

Chapter 13

The relationship between silicon and soil physical and chemical properties

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Soil minerals and organic matter control physical and chemical soil properties. Silicon (Si) is a basic mineral formatting element. The aim of our investigation was to obtain information about the effect of Si fertilization on physical and chemical soil properties. Silicon fertilization has been reported to result in increased soil exchange capacity, improved water and air regimes, transformation of P-containing minerals and formation of aluminosilicates and heavy metal silicates. All these effects are caused by the change in soil mineral composition that results from silicate addition (Si fertilizers) and/or formation of new clay minerals, which are characterized by high biogeochemical activity. They have large surface area and are able to adsorb water, phosphates, potassium (K), nitrogen (N), aluminum (Al), and heavy metals. Adsorption may occur as chemisorptions or physical sorption. Cations (Al, heavy metals) usually are chemisorbed on Si-rich surface and lose their mobility. Phosphates and N are weakly adsorbed and remain in plant-available form. Amorphous silica, montmorillonite, and vermiculite represent the newly-formed minerals. These minerals affect the soil composition, and physical and chemical properties. The amounts of amorphous silica, monosilicic acids, and polysilicic acids in the soil are closely related to each other. Monosilicic acids regulate chemical properties of the soil solution. Polysilicic acids have an effect on soil physical properties.

13.1. INTRODUCTION

Soils generally contain from 5 to 40% Si. Soil Si compounds usually are in the form of silicon dioxide and various aluminosilicates. Quartz, together with crystalline kinds of silicates (feldspar, plagioclase, orthoclase), secondary or clay Si-rich minerals (kaolin, vermiculite, smectite) and amorphous silica form the skeleton of the soil (Orlov, 1985). Numerous physical-chemical soil properties are influenced by minerals. Both mineral composition and organic matter are responsible for soil fertility.

In addition to solid Si compounds, soils contain soluble and weakly adsorbed Si substances. There are three main groups of soluble Si compounds - monosilicic acids, polysilicic acids and organosilicon compounds. However, modern investigations demonstrate that Si complexes with heavy metals, Al, Fe, and organic compounds are present in soil solution and in natural waters as well. Our investigations indicate the need to separate low and high molecular weight polysilicic acid. An analysis of our data and literature data suggest a classification system for Si substances in the soil (Figure 13.1).

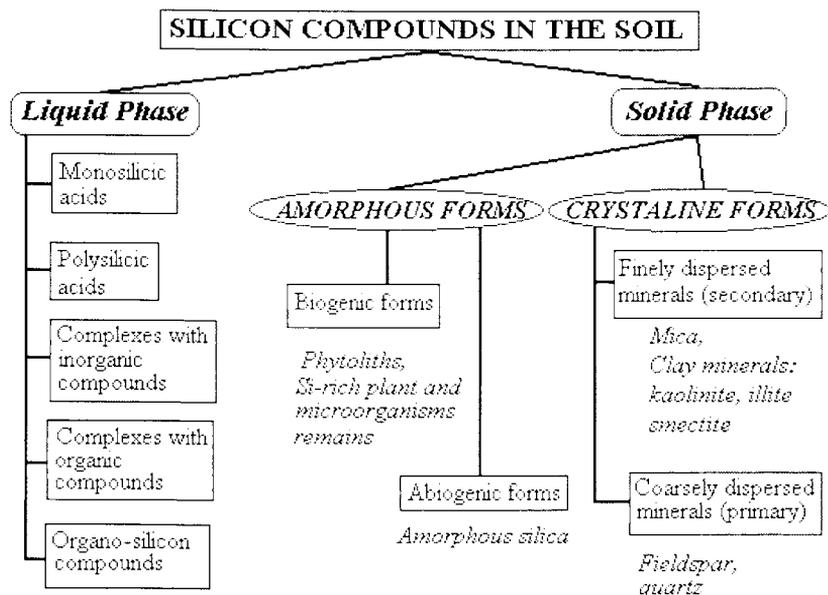


Figure 13.1. The classification of silicon compounds in the soil.

13.2. SILICIC ACIDS IN SOIL

13.2.1. Monosilicic acids

Monosilicic acid contains one atom of silicon. Orthosilicic acid (H_4SiO_4). $K = -9.85$ and its anion (H_3SiO^+) are the most widely distributed varieties of monosilicic acids. Metasilicic acid (H_2SiO_3) seldom occurs in natural waters (Babyshkin et al., 1972). The same standard methods are used for determining ortho- and meta-silicic acids, making it methodologically difficult to separate ortho- and meta-silicic acids. In the soil solution, only orthosilicic acids are presumed to be determined and are called monosilicic acids.

13.2.1.1. Interaction between silicon and phosphorus

Most investigations of monosilicic acids on soil properties concern their interaction with phosphates. Hall and Morrison (1906) presented a hypothesis about the possibility of an exchange reaction between silicate-ions and phosphate-ions due to Si fertilization. Later, it was determined that various Si fertilizers (amorphous dioxide of Si, silica-gel, silicates of calcium, K, or sodium) can increase the quantity of mobile phosphates in the soil (Gladkova, 1982; Matichenkov and Ammosova, 1996; O'Reilly and Sims, 1995; Singh and Sarkar, 1992).

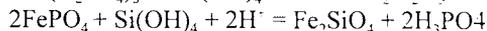
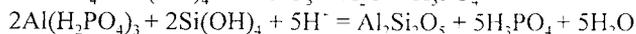
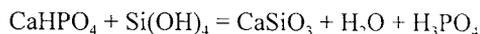
Thermodynamic calculations showed that the reaction of displacing phosphate-anion by silicate-anion from slightly soluble phosphates and formation of the corresponding silicates is possible (Matichenkov and Ammosova, 1996). The model and field experiments have completely confirmed this suggestion (Table 13.1, Figure 13.2).

Table 13.1

The effect of silicon substances on phosphate solubility.

Silicon-rich substances	CaHPO ₄		Ca ₃ (PO ₄) ₂		Al(H ₂ PO ₄) ₃		FePO ₄	
	P mg/l	pH	P mg/l	pH	P mg/l	pH	P mg/l	pH
H ₂ O	0.061	7.21	0.029	6.89	0.1124	2.23	0.1632	3.83
Super fine silica								
300 m ² /g	0.0730	6.98	0.0288	6.89	0.1124	2.23	0.1632	3.83
30 m ² /g	0.0624	7.18	0.0309	6.91	0.1893	2.30	0.1618	4.04
Quartz	0.0646	7.14	0.0256	6.98	-	-	0.1682	3.88
Calcium silicate slag	0.2564	5.55	0.0310	6.60	0.2067	2.21	0.1982	3.8

The literature and our data suggest the following stages of this process (Lindsay, 1979; Matichenkov and Ammosova, 1996). First, an increase in concentration of monosilicic acids is observed in the soil solution, along with their adsorption on slightly soluble phosphates of calcium, Al, ferric, and magnesium. The next phase is an exchange of phosphate-anion by silicate-anion:



These reactions are followed by desorption of phosphate-anion leading to increasing phosphorus in the soil solution. A new equilibrium between silicate and phosphate-anions is established. A portion of the newly-formed mobile phosphates can be adsorbed on new

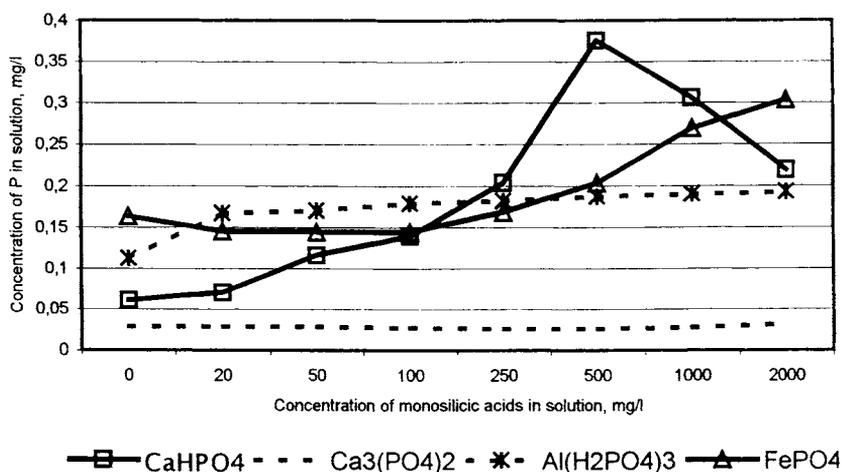


Figure 13.2. Effect of monosilicic acids on solubility of phosphates.

surfaces. On the other hand, applied Si fertilizers usually have good adsorption capacity. Our experiments were conducted with chemically pure substances (amorphous fine SiO_2 , CaCO_3 , and CaSiO_3) and with industrial by-products: slag (by-product from the electric production of phosphorus, Calcium Silicate Corp., TN) and Recmix Slag (product of processing steel slag, PRO-CHEM Chemical Company, FL).

Triplicate material samples were mixed with P-bearing solutions (prepared from KH_2PO_4) and shaken for 24 hours. The following concentrations of P were used: 0.5, 2, and 10 mg P L^{-1} . The samples were centrifuged and orthophosphate was determined by the standard method with a spectrophotometer at a wavelength of 880 nm.

The Si-rich materials varied in their capacity to adsorb P from the solution (Table 13.2). Amorphous silica significantly ($P < 0.05$) adsorbed P only from the solution with the highest concentration of P. There was no significant adsorption from the solutions with a P concentration of 0.5 and 2 mg P L^{-1} (Table 13.2). Other types of Si-rich materials adsorbed P from all P-bearing solutions. The most effective adsorption of P was observed on Recmix (Table 13.2). CaCO_3 adsorbed P from solutions with 2 and 10 mg P L^{-1} as well.

Leaching of P was modeled in a column experiment. The cultivated Spodosol was mixed with Si-rich materials at 10 Mg ha^{-1} . The plastic column had a volume of 60 cm^3 and a diameter of 2 cm. The P bearing solution with a concentration of 10 mg P L^{-1} was added to the column at 6-8 ml hr^{-1} , using a peristaltic pump. A total of 450 ml solution was applied to each column. The percolate was collected at 20 ml intervals. A minimum of 2 replications of columns and triplicate analyses of each liquid sample was conducted.

At the conclusion of the leaching period, the soils were air-dried and ground. Triplicate soil and sand samples were analyzed for mobile (water-extractable) and plant-available (acid extractable) P by standard colorimetric methods. The column experiment demonstrated that

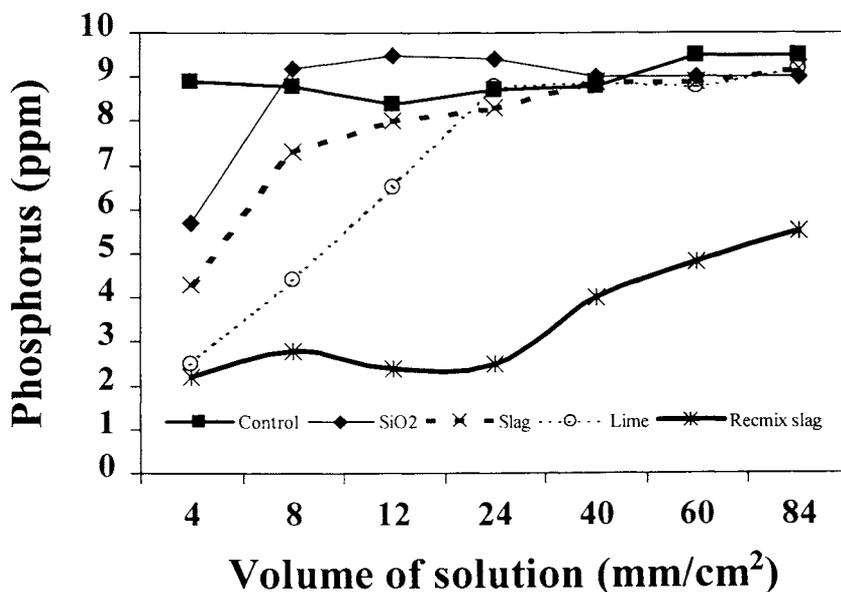


Figure 13.3. Phosphorus in percolated solution after irrigating a cultivated Spodosol with a P-bearing solution.

Table 13.2

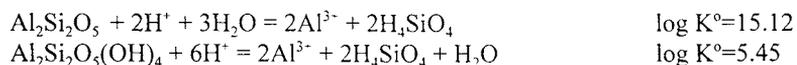
Phosphorus in supernatant after shaking with silicon materials and centrifugation.

Silicon Material	P in supernatants (mg P L ⁻¹)		
Original Solution	0.500	2.000	10.000
Amorphous SiO ₂	0.482	1.920	4.820
CaCO ₃	0.430	1.600	3.020
CaSiO ₃	0.243	0.485	0.940
Slag	0.390	0.430	0.670
Recmix Slag	0.025	0.018	0.110
LSD ₀₅	0.060	0.080	0.100

application of Si-rich material could decrease P leaching by 40-70% (Figure 13.3). Phosphorus was adsorbed by applied silicon-rich substances. The data demonstrated that adsorbed P remained in a plant-available form (Table 13.3).

13.2.1.2. Interaction between silicon and aluminum

In 1917, a study was started in the USA on the effect of Si on Al toxicity in the soil. This, and other laboratory and field experiments, has shown that the use of Si substances for reducing aluminium toxicity is very effective (Haak and Siman, 1992; Myhr and Erstad, 1996). It is possible to postulate five different mechanisms of Al toxicity reduction by Si-rich compounds. Firstly, monosilicic acids can increase soil pH (Lindsay, 1979). Secondly, monosilicic acids can be adsorbed on aluminium hydroxides, impairing their mobility (Panov et al., 1982). Thirdly, soluble monosilicic acid can form slightly soluble substances with ions of Al (Horigushi, 1988; Lumsdon and Farmer, 1995):



Another possibility for Al toxicity reduction by Si-rich compounds can be strong adsorption of mobile Al on silica surfaces. (Schulthess and Tokunda, 1996). Fifthly, mobile silicon compounds can increase plant tolerance to Al (Rahman et al, 1998). All of these mechanisms may work simultaneously, with certain ones prevailing under various soil conditions.

13.2.1.3. Interaction between silicon and heavy metals

Silicon compounds are shown to affect heavy metal behavior in the soil. Monosilicic acids are able to combine with heavy metals (Cd, Pb, Zn, Hg, and others) in soluble complex compounds (Schindler et. al., 1976) and poorly soluble heavy metal silicates (Lindsay, 1979). Low concentration of monosilicic acids in the solution leads to formation of complexes of a heavy metal with a silicic acid anion. As the result of this reaction, the content of heavy metals increases if the concentration of monosilicic acids in the soil solution slightly increases (Bocharnikova et. al. 1995; Schindler et. al., 1976). This is connected with a change in the equilibrium between soluble and solid forms of heavy metals in the soil.

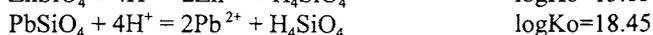
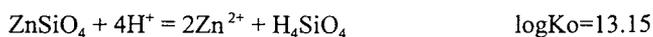
At the same time, a high concentration of monosilicic acids may cause full precipitation of

Table 13.3

The content of water and acid extractable P from a cultivated Spodosol before and after irrigation with a P-bearing solution.

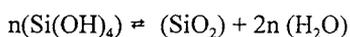
Variant	Before irrigation		After irrigation with a P-bearing solution	
	P water extractable	P acid extractable	P water extractable	P acid extractable
Control	5.9	51.1	8.6	84.3
SiO ₂	6.1	52.3	9.4	87.3
CaSiO ₃	6.0	51.4	8.4	94.2
Slag	5.8	54.2	9.7	99.7
Recmix Slag	5.7	51.6	9.8	104.5
Lime	5.7	51.2	7.5	80.4
LSD ₀₅	0.8	6.1	0.8	6.1

heavy metals with a poor formation of soluble silicates (Cherepanov et al., 1994; Lindsay, 1979).



13.2.2. Polysilicic acids

Polysilicic acids are an integral component of the soil solution. Polysilicic acid has two or more atoms of Si and does not form a yellow color complex with ammonium molybdate. These compounds can have different forms: chains, branches and spheres (Iler, 1979). The mechanism of polysilicic acid formation is not clearly understood. Silicic acid polymerization is assigned to the type of condensable polymerization (Dracheva, 1975; Iler, 1979).



In the soil, polysilicic acids mainly affect physical properties. Polysilicic acids are capable of linking soil particles. Soil structure formation takes place through the creation of silica bridges between particles (Norton et al., 1984). With increasing polysilicic acids, the degree of soil aggregation, water-holding capacity, exchange capacity and buffering capacity of a light soil increases. Soil compaction by machinery increased the polysilicic acid content (Matichenkov et al., 1996). Our investigation showed that polysilicic acids influence the mineral formation processes (Figure 13.4).

In addition to silicic acids, soil solutions and other natural waters contain organosilicon compounds (Fotiev, 1971; Matichenkov and Snyder, 1996). It is possible that Si plays an important role in specific matter formation.

13.3. EFFECT OF SOLID PARTICLES

Silicon substances usually exhibit very good adsorption ability (amorphous fine silica, calcium silicates, Si-rich clay minerals). Silicon fertilization reduced leaching of K and other

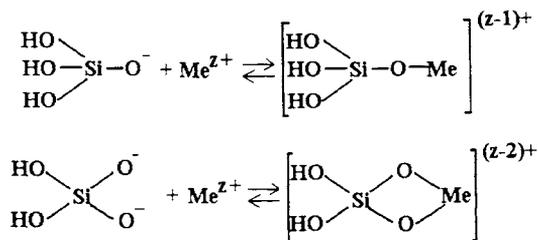


Figure 13.4. Influence of polysilicic acids on mineral formation, where Me is any heavy metal.

mobile nutrients from the surface soil horizon (Tokunaga, 1991). At present, this principle is the basis for some slow-release fertilizers (Komissarov and Panfilova, 1987; Volker et al., 1985). Our study of various textures (sand, clay-sand, sand-clay, and clay) demonstrated that treatment with Si-rich materials (10 Mg ha^{-1}) and one-month incubation under normal conditions resulted in increased water-holding capacity (Table 13.4).

13.4. SILICON FERTILIZATION

Based on information gathered from the literature on Si removal by different agricultural plants (Bazilevich et al., 1975; Reimers, 1990; Savant et al., 1997) and FAO data on world crop production (FAO Internet Database, 1998), it was calculated that 210-224 million tons of plant-available Si are removed from the soil annually. This results in acceleration of mineral weathering, depolymerization of polysilicic acids, change of P, Al, heavy metals, Fe, and Mn behavior, degradation of soil humic compounds, increased erosion, decreased microbial population, and decreased plant Si nutrition. We believe that Si fertilization is needed on all soils, except for unique soils with an abnormally high level of Si, such as recent volcanic soils, or soil formed in zones with an extremely accumulative type of geomorphology. Si fertilizers generally are Si-rich inorganic substances that increase the content of plant-available Si compounds (monosilicic acids) in the soil. Due to their large surface area, they increase the soil adsorption capacity. In addition to increasing the adsorption surface area and the content of monosilicic acids in the soil, treatment with Si fertilizer increases the amount of

Table 13.4

The change of soil water holding capacity following application of Si-rich industrial by-products.

Texture	Sand	Clay-sand	Sand-clay	Clay
Variant	W%	W%	W%	W%
Control	15.7	27.3	42.0	87.2
Amorphous silica	20.3	29.9	44.8	76.9
Slag	26.7	35.2	42.3	67.2
Cement dust	31.5	48.7	77.4	84.3

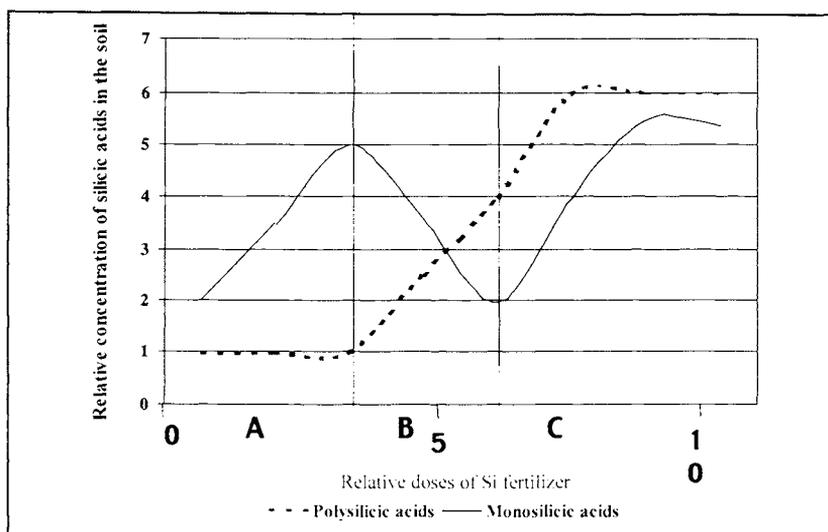


Figure 13.4. The schematic change in soluble Si compounds in soil under gradually increasing doses of Si fertilizer.

polysilicic acids. The content of monosilicic acids and polysilicic acids depends nonlinearly on the rate of Si fertilization (Figure 13.4). It is possible to identify three phases on the basis of changes in monosilicic acid and polysilicic acid concentrations.

Phase «A» represents an increase in monosilicic acid concentration in the soil solution under low doses of Si fertilizer. A further increase in Si leads to such a concentration of monosilicic acids in the soil solution that a synthesis of polysilicic acids begins. This is phase «B». During this phase, monosilicic acids that are formed are spent on the synthesis of polysilicic acids. As a result, the concentration of monosilicic acids falls and the effect from Si fertilizer decreases or disappears completely. Hereafter, an increase in the dose of Si fertilizer results in an increasing concentration of monosilicic acids, which is enough to cause both further synthesis of polysilicic acids and an increase in monosilicic acid concentration in the soil solution. This is phase «C». Further increases in the dose of Si fertilizer lead to new soil Si status, characterized by a high concentration of both mono- and polysilicic acids.

The following direct effects of Si fertilizers on soil properties have been observed:

1. Optimization of phosphate fertilizer efficiency due to transformation of slightly soluble phosphates into plant-available forms and a reduction of phosphate leaching out of the arable horizon.
2. Increase in K fertilizer efficiency.
3. Decrease in Al toxicity.
4. Change in heavy metal mobility in the soil.

5. Initiation of soil mineral formation process.
6. Improvement in adsorption properties and water-air regime of the soil.

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