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MOBILITY OF SILICON, FERTILITY OF SOD-PODZOLIC SOIL, BIOACCUMULATION OF SILICON AND YIELDS OF AGRICULTURAL CROPS UNDER THE INFLUENCE OF ZEOLITE

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Abstract

In modern arable farming, beneficial properties of silicon-containing natural materials are of interest, including zeolites which have a structuring and moisture-retaining effect on soil, can optimize conditions for development of agronomically valuable microorganisms, replenish soil solution with available forms of potassium, phosphorus and trace elements, and show activity towards excessive acidity of soils. The provision of silicon makes it possible to increase adaptation of crops to stresses caused by agroecotope factors, leading to an increase in productivity and yield quality characteristics. For the first time, in the conditions of sod-podzolic soils of the Nizhny Novgorod region, we established the beneficial influence of various doses of zeolite rock of the Khotynets deposit on the main properties of effective fertility of sod-podzolic light loamy soil and content of biologically active silicon in it. The impact of the rock on accumulation of various silicon compounds in above-ground biomass of crops is evaluated. Increase of their yield due to zeolite action was revealed and optimization of quality indices of the main part of the crop was established. The purpose of the work was to determine mobility of silicon in sod-podzolic light loamy soil, to evaluate its physicochemical and agrochemical properties, and to identify patterns of bioaccumulation of various silicon compounds by above-ground parts of plants depending on the dose of zeolite rock as a high-silicon reclamation material. Studies carried out in 2015-2017 involved crop varieties zoned in the Volga-Vyatka region, the winter wheat (*Triticum aestivum* L.) cv. Moscovskaya 39 and spring wheat cv. Kurskaya 2038, winter rye (*Secale cereale* L.) cv. Valdai, barley (*Hordeum vulgare* L.) cv. Veles, peas sown (*Pisum sativum* L.) cv. Chishminsky 95 and potato (*Solarium tuberosum* L.) cv. Red Scarlet. The design of the experiment included control (no treatment) and incorporation of 3, 6, and 12 t/ha zeolite of the Khotynetsky deposit (OOO Alsiko-Resurs, Russia) into the soil. The rock was introduced into soil once, manually, in the summer period of 2014. The soil of the field is a sod-podzolic medium-sod shallow-depressed ungelled light-ugly, formed on a cover loam. Plants were harvested upon complete ripeness (grain crops), the beginning (peas) and the end (potatoes) of drying of the tops. In above-ground plant biomass of all crops, the contents of organic, soluble mineral, insoluble polymer and general silicon compounds were determined. Soil was samples on harvest day from five points of each plot by envelope method and the content of mobile silicon compounds was evaluated. Also, in soil samples, the actual, exchange acidity, hydrolytic acidity, the content of exchange compounds of calcium and magnesium, the amount of exchange forms of potassium, the content of mobile phosphorus compounds according to Kirsanov and humus according to Tyurin were measures. It was shown that the use of 12 t/ha zeolite rock contributes to an increase in the content of water-soluble forms of silicon in the soil by 143 % ($p < 0.05$), acid-soluble forms by 2 times. The use of reclamation doses of zeolite for three years contributed to a reliable ($p < 0.05$) decrease of exchange soil acidity by 0.5 pH, hydrolytic acidity by 0.33 mg-eqv/100 g, significant increase of content of exchange compounds of calcium and magnesium (by 4.4 and 10.8 mg-eqv/100 g, respectively). In addition, there was a statistically significant ($p < 0.05$) increase in the amount of mobile phosphorus compounds (by 43 %) and potassium (by 46 %) vs. the control values. The accumulation of silicon in plant biomass depended on a crop, and in all tested cereals, it was higher in by-products than in the main yield. The use of zeolite led to an increase in absorption of silicon from soil, especially in silicon accumulators. Under the action of material, in grain of spring wheat, barley and peas accumulation of total silicon exceeded control values 1.8-, 2.3-, and 3.6-fold, respectively ($p < 0.05$). The use of zeolite activated generation of organic and mineral soluble forms of element in the grain part of crop, but did not contribute to the accumulation of insoluble silicon compounds in the plant biomass. The main yield of winter wheat increased by 0.19 t/ha, of barley by 0.98 t/ha, of sown peas by 0.24 t/ha, of potatoes by 8.6 t/ha, of spring wheat by 0.92 t/ha, and of winter rye by 0.39 t/ha ($p < 0.05$). Doses of 6 and 12 t/ha of zeolite had best effect on all crops, while the ratio of main and by-products narrowed towards grain (tuberous) part of crop. Optimization of silicon nutrition of cultivated plants and mobility of element in soil due to application of high doses of zeolite had a positive effect on quality of the main yield. The accumulation of raw gluten in grain of winter and spring wheat reached 35.3 and 31.1 %, respectively, and the grain levels of protein in barley and peas was 12.7 and 20.6 %, respectively. Improved quality of potato tubers under the influence of the zeolite was expressed in enrichment with vitamin C (up to 22.2 mg%) and higher accumulation of starch (up to 16.3 %). Consequently, use of zeolite as a fertilizer and reclamation material was agronomically feasible and necessary under conditions of sod-podzolic soils.

Keywords: silicon, zeolite, crops, efficiency and quality of harvest, bioaccumulation of silicon in biomass, contents and mobility of silicon in soil

The crop yields largely depends on the availability of mobile forms of macro and microelements, the agrophysical properties of the arable horizon, as well as on the acid-base state of the soil solution [1, 2]. In addition, there are some external dynamic factors of the agroecotope that potentially affect the realization of the agrobiological potential of any crop. These include the dynamics of free water content in the root layer of the soil, the presence of easily soluble salts, aluminum compounds, and other phytotoxicants, the phytosanitary background, and the temperature conditions of the area [3, 4]. Increasing the adaptive potential of crops to such environmental parameters is one of the priority tasks in optimizing the functioning of agroecosystems [5, 6].

In the conditions of modern agriculture, it is necessary to search for effective and environmentally acceptable ways to increase the productivity of cultivated plants, which will ensure the maintenance of effective soil fertility, its acid-base regime, harmonious activation of saprotrophic and nitrogen-fixing associations of microorganisms, and also have a prolonged effect. Such methods include the use of natural high-silicon rocks of various genesis as fertilizers and ameliorants [7-9]. These materials contain a significant amount of nutrients and reclamation components available for plants, including phosphorus, potassium, and silicon compounds, as well as a calcium-magnesium ion exchange complex [10-12].

Silicon is one of the main elements assimilated by the plant organism but its participation in biochemical and physiological processes remains poorly understood [13-15]. It has now been established that silicon compounds are involved in the thickening of epidermal tissue cells, stimulate above-ground growth and root system activity, and increase the overall resistance of the plant organism to abiotic stresses (environmental and salt factors, loss of turgor from drying out and overheating), disease and pest damage [16-18].

Plants absorb silicon from the soil solution in the form of ions (SiO_3^{2-} and SiO_4^{4-}) and monosilicon acids (H_2SiO_3 and H_4SiO_4), after which these compounds are converted to silica gel ($SiO_2 \cdot nH_2O$) in the cell fluid. Then, a biochemical binding to the polymer components of the cell (polypeptides, proteins, and complex carbohydrates), accumulation in the cell walls and the round tissues (the epidermis of leaves and roots), as well as accumulation in phytoliths, occur. It was revealed that the double cuticular layer, which is a silicon cellulose membrane, was formed during the formation of the ground tissues of the plant [19, 20].

It was found [21, 22] that silicon in the plant cell was represented by orthosilicic esters of proteins, lipids, and phospholipids, simple amino acids, hydroxy-amino acids, polysaccharides, and lignin. The amount of silicon bound in organic structures is at least 40% of its total content. As a rule, the predominant form of organically bound silicon is polymer, its amount reaches 80-85%. In particular, in grain crops, up to 60% of silicon is associated with polypeptides and proteins, more than 11% with lipids and phospholipids, about 9% with fiber and hemicellulose, no more than 5% with pectin, less than 3% with lignin.

It is assumed that the essential compounds of silicon, which form bonds in the cell walls of plants with polysaccharides (pectin and fiber), as well as with proteins and lignin, form thermally insulating structures and, as a result, determine the frost resistance of plants, optimize overwintering, and accelerate the spring acclimatization of winter and perennial crops [23-25]. In the structure of fiber and hemicellulose, silicon acts as a crosslinking agent, by forming siloxane bonds (linkages) between sugar residues [26, 27]. Due to the formation of such bonds, the strength of the straw of cereal crops increases, as well as the resistance of grain crops to lodging and arid conditions of the area [28-29]. Some authors explain this phenomenon by an increase in the content of total and organically bound silicon in plant phytomass during vegetation [21, 30, 31].

Polymer substances containing silicon serve as components of the coronary cells of the root cap and mucus secreted by the root fibrils. Recent studies confirm that the external optimization of plant silicon nutrition contributes to an increase in the accumulation of root biomass, their branching, total and adsorbing working surface, and also improves root respiration of plants [32-34]. The use of silicon-containing fertilizers and silatrane growth stimulators in agrocenoses increases the overall adaptive potential of crops with increased content of phytotoxic substances in the soil reduces susceptibility to drought and increases resistance to oxidative and salt stress [35-37]. In addition, the deficiency-free balance of mobile silicon in soils normalizes the production of cytokinins and activates the formation of phytoalexins in plant cells [17, 18], which contributes to their natural resistance to eelworms, hyphae of phytopathogenic fungi, physiological secretions of bacteria, and the action of other root pests [38-40]. These facts can determine a more effective implementation of the agrobiological potential of the crop and its cultivar in specific soil and climatic conditions under the influence of the factors under consideration.

In general, it should be noted that other authors [41-43] note the multiple positive effects of silicon and its compounds in the soil-plant system. However, there is insufficient information in the scientific literature about the reserves of mobile silicon in soils, the reclamation effect of high-silicon rocks concerning excessive soil acidity, as well as about the features of the bioaccumulation of silicon in cultivated plants [44, 45]. In particular, there is very little data on the influence of reclamation high-silicon materials on the acid-base balance of soils, which is considered an acute and urgent problem in the conditions of agriculture in Russia.

Currently, acidification of arable lands in Russia has become almost ubiquitous [46], and this phenomenon applies not only to genetically leached and depleted soils, in particular, the soils of the podzolic series of the Non-Chernozem belt of the country [47]. One of the reasons for this situation is the irrational or extremely insufficient use of chemical ameliorants and organic fertilizers, which contribute to the optimization of soil acidity [48]. Some researchers emphasize the relevance of studying highly silicon rocks as an alternative to traditional ameliorants [36, 37, 45]. In addition, the fractional composition of silicon compounds in agricultural plants is one of the least affected aspects of physiology, which is important for the development of ideas about the distribution of these substances in the plant cell and the formation of physiological mechanisms of adaptation to adverse conditions of the agroecotope. The solution of the above questions is necessary for understanding the mechanisms of silicon participation in the soil-plant system and, as a result, determines the interest in further studying the effects of the use of silicon-containing substances in agroecosystems.

For the first time in the conditions of sod-podzolic soils of the Nizhny Novgorod Region, the authors established the positive effect of various doses of zeolite rock from the Khotynets deposit on the effective fertility of sod-podzolic light-loamy soil and the content of biologically active silicon in it. The influence of the rock on the accumulation of various silicon compounds in the aboveground biomass of crops was characterized. The increase in their yield due to the action of zeolite was shown and the optimization of the quality indicators of the main part of the crop was established.

The work objective is to determine the mobility of silicon in sod-podzolic light-loamy soil, to evaluate its physicochemical and agrochemical properties, as well as to identify the features of bioaccumulation of various silicon compounds by above-ground phytomass of crops, depending on the dose of zeolite rock as a highly silicon reclamation material.

Materials and methods. The research was carried out in 2015-2017 on cultivars of crops zoned across the Volga-Vyatka region [49]: winter wheat (*Triticum aestivum* L.) of the Moskovskaya variety 39 and spring wheat Kurskaya 2038, winter rye (*Secale cereale* L.) Valdai, barley (*Hordeum vulgare* L.) Veles, peas sown (*Pisum sativum* L.) Chishminsky 95, and potatoes (*Solar tuberosum* L.) Red Scarlet. Each year, the results of the study were taken into account for two crops: in 2015, it was winter wheat and potatoes, in 2016, barley and spring wheat, in 2017, peas and winter rye.

Microplot trials with crops were laid in 2014 according to the rules generally accepted in agronomic practice [50] in the field conditions of the enterprise OOO Elitkhoz (Filippovskoye village, Bor municipal district, Nizhny Novgorod Region, 56°31'13.00" N 44°06'57.37"E). Plot (1 m^2) allocation in the experiments was randomized (4-fold replication). The experimental design included group without the use of fertilizers and ameliorants (control), as well as the incorporation of zeolite into the soil (3, 6, and 12 t/ha, Z_1, Z_2, and Z_3, respectively). The rock was introduced into the soil once, manually, in the summer of 2014, when the section was divided into working plots.

The zeolite used in the work at the Khotynets deposit (OOO Alsiko-Resurs, Russia) was represented by clinoptilolite for more than 37% of the composition, and also contained more than 15% of opal-cristobalite, about 11% of hydrous micas, 10% of fine-grained quartz, and 8-10% of montmorillonite [51]. The total composition of the zeolite rock contained SiO_2 (56.6%), CaO (13.3%), MgO (1.90%), P_2O_5 (0.23%), K_2O (1.82%), Na_2O (0.23%), SO_3 (0.13%), Al_2O_3 (10.41%), FeO + Fe_2O_3 (3.87%), and other elements.

The soil of the field was a sod-podzolic medium-sod shallow-depressed ungelled light-ugly, formed on a cover loam. At the time of the experiment, the soil was characterized by a medium acid reaction (pH_{KCl} 4.8), hydrolytic acidity (H_g) of 2.83 mg-eq/100 g, an average content of exchange compounds of calcium (5.10 mg-eq/100 g) and magnesium (1.17 mg-eq/100 g), an average degree of saturation with bases (Vs 69%), low content of humus (1.21%), an average supply of mobile compounds of phosphorus (86 mg/kg) and potassium (110 mg/kg) according to Kirsanov, as well as the average deficit in the balance of actual (16 mg/kg) and potential (213 mg/kg) silicon compounds according to Matychenkov.

The plants were harvested in the phase of complete ripeness (grain crops), as well as in the phase of the beginning (in peas) and the end (in potatoes) of the drying of the tops. The yield (biomass) of the above-ground part of grain crops, tops, and potato tubers was determined in the field on the day of harvest, and the yield (biomass) of grain was determined in the laboratory. In the aboveground phytomass of all cultures, the content of organic, soluble mineral, insoluble polymer, and general silicon compounds was determined; their extraction was carried out according to the method of Kolesnikov [21] with spectrophotometric termination according to the method of Barsukova [52] (PE-5400 VI spectrophotometer, OOO Ekroskhim, Russia). In winter and spring wheat grains, the content of raw gluten was also evaluated by washing according to GOST R 54478-2011 (Moscow, 2012); in barley and pea grains, the amount of protein was determined by wet digestion of the plant mass and protein nitrogen evaporation in the form of ammonia according to the micro-Kjeldahl method followed by conversion to the protein content [52]; in potato tubers, the starch content was determined by polarimetry [52] and the amount of vitamin C was determined fluorimetrically using a FLUORAT-02-5M analyzer (group of companies Lumex, Russia) following FR.1.31.2011.09380 [53].

The soil was selected on the day of harvesting from five points of the plot by the envelope method, prepared for analysis, and the content of mobile silicon compounds (soluble in distilled water and 0.1 n. HCl solution) was determined by spectrophotometric methods of Matychenkov et al. [54] (spectrophotometer PE-5400 VI, OO Ekroskhim, Russia). The actual, exchange acidity was also determined in the soil samples with the potentiometric method (pH meter-millivoltmeter MARK-903, OOO VZOR, Russia), hydrolytic acidity by titrimetry (GOST 26212-91. Moscow, 1992), the content of exchange compounds of calcium and magnesium by trilonometry (GOST 26487-85. Moscow, 1985), the amount of exchange forms of potassium by spectrophotometry (GOST R 54650-2011. Moscow, 2019), the content of mobile phosphorus compounds according to Kirsanov (GOST R 54650-2011), and humus according to Tyurin (GOST 26213-91. Moscow, 1992) by spectrophotometric methods (spectrophotometer PE-5400 VI) [55].

Chemical analyses of soil and plants were performed in 2015-2017. The obtained data were processed by the methods of variance and dispersion analysis [50] in the software package Microsoft Office Excel 2007. The arithmetic means and standard deviations (M±SD), the coefficient of variation (Cv, %), the error of the sample mean ($S_{X\text{mean}}$, %), the least significant difference (LSD_{05}), and Fischer's test (F_f) were calculated at a statistical significance level of $p < 0.05$ (the theoretical Fischer's criterion F_t at $n_l = 3$ and $p < 0.05$ is 3.86).

Results. The base-exchange complex of the used rock included a significant amount of exchange silicon compounds (900 mg-eq/100 g SiO_3^{2-}), calcium (480 Ca^{2+} mg-eq/100 g), and magnesium (Mg^{2+} 160 mg-eq/100 g), as well as exchange compounds of phosphorus (up to 26 mg-eq/100 g) and potassium (up to 25 mg-eq/100 g), which determined the nutritional value of the material for agrophytocenoses. The relatively high solubility and content of the exchange forms of the major cations, as well as biogenic elements in the zeolite, determined its compliance with the gradual chemical decomposition in the soil and biochemical destruction by soil-inhabiting microorganisms, which can have a positive effect on the agrochemical and agrophysical properties of the arable layer.

The positive effect of zeolite on the content of mobile silicon compounds in the soil was established in experiments (Table 1). In particular, the accumulation of water-soluble silicon substances (monosilicon acids and silicate anions) significantly ($p < 0.05$) reached a maximum in 2016 (up to 40 mg/kg of soil), and the effectiveness of the use of zeolite in 2017, when the increase in the rate of excess removal of the element by crops varied from 82 to 209%, depending on the dose of the rock.

1. Mobile silicon compounds in sod-podzolic light-loamy soil upon treatment with zeolite from the Khotynets deposit (OOO Elitkhoz, Filippovskoye village, Bor municipal district, Nizhny Novgorod Province)

Treatment	Mobile silicon compounds, mg/kg soil						On average for 3 years
	2015		2016		2017		
	M±SD	*Cv*, %	*M*±SD	*Cv*, %	*M*±SD	*Cv*, %	
Water-soluble forms of silicon							
Control	16±2	22	14±1	18	11±1	12	14
Z_1, 3 t/ha	22±1	8	25±2	14	20±1	12	22
Z_2, 6 t/ha	24±1	2	33±1	7	29±2	12	29
Z_3, 12 t/ha	29±1	6	40±1	7	34±2	13	34
Ff	24.68		363.98		41.92		
Acid-soluble forms of silicon							
Control	213±9	8	201±4	4	206±5	5	207
Z_1, 3 t/ha	281±12	8	306±3	2	292±5	4	293
Z_2, 6 t/ha	330±21	13	399±7	4	376±7	4	368
Z_3, 12 t/ha	409±26	13	429±4	2	402±6	3	413
Ff	15.56		371.65		330.94		

Note. *Ff* — Fischer's test.

In 2015 and 2016, the use of the minimum dose of zeolite (3 t/ha) statistically significantly ($p < 0.05$) contributed to an increase in the content of easily mobile silicon substances in the soil by 38 and 79%, respectively, relative to the control values, and on average for 3 years, the indicator increased by 57-143%, depending on the dose. The introduction of different doses of the material also had a significant but less expressed effect on acid-soluble forms of silicon. For example, increasing the dose of zeolite by 2 times additionally increased ($p < 0.05$) the content of silicon substances in the soil by 23-47%, depending on the year of the study. In general, the most expressed statistically justified effect was found in 2016, when the indicator increased ($p < 0.05$) by 52-113% from the control value. On average, over the years, the introduction of 12 t/ha of rock into the soil contributed to almost a 2-fold increase ($p < 0.05$) in the content of acid-soluble forms of silicon.

Such regularities were caused by the introduction of a significant amount of water-soluble silicon compounds into the soil in the form of silicates and monomers of silicic acids [56], which was facilitated by a sufficient amount of precipitation actively involved in the dissolution of the rock substance. The weather conditions of 2015 were characterized by an insignificant amount of precipitation, the year itself was generally hotter than the average climatic norms of the region (the hydrothermal coefficient of the HTI in the summer months varied in the range of 0.9-1.0). In 2016, on the contrary, no lack of precipitation was observed, the air temperature fluctuated within the normal range with its slight excess in August (HTI = 1.0-1.1). Weather conditions in 2017 were characterized by abundant precipitation in the spring and the first half of summer, the air temperature was within the average annual norms during the summer season (HTI = 1.1-1.2).

The obtained data are consistent with other reports. In particular, it was reported that when 3 t/ha of amorphous silica was introduced into the soil, the content of water-soluble forms of silicon increased by 7.3 mg/kg (36%) in ordinary chernozem and by 11.9 mg/kg (73%) in chestnut soil [19, 51]. However, the content of acid-soluble silicon compounds in these soils increased less significantly, by 15.5 mg/kg (22%) and 19.7 mg/kg (66%), respectively. The reason for a more significant increase in the content of mobile forms of silicon in sod-podzolic soil could be, on the one hand, low soil buffering, which does not prevent the release of dissolved compounds into the liquid phase, on the other hand, the average acidity of the topsoil, which actively contributes to the chemical mineralization of the substance of ameliorants and the release of their soluble components into the soil solution [1, 11].

The use of zeolite in reclamation doses led not only to the replenishment of the soil solution with mobile silicon compounds but also to a decrease in soil acidity, as well as to the accumulation of the most important biogenic elements — calcium and magnesium (Table 2).

2. Fertility indicators of the of sod-podzolic light loamy soil upon treatment with zeolite from the Khotynets deposit (OOO Elitkhoz, Filippovskoye village, Bor municipal district, Nizhny Novgorod Province)

Treatment	Soil fertility						On average
	2015		2016		2017		
	M±SD	*Cv*, %	*M*±SD	*Cv*, %	*M*±SD	*Cv*, %	
Actual acidity (pH_{H2O}), units							
Control	5.88±0.13	4	5.96±0.07	2	5.92±0.07	2	5.92
Z_1, 3 t/ha	6.54±0.10	3	6.66±0.12	4	6.71±0.09	3	6.64
Z_2, 6 t/ha	6.97±0.16	4	7.03±0.07	2	7.09±0.02	1	7.03
Z_3, 12 t/ha	6.93±0.05	1	6.99±0.12	3	7.04±0.06	2	6.99
Ff	27.81		21.69		128.45		
Exchange acidity (pH_{KCl}), units							
Control	4.81±0.04	2	4.90±0.05	2	4.86±0.09	4	4.86
Z_1, 3 t/ha	5.04±0.07	3	5.17±0.01	1	5.27±0.05	2	5.16
Z_2, 6 t/ha	5.21±0.14	5	5.31±0.02	1	5.49±0.11	4	5.34
Z_3, 12 t/ha	5.16±0.13	5	5.28±0.03	1	5.36±0.08	3	5.27
Ff	2.65		43.76		10.18		
Hydrolytic acidity (H_h), mg-eq/100 g							
Control	2.84±0.02	1	2.75±0.02	2	2.82±0.02	2	2.80
Z_1, 3 t/ha	2.76±0.02	2	2.61±0.02	2	2.67±0.03	2	2.68
Z_2, 6 t/ha	2.60±0.03	2	2.49±0.03	3	2.55±0.02	2	2.55
Z_3, 12 t/ha	2.52±0.01	1	2.41±0.03	3	2.49±0.04	3	2.47
Ff	55.16		24.43		27.51		
Calcium exchange compounds (Ca^{++}), mg-eq/100 g							
Control	5.12±0.04	2	5.23±0.05	2	5.19±0.11	4	5.18
Z_1, 3 t/ha	6.43±0.05	1	8.56±0.05	1	9.11±0.12	2	8.03
Z_2, 6 t/ha	10.30±0.02	2	13.67±0.07	1	15.83±0.28	4	13.27
Z_3, 12 t/ha	18.04±0.03	1	23.89±0.13	2	26.60±0.14	1	22.84
Ff	298.80		341.86		614.74		
Magnesium exchange compounds (Mg^{++}), mg-eq/100 g							
Control	1.19±0.02	3	1.26±0.02	4	1.22±0.01	2	1.22
Z_1, 3 t/ha	3.18±0.02	1	4.49±0.05	2	3.20±0.04	3	3.62
Z_2, 6 t/ha	5.76±0.02	2	8.11±0.05	1	6.85±0.14	4	6.91
Z_3, 12 t/ha	10.92±0.08	2	15.33±0.10	1	13.31±0.05	1	13.18
Ff	950.83		432.97		450.47		
Organic carbon content (humus), %							
Control	1.21±0.01	2	1.24±0.01	2	1.22±0.01	2	1.22
Z_1, 3 t/ha	1.21±0.02	2	1.25±0.01	2	1.23±0.03	5	1.23
Z_2, 6 t/ha	1.22±0.01	1	1.26±0.02	3	1.24±0.02	4	1.24
Z_3, 12 t/ha	1.22±0.01	2	1.26±0.01	1	1.23±0.02	3	1.24
Ff	0.44		0.96		0.11		
Mobile phosphorus compounds (P_2O_5), mg/kg							
Control	90±2	5	86±1	3	81±2	6	86
Z_1, 3 t/ha	99±4	7	103±3	5	114±4	6	105
Z_2, 6 t/ha	117±2	3	122±3	4	131±3	4	123
Z_3, 12 t/ha	112±5	9	119±3	5	125±4	6	119
Ff	19.20		41.91		194.91		
Potassium exchange compounds (K_2O), mg/kg							
Control	107±4	7	92±2	3	89±3	6	96
Z_1, 3 t/ha	118±5	8	121±2	3	126±2	4	122
Z_2, 6 t/ha	132±4	6	139±2	5	149±2	3	140
Z_3, 12 t/ha	130±6	9	133±2	4	143±2	4	135
Ff	6.04		114.04		97.19		

Note. *Ff* — Fischer's test.

For 3 years of zeolite application, the actual soil acidity decreased statistically significantly ($p < 0.05$) by more than 1 unit, and the exchange acidity by almost 0.5 units. This acid-base state of the soil solution was due to a significant ($p < 0.05$) decrease in hydrolytic acidity (by 0.33 mg-eq/100 g) due to a significant ($p < 0.05$) increase in the content of exchange forms of calcium (4.4-fold) and magnesium (10.8-fold) in the soil, as well as a significant narrowing of Ca/Mg ratio towards the latter [46, 48]. These facts, certainly, have a positive significance not only for the acid regime of the soil but also for its granulometric composition, since the interaction of magnesium with organic matter more actively contributes to the formation of Mg-humate microaggregates in the soil [1, 7].

Amid maintaining the content of humus substances, the use of zeolite caused an increase in the amount of mobile phosphorus compounds in the soil by 22-43% and potassium exchange compounds by 27-46%, depending on the dose of ameliorant ($p < 0.05$).

According to modern studies, silicon compounds are necessary for cultivated plants both in nutrition [16-18] and in providing physiological protection against stress factors of the agroecotope [15, 30, 36]. In this regard, the content of silicon and its various fractions in the biomass is an important criterion for assessing the realization of the biological potential of agrophytocenosis and the adaptation formation [38, 44, 56].

3. Silicon bioaccumulation (MP/BP) **in cultivars of various crops upon treatment with zeolite from the Khotynets deposit** (OOO Elitkhoz, Filippovskoye village, Bor municipal district, Nizhny Novgorod Province)

Treatment	Crop					
	2015		2016		2017	
	winter wheat (Moscovskaya 39)	potato (Red Scarlet)	barley (Veles)	spring wheat (Kurskaya 2038)	peas (Chishminsky 95)	winter rye (Valdai)
Total silicon compounds (Si_{tot}), % per abs. dry weight						
Total silicon compounds ($Si_{tot.}$), % per abs. dry weight						
Control	0.23/1.18	3.16/1.67	0.41/1.53	0.19/1.03	0.08/0.90	0.29/1.42
Z_1, 3 t/ha	0.26/1.22	3.20/1.78	0.68/1.69	0.21/1.08	0.19/1.11	0.35/1.50
Z_2, 6 t/ha	0.29/1.30	3.29/1.81	0.89/1.75	0.29/1.20	0.26/1.17	0.41/1.58
Z_3, 12 t/ha	0.34/1.44	3.37/1.85	0.95/1.79	0.34/1.26	0.29/1.19	0.48/1.66
Organic silicon compounds ($Si_{org.}$), % per abs. dry weight						
Control	0.09/0.50	0.70/0.50	0.21/0.92	0.09/0.52	0.01/0.23	0.15/0.78
Z_1, 3 t/ha	0.11/0.59	0.74/0.59	0.41/1.28	0.11/0.59	0.04/0.32	0.20/1.02
Z_2, 6 t/ha	0.13/0.68	0.82/0.65	0.61/1.38	0.17/0.71	0.06/0.37	0.24/1.14
Z_3, 12 t/ha	0.16/0.84	0.88/0.72	0.66/1.47	0.20/0.81	0.07/0.42	0.32/1.31
Soluble mineral compounds of silicon ($Si_{min.}$), % per abs. dry weight						
Control	0.06/0.20	1.30/0.32	0.13/0.26	0.04/0.11	0.05/0.19	0.05/0.16
Z_1, 3 t/ha	0.10/0.22	1.42/0.36	0.16/0.29	0.05/0.14	0.08/0.23	0.08/0.19
Z_2, 6 t/ha	0.11/0.24	1.48/0.37	0.20/0.30	0.05/0.14	0.15/0.25	0.13/0.20
Z_3, 12 t/ha	0.11/0.25	1.53/0.38	0.26/0.30	0.06/0.15	0.21/0.27	0.14/0.22
Insoluble polymer compounds of silicon ($Si_{polym.}$), % per abs. dry weight						
Control	0.08/0.48	1.16/0.85	0.07/0.35	0.06/0.40	0.02/0.48	0.10/0.48
Z_1, 3 t/ha	0.05/0.41	1.04/0.83	0.11/0.12	0.05/0.35	0.07/0.56	0.07/0.29
Z_2, 6 t/ha	0.05/0.38	0.99/0.79	0.08/0.07	0.07/0.35	0.05/0.55	0.04/0.24
Z_3, 12 t/ha	0.07/0.35	0.96/0.75	0.03/0.02	0.08/0.30	0.01/0.50	0.02/0.13

Note. MP/BP — the content of silicon in the main (grain, tubers) and bypass (straw, tops) parts of the crop yield. Sx_{mean} (%) by $Si_{tot.}$ (MP and BP): winter wheat vs. potato — 2 and 4 (MP and BP) vs. 3 and 2 (2015); barley vs. spring wheat — 4 and 6 vs. 3 and 3 (2016); peas vs. winter rye — 4 and 4 vs. 6 and 8 (2017). Sx_{mean} (%) by $Si_{org.}$ (MP and BP): winter wheat vs. potato — 3 and 5 vs. 6 and 7 (2015); barley vs. spring wheat — 8 and 5 vs. 4 and 8 (2016); peas vs. winter rye — 3 and 4 vs. 6 and 4 (2017). Sx_{mean} (%) by $Si_{min.}$ (MP and BP): winter wheat vs. potato — 3 and 4 vs. 4 and 5 (2015); barley vs. spring wheat — 3 and 4 vs. 3 and 3 (2016); peas vs. winter rye — 3 and 4 vs. 3 and 4 (2017). Sx_{mean} (%) by $Si_{polym.}$ (MP and BP): winter wheat vs. potatoes — 4 and 6 vs. 8 and 9 (2015); barley vs. spring wheat — 6 and 5 vs. 5 and 7 (2016); peas vs. winter rye — 5 and 8 vs. 6 and 8 (2017).

First, it should be noted that in the plant bypass of all types, as a whole, more silicon compounds ($Si_{tot.}$) accumulated than in the main part of the crop, except for potato: in this crop, the element content in the tubers was higher than in the tops (Table 3). However, the use of zeolite to the least extent contributed to an increase in the silicon content in potato phytomass, statistically significantly ($p < 0.05$) increasing the accumulation of $Si_{tot.}$ in tubers by 4-7% and in tops by 8-11%, organically bound forms ($Si_{tot.}$) by 17-26 and 30-44%, respectively, and soluble mineral forms ($Si_{min.}$) by 14-18 and 16-19%, depending on the dose of the rock.

For the remaining crops, increased efficiency in the silicon absorption was revealed when zeolite was added. In particular, in the grain part of the winter and spring wheat crop, the content of $Si_{org.}$ increased by 22-78 and 122%, respectively, in winter rye by 33-113%, in barley by 95-214% compared to the control values. In the pea seeds, the amount of $Si_{org.}$ increased 4-7 times ($p < 0.05$) amid the introduction of rock into the soil, which is probably due to its physiological characteristics. i.e., along with all grain crops, barley, as well as peas and potatoes are classified as silicophilic plants [19, 21, 25].

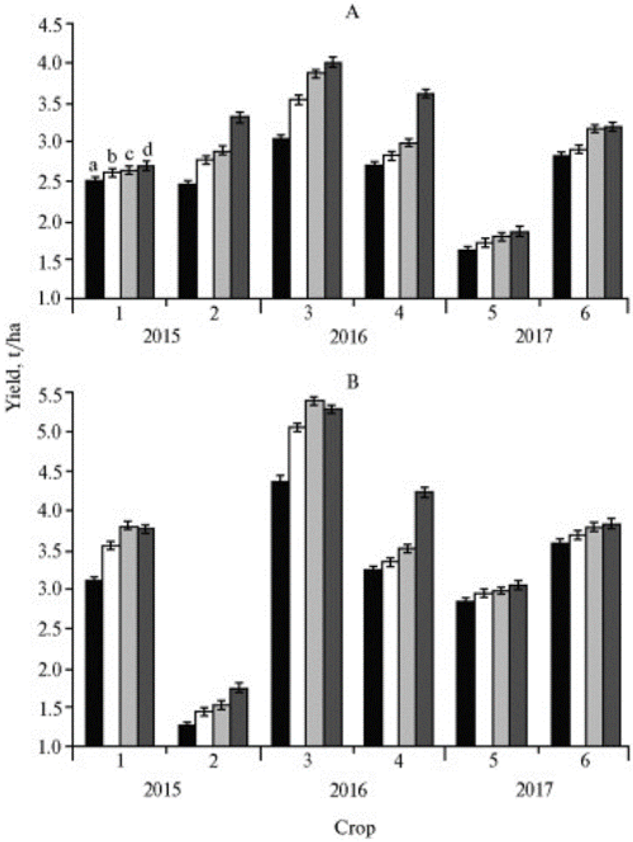
The content of mineral soluble forms of silicon in plant phytomass, which are orthosilicic acid monomers and metasilicates, also increased when the soil was fertilized with zeolite, and to a greater extent in the straw part of the crop than in the grain. The grain of winter rye and winter wheat, barley, and peas was characterized by the best and statistically justified responsiveness in the accumulation of silicon mineral compounds: amid the introduction of 12 t/ha of rock, the content of $Si_{min.}$ increased by 180, 83, 100, and 320%, respectively ($p < 0.05$).

The accumulation of organic and mineral forms of silicon in the bypass part of the crop also increased under the influence of high doses of zeolite. The greatest increase in the amount of $Si_{org.}$ increased in the straw of winter crops (by 68%) and peas (by 83%), and the content of $Si_{min.}$ in straw of spring wheat (by 36%), winter rye (by 38%), and peas (by 42%) ($p < 0.05$).

The content in plant phytomass of the insoluble fraction of silicon compounds ($Si_{polym.}$), represented by polysilicon acids, amorphous silica, and opal microaggregates in phytoliths, in the options with the use of zeolite rock, as a rule, corresponded to the control values or decreased statistically significantly ($p < 0.05$). This phenomenon undoubtedly deserves a separate study and is of value both from the point of view of plant physiology and agronomic quality of the crop. Only in the grain of barley, spring wheat, and peas, as well as in its straw, a certain excess of the insoluble forms of silicon was detected, regardless of the zeolite dose.

By assessing the overall ratio of the accumulation of organic and mineral forms of silicon in plant phytomass, it should be emphasized that the use of zeolite contributed to a greater increase in the proportion of organically bound silicon in the straw of grain crops and potato tops than in grain and tubers (except for pea crop). The proportion of mineral soluble silicon compounds under the influence of zeolite increased in the grain (tuberous) part of the crop, except for barley. At the same time, depending on the dose of the rock, the increase in the proportion of $Si_{org.}$ from the total amount of silicon in the phytomass was more expressed and was traced, as a rule, in all options, and the accumulation of $Si_{min.}$ turned out to be less active and manifested only in the C_1 option. These patterns indicate the gradual binding of silicate ions by organic substances of the cell during the plant vegetation [18, 21].

By analyzing the yield of plants under the influence of high doses of zeolite (Fig.), it should be noted that there is a very significant positive change in indicators for all crops, and, first of all, for barley, a silicophilous plant. The grain biomass of this crop increased by 32% when introducing 12 t/ha of rock into the soil, and with a minimum dose (3 t/ha), the indicator increased by 17% compared to the control ($p < 0.05$). Approximately the same responsiveness to the introduction of silicon-containing material into the soil was characterized by the yield of winter wheat grain in 2015 and peas in 2017. The indicator increased by 4 and 6%, respectively, in the option with the minimum dose of the rock, and by 8 and 15% ($p < 0.05$) for the Z_3. The biomass of the straw part of the crop also increased amid the high-silicon material, but 1.5-2.0 times weaker than the main part, i.e., on average for all treatments by 6% in peas and by 19% in barley ($p < 0.05$) compared to the control. In winter wheat, the straw biomass, on the contrary, responded more actively when zeolite was introduced into the soil, on average, by 20% ($p < 0.05$) for the treatments.



Main (grain, tubers) (A) **and bypass** (straw, tops) (B) **parts of the yield in winter wheat (*Triticum aestivum* L.) cv. Moskovskaya 39** (1), **potato (*Solarium tuberosum* L.) cv. Red Scarlet** (×10) (2), **barley (*Hordeum vulgare* L.) cv. Veles** (3), **spring wheat cv. Kurskaya 2038** (4), **peas (*Pisum sativum* L.) cv. Chishminsky 95** (5), **and winter rye (*Secale cereale* L.) cv. Valdai** (6) **upon treatment with zeolite from the Khotynets deposit:** a — control, b-d — zeolite (3 t/ha, 6 t/ha, and 12 t/ha, respectively) (OOO Elitkhoz, Filippovskoye village, Bor municipal district, Nizhny Novgorod Province). F_f (the main part MP and bypass part BP): winter wheat vs. potato — 0.97 and 35.50 vs. 11.50 and 9.77 (2015); barley vs. spring wheat — 17.97 and 11.93 vs. 48.62 and 36.42 (2016); peas vs. winter rye — 12.35 and 3.10 vs. 11.73 and 3.19 (2017). Fischer's theoretical criterion (F_t) = 3.86 for n_l = 3 and $p < 0.05$.

In general, according to the experiments, it should be noted that the responsiveness of different parts of the crop when applying the rock partly depended on the particular crop. Thus, if in 2015 and 2016, the statistically justified effectiveness of the zeolite effect on the yield of potato tops and spring wheat straw was approximately the same (for potatoes, respectively, from 13 and 16% in Z_1 to 35 and 40% in Z_3, for wheat from 3 and 5% in Z_1 to 31 and 34% in Z_3), then in 2017, when growing winter rye, the effectiveness of the rock was more pronounced with the grain part of the crop (in Z_3, 14% of the reliable increase in grain weight vs. 6% increase in straw weight). In general, the best and most reliable ($p < 0.05$) efficiency was observed for grain crops when applying 6 t/ha of zeolite to the soil (Z_2), and for potatoes and spring wheat, 12 t/ha (Z_3).

The change in the quality indicators of the main products of cultivated plants serves not only as a criterion for the agronomic efficiency of the use of fertilizers [1, 16] but also reflects the state of agrobiogeocenosis and allows assessing the implementation of the agrobiological potential of a crop or a cultivar in specific soil and climatic conditions of cultivation [3, 5].

We found that the content of raw gluten significantly ($p < 0.05$) increased in the Z_3 in winter wheat grain by 5% and in Z_1, Z_2, and Z_3 options in spring wheat grain by 9, 14, and 15%, respectively (Table 4). The greatest and statistically justified ($p < 0.05$) accumulation of protein in the main part of the crop of peas was revealed when 12 t/ha of rock was added to the soil (an increase of 16%), and in barley grain – almost equally when 6 and 12 t/ha were added (by 15-20%).

4. Quality indicators of the main part of the crop yields upon treatment with zeolite from the Khotynets deposit (*M*±SD; OOO Elitkhoz, Filippovskoye village, Bor municipal district, Nizhny Novgorod Province, 2015-2017)

Treatment	Gluten, %		Protein, %		Starch, %	Vitamin C, mg%
	winter wheat (Mosovskaya 39)	spring wheat (Kurskaya 2038)	Barley (Veles)	peas (Chishminsky 95)	potato (Red Scalet)	potato (Red Scalet)
Control	33.7±0.3	27.1±0.4	10.6±0.1	17.8±0.2	14.7±0.2	17.0±0.1
Z_1, 3 t/ha	34.0±0.1	29.4±0.2	11.9±0.2	18.9±0.3	15.0±0.2	19.6±0.1
Z_2, 6 t/ha	34.9±0.3	30.8±0.3	12.2±0.2	19.4±0.5	15.5±0.1	20.3±0.3
Z_3, 12 t/ha	35.3±0.2	31.1±0.2	12.7±0.1	20.6±0.3	16.3±0.3	22.2±0.4
LSD_{05}	1.1	1.7	1.5	1.4	0.6	2.8

A statistically significant ($p < 0.05$) increase in the starch content in potato tubers and the accumulation of vitamin C in them was found in Z_2 and Z_3, by 5-11% for starch and by 19-31% for ascorbic acid, respectively. Amid the minimum dose of high-silicon material (3 t/ha), trends in optimizing the quality indicators of the commercial part of the crop yield were mainly observed. Apparently, it is the high concentrations of mono and polysilicon acids in the soil solution, which may be due to the doses of ameliorant in 6-12 t/ha, that create the optimal background for nutrition and stability of the agrophytocenosis, which is expressed in the implementation of the cultivar (in improving quality indicators) [7, 28, 56].

In this work, the use of zeolite in high doses significantly ($p < 0.05$) contributed to the optimization of most of the considered indicators of the physical and chemical state of the soil and mineral nutrition of cultivated plants, including by replenishing the soil absorbing complex with exchangeable calcium and magnesium compounds, and the mobile nutrient fund of the arable horizon with mobile phosphorus, potassium, and silicon compounds. In turn, it increased the resistance of the agrophytocenosis to environmental factors, since it was expressed not only in increasing the overall productivity of the crop, but also in improving the quality indicators of its main part.

In many studies, the use of silicon-containing materials in a similar way contributed to an increase in crop productivity. In particular, in the work of Vasilieva [7], the use of zeolite-containing tripolite at a dose of 1.5 t/ha on sod-podzolic soil led to an increase in the yield of barley by 0.8-2.4 dt/ha, depending on the year of the study, which was 6-12% of the control values. The effectiveness of the material influence on the productivity of potato reached 27.5-53.8 dt/ha (35-39% relative to the control). In joint studies of Russian and Chinese scientists [56] in the conditions of Hunan province (China) on rice soils formed on alluvial loams, a significant ($p < 0.05$) increase in the yield of rice grain (*Oryza sativa* L.) from the use of silicon fertilizers ranged from 0.95 to 14.9 t/ha. These fertilizers were amorphous fine-dispersed silicon dioxide, as well as organosilicon fertilizer with a high content of not only silicon available for plants, but also organic matter. The obtained results confirm the positive effect of pure silicon preparations on the productivity of agrophytocenoses.

The combined use of high-silicon materials and full mineral fertilizer can have a more significant impact on plant productivity. Loboda et al. [41] studied the effect of zeolite from the Khotynets deposit and NPK fertilizers on the yield of various potato cultivars under similar soil conditions. In the option with the maximum of the studied doses of zeolite (1.2 t/ha) amid the complete mineral fertilizer ($N_{90}P_{60}K_{120}$), the efficiency of the combined action of fertilizers varied from 14.3 t/ha (47%) to 22.9 t/ha (68%) concerning the control, depending on the crop cultivar and weather conditions of the growing year. Despite the relatively low dose of zeolite, its combination with macro fertilizers contributed to a more significant increase in the yield of tubers of the crop.

Thus, when applying high doses of zeolite rock, silicon compounds are more actively ($p < 0.05$) absorbed by plants from the soil. This physiological process is activated by replenishing the soil solution with easily mobile forms of not only silicon but also calcium, magnesium, and other elements necessary for the growth and development of plants. Under the conditions of the microfield experiment based on sod-podzolic light loamy soil, the use of zeolite contributed to the increase in the implementation of the agrobiological potential of the zoned varieties of winter and spring wheat, winter rye, barley, seed sown, and potato, statistically significantly ($p < 0.05$) increasing their yield and improving the most significant quality characteristics. The interaction of the zeolite rock with the soil led to a significant and reliable decrease in its acidity, an increase in the content of exchange compounds of calcium and magnesium, as well as the main biogenic elements. The use of zeolite activated the plant uptake of silicon from the soil and its accumulation in the phytomass in the form of mineral soluble substances and organosilicon components. The established regularities allow considering zeolite as an alternative multi-component reclamation material that has a positive prolonged effect on the soil-plant system and recommending it for research in production conditions on soils of the podzolic series.

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