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Assessment of changes of some functions of Ukrainian acid soils after chemical amelioration

Abstract: The objective of the article was to determine the effectiveness of lime of different origin for chemical amelioration of soils and examine its impact on soil functions such as productivity, habitat, regulation of water quality, and the protective buffer biogeocenotic screen. Limy ameliorants were applied in small local field experiment on Luvic Chernozem, and experiment with lysimeter columns was carried out on Albic Luvisol. The number of the main groups of microflora and enzymatic activity of soil was determined in soil samples taken for the analysis from the root zone. Research concerning the influence of natural and industrial origin ameliorants on soil as habitat showed the correlation of sugar beets productivity with soil biogenic. The increase of biomultiplicity of soil microbiota after addition of a cement dust and negative influence of red sludge on soil as habitat for living organisms was observed. Research involving the influence of ameliorants on soil by lime as the protective buffer biogeocenotic screen was carried out using lysimeter columns. It was stated that the addition of limy ameliorants reduces mobility of heavy metals.

Keywords: Ecological functions of soil, lime ameliorants, heavy metals, cement dust, red sludge

INTRODUCTION

Functional and ecological approach in the soil science has its interdisciplinary and systemic nature aspects. Therefore, adverse environmental processes have led to the development of land-use doctrine of the ecological functions of soil (Anton 2004; Blum 2005; Bockheim and Gennadiyev 2010; Dobrovolsky 2000; Huntington 2006; Janzen 2004; Koster et al. 2004; Tilman et al. 2002).

In Ukraine, as all over the world, the numbers of problems related to land use are growing. Therefore, understanding of ecological consequences from realization unreasonable agriculture projects became a signal for development of ecological functions of soil doctrine and elaboration of functional and environmental approach in pedology (Baluk et. al. 2004; Dobrovolsky 2000; website 1).

Among agricultural land in Ukraine, acidic soils occupy almost 5 500 000 ha, including: highly acidic soils ($\text{pH}_{\text{aquatic}} = 4.51\text{--}5.0$ and $\text{pH}_{\text{KCl}} = 4.01\text{--}4.50$) – 636 000 ha, medium acidic soils ($\text{pH}_{\text{aquatic}} = 5.01\text{--}5.50$ and $\text{pH}_{\text{KCl}} = 4.51\text{--}5.0$) – 1 372 000 ha and slightly acidic soils ($\text{pH}_{\text{aquatic}} = 5.51\text{--}6.0$ and $\text{pH}_{\text{salt}} = 5.01\text{--}5.50$) – 3 449 900 ha. Soils with excessive acidity, which

limits the normal development of crops, are widespread in the areas of north of Polissya and forest-steppe, and in the Carpathian region (Transcarpathia, Carpathian Mountains, Prykarpattia – also known as Outer Eastern Carpathians). Acidic soils under influence of intensive agriculture are exposed to the secondary acidification and decalcification, despite of that these soils have enough anti-acid buffer ability (Baluk et. al. 2004; Program 2004).

In Ukraine, about 285 million tons of secondary raw materials and wastes are produced annually. Significant proportion of calcium waste of sugar manufacture, cement and wastes from aluminum plants is reused (Program 2004). Therefore, utilization of wastes is becoming more popular every year, first of all in agricultural application. Recognizing high economic efficiency of industrial wastes application as ameliorants, identification of possible environmental risk must be a part of amelioration actions planning.

In this article, applying the principles of ecological and functional approach, the efficacy of some lime ameliorants of different origin was studied and their impact on such functions of soil as efficiency, habitat for microbiota, regulation of hydrosphere, buffer and protective biogeocenotic screen was considered.

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MATERIALS AND METHODS

We have carried out our research on two soil types: silty clay loam Luvic Chernozem ($\text{pH}_{\text{KCl}} = 5.0$) and silty loam Albic Luvisol ($\text{pH}_{\text{KCl}} = 4.7$) (IUSS Working Group WRB, 2007). Influence of limy ameliorants on soil was conducted in small local field experiment (Table 1) on Luvic Chernozem in the NSC “O.N. Sokolovs’ky Institute for Soil Science and Agrochemistry Research” experimental farm (Slobozhan research field, Kharkiv area, Fig. 1). The cultivated plant in this experiment was the sugar beet. Research of limy ameliorants influence on soil as the protective, buffer biogeocenotic screen and the regulator of water cycling and quality was carried out based on the laboratory and model experiment on Albic Luvisol, which was selected in Obroshyno research field, Lviv area (Fig. 1).

In soil samples taken near the roots of plants, the number of major groups of microorganisms was determined (Zvyahyntsev et.al. 2005). As a result, integrated index of the soil biogenic (IIB) was determined (Azzi 1959). Enzymatic activity of soil was defined by dehydrogenase and invertase activity indexes by Galstyan’s method (Peterson and Kurilyak 1971). Polyphenol oxidase index was carried out in

the conventional way described by Karyagina and Mihaylovskaya (Karyagin and Michael 1986).

Samples of Albic Luvisol have been used in lysimeter columns which contained 1 kg of soil collected from a layer 0–20 cm. The samples to lysimetric experiments were prepared by mixing soil with ameliorants. We carried out washing of soil by the distilled water of 360 milliliter, simulating the average monthly precipitation during the vegetative period (May – September) which was about 480 mm. Doses of ameliorants were counted by the pH-buffer and hydrolytic acidity schedules. Washing of soil in columns was conducted by 4 month after 7-weeks composting at room temperature and initial soil humidity which was close to the total moisture capacity (55%). The activity of calcium ions (Ca^{2+}) and pH measurements were carried out in filtrate conditions after every washing by direct potentiometric method using ion-selective electrodes (ISO 4456:2005).

Slaked lime, dolomite and cement dust (Balakleya cement plant), and red sludge (Nikolaev aluminum plant) were used as ameliorants. Eutrophic peat from lowland (moisture content 65%; pH in water 5.1; ash-content 23.5%; degree of decomposition – 85%) was used as organic fertilizer. Thirty tones of peat

FIGURE 1. Sketch map of the research area: Slobozhan and Obroshyno research field

TABLE 1. The influence of ameliorants and organic-mineral fertilizers on sugar beet productivity and microbiological indexes of soil in the root zone

No.	Variant	IIB [%]	Polyphenol oxidase (mg 1,4-n-benzoquinone per hour)	Invertase (mg glucose per 24 hour)	Dehydrogenas (mg TFF per 24 hour)	Harvest [Hwt/ha]
1	Control (without ameliorant)	55	447.3	1.21	274.8	335
2	Slaked lime	57	865.3	1.32	220.9	358
3	Dolomite	57	243.9	1.22	311.8	360
4	Cement dust	71	166.2	1.24	206.8	391
5	Red sludge	39	661.9	1.47	208.5	334
6	NPK	41	425.1	0.83	329.6	339
7	Slaked lime + NPK	42	95.9	1.46	258.4	360
8	Dolomite + NPK	63	155.1	1.42	355.3	353
9	Cement dust + NPK	87	473.2	1.05	361.2	398
10	Red sludge + NPK	50	421.4	1.17	377.1	337
11	NPK + peat 30 t/ha	52	454.7	1.27	406.8	343
12	Slaked lime + NPK + peat 30 t/ha	71	476.9	0.74	396.1	369
13	Dolomite + NPK + peat 30 t/ha	82	210.6	1.39	403.9	381
14	Cement dust + NPK + peat 30 t/ha	75	203.2	1.12	232.2	395
15	Red sludge + NPK + peat 30 t/ha	50	454.7	1.39	409.2	345
LSD 0.05			94.25	0.29	31.05	12.3

LSD – Least Significant Difference.

were added per hectare. Mineral fertilizers (ammonium nitrate, superphosphate, potassium salt) were added in the doses of $N_{90}P_{60}K_{60}$ kilograms per hectare according to active ingredient. The determination of mobile forms of heavy metals was carried out before and after soil washing by atomic absorption spectrometry method using C-115 appliance. The extraction of heavy metals was carried out using acetate-ammonia buffer (CH_3COONH_4) with pH = 4.8 (the ratio of the soil to the solution was 1:5) according to ISO 4770.1-9:2007.

The experiment with ameliorants was conducted according to the following scheme in case where doses of ameliorants were counted by the pH-buffer schedules: 1) control (without ameliorants); 2) 1.0 g of slaked lime in 1.0 kg of soil, which corresponds to the 3.2 t/ha in industrial conditions; 3) dolomite 1 g/kg (3.5 t/ha); 4) cement dust 1.2 g/kg (3.7 t/ha); 5) red sludge 0.7 g/kg (2.2 t/ha). The experiment was conducted according to the following scheme in case where doses of ameliorants were counted by hydrolytic acidity: 6) slaked lime 1.4 g/kg (4.6 t/ha); dolomite 4.6 t/ha; 7) cement dust 1.4 g/kg (4.6 t/ha); 8) red sludge 1.4 g/kg (4.6 t/ha).

RESULTS AND DISCUSSIONS

Research of the influence of ameliorants of natural and industrial origin on soil as habitat for microorganism showed the dependence between sugar beets productivity and soil biogenic (Table 1). The most essential growth of sugar beet productivity and amount of microorganisms was found in soil amended by cement dust. After the red sludge addition, the crop of sugar beet was at the level of control. Toxic influence

of red sludge was shown in soil flora pressure and reduction of soil microbiota quantity. The increase of polyphenol oxidase activity was noticed, especially when it is added with peat. It is a sign of a possible humus accumulation. Further researches of organic substance transformation processes with application of this industrial waste is needed.

During the addition of ameliorants the pH of soil changed. Before seeding the sugar beet into the soil the dose of lime ameliorants were determined by the curves of pH-buffering (Desyatnik 2013). It was confirmed that during the cultivation of sugar beets soils have become more acidic (Desyatnik 2013; Zapko and Desyatnik 2013). In our experiments, the soil pH was decreased as follows: in the rhizosphere of sugar beet in the control (without any ameliorants) from 6.4 to 5.2; after the application of slaked lime and dolomite – from 7.5 to 6.1; after the application of cement dust – from 7.5 to 6.7; and after the application of red sludge – from 7.5 to 5.6. However one year following the harvesting, in soils on all versions of the experiment with lime ameliorants soil reaction was approximately neutral, and on the control was 5.7. The optimum value of soil pH for cultivation of sugar beet is 7.5.

Our research has showed that addition of limy ameliorants, irrespective of their origin, intensifies such functions of soil as the buffer and protective biogeocenotic screen (Table 2). First of all, this is confirmed by the increase of the soil pH by bringing ameliorants and, at the same time, decrease of mobility of the majority of trace elements (Table 2). At carrying out the experiment, the soil pH was adjusted from the initial 5.0 to 6.5, and this value throughout

TABLE 2. The content of heavy metals mobile forms in soils a number over line – before simulation of a precipitation a number under line – after simulation of a precipitation

Variants	The maintenance of heavy metals mobile forms in soil, in mg·kg ⁻¹								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Control	<u>0.2</u> 0.3	<u>0.2</u> 0.1	<u>0.9</u> 0.1	<u>0.4</u> 0.4	<u>17.1</u> 27.7	<u>95.8</u> 25.9	<u>0.4</u> 0.7	<u>1.5</u> 2.0	<u>1.3</u> 1.1
Norms of ameliorants defined by curves of pH-buffering									
Slaked lime	<u>0.3</u> 0.3	<u>0.2</u> 0.1	<u>0.4</u> 0.2	<u>0.3</u> 0.5	<u>7.4</u> 35.4	<u>67.2</u> 43.8	<u>0.3</u> 0.2	<u>0.9</u> 1.3	<u>0.9</u> 0.4
Dolomite	<u>0.2</u> 0.1	<u>0.3</u> 0.1	<u>0.6</u> 0.6	<u>0.4</u> 0.5	<u>8.6</u> 49.6	<u>54.0</u> 12.3	<u>0.2</u> 0.7	<u>1.1</u> 1.6	<u>0.8</u> 0.8
Cement dust	<u>0.2</u> 0.3	<u>0.3</u> 0.1	<u>0.6</u> 0.2	<u>0.5</u> 0.8	<u>9.4</u> 107.1	<u>98.1</u> 60.8	<u>0.2</u> 0.4	<u>1.2</u> 1.2	<u>1.5</u> 0.7
Red sludge	<u>0.3</u> 0.2	<u>0.1</u> 0.2	<u>0.5</u> 0.5	<u>0.4</u> 0.5	<u>12.1</u> 79.8	<u>50.1</u> 19.5	<u>0.3</u> 0.8	<u>0.6</u> 1.3	<u>0.8</u> 1.0
Norms of ameliorants defined by hydrolytic acidity									
Slaked lime	<u>0.3</u> 0.2	<u>0.2</u> 0.2	<u>0.3</u> 0.2	<u>0.3</u> 0.6	<u>8.1</u> 40.4	<u>79.1</u> 47.8	<u>0.3</u> 0.1	<u>0.8</u> 1.3	<u>1.1</u> 0.4
Dolomite	<u>0.2</u> 0.2	<u>0.1</u> 0.2	<u>0.3</u> 0.6	<u>0.5</u> 0.5	<u>8.1</u> 49.1	<u>62.4</u> 27.9	<u>0.6</u> 0.1	<u>1.1</u> 0.4	<u>0.8</u> 0.8
Cement dust	<u>0.3</u> 0.1	<u>0.3</u> 0.1	<u>0.3</u> 0.6	<u>0.2</u> 0.4	<u>7.4</u> 37.0	<u>57.9</u> 8.7	<u>0.4</u> 0.33	<u>1.7</u> 1.6	<u>0.7</u> 0.8
Red sludge	<u>0.2</u> 0.1	<u>0.2</u> 0.2	<u>0.5</u> 0.2	<u>0.3</u> 0.2	<u>16.1</u> 42.7	<u>74.7</u> 12.7	<u>0.3</u> 0.4	<u>1.4</u> 0.9	<u>1.1</u> 0.7
MPC	0.7–3.0	5.0	6.0	3.0	–	60.0	4.0	6.0	230

MPC – maximum permissible concentrations.

experiment remained stable. Detailed description of acid-base changes of Albic Luvisol function (pH and calcium activity) has been described in our previous publication (Zapko and Desyatnik 2013).

Application of fertilizers and ameliorants often results in an increase of total heavy metals content in soil (Kabata-Pendias 2011). Results of the experiment in the present study show that the content of mobile forms of most heavy metals (Pb, Cr, Zn, Ni, Mn) have not increased even after washing of soil, most likely due to strong fixation of metals by soil components (organic matter, carbonates, Fe-Mn oxide and others). Manganese concentration in soil samples prior the experiments was higher than maximum permissible concentration, i.e. 60 mg·kg⁻¹ (Baluk et al. 2004). After simulation of a precipitation (distilled water), manganese concentration significantly decreases. First of all, it can be connected with leaching of manganese, and also with the increase of iron mobility which serves as a factor decreasing the manganese movement (Kabata-Pendias 2011).

Application of limy ameliorants also promotes considerable decrease of lead mobility (Table 2). Lead, if the pH is growing from 5.5 to 9.5, becomes almost immobile (Azzi 1959). Therefore, actions of chemical amelioration practically reduces risk of Pb translocation to plants during vegetable production.

Zn, Co, and Cr are elements which activity is reduced at neutral and alkaline reaction of soil environment, as after addition of limy ameliorants decrease in their concentration was observed (Baluk et al. 2004). It can pose a problem, because such microelements as Zn can be almost unavailable for plants. The solution to this problem may be the addition of ameliorants containing calcium with microfertilizers which contains zinc.

Revealed reduction of majority heavy metals mobility testifies about reduction of their translocation to underground waters and vegetable production. Therefore, even though high total concentration of heavy metals in soil, the application of limy ameliorants can be an effective method to decrease of heavy metals mobility.

In order to study the influence of lime ameliorants on soil as the regulator of water cycling and quality, after each washing soil calcium content was measured in filtrates received. The research has shown a slight increase of activity of calcium ions in infiltration water as a result of application of lime ameliorants in quantities determined by curves of pH-buffer (Fig. 2). Calcium concentrations were lower than in controls in the variant with red sludge only. In our opinion, in this case calcium formed a complex compounds. While ameliorants were brought in doses defined

FIGURE 2. Calcium washing from Albic Luvisol under the influence of calcareous ameliorants (determination of ameliorants norms was carried out based on buffer action schedules)

according to hydrolytic acidity, the intensity of calcium leaching is greater (Fig. 3). This is caused by application of higher doses of ameliorants in comparison with the quantities determined by the curves of pH-buffer (Fig. 2). This fact indicates that the profitability of agricultural production can decrease and the risk of contamination of groundwater can increase, when the amounts of ameliorants will be established based on hydrolytic acidity.

Chemical amelioration for optimization acid-base regime of acidic soils has been studied by scientists for a long time in many countries all over the world (Ulrich and Pankrath 1986; Longnecker 1952), including Ukraine (Baluk et al. 2004; Program 2004). The main attention was focused on impact of chemical amelioration (e.g. liming) on agro-chemical, physico-chemical and physical properties of the acid soils. Common parameter of soil quality is their productivity, which is

FIGURE 3. Calcium washing from Albic Luvisol under the influence of calcareous ameliorants (determination of norms of ameliorants was carried out based on hydrolytic acidity of soil)

indicated by the yield of specific crop (Anton 2004; Program 2004). On the other hand, adverse impacts on indicators of soil and their quality was found in areas of reclaimed agroecosystems. The problem can arise in particular when the amounts of lime ameliorants used in the field have been exceeded. As a result this impact leads to the degradation of not only the soil environment, but also the environment in general. Today we need to modify the land use concept, because people continue to use these soils in intensive farming systems. To resolve this problem, researchers (Truckavetskiy 2003; Gorban 2008) have proposed to extend the functional-ecological approach to agricultural land.

Consequently, the problem of effective use of lime ameliorants with simultaneous assessment of the dynamics of environmental and productive functions of soil has not been studied in detail. For example, hydrospheric soil functions (transformation of surface water by soil and its role in the formation of runoff from the catchment, the impact on biological productivity of water bodies due to bringing the soil compounds) might provide the possibilities for assessment of the soils sorption barrier functions.

Soil cover plays global role include as an irreplaceable and unique part of biosphere (Blum 2005; Bockheim and Gennadiyev 2010; Dobrovolsky 2000; Huntington 2006). We need to remember about it when we provide different experiment to obtain specific results. Sometimes disruption of ecological balance at the local level threatens to escalate into global environmental problems. For example, when one is liming the acid soils we have destructive processes in terms of the environmental protection as follows:

- leaching of pollutants (for example heavy metals) with infiltration water which are present as impurities in ameliorants;
- excess of permissible level of ameliorants and as a result intensification of leaching of calcium, nitrate, water-soluble organic compounds and other substances into groundwater;
- emissions of carbon dioxide and gaseous nitrogen from the soil to the air, namely increasing of eutrophication and pollution of surface and ground water and air.

Accordingly, we have conducted laboratory and modeling research in two main directions. First of all, it was the study of the functioning of soil as a protective buffer biogeocenotic screen and regulator of the composition of natural waters under influence of different lime ameliorants (Table 2; Fig. 2 and 3). This was the initial stage of implementation of

ecological-functional approach for a particular soil in specified environmental conditions. In practice it will allow to prevent the negative effects of liming still at the stage of planning of reclamation activities. Secondly, evaluation of the role of soil as the habitat for microorganisms and the factor of biological evolution is necessary. The pH of the soil solution is crucial for the functioning of soil microorganisms, since actual acidity of the soil is essential to their metabolic and certainly for the ontogenesis of plants.

As a result of soil acidification, microbiological pool that has involved in nitrogen fixation significantly transformed. Fungi mykorrhiza which are symbiotically associated with higher plants and that contribute to more efficient use the nutrients may be killed as a result of the transformation of acidity. Consequently productivity of soil of agroecosystems will significantly reduce. Therefore, there is a need of assessment of the reaction of the soil fauna for optimization of agroecological conditions of soils under their amelioration during the planning phase of such measures. The reaction of the soil fauna is the best indicator for prevention of the degradation of ecological functions of soil cover. Our results have shown that the use of red sludge for amelioration of acid soils leads to a decrease of biodiversity of soil microorganisms, while the use of cement dust leads to a substantial increasing of the number of soil microfauna (Table 1).

CONCLUSIONS

1. The values of the biodiversity index confirmed that the most positive impact on the biodiversity of soils studied had the application of cement dust (or cement dust + NPK). On the other hand, the most adverse effect on the biodiversity of soils was observed after the application of red sludge (or red sludge + NPK).
2. The addition of limy ameliorants irrespective of their origin reduces mobility of heavy metals which testifies their role in intensification of such ecological soil function as biogeocenotic screen.
3. In order to decrease the destructive consequences of amelioration we consider that the rates of application of lime should be determined by curves of pH-buffering.

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