Fertilizer systems for detoxification of chernozem contaminated with heavy metals

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Abstract. On the podzolized chernozem, where the increased level of contamination with heavy metals (Cu, Zn, Pb, Cd) was modeled, a certain dynamics of crop yields was observed. Mineral, organo-mineral and organic fertilizer systems in crop rotation were studied as a possibility of using detoxicants. The studied fertilizer systems increase the productivity of soil contaminated with heavy metals by 34 – 109%. The most effective fertilizer system (79.4 c/ha of feed units) turned out to be organo-mineral. When using only organic or mineral fertilizers, the efficiency decreased (27.9 – 55.5 c/ha of feed units) in relation to the control variant.

1 Introduction

Currently, the harmony of ecological balance in a number of regions of the globe is broken. The result was an increase in the volume of harmful substances that are discharged into the water, air, on the soil surface by industrial, agricultural, chemical and other enterprises. All the negative unforeseen consequences of anthropogenic human activity have a significant impact on the biochemical regime of the natural environment. Soil pollution with heavy metals (HM) is one of the most dangerous types of anthropogenic degradation of the ecosystem. The environmental consequences of pollution directly depend on how firmly and a lot of pollutants are retained by the soil, how much its abiotic and biotic properties change under the influence of pollution, as well as how these changes affect soil fertility and their ability to protect adjacent environments from pollution.

Currently, there is a problem of increasing and preserving soil fertility as the basis for sustainable development of agriculture in Russia, since due to a number of subjective and objective reasons, the use of agrochemical agents is limited [1]. To date, liming is practically not produced, potash and phosphorus fertilizers are not applied, as a result, a decrease in acidity and the content of mobile forms of nutrients is recorded in a variety of soils – from chernozems to sod-podzolic.

On soils contaminated with HM, farming becomes one of their actual practical tasks. The development of agrochemical scientifically based methods of detoxification of soils at different levels of HM pollution is relevant and mandatory for obtaining clean plant products that meet all sanitary and hygienic requirements, conducting sustainable agriculture, as well as preventing the further spread of ecotoxicants through the soil into groundwater and plants, to prevent poisoning of humans and animals.

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Among the HM priority pollutants of Russian soils are the following: copper, nickel, zinc, cobalt, lead and cadmium, which belong to the first and second hazard classes. Currently, there is a complex pollution of HM lands, which increases their negative impact on environmental objects [2-6]. In this regard, the development of methods for the rehabilitation of soils of agricultural lands and their rational use becomes an urgent area of research.

The purpose of the research is to study the influence of methods of complex agrochemical reclamation of the podzolized chernozem of the Ryazan region, contaminated with HM, on the productive functions of crop production.

2 Materials and methods of research

Modeling of the increased complex level of soil contamination was performed using pre-application to the soil. Chemically pure salts were used: $Zn(CH_3COO)_2 \times 2H_2O$; $CuSO_4 \times 5H_2O$; $Pb(CH_3COO)_2$; $CdSO_4$.

To do this , a 20 cm deep soil layer was selected from the lysimeter . The calculated dose of Cu, Zn, Pb and Cd salts was thoroughly mixed with this soil and placed in the same lysimeter.

According to the research program, experience has been laid in the study of fertilizer systems: organic (cattle manure), organo-mineral and mineral, according to which double superphosphate was used periodically and annually in increased doses. For podzolized heavy loamy chernozem, the norm of manure is 100 t/ha (Table 1). The annual rates of mineral fertilizers, depending on the crop, are adopted according to the recommendations for our zone [7].

The timing and methods of fertilization in the crop rotation link were carried out in the following way. In autumn, after harvesting the crop rotation, manure of cattle (cattle) was introduced at the rate of 100 t / ha, humidity 85%.

This norm of organic matter was plowed (buried) to a depth of 25 cm. Calculated rates of mineral fertilizers were evenly distributed manually over the surface of the lysimeter, and then the soil was dug to a depth of 12 – 15 cm. The soil surface was leveled with a rake. A mixture of herbs (fescue, timothy, clover) was sown as an equalizing crop.

In the experiment, urea (N – 46%), double superphosphate (P_2O_5 – 44%), potassium sulfate (K_2O – 48%) were used.

The research was carried out in the link of crop rotation: Nevsky barley, fodder beet – Eckendorf yellow, oats – horizon.

The technology of growing crops in lysimeters imitated the generally accepted for heavy loamy chernozems of this region, but with some features of lysimetric studies. Row spacing during the cultivation of fodder beets were in a loose state and clean of weeds, due to the loosening of the soil with devices for manual work.

As can be seen from Table 1, the following fertilizer systems are presented in the formed variants: organic (biological) – option 2; organo-mineral – option 3; mineral in two modifications – options 4 and 5 (periodic application of phosphorus norms for 2 and 4 years), and option 6 was introduced against the same background (N_1K_1) with an annual increased dose of phosphates (P_{120}). The accepted fertilizer systems were compared with their long-term use. In such studies, not only the real influence of fertilizers is superimposed, but also the aftereffect of previously introduced meliorants.

It was also taken into account that with the joint and separate use of organic and mineral fertilizers, the dose of manure used (100 t/ha) will create a deficit-free humus balance in the crop rotation. The recommended dose of manure at an annual rate of more than 10 t/ha meets these requirements [8]. In mineral fertilizer systems, the effect of the action and aftereffect of doses of phosphate fertilizers was studied. Monosubstituted calcium

phosphate is able to precipitate soil compounds of lead and zinc into insoluble salts, so the toxicants may not be available to plants.

Table 1. Scheme of laying and conducting a long-term stationary lysimetric experiment on podzolized heavy loamy chernozem.

Names of variants, systems of application of fertilizers in the link of crop rotation	Abbreviations
Without fertilizers	WF
Cattle manure 100 t/ha – periodic application	M_{100}
Cattle manure 100 t/ha – periodic application, $N_{60-90}P_{60}K_{60-120}$ – annually depending on the culture	M_{100} $N_1P_1K_1$
P_2 – periodic application of phosphorus, 1 time in 2 years at a dose of 120 kg / ha, annual use $N_{60-90}K_{60-120}$	$P_2N_1K_1$
P_4 – periodic application of phosphorus, once every 4 years 240 kg/ha, annual use $N_{60-90}K_{60-120}$	$P_4N_1K_1$
$P_{2(e)}$ – annual application of an increased dose of phosphorus (120 kg/ha) and optimal doses $N_{60-90}K_{60-120}$	$P_{2(e)}N_1K_1$

Water is the main medium of transport of various substances in the landscape, therefore, the study of the dynamics of vertical water flows is extremely important to solve the problem. In the lysimetric experiment, in conditions of increasing pollution of the biosphere, it becomes necessary to assess the impact of already polluted soil on the productivity of crops and the ecological properties of the soil and plants themselves, on the qualitative composition of elements in subsurface waters.

The groundwater level was maintained at a depth of 1.9 m. The moisture layers in the experiment were differentiated by the phases of plant development, taking into account the growth of their root system. They were 20-30 cm at the beginning and 30-50 cm at the end of the growing season of plant development. Watering was carried out in volumes that increase soil moisture to the lowest moisture capacity. Irrigation norms for irrigation were calculated according to the formula of A.N. Kostyakov [9] and were 10-25 mm.

Statistical processing of the obtained results was performed according to the recommendations [10] using computer Excel programs.

Depending on the goals and objectives of the experiments, the plants were harvested during different periods of vegetation. Fodder beets – at the beginning of the drying of the tops, cereals – in the phase of full ripeness.

Cereals (barley, oats) were cut at a height of 1-2 cm from the root neck. The plants were placed in bags with the indication of the variant number and repetition. In the laboratory, the above-ground mass crop was dried to a constant weight. After threshing the grain, the refined grain was weighed. Samples were taken from the crop by repetition, numbered, according to the registration log, for shipment to the laboratory.

The research was carried out using modern methods that meet the requirements for laying and conducting experiments to study the effect of technogenesis on the bioecosystem. Agrochemical research methods are generally accepted for the Non-chernozem zone of the Russian Federation.

By the beginning of our research, the presented system of experience options had been mastered. Therefore, nitrogen (N_{60}) fertilizers were introduced for the first crop in the studied crop rotation link for spring pre-sowing tillage, and new portions (doses) of phosphate fertilizer were also introduced in accordance with the frequency of its use: 120 kg, 240 kg of P_2O_5 per 1 ha.

3 Results and Discussion

The studied fertilizer systems in the accumulation of HM by plants had their own characteristics. Thus, an increase in zinc accumulation is noted in barley and oat grains. The

content of this element in the version without fertilizers was 18.2 mg/kg, 21.6 mg/kg, respectively. All fertilizer systems increased zinc accumulation in barley by 56 – 168%, in oats – 17% - 55%. At the same time, it should be emphasized that the accumulation of zinc in the research objects depended on the applied fertilizer systems (Table 2, 3).

The maximum effect on barley was exerted by the aftereffect of organic matter with the annual introduction of the optimal norm $N_1P_1K_1$. And one organic fertilizer contributed significantly less to the absorption of this biomicroelement. In turn, mineral fertilizers used annually in an increased dose of phosphorus (P_{120}) against the background of N_1K_1, when growing oats, increased zinc in its grain by 55% compared with the option without the use of fertilizers.

Table 2. The effect of fertilizer systems on the content of Zn and Pb in the main products.

Experience options	Zn			Pb		
	Barley	Fodder beetroot*	Oat	Barley	Fodder beetroot*	Oat
WF	18.2	14.6/75.2	21.6	0.98	0.30/1.50	1.17
M_{100}	28.4	10.4/81.3	26.1	1.16	0.18/1.4	1.18
$M_{100}N_1P_1K_1$	48.7	9.9/71.3	27.0	0.71	0.21/1.6	1.18
$P_2N_1K_1$	30.0	7.8/65.1	26.4	0.98	0.17/1.4	1.24
$P_4N_1K_1$	31.3	10.1/74.5	25.2	1.07	0.14/1.1	1.34
$P_{2(e)}N_1K_1$	29.3	13.2/103.0	33.5	0.80	0.17/1.4	1.19
MPC	50	-	50	0.5	-	0.5
MDU	50	100	50	5.0	5.0	5.0

Note:* above the line, the metal content in terms of natural moisture; below the line, the dry matter

Cadmium in oat grain accumulated less under the influence of the mineral systems $P_4N_1K_1$ and $P_{2(e)}N_1K_1$. Organic and organo-mineral systems reduced its accumulation in barley grain, and the above-mentioned mineral systems, on the contrary, increased its accumulation in the main products. Copper, as a trace element, improves many biochemical processes in plants. In barley grain, its content is significantly higher than in oats. The studied fertilizer systems in crop rotation did not significantly affect the accumulation of copper in grain, with the exception of $P_{2(e)}N_1K_1$, which significantly increased the accumulation of copper in oats and reduced it in barley. The use of only organic matter affected barley by the fact that the lead content in the grain increased by 18.4%. Organics + N1P1K1 reduced the concentration of this toxicant by 27.5%. A slightly smaller difference in grain accumulation of lead was observed on variant $P_{2(e)}N_1K_1$. Other fertilizer systems have not changed the content of this metal in barley grain compared to the non-fertilizer option.

Table 3. The effect of fertilizer systems on the content of Cu and Cd in the main products.

Experience options	Cu			Cd		
	Barley	Fodder beetroot*	Oat	Barley	Fodder beetroot*	Oat
WF	4.85	1.92/9.9	2.36	0.08	0.033/0.2	0.114
M_{100}	4.93	1.30/10.1	2.49	0.07	0.024/0.2	0.104
$M_{100}N_1P_1K_1$	5.00	1.15/8.9	2.67	0.10	0.018/0.2	0.105
$P_2N_1K_1$	4.97	1.17/9.7	2.51	0.14	0.020/0.2	0.105
$P_4N_1K_1$	5.38	0.96/7.1	2.38	0.12	0.022/0.2	0.063
$P_{2(e)}N_1K_1$	3.86	1.32/10.3	2.96	0.12	0.022/0.2	0.053
MPC	10	-	10	0.1	-	0.1
MDU	30	30	30	0.3	0.3	0.3

Note:* above the line, the metal content in terms of natural moisture; below the line, the dry matter

The concentration of Zn, Pb, Cu, Cd in the root crops of fodder beet, when calculated on dry matter, was significantly higher than in the grain of cereals. The first variant revealed Zn – 75.2 mg/kg, Pb – 1.50 mg/kg, Cu – 9.9 mg/kg, Cd – 0.2 mg/kg. The maximum content

of Zn (103 mg / kg) was determined in the variant where superphosphate was used in an increased dose against the background of nitrogen and potassium ticks. Other systems tended to reduce the accumulation of metals or did not change its amount in root crops.

Studying the productivity of polluted podzolized chernozem, it was noted that the yield on the variant without fertilizers is relatively low (Table 4). Studies have shown that by creating favorable nutrition conditions for plants due to various fertilizer systems, the productivity of contaminated chernozem increases. The most effective agro-reclamation techniques proved themselves on barley, where the increase in yield ranged from 54 to 135%. Fodder beet has relatively increased the yield of root crops by 14-130%. Grain harvest on oats (the most tolerant crop to soil contamination with HM) increased by 23-56%.

Maximum productivity is obtained from the periodic application of manure at a dose of 100 t/ha, subject to the annual use of mineral fertilizers. With this use of well-available minerals and hard-to-reach nutrients in organic matter, the best conditions for plant nutrition are created. The growing conditions are slightly worse in the case of using one organic fertilizer. With the organic system, the following yield increases were obtained in the crop rotation: barley 16.4 c/ha (104%), fodder beet 280 c/ha (96%), oats 5.5 c/ha (25%). Using the organo-mineral system in crop rotation, the yield increase for these crops was 21.2 c/ha (135%), 382 c/ha (130%) and 12.4 c/ha (56%), respectively.

Mineral fertilizer systems turned out to be somewhat lower in efficiency. They differed in the method of applying phosphorus fertilizers against the background of the annual use of nitrogen and potash fertilizers and showed the greatest efficiency for cereals (Table 3). The increases were: 8.5-15.1 c/ha for barley (54-96%), 11.8-5.0 c/ha for oats (53-26%). The application of double-dose phosphate fertilizers against the background of optimal doses ($N_{60}K_{60}$) provided stable increases in all studied crops: barley 10.8 c/ha (69%), oats 12.5 c/ha (56%) and fodder beet 159 c/ha (54%). The additions of root crops in the variants with the frequency of phosphate application (2 and 4 years) amounted to 83 c/ha (28%) and 40 c/ha (14%).

Table 4. Efficiency of agrochemical methods of sanitation of polluted heavy metals of podzolized chernozem.

Experience options	Yield of main products, c/ha											
	Barley			Fodder beetroot			Oat			Feed units, c/ha		
	average	shift		average	shift		average	shift		in total	shift	
		c/ha	%		c/ha	%		c/ha	%		c/ha	%
WF	15.7	-	-	293	-	-	22.2	-	-	73.1	-	-
M_{100}	32.1	16.4	104	573	280	96	27.7	5.5	25	128.6	55.5	76
M_{100} $N_1P_1K_1$	36.9	21.2	135	675	382	130	34.6	12.4	56	152.5	79.4	109
$P_2N_1K_1$	24.2	8.5	54	375	83	28	34.0	11.8	53	103.2	30.1	41
$P_4N_1K_1$	30.8	15.1	96	333	40	14	27.2	5.0	23	98.0	27.9	34
$P_{2(e)}N_1K_1$	26.5	10.8	69	452	159	54	34.7	12.5	56	115.4	42.3	58

The maximum effect on barley was exerted by the aftereffect of organic matter with the annual introduction of the optimal norm $N_1P_1K_1$. And one organic fertilizer contributed significantly less to the absorption of this biomicroelement. In turn, mineral fertilizers used annually in an increased dose of phosphorus (P_{120}) against the background of N_1P_1, when growing oats, increased zinc in its grain by 55% compared with the option without the use of fertilizers.

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When considering the total productivity over three years, it can be noted that all agrochemical techniques have a positive pattern. At the same time, high (109%) efficiency was obtained from the use of an organo-mineral fertilizer system. The second place is occupied by an organic fertilizer system, followed by a mineral one with a systematically increased dose of phosphates (P_{120}). Studies have shown that periodic application of phosphorus for two and four years has the same effectiveness.

4 Conclusion

Organo-mineral fertilizer system enhances the ecological functions of the soil by optimizing the nutrition of plants with the necessary elements. Taking into account biological characteristics, their nutrition can be regulated by growth periods, development phases, and in crop rotation – by the aftereffect of fertilizers. According to the biological resistance to the increased content of HM in the soil, the studied crops can be arranged in the following row: oats, fodder beet, barley. At the same time, the responsiveness of crops to the use of agrochemical agents has the reverse order: barley, fodder beet, oats.

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