Chapter 3
Silicon Biogeochemistry and Bioavailability in Soil

Abstract Whether silicon (Si) deficiency occurs in plants depends largely on plant-available Si concentration in soils but not on total Si content. Si bioavailability in soils is related closely to soil Si biogeochemistry including biogeochemical cycling of Si, forms and solubility of Si in soils and solubility of Si in soils. This chapter deals in detail with soil Si biogeochemistry and bioavailability, solid forms of Si in soils, Si in natural waters, soluble and plant-available Si in soils, and Si-supplying power.

Keywords Plant-available silicon • Silicon in natural water • Silicon-supplying power • Soil silicon chemistry

3.1 Silicon in Soil

Silicon (Si), atomic number 14, molecular weight 28.0855, has 4 outer valance electrons and oxidation states of +2, +4, and −4 with its melting point of 1,410 °C and boiling point of 2,355 °C (Gascho 2001). Interestingly, in the periodic table of elements, Si is surrounded by such near neighbours as boron (B), carbon (C), nitrogen (N), oxygen (O), phosphorus (P) and sulphur (S) (all recognized as 'essential elements'), and aluminium (Al), gallium (Ga), germanium (Ge) and arsenic (As), which, together with Si itself, are all recognized as 'nonessential and/or beneficial elements' or even toxic elements.

Si is the second most abundant element after oxygen in the Earth's crust and in soil. The average content of elemental Si in the lithosphere is approximately 28 %. Total Si content in soil ranges normally from 25 to 35 % with an average of 30 %, depending greatly upon soil types. However, in some highly weathered soils such as latosols or latosolic red soils in the tropics where desilification and fersialitization processes are extremely active, Si content can be as low as less than 1 %. Si content and its availability in soil depend greatly upon soil-forming processes and consequently soil types (Fig. 3.1). Si is mainly present in soils including various categories of aluminosilicates and quartz (SiO_2), which may account for up to 75–95 % of soil inorganic constituents. Except organic soils (histosols), most mineral soils are composed of sands (largely SiO_2), various crystalline forms of primary (e.g. olivine,

Y. Liang et al., *Silicon in Agriculture*, DOI 10.1007/978-94-017-9978-2_3

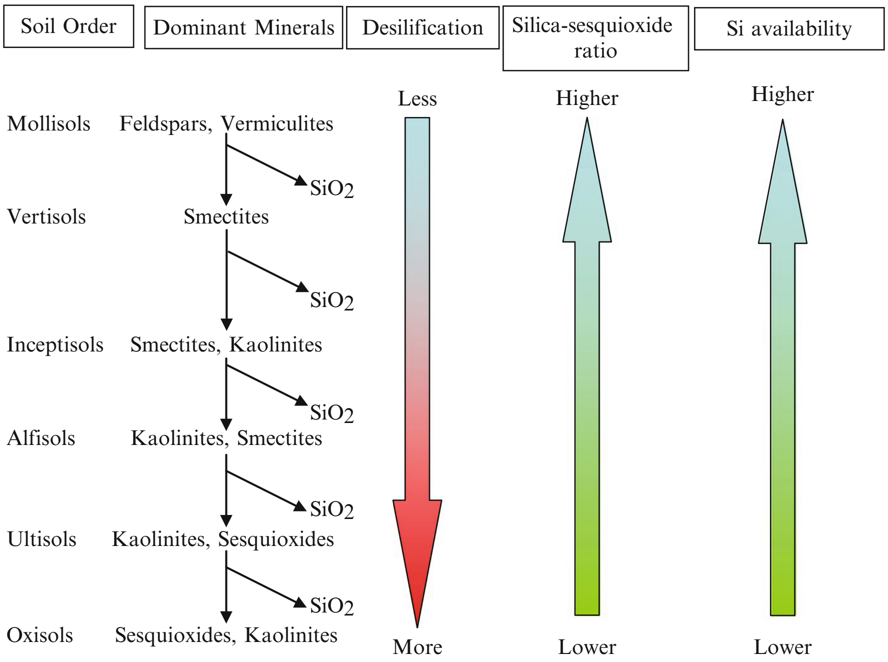


Fig. 3.1 Simplified acid weathering sequence in soil in relation to Si availability (Modified from Friesen et al. 1994; Savant et al. 1997)

augite, hornblende, quartz, feldspars-orthoclase, plagioclase, albite and mica) and secondary silicate minerals (clay minerals like illite, vermiculite, montmorillonite, chlorite and kaolinite) and amorphous (noncrystalline) Si-containing minerals such as allophone and opal. These forms of silicate compounds are only sparingly soluble and usually biogeochemically inert. Monosilicic acid or orthosilicic acid (H_4SiO_4) is the only form of water-soluble Si, while poly-silicic acid (polymerized silicic acid) is only partially water soluble in soil. Water-soluble Si is present in soil solution and can be adsorbed on the surfaces of inorganic, organic and organic–inorganic colloids in soils such as soil clays, soil organic matter and organic–inorganic complex.

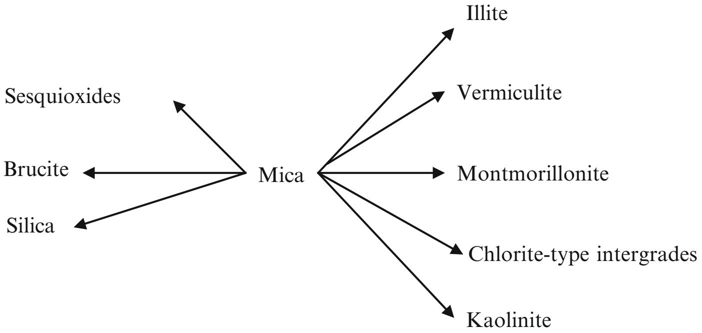
3.1.1 Solid Forms of Silicon

Solid forms of Si can be divided into two categories: one is various forms of silicates bound to Al and/or other elements; and the other is quartz (SiO_2). The commonly present primary silicate minerals are crystalline silicates and can be divided into the following five categories (Hurlbut and Klein 1985; Deer et al. 1992):

1. Nesosilicates: Nesosilicates or orthosilicates, which have isolated (insular) negatively charged silicon–oxygen tetrahedra, $[SiO_4]^{4-}$, are connected only by interstitial cations such as iron (Fe), magnesium (Mg), etc. The representative minerals are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4), which belong to the olivine group.
2. Cyclosilicates or ring silicates: Cyclosilicates, which have linked silicon–oxygen tetrahedra with $(T_xO_{3x})^{2x-}$ or a ratio of 1:3, exist usually as 3-member $(T_3O_9)^{6-}$ and 6-member $(T_6O_{18})^{12-}$ rings, where T stands for a tetrahedrally coordinated cation. The minerals typically representing this category are benitoite [$BaTi(Si_3O_9)$] (3-member ring) and axinite [$(Ca,Fe,Mn)_3Al_2(BO_3)$ $(Si_4O_{12})OH$] (6-member ring).
3. Inosilicates: Inosilicates or chain silicates consist of both single-chain and double-chain silicates. The single-chain silicates have interlocking chains of tetrahedra with a silicon–oxygen ratio of 1:3 (SiO_3), while the double-chain silicates have interlocking chains of tetrahedra with a silicon–oxygen ratio of 4:11 (Si_4O_{11}). The typical minerals representing the single-chain and double-chain inosilicates are augite [(Ca,Na) (Mg,Fe,Al) $(Si,Al)_2O_6$] and hornblende [$Ca_2(Mg,Fe)_5(OH)_2Si_8O_{22}$], respectively.
4. Tectosilicates: Tectosilicates are characterized by a three-dimensional framework of silicate tetrahedra with a silicon–oxygen ratio of 1:2 (SiO_2). This category accounts nearly for 75 % of the Earth's crust. Except for the quartz group, the minerals representing this category are aluminosilicates. The commonly present tectosilicates belong to the feldspar family including alkali feldspars (potassium feldspars) and plagioclase feldspars. The typical minerals of alkali feldspars (potassium feldspars) are microcline ($KAlSi_3O_8$), orthoclase ($KAlSi_3O_8$) and anorthoclase [$(Na,K)AlSi_3O_8$], while albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) are the representing minerals of plagioclase feldspars. The quartz group is characterized by a three-dimensional framework of silicon–oxygen tetrahedra, including quartz, tridymite and cristobalite, all corners being shared except those protruding at the outer surfaces. This category of mineral is extremely resistant to weathering.
5. Phyllosilicates: Phyllosilicates or sheet silicates form parallel sheets of silicate tetrahedra with a silicon–oxygen ratio of 2:5 (Si_2O_5). Mica group is the typical primary minerals representing phyllosilicates including biotite [$K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$], muscovite [$KAl_2(AlSi_3)O_{10}(OH)_2$], phlogopite [$KMg_3(AlSi_3)O_{10}(OH)_2$], lepidolite [$K(Li,Al)_{2-3}(AlSi_3)O_{10}(OH)_2$], margarite [$CaAl_2(Al_2Si_2)O_{10}(OH)_2$] and chlorite [$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$].

All these crystalline aluminosilicates or SiO_2 are highly weather resistant, with the resistance depending largely upon their structure. The stability of these silicates increases in the order of olivine (nesosilicates) < augite (single-chain inosilicates) < hornblende (double-chain inosilicates) < biotite (phyllosilicates) < potassium-feldspar (tectosilicates) < muscovite (phyllosilicates) < quartz (tectosilicates).

The noncrystalline silicates, which are commonly present in soil, are various layered clay minerals. The formation of these clay minerals by neogenesis implies that all polyhedra of primary minerals, especially of olivine, augite, hornblende and feldspars, are liberated by hydrolysis and then reassembled to clays either inside or adjacent to the parent crystal or after movement to a different horizon site (Jenny 1980). In soils, the commonly present clay minerals (secondary silicates) are phyllosilicates which are characterized by a structure of silicate tetrahedrons arranged in sheets. The typical phyllosilicates in soils are illites, vermiculites, montmorillonites, chlorites, kaolinites and halloysites. The principal clays that might result from the weathering of mica can be summarized as follows (Jenny 1980):



The left arrows point to the oxide clay minerals resulting from severe lattice disruption during both rock weathering and soil-forming processes, while the right arrows result in the commonly present silicate clay minerals derived from weathering of mica in soils (Jenny 1980). Clay genesis is one of the most important indicators of soil formation from parent materials or parent rocks, which is a function of the soil-forming factors. For instance, the effect of the climatic factors on clay formation processes can be illustrated by the transformations of biotite (Tardy et al. 1973): in arid climates it is typically converted to montmorillonite and in temperate environments to vermiculite, while intensive weathering in the humid tropics leads to the formation of kaolinite; on the other hand, weathering of the plagioclase feldspar progresses directly to kaolinite in all climatic conditions.

The commonly present soil amorphous aluminosilicate, which is particularly abundant in soils derived from volcanic ash in humid regions, is allophane ($Al_2O_3,SiO_2 \cdot nH_2O$), with its SiO_2/Al_2O_3 ratio and CEC being highly variable. According to Jackson (1958), allophane can be divided into two groups, unstable and stable, depending largely upon its dissolution characteristics by dilute acid (e.g. HCl) or alkali (e.g. 2 % Na_2CO_3). The amorphous SiO_2 is composed of both silica glass, which is scarce in soils, and opal, which is commonly present. The bioavailability of amorphous opal ($SiO_2 \cdot nH_2O$) to higher plants is higher than that of allophane or laterite ($Fe_2O_3 \cdot 2SiO_2 \cdot nH_2O$).

The solid forms of silicates and Si compounds may undergo weathering with their weathering rate related to not only the mineral itself and its specific surface area but also the environmental factors such as temperature, water, pH, etc.

3.1.2 Solubility of Silicon

As is well known, Si, which is surrounded by four oxygen atoms, remains tetrahedral as SiO_4 in most silicate minerals. In general, quartz is considered to be the most stable SiO_2 mineral at normal temperatures and pressures. Different forms of silica have their solubility relationships (see Table 3.1 and Fig. 3.2). The solubility of silica minerals ranges from $10^{-2.74}$ M (amorphous Si) to 10^{-4} M (quartz) (Lindsay 1979). According to Jenny (1980), the solubility of quartz dissolved in water in amounts of SiO_2 ranges from 5 to 20 mg L^{-1}. Hydration, as $SiO_2 + 2H_2O$, produces $Si(OH)_4$ molecules. The solubility of amorphous silica increases with an increase in temperature, approaching 0 at temperature < 0 °C (Iler 1979). Amorphous silica precipitates in a structure of a porous gel with its solubility in water ranging generally from 100 to 150 SiO_2 mg L^{-1} at pH 7 at room temperature (Jenny 1980). However, amorphous silica of such high solubility is thermodynamically unstable such that the silica gel is expected to form quartz. Because $Si(OH)_4$ can be strongly specifically adsorbed on the surfaces of sesquioxide clays, soluble Si concentration is less than 10 mg kg^{-1} in many highly weathered acid soils in the tropical areas (Fox et al. 1967).

Table 3.1 (Reactions 8 to 12) and Fig. 3.3 show the relationships between the dissociation of H_4SiO_4 and the polymerization of silicate species in solution under the condition that H_4SiO_4 in soil solution is controlled by SiO_2 (soil) (Lindsay 1979). The major silicate species as shown in Fig. 3.4 are the forms of silicate compounds that can be expected in soil solution. Clearly, the ionic silicates contribute significantly to total silica in solution only at $pH > 8.5$, whereas H_4SiO_4 is the major form of Si species in solution at pH values ranging from 4.5 to 8.0 (Lindsay 1979).

Table 3.1 The major equilibrium reactions of SiO_2 minerals with water and dissociation of H_4SiO_4 (Modified from Lindsay 1979).

Reaction no.	Equilibrium reaction equation	Log K^o
Hydration of SiO_2 minerals		
1	SiO_2 (silica glass) $+ 2H_2O = H_4SiO_4^o$	−2.71
2	SiO_2 (amorphous) $+ 2H_2O = H_4SiO_4^o$	−2.74
3	SiO_2 (coesite) $+ 2H_2O = H_4SiO_4^o$	−3.05
4	SiO_2 (soil) $+ 2H_2O = H_4SiO_4^o$	−3.10
5	$\alpha - SiO_2$ (tridymite) $+ 2H_2O = H_4SiO_4^o$	−3.76
6	$\alpha - SiO_2$ (cristobalite) $+ 2H_2O = H_4SiO_4^o$	−3.94
7	$\alpha - SiO_2$ (quartz) $+ 2H_2O = H_4SiO_4^o$	−4.00
Dissociation of silicic acid		
8	$H_4SiO_4^o = H_3SiO_4^- + H^+$	−9.71
9	$H_4SiO_4^o = H_2SiO_4^{2-} + 2H^+$	−22.98
10	$H_4SiO_4^o = HSiO_4^{3-} + 3H^+$	−32.85
11	$H_4SiO_4^o = SiO_4^{4-} + 4H^+$	−45.95
12	$4H_4SiO_4^o = H_6Si_4O_2^{2-} + 2H^+ + 4H_2O$	−13.32

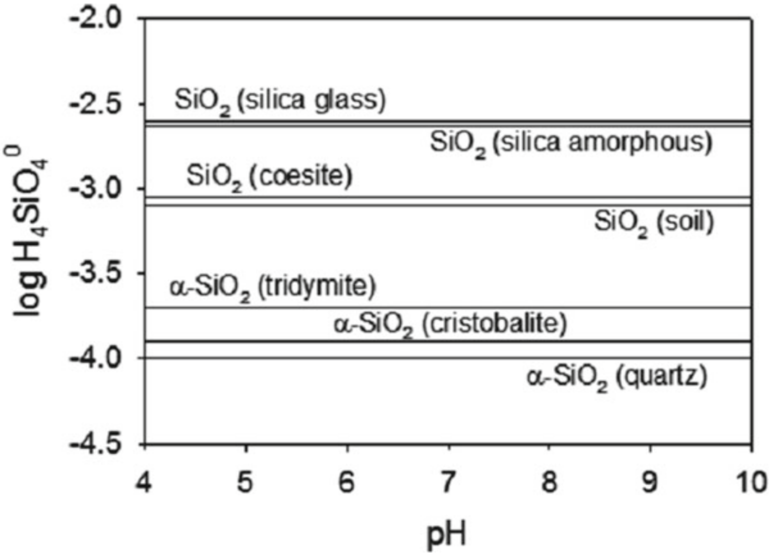


Fig. 3.2 The activity of H_4SiO_4 maintained by various forms of silica (Redrawn by Miroslav Nikolic from Lindsay 1979)

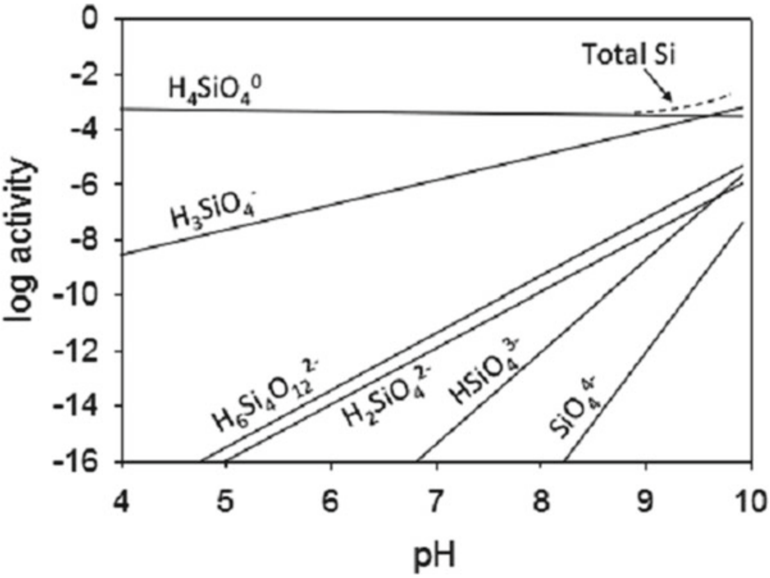


Fig. 3.3 Silicate species in equilibrium with SiO_2 (soil) represented by $10^{-3.10}$ M H_4SiO_4 (Redrawn by Miroslav Nikolic from Lindsay 1979)

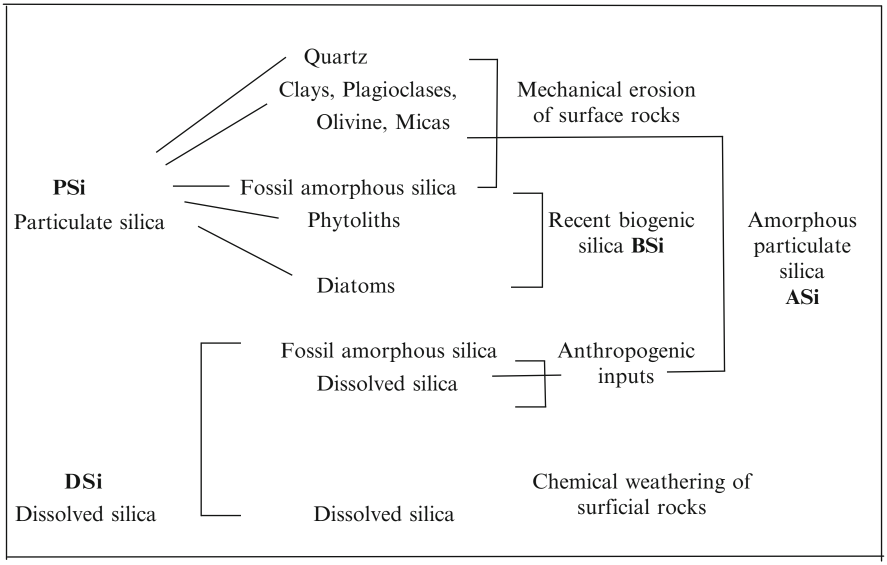


Fig. 3.4 Sources and forms of riverine Si. Amorphous Si (ASi); particulate Si (PSi); biogenic particulate Si (BSi) (Redrawn by Yongchao Liang from Dürr et al. 2011)

3.2 Silicon in Natural Waters

Si in natural waters such as rivers and lakes is primarily derived from the weathering of silicates and aluminosilicates in the bedrock and soils of an area (Berner and Berner 1996). The concentrations of Si in natural waters are much lower than 120 mg SiO_2 L^{-1} (Martin 1970) and in soil solutions decrease with an increase in pH up to about pH 8 (Jones and Handreck 1967). Si in natural waters, which accounts for a considerable proportion of Si absorbed by plants, is greatly influenced by Si in soil solution. The low concentration of silica in natural waters has been attributed largely to both adsorption of silica by Fe and Al hydroxides (Jones and Handreck 1967) and recombination of silica with aluminium silicates (Mackenzie et al. 1967).

Rainwater normally contains little Si, with Si accretion and input from rainwater being < 1 kg ha^{-1} $year^{-1}$ (Alexandre et al. 1997). The concentration of Si in irrigation water varies with the source of water used. If a form of rainwater harvesting is employed, then the water will contain little Si, whereas if the water comes from a wadi or river, the concentration of Si will be possibly higher (Imaizumi and Yoshidai 1958; Meybeck 1987; Bluth and Kump 1994; White and Blum 1995).

By calculating the averaged component of the global rivers, the US Geological Survey pioneer, Clarke (1924), showed that silica in the rivers accounted for approximately 12 % of the total dissolved solids and the dissolved Si concentration of Nile, Amazon and Mississippi waters was 17, 11 and 11 mg SiO_2 L^{-1}, respectively. By determining Si concentration of water in 225 rivers in Japan, Kobayashi (1960) showed that the averaged concentration of soluble Si was about 10 mg SiO_2 L^{-1} in the waters of rivers going through the sedimentary rock areas compared to about 45 mg SiO_2 L^{-1} in the waters of rivers going through the igneous rocks.

By making a survey on soluble Si concentrations in 43 sampling sites of the eight main streams in Zhejiang province, China, Ma et al. (1987) found that the average soluble Si concentrations ranged from 7.4 to 10.6 mg SiO_2 L^{-1} and distinct seasonal variation in soluble Si concentrations was also found in the main rivers surveyed. Furthermore, the sampling sites where soluble Si concentrations are less than 10 mg SiO_2 L^{-1} (critical value for Si deficiency in rice) accounted for 70 % of the total sampling sites (Ma et al. 1987). Investigation by Qian et al. (1995) also shows that average soluble Si concentrations of the Yangtze River and the Yellow River are about 9 and 7 mg SiO_2 L^{-1}, respectively, which are lower than the Si concentrations found in the Nile, Amazon and Mississippi waters (Clarke 1924) and below the critical value for Si deficiency in rice (*Oryza sativa*) as well.

Figure 3.4 shows sources and forms of riverine silica (Dürr et al. 2011). Dissolved silica (DSi) is composed of fossil amorphous silica coming from anthropogenic input and dissolved silica derived from chemical weathering of surface rocks. It is reported that the averaged global dissolved Si (DSi) values range from 8.3 to 13.1 mg SiO_2 L^{-1} with small variation having taken place over the last 9 decades (Dürr et al. 2011). African rivers have the highest Si concentrations (12.6 mg SiO_2 L^{-1} on average) followed by Australian rivers (11.8 mg SiO_2 L^{-1}) and Asian rivers (10.0 mg SiO_2 L^{-1}), while European rivers have the lowest silica levels on average: 5.6 mg SiO_2 L^{-1} vs. 9.5 mg SiO_2 L^{-1} for the global exorheic (externally drained water bodies) average. In addition, European rivers have the lowest averaged dissolved silica influx (13.5 Mt SiO_2 $year^{-1}$), whereas Asian rivers have the highest averaged dissolved silica influx (129.4 Mt SiO_2 $year^{-1}$) followed by South American rivers (106.5 Mt SiO_2 $year^{-1}$) (Dürr et al. 2011).

Liu et al. (2008) reported the concentrations of silicic acid and particulate biogenic Si (PBSi; μmol L^{-1}) in major streams entering into Jiaozhou Bay, China. The concentrations of silicic acid varied considerably among different streams (e.g. the Licunhe and Daguhe) and also by a factor of 1–12 between dry and flood seasons. They ranged from 10.5 to 370.8 μmol L^{-1} from March to August 2002 and from April to August 2004 with the Licunhe and Moshuihe having much higher concentrations and Daguhe, Yanghe and Baishahe having much lower concentrations.

Liu et al. (2008) also calculated the Si budget in Jiaozhou Bay, showing that among all input pathways for biologically available Si, the exchange flux between Jiaozhou Bay and the Yellow Sea is the major contribution, accounting for 72 %, followed by riverine input (21 %) and then wastewater discharge (6 %).

By measuring dissolved silica (DSi) concentrations at the Pawcatuck river-mouth in Westerly, Rhode Island, over 70 times, Fulweiler and Nixon (2005) found that DSi concentrations varied greatly during the annual cycle, with a minimum of about 90 μM Si in late spring and early summer and a maximum of about 200 μM Si during winter. Moreover, DSi concentrations are lower during spring than they are during fall at equivalent water temperatures. For example, the lowest monthly average DSi concentration and the highest occurred at approximately 12 °C (108 μM Si in April and 201 μM Si in October). A distinct seasonal variation in Si concentration was also reported in the water of the Mill Stream (downstream site), Dorset, England, between June 1991 and June 1994 (House et al. 2001) with Si concentration ranging from 25 to 180 μM. The minimum Si concentrations occurred in the spring, and the variations in concentration of Si during the periods between the spring minima were relatively small and generally ranged from 100 to 150 μM (House et al. 2001).

According to Neal et al. (2005), the Si concentration in the eastern UK rivers considerably varied, from 1.2 to 7.5 mg Si L^{-1}; the lowest averages occurred in the rural areas of Scotland and northern England, while higher concentrations were found in the industrial areas of the Humber region and in the agricultural regions of southeastern England. These trends of increased Si concentrations in rivers along the north–south gradient are consistent with the underlying north–south climatic gradient of increasing temperatures. Neal et al. (2005) also reported that dissolved Si concentrations for waters were significantly affected by temperature, pH and the type of crystalline Si with which equilibrium was established.

Husnain et al. (2008) reported that in Citarum River, Indonesia, the average Si concentration ranged from 22 to 37 mg SiO_2 L^{-1} in the upper stream and from 13 to 25 mg SiO_2 L^{-1} in the middle and lower streams, while in the Kaligarang River, the average Si concentration ranged from 34 to 54 mg SiO_2 L^{-1} in the upper stream and from 23 to 39 mg SiO_2 L^{-1} in the middle and lower streams, showing the difference was affected by the geological condition of the watersheds. Kawaguchi and Kyuma (1977) summarized that the average soluble Si concentrations in rivers on Java Island are 42.3, 30.2, 18.2 and 28.6 mg SiO_2 L^{-1}, respectively, with the geological substrate being volcanic ash, marl, lime and acid tuff loam. Ma and Takahashi (2002) also stated that the Si content was three- to fourfold higher in volcanic ash than in granite and sedimentary rocks. According to Kawaguchi and Kyuma (1977), Si concentrations in irrigation water ranged from 10.1 to 23.7 mg SiO_2 L^{-1} in Thailand, from 5.3 to 16.3 mg SiO_2 L^{-1} in West Malaysia and from 7.3 to 21.8 mg SiO_2 L^{-1} in Sri Lanka.

3.3 Soluble and Available Silicon in Soils

3.3.1 Soluble Silicon in Soils

It has been well documented that monosilicic acid (H_4SiO_4) is the only form of Si present in soil solutions (Jones and Handreck 1967; Epstein 1994). Thermodynamically, the solubility of silicate minerals in terms of H_4SiO_4 ranges from $10^{-2.74}$ M (amorphous Si) to 10^{-4} M (quartz) with the solubility of soil Si corresponding to $10^{-3.10}$ M (Lindsay 1979). Nevertheless, the measured concentrations of monosilicic acid (H_4SiO_4) in soil solutions were only 0.1–0.6 mM (Drees et al.

1989; Epstein 1994), which is much less than that in saturated monosilicic acid solution and is mainly controlled by the pH-dependent adsorption–desorption processes on sesquioxides (Jones and Handreck 1967; Mckeague and Cline 1963).

3.3.2 *Available Silicon in Soils*

Available Si in soils refers to the amount of Si that can be taken up by plants during the growing season and is usually considered an index of Si-supplying power or capacity in soil. Generally, Si is absorbed and transported by plants in the form of monosilicic acid. However, in monosilicic acid-saturated soil solution, H_4SiO_4 easily polymerizes into polymeric $Si(OH)_4$ which is in a dynamic equilibrium with noncrystalline (amorphous) and crystalline silicates, exchangeable silicates and sesquioxides. Thus, available Si in soils include monosilicic acid in soil solution and parts of silicate components that can be easily converted into monosilicic acids such as polymerized silicic acid, exchangeable silicates and part of colloidal silicates. At pH 2–9, especially at physiological pH values, Si in soil is mainly present as monosilicic acid and conversion of monosilicic acid into ionic silicates is possible only at pH >9. The main factors influencing soil Si availability or Si-supplying power include types of soil and parent material, historical land-use change, soil pH, soil texture, soil Eh, organic matter, temperature and accompanying ions (Kawaguchi and Kyuma 1977; He and Li 1995; Cai et al. 1997; Sumida 2002; Husnain et al. 2008; Struyf et al. 2010a, b).

3.3.2.1 Types of Soil and Parent Material

Soil availability and Si-supplying power vary with soil types, depending mainly on the type of parent materials, weathering and eluviation and illuviation. Soils derived from granite, quartz porphyry and peat are prone to Si deficiency, while those developed from basalt and volcanic ash are Si sufficient. The paddy soils which are subjected to intensive weathering and eluviation are prone to Si deficiency, whereas those which are subjected to slight weathering and eluviation are generally rich in plant-available Si.

He (1993) determined available Si content in 64 paddy soil samples collected from Hunan province, South China. The results showed that the available Si content in paddy soils ranged from 26 to 256 mg SiO_2 kg^{-1}. It is estimated that 51.5 % of the total area of soils is Si deficient. The paddy soils developed from plate shale, red sandstone, alluvial deposits, granite and acidic purple sandstone and those derived from quaternary red earth with lower pH and lighter soil texture were deficient in available Si, while those paddy soils derived from quaternary red earth with higher pH and heavier soil texture and those derived from lacustrine deposits contained high amount of available Si. By determining soil-available Si content of 410 paddy soil samples collected from Jiangsu province, China, Ma et al. (1993) found that 30 %

of the areas of paddy soils were Si deficient with the available Si content of less than 100 mg SiO_2 kg^{-1} and 50 % of those contained available Si of less than 150 mg SiO_2 kg^{-1}. As reported by Li et al. (1999), there are three categories of soils in terms of Si availability. The first is the soils derived from granite, quartzite and alluvial deposits. These soils, because of their sandy texture and strong leaching loss, had lowest averaged available Si contents, ranging from 33.3 to 43.3 mg SiO_2 kg^{-1} and 94 to 100 % of the tested soil samples are Si deficient or severely Si deficient. The second is the soils developed from red sandstone, pelite, lacustrine deposits and quaternary red earth. These soils, mainly due to desilification and fersialitization, had lower average available Si content, ranging from 52.9 to 66.7 mg SiO_2 kg^{-1} and 80 to 85 % of these soils are deficient or severely deficient in Si. The third is the soils derived from purple rock, limestone and Xiashu loess. These soils had higher available Si content due to their clayey soil texture, ranging from 98 to 125.8 mg SiO_2 kg^{-1} and only 33 to 60 % of these soils are Si deficient.

Cai et al. (1997) collected 179 upland and paddy rice soil samples in Fujian province, Southeast China to analyse their Si-supplying power. The results showed that the available Si content extracted by 1.0 M acetate buffer (pH 4.0) ranged from 6 to 450 mg SiO_2 kg^{-1} with an average value of 80 mg SiO_2 kg^{-1}. More importantly, according to the critical value for Si deficiency (105 mg SiO_2 kg^{-1}), 80 % of the upland soil samples and 84 % of paddy rice soil samples tested were deficient (50–100 mg SiO_2 kg^{-1}) or severely deficient in Si (< 50 mg SiO_2 kg^{-1}).

In Anhui province, out of 251 soil samples extracted by 1.0 M acetate buffer (pH 4.0), Si deficiency was established in about 54 %, with 28 % of the samples having severe Si deficiency (Zheng 1998). The available Si content was the highest in vertisols, followed by alluvial soils, limestone soils, yellow-brown soils, paddy soils, red soils and purple soils.

He and Li (1995) also reported that in Hubei province, soil-available Si content was the highest in paddy soils derived from limestone, followed by those from red-purplish sandy shale, alluvial and lacustrine deposits, quaternary red earth, granitic gneiss and sandy shale, and approximately 50 % of the 50 samples tested were Si deficient with available Si content below 100 mg SiO_2 kg^{-1}.

By analysing available Si content of 1818 surface soil samples collected from Shandong province in North China, Quan et al. (1999) reported that the available Si content ranged between 15.4 and 779.5 mg SiO_2 kg^{-1} with an average of 234 mg SiO_2 kg^{-1} and approximately 17.21 % of the soil samples tested were found to be Si deficient (<100 mg SiO_2 kg^{-1}) and 35.68 % of the soil samples were found to be potentially Si deficient (100–200 mg SiO_2 kg^{-1}). The available Si content varied with different types of soil with the highest observed in cinnamon soils (Typic Haplustalfs), followed by lime concretion black soils (Vertic Haplustalfs), saline soils (Typic Halaquepts), alluvial soils (Typic Fluvaquents), brown soils (Typic Paleustalfs) and litho soils (Lithic Ustochrepts). Investigating into 159 soil samples representing 17 major soil types distributed in Shaanxi province of Northwest China showed that available Si content extracted by 0.025 M citric acid ranged from 75 to 980 mg SiO_2 kg^{-1} with an average value of 391 mg SiO_2 kg^{-1}, suggesting that the soil Si-supplying capacity is higher (Dai et al. 2004). The available Si content varied with soil type in a descending order of paddy soils > brown soils > limestone soils > cinnamon soils.

Compared with lowland paddy soils, upland soils (i.e. ultisol and oxisol soil orders) which are often leached, acidic and highly weathered in the humid tropical areas of Southeast Asia including Indonesia, Laos, Myanmar, Thailand, Vietnam and neighbouring areas, and West Africa and South America such as Nigeria and Colombia are more prone to be Si deficient because the Si concentration and content in irrigation water, soil and crop were found to be 80 and 90 % lower in the uplands than in the lowlands (Winslow et al. 1997 and references therein).

3.3.2.2 Land-Use Pattern

Intense biogeochemical cycling of silica occurs in soils (Blecker et al. 2006; Gérard et al. 2008). It is reported that the annual ecosystem biogeochemical cycling of Si exceeds the annual export from continents to the ocean by two orders of magnitude (Conley 2002; Struyf et al. 2010a). It has been recently reported that land use is the most important controlling factor on baseflow Si mobilization in a temperate European river basin (Scheldt basin), with historical soil disturbance and sustained cultivation (> 250 years) of formerly forested areas leading to a twofold to threefold decrease in baseflow delivery of Si from the land surface to the aquatic continuum (Struyf et al. 2010b, Fig. 3.5). It seems to suggest that such human cultivation as land use can significantly alter the biogeochemical silica cycle, thus affecting terrestrial silica mobilization and the availability of Si for the growth of terrestrial plants and oceanic phytoplankton blooms (Struyf et al. 2010b).

3.3.2.3 Soil pH

The concentration of monosilicic acid is strongly dependent upon soil pH. The lowest concentration is observed at pH 8–9, below or above which the concentration of monosilicic acid increases significantly. Si concentration in soil solution may rise sharply when pH value decreases from 7 to 2 (Beckwith and Reeve 1963). Numerous studies show that soil-available Si content is closely positively correlated with soil pH values (Beckwith and Reeve 1963; Kawaguchi and Kyuma 1977; Zang 1987; He 1993; Ma et al. 1993; Wan et al. 1993; Liang et al. 1994; Shen et al. 1994; He and Li 1995; Zhang et al. 1996, 2003; Cai et al. 1997; He and Wang 1998; Zheng 1998; Li et al. 1999; Qin et al. 2012). Soil-available Si content in acid soils increased with increasing pH, organic matter and clay content (Lian 1976; He et al. 1980; Qin et al. 2012).

In contrast to South China, available Si content as extracted by acetate buffer solution in paddy soils located in the north of Yangtze River is higher (Wu et al. 1987; Ma et al. 1993; Liang et al. 1994; Zhang et al. 2003). Liang et al. (1994) showed that soil-available Si content as extracted by sodium acetate buffer was also increased with increase of pH, silt and clay content. The soils derived from river

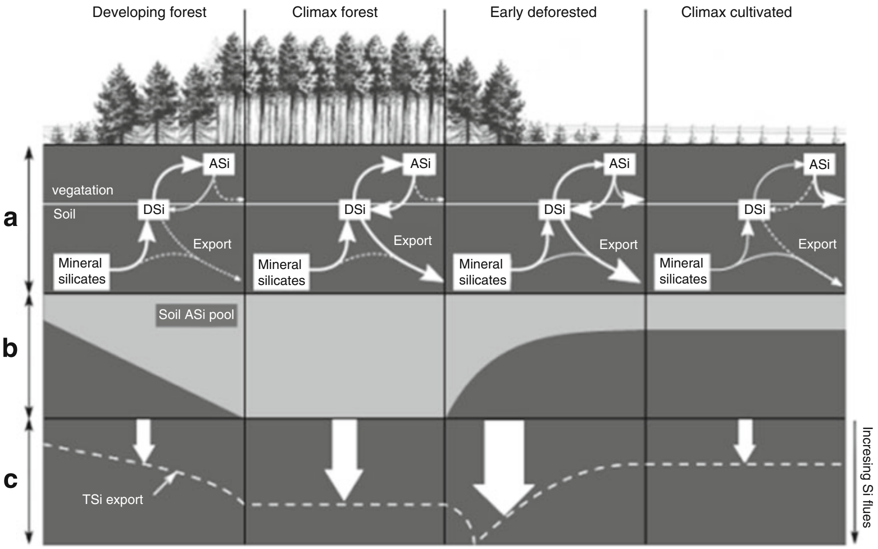


Fig. 3.5 New conceptual model for changes in Si cycling with long-term soil disturbance (From Struyf et al. 2010b). (**a**) Hypothesized Si cycling in developing forest, climax forest, early deforested areas and equilibrium cultured areas, the associated soil ASi stock (**b**) and the resultant magnitude of TSi export (**c**). *Boxes* represent stocks of Si. *Arrows* represent fluxes: the thickness of *arrows* is representative for flux size. *Dashed* arrows represent irrelevant fluxes. In (**b**), the *light grey* area represents the size of the soil ASi pool. In (**c**), the sizes of the *arrows* represent relative TSi fluxes. The *dashed line* represents the hypothesized evolution of the magnitude of the TSi fluxes: the closer the *dashed line* is to the figure *bottom*, the higher the TSi export (as also indicated by the *arrow* to the *right below*). *ASi* amorphous Si, *DSi* dissolved TSi, ASi + Dsi

alluvial and marine deposits distributed widely through the north of Yangtze River to the North China Plain to Northeast China are calcareous and alkaline. The acetate buffer-extractable Si contents in these soils ranged from 150 to 350 mg SiO_2 kg^{-1}, but the availability to plants was still lower, and rice plants responded positively to Si fertilizers (Ma et al. 1993; Liang et al. 1994; Ma et al. 1994; Zhang et al. 2003). The main reasons are that part of carbonate-bound silicates extracted by the acetate buffer solution at pH 4.0 are not plant available and the acetate buffer method overestimates the Si-supplying power of these calcareous paddy soils (Liang et al. 1994; Ma et al. 1994; Zhang et al. 2003). For these soils, there is a need either to develop a suitable extraction method or to modify the critical value of available Si content above which no positive rice yield response can be expected under field conditions (Liang et al. 1994).

Zhang et al. (2003) reported that the available Si content in Liaoning province ranged from 60 to 630 mg SiO_2 kg^{-1} with the highest levels observed in the paddy soils derived from both calcareous alluvial deposits in the North Liaoning, China, and saline marine deposits in the South Liaoning and the lowest available Si content observed in the paddy soils derived from acid alluvial deposits with light soil texture in the Central and East Liaoning. In Heilongjiang province, the available Si contents in soils tested were between 128 and 180 mg SiO_2 kg^{-1} (Wu et al. 1987). The available Si content was lower in the paddy soils derived from albic soils and meadow soils with low pH and light soil texture, but was much higher in the paddy soils derived from black soils and meadow black soils. In East Jilin province, the available Si content in soils tested ranged from 118 to 262 mg SiO_2 kg^{-1} and the lowest was found in cold-water paddy soils, followed by the paddy soils derived from albic soils, alluvial soils, black soils and meadow soils (Zhang et al. 1994).

3.3.2.4 Soil Eh

Soil Eh is one of the most important factors that influence the solubility of soil Si. Flooding results in soil reduction, lowering soil Eh and normally leading to an increase in soil-available Si concentration. Ponnamperuma (1965) reported that submergence of soil led to a marked decrease in soil Eh and concurrent increase in solubility of soil Si with submergence time. In one soil with pH of 4.8 and organic matter of 4.4 %, the concentration of Si increased from 24 to 41 mg kg in less than 50 days after submergence. However, it was also reported that Si concentration in the soil solution slightly increased after flooding and then decreased gradually and, after several months of submergence, may be lower than at the beginning (Liang et al. 1992). Liang et al. (1992) reported that the concentration of Si in soil solution ranged from 5.2 to 10.5 mg SiO_2 L^{-1} in a waterlogging paddy soil (pH 6.5) derived from Xiashu loess and a de-gleyed paddy soil (pH 7.8) developed from bog soil in Jiangsu province in China during a 60-day-period incubation. The concentration of soil-available Si in the waterlogging paddy soil doubled after submergence for 5 days and then reached a peak at 40 days and dropped slightly at 60 days. The soil-available Si content was found to have a logarithmic dependence on the days of submergence. However, for the de-gleyed paddy soil (pH 7.8) developed from bog soil, the soil-available Si concentration had a different dynamics: after 5 days of submergence, it increased only slightly, then had a peak on the 10th day, followed by a slow decrease on the 20th day, and continued to drop afterwards to a level before submergence. The distinct difference in flooding effect on soil-available Si concentration in these two paddy soils tested, especially during the early period of submergence (at 5 days), may be attributed to the differences in redox conditions; the de-gleyed paddy soil (pH 7.8) was initially more reduced than the waterlogged paddy soils (pH 6.5) (Liang et al. 1992).

The increase in Si concentration after flooding may be due to the release of silica following (a) reduction of hydrous ferric oxides which adsorb silica and (b) action of CO_2 on aluminosilicates (Imaizumi and Yoshidai 1958; Nayer et al. 1977; Ponnamperuma 1978; Liang et al. 1992). The subsequent decrease may be ascribed to recombination of Si with aluminosilicates following the decrease in the pressure of CO_2 (Ponnamperuma 1978). However, Wei et al. (1997) reported that Eh effect on Si availability depended upon soil types. For example, the available Si content increased progressively with soil reduction in a clay-textured purple soil but decreased in two sand-textured purple soils.

3.3.2.5 Soil Texture

Many studies have shown that soils with light or sandy texture are usually deficient in available Si and thus have low Si-supplying power, while those with heavy or clayey texture are Si sufficient (Kawaguchi and Kyuma 1977; He 1993; Ma et al. 1993; Wan et al. 1993; Liang et al. 1994; He and Li 1995; Zhang et al. 1996, 2003; Cai et al. 1997; Zheng 1998; Li et al. 1999). Soil-available Si content is positively correlated with clay content in soils (Wan et al. 1993; Zhang et al. 1996; Dai et al. 2004) as soil clay minerals with high specific surface have a high capacity to adsorb silicates. Some researchers reported that soil-available Si content was positively correlated with physical clay (< 0.01 mm) fraction but not with smaller clay (< 0.002 mm) in soils (Shen et al. 1994; Yu et al. 1998). He and Wang (1998) reported that the effect of soil particle size on soil-available Si content was dependent on soil acidity. In acid soils (pH bellow 6.5), pH and clay content were significantly positively related to the soil-available Si content, whereas in the soils with pH above 6.5, only pH and silt and sand fractions were negatively correlated with soil-available Si content.

3.3.2.6 Organic Matter

So far, contrasting results on the effects of soil organic matter on Si availability have been reported. Most of the authors agree that soil-available Si content is positively correlated with soil organic matter content (Lian 1976; Shen et al. 1994; Yu et al. 1998; Qin et al. 2012), while others believe that little or even negative relationship existed between soil-available Si content and organic matter content (Zang 1987; Wan et al. 1993). These contrasting results may be ascribed to the differences of soil types investigated.

3.3.2.7 Adsorption–Desorption Balance

The concentrations of plant-available Si fractions in soil were shown to be governed by processes of Si adsorption on reactive soil materials (primarily sesquioxides) and of Si desorption in the form of soluble Si in soil solution (Mckeague and Cline 1963; Jones and Handreck 1967). The properties of soil adsorption complex (its sorption and desorption characteristics) were consequently shown to largely affect the plant-available Si fraction (Elgawhary and Lindsay 1972; Wei et al. 1997; Yu and Li 1999; Yang et al. 2008, 2010, 2012).

The sorption–desorption characteristics of soils are dependent largely upon soil type and amendment with soluble or amorphous Si. The desorption of Si from a suspension of a calcareous silt loam soil was shown to be different in treatments with and without Si addition (Elgawhary and Lindsay 1972). In the soil suspension without Si addition, the concentration of Si was 18 mg Si L^{-1} at 1 day, 22 mg Si L^{-1} at 10 days and 25 mg Si L^{-1} at 50 days of incubation, while the soil suspension initially treated with 100 mg L^{-1} of soluble Si contained 27 mg Si L^{-1} at 1 day and 25 mg Si L^{-1} after 10 days and remained at 25 mg Si L^{-1} during the subsequent 50-day reaction period (Elgawhary and Lindsay 1972). This suggests that such a calcareous soil maintains an equilibrium level of Si of approximately 25 mg Si L^{-1}. The addition of 10 % amorphous Si led to a steady soil suspension Si concentration at 50 mg Si L^{-1} during the 30th to 50th day of incubation, whereas inclusion of 100 mg Si L^{-1} of soluble Si with the amorphous Si treatment showed little effect. These results seem to suggest that the solid phase of Si in this soil maintained Si levels below the solubility of amorphous Si (51 mg L^{-1}) but above that of quartz (2.8 mg L^{-1}) (Elgawhary and Lindsay 1972). By contrast, in an acidic sandy loam humid soil, the same authors found different Si adsorption–desorption behaviour. Without Si addition, the dynamics of Si in a soil suspension showed an increased trend during the 50-day experimental period and approached 19 mg Si L^{-1} after 50 days, while the addition of 100 mg L^{-1} of soluble Si caused a drop from 32 mg L^{-1} to a constant level of 19 mg L^{-1} between days 30 and 50. The amorphous Si treatment approached equilibrium at about 46 mg L^{-1}. Based on the experimental results of Elgawhary and Lindsay (1972) who measured the solubility of Si in two soils in which equilibrium was approached from both undersaturation and supersaturation, the SiO_2 (soil) concentration was $10^{-3.10}$ M and was intermediate between quartz and amorphous silica, corresponding to Reaction 4 of Table 3.1. In highly weathered tropical acid soils such as oxisols, SiO_2 may be severely leached out of the soil profiles and become depleted due to desilification and fersialitization during weathering and soil-forming processes. Consequently, sesquioxides rather than silicate clay minerals are the dominant residual secondary minerals. In such soils, the solubility of H_4SiO_4 is below that of quartz (10^{-4} M).

Using five paddy soils derived from lake and alluvial deposits and one latosol as testing materials, Yu and Li (1999) found that (1) the isothermal sorption of Si fitted well into Langmuir, Freundlich and Temkin equation and the conventional Langmuir equation seemed to be the best one to describe the sorption characteristics with high significant correlation coefficients; (2) the parameters calculated in the Langmuir equations, namely, the adsorption maximum (Xm) and maximum buffering capacity (MBC), were good parameters to assess Si sorption characteristics; (3) Xm and MBC were closely related to contents of soil clay (<0. 01 mm) and sesquioxides; and (4) approximately only 26–53 % of the adsorbed Si could be desorbed by water. However, Yang et al. (2010) reported recently that neither Langmuir equation nor Freundlich equation could be used to describe Si adsorption on meadow soils used for vegetable production in Northeast China. Rather, both the linear equation ($y=bx-a$) and Temkin equation could be used to accurately describe Si adsorption characteristics of these soils and the linear equation was more suitable for describing Si adsorption characteristics. Furthermore, significant positive linear correlations and quadratic equation existed between the regression parameters (a and b) and soil pH or organic matter. So the isothermal adsorption equation could be used to evaluate Si-supplying capability in the vegetable soils tested. It seems that soil sorption and desorption characteristics are largely dependent upon soil type, pH and clay type.

It was reported that exponential equations could be used to express the Si sorption kinetics of soils incorporated with blast furnace slag, coal fly ash and diamond slag; the accumulative releasing amount of Si at 127 days after incubation increased exponentially with time and was much higher in slag- or coal fly ash-treated soils than in control soil, suggesting that the soil Si-supplying capacities were greatly improved by addition of slag materials (Yang et al. 2008). In 20 meadow soils used for vegetable production, Yang et al. (2012) recently investigated the Si release kinetics and found that the relationship between the cumulative amount of released Si (Y) and the incubation time (X) could be expressed in the following exponential equation: $Y=kX^m$, where k and m are constants, k represents the initial Si release amount and is linearly related to soil pH, organic matter and free iron oxide contents, and m represents initial Si release rate and is also linearly correlated with soil pH, organic matter and free iron oxide contents.

3.4 Silicon-Supplying Power and Silicon Deficiency

It is critically important to understand Si-supplying power or capacity in soils in order to assess whether the amount of plant-available Si in soils is sufficient for optimized crop production. In general, Si-supplying power can be estimated by testing Si status in soils, plants and irrigation water. Generally, Si content in plant tissues is the most relevant value to directly indicate whether Si deficiency occurs or not, but soil testing can help predict Si nutritional status in plants and prevent Si deficiency by applying Si fertilizers before planting. Si level in irrigation water is also one of the useful parameters for prognosis of crop Si deficiency. In practice, it is essential to obtain information on Si status in soils, plants and irrigation water in combination with crop species and varieties to be planted for integrated crop Si nutrient management.

3.4.1 Soil Testing

Analysis of soil-available Si is one of the most commonly used approaches to determine whether Si deficiency will occur or not in a given soil. However, soil-available Si is determined by different methods involving different extracts (see Chap. 2 for more details). The most commonly used extractant is sodium acetate buffer method (pH 4.0) proposed by Imaizumi and Yoshidai (1958) as there exists a critical value or threshold value below which positive rice yield response to Si fertilization can be expected. The threshold value for soil-available Si content varies from one country to another, ranging from 105 mg SiO_2 kg^{-1} in Japan (Imaizumi and Yoshidai 1958; Lian 1976), 100 mg SiO_2 kg^{-1} in Korea (Lian 1976), 40 mg SiO_2 kg^{-1} in Chinese Taiwan (Lian 1976) and 95–100 mg SiO_2 kg^{-1} in China (He et al. 1980; Zhang et al. 2003). According to this criterion, soils low or deficient in available Si content are mainly scattered over the highly weathered acid soils in tropical and subtropical areas. In Japan, many studies were done on Si-supplying capacity and Si fertilizer application to rice crop in the 1950s (Imaizumi and Yoshidai 1958; Ma and Takahashi 2002). In Korea, investigations were carried out including testing and diagnosis of Si availability in Korean paddy soil samples taken randomly from 365 sites, modification of the acetate buffer method proposed by Imaizumi and Yoshidai (1958) and large-scale field trials on optimized application rates of various types of calcium silicates in rice crop during the 1960s (Park 2001). In South and Southeast China, Si deficiency has been frequently reported since 1970 (Qin 1979; He et al. 1980; Ma et al. 1985; Fan et al. 1989) with most of the work done in the 1990s (Yi and Zhang 1991; He 1993; Wan et al. 1993; Ma et al. 1994; Shen et al. 1994; He and Li 1995; Ge and Li 1996; Cai et al. 1997; Yu et al. 1998; Zheng 1998; He and Wang 1998; Li et al. 1999).

However, the suitability of this criterion for assessing Si deficiency, established half a century ago, is increasingly challenged by mounting evidence from field trials that has clearly demonstrated rice yield responses to Si fertilizers in soils with levels of available Si much higher than the universally recognized critical value (100–130 mg SiO_2 kg^{-1}). Si deficiency, diagnosed on the basis of the extraction with sodium acetate buffer, is reported more frequently than before in East China, Central China, Northeast China and even Northwest China (Wu et al. 1987; Ma et al. 1993, 1994; Liang et al. 1994; Zhang et al. 1994; Mao and Wang 2002).

Liang et al. (1994) reported that the sodium acetate buffer-extractable Si content of calcareous paddy soils in Nantong of North Jiangsu province ranged from 152 to 388 mg SiO_2 kg^{-1} and still rice and wheat yields responded positively to the application of Si fertilizer to these soils. Therefore, it seems that the acetate buffer probably overestimates the Si-supplying power in calcareous soils under field conditions as this buffer can extract some Si bound to carbonates which is not plant available (Liang et al. 1994; Ma et al. 1994). Similar findings of positive rice yield responses to Si fertilizers were reported in calcareous and alkaline paddy soils in Liaoning and Heilongjiang provinces of Northeast China (Li et al. 2002; Zhang et al. 2003; Luo 2004; Liu et al. 2006). For example, Li et al. (2002) investigated the Si-supplying power of the paddy soils with pH ranging from 5.2 to 8.3 during an 8-week-incubation experiment. The results indicated that the alkaline soil (pH 8.3) had the lowest Si-supplying power and the lowest water-soluble Si levels, although its acetate buffer-extractable Si content was the highest. The application of sodium metasilicate to this alkaline paddy soil increased rice yield by as much as 197 %. A pot experiment using an alkaline soil with pH of 9.24 and acetate buffer-extractable SiO_2 content of 438.5 mg SiO_2 kg^{-1} showed that application of sodium metasilicate and slag silicate fertilizer increased rice yield by 7.8 and 10.6 %, respectively (Liu et al. 2006). These results suggest that acetate buffer method is not suitable for assessing the Si-supplying power of alkaline soils, a result consistent with the reports on calcareous soils by Liang et al. (1994) and Ma et al. (1994). Liang et al. (1994) proposed that either the threshold or critical value below which positive rice yield response can be expected should be revised (raised) or a more suitable new soil testing method (probably extractant) should be developed for the high-pH calcareous soils. According to Sumida (1992), the critical value of the acetate buffer-extractable soil-available Si content for rice is 300 mg SiO_2 kg^{-1}. Based on seven field trials on slag silicate fertilizer in paddy soils derived from quaternary red earth, red sandstone and alluvial deposits in Dangyang City of Hubei province, Xu et al. (1993) proposed that the critical value of soil-available Si content for hybrid rice growth was 200 mg SiO_2 kg^{-1}. Kawaguchi and Kyuma (1977) reported that the soil-available Si content in tropical Asia ranged from 104 to 629 mg SiO_2 kg^{-1} and the available Si content was reported to be the highest in soils of Indonesia among Asian countries (Kawaguchi and Kyuma 1977). However, recent studies indicate that 12 sawah sites out of 16 in Citarum and 9 sawah out of 15 were low or deficient in available Si contents for rice growth (Husnain et al. 2008).

To summarize, soil testing for available Si using sodium acetate buffer method provides an estimate of Si-supplying power in acid soils. First, the threshold value of soil-available Si content set for acid soils generally works for rice although it differs from one country to another. Second, more and more convincing evidence shows that rice responds positively to Si fertilization in soils where available Si content is higher than the threshold value, suggesting that the threshold value should be revised (raised). Third, the sodium acetate buffer method seems to overestimate the Si-supplying power in calcareous and/or saline (alkaline) soils; thus, a new threshold value is needed for assessing whether Si is sufficient or deficient in calcareous and/or saline (alkaline) soils. Fourth, although there are many methods (mainly extractants) proposed to test soil-available Si content (see Chap. 2), no threshold values are available for the majorities of the extractants used except for the sodium acetate buffer method. Additional lab and field studies are needed to work out a universally recognized threshold value for Si extractants. Additionally, threshold values should be established for other crops of agricultural importance such as sugarcane, wheat, barley, maize, sorghum and vegetable and fruit crops.

3.4.2 Plant Testing

Soil-available Si status can affect plant growth, yield and quality and can be expressed in plant vegetative growth performance and yield and Si content in plant tissues. Although Si-deficient rice usually has some deficiency symptoms such as soft and droopy leaves, weeping willow-like appearance as described by Lewin and Reimann (1969), chemical analysis of Si content in rice straw is a reliable measure of Si status in plants. Therefore, plant Si testing is needed together with soil testing to help understand the Si nutritional status in plants. Several protocols are currently available for routine analysis of plant Si content (for details, see Chap. 2). On the basis of a large number of field trials conducted in Asian countries to correlate Si content of rice straw with rice yield response to Si fertilization, the threshold or critical Si content in straw for zero yield response to slag application was proposed. The threshold value or critical value varies from one country to another. For example, if SiO_2 content in the straw of mature rice is less than 13 % in Japan and Korea, 10 % in South China, and 11 % for both early and late rice in Chinese Taiwan, Si deficiency might occur and Si fertilization should be recommended (Lian 1976; Zang et al. 1982; Savant et al. 1997). It was reported that *japonica* rice with straw SiO_2 content of less than 11 % responded positively to slag-based calcium silicates in some cooler ecoregions (Savant et al. 1997), whereas in tropical ecoregions such as Sri Lanka and India, *indica* rice with straw SiO_2 content of less than 8 % might respond to Si applications (Nair and Aiyer 1968; Takijima et al. 1970). Snyder et al. (1986) reported that more than 6.4 % SiO_2 in rice straw was needed for good rice yield on organic soils (histosols) of the Everglades Agricultural Area in Florida. Xu et al. (1993) reported that rice with flag-leaf SiO_2 content of less than 14 % might respond positively to application of slag (averaged yield increase by 11 %). The rice yield (Y) was correlated linearly with flag-leaf SiO_2 content (X) in the following regression equation: $Y = 243.4 + 13.19X$.

3.4.3 Irrigation Water Testing

The average dissolved silica concentration (run-off weighted average) for the exorheic parts of Africa, Europe, North America, South America, Asia and Australia is 12.6, 5.6, 8.0, 9.0, 10.0 and 11.8 mg SiO_2 L^{-1}, respectively, with an average of 9.5 mg SiO_2 L^{-1} (Dürr et al. 2011). Si concentration for eastern UK rivers and tributaries ranges from 0 to 34.7 mg SiO_2 L^{-1} (Neal et al. 2005 and references therein), depending on many geological and soil factors. The Si concentration of surface waters across the UK ranges from 0 to 40.7 mg SiO_2 L^{-1} (Neal et al. 2005), which is well within that found for many rivers globally (Meybeck 1980; Berner and Berner 1996). As rice is known to be a typical Si-hyperaccumulating plant species, Si supply from irrigation water plays an important role in Si nutritional status in rice. After having analysed 400 irrigation water, soil and rice samples, Imaizumi and Yoshida (1958) pointed out that the amount of Si coming from irrigation water and from soils accounted approximately for 27 % and 73 % of the total amount of Si taken up by rice, respectively, showing that Si supply from irrigation water is of great significance to rice growth and development. Total Si content in rice straw is significantly correlated with the Si content in irrigation water. Generally, the SiO_2 concentration in irrigation water less than 10 mg L^{-1} implies a high probability of Si deficiency in rice (Liang et al. 1993). Mao (1986) found that the premature senility in rice grown in paddy soils derived from red sandstone could be attributed to both low plant-available Si content in soil and low Si concentration in irrigation water (11.8–21.3 mg SiO_2 L^{-1}). It was reported by Wang et al. (1999) that the application of slag Si fertilizers to paddy soils with an average plant-available Si content of 307 mg SiO_2 kg^{-1} still increased rice yield by 3–9 %, because the average Si concentration in irrigation water was only 4.8 mg SiO_2 L^{-1} (ranging from 1.2 to 11.8 mg SiO_2 L^{-1}), suggesting the importance of Si in irrigation water for sustainable rice production.

References

Alexandre A, Meunier JD, Colin F, Koud JM. Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochim Cosmochim Acta. 1997;61:677–82.

Beckwith RS, Reeve R. Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. Aust J Soil Res. 1963;1:157–68.

Berner EK, Berner RA. Global environment: Water, air and geochemical cycles. Upper Saddle River: Prentice Hall; 1996. 376 pp.

Blecker SW, McCulley RL, Chadwick OA, Kelly EF. Biologic cycling of silica across a grassland bioclimosequence. Global Biogeochem Cycles. 2006;20, GB3023. doi:10.1029/2006GB002690.

Bluth GJS, Kump LR. Lithologic and climatologic controls of river chemistry. Geochimica et Cosmochimica Acta. 1994;58:2341–59.

Cai AY, Xue ZZ, Peng JG, Lu HD, Lin YJ. Studies of available silica content in the soils of Fujian province and the prerequisite for its variation. J Fujian Acad Agric Sci. 1997;12(4):47–51 (In Chinese with English abstract).

Clarke FW (1924) Data of geochemistry (5th ed., No. 770). U.S. G.S. Survey Bull., 841 pp.

Conley DJ. Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem Cycles. 2002;16:1121.

Dai GL, Duanmu HS, Wang Z, Zhao YB, Zhu G, Zhou J. Study on characteristics of available silicon content in Shaanxi province. J Soil Water Conserv. 2004;18:51–3 (In Chinese with English abstract).

Deer WA, Howie RA, Zussman J. An introduction to the rock-forming minerals. 2nd ed. London: Longman; 1992.

Drees LR, Wilding LP, Smeck NE, Senkayi AL. Silica in soils: quartz, and disordered silica polymorphs. In: Dixon JB, Weed SB, editors. Minerals in soil environments. 2nd ed. Madison: Soil Science Society of America; 1989. p. 471–552.

Dürr HH, Meybeck M, Hartmann J, Laruelle GG, Roubeix V. Global spatial distribution of natural riverine silica inputs to the coastal zone. Biogeosciences. 2011;8:597–620.

Elgawhary SM, Lindsay LW. Solubility of silica in soils. Soil Sci Soc Am Proc. 1972;36:439–42.

Epstein E. The anomaly of silicon in plant biology. Proc Natl Acad Sci U S A. 1994;91:11–7.

Fan YC, Tao QX, Zhang MH. Silicon nutrition of rice and yield effect of silicon fertilizer in Jiangxi province. In: Chemical fertilizer application in China. Beijing: Beijing Science and Technology Press; 1989. p. 434–5 (In Chinese).

Fox RL, Silva JA, Younge OR, Plucknett DL, Sherman GD. Soil and plant silicon and silicate response by sugarcane. Soil Sci Soc Am Proc. 1967;31:775–9.

Friesen DK, Sanz JI, Correa FJ, Winslow MD, Okada K, Datnoff LE, Snyder GH. Silicon deficiency of upland rice on highly weathered Savanna soils in Colombia. I. Evidence of a major yield constraint. IX Conferencia Internaciaonal de arroz para a America Latina e para o Caribe, V Reuniao Nacional de Pesquisa de Arroz; 21–25 Marco; Castro's Park Hotel. Goiania, Brasil; 1994.

Fulweiler RW, Nixon SW. Terrestrial vegetation and the seasonal cycle of dissolved silica in a southern New England coastal river. Biogeochemistry. 2005;74:115–30.

Gascho GJ. Silicon Sources for Agriculture. In: Datnoff LE, Snyder GH, Korndorfer GH, editors. Silicon in agriculture. Amsterdam: Elsevier Science B.V.; 2001. p. 197–207.

Ge XL, Li SL. General introduction to silicon nutrient status and silicon fertilizer application in croplands of Zhejiang province. Zhejiang Agric Sci. 1996;2:76–7 (In Chinese).

Gérard F, Mayer KU, Hodson MJ, Ranger J. Modelling the biogeochemical cycle of silicon in soils: application to a temperate forest ecosystem. Geochim Cosmochim Acta. 2008; 72:741–58.

He DY, Zang HL, Zhang XP. The effect of silicate slags on rice in paddy soils derived from red earth. Acta Pedol Sin. 1980;17:355–63 (In Chinese with English abstract).

He DY. Form, content and availability of silicon in main farmland of Hunan province and research on furnace slag fertilizer. Res Agric Modern. 1993;14:43–7 (In Chinese).

He LY, Li XL. Content and distribution of available silicon in paddy soils of Hubei province. J Huazhong Agric Univ. 1995;14:363–8 (In Chinese with English abstract).

He LY, Wang ZL. Study on relationships between soil particle size or pH and soil available silicon content. Soils. 1998;5:243–6 (In Chinese).

House WA, Leach DV, Armitage PD. Study of dissolved silicon and nitrate dynamics in a freshwater stream. Water Res. 2001;35:2749–57.

Hurlbut CS, Klein C. Manual of mineralogy. 20th ed. New York: Wiley; 1985.

Husnain, Wakatsuki T, Setyorini D, Hermansah SK, Masunaga T. Silica availability in soils and river water in two watersheds on Java Island, Indonesia. Soil Sci Plant Nutr. 2008;54:916–27.

Iler RK. The Chemistry of Silica. New York: Wiley; 1979.

Imaizumi K, Yoshidai S. Edaphological studies on the silicon supplying power of paddy soils. Bull Natl Inst Agric Sci Tokyo. 1958;B8:261–304.

Jackson ML. Soil chemical analysis. Englewood Cliffs: Prentice-Hall; 1958.

Jenny H. The soil resource: origin and behavior, Ecological studies 37. New York: Springer; 1980. p. 95–112.

Jones LHP, Handreck KA. Silica in soils, plants and animals. Adv Agron. 1967;19:107–49.

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

Kobayashi J. A chemical study of the average quality and characteristics of river waters of Japan. Berichte Ohara Institute für Landwirtschaft Biologie. 1960;11:313–57.

Lewin J, Reimann BEF. Silicon and plant growth. Annu Rev Plant Physiol. 1969;20:289–304.

Li ZZ, Tao QX, Liu GR, Zhang HZ, Liu YR. Investigation of available silicon content in cultivated soil in Jiangxi province. Acta Agric Jiangxi. 1999;11:1–9 (In Chinese with English abstract).

Li J, Zhang YL, Liu MD, Yu N, Huang Y, Yang LJ. Study on silicon-supplying capacity and efficiency of siliceous fertilizer in paddy soils in Liaoning province. Chin J Soil Sci. 2002;33:142–4 (In Chinese with English abstract).

Lian S. Silica fertilization of rice. In: The fertility of paddy soils and fertilizer applications for rice. Taipei: Food Fertilizer Technology Center; 1976. p. 197–220.

Liang YC, Chen XH, Zhang YC, Ma TS. Effects of flooding and incorporation of organic materials on soil available silicon. Soils. 1992;5:244–7 (In Chinese).

Liang YC, Zhang YC, Ma TS. Silicon nutrition of higher plants. Prog Soil Sci. 1993;21:7–14 (In Chinese).

Liang YC, Ma TS, Li FJ, Feng YJ. Silicon availability and response of rice and wheat to silicon in calcareous soils. Commun Soil Sci Plant Anal. 1994;25:2285–97.

Lindsay WL. Chemical equilibrium in soil. New York: Wiley; 1979.

Liu MD, Zhang YL, Meng XF, Li J, Yang D, Wang YJ. Fertilizer response of silicon on rice in alkaline paddy soil. Chin J Soil Sci. 2006;37:554–9 (In Chinese with English abstract).

Liu SM, Ye XW, Zhang J, Zhang GS, Wu Y. The silicon balance in Jiaozhou Bay, North China. J Mar Syst. 2008;74:639–48.

Luo JB. Silicon effect on rice grown on soda solonchak paddy soils of Heilongjiang province. Inner Mongolia Agric Sci Technol. 2004;4:31–3 (In Chinese).

Ma TS, Qian ZR, Zhang ZF, Shu JM, Wang HY. Study on the paddy soils V. Preliminary study on the availability of silica in paddy soil of Jiangsu hilly area and the effect of slag silica fertilizer. J Nanjing Agric Univ. 1985;4:67–73 (In Chinese with English abstract).

Ma GR, He NZ, Shi WY. A survey on the concentration of sulphur, potassium and silicon and the pH value of the major water streams in Zhejiang province. Zhejiang Agric Sci. 1987;1:14–7 (In Chinese).

Ma TS, Li FJ, Liang YC, Chen XH. Silicon nutrient status and yield increase effect of silicon fertilizers. Chin J Soil Sci. 1993;24:262–3 (In Chinese).

Ma TS, Feng YJ, Liang YC, Hua W, Sun B, Wang QS, Huang SH, Zhang BK. Silicon supplying power and silicon fertilizer application in areas along Yangtze River. Soils. 1994;26:154–6 (In Chinese).

Ma JF, Takahashi E. Soil, fertilizer, and plant silicon research in Japan. Amsterdam: Elsevier; 2002. p. 1–190.

Mackenzie FT, Garrels RM, Bricker OP, Bickley F. Silica in sea water-control by silica minerals. Science. 1967;155:1404–5.

Mao DM. Analysis of causes for premature senility of rice grown on paddy soil derived from red sandstone and its prevention and control. Zhejiang Agric Sci. 1986;5:213–5 (In Chinese).

Mao GF, Wang CB. Available silicon status in croplands of Shanghai district and effectiveness of silicon fertilizers in rice. Soils. 2002;5:280–73 (In Chinese).

Martin DF. Marine Chemistry, vol. 2. New York: Dekker; 1970.

McKeague JA, Cline MG. Silica in soils. Adv Agron. 1963;15:339–96.

Meybeck M. Global chemical weathering of surficial rocks estimated from river dissolved loads. Am J Sci. 1987;287:401–28.

Meybeck M. Pathways of major elements from land to ocean through rivers. In: Martin JM, Burton JD, Eisma D, editors. Proceedings of the review and workshop on river inputs to ocean-systems; 1980. p. 18–30.

Nair PK, Aiyer RS. Status of available silica in the rice soils of Kerala State (India). II. Silicon uptake by different varieties of rice in relation to available silica contributed by soil and irrigation water. Agric Res J Kerala. 1968;6:88–94.

Nayer PK, Misra AK, Patnaik S. Evaluation of silica-supplying power of soils for growing rice. Plant Soil. 1977;47:487–94.

Neal C, Neal M, Reynolds B, Maberly SC, May L, Ferrier RC, Smitha J, Parker JE. Silicon concentrations in UK surface waters. J Hydrol. 2005;304:75–93.

Park CS. Past and future advances in silicon research in the Republic of Korea. In: Datnoff LE, Snyder GH, Korndörfer GH, editors. Silicon in agriculture. Amsterdam: Elsevier; 2001. p. 359–71.

Ponnamperuma FN. Dynamic aspects of flooded soils and the nutrition of the rice plant. In: The mineral nutrition of the rice plant. Baltimore: John Hopkins; 1965. p. 295–328.

Ponnamperuma FN. Soils and rice. Philippine: Los Banos; 1978. p. 427.

Qian FJ, Cai DL, Deng T. Silicon concentration in irrigation water and its distribution in Henan province. Area Res Dev. 1995;14:66–8 (In Chinese).

Qin RC. Effect of silicon fertilizer on disease resistance and yield increase in rice. Zhejiang Agric Sci. 1979;1:12–5 (In Chinese).

Qin FJ, Wang F, Lu H, Cen TX, Wang B, Han HX, Zhuang YQ, Zhang H. Study on available silicon contents in cultivated land and its influencing factors in Ningbo City. Acta Agric Zhejiangensis. 2012;24:263–7 (In Chinese with English abstract).

Quan WJ, Zou Q, Du CX. Available silicon content in soil and its distribution in Shandong province. Shandong Agric Sci. 1999;5:11–4 (In Chinese with English abstract).

Savant NK, Snyder GH, Datnoff LE. Silicon management and sustainable rice production. Adv Agron. 1997;58:151–99.

Shen YZ, Pan WQ, Xu JB, Fu CC. Dynamic changes of soil available silicon over last decade in Yangzhou City and application of silicon fertilizers to rice. Soil Fertil. 1994;5:23–6 (In Chinese).

Snyder GH, Jones DB, Gascho GJ. Silicon fertilization of rice on Everglades Histosols. Soil Sci Soc Am J. 1986;50:1259–63.

Struyf E, Smis A, Van Damme S, Meire P, Conley DJ. The global biogeochemical silicon cycle. Silicon. 2010a;1:207–13.

Struyf E, Smis A, Van Damme S, Garnier J, Govers G, Van Wesemael B, Conley DJ, Batelaan O, Frot E, Clymans W, Vandevenne F, Lancelot C, Goos P, Meire P. Historical land use change has lowered terrestrial silica mobilization. Nature Commun. 2010b. doi:10.1038/ncomms1128.

Sumida H. Silicon supplying capacity of paddy soils and characteristics of silicon uptake by rice plants in cool regions in Japan. Bull Tohoku Natl Agric Exp Station. 1992;85:1–46 (In Japanese with English summary).

Sumida H. Plant-available silicon in paddy soils. Proceedings of the Second Silicon in Agriculture Conference; 2002 August 22–26; Tsuruoka, Yamagata, Japan; 2002. pp. 43–49.

Takijima Y, Wijayaratna HMS, Seneviratne CJ. Nutrient deficiency and physiological disease of lowland rice in Ceylon. III. Effect of silicate fertilizers and dolomite for increasing rice yields. Soil Sci Plant Nutr. 1970;16:11–6.

Tardy Y, Bocquier G, Paquet H, Millot G. Formation of clay from granite and its distribution in relation to climate and topography. Geoderma. 1973;10:271–84.

Wan XS, He DY, Liao XL. Silicon forms of soils in Hunan province in relation to soil properties. Soils. 1993;25:146–51 (In Chinese).

Wang CB, Mao GF, Jiang ZT. Study on rice silicon nutrition status in Shanghai region and effects of silicon fertilizer. Acta Agric Shanghai. 1999;15:65–9 (In Chinese with English abstract).

Wei CF, Yang JH, Gao M, Xie DT, Li QZ, Li HL, Li J, Xiang TC. Study on availability of silicon in paddy soils from purple soil. J Plant Nutr Fertil. 1997;3:229–36 (In Chinese with English abstract).

White AF, Blum AE. Effects of climate on chemical weathering in watersheds. Geochimica et Cosmochimica Acta. 1995;66:1891–904.

Winslow MD, Okada K, Correa-Victoria F. Silicon deficiency and the adaptation of tropical rice ecotypes. Plant Soil. 1997;188:239–48.

Wu Y, Zhao XC, Li SF. Study on silicon fertilizer effect on rice in varying types of soils in Heilongjiang province. Heilongjiang Agric Sci. 1987;5:8–12 (In Chinese).

Xu SL, He SK, Gao GW, Zhou HL, Xiong BX, Shen CQ. Efficacy of calcium silicate fertilizer in hybrid rice. Chin J Soil Sci. 1993;24:264–6 (In Chinese).

Yang D, Zhang YL, Liu MD, Yu N. Silicon liberation characteristics of soil and its affecting factors after applying slag mucks. II Relationship between silicon liberation and pH. Chin J Soil Sci. 2008;39:726–9 (In Chinese with English abstract).

Yang D, Zhang YL, Liu MD, Wang CX, An J. Evaluation of silicon supplying capability in greenhouse soil with adsorption isotherm. J Shenyang Agric Univ. 2010;41:540–4 (In Chinese with English abstract).

Yang D, Zhang YL, Liu MD, Wang CX. Characteristics of silicon releasing kinetics in greenhouse soil. Chin J Soil Sci. 2012;43:42–6 (In Chinese with English abstract).

Yi XR, Zhang M. Available silicon content in paddy soils and perspectives of silicon fertilizer application in East and Central Guizhou province. Tillage Cultiv. 1991;5:51–3 (In Chinese).

Yu QY, Li XL. Study on adsorption and desorption of silicon in soils. J Anhui Agrotech Teachers Coll. 1999;13:1–6 (In Chinese with English abstract).

Yu QY, Li XL, Zhang YL. Available silicon distribution and affecting factors in paddy soils of Anhui province. J Anhui Agrotech Teachers Coll. 1998;12:5–9 (In Chinese with English abstract).

Zang HL. A preliminary study on changes in soil available silicon content. Soils. 1987;19:123–5 (In Chinese).

Zang HL, Zhang XP, He DY. On the silicon supplying capacity of paddy soils in South China. Acta Pedol Sin. 1982;19:131–40 (In Chinese with English abstract).

Zhang W, Wang WD, Zhan YL, Li DY, Zhang DL. Available silicon status and effectiveness of silicon fertilizer in paddy soils of East Jilin province. Chin J Soil Sci. 1994;25:37–9 (In Chinese with English abstract).

Zhang XM, Zhang ZY, Yin KS, Li GL, Qiu ZX, Liu YQ. Study on the available silicon content and its relationship with soil physico-chemical properties. J Heilongjiang August First Land Reclam Univ. 1996;8:42–5 (In Chinese with English abstract).

Zhang YL, Li J, Liu MD, Huang Y. A preliminary study of soil silicon status of paddy soils in Liaoning province. Chin J Soil Sci. 2003;34:543–7 (In Chinese with English abstract).

Zheng L. Available silicon content and its distribution in cultivated soils in Anhui province. Chin J Soil Sci. 1998;29:126–8 (In Chinese with English abstract).