BIO Web of Conferences **27**, 00058 (2020) https://doi.org/10.1051/bioconf/20202700058
FIES 2020

Efficiency of zeolite as maize fertilizer of Middle Volga chernozem

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Abstract. The paper presents the results of field and laboratory experiments in studying the effectiveness of zeolite of the Yushanskoye deposit based in the Ulyanovsk region being a fertilizer of maize on grain when applied both in pure form and in combination with mineral fertilizers. A positive effect of zeolite on the agrophysical, biological and agrochemical properties of medium-loamy leached chernozem and, as a result, yield and environmental safety of maize grain has been established. Its increase ranged from 0.93 t/ha (500 kg/ha of zeolite) to 2.43 and made up to 2.76 t/ha when used together with mineral fertilizers. when applying 500 kg/ha zeolite to the soil together with nitrogen fertilizer (urea) at the rate of 60 kg per hectare for 3 years on average the maize grain yield exceeded the option with mineral fertilizers (N60H60R60) by 0.27 t/ha. Zeolite contributed to more environmentally friendly products.

1 Introduction

Zeolites are the rocks extremely widespread on the globe and represented mainly by minerals of the zeolite group, specifically, clinoptilolite, mordenite, phillipsite, chabazite and montmorillonite, cristobalite, calcite, glauconite, etc. are always present in them. Zeolites are characterized by a rigid crystalline structure, which is built of four-, five-, six-membered rings and even more complex ones built by silicon-oxygen tetrahedra. As a result of this structure, a system of channels and cavities is formed in the intracrystalline space of zeolites that are connected with each other and with the environment. Exchange cations of calcium, sodium, potassium, magnesium, barium, strontium, lithium, and zeolite water molecules are located in this system. Due to this, zeolites have unique properties. Specifically, they are as follows: high absorption selectivity and the ability to separate ions and molecules of various substances by size, that is, to work as a molecular “sieve”. Their total porosity reaches 20–53 %, the exchange capacity is 0.5–1.5 gE/kg. The latter causes high adsorption and cation-exchange properties, the ability of selective absorption of substances [1].

Another unique feature of zeolites is that they belong to high-siliceous rocks. Thus, the content of SiO_2 in zeolites of the Mainsky deposit of the Ulyanovsk region is on average 56.60 %, including an amorphous one being 26.71 %. Silicon is a macroelement necessary for plants in the same way as nitrogen, phosphorus, potassium, and its removal with crops often exceeds the combined NPK-compounds. Numerous studies of Russian and foreign authors indicate the positive role of silicon in plant life [2–6]. Despite the fact that the total silicon content in soils is high (from 20–35 to 45–49 %), plants often lack movable silicon compounds due to the slow transition of its crystalline forms to orthosilicic acid and the constant uncompensated alienation of the element subtraction with crops. The lack of available silicon can be compensated by silicon-containing fertilizers, which are currently used only abroad (USA, Japan, Brazil, Mexico, China, etc.). At the same time, siliceous rocks differing by a high silicon content in an amorphous (accessible) form and having a pronounced positive effect on soil properties can be used instead of them [7]. The foregoing determines the purpose of our research, specifically, to study the effectiveness of zeolite in the maize fertilizer system on chernozems of the Middle Volga.

Herewith, the following tasks were set:

- to identify the effect of zeolite on the properties of leached chernozem (agrophysical, biological, agrochemical);
- to establish the dependence of the yield of maize grain on the use of zeolite in its fertilizer system both in pure form or together with mineral, including nitrogen, fertilizers;
- to give an environmental and economic assessment of the technology of cultivating maize using zeolite as a fertilizer.

2 Conditions, objects and research methods

The formation of crop yields occurs in specific soil and climatic conditions and when conducting field experiments aimed to study the effectiveness of any agrotechnical methods, it is important to take them into account.

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The Middle Volga belongs to the forest-steppe zone, characterized by instability of all climatic indicators throughout the year, which is reflected in sharp fluctuations in the temperature regime and distribution of precipitation, especially during the growing season. During research (2016, 2017, 2018), a rather complex interweaving of climatic conditions was observed during the periods of maize vegetation. Nevertheless, despite the frequent changes in weather events, they were quite favorable for the growth of this crop, especially in 2016, which ensured a high level of its productivity.

The soil of the experimental field where the study was conducted is represented by medium-power and medium-loamy leached chernozem with the following agrochemical parameters: humus content of 4.5 % (weak humus content), available phosphorus is 180 mg/kg (high availability), exchange potassium is 145 mg/kg (high availability), pH_{kcl} is 5.4 units (weak acid soil reaction). Boiling caused by hydrochloric acid begins at the depth equal to 84 cm.

The objects of study were:

- leached chernozem medium-power medium loamy;
- zeolite of the Yushan deposit of the Ulyanovsk region with the following content: SiO_2 56.60 % (including the amorphous substance 26.71 %); Al_2O_3 6.15 %; Fe_2O_3 2,34 %; CaO 13.31 %; MgO 1.90 %; K_2O 1.25 %; Na_2O 0.11 %; P_2O_5 0.23 %; TiO_2 0.30 %;
- maize grain, hybrid Voronezh Orzhitsa 237 MV;
- azophoska with a nitrogen, phosphorus and potassium content of 16 % (NPK) and urea with nitrogen content of 46 %.

The experimental scheme included 8 options: 1. Control (without fertilizers); 2. Zeolite 500 kg/ha; 3 Zeolite 2000 kg/ha; 4. N60P60K60 (NPK) 5. Zeolite 500 kg/ha + NPK; 6. Zeolite 2000 kg/ha + NPK; 8. Zeolite 2000 kg/ha + N60. The need for introducing urea into the experimental scheme is due to the fact that nitrogen in the zeolite cannot be restrained, which can become a yield-limiting factor in case of poor humus content of the soil, while the demand for nitrogen in maize is high (removal of nitrogen by grain is 25–30 kg).

The experiments were carried out in strict accordance with the methodological requirements: the area of the accounting plot was 60 m^2, their location was randomized, the repetition was fourfold. Harvesting was carried out on the entire plot. Zeolite and fertilizers were applied manually under pre-sowing cultivation. Soil and plant samples (maize grain) were analysed in an accredited laboratory of the Federal State Budgetary Institution SAS Ulyanovskaya in accordance with the relevant State Standard.

The research results were statistically processed by an analysis-of-variance method.

3 Results and discussion

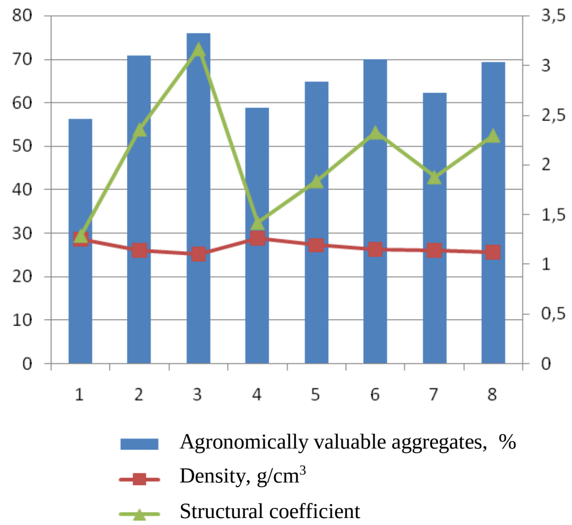
It was indicated above that highly siliceous rocks including zeolites can have a strong effect on the state of the soil especially when applied in large doses. It is possible due to their physicochemical and structural features and properties. Below are the results of changes that occurred in the soil medium when zeolite both in pure form and in combination with mineral fertilizers was introduced into it. The doses of zeolite in this case were equal to 500 and 2000 kg/ha.

3.1 Agrophysical state

The agrophysical state of the soil used for the growth of cultivated plants is extremely important from the perspective of providing them, first of all, with optimal water and air regimes in accordance with the requirements for the soil environment. The physical state of the soil, in addition, determines the direction of soil microorganisms activity. Therefore, it determines the transformation of nutrients from inaccessible forms to accessible compounds as well.

It should be noted that maize is a crop demanding soil physical condition, which is connected with the formation and structure of the root system. In the first weeks of life, it forms the first layer of primary roots, as it develops, the second layer of the root system, which extends both laterally and to the depth of 30–35 cm, and then penetrates to the depth of 60 cm or more. Therefore, for the formation of such a branched system of sensitive (feeding) roots, it is necessary to create appropriate conditions up to the depth of at least 30 cm. Aaddition of an arable layer with the density of not more than 0.9–1.1 g/cm^3 is optimal for maize.

The figure below shows the physical condition of the arable layer (0–30 cm) of leached chernozem when zeolite and mineral fertilizers are added to it.



These data showed that adding the arable layer of the soil did not meet the requirements of the cultivated crop. Specifically, the content of agronomically valuable aggregates 10–0.25 mm in size was below the optimal values, for maize it should be in the range of 58–62 % [7]. The aggregating ability of the soil was reduced and the structural coefficient was 1.29, while at least 2.3 was considered optimal. When zeolite was introduced into the soil, the indicators of the agrophysical state of leached chernozem sharply changed. These changes were as follows: the number of agronomically valuable aggregates increased to 71 and 76 %, the density of the arable layer acquired optimal values for the cultivated crop (0.9–1.1 g/cm^3).

The structure-forming ability of zeolite was evidenced by the structural coefficient, which was 2.36 when applied at the rate of 500 kg/ha and 3.17 at the rate of 2000 kg/ha. Polysilicic acids, as well as humic acids with a sufficient presence of calcium ions stick soil particles into aggregates [8, 9]. The positive effect of zeolite on the agrophysical soil state was maintained even in case of being combined with mineral fertilizers. The latter, when applied to the soil in its pure form, did not have a significant effect on the structural state and density of leached chernozem.

3.2 State of soil microflora

The physical state of the soil has a strong influence on the activity of soil microflora, which reacts most sensitively and quickly to any interventions in the soil environment both natural and man-made. The results of determining the number of ecological and physiological groups of microorganisms in the soil below (Table 1) in 3 experimental variants (as the most effective according to studies of the previous year) showed that the number of ammonifiers (MPA) and cellulose-decomposing (AGK) microorganisms when zeolite was added to the soil of 500 kg/ha was preserved, and their slight activation was observed with the joint use of the rock with urea by 14 and 4 %, respectively.

Table 1. Number of functional groups of microorganisms in the arable layer of leached chernozem under crops of maize

Option	CFU/1 g abs.-dry soil					
	MPA, x10^7	**AGK x10^4**	**ESBI x10^4**	**AMEN x10^6**	**AMUR x 10^9**	**NATx 10^5**
Control	29.46	7.13	1.48	12.74	89.18	34.16
Zeolite, 500 kg/ha	30.92	7.17	1.58	12.89	99.30	30.51
Zeolite, 500 kg/ha N_{40}	33.68	7.38	1.52	13.1	98.45	35.01

The number of non-symbiotic nitrogen fixers (ESBI) increased by 7 %. It is important to note that the number of autochthonous bacteria (NAT) in the soil decreased by 11 %. Taking into account that autochthonous microorganisms are capable of using humic substances as a food source, it can be assumed that zeolite contributes to the preservation of humus in soil.

A change in the number of the main physiological groups of microorganisms accordingly affected the soil enzyme complex (Table 2).

When pure zeolite was introduced into the soil, it remained at the control level, while when combined with nitrogen at the rate of 60 kg of the active substance per hectare, protease activity was increased by 6 %, cellulose by 10 % and phosphatase by 13 %. Against this background, peroxidase activity decreased, which indicated in the chernozems the predominance of the processes of humic substances synthesis over their mineralization strengthened when zeolite is introduced into the soil, in the chernozems.

Table 2. Enzymatic activity of leached chernozem depending on the use of zeolite as maize fertilizer

Option	Hydrolase activity			Oxidoreductase		
	Protease, mg glycine 1 g of soil/24 g	**Cellulase, mg glucose/ 10 g soil/48 g**	**Phosphatase, mg P2O5/1 g soil/30 min**	**Polyphenol oxidase, ml 0.01 per solution I2/1/1 g of soil**	**Peroxidase, ml of solution I2 / 1/1 g of soil / 2 min**	**Catalase, cm 3O2 / 1 g soil / 2 min**
Control	8.66	6.45	2.61	8.20	3.95	13.,09
Zeolite, 500 kg/ha	8.89	6.48	2.66	8.31	3.79	14.88
Zeolite, 500 kg/ha + N60	9.21	7.11	2.96	8.49	3.89	14.16

3.3 Agrochemical condition

The agrochemical state of the soil is characterized, first of all, by the content of basic nutrients in an accessible form (N-NH4, N-NO3, P2O5, K2O), as well as indicators of acid-base properties (pH of aqueous and salt extracts, hydrolytic acidity, the amount of absorbed bases, absorption capacity). Table 3 shows the data on the content of mineral forms of nitrogen, available compounds of phosphorus and potassium according to the options of experience.

Table 3. Effect of zeolite and mineral fertilizers on the agrochemical properties of leached chernozem (average for the vegetation of maize, 2018), mg/kg

Option	$(N\text{-}NH_4)+(N\text{-}NO_3)$		P_2O_5		K_2O	
	Content	**Deviation from control, ±**	**Content**	**Deviation**	**Content**	**Deviation**
Zeolite, 500 kg/ha	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, 20000 kg/ha + NPK	11.7	+3.9	183	+35	158	+39
Zeolite, 500 kg/ha + N_{60}	11.8	+4.0	150	+2	121	+2
Zeolite, 2000 kg/ha + N_{60}	11.9	+4.1	158	+10	127	+8
LSD_{05}	0.4		5		8	

The data in the table indicate that, despite the increased consumption of elements for the formation of a sufficiently high crop yield, when using zeolite in the fertilizer system, a more favorable diet of plants was maintained throughout the growing season. Thus, the content of mineral nitrogen in the soil solution according to the experimental variants exceeded the control ones by 0.6–4.0 mg/kg, available phosphorus by 2–35 mg/kg, potassium by 2–39 mg/kg.

Moreover, the introduction of zeolite in the pure form provided an increase in the availability of 0.6 nitrogen of mineral, up to 5 and 10 mg/ha of available phosphorus to plants and up to 10 and 12 mg/kg of potassium. The latter, undoubtedly, is due to the activation of the vital activity of microorganisms. It is in particular, the result of the lithotrophic microorganisms (microscopic fungi, bacteria) activity, the processes of acidolysis, alkalysis, complexolysis and biodegradation of aluminosilicates (andalusite, beryl, muscovite, nepheline, orthoclase and others). As a result, not only potassium and other elements in an accessible form but also silicon are released [10]. The latter is especially important for maize, which is a siliceous crop. In leached chernozem of the experimental field, there is a deficit of actual silicon (less than 20 mg/kg of soil).

3.4 Productivity and environmental assessment of grain

There is no doubt that the yield and quality of crops in any climatic conditions is determined by the level of their nutrition. As the research outcomes showed, the use of zeolite as a fertilizer in maize contributed to a significant improvement in the nutritional regime of leached chernozem, increasing the content of vital elements in the soil solution in the form of available compounds. The latter provided a very significant increase in the yield of maize (Table 4).

Table 4. The effect of zeolite and mineral fertilizers on the yield of maize grain (2016-2018)

Option	Years, t/ha					
	2016	2017	2018	Average	Deviation from control,	
					t/ha	%
Control	6.21	5.59	5.87	5.89	–	–
Zeolite, 500 kg/ha	7.36	6.51	6.58	6.82	+0.93	16
Zeolite, 2000 kg/ha	7.88	6.73	7.15	7.25	+1.36	23
$N_{60}P_{60}K_{60}$ (NPK)	8.36	7.27	7.58	7.74	+1.85	31
Zeolite, 500 kg/ha + NPK	8.99	7.89	8.07	8.32	+2.43/0.58*	41/7
Zeolite, 2000 kg/ha + NPK	9.35	8.14	8.47	8.65	+2.76/0.91	47/12
Zeolite, 500 kg/ha + N_{60}	8.64	7.42	7.97	8.01	+2.12/0.27*	36/3
Zeolite, 2000 kg/ha + N_{60}	9.07	7.72	8.27	8.35	+2.46/0.61*	42/8
LSD_{05}	0,42	0,27	0,31			

* In the numerator it is in relation to the control, in the denominator to the NPK variant

According to the table, maize can form grain productivity at the level of 5-6 t/ha and more under the conditions of the forest-steppe of the Middle Volga region on chernozem soils with a sufficiently high supply of mobile forms of phosphorus and potassium. The introduction of zeolite as fertilizer into the soil allowed a very significant increase in crop productivity, specifically, on average over 3 years from 0.93 t/ha (zeolite dose of 500 kg/ha) to 1.36 t/ha (zeolite dose of 2000 kg/ha).

Maize is an intensive crop and is capable of forming grain productivity under favorable conditions of more than 10 t/ha, which requires soil provision with all the nutrients in an accessible form. And it is not surprising that the use of complex mineral fertilizers (azophoska) with at the rate of 60 kg of nitrogen, phosphorus, potassium per hectare was accompanied by an increase in yield of 1.85 t/ha, that is, it increased by 31 %. An even higher increase in yield was observed when combining the use of mineral fertilizers with zeolite, which ranged from 2.12 to 2.76 t/ha. At the same time, the proportion of zeolite was at the level of 0.27 to 0.91 t/ha.

It is very important to note that the maize yield during all three years of research on applying zeolite in the proportion of 500 kg/ha to the soil together with urea with nitrogen at the rate of 60 kg per hectare was not inferior, but superior to the option using full mineral fertilizer (N60P60K60) and the average excess was 0.27 t/ha. The latter indicates that when cultivating maize on leached chernozems with a high concentration of available phosphorus and potassium compounds, a favorable soil solution medium (slightly acidic and close to neutral), using zeolite as a fertilizer can dispense with the use of phosphoric and potassium fertilizers. However, average doses of nitrogen (at least 60 kg per hectare) are necessary.

3.5 Environmental Grain Assessment

There is no need to prove that the production of environmentally friendly agricultural products is an important problem of our time. It is very important to consider this when using fertilizers, which may contain toxic substances in the form of impurities. So, cadmium in the amount of up to 50–170 kg/ha and fluorine up to 1.5 g/kg may be present in phosphorus fertilizers [11]. Zeolite in this regard is environmentally friendly material, moreover, due to its crystal-structural features (mentioned above), it can contribute to the production of environmentally safer products. The results of our studies have confirmed this statement (Table 5).

Specifically, when zeolite was introduced into the soil, there was a significant decrease in the production of heavy metals and it is as follows: zinc by 4–17 %, copper by 28–30 %, lead by 15–32 %, nickel by 6 % cadmium by 33–44 %. This is especially true for cadmium, the most toxic element that has mutagenic and carcinogenic properties and is genetically dangerous. In addition, it is the most mobile out of all heavy metals and available at any pH of the soil solution. In this case, its content in the grain of maize grown on the control version approaches the LOC, and when zeolite is introduced into the soil, the cadmium input to the product is greately reduced. The latter is associated with the transition of heavy metals in the presence of silicic acids into sparingly soluble silicates according to the following scheme:

$$2Zn^{2+} + SiO_4^{4-} = Zn_2SiO_4$$

$$2Pb + H_4SiO_4^{4-} = PbSiO_4 + 4H^+ \text{ [4].}$$

Table 5. Content of heavy metals in maize grain, mg/kg

Option	Zn	Cu	Pb	Ni	Cd
Control (without fertilizer)	10.8	4.3	0.41	1.49	0.09
Zeolite, 500 kg/ha	10.4	3.1	0.35	1.40	0.06
Zeolite, 2000 kg/ha	9.0	3.0	0.28	1.40	0.05
$N_{60}P_{60}K_{60}$ (NPK)	10.9	4.2	0.39	1.52	0.12
Zeolite, 500 kg/ha + NPK	10.5	3.2	0.37	1.43	0.08
Zeolite, 2000 kg/ha + NPK	9.1	3.0	0.30	1.37	0.06
Zeolite, 500 kg/ha + N_{60}	9.1	3.0	0.34	1.33	0.06
Zeolite, 2000 kg/ha + N_{60}	8.8	2.9	0.29	1.29	0.05
LSD_{05}	0.3	0.3	0.05	0.10	0.01
Products LOC	50.0	30.0	0.5	5.0	0.1

The economic efficiency of maize cultivation technologies using zeolite and mineral fertilizers was carried out at prices that were set in 2018: the sale price of maize grain was 9,000 rubles per ton, the cost of urea was 21.000 rubles per ton, azophoska 7.000 rubles per ton, zeolite 6.000 rubles per ton.

Maize is a high-yielding crop. In our experiments without the use of fertilizers, the grain yield on the control ranged from 5.59 to 6.21 t/ha (an average of 5.89 t/ha). This yield ensured the profitability level of 192 %. The use of zeolite as a fertilizer at the rate of 500 kg/ha (2nd option) increased it to 212 %. Higher yield (243 %) was provided only by the option of introducing zeolite into the soil at the rate of 500 kg/ha together with urea (N60). However, the level of profitability of grain production at the same time decreased by almost 2 times due to the high costs of transportation and introduction of the breed. Thus, from an economic point of view, the most effective use of zeolite in the cultivation of maize is at the rate of 500 kg/ha in conjunction with urea at the rate of 60 kg nitrogen per hectare, which provides additional 2.12 tons of grain per hectare.

4 Conclusion

1. Zeolite of the Yushanskoye deposit of the Ulyanovsk region, when introduced into the soil, had a significant positive effect on the agrophysical state of leached chernozem. The effect wass as follows: the number of agronomically valuable aggregates increased to 71 and 76 % (zeolite doses of 500 and 2000 kg/ha), whereas at control it was 56 %, the density of the arable layer acquired optimal values for maize (1.14 and 1.10 g/cm^3). The positive effect of zeolite on the agrophysical properties of the soil was maintained when combined with the use of mineral fertilizers.

2. The use of zeolite as a fertilizer for the improvement of soil agrophysical state was accompanied by an increase in the activity of soil microorganisms. Specifically, the increse was as follows: the number of ammonifiers increased by 14 % (the dose of 500 kg/ha), cellulose-decomposing microorganisms by 4 %, non-symbiotic nitrogen fixers by 11 %. Changes in the abundance of the corresponding physiological groups of microorganisms in the soil influenced the enzyme complex in the following way: it remained at a control level when zeolite was used in its pure form, and when combined with nitrogen fertilizer, it was 6 % protease, 10 % cellulose-degrading, 13 % phosphatase activity. Polyphenol oxidase activity also increased, while peroxidase activity decreased, which indicated the predominance in the chernozems of humic substances synthesis over their mineralization and strengthening of these processes when zeolite was introduced into the soil.

3. The use of zeolite in maize cultivation technology was accompanied by a significant improvement in the nutritional regime of leached chernozem. Despite the enhanced nutrition of plants with elements for the crop formation throughout the growing season, the content of mineral nitrogen in the arable layer (N-NH4+N-NO3) when adding zeolite in the pure form at the rate of 500 kg/ha was 0.6 mg/kg higher, available phosphorus at 5 mg/kg and potassium at 10 mg/kg, at the rate of 2000 kg/ha, respectively, at 0.6, 10 and 12 mg/kg of soil.

4. Introduction of zeolite as a fertilizer into the soil had a very significant effect on the maize grain yield. Its increase was 0.93 t/ha (zeolite dose 500 kg/ha) and 1.36 t/ha (dose 2000 kg/ha) when used in pure form, and 2.43 and 2.76 t/ha when combined with mineral fertilizers. The maize grain yield when applying zeolite at the rate of 500 kg/ha to the soil together with nitrogen fertilizer (urea) at the rate of 60 kg per hectare was not inferior, moreover, on average for 3 years it exceeded by 0.27 t/ha the option with using mineral fertilizers N60P60K60. Zeolite contributed to more environmentally friendly products.

5. When cultivating maize on chernozems with high availability of phosphorus and potassium compounds, it was most cost-effective and expedient to use zeolite at the rate of 500 kg/ha together with nitrogen fertilizer with the nitrogen rate of 60 kg per hectare.

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