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GEOECOLOGY

Monitoring of Chrome and Nickel Contents in Agroecosystems of the Central Chernozem Region of Russia

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Abstract—This study was performed under the state agroecological monitoring program. The purpose of this work is to conduct an environmental assessment of the contents of chromium and nickel in the agroecosystems of the southwestern part of the Central Chernozem region (CChR) from the example of Belgorod oblast. All analytical studies were carried out in the accredited testing laboratory by generally accepted methods. During this study, it was established that the average total Cr and Ni contents in the arable layer in leached chernozems are 19.8 and 24.5; in typical chernozems, 20.0 and 24.9; and in ordinary chernozems, 20.9 and 26.6 mg/kg, respectively. The average contents of mobile forms of chromium and nickel in the studied soils range within 0.13–0.14 and 0.37–0.41 mg/kg, respectively. The levels of the approximate permissible concentration of nickel and the maximum permissible concentration of mobile forms of these heavy metals in soils are not exceeded. In the agroecosystems of Belgorod oblast, Cr and Ni are mainly supplied with organic fertilizers, but this does not pose a risk for soil contamination and crop products. The highest average chromium content (0.45 mg/kg) is observed in sunflower seeds, and the lowest (0.22 mg/kg) is in corn grain. Soybeans are characterized by an anomalously high nickel content (4.81 mg/kg), and the lowest concentration (0.63 mg/kg) is recorded in corn kernels.

Keywords: clarke, soil, crops, agricultural crops, chernozem, fertilizers, heavy metals, background monitoring

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INTRODUCTION

As the industry develops, the anthropogenic impact on all components of the biosphere increases; in particular, there is a significant increase in the probability of soil contamination with heavy metals (HMs). Chrome and nickel are the HMs that are among the most abundant in nature and are widely used in industry (especially in metallurgy). According to the Russian standards, Cr and Ni are included in class 2 of toxic substances (moderately hazardous substances) [1]. The main anthropogenic sources of Cr and Ni input into the environment are the enterprises of non-ferrous and ferrous metallurgy, engineering, and the fuel-and-energy complex. Soil pollution of agroecosystems, especially near megacities, may occur when sewage sludge is used as organic fertilizers without a control.

The clarke values of these elements (average total content) in soils, established by different authors and in different years, sometimes differ considerably. For example, according to the results of the research conducted in the 1950s [2], the clarke values of Cr and Ni are 200 and 40, and according to the more recent data [3], they are 59.5 and 29.0 mg/kg, respectively.

Cr and Ni perform various physiological functions in plants; however, their role has not yet been studied in full. In particular, the minimum contents of mobile forms of Cr and Ni in soils at which the agricultural yield is limited have not been established. For example, for trace elements such as Zn, Cu, Co, Mn, and Mo, the low levels of soil provision at which it is expedient to use micronutrients are regulated by agrochemical standards [4].

The high concentrations of Cr and Ni in soils may negatively affect plant development. Therefore, their contents in soils are regulated in many countries of the world [5, 6]. In Russia, the levels of approximate permissible concentrations (APCs) are established for regulation of the total Ni content in soils, depending on their particle-size composition and acidity. For example, for heavy loamy soils with pH_{KCl} < 5.5, the

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APC of Ni is 40, and for soils with pH of salt extract (pH_{KCl}), it is greater than 5.5–80 mg/kg. The phytotoxicity of Cr depends on its oxidation state. Cr^{6+} is the most toxic, and the maximum permissible concentration (MPC) of 0.05 mg/kg is established for its content in Russian soils. The total content of Cr^{3+} is not regulated in Russia [7]. However, for example, in Germany, the MPC of Cr^{3+} in soils is specified at the level of 100 mg/kg [8]. For the contents of mobile forms of Ni and Cr^{3+}, extracted by an ammonium acetate buffer solution with pH 4.8, the MPCs are fixed at 4 and 6 mg/kg, respectively [7].

Taking into account the high potential hazard of pollution of agroecosystems with Cr and Ni, the agrochemical service of Russia monitors the contents of these toxicants in fertilizers, soils, and agricultural plants.

The aim of our studies is to conduct an environmental assessment of the Cr and Ni contents in the agroecosystems of the southwestern part of Central Chernozem region (CChR) by the example of Belgorod oblast.

PROCEDURE OF STUDIES

The studies were conducted in the southwestern part of the Central Chernozem region (CChR) of Russia on the territory of Belgorod oblast. The soil cover of the forest–steppe zone of the area is dominated by typical (44.8% of the total land area under plow) and leached (25.7%) chernozems, while in the steppe zone, ordinary chernozems (13.0%) are dominant. Selyaninov's hydrothermal coefficient (HTC) varies from 0.9 in the southeastern part of the steppe zone of this area to 1.2 in the western part of the forest–steppe zone.

Background monitoring was performed at the Yamskaya steppe site of Belogorye Nature Reserve, located in the forest–steppe zone, and on the territory of the Rovenskii nature park in the steppe zone. In the upper part of the humus-accumulative horizon of virgin leached chernozem, the contents of physical clay (particles less than 0.01 mm in size), C_{org}, and the pH of water extract (pH_{H_2O}) were 56.4, 5.63, and 6.3%; for typical chernozem 57.3, 5.86, and 7.0%; and for ordinary chernozem, 67.0, 3.77, and 7.1%, respectively.

In this work, we use the materials obtained during local agroecological monitoring performed by the agrochemical service of Russia in 2016–2023. To carry out this type of monitoring on plowed soils of the oblast, reference objects (plots of land with an area of 4–40 ha) were delineated outside the zone of influence of industrial emissions, from which soil and plant products are sampled annually for chemical analysis. The average contents of physical clay in the arable layer (0–25 cm) of leached chernozems and typical reference objects in the forest–steppe zone were 56.2 and 56.8%; C_{org}, 3.13 and 3.25%; and pH_{H_2O}, 6.3 and 6.7, respectively. The products for chemical analysis were sampled on these reference objects. The average yield was 7.0 for corn kernels, 2.2 for soybeans, and 3.0 t/ha for sunflower seeds. The arable layer of the reference objects in the steppe zone contained 72.5% of physical clay, 3.02% of C_{org}, and pH_{H_2O} 7.8.

All analytical studies were carried out in an accredited testing laboratory. The total content (extractant 5 M HNO_3) and concentration of mobile forms of Ni and Cr^{3+} extracted by the ammonium acetate buffer (AAB) solution with pH 4.8 in soil were determined by the method of atomic emission spectrometry. The total content of these HMs in the plant products was calculated using the atomic absorption method by the standard procedures in the agrochemical service [9].

RESULTS AND DISCUSSION

Chromium and nickel in soils. The background total contents of Cr and Ni were 19.8 and 25.4 in virgin leached chernozem; 19.9 and 23.3 in typical chernozem; and 20.3 and 27.0 mg/kg in ordinary chernozem, respectively.

The average total contents of Cr and Ni were 19.8 and 24.5 in arable leached chernozems, 20.0 and 24.9 in typical chernozems, and 20.9 and 26.6 mg/kg in ordinary chernozems, respectively (Fig. 1). The total content of Ni in ordinary chernozems was significantly higher than in typical and leached chernozems. At the same time, no significant differences were established in the content of Cr; however, there was a tendency toward a higher concentration of this element in ordinary chernozems compared to leached and typical chernozems. The differences in the contents of the studied HMs between the leached and typical chernozems of the forest–steppe zone and ordinary chernozems of the steppe zone are largely determined by the heavier particle- size composition of the latter.

The total contents of Cr and Ni in the arable layer (with a mass of 3000 t/ha) are, on average, 59.4 and 73.5 kg/ha in alkaline chernozems, 60.0 and 74.7 kg/ha in typical chernozems, and 62.7 and 79.8 kg/ha in ordinary chernozems, respectively.

The levels of total contents of the studied elements that we established correspond in general to the results of the studies conducted in other regions of Russia. The total content of Cr in leached chernozems of Krasnoyarsk krai is 25.7 mg/kg, on average, with variations within 19.8–33.4 mg/kg, while the content of Ni varies within 5.0–64.8 and is 25.6 mg/kg, on average [8, 10]. In Tambov oblast, the total Ni content in heavy clayey and clayey leached chernozems ranges within 20–40 mg/kg [11]. In Saratov oblast, the average total content of this metal is 18.0 mg/kg in chernozem soils [12].

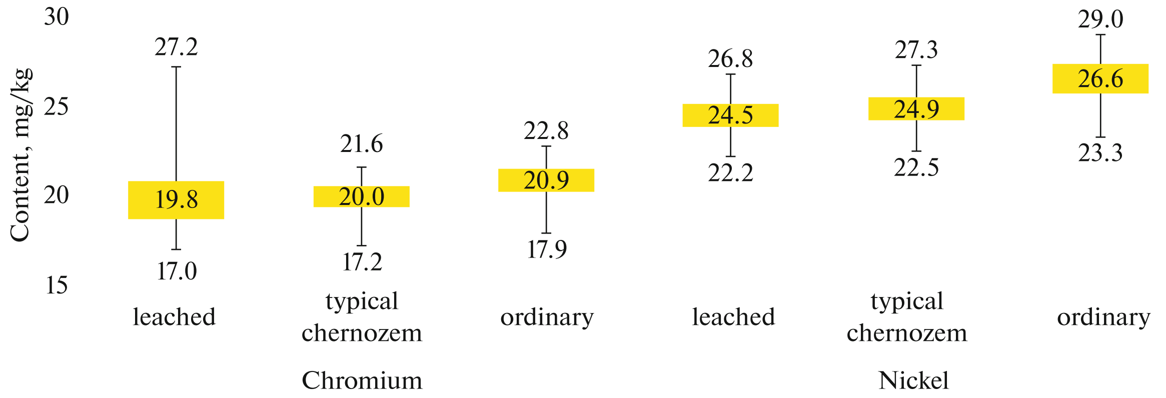

Fig. 1. Total contents of Cr and Ni in plowed soils (n = 20), mg/kg.

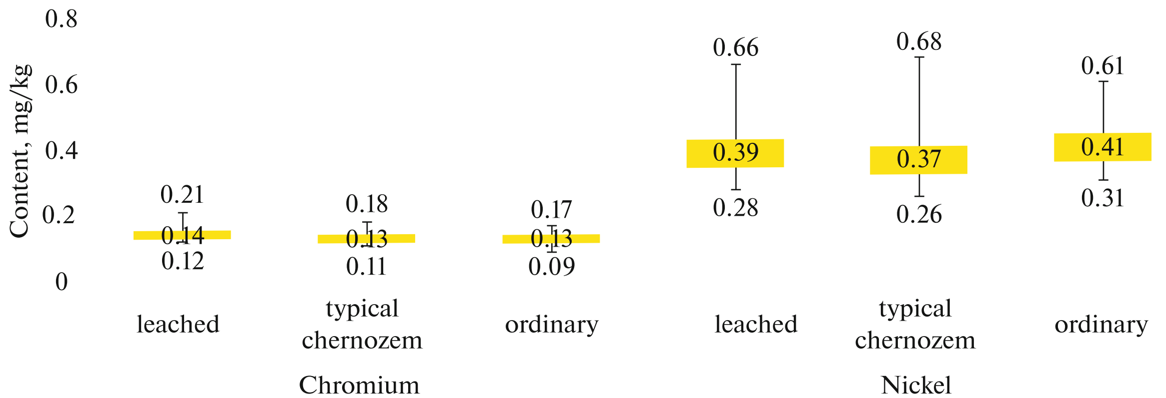

Fig. 2. Contents of mobile forms of Cr and Ni in plowed soils (n = 20), mg/kg.

The background contents of mobile Cr and Ni forms were 0.14 and 0.58 in virgin leached chernozem, 0.15 and 0.53 in typical chernozem, and 0.16 and 0.54 mg/kg in ordinary chernozem, respectively. These values were found within the range of these indicators established for plowed counterparts of virgin soils.

In plowed leached chernozems, the average contents of mobile Cr and Ni forms were 0.14 and 0.39; in typical chernozems, 0.13 and 0.37; and in ordinary chernozems, 0.13 and 0.41 mg/kg, respectively. No significant differences in these parameters were revealed between the studied soils. In plowed soils, 0.62–0.71 and 1.49–1.59% of the total amount, respectively, were present in the mobile Cr and Ni forms. The Russian levels of APC and MPC for the studied elements in soils were not exceeded.

The average contents of mobile Cr forms are 0.7 mg/kg and 0.2 mg/kg in plowed soils of Saratov oblast and Krasnoyarsk krai, respectively [12]. In plowed soils of Russia, the average content of mobile forms of this element is 0.58 mg/kg with variability in the range of 0.02–4.03 mg/kg [13]. In the chernozems of Krasnoyarsk krai, the content of mobile Ni forms ranges within 0.5–2.5 mg/kg (0.6–2.2% of the total amount), while in the chernozems of Tambov oblast, it is 1.0–2.0 mg/kg [11, 12].

Chrome and nickel in fertilizers. With respect to the chemical composition and applied doses, mineral fertilizers in Russia are not considered to be an important source of input of these HMs into the soil of agroecosystems. Monitoring the quality of mineral fertilizers performed in Belgorod oblast showed that the average content of Cr and Ni in the most common of them is the following: 1.13 and 0.31 mg/kg in ammonia nitrate and 1.32 and 0.89 mg/kg in azophoska (16 : 16 : 16), respectively. In the years 2019–2022, the average dose of application of mineral fertilizers in Belgorod oblast was 114.4 kg of active substance/ha, and nitrogen, phosphorus, and potassium were introduced in the amounts of 64.8, 17.3, and 17.9% of the total content, respectively. According to our calculations, approximately 0.36 g/ha of Cr and 0.16 g/ha of Ni will be added to the soil with this dose of mineral fertilizers.

The concentrations of chemical elements and their ratios in organic fertilizers vary strongly depending on the type of animals, feeding, amount of litter, and housing technology. Technological methods of

Table 1. Contents of Cr and Ni in organic fertilizers, mg/kg

Variation–statistical indicators	Manure stocks (2.22% of dry substance)	Straw–manure compost (56% of dry substance)	Manure of large cattle (25% of dry substance)
		Cr	
n	24	20	20
lim	0.14–0.32	0.31–0.79	0.56–1.25
$\bar{x} \pm t_{05}s\bar{x}$	0.20 ± 0.03	0.55 ± 0.07	0.90 ± 0.14
V, %	16.2	27.6	28.1
		Ni	
n	20	25	20
lim	0.19–0.36	1.59–4.00	0.30–0.70
$\bar{x} \pm t_{05}s\bar{x}$	0.28 ± 0.02	2.35 ± 0.25	0.51 ± 0.07
V, %	16.2	22.1	29.7

removal and storage of organic fertilizers exert a significant influence on this parameter. For example, the application of organic fertilizers in different amounts, such as 47.6 t/ha of manure stocks, 13.2 t/ha of large cattle manure, and 3.3 t/ha of straw-manure compost adds 100 kg/ha of nitrogen to the soil. Together with these amounts of organic fertilizers, 9.52, 11.9, and 1.80 g/ha of Cr and 13.3, 6.73, and 7.76 g/ha of Ni, respectively, will be supplied to the soil. Thus, when the same dose of nitrogen is applied with organic fertilizers, the highest amount of Cr will be supplied to the agrocenoses with large cattle manure and the highest amount of Ni will be delivered with manure stocks. The least amount of Cr will go with straw–manure compost, and the least amount of Ni, with large cattle manure (Table 1).

The average application rate of organic fertilizers in Belgorod oblast was 9.6 t/ha. The input of Cr is estimated at 8.64, and Ni, 4.9 g/ha. In general, the level of organic fertilizer use is low (1.5 t/ha) in Russian agriculture and, correspondingly, the input of Cr (1.35 g/ha) and Ni (0.77 g/ha) supplied with them is insignificant.

Thus, the average input of Cr and Ni into soils with organic fertilizers is higher than with mineral fertilizers by a factor of 24 and 30.6, respectively. Due to the application of organic fertilizers, without taking into account the export of elements with the crop and losses as a result of erosion, the total contents of Cr and Ni in the arable layer of the typical chernozems that are dominant in the area will increase on average by 0.014 and 0.0066% per year, respectively.

According to some estimates, 77% of Ni and 71% of Cr from their total input are supplied to the soils of Belgorod oblast with organic fertilizers. The balance of the studied elements in agriculture is negative, as the export of Ni and Cr with crop yield and losses with eroded soil exceed the total volumes of input from various sources [14].

Chromium and nickel in plants. Along with the biological characteristics of different plant species, the level of content and the ratio of mobile forms of elements in soils largely determine their chemical composition. The studied metals are countered as the so-called obligate elements that are always present in plants. Cr participates in protein synthesis and has an impact on the content of chlorophyll and photosynthesis. At a very high content of mobile Cr forms in soils, the input of macroelements (K, P) and microelements (Fe, Mn, Cu, B) into plants decreases, the aerial parts wither and chlorosis is formed in young leaves. Ni takes part in the structural organization and functioning of DNA, RNA, and protein. It stimulates the accumulation of symbiotically fixed nitrogen by legumes and constitutes the urease enzyme, which is involved in urea hydrolysis [15–17]. The role of Ni in various biochemical processes is similar to the role of Fe and Co. The toxicity of the element manifests itself in the inhibition of photosynthesis and transpiration processes, as well as in the formation of chlorosis in plant leaves [16].

According to the integrated data, the Cr and Ni concentrations that do not disturb physiological processes in plants vary in a very wide range and are at the levels of 0.1–0.5 and 0.2–10 mg/kg, respectively [8, 10, 16]. For both elements, the toxic level limits are estimated by some authors at 5–30 mg/kg [3]. The contents of Cr and Ni vary within 0.1–2.0 and 0.2–7.5 mg/kg, respectively, in agricultural crops of Novosibirsk oblast [16]. The contents of Cr and Ni are 0.54–2.67 and 0.12–2.58 mg/kg, respectively, in spring wheat grain and green mass of alfalfa in Western Transbaikal [8, 10, 18].

In Krasnoyarsk krai, the content of Cr and Ni ranges within 0.10–0.20 and 0.32–0.67 mg/kg in spring wheat grain, 0.18–0.22 and 0.34–0.70 mg/kg in barleycorn, and 0.12–0.22 and 2.19–2.38 mg/kg in oats, respectively. The Ni content in oat grain exceeds significantly the maximum permissible level, which is

Table 2. Contents of Cr and Ni in agricultural plants, mg/kg of absolutely dry substance

Variation-statistical indicators	Corn		Soybeans		Sunflower	
	by-product (straw)	main product (grain)	by-product (straw)	main product (grain)	by-product (stems)	main product (seeds)
			Cr			
n	20	20	22	22	22	22
lim	0.23–0.50	0.17–0.29	0.31–0.43	0.37–0.45	0.34–0.50	0.39–0.51
$\bar{x} \pm t_{05}s\bar{x}$	0.36 ± 0.02	0.22 ± 0.01	0.39 ± 0.03	0.41 ± 0.01	0.42 ± 0.02	0.45 ± 0.02
V, %	14.8	11.9	14.9	5.6	9.1	8.5
			Ni			
n	20	20	20	20	20	20
lim	0.32–0.57	0.20–0.78	0.45–0.93	4.53–5.29	0.39–0.79	0.75–1.00
$\bar{x} \pm t_{05}s\bar{x}$	0.36 ± 0.02	0.63 ± 0.07	0.62 ± 0.06	4.81 ± 0.11	0.64 ± 0.05	0.87 ± 0.04
V, %	14.8	26.1	18.4	4.5	18.8	9.7

explained by the physiological characteristics of this crop plant, rather than by soil pollution [8, 10].

In our work, the studied cultures significantly differed in their capabilities to accumulate Cr and Ni due to their biological characteristics. The minimum average content of Cr and Ni was established in corn kernels, 0.22 and 0.63 mg/kg, respectively. The highest content of Cr (0.45 mg/kg) was recorded in sunflower seeds, which is more than twice as high as in corn kernels. An abnormally high content of Ni (4.81 mg/kg) was found in soybeans, which is higher by a factor of 7.6 than the concentration of this element in corn kernels (Table 2). This is likely to be caused by a high concentration of the Ni-containing urease enzyme in soybeans. According to the estimates of other authors, the content of Ni in soybean grains is ≥3.0 mg/kg [19].

The Cr content in the by-products of the studied cultures either did not differ from the Cr content in the main products (soybean, sunflower) or was higher (corn). The contents of Ni in the main products of corn, soybeans, and sunflowers was by a factor of 1.75, 7.76, and 1.34 higher than in the by-products, which indicates its important role in the formation of the reproductive organs of plants.

The Russian regulations govern the contents of the studied elements only in products intended for feeding purposes. The maximum permissible levels of the Cr and Ni concentrations for fodder grains are 0.5 and 1.0 mg/kg, respectively [20]. In our studies, regardless of the varieties (hybrids) and agritechnologies used in the cultivation of agricultural crops, the Cr content was not recorded to exceed the maximum permissible levels; however, the Ni concentration in soybeans significantly exceeded this standard value. The facts we established, as well as the results of other authors' studies, evidence that the maximum permissible levels of the Ni content, which were approved as early as the last century, are not sufficiently studied.

CONCLUSIONS

In this research, it was established that the average total contents of Cr and Ni in the arable layer were 19.8 and 24.5 in leached chernozems, 20.0 and 24.9 in typical chernozems, and 20.9 and 26.6 mg/kg in ordinary chernozems, respectively. The average content of mobile forms in the studied soils was found in the range of 0.13–0.14 and 0.37–0.41 mg/kg for Cr and Ni, respectively. The levels of the approximate permissible concentration of nickel and the maximum permissible concentration of mobile forms of these heavy metals in soils were not exceeded. Cr and Ni were mainly supplied with organic fertilizers to the agroecosystems of Belgorod oblast, but this did not pose a risk for soil contamination and crop products. The highest average content of Cr (0.45 mg/kg) was observed in sunflower seeds, and the lowest (0.22 mg/kg) in corn kernels. Soybeans were characterized by an anomalously high Ni content (4.81 mg/kg), and the lowest concentration (0.63 mg/kg) was detected in corn kernels.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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