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ENVIRONMENTAL ASSESSMENT OF HEAVY METALS CONTENTIN AGROECONOSIS OF CENTRAL CHERNO-ZEMIC ZONEOF RUSSIA

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Abstract

The aim of the studies was to conduct an environmental assessment of heavy metals (Cr, Ni) content in agrocenoses of the forest-steppe zone in the southwestern part of the Central Chernozemic Zone(CCZ). It was established in the course of the research, that the average gross content of nickel in the arable layer of chernozemic soil in the leached CCZforest-steppe zone was 24.9;average content ofchromium was 21.0 mg/kg. With an increase of the soil profile depth the gross content of heavy metals did not change. The average content of nickel and chromium mobile forms in the 0-20 cm layer was 0.63 and 0.44 mg/kg, respectively. The content of nickel mobile forms in the 81-100 cm layer was lower than in the arable layer; there was no significant change in the content of chromium with the depth of the soil profile. MPC surplus for heavy metals mobile forms was not observed. The biological absorption factor for the main and by-products of the studied agricultural crops for nickel was in the range of 0.20-3.98; and 0.15-0.88 for chromium. The main sources of the studied elements entering the agrocenoses of the Belgorod region were organic fertilizers. The application rate of organic fertilizers on average for the years of 2010-2013 was 3.95 t/ha, wherein 86.5% of nickel and 81.0% of chromium were supplied to agrocenoses.

Keywords : Balance, biological absorption factor, heavy metals, nickel, chrome, plants, chernozem.

I. Introduction

`The term "Heavy Metals" (HM) is applied to elements (mostly metals) having an atomic mass of more than 40. Often the same elements are used with a different term - microelements. The microelements include chemical elements, obligatory for plant and animal organisms, the content of which is measured by values of the order of 0.01-0.00001% [XV, XVI, VI, IX, XVIII].

In modern Russian agro-chemistry, the problem of heavy metals is given a lot of attention - which is quite justified since the level of anthropogenic impact on the environment is constantly increasing. HM are among the main pollutants of agrocenoses. [XX, XIII, XIV, V, IV, VIII].

Given the high spatial variability in heavy metals distribution, the actual task remains to determine their content in the components of the biosphere in the context of specific regions, in particular the Central Chernozemic Zone (CCZ) of Russia. [XI, IX, XII].

The program of state agro-ecological monitoring is carried out by the agrochemical service of Russia. The program provides the content study of many heavy metals in soils and agricultural plants, including nickel and chromium [I, VII, X, XIII, II, XVII, III]. Chromium (Cr) and nickel (Ni) refer to biogenic elements that are permanently present in the tissues of plants and animals. These HM are referred to the elements of the second class of hazard (moderately hazardous substances). However, practically any elements with their high presence can become toxic; potentially toxic elements at very low concentrations do not have harmful effects on soils, plants and animals. [XIII].

Nickel performs a variety of physiological functions in plants, although its biochemical role has not yet been fully elucidated. It changes the activity of the urease enzyme, which catalyzes urea hydrolysis; nickel also participates in the transamination process. This element stimulates photosynthesis through entry into polar lipoids and through the improvement of the provision of plant's photosynthetic apparatus with plastid pigments. Nickel activates arginase, trypsin, a series of peptidases acting on nitrogen-containing moieties; it is also a catalyst for the oxidation of lecithin and linoleic acid. Nickel promotes the formation of a spiral structure of nucleic acids. However, the nature of the action of nickel is determined by its concentration in the nutrient environment. With an increased content of nickel in the soil, the growth of plants is suppressed and the content of chlorophyll in the leaves decreases.[XIII, IX, V, IV].

Chromium in plants participates in the synthesis of protein; it can increase the productivity of photosynthesis and the content of chlorophyll in the leaves. However, with an excessive content of this element, growth is reduced; there is a depression of plants, and at high concentrations - even their death. Warning signs of chromium toxicity are wilting plants, leaf ripening, the appearance of chlorosis, as well as the presence of yellow leaves with green veins. [XIII, IX, V, IV].

The aim of the research was to conduct an environmental assessment of the content of heavy metals (Cr, Ni) in agrocenoses of the forest-steppe zone in the southwestern part of the Central Chernozemic Zone.

II. Materials and Methods

The study was carried out in the forest-steppe zone on the territory of the Belgorod region, which is part of the CCZ. The paper is based on the materials of local agro-ecological monitoring, which was carried out at twenty reference points of the forest-steppe zone in 2010-2017. The reference area is a field space of 4-40 hectares. The soil cover of the reference sites is represented by leached chernozem. Revealed by Chirikov's method the average content of mobile forms of phosphorus in the 0-20 cm layer was 139;content of potassium averaged 119 mg/kg. The sum of the absorbed bases was 39.8 mmol/100g of soil. The content of manganese mobile forms was 15.0, boron - 1.3, zinc - 0.74, copper - 0.11, molybdenum (by the Grigg method) - 0.20 mg/kg. The content of organic matter and pH values over the layers of the soil profile are presented in Table 1.

Table 1: Changes in the content of organic matter, pHKCI and pH water over the layers of soil profile of leached chernozem reference objects

Soil layer, cm	Organic matter by Tyurin method,%	pH_{KCl}	pH_{water}
0-20	5,3	5,3	6,4
21-40	4,9	5,5	6,6
41-60	4,1	6,0	7,0
61-80	3,3	6,4	7,4
81-100	3,0	6,7	7,6

The total content of HM in the soil was determined by the method of atomic emission spectrometry in accordance with M-MVI-80-2008 method. The total content of HM in organic fertilizers was determined in accordance with GOST R 53218-2008 Standards and the "Guidelines for the determination of heavy metals in soils of agricultural lands and plant growing products" (TsINAO, Moscow 1992). To extract mobile elements from the soil, an acetammonium buffer solution with a pH of 4.8 was used. Determination of the chromium and nickel content in crop production was carried out in accordance with GOST 30692-2000. In the statistical processing of local monitoring data, the confidence interval calculations for the mean (± t05s) and the coefficient of variation (V, %) were used.

To characterize the selective absorption of chemical elements by crops, the biological absorption coefficient (CBP) was used, which was calculated as the ratio of the element content in the plant ash to its content in the arable layer of the soil.

The ash content indry matter of sunflower seeds draw up to 2.5%, stems and sunflower basket - 5.1, corn grain - 1.5, corn stalks - 7.3, soybeans -5.2, soybean – 5.6, pea beans - 3.1, pea straw - 8.0, white lupine beans - 4.2, lupine straws - 6.2, steppe grasses (Yamskaya steppe section of Belogorye Nature Reserve) - 6.4%

III. Results and Discussion

Sources of environmental contamination of chromium and its compounds are sewage sludge from tanneries, municipal sewage and metallurgical enterprises emissions. The main anthropogenic sources of nickel entering the environment are: burning of oil and gasoline, non-ferrous and ferrous metallurgy, burning of wood and waste. [XX, XIV, IV, V].

One of the main sources of HM supply to agrocenosisis organic fertilizers, which differ greatly in the content and correlation of macro- and microelements. The average nickel and chromium concentration in great cattle manure at a dry matter content of 44% is 4.87 and 4.20 mg/kg, respectively, concentration in composted straw (56% dry matter) - 3.04 and 2.75 mg/kg, sewage sludge (2.22% dry matter) - 0.172 and 0.066 mg/kg. To make 100 kg/ha with organic fertilizers, it will take about 3.3 tons of composted straw, 13.2 tons of great cattle manure or 47.6 tons of manure drains. With this amount of organic fertilizers there will be introduced into the soil, respectively: nickel - 10.0, 64.3, 8.2, chromium - 9.1, 55.4, 3.1 g/ha. The most common mineral fertilizers contain little HM. Nickel and chromium concentration in the ammonium nitrate draw up to 0.31 and 1.13 mg/kg, respectively, and innitrogen-phosphorus-potassium fertilizer azophoska- 0.89 and 1.32 mg/kg. In the CCZ, a certain amount of HM falls into the soil with a defecate (sugar factory lime), which is widely used as an ameliorant for liming acidic soils. The average nickel contentin the defecate (87% dry matter) is 8.24, chromium - 11.8 mg/kg.

During the period of 2010-2013 in the Belgorod region an average of 3.95 t/ha of organic fertilizers (in terms of great cattle manure) were introduced to the sown area, 100.4 kg ai./ha of mineral fertilizers and 0.31 t/ha of ameliorant (defecate). During this period, nickel was introduced to agrocenoses mainly with organic fertilizers - 19.2 g/ha (86.5%) and with ameliorants - 2.55 g/ha (11.5%). The intake of element with mineral fertilizers amounted to only 0.3 g/ha (1.4%), and with seeds - 0.14 g/ha (0.6%). The alienation of nickel from agrocenoses occurred mainly with washed soil - 48 g/ha (95.5%) and in a much smaller amount - 2.25 g / ha (4.5%) - with yield. In general, the balance of nickel was formed with a deficit (-28.06 g / ha).

The main source of chromium intake was also organic fertilizers - 16.6 g/ha (81%) and ameliorants - 3.66 g/ha (17.9%). The admission of metal with mineral fertilizers was observed at 0.2 g/ha (1%), with seeds - 0.04 g/ha (0.1%). 40.3 g/ha (97.8%) of the element were lost to the washed-out soil, and 0.92 g/ha (2.2%) to the alienated production. The balance again was formed with a deficit (-20.72 g/ha).[XIII, IX].

Clarkes of the chromium and nickel gross content in soils according to A.P. Vinogradov (1957) is 200 and 40 mg/kg, respectively [II]. According to modern estimates in the world's soils, chromium clarke constitute 59.5, nickel - 29 mg/kg [XIX]. The background gross content of chromium in the layer of 10-20 cm of the leached chernoze of the Yamskaya steppe section of Belogorye Nature Reservewas 22.6%, nickel - 25.4 mg/kg (Table 2).

Table 2: Chromium and nickel contents in the leached thick fat chernozem segment at Yamskaya steppe section of Belogorye Nature Reserve (mg/kg).

Horizon	Soil horizon, cm	Depth of sampling, cm	Gross content	Mobile forms content	
			Ni	Cr	Ni
A_1	7-45	10-20	25,4	0,54	0,91
AB	46-68	50-60	27,6	0,65	0,84
B	69-90	70-80	28,7	0,71	0,76
BC	91-120	100-110	28,7	0,92	0,92
C	121-165	140-150	28,5	2,05	1,83

For nickel approximate permissible concentrations (APC) for heavy loamy soils with pHKCI<5.5 make up 40 mg/kg. The maximum permissible concentration (MPC) of trivalent chromium in the soil is 100 mg/kg.

Based on the results of local monitoring, it was established that the average gross content in the plowing layer of chromium was 21.0, nickel - 24.9 mg/kg. There were no statistically significant changes in the distribution of these elements with the depth of the soil profile. The gross reserves of nickel in the arable layer of leached chernozem were 74.7, chromium - 63.0 kg/ha (Table 3).

Table 3: Variation-statistical indices of chromium and nickel content

in leached chernozem, mg/kg

Element	Factor	Soil layer, cm				
		0-20	21-40	41-60	61-80	81-100
Gross content						
Cr	$\bar{x} \pm t_{05}s_{\bar{x}}$	21,0±0,86	21,1±0,97	20,6±1,18	20,2±1,30	19,8±1,11
	lim	17,3-25,1	17,9-25,6	17,0-25,9	16,3-25,9	16,2-26,6
	V, %	8,7	9,8	12,3	13,8	12,0
Ni	$\bar{x} \pm t_{05}s$	24,9±0,79	25,0±0,79	24,6±0,91	23,6±1,02	23,2±1,25

	$\bar{x}$					
	lim	22,5-28,4	22,6-28,4	21,2-27,4	20,5-27,6	19,8-28,9
	V, %	6,8	6,7	7,9	9,3	11,6
Content of mobile forms						
Cr	$\bar{x}$ ±t_{05}s $\bar{x}$	0,44±0,02	0,42±0,01	0,41±0,02	0,41±0,02	0,42±0,02
	lim	0,37-0,50	0,35-0,46	0,34-0,45	0,35-0,46	0,35-0,47
	V, %	7,9	6,4	7,6	8,2	7,4
Ni	$\bar{x}$ ±t_{05}s $\bar{x}$	0,63±0,07	0,60±0,03	0,59±0,04	0,54±0,04	0,50±0,04
	lim	0,50-1,05	0,53-0,79	0,51-0,84	0,34-0,71	0,40-0,72
	V, %	22,2	11,4	14,2	16,1	15,3

The total content of chromium and nickel in the leached chernozem was lower than their clarkes and practically did not differ from the concentration of elements in the preserved chernozem soil. The content of the studied elements did not exceed the values of APC and MPC.

On the gross content of elements in soils of arable land it is difficult to determine their availability to plants. Therefore, for the environmental soil assessment determination of their mobile forms concentration is required.

The mobile forms of nickel background content in the layer of 10-20 cm of leached chernozem soil of Yamskaya steppe section was 0.91, chromium - 0.54 mg/kg. In preserved chernozem, the highest content of mobile forms of HM studied was observed in the parent rock (horizon C) (see Table 2). The content of the reference objects of chromium and nickel mobile forms in the arable layer of soils was 0.44 and 0.63 mg/kg, respectively, what is lower than in preserved chernozem (see Table 3). The content of chromium mobile forms from the total amount of the element in the arable layer of the soil was 2.1 and that of nickel 2.5%. The reserves of chromium mobile forms in the arable layer of the soil averaged 1.32, and nickel - 1.89 kg/ha.

With an increase in the depth of the soil profile of the leached chernozem, a tendency to decrease of the mobile forms content of chromium was observed. The content of nickel mobile forms in the 81-100 cm layer was also significantly lower than in the plow layer. One of the most significant parameters that determine the patterns of mobile element forms distribution along the soil profile is the pHKCI value of the soil solution. In the leached chernozems, there is a logical change in the course of the environment reaction with the depth of the process. At a depth of 40-60 cm (at the boundary of horizons A and B), the value of pHKCI varies from 5.5 to 6.0, which leads to a decrease in the mobility of most microelements.

For agro-ecological normalization of the nickel mobile forms content in soils, the level of maximum permissible concentration is 4, for chromium (Cr^{3+}) - 6 mg/kg. Arable soils with exceeding of these MPCs in the territory of the region have never been identified.

The elemental composition of the particular region vegetation cover is an important indicator of the environment quality. In the vegetation cover of the Belogorye Nature Reserve (Yamskaya steppe section), represented by the steppe herbage (up to 45 species per m2 with the prevalence of feather grass, fescue and prairie June grass), the nickel content was 0.66, chromium 0.37 mg/kg (Table 4).

Table 4: Variation-statistical indices of chromium and nickel content in agricultural crops and steppe grasses, mg/kg of dry matter

Crop		$\bar{x} \pm t_{05} s_{\bar{x}}$	lim	V, %
Cr				
Maize	grain	0,22±0,011	0,17-0,29	11,9
	straw	0,36±0,022	0,23-0,50	14,8
Soybean	beans	0,42±0,011	0,37-0,45	5,6
	straw	0,38±0,026	0,31-0,43	14,9
Peas	beans	0,30±0,04	0,22-0,59	30,5
	straw	0,26±0,03	0,19-0,46	24,0
White lupine	beans	0,34±0,03	0,23-0,45	20,1
	straw	0,41±0,04	0,29-0,64	21,9
Sunflower	seeds	0,46±0,016	0,39-0,51	8,5
	stems	0,42±0,016	0,34-0,50	9,1
Steppe grasses		0,37±0,014	0,34-0,45	8,2
Ni				
Maize	grain	0,63±0,07	0,20-0,78	26,1
	straw	0,36±0,02	0,32-0,57	14,8

Soybean	beans	5,15±0,34	4,53-7,22	15,2
	straw	0,70±0,11	0,34-1,45	32,8
Peas	beans	2,31±0,12	1,92-2,89	11,3
	straw	0,63±0,12	0,31-1,03	31,1
White lupine	beans	2,34±0,22	1,42-3,04	19,8
	straw	0,39±0,056	0,23-0,74	29,0
Sunflower	seeds	0,87±0,04	0,75-1,00	9,7
	stems	0,64±0,05	0,39-0,79	18,8
Steppe grasses		0,66±0,02	0,59-0,75	6,6

Legumes crops and especially soybeans revealed the highest accumulation of nickel. In the beans of this crop the content of nickel was 5.15 mg/kg, what is 8.2 times higher than in maize grain and 5.9 times higher than in sunflower seeds. The average nickel content in pea beans and white lupine was approximately the same - 2.31 and 2.34 mg/kg, respectively. The main products of maize, soybean and sunflower contained nickel more than the secondary. No significant differences in nickel content were found in pea and white lupine beans and straw. The highest content of chromium was found in sunflower seeds (0.457 mg/kg);and the lowest - in maize grains (0.216 mg/kg). In the main products of sunflower and soybeans, the chromium content was significantly higher than in the secondary, and maize had an inverse relationship. The main and secondary products of pea and white lupine were not significantly different in chromium content.

The values of the biological absorption factor (BAF) of nickel and chromium for steppe grasses were 0.41 and 0.26, respectively. The BAF of nickel by the main products of the studied agricultural crops was within the limits of 1.40-3.98, the secondary - 0.20-0.50. For the main products, the BAF of chromium was in the range of 0.38-0.88, and for the secondary production it was 0.15-0.39. Chromium can be attributed to the group of weakly accumulated elements, since the BAF value for all studied cultures was below 1. The BAF of nickel in plants was basically slightly higher than chromium (Table 5).

Table 5: The average content of chromium and nickel in plant ash and the factors of theirbiological absorption

Crop		Ni	Cr
The average content of elements in plant ash, mg/kg			
Maize	grain	42,0	14,7
	straw	4,93	4,93
Soybean	beans	99,0	8,08
	straw	12,5	6,79
Peas	beans	74,5	9,68
	straw	7,9	3,25
White lupine	beans	55,7	8,10
	straw	6,30	6,61
Sunflower	seeds	34,8	18,4
	stems	12,5	8,24
Steppe grasses		10,3	5,78
Biological absorption factor (ash, mg/kg) / (soil, mg/kg)			
Maize	grain	1,69	0,70
	straw	0,20	0,23
Soybean	beans	3,98	0,38
	straw	0,50	0,32
Peas	beans	2,99	0,46
	straw	0,32	0,15
White lupine	beans	2,24	0,39
	straw	0,25	0,31
Sunflower	seeds	1,40	0,88

	stems	0,50	0,39
Steppe grasses		0,41	0,26

In accordance with the current technical regulations of the Customs Union "On the safety of grain" (TR TS 015/2011), the content of the studied elements in soybeans, pea and lupine beans, maize grain, sunflower seeds used for food and feed purposes is not regulated. The content of HM in the by-products of crops on the average did not exceed the maximum permissible concentration levels established for coarse feeds.

IV. Conclusion

Thus, it was established that the average gross content of nickel in the arable layer of the leached forest-steppe zone chernozems of the CCZ was 24.9, chromium - 21.0 mg/kg. With increasing depth of the soil profile, the total content of HM did not change. The average content of mobile forms of nickel and chromium in the 0-20 cm layer was 0.63 and 0.44 mg/ kg, respectively. The content of mobile forms of nickel in the 81-100 cm layer was lower than in the arable layer, and the content of chromium with the depth of the soil profile did not significantly change. MPC surplus for mobile forms of HM was not observed. The biological absorption factor of nickel for the main and by-products of the studied agricultural crops was in the range 0.20-3.98, chromium 0.15-0.88. The main source of the studied elements entering the agrocenoses of the Belgorod region is organic fertilizers. On average for the years of 2010-2013 the application rate of organic fertilizers was 3.95 t/ha, and 86.5% nickel and 81.0% chromium were supplied to agrocenoses within this application.

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