

Optimization of Agricultural Activities in Areas Polluted with Heavy Metals

Sergey Smolentsev^{1*}, Elena Alaybysheva¹, Elena Sarbaeva¹, Alexander Volkov¹, Anastasia Demidova¹, Anastasia Korotkova¹, Anastasia Ivanova¹, Marina Polovnikova² and Olesya Savchenko^{3*}

¹ Mari State University, Lenin Square 1, Yoshkar-Ola city, 424000, Russia

² Kuban State University of Physical Culture, Sports and Tourism, Budyonny St. 161, Krasnodar city, 350015, Russia

^{3*} South Ural State Agrarian University, Gagarin street 13, Troitsk city, 457100, Russia

*Smolentsev82@mail.ru

ABSTRACT

For the first time, a comprehensive assessment of the agro ecological state of the soil and vegetation cover of agricultural land has been carried out, and critical routes of toxicants entering agricultural products have been identified. Methodological foundations have been developed and criteria for evaluating the effectiveness of technologies aimed at reducing the content of heavy metals in agricultural products have been proposed. The methodological approach to optimizing the implementation of rehabilitation measures in case of contamination of agricultural lands with heavy metals has been improved, including a comprehensive assessment of the migration parameters of heavy metals and a system of criteria for the effectiveness of rehabilitation technologies. A system for monitoring the environmental situation in the emission zone of ferrous metallurgy enterprises has been developed to assess the risk of accumulation of heavy metals in the components of agroecosystems and substantiate the need for rehabilitation measures. A comparative assessment of the impact of two metallurgical enterprises on the accumulation of heavy metals in ecosystem components is given, depending on the volume and technological features of production.

Keywords: pollution, soil, air, plant cultures, heavy metals, rehabilitation measures

INTRODUCTION

According to the Federal Service for Hydrometeorology and Environmental Monitoring, the area of soil contamination with heavy Metals in the Russian Federation is more than 18 million hectares. The most intense increase in the anthropogenic load on environmental objects, including the soil cover, is observed in the zones of impact of industrial enterprises. In this regard, the assessment of the consequences of increasing the content of chemical toxicants in the soils of natural and agricultural ecosystems is an urgent problem of ecology and environmental protection. The solution of this problem is based on monitoring the ecological state of territories, including agricultural lands, adjacent to large industrial agglomerations and developing a set of effective and economically justified rehabilitation measures (RM) that ensure the production of agricultural and food products that meet sanitary and hygienic standards [1,2].

In accordance with the Food Security Doctrine of the Russian Federation, "development of production of agricultural products, raw materials and foodstuffs that meet the established environmental, sanitary-epidemiological, veterinary and other requirements" is a priority national economic task [3,4].

Studies of domestic and foreign scientists are devoted to studying the regularities of heavy metals (HM) accumulation in agricultural crops and obtaining safe crop production in conditions of technogenic pollution. The main industrial (metallurgy, chemistry, power engineering, etc.) and agricultural (mineral fertilizers, plant protection products, animal husbandry complexes) sources of HM entering the soil and vegetation are identified [5,6].

A methodology and methods for assessing the environmental situation and the degree of its danger in conditions of technogenic pollution, as well as maximum permissible concentrations of HM in soils, veterinary requirements for feed and sanitary and hygienic standards for food products have been developed [7].

To identify the possible negative impact of HM on agroecosystems, an important task is to conduct monitoring of agricultural land, which provides an objective assessment of the toxic and ecological

situation, identify trends in its change and forecast, on the basis of which decisions are made to improve the environmental situation in the field of agricultural production [8].

Agrotechnical and agrochemical techniques have been developed and implemented to conduct agricultural production in technogenically polluted areas and produce crop products that meet sanitary and hygienic and veterinary requirements. The variety of ecological situations, the variability of soil parameters, the variety of cultivated crops, and the wide range of cultivation technologies used determine the need to optimize agricultural production in technologically polluted territories [9,10].

Objective: To assess the agroecological situation, substantiate and optimize rehabilitation measures that ensure the production of safe agricultural products in the territories adjacent to ferrous metallurgy enterprises.

MATERIALS AND METHODS

The effect of mineral fertilizer systems on HM accumulation in soil and plants was studied in the field in the form of 5 blocks: 1) control (without fertilizers); 2) variants of nitrogen fertilizer doses from 0 to 150 kg / ha at a constant background of $P_{60}K_{60}$; 3) phosphorous fertilizer doses from 0 to 120 kg/ha at a constant background of $N_{90}K_{60}$; 4) дозы potash fertilizer doses from 0 to 150 kg / ha at a constant background of $N_{90}K_{60}$; 5) application of mineral fertilizers and lime $N_{90}P_{60}K_{60} + CaCO_3$. The total number of options is 17, and the experience is repeated 4 times. Soil and plant sampling was carried out according to generally accepted methods. To identify the sources of HM input and the degree of their impact on environmental components, an agroecological monitoring network was created at different distances and directions (8 points each) from the emission flare. Snow cover, soil, and vegetation samples were taken in increments of up to 5 km. Total pollution coefficients, technogenic concentration coefficients, and dust load coefficients were calculated (GOST 17.4.3.01-2017, methodological recommendations for assessing the degree of pollution, 1990, 1995, and 2003). Background samples were taken taking into account the seasonality of the wind rose at a distance of 23 and 33 km from the source of pollution in the southern and western directions. The total content and mobile forms of HM in soil samples, plants, mineral fertilizers, snow cover, and dust precipitation were determined using the method of atomic emission spectrometry in inductively coupled plasma (ICP-OES, Hitachi-308). To determine the mobile forms of HM in the soil, an ammonium acetate buffer solution with a pH of 4.8 is used. The samples were decomposed using the MS-10 microwave sample preparation system (HDPE F 16.1:2.3:3.11-98, RD 52.18.289-2022, RD 52.19.191-2019). **определения содержания ТМ в минеральных удобрениях** Laboratory tests of 119 samples of various types and forms of fertilizers were carried out to determine the HM content in mineral fertilizers.

RESULTS AND DISCUSSION

Based on our own data and generalization of literature sources, it is shown that the content of HM in fertilizers depends on a complex of factors: the quality of incoming raw materials, the technology of its processing, the purity of the chemical reagents used, etc. At the same time, the level of HM in fertilizers from domestic raw materials is significantly lower than from raw materials from foreign deposits (China, the USA, Australia, Western Europe and the Middle East). The analysis showed that the most polluted HMS are phosphorous and complex fertilizers. On average, they contain Cd 10 times more Cd and Pb almost 20 times more Pb than nitrogen ones. The as content in these fertilizers is twice as high as in potash fertilizers. Together with the Tula Research Institute of Agricultural Research, it was established in long-term field experiments that the systematic use of unbalanced doses of mineral fertilizers or their complete absence has a significant impact on the balance of nutrients and agrochemical indicators of leached chernozem. Acidification of the soil solution was observed in most variants, and to the greatest extent in variants with unbalanced use of nitrogen-phosphorus and nitrogen - potassium fertilizers. The introduction of limestone flour into the soil (up to 7 t / ha) led to a neutralization of acidity and an increase in the pH of the soil solution by 0.4 units.

The highest yield (3.4 t/ha) was obtained when applying nitrogen fertilizers at a dose of $N_{90}P_{60}K_{60}$, and the lowest (2.5 t/ha) - when applying fertilizers without a nitrogen component ($P_{60}K_{60}$). Applying different doses of phosphorous fertilizers on a single background $N_{90}K_{60}$ leads to an increase in the yield

of spring wheat to 3.3 t / ha compared to the control of 2.4 t / ha. In the variants without potash fertilizers, the yield decreased below the control values. Unbalanced application of high doses of nitrogen and potash fertilizers increases the mobility of Pb and Cd in the soil-plant system (Table 1).

Table 1: Effect of agrochemical measures on накопление HM accumulation in spring wheat grain

No.	option	Pb		Cd		Cu	
		mg/kg	KN*	mg/kg	KN	mg/kg	KN
1	Control	0,35±0,06	0,04	0,09±0,01	1,12	5,75±0,17	0,34
2	P ₆₀ K ₆₀	0,33±0,07	0,04	0,10±0,02	1,11	5,64±0,01	0,33
3	N ₆₀ P ₆₀ K ₆₀	0,42±0,06	0,04	0,12±0,01	1,33	OF 5.13±0,19	0,30
4	N ₉₀ P ₆₀ K ₆₀	0,45±0,07	0,06	0,11±0,01	1,22	OF 5.84±0,10	0,34
5	N ₁₂₀ P ₆₀ K ₆₀	0,48±0,06	0,06	0,14±0,01	1,56	4,75±0,20	0,29
6	N ₁₅₀ P ₆₀ K ₆₀	0,54±0,06	0,05	0,15±0,01	1,40	OF 5.28±0,20	0,33
7	N ₉₀ K ₆₀	0,56±0,22	0,06	0,18±0,04	1,80	OF 5.37±0,23	0,32
8	N ₉₀ P ₃₀ K ₆₀	0,45±0,17	0,05	0,14±0,02	1,27	4,16±0,21	0,26
9	N ₉₀ P ₉₀ K ₆₀	0,33±0,18	0,04	0,14±0,02	1,40	4,41±0,17	0,28
10	N ₉₀ P ₁₂₀ K ₆₀	0,38±0,14	0,04	0,12±0,02	1,10	3,65±0,19	0,22
11	N ₉₀ P ₆₀	0,39±0,05	0,04	0,14±0,03	1,40	OF 4.04±0,17	0,29
12	N ₉₀ P ₆₀ K ₃₀	0,36±0,04	0,04	0,10±0,01	0,91	OF 5.37±0,22	0,34
13	N ₉₀ P ₆₀ K ₆₀	0,44±0,03	0,06	0,13±0,02	1,18	4,93±0,19	0,28
14	N ₉₀ P ₆₀ K ₉₀	0,47±0,04	0,06	0,12±0,01	1,20	OF 5.06±0,30	0,33
15	N ₉₀ P ₆₀ K ₁₅₀	0,46±0,02	0,06	0,15±0,01	1,50	A 4.53±0,25	0,30
16	N ₉₀ P ₆₀ K ₆₀ + CaCO ₃	0,33±0,03	0,04	0,09±0,01	0,90	3,47±0,29	0,20
SanPiN 2.3.2.1078-01		0,5		0,1		-	

* KN - accumulation coefficient

Long-term application of various doses and combinations of domestic mineral fertilizers for 20 years did not significantly affect the change in the HM content in the arable layer of chernozem soils. For grain crops **пшче** Cd, it takes 660 and 250 years to increase the content of Cd and As in the soil by 0.1 mg/kg, and Pb, Zn, Co, Ni, Cu by 1 mg/kgNi, Cu.- 285, 47, 740, 115, 130 years, respectively. When applying imported fertilizers with high levels of HM content, their accumulation in the soil can increase by an order of magnitude.

As a result of the research, 9 chemical pollutants (Fe, Cr, Zn, Mn, Ni, Co, Pb, Cu, Cd) were identified, the accumulation of which in the snow cover and soil of the surveyed territories of the location of metallurgical enterprises exceeds the background indicators. The range of elements is typical for the production of ferrous metals with the production of alloy steel. The main amount of TM is contained in solid form (metal shavings). The water-soluble fraction of HM in the snow cover is found in concentrations not higher than: Cr 0.0035; Zn 0.089; Mn 0.023; Ni 0.005; Co 0.002; Pb 0.035; Cu 0.005 and Cd 0.0005 mg/l. The HM content in solid snow cover sediment in the area of NLMK's emissions reaches Cr14 mg/kg for Cr 384, Zn 3084, Mn 3550, Ni 92, Co 6, Pb 255, Cu 71, and Cd, and is up to 20 times higher than similar indicators for NLMK-Kaluga LLC.

The maximum concentrations of pollutants and the dust load on the snow cover in the area of NLMK's location are observed in the near zone at a distance of 4-6 km from the sources of pollution in the south-east direction and exceeded the background values by up to 16 times.

As the distance from the source of contamination increases to 12 km, the dust load decreases to an average and then its low degree is recorded. In the area where NLMK is located, the maximum concentrations of HM and relatively high dust loads on the snow cover are observed in the near zone at a distance of up to 3 km from the source of contamination.

The coefficient of Cs in the snow cover indicates that dust and its components are a significant source of snow cover pollution and shows significant background exceedances in the 30 km zone of

industrial enterprises' impact.

At all sampling sites in the NLMK impact zone, the Zc of snow (up to 32) and soil (up to 13) is in the range of low values (up to 64), while in the NLMK zone, the Zc reaches 97 in the snow and 107 in the soil cover, which corresponds to the average degree of snow contamination. pokrova (64-128).

The concentration of cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and anions (SO_4^{2-} , NO_3^- , NO_2^- , NH_4^+ , Cl^-) in meltwater in the near zone of NLMK PJSC is higher (up to 10 times) than the corresponding values of the area of its location "NLMK-Kaluga", but does not exceed the maximum permissible values established for drinking water (SanPiN 1.2.3685-21). At the same time, in some cases the maximum permissible concentration for NO_2^- , NH_4^+ up to 3 times, Cu up to 5 times, and Zn up to 9 times are exceeded for water bodies of fisheries importance in the NLMK impact zone Zn (Order of the Ministry of Agriculture of the Russian Federation No. 552 of 2016).

Differences in the degree of pollutant formation are explained by the technologies used: NLMK Kaluga operates electric arc steelmaking furnaces for steel production, while NLMK PJSC operates blast furnaces with higher atmospheric emissions. In addition, NLMK-Kaluga LLC uses ferrous scrap, while NLMK PJSC uses ore. NLMK's production capacity (9.9 million tons of steel) is approximately 6 times higher than the design capacity of NLMK-Kaluga LLC (1.5 million tons of steel). Even with this adjustment, electric arc steel production using ferrous scrap is more environmentally efficient than steel production using blast furnaces and ore as raw materials. The real and hypothetical situation of contamination of agricultural land on the territory of an enterprise located in the zone of impact of NLMK's emissions is considered.

In a real-world situation, when information about a salvo aerosol release is received in the study area, it is recommended to change the harvesting time by 1-2 weeks as a protective measure. Given the relatively higher levels of air pollution in crops up to 10 km away from the source of emissions, it is recommended to place crops that are economically valuable in the soil (roots and tubers). Areas that are farthest from the source of pollutant emissions are selected for forage areas.

The developed database and DSS were used to predict the environmental situation and justify rehabilitation technologies on the territory of the agricultural enterprise LLC "Russia" in the case of a hypothetical situation of exceeding the HM content in leached medium-loamy and heavy-loamy chernozem soils. Based on the environmental, agronomic and economic efficiency of the Republic of Moldova, the most effective agrochemical measures were selected. For wheat production under conditions of Zn contamination, the use of mineral fertilizers ($\text{N}_{60}\text{P}_{60}\text{K}_{60}$) together with organic fertilizers (manure 30 t/ha) is effective. In case of Cr contamination, the use of mineral fertilizers in doses of $\text{N}_{90}\text{P}_{90}\text{K}_{90}$ is recommended, and Ni - the use of organic fertilizers (30 t/ha of manure) and mineral fertilizers in doses of $\text{N}_{60}\text{P}_{80}\text{K}_{80}$. When Cd and Pb are contaminated, the use of mineral fertilizers $\text{N}_{60}\text{P}_{60}\text{K}_{60}$ is effective (Table 2). Agrochemical measures provide a reduction in the accumulation of HM up to 1.5 times, an increase in yield up to 1.5 times, and profitability up to 55% if the products comply with sanitary and hygienic standards.

Table 2: Possible ecological and economic efficiency of the Republic of Moldova in the production of spring wheat

TM	N, kg/ha	P_2O_5 , kg/ha	K_2O , kg/ha	SaSO_3 , t /ha	Manure, t/ha	Increased Yield increase, times	Costs thousand. rubles/ha	Profitability,%	
								Acc. SanPiN	Not acc. SanPiN
Zn	90	90	90	-	-	1,3	14,3	11	-59
	120	120	120	-	-	1,3	19,0	-11	-64
	60	60	60	-	30	1,5	9,7	55	-48
	30	30	30	6	-	1,2	13,9	7	-60
	-	-	-	-	30	1,2	6,2	15	-35
Cr	60	60	60	-	-	1,2	9,7	55	-48
	90	90	90	-	-	1,3	14,3	11	-49
	90	90	120	-	-	1,3	15,7	3	-61
Ni	60	60	40	-	-	1,3	8,7	70	-45
	60	60	60	-	-	1,3	9,7	55	-48

	60	80	80	-	-	1,2	11,8	31	-54
	120	120	120	-	-	1,2	19,0	-11	-64
	-	-	-	-	30	1,2	6,2	15	-35
Cd	60	60	60	-	-	1,3	9,7	55	-48
	60	80	80	-	-	1,3	11,8	31	-54
	120	120	120	-	-	1,3	19,0	-11	-64
	-	-	-	-	30	1,2	6,2	15	-35
Pb	60	60	60	-	-	1,3	9,7	55	-48
	60	80	80	-	-	1,2	11,8	31	-64
	120	120	120			1,3	19,0	-11	-64
	-	-	-	-	30	1,2	6,2	15	-35

When cultivating potatoes, it is recommended to apply mineral fertilizers in doses of $N_{30}P_{30}K_{45}$ and manure 20 t / ha, as the main fertilizer. This combination of fertilizers reduces the Ni content by an average of 1.6 times, with an increase in yield up to 1.4 times and an increase in profitability by 23%, provided that products meet the standards are obtained. The introduction of organic fertilizers in a larger volume (manure of 30 t/ha or more) does not lead to any significant environmental and economic effects. In case of soil contamination with Zn, the most effective application of manure (30 t/ ha), the multiplicity of reducing the Zn content in potatoes in this case will be 1.2, productivity increases up to 1.3 times, profitability will be 89% if the established standards are met and 16% if they are not met.

Thus, a system of justification of optimal rehabilitation technologies in crop production in areas contaminated with HM has been developed. This toolkit (DB, DSS) provides support for decision-making by management bodies of economic entities to ensure the production of products that meet sanitary and hygienic standards. For a specific agricultural enterprise located in the area of NLMK's emissions impact, the composition, scope of implementation of measures and necessary costs are determined. The DSS allows automatic ranking of rehabilitation measures based on their effectiveness and justifying technologies, taking into account the level of HM contamination, agrochemical characteristics of the soil and the type of product.

CONCLUSION

Studies have shown that the accumulation of HM in agricultural products, soil and environmental components, depending on the source of pollution, is determined by a complex of factors. At the same time, the amount of HMS entering the soil with mineral fertilizers is determined by the time, types and doses of fertilizer application, and their long-term use has a significant impact on the balance of nutrients, agrochemical properties of soils and biological mobility of HMS. In the areas of impact of metallurgical plants, the intensity of snow and soil-plant cover pollution depends on the amount of emissions, production capacity, technologies used, direction and distance from sources of pollution, weather conditions and the nature of the underlying surface. The established regularities make it necessary to conduct agroecological monitoring in areas where industrial enterprises are located and land with a high technogenic load, providing an objective assessment of the toxic and ecological situation, identifying trends in its change and making a forecast of the agroecological situation in the field of agricultural production.

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