Article ID 240203001

# Adsorption and Desorption of Silicon in Soil

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Silicon (Si) is the second most abundant element and accounts for up to 28% of the earth's crust by weight. Silicon concentrations in the soil solution range between 3 and 17 mg $kg^{-1}$. Many plants contain a relatively high concentration of Si and its content vary in relation to Si availability in the soil. The beneficial effects of adequate Si include decreased susceptibility to fungal pathogens (and insects), amelioration of abiotic stresses, increased growth in some plants and enhanced tolerance for heavy metals in contaminated soil. In recent years, Si-containing fertilizers have been widely used in India, China, Japan and Korea for rice and sugarcane production. American Association of Plant Food Control Officials (AAPFCO) (2012) and the International Plant Nutritional Institute (IPNI) (2015) - Si as beneficial or Quasi-essential element.

Adsorption and desorption processes are key mechanisms that control the mobility and uptake of silicon by plants. Adsorption involves binding of silicon ions to soil particles, while desorption entails the release of silicon from these particles back into the soil solution. These dynamic processes are influenced by a multitude of factors, including soil properties, pH levels and presence of competing ions. Understanding the intricacies of silicon adsorption and desorption is essential for optimizing agricultural practices, improving crop yield and managing ecosystems sustainability.

**Occurrence in Soil**

Silicon is found in soil in solid, liquid and adsorbed phase. Ninety percent of the earth's crust is comprised of silica compounds. The most prevalent Si compound is silica, primary and secondary silicate minerals. In addition, biogenic Si obtained from phytolith and Si rich plants, also contribute to soil Si pool. The weathering of silicate-containing minerals releases soluble silica into the soil solution with variable contents of 0.1-0.6 mm. Young, less weathered and mineral soils usually supply more Si than completely weathered acidic and organic soils.

- pH < 9 $H_4SiO_4$
- pH > 9 $H_3SiO_4^-$
- pH > 11 $H_2SiO_4^{2-}$

**Roles of silicon in plant and soil**

Silicon is a wonderful nutrient to plant as it has potential to protect the crop from several

stresses. It is having following functions in plant safety:

**a) Biotic stress:** Silicon polymerization in shoot epidermis generally provides a protective layer against penetration of biotic entities like fungi and bacteria. It also promotes production of antibacterial and antifungal compounds known as phytoalexins. Due to enhanced rigidity, palatability and digestibility of plants, Si protects the crop from herbivore attack. Therefore, Si could be employed in integrated disease management for reducing fungicide use. Cucurbit growers, often add silicon to irrigation water to increase the plant's resistance to powdery mildew.

**b) Abiotic stresses:** Si generally has a pivotal role in stress environment. Silicon immobilizes heavy metals and removes them from rhizosphere through precipitation and improves plant resistance against heavy metals (Al, Fe, Cu, Zn, Mn *etc.*) toxicities. Further, exogenous Si application raises soil pH and decreases solubility and thus availability of toxic metals. Si stimulates root exudation of phenolic compounds which form complexes with Al ions and make them immobile. Thus, Si impart metal toxicity by increasing soil pH, metal immobilization in the growth media and also by changing metal distribution inside the plant. Under high incidence of solar radiation, Si bodies efficiently release infra-red thermal radiation and overcome heat stress. Presence of silicic acid in soil matrix reduces the salinity load on plants to some extent. Thick leaves surface due to Si deposition in cuticle, hamper transpiration mediated water loss in plants and improve water use efficiency. Moreover, Si polymerization in plant body also improves root resistance in dry soil. Thus, Si alleviates moisture stress in plants to a great extent.

**c) Crop lodging and photosynthesis:** Accumulation of Si bodies in plant vacuole increases mechanical strength and rigidity of stem and reduces crop lodging. Further, silicification also causes leaf erectness, thus, directly improves light interception and indirectly increases photosynthesis efficiency.

**d) Nutrient use efficiency:** Si is having synergetic interaction with P. Si establishes a buffer system for phosphorous as Si fertilization improves phosphate availability to plants in low phosphorous soils and vice-versa. Si increase available P in soil either by reducing P adsorbing capacity or by replacing P from adsorb site. In addition, the beneficial effect of Si under phosphorous deficiency is attributed to increased levels of organic phosphoesters, thereby improved utilization of phosphorous inside plant body.

**Deficiency symptoms**

- Symptoms appear as minute circular white leaf spot mostly on older leaves.
- Leaves and clumps become soft and droopy thus increasing mutual shading.
- Reduces photosynthetic activity.
- Severe Si deficiency reduces the number of panicles and the number of filled spikelets per panicle.
- It hampers silicification at epidermis cells which results in stalk weakness and crop lodging.

**Adsorption and Desorption**

Adsorption and desorption processes in soil play a crucial role in the movement and availability of nutrients, contaminants, and other substances in the soil environment. These processes involve the interaction of substances with the soil solid phase (soil particles and organic matter) and the soil solution (water and dissolved ions).

Adsorption is the process by which molecules or ions from the soil solution adhere to the surface of soil particles or organic matter. Adsorption occurs due to electrostatic attractions and chemical bonding between the soil and the substances in the soil solution.

Desorption is the process by which substances that were previously adsorbed onto soil particles or organic matter are released back into the soil solution. Desorption is typically driven by competition for binding sites, changes in pH, or other environmental factors that weaken the adsorption forces.

**Mechanism of silicon adsorption is soil**

The formation of bidentate surface complexes of silicon (Si) in soil involves the interaction of silicon ions or species with the surface functional groups of soil particles, such as clay minerals and organic matter. Bidentate complexes are characterized by silicon ions binding to the surface through two attachment points or ligands. Here's how the formation of such complexes typically occurs in soil:

**Silicon in Soil Solution**

Silicon can exist in the soil solution in various forms, primarily as silicic acid ($H_4SiO_4$) or silicate ions ($SiO_4^{4-}$). These forms are typically in equilibrium with each other and can be influenced by factors like pH.

**Soil Surface Functional Groups**

The surfaces of soil particles, particularly clay minerals and organic matter, are negatively charged due to the presence of hydroxyl (-OH) and carboxyl (-COOH) functional groups. These negatively charged sites attract positively charged silicon ions.

**Adsorption onto Soil Surfaces**

Silicon ions in the soil solution are attracted to the negatively charged soil surfaces through electrostatic interactions. In the case of bidentate complex formation, silicon ions attach to the soil surface through two ligands (attachment points) simultaneously.

**Formation of Bidentate Complexes**

Bidentate complexes are formed when silicon ions bind to the soil surface via two oxygen atoms (ligands) from the surface functional groups. This type of binding is characterized by the silicon ion forming two strong bonds with the soil surface.

The oxygen atoms on the soil surface act as donor atoms in the complex, sharing their electrons with the silicon ion.

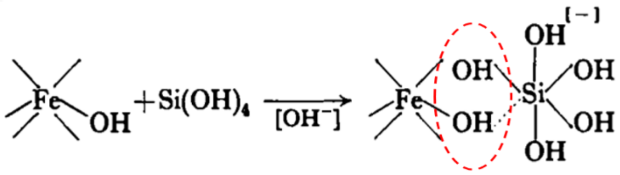
**Stability and Equilibrium**:

The stability of these bidentate complexes depends on several factors, including the nature of the soil surface functional groups, pH, ionic strength, and the concentration of silicon species in the soil solution.

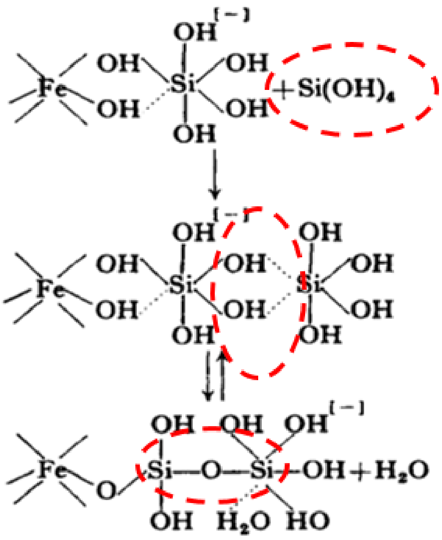
Changes in pH can affect the surface charge of the soil and, consequently, the stability of the bidentate complexes. At different pH values, the relative proportions of silicic acid and silicate ions in the soil solution can change, influencing complex formation.

Bidentate surface complexes (Si-O-Si bond) of silicon are important in soil chemistry because they play a role in the retention and release of silicon in soil, affecting its availability to plants and other organisms. Silicon is considered a beneficial element for many plants, and its uptake can be influenced by the presence of these surface complexes.

**a) Low Si concentration**



**b) High Si concentration**



**Factors affecting adsorption and desorption of silicon in soil**

**1) pH**

Adsorption of Si increases as soil pH and found to be maximum at the pH 5-7 whereas in case of allophane mineral soil the adsorption was maximum at pH 10. Further increase in pH above 10, reduced the level of Si adsorption due to repulsion action.

Increasing soil pH not only increased the magnitude of Si sorption but also increased the strength with which the Si was sorbed on to soil (Haynes and Zhou, 2020).

**2) Temperature:**

Temperature plays an important role in altering the activation energy of soil. Activation energy (Ea) indicates the size of the energy barrier that must be crossed for the reaction to proceed.

The soil with higher Ea, require higher energy to overcome the barrier and adsorb Si from the soil solution whereas, soil with lower Ea can easily adsorbed Si from soil solution because there was no need to cross any energy barrier during the process of adsorption in soil (Qiu *et al.*, 2010).

**3) Period of contact**

Si adsorption increases with increasing contact time mainly because of formation of higher energy binding to surfaces via chemical reconfiguration (e.g. transformation from monodentate to multidentate bonding) and surface precipitation (Haynes and Zhou, 2020).

**4) Type of soil and Parent material**

Quartz and feldspar contributed to less Si adsorption, while hydrous mica and montmorillonite contribute to more Si adsorption in soil.

The adsorption capacity of different paddy soils: basalt-derived > Pearl River Delta sediment-derived > granite-derived > sand-shale-derived (Huang *et al.*, 2006).

**5) Si concentration**

Adsorption of Si increases with increase in concentration of Si in soil solution. Desorption of Si takes place when its concentration is less in soil solution.

**6) Reaction Kinetics**

Reaction kinetics of Si adsorption is divided into an initial fast reaction (0-2 h) followed by a slow reaction (2-12 h). Roughly, the shape of these adsorption curve fell into the so-called "S-type" isotherm.

Multiple rate adsorption may be related to the heterogeneity of the adsorption sites, which are believed to result from differences in the accessibility of surface pores and adsorption sites in the soil, each of which have different adsorption affinities and bonding strengths.

7) **Contraction of other anion in soil**

Presence of Phosphorus decreased Si adsorption between pH 6.0 and 8.0 while the presence of Si decreased P adsorption in the pH region 6.0 and 11.

At higher pH competitive effects of $OH^-$, results in a decrease in Si adsorption (Haynes and Zhou, 2018).

## Conclusion

The adsorption and desorption of silicon in soil play essential roles in regulating the availability of silicon to plants. Notably, higher pH levels (4-9) generally enhance Si adsorption, but excessive pH (>9) levels can hinder it due to repulsion force. The presence of other anions like phosphates and hydroxyl ion can compete with Si for adsorption sites. Furthermore, Si desorption is a complex process that can vary with reaction time and soil type. Understanding these processes is crucial for managing agricultural and natural ecosystems, as silicon is considered a beneficial nutrient for many plant species and can influence plant growth and resilience. Additionally, silicon cycling in soil can have broader implications for ecosystem functions and nutrient dynamics.

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