Spatial Heterogeneity of Soil Silicon in Ukrainian Phaozems and Chernozems

Oksana Tonkha[1], Andrii Butenko[2*], Olga Bykova[3], Yuriy Kravchenko[1], Olena Pikovska[1], Vitalii Kovalenko[1], Iryna Evpak[1], Ihor Masyk[2], Elina Zakharchenko[2]

[1] National University of Life and Environmental Sciences of Ukraine, Heroyiv Oborony St. 15, Kyiv, 03041, Ukraine

[2] Sumy National Agrarian University, H. Kondratieva St., 160, Sumy, 40021, Ukraine

[3] Head of the production laboratory of soil analyses, LLC "LotikaElit" Centralstreet, building 1, building B, Lotivka Village, Shepetivskyi District, Khmelnytsky Region, 30453, Ukraine

[*] Corresponding author's e-mail: andb201727@ukr.net

ABSTRACT

This study investigated the spatial variability of the soil silicon content in relation with topography, parent materials, soil texture, soil organic matter, exchangeable cations and pH. Using the experimental data from two longterm sites in the Forest-Steppe area of Ukraine, the SiO_2 content was estimated in 60 samples taken from a soil depth 0–25 cm. The accumulation of SiO_2 was significantly greater in the soils formed in footslopes. A content of extractable silicon fraction significantly increased from a sandy loam- (366–465 mg·kg⁻¹) to medium- (670–697 mg·kg⁻¹) and heavy- (506–849 mg·kg⁻¹) textured soils. The highest amount of available silicon content was found in the soils containing: 35.0–39.9% of physical clay fraction (< 0.01 mm dia) in Hrytsiv area – 143.0 ± 46 mg·kg⁻¹ and < 25.0% of physical clay fraction in Khrolyn area – 125.0 ±6 mg·kg⁻¹. A significant relationship was found between pH_{KCl}, P_2O_5, K_2O, Mg and both forms of SiO_2. There was almost no correlation between available/ extractable SiO_2 and exchangeable Ca and $\sum$ Ca+Mg. Our studies found the best correlation between extractable SiO_2 and spring barley yield (r = 0.651; P = 0.041), as well assoluble SiO_2 and corn for grain yield (r = 0.514; P = 0.128). No significant relationships were found for sugar beet, winter wheat, sunflower.

Keywords: silicon, chernozem, fertilization, exchangeable cations, pH, soil texture

INTRODUCTION

The study of silicon in the pedosphere expands the possibilities of agronomy and relevant agricultural practices. Modern scientific research is aimed at determining the content of silicon compounds in plants, soils, establishing its critical levels in plants and soils, procedures for assessing the silicon available to plants, and the study of potential sources of silicon for agricultural production. Numerous studies have established the positive role of silicon in plant metabolism, the growth of their biomass due to the accelerated synthesis of the silicon-containing organic compounds [Richmond and Sussman, 2003]. Other authors point to the prominent role of silicon in counteracting biotic (herbivory and pathogen) and abiotic (metal toxicity) plant stresses [Epstein, 1994; Jones &Handreck, 1967]. Silicon fertilizer for industrial and grain crops can increase their yields by 21–44% [Raleigh, 1939; Lipman, 1938; Sommer, 1926; Conner, 1921]. With the intensification of agricultural production, in addition to the basic elements, i.e. nitrogen, phosphorus, potassium, the importance of which for crop yields is recognized, much attention was paid to secondary and trace elements, in particular, silicon [Bykova et al., 2020]. In some regions, fertilizing the soil with the silicon-containing materials is becoming standard agricultural practice for growing rice, sugar cane, sugar beet.

At the same time, the lack of sufficient information on the spatial provision of soils with the available forms of silicon slows down the

introduction of silicon materials into the system of agricultural cropsfertilization. In this regard, we conducted research to study the relationship of different forms of silicon with soil and relief, particle size distribution of the soil, the composition of exchangeable cations, and the soil pH.

Silicon is the second most abundant element of the Earth's crust after oxygen in terms of mass and quantity. Its content in the Earth's crust is 27.6% of its mass [Nedukha, 2019]. Due to the fact that the chemical composition of soils is determined by the elemental composition of the zone of hypergenesis, the concentration of silicon in the solid phase can vary from <1% to more than 45%, depending on the soil-forming rock. The mechanical elements of soils of sandy granulometric composition (sod, sod-podzolic, alluvial) can consist of SiO_2 in almost 100%, while in organogenic soil horizons, the content of SiO_2 may not exceed one percent [Orlov et al., 2005]. In soils, silicon is represented by free compounds SiO_2 (quartz, chalcedony, opal) and salts of silicic acids (silicates). Molecules of ortho- and polysilicon acids are present in soil solutions. In the solid state, SiO_2 is a part of such minerals as: montmorillonite (51.1%), kaolinite (45.4%), illite (49.3%), vermiculite (35.9%), chlorite (26.7%). The SiO_2 content in loesses can vary from 51.7 to 76.0% [Samofalova, 2009]. Increased SiO_2 content in soils may be associated with silica dehydration, acid reaction and mineral adsorption [Landré et al., 2020].

Silicon is a constitutional element of flora and fauna. In 1814, G. Dewey, considering the role of silicon in the construction of the skeletal framework of plants, hypothesized the mineral nutrition of plants with silicon. In 1856, Liebig established the research on the introduction of sodium silicate as a fertilizer and formed a quartet of macronutrients (N, P, K, Si), which are of paramount importance in plant nutrition [Kozlov et al., 2015; Rothamsted, 1992; Tonkha, 2018]. Later, Maxwell (1898) and Hall and Morison (1906) based on the results of field experiments onthe availability of silicon compounds in agriculture. Plantstudies offered to use them as fertilizer. According to the results of the field research conducted by scientists in the tropics [Onodera, 1917; Miyake & Adachi, 1922; Yoshida et al., 1959; Anderson, 1991; Long et al., 2018], it was recommended to use silicon fertilizer for growing rice, sugar canes, sugar beets, kiwi, some cereals. Guntzeret al. (2012) noted the important role of silicon in maintaining the productivity of corn and wheat. The oldest spore plants have the highest content of silicon in the dry matter: horsetail (9%), fern and moss (> 6%). Field crops with high content of silicon include wheat, oats, barley, rice, millet, sugar beets [Voronkov&Kuznetsov, 1984]. In plant and animal tissues, silicon is in the form of orthosilicic acid, orthosilicic ethers, polysilicic acids, amorphous silica, crystalline impurities [Kolesnikov, 2001].

Silicon is absorbed by the lateral roots of plants in the form of a monomeric molecule of silicic acid –H_4SiO_4through the active, passive and withdrawal mechanisms [Cornelis et al., 2011]. The concentration of H_4SiO_4 in the soil solution can range from 0.1 to 0.6 mM [Knight &Kinrade, 2001]. Silicic acid is adsorbed by plants from the soil solution, in which it is found in the forms of mono-silicic, oligomeric and poly-silicic acids [Iler, 1979]. Soluble silicic acid has the ability to form complexes with the organic and inorganic compounds [Williams and Crerar, 1985]. The main sources of silicic acid in the soil solution are various forms of silicon dioxide, silicates, and plant residues [Tubana& Heckman, 2015]. The amount of mono-silicic acid in the soil solution depends on many factors: solubility of the silicon-containing minerals, pH, temperature, particle size fractions, soil moisture and the organic matter content, redox potential [Savant et al., 1997]. In grassland ecosystems, the content of water-soluble silicon available to plants has a seasonal dynamics, with the highest concentrations in spring and summer, and correlates with the biological activity of the soil [Fernandes & Macias, 1987].

The Si of the solid phase of the soil and the Si of the adsorption complexcan be potential reservoirs of silicon in soils. In the solid phase of the soil, silicon is part of weakly crystalline, microcrystalline, amorphous and crystalline forms. The largest amount of Si is concentrated in the crystalline forms of primary and secondary silicates, silica. The amorphous fraction of the solid fraction Si has a biogenic and lytho/pedogenic origin [Matichencov&Bocharnikova, 2001]. The total content of amorphous silica in soils ranges from 1–30 mg g[-1][Jones, 1969; Drees et al., 1989]. Silicon of the adsorbed and liquid phases consists of H_4SiO_4, polysilicic acid, dissolved forms of organic and inorganic silicon compounds. Absorption of silicic acids in the soil occurs on clay minerals, iron and aluminum oxides [Hansen et al., 1994; Dietzel, 2002].

The basis of the mineralogical composition of the studied soils (dark gray podzolic soils and chernozems podzolic) are the silicon-containing minerals of light (quartz, orthoclase, microcline, plagioclase, mica, glauconite, chalcedony) and heavy (zircon, sphen, tuna, pomegranate), epidote, actinolite, augite, kaolinite, montmorillonite, hydromica, chlorite, nontronite) granulometric fractions [Lysenko, 1978]. These minerals are the main source of silicon in the liquid, adsorbed and solid phases in the soils of the Khmelnytsky region. As a result of natural weathering of minerals, silicon of plagioclase, orthoclase and microcline, hornblende enters the soil solution at a rate of $10^{-20.5}$ to $10^{-15.2}$ mol cm^{-2}s^{-1} [White, 1995]. In heavily weathered soils and the soils that are intensively used in agriculture, the time of release of silicon into the soil solution is longer [Tubana, Heckman, 2015]. As a result, the silicon available to plants is temporarily removed from the cycle and the plants need additional application of silicon fertilizers during this period. Most soils in Ukraine have a satisfactory supply of available silicon. However, peatlands, alluvial-sod, sod-lithogenic, sod-podzolic and light gray soils of long-term agricultural use, as well as all organogenic and cation-poor soils have a deficiency of silicon available to plants [Foy, 1992; Snyder et al., 1986; Dantoff et al., 1997]. Dark gray podzolized soils and chernozems podzolized are soils with good and high supply of exchangeable cations and, accordingly, the buffering capacity. The silicon of the soil-absorbing complex of these soils goes into the soil solution and replaces the silicon of the soil carried out by plants. At the same time, during the warm period of the year, against the background of decreasing moisture content available to plants, the concentration of orthosilicic acid increases, which leads to the polycondensation reactions of silanol groups with the formation of the siloxane-type bond in polysilicic acids, which form macromolecules of colloidal size. This process is enhanced by the presence of the hydrocarbonate ions in soils [Brinker & Scherer, 1990]. In the Forest-Steppe of Ukraine, the groundwater of the left banks of rivers and floodplain terraces often contain hydrocarbons, which contribute to the processes of polycondensation and the formation of compacted solid horizons of arable soils.

Thus, many scientists have noted the role of silicon in plant growth and development, identified the conditions and factors influencing the presence and availability of silicon compounds in soils. Given the diversity of Ukrainian soils, their spatial and mineralogical heterogeneity and the intensity of their use, it is important in agricultural production to study different forms of silicon and clarify their relationship with the adsorption complex and soil properties, spatial location of the soil in landscape and the nature of agricultural soil use.

The main purpose of our research was to determine the content of silicon compounds with different mobility in the arable layer of phaozems and chernozems podzolized of the Khmelnytsky region, to assess the spatial variation of these parameters, as well as to identify the relationship between the silicon compounds in soils with particle size distribution and calcium and magnesium exchange cations.

MATERIAL AND METHODS

Study Area

The study area is located nearby the towns of Khrolyn (50.157127N, 27.250299E) and Hrytsiv (49.970262N, 27.219525E) Shepetivka district, Khmelnytskyy region. The research sites were operated by LLC "LotivkaElit". The area is located in the Forest Steppe zone of Ukraine and has a continental climate of mild winter and warm summer. The average annual precipitation is 500–640 mm, with 70% falling from May to September. The average annual temperature is +6.8 °C and the sum of available accumulated temperature (≥10°C) is 2455°C.

The soil types were classified as Phaozems and Chernozems according to the FAO soil classification (Dark forest soil and Podzolized chernozem – in Ukrainian Soil Classification). These soils were formed during the Quaternary periodon losses under the influence of forest and grass vegetation. Farmland is a main type of a land use in this area. The crops grown on all plots included: corn for grain, winter wheat, spring barley, sugar beet, sunflower, soybean.

Sampling and Measurement

Both Phaozems and Chernozems are characterized by a good level of soil fertility parameters. The humus content in the upper soil layer reaches 3.0–3.5%. The content of available phosphorus

compounds – average and high, of available potassium compounds – high. The natural development of podzolic processes and agricultural land use with high amounts of nitrogen fertilizers led to a weakly acidic, and in some places to a moderately acidic pH of the soil solution. A random sample-method was used for taking composite soil samples from the depth of 0–25 cm by a samplingauger (length is 25 cm).A total of 60 soil samples from the cultivated fields were collected during this study: 30 samples – from Khrolyn (site numbers 1–4) and 30 samples – from Hrytsiv (site numbers 5–8) areas (Fig. 1; Table 1).

The soil samples were taken according to ISO 18400–102: 2017. Preparation for chemical analysis was carried out in accordance with DSTU ISO 11464–2007. The following parameters were determined in the soil samples: particle size distribution and content of fractions of particle size elements of different sizes according to DSTU 4730: 2007; pH of salt extract according to DSTU ISO 10390:2007; humus content (SOM) according to DSTU 4289: 2004; mobile

compounds of phosphorus and potassium according to DSTU; the content of exchangeable cations of calcium and magnesium by extraction with 1.0 M solution of KCl. The silicon compounds in soils were determined by using the method of Mullen and Riley with extraction of silicon by V.V. Matichenkov [Titova et al., 2011]. This method allows determining the content of monosilicic acids in the soil. In order to determine the different degree of availability of silicon compounds 2 types of extraction solutions were used: readily available (soluble) silicon was determined by extraction with 0.01 M $CaCl_2$ solution, hardly available (extractable) silicon was determined by extraction with 0.1 M HCl, in the ratio soil: solution 1:10, time interaction of soils with extraction solutions was 1 hour.

Statistical Analyses

IBM SPSS Statistics for Windows v. 20.0 (© SPSS, Chicago, Illinois) was used for all of the statistical analyses. The t-test was performed
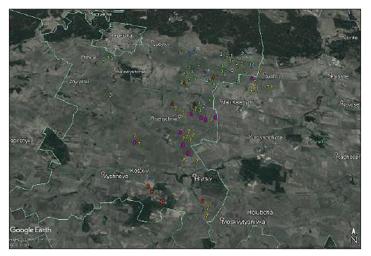

Figure 1. Location of the study area, distribution of sample sites

Table 1. Soil sampling per towns (sites)

PC	Khrolyn				Hrytsiv			
	PU	MS	SN	NS	PU	MS	SN	NS
< 25.0	Level plains	Podzolized chernozem	1	3	Level plains	Podzolized chernozem	5	3
25.0–30.0	Level plains	Podzolized chernozem	2	4	Gently slopes	Phaozem	6	8
30.0–35.0	Gently slopes	Podzolized chernozem	3	13	Gently slopes	Phaozem	7	15
35.0–40.0	Gently slopes	Podzolized chernozem	4	10	Level plains	Podzolized chernozem	8	4
Total			30		Total			30

Notes: PC – Physical clay ($\sum$ < 0.01mm dia) content, %; PU –Physiographic units; MS –Major soil; SN –Site number; NS – Number of samples

to search for the statistical differences between values. A Pearson's correlation coefficient was used to analyze the relationship between the dependent and independent variables.

RESULTS AND DISCUSSION

With long-term agricultural use of soils, a significant amount of available Si is taken up by plant biomass, which leads to a significant decrease in the content of silicon forms available to plants [Meunier et al., 2008; Dantoff et al., 1997]. The s tudies conducted in the United States showed that the removal of silicon by sugar cane and rice is about 300 and 500 kg/ha per year, respectively. U.S. natural grassland ecosystems remove only 22–67 kg/ha of silicon per year [Meyer & Keeping, 2001; Blecker et al., 2006; Makabe et al., 2009]. Overall, between 210 and 224 million tons of Si are taken up annually by agricultural plants [Bazilevich, 1993; Savant, 1997; Titova et al., 2011]. At the same time, there is almost no information in the scientific literature concerning the spatial heterogeneity of silicon compounds, their relationship to the landscape, particle size distribution, composition of exchange cations, nutrients, crop yields, etc. In accordance with the set goal, the selected soil samples were divided into four groups according to their content of physical clay ($\sum$ <0.01 mm): 1. <25.0%; 2. 25.0–30.0%; 3. 30.0–35.0%; 4. 35.0–40.0% (Table 1). The largest number of spatially selected samples (42 samples, 70%) was characterized by the medium loam texture. Site numbers 1–2 and 5–6 had a weakly acidic pH medium (pH 5.1–5.5), very low (1.7%) and low (2.4–3.0%) humus content, medium exchangeable calcium content (1120–1540 mg·kg⁻¹),

average and medium content of exchangeable magnesium (130–170 mg·kg⁻¹) (Tables 2–3). The average values of extractable silicon content were 366–849 mg·kg⁻¹ in terms of SiO_2. That is, the content of these silicon compounds in soils was 2.4–4.2 times lower than the content of exchangeable calcium. In the soils of the Hrytsiv array there are tendencies of expansion of the Ca/SiO_2 ratio with an increase in the content of physical clay in the soils. In the soils of the Khrolyn array there is no regularity in the change of this ratio. The soils of the Shepetivka district of the Khmelnytsky region had mainly low-deficit silicon balance, both soluble and hard extractable forms.

Relationship between soil silicon and soil parameters

The significant positive and negative correlation (r, P < 0.05) was found between soluble SiO_2 and soil particles > 0.05 mm dia from 1, 2, 4–6, 8 sites (Table 4). The correlation coefficient (r) was: -0.59, 0.61, 0.65, -0.57, -0.92 and -0.82 respectively. A significant relationship was also found between soluble SiO_2 and: – soil particles < 0.01 mm dia for the sites: 2 (-0.63), 4 (0.71); – soil particles < 0.001 mm dia for the site: 4 (0.89); – pH_{KCl} for the sites: 4 (0.97), 5 (0.95); – SOM for the site 5 (1.00); – P_2O_5 for the sites: 1 (0.71), 2 (0.64), 4 (0.99); – K_2O for the sites: 1 (0.99), 2 (0.80), 5 (0.87); – Mg for the sites: 1 (-0.95), 4 (0.97), 5 (0.99). Almost nocorrelation was found between soluble SiO_2 and exchangeable Ca and $\sum$ Ca+Mg. For the extractable SiO_2, the significant relationship was found with: – all soil particles for the site 4 (-0.83, -0.87, -0.98); – pH_{KCl} for the sites: 4 (1.00), 5 (0.95), 8 (0.86); – SOM for the sites 1 (0.87) and 5 (1.00); – P_2O_5

Table 2. Results of analyses of the soil samples from the study area

Site number	Content of soil particle fractions, %						pH (l:2.5 KCl)		SOM, %		$\sum$ Ca+Mg, mmol 100 g⁻¹	
	< 0.01 mm *dia*		< 0.005 mm dia		< 0.001 mm dia							
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
1	22.3	14	17.7	16	14.1	35	5.5	11	1.7	12	7.0	17
2	27.4	4	23.3	8	17.1	12	5.3	19	3.0	50	10.4	35
3	31.9	3	27.0	4	19.5	17	5.2	10	2.4	25	12.4	13
4	35.0	1	32.0	22	25.8	26	5.5	11	2.0	35	12.0	11
5	20.6	9	19.0	21	14.0	31	5.6	5	2.5	32	7.9	29
6	27.1	6	23.3	3	18.6	12	5.1	12	2.4	17	8.8	15
7	32.9	5	28.2	5	20.2	8	5.6	7	3.0	17	13.6	7
8	35.8	2	27.6	12.7	20.0	10	5.7	9	3.1	17	14.7	12

Note: SD – standard deviation, %

Table 3. Results of analyses of the soil samples from the study area

Site number	Exchangeable Ca, mg kg^{-1}		Exchangeable Mg, mg kg^{-1}		Soluble SiO$_2$ SiO$_2$, mg kg^{-1}		Extractable SiO$_2$ SiO$_2$, mg kg^{-1}		Exchangeable Ca/ Extractable SiO$_2$
	mean	SD	mean	SD	mean	SD	mean	SD	
1	1120	17	170	36	127	76	465	30	2.4
2	1800	39	165	31	112	36	583	41	3.1
3	2200	13	170	25	131	44	692	21	3.2
4	2130	11	165	10	143	46	506	24	4.2
5	1370	31	130	27	125	6	366	76	3.7
6	1540	16	135	13	120	75	514	41	3.0
7	2380	8	205	23	117	48	670	25	3.6
8	2580	12	213	35	119	33	849	46	3.0

Note: SD – standard deviation, %

for the sites: 2 (0.82), 4 (-0.97), 6 (0.87); – K$_2$O for the sites: 1 (-0.95), 2 (0.76), 5 (0.85); – Mg for the sites: 1 (0.99), 5 (0.99); – Ca/SiO$_2$ for the sites: 1 (-0.78), 5 (-0.72);– $\sum$ Ca+Mg for the sites: 1 (-0.64), 4 (-0.94); 6 (-0.99). There were almost not found correlation between extractable SiO$_2$ and exchangeable Ca.

The data obtained indicate a certain pattern of changes in the SiO$_2$ content from the spatial position of the experimental site and soil parameters. The highest content of soluble SiO$_2$ was observed at site number 4 (143 mg·kg^{-1}) (Table 3). Geomorphologically, this area is the lower part of the steep slope of arable land, which accordingly affected the migration of soluble SiO$_2$ in this area. The highest content of extractable SiO$_2$ was observed at site 8, the study areas of which were located mainly at the beginning of the ravines, which also indicates the influence of the migration processes on the accumulation of the extractable SiO$_2$ in these micro-sites. The content of soluble SiO$_2$ was most correlated with the fraction of sand, pH$_{KCl}$, K$_2$O and Mg and almost did not depend on the content of SOM, Ca and $\sum$ Ca + Mg (Table 4). The largest number of significant correlations of extractable SiO$_2$ was found with pH$_{KCl}$, P$_2$O$_5$, K$_2$O and Mg (Table 5).

Relationship between soil silicon and crop yields

As noted above, silicon is a constitutional element of plants, most of which respond well to the application of silicon fertilizer [Voronkov & Kuznetsov, 1984; Onodera, 1917; Miyake and Adachi, 1922; Yoshida et al., 1959; Anderson, 1991; Long et al., 2018, Raleigh, 1939; Lipman, 1938; Sommer, 1926; Conner, 1921]. Our studies showed the best correlation between extractable SiO$_2$ with spring barley yield (r = 0.651; P = 0.041) and soluble SiO$_2$ with corn for grain yield (r = 0.514; P = 0.128) (Table 6). Other crops did not have a significant correlation with the content of SiO$_2$ in soils.

Table 4. Pearson correlation (*r*) between the soluble SiO$_2$ (mg·kg^{-1}) and the soil parameters of sites 1–8

Soil parameters	Sites							
	1	2	3	4	5	6	7	8
> 0.05 mm dia	-0.59	0.61	0.11	0.65	-0.57	-0.92	0.23	-0.82
< 0.01 mm dia	-0.35	-0.63	0.24	0.71	0.28	0.45	0.19	-0.29
< 0.001 mm dia	0.03	-0.05	-0.08	0.89	-0.60	0.31	-0.05	-0.39
pH(l:2.5 KCl)	0.43	0.36	0.40	0.97	0.95	0.64	0.18	0.34
SOM, %	0.86	-0.18	-0.20	0.12	1.00	-0.22	0.02	0.06
P$_2$O$_5$	0.71	0.64	0.47	0.99	0.44	0.32	0.21	0.55
K$_2$O	-0.99	0.80	0.37	-0.07	0.87	0.07	-0.01	0.46
$\sum$ Ca+Mg, mM/100 g^{-1}	-0.43	-0.24	-0.08	0.82	0.62	-0.62	-0.06	0.02
Ca, mg kg^{-1}	-0.30	0.50	-0.06	-0.08	0.49	-0.11	0.07	-0.08
Mg, mg kg^{-1}	-0.95	0.58	0.22	0.97	0.99	-0.31	0.18	0.03
Ca/SiO$_2$	-0.60	0.57	-0.09	0.05	0.73	-0.12	0.10	-0.06

Table 5. Pearson correlation (r) between the extractable SiO_2 (mg·kg^{-1}) and the soil parameters of sites 1–8

Soil parameters	Sites							
	1	2	3	4	5	6	7	8
> 0.05 mm dia	-0.36	0.71	-0.34	-0.83	0.57	-0.54	-0.13	-0.40
< 0.01 mm dia	-0.58	-0.38	0.43	-0.87	-0.27	-0.17	0.42	-0.11
< 0.001 mm dia	-0.22	-0.19	0.03	-0.98	0.61	-0.02	0.46	-0.55
pH(l:2.5 KCl)	0.64	0.40	0.52	-1.00	-0.95	0.58	0.62	0.86
SOM, %	0.87	0.12	0.09	0.15	-1.00	0.40	-0.27	0.64
P_2O_5	0.50	0.82	0.39	-0.97	-0.43	0.87	0.21	0.21
K_2O	-095	0.76	0.12	0.33	-0.85	-0.54	0.04	0.34
$\sum$ Ca+Mg, mM/100 g^{-1}	-0.64	-0.12	0.36	-0.94	0.62	-0.99	0.69	0.09
Ca, mg kg^{-1}	-0.54	0.54	0.29	0.34	-0.48	0.60	0.38	0.63
Mg, mg kg^{-1}	-0.99	-0.06	0.36	-0.86	-0.99	-0.45	0.27	0.37
Ca/SiO_2	-0.78	0.53	0.30	0.22	-0.72	0.53	0.40	0.71

Table 6. Pearson correlation (r) between soluble and extractable SiO_2 with crop yields

Soil parameters	Correlation	Sugar beet	Winter wheat	Sunflower	Spring barley	Corn
Soluble SiO_2 (mg kg^{-1})	r	-0.271	-0.167	0.137	-0.212	0.514
	P Value	0.162	0.623	0.480	0.556	0.128
Extractable SiO_2 (mg kg^{-1})	r	-0.355	-0.451	0.230	0.651	0.354
	P Value	0.0639	0.163	0.230	0.041	0.316
Si soluble / Si extractable	r	-0.0097	0.0710	0.083	0.183	0.020
	P Value	0.961	0.836	0.670	0.614	0.956

This fact can be explained by the significant influence of other factors on crop yields, such as: fertilizer system, soil organic matter content, available moisture content, nutrient content, etc. Thus, the spatial studies of soils are significantly influenced by the diversity of natural conditions and various agronomic measures. In determining the impact of soil silicon on crop yields, it is advisable to organize a system of scientific field experiments that would take into account geomorphological morphosculptures, lithology, different SiO_2 content in soils, fertilizer system, crop rotation, crops, etc. By organizing such studies, it is possible to determine the weight and significance of each criterion, which would depend on the content and forms of SiO_2 and predict its role in the formation of future crop yields under their normal and stressful growing conditions.

CONCLUSIONS

The spatial distribution of SiO_2 was significantly greater in the soils that formed in footslopes. The content of an extractable silicon fraction significantly increased from a sandy loam- (366–465 mg·kg^{-1}) to medium- (670–697 mg·kg^{-1}) and heavy- (506–849 mg·kg^{-1}) textured soils. The content of soluble SiO_2 was not related to soil texture. The significant positive and negative correlation (r, P < 0,05) was found between soluble SiO_2 and soil particles > 0.05 mm dia from: 1 (-0.59), 2 (0.61), 4 (0.65), 5 (-0.57), 6 (-0.92) and 8 (-0.82) sites. The significant relationship was between pH_{KCl}, P_2O_5, K_2O, Mg and both forms of SiO_2. There was almost no correlation between soluble/extractable SiO_2 and exchangeable Ca and $\sum$ Ca+Mg. Our studies found the best correlation between extractable SiO_2 and spring barley yield ($r = 0.651$; P = 0.041), and soluble SiO_2 and corn for grain yield ($r = 0.514$; P = 0.128). No significant relationships were found for sugar beet, winter wheat, sunflower. This fact can be explained by the significant influence of other factors on crop yields, such as: fertilizing system, soil organic matter content, available moisture content, major nutrients content in soil, etc.

REFERENCES

1. Anderson D.L. 1991. Soil and leaf nutrient interactions following application of calcium silicate slag to sugarcane. Fertilizer Research, 30, 9–18.

2. Bazilevich N.I. 1993. The Biological Productivity of North Eurasian Ecosystems. RAS Institute of Geography. Moscow, Nayka, pp. 293.

3. Blecker S.W., McCulley R.L., Chadwick O.A. et al. 2006. Biological cycling of silica across a grassland bioclimosequence. Glob Biogeochem Cycles 20: 1–11.

4. Brinker C.J., Scherer G.W. 1990. The Physics and Chemistry of Sol-Gel Processing. Academic Press, Inc., Am Imprint of Elsevier, pp. 908.

5. Bykova O., Tonkha O., Pikovska O. & Pak O. 2020. Soluble silicon compounds in soils of different granulometric composition of the western region of Ukraine. Scientific journal «Plant and Soil Science». 11(2), 22–29. doi:http://dx.doi.org/10.31548/agr2020.02.022

6. Cornelis J. T., Delvauz B., Georg R.B., Lucas Y., Ranger J., Opfergelt S. 2011. Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: A review. Biogeosciences, 8: 89–112.

7. Datnoff L.E., Deren C.W., Snyder G.H. 1997. Silicon fertilization for disease management of rice in Florida. Crop Prot 16:525–531 Jones R.L. (1969) Determination of opal in soil by alkali dissolution analysis. Soil Sci Soc Am Proc 33: 976–978.

8. Dietzel M. 2002. Interaction of polysilicic and monosilicic acid with mineral surfaces. In: Stober I, Bucher K (eds) Water–rock interaction. Kluwer, Dordrecht, pp. 207–235.

9. Drees L.R., Wilding L.P., Smeck N.E. et al. 1989. Silica in soils: quartz and disorders polymorphs. In: Minerals in soil environments. Soil Science Society of America, Madison, pp. 914–974.

10. DSTU 4115–2002 Soils. Determination of mobile compounds of phosphorus and potassium by the modified Chirikov method [Valid from 2003–01–01] (State standard of Ukraine).

11. DSTU 4289:2004 Soil quality. Methods for determination of organic matter [Valid from 2005–07–01] (State standard of Ukraine).

12. DSTU 4730:2007 Soil quality. Determination of particle size distribution by pipette method in the modification of N.A. Kachynskiy. [Valid from 2008–01–01]. (State standard of Ukraine).

13. DSTUISO 10390:2007 Soil quality. Determination of pH (ISO 10390:2005, IDT). – [Valid from 2009–10–01] (State standard of Ukraine).

14. DSTUISO 11464–2001 2007 Soil quality. Pre-treatment of samples for physicochemical analysis (ISO 11464:2006, IDT) [Valid from 2009–10–01] (State standard of Ukraine).

15. Epstein E. 1994. The anomaly of silicon in plant biology. Proc. Natl. Acad. Sci. U.S.A., 91: 11–17.

16. Fernandes M.L., Macias F. 1987.Variacionestansional de la composicion de la disolucion de suelos de Galicia enrelacion, 1994.

17. Foy C.D. 1992. Soil chemical factors limiting plant root growth. Adv Soil Sci 19: 97–149.

18. Guntzer F., Keller G., Meunier J. .2012. Benefits of plant silicon for crops: a review. Agron Sustain Dev 32: 201–213.

19. Hall A.D., Morison G.T. 1906. On the function of silica in the nutrition of cereals. Part 1. Proc. Royal Soc. Ser. B, 77: 455–477.

20. Hansen H.C.B., Raben-Lange B., Raulund-Rasmussen K. et al. 1994.Monosilicate adsorption by ferrihydrite andgoethite at pH 3–6. Soil Sci 158: 40–46.

21. IlerR.K. 1979. The chemistry of silica. Wiley, New York, p. 621.

22. ISO 18400–102:2017 Soil quality – Sampling – Part 102: Selection and application of sampling techniques.

23. Jones R.L. 1969. Determination of opal in soil by alkali dissolution analysis. Soil Sci Soc Am Proc 33: 976–978.

24. Jones L.H.P., Handreck K.A. 1967. Silica in soils, plants, and animals. Adv. Agron., 19: 107–149.

25. Knight C.T.G., Kinrade S.D. 2001. A primer on the aqueous chemistry of silicon. In: Silicon in Agriculture, Vol. 8, Studies in Plant Science. Datnoff, L.E., G.H. Snyder, and G.H. Korndörfer (eds.). Amsterdam, The Netherlands: Elsevier, 57–84.

26. Kolesnikov M.P. 2001. Forms of Silicon in Nature. Successes of Biological Chemistry, 41: 301–332 (In Russian).

27. Kozlov A.V., Uromova I.P., Frolov E.A., MozolevaK.Yu.(2015. Physiological Value Of Silicon In Ontogenesis Of Cultural Plants And At Their Protection Against Phytopathogens. The Nizhniy Novgorod State Pedagogical University n.a. K. Minin1: 39.

28. Landré A., Cornu S., Meunier J., Guerin A., Arrouays D., Caubet, M., Saby N.P.A. 2020. Do climate and land use affect the pool of total silicon concentration? A digital soil mapping approach of frenchtopsoils.Geoderma, 364doi:10.1016/j.geoderma.

29. LipmanC.B. 1938. Importance of silicon, aluminum and chlorine for higher plants. Soil Sci. 45: 189–198.

30. Long Jiang-xue, Cheng Hui-yan, Dai Zhi-neng, Liu Jian-fu. 2018. The Effect of Silicon Fertilizer on The Growth of Chives. IOP Conference Series: Earth

and Environmental Science, Volume 192: 1–6.

31. Lysenko M.P. 1978. Loesses: Composition and Engineering Properties. Leningrad, Nedra, pp.208.

32. Makabe S., Kakuda K., Sasaki Y. et al. 2009.Relationship between mineral composition or soil texture and available silicon in alluvial paddy soils on the Shounai Plain, Japan. Soil Sci Plant Nutr 55: 300–308.

33. Matichencov V.V., Bocharnikova E.A. 2001. The relationship between silicon and soil physical and chemical properties. In: Silicon in Agriculture, Vol. 8, Studies in Plant Science. Datnoff L. E., G.H. Snyder, and G. H. Korndörfer (eds.). Amsterdam, The Netherlands: Elsevier, 209–219.

34. Maxwell W. 1898. Lavas and Soils of the Hawaiian Islands. Hawaii. Honolulu: Hawaiian Sugar Planters' Association, pp. 186.

35. Meunier J.D., Guntzer F., Kirman S. 2008. Terrestrial plant-Si and environmental changes. Mineral. Mag., 72: 263–267.

36. Meyer J.H., Keeping M.G. 2001. Past, present and future research of the role of silicon for sugar cane in southern Africa. In: Datnoff LE, Snyder GH, Korndörfer GH (eds) Silicon in agriculture. Elsevier, Amsterdam, pp. 257–275.

37. Miyake, K., Adachi, M. (1922). Chemischeuntersuchungen uber die widerstandsfahigkeit der reisartengegen die "Imochikrankheit". J. Biochemistry. Tokyo, 1 (2): 223–229.

38. Nedukha O.M. 2019. Participation of ions of silicon in adaptation of plants to adverse factors. The bulletin of Kharkiv national agrarian university. Series biology 2 (47): 23–38. (In Ukrainian).

39. Onodera I. 1917. Chemical studies on rice blast. J. of the Scientific Agric. Soc., 180: 606.

40. Orlov D.S., Sadovnikova L.K., Suhanova M.I. 2005. Soil Chemistry. Textbook, Moskow, Higher Education. – 558 p. (In Russian).

41. Richmond K.E., Sussman M. 2003. Got silicon? The non-essential beneficial plant nutrient. Curr. Opin. Plant Biol., 6: 268–272.

42. Rothamsted Experimental Station. 1992. Guide to the Classical Experiment. Details and Guides to the Rothamsted Experiments. Institute of Arable Crops Research Harpenden, Lawes Agricultural Trust, HERTS, pp. 35.

43. Samofalova I.A. 2009. Chemical composition of soil and parent materials. Textbook, Perm, Permskaya SAA, 132 pp. (In Russian).

44. Savant N.K., Snyder G.H., Datnoff L.E. 1997. Silicon management and sustainable rice production. Adv Agron 58: 151–199.

45. Savant N.K., Datnoff L.E., Snyder G.H. 1997. Depletion of plant-available silicon in soils: A possible cause of declining rice yields. Commun. Soil Sci. Plant Anal. 28: 1145–1152.

46. Snyder G.H., Jones D.B., GaschoG.J. 1986. Silicon fertilization of rice on Everglades Histosols. Soil Sci Soc Am J 50: 1259–1263.

47. Suzuki H. 1934. Studies on the Influence of some environmental factors on the susceptibility of the rice plant to blast and hemlminthosporim diseases, and on the anatomical characters of the plant. J. Coll. Agric., 13 (1): 45–108.

48. Titova V.I., Dabahova E.V., DabahovM.V. 2011. Agro- and biochemical methods of investigation of agroecosystems stage. Manual for higher educational institutions. N.Novgorod, 73–84. (In Russian).

49. Tonkha O.L., SychevskyiS.O., PikovskayaO.V, Kovalenko V.P. 2018. Modern approach in farming based on estimation of soil properties variability/ 12th International Conference on Monitoring of Geological Processes and Ecological Condition of the Environment, 68–74.

50. Tubana B.S., Heckman J.R., Silicon in Soils and Plants In: Rodriges F.A., Datnoff L.E. (eds). 2015. Silicon and Plant Diseases, DOI 10.1007/978–3–319–22930–0_2 Springler International Publishing Switzerland, pp. 7–51.

51. Voronkov M.G., KuznetsovI.G. 1984. Silicon in Nature. Seria: People and Environment. Novosibirsk, Nauka, pp. 157 (In Russian).

52. White A.F. 1995. Chemical weathering rates of silicate minerals in soils. In: White A. F., and S.L Brantley. (eds.) Chemical Weathering Rates of Silicate Minerals. Rev. Min. 31: 407–461.

53. Williams L.A., Crerar D.A. 1985. Silica diagenesis. II. General mechanisms. J Sed Pet 55:312–321 Winslow MD (1995) Silicon: A new macronutrient deficiency in upland rice. Working document No 10. International Center of Tropical Agriculture, Cali.

54. Yoshida S., Onishi Y., Kitagishi K. 1959. The chemical nature of silicon in rice plant. Soil and Plant Food , 5 (1): 23–27.