol is negligible. This is in agreement with the content of Fe/Al hydrous oxides for these soils (Table 3.1). Soil positive surface charge mainly originates from the protonation of surface hydroxyl groups of Fe/Al hydrous oxides (van Raij and Peech, 1972a; Taubaso *et al.*, 2004). The higher content of Fe/Al hydrous oxides in the Palmerston Ferrosol yields greater amounts of positive surface charge compared to the other three soils, particularly at low pH. On the other hand, the negative surface charge (CEC_B and CEC_T) of the Palmerston Ferrosol is much lower than that of the other three soils. This is probably due to the different mineralogical components in the soils. The mineralogy of the Palmerston Ferrosol is dominated by kaolinite, hematite and goethite. However, the mineralogy of the Dorrigo Ferrosol is dominated by kaolinite with gibbsite influence. The Hydrosol and Vertisol have similar mineralogical compositions to the Dorrigo Ferrosol, but they may also contain a small amount of the 2:1 clay minerals such as

illite and vermiculite (Gillman, 1984). Therefore, the amounts of negative surface charge in the Hydrosol and Vertosol are higher than that in the Dorriggo Ferrosol.

The subsoil of the Palmerston Ferrosol was very low in TOC content (1.55 %), and very high in Fe/Al hydrous oxides (15.9 %) resulting from the soil being dominated by kaolinite, hematite and goethite. Consequently, the subsoil exhibited a high value for pH_0 (4.63) and it was higher than the soil pH (4.26) (Table 3.5) leading to the net positive charge surface at soil pH as indicated by high AEC ($-0.62 \text{ cmol}_c \text{ kg}^{-1}$) and very low CEC ($0.23 \text{ cmol}_c \text{ kg}^{-1}$) (Table 3.6). These results are strongly supported by the finding of Gillman (1984) on another Pin Gin series Ferrosol from the wet tropical coast of north Queensland under sugarcane cultivation. He found that the increase in pH_0 values with soil depth reflected the rapid decrease in OM and dominance of oxidic minerals such as goethite and haematite in the clay fraction. The greater amount of AEC in the subsoil reflects the influence of Fe and Al hydrous oxides, which are positively charged below their points of zero charge (Gillman and Sumpter, 1986). Thus, even though soil pH values did not alter appreciably with soil depth, pH_0 values well above soil pH indicated that the variable charge components of the soil would be positively charged. In consequence, the negative charge was very low, and the loss of CEC with an associated increase in acidity resulted in the loss of basic cations such as calcium, magnesium and potassium from the exchange complex (Uehara and Keng, 1975; Gillman, 1984; Noble *et al.*, 2001). On the other hand, an appreciable amount of positive charge (AEC) would be beneficial in the prevention of leaching of anion nutrients such as sulphate and nitrate, thus mitigating contamination of groundwater (Gillman, 1984; Eick *et al.*, 1999).

The interesting result observed in this study is that the subsoil of the Palmerston Ferrosol exhibited a PZNC of 4.88 (Table 3.5) higher than the pH_0 value (4.63), and reflecting that the soil generated permanently positive charge which accounted for $-0.18 \text{ cmol}_c \text{ kg}^{-1}$ out of $-0.39 \text{ cmol}_c \text{ kg}^{-1}$ of the total net positive charge (Table 3.7). This result usually occurs in some highly weathered soil, particularly oxide-rich Oxisols, and is in agreement with the theory of charge characteristics of soils with variable and permanent charge minerals (Uehara and Gillman, 1980). Permanent positive charge was also found in the lower subsoils from north Queensland (Acrohumox-B2 sample) (Gillman and Uehara, 1980), and also in the A_{12} horizon (35 - 45 cm) of a Dystrandep (a volcanic ash soil) in Papua New Guinea (Bleeker and Sageman, 1990).

Delta $CEC_{4.5-5.5}$ (ΔCEC , expressed as the change of CEC_T with 1 unit pH change) was significantly ($P < 0.05$) positively correlated with TOC, Al_{Ox} and Fe_{Ox} (Table 3.11). This indicates that the main sites for variable negative charge generation as pH increases are mainly associated with the soil organic matter and amorphous Fe and Al hydrous oxides. Aitken *et al.* (1990b) also found a significant correlation of ΔCEC with TOC and clay content in a diverse suite of acidic soils. These authors suggested that the extent of deprotonation of functional organic groups and variable charge minerals (such as hydrous oxides of Fe and Al) as pH increases determines the increase in net negative charge on surfaces, and this increase is reflected in the magnitude of ΔCEC . They also stated that as the amounts of hydrous oxides of Fe and Al relative to other clay minerals (for example kaolinite) increased at a given clay content, effective cation exchange capacity (ECEC) would also increase.

Variations in phosphorus sorption capacity

Variable charge soils usually show appreciable adsorption and fixation capacity for P (Pardo *et al.*, 1992; Wang *et al.*, 2009). Phosphorus sorption has been shown to be influenced by variables such as pH, composition and properties of the electrolyte, and the nature of the sorbent surfaces. These effects are ascribed to the variations produced in the charge and in the electric potential of the reacting surfaces (Ryden *et al.*, 1977; Barrow *et al.*, 1980; Barrow, 1984; Bolan *et al.*, 1986). Phosphorus buffering indices of the two Ferrosols range from 463 to 1245, and increase significantly ($P < 0.05$) with depth (Figures 3.8 and 3.9). This result is consistent with the work of Fox (1982) for some highly weathered soils (Oxisols and Ultisols) in Brazil. In contrast, PBIs of the Hydrosol and Vertisol subsoils are very low (60 and 174, respectively) (Figure 3.9). Table 3.11 indicates that across all soils and depths, PBI is highly correlated with clay content and crystalline Fe and, to a lesser extent, crystalline Al. The Hydrosol has low contents of clay and Fe and Al hydrous oxides and this is reflected in its very low PBI. The Vertisol, while having a similar clay content to the Ferrosols, has a much lower content of Fe and Al hydrous oxides than the Ferrosols (Table 3.1) and therefore a lower PBI than these soils. Wang *et al.* (2009) found that the greater P adsorption by two Oxisols than an Ultisol in China was attributed to the higher content of Fe/Al hydrous oxides in the former soils than in the latter. These results are consistent with many previous studies for P adsorption in several VCS (Hanafi *et al.*, 1992; Sei *et al.*, 2002; Arai *et al.*, 2005; Arai and Parks, 2007; Wang *et al.*, 2009).

3.5 Summary and conclusions

This study highlights the linkages between the chemical and mineralogical compositions of four soils from New South Wales and north Queensland, and their surface charge characteristics and P sorption capacities. The results clearly show that the Red Ferrosols have many constraints such as extreme acidity, very low CEC and very high P sorption capacity, and these problems are more pronounced in the subsoil. In particular, the subsoil of the Palmerston Ferrosol exhibits higher pH_0 than the existing soil pH and higher PZNC than pH_0 . Therefore, the soil has developed net positive surface charge with its AEC exceeding its CEC. In contrast, the Hydrosol and Vertosol are less acidic, have lower pHBC, higher net negative charge (i.e., CEC) and much lower P sorption capacity than the two Red Ferrosols. These differences are attributed to variations in the chemical and mineralogical compositions of these soils. For instance, TOC and Fe/Al hydrous oxides in the clay fraction significantly affect pHBC, delta CEC and PBI. In addition, OM has a great influence on the pH_0 of variable charge components, and thus on CEC. Consequently, OM addition to these soils will be an important management strategy to increase nutrient retention (Ca, K, Mg) against leaching losses and to increase the ability of the soil to resist acidification. Although there is no significant effect of the existing 'native' Si on these properties, Si addition should be assessed as a management strategy because freshly added Si would be expected to affect the charge characteristics of VCS. The effect of inorganic Si and organic amendments on surface charge characteristics and P sorption capacity of these soils has been investigated in the following chapters.

Chapter 4 Effects of silicon on surface charge characteristics and phosphorus sorption capacity of variable charge soils

4.1 Introduction

Since variable charge soils (VCS) have often developed under intensive weathering in subtropical and tropical regions (Qafoku *et al.*, 2004), they are strongly subjected to the process of desilication which leads to the soils being dominated by variable charge constituents (Savant *et al.*, 1999). As previously discussed in Chapter 3, VCS exhibit many constraints, creating plant nutritional problems and reducing agricultural production. Constraints of VCS include soil acidity, aluminium toxicity, low cation retention and high fixation of anions (such as P). Thus, basic cations are easily leached out of the soil profile and the soils have low nutrient supplying capacity.

Surface charge characteristics of VCS are critical to soil management (Qafoku *et al.*, 2004) because the majority of the reactions that control nutrient availability, and many physical properties, are dependent upon the physicochemical processes that occur at the soil particle surface (Uehara and Gillman, 1981). Options for management of VCS include liming, organic matter addition, P and silicon amendment (Uehara and Gillman, 1981; Bolan *et al.*, 1999; Qafoku *et al.*, 2004). All these management strategies manipulate the surface charge characteristics in order to control the retention of cations and anions of VCS. Because variable charge characteristics largely depend on the pH of the soil solution, soil treatment with pH amendments has usually been applied to control the reactions of nutrient ions and toxic heavy metals (Uehara and Gillman, 1981; Bolan *et al.*, 1999). In addition, application of specifically adsorbed anions, such as P and Si (Noble *et al.*, 2003), and organic matter (Phan, 2000) can increase the cation exchange capacity (CEC) of the soils.

Lime application is the most common practice used for neutralizing acidity and increasing pH, thereby influencing the surface charge characteristics of variable charged components in the soil (Mora and Barrow, 1996). In addition, an increase in soil pH has been shown to reduce phytotoxic aluminium (Al^{3+}), decrease the retention of anions such as SO_4^{2-} and HPO_4^{2-} (Marsh *et al.*, 1987; Bolan *et al.*, 1988; Naidu *et al.*, 1990) and increase the ability of soils to retain nutrient ions and potentially toxic heavy metals (Adams, 1984; Helmke and Naidu, 1996). However, large amounts of lime need to be applied to VCS to increase pH

above a certain level (e.g., pH 6.0), because of the high buffering capacity of these soils due to deprotonation of surface hydroxyls (Uehara and Gillman, 1981). This could be very costly and may result in induced micronutrient deficiencies. Therefore, another option to increase the CEC of VCS is to lower the point of zero charge value (pH_0). As previously discussed in Chapter 2, organic matter, Si and P application can shift pH_0 of VCS to a lower value. The pH_0 values of organic matter and of silanol surfaces (Si-OH) are about pH 2.0 (Sposito, 1984), so overall lowering of the soil pH_0 can be achieved by sorption of organic anions or silanol groups onto particle surfaces, thereby masking some positive charge of variable charge components of VCS. On other hand, P and Si anions can be specifically adsorbed and increase CEC of the soils. Another beneficial effect of Si is that Si can compete with P on the adsorbed sites of VCS, thus reducing the P sorption capacity of the soils.

Surface charge characteristics and P sorption capacity of selected VCS have been examined in Chapter 3. Subsequently, the role of Si, derived from both inorganic and organic amendments, will be investigated in this chapter. In addition to monosilicic acid, acidulated calcium silicate, acidulated magnesium silicate and mulched sugarcane trash amendments were used in this investigation. Fused magnesium phosphate, a product of Vietnam, and *Tithonia diversifolia*, a green manure, are also used to investigate the effect of Si on surface charge characteristics and P sorption capacity of selected VCS. Fused magnesium phosphate is high in Ca, Mg, P and Si content, and is commonly used in farming systems of Vietnam as a P fertiliser agent. It has recently been imported to Australia and used as a P and lime material. Although the benefit of fused magnesium phosphate is well known in association with its liming effect and P content, the Si content of this product has been neglected and the beneficial effect of Si on surface charge characteristics is still unknown. *Tithonia diversifolia* has been widely applied in Vietnam as a green manure because it grows in the wild, and is highly productive and easily collected, particularly in the central highlands of Vietnam where VCS (Ferrosols) dominate. *Tithonia* not only contains Si, but also high amounts of Ca, Mg and P compared to other green manures.

4.2 Materials and methods

4.2.1 Soil collection and preparation

The three soil types used in this study were the Palmerston Ferrosol (0 - 20 and 20 - 40 cm), the Hydrosol (20 - 40 cm) and the Vertosol (20 - 40 cm). Details of the soil classification, locations, land use, mineralogical compositions and properties are presented in Section 3.2.1 (Chapter 3) and given in Table 4.1. The soil samples were air-dried and passed through a 2 mm-sieve before taking representative samples for experimentation.

Table 4.1 Selected characteristics of the Palmerston Ferrosol, Hydrosol and Vertosol

Soil type	Depth	¹ BD	² FC	³ Δ pH	P	Si	⁴ P _{avail.}	⁵ Si _{avail.}	⁶ PBI _{Colwell}
	(cm)	(Mg m ⁻³)	(%)		(%)		(mM)		
Palmerston	0 - 20	1.1	30.40	-0.07	0.23	7.16	0.02	0.42	616
Ferrosol	20 - 40	1.3	30.37	0.26	0.18	6.48	0.01	0.02	1245
Hydrosol	20 - 40	1.3	18.65	-1.03	0.02	35.48	0.00	0.88	60
Vertosol	20 - 40	1.1	29.67	-1.69	0.01	25.32	0.00	2.13	174

¹ bulk density; ² field capacity; ³ delta pH = pH(1:5, 1 M KCl) – pH (1:5, water);

⁴ P_{avail} = 0.01 M CaCl₂ extraction; ⁵ Si_{avail} = 0.01 M CaCl₂ extraction; ⁶ phosphorus buffering index

4.2.2 Silicate amendments, soil treatments and incubation

Silicate amendments

Several silicate amendments were used in this study to investigate the effect of Si on surface charge characteristics and P sorption capacity of the above soils. The amendments comprised both inorganic Si sources and organic amendments. The inorganic silicate amendments were monosilicic acid (Mono-Si), acidulated calcium silicate (Ac-Ca-Si), acidulated magnesium silicate (Ac-Mg-Si) and fused magnesium phosphate (FMP); while mulched sugarcane trash and *Tithonia diversifolia* whole plant tops are described as organic silicate amendments (hereafter referred to as sugarcane and *Tithonia*, respectively). These amendments were chosen for this study due to their popular use in Vietnam (FMP and *Tithonia*) and Australia (FMP and sugarcane), and to investigate the effect of Si alone (Mono-Si) and its interaction with other accompanying elements (Ca, Mg and P) contained in Ac-Ca-Si, Ac-Mg-Si and FMP. In order to prevent alkaline effects on soil pH (and thus the development of variable surface charge) Ac-Ca-Si and Ac-Mg-Si were used instead of calcium- (Ca-Si) and

magnesium silicate (Mg-Si) amendments for comparison with Mono-Si. Lime (CaCO_3) and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Ca-P) were also used to compare with the effect of Ca and P contained in FMP. Chemical compositions of the investigated amendments are presented in Table 4.2.

Table 4.2 Chemical compositions of the investigated amendments

Amendment	Ca	Mg	Fe	P	Si	¹ P _{avail.}	² Si _{avail.}	³ NV	Ash alkalinity
	(%)					(mM)		(%)	(M OH ⁻ kg ⁻¹)
Mono-Si	0.00	0.00	0.00	0.00	0.09	⁴ nd	nd	nd	nd
Ac-Ca-Si	14.1	0.04	0.05	0.02	15.2	0.51	17.6	0.0	nd
Ac-Mg-Si	1.48	10.3	1.61	0.00	7.23	0.00	67.7	0.0	nd
FMP	18.8	8.86	1.67	7.24	12.0	1.02	25.9	47.7	nd
Lime	37.8	0.08	0.11	0.00	0.46	0.00	1.54	97.6	nd
Ca-P	23.3	0.00	0.00	18.0	0.00	nd	nd	nd	nd
Sugarcane	0.17	0.15	0.29	0.06	3.14	10.9	2.51	nd	0.25
<i>Tithonia</i>	1.58	0.40	0.03	0.42	0.44	63.9	80.3	nd	1.04

¹ P_{avail} = 0.01 M CaCl_2 extraction; ² Si_{avail} = 0.01 M CaCl_2 extraction;

³ neutralizing value (expressed as percentage of CaCO_3); ⁴ not determined

Soil treatments and incubation

Each amendment was added and thoroughly mixed with 150 g of each investigated soil sample in an air-filled 2-kg-plastic bag (Table 4.3). The mixture was then transferred into a labelled polypropylene pot of 10 cm height and 6.5 cm diameter. All pots were adjusted to 85% field capacity with deionized water and covered with lids with four 2-cm-diameter holes, thus ensuring the moist soil samples were ventilated but restricting evaporation under the high incubation temperature (40°C). The amendments were added at rates equivalent to 250 kg Si ha⁻¹ (calculated on a surface area basis per 10 cm depth with the specific bulk density of a given soil) for inorganic silicate amendments (Mono-Si, Ac-Ca-Si, Ac-Mg-Si and FMP), and 125 kg Si ha⁻¹ for organic amendments (sugarcane and *Tithonia*). A treatment comprising 125 kg Si ha⁻¹ as Mono-Si was also applied in order to equal the amount of Si added in the organic amendments. In addition, lime and Ca-P were applied at rates equivalent to the neutralizing value and P applied by the FMP treatment, respectively (Table 4.3). Note that the Mono-Si solution was immediately diluted with deionized water prior to addition to the soil samples to prevent polymerisation at the high Si concentration. It was observed from our laboratory work

that if the generated Mono-Si solution was higher than 0.1% Si, then polymerisation occurred and if the amount of Si applied as Mono-Si was more than 250 kg Si ha⁻¹, the volume of applied Mono-Si solution exceeded 85% field capacity (determined as water retained following 48 hours free drainage) of the investigated soils. Half of this rate of Si was applied as organic amendments (125 kg Si ha⁻¹) because of the large amount of organic matter needed to supply this rate of Si. In particular, more than 28 tonnes of *Tithonia* was required (Table 4.3); this amount can be practically applied under field conditions, particularly in Vietnamese farming systems.

Table 4.3 The amounts of amendments applied to the investigated soils in the incubation experiments. Application rates calculated on a soil surface area basis per 10 cm depth at the bulk density of a given soil

Amendment	Si	P	Ca	Mg	¹ OM
	(kg ha ⁻¹)				
Mono-Si-1	250	0	0	0	0
Ac-Ca-Si	250	0	232	1	0
Ac-Mg-Si	250	0	51	356	0
FMP	250	151	391	184	0
Ca-P	0	151	195	0	0
Lime	5	0	383	0	0
Mono-Si-2	125	0	0	0	0
Sugarcane trash	125	2	7	6	3977
<i>Tithonia</i>	125	119	448	114	28373

¹ air-dried organic materials applied after passing through a sieve to ensure homogeneity

All treatments including the control treatment (unamended soil) of all investigated soils were replicated three times. The pots were randomly placed in a tray approximately 5 cm apart and incubated at constant temperature of 40°C for 30 days. All pots were maintained at the initial moisture content by daily watering to weight. After 30 days of incubation, vertical soil samples were taken from the soil surface to the bottom of the pot using a plastic tube of 15 cm length and 1.5 cm diameter. Three cores were taken from each pot. Soil samples were dried at 25°C for 5 days, gently hand-broken and then passed through a 2-mm sieve before collecting for analysis. Note that all processes were performed on all investigated soils over the same time period.

4.2.3 Analytical determinations

Monosilicic acid generation

The monosilicic acid generation method was modified from the method described by Ma *et al.* (1997) using sodium silicate solution ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), resin [Amberlite IR-120 (H^+ form) beads, particle size 0.30 - 1.18 mm (14 - 52 mesh)] and 1 M HCl solution. The procedure is briefly described as follows: a) the beads were washed three times and soaked overnight with deionized water before filling a column (a burette); b) hydrochloric acid (1 M) solution was first passed through the column and the beads were again washed with deionized water several times until the pH of the effluent water was around 4.0; c) sodium silicate solution was then passed through the column; and d) the latter two thirds of the effluent solution were collected (considered as pure silicic acid solution, i.e. without any sodium contamination) and analysed using inductively coupled plasma - atomic emission spectrometry (ICP-AES) to obtain the concentration of Si and ensure that the solution contained non-detectable levels of sodium.

Chemical properties

Soil pH was measured in water ($\text{pH}_{\text{H}_2\text{O}}$) and in 1 M KCl (pH_{KCl}) at a 1:5 soil to solution ratio using a pH meter (901-CP model, TPS Pty. Ltd., Australia). Delta pH (ΔpH) was then calculated as the difference between $\text{pH}_{1 \text{ M KCl}}$ and $\text{pH}_{\text{H}_2\text{O}}$.

Total Ca, Mg, Fe, P and Si concentrations in the soils and the amendments were determined by the microwave digestion technique using a digestion solution of nitric acid (70%), hydrogen peroxide (30%) and hydrofluoric acid (50% w/w), and a Milestone Ethos Plus with a HPR-1000/10S high pressure segment rotor with temperature control (Ethos Plus). Available P ($\text{P}_{\text{avail.}}$) and Si ($\text{Si}_{\text{avail.}}$) of the soils and the amendments were extracted using 0.01 M CaCl_2 solution as described by Kuo (1996) and Berthelsen *et al.* (2003), respectively. Both extractions were modified using a 1:10 and a 1:100 soil (or amendment) to solution ratio for the soils and the amendments, respectively, and shaken end-over-end (12 rpm) for 16 h at 25°C. The extracts were centrifuged and the supernatants were analysed for P and Si by colorimetry; the malachite green method was used for P determination (Motomizu *et al.*, 1983), and Si was determined using the modified blue silicomolybdous acid procedure

(Weaver *et al.*, 1968). The neutralizing values of lime and FMP were determined using the 6.4 method (Faithfull, 2002).

Surface charge characteristics, oxalate extractable Fe, Al and Si (Fe_{Ox} , Al_{Ox} and Si_{Ox} , respectively), Colwell P ($\text{P}_{\text{Colwell}}$) and P buffer index ($\text{PBI}_{\text{Colwell}}$) were determined using the methods described in Section 3.2.2 (Chapter 3). Note that surface charge characteristic values of all soils were performed with two replications, and the effect of organic amendments on these properties was only determined for the Palmerston Ferrosol.

4.2.4 Data analysis

Charge fingerprint curves were plotted using Microsoft Office Excel 2007 for Windows XP Professional 2002. Surface charge characteristic values were calculated using regression equations derived from charge fingerprint curves. General analysis of variance (ANOVA) and least significant differences of means ($\text{LSD}_{0.05}$) were used to compare treatment effects. Differences between the inorganic silicate treatments were compared at the rate of $250 \text{ kg Si ha}^{-1}$, while the organic amendments treatments, including a Mono-Si treatment, were compared at the rate of $125 \text{ kg Si ha}^{-1}$ to examine the effect of Si on surface charge characteristics and P sorption capacity. Differences between the lime and Ca-P treatments were also compared to the FMP treatment within a given soil to examine the combined effects of Ca, P and Si on surface charge characteristics and P sorption capacity. Linear correlation coefficient (r) matrices and regression equations were computed for the various analyses of all treatments and soils to express the relationships of surface charge characteristics and P sorption capacity with soil properties. In addition, stepwise (forward and backward) multiple linear regression was used to further explore the combined effect of measured soil variables on charge surface characteristics and P sorption capacity, with Akaike information set as a criterion to select the best model. Significant levels were set to $P \leq 0.05$ for all tests. All analyses were undertaken in the GenStat Discovery Edition 3 (seventh edition, version - 7.2.2.222) Copyright 2008 for Windows XP.

4.3 Results

4.3.1 Changes in soil pH and surface charge characteristics

The effect of inorganic silicate amendments (Mono-Si, Ac-Ca-Si, Ac-Mg-Si and FMP equivalent to 250 kg Si ha⁻¹) on soil pH (1:10, 0.002 M CaCl₂) (hereafter referred as to soil pH), delta pH, point of zero charge (pH₀), total cation exchange capacity (CEC_T) and anion exchange capacity (AEC) of the Palmerston Ferrosol topsoil (0 - 20 cm) and subsoil (20 - 40 cm) are presented in Table 4.4. In general, the topsoil pHs of all treatments (4.38 – 4.88) were higher than those of the subsoil (4.29 – 4.87); whereas the topsoil pH₀s (4.08 – 4.24) and delta pHs [(-0.29) – (-0.06)] were lower in all treatments than those in the subsoil, (4.31 – 4.63) and [(-0.23) – 0.16] for pH₀ and delta pH, respectively. Therefore, the topsoil exhibited higher CEC_T values (0.60 – 1.11 cmol_c kg⁻¹) than the subsoil (0.31 – 0.65 cmol_c kg⁻¹), and the topsoil had lower AEC values [(-0.10) – 0.03 cmol_c kg⁻¹] than the subsoil [(-0.32) – (-0.58) cmol_c kg⁻¹] in all treatments. The results also show that the pH₀ values were generally higher than the soil pH values in the subsoil, but the reverse situation occurred in the topsoil (Table 4.4).

Application of inorganic silicate amendments, except for Mono-Si, to the topsoil of the Palmerston Ferrosol significantly ($P < 0.05$) increased soil pH and negative values of delta pH, reduced pH₀ compared to the unamended soil (the control treatment), thus these amendments significantly increased CEC_T by 28 to 85% and reduced AEC by 22 to 67% compared to the control treatment. The highest CEC_T increase was observed in the FMP treatment (85%) and there was no AEC in this treatment. Although Mono-Si lowered the pH of the soil, it shifted the pH₀ to a lower value than the control treatment, thereby increasing the CEC_T of the soil by 18% compared to the control treatment (Table 4.4). Greater inorganic silicate amendment effects were observed in the subsoil than in the topsoil. In the subsoil, all treatments significantly ($P < 0.05$) increased soil pH (except for the soil pH of the Mono-Si treatment), reduced delta pH from positive to negative values, and shifted the pH₀ to lower values compared to the unamended soil; in particular the Ac-Mg-Si and FMP amendments shifted the pH₀ values below the soil pH values. These effects on pH₀ accounted for an increase in CEC_T (29 – 210%) and a decrease in AEC (29 – 46%) by inorganic silicate amendments compared to the control treatment (Table 4.4). Of all amendments, Mono-Si exhibited the least effect, while FMP had the greatest effect, and Ac-Mg-Si had more effect than Ac-Ca-Si amendment on soil pH, delta pH and surface charge characteristics of the Palmerston Ferrosol in both soil depths.

Table 4.4 Effect of inorganic silicate amendments on pH, delta pH, point of zero charge, total cation exchange capacity and anion exchange capacity of the Palmerston Ferrosol at different soil depths (0 - 20 and 20 - 40 cm)

Amendment	¹ pH	² Δ pH	³ pH ₀	⁴ CEC _T	⁵ AEC	Percentage change	
						CEC _T	AEC
	(cmol _c kg ⁻¹)					(%)	
	0 - 20 cm						
Control	4.43 b	-0.07 c	4.24 c	0.60 a	-0.09 a		
Mono-Si-1	4.38 a	-0.06 c	4.19 b	0.71 b	-0.10 a	18	11
Ac-Ca-Si	4.47 c	-0.11 b	4.19 b	0.77 c	-0.07 ab	28	-22
Ac-Mg-Si	4.56 d	-0.29 a	4.08 a	0.87 d	-0.03 b	45	-67
FMP	4.88 e	-0.26 a	4.18 b	1.11 e	0.03 c	85	-
LSD _(0.05)	0.01	0.03	0.04	0.05	0.05		
<i>P</i>	< 0.001	< 0.001	0.004	< 0.001	0.009		
	20 - 40 cm						
Control	4.27 a	0.16 e	4.63 e	0.31 a	-0.58 a		
Mono-Si-1	4.29 a	0.12 d	4.54 d	0.40 b	-0.41 bc	29	-29
Ac-Ca-Si	4.33 b	0.02 c	4.46 c	0.42 b	-0.47 b	35	-19
Ac-Mg-Si	4.44 c	-0.23 b	4.31 a	0.49 c	-0.36 c	58	-38
FMP	4.87 d	-0.19 a	4.41 b	0.65 d	-0.32 c	210	-46
LSD _(0.05)	0.03	0.01	0.04	0.04	0.10		
<i>P</i>	< 0.001	< 0.001	< 0.001	< 0.001	0.009		

¹ soil pH (1:10, 0.002 M CaCl₂); ² delta pH; ³ point of zero charge;

⁴ total cation exchange capacity; ⁵ anion exchange capacity

Means in the same column followed by different letters are significantly different at *P* < 0.05.

The effects of inorganic silicate amendments on soil pH, delta pH and CEC_T of the Hydrosol and Vertosol subsoils (20 - 40 cm) were different from those observed for the Palmerston Ferrosol (Table 4.4 compared to Table 4.5). Note that the pH₀ values of the two former soils could not be estimated from the charge fingerprint curves within the pH range of 4.0 – 7.0. The AEC values in all treatments of both soils were not negative and nearly zero (Table 4.5). In contrast, the control CEC_T values of both soils, particularly the Vertosol, were much higher than those of the Palmerston Ferrosol (cf, Tables 4.4 and 4.5). The effect of inorganic silicate amendments (applied at the same rate as that applied to the Palmerston Ferrosol, 250 kg Si ha⁻¹) on soil pH, delta pH and CEC_T of the Hydrosol and Vertosol were proportionally less than

their effects on the Palmerston Ferrosol. In comparison to the control treatment, Mono-Si, Ac-Ca-Si and Ac-Mg-Si amendments had little (although significant) effect on soil pH, delta pH and CEC_T of the Hydrosol and caused a small increase (<10%) in CEC_T of the Vertosol (Table 4.5). However, the results observed in the FMP amendment were much greater; in addition to increasing pH of both soils compared to the other amendments and the control treatment, there was an increase in CEC_T of 17 and 20% for the Hydrosol and the Vertosol, respectively (Table 4.5).

Table 4.5 Effect of inorganic silicate amendments on pH, delta pH, total cation exchange capacity and anion exchange capacity of a Hydrosol and Vertosol at the soil depth of 20 - 40 cm

Amendment	¹ pH	² Δ pH	³ CEC _T	⁴ AEC	Percentage change	
					CEC _T	AEC
			(cmol _c kg ⁻¹)		(%)	
Hydrosol						
Control	4.78 b	-0.64 c	1.57 a	0.01 a		
Mono-Si-1	4.74 a	-0.76 b	1.63 a	0.02 a	4	-
Ac-Ca-Si	4.77 ab	-0.50 d	1.54 a	0.02 a	-2	-
Ac-Mg-Si	4.83 c	-0.47 e	1.54 a	0.02 a	-2	-
FMP	5.33 d	-0.83 a	1.83 b	0.05 b	17	-
LSD _(0.05)	0.03	0.02	0.09	0.01		
<i>P</i>	< 0.001	< 0.001	0.003	0.003		
Vertosol						
Control	5.13 b	-1.34 a	5.55 a	0.02		
Mono-Si-1	5.03 a	-1.28 b	5.78 b	0.02	4	-
Ac-Ca-Si	5.15 bc	-0.90 c	5.97 d	0.00	8	-
Ac-Mg-Si	5.18 c	-0.74 d	5.91 c	0.00	6	-
FMP	6.00 d	-1.34 a	6.67 e	0.06	20	-
LSD _(0.05)	0.03	0.04	0.04	⁵ ns		
<i>P</i>	< 0.001	< 0.001	< 0.001	0.231		

¹ soil pH (1:10, 0.002 M CaCl₂); ² delta pH; ³ total cation exchange capacity; ⁴ total net charge; ⁵ not significant
Means in the same column followed by different letters are significantly different at *P* < 0.05.

Since the FMP amendment also contains P and Ca in addition to Si (Table 4.2), lime and Ca-P treatments at an equivalent neutralizing value and P addition rate, respectively, were used to investigate the contribution of pH and P in combination with Si to the FMP effect. The results of these amendments on soil pH and surface charge characteristics are given in Table 4.6 for the Palmerston Ferrosol (0 - 20 cm and 20 - 40 cm) and in Table 4.7 for the Hydrosol and Vertosol (20 - 40 cm).

Table 4.6 Combined effects of Ca, P and Si amendments on pH, delta pH, point of zero charge, total cation exchange capacity and anion exchange capacity of the Palmerston Ferrosol at different soil depths (0 - 20 cm and 20 - 40 cm)

Amendment	¹ pH	² Δ pH	³ pH ₀	⁴ CEC _T	⁵ AEC	Percentage change	
						CEC _T	AEC
	(cmol _c kg ⁻¹)					(%)	
0 - 20 cm							
Control	4.43 a	-0.07 d	4.24 b	0.60 a	-0.09 a		
Lime	4.79 c	-0.19 b	4.25 b	0.96 c	-0.03 b	60	-67
Ca-P	4.56 b	-0.13 c	4.19 a	0.83 b	-0.03 b	38	-67
FMP	4.88 d	-0.26 a	4.18 a	1.11 d	0.03 c	85	-
LSD _(0.05)	0.02	0.03	0.03	0.07	0.05		
<i>P</i>	< 0.001	< 0.001	0.015	< 0.001	0.009		
20 - 40 cm							
Control	4.27 a	0.16 c	4.63 c	0.31 a	-0.58 a		
Lime	4.76 c	-0.09 b	4.70 d	0.55 c	-0.46 b	77	-21
Ca-P	4.58 b	-0.08 b	4.51 b	0.48 b	-0.47 b	55	-19
FMP	4.87 d	-0.19 a	4.41 a	0.65 d	-0.32 c	210	-46
LSD _(0.05)	0.03	0.03	0.05	0.04	0.10		
<i>P</i>	< 0.001	< 0.001	< 0.001	< 0.001	0.009		

¹ soil pH (1:10, 0.002 M CaCl₂); ² delta pH; ³ point of zero charge;

⁴ total cation exchange capacity; ⁵ anion exchange capacity

Means in the same column followed by different letters are significantly different at *P* < 0.05.

All treatments (lime, Ca-P and FMP) significantly (*P* < 0.05) increased soil pH, negative values of delta pH and CEC_T, and significantly (*P* < 0.05) decreased pH₀ (except the lime treatment) and AEC in both the soil depths of the Palmerston Ferrosol (Table 4.6). However, the proportional effects of the lime and Ca-P treatment were not as great as those of the FMP

treatment. Therefore, the increase in CEC_T and the decrease in AEC caused by the lime and Ca-P treatments were much less than those caused by the FMP treatment, particularly in the subsoil (Table 4.6). These results can be attributed to the additional effect of Si or the synergistic effect of Ca, P and Si contained in the FMP amendment. Similarly, the soil pH and CEC_T of the Hydrosol and Vertosol were significantly increased by lime, Ca-P and FMP treatment compared to the control (Table 4.7). Fused magnesium phosphate exhibited greater effects than lime and Ca-P, particularly increasing CEC_T of the Vertosol by 20% for FMP, compared with 18% for lime and 14% for Ca-P. However, the extent of the increased CEC_T (17%) caused by lime in the Hydrosol was the same as that by FMP, and the extent of the decreased AEC of both soils was also similar between these treatments (Table 4.7).

Table 4.7 Combined effects of Ca, P and Si amendments on pH, delta pH, total cation exchange capacity and anion exchange capacity of the Hydrosol and Vertosol at the soil depth of 20 - 40 cm

Amendment	¹ pH	² Δ pH	³ CEC _T	⁴ AEC	Percentage change	
					CEC _T	AEC
	(cmol _c kg ⁻¹)				(%)	
Hydrosol						
Control	4.78 a	-0.64 c	1.57 a	0.01 a		
Lime	5.27 c	-0.77 b	1.83 b	0.04 b	17	-
Ca-P	4.89 b	-0.75 b	1.59 a	0.04 b	1	-
FMP	5.33 d	-0.83 a	1.83 b	0.06 c	17	-
LSD _(0.05)	0.01	0.02	0.11	0.01		
<i>P</i>	< 0.001	< 0.001	0.007	0.009		
Vertosol						
Control	5.13 a	-1.34 a	5.55 a	0.02		
Lime	6.01 c	-1.29 b	6.55 bc	0.04	18	-
Ca-P	5.41 b	-1.33 a	6.35 b	0.04	14	-
FMP	6.00 c	-1.34 a	6.67 c	0.05	20	-
LSD _(0.05)	0.01	0.02	0.30	⁵ ns		
<i>P</i>	< 0.001	0.005	0.005	0.201		

¹ soil pH (1:10, 0.002 M CaCl_2); ² delta pH; ³ total cation exchange capacity; ⁴ total net charge; ⁵ not significant

Means in the same column followed by different letters are significantly different at $P < 0.05$.

The effects of organic amendments (applied as sugarcane and *Tithonia* equivalent to 125 kg Si ha⁻¹) on soil pH, delta pH and surface charge characteristics was examined for the Palmerston Ferrosol subsoil (20 - 40 cm), and results are given in Table 4.8. The application of sugarcane or *Tithonia* significantly ($P < 0.05$) increased soil pH, and decreased delta pH and pH₀ compared to those of the control treatment. In particular, the large increase in soil pH (1.40 unit) and significant reduction in pH₀ (nearly 0.4 unit) caused by *Tithonia* markedly increased CEC_T and significantly decreased AEC compared to the control treatment by approximately 500 and 100% respectively (Table 4.8). Although sugarcane significantly increased soil pH and decreased pH₀ of the soil, the extent of these changes was not sufficient to significantly increase CEC_T of the soil compared to the control treatment, but AEC of the soil was significantly decreased by 26% (Table 4.8). The results show that Si applied as Mono-Si at the same rate as for *Tithonia* and sugarcane at the low rate (125 kg Si ha⁻¹) did not significantly affect either CEC_T or AEC of the Palmerston Ferrosol subsoil.

Table 4.8 Effect of organic amendments on pH, delta pH, point of zero charge, total cation exchange capacity and anion exchange capacity of the Palmerston Ferrosol at the soil depth of 20 - 40 cm

Amendment	¹ pH	² Δ pH	³ pH ₀	⁴ CEC _T (cmol _c kg ⁻¹)	⁵ AEC	Percentage change	
						CEC _T	AEC
						(%)	(%)
Control	4.27 b	0.17 c	4.63 d	0.31 a	-0.58 a		
Mono-Si-2	4.24 a	0.19 c	4.57 c	0.34 a	-0.64 a	10	10
Sugarcane	4.34 c	0.04 b	4.53 b	0.36 a	-0.43 b	16	-26
<i>Tithonia</i>	5.67 d	-0.42 a	4.26 a	1.54 b	-0.02 c	497	-97
LSD _(0.05)	0.01	0.02	0.02	0.11	0.09		
<i>P</i>	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001		

¹ soil pH (1:10, 0.002 M CaCl₂); ² delta pH; ³ point of zero charge;

⁴ total cation exchange capacity; ⁵ anion exchange capacity

Means in the same column followed by different letters are significantly different at $P < 0.05$.

Variably charged soils are often mixed systems of permanent- and variable charge components. Net permanent charge (NPC) values can be estimated from charge curves and pH₀ values derived from the charge fingerprint method; accordingly net variable charge (NVC) values can be computed from the difference between total net charge and NPC values (see Section 3.2.2 in Chapter 3). In order to further investigate the effect Si on changes of NPC and NVC of VCS, calculations of these parameters were made for the Palmerston

Ferrosol (both soil depths). Note that NPC and NVC values of the Hydrosol and Vertosol could not be estimated from the pH range used in the charge fingerprint method.

Application of inorganic silicate amendments significantly ($P < 0.05$) increased both NPC and NVC of the Palmerston Ferrosol topsoil (0 - 20 cm), except for Mono-Si (Figure 4.1a). Although the soil exhibited more permanent negatively charged surfaces than variable charged surface in all inorganic silicate amendment treatments. The order of increase was as follows: FMP > Ac-Mg-Si > Ac-Ca-Si > Mono-Si (Figure 4.1a). Since the unamended subsoil of the Palmerston Ferrosol exhibited net positive charge (i.e. higher AEC value than CEC_T value), the application of inorganic silicate amendments significantly ($P < 0.05$) reduced both permanent charged surfaces and variable charged surfaces of the soil compared to the control treatment (Figure 4.1b). Fused magnesium phosphate and Ac-Mg-Si amendment also shifted variable charged surfaces from positive to negative values. These changes can be attributed to the reduction in both pH_0 and point of zero net charge (PZNC) of the soil caused by the application of inorganic silicate amendments (Figure 4.1b). Similarly, the application of lime and Ca-P amendment significantly increased both NPC and NVC in both soil depths of the Palmerston Ferrosol, and changed the sign of the variable charged surfaces from positive to negative values in the subsoil (Figures 4.2a and b). However, the effects of these amendments were not as great as those caused by FMP amendment. The results in Figures 4.1b and 4.2b also show that the PZNC values were higher than the pH_0 values of all treatments, thus the soil still carried some positive permanent charge with the magnitude reflected by the difference between PZNC and pH_0 .

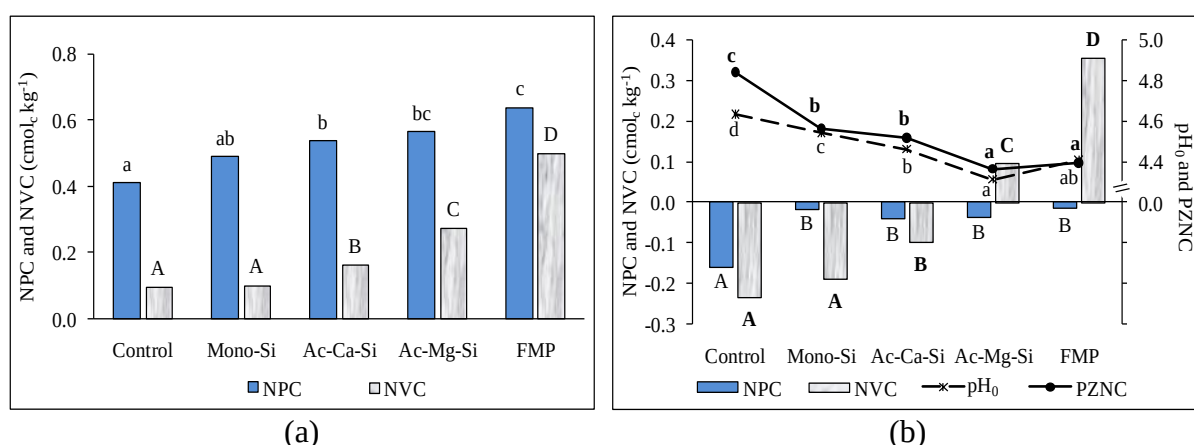


Figure 4.1 Effect of inorganic silicate amendments on net permanent- (NPC) and net variable charge (NVC) of the Palmerston Ferrosol at different soil depths [(a) 0 - 20 cm and (b) 20 - 40 cm]. Treatment means with different letters at the same pattern columns (or lines) are significantly different at $P < 0.05$

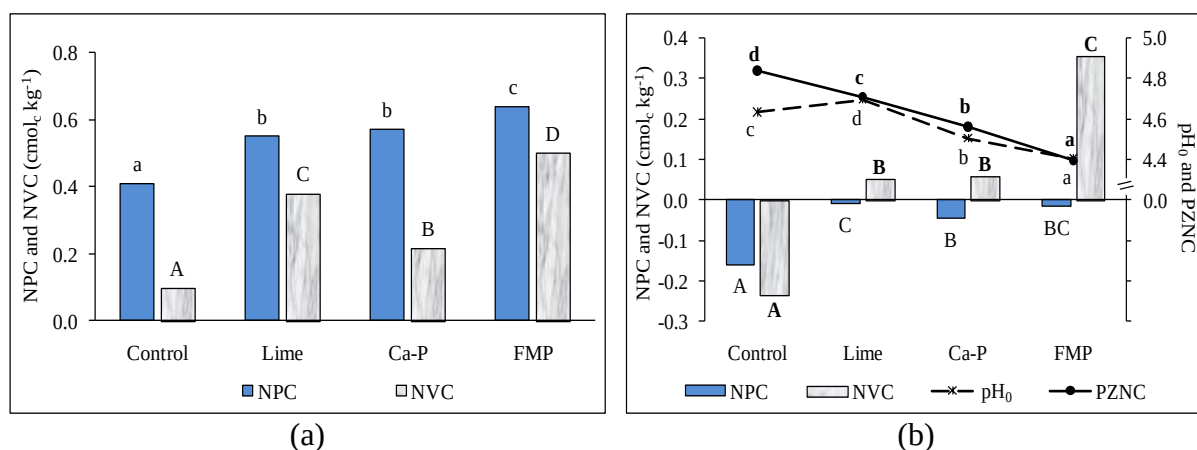


Figure 4.2 Combined effects of Ca, P and Si amendments on net permanent- (NPC) and net variable charge (NVC) of the Palmerston Ferrosol at different soil depths [(a) 0 - 20 cm and (b) 20 - 40 cm]. Treatment means with different letters at the same pattern columns (or lines) are significantly different at $P < 0.05$

Changes of NPC, NVC, pH₀ and PZNC of the Palmerston Ferrosol subsoil following the application of organic amendments and Mono-Si (125 kg Si ha⁻¹) are presented in Figure 4.3. Although only *Tithonia* amendment markedly changed the magnitude and sign of NVC both sugarcane and *Tithonia* amendments significantly shifted the small positive NPC to negative values compared to that of the Mono-Si amendment. These results are obviously due to the PZNC being shifted to lower values than the pH₀ following the application of sugarcane and *Tithonia* amendments (Figure 4.3).

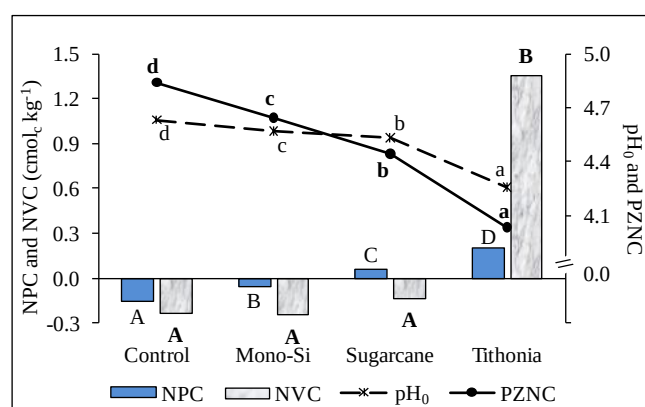


Figure 4.3 Effect of organic amendments on net permanent- (NPC) and net variable charge (NVC) of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters at the same pattern columns (or lines) are significantly different at $P < 0.05$

Apart from increasing soil pH, it is considered that lowering soil pH_0 is another option to increase nutrient retention capacity (i.e. cation exchange capacity, CEC) of VCS. Total cation exchange capacity computed at soil pH 5.0 [$CEC_T(pH_{5.0})$] and delta CEC_T (derived from different CEC_T values between soil pH 4.5 and 5.5) of all treatments were compared to changes in the pH_0 values following silicate amendment. By doing this, it can be investigated whether lowering pH_0 by silicate amendments increased the CEC_T of VCS in this study. All inorganic silicate amendments significantly decreased pH_0 values, and increased both $CEC_T(pH_{5.0})$ and delta CEC_T of the Palmerston Ferrosol (both soil depths) compared to the control treatment (Figures 4.4a and 4.4b). Similar trends were observed for the organic amendments (sugarcane and *Tithonia*) applied to the Palmerston Ferrosol subsoil (Figure 4.6). In comparison of these effects between lime, Ca-P and FMP amendment, the FMP amendment resulted in the greatest effects in both soil depths of the Palmerston Ferrosol (Figure 4.5). These results demonstrate that lowering soil pH_0 by silicate amendment increased nutrient retention capacity of the Palmerston Ferrosol. For all investigated amendments, FMP and *Tithonia* amendment exhibited greater effects on nutrient retention capacity of the soil than the other amendments. This is attributed to additional effects of accompanying elements such as Ca, Mg and P contained in FMP and *Tithonia*, and organic carbon also contained in *Tithonia* (Tables 4.2 and 4.3).

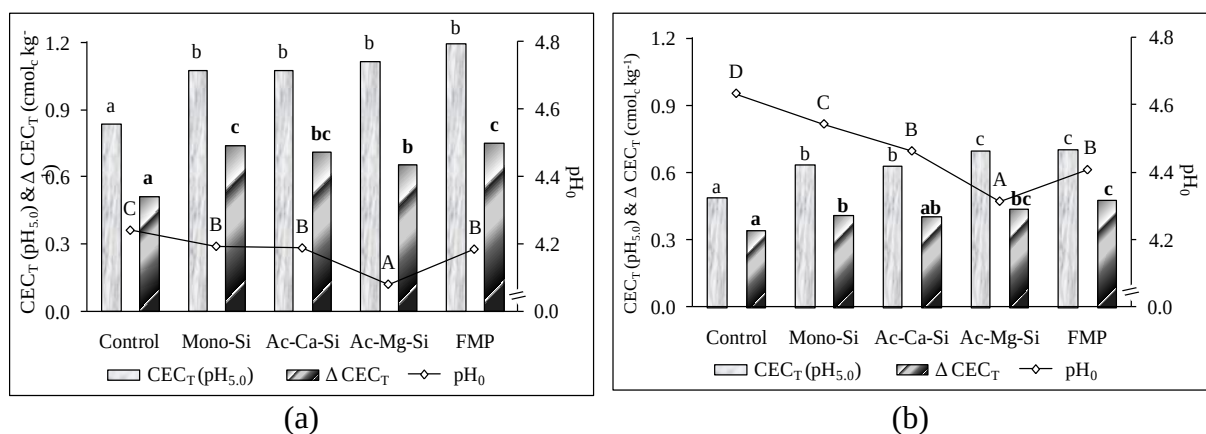


Figure 4.4 Effect of inorganic silicate amendments on $CEC_T(pH_{5.0})$ and delta CEC_T of the Palmerston Ferrosol at two soil depths [(a) 0 - 20 cm and (b) 20 - 40 cm]. Treatment means with different letters on the same pattern columns (or line) are significantly different at $P < 0.05$

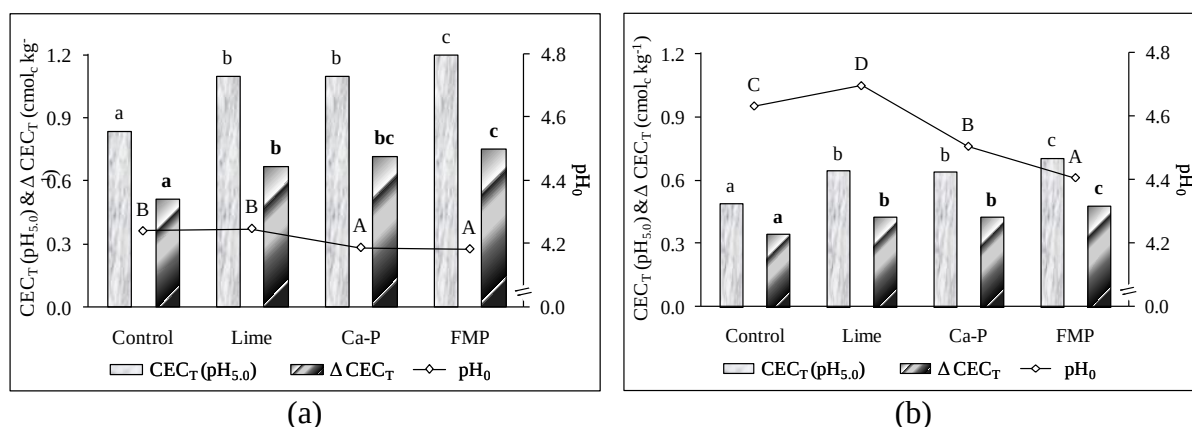


Figure 4.5 Combined effects of Ca, P and Si amendments on CEC_T (pH_{5.0}) and delta CEC_T of the Palmerston Ferrosol at two soil depths [(a) 0 - 20 cm and (b) 20 - 40 cm]. Treatment means with different letters on the same pattern columns (or line) are significantly different at *P* < 0.05

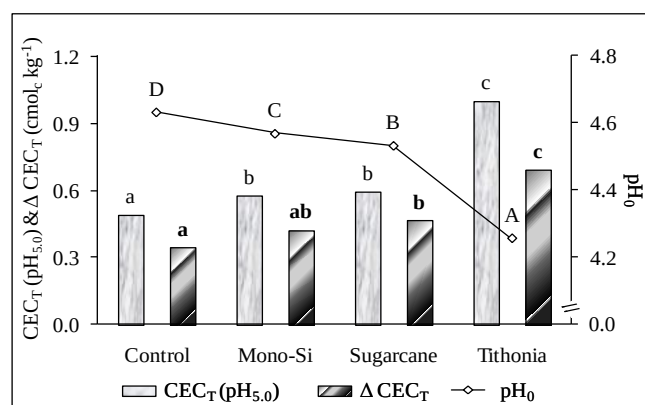


Figure 4.6 Effect of organic amendments on CEC_T (pH_{5.0}) and delta CEC_T of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns (or line) are significantly different at *P* < 0.05

4.3.2 Changes in silicon-, phosphorus availability and phosphorus sorption capacity

As previously discussed in Chapter 2 and 3, high P fixation is one of the major constraints of VCS, particularly those containing large amounts of Fe and Al hydrous oxides. For example, the results presented in Chapter 3 show that the Palmerston Ferrosol contains high amounts of Fe and Al hydrous oxides, and has a correspondingly high P sorption capacity, whereas the Hydrosol and Vertosol have low contents of Fe and Al hydrous oxides and a low P sorption capacity (see Chapter 3). With a theory that Si can reduce P fixation of VCS by competing with the sorption sites of P (see Chapter 2) the effect of Si on P sorption capacity of the selected VCS will be presented in this section.

The application of inorganic silicate amendments to the Palmerston Ferrosol topsoil did not significantly increase P availability (estimated by 0.01 M CaCl₂ extraction) except for the FMP amendment. Si availability (estimated by 0.01 M CaCl₂ extraction) was significantly ($P < 0.05$) increased by these amendments compared to the control treatment, particularly with the application of Mono-Si and FMP amendment (Figure 4.7a). Compared to the control, the Colwell P (P_{Colwell}) values of all inorganic silicate treatments were significantly increased, and the P buffering index ($\text{PBI}_{\text{Colwell}}$) significantly reduced, following the application of inorganic silicate amendments (Figure 4.7b). In the case of the Palmerston Ferrosol subsoil, all amendments significantly increased Si and P availability, and decreased $\text{PBI}_{\text{Colwell}}$ compared to the control treatment (Figures 4.8a and 4.8b). For both soil depths, the Mono-Si amendment resulted in the highest Si availability, while the FMP amendment resulted in the highest P_{Colwell} and the lowest $\text{PBI}_{\text{Colwell}}$ value. The values of $\text{PBI}_{\text{Colwell}}$ decreased as follows: Control > Mono-Si = Ac-Ca-Si > Ac-Mg-Si > FMP (Figures 4.7 and 4.8).

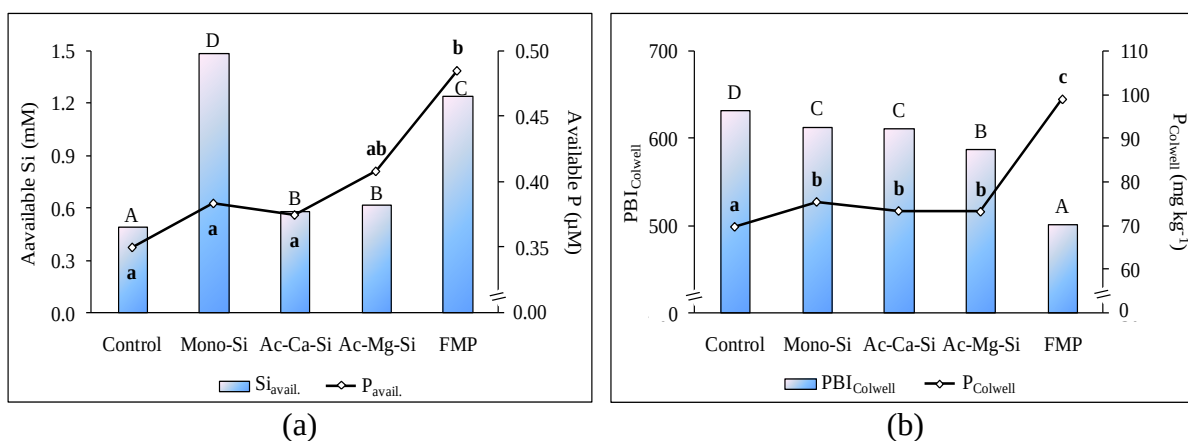


Figure 4.7 Effect of inorganic silicate amendments on (a) Si, and P availability and (b) P sorption capacity and Colwell-P of the Palmerston Ferrosol at the soil depth of 0 - 20 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

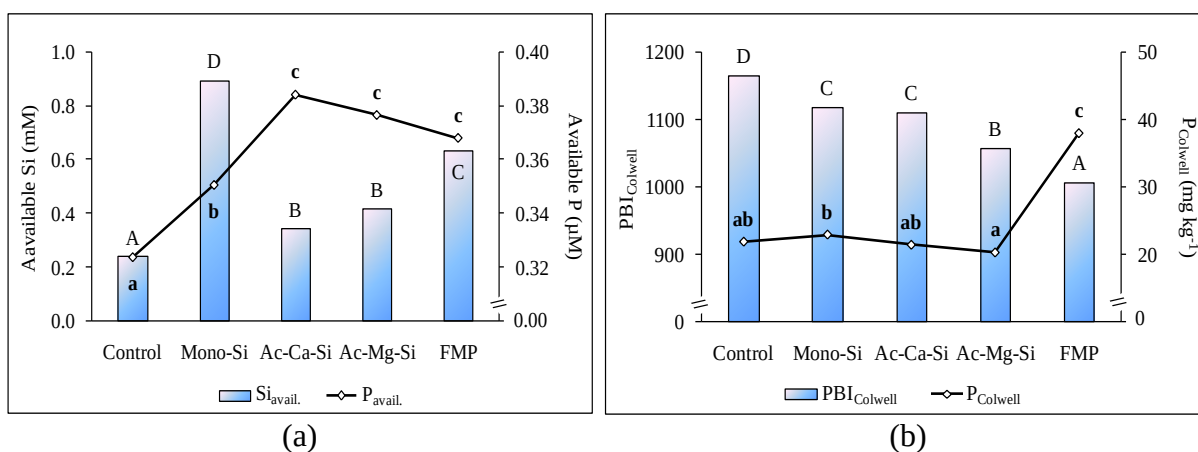


Figure 4.8 Effect of inorganic silicate amendments on (a) Si and P availability and (b) P sorption capacity and Colwell-P of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

In order to investigate the combined effect of Ca, P and Si contained in the FMP amendment on P sorption capacity, lime and Ca-P treatments were compared with the FMP treatment to separate out the Ca and Ca plus P effects, respectively, and the results for the Palmerston Ferrosol topsoil and subsoil are given in Figures 4.9 and 4.10, respectively. In comparison with the control treatment, a significant increase in Si availability was only found in the FMP treatment (Figure 4.9a); the Ca-P and FMP treatments significantly increased both P availability and P_{Colwell} , but the lime treatment had no significant effect (Figures 4.9a and 4.9b). The $\text{PBI}_{\text{Colwell}}$ values of all treatments decreased significantly, and the greatest effect was found in the FMP treatment (Figure 4.9b). In the case of the subsoil, the only significant increase in Si availability was observed in the FMP treatment and, in P availability, the only significant effect was observed in the Ca-P treatment (Figure 4.10a). Both Ca-P and FMP treatments significantly increased P_{Colwell} , whereas the lime treatment had no effect (Figure 4.10b). The $\text{PBI}_{\text{Colwell}}$ values decreased significantly in all treatments in the order: Ca-P = FMP > Lime > Control (Figure 4.10b).

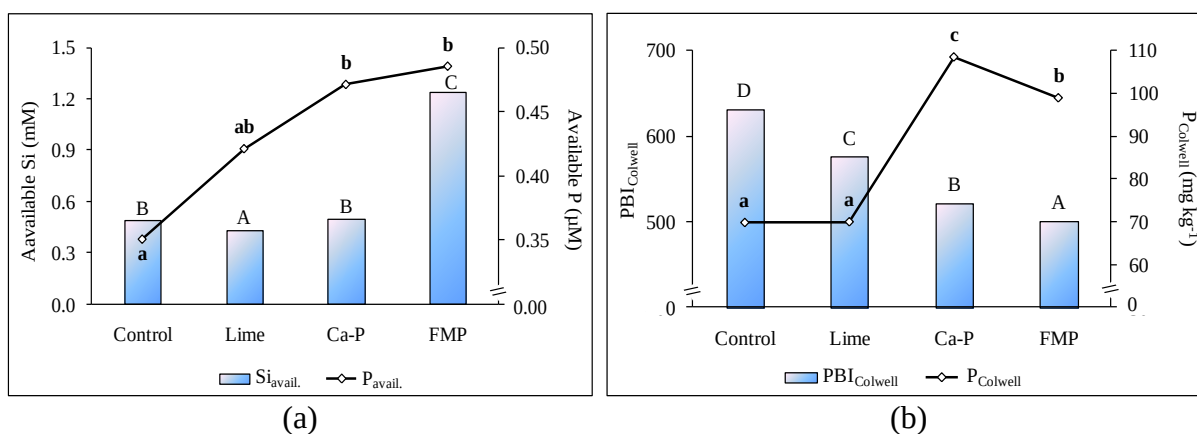


Figure 4.9 Combined effects of Ca, P and Si amendments on (a) Si and P availability and (b) P sorption capacity and Colwell-P of the Palmerston Ferrosol for the soil depth of 0 - 20 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

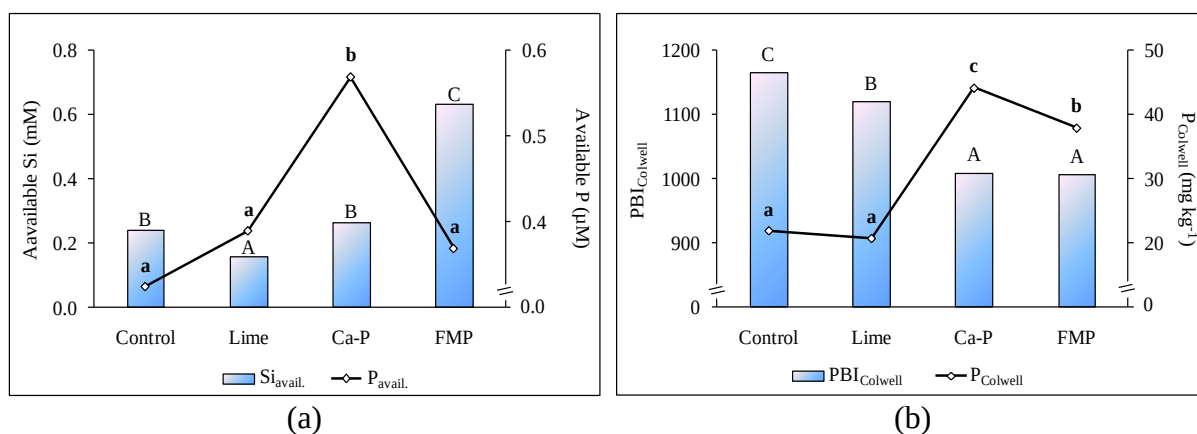


Figure 4.10 Combined effects of Ca, P and Si amendments on (a) Si and P availability and (b) P sorption capacity and Colwell-P of the Palmerston Ferrosol for the soil depth of 20 - 40 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

The effect of organic amendments ($125 \text{ kg Si ha}^{-1}$) on Si and P contents and P sorption capacity of the Palmerston Ferrosol subsoil are presented in Tables 4.11a and 4.11b. Silicon availability and P_{Colwell} increased significantly, and $\text{PBI}_{\text{Colwell}}$ decreased in the *Tithonia* treatment compared to the sugarcane and the control treatments. In comparison with the control treatment, although the sugarcane treatment significantly increased P availability to the same extent as *Tithonia*, it did not increase Si availability, P_{Colwell} or $\text{PBI}_{\text{Colwell}}$ (Figures 4.11a and 4.11b). In the case of the Mono-Si treatment ($125 \text{ kg Si ha}^{-1}$), there was no significant increase in P availability or P_{Colwell} , but Si availability increased significantly. The $\text{PBI}_{\text{Colwell}}$ of this treatment was significantly lower than that of the control treatment (Figures

4.11a and 4.11b). These results, together with the results of the topsoil, suggest that Si concentration in the soil solution played an important role in the reduction of P sorption capacity of the Palmerston Ferrosol.

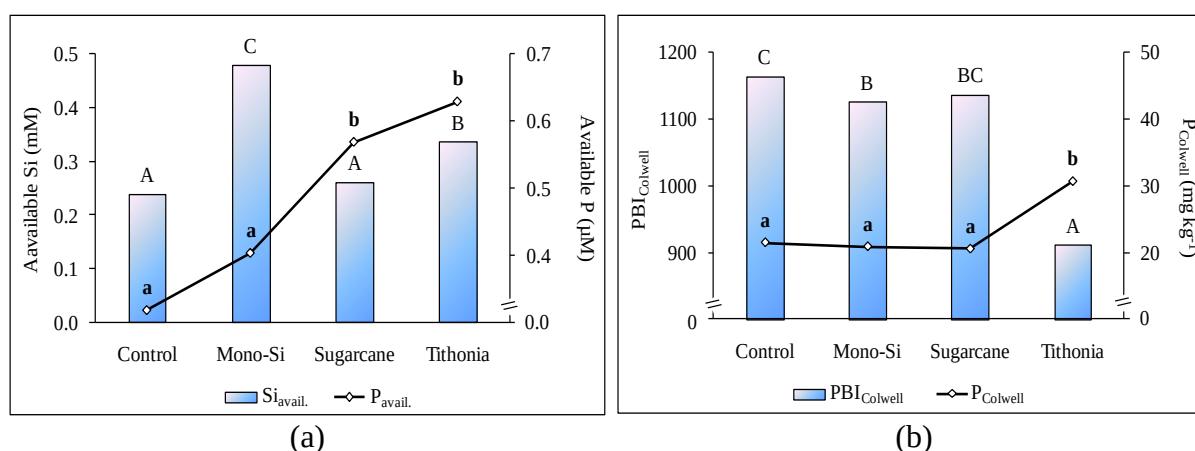


Figure 4.11 Effect of organic amendments on Si-, P availability (a) and P sorption capacity (b) of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters at the column (or line) are significantly different at $P < 0.05$

The Hydrosol and Vertosol

The effect of inorganic silicate amendments on P sorption capacities of the Hydrosol and Vertosol subsoil are presented in the Figures 4.12 and 4.13. In comparison with the Palmerston Ferrosol subsoil ($PBI_{Colwell} > 1000$, Figures 4.10b and 4.11b), the Hydrosol and Vertosol subsoils exhibited comparatively low P sorption capacity ($PBI_{Colwell} < 200$, Figures 4.12b and 4.13b), particularly that of the Hydrosol ($PBI_{Colwell} < 60$, Figure 4.12b). For the Hydrosol subsoil, only the FMP amendment caused a significant increase in P availability and $P_{Colwell}$, while the application of both Mono-Si and FMP amendments significantly increased Si availability and significantly decreased $PBI_{Colwell}$ (Figures 4.12a and 4.12b). The same trends were observed in the Vertosol subsoil where both Mono-Si and FMP treatments significantly increased Si availability and decreased $PBI_{Colwell}$ compared to the control treatment (Figures 4.13a and 4.13b). In contrast, the Ac-Ca-Si and Ac-Mg-Si treatments did not significantly affect Si availability, and they exhibited an insignificant decrease in $PBI_{Colwell}$ compared to the control treatment (Figures 4.12 and 4.13).

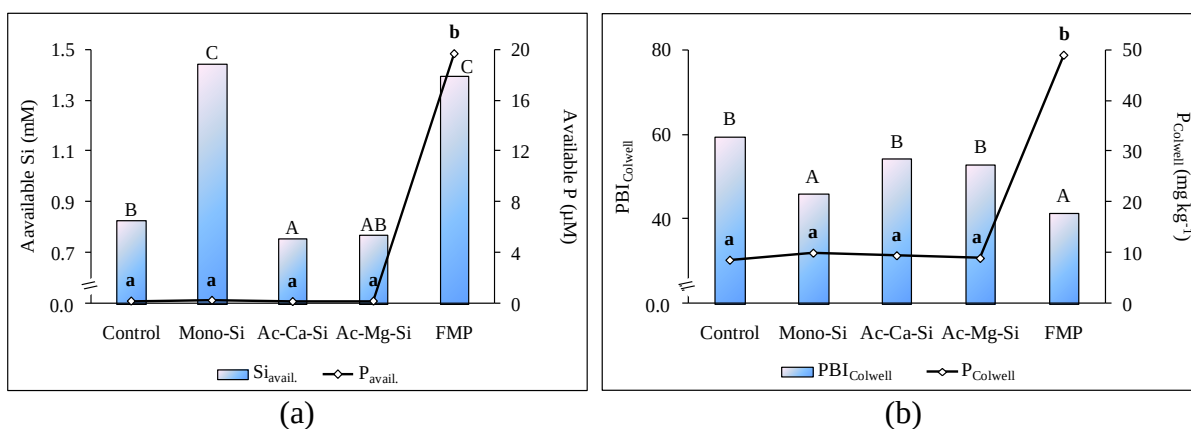


Figure 4.12 Effect of inorganic silicate amendments on (a) Si and P availability, and (b) P sorption capacity and Colwell-P of the Hydrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

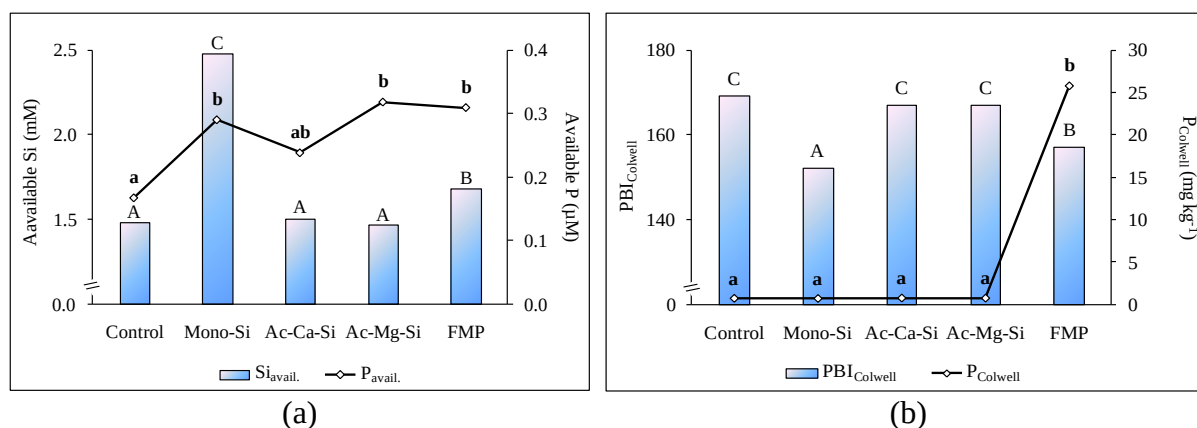


Figure 4.13 Effect of inorganic silicate amendments on (a) Si and P availability and (b) P sorption capacity and Colwell-P of the Vertosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

The combined effects of Ca, P and Si on P sorption capacities of the Hydrosol and Vertosol are given in Figures 4.14 and 4.15, respectively. The application of lime did not increase soil P availability or $\text{P}_{\text{Colwell}}$, but the Ca-P treatment significantly increased both P availability and $\text{P}_{\text{Colwell}}$ compared to the control and even to the FMP treatment. However, the Ca-P treatment did not cause any increase in Si availability (Figure 4.14a), thus $\text{PBI}_{\text{Colwell}}$ of this treatment did not decrease in comparison with the control treatment (Figure 4.14b). In contrast, the lime treatment significantly decreased $\text{PBI}_{\text{Colwell}}$, and this may be attributed to both a significant increase in soil pH (Table 4.7) and increased Si availability caused by lime amendment (Figure 4.14a). However, the $\text{PBI}_{\text{Colwell}}$ value of the lime treatment (50) was still higher than

that of FMP treatment (47) (Figure 4.14b). In contrast to its lack of effects in the Hydrosol, the Ca-P treatment significantly increased Si availability (Figure 4.15a), and significantly decreased $PBI_{Colwell}$ of the Vertosol subsoil compared to the control treatment (Figure 4.15b). The lime treatment significantly decreased Si availability in the Vertosol and significantly increased $PBI_{Colwell}$ of the soil compared to the control treatment (Figure 4.15). In conclusion, lime tended to increase (but not significantly) Si availability in the Hydrosol and P (as Ca-P) promoted Si availability in the Vertosol; these increases in Si availability were accompanied by decreases in the P sorption capacities in both soils.

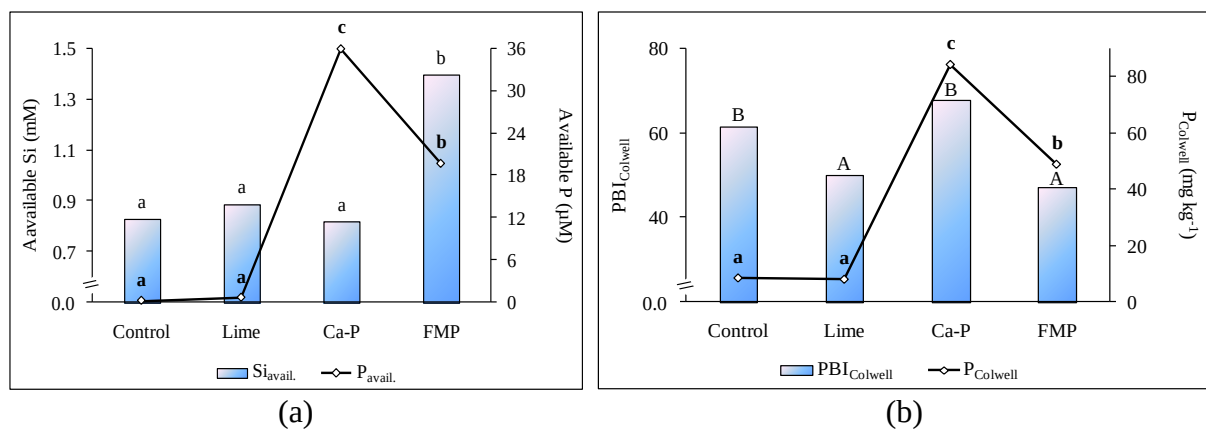


Figure 4.14 Combined effects of Ca, P and Si amendments on (a) Si and P availability and (b) P sorption capacity and Colwell P of the Hydrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

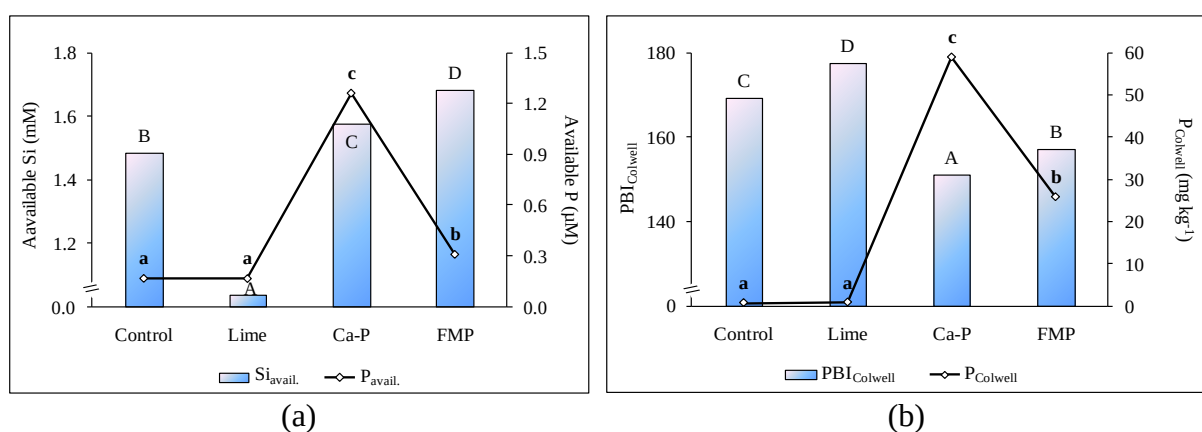


Figure 4.15 Combined effects of Ca, P and Si amendments on (a) Si and P availability and (b) P sorption capacity and Colwell P of the Vertosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the column (or line) are significantly different at $P < 0.05$

4.3.3 Changes in Fe-, Al- and Si hydrous oxides

The Palmerston Ferrosol topsoil and subsoil

The effect of inorganic silicate amendments on oxalate extractable Fe, Al and Si (Fe_{Ox} , Al_{Ox} and Si_{Ox} , respectively) of the Palmerston Ferrosol topsoil and subsoil are shown in Figures 4.16 and 4.17, respectively. The highest levels of Si_{Ox} in both soil depths were observed in the Mono-Si and FMP treatments and these were significantly ($P < 0.05$) different from the control, Ac-Ca-Si and Ac-Mg-Si treatments. The Ac-Mg-Si treatment significantly increased Si_{Ox} only in the subsoil, with Si_{Ox} being lower in the topsoil for both Ac-Ca-Si and Ac-Mg-Si treatments compared to the control treatment (Figures 4.16 and 4.17). Except for the Mono-Si treatment, the other silicate treatments significantly decreased Fe_{Ox} in the topsoil (Figure 4.16), whereas only the Ac-Ca-Si treatment significantly reduced Fe_{Ox} in the subsoil compared to the control treatment (Figure 4.17). Oxalate extractable Al tended to decrease in all inorganic silicate treatments, but these differences were not significant ($P=0.05$). Similarly, the application of lime or Ca-P amendment did not decrease Al_{Ox} or increase Si_{Ox} in either soil depth (Figures 4.18 and 4.19), but they did decrease Si_{Ox} in the topsoil compared to the control treatment (Figure 4.18). Lime significantly decreased Fe_{Ox} in the topsoil (Figure 4.18), yet it increased Fe_{Ox} in the subsoil (Figure 4.19). The only difference between the lime and Ca-P treatments in comparison to the FMP treatment was the lower Si_{Ox} in the former treatments at both soil depths.

In comparison with the control treatment, the application of *Tithonia* amendment to the Palmerston Ferrosol subsoil significantly increased Si_{Ox} and significantly decreased both Al_{Ox} and Fe_{Ox} (Figure 4.20). Compared to the control treatment, sugarcane caused significantly ($P < 0.05$) increased Fe_{Ox} (Figure 4.20).

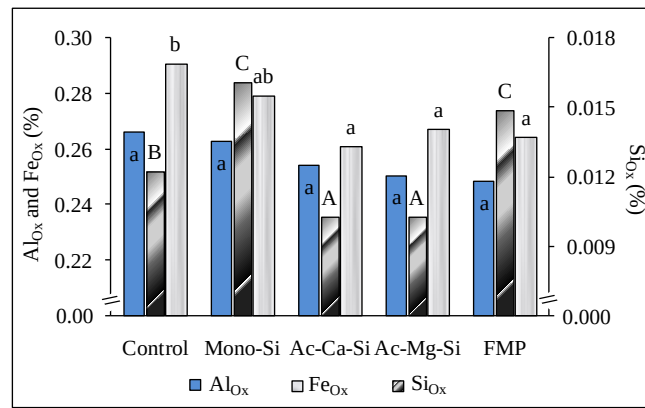


Figure 4.16 Effect of inorganic silicate amendments on Al_{Ox} , Fe_{Ox} and Si_{Ox} of the Palmerston Ferrosol at the soil depth of 0 - 20 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

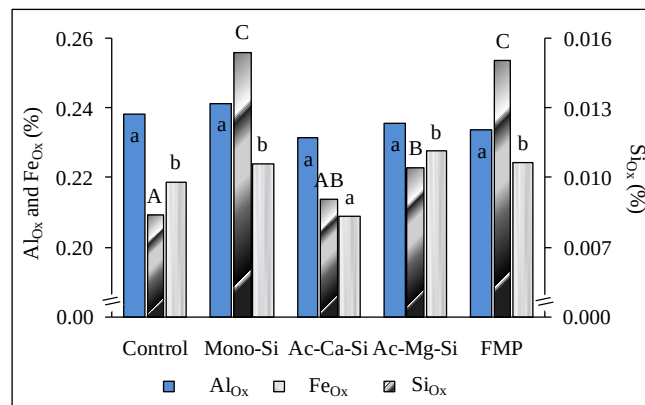


Figure 4.17 Effect of inorganic silicate amendments on Al_{Ox} , Fe_{Ox} and Si_{Ox} of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

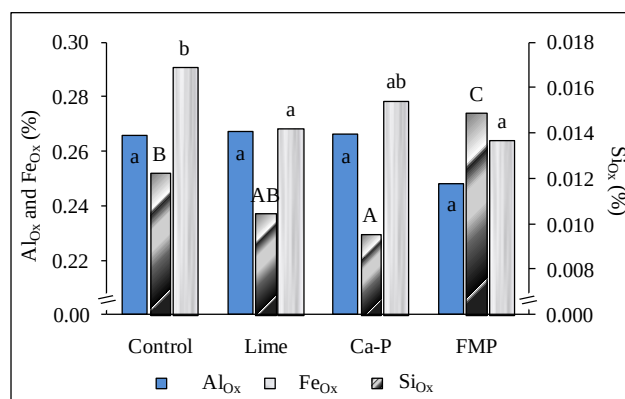


Figure 4.18 Combined effects of Ca, P and Si on Al_{Ox} , Fe_{Ox} and Si_{Ox} of the Palmerston Ferrosol at the soil depth of 0 - 20 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

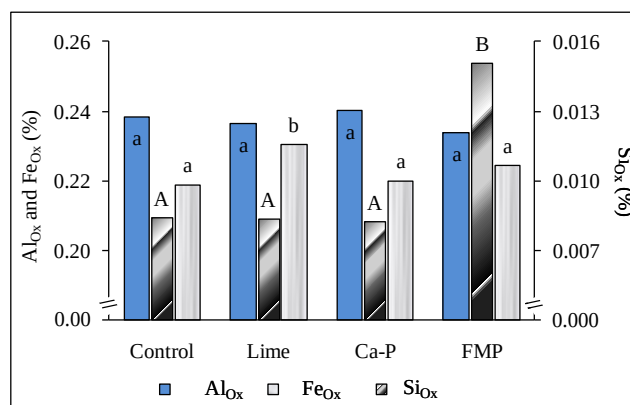


Figure 4.19 Combined effects of Ca, P and Si on Al_{Ox}, Fe_{Ox} and Si_{Ox} of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

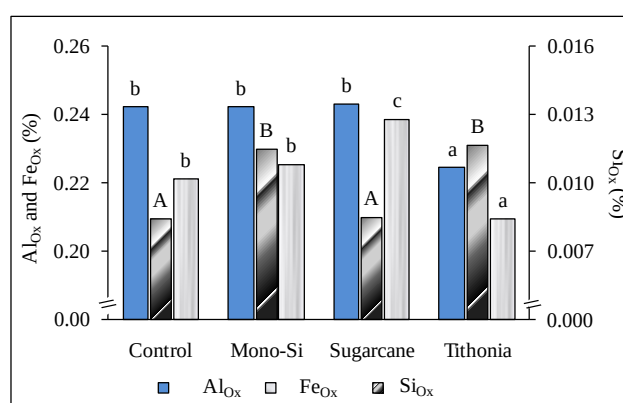


Figure 4.20 Effect of organic amendments on Al_{Ox}, Fe_{Ox} and Si_{Ox} of the Palmerston Ferrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

The Hydrosol and Vertosol

Changes in Al_{Ox}, Fe_{Ox} and Si_{Ox} of the Hydrosol and Vertosol following the application of inorganic silicate amendments are presented in Figures 4.21 and 4.22, respectively. Although Fe_{Ox} of the Hydrosol was not changed significantly by applying the inorganic silicate amendments, a significant decrease in Al_{Ox} was observed (Figure 4.21). In the Vertosol, the silicate treatments did not change Al_{Ox} while Fe_{Ox} values were higher in the FMP and Ac-Mg-Si treatments than in the control treatment (Figure 4.22). Oxalate extractable Si concentrations in both the Hydrosol and Vertosol were only significantly increased in the Mono-Si and FMP treatments (Figures 4.21 and 4.22).

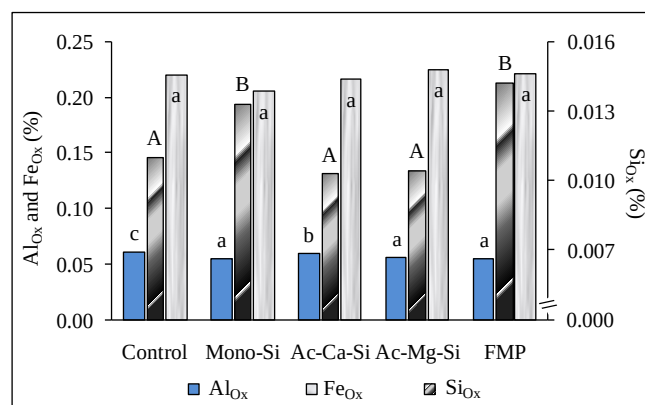


Figure 4.21 Effect of inorganic silicate amendments on Al_{Ox}, Fe_{Ox} and Si_{Ox} of the Hydrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

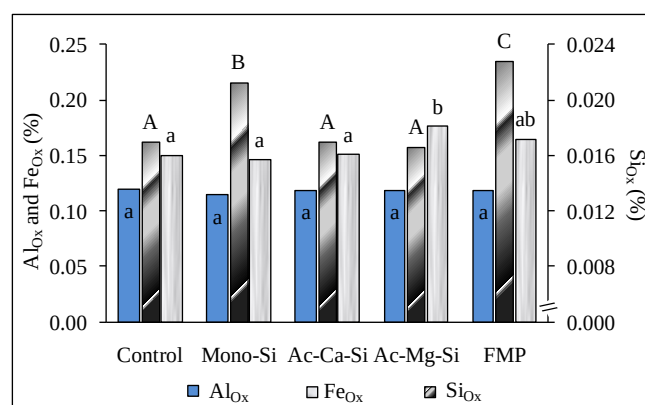


Figure 4.22 Effect of inorganic silicate amendments on Al_{Ox}, Fe_{Ox} and Si_{Ox} of the Vertosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

Lime and Ca-P treatments were used to compare the effect of these treatments with the FMP treatment on changes in Al_{Ox}, Fe_{Ox} and Si_{Ox} of the Hydrosol and Vertosol (Figures 4.23 and 4.24). Similar to the FMP treatment, both lime and Ca-P treatments significantly decreased Al_{Ox}, but had no effect on Fe_{Ox} of the Hydrosol compared to the control treatment (Figure 4.23). In the Vertosol, similar results were observed for Al_{Ox} and Fe_{Ox}, with the values being similar to that of the control treatment (Figure 4.24). The Ca-P treatment did not significantly change Si_{Ox} in either soil, but the lime treatment significantly increased Si_{Ox} in the Vertosol but not in the Hydrosol (Figures 4.23 and 4.24). It can be concluded that the main difference between both lime and Ca-P, and FMP amendment in both soils is the higher Si_{Ox} observed in the latter treatment.

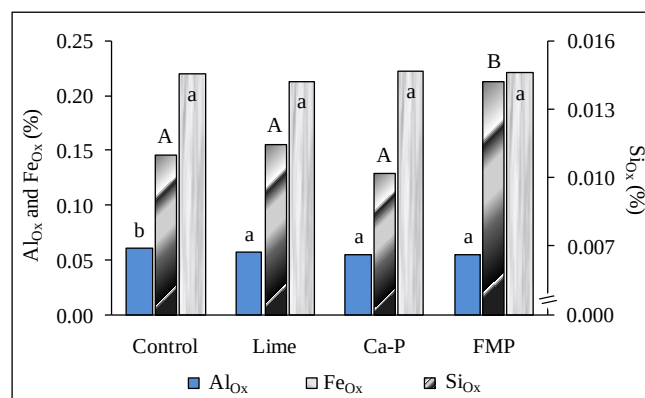


Figure 4.23 Combined effects of Ca, P and Si on Al_{Ox} , Fe_{Ox} and Si_{Ox} of the Hydrosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

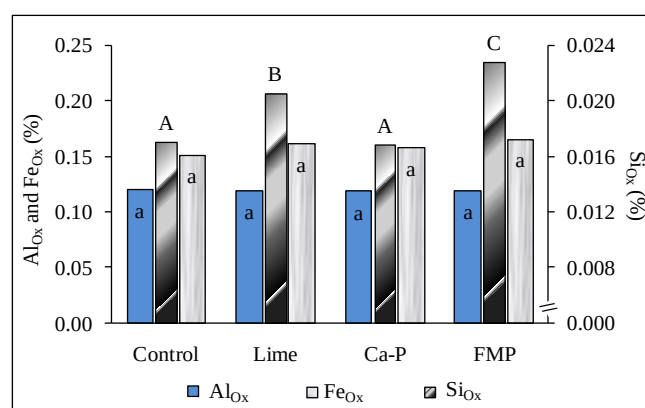


Figure 4.24 Combined effects of Ca, P and Si on Al_{Ox} , Fe_{Ox} and Si_{Ox} of the Vertosol at the soil depth of 20 - 40 cm. Treatment means with different letters on the same pattern columns are significantly different at $P < 0.05$

4.4 Discussion

The initial surface charge characteristics and P sorption capacities of selected VCS have been discussed in Chapter 3. Changes in these properties following the application of inorganic silicate and organic amendments are discussed in this section.

4.4.1 Effect of silicon on surface characteristics of variable charge soils

Effect of inorganic silicate amendments

As previously discussed in Chapter 2 and 3, soil pH is known to be one of the most important factors in the development of charge on variable charge surfaces. In all investigated soils, pH

increased following the application of inorganic silicate amendments in the order: FMP > Ac-Mg-Si > Ac-Ca-Si (Tables 4.4 and 4.5). Although it has previously been demonstrated that Ac-Mg-Si (Berthelsen *et al.*, 2003) and Ac-Ca-Si (Tavakkoli *et al.*, 2011) had no effect on pH following application, Ac-Mg-Si increased pH of all investigated soils and Ac-Ca-Si increased pH of the Palmerston Ferrosol (both soil depths), but not of the Hydrosol or Vertosol. However, these increases were much less than those caused by FMP amendment. This can be explained by the Neutralising Value of the FMP; neither Ac-Mg-Si nor Ac-Ca-Si had measureable Neutralising Values (Table 4.3). Also, P contained in FMP was involved in this effect. Displacement of OH⁻ into solution by ligand exchange with P anions on variable charge surfaces is well known and would increase soil pH following P application.

The pH of the applied Mono-Si solution was around 4.0, which was lower than the actual pH of all investigated soils (4.27 – 5.13). Therefore, the overall soil pH was reduced by the application of Mono-Si; a reduction of 0.05 pH unit occurred for the Palmerston topsoil and the Hydrosol, and 0.10 pH unit for the Vertosol compared to that of the control treatment (Tables 4.4 and 4.5). However, Mono-Si application did not decrease the pH of the Palmerston Ferrosol subsoil which had a low initial pH (4.27) and the highest pH buffer capacity of all the studied soils (Table 4.8).

The sign and magnitude of delta pH reflects the sign and magnitude of the surface charge of soil systems with a mixture of variable and permanent charge minerals (Uehara and Gillman, 1981). These authors asserted that a delta pH value of positive, zero or small negative (< -0.5) generally indicates a soil dominated by variable charge minerals, whereas a large negative value of delta pH indicates a high negative charge density. The results of this current study are consistent with these statements. For example, the Palmerston Ferrosol is dominated by variable charge minerals (see Chapter 3) and the delta pH value was nearly zero for the topsoil and positive for the subsoil; thus the total net negative charge (CEC_T plus AEC) was very low and less than 1.0 cmol_c kg⁻¹ for the topsoil, and the subsoil had a total net positive charge (Table 4.4). On the other hand, the Hydrosol and Vertosol subsoils were dominated by permanent charge surfaces and the negative values of delta pH were higher than -0.5 and -1.0, respectively; thus the total net negative charges of these soils (particularly the Vertosol) were much higher than those of the Palmerston Ferrosol, (Table 4.5). Similar results were observed by Berthelsen *et al.* (2003) for Ferrosols and Hydrosols from north Queensland. In their study of several highly weathered soils, Uehara and Gillman (1981) postulated that the differences in charge characteristics between a Hydrandept with low negative or zero delta pH values and

low CEC compared to a Eutrandept with high negative delta pH values and high CEC was due to the former soil being more highly weathered, and therefore more de-silicated than the latter soil. Our findings confirm this situation, with the Palmerston Ferrosol having very low total, amorphous and available Si contents compared to the Hydrosol and Vertosol (Tables 3.1 and 4.1), and highly significant correlation coefficients (around 0.9) being observed for the relationship of CEC_T and TNC with Si_{Ox} and available Si (Table 4.9).

Following the application of inorganic silicates, the negative delta pH value of the Palmerston Ferrosol topsoil increased (Table 4.4), but those of the Hydrosol and Vertosol did not change or even decreased (Table 4.5). These results are consistent with the work of Berthelsen *et al.* (2003) who found that silicate amendments significantly increased negative delta pH values of a Ferrosol dominated by variable charge minerals with a low negative delta pH value, but did not change those of a soil dominated by permanent charge minerals with a high negative delta pH value. They suggested that the increases were likely due to the formation of amorphous alumino-silicate surfaces as a result of silicate amendments applied to the soil. According to the definition of delta pH, a high negative delta pH value is the result of a high pH in water and/or a low pH in 1 M KCl. Because soils with dominantly negative charge exhibit major exchange of H^+ and Al^{3+} by K^+ causing the pH in 1 M KCl to be more acidic than that in water (Berthelsen *et al.*, 2003). In our study, the lower negative delta pH values of the Ac-Ca-Si and Ac-Mg-Si treatments compared to the other treatments in the Hydrosol and Vertosol (Table 4.5) can be primarily ascribed to the Ca and Mg contained in these amendments partly displacing exchangeable H^+ and Al^{3+} ions, thus resulting in a lower pH in KCl.

Table 4.9 Linear correlation coefficient (r) matrix for the relationships between soil properties and surface charge characteristics for all soils

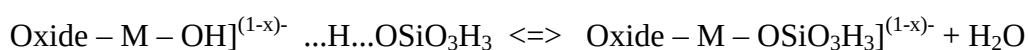
	¹ CEC_T	² TNC	³ NPC	⁴ NVC
pH _(0.002 M CaCl2)	0.77***	0.79***	0.71***	0.77***
Δ pH	-0.89***	-0.91***	-0.90***	-0.78***
Al_{Ox}	-0.53***	-0.56***	-0.59***	-0.42***
Fe_{Ox}	-0.80***	-0.76***	-0.73***	-0.68***
Si_{Ox}	0.81***	0.80***	0.77***	0.72***
Available Si	0.76***	0.77***	0.78***	0.63***

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

¹ total cation exchange capacity; ² total net charge; ³ net permanent charge; and ⁴ net variable charge

In our study, the application of inorganic silicate amendments reduced pH_0 of the Palmerston Ferrosol, thus increasing CEC_T and decreasing AEC of the soil. These results can be attributed to the specific adsorption of Si on variable charge surfaces of the soil causing a lowering of pH_0 to about 2.0 (Sposito, 1984) in contrast to the high pH_0 of the Fe and Al hydrous oxides (about 8.0, Sposito, 1984) that dominate in the soil (Parfitt, 1980; Uehara and Gillman, 1981). Specific adsorption of anions (silicate and to a greater extent, phosphate) by goethite, gibbsite (Hingston and Raupach, 1967; Hingston *et al.*, 1968; Hingston *et al.*, 1972; Parfitt, 1978; Mott, 1981) and soils (Obihara and Russell, 1972; Parfitt, 1978; Wann and Uehara, 1978a; Uehara and Gillman, 1981) have been extensively studied over the last 40 years. All these authors suggest that these anions are adsorbed on soil minerals by ligand exchange with surface OH^- or OH_2 groups, reducing positive surface charge and/or increasing negative surface charge. This simply means that the adsorption of anions makes the surface more negative and it requires a higher concentration of H^+ in solution to reach the point of zero charge (Mott, 1981).

According to Hingston *et al.* (1972), the Langmuir equation has been used to determine the specific adsorption of a range of anions, including silicate and phosphate, on surfaces over a pH range from 2.5 to 12.5. The authors determined the maximum adsorption of anions (termed the ‘adsorption envelope’) by plotting Langmuir curves over this pH range. This shows the influence of H^+ on the adsorption process and indicates that the important effect is not the charge on the hydrous oxide surfaces but the dissociation of the conjugate acid of the anion. The adsorption envelope clearly showed that the amount of specific adsorption was not only a function of the concentration of the anion in solution because there was a considerable sorption of Si at pH 5.0, at which pH the concentration of the anion $H_3SiO_4^-$ relative to the undissociated acid H_4SiO_4 is less than 0.01% (Mott, 1981). Hingston *et al.* (1972) also found that a weak acid, such as H_4SiO_4 , can be adsorbed on negative or neutral surfaces. They explained this observation by proposing that the negative free energy of adsorption of the anion ligand is sufficiently high to dissociate the acid at the hydrous oxide surface. The proton released from this process reacts with the $OH^{(1-x)-}$ surface site to form an OH_2^{x+} group. This is then replaced by the negatively charged anion remaining after the surface-induced dissociation, as shown in the following equation.



This mechanism does not contribute to any negative charge on the surface, but the new ligand alters the charge distribution at the site, and because H_4SiO_4 dissociates less easily than H_2O , there is a tendency for a neighbouring water ligand to dissociate to hydroxyl (Mott, 1981). Therefore, the change in negative charge observed on addition of each Si group is not one unit but about 0.5 unit of charge, and this change seems to be virtually independent of pH and the $\text{OH}^-/\text{OH}_2^+$ ratio on the surface (Hingston *et al.*, 1972). All these reactions can be used to explain the lesser extent of increases in CEC_T for the Hydrosol and Vertosol than that of the Palmerston Ferrosol, and also for the lesser extent of changes in the topsoil than the subsoil of the Palmerston Ferrosol following the application of inorganic silicate amendments (Tables 4.4 and 4.5). The FMP amendment showed the greatest effect on all investigated soils. This suggests that specific adsorption of P was involved in generating more negative charge (higher CEC_T) than that produced by the other amendments. Phosphorus sorption curves indicate that specific adsorption of P on synthetic oxides, goethite, gibbsite (Hingston *et al.*, 1972) and soils (Obihara and Russell, 1972) decreases with increasing pH. All these authors postulate that greater specific adsorption of anions will contribute more negative charge and less positive charge to variable charge surfaces. Therefore, the greatest effect of FMP was observed in the Palmerston subsoil with lowest pH compared to the other soils.

In terms of causing increases in CEC_T and decreases in AEC of all soils, FMP had a greater effect than any other inorganic amendment (Tables 4.4 to 4.7). This can be attributed to the combined effect of Ca, Mg, P and Si contained in FMP causing soil pH and negative delta pH to increase and pH_0 to decrease. These effects can be confirmed by the significant positive correlation of soil pH, and negative correlation of delta pH and pH_0 , with CEC_T (Tables 4.9 and 4.10). However, although pH_0 values were lower in the Ac-Mg-Si treatment than those in the FMP treatment for both depths of the Palmerston Ferrosol, CEC_T in the former was lower than that in the latter for both soil depths (Table 4.4). This can be explained by specific adsorption of Ca contained in FMP partly increasing pH_0 . Uehara and Gillman (1981) demonstrated that specifically adsorbed cations on an hydrous oxide surface at zero net charge would cause a net positive charge, and the pH would have to be raised to reach a new pH_0 . Uehara and Keng (1975) observed that specifically adsorbed cations shifted the pH_0 to a higher value and changed total net surface charge towards a more positive value (McBride, 1994). For example, the adsorption of Ca^{2+} into the Stern layer has been shown to cause charge reversal in an Oxisol (Wann and Uehara, 1978a, b). In our study, the pH_0 values of the Palmerston Ferrosol in the lime treatment were higher than those in the control treatment (Table 4.6). When making comparisons between lime, Ca-P and FMP treatments, the results

consistently showed that the FMP treatment had a greater effect on increases in CEC_T and decreases in AEC than the lime and Ca-P treatments, particularly for the Palmerston Ferrosol (Tables 4.6 and 4.7). These results suggest that Si, again, had a beneficial effect on surface charge characteristics of VCS. However, except for the FMP treatment, none of the inorganic silicate amendments (Mono-Si, Ac-Ca-Mg and Ac-Mg-Si) caused any changes in CEC_T or AEC for the Hydrosol (Table 4.5). This may be due to the following reasons: a) these amendments do not change pH of the soil; b) the native Si of the soil is very high (35.5%; Table 4.1); and c) permanent charge is dominant in this soil (see Chapter 3). Therefore, Si added by the amendments did not have any effect on the change of charge surfaces of this soil.

Although surface charge characteristics of all investigated soils were significantly negatively correlated with Fe_{Ox} and to a lesser extent with Al_{Ox} (Table 4.9), there were only significant reductions in Fe_{Ox} of the Palmerston Ferrosol topsoil following application of Ac-Ca-Si, Ac-Mg-Si, lime and Ca-P (Figures 4.16 and 4.18). These reductions tended to be associated with reductions in Si_{Ox} suggesting the formation of a crystalline phase of Fe silicates that was not mirrored in the formation of a crystalline Al silicate because Al_{Ox} levels were not affected by treatment (Figures 4.7, 4.8, 4.12 and 4.13). However, the neoformation of crystalline Fe is highly speculative and biological processes may also be involved. Surface charge characteristics of the soils showed significant positive correlations with Si_{Ox} and Si availability (Table 4.9), and the multiple linear regression equations of best fit for surface charge characteristics show that soil pH, Fe_{Ox} and/or Al_{Ox} and Si_{Ox} and/or Si availability are all significant factors in determining these characteristics (Table 4.11). This indicates that the impacts of inorganic silicate amendments on surface charge characteristics of the soils are due to their effects on soil pH, Si_{Ox} and Si availability.

Table 4.10 Linear correlation coefficient (r) matrix for the relationships between point of zero charge (pH₀) and point zero of net charge (PZNC), and surface charge characteristics

	¹ CEC _T (pH _{5.0})	² Δ CEC _T	³ TNC	⁴ NPC	⁵ NVC
pH ₀ ^A	-0.90***	-0.85***	-0.81***	-0.87***	-0.53***
PZNC ^B	-0.91***	-0.90***	-0.86***	-0.86***	-0.84***

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$;

^A pH₀ of the Hydrosol and Vertosol omitted from correlations; ^B only Palmerston Ferrosol PZNC used

¹ total cation exchange capacity at soil pH of 5.0; ² delta CEC_T at different soil pHs of 5.5 and 4.5;

³ total net charge; ⁴ net permanent charge; ⁵ net variable charge

Table 4.11 Multiple linear regressions for the relationships between soil properties and surface charge characteristics

Multiple linear regression equations	R ²
¹ CEC _T = -2.3 (±1.9) + 1.3 (±0.3) pH*** - 20.1 (±3.4) Fe _{Ox} *** + 132.2 (±57.7) Si _{Ox} * + 0.9 (±0.4) Si _{availability} *	85.7
² TNC = -5.8 (±2.0) + 2.0 (±0.3) pH*** - 16.6 (±3.7) Fe _{Ox} *** + 1.8 (±0.3) Si _{availability} ***	85.4
³ NPC = -2.3 (±1.6) + 1.0 (±0.3) pH*** - 10.8 (±2.9) Fe _{Ox} *** + 1.3 (±0.2) Si _{availability} ***	78.2
⁴ NVC = -4.5 (±1.3) + 1.2 (±0.2) pH*** + 2.7 (±1.1) Al _{Ox} * - 6.9 (±2.2) Fe _{Ox} ** + 0.6 (±0.2) Si _{availability} ***	71.5

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

¹ total cation exchange capacity; ² total net charge; ³ net permanent charge and ⁴ net variable charge

Because the pH₀ values of the Palmerston Ferrosol (both soil depths) were estimated from the regression curves within the pH range used in the charge fingerprint method, the amounts of net permanent charge (NPC) and net variable charge (NVC) were computed for these soils (Figures 4.1 and 4.2). The inorganic silicate amendments, lime, Ca-P and FMP increased both NPC and, to a lesser extent, NVC in the surface soil (Figure 4.1). These results are consistent with the work of Berthelsen *et al.* (2003) who found that NVC increased to a greater extent than NPC on several VCS from north Queensland following application of silicate amendments. For the Palmerston Ferrosol subsoil, inorganic silicates, lime, Ca-P and FMP all

reduced the AEC due to NPC to very low levels, and Ac-Mg-Si, Lime, Ca-P and FMP treatments changed the sign of the NVC from positive to negative. The PZNC for this subsoil was also estimated within the pH range of the charge fingerprint method, and it was higher than pH_0 , and thus the soil exhibited both positive NPC and NVC (Figure 4.1b). This is in agreement with the model of soils containing mixtures of permanent and variable charge surfaces reported by Uehara and Gillman (1981) and McBride (1994); these authors suggested that a reduction in PZNC is mainly due to an increase in ionic strength of the soil solution.

In order to examine the effect of inorganic silicate amendments on increases of CEC_T due to the reduction of pH_0 resulting from specific adsorption of Si, CEC_T at a constant pH 5.0 [$CEC_T(pH_{5.0})$] and the increment of CEC_T caused by 1.0 pH unit increase (ΔCEC_T) were computed for the Palmerston Ferrosol topsoil and subsoil. Both $CEC_T(pH_{5.0})$ and ΔCEC_T increased significantly with decreasing pH_0 (Figures 4.4 and 4.5) following silicate application, and this is reflected in the significant negative correlations of pH_0 with both $CEC_T(pH_{5.0})$ and ΔCEC_T (Table 4.10). Of all inorganic amendments including lime and Ca-P, FMP had the greatest effects on both soil depths. These results are consistent with the work of Van Ranst (1995, cited by Qafoku *et al.*, 2004) which suggested that increases in the negative charge of surfaces of highly weathered soils were due to a decrease in pH_0 resulting from adsorption of silicate anions on positively charged sites. In support, Noble *et al.* (2003) reported that the application of relatively small amounts of Ca silicate slag significantly increased the CEC at pH 5.5 of an Oxisol from north Queensland.

Effect of organic amendments

Soil organic matter (SOM) is the only major soil component other than silicate clays with a low pH_0 . Thus SOM compensates for the effects of desilication, maintaining a low pH_0 (Sollins *et al.*, 1988) and, therefore, at least some CEC in highly weathered VCS (Gillman, 1985). Silicon derived from the organic matter sources, mulched sugarcane trash and *Tithonia diversifolia*, were used at the rate of 125 kg Si ha⁻¹ in this study in order to investigate the effect of organic amendments on surface charge characteristics of the Palmerston Ferrosol subsoil (20 - 40 cm). The significant increase in CEC_T and decrease in AEC of the soil following application of the amendments are attributed to the increment of soil pH and decrement of pH_0 (Table 4.8). Organic matter (OM) has a low pH_0 (less than 2.5, Sollins *et al.*, 1988), and sorption of large organic anions onto particle surfaces results in an overall lowering of the soil pH_0 (Uehara and Gillman, 1981; Gillman, 1985). In addition, negatively

charged organic surfaces may combine (or mask) with positively charged Fe and Al hydrous oxides or with the positive sites at edges of clay minerals (Gillman, 1985; Zhang and Zhao, 1997). In our study, significant negative correlations between pH_0 and CEC_T ($\text{pH}_{5.0}$) as well as ΔCEC_T , were observed (Figure 4.6 and Table 4.10), and this is consistent with the observation of Sollins *et al.* (1988). In addition, the results show the organic amendments shifted the PZNC of the soil from values higher than the pH_0 to values lower than the pH_0 ; consequently, total net surface charge changed from being positive to being negative (Figure 4.3). This result is in agreement with the finding of Zhang and Zhao (1997) for a Rhodic Ferralsol in China. These authors found that after the removal of OM from this soil which contained a large amount of Fe hydrous oxides, a significant decrease in the amount of net negative charge surface and an increase in PZNC were observed. They suggested the importance of Fe hydrous oxides in the information of organo-mineral complexes in the soil. Significant negative correlations between Fe_{Ox} and NPC and NVC were found in our study (Table 4.9).

A comparison of the effects of sugarcane and *Tithonia* amendment on surface charge characteristics indicates that *Tithonia* causes a greater increase in CEC_T and a greater decrease in AEC of the soil than sugarcane. As previously discussed, this could be caused by a number of factors: a) higher soil pH caused by the higher ash alkalinity of *Tithonia* (Table 4.3); b) the lower pH_0 value observed in the *Tithonia* treatment (Table 4.8) due to specific adsorption of P and organic anions on variable charge surfaces; c) larger decreases in Fe_{Ox} and Al_{Ox} and increases in Si_{Ox} and available Si caused by *Tithonia* application (Figures 4.11 and 4.17); and d) faster decomposition of *Tithonia* than sugarcane, causing the release of a greater amount of dissolved organic C (see Chapter 6).

Tithonia application to two Ferralsols in the eastern region of South Vietnam has been shown to significantly increase soil pH and CEC and to decrease AEC (Phan, 2000). The author reported that the greater the amount of *Tithonia* applied (from 2.5 to 40 g kg⁻¹ soil, after 7 weeks of incubation at 25°C), the greater the CEC and the lower the AEC; there was up to 344% increase in CEC and 92% decrease in AEC. In our study, there was nearly a five-fold increase in CEC_T and a 100% decrease in AEC of the Palmerston Ferrosol subsoil following application of *Tithonia* at about 22 g kg⁻¹ soil and seven days of incubation at 40°C. In context however, these large percentage changes in surface charge also reflect the very low starting charge of these VCS.

It is postulated that the increase in negative charges associated with *Tithonia* application is due to the selective adsorption of organic molecules containing a high concentration of anionic groups (Perrott, 1978). Organic acids produced during *Tithonia* decomposition and their actions on pH and exchangeable Al may change surface charges (Iyamuremye and Dick, 1996). These mechanisms can be used to explain the different effects on surface charge characteristics between the organic amendment (*Tithonia*) and inorganic silicate (Mono-Si) amendment at the same application rate of 125 kg Si ha⁻¹. In fact, if the effect of Si applied in *Tithonia* or as an inorganic silicate amendment on surface charge characteristics is compared, the greatest effect is observed in the *Tithonia* treatment even though Si was applied at only half the rate of the inorganic amendments. This can be thought of as an effect of OM over and above that due to the Si contained in the organic amendment, demonstrating that OM is a very important factor in the management of VCS. However, in the case of sugarcane the effect was much less than that of the inorganic silicate amendments; this may be due to very low Si availability in sugarcane perhaps because of physical protection of the Si in cellular structures (Table 4.2) and/or the 30-day incubation period not being long enough for sugarcane decomposition. It has been shown in Chapter 6 that the amount of dissolved organic C in soil solution is much lower in sugarcane than that in the *Tithonia* treatment.

4.4.2 Effect of silicon on phosphorus sorption capacity of variable charge soils

Effect of inorganic silicate amendments

Many studies have demonstrated an improvement in P availability from soils following the addition of Si (Laws, 1951; Raupach and Piper, 1959; Roy, 1969; Roy *et al.*, 1971; Smyth and Sanchez, 1980; Exley *et al.*, 1993; Guadalix and Pardo, 1994; Owino-Gerroh and Gascho, 2004). As mentioned previously, the adsorption of the silicate ion increases with increasing pH, but the adsorption of phosphate by goethite, gibbsite and soils decreases with increasing pH, and maximum P adsorption occurs at about pH 6.4 and 11.6, a little below the two relevant phosphate ion pKs (7.2 and 12.7) (Hingston *et al.*, 1967; Hingston *et al.*, 1968; Hingston *et al.*, 1972; Obihara and Russell, 1972; Mott, 1981). The intersection point between silicate and phosphate adsorption curves is about pH 6.5. Together with the development of surface charge on variable charge minerals, this mechanism explains the preferential adsorption of phosphate anions dissociated from the strong acid (H₃PO₄) at low pH over that of silicate anion dissociated from the weak acid (H₄SiO₄) (McBride, 1994). The adsorption sites for both P and Si are mainly attributed to Fe and Al hydrous oxides contained in VCS

(Parfitt, 1980; Uehara and Gillman, 1981; Zhang and Zhao, 1997). In an early study of P and Si interactions in four acidic soils in Hawaii (Tropoctic Entrothox, Humoxic Tropohumult, Typic Hydrandept and Typic Gibbsihumux) dominated by kaolinite and Fe and Al hydrous oxides, Roy (1969) concluded that P decreased Si sorption and Si decreased P sorption, but the former effect was greater; silicon decreased P sorption most effectively at low pH, whereas the effect of P was most pronounced at high pH levels. The interactive effects of Si and P on P and Si sorption by soils are related to their solubilities in the soil solution and P desorption increases in the presence of sorbed Si (Roy, 1969). Although recent studies have been unable to confirm an effect of Si on P availability in acid soils (Ma and Takahashi, 1990a, 1991), others have demonstrated the effect of Si in decreasing P sorption, thus increasing P availability (Smyth and Sanchez, 1980; Guadalix and Pardo, 1994; Owino-Gerroh and Gascho, 2004; Lee and Kim, 2007). These results were accounted for as being the result of both increases in soil pH by applied CaSiO_3 and Na_2SiO_3 amendments (Smyth and Sanchez, 1980; Owino-Gerroh and Gascho, 2004) and specific adsorption of the silicate anion that competes with phosphate for sorption sites (Guadalix and Pardo, 1994; Lee and Kim, 2007). In relation to the present study, the inorganic silicate amendments decreased the P sorption capacity of all investigated soils, as expressed as the reduction of P buffering index, PBI (Figures 4.7, 4.8, 4.12 and 4.13). This effect can be attributed to specific adsorption of the Si anion, lowering pH_0 and increasing surface negative charge for the Mono-Si, Ac-Ca-Si, Ac-Mg-Si and FMP amendments, and the additional effect of increasing pH by FMP amendment. However, the decreases in PBI were not significant for the Ac-Ca-Si and Ac-Mg-Si treatments in the Hydrosol and Vertosol (Figures 4.12 and 4.13). As previously discussed, these two soils are dominated by permanent charge surfaces and there is therefore a low capacity for Si to be specifically adsorbed on variable charge surfaces. The Hydrosol and Vertosol also have high native Si and low PBI compared to the Palmerston Ferrosol (Table 4.1) and this may cause the negligible effect of added Si. Obihara and Russell (1972) postulated that for soils with very low adsorbed P, the ability of the silicate anion to displace phosphate increases with increasing soil pH, and that the silicate anion would be expected to release phosphate more effectively from neutral or calcareous soils than from acid soils. Exley *et al.* (1993) reported that Al was bound by both P and Si in solution to form highly insoluble aluminophosphates and hydroxyaluminosilicates, respectively, and the competitive binding was highly pH dependent, with hydroxyaluminosilicates being preferentially formed at pH above 6.6. In addition, Ca and Mg contained in Ac-Ca-Si and Ac-Mg-Si amendments should be taken into account for their effects on P sorption. It has been suggested that an increase of the Ca^{2+} concentration in solution results in the potential of the surface of adsorption

becoming less negative and consequently P sorption increases; this effect of Ca^{2+} to promote P sorption may be more important than the effect of the formation of new phosphate-sorbing surfaces in the soils as a result of the exchangeable Al precipitation (Guadalix and Pardo, 1994).

In the case of FMP amendment, a lower PBI value was observed in all soils compared to the other inorganic silicate, lime and Ca-P amendments. This result is not only due to the increase in soil pH by FMP, to Si competing with P for sorption sites and to specific adsorption of Si and P, but also to the effect of P contained in FMP desorbing Si into solution. Simultaneously applied Si and P significantly decreased P sorption by soils and increased both Si and P solubility in soil solution (Raupach and Piper, 1959; Smyth and Sanchez, 1980; Guadalix and Pardo, 1994); an increase in Si solubility alone, on the other hand, has been shown to decrease P sorption (Owino-Gerroh and Gascho, 2004; Hartono, 2008), and this effect is demonstrated by the significant negative correlation between PBI and Si availability and Si_{Ox} found in Table 4.12.

Table 4.12 Linear correlation coefficient (r) matrix and multiple linear regressions for the relationships between phosphorus sorption capacity (PBI) and soil properties

	Al_{Ox}	Fe_{Ox}	Si_{Ox}	$\text{Si}_{\text{availability}}$	$\text{P}_{\text{Colwell}}$	$\text{P}_{\text{availability}}$	CEC_{T}
PBI	0.83***	0.40***	-0.44***	-0.65***	-0.26**	0.20**	-0.70***
Multiple linear regression equation							R^2
$\text{PBI} = 988 (\pm 158) + 4103 (\pm 268) \text{Al}_{\text{Ox}}^{***} + 3563 (\pm 568) \text{Fe}_{\text{Ox}}^{***} - 17133$ $(\pm 6799) \text{Si}_{\text{Ox}}^* - 225 (\pm 54) \text{Si}_{\text{availability}}^{***}$							82.1

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

Although Al_{Ox} and Fe_{Ox} were significantly positively correlated with PBI, and the multiple linear regression equation estimated the main factors that affected PBI were also Al_{Ox} and Fe_{Ox} (Table 4.12), the inorganic silicate amendments had little or no effect on these parameters. This may be due to Fe and/or Al impurities in these amendments, particularly high Fe contained in FMP (1.67%) and Ac-Mg-Si (1.61%) (Table 4.2), and these relationships need to be investigated in further research.

Effect of organic amendments

The previous discussion of the effect of the organic amendments on surface charge characteristics of the Palmerston Ferrosol subsoil (Section 4.4.1) showed that *Tithonia* was most effective in comparison with the other silicate amendments, including sugarcane in increasing surface negative charge (CEC_T). A similar observation can be made on the relative effects of these silicate amendments on soil P sorption capacity, as measured by PBI. Because there was a significant ($P < 0.001$) negative correlation ($r = 0.70$) between PBI and CEC_T (Table 4.12). In addition, there are some other factors originating from OM that may affect soil P sorption capacity. High levels of extractable Al and/or Fe play an important role in controlling orthophosphate concentration in the soil solution of acid soils (Iyamuremye and Dick, 1996). Thus reduction of exchangeable Al and Fe by complexation/precipitation with OM amendments could have a significant effect on P sorption. In our results, *Tithonia* amendment caused a significant reduction in monomer Al concentration in soil solution of a Ferrosol from New South Wales, and the effect was much greater than that of the sugarcane treatment (see Chapter 6). This is consistent with the report of Iyamuremye and Dick (1996). These reductions may be accounted for by precipitation of Al ions by OH ions released from the exchange of ligands between organic ions and terminal hydroxyl groups of Fe and Al hydrous oxides, and/or the complexation of Al by organic molecules (Hoyt and Turner, 1975; Hue, 1992). Singh and Jones (1976) found that only organic residues with more than 0.3% P decreased P sorption and increased desorption. This can help explain the greater decrease in PBI (Figure 4.11) caused by *Tithonia* (0.42% P) than by sugarcane (0.06% P) in this study (Table 4.2). As previously discussed, Si and P availability are positively related to P sorption and the competition of Si with P on sorption sites. This is another factor leading to *Tithonia* having a greater effect on reduction of P sorption capacity of the soil than all other amendments because it contained the highest amounts of Si (80 mM) and P (64 mM) (Table 4.2). This result confirms the previous findings that *Tithonia* increased P solubility in soils more than inorganic P fertilisers (Phan, 2000; Kwabiah *et al.*, 2003b) and other organic residues (Kwabiah *et al.*, 2003a; Kwabiah *et al.*, 2003c) at the same rate of applied P.

4.5 Summary and conclusions

The effects of inorganic silicates and organic amendments during a 30-day incubation at 40°C on surface charge characteristics and P sorption capacities of the selected VCS are summarised as follows:

- Inorganic silicate amendments (Mono-Si, Ac-Ca-Si, Ac-Mg-Si and FMP) increased surface negative charge of all investigated soils and therefore the total cation exchange capacity of the soils. These amendments also decreased surface positive charge of the Palmerston Ferrosol at both soil depths. These effects were due to increases in soil pH and negative delta pH values, with specific adsorption of silicate anions resulting in lower pH_0 values of the soils.
- Inorganic silicate amendments decreased P sorption capacities of the soils by increasing surface negative charge and/or decreasing surface positive charge; by increasing soil pH and providing soluble Si to compete with P on sorption sites.
- The effects of the FMP amendment on surface charge characteristics and P sorption capacity were more pronounced than for the other inorganic silicate amendments. This amendment is a combination of Ca, Mg, P and Si elements all of have influences on surface charge characteristics and soil P sorption capacity.
- The Hydrosol and Vertosol, which are dominated by permanent negative charges, exhibited high total Si and Si availability, and low oxalate extractable Fe/Al. Therefore, they demonstrated lesser effects of inorganic silicate amendments than the Palmerston Ferrosol which is dominated by variable charge, has low Si contents and high oxalate extractable Fe/Al. Inorganic silicate amendments produced greater effects in the Palmerston Ferrosol subsoil than the surface soil because of the net positive charge occurring in this soil depth.
- Although oxalate extractable Fe and Al were closely related to surface charge characteristics and P sorption capacity of the soils, inorganic silicate amendments had little effect on these properties.
- Organic amendments (sugarcane and *Tithonia*) significantly increased surface negative charge and reduced surface positive charge of the Palmerston Ferrosol subsoil. *Tithonia* markedly decreased P sorption capacity of the soil, but application of sugarcane had lesser effects. The changes caused by *Tithonia* were much greater than those of the inorganic silicate amendments with Si applied at double the rate of that as *Tithonia*. This is due to the large amounts of Ca, Mg, P and OM applied together with the Si applied to the soil from *Tithonia*. Therefore, this amendment has an optimum effect on rectifying problems of the soil.
- Due to the additional effect of OM contained in *Tithonia* on soil properties, the effect of Si derived from *Tithonia* was not clearly verified in this study. Therefore, further research is required to confirm the effect of Si from *Tithonia* on the properties of VCS.

Chapter 5 Changes in surface charge characteristics and phosphorus sorption capacity of an acidic Red Ferrosol caused by different silicon rates and silicate amendments

5.1 Introduction

Surface charge characteristics and P sorption capacities of variable charge soils (VCS) from north Queensland and New South Wales (NSW) have been examined in Chapter 3 and the beneficial effect of Si on enhancing negative charge surface (total cation exchange capacity, CEC_T) and reducing P sorption capacity (phosphorus buffer index, PBI) of these VCS have been demonstrated in Chapter 4. The results showed that both inorganic silicate and organic amendments had greater effects on the soils dominated by variable charge surfaces (e.g., the Palmerston Ferrosol) than on the soils dominated by permanent charge surfaces (i.e., the Hydrosol and Vertosol). These effects were attributed to increases in soil pH, and lowering of the point of zero charge (PZC or pH_0) and/or point of zero net charge (PZNC) following a 30-day incubation at 40°C of the soils with silicate amendments.

As previously discussed in Chapter 2, different doses of Si application caused different results in mitigating the main problems of VCS. Therefore, the effects of a variety of silicate amendments at different rates on surface charge characteristics and P sorption capacity of another acidic Red Ferrosol from NSW following different incubation periods are investigated and presented in this chapter. In order to further examine the effect of Si on the amelioration of Al toxicity of this soil, the solutions of Si amended soil are used and presented in Chapter 6.

5.2 Materials and methods

5.2.1 Soil collection, preparation and physicochemical properties

An acidic Red Ferrosol (0 - 30 cm) (Isbell, 1996) was collected from Alstonville Horticultural Research Station, Alstonville, NSW (hereafter referred as to Alstonville Ferrosol). The soil was air-dried, passed through a 2mm-sieve and well mixed before taking representative samples for initial soil analysis, and setting up of treatments. The results from a mid-infrared reflectance (MIR) scan showed that the soil has clay mineralogy dominated by kaolinite, goethite and gibbsite.

Selected physicochemical properties of the soil are as follows: bulk density, 1.3 Mg m^{-3} ; field capacity, 35 %; clay, 71 %; total organic carbon, 5.05 %; pH(1:5) in 0.01 M CaCl_2 , 4.02; electrical conductivity, 0.053 dS m^{-1} ; oxalate extractable Fe, Al and Si, 0.70, 0.60 and 0.03 %, respectively; crystalline Fe and Al, 11.1 and 1.4 %, respectively; and exchangeable acidity, $2.34 \text{ cmol}_c \text{ kg}^{-1}$ of which exchangeable Al^{3+} and H^+ are 2.08 and $0.26 \text{ cmol}_c \text{ kg}^{-1}$, respectively.

5.2.2 Silicate amendments, soil treatments and incubations

Silicate amendments

Using the same treatments and methodologies as described in Section 4.2.2 (Chapter 4), both inorganic silicate and organic amendments were used to investigate the effect of Si on surface charge characteristics and P sorption capacity of this Ferrosol. The inorganic silicate amendments comprised monosilicic acid (Mono-Si), calcium silicate (Ca-Si), acidulated calcium silicate (Ac-Ca-Si), magnesium silicate (Mg-Si), acidulated magnesium silicate (Ac-Mg-Si) and fused magnesium phosphate (FMP); mulched sugarcane trash and whole plant tops of *Tithonia diversifolia* were utilised as organic amendments (hereafter referred to as sugarcane and *Tithonia*, respectively). Chemical composition of the investigated amendments are presented in Table 5.1 (as shown in Chapter 4 for the measured methods).

Table 5.1 Chemical compositions of the investigated amendments

Amendment	Ca	Mg	Fe	P	Si	¹ P _{avail.}	² Si _{avail.}
	(%)					(mM)	
Mono-Si	0.00	0.00	0.00	0.00	0.09	³ nd	nd
Ca-Si	22.56	0.03	0.18	0.05	27.01	0.23	25.70
Ac-Ca-Si	14.08	0.04	0.05	0.02	15.18	0.51	17.64
Mg-Si	0.13	23.93	2.17	0.00	17.46	0.00	5.35
Ac-Mg-Si	1.48	10.30	1.61	0.00	7.23	0.00	67.75
FMP	18.80	8.86	1.67	7.24	12.01	1.02	25.90
Sugarcane	0.17	0.15	0.29	0.06	3.14	10.92	2.51
<i>Tithonia</i>	1.58	0.40	0.03	0.42	0.44	63.88	80.29

¹ P availability (0.01 M CaCl₂ extraction); ² Si availability (0.01 M CaCl₂ extraction); ³ not determined

Soil treatments and incubations

All silicate amendments were individually added to the air-dried soil at the rate of 210 kg Si ha⁻¹ (calculated on a soil surface area basis per 10 cm depth with the bulk density of the soil) to investigate the effect of Si derived from different silicate amendments on surface charge characteristics and P sorption capacity of the soil. In addition, in order to investigate the effect of different rates of Si on these soil characterisations, Mono-Si, FMP and *Tithonia* amendments were added to the soil at the rates of 420, 112 and 71 kg Si ha⁻¹, respectively (Table 5.2). Unamended soil is referred to as the control treatment. All treatments were replicated three times, completely randomised in separate incubators (one for 7 days and the other for 30 days) and incubated at field capacity at a constant temperature of 40°C. The method of silicate application was the same as described in Section 4.2.2 (Chapter 4). Note that, as described in Section 4.2.2 (Chapter 4) in regards to the issue of high concentration of Si applied as Mono-Si, the rate of 420 kg Si ha⁻¹ applied as Mono-Si in this study required two applications, the first on the first day of the incubation and the second two days later. This prevented the soil from becoming saturated following addition of the Mono-Si solution. After 7 and 30 days of incubation (7-DAI and 30-DAI, respectively), soil solutions were extracted for the bioassay trial (see Chapter 6), and soil sampling was then undertaken vertically from the soil surface to the bottom of the pot using a plastic tube 15 cm in length and 1.5 cm in diameter. Three cores were sampled for each pot. Soil samples were dried at 25°C for 5 days, gently hand-broken and then passed through a 2-mm sieve before analysis.

Table 5.2 The amounts of silicate amendments applied to pots (10 cm diameter and 11 cm height) containing the Alstonville Ferrosol (0 - 30 cm) in the incubation experiment

Amendment	Si	P	Ca	Mg	¹ OM
	(kg ha ⁻¹)				
Mono-Si-1	210	0	0	0	0
Mono-Si-2	420	0	0	0	0
FMP-1	112	68	175	83	0
FMP-2	210	127	329	155	0
<i>Tithonia</i> -1	71	68	255	65	16170
<i>Tithonia</i> -2	210	199	753	192	47666
Ca-Si	210	0	175	0	0
Ac-Ca-Si	210	0	195	1	0
Mg-Si	210	0	2	288	0
Ac-Mg-Si	210	0	43	299	0
Sugarcane trash	210	4	11	10	6681

¹ amount of air-dried organic materials applied

5.2.3 Analytical methods

All analytical methods used in this study were described in Section 3.2.2 (Chapter 3), 4.2.2 (Chapter 4) and 6.2.6 (Chapter 6). Due to the very low pH of this soil (4.02), surface charge characteristics in this study were determined using the charge fingerprint procedure over the pH range of 4.0; 4.5; 5.0; 5.5 and 6.0. The phosphorus buffer index (PBI) (Burkitt *et al.*, 2002) was calculated using the Olsen extractable P (P_{Olsen}) (Olsen *et al.*, 1954) according to the following equation and Olsen P was used to indicate P availability in this chapter as it is faster and correlates directly with PBI calculations made using Colwell:

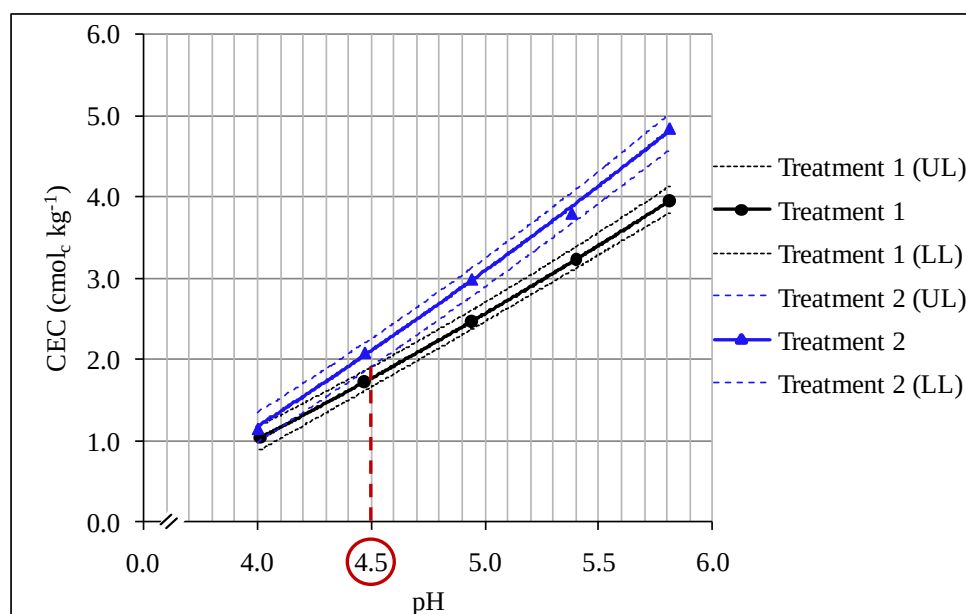
$$PBI_{Olsen} = \frac{Ps \text{ (mg P kg}^{-1}\text{)} + 4.59 \times P_{Olsen} \text{ (mg kg}^{-1}\text{)}}{c \text{ (mg P L}^{-1}\text{)}^{0.41}}$$

Surface charge characteristics of all treatments were determined using a composite sample of the three replications, but P_{Olsen} and PBI_{Olsen} were measured on individual replicates.

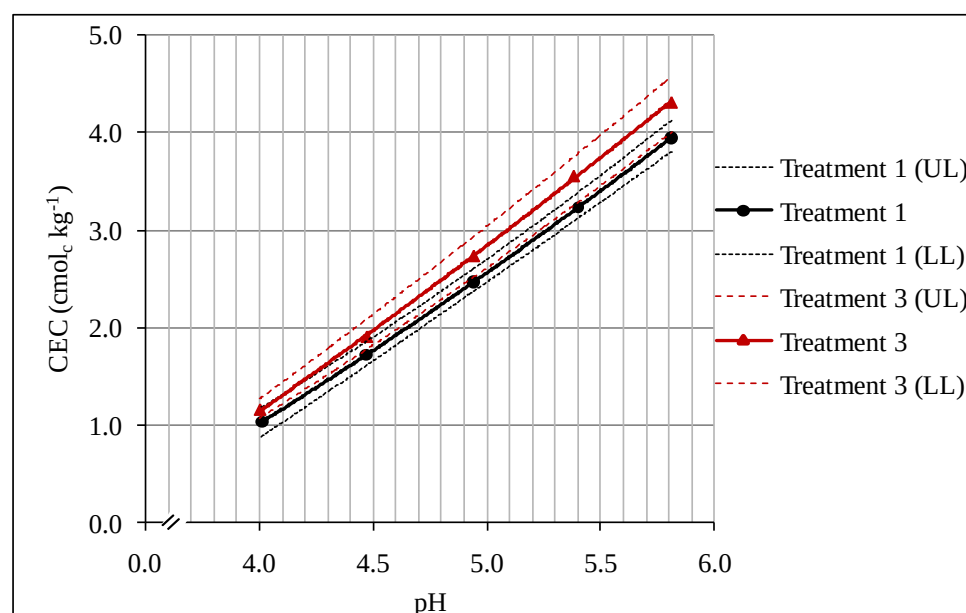
5.2.4 Data analysis

Charge fingerprint curves and surface charge characteristic values at soil pH were calculated as described in Section 4.2.3 (Chapter 4). Because the charge fingerprint data were obtained from five pH points (4.0; 4.5; 5.0; 5.5 and 6.0), composite treatment samples were used, and the R software package (R Development Core Team, 2009) was used to estimate confidence limits [upper limit (UL) and lower limit (LL)] of an individual treatment from the regression curve of five pH points (on x axis) in accordance with the values of surface charge characteristics (on y axis). In the context of this dataset, the pH value at which the UL curve of one treatment and the LL curve of another treatment diverge is considered to be the starting pH value of significant differences between treatments. On the other hand, if the confidence boundaries of two curves overlap each other, there is no evidence of a statistical difference between treatments. For example, as shown in Figure 5.1, the CEC of treatment 2 is significantly different to that of treatment 1 when soil pH is higher than 4.5 (Figure 5.1a); there is no evidence of statistical difference in CECs of treatment 3 and of treatment 1 over the whole pH range (Figure 5.1b).

General analysis of variance (ANOVA) and least significant differences of means ($LSD_{0.05}$) in the GenStat Discovery Edition 3 (seventh edition, version - 7.2.2.222) Copyright 2008 for Windows XP were used to compare differences between the means of P_{Olsen} and PBI_{Olsen} . Surface charge characteristics and P sorption capacities of silicate treatments at the rate of 210 kg Si ha⁻¹ and at different addition rates were compared to the control treatment (unamended treatment) 7-DAI and 30-DAI to examine the effect of Si derived from inorganic or organic amendments. A linear correlation coefficient (r) matrix was computed for the various properties of all treatments at 7-DAI and 30-DAI to determine the relationships of surface charge characteristics and P sorption capacity with soil properties. Significant levels were set to $P \leq 0.05$ for all tests.



(a)



(b)

Figure 5.1 Illustrative relationships between CEC and soil pH for the Alstonville Ferrosol for selected treatments. Figure 5.1(a) shows the starting pH value at which significant differences occurred, but there is no evidence of statistical difference in Figure 5.1(b)

5.3 Results

5.3.1 Changes in soil pH and surface charge characteristics

Different curves expressing the variation in pH_0 , total cation exchange capacity (CEC_T), basic cation exchange capacity (CEC_B), total net charge (TNC) and anion exchange capacity (AEC) at a CaCl_2 concentration of 0.002 M (ionic strength = 0.006 M) over the soil pH range 4.0 to 6.0 for all treatments (7-DAI and 30-DAI) are presented in Appendix 2, and results are summarized in this section. All measured parameters (soil pH, pH_0 , CEC_T , CEC_B , AEC, TNC, NPC and NVC) decreased with increasing incubation period over all Si rates (Tables 5.3 and 5.4) and silicate amendments (Tables 5.6 and 5.7). Larger differences between CEC_T and CEC_B were observed at lower soil pH and similar values between these parameters were found where soil pH was higher than 5.0 (see Appendix 2 and here in the case of the *Tithonia*-2 treatment). The soil exhibited higher values of NPC than those of NVC in all treatments (except for the *Tithonia*-2 treatment) (Tables 5.4 and 5.7). This indicated that the soil was dominated by permanent charge surface.

Effect of silicon rate

Neither rate of Mono-Si application (210 and 420 kg Si ha⁻¹) increased soil pH compared to the control treatment at 7-DAI, but the higher rate (420 kg Si ha⁻¹) increased soil pH relative to the control at 30-DAI (Table 5.3). Similar to the results shown in Chapter 4 for the other VCS, the application of FMP significantly increased the pH of the Alstonville Ferrosol, as did the *Tithonia* treatment, and the higher the rate of applied Si, the higher the soil pH. Although the soil pH in most treatments decreased with increasing incubation period, the soil pH at 30-DAI (5.55) in the *Tithonia*-2 treatment (210 kg Si ha⁻¹) was higher than at 7-DAI (5.52) (Table 5.3). At 7-DAI, the only significant decrease in soil pH_0 compared to the control treatment occurred in the *Tithonia*-2 treatment (3.90 compared to 4.04, respectively). However, lower pH_0 values were observed in all treatments at 30-DAI and the higher the rate of applied Si in a given silicate amendment, the lower the pH_0 observed (Table 5.3).

Table 5.3 Effect of monosilicic acid (210 and 420 kg Si ha⁻¹), fused magnesium phosphate (112 and 210 kg Si ha⁻¹) and *Tithonia diversifolia* (71 and 210 kg Si ha⁻¹) on pH, point of zero charge, total cation-, basic cation- and anion exchange capacity at soil pH of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	¹ pH	² pH ₀	³ CEC _T	⁴ CEC _B	⁵ AEC	Percentage change		
						CEC _T	CEC _B	AEC
			(cmol _c kg ⁻¹)			(%)		
7-DAI								
Control	4.65	4.04	2.24	2.00	-0.07			
Mono-Si-1	4.63	4.02	2.51	2.16	-0.06	12	8	-14
Mono-Si-2	4.64	3.98	2.58	2.33	-0.06	15	17	-14
FMP-1	4.80	4.07	2.48	2.30	-0.02	11	15	-71
FMP-2	4.92	4.04	2.91	2.78	0.00	30	39	⁶ -
<i>Tithonia</i> -1	4.99	4.03	2.90	2.81	-0.01	30	41	-86
<i>Tithonia</i> -2	5.52	3.90	4.66	4.66	0.06	208	233	-
30-DAI								
Control	4.59	3.98	1.99	1.72	-0.07			
Mono-Si-1	4.57	3.95	1.97	1.69	-0.08	-1	-2	14
Mono-Si-2	4.64	3.90	2.08	1.85	-0.04	5	8	-43
FMP-1	4.74	3.96	2.10	1.89	-0.02	6	10	-71
FMP-2	4.77	3.90	2.63	2.41	-0.02	32	40	-71
<i>Tithonia</i> -1	4.89	3.96	2.55	2.42	0.02	28	41	-
<i>Tithonia</i> -2	5.55	3.68	3.86	3.86	0.04	194	224	-

¹ soil pH (1:10, 0.002 M CaCl₂); ² point of zero charge; ³ total cation exchange capacity;

⁴ basic cation exchange capacity; ⁵ anion exchange capacity; ⁶ cannot be calculated

The increases in soil pH and/or decreases in pH₀ at both incubation periods associated with different rates of silicate amendments increased both CEC_T and CEC_B, and decreased AEC of the soil compared to those of the control treatment (Table 5.3). The order of magnitude in these changes was *Tithonia* > FMP > Mono-Si. In comparison with the control treatment, the results in Table 5.3 show that the extents of increments in CEC_T and CEC_B were similar for the Mono-2 (420 kg Si ha⁻¹) and FMP-1 (112 kg Si ha⁻¹) treatments, and for the FMP-2 (210 kg Si ha⁻¹) and *Tithonia*-1 (71 kg Si ha⁻¹) treatments at both incubation periods. The highest and lowest of these increments were observed in the *Tithonia*-2 (210 kg Si ha⁻¹) and Mono-Si-1 (210 kg Si ha⁻¹) treatments, respectively. Comparing the two incubation periods for a given

silicate amendment (both rates) with the control treatment, the results show that the Mono-Si (both rates, 210 and 420 kg Si ha⁻¹) and FMP (lower rate, 112 kg Si ha⁻¹) obtained greater effects in CEC_T and CEC_B increments at 7-DAI than at 30-DAI, whereas the increments for the FMP (higher rate, 210 kg Si ha⁻¹) and *Tithonia* amendments (both rates, 71 and 210 kg Si ha⁻¹) were similar at both incubation periods. In all but the Mono-Si-1 treatment at 30-DAI, AEC decreased compared to the control treatment, especially for both *Tithonia* treatments at both incubation periods (Table 5.3).

The effect of silicate amendments at different rates on TNC of the soil showed the same trends as those on CEC_T and CEC_B at both incubation periods; the more Si applied, the greater the observed effect (Table 5.4). Except for the Mono-Si-1 treatment at 7-DAI, NPC and NVC increased with increasing Si application at both incubation periods. As expected for VCS, the extent by which NVC increased following Si application was much larger than that of NPC. In comparison between two incubation periods, the increment of NVC was lower at 30-DAI than at 7-DAI for all treatments except *Tithonia*. For both *Tithonia* treatments, NVC increased with increasing time of incubation, from 68 – 96% and 403 – 449% for the *Tithonia*-1 and *Tithonia*-2 treatment, respectively (Table 5.4).

Because only composite samples were used for the measurement of surface charge characteristics using the charge fingerprint method (as mentioned in Section 5.2.3), it is not possible to make direct statistical comparisons of the surface charge characteristic values presented in Tables 5.3 and 5.4. However, confidence intervals (or limits) for the soil pH-charge characteristic curves were estimated using the R software and these were used to derive statistical differences (as described in Section 5.2.4). Soil pH values at which significant differences ($P < 0.05$) in surface charge characteristics of the soil started occurring between the control and different rates of silicate treatments are given in Table 5.5. There was no evidence of statistical difference ($P < 0.05$) in surface charge characteristics between the control and both rates of Mono-Si treatments at 30-DAI. However, significant differences in CEC_T, CEC_B and TNC were observed in the Mono-Si-2 treatment (420 kg Si ha⁻¹) at 7-DAI. This is due to the actual soil pH (4.64) of this treatment at 7-DAI (Table 5.3) being higher than the pH values of 4.37; 4.24 and 4.25 (Table 5.5) at which significant differences were observed for CEC_T, CEC_B and TNC, respectively. On the other hand, the application of Mono-Si at 210 kg Si ha⁻¹ (Mono-Si-1) was only significantly different for TNC at 7-DAI compared with the control treatment, because the actual soil pH (4.63) of this treatment at 7-DAI (Table 5.3) was higher than the pH value (4.40) at which the significant difference was observed for this treatment at 7-DAI (Table 5.5). Similarly, it can be shown that the

application of FMP at 210 kg Si ha⁻¹ (FMP-2) and *Tithonia* at both rates (71 and 210 kg Si ha⁻¹) were significantly different in CEC_T, CEC_B and TNC compared with the control treatment for both incubation periods (Tables 5.3 and 5.5).

Table 5.4 Effect of monosilicic acid (210 and 420 kg Si ha⁻¹), fused magnesium phosphate (112 and 210 kg Si ha⁻¹) and *Tithonia diversifolia* (71 and 210 kg Si ha⁻¹) on total net charge, net permanent charge and net variable charge of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	¹ TNC	² NPC	³ NVC	Percentage change		
				TNC	NPC	NVC
				(%)		
7-DAI						
Control	2.17	1.52	0.65			
Mono-Si-1	2.36	1.66	0.70	9	9	8
Mono-Si-2	2.53	1.56	0.97	17	3	49
FMP-1	2.46	1.71	0.75	13	13	15
FMP-2	2.91	1.84	1.08	34	21	66
<i>Tithonia</i> -1	2.88	1.80	1.09	33	18	68
<i>Tithonia</i> -2	4.70	2.08	2.62	217	37	403
30-DAI						
Control	1.92	1.43	0.49			
Mono-Si-1	1.89	1.44	0.45	-2	1	-8
Mono-Si-2	2.04	1.51	0.53	6	6	8
FMP-1	2.08	1.53	0.55	8	7	12
FMP-2	2.61	1.87	0.74	36	31	51
<i>Tithonia</i> -1	2.57	1.62	0.96	34	13	96
<i>Tithonia</i> -2	3.88	1.68	2.20	202	18	449

¹ total net charge; ² net permanent charge; ³ net variable charge

Table 5.5 Soil pH values at which significant differences ($P < 0.05$) in surface charge characteristics of the Alstonville Ferrosol (0 - 30 cm) occurred for silicate amendments at different rates after 7 and 30 days of incubation

Treatment	7-DAI				30-DAI			
	¹ CEC _T	² CEC _B	³ AEC	⁴ TNC	CEC _T	CEC _B	AEC	TNC
Control vs Mono-Si-1	> 4.72	> 4.85	⁵ ns	> 4.40	ns	ns	ns	ns
Control vs Mono-Si-2	> 4.37	> 4.24	ns	> 4.25	ns	ns	ns	ns
Control vs FMP-1	> 5.64	> 5.75	ns	> 5.22	ns	> 5.00	ns	ns
Control vs FMP-2	> 4.43	> 4.45	> 5.10	> 4.25	> 4.00	> 4.00	ns	> 4.00
Control vs <i>Tithonia</i> -1	> 4.37	> 4.24	ns	> 4.00	> 4.65	> 4.35	ns	> 4.53
Control vs <i>Tithonia</i> -2	> 4.00	> 4.00	ns	> 4.00	> 4.12	> 4.08	ns	> 4.16

¹ total cation exchange capacity; ² basic cation exchange capacity; ³ anion exchange capacity; ⁴ total net charge;

⁵ no evidence of statistical difference

Effect of silicate amendments

At 7-DAI, all silicate treatments (Ca-Si, Ac-Ca-Si, Mg-Si, Ac-Mg-Si and Sugarcane) increased soil pH compared with the control treatment (Table 5.6). The highest soil pH value (4.80) was observed for the Ca-Si treatment and the pH₀ values of all silicate treatments were higher than that of the control treatment (Table 5.6). At 30-DAI, however, although the soil pH of the control and Ca-Si treatment were lower compared with those at 7-DAI, the soil pH of all other silicate treatments remained constant or increased after 30 days of incubation. Therefore, increases in soil pH following silicate treatments at 30-DAI were greater than those at 7-DAI in comparison with the control treatment. In addition, the pH₀ values of all silicate treatments were lower than that of the control treatment at 30-DAI (Table 5.6). In this incubation period, the Ac-Si-Mg treatment exhibited the highest soil pH (4.77) and lowest pH₀ (3.92). As a result, in comparison with the control treatment, CEC_T and CEC_B of the silicate treatments at 30-DAI increased to a greater extent than those at 7-DAI, and the Ac-Si-Mg treatment was most effective, with an increase of 28% in CEC_T and 34% in CEC_B (Table 5.6). With the exception for the Ca-Si treatment at 7-DAI, all silicate treatments decreased AEC of the soil at both incubation periods.

Table 5.6 Effect of different silicate amendments (210 kg Si ha⁻¹) on pH, point of zero charge, total cation-, basic cation- and anion exchange capacity at soil pH of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	¹ pH	² pH ₀	³ CEC _T	⁴ CEC _B	⁵ AEC	Percentage change		
						CEC _T	CEC _B	AEC
	(cmol _c kg ⁻¹)					(%)		
7-DAI								
Control	4.65	4.04	2.24	2.00	-0.07			
Ca-Si	4.80	4.07	2.30	1.93	-0.09	3	-4	29
Ac-Ca-Si	4.73	4.07	2.49	2.27	-0.04	11	14	-43
Mg-Si	4.71	4.08	2.28	2.07	-0.02	2	4	-71
Ac-Mg-Si	4.70	4.05	2.72	2.49	-0.01	21	25	-86
Sugarcane	4.69	4.06	2.48	2.24	-0.05	11	12	-29
30-DAI								
Control	4.59	3.98	1.99	1.72	-0.07			
Ca-Si	4.72	3.94	2.13	1.91	-0.05	7	11	-29
Ac-Ca-Si	4.74	3.95	2.40	2.18	-0.03	21	27	-57
Mg-Si	4.70	3.95	2.33	2.09	-0.05	17	22	-29
Ac-Mg-Si	4.77	3.92	2.54	2.31	-0.04	28	34	-43
Sugarcane	4.70	3.97	2.00	1.77	-0.02	1	3	-71

¹ soil pH (1:10, 0.002 M CaCl₂); ² point of zero charge; ³ total cation exchange capacity;

⁴ basic cation exchange capacity; ⁵ anion exchange capacity

Total net charge as well as both NPC and NVC of the soil increased following application of the silicate amendments, but the increment of NVC was much higher than that of NPC at both incubation periods (Table 5.7). Although the highest NVC value of the Ca-Si treatment (1.08 cmol_c kg⁻¹, an increase of 66% compared to that of the control treatment) was observed at 7-DAI, it was reduced to a low value at 30-DAI (0.61 cmol_c kg⁻¹, an increase of 25% compared to that of the control treatment). In contrast, the Ac-Mg-Si treatment consistently exhibited high NVC values at both incubation periods, 1.01 and 0.74 cmol_c kg⁻¹ for 7-DAI and 30-DAI, respectively, and an increase of over 50% compared to that of the control treatment at both incubation periods (Table 5.7).

Table 5.7 Effect of different silicate amendments (210 kg Si ha⁻¹) on total net charge, net permanent charge and net variable charge of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	¹ TNC	² NPC	³ NVC	Percentage change		
				TNC	NPC	NVC
	(cmol _c kg ⁻¹)			(%)		
7-DAI						
Control	2.17	1.52	0.65			
Ca-Si	2.71	1.63	1.08	25	7	66
Ac-Ca-Si	2.45	1.76	0.69	13	16	6
Mg-Si	2.26	1.62	0.64	4	7	-2
Ac-Mg-Si	2.71	1.71	1.01	25	13	55
Sugarcane	2.43	1.72	0.71	12	13	9
30-DAI						
Control	1.92	1.43	0.49			
Ca-Si	2.08	1.48	0.61	8	4	25
Ac-Ca-Si	2.37	1.62	0.74	23	13	51
Mg-Si	2.28	1.54	0.74	19	8	51
Ac-Mg-Si	2.49	1.75	0.74	30	22	51
Sugarcane	1.98	1.42	0.55	3	-1	12

¹ total net charge; ² net permanent charge; ³ net variable charge

According to the statistical analysis comparing significant ($P < 0.05$) differences between the control and silicate treatments given in Table 5.8 and the soil pH values of these treatments given in Table 5.6 for both incubation periods, there was no evidence of statistical differences between the control and silicate treatments at 7-DAI. At 30-DAI, however, significant ($P < 0.05$) differences in CEC_T, CEC_B and TNC were observed for the Ac-Ca-Si, Mg-Si and Ac-Mg-Si treatments compared to those for the control treatment.

The linear correlation coefficient matrix expressing the relationships between soil pH, pH₀ and surface charge characteristics of the soil are presented in Table 5.9. In all but the NPC parameter at 30-DAI, there were highly significant positive correlations in soil pH and highly significant negative correlations in pH₀ with surface charge characteristics at both incubation periods.

Table 5.8 Soil pH values at which significant differences ($P < 0.05$) in surface charge characteristics of the Alstonville Ferrosol (0 - 30 cm) occurred following amendment with different silicate sources after 7 and 30 days of incubation

Treatment	7-DAI				30-DAI			
	¹ CEC _T	² CEC _B	³ AEC	⁴ TNC	CEC _T	CEC _B	AEC	TNC
Control vs Ca-Si	⁵ ns	ns	ns	ns	ns	> 5.45	ns	ns
Control vs Ac-Ca-Si	> 5.35	> 5.35	ns	> 5.25	> 4.00	> 4.00	ns	> 4.00
Control vs Mg-Si	ns	ns	ns	ns	> 4.24	> 4.35	ns	> 4.43
Control vs Ac-Mg-Si	ns	ns	ns	> 4.82	> 4.00	> 4.00	ns	> 4.00
Control vs Sugarcane	ns	ns	> 5.20	ns	> 5.12	> 4.88	ns	> 5.25

¹ total cation exchange capacity; ² basic cation exchange capacity; ³ anion exchange capacity; ⁴ total net charge;

⁵ no evidence of statistical difference

Table 5.9 Linear correlation coefficient (r) matrix for the relationships between soil pH, pH₀ and surface charge characteristics of the Altonsville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

	¹ CEC _T	² CEC _B	³ TNC	⁴ NPC	⁵ NVC
7-DAI					
pH _(0.002 M CaCl2)	0.94***	0.95***	0.95***	0.55*	0.96***
pH ₀	-0.85***	-0.83***	-0.83***	-0.79***	-0.71**
30-DAI					
pH _(0.002 M CaCl2)	0.93***	0.95***	0.94***	0.39	0.95***
pH ₀	-0.90***	-0.90***	-0.90***	-0.38	-0.91***

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

¹ total cation exchange capacity; ² basic cation exchange capacity; ³ total net charge; ⁴ net permanent charge; and

⁵ net variable charge

5.3.2 Changes in phosphorus sorption capacity

Effect of silicon rate

The application of Mono-Si, FMP and *Tithonia* amendment at different Si rates significantly ($P < 0.05$) increased P_{Olsen} of the soil compared to that of the control treatment at both incubation periods (Table 5.10). Except for the Mono-Si amendment at 7-DAI, all higher rates of silicate treatments resulted in significant increases of P_{Olsen} , and the highest values

observed were about 10 mg kg⁻¹ P for both FMP-2 and *Tithonia*-2 treatments (210 kg Si ha⁻¹) at both incubation periods. The PBI_{Olsen} values given in Table 5.10 show that phosphorus sorption capacity of the soil was significantly decreased by the FMP-2, *Tithonia*-1 and *Tithonia*-2 treatments at 7-DAI; however, all treatments significantly decreased PBI_{Olsen} at 30-DAI; these decreased in the order: *Tithonia*-2 > FMP-2 = Mono-Si-2 > *Tithonia*-1 = FMP-1 > Mono-1 (Table 5.10).

Table 5.10 Effect of monosilicic acid (210 and 420 kg Si ha⁻¹), fused magnesium phosphate (112 and 210 kg Si ha⁻¹) and *Tithonia diversifolia* (71 and 210 kg Si ha⁻¹) on phosphorus sorption capacity of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	P _{Olsen} (mg kg ⁻¹)		PBI _{Olsen}	
	7-DAI	30-DAI	7-DAI	30-DAI
Control	3.79 a	3.74 a	1017 c	962 e
Mono-Si-1	4.27 b	3.96 a	1126 d	856 d
Mono-Si-2	4.47 b	4.33 b	1018 c	694 b
FMP-1	7.41 d	6.88 d	1046 c	773 c
FMP-2	9.93 e	10.48 f	924 b	692 b
<i>Tithonia</i> -1	6.57 c	6.12 c	913 b	766 c
<i>Tithonia</i> -2	10.12 e	9.84 e	666 a	603 a
LSD _{0.05}	0.47	0.24	44	25
CV(%)	4.0	2.1	2.6	1.9

Means in the same column followed by different letters are significantly different at $P < 0.05$

Effect of silicate amendments

The effects of different inorganic amendments at the rate of 210 kg Si ha⁻¹ on phosphorus sorption capacity of the soil after 7 and 30 days of incubation are given in Table 5.11. At 7-DAI, all inorganic silicate treatments except the Ca-Si treatment, significantly increased extractable P (P_{Olsen}), but P sorption capacity (PBI_{Olsen}) of the soil was only significantly reduced by the FMP-2 and *Tithonia* treatments in comparison with the control treatment. With increasing time of incubation (30-DAI), P_{Olsen} of the FMP treatment increased considerably, whereas that of all other inorganic silicate treatments declined and significant differences in P_{Olsen} compared to the control treatment were only observed in the Ac-Ca-Si, Ac-Mg-Si and

FMP treatments. However, the P_{Olsen} values of all treatments were significantly ($P < 0.05$) lower than that of the control treatment at 30-DAI, and decreased in the order: FMP = Ac-Mg-Si > Mg-Si = Ac-Ca-Si > Ca-Si = Mono-Si (Table 5.11).

As previously shown in Table 5.10, *Tithonia* application at the high Si rate ($210 \text{ kg Si ha}^{-1}$) caused the greatest effect in increasing P_{Olsen} and decreasing PBI_{Olsen} . Results are shown in Table 5.12 in order to compare the effects of the organic amendments. The sugarcane treatment did not cause any change in P_{Olsen} in either incubation period; this treatment increased P sorption capacity of the soil at 7-DAI, but significantly decreased it compared to the control treatment at 30-DAI (Table 5.12).

Table 5.11 Effect of inorganic silicate amendments ($210 \text{ kg Si ha}^{-1}$) on phosphorus sorption capacity of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	P_{Olsen} (mg kg^{-1})		PBI_{Olsen}	
	7-DAI	30-DAI	7-DAI	30-DAI
Control	3.79 a	3.74 a	1017 b	962 d
Mono-Si-1	4.27 b	3.96 ab	1126 cd	856 c
Ca-Si	3.86 a	3.73 a	1116 c	838 c
Ac-Ca-Si	4.33 bc	4.19 bc	1142 cde	766 b
Mg-Si	4.19 b	3.75 a	1173 e	764 b
Ac-Mg-Si	4.62 c	4.41 c	1156 de	707 a
FMP-2	9.93 d	10.48 d	924 a	692 a
LSD _{0.05}	0.29	0.26	39	41
CV(%)	3.2	3.0	2.0	2.9

Means in the same column followed by different letters are significantly different at $P < 0.05$

The correlations between P sorption capacity (PBI_{Olsen}) of the soil and soil pH, surface charge characteristics and extractable P (P_{Olsen}) are given in Table 5.13 and show that these relationships are different between 7-DAI and 30-DAI. At 7-DAI, PBI_{Olsen} of the soil was highly positively correlated with pH_0 and highly negatively correlated with soil pH, CEC_T , TNC and NVC, but not correlated with P_{Olsen} . At 30-DAI, however, it was moderately correlated with all measured parameters.

Table 5.12 Effect of organic amendments (210 kg Si ha⁻¹) on phosphorus sorption capacity of the Alstonville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

Amendment	P _{Olsen} (mg kg ⁻¹)		PBI _{Olsen}	
	7-DAI	30-DAI	7-DAI	30-DAI
Control	3.79 a	3.74 a	1017 b	962 c
Sugarcane	3.95 a	3.66 a	1183 c	753 b
<i>Tithonia</i> -2	10.12 b	9.84 b	666 a	603 a
LSD _{0.05}	0.65	0.32	66	18
CV(%)	4.8	2.5	3.1	1.0

Means in the same column followed by different letters are significantly different at $P < 0.05$

Table 5.13 Linear correlation coefficient (r) matrix for the relationships between soil pH, pH₀, surface charge characteristics and phosphorus sorption capacity of the Altonsville Ferrosol (0 - 30 cm) after 7 and 30 days of incubation

	¹ Soil pH	pH ₀	² CEC _T	³ TNC	⁴ NVC	P _{Olsen}
7-DAI						
PBI _{Olsen}	-0.87***	0.82***	-0.86***	-0.86***	-0.79***	-0.50
30-DAI						
PBI _{Olsen}	-0.64*	0.65**	-0.61*	-0.63*	-0.59*	-0.56*

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

¹pH (1:10, 0.002 M CaCl₂); ²total cation exchange capacity; ³total net charge; and ⁴net variable charge

5.4 Discussion

As previously shown, most of the silicate amendments used in this study were the same in Chapter 4 and Chapter 6, and the effects of different silicate amendments on surface charge characteristics and P sorption capacity of this soil type had similar trends to those shown in soils in Chapter 4, especially the Palmerston Ferrosol from north Queensland. Therefore, the following statements will not be discussed from a mechanistic viewpoint because this can be obtained in Chapter 4 and/or Chapter 6. However, the effects of different Si application rates at different incubation periods will be focused on here and, where needed, the effects of different silicate amendments will be mentioned.

5.4.1 Effect of different silicon rates and silicate amendments on surface charge characteristics at two incubation periods

It is well known that the negative charge surface of VCS increases with increasing Si rate applied by various silicate amendments. For example, the greater the Ca-Si application rate, the more the CEC increased for a Red Ferrosol and a Tenosol from north Queensland (Berthelsen *et al.*, 2003), an Andisol from west Sumatra, Indonesia (Fiantis *et al.*, 2002), and a Red Latosol from Brazil (Smyth and Sanchez, 1980); similarly, the higher rates of *Tithonia* and FMP application markedly increased CEC of two Ferralsols from Vietnam (Phan, 2000) and of a Red Ferrosol from north Queensland (Nguyen *et al.*, 2010), respectively. The results of this study are consistent with these previous findings for the Mono-Si, FMP and *Tithonia* amendments through both incubation periods. This is due to greater increases in soil pH and/or decreases in pH_0 following the application of the higher Si rate, and similar results were observed by Berthelsen *et al.* (2003) and Nguyen *et al.* (2010). In addition, significant and high correlations between soil pH (positive) and pH_0 (negative) with surface charge characteristics of the soil were observed in this study (Table 5.9). The above discussion can also be used to explain the effect of different silicate amendments on negative charge surface (Table 5.6).

Although the pH_0 values of all treatments (different Si rates, different amendments and control treatment) were lower at 30-DAI, soil pH values also tended to be lower, resulting in the negative surface charge of all treatments decreasing over the incubation period (i.e., lower values at 30-DAI than those at 7-DAI) (Tables 5.3; 5.4; 5.6 and 5.7). This can be attributed to the oxidation/mineralisation of the relatively high organic carbon content (5.05%, see Section 5.2.1) of the topsoil (0 - 30 cm) during incubation at high temperature (40°C) reducing the negative charge surface derived from the native organic carbon in the soil. In addition, if the comparison is made between the effect of Mono-Si (both rates) and that of other inorganic silicate amendments (Ca-Si, Ac-Ca-Si, Mg-Si and Ac-Mg-Si) on surface charge characteristics of the soil at 7-DAI and 30-DAI, it can be seen that the Mono-Si amendment achieved a greater effect at 7-DAI than at 30-DAI, whereas the other inorganic silicate amendments showed the reverse trend. These effects can be explained by more available Si being released to the soil from the Mono-Si amendment applied as pure monosilicic acid solution and it would be, then, quickly involved in actions with soil surfaces. On the other hand, Si in the other inorganic silicate amendments is present with Ca or Mg and generally considered to contain a readily released fraction and a slowly released fraction (Kato and

Owa, 1997). As a result, these amendments would need more time than Mono-Si to react with soil surfaces. However, in the cases of the FMP (210 kg Si ha⁻¹) and *Tithonia* (both rates, 71 and 210 kg Si ha⁻¹) amendments, the effects were constant through both incubation periods. These effects are not only due to the high available Si in these amendments (Table 5.1), but also the synergistic effect of other elements as discussed in Chapter 4.

Among silicate amendments (Ca-Si, Ac-Ca-Si, Mg-Si and Ac-Mg-Si), although Ac-Mg-Si did not increase soil pH as much as Ca-Si, Ac-Ca-Si and Mg-Si at 7-DAI, it was the most effective amendment in terms of reducing pH₀ and increasing the negative charge surface of the soil at 30-DAI (Table 5.6). These effects can be explained by more available Si being released to the soil from this amendment than the others, as salt extractable Si of Ac-Mg-Si is much higher than that in the other silicate amendments (Table 5.1). This confirms the results observed by (Nguyen *et al.*, 2010) on a Red Ferrosol from north Queensland. From the above discussion, it is of practical importance to note that the effects of application rate and timeline of different silicate amendments should mainly depend on the available Si content.

In comparison to the results shown in Chapter 4, especially for the Palmerston Ferrosol from north Queensland, it should be noted that the Alstonville Ferrosol from NSW demonstrated a larger difference between CEC_T and CEC_B at low pH (< 5.0). This can be explained by the high exchangeable Al³⁺ content in the latter soil (see Section 5.2.1 and Chapter 6) contributing to CEC_T at low soil pH. A similar result was found by Berthelsen *et al.* (2003) on a Tenosol from north Queensland, and the authors suggested that an increase in exchangeable Al³⁺ on the exchange complex as soil pH decreased below 5.5, is associated with a decline in exchangeable Ca²⁺, Mg²⁺ and K⁺, and this is likely to have a significant impact on crop performance.

5.4.2 Effect of different silicon rates and silicate amendments on phosphorus sorption capacity at two incubation periods

The effects of different Si rates and different amendments on P sorption capacity of the soil (Tables 5.10; 5.11 and 5.12) were very similar to those on the surface charge characteristics in this study as previously discussed and with those on the P sorption capacity of the soils in Chapter 4. This means that where there is an increase in negative- and a decrease in positive charge surfaces following the application of a amendment, it would reduce the capacity of the soil to adsorb P. As shown in Table 5.13, there were significant correlations between PBI and surface charge characteristics of the soil at both incubation periods. However, while the FMP-

2, *Tithonia*-1 and *Tithonia*-2 treatments reduced PBI at both incubation periods, the others were only significantly different from the control treatment in PBI reduction at 30-DAI. This suggests that there is a lower affinity of adsorbents for the Si anion than with P anions. Therefore, the silicate amendments might require longer time (30-DAI) to release enough available Si to compete with the P anions for sorption sites.

5.5 Summary and conclusions

The Alstonville Ferrosol (0 - 30 cm) is a VCS with permanent charge surface dominated by low cation exchange capacity and high P sorption capacity. The soil is very acidic and high in exchangeable Al and thus the CEC_T of the soil is relatively higher than the CEC_B at low pH. The effects of different silicate amendments at different Si rates following incubation for 7 and 30 days at 40°C on these soil properties are as follows:

- All inorganic silicate and organic amendments (Mono-Si, Ca-Si, Ac-Ca-Si, Mg-Si, Ac-Mg-Si, FMP, *Tithonia* and sugarcane) affected surface charge characteristics, particularly increasing CEC_T , CEC_B , TNC and NVC, decreasing pH_0 and AEC; and reducing P sorption capacity of the soil at 7-DAI and/or 30-DAI. The order of magnitude of these effects can be arranged as: a) surface charge characteristics improved: *Tithonia* > FMP = Ac-Mg-Si > Ac-Ca-Si > Mg-Si > Sugarcane = Ca-Si = Mono-Si; b) phosphorus sorption capacity reduced: *Tithonia* > FMP = Ac-Mg-Si > Sugarcane = Mg-Si = Ac-Ca-Si > Ca-Si = Mono-Si.
- The application of a higher Si rate more effectively increased negative surface charge and decreased P sorption capacity than a lower Si rate.
- Apart from the FMP amendment which also contains high P, the inorganic silicate amendments with high available Si (Mono-Si and Ac-Mg-Si) achieved faster effects on surface charge characteristics (at 7-DAI) than those with low available Si content (Ca-Si, Ac-Ca-Si and Mg-Si).
- Due to the additional effects of basic cations (Ca and Mg), P and organic matter, FMP and *Tithonia* were the two most effective amendments for improving surface charge characteristics and decreasing P sorption capacity of the soil at both incubation periods.
- There were highly significant correlations between soil pH and pH_0 with negative charge surface, and between P sorption capacity and these former soil properties. Therefore, if a silicate amendment can increase soil pH and/or decrease pH_0 , it will not only increase negative charge surface but also decrease P sorption capacity of the soil.

Chapter 6 Silicon-induced amelioration of aluminium induced root toxicity generated from an acidic Red Ferrosol

6.1 Introduction

Silicon (Si) and aluminium (Al) are not generally regarded as essential elements for higher plants, yet they are respectively the second (28 - 31%) and third most (8%) abundant elements, after oxygen (46 - 49%), in the Earth's crust (Greenland and Hayes, 1978; Sposito, 1989; Wehr *et al.*, 2007). Both elements are major components of ubiquitous silicates, oxides, hydroxides, natural rocks, sediments and soils. Most such minerals are unstable with respect to aqueous surface conditions; accordingly, chemical weathering releases dissolved Si and Al (Wonisch *et al.*, 2008). Silicon- and Al-containing minerals are weathered to initially form 2:1 layer aluminosilicate clay minerals, such as vermiculites and smectites, which upon further weathering form 1:1 layer aluminosilicates such as kaolinite and halloysite. Further weathering of clay minerals results in leaching of silica (SiO₂) (see Figure 3.1 in Chapter 2) and base cations leaving behind hydrous aluminium oxide (gibbsite). Subsequently, dissolution of Al minerals at low pH releases Al³⁺, which is hexacoordinated with water molecules as Al(H₂O)₆³⁺. This species is well known as one of the most toxic Al forms to plants (Parker *et al.*, 1989; Kinraide, 1991; Kochian, 1995; Kinraide, 1997, 2003; Wehr *et al.*, 2007; Poschenrieder *et al.*, 2008).

Aluminium toxicity is an important growth limiting factor for plants in many acid soils with pH(water, 1:5) below 5.0 and can even occur at pH(water, 1:5) as high as 5.5 (Foy *et al.*, 1978). The form of soluble Al largely depends on pH (Prabagar *et al.*, 2011). As pH of an acidic Al solution is increased above 4.0, hydrolysis of Al occurs, giving rise to a series of Al hydroxyl species (AlOH²⁺, Al(OH)₂⁺ and Al(OH)₃⁰). If the pH is less than 4.0, the Al³⁺ species predominates in solution (Wehr *et al.*, 2007). Aluminium as a toxic element of acidic soils has been recognized through the tropics and subtropics for more than a hundred years (Poschenrieder *et al.*, 2008). Early studies on Al toxicity in plants date from the beginning of the last century (Miyake, 1916). Since then, many studies have focused on Al toxicity in plants and shown that Al toxicity reduces plant rooting depth, increases susceptibility to drought, decreases the use of subsoil nutrients, and eventually limits crop production. Aluminium toxicity inhibits root elongation more than shoot growth; consequently, yield may be significantly reduced by Al in acid soils without developing clear and diagnostic foliar symptoms. Root elongation restriction leads to short, stubby, and brittle roots and an absence

of root hairs (Foy *et al.*, 1978). The main root zone affected by Al is from 1 to 4 mm behind the root tip (Sivaguru and Horst, 1998; Blamey *et al.*, 2004; Wehr *et al.*, 2007). Such root tips thicken and turn brown, and these symptoms indicate a root that is inefficient in absorbing nutrients and water (Foy *et al.*, 1978).

Much of the physiological research on the mechanism of Al toxicity has suggested that the primary site of Al toxicity is in the cell wall (Kochian *et al.*, 2005; Zheng and Yang, 2005; Wehr *et al.*, 2007). In general, Al binds to negative charges of the cell wall leading to interference with cell division in plant roots and processes necessary for cell expansion and thus root elongation (Ma *et al.*, 1999; Tabuchi and Matsumoto, 2001). For example, binding of Al to pectin renders pectin resistant to degradation by enzymes (Wehr *et al.*, 2004), in turn reducing mobility of enzymes necessary to cleave load-bearing hemicellulose molecules (Kenjebaeve *et al.*, 2001), resulting in stiffening of the cell wall (Tabuchi and Matsumoto, 2001; Ma *et al.*, 2004). In addition, Al fixes P in less available forms in the soil and in or on plant roots, decreases root respiration, and interferes with the uptake, transport, and use of several elements (Ca, Mg, P, K) and water by plants (Rorison, 1965; Foy *et al.*, 1978).

The beneficial role of Si in stimulating the growth and development of many plant species has been generally recognized. Silicon is known to effectively mitigate various abiotic stresses such as Mn, Al and heavy metal toxicities, as well as salinity, drought, chilling and freezing stresses. However, mechanisms of Si-mediated alleviation of abiotic stresses remain poorly understood. Liang *et al.* (2007) stated that the key mechanisms of Si-mediated alleviation of abiotic stresses in higher plants include: a) stimulation of antioxidant systems in plants; b) co-precipitation of toxic metal ions with Si; c) immobilisation of toxic metal ions in growth media; d) plant Si-uptake processes; and e) compartmentalisation of metal ions within plants. In early research, Williams and Vlamis (1957b) discovered that Mn toxicity in barley in culture solution was mitigated by addition of Si. Subsequently, the role of Si in mitigating Mn toxicity has been extensively investigated in barley (Horiguchi and Morita, 1987), rice (Horiguchi, 1988), bean (Horst and Marschner, 1978), pumpkin (Iwasaki and Matsumura, 1999), cowpea (Iwasaki *et al.*, 2002a, b), tomato (Peaslee and Frink, 1969) and cucumber (Rogalla and Römheld, 2002).

The discovery that Si alleviated Mn phytotoxicity in turn led to the finding that this role of Si can also be applied to other metal ions, particularly Al (Epstein, 1999). Therefore, considerable research has been recently conducted to investigate the role of Si in ameliorating

Al toxicity (Hodson and Evans, 1995). Although the alleviation effect on Al toxicity by Si and its possible mechanisms have been extensively examined, no appropriate explanation could be drawn regarding this effect in many of these investigations. Hodson and Evans (1995) reported that interactions of Si and Al have been studied in at least eight plant species, but contradictory findings have been shown. Sorghum (*Sorghum bicolor* L.), barley (*Hordeum vulgare* L.), teosinte (*Zea mays* L. Ssp. Mexicana), and soybean [*Glycine max* (L.) Merr.] showed significantly ameliorative effects of Si on Al toxicity, whereas there was little or no such effect on rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), cotton (*Gossypium hirsutum*) and pea (*Pisum sativum* L.).

Many researchers have reported that Si-induced amelioration of Al toxicity is attributed to both external (nutrient solutions) and internal mechanisms (within plant) related to the formation Al-Si complexes. Hiradate *et al.* (1998) reported that interaction between Si and Al, reducing the activity of Al in the medium, is one possible external mechanism for the amelioration of Al toxicity by Si. Such external effects are also supported by the finding that Si alleviated the Al toxicity to soybean (Baylis *et al.*, 1994). Ma *et al.* (1997) concluded that the formation of Al-Si complexes was responsible for the lack of inhibition of corn root elongation by Al. The precipitation of sub-colloidal, inert hydroxyaluminosilicates (HAS) seems to be responsible for the diminished concentration (activity) of phytotoxic Al in solution (Liang *et al.*, 2007). In addition, the co-deposition of Si and Al also seems to occur within plants (Liang *et al.*, 2001). Cocker *et al.* (1998a) proposed that HAS or low-solubility aluminosilicates (or both) were formed within the root cell wall (apoplastic) space, thereby reducing the concentration of free, toxic Al^{3+} ions. Silicon application also results in the formation of HAS in the apoplast of the root apex of maize and wheat, thus detoxifying Al (Cocker *et al.*, 1998b; Wang *et al.*, 2004).

Although it is now well recognized that Si can have ameliorative effects on the phytotoxicity of Al, the effect of Si on Al toxicity has been mostly conducted in hydroponic culture (or nutrient solution) and field studies in soil systems. Such conditions may confound Al-Si chemistry and the equilibrium between solid and liquid phases in the soil. For example, using soil bioassays, the results of the effects of Al toxicity and Ca deficiency on root growth have been difficult to interpret (Adams and Moore, 1983; Adams and Hathcock, 1984; Bruce *et al.*, 1988; Aitken *et al.*, 1990a). Aitken *et al.* (1990a) found that relative root elongation in soil bioassay had a good linear relationship ($R^2 = 0.96$) with that in soil solution bioassay, and indicated that soil solution bioassay could be used to diagnose Al toxicity in soil.

Furthermore, most such studies have involved monocotyledons and a few herbaceous dicotyledons (Prabagar *et al.*, 2011), generally with alkaline Si sources as Si amendments such as Na-, Ca silicate and other silicate slags. Therefore, the amelioration of Al toxicity has been mainly attributed to the effect of increased pH rather than Si (Baylis *et al.*, 1994; Morikawa and Saigusa, 2002). Moreover, applying dolomite, calcite limestone or phosphate is also an effective way to deal with Al toxicity (Wehr *et al.*, 2007). Thus, various Si amendments including lime and phosphorus were used in this current study, in order to investigate the effect of Si only and Si-combined with other elements (Ca, Mg and P) on amelioration of Al toxicity. A bioassay was conducted on mungbean root elongation using soil solution extracted from an acidic Red Ferrosol.

6.2 Materials and methods

6.2.1 Soil collection, preparation, physicochemical properties and incubation

Details of the location, preparation and selected physicochemical properties of the soil are presented in Section 5.2.1 (see Chapter 5).

Monosilicic acid (Mono-Si), calcium silicate (Ca-Si), acidulated calcium silicate (Ac-Ca-Si), magnesium silicate (Mg-Si), acidulated magnesium silicate (Ac-Mg-Si), fused magnesium phosphate (FMP), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Ca-P), lime (CaCO_3), and mulched sugarcane trash and *Tithonia diversifolia* whole plant tops, were added to air-dried soil samples (Table 6.1a) and thoroughly mixed before adding deionized water to bring the soil to field capacity (35% w/w moisture). Note that only Mono-Si was added as solution and the added plant materials (mulched sugarcane trash and *Tithonia diversifolia*) were passed through a 0.5 mm sieve. Each plastic pot (10 cm diameter and 11 cm height) contained 600 g air-dried soil plus amendment and 210 mL deionized water, thus all pots were adjusted to a 35% w/w field capacity (determined by free drainage for 48 hours). Unamended soil is referred to as the control treatment. All treatments were replicated three times and incubated at constant temperature of 40°C for 7 and 30 days before extracting soil solution for bioassay. Pots were maintained at field capacity by daily watering to weight.

6.2.2 Soil solution extraction

Soil solutions were extracted at seven days after incubation (7-DAI) and 30 days after incubation (30-DAI) using hollow-fiber soil solution samplers (Menzies and Guppy, 2000),

which were vertically inserted through the soil from 5 mm under the soil surface to 5 mm above the bottom of the plastic pot. The soil solution sampler was made up of three main parts: a length of polyacrylonitrile micro-pore tubing (Microza AP2010™) blocked at one end and connected to a section of stiff Teflon™ tubing with a double ended hypodermic needle on the end. The needle was inserted into the septum of a 10 mL evacuated vacuum tube at the time of soil solution extraction. In order to prevent the soil solution from contamination, all connections between the tubes were sealed and the sampler was gently inserted into the soil before adding deionized water on the first day of the incubation period. Five soil solution samplers were inserted in each pot (600 g soil) to ensure sufficient soil solution was extracted for the bioassay.

Table 6.1a Rates of different silicate amendments applied to pots (10 cm diameter and 11 cm height) of a Red Ferrosol from Alstonville, NSW in the incubation experiment. Application rates calculated on a soil surface area basis per 10 cm depth at the bulk density of the soil

Amendment	Si	P	Ca	Mg	¹ OM
	(kg ha ⁻¹)				
Mono-Si-1	210	0	0	0	0
Mono-Si-2	420	0	0	0	0
Ca-Si	210	0	175	0	0
Ac-Ca-Si	210	0	195	1	0
Mg-Si	210	0	2	288	0
Ac-Mg-Si	210	0	43	299	0
FMP-1	112	68	175	83	0
FMP-2	210	127	329	155	0
Ca-P-1	0	68	87	0	0
Ca-P-2	0	136	175	0	0
Lime	2	0	175	0	0
Sugarcane trash	210	4	11	10	6681
<i>Tithonia</i> -1	71	68	255	65	16170
<i>Tithonia</i> -2	210	199	753	192	47666
Mono-Si + lime	210	0	175	0	0
Mg-Si + lime	210	0	175	288	0

¹ air-dried organic materials applied

6.2.3 Seedling pre-germination

Mungbean (*Phaseolus aureus* Roxb.) has been known as an Al sensitive crop (Aitken *et al.* 1990a); therefore, it was chosen in this study. Seeds of mungbean were manually selected for uniform size, thoroughly washed with deionized water, and then soaked in 0.002 M CaSO₄ for 24 hours (referred to as ‘normal pre-germination’). In order to investigate the effect of silicon pre-treatment on root elongation of mungbean seedlings, another set of seeds was soaked for 24 hours in 0.002 M CaSiO₃ rather than 0.002 M CaSO₄ (referred to as ‘silicate pre-germination’). Seedlings with white root tips and roots about 1 to 2 mm long were selected, and then transferred into a tray containing clean washed and dried sand (passed through a 2-mm sieve) 5 cm deep. The seedlings were carefully placed in the sand with the root tip facing down and covered with 1 cm sand. Note that 0.002 M CaSO₄ or 0.002 M CaSiO₃ solution was immediately added to separate trays for normal- or silicate pre-germination, respectively. The trays were placed in an incubator at a constant temperature of 25°C for 48 hours. This procedure produces a higher proportion of seedlings with straight roots of uniform length than other methods such as pre-germinating seeds on germination pads in trays (Aitken *et al.*, 1990a). In addition, a small amount of fine sand adhered to the developing root hairs (but not to the stem) making it easier to discern the junction of root and stem. This facilitated screening the seedlings for uniform root length. Seedlings were then recovered by gently washing the contents of the trays through an appropriately sized sieve with 0.002 M CaSO₄ or 0.002 M CaSiO₃ solution for normal- or silicate pre-germination, respectively.

6.2.4 Soil solution bioassay

For each treatment, pH and electrical conductivity (EC) were measured on the soil solution extracted 7-DAI and 30-DAI from three separate replications. The three replicate samples were reduced to duplicates by proportional volumetric mixing of the triplicates, and subsamples of the duplicates taken for chemical analysis. The duplicate soil solutions from each treatment were then bulked and thoroughly mixed for use in the bioassay.

A set of soil solution treatments was created from the control treatment (7-DAI and 30-DAI) by adding saturated Ca(OH)₂ to adjust soil solution to pH 5.50 so that relative root elongation (RRE) can be calculated for the studied treatments. Two more treatments (only for soil solution of 7-DAI) are as follows: soil solution treated with Ca (0.5 mM as CaCl₂) and soil solution treated with CaCl₂ and MgCl₂ to give equilibrated concentrations of Ca and Mg respectively, equivalent to those in the soil solution of FMP-1 amendment (Table 6.1a). The

same process was performed for the bioassay of the mungbean seedlings with silicate pre-germination, but only using extracted soil solution 7-DAI. The soil solution bioassay treatments are shown in Table 6.1a as different amendments for 7-DAI, and in Table 6.1b as additional treatments created from the control treatment (unamended soil) for 7-DAI and/or 30-DAI.

Table 6.1b Additional soil solution bioassay treatments

Treatment	Extracted soil solution (DAI)
0.002 M CaSO ₄ pre-germinated	
Control (unamended soil)	7 and 30
Control with adjusted to pH 5.50	7 and 30
Control + 0.5 mM Ca (as CaCl ₂)	7
Control + Ca and Mg (as CaCl ₂ and Mg Cl ₂)	7
0.002 M CaSiO ₃ pre-germinated	
Control (unamended soil)	7
Control with adjusted to pH 5.50	7

Aliquots (11 mL) of the bulked soil solution from each treatment were dispensed into each of five polypropylene tubes (12 mm internal diameter and 110 mm height) designated as five replications per treatment. Pre-germinated mungbean seedlings with 25 ± 2 mm root length were selected and one seedling was placed into each tube and retained by an 8-mm thick circular foam plug with a central hole such that the root was suspended in the soil solution. All tubes with the seedlings were placed in racks with tubes about 5 cm apart, and the racks placed in an incubator with a constant temperature of 25°C, 14-hour light and 10-hour dark for a period of 72 hours.

6.2.5 Measurement of root elongation and root staining

Root elongation and relative root elongation measurement

Seedlings were removed from the polypropylene tubes and the foam plugs and the main root length was measured. As described in the following equations, root elongation (RE) was calculated by subtracting the final root length from the initial root length, Relative root

elongations were then obtained by expressing the RE in indicated treatments as a percentage of the RE in the pH adjusted (pH = 5.50) treatment.

$$\text{RE (mm 72h}^{-1}\text{)} = \text{Final root length} - \text{Initial root length}$$

$$\text{RRE (\%)} = \frac{\text{RE of indicated treatments}}{\text{RE of adjusted pH (5.5)treatment}} \times 100$$

Root staining

Root tips were stained using hematoxylin (HEM), chromeazurol S (CAS) and eriochrome cyanine R (ECR) dye to detect Al sensitivity of mungbean root tips. These dyes were prepared as follows: 0.5 g hematoxylin dissolved in 250 mL deionized water, stirred overnight, 0.05 g potassium iodide (KI) added, the solution stirred again and then filtered. Chromeazurol S and eriochrome cyanine R were used as 0.05% solutions in deionized water. These three staining solutions were stored in dark bottles at 4°C and used within 10 days (Wehr *et al.*, 2010 and Wehr personal communication 2011).

Whole roots (after root elongation was measured) were rinsed under running deionized water for approximately 1 minute using an eppendorf tube, and root tips (1 cm long) were excised and separately collected in polypropylene tubes for staining. The three above staining solutions (1 mL) were separately added and roots were stained overnight at 4°C, followed by de-staining with deionized water over 2 days (the staining solution was replaced with 3 batches of deionized water). Stained root tips were then scanned under 40-time magnification with a microscope in both light- and dark-field illumination.

6.2.6 Chemical components analysis

Soil exchangeable acidity was extracted with 1 M KCl and analysed for Al^{3+} and exchangeable acidity by the 15G1 method (Rayment and Higginson, 1992); H^{+} was obtained by the difference between exchangeable acidity and Al^{3+} .

Soil solutions were immediately measured for pH and EC after extraction using a pH meter (901-CP model, TPS Pty. Ltd., Australia) and an EC meter (labCHEM cond. model, TPS Pty. Ltd., Australia), respectively. The samples were then stored at 4°C for further analysis. Total

concentrations of dissolved Al, Ca, Mg, Mn, P and Si were measured using inductively coupled plasma - atomic emission spectrometry (ICP-AES) (Vista MPX-radial model, Varian, Australia). Monomeric Al was measured by the pyrocatechol violet colorimetric method (Kerven *et al.*, 1989). The concentration of monomeric Al in soil solution was then used to estimate Al^{3+} activities using a multi-function chemical speciation program, GEOCHEM-EZ (Shaff *et al.*, 2010). Soluble P was analysed by the malachite green colorimetric method (Motomizu *et al.*, 1983), and available Si was determined using a modified approach (Berthelsen *et al.*, 2003) to the blue silicomolybdous acid colorimetric procedure (Weaver *et al.*, 1968). Dissolved organic carbon (DOC) was analysed by a Sievers Innovative Oxidation Laboratory Total Organic Carbon Analyzer (GE Analytical Instruments, USA). Nitrate-N and ammonium-N were analysed by the Skalar methods M461-318 and M155-008R, respectively, on a Continuous Flow Analyzer (Skalar Analytical B.V., The Netherlands).

6.2.7 Statistical analysis

Root elongation and relative root elongation were calculated using Microsoft Office Excel 2007. Relative root elongation and chemical components of soil solutions from the bioassay were statistically analysed using one-way analysis of variance (ANOVA) to compare differences between the means in regards to the components of different amendments. Simple linear regressions were used as a data exploration tool to determine any possible associations between RRE and each measured soil solution variable. Stepwise (forward and backward) multiple regression was also used to further explore the combined effect of measured soil solution variables on RRE, using the AIC (Akaike's Information Criterion) to select the best model. The linear correlation coefficient (r) was used to express the relationships between selected soil solution variables and RRE. Significant levels were set to $P < 0.05$ for all tests. All analyses were undertaken in the GenStat Discovery Edition 3 (seventh edition, version - 7.2.2.222) for Windows XP. Normality of the dataset was tested and where appropriate, transformations to meet normality assumptions were performed.

6.3 Results

6.3.1 Changes in selected chemical components of the soil solution and root elongation following different incubation periods

Differences of chemical components in soil solution and root growth between 7 and 30 days after incubation

Chemical components in soil solutions of the control, Mono-Si and FMP treatments changed between 7 days after incubation (7-DAI) and 30 days after incubation (30-DAI) (Table 6.2). Electrical conductivity of all treatments increased, but pH decreased, with increasing incubation period. The extent of pH decrease was larger in the control treatment (0.41 unit) than in the Mono-Si and FMP treatment (0.20 and 0.25 unit, respectively). Aluminium concentrations in the soil solutions were much higher at 30-DAI than at 7-DAI. The Al concentration of the control treatment (unamended treatment) at 30-DAI increased nearly 10-fold compared to that at 7-DAI, but it was about 4- and 5-fold for the FMP and Mono-Si treatment, respectively. Phosphorus and Si concentrations in the soil solutions did not vary with incubation time in the control treatment. Whereas Si decreased with increasing incubation time for both Mono-Si and FMP treatments; the P concentrations in these treatments were not changed much between two incubation periods and were higher than in the control treatment (Table 6.2). Hence Si application can release P into soil solution at least as much as direct P additions in Ferrosol soils.

Table 6.2 Means and standard errors (in brackets) of changes in electrical conductivity (EC), pH, Al, P, and Si in soil solutions of selected treatments following 7 and 30 days incubation of a Red Ferrosol at field capacity

Treatment	Incubation period	EC (dS m ⁻¹)	pH	Al		P	Si
				(μM)			(mM)
Control	7-DAI	0.73 (±0.00)	4.29 (±0.02)	20.9 (±0.4)	0.02 (±0.00)	0.17 (±0.00)	
	30-DAI	1.09 (±0.04)	3.88 (±0.02)	193 (±0.3)	0.02 (±0.01)	0.19 (±0.00)	
Mono-Si-1	7-DAI	0.75 (±0.01)	4.14 (±0.01)	24.4 (±0.43)	0.11 (±0.01)	0.69 (±0.00)	
	30-DAI	0.99 (±0.07)	3.94 (±0.02)	127 (±0.06)	0.08 (±0.01)	0.44 (±0.00)	
FMP-2	7-DAI	0.74 (±0.01)	4.69 (±0.03)	2.9 (±0.02)	0.08 (±0.00)	0.43 (±0.00)	
	30-DAI	1.12 (±0.04)	4.44 (±0.06)	12.5 (±0.05)	0.10 (±0.01)	0.39 (±0.00)	

Relative root elongation of mungbean 7-DAI in the unamended soil solution compared to the pH (5.5) adjusted treatment was approximately 45% (Figure 6.1). Relative root elongation in the unamended soil solution 30 days after incubation (30-DAI) was about 30%, a significant reduction from the 7-DAI value. This is attributed to the increase in Al concentration associated with a decline in pH in the unamended soil solution of 30-DAI compared to that 7-DAI (Figure 6.1).

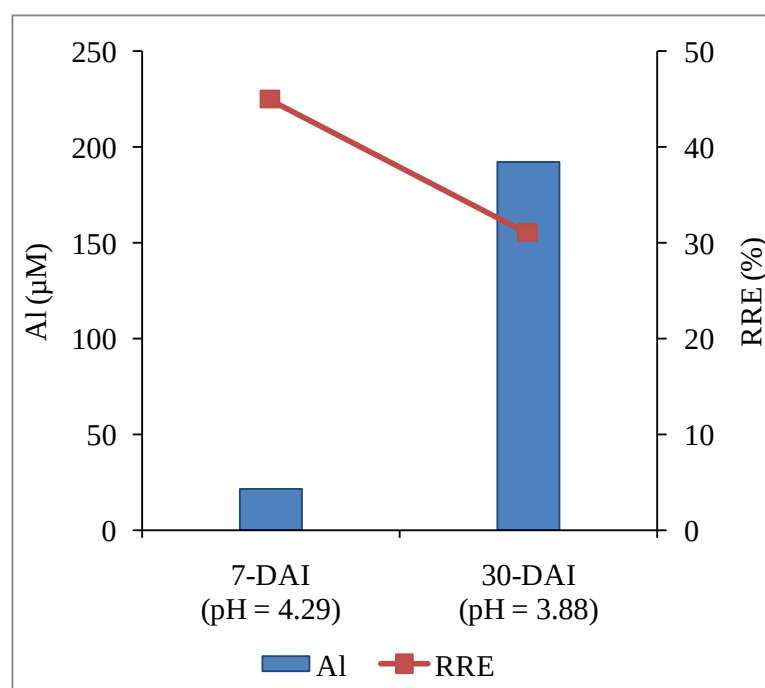


Figure 6.1 Relative root elongation (RRE) of mungbean and differences of pH and Al concentration in unamended soil solution at 7- and 30-DAI (LSD_{0.05} = 0.14; 8.80 µM and 12 % for pH, Al and RRE, respectively)

Because of the extremely low pH and high Al concentrations present in some of the 30-DAI soil solutions, it was decided to restrict the examination of Si-induced amelioration of Al toxicity for mungbean seedling primarily to the 7-DAI soil solutions, and the results are reported in the following sections.

Relationship of chemical components in soil solution with relative root elongation

The relationships between selected chemical components in soil solutions at 7-DAI and RRE in some selected treatments were examined using a linear correlation matrix in order to separately describe the effects of Si only, Si + Ca, Si + Ca + Mg, and Si + organic matter (OM) on RRE (Table 6.3). Generally, in all selected treatments Al significantly ($P < 0.05$) and negatively correlated with RRE, while pH and Si showed significant positive correlations

with RRE. The application of Mono-Si may reduce soil solution pH, but it also significantly decreased Al concentration, thus improving RRE. Stronger correlations with pH and Si were observed where Ca, Mg and P were also present due to potentially synergistic effects of associated these ions on root growth (Table 6.3). The applications of organic amendments did not only show the significantly positive correlation of DOC, but also of Ca and Mg with RRE (Table 6.3 – column d). However, the negative correlation of Si and RRE observed in these treatments suggesting that Si may form complexes with organic matter which could not be detected by the blue silicomolybdous acid colorimetric method. The evidence is that the lowest of measured available Si was observed in the *Tithonia*-2 treatment, which was the highest DOC content, compared to the other treatments.

Table 6.3 Linear correlation coefficient (r) for the relationships between soil solution properties of (a) Si treatments (control, Mono-Si-1, Mono-Si-2); (b) Si, Ca and P treatments (control, Ca-Si, FPM-2, Ca-P-2); (c) Si, Ca and Mg treatments (control, Mg-Si, Ac-Mg-Si, FPM-2, Mg-Si + lime, Ac-Mg-Si + lime); (d) organic amendment treatments (control, sugarcane trash, *Tithonia*-1, *Tithonia*-2) and relative root elongation

Soil solution properties	Relative root elongation			
	(a) (n = 6)	(b) (n = 10)	(c) (n = 12)	(d) (n = 8)
pH	-0.70	0.97***	0.99***	0.84*
Al	-0.13	-0.92***	-0.71***	-1.00**
Mn	0.78	-0.98**	0.38	0.76
Ca	-0.77	-0.17*	0.60*	0.96*
Mg	-0.60	-0.05	0.76***	0.93**
P	0.91	0.40**	0.03	0.77
Si	0.97*	0.72***	0.71*	-0.81
DOC	nd ⁽¹⁾	nd	nd	0.85*

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; ⁽¹⁾ not determined due to none organic amendment in these treatments

Stepwise multiple linear regressions were used to investigate interactions between various soil solution components and RRE. Due to the strong root growth effects of DOC the three organic amendment treatments were not included in the following stepwise regression.

The following regression equation best described RRE:

$$\text{RRE} = 158.9 (\pm 22.2) \text{pH}^{***} + 11.4 (\pm 4.2) \text{Mg}^* + 47.1 (\pm 13.1) \text{Si}^{**} - 630.2 (\pm 101.4) \text{R}^2 = 0.82$$

Where *** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$

None of the additional variables of EC, NO₃-N, NH₄-N, Ca, Mn, P or monomeric Al significantly ($P = 0.05$) increased the variation in RRE explained by the model.

Because pH was correlated ($P < 0.05$) with several of the measured soil solution attributes (DOC, Mn, Al, P and Si), the step-up regression was repeated with all attributes except pH.

The following regression equation best described RRE:

$$\text{RRE} = 0.08 (\pm 0.03) \text{EC}^{**} + 0.93 (\pm 0.44) \text{DOC}^* - 1.09 (\pm 0.70) \text{Al}^* + 37.9 (\pm 25.0) \text{R}^2 = 0.69$$

Where *** $P < 0.001$; ** $P < 0.01$.

None of NO₃-N, NH₄-N, Ca, Mg, Mn, P or Si significantly ($P = 0.05$) increased the variation in RRE explained by the model.

When the soil solution characteristics and RRE data of the sugarcane trash and *Tithonia* treatments were included in the step-up regression analysis, RRE was again best predicted by a combination of Al ($P < 0.001$) and Mg ($P < 0.05$) with $\text{R}^2 = 0.65$. These results indicate that RRE was primarily inhibited by monomeric Al and suggest ameliorative effects of Mg, Si and DOC.

6.3.2 Effect of silicon amendments on aluminium toxicity and relative root elongation

Monosilicic acid and silicate pre-treatment effects

Relative to the unamended soil solution, pH decreased in the presence of Si applied as monosilicic acid (Mono-Si), particularly at the lower rate of soil amendment (210 kg Si ha⁻¹) (Figure 6.2). Soil solution Al concentration increased significantly in response to the lower pH of the 210 Si treatment but was lower at 420 Si than in the unamended soil solution even though the soil solution pH of this treatment was lower than the unamended solution. In spite of the lower soil solution pH and higher Al of the 210 Si treatment compared to the

unamended solution, RRE was higher indicating an ameliorative Si effect on Al toxicity. The higher Si rate increased RRE further and decreased solution Al concentration, suggesting that the Si complexed the Al, reducing the concentration of the toxic monomeric form despite the low solution pH (Figure 6.2).

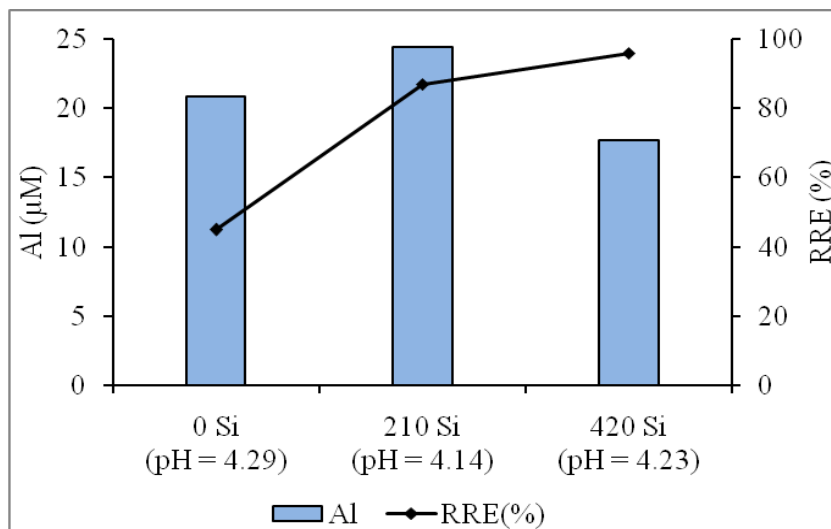


Figure 6.2 Effect of monosilicic acid on pH, monomeric Al concentration in soil solution and relative root elongation (RRE) of mungbean ($LSD_{0.05} = 0.05$; 1.6 and 11 for pH, Al and RRE, respectively)

Although mungbean seedlings were grown in unamended soil solutions with identical pH (4.29) and monomeric Al concentration (20.9 μM), the mean RRE of the seedlings with 0.002 M CaSiO_3 pre-germination was significantly higher, and at 85%, nearly double that of the 0.002 M CaSO_4 pre-germination treatment (Table 6.4). Thus, the Si amelioration effect is not only related to the reduction of monomeric Al concentration in soil solution, but is also related to inhibition of Al-uptake by the root.

Table 6.4 Root growth and relative root elongation of mungbean in unamended soil solution as affected by calcium silicate (0.002 M) pre-germination

Treatment	pH	Al (μM)	Relative root elongation (%)
CaSO_4 pre-germinated	4.29	20.9	45 b
CaSiO_3 pre-germinated			85 a
$LSD_{(0.05)}$	-	-	8.0
CV(%)	-	-	6.7

Means in the same column followed by different letters are significantly different at $P = 0.05$

Different silicate sources effects

In order to compare the pure Si (Mono-Si) and other Si containing products, several Si amendments (including inorganic silicate and organic amendments) were used, at the equivalent rate of 210 kg Si ha⁻¹, to investigate the effects of these products on amelioration of Al toxicity to mungbean seedlings. The results shown in Table 6.5 illustrate that all Si-containing treatments significantly ($P < 0.05$) increased soil solution pH and substantially decreased Al concentration compared to those in Mono-Si treatments. The largest effects on RRE were attributed to *Tithonia* and FMP amendments with RRE figures of 150% and 141% respectively (Table 6.5). Relative root elongation in other Si containing products was also higher than that in Mono-Si treatment, with the exception of sugarcane trash amendment. The effects of all amendments on RRE ranged as follows: *Tithonia* > FMP > Ac-Mg-Si > Ca-Si = Ac-Ca-Si > Mg-Si > Mono-Si > sugarcane trash.

Table 6.5 Effect of different silicate amendments (at 210 kg Si ha⁻¹) on pH, monomeric Al concentration in soil solution and relative root elongation of mungbean

Amendments	pH	Al (μ M)	Relative root elongation (%)
Mono-Si	4.14 g	24.4 a	87 c
Ca-Si	4.55 c	6.0 e	103 b
Ac-Ca-Si	4.46 de	10.4 d	100 bc
Mg-Si	4.39 e	9.9 d	93 c
Ac-Mg-Si	4.48 cd	13.0 c	117 b
FMP	4.69 b	2.9 f	141 a
Sugarcane trash	4.30 f	22.7 b	60 d
<i>Tithonia</i>	5.70 a	1.6 g	150 a
LSD _(0.05)	0.07	0.8	19.0
CV(%)	0.9	3.0	13.6

Means in the same column followed by different letters are significantly different at $P = 0.05$

Fused magnesium phosphate and *Tithonia diversifolia* effects

A comparison of the soil solution compositions at two rates of FMP (112 and 210 kg Si ha⁻¹) with the unamended control treatment indicates that the more Si that was applied, the more the soil solution pH increased and the more the Al concentration in the soil solution decreased

(Figure 6.3). In response, RRE increased greatly with increasing Si applied by FMP; however, there was no significant difference in RRE between 112 and 210 kg Si ha⁻¹ (Figure 6.3). The same trend was observed with *Tithonia* applications of 71 and 210 kg Si ha⁻¹ (Figure 6.4). Soil solution pH increased markedly, Al concentration decreased and RRE increased considerably at the lower Si rate, but RRE was not significantly different between the two rates of *Tithonia* application.

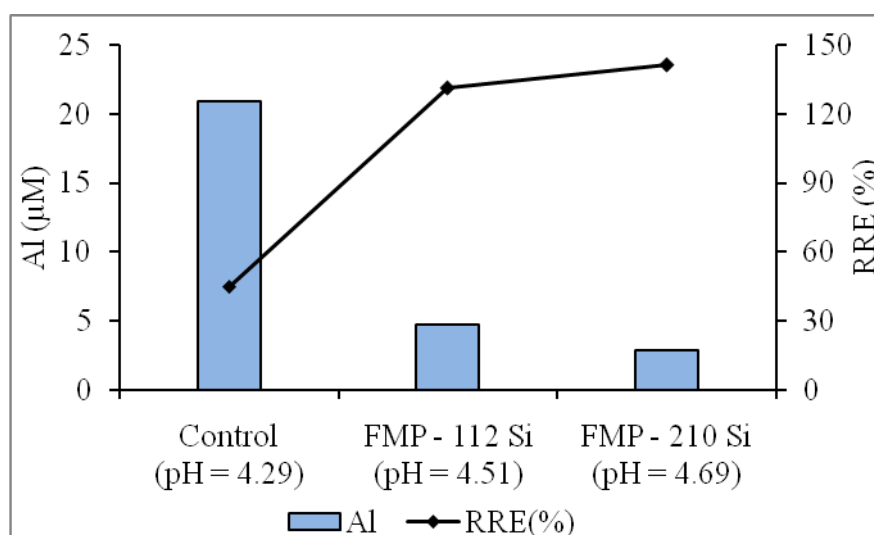


Figure 6.3 Effect of fused magnesium phosphate (FMP) (at 112 and 210 kg Si ha⁻¹) on pH, monomeric Al concentration in soil solution and relative root elongation of mungbean (LSD_{0.05} = 0.09; 1.6 and 18 for pH, Al and RRE, respectively)

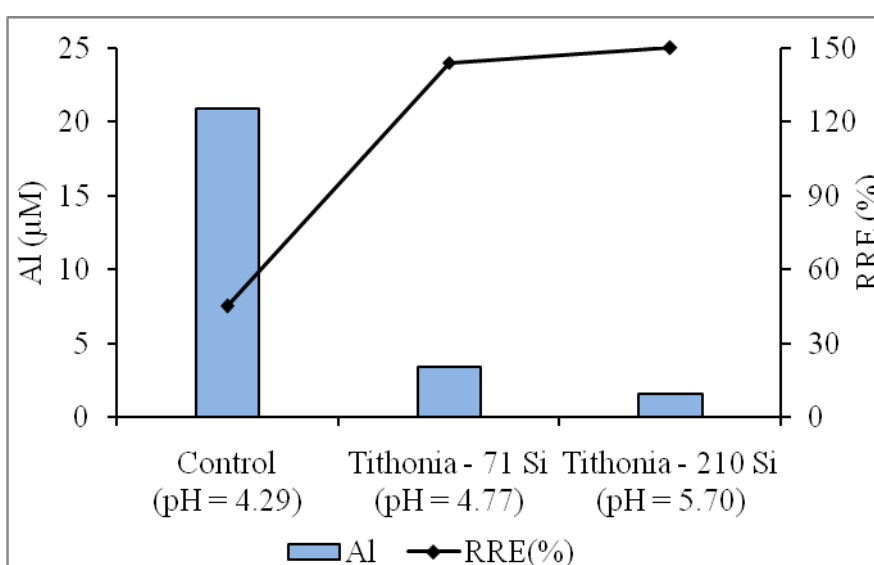


Figure 6.4 Effect of *Tithonia diversifolia* (at 71 and 210 kg Si ha⁻¹) on pH, monomeric Al concentration in soil solution and relative root elongation of mungbean (LSD_{0.05} = 0.09; 1.6 and 18 for pH, Al and RRE, respectively)

As previously observed for data in Table 6.5, the results show that all inorganic Si containing amendments (Ca-Si, Mg-Si and FMP) are more effective at increasing pH, reducing monomeric Al and improving RRE than the Mono-Si amendment. This can be attributed to the combined effects of Ca and/or Mg and/or P with Si. For instance, besides Si, Ca is also contained in Ca-Si, Mg in Mg-Si and, Ca, Mg and P in FMP. In order to examine the combined effects of Si and Ca on pH, Al and RRE, lime and mono calcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$] (Ca-P) were used as additional amendments, and lime was added to those without Ca, such as Mono-Si and Mg-Si amendments. By doing this, all amendments had equivalent Ca at 175 kg ha^{-1} (Table 6.6). The addition of lime to Mono-Si and Mg-Si amendments increased pH, reduced monomeric Al and increased RRE relative to these amendments without lime (cf. Tables 6.5 and 6.6). Thus, Ca in combination with Si increases RRE relative to Ca (as lime) alone. In addition, Ca combined with P (as Ca-P amendment) does not increase RRE over that obtained with lime alone (Table 6.6). Although the rate of Si applied in the FMP treatment was lower ($112 \text{ kg Si ha}^{-1}$) than that in other treatments ($210 \text{ kg Si ha}^{-1}$) such as Ca-Si and Mg-Si + lime, the RRE of the FMP treatment was significantly ($P < 0.05$) higher than for any other treatment (Table 6.6). This must be due to the combined effects of Si, Ca, Mg and P contained in FMP on root growth.

Table 6.6 Relative root elongation, pH and monomeric Al concentration in soil solution affected by different amendments equivalent to $175 \text{ kg Ca ha}^{-1}$

Treatment	pH	Al (μM)	Relative root elongation (%)
Ca-Si ($210 \text{ kg Si ha}^{-1}$)	4.55 a	6.0 d	103 bc
FMP ($112 \text{ kg Si ha}^{-1}$)	4.51 ab	4.7 f	131 a
Ca-P (0 kg Si ha^{-1})	4.37 c	9.2 a	77 d
Lime (0 kg Si ha^{-1})	4.43 c	6.3 c	87 cd
Mono-Si + Lime ($210 \text{ kg Si ha}^{-1}$)	4.37 c	7.8 b	99 bc
Mg-Si + Lime ($210 \text{ kg Si ha}^{-1}$)	4.44 bc	5.9 e	107 b
LSD _(0.05)	0.07	0.0	18.0
CV(%)	0.8	0.0	13.8

Means in the same column followed by different letters are significantly different at $P = 0.05$

It is noteworthy that the addition of *Tithonia* to the soil was the only other treatment that resulted in a RRE higher (although not significant at $P = 0.05$) than that obtained with FMP (Table 6.5). When these amendments were compared with Ca-P at equivalent P additions of

68 kg ha⁻¹ but different Si doses of 0, 71 and 112 kg Si ha⁻¹, RRE was significantly higher for the *Tithonia* and FMP amendments as was pH, while monomeric Al was lower (Figure 6.5). Although Si applied in *Tithonia* (71 kg Si ha⁻¹) was lower than that from FMP (112 kg Si ha⁻¹), the effect of *Tithonia* application on RRE was greater than that of FMP (Figure 6.5). This suggests that apart from the effects of Si, Ca, Mg and P on RRE, organic matter may also play an important role in the amelioration of Al toxicity for root growth.

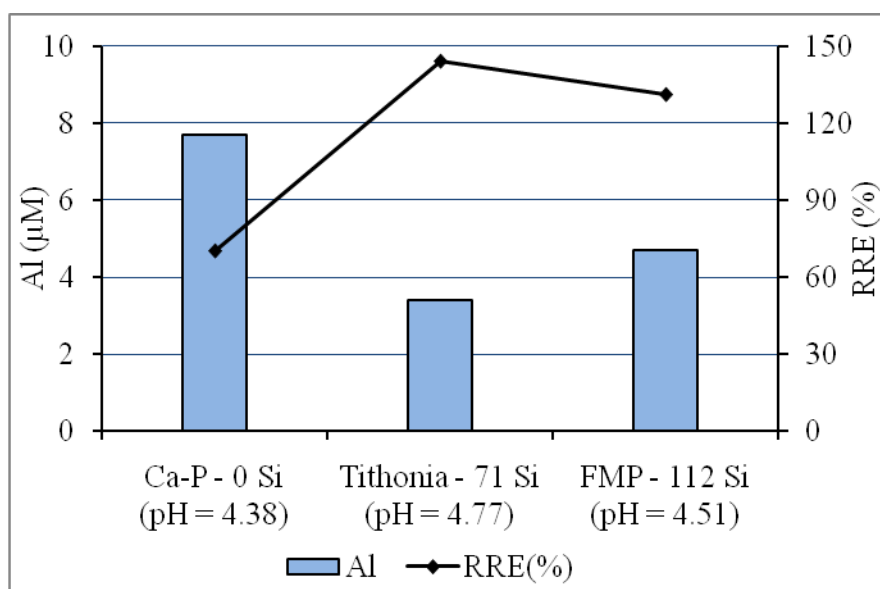


Figure 6.5 Relative root elongation, pH and monomeric Al concentration in soil solution affected by different amendments equivalent to 68 kg P ha⁻¹ and different rates of Si application (at 0; 71 and 112 kg Si ha⁻¹) (LSD_{0.05} = 0.08; 1.6 and 15 for pH, Al and RRE, respectively)

Reactions of Al³⁺ and hydrolysed Al bound on root tips with three different dyes

The binding of Al³⁺ and hydrolysed Al to negative charges on plant cell walls exerts initial toxic effects on root growth and the greater tendency for Al³⁺ to bind to plant root tips also results in inhibition of root elongation (Schmohl and Horst, 2000). Staining of roots affected by Al toxicity with dyes, such as chromeazurol S (CAS), eriochrome cyanine R (ECR) and hematoxylin (HEM), can be used to detect Al sensitivity of plant roots instead of analytical techniques such as atomic absorption spectroscopy and inductively-coupled plasma atomic emission spectroscopy (ICPAES) (Hawke *et al.*, 1996). In this study the three dyes above were used to stain root tips and detect Al sensitivity of mungbean roots. Hematoxylin is a dye reacting with Al and P, thereby forming a purple precipitate in roots. The P is released from roots due to Al-induced membrane damage (Ownby, 1993); HEM therefore indicates the

extent of Al damage. On the other hand, ECR is related to the amount of Al bound to the cell wall and CAS detects both the amount of Al and the extent of Al hydrolysis in roots (Wehr *et al.*, 2009).

In general, root tips of most treatments reacted strongly with all three dyes except for both *Tithonia* treatments. Depending on Al concentration and active Al^{3+} in each treatment, root tips were stained from dark violet to light purple or light yellow with CAS or HEM, and stained from dark blue to light blue in whole or parts of root tips with ECR (Figures 6.6 - 6.9).

The control and Mono-Si treatments, with high Al concentrations in soil solution, resulted in staining with all three dyes; in particular the whole root tips of the control treatment developed very dark violet and dark blue staining with CAS and ECR, respectively. The light purple staining with HEM exposes the large damaged area on the root tip of the control treatment (Figure 6.6). However, the extent of staining on the root tips of the higher rate ($420 \text{ kg Si ha}^{-1}$) of Mono-Si was less than for the lower rate ($210 \text{ kg Si ha}^{-1}$). When lime was used together with Mono-Si ($210 \text{ kg Si ha}^{-1}$), the root tips showed only a limited effect at the root tip. The root tips with Si pre-treated also showed less effect than without Si pre-treated (Figure 6.6).

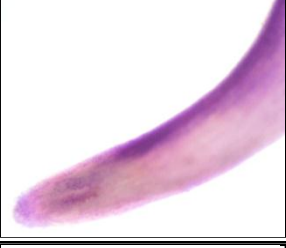
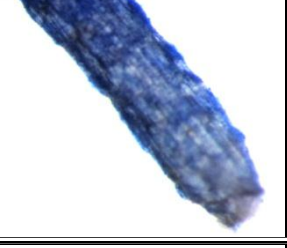
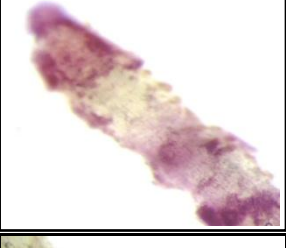
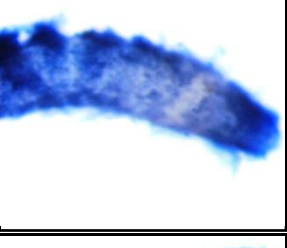
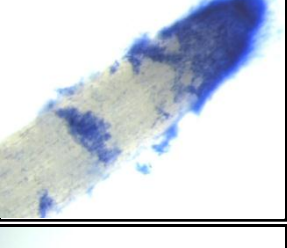
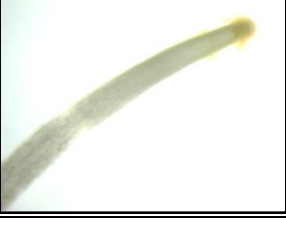
Treatment	Chromazurol S	Eriochrome cyanine R	Hematoxylin
Control (0 kg Si ha ⁻¹) pH 4.29; 20.9 µM Al			
Control + Si pre-treated pH 4.29; 20.9 µM Al			
Mono-Si (210 kg Si ha ⁻¹) pH 4.14; 24.4 µM Al			
Mono-Si (420 kg Si ha ⁻¹) pH 4.23; 17.7 µM Al			
Mono-Si + lime (kg ha ⁻¹) (210 Si + 175 Ca) pH 4.37; 7.8 µM Al			

Figure 6.6 Reactions of Al³⁺ and hydrolysed Al bound on mungbean root tips grown in soil solution treated with Mono-Si, Mono-Si plus lime and pre-treated by Ca-Si

The amendments with combinations of Si and Ca or/and Mg (Ca-Si, Mg-Si and FMP) had less effect with the staining dyes than those with Si only (Mono-Si). The treatments of Ca-Si, Mg-Si + lime and Ac-Mg-Si resulted in less reaction with all stains than the Mg-Si, Ac-Ca-Si and lime treatments (Figure 6.7). Similarly, FMP treatments showed less intensive staining than Ca-P treatments (Figure 6.8).

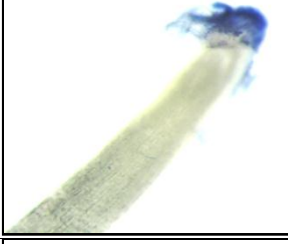
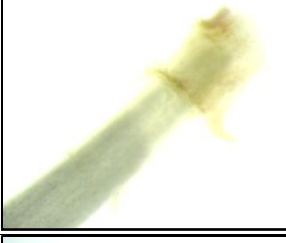
Treatment	Chromeazurol S	Eriochrome cyanine R	Hematoxylin
Ca-Si (kg ha ⁻¹) (210 Si + 175 Ca) pH 4.55; 6.0 µM Al			
Ac-Ca-Si (kg ha ⁻¹) (210 Si + 195 Ca) pH 4.46; 10.4 µM Al			
Mg-Si (kg ha ⁻¹) (210 Si + 288 Mg) pH 4.39; 9.9 µM Al			
Ac-Mg-Si (kg ha ⁻¹) (210 Si + 43 Ca + 299 Mg) pH 4.48; 10.3 µM Al			
Lime (175 kg Ca ha ⁻¹) pH 4.43; 6.3 µM Al			
Mg-Si + lime (kg ha ⁻¹) (210 Si + 175 Ca + 285 Mg) pH 4.44; 5.9 µM Al			

Figure 6.7 Reactions of Al³⁺ and hydrolysed Al bound on mungbean root tips grown in soil solution treated with Ca-Si, Mg-Si and lime

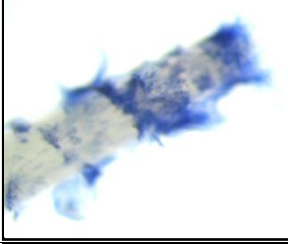
Treatment	Chromeazurol S	Eriochrome cyanine R	Hematoxylin
FMP (kg ha ⁻¹) (112 Si + 175 Ca + 83 Mg + 68 P) pH 4.51; 4.7 µM Al			
FMP (kg ha ⁻¹) (210 Si + 327 Ca + 155 Mg + 129 P) pH 4.69; 2.9 µM Al			
Ca-P (kg ha ⁻¹) (87 Ca + 68 P) pH 4.37; 9.2 µM Al			
Ca-P (kg ha ⁻¹) (175 Ca + 136 P) pH 4.38; 7.7 µM Al			

Figure 6.8 Reactions of Al³⁺ and hydrolysed Al bound on mungbean root tips grown in soil solution treated with Ca-P and FMP

Root tips from treatments with very low Al concentration in soil solution did not stain with any of three dyes, e.g. the two *Tithonia* treatments (Figure 6.9). On the other hand, due to high Al concentration, the sugarcane treatment was similar to the results of the control and Mono-Si treatments, thus the root tips of this treatment exhibited a strong reaction with all three stains (Figure 6.9). These results are consistent with the work of Wehr *et al.* (2010) who worked with roots of teak (*Tectona grandis* Linn. F.) clones. In a study with maize roots grown in culture media containing 50 µM Al with- and without 1 mM Si application, Corrales *et al.* (1997) observed roots without Si exhibited considerable HEM staining, not only in epidermal and outer cortex cells, but also in cell walls of endodermal cells. In contrast, roots with Si treatment showed only light staining in parts of cell walls of the epidermis and outer cortex (Corrales *et al.*, 1997). This suggests that Si prevented Al entering the roots where it could cause membrane damage. Wehr *et al.* (2010) proposed that roots staining positive with

two out of three dyes were Al-sensitive (i.e., suffered Al damage), whereas roots reacting with only one dye were considered Al resistant.

These qualitative staining results, together with previously discussed RRE and soil solution composition data suggest that soil solution Al concentration and Al activity are closely related to Al bound on root tips or inside the root, thus causing root damage. Silicon plays an important role in ameliorating Al toxicity in mungbean roots.

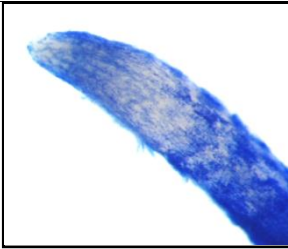
Treatment	Chromeazurol S	Eriochrome cyanine R	Hematoxylin
Sugarcane (kg ha ⁻¹) (210 Si + 11 Ca + 10 Mg + 4 P + 6.68 tonnes OM) pH 4.30; 19.3 µM Al			
Tithonia (kg ha ⁻¹) (71 Si + 255 Ca + 65 Mg + 68 P + 16.2 tonnes OM) pH 4.77; 3.4 µM Al			
Tithonia (kg ha ⁻¹) (210 Si + 753 Ca + 192 Mg + 199 P + 4.77 tonnes OM) pH 5.70; 1.6 µM Al			

Figure 6.9 Reactions of Al³⁺ and hydrolysed Al bound on mungbean root tips grown in soil solution treated with sugarcane trash and Tithonia

6.4 Discussion

Silicon has been reported by some authors to have an ameliorative effect on Al toxicity in higher plants, yet others have reported little or no effect. Such inconsistencies may result from different experimental conditions, such as nutrient media, applied Si sources and rates, plant species and cultivars, the initial Si status of plants used and the growth period (reviewed by Hodson and Evans, 1995; Cocker *et al.*, 1998a; Ma, 2004; Liang *et al.*, 2007). Although the mechanisms of the amelioration still remain unclear, three suggestions have been proposed: a) solution chemistry effects by which a Si-induced increase in solution pH reduces Al bioavailability due to the formation of hydroxylaluminosilicate (HAS) species; b) in-plant

detoxification of Al in which co-deposition of Al and Si occur; and c) indirect effects which relate to the uptake and transport of other essential nutrients, such as Ca, Mg and P (Hodson and Evans, 1995; Cocker *et al.*, 1998a). This study investigated the ameliorative effects of Si on Al toxicity in mungbean seedlings, which were grown in extracted solutions of an acidic Red Ferrosol from New South Wales with various applied Si sources. These effects will be discussed in the following sections.

Monosilicic-induced amelioration of aluminium toxicity and enhancement of mungbean root growth

Monosilicic acid (Mono-Si) was used in this study in order to investigate the effect of Si, by itself, on Al toxicity by preventing confounding effects caused by accompanying basic cations (Ca, K or Na). The RRE of mungbean seedlings increased markedly in the presence of Si compared to that in the absence of Si (Figure 6.2). Soil solution pH decreased significantly ($P < 0.05$) in the presence of Si, applied as monosilicic acid (Mono-Si) at both rates of 210 and 420 kg Si ha⁻¹. This is due to the low pH (4.15) of the added Mono-Si solution and that there is not any effect of the accompanying basic cations. Soil solution pH at the higher rate (420 kg Si ha⁻¹) of Mono-Si was nearly 0.1 unit higher than that at the low rate (210 kg Si ha⁻¹), suggesting that specific adsorption of Si occurred on clay surfaces of the variable charge soil used in this study when the higher rate of Si was applied. The mechanism possibly responsible for the pH change is ligand exchange between OH⁻ and SiO₄⁴⁻ ions (Parfitt, 1978). Due to pH decrease relative to the unamended soil solution, Al increased significantly at the lower Si rate (24.4 µM), but decreased at the higher Si rate (17.7 µM) compared to that in the absence of Si (20.9 µM) (Table 6.7). Although pH was still lower in the 420 kg Si ha⁻¹ treatment than in the absence of Si, Al significantly decreased at the high rate of Si. This is attributed to the formation of HAS in this treatment which has a high Si concentration (1.02 mM) (Table 6.7). Working on corn roots (*Zea mays* L.) in solution pH 4.3, Ma *et al.* (1997) demonstrated that amelioration of Al toxicity was due to the formation of Al and Si complexes in solution. They found that the concentration of toxic Al³⁺, as determined by pyrocatechol violet, was markedly reduced in the presence of 2.0 mM Si compared to 1.0 mM Si. Our findings confirmed this phenomenon at the high rate of applied Mono-Si. Many researchers have reported that HAS species start to form at pH > 4.0 (Birchall, 1990; Exley and Birchall, 1992, 1993; Ma *et al.*, 1997; Perry and Tucker, 1998), and are stable with increasing pH and higher Si concentration (Exley and Birchall, 1992; Hodson and Evans, 1995; Perry and Tucker, 1998). These conditions support our finding that Al concentration

was higher in the lower rate than in the higher rate of Si applied. The results of staining root tips (Figure 6.6) also indicated that the higher rate of Si application resulted in less reaction with the staining dyes.

Table 6.7 Aluminium, silicon and phosphorus concentration and aluminium speciation in soil solution predicted by the GEOCHEM-EZ program at different rates of monosilicic acid application

Treatment	Al	Si	P	Al ³⁺ (a)	Al+PO ₄ ^(b)	Al+OH ^(c)
	(μM)	(mM)	(μM)	(%)		
Control (0 kg Si ha ⁻¹)	20.9	0.17	0.02	81.7	5.6	12.7
Mono-Si (210 kg Si ha ⁻¹)	24.4	0.69	0.11	77.2	14.6	8.2
Mono-Si (420 kg Si ha ⁻¹)	17.7	1.02	0.22	69.6	19.5	10.9

^(a) active Al³⁺ free; ^(b) Al³⁺ complexed with PO₄³⁻; ^(c) Al³⁺ complexed with OH⁻

In addition, other mechanisms may occur for Si-induced amelioration of Al toxicity. Firstly, according to the chemical components of soil solution and Al speciation predicted by GEOCHEM-EZ, it can be seen that Si and P concentrations significantly increased with increasing rate of Si application and that more Al complexed with P; accordingly, active Al³⁺ was reduced following Si application (Table 6.7). In a study of Si amelioration of Al toxicity in barley (*Hordeum vulgare* L.) grown in two non-allophanic Andosols, Morikawa and Saigusa (2002) reported that nearly 100% of Si in the soil solutions was in silicic acid (H₄SiO₄) form. However, use of the programs GEOCHEM and MINTEQ to predict Al activity and speciation in solutions containing Si has been questioned (Li *et al.*, 1989; Barceló *et al.*, 1993), so using speciation modelling to interpret responses is tenuous. Another possible mechanism for Al toxicity amelioration is that Si inhibits Al uptake by roots and/or detoxifies Al in roots. This mechanism can be used to explain the finding that in spite of the high Al concentration in the 210 kg Si ha⁻¹ treatment, RRE of mungbean seedlings was significantly enhanced (Figure 6.2 and Table 6.7).

Many studies have confirmed that the detoxification of Al by Si in plants is due to interactions of the two elements within the plant (reviewed by Hodson and Evans, 1995; Cocker *et al.*, 1998a).

These authors concluded that Al/Si deposition occurs in plants, and that it may play an important role in the mitigation of Al toxicity by Si. With respect to our results, although we

did not undertake chemical analysis for phytoliths or microanalysis [which are the two main methods for demonstrating Al/Si deposition in plants (Hodson and Evans, 1995)], Si pre-treatment was undertaken in order to investigate the effect of Si on Al toxicity occurring within the plant. In the same soil solution of pH 4.29 and 20.9 μM Al, RRE was markedly increased in mungbean seedlings pre-treated with Si compared to those without Si pre-treatment (Table 6.4). This suggests that Si in the root inhibited Al uptake and/or deposition of Al and Si occurred inside roots. Images of the roots pre-treated or not with Si provide evidence for this effect; the staining in roots pre-treated with Si is considerably less than those which were not pre-treated (Figure 6.6). Our results are consistent with the finding of Corrales *et al.* (1997), who studied the effect of Si pre-treatment on Al toxicity in maize roots. They found that plants pre-treated with 1 mM Si and exposed to Al (up to 50 μM) had higher root growth rates than plants without Si pre-treatment. In addition, the authors showed that less Al was taken up into root tips of plants that were pre-treated with Si. In an experiment with barley, Hammond *et al.* (1995) also reported that Si exhibited significant ameliorative effects on Al toxicity and the amelioration was most marked where the toxic effects of Al were the greatest. As much as 80% amelioration of the decrease in root length was achieved using 2.8 mM Si and 50 μM Al, and the addition of Si reduced Al uptake into the roots (Hammond *et al.*, 1995).

Role of inorganic silicon on aluminium toxicity and mungbean root growth

It is well known, and supported by results discussed in the previous section, that one mechanism of Si alleviation of Al toxicity in plants occurs directly as a result of Si and Al interactions in the external growth media. Si amendments containing basic cations have also been shown to promote such interactions (Li *et al.*, 1996). For instance, the addition of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) results in an increase in pH that subsequently leads to precipitation of Al (Cocker *et al.*, 1998a). In comparison with Mono-Si treatment, all inorganic Si amendments containing Ca or/and Mg (Ca-Si, Mg-Si, Ac-Ca-Si, Ac-Mg-Si and FMP) significantly increased soil solution pH and decreased Al concentration. Hence, the root staining images of these treatments show a significant reduction of Al bound on root surface (Figure 6.7), thus reducing reactions with all three dyes. Consequently, RRE of mungbean seedlings in these treatments were higher than that in the Mono-Si treatment (Table 6.5). Additionally, soil solution pH increased and Al concentration reduced when lime was added together with Mono-Si or Mg-Si. Therefore, RRE of these treatments were similar to that of the Ca-Si treatment and higher than that of Mono-Si or Mg-Si applied alone (Tables 6.5 and

6.6). Consequently all of these results are attributed to the additional effects of Ca or/and Mg contained in these products. In particular, the FMP product which contained both Ca and Mg, had the greatest effect in terms of increasing RRE (Table 6.5), even though Si added by the FMP (112 kg Si ha⁻¹) was less than that added in the other treatments (210 kg Si ha⁻¹) (Table 6.6). This result is supported by the comparison of the staining root images between these treatments (Figure 6.8).

In order to remove the confounding effect of changing pH, Ac-Ca-Si and Ac-Mg-Si were also used in this study. The results show that soil solution pH was lower and Al concentration was higher in these treatments than those in the Ca-Si treatment, but RRE was similar or even higher in the Ac-Mg-Si treatment than in Ca-Si treatment (Table 6.5). Effects of Ca and Mg on Al toxicity in two soybean genotypes grown in nutrient solutions at pH 4.3 were found by Silva *et al.* (2001). The authors reported that Al toxicity was completely alleviated in both genotypes by Ca and Mg, and the response to 2.5 µM Mg was equivalent to at least 3 mM Ca. Tan *et al.* (1992) studied Mg-induced amelioration of Al toxicity in twelve sorghum genotypes grown in nutrient solutions with pH 4.2, and found that increasing Mg concentrations (from 2.5 to 7.5 mM) in the solutions not only reduced the concentrations of Al in/on the roots, but also decreased Al-induced Mg deficiency. Our results show that Ca and Mg significantly increased soil solution pH and enhanced RRE of mungbean seedlings (Figure 6.10), suggesting that Ca and, to a lesser extent, Mg may reduce Al concentration by increasing pH and correcting the deficiencies of these nutrients for root growth. Ca-Si, Ac-Mg-Si and FMP caused higher soil solution P concentrations than Ac-Ca-Si and Mg-Si application (Table 6.8). Therefore, it would be expected that more Al would be complexed with P, resulting in lower Al³⁺ activities in soil solutions of these treatments than in the case of Ac-Ca-Si and Mg-Si.

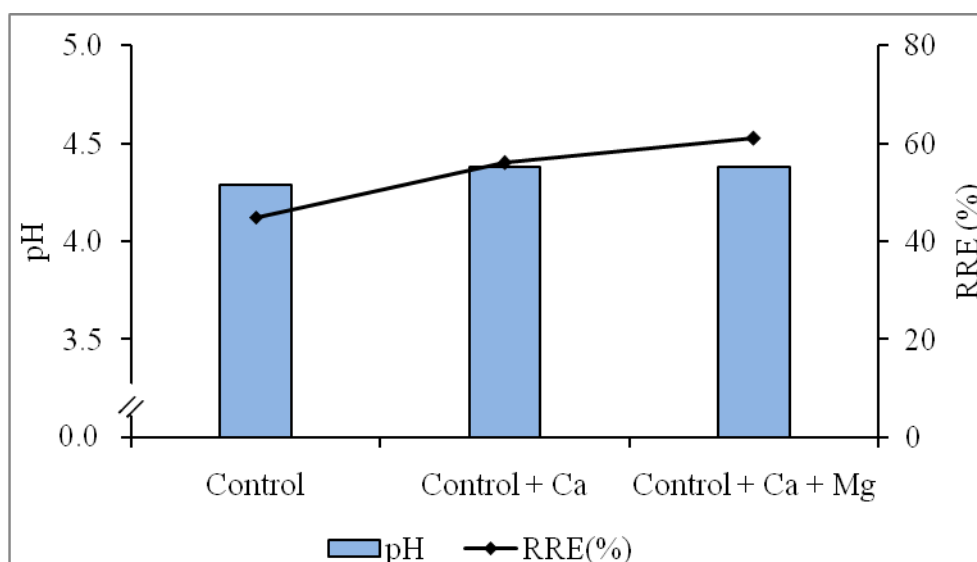


Figure 6.10 Effect of calcium and magnesium (0.5 mM as CaCl_2 for Control + Ca treatment; added CaCl_2 and MgCl_2 equivalent to Ca and Mg in the FMP-1 treatment for Control + Ca + Mg treatment) on soil solution pH and relative root elongation of mungbean ($\text{LSD}_{0.05} = 0.08$ and 10 for pH and RRE, respectively)

Table 6.8 Calcium, magnesium, aluminium, silicon and phosphorus concentrations and aluminium speciation in soil solution predicted by GEOCHEM-EZ program in different inorganic silicate amendments with the equivalence of $210 \text{ kg Si ha}^{-1}$

Treatment	Ca	Mg	Al	Si	P	$\text{Al}^{3+ \text{(a)}}$	$\text{Al} + \text{PO}_4^{3- \text{(b)}}$	$\text{Al} + \text{OH}^- \text{(c)}$
	(mM)	(mM)	(μM)	(mM)	(μM)	(%)		
Mono-Si	0.47	0.79	24.4	0.69	0.11	77.2	14.6	8.2
Ca-Si	0.43	0.41	6.0	0.17	0.13	61.8	17.9	20.3
Ac-Ca-Si	0.87	0.61	10.4	0.20	0.07	76.5	5.5	18.0
Mg-Si	0.35	1.02	9.9	0.21	0.03	74.6	10.4	15.0
Ac-Mg-Si	0.55	2.80	13.0	0.23	0.13	67.2	18.6	14.2
FMP	0.53	0.82	2.9	0.43	0.18	54.1	21.2	24.7

^(a) active Al^{3+} free; ^(b) Al^{3+} complexed with PO_4^{3-} ; ^(c) Al^{3+} complexed with OH^-

The Ac-Mg-Si treatment gave higher RRE than the other treatments (except FMP treatment). This may be due to the high Mg concentration (2.80 mM) in the soil solution of this treatment (Table 6.8). Another explanation is that the Ac-Mg-Si product has higher soluble Si extracted by 0.01 M CaCl_2 using the blue silicomolybdous acid procedure than the other products (Table 4.2 in Chapter 4). Relative root elongation in the FMP treatment was significantly higher than in the other treatments (Table 6.5), suggesting that there are not only effects of Si,

Ca and Mg, but also an additional effect from the P contained in this product (Table 6.1). Although our results show that RRE of the Ca-P treatment was lower than that of the other treatments (Table 6.6). It is still evident from the images in Figure 6.8 that there is less staining at the higher rate of Ca-P despite similar pH and Al values in both treatments. Previous evidence has shown that Al toxicity can be alleviated by P in some plants, including maize (Gaume *et al.*, 2001), sorghum (Tan and Keltjens, 1990) and *Citrus grandis* (Jiang *et al.*, 2009). Pierre and Stuart (1933) reported that P could alleviate Al toxicity due to direct precipitation of Al-P in the zone of P incorporation. In a study of mechanisms of Al tolerance in two citrus species by P application, Yang *et al.* (2011) concluded that P could ameliorate Al toxicity through increasing immobilisation of Al in the roots. As previously discussed and also illustrated in Table 6.8, it is evident that FMP not only increases soil solution pH and decreases Al concentration, but also significantly reduces Al^{3+} activity because a considerable amount of P is released into solution, and favours Al forming complexes with P (Table 6.8). In the case of FMP, based on the evidence that there is a highly significant relationship between RRE and the significantly ($P < 0.05$) integrated correlations of pH, Al, Si, Mg and P with RRE (Table 6.3), and of root staining images which have less reactions with the dyes than those of inorganic Si amendments (Figures 6.7 and 6.8). It can be concluded that there is an interactive effect of Si, Mg, Ca and P on amelioration of Al toxicity and improvement of RRE of mungbean seedlings.

Role of organic amendments on aluminium toxicity and mungbean root growth

The addition of green manures or organic residues to acid soils can reduce the total Al concentration in soil solution and/or the monomeric Al concentration in solution, and thus reduce Al phytotoxicity and increase crop growth (Asghar and Kanehino, 1980; Hue and Amien, 1989; Wong *et al.*, 1995). Suggested mechanisms include an increase in soil pH (Noble *et al.*, 1996), a reduction in exchangeable Al due to complexation of solid phase organic matter (Hoyt and Turner, 1975), and complexation of Al in soil solution by soluble organic matter (OM) thus reducing active Al^{3+} in solution (Hue *et al.*, 1986). In our experiment, soil solution pH increased 1.4 units and Al concentration decreased 19.3 μM with the *Tithonia* treatment compared to the control treatment (Table 6.5 and Figure 6.2). This result is consistent with the work of Pypers *et al.* (2005) who measured similar effects on the soil solution composition of two red weathered soils after the application of 13.2 tonnes ha^{-1} of *Tithonia* and seven days incubation under field conditions. However, in the current work, it was necessary to add the equivalent of 47.7 tonnes *Tithonia* ha^{-1} in order to apply 210 kg Si

ha⁻¹. Thus large amounts of Mg, P and particularly Ca (753 kg ha⁻¹) were applied (Table 6.1). The RRE of mungbean in the *Tithonia* treatment was 150% compared to the adjusted pH 5.5 treatment (Figure 6.4). In a study of the amelioration of Al toxicity in mungbean by organic matter, Bessho and Bell (1992) concluded that high rates (40 and 80 tonnes ha⁻¹) of legume leaves and barley straw were effective in Al detoxification. They believed that the dominant mechanism of this effect was due to a decrease in monomeric Al activity in soil solution as the result of precipitation of soluble Al, following increases in soil solution pH, and to a lesser extent complexation of Al by DOC. The reduction in phytotoxic monomeric Al was larger for the legume leaves which contained relatively high concentration of Ca and Mg than for the barley straw (Bessho and Bell, 1992). Likewise, Shen and Shen (2001) suggested that the beneficial effects of wheat straw (30 g kg⁻¹ soil) containing relatively high concentrations of P, Ca and K on mungbean was likely due to decreasing concentration of monomeric Al in soil solution and improvement of mineral nutrition. Our results show that both Al concentration and active Al³⁺ are very low (1.6 µM of which only 2.6% is active Al³⁺) following *Tithonia* application (Table 6.9). In contrast, the application of 210 kg Si ha⁻¹ as sugarcane trash (equivalent to 6.7 tonnes OM ha⁻¹) resulted in very low pH (4.30) and high Al concentration (22.7 µM) similar to those of the control treatment (Table 6.5 and Figure 6.2) and resulting in a very low RRE (Table 6.5). This is probably due to the very low concentrations of Ca, Mg and P in sugarcane trash compared to the Si content of this product, and only 10 kg ha⁻¹ of Ca and Mg, and 4 kg P ha⁻¹ were applied at the rate equivalent to 210 kg Si ha⁻¹ (Table 6.1). In addition, the rate of application of sugarcane trash was much lower than that of *Tithonia* (6.7 and 47.7 tonnes ha⁻¹, respectively), resulting in soil solution DOC being much lower in the sugarcane trash treatment (18 mg C mL⁻¹) than in the *Tithonia* treatment (485 mg C mL⁻¹) (Table 6.9). Fundamental reasons for the lower effect of sugarcane trash on Al amelioration than *Tithonia* are that sugarcane is a non-leguminous residue, whereas *Tithonia* is leguminous, and the short incubation period (7 days) used for the experiment. Because of its wide C:N ratio, sugarcane trash would decompose more slowly than *Tithonia*. Berek *et al.* (1995) demonstrated that growth of soybean in residue-amended soils was better for legume- (*Calopogonium*, soybean and *Leucaena*) than for non-legume-amended treatments (sugarcane and rice). In order to examine the DOC effect on Al amelioration, another *Tithonia* treatment contained the equivalent amount of P (68 kg ha⁻¹) as the FMP treatment, and thus the amounts of Si and Mg derived from this *Tithonia* treatment were lower than those from FMP, although Ca was still higher than for the FMP treatment (Table 6.1). In comparison of these two treatments, soil solution pH was higher and Al concentration was lower in the *Tithonia* treatment than in the FMP treatment, resulting in a higher RRE in the *Tithonia* treatment than

in the FMP treatment (Figure 6.5). It is also apparent from the root images that while there was some staining with all three dyes for the FMP treatment (Figure 6.8), there was no root staining for the *Tithonia* treatment (Figure 6.9). Therefore, it can be suggested that the ameliorative effect is attributed to OM contained in *Tithonia* rather than Si.

Table 6.9 Calcium, magnesium, aluminium, silicon, phosphorus and dissolved organic carbon concentrations in soil solutions and aluminium speciation predicted by GEOCHEM-EZ program in different organic amendments applied at rates equivalent to 210 kg Si ha⁻¹

Treatment	Ca	Mg	Al	Si	P	DOC ^(a)	Al ³⁺ ^(b)	Al+PO ₄ ^(c)	Al+OH ^(d)
	(mM)	(mM)	(μM)	(mM)	(μM)	(mg mL ⁻¹)	(%)		
Sugarcane	0.46	0.82	22.7	0.17	0.00	18	64.9	24.8	10.3
<i>Tithonia</i>	1.12	1.34	1.6	0.10	0.14	485	2.6	60.0	37.4

^(a) dissolved organic carbon; ^(b) active Al³⁺ free; ^(c) Al³⁺ complexed with PO₄³⁻; ^(d) Al³⁺ complexed with OH⁻

6.5 Summary and conclusions

The Red Ferrosol from New South Wales that was used in this study is very acidic and Al toxic. The pH of the unamended soil solution decreased approximately 0.5 unit (from 4.29 to 3.88) and Al concentration increased nearly 10-fold (from 21 to 193 μM) following 7 and 30 days incubation at 40°C. Monosilicic acid, inorganic Si and organic amendments significantly ameliorated Al toxicity through several mechanisms, thereby enhancing relative root elongation of mungbean seedlings grown in soil solutions from these treatments. Based on the chemical components contained in an individual product, the order of magnitude of the ameliorative effects from these amendments are as follows: *Tithonia diversifolia* > FMP > Ac-Mg-Si > Ca-Si = Ac-Ca-Si > Mg-Si > Mono-Si > sugarcane trash. The mechanisms for the amelioration of Al toxicity by these treatments are different, including: a) external effects on soil solution composition through pH increase, reduced Al concentrations by the formation of hydroxyaluminosilicates or insoluble Al-organic complexes; b) internal plant effects which are due to Si interference with Al uptake into the root and co-deposition of Al and Si in plants; and c) indirect effects on the supply of essential nutrients for short term root elongation.

Chapter 7 General conclusions and suggestions for further research

7.1 General conclusions

The investigated variable charge soils (VCS) (Redoxic Hydrosol and Aquic Grey Vertosol from north Queensland, and Red Ferrosols from both north Queensland and New South Wales) are very acidic with very low CECs. The Red Ferrosols from both north Queensland and New South Wales exhibited very high P sorption capacities, much higher than those of the Hydrosol and Vertosol. The subsoils of the two Red Ferrosols were more acidic, had lower CECs and much higher P sorption capacities than their topsoils. These differences between the soils and between the soil layers are associated with differences in clay and Fe/Al hydrous oxide contents, mineralogical composition, and variations in organic matter contents.

The subsoil of the Red Ferrosol from north Queensland exhibited higher pH_0 than the existing soil pH and higher PZNC than pH_0 . Therefore, the soil had developed net positive surface charge with its AEC exceeding its CEC. This is a similar characteristic to that of the geric Ferralsols of the uplands in Vietnam. Therefore, I am confident that any beneficial effects of Si based amendments to these Australian soils will translate into similar effects on the geric upland soils in Vietnam, and in fact wherever geric soils are found.

Although Mono-Si did not increase soil pH, it decreased pH_0 of the soils. As a result, surface negative charge increased, and was expressed as an increase in CEC of the soils. This effect can be attributed to specific adsorption of silicate anions resulting in the reversal of positively charged surfaces to negatively charged surfaces in these VCS. In addition to Si, the basic elements (Ca or Mg) also added to the soils by the other inorganic silicate amendments (Ca-Si, Ac-Ca-Si, Mg-Si and Ac-Mg-Si) had the effects of increasing soil pH and decreasing pH_0 . Therefore, these amendments caused greater increases in CEC than those caused by Mono-Si. The beneficial effect of the FMP amendment on surface charge characteristics was more pronounced than that of the other inorganic silicate amendments. This was due to a combination of Ca, Mg, P and Si elements as well as its liming value, all of which had synergistic influences on surface charge characteristics. Organic amendments (sugarcane and *Tithonia*, 125 kg Si ha⁻¹) also had a significant effect on enhancing surface negative charge and reducing surface positive charge of the soils. The effects caused by *Tithonia* were much

greater than those of sugarcane and even of the inorganic silicate amendments with Si applied ($250 \text{ kg Si ha}^{-1}$) at double the rate of that added as *Tithonia*. This efficacy is attributed to the large amounts of Ca, Mg, P and functional organic groups applied, together with Si, in the *Tithonia*. Therefore, this amendment has the optimum effect. Since P sorption capacity of the soils was shown to be strongly negatively correlated with the development of negative surface charge, the greater the increase in CEC caused by a given amendment, the lower the P sorption capacity obtained.

In a Vietnamese context, these results support further field trials and investigation into strategies to increase soil pH and decrease pH_0 in association with amendments that supply a range of needed base cations and phosphorus in the most cost effective manner. In Vietnam FMP is a widely available fertiliser, and *Tithonia* grows wild by roadsides and is able to be harvested and incorporated into soil as an amendment or applied as surface mulch for erosion control. As both FMP and *Tithonia* are locally available and supply multiple benefits to the soil chemical properties of geric soils, significant investment in expanding their use would be worthwhile. Particular focus should be given to the economic benefits of these amendments to smallhold farmers, particularly as lime is a relatively straightforward method to increase pH, but is likely to be less cost effective at the smallholder scale. The capacity of smallholders to implement increased *Tithonia* incorporation is affected by economic considerations such as labour availability. Increasing trends towards urbanization results in labour shortages that preclude development of cut-and-carry methods of harvesting, distributing and spreading *Tithonia* material in Vietnam. As *Tithonia* is an environmental, road-side weed, mechanical harvesting is also difficult. Trials of small plots of machine-harvestable and mulchable *Tithonia* may be necessary to develop this amendment's potential to improve the soil chemistry of geric soils in Vietnam.

Lesser effects of the amendments on these properties were obtained for the soils dominated by permanent negative charges (the Hydrosol and the Vertosol). These soils exhibited high total Si and Si availability, and low Fe/Al hydrous oxides, but also contained significant variable negative charges. The amendments produced greater effects in the subsoils of the VCS than in the topsoils because of the net positive charge occurring in the subsoil. However, although Fe/Al hydrous oxides were strongly correlated with surface charge characteristics and P sorption capacity of the soils, inorganic silicate amendments had little effect on these properties. The effect of Si derived from *Tithonia* was not clearly verified in this study

because the effects of its liming value on soil surface charge characteristics and its high content of functional organic groups confounded the effect of Si on soil properties.

As these affects on soil chemistry were most pronounced in the subsoils of these geric Australian soils, the question remains as to how to amend the subsoils of geric Vietnamese upland soils. Further research would be necessary to determine the extent to which the effective properties of these materials are soluble and able to move through the soil profile. In the case of *Tithonia* residues this may occur, but the P components of FMP material are definitely not mobile in these soils. Recent research in southern Australia has developed a subsoil slotting implement to place amendments, including tonnes of manure material, at considerable depth, although this technology is unlikely to be developed and implemented rapidly in Vietnam. As is typical of subsoil constraints the world over, solving this issue will take considerable time.

The effect of Si rates for different incubation periods on surface charge characteristics and P sorption capacity of a Red Ferrosol from NSW (the Alstonville Ferrosol, 0 - 30 cm) was also studied. Silicon applied at a high rate was more effective at increasing surface negative charge and decreasing P sorption capacity of the soil than a low rate. Between the two incubation periods (7-DAI and 30-DAI), amendments with high soluble Si contents (Mono-Si and Ac-Mg-Si) were found to have faster effects than those with lower soluble Si content (Ca-Si, Ac-Ca-Si and Mg-Si). The effects of the acidulated silicate amendments (Ac-Mg-Si and Ac-Ca-Si) were greater than those of the raw silicate amendments (Mg-Si and Ca-Si) because they had higher soluble Si contents.

The soil became more acidic and Al toxic with increasing incubation time. All investigated inorganic silicate and organic amendments significantly ameliorated Al toxicity, thereby enhancing relative root elongation of mungbean seedlings grown in soil solutions from these treatments. The order of magnitude of the ameliorative effects from these amendments is as follows: *Tithonia diversifolia* > FMP > Ac-Mg-Si > Ca-Si = Ac-Ca-Si > Mg-Si > Mono-Si > sugarcane trash. The amelioration of Al toxicity by these treatments can be attributed to different mechanisms, including: a) external effects on soil solution composition through pH increase and reduced Al toxicity by the formation of hydroxyaluminosilicates or insoluble Al-organic complexes; b) internal plant effects which are due to Si interference with Al uptake into the root and co-deposition of Al and Si in plants; and c) indirect effects on the supply of essential nutrients for short term root elongation. These results suggest that, when compared

with lime, application of Si to acidic, geric soils confers greater advantages because of more effective mitigation of Al toxicity. In practice this means that productivity of Al-sensitive species is likely to be higher for a longer period of time where charge has been increased by both raising pH (which might be ephemeral) and lowering pH_0 (more likely to be permanent) because of small increases in solution Si concentration.

7.2 Suggestions for further research

Although the beneficial effects of Si on major constraints of selected VCS and the mechanisms of these effects were investigated, a number of issues were not covered in this study and need further research.

- Investigation of the interactions between Fe/Al hydrous oxides and Si availability in VCS should be undertaken to aid understanding of the relationship between soil Si and Fe/Al hydrous oxides, and how this affects surface charge characteristics and P sorption capacity. Specifically, this study did not investigate the nature of the ligand exchange reactions occurring at oxide surfaces between Si and metal species, and the effects on the equilibrium solution Si concentration in geric soils following amendment needs further elucidation.
- Other plant residues with high Si content (e.g., rice stubble in the Vietnamese context) and other leguminous species (e.g., *Dolichos* and *Peuraria* spp. in the Vietnamese context) should be assessed for their effects on the properties of VCS. In particular, this study should clarify the interactions between Si and organic carbon contained in organic amendments to verify the longevity of the effect of Si derived from organic amendments on soil properties, and the formation of organo-silicates complexes for ameliorating Al toxicity.
- Field evaluation of Tithonia in Vietnam is the next step in determining the efficacy of this material as an amendment that alleviates soil constraints associated with low charge.

The results from this study indicate that a Si fertilisation strategy could be beneficial for VCS in Vietnam where inorganic silicate (FMP) and organic (*Tithonia*) amendments are locally available, yet the current use of these amendments is not widely practised. Soil Si repletion by applying relevant Si sources is necessary for rice-based and sugarcane-based farming systems in Vietnam and should be researched.

Appendices

Appendix 1 - Charge fingerprint curves for surface charge characteristics of selected variable charge soils affected by inorganic silicate and organic amendments

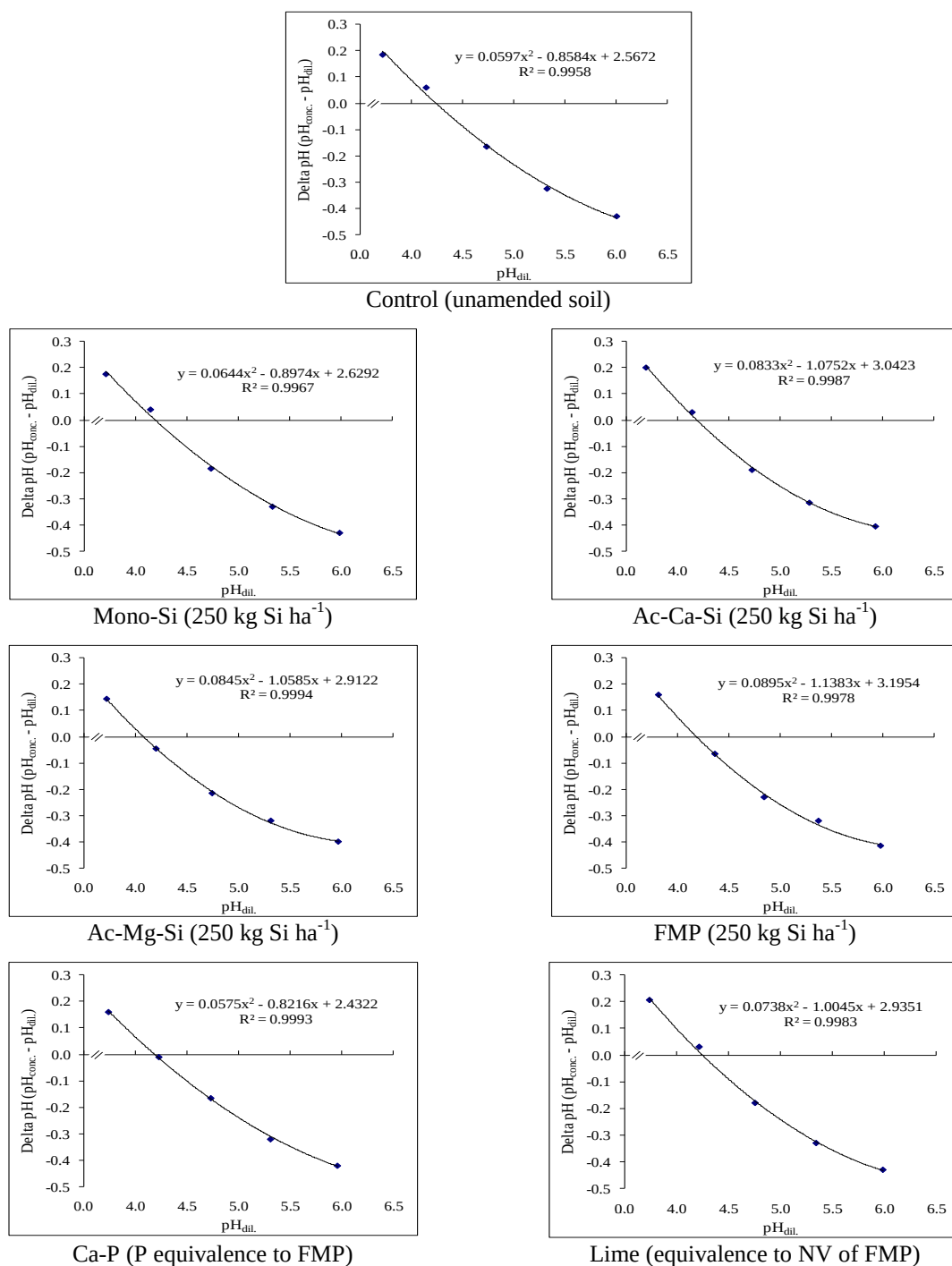


Figure A.1 Soil pH_0 of the Palmerston Ferrosol topsoil (0 - 20 cm) affected by the amendments after 30 days of incubation at 40°C

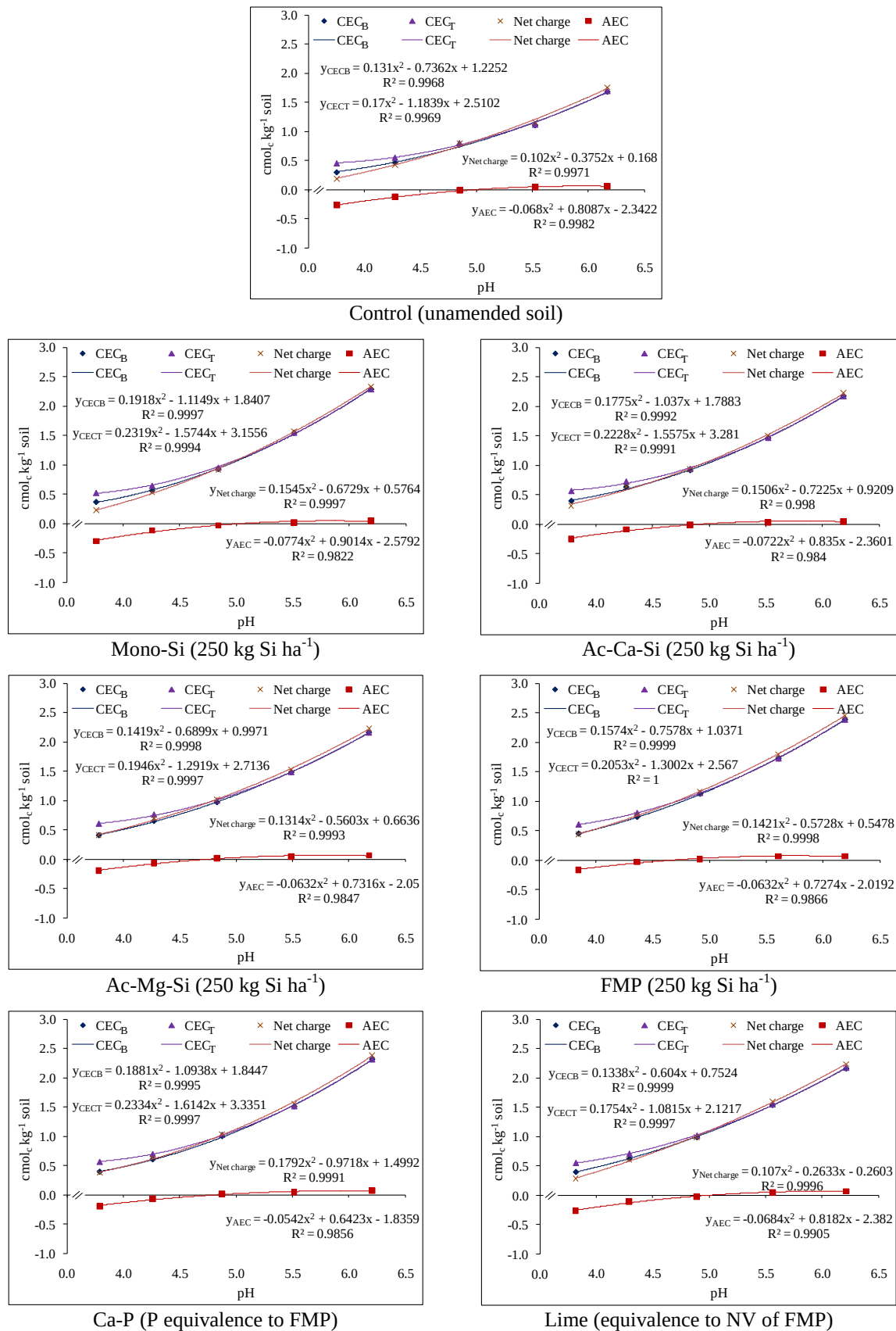


Figure A.2 Surface charge characteristics of the Palmerston Ferrosol topsoil (0 - 20 cm) affected by the amendments after 30 days of incubation at 40°C

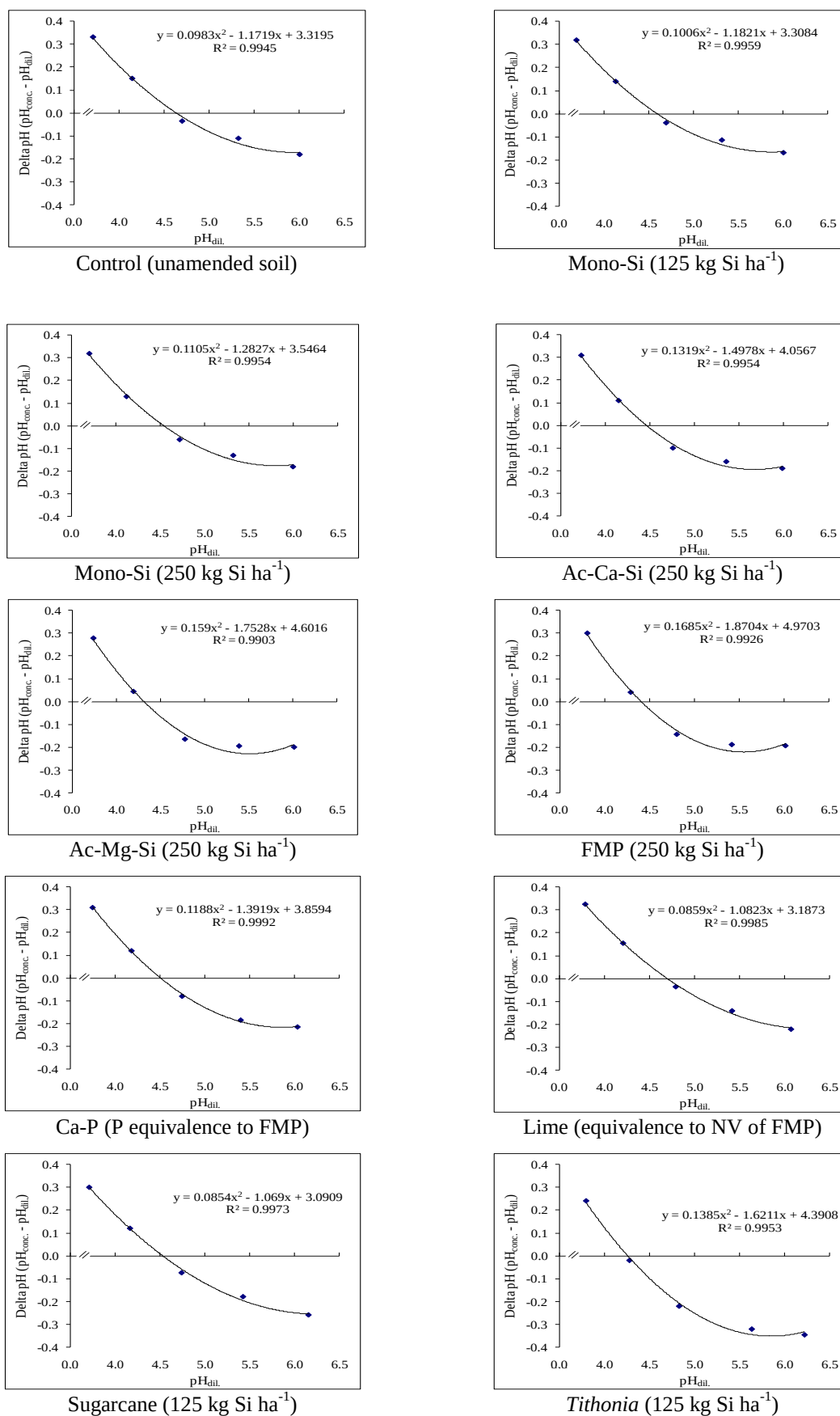


Figure A.3 Soil pH_0 of the Palmerston Ferrosol subsoil (20 - 40 cm) affected by the amendments after 30 days of incubation at 40°C

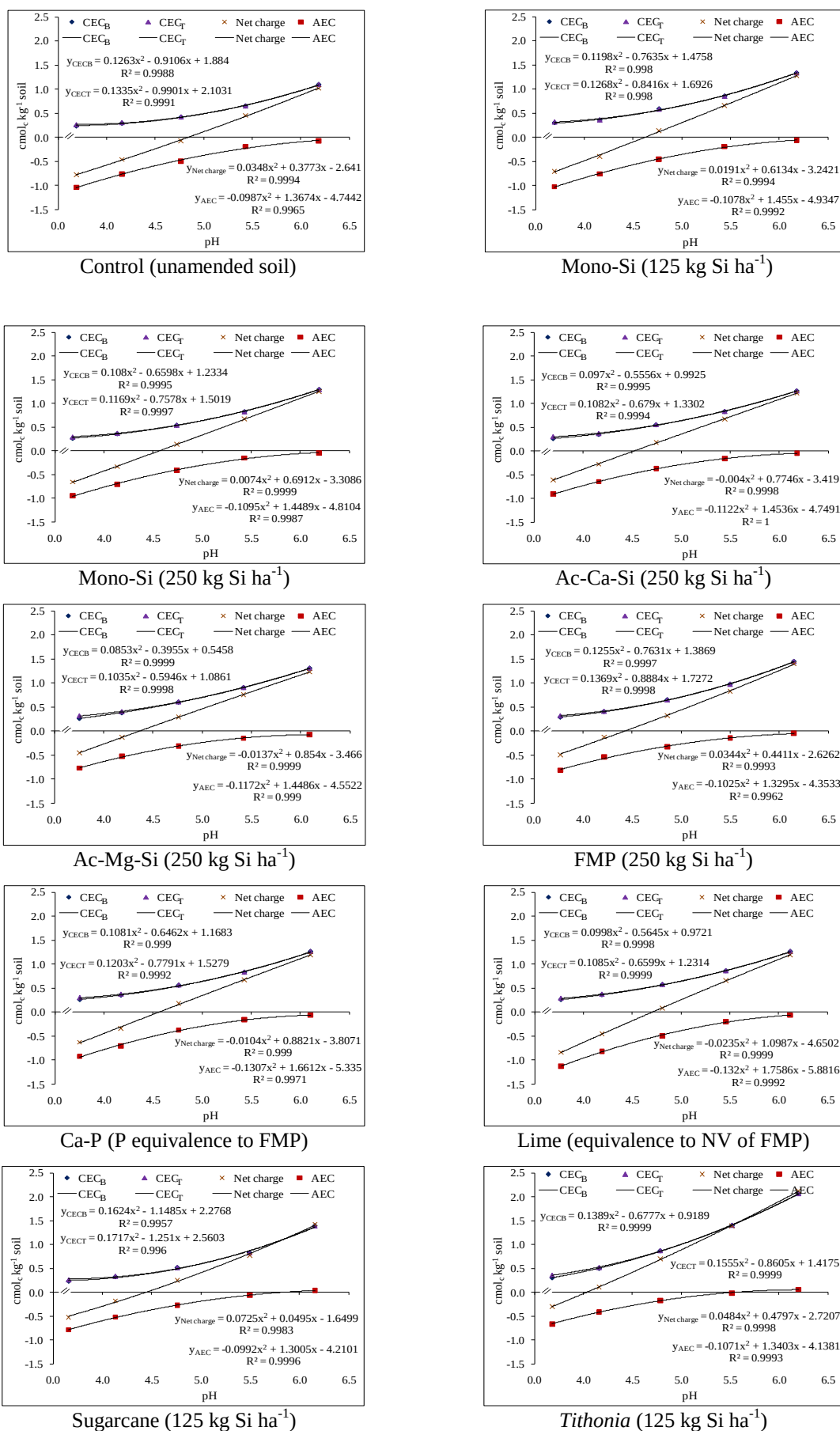


Figure A.4 Surface charge characteristics of the Palmerston Ferrosol subsoil (20 - 40 cm) affected by the amendments after 30 days of incubation at 40°C

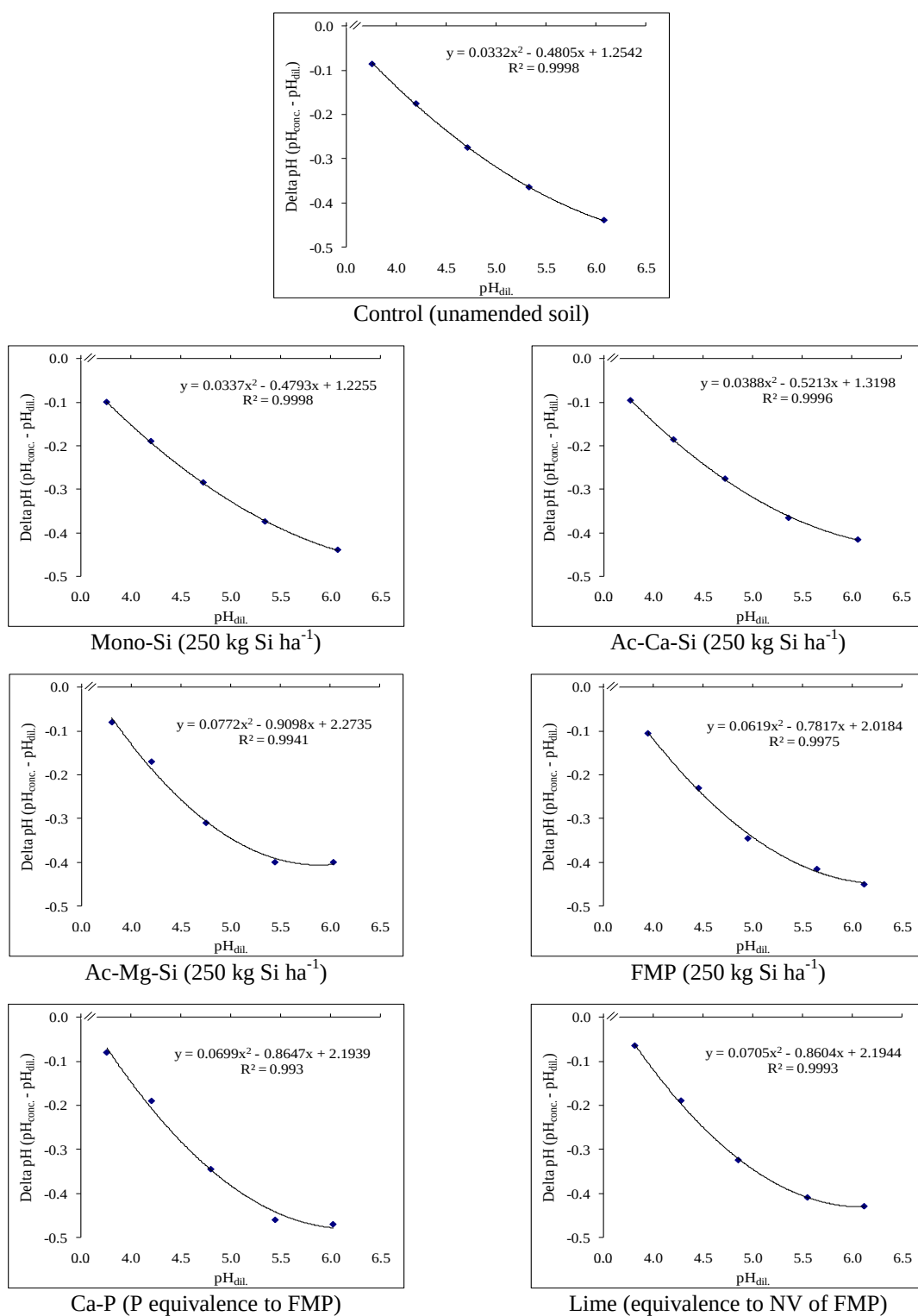


Figure A.5 Soil pH_0 of the Hydrosol subsoil (20 - 40 cm) affected by the amendments after 30 days of incubation at 40°C

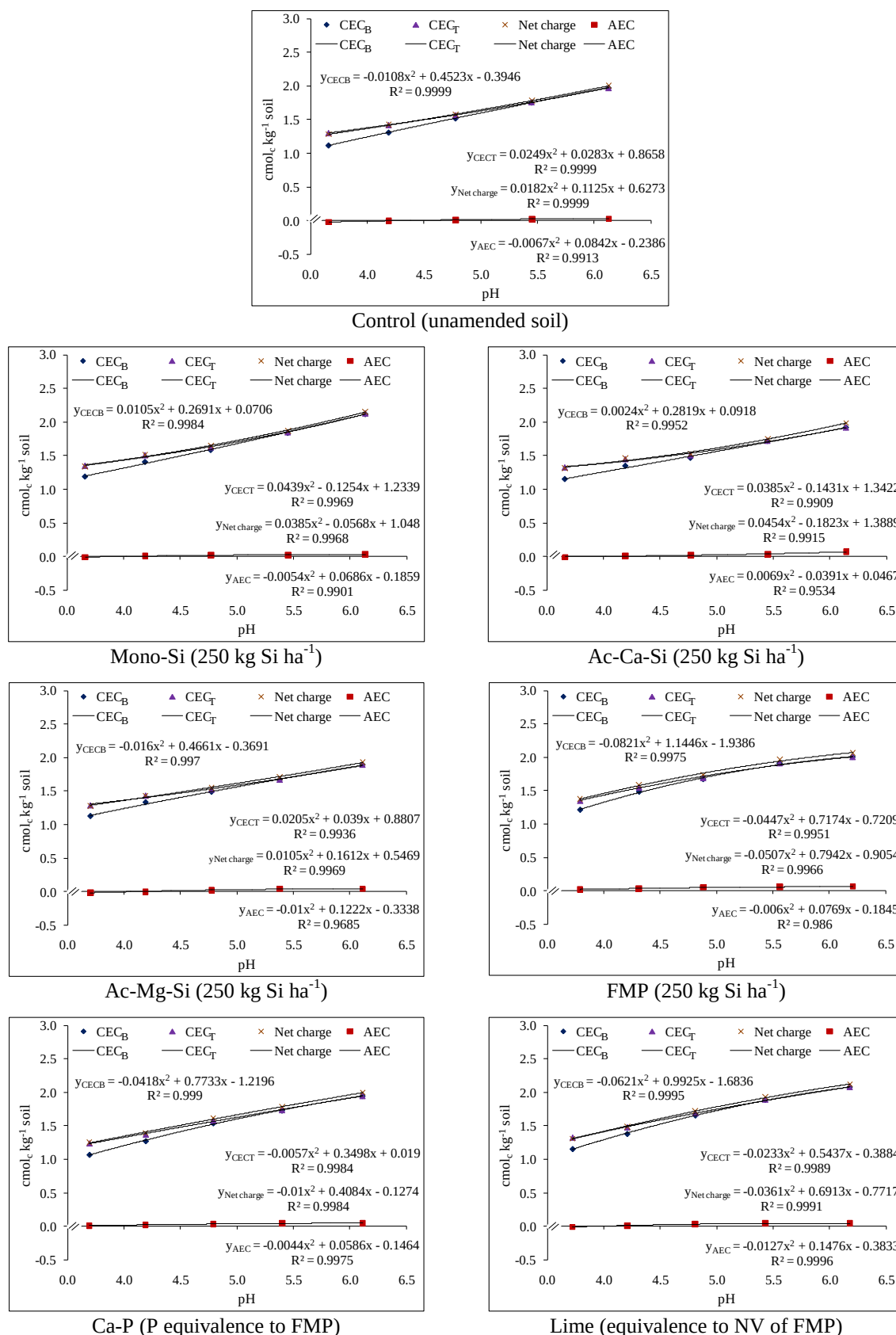


Figure A.6 Surface charge characteristics of the Hydrosol subsoil (20 - 40 cm) affected by the amendments after 30 days of incubation at 40°C

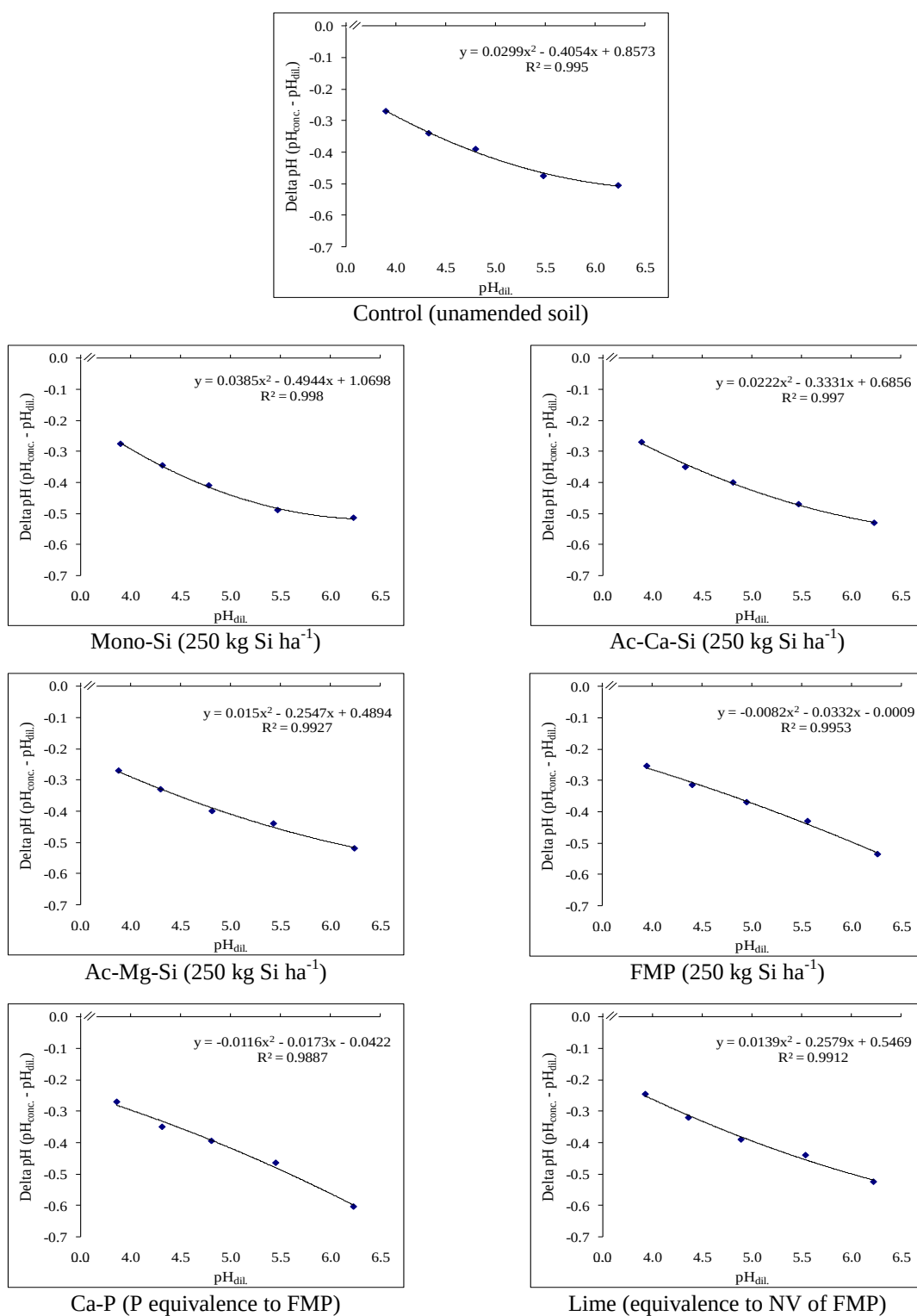


Figure A.7 Soil pH_0 of the Vertosol subsoil (20 - 40 cm) affected by the amendments after 30 days of incubation at 40°C

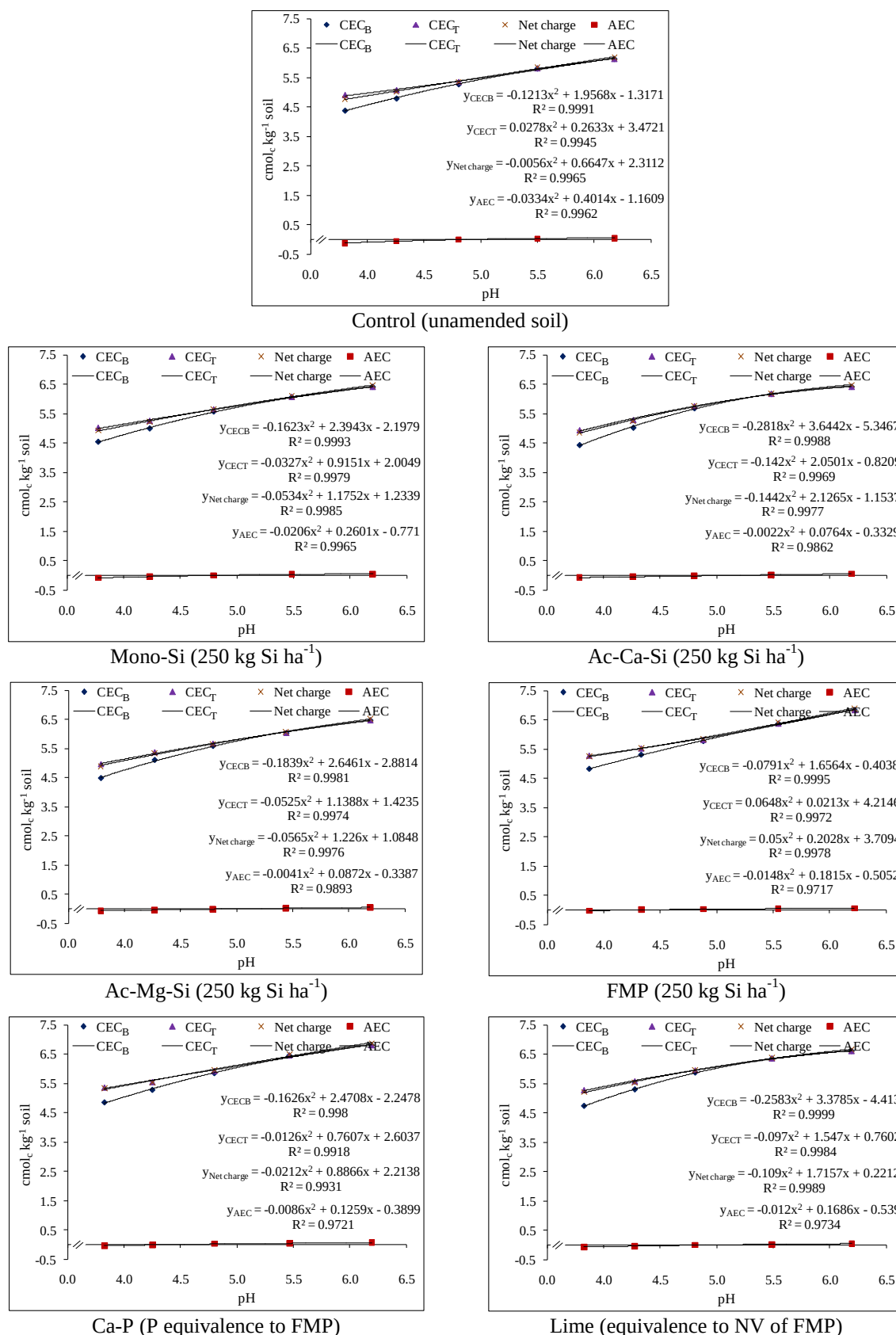


Figure A.8 Surface charge characteristics of the Vertisol subsoil (20 - 40 cm) affected by the amendments after 30 days of incubation at 40°C

Appendix 2 - Charge fingerprint curves for point of zero charge (pH₀) surface charge characteristics of the Alstonville Ferrosol (0 - 30 cm) affected by inorganic silicate and organic amendments

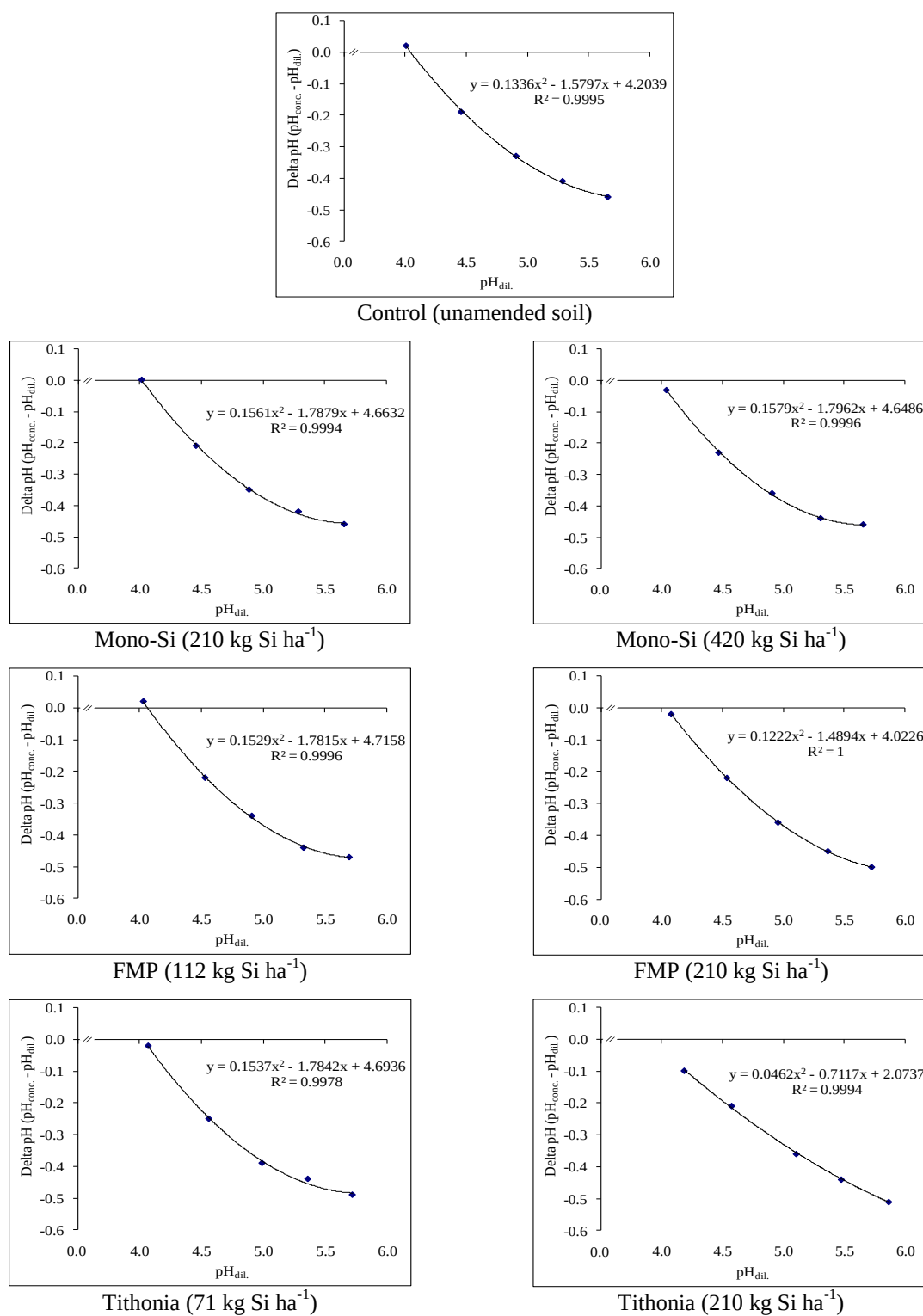


Figure A.9 Soil pH₀ of the Alstonville Ferrosol (0 - 30 cm) affected by different rates of amendments after 7 days of incubation at 40°C

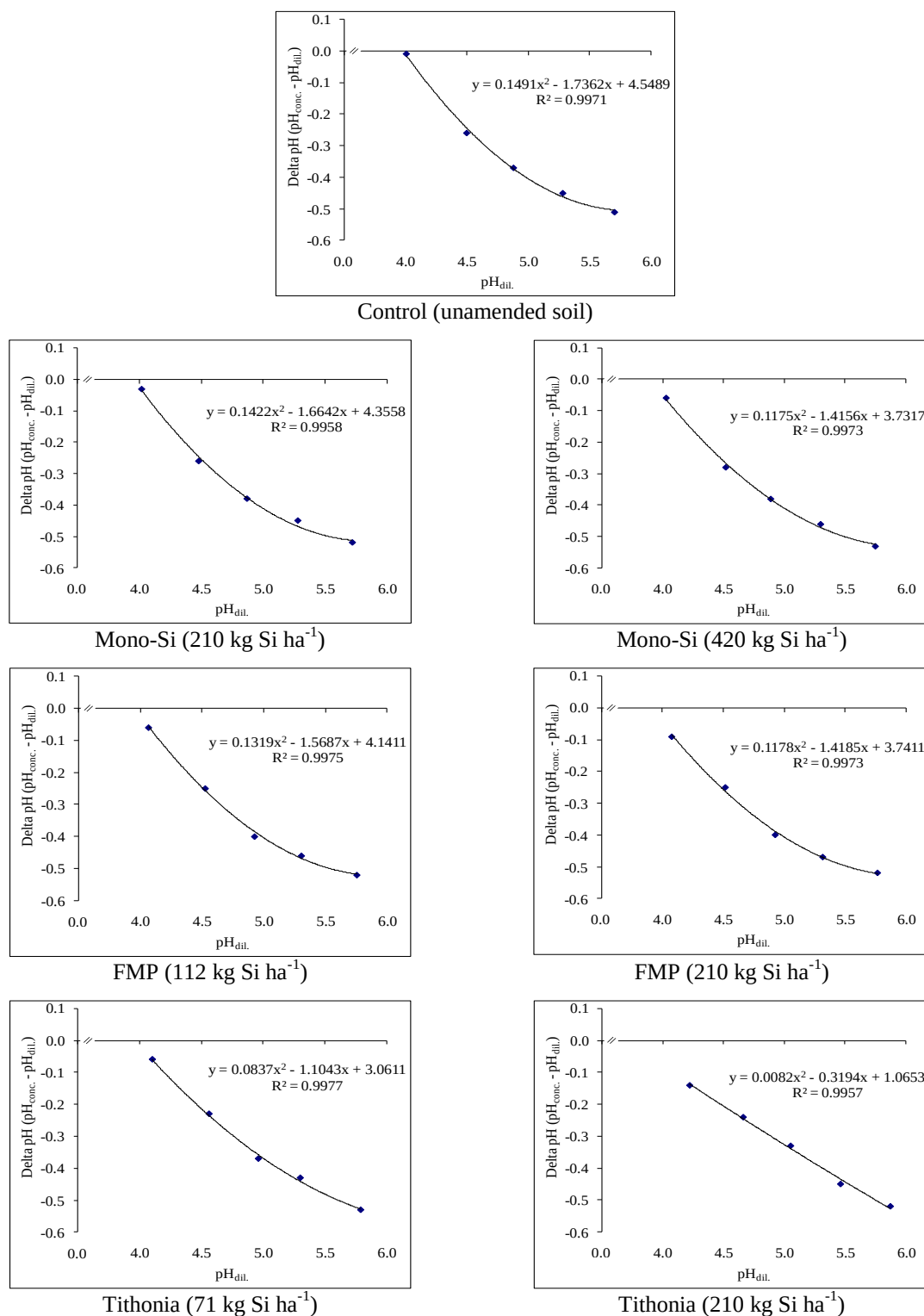


Figure A.10 Soil pH_0 of the Alstonville Ferrosol (0 - 30 cm) affected by different rates of amendments after 30 days of incubation at 40°C

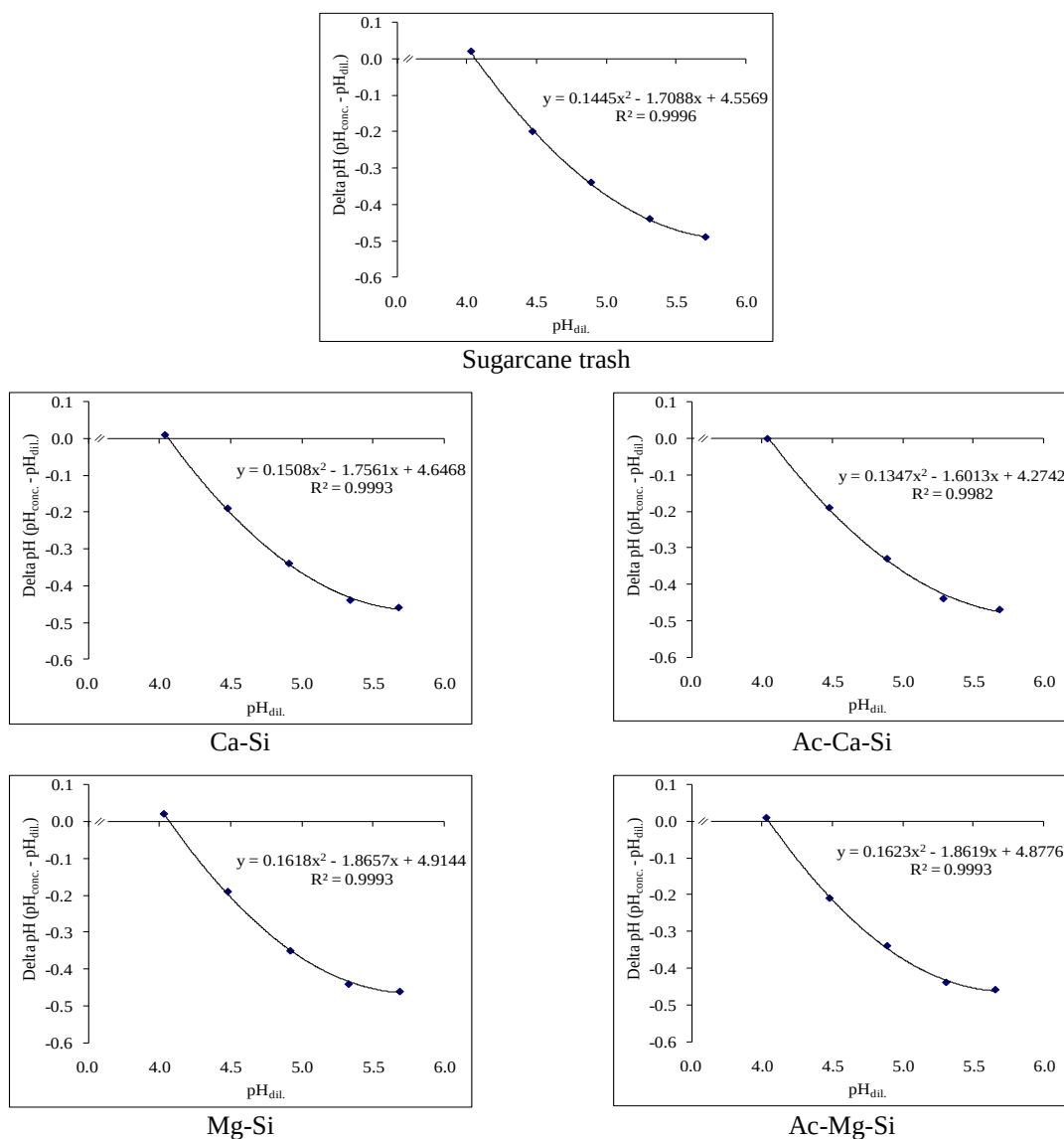


Figure A.11 Soil pH_0 of the Alstonville Ferrosol (0 - 30 cm) affected by different amendments ($210 \text{ kg Si ha}^{-1}$) after 7 days of incubation at 40°C

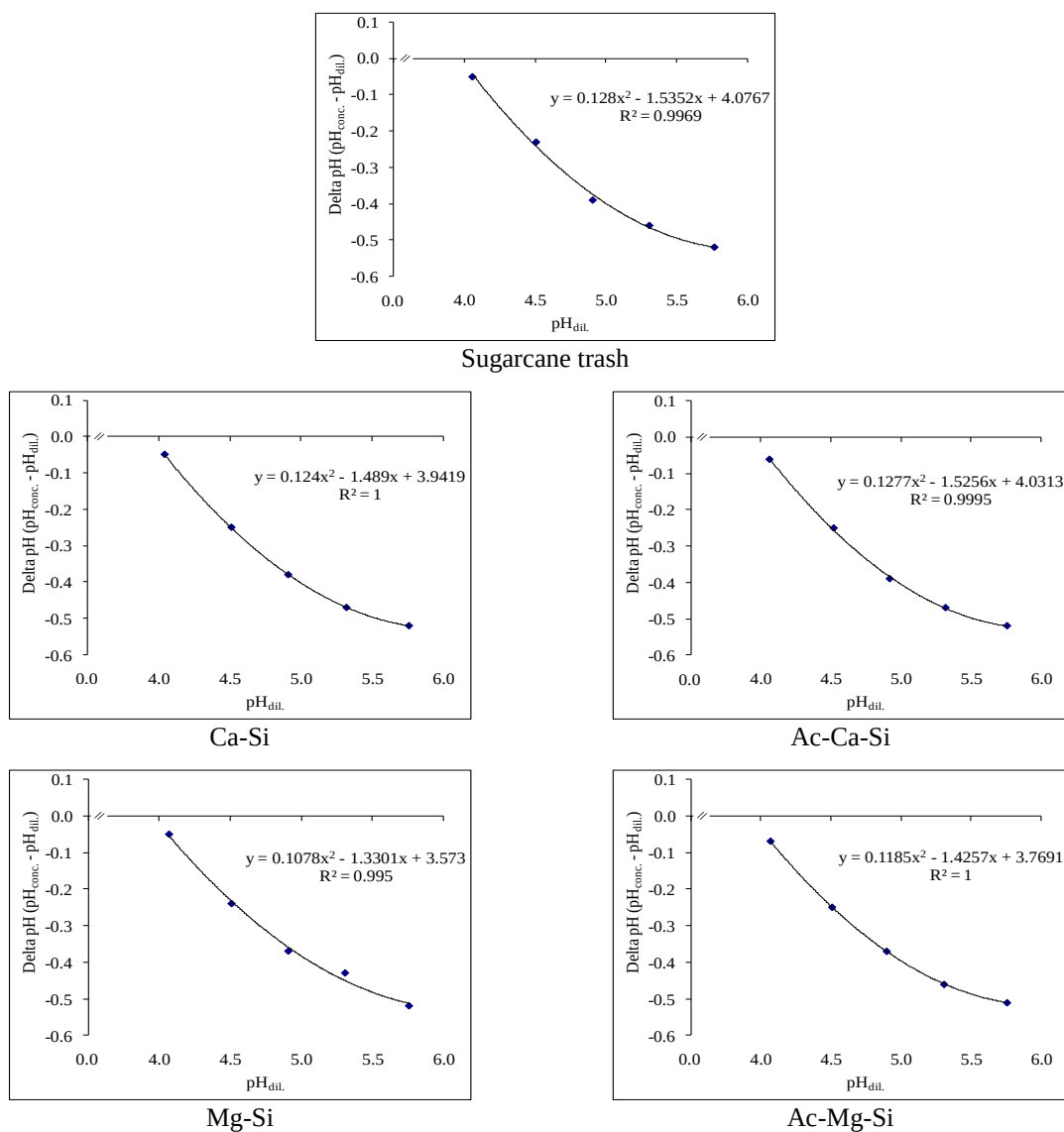


Figure A.12 Soil pH_0 of the Alstonville Ferrosol (0 - 30 cm) affected by different amendments ($210 \text{ kg Si ha}^{-1}$) after 30 days of incubation at 40°C

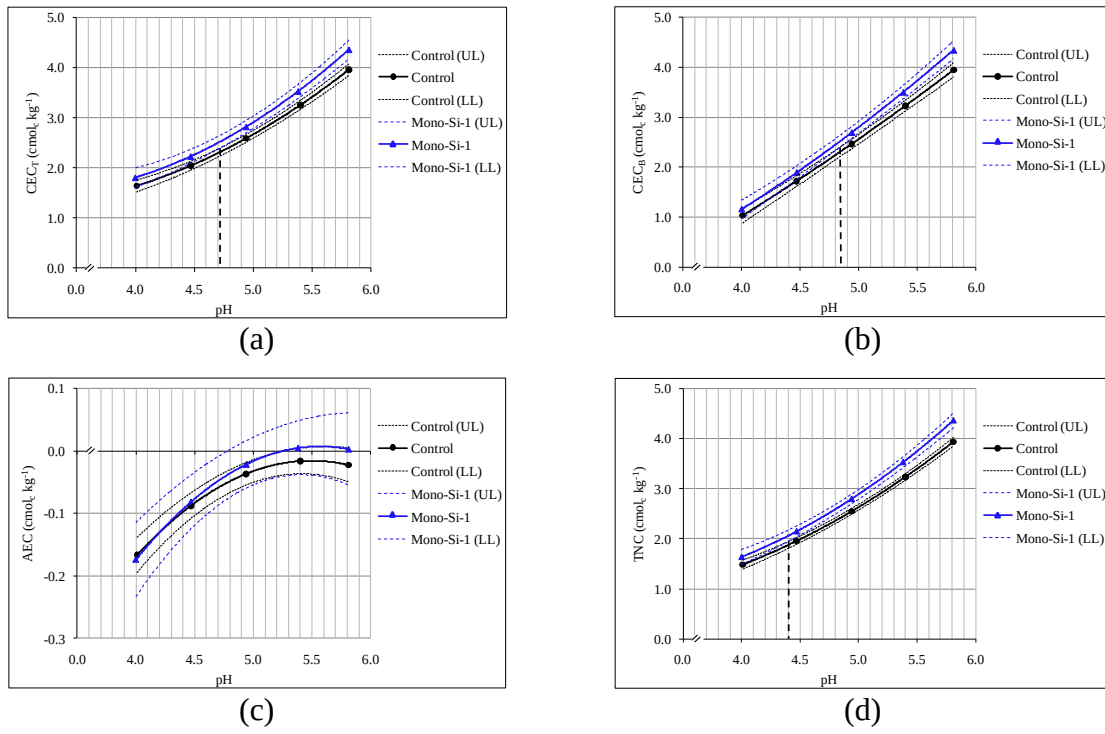


Figure A.13 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following Mono-Si amendment (210 kg Si ha⁻¹) after 7 days of incubation

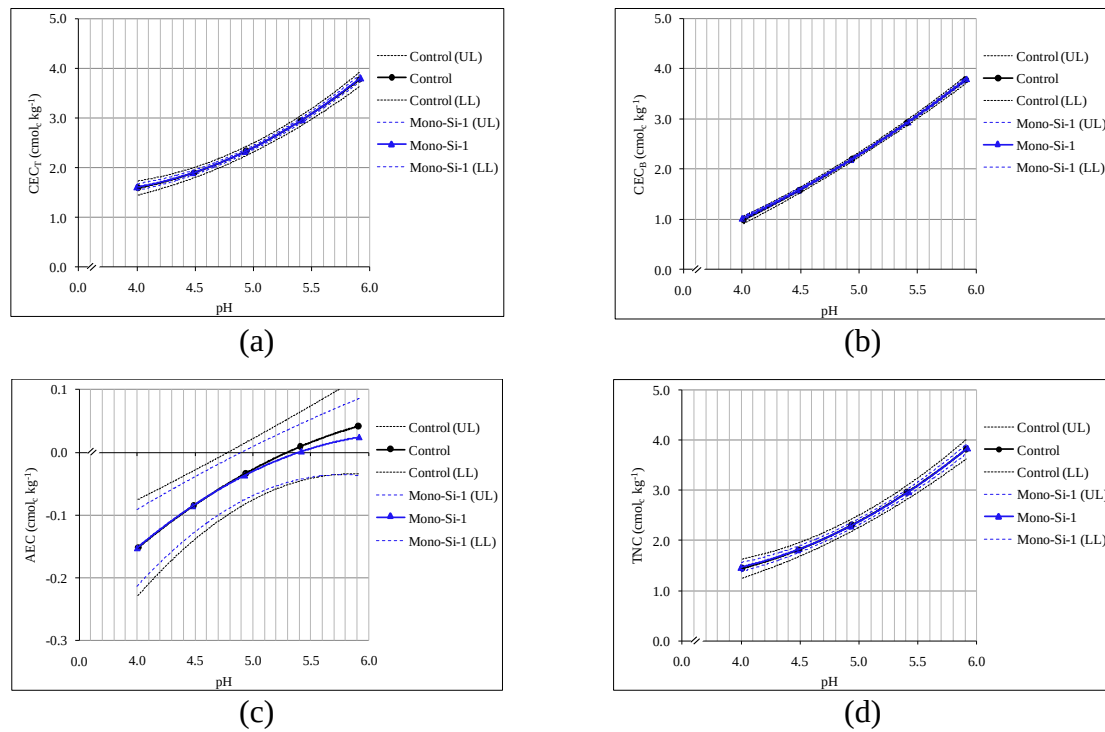


Figure A.14 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following Mono-Si amendment (210 kg Si ha⁻¹) after 30 days of incubation

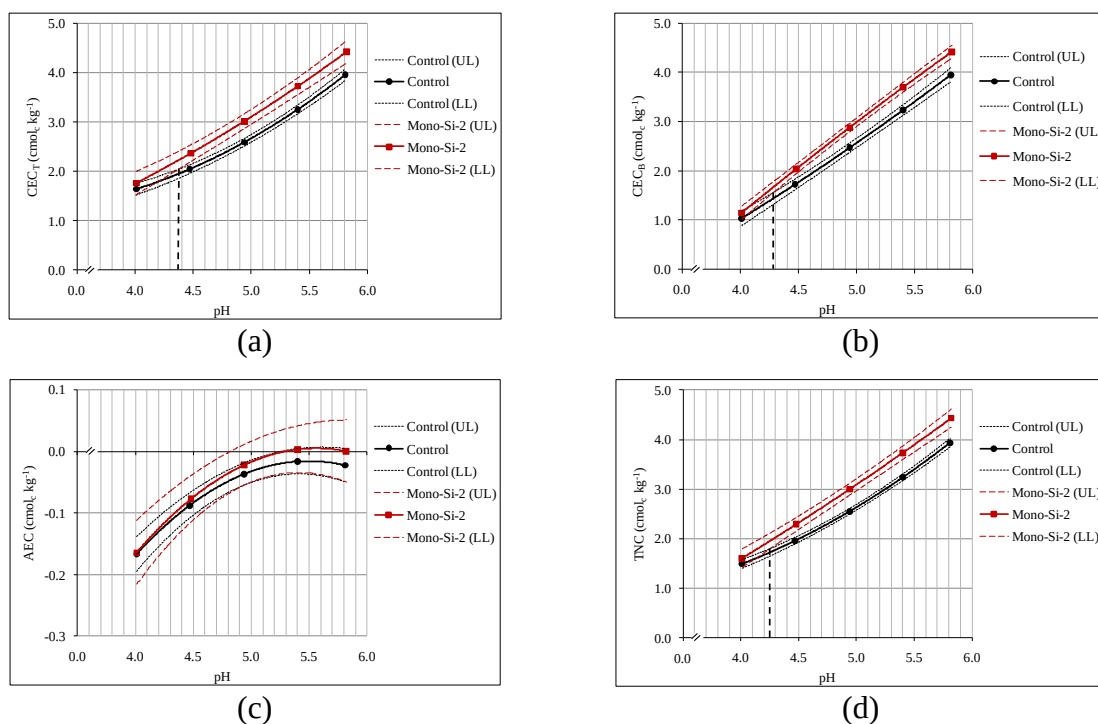


Figure A.15 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following Mono-Si amendment (420 kg Si ha⁻¹) after 7 days of incubation

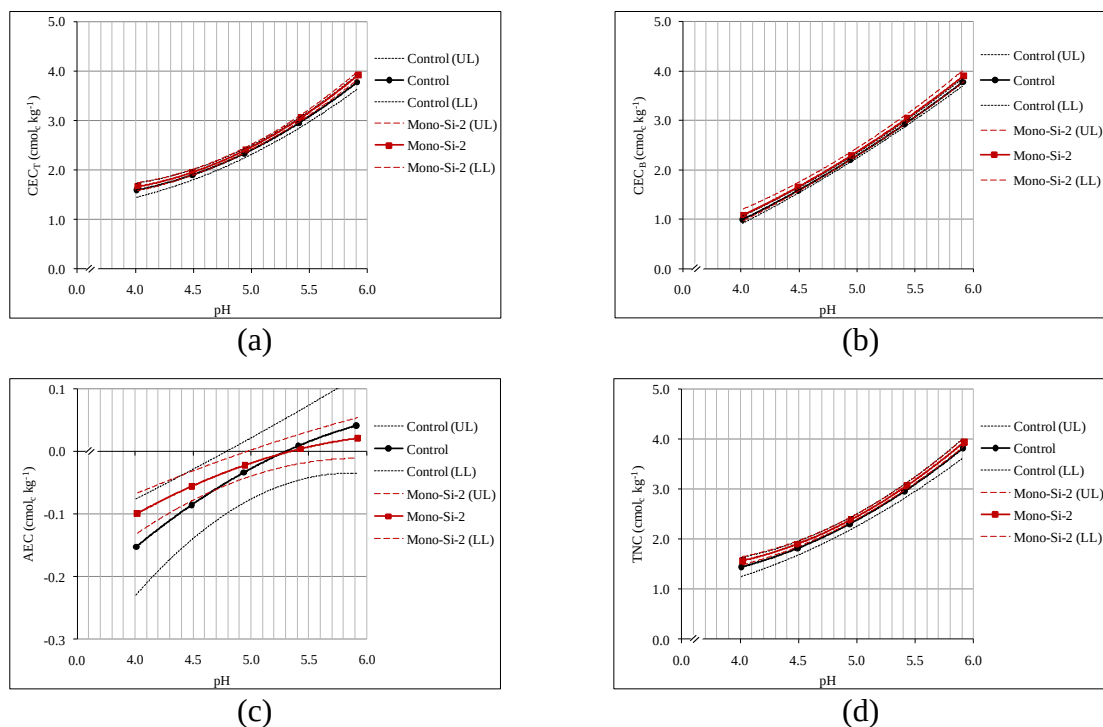


Figure A.16 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following Mono-Si amendment (420 kg Si ha⁻¹) after 30 days of incubation

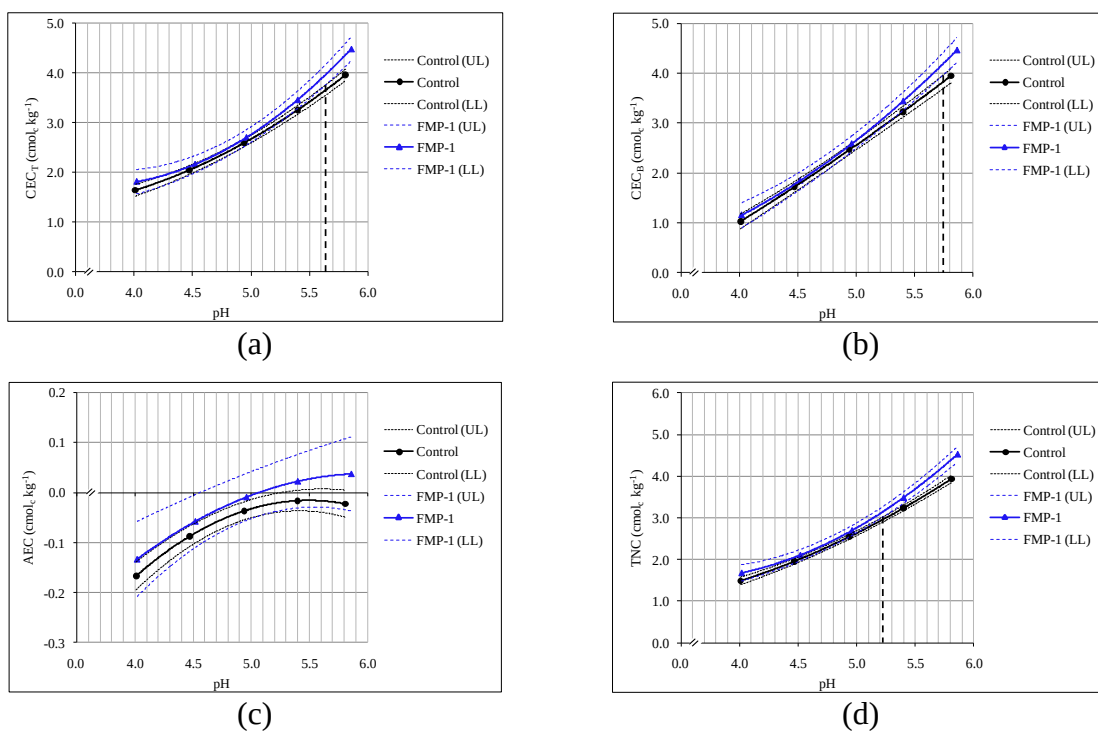


Figure A.17 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following fused magnesium phosphate amendment (112 kg Si ha⁻¹) after 7 days of incubation

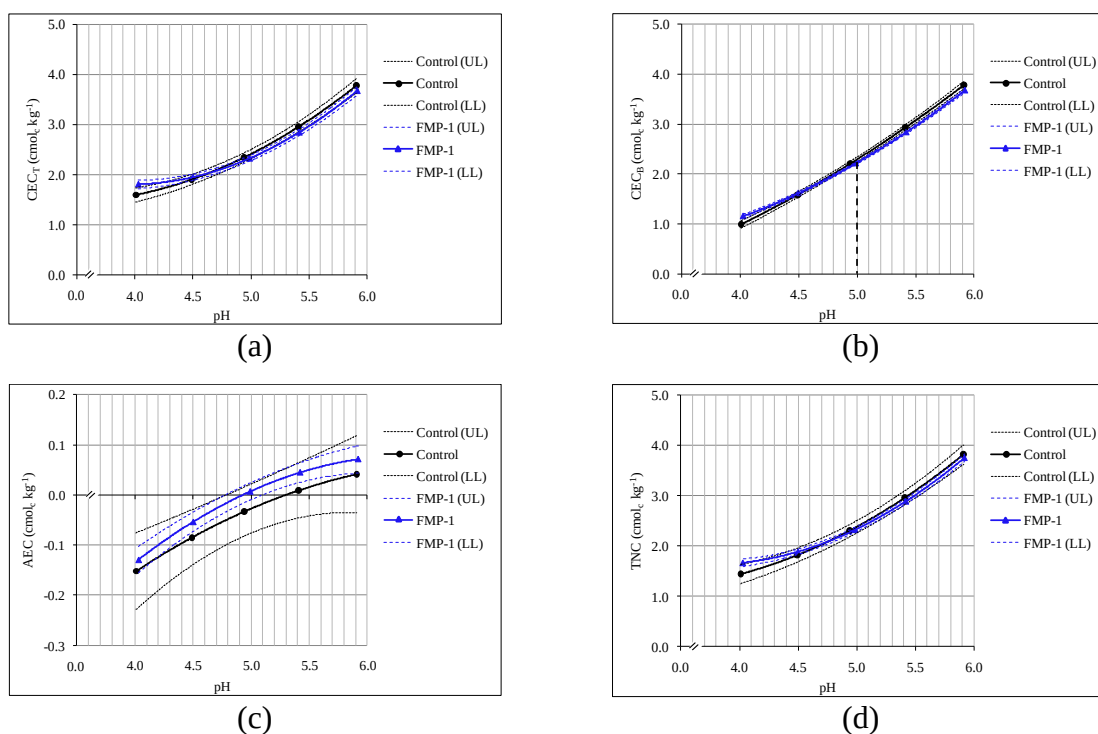


Figure A.18 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following fused magnesium phosphate amendment (112 kg Si ha⁻¹) after 30 days of incubation

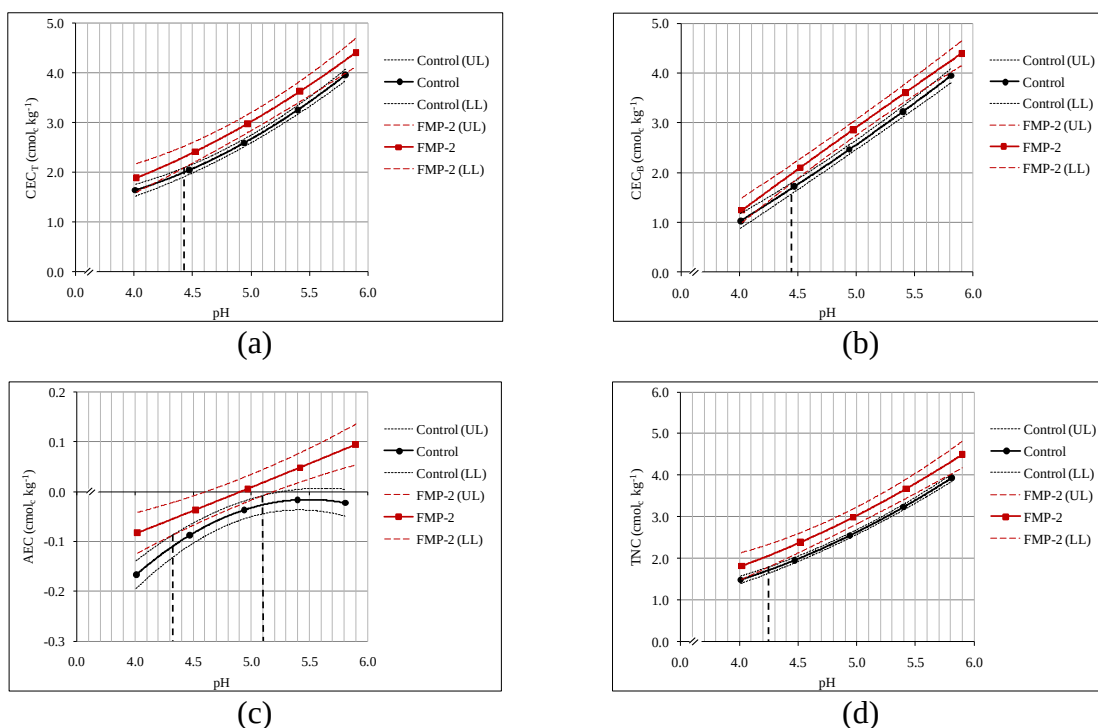


Figure A.19 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following fused magnesium phosphate amendment (210 kg Si ha⁻¹) after 7 days of incubation

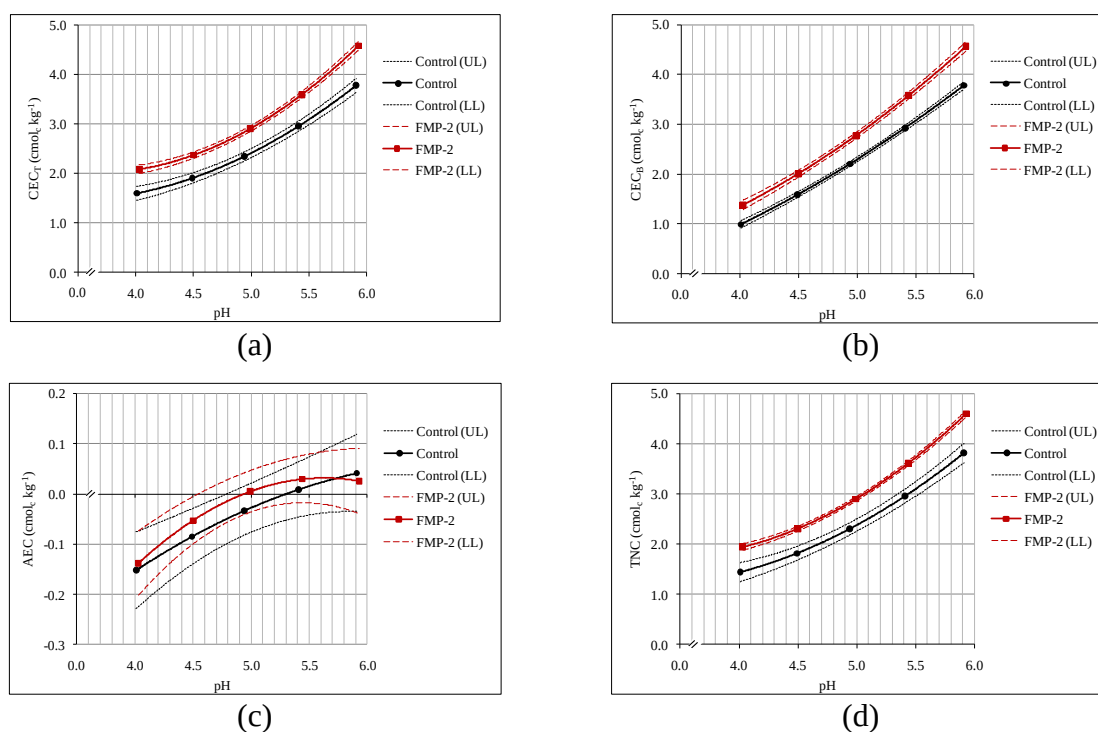


Figure A.20 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following fused magnesium phosphate amendment (210 kg Si ha⁻¹) after 30 days of incubation

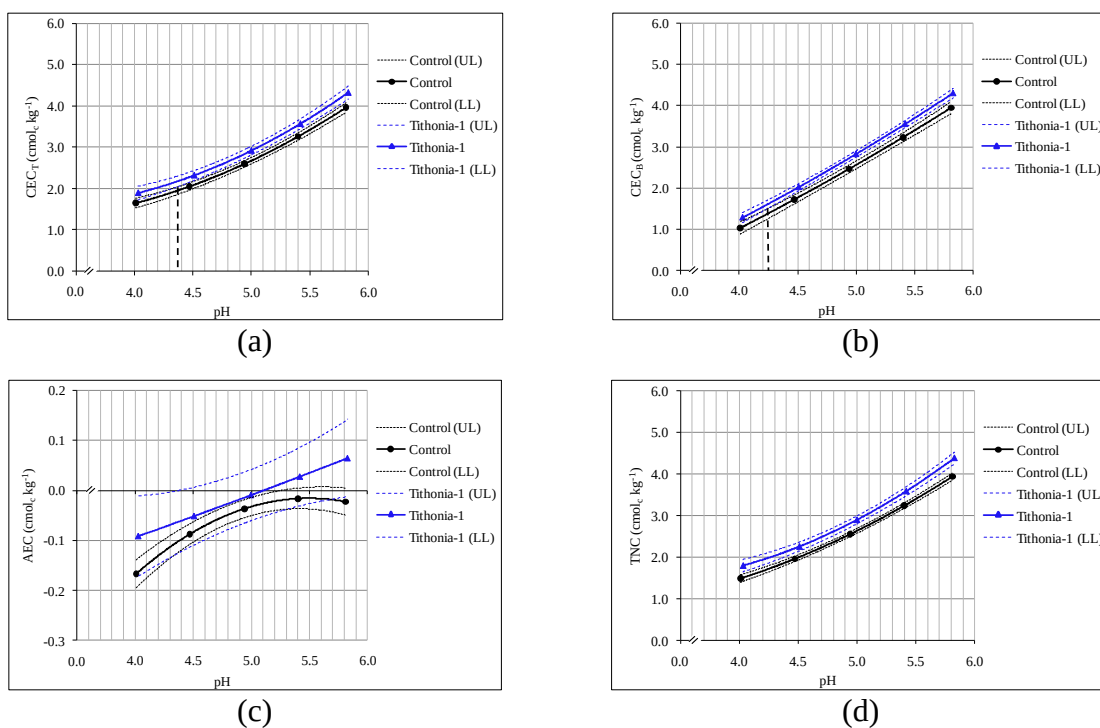


Figure A.21 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following *Tithonia diversifolia* amendment (71 kg Si ha⁻¹) after 7 days of incubation

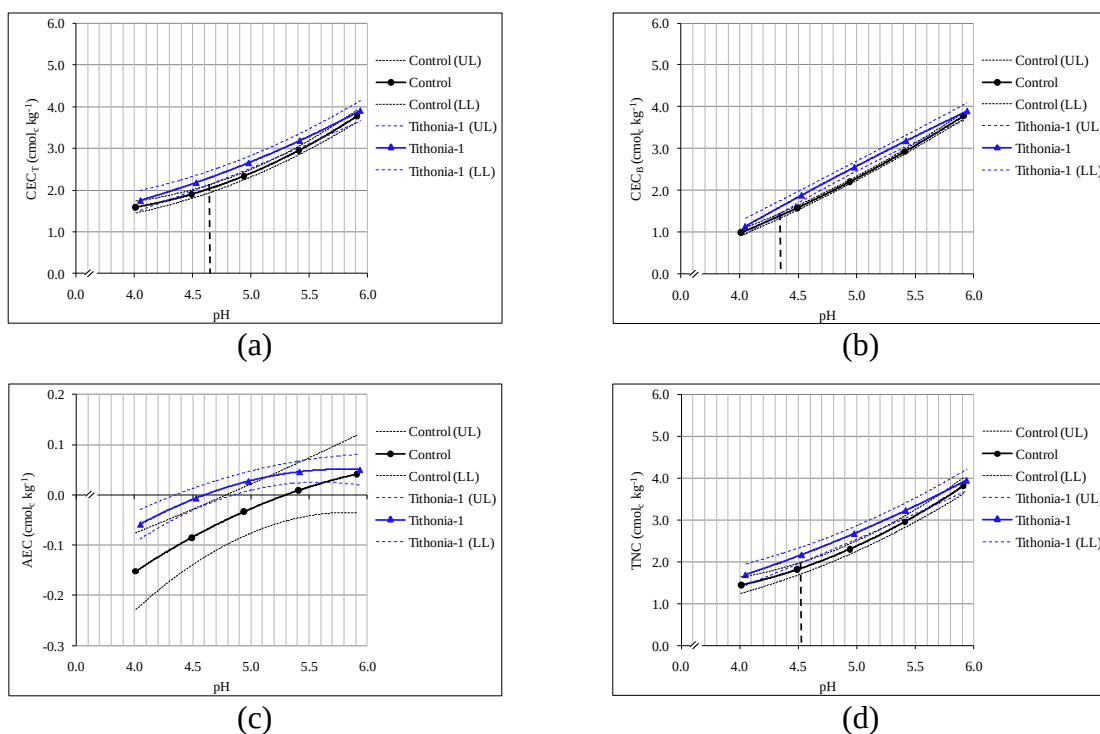


Figure A.22 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following *Tithonia diversifolia* amendment (71 kg Si ha⁻¹) after 30 days of incubation

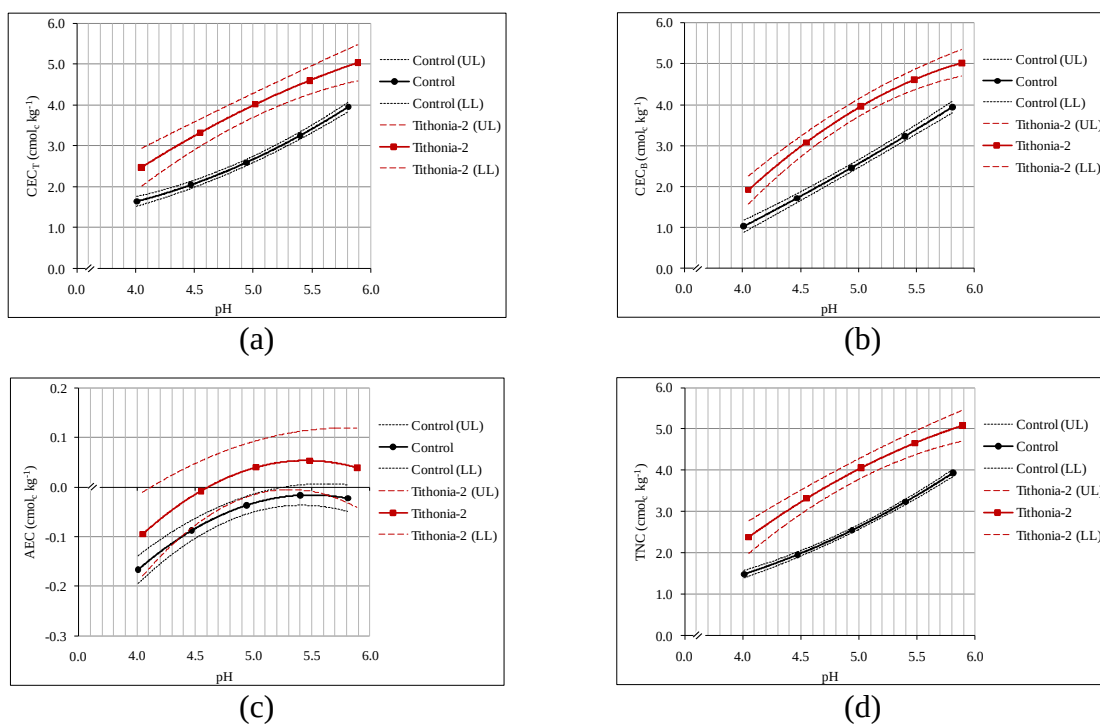


Figure A.23 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following *Tithonia diversifolia* amendment (210 kg Si ha⁻¹) after 7 days of incubation

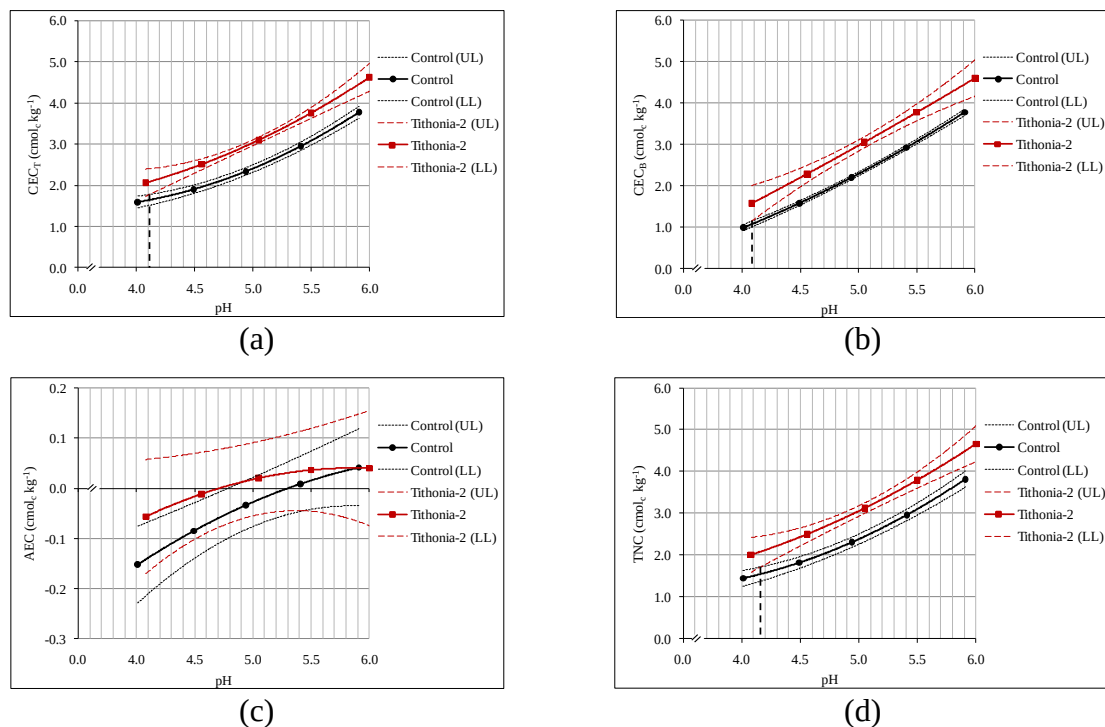


Figure A.24 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following *Tithonia diversifolia* amendment (210 kg Si ha⁻¹) after 30 days of incubation

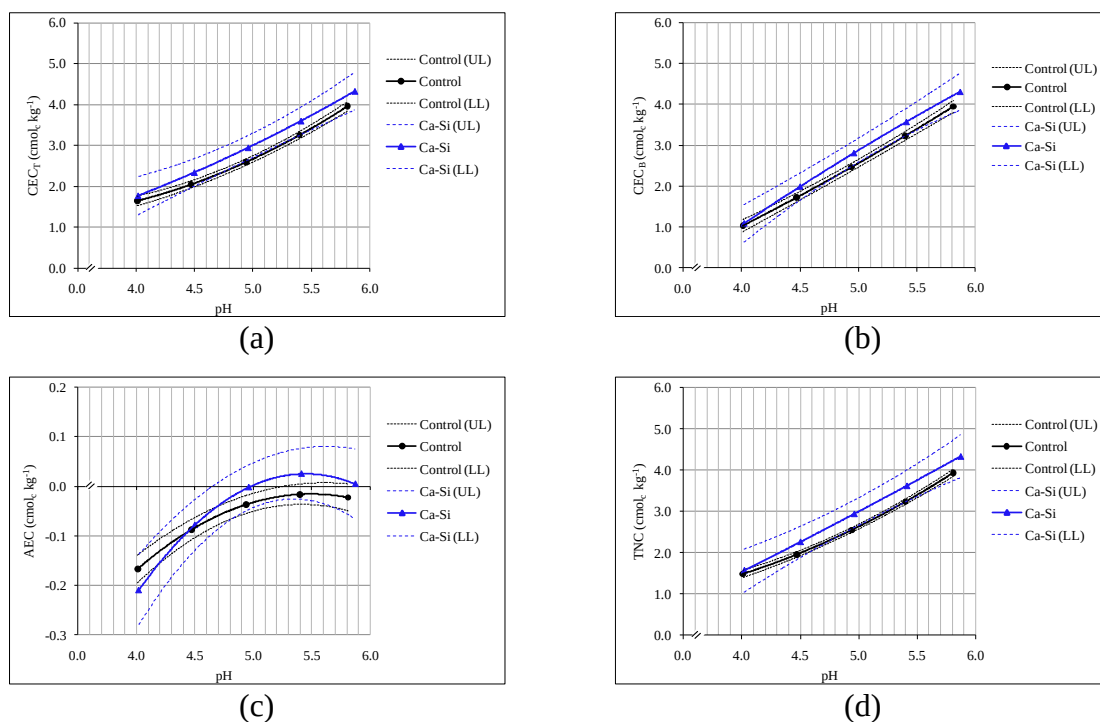


Figure A.25 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following calcium silicate amendment (210 kg Si ha⁻¹) after 7 days of incubation

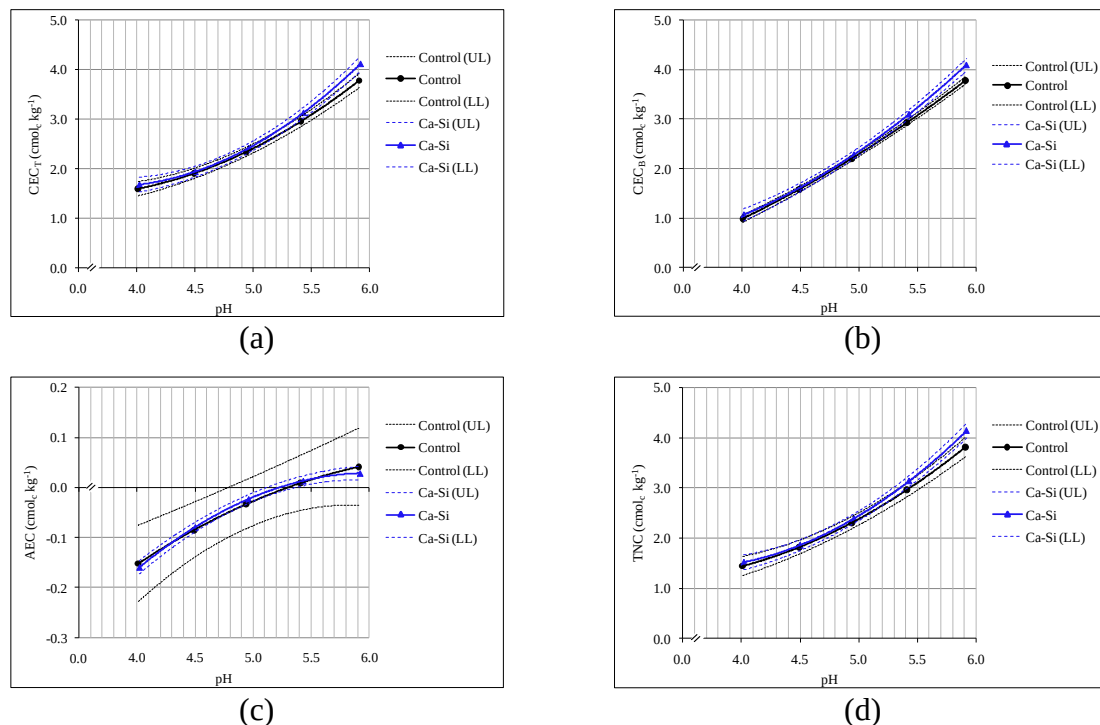


Figure A.26 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following calcium silicate amendment (210 kg Si ha⁻¹) after 30 days of incubation

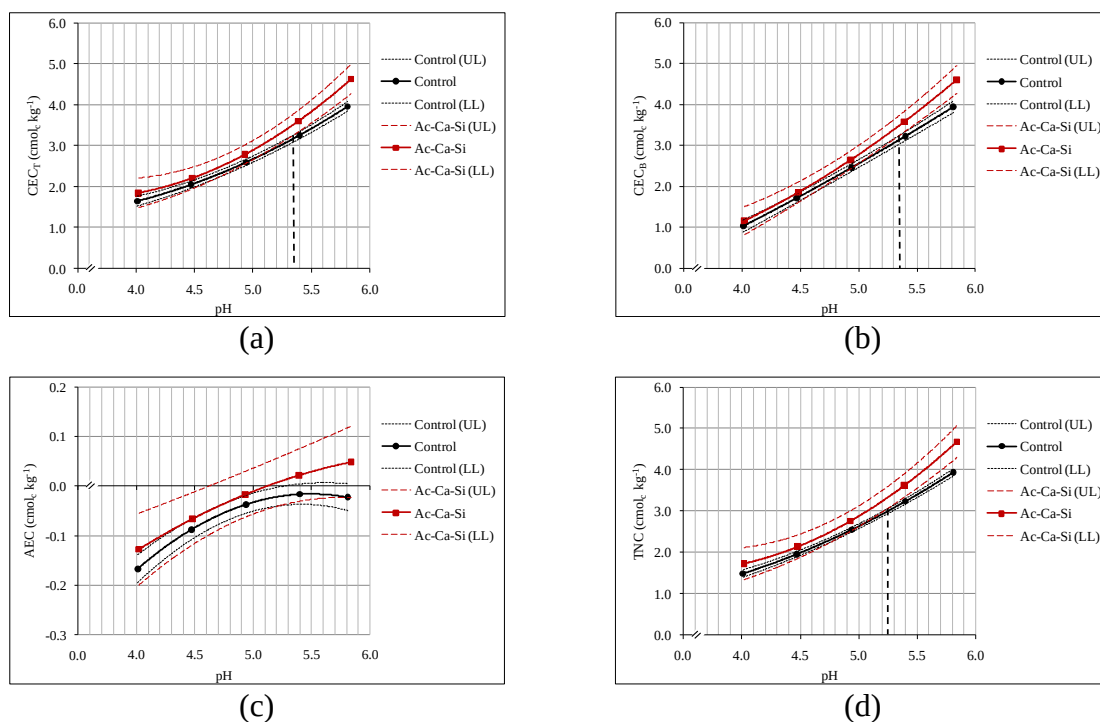


Figure A.27 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following acidulated calcium silicate amendment ($210 \text{ kg Si ha}^{-1}$) after 7 days of incubation

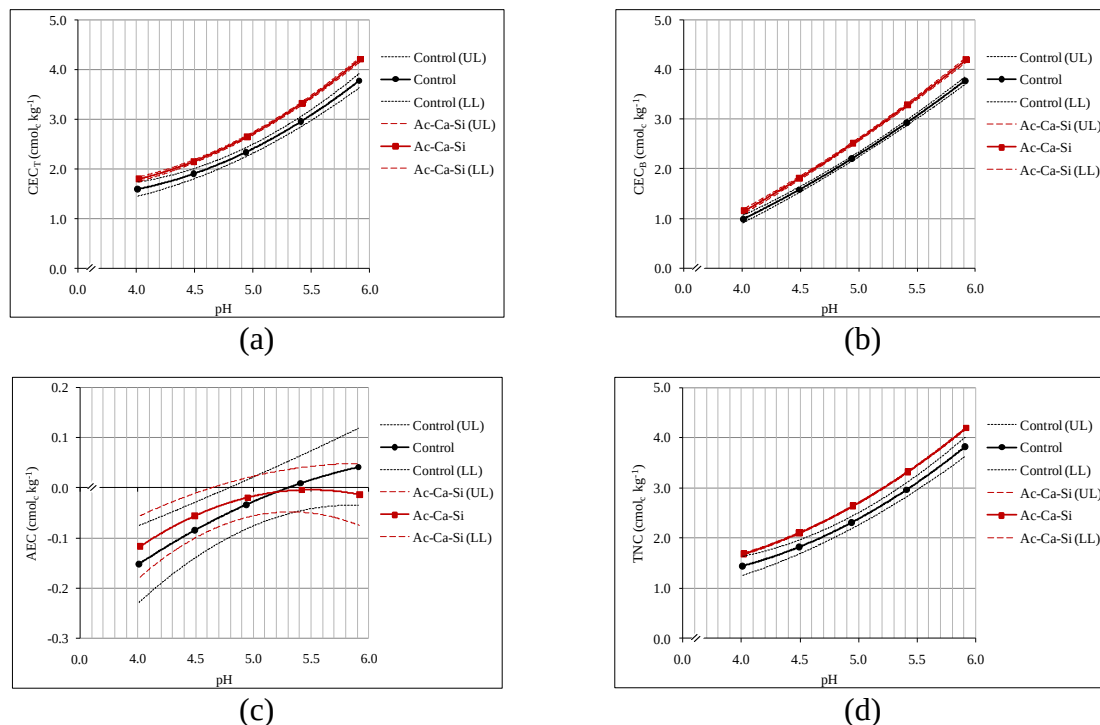


Figure A.28 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following acidulated calcium silicate amendment ($210 \text{ kg Si ha}^{-1}$) after 30 days of incubation

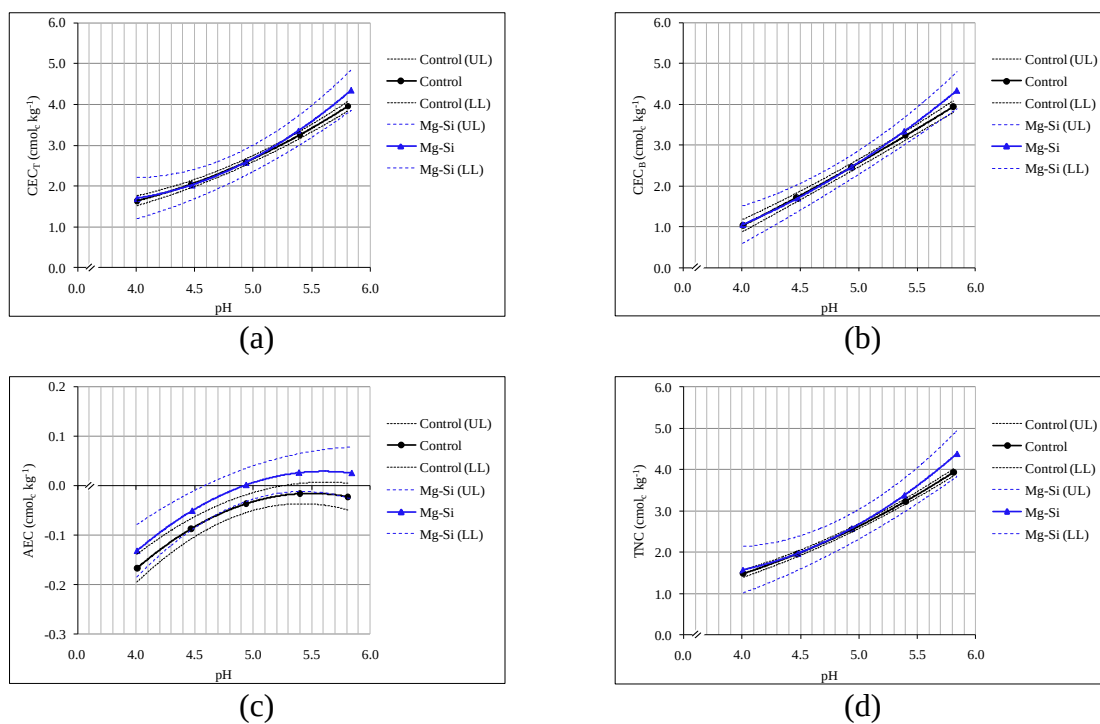


Figure A.29 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following magnesium silicate amendment ($210 \text{ kg Si ha}^{-1}$) after 7 days of incubation

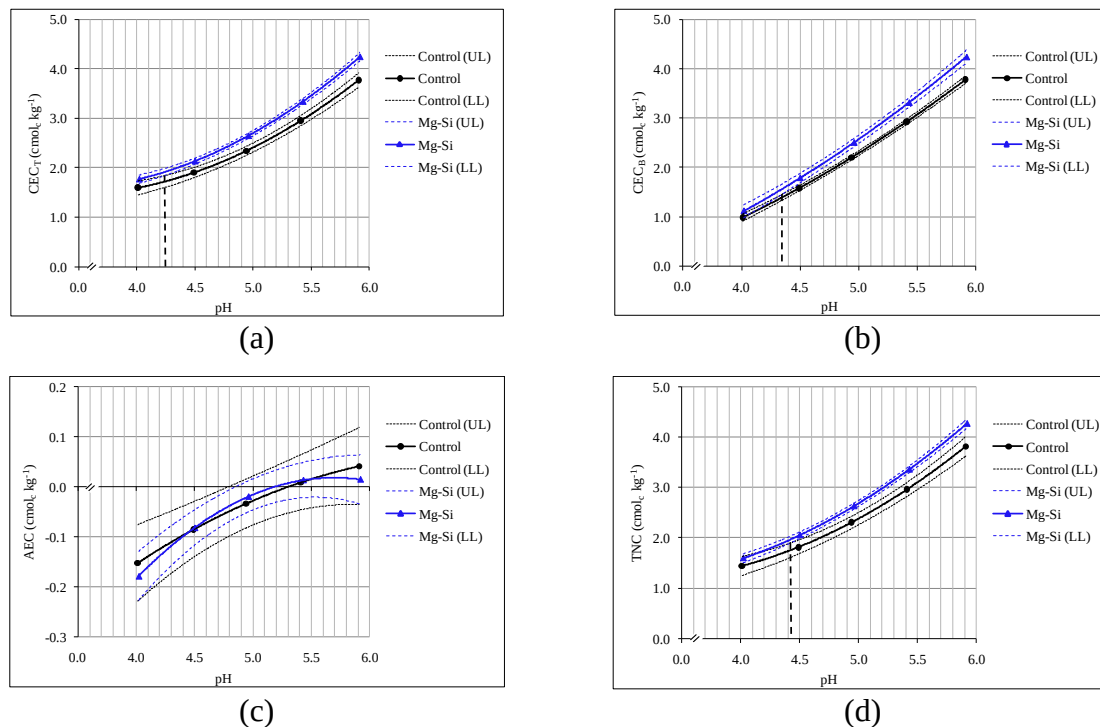


Figure A.30 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following magnesium silicate amendment ($210 \text{ kg Si ha}^{-1}$) after 30 days of incubation

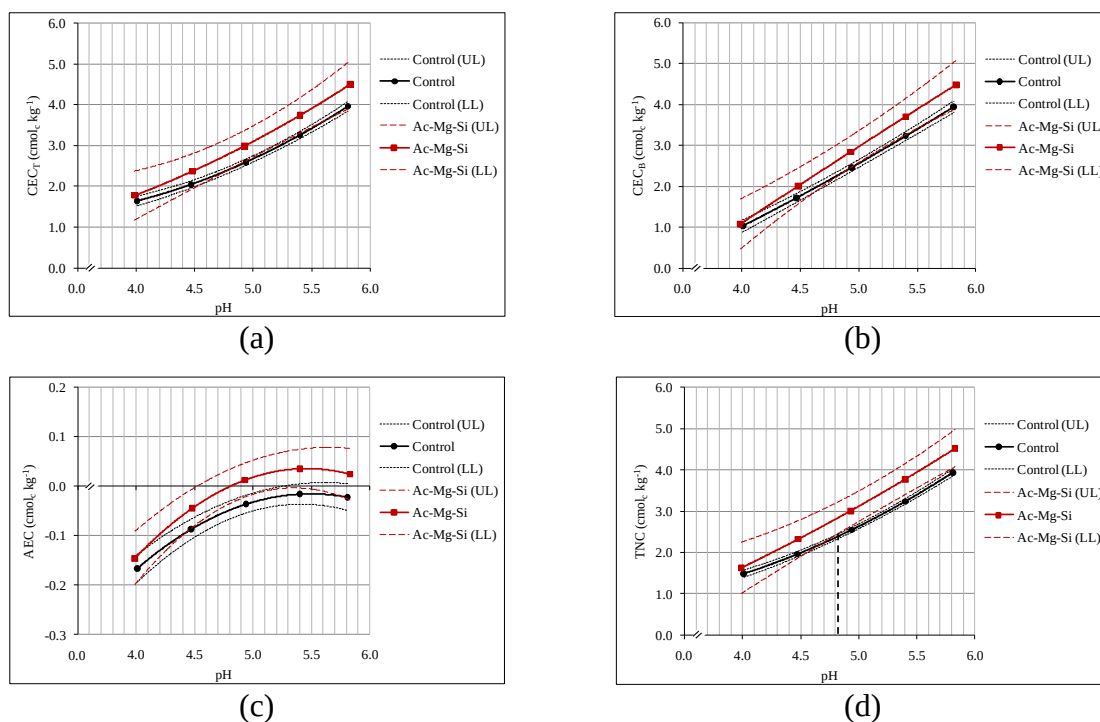


Figure A.31 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following acidulated magnesium silicate amendment (210 kg Si ha⁻¹) after 7 days of incubation

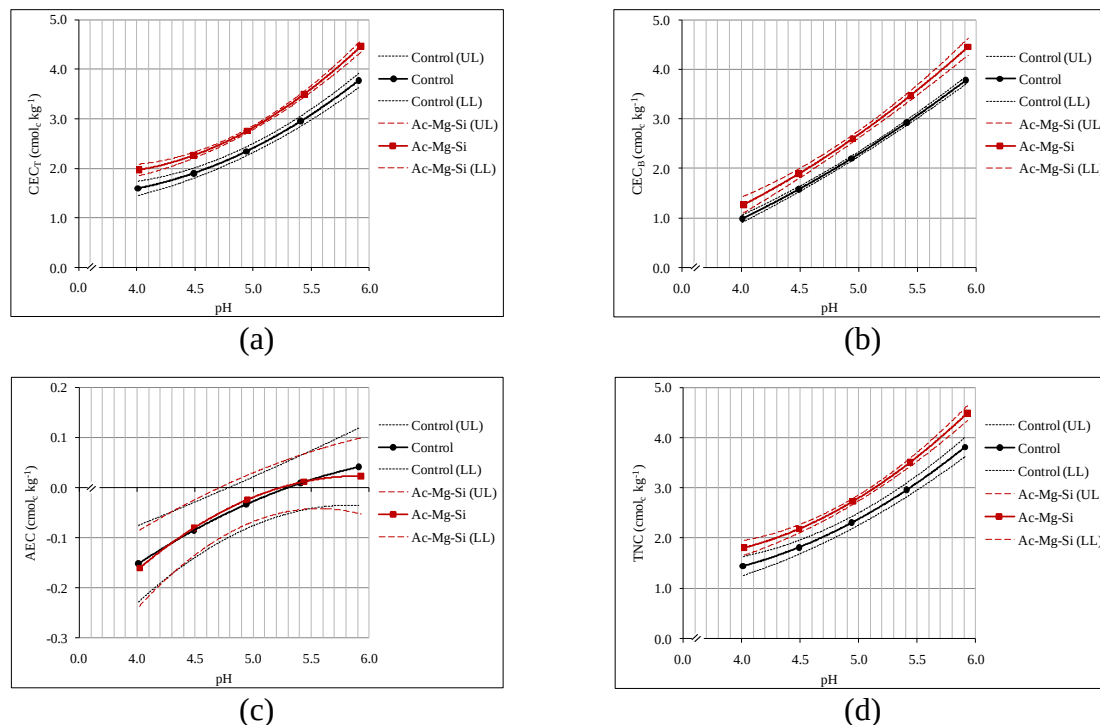


Figure A.32 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following acidulated magnesium silicate amendment (210 kg Si ha⁻¹) after 30 days of incubation

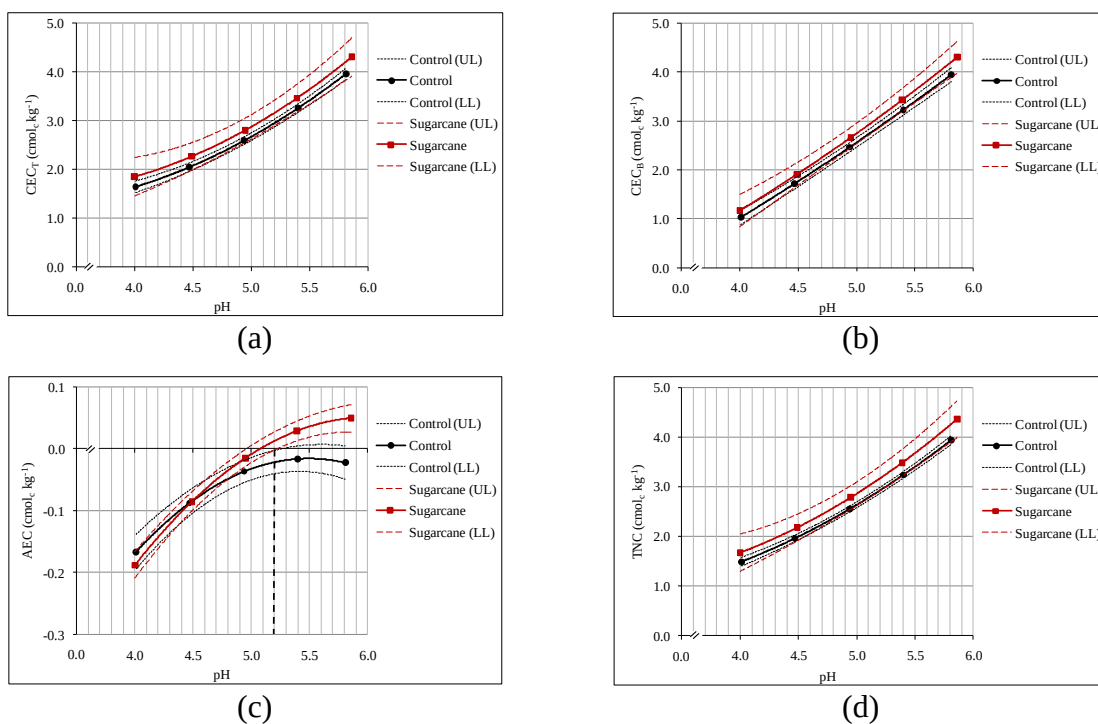


Figure A.33 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following sugarcane amendment ($210 \text{ kg Si ha}^{-1}$) after 7 days of incubation

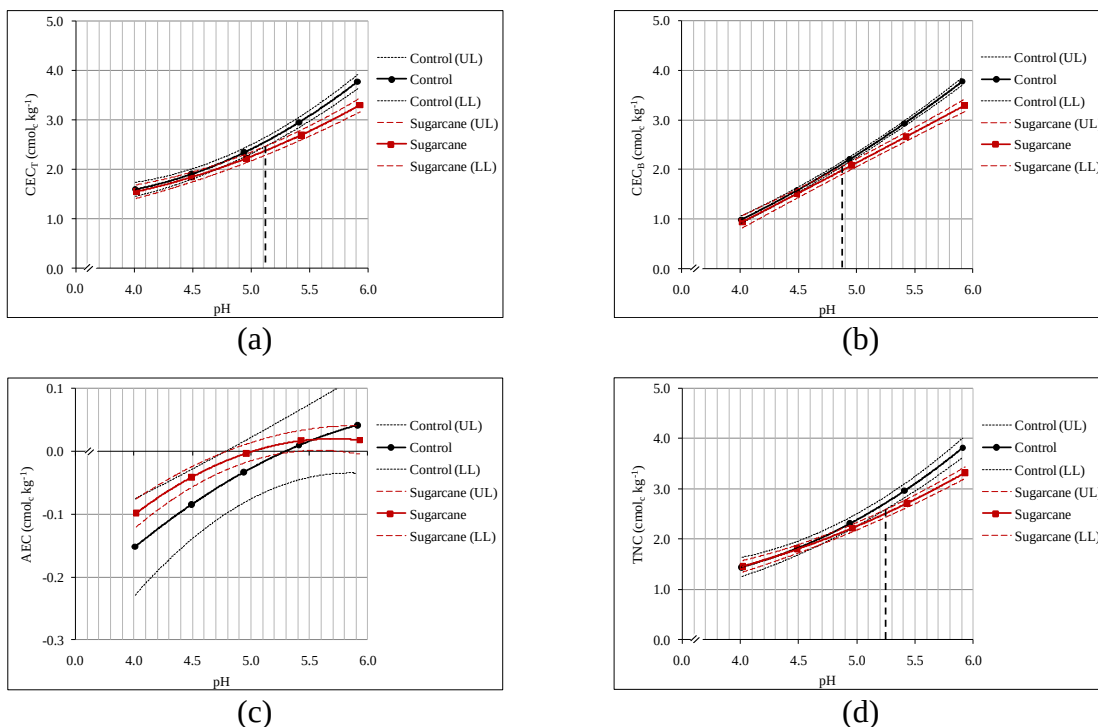


Figure A.34 Changes in (a) total cation exchange capacity; (b) basic cation exchange capacity; (c) anion exchange capacity; and (d) total net charge following sugarcane amendment ($210 \text{ kg Si ha}^{-1}$) after 30 days of incubation

References

- Adams, E., 1984. Soil acidity and liming. Soil Science Society of America, Inc., Madison, WI.
- Adams, F., Hathcock, R., 1984. Aluminum toxicity and calcium deficiency in acid subsoil horizons of two coastal plains soil series. *Soil Science Society of America Journal* **48**, 1305-1309.
- Adams, F., Moore, B., 1983. Chemical factors affecting root growth in subsoil horizons of coastal plain soils. *Soil Science Society of America Journal* **47**, 99-102.
- Aitken, R., Moody, P., 1994. The effect of valence and ionic strength on the measurement of pH buffer capacity. *Australian Journal of Soil Research* **32**, 975-984.
- Aitken, R., Moody, P., Compton, B., 1990a. A simple bioassay for the diagnosis of aluminium toxicity in soils. *Communications in Soil Science and Plant Analysis* **21**, 511-529.
- Aitken, R., Moody, P., Dickson, T., 1998. Field amelioration of acidic soils in south-east Queensland. I. Effect of amendments on soil properties. *Australian Journal of Agriculture Research* **49**, 627-637.
- Aitken, R., Moody, P., McKinley, P., 1990b. Lime requirement of acidic Queensland soils. I. Relationship between soil properties and pH buffer capacity. *Australian Journal of Soil Research* **28**, 695-701.
- Alexander, G.B., Heston, W.M., Iler, R.K., 1954. The solubility of amorphous silica in water. *Physical Chemistry* **58**, 453-455.
- Amarasiri, S.L., Perera, W.R., 1975. Nutrient removal by crops in the dry zone of Sri Lanka. *Tropical Agriculture* **131**, 61-70.
- Anda, M., Shamshuddin, J., Fauziah, C.I., Syed Omar, S., 2008. Mineralogy and factors controlling charge development of three Oxisols developed from different parent materials. *Geoderma* **143**, 153-167.
- Arai, Y., Livi, K., Sparks, D., 2005. Phosphate reactivity in long-term poultry litter-amended Southern Delaware sandy soils. *Soil Science Society of America Journal* **69**, 616-629.
- Arai, Y., Parks, D., 2007. Phosphate reaction dynamics in soil and soil components: A multiscale approach. *Advances in Agronomy* **94**, 135-179.
- Asghar, M., Kanehino, Y., 1980. Effects of sugarcane trash and pineapple residue on soil pH, redox potential, extractable Al, Fe and Mn. *Tropical Agriculture* **57**, 245-258.
- Aweto, A., Obe, O., Ayanniyi, O., 1992. Effects of shifting and continuous cultivation of cassava (*Manihot esculenta*) intercropped with maize (*Zea mays*) on a forest alfisol in south-western Nigeria. *Agricultural Science* **118**, 195-198.
- Bache, B., 1988. Measurements and mechanisms in acid soils. *Communications in Soil Science and Plant Analysis* **19**, 775-792.
- Barceló, J., Guevara, P., Poschenrieder, C., 1993. Silicon amelioration of aluminum toxicity in teosinte, *Zea mays* L. ssp. *mexicana*. *Plant and Soil* **154**, 249-255.
- Barrow, N., J., 1984. Modeling the effects of pH on phosphate sorption by soils. *Soil Science* **35**, 283-297.
- Barrow, N., J., 1986. Reaction of anions and cations with variable-charge soils. *Advances in Agronomy* **38**, 183-230.
- Barrow, N., J., 1996. The reaction of anions and cations with metal oxides as models for their reaction with soil. In: Dabrowski, A., Tertykh, V.A. (Eds.), Adsorption on new and modified inorganic sorbents. Elsevier Science B.V., pp. 829-856.

- Barrow, N., J., Bowden, J.W., Posner, A.M., Quirk, J.P., 1980. Describing the effects of electrolyte on adsorption of phosphate by variable charge surface. *Australian Journal of Soil Research* **18**, 395-404.
- Baylis, A.D., Gragopoulou, C., Davidson, K.J., Birchall, J.D., 1994. Effects of silicon on the toxicity of aluminum to soybean. *Communications in Soil Science and Plant Analysis* **25**, 537-546.
- Beckwith, R.S., Reeve, R., 1963. Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. *Australian Journal of Soil Research* **1**, 157-168.
- Beckwith, R.S., Reeve, R., 1964. Studies on soluble silica in soils. II. The release of monosilicic acid from soils. *Australian Journal of Soil Research* **2**, 33-45.
- Bellini, G., Sumner, M.E., Radcliffe, D.E., Qafoku, N.P., 1996. Anion transport through columns of highly weathered acid soil: adsorption and retardation. *Soil Science Society of America Journal* **60**, 132-137.
- Berek, A., Radjagukguk, B., Maas, A., 1995. The effect of different organic materials on the alleviation of Al toxicity in soybean on a red-yellow podzolic soil. In: Date, R., Grundon, N., Rayment, G., Probert, M.E. (Eds.), *Plant-soil interactions at low pH: Principles and management*. Kluwer Academic Publishers, Dordrecht, pp. 579-584.
- Berthelsen, S., Noble, A.D., Kingston, G., Hurney, A., Rudd, A., Garside, A., 2003. Improving yield and ccs in sugarcane through the application of silicon based amendments. Final report: SRDC Project CLW009. CSIRO Land and Water, Townsville, Queensland, pp. 1-138.
- Bessho, T., Bell, L., 1992. Soil solid and solution phase changes and mungbean response during amelioration of aluminium with organic matter. *Plant and Soil* **140**, 183-196.
- Betz, L.D., Noll, C.A., Maguire, J.J., 1941. Adsorption of soluble silica from water. *Industrial and Engineering Chemistry* **33**, 814-820.
- Birchall, J.D., 1990. The role of silicon in biology. *Chemistry in Britain* **26**, 141-144.
- Blamey, F.P.C., Nishizawa, N.K., Yoshimura, E., 2004. Timing, magnitude, and location of initial soluble aluminum injuries to mungbean roots. *Soil Science and Plant Nutrition* **50**, 67-76.
- Bleeker, P., Sageman, R., 1990. Surface charge characteristics and clay mineralogy of some variable charge soils in Papua New Guinea. *Australian Journal of Soil Research* **28**, 901-917.
- Bolan, N.S., Naidu, R., Syers, J.K., Tillman, R.W., 1999. Surface charge and solute interactions in soils. *Advances in Agronomy* **67**, 87-140.
- Bolan, N.S., Naidu, R., Syers, J.K., Tillman, R.W., 2000. Surface charge and solute interactions in soils. *Advances in Agronomy* **67**, 87-140.
- Bolan, N.S., Syers, J.K., Tillman, R.W., 1986. Ionic strength effects on surface charge and adsorption of phosphate and sulfate by soils. *Soil Science* **37**, 379-388.
- Bolan, N.S., Syers, J.K., Tillman, R.W., Scotter, D.R., 1988. Effect of liming and phosphate additions on sulfate leaching in soils. *Soil Science* **39**, 493-504.
- Bolland, M.D.A., Posner, A.M., Quirk, J.P., 1976. Surface charge on kaolinite in aqueous suspension. *Australian Journal of Soil Research* **14**, 197-216.
- Bowden, J.W., Posner, A.M., Quirk, J.P., 1980. Adsorption and charging phenomena in variable charge soils. In: Theng, B.K.G. (Ed.), *Soils with available charge*. New Zealand Society of Soil Science, Lower Hutt, pp. 147-166.
- Breeuwsma, A., Lyklema, J., 1971. Interfacial Electrochemistry of Haematite (α -Fe₂O₃). *Discussions of the Faraday Society* **52**, 324-333.
- Brown, T.H., Mahler, R.L., 1987. Effects of phosphorus and acidity on level of silica extracted from Palouse Silt Loam. *Soil Science Society of America Journal* **51**, 674-677.

- Bruce, A., Warrell, L., Edwards, D., Bell, L., 1988. Effects of aluminium and calcium in the soil solution of acid soils on root elongation of *Glycine max* cv. Forrest. *Australian Journal of Agriculture Research* **39**, 319-338.
- Bui, B.B., 1998. Bridging the rice yield gap in Vietnam In: Rigi, C.P., Pradhan, D., Ofren, R.S., Kratzschmar, E. (Eds.), Land use/land cover change in south-east Asia. UNEP Environment Assessment Program for Asia and the Pacific, Bangkok.
- Burkitt, L., Moody, P., Gourley, C., Hannah, M., 2002. A simple phosphorus sorption index for Australian soils. *Australian Journal of Soil Research* **40**, 497-513.
- Charlet, L., Sposito, G., 1987. Monovalent ion adsorption by an Oxisol. *Soil Science Society of America Journal* **51**, 1155-1160.
- Charlet, L., Sposito, G., 1989. Bivalent ion adsorption by an Oxisol. *Soil Science Society of America Journal* **53**, 691-695.
- Chorover, J., 2005. Zero-charge point. In: Hillel, D. (Ed.), Encyclopedia of soils in the environment, four-volume set. Elsevier Inc., New York.
- Clarke, J., 2003. The occurrence and significance of biogenic opal in the regolith. *Earth Science Reviews* **60**, 175-194.
- Cocker, K.M., Evans, D.E., Hodson, M.J., 1998a. The amelioration of aluminium toxicity by silicon in higher plants: solution chemistry or an in plants mechanism? *Plant Physiology* **104**, 608-614.
- Cocker, K.M., Evans, D.E., Hodson, M.J., 1998b. The amelioration of aluminum toxicity by silicon in wheat (*Triticum aestivum* L.): malate exudation as evidence for an in planta mechanism. *Planta* **204**, 318-323.
- Colwell, J., 1963. The estimation of the phosphorus fertiliser requirements of wheat in southern New South Wales by soil analysis. *Australian Journal of Experimental Agriculture and Animal Husbandry* **6**, 105-120.
- Conyers, M., Helyar, K., Poile, G., 2000. pH buffering: The chemical response of acidic soil to added alkali. *Soil Science* **165**, 560-566.
- Cooke, G.M., 1956. The effect of some silicate slags on the utilization of soil and fertilizer phosphorus. *Science of Food and Agriculture* **7**, 56-61.
- Corrales, I., Poschenrieder, C., Barceló, J., 1997. Influence of silicon pretreatment on aluminium toxicity in maize roots. *Plant and Soil* **190**, 203-209.
- Cresser, M., Killham, K., Edwards, T., 1993. Soil chemistry and its applications. Cambridge environmental chemistry series 5. Cambridge University Press, New York.
- Dahlgren, R.A., Shoji, S., Nanzoy, M., 1993. Mineralogical characteristics of volcanic ash soils. In: Shoji, S., Nanzoy, M., Dahlgren, R.A. (Eds.), Volcanic ash soils: Genesis, properties and utilization. Elsevier, Amsterdam, pp. 101-144.
- Dahlgren, R.A., Ugolini, F.C., 1989. Aluminum fractionation of soil solution from unperturbed and tephra-treated Spodosols, Cascade Range, Washington, USA. *Soil Science Society of America Journal* **53**, 559-566.
- Davies, S.N., 1964. Silica in streams and ground water. *American Journal of Science* **262**, 870-891.
- Demumbrum, L.E., Chesters, G., 1964. Isolation and characterization of some soil allophanes. *Soil Science Society of America Proceedings* **28**, 355-359.
- Dietzel, M., 1998. Polysilicic acid and the dissolution of silicates. *Mineralogical Magazine* **62A**, 385-386.
- 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: Stober, I., Bucher, K. (Eds.), *Water-rock interaction*. Kluwer Academic, Dordrecht, pp. 207-235.
- Drees, L.R., Wilding, L.P., Smeck, N.E., Senkayi, A.L., 1989. Silica in soils: quartz and disordered silica polymorphs. In: Dixon, J.B., Weed, S.B., Dinauer, R.C. (Eds.), *Minerals in soil environment*. *Soil Science Society of America. Book Series 1*, Madison WS, pp. 913-974.
- Eick, M., Brady, W., Lynch, C., 1999. Charge properties and nitrate adsorption of some acid Southeastern soils. *Environmental Quality* **28**, 138-144.
- Epstein, E., 1994. The anomaly of silicon in plant biology. *Proceedings of the National Academy of Sciences* **91**, 11-17.
- Epstein, E., 1999. Silicon. *Annual Review of Plant Physiology and Plant Molecular Biology* **50**, 641-664.
- Ethos Plus, 2000. Milestone application note 031. Application field environment, soil.
- Exley, C., Birchall, J.D., 1992. Hydroxyaluminosilicate formation in solutions of low total aluminium concentration. *Polyhedron* **11**, 1901-1907.
- Exley, C., Birchall, J.D., 1993. A mechanism of hydroxyaluminosilicate formation. *Polyhedron* **12**, 1007-1017.
- Exley, C., Tollervey, A., Gray, G., Roberts, S., Birchall, J.D., 1993. Silicon, aluminium and the biological availability of phosphorus in algae. *Proceedings of Biological Sciences* **253**, 93-99.
- Faithfull, N.T., 2002. *Methods in agricultural chemical analysis: A practical handbook*. CABI Publishing, Wallingford.
- Fiantis, D., Van Ranst, E., Shamshuddin, J., Fauziah, I., Zauyah, S., 2002. Effect of calcium silicate and superphosphate application on surface charge properties of volcanic soils from West Sumatra, Indonesia. *Communications in Soil Science and Plant Analysis* **33**, 1887-1900.
- Fleck, A., T, N., Repenning, C., Stahl, F., Zahn, M., Schenk, M., 2011. Silicon enhances suberization and lignification in roots of rice (*Oryza sativa*). *Experimental Botany* **62**, 2001-2011.
- Fox, R.L., 1978. Studies phosphorus nutrition in the tropics. In: Andrew, C.S., Kamprath, E.J. (Eds.), *Mineral nutrition of legumes in tropical and subtropical soils*. Commonwealth Scientific and Industrial Research Organization, Melbourne, pp. 168-187.
- Fox, R.L., 1980. Soils with available charge: agronomic and fertility aspects. In: Theng, B.K.G. (Ed.), *Soils with available charge*. New Zealand Society of Soil Science, Lower Hutt, pp. 195-224.
- Fox, R.L., 1982. Some highly weathered soils of Puerto Rico, 3. Chemical properties. *Geoderma* **27**, 139-176.
- Foy, C.D., Chaney, R.L., White, M.C., 1978. The physiology of metal toxicity in plants. *Annual Review of Plant Physiology* **29**, 511-566.
- Gallez, A., Juo, A.S.R., Herbillon, A.J., Moormann, F.R., 1975. Clay mineralogy of selected soils in southern Nigeria. *Soil Science Society of America Proceedings* **39**, 577-585.
- Gaume, A., Machler, F., Frossard, E., 2001. Aluminum resistance in two cultivars of *Zea mays* L.: root exudation organic acids and influence of phosphorus nutrition. *Plant and Soil* **234**, 73-81.
- Gillman, G.P., 1984. Using variable charge characteristics to understand the exchangeable cation status of oxic soils. *Australian Journal of Soil Research* **22**, 71-80.
- Gillman, G.P., 1985. Influence of organic matter and phosphate content on the point of zero charge of variable charge components in oxidic soils. *Australian Journal of Soil Research* **23**, 643-646.
- Gillman, G.P., 2007. An analytical tool for understanding the properties and behaviour of variable charge soils. *Australian Journal of Soil Research* **45**, 83-90.

- Gillman, G.P., Murtha, G., 1983. Effects of handling on some chemical properties of soils from high rainfall coastal North Queensland. *Australian Journal of Soil Research* **21**, 67-72.
- Gillman, G.P., Sumner, M.E., 1987. Surface charge characterization and soil solution composition of four soils from the Southern Piedmont in Georgia. *Soil Science Society of America Journal* **51**, 589-594.
- Gillman, G.P., Sumpter, E.A., 1986. Surface charge characteristics and lime requirements of soils derived from basaltic, granitic, and metamorphic rocks in high-rainfall tropical Queensland. *Australian Journal of Soil Research* **24**, 173-192.
- Gillman, G.P., Uehara, G., 1980. Charge characteristics of soils with variable and permanent charge minerals: II. Experimental. *Soil Science Society of America Journal* **44**, 252-255.
- Gladkova, K.F., 1982. The role of silicon in phosphate plant nutrition. *Agrochemistry* **2**, 133-144.
- Greenland, D.J., Hayes, M.H.B., 1978. Soils and soil chemistry. In: Greenland, D.J., Hayes, M.H.B. (Eds.), *The chemistry of soil constituents*. John Wiley & Sons, London, pp. 1-27.
- Greenland, D.J., Mott, C.J.B., 1978. Surfaces of soil particles. In: Greenland, D.J., Hayes, M.H.B. (Eds.), *The chemistry of soil constituents*. John Wiley & Sons, London, pp. 321-353.
- Guadalix, M.E., Pardo, M.T., 1994. Effects of liming on soil properties and P solubility in some Spanish Andosols. *Geoderma* **63**, 53-61.
- Hammond, K.E., Evans, D.E., Hodson, M.J., 1995. Aluminium/silicon interactions in barley (*Hordeum vulgare* L.) seedling. *Plant and Soil* **173**, 89-95.
- Hanafi, M., Syers, J.K., Bolan, N.S., 1992. Effect of lime on the dissolution of two phosphate rocks in acid soils. *Science of Food and Agriculture* **60**, 155-164.
- Hartono, A., 2008. The effect of calcium silicate on the phosphorus sorption characteristics of Andisols Lembang West Java. *Jurnal Tanah dan Lingkungan* **10**, 14-19.
- Hawke, D., Powell, H., Simpsons, S., 1996. Equilibrium modelling of interferences in the visible spectrophotometric determination of aluminium (III) : Comparison of the chromophores chrome azurol S, eriochrome cyanine R and pyrocatechol violet, and stability constants for eriochrome cyanine R-aluminium complexes. *Analytica Chimica Acta* **319**, 305-314.
- Helmke, P.A., Naidu, R., 1996. Fate of contaminant in the soil environment: Metal contaminants. In: Naidu, R., Kookana, R.S., Oliver, D., Rogers, S., McLaughlin, M.J. (Eds.), *Contaminants and soil environment in the Australasia - Pacific region*. Kluwer, Dordrecht, pp. 69-94.
- Hendershot, W.H., Lavkulich, L.M., 1978. The use of zero point of charge (ZPC) to assess pedogenic development. *Soil Science Society of America Journal* **42**, 468-472.
- Herbillon, A.J., 1980. Mineralogy of Oxisols and oxic materials. In: Theng, B.K.G. (Ed.), *Soils with variable charge*. New Zealand Society of Soil Science, Lower Hutt, pp. 109-126.
- Hingston, F.J., Atkinson, R.J., Quirk, J.P., 1967. Specific adsorption of anions. *Nature* **215**, 1459-1461.
- Hingston, F.J., Posner, A.M., Quirk, J.P., 1968. Specific adsorption of anions on goethite. *The Transactions of the 9th International Congress of Soil Science* **1**, 669-678.
- Hingston, F.J., Posner, A.M., Quirk, J.P., 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *Soil Science* **23**, 177-192.
- Hingston, F.J., Posner, A.M., Quirk, J.P., 1974. Anion adsorption by goethite and gibbsite: II. Desorption of anions from hydrous oxide surface. *Soil Science* **25**, 16-26.
- Hingston, F.J., Raupach, M., 1967. The reaction between monosilicic acid and aluminum hydroxide. I. Kinetics of adsorption of silicic acid by aluminum hydroxide. *Australian Journal of Soil Research* **5**, 295-309.

- Hiradate, S., Taniguchi, S., Sakurai, K., 1998. Aluminum speciation in aluminum-silica solutions and potassium chloride extracts of acidic soils. *Soil Science Society of America Journal* **62**, 630-636.
- Hodson, M.J., Evans, D.E., 1995. Aluminium/silicon interactions in higher plants. *Experimental Botany* **46**, 161-171.
- Horiguchi, T., 1988. Mechanism of manganese toxicity and tolerance of plants. VI. Effect of silicon on alleviation of manganese toxicity of rice plants. *Soil Science and Plant Nutrition* **34**, 65-73.
- Horiguchi, T., Morita, S., 1987. Mechanism of manganese toxicity and tolerance of plants. VI. Effect of silicon on alleviation of manganese toxicity of barley. *Plant Nutrition* **10**, 2299-2310.
- Horst, W.J., Fecht, M., Naumann, A., Wissemeier, A.H., Maier, P., 1999. Physiology of manganese toxicity and tolerance in *Vigna unguiculata* (L.). *Soil Science and Plant Nutrition* **162**, 263-274.
- Horst, W.J., Marschner, H., 1978. Effect of silicon on manganese tolerance of bean plants (*Phaseolus vulgaris* L.). *Plant and Soil* **50**, 287-303.
- Hoyt, P., Turner, R., 1975. Effects of organic materials added to very acid soils on pH, aluminium, exchangeable NH₄ and crop yields. *Soil Science* **119**, 227-237.
- Huang, L.Y., Li, H.X., Zhang, X.M., Lu, W.S., Liu, Y.J., 2006. Silicate adsorption in paddy soils of Guangdong province, China. *Phedosphere* **16**, 654-659.
- Hue, N., 1992. Correcting soil acidity of a highly weathered Ultisol with chicken manure and sewage sludge. *Communications in Soil Science and Plant Analysis* **23**, 241-246.
- Hue, N., Amien, I., 1989. Aluminium detoxification with green manures. *Communications in Soil Science and Plant Analysis* **20**, 1499-1511.
- Hue, N., Craddock, G., Adams, F., 1986. Effect of organic acids on aluminium toxicity in subsoils. *Soil Science Society of America Journal* **50**, 28-34.
- IFA, 1992. Rice. In IFA world fertilizer use manual. International Fertilizer Industry Association, Paris, p. 38.
- Iler, R.K., 1955. The Colloid Chemistry of Silica and Silicates. Cornell University Press, New York.
- Iler, R.K., 1979. The chemistry of silica : solubility, polymerization, colloid and surface properties, and biochemistry. Wiley - Interscience, New York.
- IRRI, 1965. Annual report 1964. International Rice Research Institute, Los Banos.
- Isbell, R.F., 1996. The Australian soil classification. CSIRO Publishing, Melbourne.
- Iwasaki, K., Maier, P., Fecht, M., Horst, W.J., 2002a. Effect of silicon supply on apoplastic manganese concentrations in leaves and their relation to manganese tolerance in cowpea (*Vigna unguiculata* L. Walp.). *Plant and Soil* **238**, 281-288.
- Iwasaki, K., Maier, P., Fecht, M., Horst, W.J., 2002b. Leaf apoplastic silicon enhances manganese tolerance of cowpea (*Vigna unguiculata*). *Plant Physiology* **159**, 167-173.
- Iwasaki, K., Matsumura, A., 1999. Effect of silicon on alleviation of manganese toxicity in pumpkin (*Cucurbita moschata* Duch cv. Shintosa). *Soil Science and Plant Nutrition* **45**, 909-920.
- Iyamuremye, F., Dick, R., 1996. Organic amendments and phosphorus sorption by soils. *Advances in Agronomy* **56**, 139-185.
- Jiang, H., Tang, N., Zheng, J., Li, Y., Chen, L., 2009. Phosphorus alleviates aluminum-induced inhibition of growth and photosynthesis in *Citrus grandis* seedlings. *Physiologia Plantarum* **137**, 298-311.
- Jiang, J., Xu, R., Zhao, A., 2010. Comparison of the surface chemical properties of four soils derived from Quaternary red earth as related to soil evolution. *Catena* **80**, 154-161.

- Jones, L.H.P., Handreck, K.A., 1963. Effect of iron and aluminum oxides on silica in solution in soils. *Nature* **108**, 852-853.
- Jones, L.H.P., Handreck, K.A., 1965. Studies of silica in the oat. III. Uptake of silica from soils by the plant. *Plant and Soil* **23**, 79-96.
- Jones, L.H.P., Handreck, K.A., 1967. Silica in soils, plants, and animals. *Advances in Agronomy* **19**, 107-149.
- Jones, R.L., Beavers, A.H., 1964. Aspects of catenary and depth distribution of opal phytolites in illinois soils. *Soil Science Society of America Proceedings* **28**, 413-416.
- Juo, A.S.R., Franzluebbers, K., 2003. Tropical soils: properties and management for sustainable agriculture. Oxford University Press, Inc., New York.
- Kamprath, E.J., 1970. Exchangeable Al as a criterion for liming leached mineral soils. *Soil Science Society of America Proceedings* **34**, 252-254.
- Kato, N., Owa, N., 1997. Dissolution of slag fertilizers in Paddy soil and Si uptake by rice plant. *Soil Science and Plant Nutrition* **43**, 329-341.
- Keng, J.C.W., Uehara, G., 1973. Chemistry, Mineralogy and Taxonomy of Oxisols and Ultisols. *Soil and Crop Science Society of Florida* **33**, 120-126.
- Kenjebaeve, S., Yamamoto, Y., Matsumoto, H., 2001. The impact of aluminium on the distribution of cell wall glycoproteins of pea root tip and their Al-binding capacity. *Soil Science and Plant Nutrition* **47**, 629-636.
- Kerven, G., Edwards, D., Ascher, C., Hallmer, P., Kokot, S., 1989. Aluminium determination in soil solution. II. Short-term colorimetric procedures for the measurement of inorganic monomeric aluminium in the presence of organic acid ligands. *Australian Journal of Soil Research* **27**, 9-102.
- Kinjo, T., Pratt, P.F., 1971. Nitrate adsorption: II. In competition with chloride, sulphate, and phosphate. *Soil Science Society of America Proceedings* **35**, 725-728.
- Kinraide, T., 1991. Identity of the rhizotoxic aluminium species. In: Wright, R., Baligar, V., Murrmann, R. (Eds.), Plant-soil interactions at low pH. Kluwer Academic Publishers, Dordrecht, pp. 717-728.
- Kinraide, T., 1997. Recondisering the rhizotoxicity of hydroxyl, sulphate, and fluoride complexes of aluminium. *Experimental Botany* **48**, 1115-1124.
- Kinraide, T., 2003. Toxicity factors in acidic forest soils: attempts to evaluate separately the toxic effects of excessive Al^{3+} and H^+ and insufficient Ca^{2+} and Mg^{2+} upon root elongation. *European Journal of Soil Science* **54**, 323-333.
- Kochian, L., 1995. Cellular machenisms of aluminum toxicity and resistance in plants. *Annual Review of Plant Physiology and Plant Molecular Biology* **46**, 237-260.
- Kochian, L., Pineros, M., Hoekenga, O., 2005. The physiology, genetics and molecular biology of plant aluminum resistance and toxicity. *Plant and Soil* **274**, 175-195.
- Koski-Vahala, J., Hartikainen, H., Tallberg, P., 2001. Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. *Environmental Quality* **30**, 546-552.
- Kuo, S., 1996. Phosphorus. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E. (Eds.), Methods of soil analysis: Part 3 chemical methods. Soil Science Society of America, Inc. and American Society of Agronomy, Inc., Madison, VI, pp. 869-919.
- Kwabiah, A.B., Palm, C.A., Stoskopf, N.C., Voroney, R.P., 2003a. Response of soil microbial biomass dynamics to quality of plant materials with emphasis on P availability. *Soil Biology and Biochemistry* **35**, 207-216.

- Kwabiah, A.B., Stoskopf, N.C., Palm, C.A., Voroney, R.P., 2003b. Phosphorus availability and maize response to organic and inorganic fertilizer inputs in a short term study in western Kenya. *Agriculture, Ecosystems and Environment* **95**, 49-59.
- Kwabiah, A.B., Stoskopf, N.C., Palm, C.A., Voroney, R.P., 2003c. Soil P availability as affected by the chemical composition of plant materials: implications for P-limiting agriculture in tropical Africa. *Agriculture, Ecosystems and Environment* **100**, 53-61.
- Laws, W.D., 1951. Water-soluble silicate application to a calcareous clay soil and effect on soil properties and nutrient uptake by plants. *Soil Science Society of America Proceedings* **15**, 89-92.
- Le Roux, J., 1973. Quantitative clay mineralogical analysis of Natal Oxisols. *Soil Science* **115**, 137-144.
- Lee, Y.B., Hoon, C., Hwang, J.Y., Lee, I.B., Kim, P.J., 2004. Enhancement of phosphate desorption by silicate in soils with salt accumulation. *Soil Science and Plant Nutrition* **50**, 493-499.
- Lee, Y.B., Kim, P.J., 2007. Reduction of phosphate adsorption by Ion competition with silicate in soil. *Korean Journal of Environmental Agriculture* **26**, 286-293.
- Li, Y., Alva, A., Sumner, M.E., 1989. Response of cotton to aluminum in solutions with varying silicon concentrations. *Plant Nutrition* **12**, 881-892.
- Li, Y., Sumner, M.E., Miller, W., Alva, A., 1996. Mechanism of silicon induced alleviation of aluminum phytotoxicity. *Plant Nutrition* **19**, 1075-1087.
- Liang, Y., Sun, W., Zhu, Y., Christie, P., 2007. Mechanisms of silicon-mediated alleviation of abiotic stresses in higher plants: A review. *Environmental Pollution* **147**, 422-428.
- Liang, Y.C., Yang, C.G., Shi, H.H., 2001. Effects of silicon on growth and mineral composition of barley grown under toxic levels of aluminum. *Plant Nutrition* **24**, 229-243.
- Lindsay, W.L., 1979. Chemical equilibria in soils. John Wiley and Sons, New York.
- 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., Miyake, Y., Takahashi, E., 2001. Silicon as beneficial element for crop plants. In: Datnoff, L.E., Snyder, G.H., Korndorfer, G.H. (Eds.), *Silicon in agriculture. Studies in plant science* 8. Elsevier, Amsterdam.
- Ma, J.F., Sasaki, M., Matsumoto, H., 1997. Al-induced inhibition of root elongation in corn, *Zea mays* L. is overcome by Si addition. *Plant and Soil* **188**, 171-176.
- Ma, J.F., Shen, R., Nagao, S., Tanimoto, E., 2004. Aluminum targets elongation cells by reducing cell wall extensibility in wheat roots. *Plant and Cell Physiology* **45**, 583-589.
- Ma, J.F., Takahashi, E., 1990a. The effect of silicic acid on rice in a P-deficient soil. *Plant and Soil* **126**, 121-125.
- Ma, J.F., Takahashi, E., 1990b. Effect of silicon on the growth and phosphorus uptake of rice. *Plant and Soil* **126**, 115-119.
- Ma, J.F., Takahashi, E., 1991. Effect of silicate on phosphate availability for rice in a P-deficient soil. *Plant and Soil* **133**, 151-155.
- Ma, J.F., Takahashi, E., 2002. Soil, fertilizer, and plant silicon research in Japan. Elsevier Science, Amsterdam.
- Ma, J.F., Yamamoto, R., Nevins, D., Matsumoto, H., Brown, P., 1999. Al binding in the epidermis cell wall inhibits cell elongation of okra hypocotyl. *Plant and Cell Physiology* **40**, 549-556.
- Marsh, K.H., Tillman, R.W., Syers, J.K., 1987. Charge relationships on sulfate sorption by soils. *Soil Science Society of America Journal* **51**, 318-323.

- Matichenkov, V.V., Ammosova, Y.M., 1996. Effect of amorphous silica on soil properties of a sod-podzolic soil. *Eurasian Soil Science* **28**, 87-99.
- Matichenkov, V.V., Bocharnikova, E.A., 2001. The relationship between silicon and soil physical and chemical properties. In: Datnoff, L.E., Snyder, G.H., Korndörfer, G.H. (Eds.), *Silicon in agriculture. Studies in plant science* 8. Elsevier, Amsterdam.
- Matichenkov, V.V., Bocharnikova, E.A., 2002. Effect of Si-rich slag and lime on P leaching in sandy soils. *American Society of Sugarcane Technologists* **22**, 9-15.
- Matichenkov, V.V., Calvert, D.V., 2002. Silicon as a beneficial element for sugarcane. *American Society of Sugarcane Technologists* **22**, 21-30.
- McBride, M.B., 1994. *Environmental chemistry of soils*. Oxford University Press, New York.
- McKeague, J.A., Cline, M.G., 1963a. Silica in soil solutions. I. The form and concentration of dissolved silica in aqueous extracts of some soils. *Canadian Journal of Soil Science* **43**, 70-82.
- McKeague, J.A., Cline, M.G., 1963b. Silica in soil solutions. II. The adsorption of monosilicic acid by soil and by other substances. *Canadian Journal of Soil Science* **43**, 83-96.
- McKeague, J.A., Cline, M.G., 1963c. Silica in soils. *Advances in Agronomy* **15**, 339-396.
- McLaren, R.G., Cameron, K.C., 1996. *Inorganic Soil Colloids., Soil Science - Sustainable Production and Environmental Protection*. Oxford University Press, New York.
- Melo, V.F., Singh, B., Schaefer, C.E.G.R., Novais, R.F., Fontes, M.P.F., 2001. Chemical and mineralogical properties of kaolinite-rich Brazilian soils. *Soil Science Society of America Journal* **65**, 1324-1333.
- Mengel, K., Kirkby, E.A. (Eds.), 2001. *Principles of plant nutrition*. Kluwer Academic, Dordrecht.
- Menzies, N., Guppy, C., 2000. In-situ soil solution extraction with polyacrylonitrile hollow-fibers. *Communications in Soil Science and Plant Analysis* **31**, 1875-1886.
- Mitchell, B.D., Farmer, V.C., McHardy, W.J., 1964. Amorphous inorganic materials in soils. *Advances in Agronomy* **16**, 327-383.
- Miyake, K., 1916. The toxic action of aluminum salts upon the growth of the rice plant. *Biological Chemistry* **25**, 23-28.
- Moody, P.W., Phan, T.C., 2008. Soil constraints and management package (SCAMP): guidelines for sustainable management of tropical upland soils. Australian Centre for International Agricultural Research. Canberra.
- Moody, P.W., Yo, S., Aitken, R., 1997. Soil organic carbon, permanganate fractions, and the chemical properties of acidic soils. *Australian Journal of Soil Research* **35**, 1301-1308.
- Mora, M.L., Barrow, N., J., 1996. The effect of time incubation on the relation between charge and pH of soil. *European Journal of Soil Science* **47**, 131-136.
- Morikawa, C., Saigusa, M., 2002. Si amelioration of Al toxicity in barley (*Hordeum vulgare* L.) growing in two andosols. *Plant and Soil* **240**, 161-168.
- Motomizu, S., Wakimoto, T., Toei, K., 1983. Spectrophotometric determination of phosphate in river waters with molybdate and malachite green. *Analyst* **108**, 361-367.
- Mott, C.J.B., 1981. Anion and ligand exchange. In: Greenland, D.J., Hayes, M.H.B. (Eds.), *The chemistry of soil processes*. John Wiley and Sons, Chichester, pp. 179-219.
- Murali, V., Sarma, V.A.K., Krishna-Murti, S.R., 1974. Mineralogy of two red soils (Alfisol) profiles of Mysore Stare, India. *Geoderma* **11**, 147-155.
- Naidu, R., Syers, J.K., Tillman, R.W., Kirkman, J.H., 1990. Effect of liming on phosphate sorption by acid soils. *Soil Science* **41**, 165-175.

- Nguyen, Q.C., Guppy, C., Moody, P., 2010. Effect of P and Si amendment on the charge characteristics and management of a geric soil. In: Gilkes, R.J., Prakongkep, N. (Eds.), 19th World Congress of Soil Science Proceedings, Brisbane, Australia.
- Nguyen, T.S., Thai, P., 1999. Upland soils in Vietnam, degradation and rehabilitation (in Vietnamese). Agricultural Publishing House, Hanoi.
- Nkhalamba, J., Rowell, D., Pilbeam, C., 2003. The development and contribution of surface charge by crop residues in two Malawian acid soils. *Geoderma* **115**, 281-302.
- Noble, A., Gillman, G.P., Nath, S., Srivastava, R., 2001. Changes in the surface charge characteristics of degraded soils in the wet tropics through the addition of beneficiated bentonite. *Australian Journal of Soil Research* **39**, 991-1001.
- Noble, A., Zenneck, I., Randall, P., 1996. Leaf litter ash alkalinity and neutralisation of soil acidity. *Plant and Soil* **179**, 293-302.
- Noble, A.D., Moody, P., Liu, G., Ruaysoongnern, S., Qi, Z., Berthelsen, S., 2003. Quantification of soil chemical degradation and its remediation in tropical Australia, China and Thailand. *Pedosphere* **13**, 31-39.
- Obihara, C.H., Russell, E.W., 1972. Specific adsorption of silicate and phosphate by soils. *Soil Science* **23**, 105-117.
- Okuda, A., Takahashi, E., 1961. Studies on the physiological role of silicon in crop plants. 4. Effect of silicon on the growth of barley, tomato, raddish, green onion, chinese cabbage and their nutrients uptake. *The Science of Soil and Manure* **32**, 623-626.
- Olsen, S., Cole, C., Watanabe, F., Dean, L., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA CIRC, Washington, pp. 171-189.
- Oorts, K., Vanlauwe, B., Pleysier, J., Merckx, R., 2004. A new method for the simultaneous measurement of pH-dependent cation exchange capacity and pH buffering capacity. *Soil Science Society of America Journal* **68**, 1578-1585.
- Owino-Gerroh, C., Gascho, G.J., 2004. Effect of silicon on low pH soil phosphorus sorption and on uptake and growth of maize. *Communications in Soil Science and Plant Analysis* **35**, 2369-2378.
- Ownby, J., 1993. Mechanisms of recation of hematoxylin with aluminium-treated wheat roots. *Physiologia Plantarum* **87**, 371-380.
- Pardo, M.T., Guadalix, M.E., Garcia-Gonzalez, M., 1992. Effect of pH and background electrolyte on P sorption by variable charge soils. *Geoderma* **54**, 275-284.
- Parfitt, R.L., 1978. Anion adsorption by soils and soil materials. *Advances in Agronomy* **30**, 1-50.
- Parfitt, R.L., 1980. Chemical properties of variable charge soils. In: Theng, B.K.G. (Ed.), Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt, pp. 167-193.
- Parfitt, R.L., Russel, M., Orbell, G.E., 1983. Weathering sequence of soils from volcanic ash involving allophane and halloysite, New Zealand. *Geoderma* **29**, 41-57.
- Parfitt, R.L., Saigusa, M., Cowie, J.D., 1984. Allophane and halloysite formation in a volcanic ash bed under different moisture conditions. *Soil Science* **138**, 360-364.
- Parker, D., Kinraide, T., Zelazney, L., 1989. On the phytotoxicity of polynuclear hydroxy-aluminum complexes. *Soil Science Society of America Journal* **53**, 789-796.
- Peaslee, D.E., Frink, C.R., 1969. Influence of silicic acid on uptake of Mn, Al, Zn, and Cu by tomatoes (*Lycopersicum esculentum*) grown on an acid soil. *Soil Science Society of America Proceedings* **33**, 569-571.
- Perrott, K.W., 1978. The influence of organic matter extracted from humified clover on the properties of amorphous aluminosilicates. II. Phosphate retention. *Australian Journal of Soil Research* **16**, 341-346.

- Perry, C., Tucker, T., 1998. Aspects of the bioinorganic chemistry of silicon in conjunction with the biometals calcium, iron and aluminium. *Inorganic Biochemistry* **69**, 181-191.
- Phan, T.C., 2000. Improving phosphorus availability in selected soils from the upland of South Vietnam by residue management - A case study: *Tithonia diversifolia*. Departement Landbeheer. Katholieke Universiteit Leuven, Leuven, p. 191.
- Phan, T.C., Cong, D.S., Nguyen, Q.C., Nguyen, B.D., 2005. Replenishing the phosphorus capital in depleted soils of the central highlands and the eastern region of south Vietnam (in Vietnamese). Project ET-2000/PRV (VLIR) - 05, Hochiminh city.
- Pierre, W., Stuart, A., 1933. Soluble aluminum studies. IV. The effects of phosphorus in reducing the detrimental effects of soil acidity on plant growth. *Soil Science* **36**, 211-227.
- Poschenrieder, C., Gunse, B., Corrales, I., Barceló, J., 2008. A glance into aluminum toxicity and resistance in plants. *Science of the Total Environment* **400**, 356-368.
- Prabagar, S., Hodson, M.J., Evans, D.E., 2011. Silicon amelioration of aluminium toxicity and cell death in suspension cultures of Norway spruce (*Picea abies* (L.) Karst.). *Environmental and Experimental Botany* **70**, 266-276.
- Probert, M.E., 1983. The sorption of phosphate by soils. In: Lenaghan, J.J., Katsantoni, G. (Eds.), *Soils, an Australian viewpoint*. Academic Press, London, pp. 427-435.
- Pypers, P., Verstraete, S., Phan, T.C., Merckx, R., 2005. Changes in mineral nitrogen, phosphorus availability and salt-extractable aluminium following the application of green manure residues in two weathered soils of South Vietnam. *Soil Biology and Biochemistry* **37**, 163-172.
- Qafoku, N.P., Ranst, E.V., Noble, A., Baert, G., 2004. Variable charge soils: Their mineralogy, chemistry and management. *Advances in Agronomy* **84**, 159-215.
- Qafoku, N.P., Summer, M.E., West, L.T., 2000. Mineralogy and chemistry of some variable charge subsoils. *Communications in Soil Science and Plant Analysis* **31**, 1051-1070.
- Qafoku, N.P., Sumner, M.E., 2002. Adsorption and desorption of indifferent ions in variable charge subsoils: The possible effect of particle interactions on the counter-ion charge density. *Soil Science Society of America Journal* **66**, 1231-1239.
- R Development Core Team, 2009. R: A language and environment for statistical computing. R Foundation for Statistical Computing. Institute for Statistics and Mathematics, Vienna.
- Raupach, M., Piper, C.S., 1959. Interaction of silicate and phosphorus in a lateritic soil. *Australian Journal of Agriculture Research* **10**, 818-831.
- Rayment, G., Higginson, F., 1992. Australian soil and land survey handbook - Australian laboratory handbook for soil and water chemical methods. Inkata Press, Melbourne.
- Rayment, G., Lyons, D., 2011. Soil chemical methods-Australasia. CSIRO Publishing, Collingwood, Victoria.
- Rimstidt, J.D., 1997. Quartz solubility at low temperature. *Geochimica et Cosmochimica Acta* **61**, 2553-2556.
- Rogalla, H., Römhild, V., 2002. Role of leaf apoplast in silicon-mediated manganese tolerance of *Cucumis sativus* L. *Plant, Cell and Environment* **25**, 549-555.
- Rorison, I., 1965. The effect of aluminum on the uptake and incorporation of phosphate by excised sanfoin roots. *New Phytologist* **63**, 23-27.
- Rowell, D., Wild, A., 1985. Causes of soil acidification: a summary. *Soil Use and Management* **1**, 32-33.
- Roy, A.C., 1969. Phosphorus-silicon interactions in soils and plants. Agriculture and Soil Science. University of Hawaii, p. 218.

- Roy, A.C., Ali, M.Y., Fox, R.L., Silva, J.A., 1971. Influence of calcium silicate on phosphate solubility and availability in Hawaiian Latosols. *Proceedings of the International Symposium on Soil Fertility Evaluation*, New Delhi, pp. 757-765.
- Ryden, J., Syers, J.K., McLaughlin, J., 1977. Effects of ionic strength on chemisorption and potential determining sorption of phosphate by soils. *Soil Science* **28**, 62-71.
- Savant, N.K., Datnoff, L.E., Snyder, G.H., 1997a. Depletion of plant-available silicon in soils: a possible cause of declining rice yields. *Communications in Soil Science and Plant Analysis* **28**, 1145-1152.
- Savant, N.K., Korndörfer, G.H., Datnoff, L.E., Snyder, G.H., 1999. Silicon nutrition and sugarcane production: A review. *Plant Nutrition* **22**, 1853-1903.
- Savant, N.K., Snyder, G.H., Datnoff, L.E., 1997b. Silicon management and sustainable rice production. *Advances in Agronomy* **58**, 151-199.
- Schmohl, N., Horst, W.J., 2000. Cell-wall composition modulates aluminium toxicity. *Plant, Cell and Environment* **23**, 735-742.
- Schroth, B.K., Sposito, G., 1997. Surface charge properties of kaolinite. *Clays and Clay Minerals* **45**, 85-91.
- Schwertman, U., Taylor, R.M., 1989. Iron oxides. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. Soil Science Society of America, Madison, Wisconsin, pp. 379-438.
- Segalen, P., 1971. Metallic oxides and hydroxides in soils of the warm and humid areas of the world: Formation, identification, evolution. UNESCO, Bandung Symposium, pp. 15-24.
- Sei, J., Jumas, J., Olivier-Fourcade, J., Quiquampoix, H., Staunton, S., 2002. Role of iron oxides in the phosphate adsorption properties of kaolinites from the Ivory Coast. *Clays and Clay Minerals* **50**, 217-222.
- Shaff, J., Schultz, B., Craft, E., Clark, R., Kochian, L., 2010. GEOCHEM-EZ: a chemical speciation program with greater power and flexibility. *Plant and Soil* **330**, 207-214.
- Shariatmadari, H., Mermut, A.R., 1999. Magnesium- and silicon-induced phosphate desorption in smectite-, palygorskite-, and sepiolite-calcite systems. *Soil Science Society of America Journal* **63**, 1167-1173.
- Shen, Q., Shen, Z., 2001. Effects of pig manure and wheat straw on growth of mung bean seedlings grown in aluminium toxicity soil. *Bioresource Technology* **76**, 235-240.
- Silva, I., Smyth, T.J., Israel, D., Raper, C., Rufty, T., 2001. Magnesium is more efficient than calcium in alleviating aluminum rhizotoxicity in soybean and its ameliorative effect is not explained by the Gouy-Chapman-Stern model. *Plant and Cell Physiology* **42**, 538-545.
- Silva, J.A., 1971. Possible mechanisms for crop response to silicate applications. *International Symposium on Soil Fertility Evaluation: Proceedings* **1**, 805-814.
- Singh, B.B., Jones, J.P., 1976. Phosphorus sorption and desorption characteristics of soil as affected by organic residues. *Soil Science Society of America Journal* **40**, 389-394.
- Sivaguru, M., Horst, W.J., 1998. The distal part of the transition zone is the most aluminium-sensitive apical root zone of maize. *Plant Physiology* **116**, 155-163.
- Slattery, W., Morrison, G., Coventry, D., 1995. Liming effects on soil exchangeable and soil solution cations of four soil types in north-eastern Victoria. *Australian Journal of Soil Research* **32**, 277-295.
- Smyth, T.J., Sanchez, P.A., 1980. Effects of lime, silicate, and phosphorus applications to an Oxisol on phosphorus sorption and ion retention. *Soil Science Society of America Journal* **44**, 500-505.
- Soil Survey Staff, 2003. Keys to soil taxonomy. United States Department of Agriculture, Soil Conservation, USA.

- Sollins, P., Robertson, G.P., Uehara, G., 1988. Nutrient mobility in variable- and permanent-charge soils. *Biogeochemistry* **6**, 181-199.
- Sommer, M., Kaczorek, D., Kuzyakov, Y., Breuer, J., 2006. Silicon pools and fluxes in soils and landscapes - a review. *Plant Nutrition and Soil Science* **169**, 310-329.
- Sposito, G., 1984. The surface chemistry of soils. Oxford University Press, New York.
- Sposito, G., 1989. The chemistry of soils. Oxford University Press, New York.
- Sposito, G., 2008. The chemistry of soils. Oxford University Press, New York.
- Stace, H., Hubble, G., Brewer, R., Northcote, K., Sleeman, J., Mulcahy, M., Hallsworth, E., 1968. A Handbook of Australian Soils. Rellim Technical Publications, Glenside, South Australia.
- Stumm, W., Morgan, J.J., 1970. Aquatic chemistry: An introduction emphasizing chemical equilibria in natural water. John Wiley, New York.
- Sumner, M.E., 1963. Effect of iron oxides on positive and negative charges in clays and soils. *Clay Minerals Bulletin* **5**, 218-226.
- Sumner, M.E., 1993. Gypsum and acid soils: the world scene. *Advances in Agronomy* **51**, 1-32.
- Sumner, M.E., 1995. Soil chemistry: past, present, and future. In: Huang, P.M. (Ed.), Future prospects for soil chemistry. Soil Science Society of America, Inc., Madison, WI, pp. 1-38.
- Tabuchi, A., Matsumoto, H., 2001. Changes in cell-wall properties of wheat (*Triticum aestivum*) roots during aluminum-induced growth inhibition. *Physiologia Plantarum* **112**, 353-358.
- Tan, K., Keltjens, W., 1990. Interaction between aluminum and phosphorus in sorghum plants. I. Studies with the aluminum sensitive sorghum genotype TAM428. *Plant and Soil* **124**, 15-23.
- Tan, K., Keltjens, W., Findenegg, G., 1992. Aluminium toxicity with sorghum genotypes in nutrient solutions and its amelioration by magnesium. *Z. Pflanzenernähr. Bodenk.* **155**, 81-86.
- Tan, K.H., 1994. Environmental soil science. Marcel Dekker, Inc., New York.
- Tan, K.H., 2000. Environmental soil science. Marcel Dekker, Inc., New York.
- Tan, K.H., 2009. Environmental soil science. CRC Press, New York.
- Tate, K.R., Theng, B.K.G., 1980. Organic matter and its interactions with inorganic soil constituents. In: Theng, B.K.G. (Ed.), Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt, pp. 225-249.
- Taubaso, C., Dos Santos Afonso, M., Torres Sanchez, R., 2004. Modelling soil surface charge density using mineral composition. *Geoderma* **121**, 123-133.
- Tavakkoli, E., English, P., Guppy, C., 2011. Interaction of silicon and phosphorus mitigate manganese toxicity in rice in a highly weathered soil. *Communications in Soil Science and Plant Analysis* **42**, 503-513.
- Tedrow, J.C.F., 1954. Clay minerals in three podzol profiles. *Soil Science Society of America Proceedings* **18**, 479-481.
- Theng, B.K.G., 1980. Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt.
- Thomas, G.W., 1977. Historical development in soil chemistry: ion exchange. *Soil Science Society of America Journal* **41**, 230-238.
- Thorburn, P., Shaw, R., 1987. Effects of different dispersion and fine fraction determination methods on results of routine particle size analysis. *Australian Journal of Soil Research* **25**, 347-360.
- Ton, T.C., Tran, K.T., Nguyen, T.D., Nguyen, T.S., Le, T.B., 1996. Soils in Vietnam (in Vietnamese). Agricultural Publishing House, Hanoi.

- Tran, T.T.L., Vo, D.Q., Le, T.L.H., Phan, L., 2005a. The effect of silicate (SiO_3^{2-}) and silicofluoride (SiF_6^{2-}) anions on phosphorus adsorption capacity and desorption capacity of an actual acid sulphate soil (in Vietnamese). *Science and Technology Journal of Agriculture and Rural Development* **No. 1**, 64-67.
- Tran, T.T.L., Vo, D.Q., Le, T.L.H., Phan, L., 2005b. Effects of applying phosphate, sodium silicate and sodium silicofluoride on the growth and nutrient absorption of rice on an actual acid sulphate soil (in Vietnamese). *Science and Technology Journal of Agriculture and Rural Development* **No. 3 + 4**, 33-36.
- Uehara, G., Gillman, G.P., 1980. Charge characteristics of soils with variable and permanent charge minerals: I. Theory. *Soil Science Society of America Journal* **44**, 250-252.
- Uehara, G., Gillman, G.P., 1981. The mineralogy, chemistry, and physics of tropical soils with variable charge clays. Westview Press, Inc., Boulder, Colorado.
- Uehara, G., Keng, J., 1975. Management implications of soil mineralogy in Latin America. In: Bornemisza, E., Alvarado, A. (Eds.), *Soil management in Latin America*, New York.
- van Olphen, H., 1977. Introduction to clay colloid chemistry. Interscience, New York.
- van Raij, B., Peech, M., 1972a. Electrochemical properties of some Oxisols and Alfisols of the tropics. *Soil Science Society of America Journal* **36**, 587-593.
- van Raij, B., Peech, M., 1972b. Electrochemical properties of some Oxisols and Ultisols of the tropics. *Soil Science Society of America Journal* **36**, 587-593.
- van Ranst, E., Awah, E.T., Hof, J., 1990. Volcanic soil patterns as related to the geomorphology of the lower southern slopes of Mount Cameroon (West Africa). *Pedologie* **XL**, 65-78.
- Violante, A., Pigna, M., Ricciardella, M., Gianfreda, L., 2002. Adsorption of phosphate on variable charge minerals and soils as affected by organic and inorganic ligands. In: Violante, A., Huang, P.M., Bollag, J.M., Gianfreda, L. (Eds.), *Developments in soil science*. Elsevier Science B.V., pp. 279-295.
- Vlamis, J., Williams, D.E., 1967. Manganese and silicon interactions in the graminates. *Plant and Soil* **27**, 131-140.
- Wada, K., 1980. Mineralogical characteristics of Andosols. In: Theng, B.K.G. (Ed.), *Soils with variable charge*. New Zealand Society of Soil Science, Lower Hutt, pp. 87-107.
- Wada, K., 1985. The distinctive properties of Andosols. In: Stewart, B.A. (Ed.), *Advances in soil science*. Springer, Berlin, pp. 173-229.
- Wada, K., 1987. Mineral formed and mineral formation from volcanic ash by weathering. *Chemical Geology* **60**, 17-28.
- Wada, K., Harward, M.E., 1974. Amorphous clay constituents of soils. *Advances in Agronomy* **26**, 211-260.
- Wada, K., Inoue, A., 1974. Adsorption of monomeric silica by volcanic ash soils. *Soil Science and Plant Nutrition* **20**, 5-15.
- Wang, Y., Jiang, J., Xu, R., Tiwari, D., 2009. Phosphate adsorption at variable charge soil/water interfaces as influenced by ionic strength. *Australian Journal of Soil Research* **47**, 529-536.
- Wang, Y., Stass, A., Horst, W.J., 2004. Apoplastic binding of aluminum is involved in silicon-induced amelioration of aluminum toxicity in maize. *Plant Physiology* **136**, 3762-3770.
- Wann, S.S., Uehara, G., 1978a. Surface charge manipulation of constant surface potential soil colloids: I. Relation to sorbed phosphorus. *Soil Science Society of America Journal* **42**, 565-570.
- Wann, S.S., Uehara, G., 1978b. Surface charge manipulation of constant surface potential soil colloids: II. Effect on solute transport. *Soil Science Society of America Journal* **42**, 886-888.

- Weaver, R., Jacson, M., Syers, J.K., 1968. Determination of silica in citrate-bicarbonate-dithionite extracts of soils. *Soil Science Society of America Proceedings* **32**, 497-501.
- Wehr, J., Blamey, F., Menzies, N., 2007. Aluminium. *Encyclopedia of Soil Science*. Taylor & Francis, London, pp. 1-6.
- Wehr, J., Blamey, F.P.C., Kerven, G., Horst, W.J., Hanna, J., Menzies, N., 2009. Aluminium bound to plant cell walls - does staining give clues about the bound Al species? In: Hong, L., Yan, X., Kocian, L. (Eds.), *Proceedings of the 7th International Symposium on plant-soil interactions at low pH*, Guangzhou.
- Wehr, J., Menzies, N., Blamey, F.P.C., 2004. Inhibition of cell wall autolysis and pectin degradation by cations. *Plant Physiology and Biochemistry* **42**, 485-492.
- Wehr, J., Smith, T., Blamey, P., Menzies, N., 2010. Aluminium sensitivity and optimum Ca and pH requirement of teak (*Tectona grandis* Linn. f.) clones used for forestry plantations in Australia. 19th World Soil Congress of Soil Science, Brisbane.
- Wieland, E., Stumm, W., 1992. Dissolution kinetics of kaolinite in acidic aqueous solution at 25°C. *Geochimica et Cosmochimica Acta* **56**, 3339-3355.
- Wilding, L., 2000. Classification of soils. In: Summer, M.E. (Ed.), *Handbook of soil science*. CRC Press LLC, Florida, pp. E-175-E-183.
- Williams, D.E., Vlamis, J., 1957a. The effect of silicon on yield and manganese-54 uptake and distribution in the leaves of barley plants grown in culture solutions. *Plant Physiology* **32**, 404-409.
- Williams, D.E., Vlamis, J., 1957b. Manganese toxicity in standard culture solution. *Plant and Soil* **8**, 183-193.
- Wong, M., Akyeampong, E., Nortcliff, S., Rao, M., Swift, R., 1995. Initial responses of maize and beans to decreased concentrations of monomeric inorganic aluminium with application of manure or tree prunings to an Oxisol in Burund. *Plant and Soil* **171**, 275-282.
- Wonisch, H., Gerard, F., Dietzel, M., Jaffrain, J., Nestroy, O., Boudot, J., 2008. Occurrence of polymerized silicic acid and aluminum species in two forest soil solutions with different acidity. *Geoderma* **144**, 435-445.
- Yang, L., Jiang, H., Tang, N., Chen, L., 2011. Mechanisms of aluminum-tolerance in two species of citurs: Secretion of organic acid anions and immobilization of aluminum by phosphorus in roots. *Plant Science* **180**, 521-530.
- Yoshinaga, N., Aomine, S., 1962a. Allophane in some Ando soils. *Soil Science and Plant Nutrition* **8**, 6-13.
- Yoshinaga, N., Aomine, S., 1962b. Imogolite in some Ando soils. *Soil Science and Plant Nutrition* **8**, 22-29.
- Yu, T.R., 1997. Introduction: Characteristics of variable charge soils. In: Yu, T.R. (Ed.), *Chemistry of variable charge soils*. Oxford University Press, New York, pp. 6-16.
- Zhang, G.Y., Yu, T.R., 1997. Coordination and adsorption of anions. In: Yu, T.R. (Ed.), *Chemistry of variable charge soils*. Oxford University Press, New York, pp. 175-218.
- Zhang, X.N., Zhang, G.Y., Zhao, A.Z., Yu, T.R., 1989. Surface electrochemical properties of the B horizon of a Rhodic Ferralsol, China. *Geoderma* **44**, 275-286.
- Zhang, X.N., Zhao, A.Z., 1997. Surface charge. In: Yu, T.R. (Ed.), *Chemistry of variable charge soils*. Oxford University Press, New York, pp. 17-63.
- Zheng, S., Yang, J., 2005. Target sites of aluminum phytotoxicity. *Biological Plant* **49**, 321-331.