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RESEARCH ARTICLE

STUDYING THE SOLUBILITY, AVAILABILITY, AND UPTAKE OF SILICON (Si) FROM SOME ORE MINERALS IN THE SANDY SOIL

Rama T. Rashad* and Rashad A. Hussien

Soils, Water and Environment Research Institute,
Agricultural Research Center, Giza, Egypt
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ABSTRACT

The solubility and availability of Si from the feldspar, silica, and zeolite as Si-bearing minerals were studied in a sandy soil. Silicon uptake by the soybean (*Glycine max L.*) plant was discussed. The minerals used were applied before planting in two separate rates; rate 1 ≈ 595.2 and rate 2 ≈ 1190.5 kg ha^{-1} accompanied by a ≈ 4.8 kg ha^{-1} constant rate of the K-humate sprayed as a solution on soil after planting in a complete randomized block design. The dissolved Si from the different minerals at rate 2 followed an opposite direction to their SiO_2 percentage which may be due to their structural differences: silica (1.46 mg kg^{-1} - $SiO_2 = 98.4\%$) < zeolite (1.71 mg kg^{-1} - $SiO_2 = 75.9\%$) < feldspar (2.09 mg kg^{-1} - $SiO_2 = 71.9\%$). The individual mineral treatments at rate 2 have almost decreased the available NPK estimated after soybean harvesting. The K-humate has enhanced the effect of silica at rate 2 for the available N and P. The soybean seed yield (kg ha^{-1}) increased significantly by 117.9% for the S1 + H, 109.2% for K-humate and 57.5% for the Z2 + H treatment. The seeds' Si (mg kg^{-1}) increased significantly from 3.6% to 102.9% affected by the silica treatments.

Keywords: Feldspars, Sandy soil, Si, Silica, Zeolite

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INTRODUCTION

The regular application of the chemical fertilizers to increase the crop yield sometimes degrades the soils physically and chemically. The partial replacement of the chemical fertilizer by more environment-friendly minerals under the sandy soil conditions is highly recommended (Savci, 2012). A promising way of a green chemistry perspective is to achieve nutrient availability from minerals by their exposure to an aqueous solution simulates the geochemical weathering (Wada, 2005).

The silicate mineral-based fertilizers can optimize the soil properties and thus the nutrient cycling when they provide the sufficient water-soluble Si to meet the plant needs and do not contaminate the soil (Ji et al., 2016). The inorganic materials such as clays, micas, feldspars, and quartz (SiO_2) although being rich in Si, are poor Si-fertilizer sources because of the low Si solubility. The highly soluble but expensive Ca-silicate, K-silicate, and silica gel are widely used (Snyder et al., 2006).

The silicate fertilizers may increase the fertilizers use efficiency and silicon (Si) is becoming an 'agronomically essential element' especially for the plants that are able to control the accumulation, transport, and

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** Corresponding Author:*
Email: rtalat2005@yahoo.com

polymerization of the Si (Liang et al., 2015; Matychenkov et al., 2016; Rodrigues & Datnoff, 2015). The toxicity of some metals (Mn, Cd, Al, and Zn) could be inhibited and the protective role of the Si may be due to the production of biologically active agents (Wiese et al., 2007).

Silicon in soil is usually in a sparingly soluble form, bio-geochemically inert amorphous silica (SiO_2) and various aluminosilicates. Amorphous SiO_2 in the surface soil horizons is of biogenic forms (plant and microorganism phytoliths) and abiogenic substances formed by the precipitation and dehydration of the soluble Si compounds in the biogeochemical cycle of Si. The molecular biology techniques have indicated defence-related genes responsible for the Si polymerization (Snyder et al., 2006).

The presence of Si-binding compounds revealed some interaction between the inorganic SiO_2 phase and the organic matrix (Moriguchi et al., 2005). The organic environment includes a range of proteins, carbohydrates, metal ions and (in plants) phenolic compounds. Possible electrostatic interactions exist between the positively charged side-chains of the organic moiety with the negatively charged SiO_2 species containing the – OH groups. Whereas the hydrophobicity of the side-chain correlates with the surface area of the SiO_2 material. Bridge particles may be formed to produce extended structures (Sarawade et al., 2010).

The principal soluble forms of the Si in the soil are the mono- and polysilicic acids. The monosilicic acid is produced by the dissolution of the Si-containing minerals depending on the chemical structure and the particles' size. The highest solubility is inherent in the amorphous SiO_2 with the high surface area (Bocharnikova & Matichenkova, 2012). The soluble form of the Si as the weakly acidic orthosilicic acid monomer [$Si(OH)_4$] (or its ionized form, $Si(OH)_3O_2^-$) allows its uptake by the plants from the soil (Bocharnikova et al., 2010). Sometimes, the extractable Si is correlated with the plant yield. The polysilicic acid is leachable, chemically inert, acts as an adsorbent forming colloidal particles, and may be sorbed by the minerals to form siloxane bridges. It is a high water saturated, affect the soil water-holding capacity and the formation of the soil structure (Snyder et al., 2006).

The feldspars are "framework silicates" called tectosilicates (Skorina & Allanore, 2015). Some nutrients from them had been solubilized into the available form when added with organic materials to the sandy soil (Badr, 2006). Zeolites are a group of the crystalline hydrated aluminosilicate minerals used as fertilizers and are often highly selective for loading by NH_4^+ and K^+ (Li et al., 2013; Perez-Caballero et al., 2008).

The dissolution of the feldspars and silica takes place in all soils depending on numerous factors and is a one-way irreversible process with a minimum rate under the neutral conditions. Their very low aqueous solubility is while destroying the silicate matrix and increases in the presence of the polybasic organic anions in the solution (Smith, 1998). The dissolution of the K-bearing silicates begins from the release of charge-balancing alkali metal cations (e.g. K^+) from the surface of the crystal lattices into the solution. This is via the ion exchange, adsorption/desorption of the dissolved species at the surface exposed to the fluid, and the hydrolytic degradation, i.e. the removal of the hydrated alumina and silica species from the crystal lattice (Skorina & Allanore, 2015).

The dissolution of the quartz and amorphous SiO_2 proceeds via the adsorption of the water molecules on the surface with the further formation of four silanol groups (Si–OH) around the Si atom and the detachment of the molecules of the orthosilicic acid from the surface (Ehrlich et al., 2010; Sokolova, 2013).

The humic substances (HS) increase the fertilizers use efficiency (Selim et al. 2010). They behave as a polyelectrolyte with predominantly negative charges in the aqueous solution (Li et al., 2011). The carboxylic and phenolic groups contribute to the surface charge and the reactivity of the humate derivatives and are capable of binding metal ions and forming complexes (Boguta et al., 2016).

The soybean plant (*Glycine max L.*), is one of the most important and economic plants in the world. It is a very rich in nutrients and used for various purposes (Xie et al., 2011). Well-characterized Si transporters have been stated in the soybean giving a natural ability for the Si absorption (Cruz et al., 2014).

The present work aims to study the dissolution and availability of the Si from the feldspar, silica, and zeolite as Si-bearing minerals by the effect of the K-humate as well as the uptake of the Si by the soybean (*Glycine max L.*) plant in a sandy soil.

MATERIALS AND METHODS

A field experiment has been carried out during the summer seasons of the 2016 and 2017 at the Ismailia Agricultural Research Station, Agricultural Research Center (ARC) – Egypt. It was under the sandy soil conditions (Typic Torripsamment; Entisol [Arenosol AR] (FAO, 2014)). Some physical and chemical properties of the experiment soil are shown in Table 1.

Materials

The minerals used; feldspar, silica, and zeolite, were obtained as free samples for the research and their chemical analysis results are presented in Table 2. The zeolite XRD analysis indicated that it is 100% Clinoptilolite – Ca with the chemical formula $Si_{29.04}Al_{6.96}O_{96.40}Na_{1.92}Ca_{1.57}Ba_{0.32}K_{0.56}Mg_{0.72}$. The particle size distribution and Zeta potential for the studied minerals have been measured using the Zeta sizer nano series (Nano ZS), Malvern, UK - Size range (nm):0.6:6000 nm and Zeta potential range (mV): (-200:200 mV) and the analysis results are presented in Table 3.

Table 1. Some characteristics of the experiment soil before cultivation

Character		
Particle size distribution (%)	**Coarse sand**	72.12
	Fine sand	14.32
	Silt	3.22
	Clay	10.34
Texture class		Sandy
$CaCO_3$ (%)		0.36
Organic Matter, OM (%)		0.23
pH (1:2.5 soil : water suspension)		8.01
Saturation Percent, SP		25.00
Electrical Conductivity, EC (dS m^{-1}) (1:5 soil : water extract)		0.30
Available nutrients (mg kg^{-1})	**N**	20.50
	P	2.01
	K	50.13

Table 2. Chemical Analysis of the minerals used in the study

Character (%)	Feldspar	Silica	Zeolite
SiO_2	71.94	98.38	75.94
Al_2O_3	16.5	0.07	12.97
Fe_2O_3	0.3	0.03	1.32
CaO	0.56	0.08	3.22
MgO	0.00	0.01	1.06
SO_3	0.02	0.19	0.00
K_2O	6.8	0.13	0.96
Na_2O	3.1	0.59	2.17
TiO_2	0.06	0.03	0.00
MnO_2	0.03	0.02	0.00
P_2O_5	0.00	0.01	0.00
Cl^-	0.03	0.05	0.00
Total	**99.98**	**99.88**	**97.64**

Table 3. Particle Size Distribution and Zeta Potential of the used minerals

Particle Size Distribution (%)			
	Feldspar	**Silica**	**Zeolite**
Size (nm)	528.0 (11.1%) 133.5 (88.9%)	584.4 (11.4%) 130.8 (88.6%)	345.2 (100%)
PdI *	0.583	0.669	0.837
Zeta Potential (mV) and Conductivity (mS cm^{-1})			
	Feldspar	**Silica**	**Zeolite**
Zeta Potential (mV)	**- 24.1**	**- 29.2**	**- 26.5**
Zeta Deviation (mV)**	4.44	4.60	5.39
Conductivity (mS cm^{-1})	0.016	0.025	0.017

Remarks: * Poly dispersity index (a statistical parameter); ** 12 Run

Table 4. Released Si (mg kg^{-1}) from different minerals at 1190.48 kg ha^{-1} application rate by the cK-Humate in distilled H_2O

	Maximum Si (mg) available for kg soil*	Soluble Si (mg kg^{-1}) at Rate 2	(%) of soluble Si from the maximum available
K-Humate	0.002	0.000008	0.400
Feldspar + K-Humate	359.7	2.09	0.581
Silica + K-Humate	491.9	1.46	0.297
Zeolite + K-Humate	379.7	1.71	0.450

Remarks: * Calculated on the basis of SiO_2 % for each mineral at an application rate of 0.5 g kg^{-1} soil (Rate 2)

The minerals were applied before planting in two separate rates ≈ 595.2 and 1190.5 kg ha^{-1} (= 0.25 and 0.5 g kg^{-1} soil). An aqueous solution of the K-humate (11.2% K_2O) was sprayed on the soil 30 days after planting at a constant recommended rate of 4.8 kg ha^{-1}

= 0.002 g kg^{-1} soil. A treatment includes the higher mineral rate 1190.5 kg ha^{-1} without the K-humate was used for comparison.

The K-humate was added as a source of the polybasic organic anions to enhance the solubility and availability of Si released from the applied minerals. The solubility of Si from the minerals by the humate ligand was tested in distilled water on the laboratory scale. Three separate flasks each of which contains a 0.5 g of K-humate salt dissolved in 50 mL distilled H_2O (1% K-humate solution). Five grams of each mineral was then added to this solution giving a partial suspension of pH 9.8 without modification. The mixture was shaken at room temperature, left overnight, filtered and the concentration of soluble Si was measured in the filtrate by the Inductively Coupled Plasma Spectrometry (ICP-*Ultima 2 JY* Plasma). The total soluble Si released from the minerals in the humate solution in (mg kg^{-1}) for the studied mineral rates was calculated (Table 4).

Planting

The soybean seeds were inoculated by efficient strained *Bradyrhizobium Jabonicum* (supplied by the Department of Microbiology at SWERI/ARC) as follows: an amount of the starch as an adhesive glue material suitable for the seeds quantity was wetted by 50 mL of warm water then mixed thoroughly with the seeds. The bacteria were mixed with the starch-wetted seeds and air dried for 90 min. The nitrogen fertilization was applied before the first irrigation at the rate of 35.7 kg ha^{-1}. Giza-111 soybean variety, 2–3 seeds were hand sown in hills (four ridges per plot of (=9.6 m^2)), at 15 cm apart.

The treatments in Table 5 were applied in a complete randomized block design with three replicates in 33 plots. Planting and the other agronomic practices were applied as recommendations. At the harvest time, ten plants were randomly collected from each treatment and air-dried to estimate the: Number of pods/ plant, Pods weight/ plant (g), Number of seeds/ plant, Number of seeds/ pod, 100-seed weight (g), Seeds weight/ plant (g), and seed yields (kg ha^{-1}) that calculated according to the total seed yield per the plot area.

Analysis of plant and soil samples

After the harvesting, a half gram of the ground seeds and/or straw was wet digested using the acid mixture (1:1 H_2SO_4:$HClO_4$) (Chapman & Pratt 1961). The soil available N, P, K, and Si were extracted by 1% K_2SO_4, 0.5 N $NaHCO_3$, 1 N NH_4OAc (pH 7.0) and 0.5 N CH_3COOH (Heckman & Wolf, 2009), respectively. The total percentage of the N, P, and K in the digested plant samples and the available in the soil extracts were estimated by the distillation using the Kjeldahl apparatus, colorimetrically by the UV-Vis. Spectrophotometer and by the flame photometer, respectively (Black, 1965; Jackson, 1973). The protein percentage in the seeds was calculated as the N (%) × 6.25. The Si concentrations in the soil extracts as well as the Cu, Fe, Mn, Zn, and Si for both the seeds and straw were measured by the ICP Spectrometry (ICP-*Ultima 2 JY* Plasma).

Statistical Analysis

The one-way analysis of variance (ANOVA) was carried out using the Co-State software to determine the statistical significance of the treatment effects at a significance level of $P = .05$ (Gomez & Gomez, 1984).

RESULTS

The soil available macronutrients

The variation in the soil available NPK mentioned in Table 6 after the harvesting was non-significant for the studied treatments based on the LSD values. Compared to the control treatment, the maximum values of the available NPK were increased by 24.2%, 31.0% and 33.5% affected by the treatments S2 + H, F2 + H and Z1 + H, respectively. While the minimum available NPK values were decreased by 45.5%, 13.8% and 15.8%, respectively, affected by the treatments F2 + H for the N and the Z2 + H one for the P and K.

Table 5. The treatments used in the experiment

Additive	Treatment	Symbol
	Control (No additives)	C
	K-Humate	H
Feldspar (F)	Feldspar (Rate 1) + K-Humate	F 1 + H
	Feldspar (Rate 2) + K-Humate	F 2 + H
	Feldspar (Rate 2)	F 2
Silica (S)	Silica (Rate 1) + K-Humate	S 1 + H
	Silica (Rate 2) + K-Humate	S 2 + H
	Silica (Rate 2)	S 2
Zeolite (Z)	Zeolite (Rate 1) + K-Humate	Z 1 + H
	Zeolite (Rate 2) + K-Humate	Z 2 + H
	Zeolite (Rate 2)	Z 2

Table 6. Available NPK nutrients in the soil after harvest (mg kg^{-1})

		Available NPK (mg kg^{-1})		
		N	**P**	**K**
	Control	23.1 ^{abc}	2.9 ^{a}	115.79 ^{a}
	F 2	18.6 ^{abc}	3.1 ^{a}	111.15 ^{a}
	S 2	13.3 ^{c}	2.6 ^{a}	104.33 ^{a}
	Z 2	21.4 ^{abc}	2.9 ^{a}	99.69 ^{a}
K-Humate (H)	**Feldspar 0**	26.3 ^{ab}	2.9 ^{a}	134.32 ^{a}
	F 1 + H	20.3 ^{abc}	3.0 ^{a}	129.68 ^{a}
	F 2 + H	12.6 ^{c}	3.8 ^{a}	115.79 ^{a}
K-Humate (H)	**Silica 0**	26.3 ^{ab}	2.9 ^{a}	134.32 ^{a}
	S 1 + H	14.7 ^{bc}	3.4 ^{a}	120.43 ^{a}
	S 2 + H	28.7 ^{a}	3.1 ^{a}	129.68 ^{a}
K-Humate (H)	**Zeolite 0**	26.3 ^{ab}	2.9 ^{a}	134.30 ^{a}
	Z 1 + H	22.4 ^{abc}	3.1 ^{a}	154.56 ^{a}
	Z 2 + H	19.3 ^{abc}	2.5 ^{a}	97.50 ^{a}
L.S.D $_{5\%}$		**11.73**	**1.56**	**57.82**

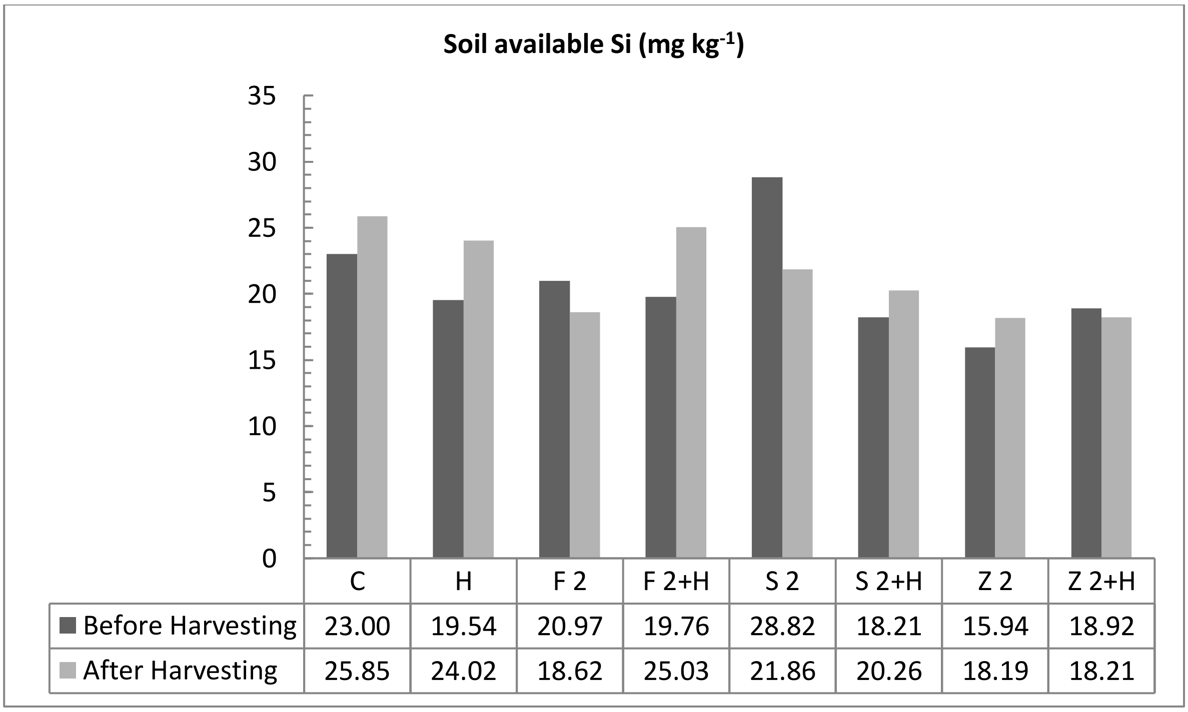
Remarks: The footnotes (a–c) indicate the non-significance ranges for the different treatments.

The individual treatment of the K-humate fertilizer increased the available N and K but had no effect on the available P. The mineral individual treatments (all at rate 2) decreased the available NPK (except the F2 one). The application of the feldspar and zeolite minerals to the studied soil might inhibit the K-humate fertilizer efficiency to some extent. The K-humate enhanced the silica effect at rate 2 for the available N and P but probably limited the K. Previous studies had indicated that the application of the Si to soybean seedlings grown in a K-deficient medium had enhanced the K use efficiency because Si ameliorates symptoms associated with the deficiency in the essential nutrients in the plants (Gonzalo et al., 2013). A suitable NPK soil fertilization may be necessary for the Si accumulation in the seeds and straw.

The soil available silicon

Many studies had mentioned that the 0.5 N acetic acid method is appropriate for testing the soil-Si levels across a wide range of soils of low clay content with a range of extractable soil-Si from 1 to 239 mg L^{-1} soil. A soil was classified as deficient (requiring Si fertilization for rice and/or sugarcane), based on critical soil Si test values of 24 mg L^{-1} soil published for organic and mineral soils. Soluble Si in the soil solution is mainly the orthosilicic acid (H_4SiO_4) over a wide pH range (2 to 9) and is in equilibrium with amorphous SiO_2 (Rodrigues et al., 2003).

In the present study, the soil available Si was decreased by the different treatments except for the S2 compared with the control (Figure 1). Before harvesting, the Si available from the F2 (F2 +H) and S2 (S2 + H) was decreased under the effect of the K-humate application but increased from the Z2 (Z2 + H) compared with the mineral individually applied. The Si solubilized from minerals may be captured by the humate effect then absorbed by plant or leached. After harvesting, the opposite was observed. The available Si from the feldspar and silica was higher by the K-humate application because it might not absorbed by plant.



	C	H	F 2	F 2+H	S 2	S 2+H	Z 2	Z 2+H
■ Before Harvesting	23.00	19.54	20.97	19.76	28.82	18.21	15.94	18.92
▨ After Harvesting	25.85	24.02	18.62	25.03	21.86	20.26	18.19	18.21

Fig. 1 Soil available Si (mg kg^{-1}) affected by different treatments before and after harvesting

Among treatments, the soil available Si increased in the order: S2 > F2 > Z2. Upon application of the K-humate, the available Si before harvesting increased in the direction: F2 + H > Z2 + H > S2 + H while after harvesting, the available Si followed the order F2 + H > S2 + H > Z2 + H.

Yield and yield components

The soybean yield is a complex function dependent on a number of variables differ in sensitivity at different growth stages (El-Mohsen et al., 2013). The applied treatments significantly affected the yield components compared to the control based on the LSD value (Table 7). The first three maxima often included the K-humate (H) and Silica (either 1 or 2) + H treatments and sometimes the Zeolite ones (Z + H) for the plant weight (g), number of pods/plant, the pod weight/plant, the number of seeds/plant, the number of seeds/pod, and the seed weight/plant. The last three minima often included the feldspar as an individual treatment or with the K-humate.

The variation in the 100-seed weight was non-significant except for the treatments F2, Z2, and Z2 + H. The seed yield (kg ha^{-1}) increased significantly by 117.9%, 109.2% and 57.5% affected by the treatments S1 + H, H and Z2 + H, respectively. However, it decreased significantly by 67.4% and 9.5% for the treatments F2 and F2 + H, respectively.

The macronutrient content of seeds and straw

Table 8 indicates that the Z1 + H treatment was the most significant for the N (mg kg^{-1}) in seeds by 6.6% compared to the control. While the least significant were those of the feldspar and silica, as individual and with the K-humate. The zeolite application to the soil increased the N retention capacity as stated previously (Perez-Caballero et al., 2008; Li et al., 2013). The most significant treatment for the P (mg kg^{-1}) was the F2 + H (26.9%). The variation due to the other studied treatments was non-significant.

No significant increase in the K (mg kg^{-1}) can be observed, while some significant decrease was by 22.9% and 10.6% for the S 1 and S 2 + H treatments, respectively. For the straw, no significant increase compared with the control was observed for its N (mg kg^{-1}) that decreased significantly due to the treatments F1 + H and the Z2 from 10.6% to 42.1%, respectively. The P (mg kg^{-1}) increased significantly by 154.6% for the F2 + H treatment and other variation values were non-significant. The maximum significant increase for K (mg kg^{-1}) was 34.9% by the F2 treatment while the only significant decrease was 22.9% by the F2 + H one.

Silicon and micronutrients content in the soybean seeds and straw

Some general trends can be observed regarding the concentration of the estimated micro-elements affected by the studied treatments according to Table 9.

A Significant increase compared to the control was observed by all studied treatments for the Fe, Zn, and Si while for the Mn only the K-humate increased it by 192.0% and the F2 one by 6.2%. Significant decrease ranges were from 39.4% to 66.7% for the Cu and from 11.5% to 46.9% for the Mn. Some nutrients perhaps either immobilized by precipitation or coagulation with mineral particles or leached in more soluble forms.

All studied treatments increased the Si concentration (mg kg^{-1}) significantly in the seeds from 3.6% to 102.9% affected by the S2 and the S2 + H treatments, respectively. The Si concentration in both seeds and straw (except for the straw at the H treatment) increased as the SiO_2% in the source mineral increases for the K-humate + mineral treatments but in an opposite direction to the Si solubility presented in Table 4. The Si uptake mode of the soybean plant was stated as of the intermediate type stand between the active uptake type and the rejective type (Miyake & Takahashi, 1985).

The pure mineral treatment decreased the absorbed elements when mixed with the K-humate for feldspar (Cu, Fe, Mn, and Si) and for zeolite (Fe, Mn) but increased it for the silica.

DISCUSSION

Particle properties of the studied minerals in the aqueous solution

The SiO_2% in the studied minerals follows the order: feldspar (71.9%) < zeolite (75.9%) < silica (98.4%), Table 2. Each mineral exhibits different particle sizes that have negative surface charge expressed as Zeta potential (ZP). The ZP values increase as the SiO_2% increases in the mineral (Table 3). The silica possessed the smallest particle size nearby the nano-scale (130.8 nm by 88.6%) and the highest ZP (-29.2 mV). The charged particles indicate that the studied minerals are not inert materials but have a degree of chemical activity that will strongly affect the chemical and biological processes in both the soil and the plant. The released Si by the partial dissolution of the mineral in the K-humate aqueous solution at pH 9.8 (Table 4) followed an opposite direction to its SiO_2%; silica (1.46 mg) < zeolite (1.71 mg) < feldspar (2.09 mg) at a rate of 0.5 g kg^{-1} soil. The dissolution of the silica species in water is given by (Júnior & Baldo, 2014):

$$SiO_{2(s)} + 2H_2O_{(L)} \leftrightarrow H_4SiO_{4(aq)} \qquad [1]$$

The H_4SiO_4 is the weak monosilicic acid and is the plant available form of the Si (PAS) that dissociates as the pH value increases

$$H_4SiO_{4(aq)} \rightarrow H_3SiO_{4(aq)} + H^+ \qquad [2]$$

Role of surface and electric properties of the minerals' particle

The ZP is an electro-kinetic parameter indirectly determined by the surface charge of particles when suspended in a polar media. The ZP values of some forms of silica get gradually more negative as the pH and the powder surface area increased. The ZP values of ±30 mV are enough to promote stable water suspensions because the particles of like charge repel each other, overcoming the aggregation and sedimentation caused by the Van der Waals forces. In the aqueous suspensions of the silica particles, unsaturated free bonds of the tetrahedron coordination at the particle surface, SiO_4^{4-} are neutralized by the OH^- and H^+ species. The partial or total particle surface hydroxylation can result in the formation of silanol groups $[Si(OH)_n]$ that dissociate in pure water as follows (Júnior & Baldo, 2014):

$$\equiv Si\text{–}OH + OH^- \rightleftharpoons Si\text{–}O^- + H_2O \qquad [3]$$

$$\equiv Si\text{–}OH + H^+ \rightleftharpoons Si\text{–}OH_2^+ + H_2O \qquad [4]$$

This phenomenon is related to the structural properties, exposed planes on the fractured surface of particles, and the presence of contaminants in the SiO_2 source.

Effect of K-humate

The humate salts partially ionize in the aqueous media to produce the K^+ cation and the humate anion (ligand) giving the basic character of the solution and enhancing the mineral particle dissolution and formation of the PAS form according to the eqns. [1-4]. Some possible mechanisms in the complex soil solution are (Boguta et al., 2016; Brigante et al., 2010; Selim et al., 2010): Mono- and polyatomic ions in solution can exchange with K^+ for the humate active sites or interact with it to form more stable humate moieties like K-silicate moieties.

Adsorption of humate moieties may occur on the mineral particles. The partial dissolution of the mineral particle releases cations that can interact with the humate then absorbed by the plant roots.

Table 7. Yield and yield components

	Treatment	Plant wt (g)	No. of pods/ plant	Pod wt/ plant (g)	No. of seeds/ plant	No. of seeds/ pod	100 seed wt. (g)	seed wt/ plant (g)	Seed yield* (kg ha^{-1})
	Control	27.50	53.59	11.10	96.47	1.80	17.44	16.4	3280
	F 2	16.88	18.07	11.54	35.60	1.97	15.33	5.34	1068
	S 2	35.94	60.10	17.19	117.19	1.96	16.35	18.75	3750
	Z 2	27.50	59.39	10.04	116.40	1.95	14.52	17.46	3492
K- Humate	**Feldspar 0**	57.50	95.76	23.20	190.56	1.99	18.04	34.3	6860
	F 1 + H	37.50	74.62	13.74	148.50	1.99	15.95	23.76	4752
	F 2 + H	27.50	43.89	12.65	87.35	1.99	16.71	14.85	2970
K- Humate	**Silica 0**	57.50	95.76	23.20	190.56	1.99	18.04	34.3	6860
	S 1 + H	47.00	107.29	11.25	210.29	1.97	17.01	35.75	7150
	S 2 + H	38.75	59.26	17.63	117.33	1.99	17.92	21.12	4224
K- Humate	**Zeolite 0**	57.50	95.76	23.20	190.56	1.99	18.04	34.3	6860
	Z 1 + H	32.50	71.51	9.96	140.88	1.96	16.01	22.54	4508
	Z 2 + H	37.50	185.43	11.67	369.00	1.98	14.30	25.83	5166
L.S.D $_{5\%}$		1.73	1.59	1.78	1.72	0.06	1.78	1.72	62.01

Remark: *on calculation basis from the data of 10 plants selected from each plot.

Table 8. Total NPK in soybean seeds and straw (g kg^{-1}).

		Seeds (g kg^{-1})				**Straw (g kg^{-1})**		
		Protein %	**N**	**P**	**K**	**N**	**P**	**K**
	Control	33.61	53.78 ^{b}	6.7 ^{bc}	19.09 ^{ab}	20.75 ^{a}	1.65 ^{b}	8.05 ^{cde}
	F 2	27.98	44.77 ^{ef}	7.9 ^{abc}	18.78 ^{abc}	13.10 ^{e}	2.55 ^{ab}	10.86 ^{a}
	S 2	29.01	46.41 ^{e}	7.7 ^{abc}	19.67 ^{a}	16.11 ^{d}	2.23 ^{b}	6.84 ^{ef}
	Z 2	33.78	54.05 ^{b}	7.5 ^{abc}	15.93 ^{de}	12.01 ^{e}	1.95 ^{b}	8.05 ^{cde}
K-Humate	**Feldspar 0**	33.44	53.51 ^{bc}	6.3 ^{c}	15.93 ^{de}	18.02 ^{bc}	2.00 ^{b}	7.07 ^{def}
	F 1 + H	30.71	49.14 ^{d}	7.3 ^{abc}	17.68 ^{bcd}	18.56 ^{b}	2.10 ^{b}	8.66 ^{bcd}
	F 2 + H	32.42	51.87 ^{c}	8.9 ^{a}	19.38 ^{ab}	15.83 ^{d}	4.20 ^{a}	6.21 ^{f}
K-Humate	**Silica 0**	33.44	53.51^{bc}	6.3 ^{c}	15.93 ^{de}	18.02 ^{bc}	2.00 ^{b}	7.07 ^{def}
	S 1 + H	27.30	43.68 ^{f}	6.8 ^{bc}	14.72 ^{e}	18.02 ^{bc}	1.68 ^{b}	9.02 ^{bc}
	S 2 + H	27.30	43.68 ^{f}	7.3 ^{abc}	17.08 ^{cd}	16.66 ^{cd}	2.33 ^{b}	10.06 ^{ab}
K-Humate	**Zeolite 0**	33.44	53.51 ^{bc}	6.3 ^{c}	15.93 ^{de}	18.02 ^{bc}	2.00 ^{b}	7.07 ^{def}
	Z 1 + H	35.83	57.33 ^{a}	8.3 ^{ab}	19.38 ^{ab}	13.10 ^{e}	2.15 ^{b}	7.80 ^{cdef}
	Z 2 + H	33.44	53.51 ^{bc}	7.7 ^{abc}	19.09 ^{ab}	15.83 ^{d}	2.55 ^{ab}	7.80 ^{cdef}
L.S.D $_{5\%}$			1.72	1.80	1.78	1.72	1.78	1.72

Remark: the footnotes (a–f) indicate the non-significance ranges for the different treatments.

Table 9. Trace elements in soybean (mg kg^{-1}).

Sample	**Seeds (mg kg^{-1})**					**Straw (mg kg^{-1})**				
	Cu	**Fe**	**Mn**	**Zn**	**Si**	**Cu**	**Fe**	**Mn**	**Zn**	**Si**
C	82.5^{a}	48.25^{b}	28.25^{a}	58.75^{c}	79.6^{g}	4.9^{d}	56.21^{e}	59.6^{b}	40.2^{c}	57.7^{g}
H	50.0^{b}	74.5^{d}	82.5^{b}	74.5^{e}	103.7^{d}	3.7^{g}	50.16^{h}	42.3^{f}	44.5^{b}	49.7^{h}
F 2	37.5^{c}	195.0^{f}	30.0^{c}	77.0^{b}	109.5^{c}	4.1^{f}	74.18^{c}	45.4^{d}	29.3^{g}	77.7^{f}
F 2 + H	27.5^{e}	105.0^{g}	20.0^{f}	165.0^{h}	107.9^{c}	4.5^{e}	50.71^{g}	38.6^{g}	35.6^{e}	94.5^{e}
S 2	27.5^{e}	92.5^{h}	15.0^{h}	172.5^{g}	82.5^{f}	5.6^{c}	100.90^{a}	74.2^{a}	80.1^{a}	151.5^{a}
S 2 + H	27.5^{e}	572.5^{a}	17.5^{g}	335.0^{d}	161.5^{a}	6.3^{b}	52.44^{f}	38.6^{g}	38.9^{d}	121.5^{b}
Z 2	30.0^{d}	397.5^{c}	27.5^{d}	167.0^{a}	96.0^{e}	4.8^{d}	93.48^{b}	58.6^{c}	26.9^{h}	108.8^{c}
Z 2 + H	30.0^{d}	222.5^{e}	25.0^{e}	207.5^{f}	128.9^{b}	6.9^{a}	62.83^{d}	43.2^{e}	32.4^{f}	100.7^{d}
L.S.D $_{5\%}$	1.81	1.24	1.88	1.87	1.85	0.17	0.62	0.18	0.12	0.17

Remark: the footnotes (a–h) indicate the non-significance ranges for the different treatments.

The hydrophilic/hydrophobic, as well as the electrostatic are possible modes of interactions.

Different mechanisms may proceed more successful for the more negatively charged smaller particle size. Therefore, the silica mineral shall be the best in the presence of the K-humate although it is the least soluble (from Table 4). It can be considered as a slow release source of the active Si compared to the feldspar and zeolite. The readily soluble Si from the feldspar and zeolite may be lost by leaching or immobilized through precipitation or adsorption within the soil matrix before absorption by the plant. The fertilization efficiency of the K-humate is expected affected by the presence of the charged particles from the different sources like the feldspar, silica, and zeolite.

Soil available silicon

The Si absorption by plants as the H_4SiO_4 depends on the Si concentration in the soil solution. Only 2 mg kg^{-1} is ionized ($H_3SiO_4^-$) at pH 7.0 and the degree of ionization increases as pH increases. The monosilicic acid solubility and concentration in the soil solution are variable, from 1 to 100 mg L^{-1} SiO_2, related with the clay content, iron and aluminum oxides and the pH (Camargo et al., 2013).

Table 4 shows the dissolved Si concentration from the studied minerals by mixing with the humate on the laboratory scale at rate 2 and its percentage from the maximum mineral content of Si as follows: silica (1.46 mg Si = 0.297%) < zeolite (1.71 mg Si = 0.45%) < feldspar (2.09 mg Si = 0.581%). The studied minerals may act as slow release Si sources throughout the cultivation season because their total Si content dissolves gradually affected by the soil solution conditions of a specific pH and organic and inorganic species present in the solution.

Three main pathways of the Si migration and transformation within the soil matrix could be suggested (Bocharnikova & Matichenkova, 2012):

1. Leaching of the soluble Si-rich compounds like polysilicilic acid without transformation,
2. Adsorption of the monosilicilic acid by the plant roots then transformed into the amorphous silica. Translocation of the nutrients within the plant parts and the nutrient uptake may be increased by increasing the PAS,
3. Transformation of soluble forms of the Si into the soil without movement from the soil profile,

The promoted or inhibited different growth stages are often Si-related, affecting the absorption and accumulation of some nutrients by the plant tissues and depending on the chemical equilibria at the root zone distribution (RZD). Some genes were expressed specifically in developing seeds and/or to seed maturation and for the different organs (Deshmukh et al., 2013). Although the Si never directly binds to the hydrogen (H), the hydrated silica moieties may interact with the plant organic constituents through the –OH groups (Rashad & Hussien, 2014). The plant Si uptake acts as a "terrestrial Si filter" controlling the continuous delivery of Si and the absorbed Si species show strong interactions with many plant bio-molecules.

CONCLUSION

The studied minerals may act as slow release Si sources throughout the cultivation season because their total Si content dissolves gradually affected by the soil solution conditions of the specific pH, organic and inorganic species present in the solution. Formation of more biocompatible Si-humate or Si-organo species may be promoted in the absence of some competing species, which may be dissolved from the minerals that are not pure silica like feldspar and zeolite. Formation and absorption of PAS may depend on the Si source whether it is pure silica or an aluminosilicate mineral. The application of the Si minerals as soil amendments should be accompanied by an organic amendment.

CONFLICT OF INTEREST DECLARATION

The author declares that no conflict of interest regarding the present article exists.

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