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Plant Growing

Natural Zeolite – One of the Possibilities of Transition from Chemical to Biological Agronomy

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ABSTRACT. Some aspects of transition from chemical to biological agronomy are discussed in the article. Attention is focused on the questions of use of natural zeolites of sedimentary origin in practice of plant growing. On the basis of the researches carried out at the end of the 20th and at the beginning of the 21st centuries, positive influences of the natural zeolites on its physical and chemical properties, biological activity and efficiency are established. *© 2012 Bull. Georg. Natl. Acad. Sci.*

Key words: *soil, properties, clinoptilolite-containing tuff, organo-zeolitic fertilizer.*

In the nearest future the danger of losing agricultural soils arises in the world because of global natural cataclysms and irrational activity of man [1]. One of the reasons of the development of the negative processes in the soil is the increasing utilization of mineral fertilizers and pesticides. All these cause an increase in crop yield but at the same time create the danger of the contamination of the environment by toxic substances.

Therefore, development of new solutions becomes necessary in order to feed the growing world population and maintain a safe environment at the same time.

In the middle of the past century, calls for renouncing chemical (industrial) arable farming and moving to its biological counterpart appeared in scientific journals. However, in many scientists' opinion, not absolute rejection of mineral fertilizers and pesticides but "balanced utilization of agro techniques, agrochemical and biological methods together with the system of integral plant protection" is more reasonable [2]. G. Kahnt, a German scientist, holds this opinion and advances three main factors for transition to biological arable farming:

1. Transition of nitrogen of the air into plant protein by means of bean culture and specific soil bacteria, but not by means of synthetic nitrogen fertilizers.
2. Loosening and aggregation of the soil by means of plant roots, small soil-inhabiting animals and soil microorganisms, but not by means of tools and mechanisms.
3. Struggle against weeds, plant diseases, and pests is to be carried out by means of proper alternation of crop-rotation of cultures, choice of species

and sorts applicable to specific conditions and methods of activation of natural enemies of pests; but not at the expense of application of chemical against (herbicides, insecticides, fungicides, etc.).

In this case, biological arable farming does not exclude utilization of mineral fertilizers:- "goal-directed tilling of the soil, crop rotation, fertilization by manure (organic), and harmonic addition of mineral nutritious substances are the prerequisites for good harvest" [2].

At present, natural zeolites of sedimentary origin are widely used in plant-growing [3-7]. Their application in the soil (both individually and in combination with minerals and organic fertilizers) not only increases the capacity of the crops but also improves their qualitative indices [8].

Zeolites belong to a special class of crystalline alumo-silicate minerals and are characterized by their inherent alkaline reactions [9]. Combination of well-defined adsorption and ion-exchange capacity with considerable biological activity is a specific characteristic of zeolites [9]. Furthermore, the cation-exchange capacities of zeolites are one order higher than those for any other types of soils [10, 11].

It is due to this specificity that addition of zeolites to the soil improves its physical and chemical properties.

At present, more than forty types of zeolites are known but only the following zeolites of sedimentary origin have practical utilization: clinoptilolite, heulandite, mordenite, phillipsite, faujasite, laumontite,analcime, chabazite and erionite. Industrial deposits of these zeolites, with the main mineral content above 50-60% in rocks, are widely represented on all the continents of our planet. They are inexpensive, easily accessed for extraction and exploration [9-10].

According to the specificity of these minerals, their utilization is more reasonable for acidic (infertile) soil, but this does not exclude the possibility of their use for other types of soils as well. Acidic soil (podzolic, soddy podzolic, gray forest, boggy, peat, red, yellow) are widely distributed on all the continents and are characterized by high acidity (pH of water extracts of these soils ranges from 3-3.5 up to 4.6-6.0) [12]. Such soils are useless for growing the majority of the crops successfully grown on neutral soils (pH=7 for the soil solution). The method of liming [12] is used in the practice of plant-growing in order to decrease the acidity and increase the fertility of such soils. This method is based on the enrichment of soil exchangeable complex with cations of calcium characterized by clearly shown alkaline reaction. However, already at the end of the past century, it appeared that natural zeolites can fulfill this positive role [5]. Effects of zeolites on pH of soil solutions are mainly noticed for acidic soils, depending on the doses of the applied minerals.

Laboratory experiments showed that application of 2% zeolite-bearing rocks (deposits of Bulgaria) to weakly alkaline soils of that country changes pH of the surrounding only by 0.44 units; for weakly acidic soils of Central Greece – by 0.44 units as well [13]. Identical results were obtained in the case of application of 1% clinoptilolite-bearing tuff (Ai-Dag deposit, Azerbaijan) to weakly cultivated soddy podzolic soils (Moscow region) where alkalinity also increased only by 0.3 units [14].

The experiments, carried out in Georgia [15], proved that application of clinoptilolite-bearing tuffs to red and podzolic soils in the amount of 0.5% did not change the pH of the medium; only application of 1.0-1.5 % of zeolites increased alkalinity by 0.2-0.3 units. Appreciable results were obtained by enrichment of this soil with 15% zeolites. On red soils alkalinity increased by 2.5 units but that on podzolic soil by 2.4 units, i.e. became neutral (pH=6.8-7.4). Similar results are given in [14] according to which application of zeolites in the amount of 5 and 10 % increases alkalinity by 2.3 and 3.0 units respectively for the first year and preserves that effect for the following two years.

Field experiments carried out in Ukraine and Yakutia fully confirmed the experiments done in laboratory conditions. So, application of clinoptilolite-bearing tuff to soddy podzolic soils (Ukraine) in the amount of 30 t/ha (against the background of NPK) increased the pH of the water extraction from 5.3 to 6.7, i.e. by 1.4 units [16].

Introduction of calcium forms of zeolite (Khonguruu deposit, Yakutia) into podzolic, sandy loam (against the background of NPK) in the amount of 50t/ha increased alkalinity by 0.6 units, from 5.2 to 5.8; but enrichment of the boggy-high soil of South Yakutia with the same type of zeolites in the amount of 100 t/ha contributed to an increase in pH by 1.6 units, from 5.2 to 6.8 [17]. It has been established by the field experiments that the change in pH is preserved for a long time (2-3 years) after a single application of zeolite [16]; according to other data - for 4-5 years [18]. Thus, a new possibility of reclamation of acidic soils without liming has become available.

Other important properties of zeolites, such as ability to adsorb a lot of quantity of moisture and retain it in their pores at increased temperature attracted the attention of growers.

In [19-20] carried out in Azerbaijan on chestnut soils of Karabakh steppe it has been found that introduction of clinoptilolite-bearing tuffs of a local deposit (Ai-Dag) into the soil increased the water-content in the latter.

In this case, moisture of the soil in an arable layer (a month prior to the harvesting) changed in a wide range depending on the dose of the applied zeolite. On non-irrigated plots of these soils, moisture in the control against the background of NPK totaled 8.26 %, enrichment of the soil by zeolite in the amount of 5.10 and 20 t/ha has led to the increase in moisture up to 11.50; 15.38 and 21.79% respectively. The same regularity was observed on irrigated plots: 12.99%, 18.56%, 22.12%, 20.80%. On the average, over three years of use of the same doses of zeolites on non-irrigated plots, the moisture of soil increased from 21.2% up to 24.0; 25.4; and 27.8%; and on irrigated - from 25.3 up to 29.6; 30,5; and 32.2%.

A similar fact is observed on soddy-podzolic soils of Ukraine [16]. On the average over five months of the vegetative period (1980), application of zeolites in the amount of 10; 20; 30 and 50 t/ha against the background of NPK, moisture of soil exceeded that of the control by 6.7; 13.3; 9.2 and 10.8 %. Increase in norms of zeolites up to 30 and 50 t/ha has not led to an adequate change in moisture compared to 10 and 20 t/ha. It should be noted that the positive influence on the increase of water-content in soils and their retention capacity is evidenced with all types of soil.

Application of zeolites to the soil promotes improvement of some of its physical and chemical properties. So, it is shown [21-22] that as a result of enrichment of serozemic-meadow soil of Shirvan steppes (Azerbaijan) with clinoptilolite-containing tuff, granulated in 0.5-1.0 mm, in a dose of 5 t/ha, contributed to the improvement of such indices of soil as aggregation, swelling, and filtration capacity. The quantity of agronomically valuable aggregates of 1-10 mm size in an arable layer has increased up to 75.25 % in comparison with the control (51.08 %); but aggregates of greater sizes <25 mm – 96.13 % (in the control – 81.62 %), attesting to the aggregation (structuration) of the soil.

The size of swelling in an arable layer, on the contrary, has decreased to 6.9 % (in the control 8.9 %), filtration capacity has increased within 9 min from 13 ml (in the control) to 23.7 ml. The same effect was obtained by application of clinoptilolite-containing tuff to the chestnut soil of Azerbaijan in the amount of 5, 10 and 20 t/ha [22]. Thus, positive influence of zeolites is more clearly shown on non-irrigated soil than on its irrigated counterpart and depends on the dose of zeolites used. The amount of water-stable micro aggregates of 1.0 – 0.25 mm in size has noticeably increased, and the difference between the contents of these aggregates in the control and non-irrigated plots amounted to 5.7 %; but that on irrigated one to only 1.9 % (the norm of the used zeolite – 10 t/ha). On non-irrigated plots the swelling decreased from 8.5 % (in the control) to 5.5 %, and that on irrigated one from 11.6 up to 7.8 %. Filtrational properties of the arable layer have noticeably improved. Thus, whereas on the non-irrigated plots it amounted to 21.3 ml/10 min, after application of zeolites it increased up to 39 ml/10 min. A similar picture was observed on irrigated plots as well: a maximal increase of these parameters (from 43.6 ml/10 of min up to 65.2 ml/10 min) took place.

The researches carried out in Georgia established that application of clinoptilolite-containing tuffs to acidic soil, characteristic of the humid subtropics of Western Georgia, contributed to the formation of giant (up to 50-60 mk) amoebas, being an indirect evidence of the increase in porosity of soil and improvement of its structure [15]. In a later work [23], it has been shown that enrichment of acidic soil of Kolkheti lowland (belonging to the category of light-clay) by natural zeolite - laumontite (20 t/ha) reduces the content of physical clay from 62 % to 58 %, transferring it to the category of heavy loam. The factor of structure formation in this case increases from 76.9 up to 80.6 %; but the total porosity of the test plots from 52.3 % up to 55.5 %.

Bulgarian scientists [24] made an attempt to recultivate yellow and green clay by means of clinoptilolite-containing tuffs. By laboratory experiments, it has been established that the total porosity increased from 43 up to 49.6 % and approached the control variant – 51.80 (humus layer of soil without fertilizers).

Fertility of soils in many respects depends on the exchange-absorption capacity of the arable layer (absorbing complex). In the scientific literature the terms "absorbing capacity", "cation-exchange capacity" [11, 12] and sometimes "capacity of base exchange" [25] are used for its designation. These terms imply the total amount of all absorbed (exchange) cations which can probably be ejected from soil. This index is expressed in milligram-equivalents per 100 gram of soil. Reaction of soil solution, dispersity of soil, aggregation ability, and stability of an absorbing complex to the destructive action of water in the process of soil formation depends on the composition of the absorbed cations. The absorbed H^+, Al^{3+} and especially Na^+ contribute to destruction of the absorbing complex, reduction of the ability of retention and fixation of humus substances. Saturation of the absorbing complex by calcium, on the contrary, provides favorable conditions for plants by protecting the absorbing complex from destruction, promotes its aggregation and fixation of humus in it. Therefore, calcium is called "guard" of fertility [11]. As the cation composition of zeolites is identical with the cations of the absorbing complex of soil in composition, its enrichment with zeolite-containing rocks seems advisable. Utilization of zeolites with prevailing Ca^{+2} composition, (for example heulandites or laumontite) is desirable. In the case of utilization of clinoptilolite for this purpose, samples differing by high content of Ca^{2+} and K^+ and absence or negligible content of Na^+ should be selected. Thus, application of zeolites to the soil: in the first place, increases many times its cation capacity and in the second place enriches it with "useful" Ca^{+2}. In 1975-1976, the first studies were carried out in Ukraine on soddy-podzolic sandy and sandy loam, for which the absorbing capacity varied within the limits of 3-4 mg-eq/100g soil for sandy and 5-7 mg-eq/100g for sandy loam. Introduction of clinoptilolite-containing tuff to such soil in the amount of 15-30 t/ha increases the content of exchangable cations and absorbing capacity by 15-25 % which is stably observed for five years [25]. In this case, enrichment of the absorbing complex occurs at the expense of calcium, potassium and magnesium. In [14], carried out on soddy-podsolic soils under influence of 10 % zeolite, cation exchangable capacity increased from 15.2 up to 34.6 mg-eq/100gr of soil (more than twice), and the sum of the absorbed bases - from 6.5 up to 15.8 mg-eq/100g of soil. The calcium content in the soil increased 2-3 times, but magnesium content decreased 5-8 times.

The same effect was observed by application of the càlcium form of natural zeolite khongurin in acidic, podzolic, sandy loam and boggy-upper soils of Yakutia [17]. In the first case, at application of zeolite in the amount of 50 t/ha against the background of NPK, the sum of the exchangeable cations increased from 15 (in the control) to 24.2 mg-eq/100g of soil, the amount of calcium has increased 2.5 times. In the second case, with application of 100 t/ha khongurin the sum of exchangeable cations increased from 35.3 to 69.8 mg-eq/100g of soil, and the amount of calcium and magnesium – 2.0 and 2.3 times. Such positive effect is observed independently of the type of soil. Thus, application of zeolite in the amount of 10 t/ha to chestnut soils of Azerbaijan led to an increase of the sum of the absorbing bases in comparison with the control; but further increase in doses of zeolites does not exert an influence on this index [22].

Application of zeolite-containing rocks exerts a certain influence on the content of such nutritious elements as NH_4^+ + and K^+. At application of clinoptilolite-containing tuffs to soddy-podzolic soils, an increase in the fixed ammonium (~77 %) and creation of the best conditions for its assimilation by plants is observed; the process of nitrification is slowed down; loss of nitrogen by washing away and denitrification is reduced [16]. Introduction of zeolite-containing rocks in the amount from 5 up to 15 t/ha in meadow, grey, heavy-loamy soil of the Far East contributed to the adsorption of ammonium on the average more than 50 % in comparison with the control (untreated plots) [26]. By laboratory studies it has been established that at introduction of 15 % clinoptilolite-containing tuff to red and podzolic soils of Georgia, the absorption capacity of potassium increases almost three times [14].

Microorganisms, living in the soil, considerably contribute to soil fertility. Accumulation of organic substances, formation of humus in the arable layer depend on the number of these microorganisms and their composition. Activity of microorganisms is determined by a number of factors, such as: humidity, temperature and acidity of the soil, and so on. Application of mineral, and especially organic, fertilizers exerts a certain influence on the increase of their number in the soil [27]. In the second half of the last century, biological activity of zeolites was also revealed. It was shown that their application to the soil increased the number of microbial coenosis [15]. A number of studies were carried out in this direction.

In the laboratory investigations carried out in 1984, the dynamics of the variation of the number and biomass of microorganisms in acidic soil under the influence of clinoptilolite-containing tuff and peat [28] was studied. Duration of the experiment: 22 days. The best results were obtained for the mixture soil+clinoptilolite in the ratio 8.5/1.5. The weight of the formed bacteria for this period of time amounted to 5.32 mg/g. The weight of the bacteria in the control (on pure soil) was 2.69 mg/g. The increase in number of microorganisms has pulsating character. Such fluctuations are probably caused by periodic reproduction and necrosis of microorganisms during the experiment.

Biological activity of zeolites became apparent in the process of their impact on the decomposition of organic substances in soil (red) [29, 30]. To determine the dynamics of decomposition of organic substances in the soil, such highly informative index as rate of release of CO_2 from the surface of the soil in a unit of time, so-called respiration of soil, has been used [11]. Laboratory studies [29, 30] established that application of clinoptilolite-containing tuff to an acidic soil in the amount of 10-20 % sharply increased the intensity of decomposition of organic substances in comparison with the control (soil without fertilizer) 3.2-5.0 times and thus worsened the agronomical properties of the soil. Application of the same amount of peat practically does not exert any influence on this process. At application of a mix of clinoptilolite (20 %) and peat (20 %), the intensity of the process of decomposition of organic substances in the soil increased only 1.8 times in comparison with the control. This contributed to more regular decomposition of organic substances and createed favorable conditions for growth and development of plants.

The positive effect of zeolites on the increase of the number of microorganisms in the soil depends on the type of the latter as well. Application of 10 % clinoptilolite-containing tuff to humus-carbonated soil even causes slight decrease in the number of the microflora to 880 thousand/g of soil (in the control 890 thousand/g of soil). Application of the same doses of zeolites to podzolic and red soils doubled the number of the microorganisms in the soil in comparison with the control 1646 and 1642 thousand/g of soil (in the control 830 and 820 thousand/g of soil) [30].

In the presence of natural zeolites in the soil, not only an increase in the number of microorganisms but also change of their qualitative composition have been observed. Thus, in acidic soils containing 15 % clinoptilolite, mycolytic bacteria dominate, inducing lysis (eating up mold fungi) and reducing their content 2-3 times [15]. Almost threefold increase in the number of actinomyces that have bacterial activity and therefore contribute to the sterilization of soil from undesirable microflora has also been noted. The fact of positive influence of zeolites on the increase in the number of blue-green algae and azotobacter in soils, which play an important role in atmospheric nitrogen fixation and their conversion into forms that are available for plants has been established also. Only in acidic soils the number of azotobacter increased by 30-40 % [15].

Similar field experiments fully confirmed the laboratory study of change in the qualitative composition of microflora under the influence of natural zeolites.

By the experiments carried out in Azerbaijan [31] in 1985-1987, it was shown that application of 10 t/ha clinoptilolite-containing tuff to mountain-gray-brown soils increased the number of microorganisms from 5707 thousand/g soil in the control (soil without fertilizer) up to 6901 thousand/g soil ; and the number of actinomyces increased 1.4 times. The same effect was observed on soddy podzolic soils of Ukraine [16]. After application of 10 t/ha zeolite-containing tuff to this soil only once, increase in the number of microorganisms from 3844 thousand/g soil in the control against a background of NPK and manure up to 6139 thousand/g soil took place even in the third year of the experiment. It is necessary to note that the number of actinomyces increased 2.5 times, and the number of ammonium fixators was doubled compared to the control.

By the field experiments carried out on the grey-brown soils of Eastern Georgia in 1989-1992, [30] it was established that introduction of organo-zeolitic fertilizers (a mixture of clinoptilolite-containing tuff and fresh poultry manure) in the ratio 1: 1 also contributed to the increase in the number of such microorganisms as nitrogen fixers. From the obtained results it follows:

1. Introduction of these fertilizers in the amount of 20-40 t/ha into soils increases the number of nitrogen fixers to a greater extent than utilization of mineral fertilizers ($N_{60}P_{60}K_{45}$ kg/ha);
2. Increase in the doses of the applied organo-zeolitic fertilizers contributed to the increase in the number of microorganisms in the soil;
3. Vital activity of nitrogen fixers in the autumn-winter period is noticeably decreased in the control soil and in soils with mineral fertilizers that takes place with application of organo-zeolitic fertilizers but to a lesser extent.
4. Considerable effect of the after-action in the case of utilization of organo-zeolitic fertilizers has been noted: in 1991, the number of microorganisms almost doubled in comparison with that in 1990.

A similar regularity was observed in the case of application of organo-zeolitic fertilizers in acidic soils characteristic of humid subtropics of Western Georgia in 1989-91 [32]. The total number of microorganisms increased 1.5-2.0 times in comparison with the control against a background of mineral fertilizers $N_{60}P_{90}K_{45}$.

At present, there are a few works about the possibility of utilization of natural zeolites to combat diseases, pests and weeds of crops. However, the necessity of development of this direction is seen to be prospective in some of them.

In the work of Russian scientists [33] it has been shown that application of natural zeolites to soil prevents disease of the root system of plants and holds back the development of diseases. Vegetative laboratory tests have shown that zeolites reduce lesion of sprouts of ginseng and purple coneflower with root rots. Application of zeolites in the amount of 2 t/ha (in field conditions) led to the decrease in the number of sick plants in comparison with the control by 30 % for ginseng and 15 % for coneflower. This is apparently related to the fact that zeolites increase the physiological and biological activity of soils, their aeration and normalization of water balance. Also it has been found that growing of seeding of common valerian on a substratum-containing zeolite, decrease lesion of plants by root rots up to 4.9 %; in the control (sand-peat-soil) it amounted to 14.8 %.

In Italy [10] natural zeolites have been used as dusting agents to kill aphids affecting fruit trees. The mechanism of this reaction is not known: the zeolite could act as a desiccant, although it is almost completely saturated with water before use, or its highly alkaline character in water could simply kill individual insects that come in contact with it.

Laboratory investigations have been carried out in Georgia to study the influence of natural zeolites on germination of seeds of wheat and weeds, characteristic of this culture [34]. In vegetative vessels filled with podzolic soil (control) and the same soil enriched with finely ground clinoptilolite-containing tuffs in the amount of 5, 10, and 15 %, were sown with wheat and weeds. Germination of weeds in the control was found to be 100 %, and that of wheat - 91%. Along with enrichment of the soil with zeolite, the germination of weeds decreased to 77.5 %, while the germination of wheat increased up to 97 %.

Thus, from the analysis of numerous studies of the utilization of natural zeolites in plant-growing it follows that all the three propositions presented in the monograph of G.Kahnt [2] in many cases can be carried out by means of natural zeolites of sedimentary origin - an inexpensive and available mineral raw material.

მემცენარეობა

ბუნებრივი ცეოლითები - ქიმიური აგრონომიიდან ბიოლოგიურზე გადასვლის ერთ-ერთი შესაძლებლობა

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სტატიაში განხილულია ქიმიური აგრონომიიდან ბიოლოგიურ მიწათმოქმედებაზე გადასვლის ზოგიერთი ასპექტი. დიდი ყურადღება ეთმობა მემცენარეობის პრაქტიკაში სედიმენტაციური წარმოშობის ბუნებრივი ცეოლითების გამოყენებას. XX ს-ის ბოლოს და XXI ს-ის დასაწყისში ჩატარებული კვლევების ანალიზის საფუძველზე დადგენილია ნიადაგში შეტანილი ბუნებრივი ცეოლითების დადებითი ზეგავლენა მის ფიზიკურ-ქიმიურ თვისებებზე, ბიოლოგიურ აქტიურობასა და პროდუქტიულობაზე.

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