

The role of highly silicious rocks in increasing productivity and obtaining ecologically-safe agricultural products

Alevtina Kulikova¹, Andrei Kozlov², Nikolai Zakharov¹, Evgeny Yashin¹, and Natalya Khairtdinova^{1,*}

¹Ulyanovsk State Agrarian University, 432017 Ulyanovsk, Russia

²Nizhny Novgorod State Teacher Training University, 603005 Nizhny Novgorod, Russia

Abstract. The paper presents results of long-term research on effectiveness of application of highly-siliceous rocks (diatomite and zeolite) in crop cultivation technology in the conditions of leached black soil of the Middle Volga region. Crop yields and content of heavy metals (Zn, Cu, Pb, Cd, Ni) in products are given in two variants: control and variant with introduction of the highly-siliceous rocks into the soil. It has been established that diatomite from Inza deposit and zeolite from Yushanskiy deposit of Ulyanovsk region are highly effective non-traditional fertilizers due to a complex positive effect on the “soil-plant” system. Thus, the yield increase of sugar beet roots amounted to 6.4 t/ha (+23 %) when diatomite was introduced into the soil at the dose of 5 t/ha, barley – 0.93 t/ha (+52 %), spring wheat – 0, 67 t/ha (+42 %). Highly-siliceous rocks with a highly developed specific surface area, possessing unique physicochemical properties, contribute to production of ecologically safe products. At the same time, the intake of heavy metals in agricultural products for some crops and metals decreased by more than 2 times.

1 Introduction

Ensuring environmental safety of agricultural production is undoubtedly the most important and preferred task worldwide. The problem is escalated due to constant increase of man-made loads on agroecosystems, including heavy metals. The latter specifies the necessity to develop techniques to use polluted lands, which will reduce the supply of toxicants in agricultural products. It is advisable to maximize the usage of techniques that help to improve the soil environment and at the same time to transfer heavy metals to poorly soluble compounds unavailable for plants. In this regard, natural sorbents are of great interest, which, are basically, highly-siliceous rocks (diatomites, zeolites, tripoli, bentonite clays, etc.), represented predominantly by amorphous (active) silica.

Highly-siliceous rocks have specific porosity, high adsorption and ion-exchange capacity (0.8–0.12 g-eq/kg), due to which they are able to hold heavy metals, and amorphous silicon – to transfer them to an inaccessible state for plants. In addition, they contain a number of elements important from an agronomical point of view (P₂O₅, K₂O, CaO, MgO, MnO). It also should be noted that highly-siliceous rocks are affordable (their reserves in the country are huge), cheap and environmentally friendly raw materials [1, 2]. In connection with the above mentioned, the purpose of our research was to study the effectiveness of application of highly-siliceous rocks in crop cultivation to increase their yield and obtain ecologically safe products. Research has been conducted since 2000 up to the present. This paper

presents parameters of yield and environmental safety of grain, tilled and vegetable crops.

2 Objects and methods of the research

Research, as noted above, has been conducted for almost 20 years at the experimental field of Ulyanovsk State Agrarian University in field small-plot experiments using Inza diatomite and Yushanskiy zeolite of Ulyanovsk region in cultivation technologies of grain (winter and spring wheat, barley), tilled (corn, sugar beetroot and feed beetroot) and vegetable (cucumbers, tomatoes, carrots, table beetroot) crops. All experiments were performed in fourfold repetition with strict adherence to methodological requirements. The area of registered plots was 10 m² (vegetable), 20 m² (grain) and 60 m² (tilled) with randomized placement. Analyses of soil and plant samples were carried out according to the corresponding State Standards of two-fold repetition.

The soil of the experimental field is leached black soil with humus content of 4.5–4.7 %, phosphorus (according to Chirikov) of 140–162 mg/kg, potassium – 141–161 mg/kg, the reaction of the soil solution is 5.4–5.6 units of pH_{KCl}.

The composition of highly-siliceous rocks is the following:

- diatomite: SiO_{2 total} – 81.7 %; SiO_{2 amorphous} – 42.1 %; CaO – 0.52 %; MnO – 0.01 %; K₂O – 1.25 %; P₂O₅ – 0.05 %; SO₃ – 0.23 %.
- zeolite: SiO_{2 total} – 56.6 %; SiO_{2 amorphous} – 26.7 %; CaO – 13.3 %; MnO – 0.003 %; K₂O – 1.25 %; P₂O₅ – 0.23 %; SO₃ – 0.5 %.

* Corresponding author: hairtdinova.natalia@yandex.ru

3 Results and discussion

Below are the results of the research and production testing carried out in different years of the study on effectiveness of diatomite and zeolite crop cultivation technology, relating to their yield and product ecological assessment on the content of heavy metals compared to the control variants. All data are average for 3 years (except production experiments), the difference between the variants is reliable (table 1).

Table 1. The effect of diatomite and zeolite on crop yield (t/ha) and content of heavy metals in products (mg/kg in natural substance)

Crop	Variant	Yield	Zn	Cu	Pb	Cd	Ni
Tomatoes (2000–2002)	Contol	38.1	15.3	3.3	0.59	0.18	1.15
	Diatomite 5 t/ha	43.0	14.4	2.2	0.09	0.12	1.00
Cucumbers under cover, (2005–2007)	Contol (turfy sub-strate)	26.6*	11.3	1.2	0.07	0.08	0.50
	Organic Soil 90 % + Diato-mite 5 t/ha 10 %	35.1	5.9	0.5	0.01	0.04	traces
Carrots (production tests, area of 1 plot is 5 ha, 2002)	Contol	13.2	10.9	3.5	0.12	0.09	1.19
	Diatomite 5 t/ha	26.7	9.9	2.7	0.11	0.08	0.77
Spring wheat (2003–2005)	Contol	1.58	8.3	1.5	0.30	0.06	n/a
	Diatomite 5 t/ha	2.25	6.6	0.8	0.14	0.02	n/a
Barley (2003–2005)	Contol	1.79	16.4	2.7	0.33	0.14	n/a
	Diatomite 5 t/ha	2.72	11.0	1.9	0.15	0.07	n/a
Sugar beet-root (2007–2009)	Contol	27.6	72	3.8	0.07	0.05	0.20
	Diatomite 5 t/ha	34,0	6.7	3.1	0.06	0.04	0.17
Corn (2016–2017)	Contol	5.90	9.8	3.1	0.41	0.09	1.50
	Zeolite 0.5 t/ha	6.94	9.5	2.9	0.36	0.06	1.39

*kg/m²

The data in the table convincingly prove high efficiency of diatomite and zeolite as, first of all, silicon fertilizer for crops. Thus, the yield of vegetable crops in both open and protected conditions increased from 13 (tomatoes) to 32 % (cucumbers). The yield of carrots doubled [3] under the production conditions of the training and experimental farm of Ulyanovsk Agrarian University on the area of 5 hectares.

The yield increase of sugar beetroot amounted to 6.4 t/ha (+23 %) when diatomite was introduced into the soil at the dose of 5 t/ha, barley – 0.93 t/ha (+ 52 %), spring wheat – 0.67 t/ha (+42 %). Application of zeolite at the dose of only 0.5 t/ha in corn cultivation provided an increase of grain by 1.04 t/ha, or 18 %.

High efficiency of highly-siliceous rocks in raising the crop yield (according to the results of our research) is caused by their complex positive impact on the “soil-plant” system, which is briefly described by the following:

- the introduction of both diatomite and zeolite had a favorable effect on the physical state of the soil, structuring and loosening it, due to which the arable layer gets appropriate composition for cultivation of any crop [4];

- improvement of soil agrophysical parameters was accompanied by an increase of the activity of soil organisms by 20–30 %, which positively influenced the agrochemical properties of the soil, contributing to transition of nutrients (including silicon) to a more accessible form;

- highly-siliceous rocks greatly increased the water holding capacity of the soil, ensuring the economical and rational usage of reserves of productive moisture during the growing season of crops;

- highly-siliceous rocks have undoubted protective properties due to high content of amorphous silicon, reducing the susceptibility of plants to diseases, insects and pests [5];

- due to the highly developed specific surface area, the porosity, and other unique physicochemical properties, diatomite and zeolite contribute to production of ecologically safer products, as the data in the tables clearly show.

The research results in the table persuasively prove the detoxification ability of highly-siliceous rocks. Thus, for example, the grain of spring wheat and barley accumulated such toxic elements as lead and cadmium two times less, when diatomite was introduced at the dose of 5 t/ha.

Ecological safety is especially important when the products directly go to the table of the consumer, as it is in the case of vegetables. When growing cucumbers in protected soil, 90 % consisting of organic material (turf + sawdust) and only 10 % of diatomite, the vegetables absorbed 7 times less lead and 3 times less cadmium. Studies conducted in the recent years have shown that zeolite in this regard is not inferior to diatomite. Introducing it in the soil at a significantly lower dose (0.5 t/ha) made it possible not only to receive more than one ton of corn from each hectare, but also to significantly reduce the flow of heavy metals into the products, primarily lead, by 12 % and cadmium by 33 %.

The decrease of toxicants in the products of agricultural crops in case of introduction of highly-siliceous rocks into the soil may result from a number of factors. The main ones, apparently, are the following:

- plants are able to protect themselves from an excessive amount of heavy metals and xenobiotics. At the same time, the plant tries to prevent toxicants from entering the protoplast by immobilizing it in the soil with root secretions. Then they are bound by special protein compounds which further become non-reactive [6];

- Silicon-containing materials, when entering the soil, contribute (as noted above) to improvement of nutritional regime and, thus, increase their competitiveness in relation to toxicants [4, 7];

- There is a large number of publications on reduction of stresses caused by heavy metals by means of silicon. It is assumed that it results in subsidence of metals or formation of their complexes with silicon, inhibition of metal transportation from the roots to the

aerial part, their distribution in the plant, enhancement of the immune system [8, 9].

Simultaneous and interrelated action of these factors ensures a reduction of heavy metals in agricultural products, ensuring their ecological safety when highly-siliceous rocks are introduced into the soil.

The simultaneous and interconnected action of these factors when applying high-siliceous rocks to the soil leads to a decrease in the intake of heavy metals by agricultural products, ensuring their ecological safety.

In support of the foregoing, we would like to present the results of experiments conducted by us in 2016–2018. The experiments involved cultivating corn for grain and using zeolite (from Yushanskoye deposit in the Ulyanovsk region) in the fertilization system. Zeolite was used both in pure form and together with mineral fertilizers (the design of the experiment is shown in the table, the soil of the experimental plot is leached black soil, of medium thickness, medium loamy).

Table 2 shows the agrophysical indicators of leached black soil depending on the use of zeolite in the technology of its cultivation according to 6 experimental options.

Table 2. Density and structural condition of the soil when applying zeolite (0-30 cm)

Option	Soil density, g/cm ³	Content of aggregates, % (dry sifting)			Content of water resistant aggregates, %		Kc (coefficient of soil pedality)
		>10 mm	10-0,25 mm	<0,25 mm	3-0,25 mm	<0,25 mm	
Control	1.25	38.5	56.3	5.2	69.8	30.2	1.29
Zeolite 500 kg/ha	1.14	25.2	70.9	4.5	73.5	26.5	2.36
Zeolite 2000 kg/ha	1.10	20.0	76.0	4.0	75.2	24.8	3.17
N ₆₀ P ₆₀ K ₆₀ (NPK)	1.26	35.2	58.8	6.1	69.0	31.0	1.42
Zeolite 500 kg/ha + NPK	1.19	31.2	64.8	4.0	70.8	29.2	1.84
Zeolite 2000 kg/ha + NPK	1.15	27.9	70.0	2.1	75.1	24.9	2.33
LSD ₀₅	0.04	3.9	4.8	0.8	3.9	2.1	

It is necessary to point out that corn is a very demanding plant in terms of the physical state of the soil, due to the structure of its root system. In the first weeks of life, it forms the first tier of primary roots. As the plants develop, they form a second tier of roots, which extend both to the side and in depth up to 30–35 cm, and then penetrate the soil up to 60 cm or more. Thus, the major part of the sensitive roots that nourish the plant is in a layer of 20–40 cm and, therefore, it is necessary to create an optimal agrophysical state of the soil to a depth of at least 30 cm. The density of the arable layer of

0.9–1.1 g/cm³ is optimal for corn, the content of water-resistant aggregates is more than 58 %.

As the results of the study have shown, the agrophysical state of leached black soil does not meet the requirements of the cultivated crop: the density of the soil in the control group is 1.25 g/cm³; the number of agronomically valuable aggregates with sizes of 10–0.25 mm, as well as the coefficient of soil pedality below the optimal values: for row crops, they should be 58–62 % and 2.3, respectively [3].

The application of zeolite to the soil contributed to a significant improvement in the agrophysical state of the arable layer, and its indices reached optimal values for the given crop with a density of 1.10–1.14 g/cm³, with the content of agronomically valuable water-resistant aggregates of 73.5 and 75.2 %. Soil loosening occurred, undoubtedly, due to the structural effect of zeolite on the aggregate composition of the soil: poly-silicic acids are able to bind soil particles into aggregates due to silicon bridges between them [10].

The agrophysical state of the soil has the strongest direct effect on its biological properties, primarily on the activity of microorganisms. Table 3 shows the abundance of the main ecological and physiological groups of microorganisms in the soil of three experimental options identified in 2017. The options were selected as the most promising according to the research results in 2016.

Table 3. Count of functional groups of microorganisms depending on the use of zeolite in corn cultivation

Option	Colony-forming units/1 g of absolutely dry soil*					
	MPA,** x 10 ⁷	Hutchinson-Clayton agar,** x 10 ⁴	Ashby agar,** x 10 ⁴	Menkina agar, x 10 ⁶	Muromtsev agar, x 10 ⁶	Nitrate agar x 10 ⁶
Control	29.46	7.13	1.48	12.74	89.18	34.15
Zeolite 500 kg/ha	3.92	7.17	1.58	12.89	99.30	30.51
Zeolite 500 kg/ha + N ₆₀ (urea)	33.68	7.38	1.52	13.11	98.45	35.01

*Colony-forming units; ** culture medium for counting:

- MPA ammonifying microflora;
- HCA cellulose-decomposing microorganisms;
- Ashbynon-symbiotic nitrogen fixing agents;
- Menkinagarorganotrophic phosphate-reducing microorganisms;
- Muromtsevarolithotrophic phosphate-reducing organisms;
- Nitrateagargroups of organisms that are capable of absorbing humic substances.

According to the table, when zeolite is applied to the soil, the activity of the main groups of microorganisms that determine plant nutrition: ammonifiers, diazotrophs, phosphate-reducing (especially lithotrophic ones, whose activity increased by 11 %) is enhanced.

Changes in the number of physiological groups of microorganisms in the soil were accompanied by

corresponding variability of enzymes, since the latter are produced by microorganisms. Enzymes are biological catalysts that play a crucial role in material and energy metabolism in soils and in all biochemical processes in it. Because of this, they are sensitive indicators of the impact of any factors (both natural and man-made) on the soil ecosystem. The research results showed that when applied to the soil, the enzyme complex is completely preserved in the soil. Their marked activation was observed in the options of the joint use of zeolite with nitrogen fertilizer – by 6 % for protease, 10 % for cellulase and 13 % for phosphatase activity.

Changes in the activity of soil microbiota had a direct influence on the nutrient regime of the soil, as evidenced by the data in the following table (Table 4).

Table 4. Influence of zeolite and mineral fertilizers on the content of available forms of nitrogen, phosphorus and potassium in the soil, mg/kg (average values during vegetation)

Option	(N-NH ₄) ⁺ (N-NO ₃)		P ₂ O ₅		K ₂ O	
	content	deviation from control	content	deviation from control	content	deviation from control
Control	7.8	–	148	–	119	–
Zeolite 500 kg/ha	8.4	+0.6	153	+5	129	+10
Zeolite 2000 kg/ha	8.4	+0.6	158	+10	131	+12
N ₆₀ P ₆₀ K ₆₀ (NPK)	11.3	+3.5	180	+32	149	+30
Zeolite 500 kg/ha+NPK	11.5	+3.7	181	+33	153	+34
Zeolite 2000 kg/ha + NPK	11.7	+3.9	183	+35	158	+39
LSD ₀₅	0.4		5		8	

An analysis of the data in the table demonstrates that when zeolite and mineral fertilizers are added to the soil, despite the increased intake of nutrients by plants for yield formation, an elevated level of nutritional regime is maintained over the vegetation season on average, compared to control. When zeolite was applied in its pure form, the content of mineral forms of nitrogen (ammonium and nitrate) increased by 8 %, when added together with mineral fertilizers, depending on the dose, by 47–50 %. Similar changes occurred in the content of available forms of phosphorus and potassium: the amount of P₂O₅ increased by 32–35 mg/kg, potassium – by 30–39 mg/kg of soil.

Thus, the results of the experiments indicate the undoubted role of zeolite in improving the nutritional regime of the soil.

The detected favorable effect of zeolite on the condition and properties of the soil had an effect on the yield and ecological safety of crop products (figure).

The yield and product quality are a reflection of all the interacting factors in their formation. In relation to fertilizers – they must provide a balanced optimal nutrition of plants under any soil and climatic conditions. The latter is connected not only with the basic nutrients (nitrogen, phosphorus and potassium), but also silicon, as well as trace elements. Judging by the yield data, the

application of zeolite in its pure form, depending on the application dose, was accompanied by a very significant increase in the yield of corn grain by 0.93 and 1.36 t/ha, which indicates the optimization of all environmental factors of the soil (primarily, agrophysical and agrochemical).

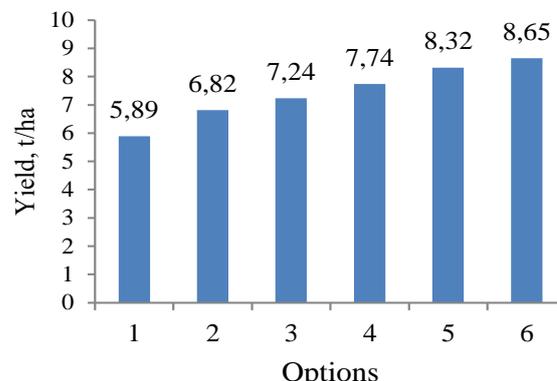


Fig. 1. Yield of corn grain, depending on the application of zeolite and mineral fertilizers in the cultivation technology, t/ha (2016-2018, the differences between the options are reliable) (1 – Control; 2 – Zeolite 2000 kg/ha; 3 – Zeolite 500 kg/ha; 4 – N₆₀P₆₀K₆₀ (NPK); 5 – Zeolite 500 kg/ha+NPK; 6 – Zeolite 2000 kg/ha +NPK)

Corn is an intensive crop and, if it is provided with all life factors, it can give a grain yield of up to 10 t/ha and more. At the same time, the removal of nutrients from the soil is very high: the average content of nitrogen in the grain is 1.80 %, phosphorus (P₂O₅) is 0.57 % and potassium is 0.37 % (K₂O). Therefore, a high level of nutrition with relevant elements is required to obtain a high yield. It is not surprising that when nitrogen-phosphorus-potassium fertilizers of 60 kg per 1 hectare were applied, the yield of corn grain increased in relation to the control variant by 1.85 t/ha.

The use of zeolite with a full dose of mineral fertilizers made it possible to form a crop yield exceeding the control variant by 2.43 t/ha (zeolite dose 500 kg/ha) and 2.71 t/ha (dose 2000 kg/ha), i.e. increase the level of grain increase by 31 and 41 %. Thus, zeolite is a highly effective non-traditional fertilizer of corn.

When cultivating corn with application of zeolite as a fertilizer, all grain quality indicators improved (Table 5).

Table 5. Quality of corn grain

Option	Nitro- gen	Phospho- rus	Potas- sium	Protein
Control	1.49	0.49	0.28	8.94
Zeolite 500 kg/ha	1.54	0.52	0.28	9.24
Zeolite 2000 kg/ha	1.52	0.51	0.31	9.12
N ₆₀ P ₆₀ K ₆₀ (NPK)	1.61	0.55	0.31	9.66
Zeolite 500 kg/ha + NPK	1.70	0.55	0.35	10.20
Zeolite 2000 kg/ha + NPK	1.62	0.57	0.31	9.90

Thus, the content of nitrogen in the grain with application of zeolite in 500 kg/ha increased from 1.49 to 1.54 %, protein from 8.94 to 9.24 %, respectively. A more significant accumulation of nitrogen and protein in

the grain occurred with the combined use of zeolite and mineral fertilizers.

It was stated above that high-siliceous rocks, including zeolites, contribute significantly to growing environmentally clean agricultural products. The studies conducted in this experiment once again confirmed the results of previous studies (Table 6).

Table 6. Influence of zeolite and mineral fertilizers on the content of heavy metals in corn grain, mg/kg

Option	Zn	Cu	Pb	Ni	Cd
Control	10.8	4.3	0.41	1.49	0.09
Zeolite 500 kg/ha	10.4	3.5	0.35	1.40	0.07
Zeolite 2000 kg/ha	9.0	3.1	0.28	1.40	0.06
N ₆₀ P ₆₀ K ₆₀ (NPK)	10.9	4.2	0.39	1.52	0.12
Zeolite 500 kg/ha + NPK	10.5	3.2	0.37	1.43	0.09
Zeolite2000kg/ha + NPK	9.1	3.0	0.30	1.37	0.06
LSD ₀₅	0.3	0.3	0.05	0.1	0.01

This table provides clear evidence that zeolite significantly reduces the intake of heavy metals in corn grain. The latter depends on the dose of zeolite: the larger the dose, the less heavy metals are accumulated in the grain. For instance, at a dose of 500 kg/ha, the content of the most toxic elements of lead and cadmium decreased by 15 and 32 %, respectively, at a dose of 2000 kg/ha – by 32 and 33 %.

According to V.V. Matychenkov et al. [2], in the presence of mono-silicic acid in the medium, a number of elements, which heavy metals are referred to, pass into an insoluble state of the type $2Pb + H_4SiO_4 = PbSiO_4 + 4H^+$, which sharply reduces their availability. Thus, the environmental expert assessment showed that zeolite is not only a means of increasing the yielding capacity, but also growing ecologically clean products.

4 Conclusion

Long-term studies have demonstrated that high-siliceous rocks, diatomites, zeolites, have a beneficial effect on soil properties (physical, biological, agrochemical, etc.); not only contribute to a significant rise in crop yields, but also growing ecologically clean products.

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