SILICON DEFICIENCY AND FUNCTIONALITY IN SOILS, CROPS AND FOOD

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Si is a second widespread element on the Earth. Besides inert Si forms (quartz, glass *et al.*), biogeochemically active Si-rich substances present in the nature. There are monosilicic acid, oligomers of silicic acid and polysilicic acids. Silicon plays a distinctive and significant role in soil formation processes, affecting the soil fertility and plant nutrition [2, 6, 8]. Positive influence of silicon on plant growth and development had been known since Justius von Leibigh published the work in 1840 about minaeral nutrition of plants. Beginning in 1840, numerous laboratory, greenhouse, and field experiments have shown benefits of Si fertilization for crop productivity of rice (*Oryza sativa* L.) (15-100%), corn (*Zea mays* L.) (15-35%), wheat (*Triticum aestivum* L.) (10-30%), barley (*Hordeum vulgare* L.) (10-30%), sugar cane (*Saccharum officinarum* L,) (15-40%), cucumber (*Cucumus sativus* L.) (10-40%), strawberry (*Fragaria* spp.) (10-30%), citrus (*Citrus* spp.) (5-15%), tomato (*Lycopersicon esculentum* Mill.) (10-40%), grasses (*Stenotaphrum secundatum* Kuntze, *Cynodon dactulon* L., *Lolium multiforum* Lam, *Paspalum notatum* Fluegge) (10-25%), banana (*Musa paradisiaca*) (20-40%) [6, 9].

Silicon in soil

Soluble silicon compounds, such as monosilicic acid and polysilicic acid, affect many chemical and physical-chemical soil properties. Monosilicic acid possesses high chemical activity [3, 6]. Monosilicic acid can react with aluminum, iron, and manganese with the formation of slightly soluble silicates [2, 6]:

$$Al_2Si_2O_5 + 2H^+ + 3H_2O = 2Al^{3+} + 2H_4SiO_4 \qquad \log K^o = 15.12$$
$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O \qquad \log K^o = 5.45$$
$$Fe_2SiO_4 + 4H^+ = 2Fe^{2+} + 2H_4SiO_4 \qquad \log K^o = 19.76$$
$$MnSiO_3 + 2H^+ + H_2O = Mn^{2+} + 2H_4SiO_4 \qquad \log K^o = 10.25$$

Monosilicic acid under different concentrations is able to combine with heavy metals (Cd, Pb, Zn, Hg, and others), forming soluble complex compounds if monosilicic acid concentration is less [6], and slightly soluble heavy metal silicates when the concentration of monosilicic acid is greater in the system [2]. By this means the application of active form f Si give possibility to manage the heavy metal mobility.

$$ZnSiO_4 + 4H^+ = 2Zn^{2+} + H_4SiO_4 \qquad \log K^o = 13.15$$
$$PbSiO_4 + 4H^+ = 2Pb^{2+} + H_4SiO_4 \qquad \log K^o = 18.45$$

Silicon may play a prominent part in the effects of aluminum on biological systems [5]. Significant amelioration of aluminum toxicity by silicon has been noted by different groups and in different species [3]. The main mechanism of the effect of silicon on aluminum toxicity is probably connected with the formation of nontoxic hydroxyaluminosilicate complexes [8, 9].

The anion of monosilicic acid $[Si(OH)_3]^-$ can replace the phosphate anion $[HPO_4]^{2-}$ from calcium, magnesium, aluminum, and iron phosphates [6].

$CaHPO_4 + Si(OH)_4 = CaSiO_3 + H_2O + H_3PO_4$
$2Al(H_2PO_4)_3 + 2Si(OH)_4 + 5H^+ = Al_2Si_2O_5 + 5H_3PO_4 + 5H_2O$
$2FePO_4 + Si(OH)_4 + 2H^+ = Fe_2SiO_4 + 2H_3PO_4$

These reactions are followed by desorption of phosphate-anion leads to increasing phosphorus in the soil solution and improve plant P nutrition by application of Si fertilizers. The maximum effect can be expected on alkaline soils, like calcareous (Table 1).

Table 1.- Content of water-extractable and alkaline extractable P in the calcareous soil (Granada region) before and after incubation with monosilicic acid (200 mg/l of Si)

Soil, location	Before incubation		After incubation	
	Water-extractable	Alkaline extractable	Water-extractable	Alkaline extractable
	---------------------P, mg/kg--------------------------------			
Calcareous, Jordan	11.5	58.5	22.4	75.4
Calcareous, Granada 1	2.2	20.8	13.6	49.7
Calcareous, Granada 2	2.3	5.6	4.6	29.3

Rainfalls and widespread use of irrigation and drainage lead to 20 to 80% of nutrients and chemicals added to leach from a sandy soil profile. Si-rich biogeochemically active substances (Si fertilizers) usually exhibit very good adsorption properties [2, 9]. In the result this material can physically adsorb mobile P, N or K and keeping them in a plant-available form [6].

Polysilicic acids are an integral component of the soil solution. Polysilicic acid has two or more atoms of silicon. In the soil, polysilicic acids have mainly affect on physical properties. Polysilicic acids are capable of linking soil particles. Soil structure formation takes place through creation of silica bridges between particles [6]. With increasing polysilicic acids, the degree of soil aggregation, water-holding capacity, exchange capacity and buffering capacity of light soil increases.

The absence of simple, universal, and informative methods for soil classification on the deficiency of plant-available and active forms of silicon had a great negative influence on the practical use of Si fertilizers in the world. Various methods for determining plant-available Si in a growing media have been suggested: water. alkaline, acid or organic extractions [5]. All these methods have limitations, because the drying process transform both polysilicic and monosilicic acids to silicon dioxide, which give problem in data interpretation. We offer to determine the content of monosilicic acids (plant-available Si) on water extracted from fresh soil sample. An analysis of monosilicic acid in the soil seems not to be enough for complete characterization of the soil Si deficiency. Monosilicic acid is an active form of Si controlling the Si plant nutrition and primary soil biogeochemical processes. This is **actual Si**, which exist in the soil solution right now. Besides actual Si, it is necessary to have information about soil Si compounds that can transform (dissolve) to actual form in the future. This is **potential Si**. The potential Si may be determined by the hydrochloric acid (0.1 n) extraction method form dry soil. The method provides a close correlation with Si in plant tissue as well (r^2=0.98) [5].

The dissolving of Si-rich compounds proceeds fast. During one growing season as far as plants take up Si, the monosilicic acid concentration in the soil is restored. The values of plant Si absorption definitely prove this. For example, during one season rice absorbs from 150 to 250 kg of Si ha^{-1}, whereas the soil contains only from 5 to 30 kg of actual or plant-available Si ha^{-1} in 10-cm soil layer. Therefore, the concentration of monosilicic acid should be restored about 10 times. Our data on soil examination in Russia, Ukraine, Great Britain, USA and other countries has demonstrated that usually actual Si to be in the ration to potential Si as 1:10. That let us to suggest the following formula for active Si:

Active Si = 10*Actual Si + Potential Si

The results of greenhouse experiment showed the coefficient of correlation between active Si (calculated parameter) and Si concentration in rice shoots had high values both for linear function (R^2=0.95) and for polynomial function (R^2=0.95). Both actual and potential Si compounds are important for successful Si plant nutrition and should be examined for determining Si deficiency in the soil. To assess the need in Si fertilization (1) the soil classification on deficiency of actual, potential and active Si should be developed; (2) mapmaking for various regions. We suggest the following gradations of soil Si deficiency (Table 2).

- **Not deficient soil** - Si fertilization or Si-rich soil amendments are not required. Sometimes the application of Si-rich soil amendments would have beneficial effect via acting Si compounds on soil properties and NPK behavior in the soil-plant system.
- **Low deficient soil** - Si fertilization is necessary for Si-accumulating plants (cereals, grasses). Si-rich soil amendments are required for optimizing P plant nutrition.
- **Deficient soil** - Si fertilizers and Si-rich soil amendments have stable and significant effect on all crops and increase soil fertility. A standard rate of Si application is necessary.
- **Critically deficient soil** - lack of active Si has a negative effect on crop productivity and environment. High rates of Si fertilizers or Si soil amendments are necessary.

Table 2.- Soil classification on deficiency of actual and potential Si

Deficiency level	Actual Si	Potential Si	Active Si	Soil
	-------------mg kg^{-1} of Si in soil---------			
Not deficient soil (W)	>40	>600	>1000	Virgin Mollisols (Chernozems), volcanic ash soils
Low deficient soil (L)	20-40	300-600	500-1000	Cultivated Mollisols, greenhouse potting mixtures
Deficient soil (D)	10-20	100-300	200-500	Most cultivated soils
Critically deficient soil (C)	0-10	0-100	0-200	Tropical soil, sandy soils, degraded cultivated soils

Silicon in plant

Silicon is an integral part of plants. Distribution of silicon between plant organs is not equal and may vary from 0.001% in the pulp of fruit to 10–15% in the epidermal tissue [3]. Plants have a special mechanism for selective uptake of monosilicic acid from the soil solution [4]. Plant tissues are characterized by extremely high concentration of mono and polysilicic acid in sap and has possibility for fast redistribution of this element [2]. Silicon provides the protective functions of plants on the mechanical, physiological, chemicals and biochemical levels.

Mechanical

The accumulation of Si in the epidermal tissue creates mechanical plant protection. Absorbed molecules of monosilicic acid are accumulated in the epidermal tissues [10] and form the silicon-cellulose envelope where silicon is bonded with pectin and calcium [3]. As a result, the double cuticle layer protecting and mechanically strengthening the plants is formed [3, 10]. The mechanical protection of plants against biotic (fungi and insect attacks) and abiotic (lodging) stresses, probably most investigated and popular for explanation of Si fertilizer direct effect on plant resistance.

Physiological

The physiological effect of Si on plants proceeds via the formation of better developed root system (Figure 1). Monosilicic acid support stability of chlorophylls molecules and other organelles, which reinforce physiological plant stability [2,6, 9]. We hypothesized that increasing of plant drought resistance by application of active forms of Si also realized via physiological mechanism. High concentration of polysilicic acid in the symplast and apoplast of plant can keep water and these molecules can be used as rechargeable water tank [7]. Unfortunately this type of mechanism the active Si influence on the plant investigated very poor.

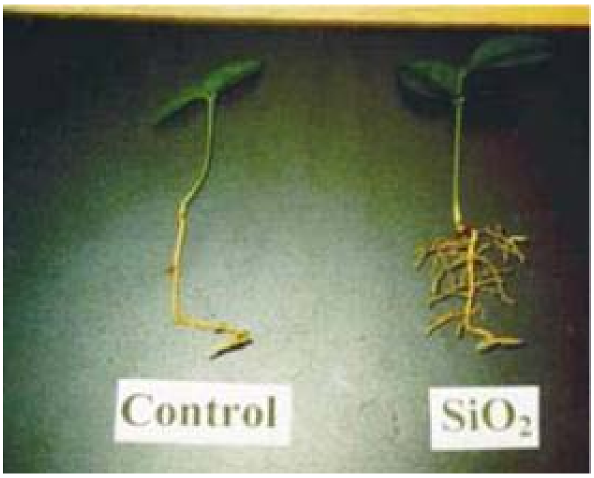

Figure 1.- Effect of Si fertilization on the citrus plant growth

Chemical

Salt toxicity is a worldwide agricultural problem. Approximately one-third of the world land surface is arid and semi-arid, of which half is affected by salinity. In the nearest future, under global warming, the problem will increase. There are several hypothesis can explain the effect of active Si on the plant salt resistance. They are (i) improved photosynthetic activity, (ii) enhanced K:Na selectivity ratio, (iii) increased enzyme activity, and (iv) increased concentration of soluble substances in the xylem, which results in reduced sodium adsorption by plants [2, 6, 9]. The application of Si fertilizer also chemically protects plants against heavy metal toxicity [2].

Biochemical

Si can play important part in all above described mechanisms. But some effects of active Si on plant protection (for example the increasing frost resistance), cant be explained by mechanical, physiological or chemical processes. We hypothesized that it is available additional mechanism for synthesis of specific and non-specific stress protectors in plant cells, which provided by catalytic properties of polysilicic acid matrix [2]. The additional pre-suppositions for organic compounds synthesis on gels of polysilicic acids in living cell are following:

- Active Si increases plant resistance against ANY type of stresses [3, 6, 8, 9, 10];
- Any stress initiates increasing Si in plant tissue [2, 6, 9];
- Plant tissue contain very high concentrations of mono- and polysilicic acids [7];
- Optimization of Si plant nutrition increases the antioxidants and stress-ferments amounts in plant tissue 2, 6];
- Polysilicic acids are used for synthesis of organic molecules [1].

The influence of any stress stimulates nuclear control of the cell for identification the type of stress (Figure 3). After this identification the signal system of plant cell initiates metabolism and protein synthesis for formation of specific and non-specific stress-protectors. The several points in this process are critical for realization of the plant defense. First, there is time period, which require for stress identification. Second, it is time and energy for synthesis of anti-stress proteins and anti-stress metabolites. The time and energy deficiency are main factors of negative influence of stresses on plant production and possibility to surviving of plant, which attacked by stress agent.

High concentration of polysilicic acid in the plant cell and possibility to use polysilicic acid for directed catalytic synthesis of organic molecules can strengthen this process by following. The stress initiates nuclear control for identification of stress and asking for additional transport of Si into problematic cell. After identification the synthesis of specific and non-specific stress-protectors is realized by well-known mechanisms and by additional low-energy required (catalytic) synthesis of these substances on polysilicic-acid matrix (Figure 2). This hypothesis gives possibility to use active Si for reinforce the plant protection system and give ecologically safe alternative for pesticides.

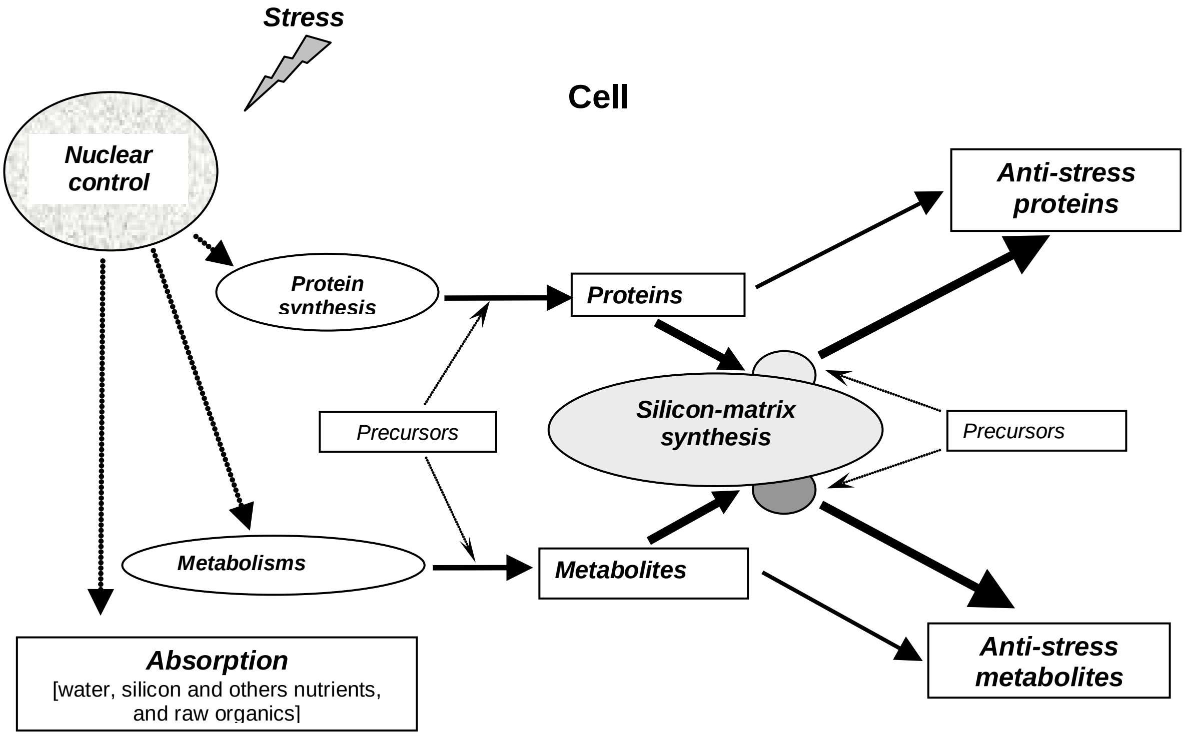

Figure 2.- Schematic of stress-protection system of plant call

The discovery of this mechanism gives new opportunities for elaboration new, very powerful, but completely environmentally friendly materials for protection of cultivated plants. The cauliflower (*Brassica oleracea* L) was used as tested plant in greenhouse. The plant-louse (*Aphidae, Myzodes persicae*) was used as stress factor for infection of cultivated plant. Activated and non activated Si fertilizers were tested, compare with such insecticide as Actara Sergenta. The obtained result with cauliflower is present in the table 3 and 4. The application of non activated, activated Si fertilizers and Actara Sergenta had positive effect on the biomass of shoots and roots of cauliflower and reduced the plant infection by plant-louse. The maximum effect was observed for activated Si fertilizer (Table 3). The application of non active Si had lowest effect compare with activated Si. Considering that Actara Sergenta had also positive effect on cauliflower.

Table 3.- Effect of Si fertilizers and Syngenta's insecticide on biomass of 1 month old plant (roots and shoots) the % of cauliflower leaves infected by louse-plant

Treatment	Weight of one plant, g		% of infected leaves
	Shoots	Roots	
Control	6.79	0.10	75
Non activated Si fertilizer	7.27	0.11	58
Activated Si fertilizer	8.82	0.13	7
Actara Sergenta	7.54	0.13	24
LSD_{05}	0.25	0.01	3

On the table 4 present the crop of cauliflower which was obtained in the greenhouse. The maximum crop was obtained on plot with activated Si fertilizer (increasing on 173%, compare with control). The application of Actara Sergenta also had high effect (increasing on 142%, compare with control). But this pesticide can't be approval for organic farming, activated Si fertilizer is approved by CERES (Certification of Environmental Standards GmbH) for Organic Farming.

Table 4.- Effect of Si fertilizers on the cauliflower crop

Treatment	t/ha	
	Average	Increasing, %
Control	5.30	-
Non activated Si fertilizer	8.56	61
Activated Si fertilizer	14.49	173
Actara Sergenta	12.82	142
LSD_{05}	0.2	

Using soil under agricultural plants destroys a balance of nutrients through their annual harvesting with crop. The active Si removal from cropland ranges from 40 to 300 kg Si per ha [6]. Increasing Si deficit causes a number of negative consequences for soil and plant. Si deficient accelerate soil degradation processes manifested as reduction of soil organic matter, decreasing water holding and adsorption capacities, increasing the Al activity. Reduction of plant-available Si in the soil dramatically reduces natural plant defense system against biotic and abiotic stresses [2, 6].

The modern technologies of using Si-rich substance allow reducing pesticide application form 50 to 70% or removing this type of agrochemicals form plant cultivation [2]. Silicon fertilizers promote transformation of plant-unavailable phosphates into available forms and prevent the transformation of phosphate fertilizers into immobile compounds. Si soil amendment can sharply reduce nutrient leaching from sandy soils and keep nutrients in a plant-available form [6, 9]. In the result the application of traditional mineral fertilizers (N, P, K) also can be reduced under Si fertilization on 30-50%. This effect of active Si dramatically reduces the maintenance cost for agriculture activity and gives pest opportunity for organic agriculture.

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