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Agrochemical methods for reducing the translocation ability of heavy metals in sod-podzolic soil

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Abstract. The impact of technogenesis on the agricultural landscape contributes to the contamination of all its components by heavy metals. The main measure to protect the environment from the input of heavy metals is the prevention of pollution, which is achieved by improving the technology of agricultural production. The development of methods for the agrochemical rehabilitation of technogenically polluted soil, which ensure the receipt of environmentally safe crop products, is an urgent task. The paper presents the results of a lysimetric experiment on the study of the use of fertilizer systems for the purpose of remediation of heavy-metal-contaminated soddy-podzolic soil. It has been experimentally established that the translocation ability of heavy metals and, as a result, the accumulation of toxicants in grain and tilled crops is reduced when using an organomineral fertilizer system. All the studied fertilizer systems reduced the entry of dangerous ecotoxicants - lead and cadmium, into the infiltration water, and also caused the immobilization of Cu and Zn.

Key word: mineral fertilizers, organic fertilizers, soddy-podzolic soil, soil remediation, heavy metals, translocation, chemical reclamation, crop production, environmental safety.

INTRODUCTION

Preservation of soil, improvement of its properties and increase in fertility is one of the main conditions for the existence of mankind. However, at present, on a global scale, there is a systematic decrease in the area of soil in agricultural use. Therefore, it is very important to increase soil fertility, which is achieved through land reclamation measures, favorable for the development of agricultural crops, the mode of use. Soil fertility depends on natural soil formation, agrochemical and agrophysical properties, the influence of cultivating factors in the technology of growing crops and, more recently, on the impact of technogenesis. Heavy metals (HMs) pose a serious threat to the soil cover. All major HM migration cycles in the biosphere begin in the soil, since it is there that metals are mobilized and their migratory forms are formed. A significant reaction surface of mineral matter, the presence of soil solutions and organic matter, saturation with microorganisms, mesofauna, and roots of higher plants create the most complex system of transformation of heavy metal compounds in the soil (Borisochkina & Kaydanova, 2021; Mazhaiskiy & Guseva, 2021). In the process of interaction between soil and metals, they are sorbed by organic matter, iron hydroxides, and clay minerals. Soddy-podzolic sandy soil is the least resistant to the action of technogenesis, since they are poorly provided with nutrients and are permeable. According to many authors, the most acceptable method of rehabilitation and restoration of the fertility of technogenically polluted soil is a rational fertilizer system (Ignatova, 2020; Chernyakova, 2020; Patrikeev & Yanchas, 2020). Organic and phosphate fertilizers are effective as a means of reducing the mobility of heavy metals. Mineral fertilizers improve the trophic indicators of agricultural crops, improving the resistance of plants to adverse environmental influences (Lasmini et al., 2019; Skudra & Ruza, 2019; Burdin et al., 2020; Hlisnikovský et al., 2020; Khajbullin et al., 2020; Murtić et al., 2020; Wiśniewska-Kadżajan & Jankowski, 2020; Kołodziejczyk, 2021; Radchenko et al., 2021). In this regard, the development of scientifically based systems for the use of fertilizers on technogenically modified soddy-podzolic soil is an urgent task. The aim of the research is to evaluate agrochemical methods for reducing the translocation ability of heavy metals in sod-podzolic soil. The results of such studies allow us to offer more effective reclamation recommendations for unproductive soils of light granulometric composition in order to increase their fertility and maintain a positive balance of nutrients due to the normalized application of organic and mineral fertilizers, as well as the conservation and sustainable use of sod-podzolic soils of agricultural landscapes transformed as a result of technogenesis.

MATERIALS AND METHODS

The research was carried out in the conditions of the Meshcherskaya lowland on the territory of the Ryazan region, located in the southeastern part of the central zone of the European part of Russia. For the Ryazan Meshchera, zonal soil is soddy-podzolic soil, which occupies about 70% of the area. It is characterized by a light granulometric composition, low content of organic matter and low fertility (Table 1).

Table 1. Agrochemical characteristics of sod-podzolic soils

Soil layer, cm	Humus, %	$pH_{сол}$	N, %	P_2O_5, mg kg^{-1}	K_2O, mg kg^{-1}
0–10	1.33	5.2	0.032	113	78
10–20	1.29	4.9	0.024	95	66
20–30	1.18	4.8	0.016	76	37
30–40	1,06	4.6	0.010	57	21
0–40	1.22	4.9	0.017	85	51

According to long-term environmental monitoring, this soil is under a significant technogenic load, which has led to the accumulation of zinc, cadmium, lead, copper to levels of medium and high pollution (Mazhaiskiy & Guseva, 2019).

To study the effectiveness of agro-reclamation methods for the rehabilitation and detoxification of soddy-podzolic sandy loamy soil contaminated by heavy metals, a long-term lysimetric experiment (2010–2020) was carried out, the scheme of which is presented in the 2st Table. A complex soil contamination by HMs, corresponding to the data of monitoring of the technogenic load on soddy-podzolic soil, is modeled in the experiment, taking into account the background content of elements, which amounted to: Cu - 90 mg kg^{-1}, Zn - 110 mg kg^{-1}, Pb - 40 mg kg^{-1}, Cd - 0.6 mg kg^{-1}. The doses of elements per lysimeter were calculated from their content in chemically pure salts ($ZnSO_4 \cdot 7H_2O$ (22.8% Zn), $CuSO_4 \cdot 5H_2O$ (25.5% Cu), $Pb(CH_3COO)_2 \cdot 3H_2O$ (54.6% Pb), $CdSO_4$ (53.9% Cd)).

Table 2. The scheme of the lysimetric experiment

Variant	Fertilizer system
Control	Without fertilizer
1	Cattle manure 40 t ha^{-1}, N90P60K120
2	Cattle manure 40t ha^{-1}, N90P120K120
3	Cattle manure 40t ha^{-1}, N90P240K120
4	Cattle manure 80 t ha^{-1}
5	N90P480K120

For experiments, we used lysimeters designed by the NRIHEM with an area of 1.17 m^2, soil (soddy-podzolic sandy loam) of undisturbed composition. As experimental crops used in crop rotation: potatoes, beets, grain crops (oats, barley). After the end of the experiment in 2020, the content of copper, zinc, lead and cadmium was determined in crop production and lysimetric waters by atomic absorption spectrometry on the AAS–1 spectrophotometer. The mineralization of plant samples was carried out by dry salting, water samples were mineralized by evaporation with concentrated nitric acid (Guidelines for the determination of heavy metals in agricultural soil and crop products, 2021; GOST R 55447–2013). Trial establishment - the introduction of heavy metals and the use of organic-mineral, organic and mineral fertilizer systems took place in 2010. Background liming and manure application was carried out in 2014. Urea (N–46%) or ammonium nitrate (N–34.5%), double superphosphate (P_2O_5–46%), potassium chloride (K_2O–60%), and cattle manure were used in the experiment. Fertilizers were applied before spring tillage. The experiment was carried out in four repetitions, the results were computer statistically processed.

RESULTS AND DISCUSSION

The task of agrochemical means is to create a balanced diet and neutralize the phytotoxic effect for crops in conditions of technogenic soil pollution. A scientifically based fertilizer system is designed to influence a more complete use of nutrients by various crops and prevent the accumulation of heavy metals in crop products (Guseva et al., 2017; Guseva, 2019).

Tables 3–6 present data on the effect of the developed fertilizer systems on the content of pollutants in agricultural crops grown on soddy-podzolic soil contaminated by heavy metals, obtained from the results of a long-term lysimetric experiment.

The content of Pb in potato tubers, fodder beet, grain biomass, as well as in by-products does not exceed the standard values for plant feed. In the main barley production in the variant without the usage of fertilizers, the accumulation of lead was recorded in excess of the maximum allowable concentration (MAC) for food raw materials by 36%.

Table 3. Lead content in crop products, mg kg^{-1}*

Variant		Potato	Barley	Oats	Fodder beet
Control		0.43 ± 0.04 2.95 ± 0.1	0.68 ± 0.04 1.4 ± 0.02	0.75 ± 0.04	0.21 ± 0.01
1	Cattle manure 40 t ha^{-1}, N90P60K120	0.26 ± 0.01 3.12 ± 0.2	0.33 ± 0.01 1.68 ± 0.03	0.84 ± 0.05	0.19 ± 0.01
2	Cattle manure 40 t ha^{-1}, N90P120K120	0.25 ± 0.01 2.92 ± 0.3	0.33 ± 0.01 1.67 ± 0.01	0.83 ± 0.05	0.18 ± 0.02
3	Cattle manure 40 t ha^{-1}, N90P240K120	0.24 ± 0.02 3.39 ± 0.2	0.44 ± 0.02 0.78 ± 0.01	1.34 ± 0.09	0.19 ± 0.01
4	Cattle manure 80 t ha^{-1}	0.42 ± 0.03 2.50 ± 0.1	0.32 ± 0.01 0.96 ± 0.02	1.08 ± 0.08	0.20 ± 0.01
5	N90P480K120	0.27 ± 0.02 2.39 ± 0.2	0.32 ± 0.01 1.03 ± 0.03	0.92 ± 0.07	0.17 ± 0.01
MACp. **		0.5	0.5	–	–
MACf. ***		5.0	5.0	5.0	5.0

*Note: numerator – lead content in main products, denominator - lead content in by-products.

MACp. – maximum allowable concentration of lead in plant products (Temporary maximum allowable level .... 123-4 / 281, 1987).

MACf. – maximum allowable concentration of lead for feed (Maximum allowable concentrations of heavy metals and arsenic in plant raw materials and food products, 1992).

Table 4. Cadmium content in crop products, mg kg^{-1}*

Variant		Potato	Barley	Oats	Fodder beet
Control		0.04 ± 0.003 0.24 ± 0.03	0.21 ± 0.03 0.14 ± 0.01	0.09 ± 0.002	0.02 ± 0.001
1	Cattle manure 40 t ha^{-1}, N90P60K120	0.03 ± 0.001 0.21 ± 0.01	0.07 ± 0.003 0.10 ± 0.01	0.09 ± 0.002	0.02 ± 0.001
2	Cattle manure 40 t ha^{-1}, N90P120K120	0.03 ± 0.001 0.22 ± 0.01	0.10 ± 0.02 0.09 ± 0.004	0.07 ± 0.001	0.02 ± 0.002
3	Cattle manure 40 t ha^{-1}, N90P240K120	0.03 ± 0.002 0.20 ± 0.03	0.07 ± 0.003 0.13 ± 0.02	0.10 ± 0.01	0.02 ± 0.001
4	Cattle manure 80 t ha^{-1}	0.03 ± 0.003 0.23 ± 0.01	0.10 ± 0.02 0.11 ± 0.01	0.10 ± 0.02	0.02 ± 0.002
5	N90P480K120	0.03 ± 0.003 0.23 ± 0.02	0.10 ± 0.01 0.11 ± 0.02	0.09 ± 0.002	0.02 ± 0.001
MACp.**		0.03	0.1	–	–
MACf.***		0.3	0.3	0.3	0.3

*Note: numerator – cadmium content in main products, denominator - cadmium content in by-products.

MACp. – the maximum allowable concentration of cadmium in plant products (Temporary maximum allowable level .... 123-4 / 281, 1987).

MACf. – maximum allowable concentration of cadmium for feed (Maximum allowable concentrations of heavy metals and arsenic in plant raw materials and food products, 1992).

According to the content of cadmium in vegetation in the experiment, the following results were obtained. The content of this element in beets and grain biomass, as well as by-products of potatoes and barley, is within the MAC for plant feed. The accumulation of Cd, in relation to the MAC for food raw materials, occurred in potato tubers in the variant of the experiment without fertilizers, and the accumulation of this element was also observed in the main barley production in the control (the excess was 33% and 110%, respectively).

Table 5. Zinc content in crop products, mg kg^{-1}*

Variant		Potato	Barley	Oats	Fodder beet
Control		10.71 ± 1.2	76.1 ± 6.2	72.3 ± 3.1	11.4 ± 1.2
		103.1 ± 8.9	111.2 ± 10.1		
1	Cattle manure 40 t ha^{-1},	6.62 ± 0.7	48.7 ± 4.1	45.7 ± 4.2	13.1 ± 1.1
	N90P60K120	100.5 ± 10.2	65.2 ± 3.7		
2	Cattle manure 40 t ha^{-1},	6.68 ± 0.9	46.4 ± 4.9	50.1 ± 5.6	16.3 ± 1.5
	N90P120K120	74.8 ± 5.1	59.3 ± 4.9		
3	Cattle manure 40 t ha^{-1},	6.02 ± 0.5	49.2 ± 4.1	50.01 ± 4.8	14.4 ± 1.1
	N90P240K120	67.9 ± 4.9	73.9 ± 5.5		
4	Cattle manure 80 t ha^{-1}	6.10 ± 0.7	37.6 ± 2.2	49.4 ± 4.1	27.3 ± 1.9
		51.7 ± 4.6	72.3 ± 5.2		
5	N90P480K120	9.6 ± 1.1	49.0 ± 4.7	49.7 ± 4.6	21.5 ± 2.2
		99.5 ± 9.9	72.5 ± 6.1		
MACp.**		10	50	–	–
MACf.***		100	50	50	100

*Note: the numerator is the zinc content in the main product, the denominator is the zinc content in the by-products.

MACp. – maximum allowable concentration of zinc in plant products (Temporary maximum allowable level .... 123-4 / 281, 1987).

MACf. – maximum allowable concentration of zinc for feed (Maximum allowable concentrations of heavy metals and arsenic in vegetable raw materials and food products, 1992).

Table 6. Copper content in crop products, mg kg^{-1}*

Variant		Potato	Barley	Oats	Fodder beet
Control		2.06 ± 0.008	6.02 ± 0.8	1.62 ± 0.03	2.26 ± 0.08
		9.06 ± 1.02	8.77± 0.8		
1	Cattle manure 40 t ha^{-1},	1.72 ± 0.07	4.36 ± 0.4	3.67 ± 0.1	1.53 ± 0.02
	N90P60K120	4.72 ± 0.3	2.36 ± 0.08		
2	Cattle manure 40 t ha^{-1},	1.60 ± 0.03	4.00 ± 0.6	2.92 ± 0.07	1.33 ± 0.03
	N90P120K120	8.67± 0.9	5.68 ± 0.5		
3	Cattle manure 40 t ha^{-1},	1.38 ± 0.04	4.75 ± 0.4	3.02 ± 0.2	1.93 ± 0.03
	N90P240K120	6.55 ± 0.8	4.44 ± 0.2		
4	Cattle manure 80 t ha^{-1}	1.86 ± 0.02	3.5 ± 0.1	2.09 ± 0.08	2.79 ± 0.05
		2.67 ± 0.09	4.38 ± 0.3		
5	N90P480K120	1.70 ± 0.04	4.43 ± 0.4	3.36 ± 0.1	2.21 ± 0.04
		10.91 ± 1.1	3.88 ± 0.1		
MACp.**		5	10	–	–
MACf.***		30	30	30	30

*Note: numerator – copper content in the main product, denominator - copper content in by-products.

MACp. – maximum allowable concentration of copper in plant products (Temporary maximum allowable level .... 123-4 / 281, 1987).

MACf. – maximum allowable concentration of copper for feed (Maximum allowable concentrations of heavy metals and arsenic in vegetable raw materials and food products, 1992).

The results of the experiment on the effect of various fertilizer systems on the accumulation of zinc by agricultural plants are as follows. The content of this metal in beets, the main and by-products of potatoes is within the MAC for both plant products and feed. A slight excess of the standards for potatoes and oats was observed in the control variant. The content of Zn in fodder beet did not exceed the standard values in all variants of the experiment. In the biomass of oats, there was an accumulation of zinc in the variant without fertilizers by 45% compared with MAC. In the main and by-products of barley, there was also an excess of the content of this element in the control variant (by 32% and 122%, respectively, compared with the maximum allowable concentrations). Also, an excess of the content of Zn in the by-products of barley was noted in all variants of the experiment, but these values are below the control.

The analysis of the experimental results showed that the Cu content in all test cultures, including by-products, did not exceed the normative values for plant feed and food products.

Thus, the obtained results showed a positive effect of the studied fertilizer system as a factor in the remediation of technogenically polluted soddy-podzolic soil.

The use of organic and mineral fertilizers against the background of liming on soil contaminated by heavy metals causes physicochemical and biological processes in the soil, which lead to the immobilization of HMs, making them not only inaccessible to plants, but also reducing their penetration into soil runoff (Stehlík et al., 2019). The results of the research of lysimetric water are presented in the 7th Table.

Table 7. Content of heavy metals in lysimetric water, mg $L^{-1} \cdot 10^{-3}$

Variant		Cu	Zn	Pb	Cd
Control		2.7 ± 0.1	19.5 ± 1.3	12.0 ± 1.8	3.9 ± 0.4
1	Cattle manure 40 t ha^{-1}, N90P60K120	6.5 ± 0.8	88.5 ± 5.2	3.7 ± 0.5	3.6 ± 0.3
2	Cattle manure 40 t ha^{-1}, N90P120K120	2.6 ± 0.1	44.9 ± 1.7	11.6 ± 1.1	3.7 ± 0.4
3	Cattle manure 40 t ha^{-1}, N90P240K120	6.7 ± 1.1	64.9 ± 9.3	10.6 ± 1.2	3.5 ± 0.2
4	Cattle manure 80 t ha^{-1}	1.8 ± 0.06	10.7 ± 1.3	9.8 ± 0.9	3.2 ± 0.3
5	N90P480K120	3.7 ± 0.3	59.1 ± 1.8	7.2 ± 0.3	2.3 ± 0.1

Copper is able to form many complexes with organic and mineral compounds of various solubility. The ability of a soil to fix Cu is highly dependent on the nature and amount of organic matter. Zinc is a mobile element, practically incapable of complex formation (Medvedev & Derevyagin, 2017). The experiment recorded the removal of these HMs outside the soil profile, but the immobilization of Cu and Zn was noted in the 4th variant of the experiment, the concentration of these elements in lysimetric water decreased by 33% and 45%, respectively, compared with the variant without fertilizers. All studied fertilizer systems reduced the infiltration water of hazardous environmental toxicants - lead and cadmium.

CONCLUSIONS

Agrochemical methods of rehabilitation of technogenically polluted soil must be implemented through the introduction of a scientifically based organo-mineral fertilizer system. In crop rotations, about 40% should be allocated to crops, the roots of which will concentrate a significant part of the HM. After harvesting the above-ground part, crop residues and roots must be plowed to the entire depth of the humus horizon of the contaminated soil. Organic and mineral fertilizers are recommended to be used systematically in crop rotations. A system of periodic (once every four years) application of organic and phosphate fertilizers is proposed. The recommended dose of manure - 40 t ha^{-1} (1 time per four years) is not deficient in the balance of humus, doses of mineral fertilizers, depending on the crop: N - 30–90 kg ha^{-1}, P_2O_5 - 60–120 kg ha^{-1}, K_2O - 60–120 kg ha^{-1} (per year).

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