

Chapter 2

Silicon in Soils and Plants

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Abstract The crust of the earth is largely composed of silicon that is found primarily as silicate minerals, secondary aluminosilicates and various forms of silicon dioxide. However, the abundance of silicon in soils is not an indication that sufficient supplies of soluble silicon are available for plant uptake. In this chapter, the outcomes of many years of research conducted on silicon are consolidated to understand the state of knowledge for silicon fertilization guidelines in crop production. Monosilicic acid (H_4SiO_4) is the form of silicon used by plants, which is found both in liquid and adsorbed phases of silicon in soils. The concentration of the H_4SiO_4 in the soil solution is influenced by the soil pH and the amounts of clay, minerals, organic matter and Fe/Al oxides/hydroxides, which are collectively related to the geologic age of the soil. Fertilization can rapidly increase the concentration of H_4SiO_4 in the soil solution; therefore, fertilization has become a common practice in areas with intensive cropping systems, particularly for those soils that are inherently low in soluble silicon. The establishment of procedures to estimate the plant-available silicon and the critical soil silicon levels and the method (5-day Na_2CO_3 - NH_4NO_3 extraction) to analyze the soluble silicon fraction in solid fertilizers were among the advances in research on silicon in agriculture in recent years. These measurements were the key components required for the development and implementation of effective silicon fertilizer management in crop production. However, many aspects of the role of silicon in soil science remain understudied, and these aspects should be the focus of future research.

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Introduction

The silicon in the crust of the earth is ubiquitous. Over 100 years ago, man linked silicon fundamentally to his life style with the use of silicon in the household, in industrial applications, and in construction (Vasanthi et al. 2012). In agriculture, silicon is a nutrient for which an enormous amount of literature examines the value of silicon fertilization in improving overall crop productivity and health. Silicon is abundant in the soil but is primarily in an inert form and consequently is unavailable for plant uptake. Although years of research have focused on understanding the role of silicon in plant growth and development, to date, this element has been determined to be essential only for scouring rushes and diatoms and other members of the yellow-brown or golden algae (Epstein 1999). Nevertheless, the benefits of silicon fertilization to crop production are too significant to be overlooked, and in some agricultural areas, fertilization with silicon is the common agronomic practice. Thus, a renewed research effort was directed to develop guidelines and management practices for silicon fertilization for a number of agronomic and horticultural crops. In this chapter, the results from many years of research on silicon in soils and plants were consolidated, and the analysis included the chemical dynamics of the different forms of silicon in soils, specifically the form used by plants, monosilicic acid (H_4SiO_4), the assimilation and the role of silicon in plants, the critical levels of silicon in soils and plants, the procedures to estimate the plant-available silicon in soils, and the potential sources of silicon.

Silicon in Soils

Silicon is the second most abundant element in the crust of the earth after oxygen, with a mean content of 28.8 % (weight) and an occurrence that ranges from 0.52 to ~47 wt% (McKeague and Cline 1963; Wedepohl 1995). In rocks, the concentrations of silicon range from 23 % (e.g., basalt) to 46.5 % (e.g., orthoquartzite) (Monger and Kelly 2002). Trace amounts of silicon are also in carbonaceous rocks such as the limestones and the carbonites (Monger and Kelly 2002). The silcretes are the component of derived soils that contain significant amounts of silicon (as high as 46 %). The amount of silicon in the petrocalcic horizon is much lower than (~8 %) that in the silcretes, and the amount of silicon in the minerals found in some highly weathered Oxisols such as bauxites and ferricretes is even less (Monger and Kelly 2002). Whereas most soils are abundant in silicon, certain soils contain low levels of this element, particularly the plant-available form of silicon. These soils include the Oxisols and the Ultisols, which are typically characterized as highly weathered, leached, acidic and low in base saturation (Foy 1992), and the Histosols, which contain high levels of organic matter and very low mineral contents (Snyder et al. 1986). Additionally, the soils that are composed of a large fraction of quartz sand

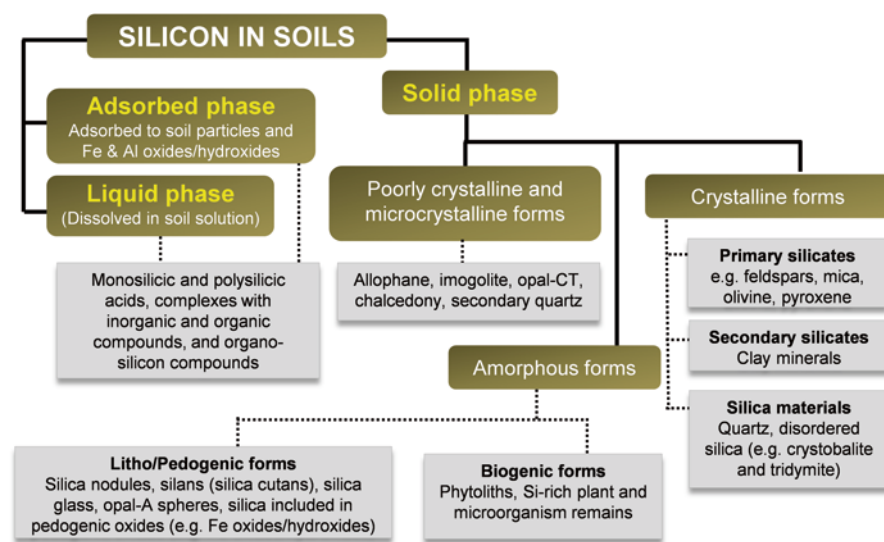


Fig. 2.1 Different fractions of silicon in soils (Modified from Matichencov and Bocharnikova (2001) and Sauer et al. (2006))

and those that have been under long-term crop production typically have low plant-available silicon (Datnoff et al. 1997).

In soils, silicon is generally grouped into three different fractions: the liquid phase, the adsorbed phase and the solid phase (Matichencov and Bocharnikova 2001; Sauer et al. 2006). The compositions of these different fractions are detailed in the classification of silicon compounds in soils that is presented in Fig. 2.1. The silica material was included by Sauer et al. (2006) among the crystalline forms of silicon in the solid phase fraction. Previously, the crystalline form consisted only of the primary and the secondary crystalline silicates, which are abundant in mineral soils that developed from rocks and sediments (Iler 1979; Conley et al. 2006). The silica materials consist primarily of quartz and disordered silica. The amorphous and poorly crystalline and microcrystalline forms are also components of the silicon fractions in the solid phase (McKeague and Cline 1963). The components of silicon in the liquid and the adsorbed phases are similar, with exception that those in liquid phase are dissolved in the soil solution, whereas those that are adsorbed are held onto soil particles and the Fe and Al oxides/hydroxides.

1. Solid Phase Silicon forms in the solid phase are divided into three primary groups: the amorphous forms, the poorly crystalline and microcrystalline forms, and the crystalline forms (Fig. 2.1). The largest fraction of silicon in the solid phase is the crystalline forms that occur primarily as primary and secondary silicates and silica materials. The primary mineral-bearing silicates that are inherited in soils are concentrated in the sand and silt particles; whereas the clay particles that are produced from the pedogenic processes that involve phyllosilicates and Al-Fe oxides/

hydroxides contain the secondary silicates (Allen and Hajek 1989). Furthermore, Allen and Hajek (1989) found that silicon is also in poorly crystalline forms such as the short-range ordered silicates and in the microcrystalline forms such as chalcedony and secondary quartz. The formation of the short-range ordered silicates (e.g., allophane and imogolite) in soil horizons is favored with $\text{pH}_{\text{H}_2\text{O}} > 5.0$ (Wada 1989), and the formation of the imogolite originates from the precipitation of H_4SiO_4 with Al hydroxides (Exley 1998; Doucet et al. 2001). Conversely, the formation of allophane and imogolite is inhibited in environments in which the decomposition rate of organic materials is high and the accumulation of humus is prevalent. The organic matter components bind the Al hydroxides to prevent the formation of the short-ranged silicates, but the formation of opaline silica is favored (Huang 1991). When the H_4SiO_4 concentration exceeds the solubility of the amorphous silica, the formation of opal-A, opal-CT and microquartz is promoted, whereas the secondary microcrystalline quartz is produced from the re-precipitation of the opal-CT from the dissolved opal-A (Chadwick et al. 1987).

The amorphous forms include the forms of both biogenic and litho/pedogenic origins and are in soils in amounts that range from <1 to 30 mg g^{-1} on a total soil basis (Jones 1969; Drees et al. 1989). The biogenic forms originate from plant residues and the remains of microorganisms and are collectively known as biogenic opal. The silicon absorbed by plants accumulates in the leaf, culm and stem as silica bodies or phytoliths, whereas the contributions of microorganisms are found as microbial and protozoic silicon (Sauer et al. 2006; Sommer et al. 2006; Aoki et al. 2007). The litho/pedogenic forms consist of silicon complexes with Al, Fe, heavy metals and soil organic matter (Matichencov and Bocharnikova 2001; Farmer et al. 2005). Furthermore, the pedogenic forms are characterized as the noncrystalline inorganic fractions, which include opal A, glasses and opal coatings on secondary minerals (McKeague and Cline 1963; Chadwick et al. 1987; Drees et al. 1989). The opal A is formed when the soluble silicon in the soil is at supersaturated levels (Drees et al. 1989). The formation of the opal coatings, such as the silcretes and the cements, is common in most soils and is classified as a secondary product of weathering (Dove 1995; Basile-Doelsch et al. 2005). According to Drees et al. (1989), the biogenic-based opal is commonly found in significant amounts under a wide range of environmental conditions, whereas the formation of the pedogenic opal occurs under specific physico-chemical soil conditions.

The solubility of the different forms of silicon in the solid phase significantly affects the concentration of silicon in the soil solution. The packing density of the silica tetrahedral and the long-range crystal order influences the solubility of the silica-bearing minerals (Iler 1979; Lindsay 1979; Drees et al. 1989). For example, larger contributions are expected from amorphous silica because of the higher solubility ($1.8\text{--}2 \text{ mM}$ silicon) than those from quartz. The dissolution rates of amorphous silica linearly increased with saturation but exhibited an exponential dependence on the electrolytes that was similar to quartz (Dove et al. 2008). The solubility of quartz ranged only from 0.10 to 0.25 mM silicon because quartz is highly stable and thermodynamically resistant to weathering (Drees et al. 1989; Monger and Kelly 2002). Thus, if quartz is ubiquitous in both the residual and the

transported parent materials, the contribution of quartz to the silicon in soil solution will be minimal. Fraysse et al. (2006) noted that the solubility of biogenic-based silica is 17-fold higher than that of quartz. The silica contained in the phytoliths is classified as a pure inorganic pool, because the rate of release from plant litter is independent of cellulose hydrolysis, and the released silica does not form complexes with organic matter (Fraysse et al. 2010). The solubility of both the crystalline and the amorphous silica is approximately constant between pH values 2 and 8.5 but increases rapidly at pH ~9 because of the reduction of the H_4SiO_4 concentration in the soil solution. At pH ~9, the H_4SiO_4 dissociates to $\text{H}_3\text{SiO}_4^- + \text{H}^+$ (Dove 1995), which initiates the dissolution of the crystalline and the amorphous silica to replenish or buffer the reduced concentration of the H_4SiO_4 in the soil solution.

2. Silicon in Soil Solution Silicon is in the soil solution in different forms and occurs primarily as monomeric (H_4SiO_4 , the plant bioavailable form), oligomeric or polysilicic acid (Iler 1979). Some dissolved silicic acid in the soil solution forms complexes with organic and inorganic compounds. The numerous chains of H_4SiO_4 up to ten silicon atoms in length are classified as the oligomeric or low-molecular-weight-silica, whereas the polysilicic acids with a higher degree of polymerization are the polymeric or the high-molecular-weight-silica (Williams and Crerar 1985). The oligomeric and polysilicic acids are found in chain, branch and sphere forms (Iler 1979). The monosilicic acid form is relevant to plant absorption and nutrition, whereas the polysilicic acid influences soil aggregation. According to Norton (1984), the polysilicic acid links soil particles through the creation of silica bridges that eventually improve soil aggregation, water-holding capacity and buffering capacity, particularly in light-textured soils. Matichencov and Bocharnikova (2001) reported an increase in the water-holding capacity of soils with varying textures (light to heavy) after a month of incubation with silicon-rich materials.

The uncharged H_4SiO_4 is in common soils with pH values <8 (Iler 1979). In most soils and natural waters, the silicic acid is commonly in an undissociated monomeric form (McKeague and Cline 1963; Dietzel 2000). However, the H_4SiO_4 dissociates into $\text{H}^+ + \text{H}_3\text{SiO}_4^-$ at pH values above 9 and further dissociates into $2\text{H}^+ + \text{H}_2\text{SiO}_4^{2-}$ at pH values above 11. For alkaline soils, such as the Solonetz and the Solonchaks, both the undissociated and the dissociated monosilicic acids occur. The formation of stabilized, numerous chains of H_4SiO_4 occurs when the concentration of the silicic acid is high and the pH >9 (Knight and Kinrade 2001). However, significant concentrations of polymerized silicic acid were observed in two acidic, forest soils in Europe, with concentrations as high as 20 % of the total silicon measured in the soil (Wonisch et al. 2008). The stability of the oligomeric form of silicic acid from the dissolution of minerals is short-term and lasts only for a few hours or days under most natural conditions before the breakdown into H_4SiO_4 (Dietzel 2000). The oligomer, polymer and silicon-organic forms of silicic acid are found at high pH values, with the amounts becoming significant at pH values of 11–12 (Iler 1979). The concentration of silicon in soil solutions ranges from 0.09 to 23.4 mg L⁻¹,

but the concentrations can be as high as 46.7–93.4 mg L⁻¹ in soils with pH values of 10–11 and that contain sodium carbonate (Volkova 1980; Kovda 1985).

The primary sources of H₄SiO₄ in the soil solution are the various forms of silicon dioxide, silicate minerals and plant residuum. The amount of H₄SiO₄ released by the various forms of SiO₂ is dependent on the physico-chemical properties. The SiO₂ in the soil influences the concentration of the H₄SiO₄ in the soil solution. Those forms that occur as nepheline, diopside, and augite in a dispersed state may supply between 7 and 9 mg silicon L⁻¹, whereas the biotite, microcline and labradorite may supply between 2.3 and 3.5 mg silicon L⁻¹. However, quartz has a low solubility rate and releases only 1.6–1.9 mg silicon L⁻¹ (Keller 1955; Lindsay 1979; Drees et al. 1989). The weathering of the silicate minerals releases silicon into the soil solution, which can be combined with other elements to form clay minerals, be released into the streams and the oceans or be used for uptake by plants and micro-organisms. A small amount of silicon is contributed to the soil solution by minerals that are insoluble and resistant to weathering, which include feldspar and a number of complex silicates such as circone, garnet and tourmaline (Kovda 1985).

The amount of H₄SiO₄ in the soil solution is affected by many factors and the solubility of silicon containing minerals is affected by pH, temperature, particle size, water and organic matter contents, and redox potential (Savant et al. 1997). Overall, the soil pH regulates the solubility and the mobility of silicon. The adsorption-desorption processes affect the concentration of H₄SiO₄ in the soil solution and are very dependent on the soil pH (McKeague and Cline 1963). The maximum adsorption of H₄SiO₄ occurs at a pH of 9–10, and at pH values below or above these levels, the amount of adsorption is reduced. The adsorption, polymerization and coagulation of H₄SiO₄ in saline soils are high (Brown and Mahler 1988). The amount of adsorbed H₄SiO₄ also increases in soils that contain large amount of allophanes, Fe-enriched crystal minerals, and particularly, the more reactive hydroxides of multivalent metals. The production of silicon dioxide (SiO₂) deposits in the form of crusts is enhanced during the evaporation, transpiration and freezing processes (McKeague and Cline 1963). The application of acid-producing fertilizer increases the concentration of H₄SiO₄ in the soil solution, whereas liming and high organic matter content result in a reduction in the concentration and mobility of the H₄SiO₄ (Panov et al. 1982; Allmaras et al. 1991). The alkalized H₄SiO₄ can be redeposited as a cementing and a blocking agent in the lower horizons of the soil profile.

The concentration of H₄SiO₄ in the soil solution also changes seasonally within ecosystems. In grassland ecosystems, the maximum concentration of H₄SiO₄ is observed during the spring and summer when the temperature favors biological activity (Volkova 1980; Bystritskaya 1987; Fernandes and Macias 1987). However, in forests, the highest concentration of H₄SiO₄ was observed during the autumn leaf fall (Volkova 1980; Pervova and Evdokimova 1984).

3. Silicon Adsorbed on Solid Phases The fractions of dissolved silicic acid in the soil solution are adsorbed onto a variety of solid phases in soils, including clay particles and Fe and Al hydroxides (Hansen et al. 1994; Dietzel 2002). A minimal reduction in the concentration of silicon in the soil solution is attributed to the

adsorption by secondary clay minerals (Siever and Woodford 1973). However, the Fe and Al hydroxides have strong adsorption capacity, which can remove significant amounts of dissolved silicon from the soil solution (Beckwith and Reeve 1963; McKeague and Cline 1963; Cornell and Schwertmann 1996).

The pH, soil redox potential (Eh), and the type of metal influence the adsorption of monosilicic acid by oxides. The amount of monosilicic acids that is adsorbed by oxides increases from pH 4 to pH 9, and the amount is notably higher when the metal oxides in the soil are Al-based rather than Fe-based. Ponnampetuma (1965) reported that with the increased submergence time of soil the corresponding reduction in the Eh was accompanied with an increase in the solubility of the soil silicon. This increase in silicon in the soil solution was attributed to the release from ferri-silica complexes under anaerobic soil conditions. The Al hydroxides are more effective than the Fe oxides in adsorbing the H_4SiO_4 in the soil solution (Jones and Handreck 1963, 1965, 1967; McKeague and Cline 1963). In general, the silicic acid is adsorbed onto secondary Fe-based oxides; a higher amount of silicic acid is adsorbed on the short-range, ordered ferrihydrite than that on the crystalline goethite (Delstanche et al. 2009). The OH group of the Fe-oxide surface is replaced with the H_4SiO_4 through ligand exchange, which eventually forms a silicate bidentate inner-sphere complex (Parfitt 1978; Pokrovsky et al. 2003; Hiemstra et al. 2007). The polysilicic acid is also formed through specific interaction of the Fe-oxide surface with the orthosilicic acid (Dietzel 2002). The iron oxides are commonly found in soils, and therefore even if the silicon adsorbing capacity is less effective compared with the Al oxides, the iron oxides will control, to some degree, the concentration of H_4SiO_4 in the liquid phase (McKeague and Cline 1963; Schwertmann and Taylor 1989; Opfergelt et al. 2009).

Silicon Cycle in Soil

The solid, liquid, and adsorbed phases of silicon are the key components of the silicon cycle in soil (Fig. 2.2). The liquid silicon phase consists of H_4SiO_4 and the polymerized and complexed silicic acid in soil solution, and the uncharged form of H_4SiO_4 is the only form that is absorbed by plants and microorganisms. The absorbed silicon is later deposited as polymerized silica within the plant tissues or the cell structure of the microorganisms. These polymerized silica bodies return to the topsoil in the litter fall and the remains of microorganisms and eventually enter the highly soluble biogenic silica pool that contributes to the silicon in the soil solution (Drees et al. 1989; Van Cappellen 2003; Farmer et al. 2005; Saccone et al. 2007; Fraysse et al. 2010). Conley (2002) estimated that 60–200 Tmol silicon per year is stored in plants. Silicon is also added to soils with applications of manure and compost, and the decomposition of silicon-rich manure can increase the level of available soil silicon (Song et al. 2013). The silicon rarely interacts with dissolved organic matter but does form colloidal aluminum-silicon polymers (suspended silicon particles) at many soil solution pH values (Doucet et al. 2001). The chemistry

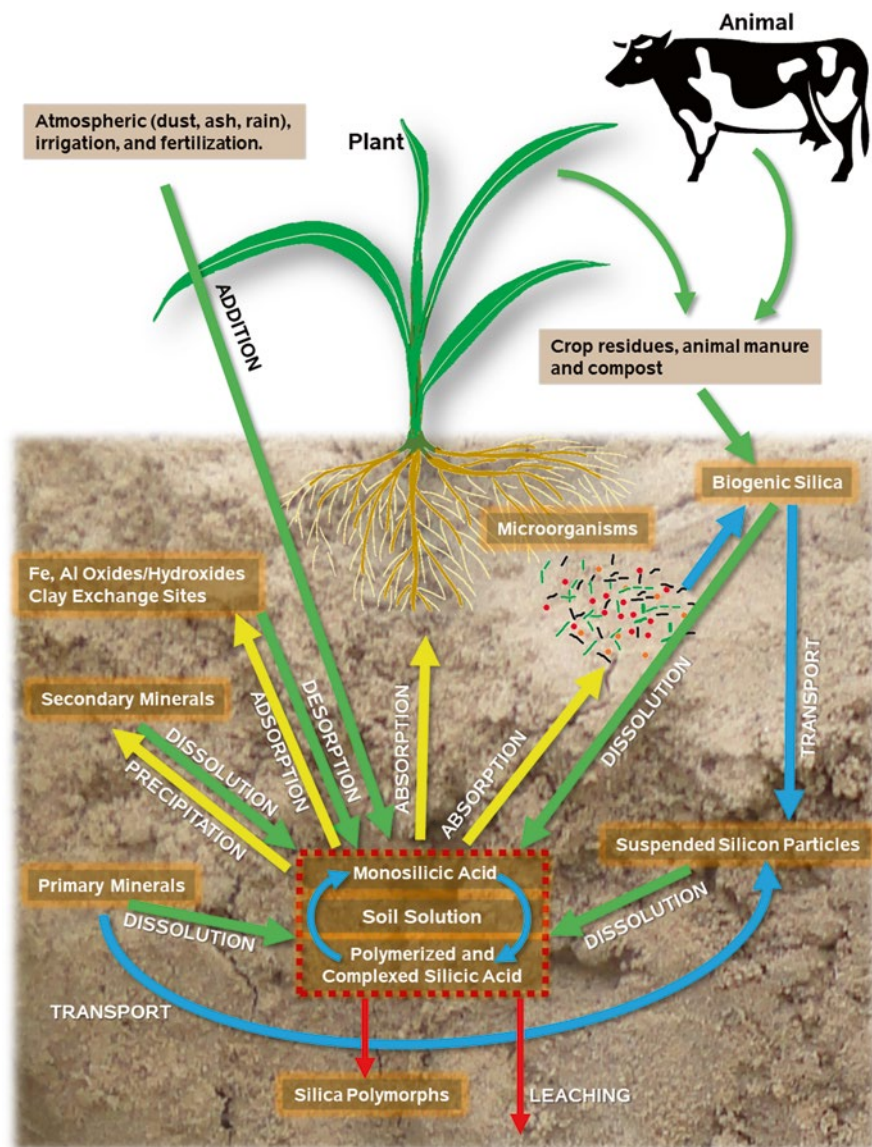


Fig. 2.2 Comprehensive cycle of silicon in soil (Green arrows represent transformation or processes which raise silicon concentration in soil solution. Yellow arrows represent the transformation or processes which reduce silicon concentration in soil solution. Red arrows represent processes that result in silicon loss from the soil system or production of stable, plant unavailable form of silicon. Blue arrows represent transformation processes of silicon into a silica pool that contributes this element into the soil solution)

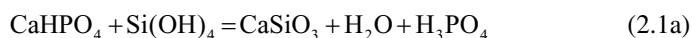
of silicon in the liquid phase is regulated by a number of processes: (a) the dissolution of silicon that contains primary and secondary minerals, (b) the absorption of H_4SiO_4 in the soil solution by the vegetation and microorganisms, (c) the silicon adsorption on and the desorption from various solid phases, (d) the preservation of the stable silicon in the soil profile (silica polymorphs), (e) leaching, and (f) addition (i.e., fertilization, irrigation, atmospheric, plant litter, animal manure, and remains of microorganisms). The natural waters used as irrigation may contain different forms of silicon, including ionic, molecular, and aggregate silicon. Silicon is also added to the soil in atmospheric deposition via wind-blown dust and phytolith particles from savanna fires (Kurtz et al. 1987; Street-Perrott and Barker 2008; Opfergelt et al. 2010). However, the contribution of silicon to the soil solution from the atmosphere is very low compared with the other silicon inputs to the soil-plant system (Street-Perrott and Barker 2008).

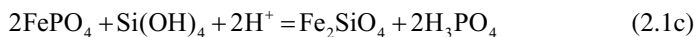
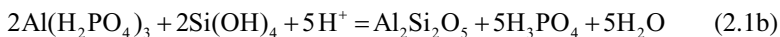
Interaction of Silicon with Other Plant Nutrients in the Soil

The application of a silicon-rich material influences the dynamics of different elements in the soil. The outcome of the reactions maybe beneficial (e.g., alleviate heavy metal toxicity) but may also be negative with the reduced availability of several plant-essential nutrients. The ability of silicon to influence the dynamics of elements in the soil is because of the high adsorptive capacity of the form of the silicon-rich materials that are commonly found in and added to the soil. Additionally, an increased concentration of silicic acid ions in the soil solution leads to the formation of complexes with heavy metals in the soil and to competition with other ions for adsorption sites.

The nutrients in the soil solution with a positive charge are adsorbed onto a silica surface. In a study conducted by Tokunaga (1991), the leaching losses of K and other mobile nutrients from the surface soil horizon were reduced because of a silica surface. The nutrients adsorbed onto the silica surface remain available to plants and formed the basis for slow-release fertilizer technology (Volker et al. 1985; Komisarov and Panfilova 1987).

According to a plethora of published information, phosphate availability increases following silicon fertilization (Gladkova 1982; Singh and Sarkar 1992; O'Reilly and Sims 1995; Matichenkov and Ammosova 1996). Matichenkov and Ammosova (1996) and Lindsay (1979) outlined the series of reactions involved between the silicate and the phosphate ions in which in the final reaction resulted in the release of phosphates into the soil solution (Eqs. 2.1a, 2.1b, and 2.1c). The fertilization with silicon increased the amount of dissolved silicon in the soil solution (H_4SiO_4), and the amount of silicon adsorbed onto the slightly soluble phosphates of Al, Ca, ferric and Mg was followed by the desorption of the phosphate anion.





Notably, a silicon fertilizer has the capacity to adsorb the dissolved phosphates in the soil solution, including those released from the exchange reaction between the silicate and the phosphate ions. In one experiment, Matichencov and Bocharnikova (2001) showed that a silicon source in the form of steel slag was the most effective in the adsorbing of phosphate in solution compared with amorphous fine SiO_2 , calcium carbonate, calcium silicate, and the industrial silicon by-product from the electric production of P. The steel slag consistently adsorbed >95 % of the phosphate in solution, whether the phosphate concentration in solution was as low as 0.5 mg P L⁻¹ or as high as 10 mg P L⁻¹. However, the amount of phosphate adsorbed by the other silicon sources increased significantly with the increase in the phosphate concentration in solution. For example, the amorphous SiO_2 adsorbed 2 %, 4 %, and 52 % of the 0.5, 2, and 10 mg P in a liter of solution, respectively.

In the soil system, the relationship between the phosphate and the H_4SiO_4 is antagonistic; the amount of phosphate ion that is released into the soil solution increases with increasing concentrations of H_4SiO_4 . The antagonistic reaction between the phosphate and the H_4SiO_4 ions is explained by the strong competition for specific sorption sites (Brown and Mahler 1987). However, Jones and Handreck (1967) noted that this competition is more likely a long-term effect of the silicic acid; for example, gibbsite, when silicified into kaolinite, has reduced affinity for phosphate ions. The short-term competition between the silicic acid and the phosphate ions for adsorption sites has a minimal contribution, or possibly none, to the concentrations in the soil solution. The silicic acid is attracted to the hydrogen bond of an oxygen atom that bridges two metal atoms, whereas the phosphate (basic) is attracted to the metal atoms; these two sites are different types. The high P sorption capacity of a low pH soil from the coastal plain of Georgia was markedly reduced with the application of sodium silicate, an effect attributed to the increase in soil pH by Owino-Gerroh and Gascho (2004). These authors noted that the amorphous silicic acid (from silicate ions) had a lower negative surface charge than that of the phosphate ion. Thus, when these two ions are present in the soil solution, the amorphous silicic acid is preferentially adsorbed over the phosphate ion. Earlier propositions were also considered and include the following: (1) the increase in alkalinity caused by the increase in the concentration of monosilicic acid liberated the phosphate with the dissolution of iron and aluminum oxides, and (2) the monosilicic acid lowered the activity of aluminum ions in solution by preventing these ions from precipitating the phosphate (Jones and Handreck 1967).

The application of the silicon rich materials fly ash and steel slag resulted in an increase in the soil pH (>1 unit), which decreased the phytoavailability of Cd, Cu, Pb and Zn by 60 % and eventually reduced the uptake of the heavy metals in rice (Chen et al. 2000; Gu et al. 2011). Additionally, the heavy metal diffusion fluxes

from the soil to the solution were reduced by 84 % because of precipitations with silicates, phosphates, and hydroxides. Moreover, the solubility of these heavy metal silicates was very low (Schindler et al. 1976). A recent study conducted by Tubaña et al. (2012a) showed that the addition of increasing rates of steel slag resulted in a steady decline in the concentrations of the Mehlich-3 extractable Fe and Ni, and the decline was attributed to the increase in soil pH as the application rates of the applied steel slag were also increased. Wallace (1993) explained that despite the high soluble Fe content in the anaerobic soils in which paddy rice is grown, the high concentration of silicon in rice creates an alkaline rhizosphere that decreases the availability of Fe. However, the heavy metal content in the soil solution also increased when the concentration of the H_4SiO_4 was increased (Schindler et al. 1976; Bocharnikova et al. 1995). This result was caused by the ability of the H_4SiO_4 ion (even at low concentrations) to form slightly soluble complexes with heavy metals. However, at a high concentration of H_4SiO_4 in the soil solution, the heavy metals are immobilized by the precipitation of silicates, which leaves a low concentration of soluble silicates for plant uptake (Jones and Handreck 1967; Lindsay 1979; Snyder et al. 2007). Ma and Yamaji (2006) noted that the silicon in soil becomes unavailable for plant uptake when it forms silicates or oxides with other compounds.

Earlier studies showed that the application of silicon-rich materials effectively reduced the Al toxicity in plants through the reduced uptake of Al (Haak and Siman 1992; Myhr and Estad 1996). The potential mechanisms for this effect include the following: (1) the precipitation of Al caused by the increased soil pH as a result of the elevated concentration of H_4SiO_4 (Lindsay 1979); (2) the H_4SiO_4 was adsorbed on Al hydroxides, which formed a less mobile compound and diminished the activity of the phytotoxic Al in solution (Panov et al. 1982; Baylis et al. 1994); and (3) the mobile Al was strongly adsorbed on the silica surfaces (Schulthess and Tokunaga 1996). The reduction in Al toxicity to plants was not caused entirely by the immobilization of Al in the soil or growth media. Rahman et al. (1998) reported that an increase in silicon nutrition increases the tolerance of the plant to excessive amounts of absorbed Al. Similarly, Liang et al. (2005a) showed that the silicon-enhanced tolerance of corn to Cd toxicity was attributed to both the Cd immobilization caused by the increase in soil pH and the silicon-mediated detoxification of the Cd in the plant. In rice, the oxidation of ferrous to ferric ion is increased because of an increase in the silicon-induced oxidizing capacity of the roots (Ma and Takahashi 2002). The ferrous form of iron is preferred for plant uptake compared with the ferric form, which prevents the excessive accumulation of Fe in flooded rice. Wallace (1993) suggested that silicon increased the release of OH^- from the roots, and the increase in the soil pH eventually led to the decrease in the solubility of Fe. Unlike the *in planta* mechanisms (the internal silicon-mediated mechanisms in plants; Table 2.1), the silicon-mediated mechanisms involved in the prevention of excessive uptake of metals from the soil and the roots require further study (Kirkham 2006).

Table 2.1 Internal silicon-mediated mechanisms involve in enhancing the plant's tolerance to heavy metal toxicity

Heavy metal	Crop	References	Mechanisms
Aluminum	Barley	Hammond et al. 1995	Exclusion of Al from the subtending tissue as a result of silicon deposition at the epidermis, restricting total overall Al uptake into the root
	Corn	Wang et al. 2004	Formation of hydroxyaluminosilicates in the apoplast of the root apex reducing the mobility of apoplastic Al
		Kidd et al. 2001	Mediates the metabolism of flavonoid-phenolic compounds which strongly chelate Al
Arsenic	Rice	Seyfferth and Fendorf 2012	Silicon competes with arsenate ions for root entry points
Cadmium	Corn	Liang et al. 2005a	Co-precipitation of Cd with silicates resulting in strong binding of Cd to cell walls thereby reducing the concentration of Cd in cytosols or symplast
		Wang et al. 2000	Formation of colloidal silicon in cell walls which has high specific adsorption property to Cd preventing Cd uptake into the cell
		Cunha and Nascimento 2009	Structural alterations on xylem diameter, mesophyll and epidermal thickness, and transversal area occupied by collenchyma and midvein; deposition of silica in the endodermis and pericycle of roots
	Rice	Nwugol and Huerta 2008	Cell wall-bound silicon inhibit apoplastic Cd uptake by covalently bonding with Cd and trapping Cd as it diffuses through the cell wall and intracellular spaces.
	Peanut	Shi et al. 2010	Increased activities of antioxidant enzymes; inhibition of Cd transport from roots to shoots possibly due silicon-mediated changes on cell wall properties and competition for uptake sites
Lead	Cotton	Bharwana et al. 2013	Enhanced the activities of major antioxidant enzymes preventing plant tissue from membrane oxidative damage
	Cowpea	Iwasaki et al. 2002a	Enhanced adsorption of Mn on cell walls reducing the amount of soluble apoplastic Mn
		Iwasaki et al. 2002b	Interaction of silicon with phenolic substances maintains the apoplast in reduced state preventing the oxidation of Mn by guaiacol-peroxidase
	Cucumber	Rogalla and Römhild 2002	Strong binding of Mn to cell walls and a lowering of the Mn concentration within the symplast
		Shi et al. 2005	Enhanced production of enzymatic (e.g. superoxide dismutase, ascorbic peroxidase, glutathione reductase) and non-enzymatic (e.g. ascorbate and glutathione) antioxidants resulting in reduced membrane lipid peroxidation

(continued)

Table 2.1 (continued)

Heavy metal	Crop	References	Mechanisms
Zinc	Corn	Kaya et al., 2009; Neumann and zur Nieden 2001	Formation of less soluble zinc-silicates in cytoplasm
		Cunha and Nascimento 2009	Structural alterations on xylem diameter, mesophyll and epidermal thickness, and transversal area occupied by collenchyma and midvein; deposition of silicon in the endodermis and pericycle of roots

Silicon in Plants

1. Silicon Uptake, Transport and Deposition in Plant Plants uptake silicon from the soil solution in the form of H_4SiO_4 , which is commonly found at concentrations that range from 0.1 to 0.6 mM at the pH levels found in most agricultural soils (Knight and Kinrade 2001). According to Ma et al. (2001a), the lateral roots of rice are involved in the uptake of silicon. Cornelis et al. (2011) described the different mechanisms by which the silicon is absorbed by plants, i.e., active, passive and rejective. The amount of uptake of silicon by the active mechanism is typically larger than that predicted based on the mass flow and is attributed to the density of silicon transporters in the roots and shoots that facilitate the absorption process across the membranes of root cells. In rice, the transporters mediate both the radial transport and the xylem loading of silicon (Mitani and Ma 2005). Moreover, these transporters were recently identified and were coded by low-silicon genes such as the *Lsi1* and *Lsi2* in roots and the *Lsi6* in shoots (Mitani and Ma 2005; Ma et al. 2006, 2007; Yamaji et al. 2008). The *Lsi1* may encode a membrane protein similar to the water channel proteins, also known as aquaporins (Ma et al. 2006). The amount of uptake of silicon by the plant via the passive mechanism is likely entirely driven by mass flow. In the rejective mechanism, the buildup of the concentration of H_4SiO_4 in the soil solution typically results from the low concentrations of silicon that are absorbed by plants.

Takahasi et al. 1990 categorized plant species based on the mechanisms of silicon uptake. The plants that rely primarily on active, passive or rejective mechanisms are classified as high-, intermediate- or non-accumulators, respectively. The plants in the high-accumulator category have a silicon content in the shoot that ranges from 1.0 % to 10 % dry weight and are primarily monocotyledons such as bamboo (*Bambuseae*), barley (*Hordeum vulgare*), rice (*Oryza sativa*), sorghum (*Sorghum bicolor*), sugarcane (*Saccharum officinarum*), and wheat (*Triticum aestivum*) (Liang et al. 2007; Ma et al. 2001b; Ma and Takahashi 2002). Because of the efficient silicon uptake system of the high-accumulators, the amount of silicon uptake by the plant from the soil is several times higher than the uptake of some of the essential macro- or micronutrients. For example, the uptake of N is the largest among the essential nutrients, but the accumulation of silicon may be twice the amount of N in rice.

The intermediate-accumulator plants are mostly dryland Gramineae with shoot silicon contents that range between 0.5 % and 1.5 % dry weight. The dicots, which accumulate <0.2 % shoot dry weight silicon, form the low-accumulator group. Mitani and Ma (2005) attributed the low silicon accumulation in this group of plants to a lack of specific transporters to facilitate the radial transport and the xylem loading of silicon and suggested that the transport of silicon across cells was accomplished via a passive diffusion mechanism. Later, Liang et al. (2006) showed that both the active and the passive uptake of silicon, which occur in high-accumulator plants, are also found in the intermediate-accumulator plants (e.g., sunflower and wax gourd).

The absorbed H_4SiO_4 is transported through the xylem and is deposited in the leaf epidermal surfaces in which it is condensed into a hard, polymerized silica gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), also known as a phytolith (Yoshida et al. 1962; Jones and Handreck 1965, 1967; Raven 1983). The absorbed H_4SiO_4 is preferentially deposited in the abaxial epidermis, but as the leaf grows, the deposition occurs in the epidermis (Hodson and Sangster 1988). In wheat, the silicon is in all tissues but high concentrations are found in the inner tangential and radial walls of the endodermis (Bouzoubaa 1991). The phytoliths are found in specific cells, the silica cells, which are in vascular bundles and in silica bodies in bulliform cells, fusoid cells or prickly hairs in rice, wheat, and bamboo, respectively (Dietrich et al. 2003; Motomura et al. 2004; Ma and Yamaji 2006). According to Lanning (1963), the phytoliths are best classified as biogenic opal (Si-O-Si bonding). The SiO_2 precipitation in plants occurs at concentrations of H_4SiO_4 greater than 2 mol m^{-3} (Osuna-Canizales et al. 1991) and occurs primarily in the epidermis of the shoots, in addition to the vascular system and the endodermis of roots of some plant species (Raven 1983; Lux et al., 2003a, b). The deposited silica is immobile and is not transferred to actively growing or meristematic tissues (Elawad and Green 1979; Ma et al. 1989; Epstein 1999). Transpiration remains a viable option as one of the primary drivers in silicon transport and deposition in plants, and therefore, the duration of plant growth significantly affects the concentration of silicon; for example, older leaves contain more silicon than younger leaves (De Saussure 1804; Henriet et al. 2006). Based on earlier research, the $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ framework possibly binds with organic components (Lanning 1963). Conversely, the studies by Casey et al. (2003) and Ma et al. (2004) confirmed that only the mono- and the di-silicic acids but not the organosilicic complexes were found in the xylem exudates of rice and wheat.

2. Effects on Plant Growth Silicon is a known essential nutrient to only two groups of plants, i.e., the scouring rushes and the diatoms and other members of the yellow-brown or golden algae (Epstein 1999). To date, whether silicon is essential for higher plants remains uncertain because no evidence to demonstrate the direct involvement of silicon in plant metabolism has been found and no silicon-bearing organic compound has been identified in higher plants (Ma et al. 2001b; Knight and Kinrade 2001; Ma and Takahashi 2002; Richmond and Sussman 2003). However, the amount of literature that documents the benefits of silicon on the growth of a wide variety of agronomic and horticultural crops is vast and continues to increase. The beneficial

effects of silicon become more evident when plants are in stressed (biotic or abiotic stress) environments than in those growing under optimal conditions (Li et al. 2007; Epstein 1999; Bélanger et al. 1995; Datnoff et al. 1997). The beneficial effects of silicon on plant growth and development are based on several mechanisms, which include the formation of a protective outer layer composed of silica deposits, the reactivity of the absorbed silicon with the heavy metals ions and other compounds within plants and the metabolic functions of silicon in stressed plants.

2.1. Reinforced Plant Protective Layer and Mechanical Structure In the amelioration of biotic-related stresses, the role of silicon was first recognized in the modification of plant cell wall properties (Horst et al. 1999; Fawe et al. 2001; Lux et al. 2002; Iwasaki et al. 2002a, b). The deposition of biogenic silica in shoots increases the structural component of the plant and creates a hard outer layer (Rafi et al. 1997; Bélanger et al. 2003). Most of the reported benefits in crop quality and yield following silicon fertilization resulted from the improved overall mechanical strength and an outer layer of enhanced protection for the plant (Epstein 1999, 2001; Ma and Takahashi 2002; Epstein and Bloom 2005).

The silicon-enhanced mechanical defense of plants significantly reduces the damage caused by insects and grazing animals. For example, wild rabbits (Cotterill et al. 2007) and locusts (Hunt et al. 2008) preferred to eat unfertilized grasses compared with silicon-fertilized grasses. Savant et al. (1997) reported that silicon fertilization in rice reduced the damage caused by insect borers, yellow borers, rice chlorops, rice leafhoppers, brown leafhoppers, and mites. Gomes et al. (2005) attributed the reduction in aphid damage to the decreased number of aphids that were observed in infested plants fertilized with silicon. According to Goussain et al. (2005), the silicification did not create a physical barrier against penetration of the stylus of aphids, but they did observe a chemical-induced removal of the stylus, which eventually reduced the amount of sap consumed by the aphids.

Reports also indicate that silicon fertilization improved the tolerance of plants to stress from the lack of moisture (Janislampi 2012; Rizwan et al. 2012). The silicon fertilized crops maintained higher biomass and grain yields with a deficiency of water (Eneji et al. 2005, 2008; Pei et al. 2010). The wheat plants treated with silicon fertilizer under drought stress had higher stomatal conductances, relative water contents, and water potentials than nontreated plants (Pei et al. 2010). The reduction in water loss through transpiration (Hattori et al. 2005) and the decreased uptake of water (Eneji et al. 2005) were attributed to the larger and thicker leaves of silicon-treated plants and to the higher silicon deposition in the cell walls of epidermal tissues (prevents excessive water loss through transpiration) and the xylem vessels (prevents compression of the vessels) than nontreated plants. The thickened silicate layer on the leaf surface also reduces cuticular transpiration. Thus, the silicon increased the drought tolerance of plants not only by maintaining water balance, photosynthetic efficiency, erectness of plant canopy structure, and structure of the xylem vessels under high transpiration rates (Hattori et al. 2005), but also improved the development of secondary and tertiary cells of the endodermis for a better root resistance to dry soils and a faster growth of roots to explore a larger volume of soils

than plants not treated with silicon (Hattori et al. 2003, 2005). Ma et al. (2001b) also reported an increase in the resistance of rice to typhoon damage, which was attributed to the increase in rigidity with the silicification of shoots.

2.2. Reactivity of Silicon with Other Elements and Compounds Inside the Plants According to Cocker et al. (1998), the beneficial effects of silicon in plants are based on two aspects, i.e., solution chemistry and *in planta* mechanisms. These authors described the co-deposition of silicon and Al that formed less soluble aluminosilicates or hydroxyaluminosilicates within the root cell wall as responsible for the reduced concentration of free, toxic Al^{3+} ions in plants. A more recent and comprehensive review of the silicon-mediated mechanisms used to alleviate the abiotic stress caused by heavy metal toxicity, salinity, drought and freezing was conducted by Liang and his colleagues (2007). These authors grouped the mechanisms for the alleviation of metal toxicity with the increased level of silicon within the plant into two groups, external and internal. The external mechanisms are characterized by the inhibition of the absorption of metal ions by plants through the following processes: (1) the reduction in metal activity via increased ionic strength or pH, (2) the formation of metal-phenolic complexes caused by the silicon-mediated release of phenolic compounds, and (3) the co-deposition between the silicon and the metal ions in growth media. In contrast to the external mechanisms, the internal mechanisms occur within the plant and involve the following processes: (1) the enhancement of the antioxidant systems in the plant, (2) the complexation or co-precipitation of metal ions with silicon, (3) the uptake processes, and (4) the compartmentalization of metal ions. The changes in the plant cell wall properties not only contributed to the mechanical strength in the *Gramineae* but also inhibited the transport of metals (Cunha and Nascimento 2009). According to the authors, the reduction in metal transport from the roots to the shoots may have resulted from the thickening of the Casparian strips in the endodermis and the cell wall of the xylem and the pericycle, in addition to the deposition of lignin (endodermis, epidermis and exodermis) and silicon (endodermis) in the cell walls (Shi et al. 2005; Cunha and Nascimento 2009).

Many studies demonstrated that silicon fertilization of several types of crops reduced the metal uptake and toxicity. However, the mechanisms for the alleviating action of silicon on metal toxicity were not determined in all of the studies, including those on the toxic effects of Cu on spring wheat (Nowakowski and Nowakowska 1997) and of As on rice (Guo et al. 2005). Several silicon-mediated mechanisms to alleviate heavy metal toxicity in a wide array of crops were reported in the literature (Table 2.1). Silicon is generally reactive to heavy metals and impairs the translocation inside the plants and eventually reduces the toxic effect to the plant (Rahman et al. 1998; Neumann and Nieten 2001; Richmond and Sussman 2003; Ma et al. 2004). The reduced translocation of absorbed heavy metals in plants was attributed to the buildup of silica deposits in the cell walls that bound the metal ions and prevented the distribution of the ions from the roots to the shoots, in addition to the complex formation of silicon with metal ions that limited the translocation to different parts of the plants (Gu et al. 2011; Ma et al. 2001b). In cucumber, the binding of Mn to the cell walls resulted in decreased Mn content in the symplasts (Rogalla and

Romheld 2002), whereas a similar mechanism was reported for Cd in peanut and Al in barley (Baylis et al. 1994; Shi et al. 2010). The formation of an aluminum-silicon complex eventually prevented the penetration of Al into the root cortex of sorghum (Liu et al. 2004). The plants that suffer from heavy metal toxicity may benefit from silicon application through the increased release of compounds that immobilize the heavy metal ions. Additionally, the release of a phenolic compound was associated with the silicon-mediated increased resistance to Al in an Al-resistant maize cultivar (Kidd et al. 2001).

Silicon also reduced the oxidative stress induced by B (semi-heavy metal) toxicity (Gunes et al. 2007; Inal et al. 2009). Additionally, silicon inhibited the accumulation of Na in salt-stressed plants through a silicon-induced reduction of the transpiration rate and a partial blockage of the transpirational bypass flow (Matoh et al. 1986; Yeo et al. 1999) and a silicon-induced stimulation of the root plasma membrane H^+ -ATPase (Liang 1999; Liang and Ding 2002; Liang et al. 2005, 2006). In the latter study, an eventual reduction in the Na content in the shoots of barley was the result of an increase in the uptake and transport of K and a decrease in the uptake and transport of Na from roots to shoots. In addition to altering the structure, integrity, and functions of the plasma membrane, silicon alleviates the problems associated with salinity with a reduction in the stress-dependent peroxidation of membrane lipids through the stimulation of antioxidant enzyme and nonenzyme activities in the plants (Liang et al. 1996, 2003, 2005, 2006; Liang 1999). These observations were consistent with the research conducted on several intermediate- or low-silicon accumulator plants, such as cucumber (Zhu et al. 2004) and tomato (Al-Aghabary et al. 2004).

As described above, silicon fertilization also alleviates problems associated with moisture stress in plants. Gong et al. (2005) and Pei et al. (2010) documented the benefits of silicon fertilization to drought-stressed plants at the metabolic level in wheat. In Gong et al. (2005), in silicon-treated wheat plants under moisture stress, a corresponding increase in the antioxidant defenses helped to maintain physiological processes such as photosynthesis. The improvement in the growth of wheat under short-term water stress when supplied with a silicon fertilizer was attributed to an enhancement of the antioxidant defense system rather than to the adjustment in the osmotic pressure.

Silicon Sources

From a global perspective, Guntzer et al. (2012) highlighted the important role of silicon in the maintenance of crop productivity. According to Guntzer et al. (2012), among the top ten most produced crops worldwide, seven of these crops are silicon accumulators, which include maize, rice, sugar beet, sugarcane, and wheat. The estimated amount of silicon removed annually by the different agricultural crops on a global scale is between 210 and 224 million tons (Bazilevich 1993; Reimers 1990; Savant et al. 1997). For the high silicon-accumulator crops (e.g., rice,

sugarcane, and wheat), the removal of silicon from the soil is significantly higher than the removal in natural systems. For example, for sugarcane and rice, the silicon removal rates were between 300 and 500 kg ha⁻¹ year⁻¹, respectively, compared with the US grasslands that averaged only between 22 and 67 kg ha⁻¹ year⁻¹ (Meyer and Keeping 2001; Blecker et al. 2006; Makabe et al. 2009). With years of continuous and intensive cropping, the harvest of silicon-accumulator crops results in a significant reduction in the amount of plant-available silicon in soils (Meunier 2003; Meunier et al. 2008). Desplanques et al. (2006) noted that if the rice production in the fields of Camarque relied entirely on amorphous silica as the source of silicon, the reserve of plant-available silicon would be exhausted after five years of cultivation. According to Hodson et al. (2005), the concentration of silicon in plants depends primarily on the phylogenetic position of the plant, compared with the environmental effects that encompass silicon concentrations in the soil and soil solution and the pH. Nevertheless, various amounts of silicon uptake are reported for a given plant species; thus, although silicon accumulation is primarily a phylogenetic feature, the amount of plant-available silicon in the soil affects the amount of silicon that is absorbed by the plant (Deren et al. 1992; Ma and Takahashi 2002; Henriot et al. 2006).

The processes that regulate the concentration of silicon in the soil solution occur immediately to replenish the silicon that is removed by plants until equilibrium is reached between the liquid and the solid phases of silicon (Fig. 2.2). The soils with high buffering capacity (e.g., recent volcanic soils) easily replenish the lost silicon and maintain high levels of dissolved silicon for plant uptake. However, the removal of silicon from some types of soil (e.g., highly weathered, organic, and intensively cropped) may require some time to replenish, even with accelerated mineral weathering, depolymerization of polysilicic acid, and dissolutions of silicate complexes with heavy metals, hydroxides and organic matter; thus, these types of soils require the addition of silicon through fertilization with Si-rich materials.

The purpose of silicon fertilization is to increase the concentration of H₄SiO₄ in the soil solution. Matchencov and Bocharnikova (2001) provided an overview of the formation of the different silicic acid species in soil solution as affected by the rates of silicon fertilization. Three phases were established based on the changes in the concentrations of monosilicic and polysilicic acids (Fig. 2.3). Phase A occurs at the low end of the range of silicon fertilization rates for which the concentration of the H₄SiO₄ in the soil solution increases. As the rate of added silicon increases, the concentration of the monosilicic acid reaches a certain point and then begins to polymerize (the formation of polysilicic acid). The concentration of the silicon in the soil solution ranges between 0.01 and 1.99 mM silicon (Karathanasis 2002). Tan (1994) and Matchenkov and Ammosova (1994) further reported that polymerization occurs when the silicon concentration in the soil solution exceeds 65 mg L⁻¹. At this concentration and above, a mixture of H₄SiO₄, polysilicic acid and silicon-organic compounds is found in the soil solution, which indicates that ~2 mM silicon is potentially the concentration at which polymerization begins (phase B). During phase B, the H₄SiO₄ from the addition of silicon fertilizer produces polysilicic acid. Thus, even when the amount of silicon added to the soil is increased, the level of the

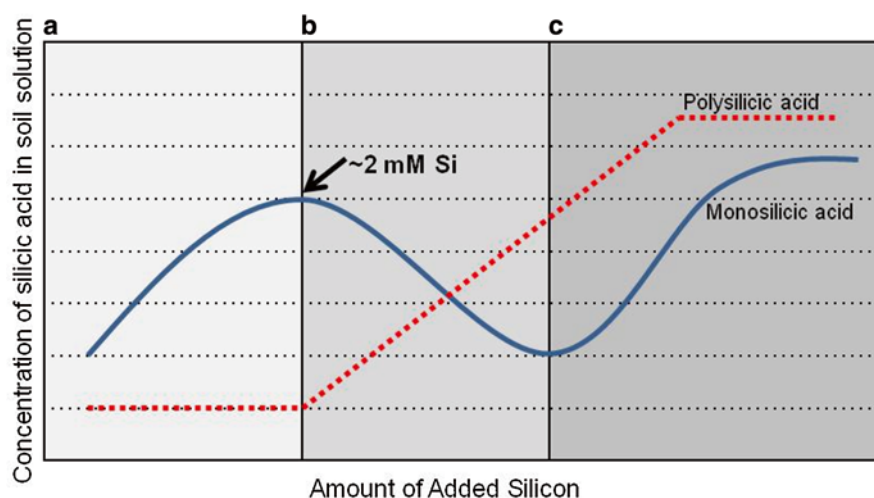


Fig. 2.3 Monosilicic and polysilicic acid fractions in the soil solution as affected by the amount of added silicon. Letters on the x axis represent a range of silicon fertilization rates where A is the low end, B is the middle and C is the high end rate (Adapted from Matichencov and Bocharnikova (2001))

H_4SiO_4 continuously declines, and the amount of polysilicic acids increases. In phase B, the effect of silicon fertilization is evident only in the amount of polysilicic acid. Phase C is characterized by both the synthesis of the polysilicic acids and the increase in the H_4SiO_4 concentration in the soil solution, within the range of rates of added silicon to the soil. Within phase C, both the polysilicic and H_4SiO_4 acids increase in concentration with the increased rate of added silicon. Notably, the processes that occur within these three phases (Matichencov and Bocharnikova 2001) are exclusively dependent on the concentration of silicic acid (because of the silicon addition). Therefore, the influences of pH, temperature, and the concentration of heavy metal ions were not included in this illustration (Fig. 2.3); however, these factors have a strong influence on the stability of both the H_4SiO_4 and the polysilicic acids in soil solution (Yates et al. 1998).

Calcium silicate occurs as prismatic crystals of wollastonite (Maxim et al. 2008), and pulverized wollastonite is commonly used in many silicon studies because of the high content of calcium silicate (at least 50 % SiO_2). The deposits of wollastonite are not typically found in the pure form (calcium silicate), and therefore, labor-intensive, expensive refining processes are required, which limit the mass production of wollastonite as a fertilizer (Park 2001; Maxim et al. 2008). Materials, such as magnesium silicate, contain large amounts of silicon, but are not considered a suitable source for silicon fertilizer because of the poor solubility (Weast et al. 1985). Currently, the silicon-containing industrial by-products or slags are most commonly used as silicon fertilizers. These industrial by-products, such as those from the electric production of P and the production of steel/iron, are inexpensive and accessible sources of silicon for the production of crops. The silicate slags often contain a

small fraction of easily soluble silicon (Gascho 2001) but have the added benefit as liming agents, typically with similar calcium carbonate equivalents (Heckman et al. 2003).

The composition and the amount of plant-available silicon found among these silicon-containing slags are highly variable (Datnoff et al. 2001; Ma and Takahashi 2002). These differences are caused by the variation in the speed of cooling and the granular size of the material (Takahashi 1981; Datnoff et al. 1992). Additionally, the silicate slags are more cost-effective than the wollastonite. Thus, for the purposes of silicon fertilizer management and economics, it is important to know the amount of plant-available silicon in the silicon-rich industrial by-products that are commercially available for crop production. Buck et al. (2011) evaluated several of the methods used to quantify the plant-available silicon from the industrial by-products (solid or liquid). The $\text{Na}_2\text{CO}_3 + \text{NH}_4\text{NO}_3$ extraction method was optimal to estimate the plant-available silicon in solid fertilizers, whereas quantifying the total silicon content via $\text{HCl} + \text{HF}$ digestion was suitable for liquid fertilizers. Recently, the 5-day $\text{Na}_2\text{CO}_3\text{-NH}_4\text{NO}_3$ soluble silicon extraction method was recognized as the official method in the United States and was approved by the Association of American Plant Food Control Officials to quantify the plant-available silicon in solid fertilizer products (Sebastian 2012; Sebastian et al. 2013). This method originated from the research conducted by Pereira et al. (2003) and Buck et al. (2011). The total silicon (both elemental and SiO_2) and the amount of plant-available silicon from several sources of silicon are summarized in Table 2.2. The other sources that are not listed in Table 2.2 include mill furnace ashes, crushed basalt, cement, wood biochar and volcanic cinders (Elawad and Green 1979; Savant et al. 1999; Gu et al. 2011; Varela-Milla et al. 2013).

Because of the added value of plant-based silicon sources to overall soil quality, the silicon-rich materials from plant biomass as potential sources of bioavailable silicon were evaluated. The application of biochar improved the soil chemical properties (e.g., the pH and cation exchange capacity, among others) and the soil physical properties, such as water-holding capacity and aggregation (Glaser et al. 2002; Chan et al. 2007). Rice husks are a major waste that is generated by the rice mills, and the carbonized rice husk has been used as an on-farm source of silicon in rice production systems (Sistani et al. 1997; Hossain et al. 2001). The application of biochar (the product of plant biomass pyrolysis) from *Miscanthus* not only increased both soil carbon sequestration and fertility, but also increased the bioavailable silicon that was extracted by CaCl_2 solution (Houben et al. 2014). Among the biochars produced from three plant-derived feedstocks (coffee husk, woody material, and *Miscanthus*), the biochar from the *Miscanthus* had the highest release rate of bioavailable silicon at $25.8 \text{ mg kg}^{-1} \ln (\text{min})^{-1}$. According to Ma and Takahashi (2002), rice straw has been widely used as source of silicon primarily because of the long-term effect (40 years) of rice straw on the plant-available silicon concentrations in soil. The silicon in the rice straw is not fully available in the short-term, but the amount of silicon that becomes plant-available in the long-term could exceed 70 % of the amount applied.

The silicon-rich materials from industrial wastes and plant biomass are applied in large amounts. Because most of these materials are also good liming agents, the

Table 2.2 Total and soluble silicon content of different silicon fertilizer sources

Source	Silicon content		Chemical composition	References
	Total Si, %	Soluble Si ^a , %		
Wollastonite	24.2	3.6	CaSiO ₃	Sebastian et al. 2013
	24.2	6.5	CaSiO ₃	Haynes et al. 2013
MgSiO ₃ (Talc)	28.5	0.1	MgSiO ₃	Sebastian et al. 2013
Silica gel	46.7	5.8	Not known	Sebastian et al. 2013
K ₂ SiO ₃ -liquid	9.7	7.6	K ₂ SiO ₃	Sebastian et al. 2013
NaSiO ₃ -liquid	5.6	–	Na ₂ SiO ₃	Abed-Ashtiani et al. 2012
Silicic acid	36.0	6.4	–	Sebastian et al. 2013
Silica blend (monocal or with FeSO ₄ , NH ₄ NO ₃ , KCl)	12.1	1.8	CaSiO ₃ (mainly)	Sebastian et al. 2013
CaSiO ₃ /MgSiO ₃ blend	12.0	2.2	CaSiO ₃ /MgSiO ₃	Sebastian et al. 2013
Industrial by-product				
Iron/steel slag	5.4	0.46	CaSiO ₃	Haynes et al., 2013
Electric furnace slag	21.1 20.3	14.8 ^b 0.5	CaSiO ₃ /MgSiO ₃	Gascho and Korndorfer 1998 Sebastian et al. 2013
Blast furnace slag	17.3	1.7	CaSiO ₃ /MgSiO ₃	Haynes et al. 2013
Processing mud	6.8	0.04	–	Haynes et al. 2013
Fly ash	29.1 23.0	0.03 0.01	–	Haynes et al. 2013 Raghupathy 1993
Plant material-based silica				
Miscanthus biochar	38.3	–	SiO ₂	Houben et al. 2014
Rice hull fresh	7–9.2	–	SiO ₂	Sun and Gong 2001
Rich hull ash	>28.0	–	SiO ₂	Kalapathy et al. 2002

^a5-day Na₂CO₃-NH₄NO₃ Soluble Silicon Extraction Method (SLV 5-day)^b2 % Citric acid procedure

pH values of the soils that receive these materials commonly increase substantially (Tubaña et al. [2012a](#); Haynes et al. [2013](#)). Using a liquid silicon formulation has advantages in the ease of application at manageable rates when compared with the sources of solid silicon. Both potassium and sodium silicate solutions are used as either a foliar supplement or a soil drench (Menzies et al. [1992](#); Bélanger et al. [1995](#); Kanto et al. [2006](#); Rodrigues et al. [2009](#); Kamenidou et al. [2010](#)). In greenhouses with hydroponic crop production systems, the liquid silicon formulation is

added to the recirculating nutrient solutions (Adatia and Besford 1986). Additionally, several studies showed positive crop responses to a foliar silicon spray. For example, the rice grain yield increased after a foliar application of soluble silicic acid (Prakash et al. 2011).

Measuring Silicon Concentration

The molybdenum blue colorimetry is commonly used to quantify the silicon concentrations in water and extracted/digested samples (Hallmark et al. 1982). The monosilicic acid is the only form of silicon that is molybdate-reactive, and the other forms of silicon (e.g., polysilicic acid) have little to no effect on the formation of the silicon-molybdate complex. This complex forms an intense blue color in the solution, which increases in intensity with an increase in the concentration of the H_4SiO_4 (Hallmark et al. 1982; Sparkman 2006). Although the concentration of silicon is also measured with the inductively coupled plasma-optical emission spectrometry (ICP-OES), notably, this analysis measures all the forms of silicon in solution, including polysilicic acid, which is not plant-available. The measurement of all forms may confuse the interpretation of the results when the silicon is analyzed in soil extracts because large amounts of polysilicic acid in the soil solution may lead to an overestimation of the plant-available silicon. However, to quantify the total silicon content in plant samples, the ICP-OES analysis may be suitable because for the molybdenum blue colorimetry, fluoride ions must be in the plant digest to facilitate the complete ionization of the polysilicic acids (Iler 1955), which eventually optimizes and stabilizes the absorbance readings (Kraska and Breitenbeck 2010). Moreover, because the molybdenum blue colorimetry is highly sensitive, a large dilution of the sample extract is required, which may magnify any errors of measurement (van der Vorm 1987).

Based on the vast amount of literature, many researchers in general have focused on the standardization of the procedures to extract the different fractions of silicon from the soil. To date, although many procedures have been established and modified for different soil types, no universal method has been accepted as the standard. The methods for plant tissue digestion have also undergone multiple modifications, primarily to simplify the method and to improve the precision.

1. Methods for Extraction of Different Silicon Fractions from Soil In the past 50 years, many procedures were identified and used to extract the different forms of silicon from the soil (Hashimoto and Jackson 1960; Beckwith and Reeve 1963, 1964; Schachtschabel and Heinemann 1967). Sauer et al. (2006) reviewed the various methodologies that are used not only to quantify plant-available silicon, but also to extract silicon from amorphous silica and allophane in soils and sediments. Because the solubility of the amorphous silica markedly increases at higher pH values (Iler 1979), the majority of the extraction procedures use alkaline solutions to quantify the silicon bound in this fraction (Table 2.3).

Table 2.3 Extraction procedures used for determining silicon in the solid phase

Solution	Procedure	Silicon fractions	References
NaOH	0.5 M NaOH; 1 g soil in 50 mL solution; 4 h boiling	Amorphous (biogenic and minerogenic)	Foster 1953
	0.5 NaOH; 2.5 min boiling	Amorphous and oxides	Hashimoto and Jackson 1960
	0.5 M NaOH; light fraction of coarse silt (20–50 μm), filter content in 15 mL solution; 16 h at 150 °C	Amorphous (biogenic)	Herbauts et al. 1994
	0.5 M NaOH; 1 g coarse silt (20–50 μm) sample in 100 mL solution; 20 boiling	Amorphous (biogenic)	Jones 1969
KOH + HCl	2.5 min boiling in 0.5 M KOH solution followed by centrifugation and 1 h shaking with 6 M HCl	Amorphous	McKeyes et al. 1974; Karathanasis 1989
Na ₂ CO ₃	0.5 M Na ₂ CO ₃ ; sequential extraction; 100 mg clay in 80 mL cold solution for 16 H shaking followed by 2 h boiling; repeat extraction until silicon content is low and constant	Amorphous	Follett et al. 1965
	0.5 M Na ₂ CO ₃ ; 1 g sample in 25 mL solution; agitate for 10 min at 80 °C, repeat extraction until silicon content is low and constant	Amorphous	Arnseth and Turner 1988
	0.5 M Na ₂ CO ₃ ; 2 g sample in 50 mL solution; 16 h shaking at room temperature	Amorphous	Breuer 1994; Breuer and Herrmann 1999
NaOH + Na ₂ CO ₃	2 % Na ₂ CO ₃ digestion of iron oxides-pre-extracted samples at 90 °C for 15 min then treated with 0.5 N NaOH and heated at 90 °C for 15 min	Amorphous	Wada and Greenland, 1970
Tiron	0.1 M Tiron (4, 5-dihydroxy-1, 3-benzene-disulfonic acid [disodium salt]) (pH 10.5); 25 mg sample in 30 mL solution; 1 h at 80 °C	Amorphous	Biermans and Baert 1977; Kodama and Ross 1991

A wet chemical dissolution process that uses the strong base NaOH is a standard technique that was developed in 1950s to analyze the amorphous silicon in soils (Foster 1953). Although this procedure also dissolves biogenic and minerogenic silica, the amorphous silica that is bound in the sesquioxides remains intact even under prolonged exposure to a high temperature and an alkaline solution. Nevertheless, a tendency to overestimate the silicon content of soils from this fraction occurs because the silicate minerals partially dissolve using this method and eventually release silicon (Wada and Greenland 1970). This tendency for overestimation has prompted modifications to the length of time for which samples are exposed to a boiling temperature and to the composition of the solutions to (1) ensure that the silicon measured in the extracts is from the dissolved amorphous silicon and (2) effectively remove the amorphous silica from soils (Hashimoto and Jackson 1960; McKeyes et al. 1974; Karathanasis 1989). This standard technique was also modified to specifically quantify the biogenic silica content of soils (Jones 1969; Herbauts et al. 1994), which generally involves a wet chemical dissolution using the NaOH on only the light fraction of the coarse silt (20–50 μm).

Follett and his colleagues (1965) proposed a sequential extraction procedure to quantify the silicon from the graded clay fraction of the soil in which soil samples were subjected to cold (16 h shaking) and hot (2 h boiling) extraction steps with a 5 % Na_2CO_3 solution. The entire extraction procedure was repeated until low and constant levels of silicon were measured in the extracts. In modifications of the procedure, Arnseth and Turner (1988) reduced the shaking time to 10 min and removed the cold extraction step, whereas Breuer (1994) and Breuer and Herrmann (1999) maintained the 16-h shaking time but removed the cold and the hot extraction steps. Nevertheless, Sauer et al. (2006) noted that the silicon fractions dissolved by the modified methods were assumed to be similar to those extracted by the original sequential extraction procedure of Follett et al. (1965).

In 1970, a procedure was established that combined the NaOH and the Na_2CO_3 solutions in the extraction to address the limitations of the NaOH-sequential cold and hot extraction procedure (Wada and Greenland 1970). When subjected to the cold and hot extraction with NaOH, varying amounts of silicic acid were released from pure clay minerals. Thus, Follett et al. (1965) assumed that the silicic acid originated from the amorphous materials, and therefore, the amount and the type of material found in the soil clay (from completely disordered to well crystallized material) that was dissolved was dependent on the type of the solution. However, Wada and Greenland (1970) indicated that initial mineral composition was the predominant influence on this reaction. Later, Krausse et al. (1983) showed that the extent of the mineral dissolution was also dependent on the digestion time, temperature, pH, concentration, and volume of the reagent.

For soil nutrient management, the abundance of silicon in the soil is interpreted differently. Because the agronomic value of silicon fertilization is well recognized in production agriculture, the research interest shifted in recent years, and many methodologies were established to determine the plant-available silicon (Datnoff et al. 2001). The most important fraction of the silicon that is subject to interpretation is the form available for plant uptake, because the amount of plant-available

silicon determines whether silicon fertilization is required. The plant-available silicon is presumably composed of silicic acid, both in the liquid (in the soil solution) and in the adsorbed phases (to the soil particles). The suitable solutions identified to extract plant-available silicon include water, CaCl_2 , acetate, acetic acid, phosphate, H_2SO_3 , H_2SO_4 , and citrate (Table 2.4). These solutions also extract the desorbed silicic acid, with the H_2SO_3 , H_2SO_4 , and citrate as the most effective solutions.

The procedures summarized in Table 2.4 experienced a series of modifications, most of which generally resulted in a shorter extraction time. As reported by McKeague and Cline (1963), a prolonged shaking time, even with water only, can

Table 2.4 Extraction procedures used for determining soluble and adsorbed silicon in soil

Solution	Procedure	Silicon fractions	References
H_2O	10 g in 50 mL + 0.1 % NaN_3 to reduce biological activity; incubate 21 days at room temperature with manual shaking 2 times a day	Water-soluble	Schachtschabel and Heinemann 1967
	10 g in 100 mL; 4 h shaking	Water-soluble	Fox et al. 1967; Khalid et al. 1978
	10 g in 60 mL; incubate at 40 °C for 2 weeks	Water-soluble	Nonaka and Takahashi 1988, 1990
	10 g in 100 mL; 1 h shaking	Water-soluble	Korndörfer et al. 1999
CaCl_2	0.01 M CaCl_2 ; 1 g sample in 20 mL solution; 16 h shaking	Liquid phase; readily available	Haysom and Chapman 1975
	0.01 M CaCl_2 ; 10 g sample in 100 mL solution; 1 h shaking	Liquid phase; readily available	Korndörfer et al. 1999
Na acetate + acetic acid	0.18 N Na acetate + 0.87 M acetic acid, adjusted to pH 4; 10 g sample in 100 mL solution; 5 h occasional shaking at 40 °C	Soluble and some exchangeable	Imaizumi and Yoshida 1958
	0.18 N Na acetate + 0.87 M acetic acid, adjusted to pH 4; 10 g sample in 100 mL solution; 1 h shaking	Soluble and some exchangeable	Korndörfer et al. 1999

(continued)

Table 2.4 (continued)

Solution	Procedure	Silicon fractions	References
NH ₄ acetate	5 % (0.5 M) NH ₄ acetate, adjusted to pH 4.5–4.8 with 0.1 M acetic acid; 1 g sample in 20 mL solution; 1 h shaking	Soluble and some exchangeable	Ayres 1966 ; Cheong and Halais 1970
	5 % (0.5 M) NH ₄ acetate, adjusted to pH 4.8 with 0.1 M acetic acid; 1 g sample in 10 mL solution; 1 h shaking	Soluble and some exchangeable	Korndörfer et al. 1999
Acetic acid	0.5 M acetic acid; 1 g sample in 10 mL solution; 1 h shaking with 12 h resting	Soluble and some exchangeable	Snyder 1991
	0.5 M acetic acid; 1 g sample in 10 mL solution; 1 h shaking	Soluble and some exchangeable	Korndörfer et al. 1999
	0.5 M acetic acid; 10 g sample in 25 mL solution; overnight resting followed by 2 h shaking	Soluble and some exchangeable	Snyder 2001
Phosphate acetate	0.016 M P as Ca (H ₂ PO ₄) ₂ dissolved in 0.1 M NH ₄ acetate, adjusted to pH 3.5 with 0.1 M acetic acid; 1 g sample in 10 mL solution; 4 h shaking	Soluble and some exchangeable	Fox et al. 1967
	0.0016 M P as Ca(H ₂ PO ₄) ₂ dissolve in 0.1 M acetic acid adjusted to pH 3.5; 1 g sample in 10 mL solution; 4 h shaking	Soluble and some exchangeable	Khalid et al. 1978
Citric acid	0.1 M citric acid; 1 g sample in 50 mL solution; 2 h shaking, resting overnight then 1 h shaking	Soluble, exchangeable, and adsorbed	Acquaye and Tinsley 1964
Na citrate + NaHCO ₃	80 % 0.3 M Na citrate and 20 % 1 M NaHCO ₃ ; 2 g sample in 50 mL solution; 5 min at 80 °C	Soluble, exchangeable, and adsorbed to sesquioxide surfaces	Breuer 1994

(continued)

Table 2.4 (continued)

Solution	Procedure	Silicon fractions	References
NH ₄ citrate	1 M NH ₄ citrate; 10 g sample in 25 mL solution; 80 h shaking	Soluble, exchangeable, and adsorbed	Sauer and Burghardt 2000, 2006
H ₂ SO ₃ + (NH ₄) ₂ SO ₄	0.02 N H ₂ SO ₃ containing 0.02 M (NH ₄) ₂ SO ₄ ; 1 g sample in 100 mL solution; 30 min shaking	Soluble, exchangeable, and adsorbed	Fox et al. 1967
H ₂ SO ₄	0.005 M H ₂ SO ₄ ; 1 g sample in 200 mL solution; 16 h shaking	Soluble, exchangeable, and adsorbed	Hurney 1973

increase the amount of silicon extracted from a soil because of the abrasion. By contrast, a prolonged shaking time results in equilibration between the soil and the solution (Schachtschabel and Heinemann 1967; Nonaka and Takahashi 1988, 1990); however, the time required for the completion of the procedure is too long, and therefore, the adoption of this approach in commercial soil testing laboratories will be limited. With water, the least amount of soluble silicon is extracted in soils, whereas the silicon extracted with CaCl₂ is the most easily removed of the soluble fractions (Berthelsen et al. 2001). Haysom and Chapman (1975) reported a high correlation between the silicon extracted with distilled water and that extracted with a 0.01 M CaCl₂ solution from the acidic soils of northern Queensland. Mengel and Kirkby (2001) found that the amount of soluble silicon extracted with both distilled water and the CaCl₂ solution was primarily H₄SiO₄, which was present at pH values from 2 to 9 and was in equilibrium with the amorphous silica. Nevertheless, the amount of silicon extracted with the CaCl₂ solution obtained the highest correlation with the sugar yield ($r^2=0.82$) compared with the silicon extracted with the 0.5 M NH₄ acetate and the 0.005 M H₂SO₄ (Haysom and Chapman 1975).

The soil silicon extracted with the acetic acid/acetate-based solutions is the soluble silicon and some of the exchangeable silicon, primarily the silicon from exchange sites. Nonaka and Takahashi (1990) reported that the amount of silicon extracted by the acetate solution overestimated the plant-available silicon for soils that were previously amended with calcium silicate. Moreover, these authors found that not all the silicon extracted from the calcium silicate was plant-available. Snyder (2001) noted that phosphate buffer used as an extractant did not overestimate the plant-available silicon in soils with silicates applied, likely because the phosphate (anion) only displaced the adsorbed silicic acid rather than dissolving the residual calcium silicate.

The amount of silicon extracted by citric acid, citrate-based solutions and diluted H₂SO₄ is generally higher than the amount extracted with acetate-based solutions. This result was attributed to the silicon contributed by the adsorbed fractions (both particles and hydroxides). Beckwith and Reeve (1964) also noted that the citrate

ions not only competed for the sorption sites for silicic acid but also formed complexes with metal ions that are known to bind silicic acid. The assumption of Breuer (1994) that the Na citrate+NaHCO₃ solutions extracted the silicon fraction that was specifically adsorbed to the sesquioxide surfaces was supported by the close correlation between the silicon extracted with this method and the silicon content in dithionite extracts (Mehra and Jackson 1960). Although the Na citrate+NaHCO₃ solutions extracted only 17 % of the amount of silicon found in the dithionite extracts, a strong correlation ($r^2=0.81$) between the silicon that was extracted by these two methods was observed. The dithionite solution effectively dissolves pedogenic sesquioxide; thus, the silicon quantified in the extract originates not only from the surface, but also as the silicon bound inside of the sesquioxides. Similar to phosphate, the sulfate-based solutions were noted to effectively extract silicon from a wider array of soil types than the acetate-based solutions (Fox et al. 1967). The acidity of the citric and sulfate-based solutions combined with a long shaking time (Hurney 1973) chemically and mechanically abraded the silicon from the silicates and the clay minerals, which resulted in an overestimation of the plant-available silicon. The actual amount of readily soluble silicon in the soil regardless of the origin (biogenic or pedogenic) is quantified with alkaline dissolution (Sauer et al. 2006; Saccone et al. 2007; Cornelis et al. 2011).

The amount of silicon that is extracted is different among these procedures, presumably, because the silicon extracted did not originate from the identical fractions. This problem poses a complication for the determination of the silicon fertilizer requirement, because the determination will be based on the choice of the extractant. The assumption is that these solutions all extract the dissolved plant-available silicon. Fox et al. (1967) used Ca(H₂PO₄)₂, H₂SO₄, and acetic acid to extract silicon from the soils of Hawaii with different mineral compositions. Based on the results, water consistently extracted the least amount of silicon in all the soils, and in the soils dominated by montmorillonite, kaolinite, goethite and gibbsite, the Ca(H₂PO₄)₂ extracted the most silicon. With the exception of the desert soils, the rest of the soils from the volcanic ashes that were dominated by allophane had the highest amount of silicon extracted with the H₂SO₄ as the extractant. The amount of silicon extracted with the acetic acid solution was between the amounts extracted with water and with Ca(H₂PO₄)₂ or H₂SO₄. The comparisons of Berthelsen et al. (2001) for different extractants revealed similar results; the solutions that contained diluted H₂SO₄ and citric acid extracted 12- and 16-fold more silicon than the CaCl₂ solution, respectively. For calcareous soils, the acidic extractants (e.g., acetic acid and sulfuric acid) tended to remove the greatest amount of silicon, which originated from the highly acid-soluble calcium silicates. However, the silicon of this form was not easily absorbed by plants (Xu et al. 2001). Large amounts of silicon were removed from the acidic volcanic soils of northern Queensland using 0.005 M H₂SO₄ because of the ability to dissolve the sesquioxide compounds that contained the adsorbed silicon Hayson and Chapman (1975).

Tubaña et al. (2012b) and Babu et al. (2013) also demonstrated that the amounts of silicon extracted were variable using different procedures for soils collected from the Midwest and the southern USA. Tubaña et al. (2012b) showed that 0.1 M citric

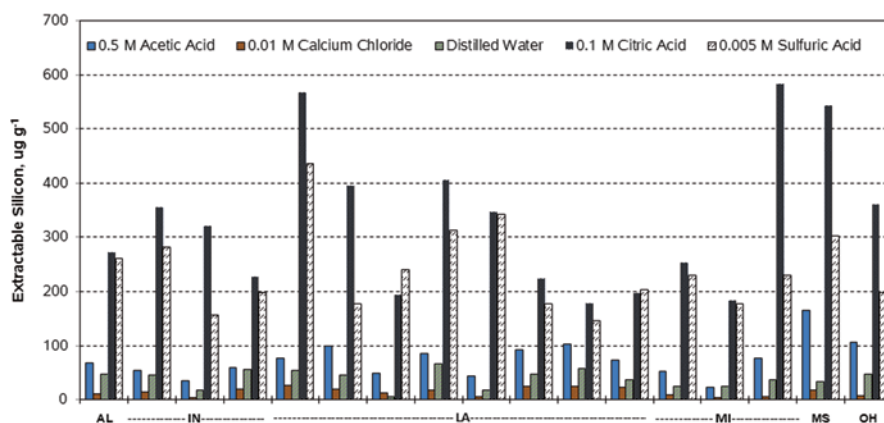


Fig. 2.4 Silicon concentration extracted from soils collected from Alabama, Indiana, Louisiana, Michigan, Mississippi, and Ohio using different extraction procedures (Tubaña et al. 2012b)

acid consistently extracted the largest amount of silicon from soils collected from selected states in the US (Fig. 2.4). Babu et al. (2013) noted that the amount of extractable silicon was in the order of citric acid > acetic acid (24 h rest + 2 h shaking > 1 h shaking) > sodium acetate > ammonium acetate > calcium chloride > water. Similarly, the 0.025 M citric acid solution also extracted higher quantities of silicon in calcareous soils than the Na acetate–acetic acid (pH 4) and the 0.19 M Na_2CO_3 –0.5 M NaHCO_3 (pH 8.5) solutions (Xu et al. 2001).

Lima Rodrigues et al. (2003) correlated the amounts of silicon extracted by acetic acid (Snyder 2001), acetate/acetic acid (Imaizumi and Yoshida 1958), and CaCl_2 (Haysom and Chapman 1975) solutions from soils collected from 31 countries. These soils collectively represented 137 mineral soils, primarily as Oxisols, Ultisols, and coarse-textured soils. The relationship between the silicon extracted with acetic acid and acetate/acetic acid ($r^2=0.59$) was relatively stronger than that between the silicon extracted with acetic acid and CaCl_2 ($r^2=0.53$). Babu et al. (2013) obtained similar results for the relationship between the silicon extracted with acetic acid and sodium acetate ($r^2=0.56$) from the soils (~130 samples) of Louisiana that were farmed for different field crops.

Korndörfer et al. (1999) standardized the soil to solution ratio (1:10) and the shaking time (1 h) before filtration for the water, acetic acid, CaCl_2 , and Na acetate+acetic acid extraction procedures (Table 2.4). The authors used these procedures to determine the silicon contents of four soil types from Brazil that were treated with five levels of wollastonite and were grown with upland rice. For the extraction procedures, the amount of silicon extracted from the soil and the silicon content of the rice had strong correlations (r^2 values > 0.69). Barbosa-Filho et al. (2001) also evaluated a similar set of methods using the predominantly organic soils of the Everglades agricultural areas in southern Florida. In general, the soil silicon values obtained from the different methods were correlated with the straw and the panicle silicon content. However, the soil silicon extracted with 0.5 M acetic acid

obtained the highest correlation with the silicon contents of the rice straw ($r^2=0.90$) and the panicle ($r^2=0.84$).

2. Soil Silicon Critical Levels To interpret soil tests and to determine fertilization guidelines for a nutrient requires knowledge of the critical level in the soil. The critical nutrient level is the point in a crop response curve that corresponds to the level of a plant-available nutrient that generates the maximum yield. Above the critical nutrient level, fertilization of the crop is in excess, whereas at levels below this point, a crop response to higher levels of fertilization is likely. To date, the published critical silicon levels varied with soil type, crops, and soil testing procedure. The critical silicon levels that were established using the different extraction procedures to determine plant-available silicon are summarized in Table 2.5. Lima Rodrigues et al. (2003) observed that the different extraction procedures would predict different levels of silicon deficiency in soil and therefore, different resultant silicon requirements for a crop. Using the published critical soil test silicon values for the Na acetate buffer, acetic acid and CaCl_2 extraction procedures, the authors created a subset of 137 mineral soils from 31 countries. The results of the tests on the subset of soils were at or below the published critical silicon levels for each of the extraction procedures. The silicon extracted with the Na acetate buffer correlated well with the acetic acid ($r^2=0.71$), but not with the CaCl_2 ($r^2=0.33$).

Based on the calibration tests conducted by Xu et al. (2001) that involved 17 field trials, the sodium acetate + acetic acid solution of Imaizumi and Yoshida (1958) was the optimal extraction method to assess plant-available silicon in calcareous soils. Using wheat biomass as a response variable, the authors established the critical level at 80 mg silicon kg^{-1} (171 mg SiO_2 kg^{-1}). These soils were classified as Inceptisols with a high soil pH that ranged from 7.40 to 8.25 and CaCO_3 concentrations that ranged from 26.5 to 52.6 g kg^{-1} . The acetic acid (0.5 M) extraction procedure was suitable for the organic and mineral soils in south Florida that were characterized by low clay, Al, and Fe contents (Korndörfer et al. 2001). The established critical silicon level for these soils was 19 mg kg^{-1} (Table 2.5). Korndörfer et al. (2001) categorized the soil silicon test values below this critical level such that >24 , 6–24, and <6 mg silicon kg^{-1} soil were interpreted as high, medium and low soil silicon test values, respectively, and should be fertilized with 0, 1120, and 1500 kg silicon ha^{-1} , respectively. The calcium chloride (0.01 M) extraction procedure was developed in Australia as an alternative to the extraction method of distilled water; the latter method has problems with the interference by dispersed clay fractions in a water suspension (Haysom and Chapman 1975). These authors established the soil silicon critical level based on the extraction with calcium chloride solution at 20 mg kg^{-1} for sugarcane. McCray et al. (2011) reported that the soil silicon critical level based on an acetic acid extraction of the soils used to grow sugarcane in Florida was 32 g m^{-3} .

3. Methods to Extract Silicon from Plant Tissue Samples The silicon from plant tissue samples can be extracted using a gravimetric method, a hydrofluoric acid solubilization, an autoclave-induced digestion with a strong NaOH solution or a microwave digestion assisted with nitric and hydrofluoric acids (Yoshida et al. 1976;

Table 2.5 Critical silicon levels established in different soils using different extraction procedures for different crops

Solutions	Critical levels mg Si kg ⁻¹	Soil types/ orders	Crops	References
Acetic acid	19	Histosols	Rice	Snyder 1991; Korndörfer et al. 2001
	54	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
	32 ^a	Histosol	Sugarcane	McCray et al. 2011
Acetic acid w/ 24 h rest	87	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
Acetate – buffer	33 28	Tropical soils	Rice	Kawaguchi 1966 Takijima et al. 1970
Na acetate – acetic acid	80	Calcareous	Wheat	Xu et al. 2001
	71–181	Calcareous	Rice, Wheat	Liang et al. 1994
	38	Acid and neutral	Rice	Takijima et al. 1970
	60	Acid and neutral	Rice	Imaizumi and Yoshida 1958
	38–60	Acid and neutral	Rice	He 1980
Na acetate	60	Acid and neutral	Rice	Lian 1976
	85	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
NH ₄ acetate	32	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
H ₂ O – 1 h shaking	14	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
H ₂ O – 4 h shaking	30	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
CaCl ₂	43	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
	20	Acid	Sugarcane	Haysom and Chapman 1975
Citric acid	185	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009
H ₂ SO ₄	207	Acid/Ultisol	Rice	Narayanaswamy and Prakash 2009

^aCritical level of Si expressed as g/m³

NovozamskyI et al. 1984; Elliot and Snyder 1991; Feng et al. 1999). The silicon in these extracts is analyzed colorimetrically or by ICP-OES. The standardization of the procedures in silicon plant tissue testing has not encountered as many challenges as the standardization of the soil silicon testing. The modifications of the procedures were to address safety (e.g., the nitric acid-hydrofluoric acid digestion), the availability of instruments, and the time-consuming and difficult-to-perform procedures (Fox et al. 1969; Elliot and Snyder 1991; Ostatek-Boczynski and Haysom 2003). The gravimetric method, which was established in 1960 by Horwitz, is time consuming and requires platinum ware at each stage of the extraction. The bomb

technique proposed by Novozamsky et al. (1984) uses a mixture of very reactive and hazardous chemicals (hydrochloric, nitric, and hydrofluoric acids) during autoclaving. The procedures were also modified to ensure accurate and reproducible results. Whereas the widely used autoclave-induced digestion method of Elliot and Snyder (1991) is relatively rapid, inexpensive and specialized instrumentation is not required (Bell and Simmons 1997), others have reported that the results are highly variable and tend to underestimate the silicon content of the plant (Taber et al. 2002; Haysom and Ostatek-Boczynski, 2006). The underestimation of the silicon values in plant tissue samples is attributed to the vigorous foaming that occurs when the H_2O_2 and the NaOH are combined in the sample tube, which deposits samples on the upper tube wall. During autoclaving, the sample particles on the upper tube wall are not well digested. Before the addition of the hydrogen peroxide, the addition of five drops of octyl-alcohol was incorporated into the method (Modified Autoclave Digestion–MAD) to eliminate the excessive foaming. The MAD procedure was later simplified to use an oven instead of the autoclave during digestion (Kraska and Breitenbeck 2010). To ensure that the color development is stable during the colorimetric procedure, the addition of 1 mL of 5 mM ammonium fluoride was also introduced to the procedure, now the Oven-Induced Digestion (OID). The ammonium fluoride ions facilitate the complete ionization of the polysilicic acid in the plant digests, which provides for more stable absorbance readings.

Among the published studies on which plant part should be analyzed for the concentration of silicon, there is relatively good agreement. For example, for the most practical testing procedure, the straw of rice plants at harvest was used as the sample material. Park et al. (1964) used the rice flag leaf as the sample material for silicon content determination, which they also used as an index of the available silicon in soil. To attain high levels of accuracy and sensitivity, low coefficients of variation and practical convenience, Winslow (1995) proposed the use of rice hull as the sample material for silicon content determinations in rice.

4. Critical Silicon Concentration in Plant Tissue Samples The plant silicon content is an accepted parameter for the routine monitoring of the silicon status in crops. Currently, only a few published critical silicon levels in plant tissue are available, and these were published primarily for rice and sugarcane. The critical silicon content in rice straw was established at 37 g kg^{-1} by Nair and Aieyer (1968) and Takijima et al. (1970). The critical silicon level established by Snyder et al. (1986) for rice straw was 30 g kg^{-1} ; a value that was closer to 37 g kg^{-1} than the level reported by DeDatta in 1981 at 5 g kg^{-1} . Using the Y-leaf of rice, Dobermann and Fairhurst (2000) reported a similar critical level to that of De Datta (1981). Lian (1976) reported that the critical silicon levels for rice straw as the sample material were 51, 47, and 42 g kg^{-1} for Japan, Korea, and Taiwan, respectively. Korndörfer et al. (2001) established a range of critical levels using straw as the sample material (from 17 to 34 g kg^{-1}) for rice grown in Florida soils; these values are lower than the critical levels reported by Lian (1976) for other rice producing countries. Narayanaswamy and Prakash (2009) established a critical level at 29 g kg^{-1} for straw and at 12 g kg^{-1} for grain for rice grown in southern India.

Only a few studies were conducted to determine the critical silicon level in sugarcane. A narrow range of critical silicon levels in sugarcane leaf was established at 10 g kg^{-1} (Anderson and Bowen 1990), 5.5 g kg^{-1} (Bethelsen et al. 2003), and 5 g kg^{-1} (McCray and Mylavarapu 2010). The critical silicon level that was established many decades ago by Halais (1967), who used the sixth leaf sheath, was the highest (12.5 g kg^{-1}) among the published critical silicon levels.

To attain satisfactory yields, the silicon content in a plant should be above the reported critical silicon level (Snyder et al. 1986). The critical silicon levels currently reported are very specific not only to the crop species but also to the location and the sample material used, which underscores the necessity to establish site-specific plant-silicon content interpretations.

Conclusions

The benefits of silicon to a wide variety of crops are well-documented and strongly demonstrate the value of silicon fertilization in agriculture. Agricultural areas under intensive cropping systems, especially those with soils inherently low in soluble silicon, are amended with silicon-rich materials to ensure plant productivity. In fact, in some parts of the world silicon fertilization is an accepted agronomic practice. While the development and standardization of different procedures to extract and quantify different silicon fractions in soils is considered significant progress in silicon research specifically and the realm of soil science more generally, their applications in soil fertility and nutrient management have been very limited. The development of soil silicon interpretation test and fertilization guidelines in crop production require the establishment of critical soil silicon levels and robust, high-precision soil testing procedures suitable for a wide array of soil types. Thus far, a few extraction procedures (e.g., 0.5 M acetic acid and 0.01 M CaCl_2) have been identified and are rigorously employed in calibration/correlation research in many parts of the world, including the US and Brazil. Initial critical soil-based silicon levels using these procedures have been reported but appear to require further refinement. No elaborate soil interpretation test has been derived from these calibration/correlation studies. A soil interpretation test can be used as a tool to determine whether silicon fertilization is needed or not, but it does not provide the concentration of silicon required to raise plant-available silicon to a desired level, nor does it indicate the probability that the crop in question will respond to and benefit from silicon fertilization. The availability of high-precision method(s) for quantifying plant-available silicon in silicon fertilizer is equally as important as an established, well-refined soil silicon interpretation test in providing effective silicon recommendations. One remarkable achievement in silicon research was the development and recognition of the 5-days $\text{Na}_2\text{CO}_3\text{-NH}_4\text{NO}_3$ method for extracting plant-available silicon from solid fertilizer. This method is currently being evaluated in terms of its applicability to many silicon-containing fertilizers. Clearly, silicon research has made progress, particularly in those areas that are critical to the development of

effective silicon fertilization guidelines. Even so, there are many soil science aspects of silicon that are understudied (e.g., chemical dynamics and soil-plant interaction). It is strongly believed that the outcomes from these future soil science-based research studies on silicon will significantly advance the current established knowledge of silicon in soil and fertilization guidelines for crop production.

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