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NITROGEN SORPTION AND ITS RELEASE IN THE SOIL AFTER ZEOLITE APPLICATION

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Abstract

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The dynamics of nitrate and ammoniac nitrogen in soil after the application of zeolite of various amounts was monitored. The decreased ammonium content was apparent one month after zeolite application compared to the variants without zeolite due to the specific fixation of NH_4^+ cations on the zeolite lattice (92.5 mg at the control variant and 77.2 - 81.0 mg per kg of soil at the tested variants). Three months later, an ammonium content increase of 24-59 % at the variants with zeolite was observed in comparison with the control variant due to the gradual ammonium release from the zeolite lattice. Six months after zeolite application into the soil, statistically significant differences were found not only between the control variant and variants with zeolite, but also among individual variants with various zeolite dose (H=14.201; p=0.003 according to the Kruskall-Wallis test).

The nitrification process in the soil is less intense due to the influence of applied zeolite. In the autumn period, the nitrate nitrogen content in the soil decreases by 66-78 % compared to the control variant, therefore, the nitrate leaching from the soil horizons to the ground water is less. In summary, zeolite can be considered as a slow releasing nitrogen fertilizer.

*Key words***:** zeolite, soil nitrogen dynamics, nitrate and ammoniac nitrogen

Abbreviations: N_{an} – inorganic nitrogen, N_{total} – total nitrogen, C_{org} – organic carbon

Introduction

Swedish mineralogist Alex Fredrik Cronstedt (Cronstedt, 1756) originally coined the term zeolite in 1756. Regardless of the considerable physical-chemical properties of zeolites they had not found a practical utilization for a long time which was due to the research only on the zeolites of volcanic origin. Their share of the total volume of rocks rarely exceeds a few percent. Zeolites belong to a group of hydrated aluminosilicate monohydric elements sodium, potassium and bivalent calcium. Their basic building unit is a crystalline lattice of silicon tetrahedrons and aluminum octahedrons. The discovery of zeolites of sedimentary origin allowed their utilization to be developed seriously. Due to their extremely high sorptive capacity, which depends on dominant mineral, zeolites can be applied in different area of national economy, including agriculture.

The zeolite utilization in agriculture as a “carrier” of fungicides, herbicides or plants’ mineral nutritive elements is feasible just because of the high sorptive capacity of this mineral. The experiments of Manolov

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(2000) show that a nitrogen and phosphorus saturated zeolite applied into the soil leads to higher content of mentioned nutrients at barley. By applying nutrients into the soil in this way, their consumption could be reduced. There is no need of redundant delivery of raw materials and consequently, fewer nutrients (mostly nitrogen that causes ineligible eutrophication of water sources) are leached into the ground and surface water.

The first zeolite deposit in Slovakia, verified by research, is near the village Nizny Hrabovec (48°51’36’’N, 21° 45’54’’E), Eastern Slovakia. Singliar (1992) claims that the average content of cliniptillolite is 57.2 %. According to Hanes (1999) and Singliar (1992) the chemical composition of zeolite from Nizny Hrabovec deposit is as follows: SiO_2 – 58.83-70.90 %, Al_2O_3 – 12.07-12.67 %, Fe_2O_3 – 1.38-2.30 %, CaO – 2.91-7.88 %, K_2O – 2.16-3.29 %, MgO – 0.80-1.10 %, Na_2O – 0.54-0.69 %, H_2O – 3.86-4.63 % . Michalik and Missik (1995) who used radionuclide ^{45}Ca and ^{32}P confirmed the excellent sorptive properties of Nizny Hrabovec zeolite deposit. They recommended using zeolites as adsorbents, suitable for the risk reduction of heavy metal soil contamination. Zeolite can be used also to decrease the heavy metals’ content of plants. Such results were obtained by Petkova et al. (2000) when zeolite-glauconite and zeolite-phosphorite mixture was applied into the soil the lead content in radish plants decreased approximately twice compared to the radish grown on contaminated soil.

Material and Methods

The natural zeolite impact on the dynamics of mineral nitrogen (both nitrate and ammoniac forms) was observed in soil depth of 0.0-0.3 m.

Because of the results of the laboratory experiments in which the sorption speed of NH_4^+ on the powdered zeolite mineral was observed (Hronec et al., 1989) the impact of natural zeolite on the dynamics of mineral nitrogen in soil depth of 0.0-0.3 m was verified. The solution of the above-mentioned objectives was ensured by the field experiment, which was based on clay Eutric Cambisols the basic chemical properties of which are illustrated in Table 1 (nutrient analyses according to Mehlich II., organic carbon according to Tjurin).

Zeolite rock with dominating mineral clinoptillolite was from Nizny Hrabovec deposit and its granulometric composition was as follows:

Fraction	0.06 – 0.02 mm -	11.10 %
	0.02 – 0.01 mm -	16.36 %
	< 0.01 mm -	72.54 %

The heavy metals’ content in zeolite was not higher than the allowed at waste application into the agricultural soils in Slovakia (Table 2).

There were four variants of the experiment:

K - control variant without any fertilization; Z_1 - 600 kg of zeolite per hectare; Z_2 - 900 kg of zeolite per hectare and Z_3 - 1200 kg of zeolite per hectare.

All variants were carried out four times. The experimental field was 50 m^2 (10 x 5 m). The experimental

Table 1
Selected chemical soil indicators (Eutric Cambisols)

Depth, m	pH	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	N_{min}	N_{total}	P	K	Mg	C_{org}
		mg.kg^{-1}							%
0.0-0.3	7.2	34.3	26.8	61.1	2043	118	411	166	1.62
0.3-0.6	7.3	24.6	27.8	52.4	1717	89	294	173	1.31

Table 2
Content of heavy metals in zeolite (in mg kg^{-1} of solids in lixivium 2 M HNO_3)

	Pb	Cd	Cr	Cu	Zn	Ni
Zeolite	16.80	0.15	3.00	15.00	111.00	1.90
Maximum allowed content *	750	10	1000	1000	2500	300

* according to the Act of National Council of the Slovak Republic No. 188/2003 about waste application into the agricultural soils

crop was medium-ripening white cabbage (*Brassica oleracea, L.)* (Slava variety) grown at the ordinary agricultural agrotechnics. Seedlings were planted on April 26th; harvest was finished on August 25th, 2011. The average soil samples were taken and analyzed for pH, nitrogen (ammonia and nitrate) content, the content of available phosphorus, potassium and magnesium and organic carbon before setting up the experiment and after its completion from each site. In addition, once a month, soil samples from a depth of 0.0-0.3 m of each site were taken in order to monitor the dynamics of ammonia and nitrate nitrogen in soil.

The statistical processing went out from the assumption that the zeolite dose influences on both ammonium and nitrate content in the soil. Kruskall-Wallis test was chosen for verification of this hypothesis. In case of rejection of the null hypothesis, the non-parametric Mann-Whitney test was used.

Results and Discussion

The exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ cations of zeolite mineral are already present in the natural deposits. The zeolite can exchange these cations for NH_4^+ and other metal cations, depending on the pH value of the solution and their concentrations. The principles of sorption equilibrium creation are applied at the exchange of zeolite rock cations in the solution or sorption of the solution. According to Ames (1964) at sorption of cations in zeolite rock, the following range selection is kept: $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$.

In our previous paper (Hronec et al., 1989) was demonstrated that the sorption especially of ammoniac nitrogen on the zeolite rock is extraordinary fast. In the first minute, the sorption of more than 90 % of the maximum potential ammonia concentration on zeolite rock by infinite time scale was observed. During the next period from 2 minutes up to several hours, the concentration of NH_4^+ did not change significantly and it remained almost constant.

However, it can be assumed that this process will depend on the size of the zeolite particles, so increasing it the stabilization of sorption equilibrium in time, especially NH_4^+ will be slower. This assumption is confirmed by Horvathova and Kachnak (1987) who measured the time dependence of sorption on zeolite-grained rocks fraction 0.2-3.2 mm with heavy metals. The stabilization of exchange equilibrium was reached only in a few hours.

Regarding now, the zeolite rock performs in the soil for several years, the stabilization of ionic exchange balance in several minutes or hours can be considered very quickly. This knowledge can be applied to liquid nitrogen based plant nutrition on the basis that zeolite rock put into the soil would prevent the escape of redundant ammonium ions because these would be bound by zeolite rock in moist soil very quickly and would be gradually released to plants as soil solution. The observed phenomenon of ammonium cation fixation was verified directly in field conditions. Three doses of zeolite were used – 600, 900 and 1200 kg per hectare. A month later, after application of zeolite to soil, the Eutric Cambisols topsoil contained 14-20% more ammonia nitrogen (92.5 $mg.kg^{-1}$ of soil) in the control variant compared to the experimental variants (77.2-81.0 $mg.kg^{-1}$ of soil). This reduction of the contents in experimental variations can probably be attributed to fixation of ammonium ions by specific areas in the zeolite crystal lattice because they are bonded to the zeolite with the most intensity of all cations (Cicisvili and Andronikasvili, 1988). Similar findings were reached in our previous research (Torma and Chimic, 1992). There is a change in this subsequent period: the content of ammonia nitrogen in the topsoil in the variants with applied zeolites increases and reaches 24-59% higher values after three months (depending on the amount of zeolite) comparing to the control variant. At the end of the field experiment (five months after the application of zeolite), the experimental variants achieve 68.5-86.9 mg, and the control variant achieves only 55.2 mg per kilogram of soil (Figure 1).

Based on the calculated values of the Mann-Whitney test we could conclude that statistically significant differences of average value of NH_4^+ concentrations in the soil were confirmed not only between the control variant and observed ones but among all observed variants with each other, as well (Table 3).

Statistical analysis of the results according to the Kruskall-Wallis test confirmed significant differences between the average values of all observed variants

(H=14.201 with p-value 0.003). The Mann-Whitney test results are contained in Table 4.

Russian and Georgian authors (Chelischeva and Chelischev, 1984; Tukvadze, 1984) have found a similar effect after zeolite application. Although, their experiments contained significantly higher zeolite amounts. Application of 2 tons of zeolite in heavy soils increased twice the hydrolysis able nitrogen content, four times at 4 tons and five times at 6 tons of zeolite. Sopkova et al. (1993), Ming and Aleln (2001), Rehakova et al. (2003), Uher and Balogh (2004) indicate the fertilizer with the addition of zeolite as a "slow releasing fertilizer". Although, this term was considered, with regard to the zeolites, quite disputable by Ruzek and Kovanda (1996). The researchers in many countries get positive results with zeolite application at nitrogen loss decreasing due to leaching from the soils (Bernardi et al., 2010; Gholam et al., 2009; Ippolito et al., 2011; Sepaskhah and

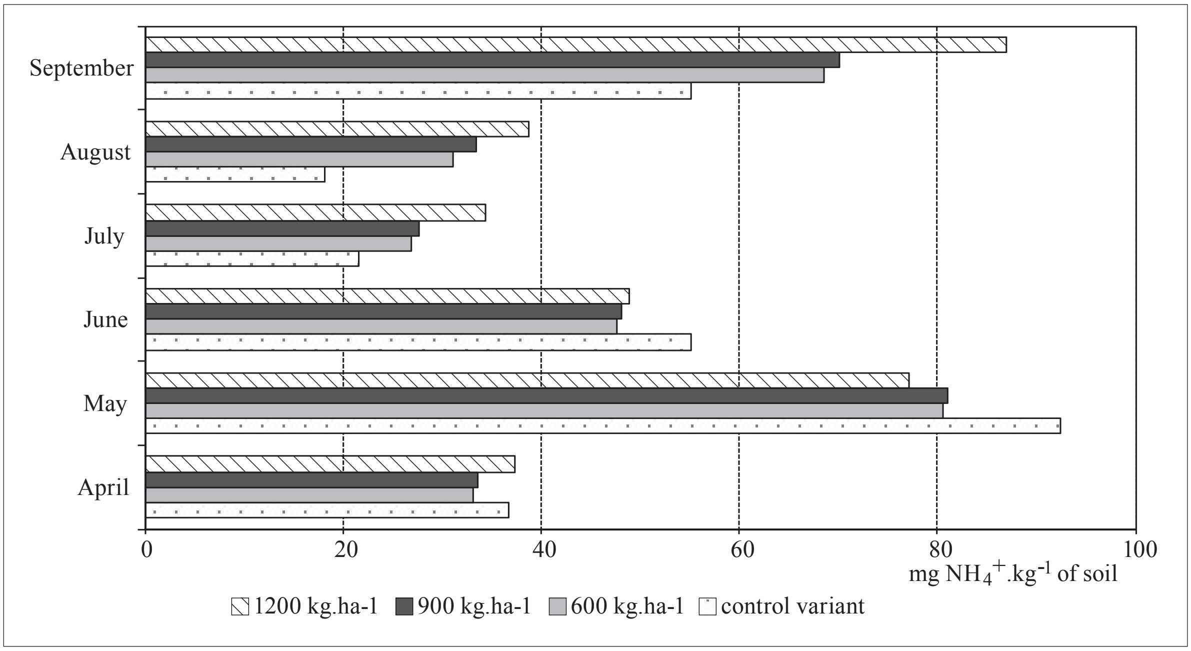

Fig. 1. Dynamics of ammonia nitrogen in the soil horizon 0.0-0.3 m after application of different amounts of zeolite

Table 3
The main statistical parameters from the last measurement in the end of field experiment

	Minimum	Maximum	Median	Arithmetic mean	Standard deviation
Control variant	54.5	56.1	55.2	55.25	0.733
600 kg zeolite	67.3	68.9	68.9	68.5	0.800
900 kg zeolite	69.4	70.5	70.25	70.1	0.483
1200 kg zeolite	86.1	87.4	87.05	86.9	0.572

Table 4
Mann-Whitney test results of observed variants (regarding ammonium nitrogen)

	Control variant	600 kg zeolite per ha	900 kg zeolite per ha
600 kg zeolite per ha	0.000^{+} (0.029)		
900 kg zeolite per ha	0.000^{+} (0.029)	0.000^{+} (0.029)	
1200 kg zeolite per ha	0.000^{+} (0.029)	0.000^{+} (0.029)	0.000^{+} (0.029)

Yousefi, 2007; Aghaalikhani et al., 2011 and others). Furthermore, zeolite is used also as a means for nitrate removing from water (Mazeikiene et al., 2010).

After the zeolite application, the content of nitrate nitrogen changed during the observed period (Figure 2). All variants kept the spring maximum in April (24.3 - 27.5 mg.kg^{-1} of soil) and the summer minimum in June and July (1.4 - 4.9 mg.kg^{-1} of soil). At the time of crop harvest (in August), there is an apparent increase of nitrate nitrogen (12 mg.kg^{-1} of soil) in the control variant, which corresponds to the so-called autumn maximum. This fact was not confirmed by the variants with zeolite because the nitrification process of ammonia nitrogen gets slower due to presence of zeolite in the soil. Barbarick and Pirola (1984) explain the process of catching and keeping the nitrogen in the soil after zeolite application: NH_4^+ cations penetrate into the zeolite channels, the small size of which does not allow the nitrifying bacteria to penetrate. From this perspective, the application of zeolite holds back the chemical change of ammonium cations into nitrate anions, thereby decreasing the amount of nitrate leaching into groundwater. In this way, it is possible to reduce significantly nitrogen loss, which reaches, by several authors, 25-35% of the total amount of applied nitrogen in mineral fertilizers.

In our case, the content of nitrate nitrogen in the soil in the experimental variants is 66-78 % lower in comparison with the control variant. Similar results were obtained by Bajrakov and Shevchenko (1984) where after the zeolite application was observed decrease of the $N\text{-}NO_3^-$ in soil only to the level 41-48 % compared to the nitrate nitrogen content in the control variant.

Statistical analysis of the results according to Kruskall-Wallis test confirmed the significant differ-

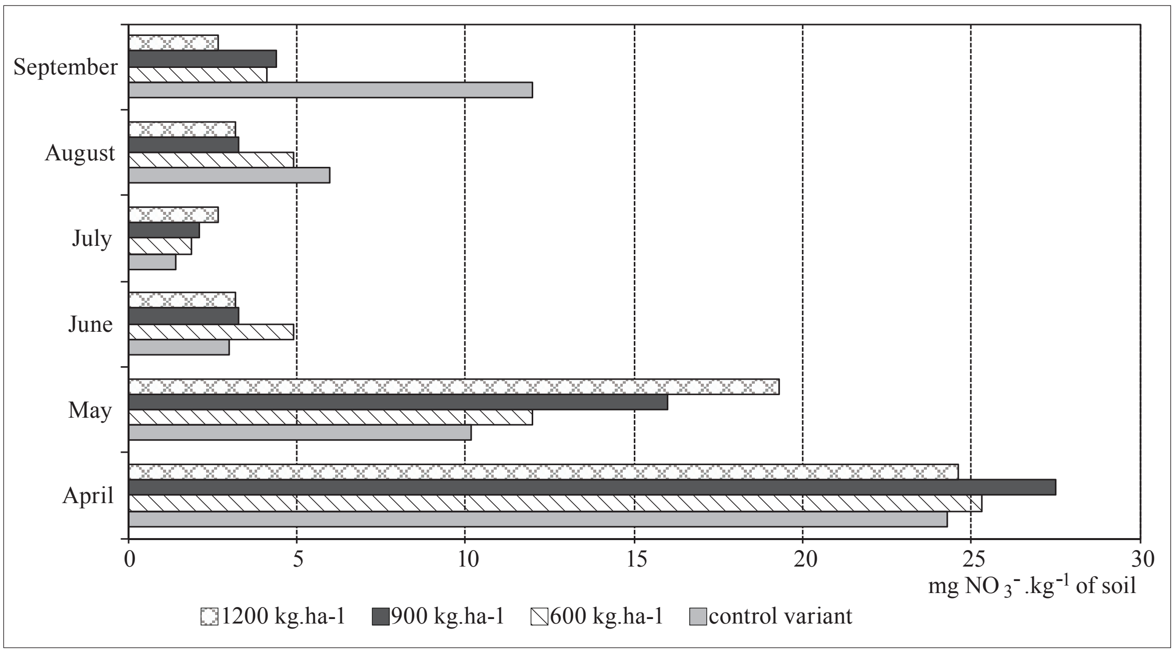

Fig. 2. Dynamics of nitrate nitrogen in the soil horizon 0.0-0.3 m after application of different amounts of zeolite

Table 5
Mann-Whitney test results of observed variants (regarding nitrate nitrogen)

	600 kg zeolite per ha	900 kg zeolite per ha	1200 kg zeolite per ha
Control variant	0.000 $^+$ (0.029)	0.000 $^+$ (0.029)	0.000 $^+$ (0.029)
600 kg zeolite per ha		1.500 $^-$ (0.570)	0.000 $^+$ (0.029)
900 kg zeolite per ha			0.000 $^+$ (0.029)

ences between average values of all observed variants (H=13.780 with p-value 0.003). The Mann-Whitney test results are contained in Table 5.

Regarding to the obtained results it is possible to conclude the zeolite tendency to become a sort of slow-releasing nitrogen fertilizer with NH_4^+ ions and indirectly it limits the intensity of nitrification in the soil. In one hand, the cultivated plants are provided with the sufficient amount of nutrients throughout the vegetation period and on the other hand, zeolites high sorption capacity prevents the leaching of nitrogen from the root zone of plants. It is believed that natural zeolites can play a positive role in plant nutrition.

Conclusions

The following conclusions can be drowning based on the obtained results:

The dynamics of ammonia nitrogen in the soil during the five months of observation coined the term "slow-releasing nitrogen fertilizer" for zeolite. In a short time after zeolite application the content of nitrogen in the soil compared to the control variant decreased because of NH_4^+ fixation by zeolite but after 3-4 months the opposite was true, the increase probably caused by the gradual release of nitrogen from the zeolite crystal lattice.

In the beginning of the experiments statistical significant differences were confirmed only between the control variant and observed variants. In the last month of experiment, they were also confirmed among all observed variants and each other.

The presence of zeolite in the soil is to a certain extent-inhibited process of nitrification, which in the case of zeolite application to the soil results in decrease of nitrate nitrogen content in soil. Consequently, neither the nitrates leaching into deeper soil horizons is so intensive.

Zeolite application into the soil favorably effects the environment by preventing the leakage of mineral nutrients (especially nitrogen) into the groundwater, increases the efficiency of nutrients occurring in soil while it does not affect negatively the quality of cultivated products.

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