Emir. J. Food Agric. 2013. 25 (12): 980-985
doi: 10.9755/ejfa.v25i12.16736
http://www.ejfa.info/

REGULAR ARTICLE

The use of natural zeolites impregnated with zinc and copper ammoniates as carriers of micronutrients in growing vegetables

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Abstract

The aim of our study was to obtain prolonged micronutrients for use in organic agriculture and production of row materials for baby food. For this purpose, we proposed to use impregnated with ammoniates of zinc and copper zeolite. Field experiments were conducted during 2011 – 2012 on the territory of Kyiv region. Results of two-year experiments revealed that during the first year of impregnated zeolite implementation statistically reliable (confidence level 0.95) increase of zinc and copper in carrot and beetroot. On the second year after zeolite implementation, their influence on zinc and copper concentration in spring oats and spring barley grains was observed. Concentration of these micronutrients in oats and barley grains was significantly larger than in the control sample. Implementation of zeolites, impregnated with zinc and copper ammoniates, can be recommended for improving the soil quality and micronutrients level in grain and vegetable production.

Key words: Micronutrients, Soil, Zeolite, Baby food, Organic agriculture

Introduction

Ukraine has vast areas of fertile lands. The most fertile soils in the world – humus soils – occupy almost 27.8 million ha, which is 67.7% of total arable Ukrainian lands and 8.7% of all world humus (Pozniak, 2008). Availability of large areas of fertile lands enables the development of organic agriculture production. According to the IFOAM data, in 2011 in Ukraine there were 118 farms registered and certified by international accreditation bodies as farms with organic farming. Total area of certified for organic farming agricultural lands is of 270226 ha. Nowadays, Ukraine is ranked first in the east-European region by the area of lands certified for organic farming. These farms specialize mostly on production of grain, bean and oil cultures. The area of certified lands is almost 0.7% of all arable lands of Ukraine (Data collection, 2013).

Besides, production of baby food in Ukraine can only take place in a special raw area. The status of such zone is given after the detailed analysis of quality of soils and their pollution with radionuclides, heavy metals and persistent organic pollutants (Law of on Baby Food, 2006). The main criterion for organic farms and special raw areas is the concentration of radionuclides in their soils. This is important since almost one third of Ukraine, or 15 thousand of square kilometers, is polluted with radioactive wastes (National Report of Ukraine, 2011). This area is inhabited by almost 2.4 million people. According to the Ukrainian "Law on Baby Food", the status of special raw area can be granted to the farm with concentration of 10 kBk/m^2 for ^{137}Cs and 0.75 kBk/m^2 for ^{90}Sr. Pollution of agricultural lands with heavy metals and persistent organic pollutants also limits number of farms that can receive the special raw area status.

The important criterion for organic farms and farms with special raw area status is sufficient concentration of micronutrients in soil. Agricultural

Received 07 March 2013; Revised 17 April 2013; Accepted 10 May 2013; Published Online 25 August 2013

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activities on such lands require introduction of required microelements. Important requirement for organic farming is the reduction of solubility of introduced micronutrients. That is why our research is focused on microfertilizers with prolonged action for usage in organic farming and baby food production.

Materials and Methods

Zeolite-Sokyrnit (clinoptilolite) was chosen for the prolongation of microelements effect. Usage of zeolites is allowed in organic farming without any restrictions. The necessity of application of microelements (e.g., boron, copper, iron, manganese, molybdenum, zinc) has to be recognized by the certification body or authority (Codex Alimentarius, 2007). Zeolite-Sokyrnit is the mineral of volcano origin with deposit in Zakarpattya region of Ukraine. Low cost and simplicity of application are the main reasons of economical effectiveness of zeolite technologies. Zeolite-Sokyrnit consists of: $(Na, K)_4\ CaAl_6Si_{30}O_{72}\cdot 24H_2O$ (Tarasevich Yu et al., 1979). Natural zeolite is widely used in agriculture since due to its unique properties it improves the soil quality, capable of retaining the moisture and reducing the mobility of pollutants.

We have used zeolite with the grain size of 3-10mm. Crystal structure of zeolite is formed by tetrahedral groups of $SiO_2/4$ and $AlO_2/4$, connected by common vertexes in the 3d-frame pierced with cavities and canals. Quantities of the microelements used for the impregnation were evaluated basing on adsorption capabilities of zeolite (using the data from adsorption isotherm).

To obtain zeolites impregnated with zinc and copper ammoniates they were held in the water solution of these substances for 14 hours. Quantities of zinc and copper salts were calculated according to the plants need in microelements. Quantity of zeolites was calculated provided that water capability of zeolites to be of 20%. To introduce the test plots in soil of total area of 0.4 ha, we processed 35.2 kg of 3-10mm zeolite grains with 7 liters of ammoniates solution containing 79.0 g of Zn^{2+} and 15.4 g of Cu^{2+}.

Field experiments were conducted over 2011 – 2012 on the territory of Kyiv region according to the Technique of field experiment (Dospehov, 1985). Soil of the region of experiment is the low-humus chromosomes soil (humus concentration of about 2.7– 4%). The experiment was conducted to study the effect of zeolites impregnated with zinc and copper ammoniates ($Zn(NH_3)_4SO_4$ and $Cu(NH_3)_4SO_4$) on the concentration of micronutrients in carrot and beet.

Experiment scheme for carrot

1. Control – without introduction of zeolite and microelements;
2. Non-impregnated Zeolite introduction;
3. Impregnated Zeolite introduction - 0.275 kg/m^2 (Zn – 200mg/m^2; Cu – 40 mg/m^2).

Experiment scheme for beetroot

1. Control – without introduction of zeolite and microelements;
2. Non-impregnated Zeolite introduction;
3. Impregnated Zeolite introduction - 0.275 kg/m^2; (Zn – 200mg/m^2; Cu – 40 mg/m^2)

To study the prolonged effect of zeolites impregnated with zinc and copper complexes on the content of micronutrients in agricultural raw materials, in 2012 we conducted additional experiments. We planted grains – spring oats and spring barley - at the same location without adding new portions of zeolites. Barley was planted instead of carrot and oats was planted instead of beetroot.

The experiment was repeated 3 times. The area of each test site was 0.02 ha. Plots have random positions. Root-crop samples were selected using the envelope method – in 5 points on each site 10 carrots, 5 beetroots and grain were sampled. Grain yield were collected from each plot separately.

Determination of metal concentrations in products of mineralization of samples was conducted using the method of atomic adsorption in the propane-air flame (atomic-adsorption spectrometer AAS-3, Germany). The sources of radiation were hollow cathode lamps, working wavelengths – 324.8 nm for copper and 213.9 nm for zinc.

Total metal concentration in the soil was determined using the method of dissolution of soil in hydrofluoric and perchloric acids according to ISO 14869-1:2001 followed by atomic-absorption determination according to ISO 11466:1995. Determination of metal concentrations in root-crop was repeated 3 times according to GOST 30178-96 (closest analogs - ISO 7952:1994; ISO 6636-2:1981; ISO 6869:2000).

Determination of metal concentrations in samples was conducted using atomic-absorption method in the propane-air flame (spectrometer AAS-3, Carl Zeiss, Germany). Statistical data processing was made using the StatSoft Statistica 7 software.

Measurements

Pore structure of the Zeolite-Sokyrnit (clinoptiolite) was studied using low-temperature (77.4 K) adsorption/desorption of nitrogen on the high-speed gas sorption analyzer “Autosorb-6” (“Quantachrome”, USA). Before the footage samples were degassed for 20hrs under the temperature of 473K and vacuum $6.58 \cdot 10^{-5}$ Torr. Processing of the obtained results of the nitrogen adsorption/desorption was made automatically using the software Quantachrome Instruments, version 3.0. We measured specific surface area (S), specific volume (V) and average radius (R) of zeolite (clinoptiolite) pores. We also studied dependence of pore volume distribution on the radius of pores using Density Functional Theory (DFT) (Webb et al., 1997).

Mean specific surface area is 18.5 m^2/g. Mean specific pore volume (V) is 0.1 cm^3/g. Mean pore radius (R) is 5.3 nm. Differential curve obtained contains the series of peaks that correspond to the radii of 2.8, 12 nm, and the wide range of values from 12 to 22 nm, which reflects a multimodal distribution of pores in the sample. These pores are primary for the impregnation of zeolite (clinoptiolite) with zinc and copper ammoniates.

Measurements of metals concentrations in root-crop and grain-crop were made three times. Beetroot and carrot samples from each site were washed, peeled and chopped. After thorough mixing, three samples of 15-20g were selected from each variant. (Samples of root-crop and grain were 3-5 times larger compared to the minimum required sizes to obtain more representative results). Mineralization of samples was made using the method of dry ashing. Every sample was put in the heat-resisting bulb. After drying samples in a dessicator, the samples were flied ash in a muffle furnace at the temperature of 400°C. Ash of each sample was preliminary processed with nitric acid (1:1) with a few drops of hydrogen peroxide. After evaporation to the state of moist salts samples were dissolved in 1H nitric acid. The solution was then filtered and diluted to obtain the volume of 25 cm^3. As for grain, we sampled 3 samples of 10 grams each from each variant. Product of grain mineralization we obtained using the same way as described above, except drying.

Results

Concentration of microelements in vegetables in each sample is presented in Figure 1, in grain – in Figure 2. Reliability of data on metal concentrations in different samples was tested using t-test for independent samples (Table 1, 2). Averaged metal concentrations for each sample are also presented.

Concentration of zinc and copper in root-crop of carrot in control sample (Var 1) and in sample where non-impregnated zeolites were used (Var 2) is statistically insignificant (see in Table 1). At the same time, in the root-crop of beetroot there is a reliable increase in the concentration of copper when using non-impregnated zeolites as well as impregnated ones. Implementation of impregnated zeolites (Var 3) causes an increase in both metals concentrations comparing to both control (Var 1) and non-impregnated zeolite variants (Var 2). Besides, the crop increase is observed in both zeolite variants - (Var 2) and (Var 3) - comparing to the control (Var 1).

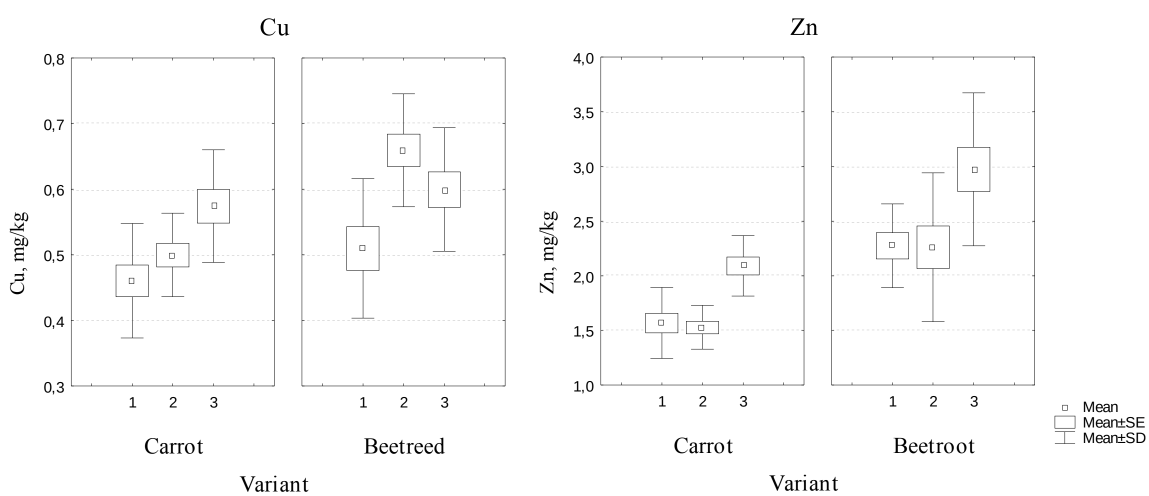

Figure 1. Concentration of Copper and Zinc in carrot and beetroot roots.

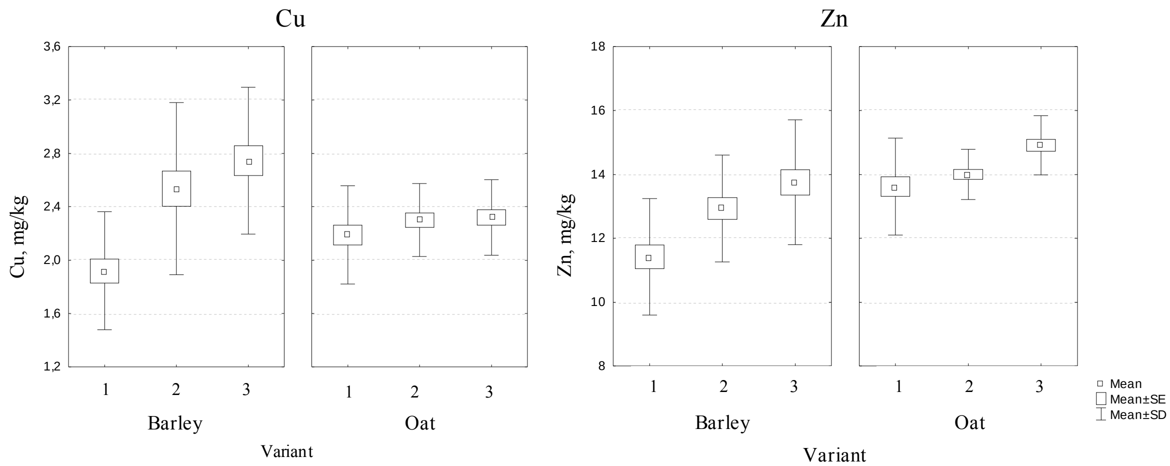

Figure 2. Concentration of Copper and Zinc in barley and outs grains.

Table 1. Averaged values and statistical significance level of the hypothesis about coincidence of group means for root-crop.

Parameters	Carrot Mean		Statistical significance	Beetroot Mean		Statistical significance
	Var 1	Var 2		Var 1	Var 2	
Cu, mg/kg	0.46	0.50	0.19	0.51	0.66	0.002
Zn, mg/kg	1.52	1.53	0.92	2.27	2.26	0.96
Yild, t/ha	21.8	22.3	0.055	17.0	19.9	<0.0001
	Var 1	Var 3		Var 1	Var 3	
Cu, mg/kg	0.46	0.57	0.00416	0.51	0.60	0.049
Zn, mg/kg	1.52	2.09	<0.0001	2.27	2.97	0.010
Yild, t/ha	21.8	22.9	<0.0001	17.0	20.6	<0.0001
	Var 2	Var 3		Var 2	Var 3	
Cu, mg/kg	0.50	0.57	0.027	0.66	0.60	0.118
Zn, mg/kg	1.53	2.09	<0.0001	2.26	2.97	0.019
Yild, t/ha	22.3	22.9	0.0004	19.9	20.6	0.016

Table 2. Averaged values and level of statistical significance of hypothesis about samples coincidence for grain crop.

Spring barley				Spring oat			
	Mean		statistical significance		Mean		statistical significance
	Var. 1	Var. 2			Var. 1	Var. 2	
Cu	1.9	2.5	<0.001	Cu	2.2	2.3	0.24
Zn	11.4	12.9	0.004	Zn	13.6	14.0	0.28
	Var. 1	Var.3			Var. 1	Var.3	
Cu	1.9	2.7	<0.001	Cu	2.2	2.3	0.17
Zn	11.4	13.8	<0.001	Zn	13.6	14.9	<0.001
	Var.2	Var.3			Var.2	Var.3	
Cu	2.5	2.7	0.23	Cu	2.3	2.3	0.79
Zn	12.9	13.8	0.125	Zn	14.0	14.9	<0.001

On the next year after the implementation of zeolites intake of microelements into agricultural crops was changed (Table 2). For grain crops concentrations of both metals increased after zeolite implementation, both impregnated and non-impregnated (beside copper in Var.2 - Var.3). Besides, for spring barley statistically significant difference in data (p = 0.95) is observed when compared to control. This difference is much less significant when comparing non-impregnated and impregnated zeolites. For oats, an increase in zinc concentration in the variant with impregnated zeolite compared to other two variants is statistically reliable only.

Discussion

Zeolites are porous crystalline aluminum silicates. They consist of combined oxides of silicon, aluminum and alkali or alkaline earth metals. They can also include different chemical elements and crystal water. Properties of zeolites are defined by nano-channels and cavities that can contain extraneous ions and neutral molecules. It is known that Natural zeolite is widely used in agriculture. Thanks to its unique properties and chemical composition it improves soil quality, can retain moisture and decrease pollutants mobility. (Salavati-Niasari et al., 2011).

In our research we used the ability of zeolites to adsorb metal-ammonium complexes. Using electron paramagnetic resonance EPR (Clark et al., 1984) the mechanism of interaction of copper ammoniate complexes with aluminum silicates Allophane and Imogolite (zeolite (clinoptiolite) analogs) was studied. It was shown that during sorption of ammoniate complexes several types of complexes are formed on the surface of aluminum silicates. Aluminum silicate groups of the carrier (≡Si-OH и =Al-OH) take part in the formation of these complexes:

$$\equiv Si\text{-}OCu(H_2O)_4^+ + 4NH_3 \leftrightarrow \equiv Si\text{-}OCu(NH_3)_4^+ + 4H_2O \quad (1)$$

$$\equiv Si\text{-}OH + NH_3 + Cu(NH_3)_4(H_2O)_2^{2+} \leftrightarrow \equiv Si\text{-}OCu(NH_3)_4^+ + NH_4^+ + 2H_2O \quad (2)$$

$$=Al\text{-}OCu(NH_3)_2OH + NH_3(aq) \leftrightarrow =Al\text{-}OCu(NH_3)_3^+ + OH(aq)^- \quad (3)$$

We must admit that chemical composition of a copper ammoniate complex with aluminum silicate surface and its hydrolytic stability depends on $Cu/NH_3(aq)$ proportion. If NH_3 is insufficient, the balance in reaction (1) shifts left. If the proportion is equimolar or ammonia is prevailing, the balance in reaction (1) shifts right. Besides, when ammonia is prevailing, reactions (2) and (3) become possible. Ammonium ions, which results from these reactions, are adsorbed by aluminum silicates. We can assume that cation $[Cu(NH3)_4]^{2+}$ is adsorbed by the narrow mesopores following the ion-exchange mechanisms (reactions 1-3), and the $Cu(NH3)_4SO_4{\cdot}H_2O$ molecules are adsorbed by wide mesopores.

We proposed that implementation the soil of micronutrients in the form of complexes with natural zeolites of Sokirnya deposit can help to increase the zinc and copper concentration in agricultural production and prolong micronutrients presence in soil by reducing their mobility.

In field experiment in 2012 we studied the influence of non-impregnated and impregnated with copper and zinc ammoniates zeolites on the concentration of zinc and copper micronutrients in carrot and beetroot (see Figure 1).

Concentration of zinc and copper in carrot of control sample (Var. 1) non-impregnated zeolites sample (Var. 2) is statistically insignificant (Table 1). At the same time, in root-crop of beetroot a reliable increase in copper levels is observed when using both impregnated and non-impregnated zeolites. Implementation of impregnated zeolites (Var. 3) leads to an increase in concentrations of both metals comparing both to the control (Var. 1) and to non-impregnated zeolite variant (Var 2). Crop increase is observed when using both non-impregnated (Var 2) and impregnated zeolites variants (Var 3) compared to the control. These results confirmed field experiment conducted under the same soil conditions in 2011.

We also studied a prolonged effect of implementation of impregnated zeolites on the crop production (Figure 2). The next year after implementation of zeolites we observed new data, which are presented in Table 2. For grain-crop an increase in concentrations of both metals is observed when using any combination of impregnated and non-impregnated zeolites (beside copper in Var.2 - Var.3). Particularly, for barley we observe statistically reliable (confidence level 0.95) differences of implementation of impregnated zeolites (Var. 3) compared to the control; but, compared to the non-impregnated zeolites (Var. 2) there is less difference between these two. For oats, only the difference in zinc levels is statistically reliable when comparing impregnated zeolite (Var. 3) both to control (Var. 1) and non-impregnated zeolite variant (Var. 2).

Conclusions and recommendations

Environmentally safe method for improving the quality of vegetables and grain is proposed. Based on field experiments conducted in 2011 and 2012 it was shown that implementation of zinc and copper ammoniates in their complex with natural zeolites from Sokirnya deposit (Ukraine) helps to increase the concentration of zinc and copper in agricultural production.

Results of two-year experiments revealed that during the first year of impregnated zeolite implementation a statistically reliable (confidence level 0.95) increase in zinc and copper content in carrot and beetroot is observed.

On the second year after zeolite implementation, their influence on zinc and copper concentration in spring oats and spring barley was observed. Concentration of these microelements in oats and barley grains was significantly larger than in the control sample. For oats, an increase in zinc concentration compared to control variant and non-impregnated zeolite variant is statistically reliable. For barley, difference between control and impregnated zeolite samples is statistically reliable (confidence level 0.95), but difference between the impregnated zeolite variant and non-impregnated zeolite variant is not statistically significant.

Implementation of zeolites, impregnated with zinc and copper ammoniates, can be recommended for improving the soil quality and micronutrients level in grain and vegetable production.

Acknowledgments

Authors express their thanks to Cost Action FA 0905 “Mineral Improved Crop Production for Healthy Food and Feed” for consulting and financial support.

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