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GEOECOLOGY

Monitoring of the Cadmium Content in Agroecosystems in the Central Black Earth Region of Russia

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Abstract—Under the state agroecological monitoring program, the Cd content in the main components of the forest–steppe agroecosystems in the Belgorod region located in the southwestern part of the Central Black Earth Region was studied. The soil cover was mainly composed of leached and typical chernozems. According to the study results, the average total Cd was 0.32 mg/kg in the 0- to 20-cm layer of arable leached black soil, while mobile forms were 0.08 mg/kg, corresponding to the background values and much lower than the approximate allowable concentrations. The background Cd concentrations were excessive in the soils of roadside ecosystems at a distance of up to 60 m from the roadbed. Most Cd was brought into the Belgorod agroecosystems with organic fertilizers, but it did not cause contamination of the soil or crop products. Out of the crops studied, the minimum level of Cd was in white lupine grain (0.011 mg/kg), and the maximum was in sunflower seeds (0.086 mg/kg). The average Cd contents of corn, barley, and winter wheat grains were not drastically different and ranged from 0.037 to 0.042 mg/kg. In clover and alfalfa hay, the average Cd was almost the same: 0.012–0.013 mg/kg; these values were much lower than in natural forbs (0.045 mg/kg). The maximum allowable Cd concentrations of food grains and maximum allowable Cd level of feed were not excessive in the crop products studied.

Keywords: agroecological monitoring, cadmium, roadside ecosystems, agricultural crops, heavy metals, chernozem, fertilizers

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INTRODUCTION

Among heavy metals (HMs), cadmium is one of the most toxic for living organisms and the most mobile in the soil–plant system. This element belongs to highly hazardous substances, and all its compounds are toxic. Animal and plant bodies always contain Cd, but its role and necessity for the course of biochemical processes has not yet been revealed. However, Cd phytotoxicity has been studied well: it is expressed in an inhibitory effect on photosynthesis, disruption of transpiration and carbon dioxide fixation, and inhibition of various biochemical processes. It is largely due to the fact that Cd is similar in chemical properties to Zn and can replace it in various enzymes, thereby disrupting their work [1, 2].

Cd-containing minerals do not form ore clusters, but occur as Zn companions in Zn and polymetallic ores. According to different scientists, the clarke value of the element ranges from 0.41 [2] to 0.5 mg/kg [3] in soils. Out of the soil-forming rocks, the highest Cd is typical for clays and loesses, and the lowest Cd, for sands and sandy loams [4].

The main sources of biosphere pollution with this element include nonferrous metallurgy plants, Ni–Cd battery production and disposal plants, and thermal power plants operating with the use of coal and fuel oil. Rubber and plastics combustion causes a large supply of Cd into the atmosphere [1, 2]. Soil can be polluted from the uncontrolled use of sewage sludge as a fertilizer.

Given the high toxicity and mobility of Cd compounds, the total content of this HM in soils is standardized in Europe, the United States, Canada, South Africa, Australia [5], and China [6]. In Russia, the approximate allowable concentrations (AAC) were adopted to normalize the total Cd in soils. The AAC of Cd is 1.0 mg/kg for heavy loamy soils with $pH_{KCl} < 5.5$; it is 2.0 mg/kg for soils with $pH_{KCl} > 5.5$. The AAC is

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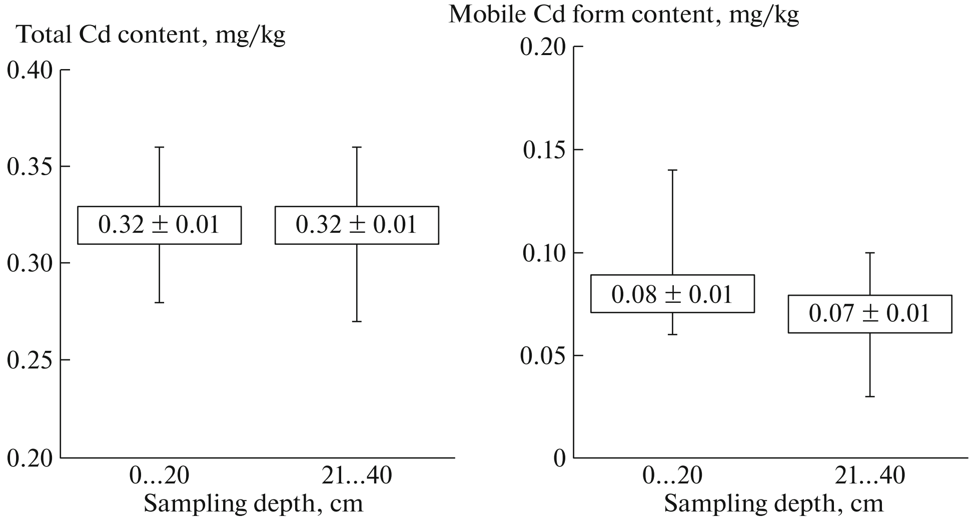

Fig. 1. Cd content in leached chernozems, mg/kg.

0.5 mg/kg for sandy and sandy loamy soils with $pH_{KCl} < 5.5$, corresponding to the clarke value of this element [7]. The maximum allowable concentration (MAC) of Cd mobile forms in soils has not been established by the Russian standards. For this reason, it is very hard to provide a correct environmental assessment of the contamination of agricultural land. Due to the fact that a large amount of this element is brought into the human body with food, its content in food products and animal feed is standardized [8, 9].

Taking into account the high toxicity of Cd, the state agroecological monitoring program provides for the determination of its content in the main agroecosystem components [10].

The objective of this study is to carry out an environmental assessment of the Cd content in arable soils, fertilizers, and crop products.

METHODS

The basic studies were carried out in the period 2016–2022 in the forest–steppe zone of Belgorod region located in the southwestern part of the Central Black Earth Region (CBER). The most common soils in this zone include leached and typical chernozems. Leached chernozem samples were taken from the background object selected: the virgin area "Yamskaya Steppe" in the Belogorye State Nature Reserve. Twenty reference plots were arranged in arable chernozems of the leached forest–steppe zone. Soil sampling was carried out in accordance with the method generally accepted in the agrochemical service [11].

In the leached arable chernozem layer of 0–20 cm, the average content of physical clay was 56.8%; organic matter, according to Tyurin, 5.6%; and pH_{KCl}, 5.3; and in the virgin soils, 56.4%, 9.7%, and 5.3, respectively. In a typical roadside chernozem (0- to 20-cm layer), the average content of physical clay was 55.2%; organic matter, 5.3%; and pH_{KCl}, 5.6.

The Cd content was determined in soil samples, crop products, and fertilizers by atomic emission spectrometry by means of the ICPE-9000 Shimadzu equipment according to the methods generally accepted in the agrochemical service [12]. To extract gross Cd from the soil, 5 M HNO_3 was used; mobile forms of this element were extracted using an ammonium acetate buffer (AAB) solution with pH 4.8. All chemical analyses were carried out in the certified testing laboratory of Belgorod Agrochemical Service Center.

RESULTS AND DISCUSSION

Cd in soils. The background total Cd is 0.33 in the upper part (10–20 cm) of the humus–accumulative horizon (A) of the leached virgin chernozem in the Yamskaya Steppe area of the Belogorye Nature Reserve, while its mobile forms reach 0.07 mg/kg (21.2% of total).

In the leached arable chernozem (0- to 20-cm layer), the average total Cd is 0.32 and its mobile forms reach 0.08 mg/kg (25% of the total). These values are almost consistent with those of the background soil. The content of this element was not drastically different in the arable soil layers of 0–20 and 21–40 cm (Fig. 1). The total Cd in the arable soil layer (weight 3000 t/ha) was estimated at 0.96 kg/ha; mobile forms, 0.24 kg/ha.

In the Lipetsk region, in podzolized and leached virgin chernozems (horizon A), the average content of mobile Cd forms was 0.06 and 0.04 mg/kg, respectively, and in arable analogs of these soils, 0.04 and 0.03–0.08 mg/kg [13]. In arable chernozems of the Saratov region, mobile Cd was 0.03–0.07 mg/kg [1].

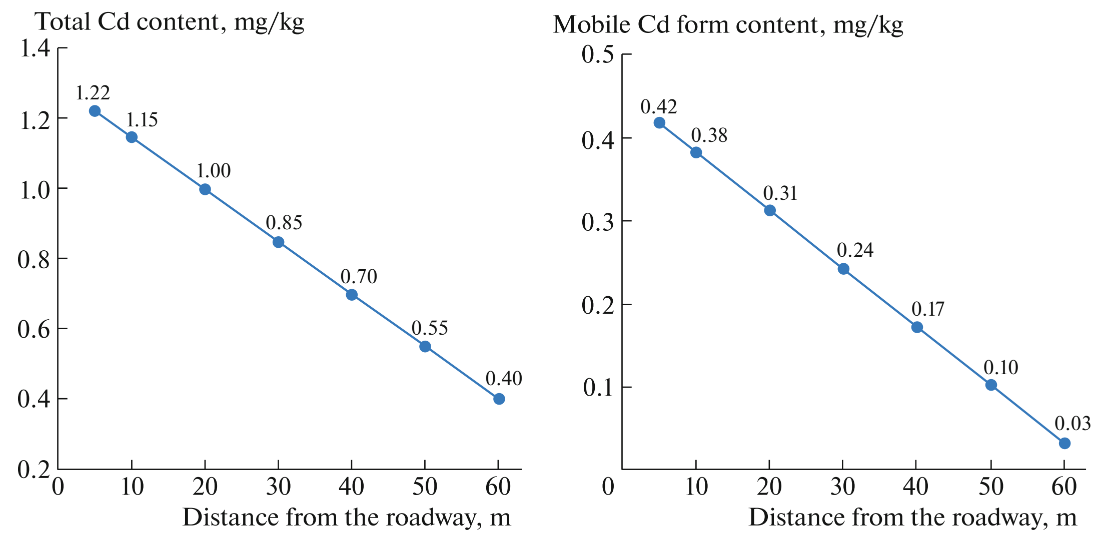

Fig. 2. Influence of the distance from the roadway on Cd content in the soil (0- to 20-cm layer) of the roadside ecosystem (M2 Crimea motorway, Belgorod region).

Numerous research results are indicative of Cd contamination of roadside ecosystems due to car tire wear [1, 14]. The main factors affecting the soil pollution level include terrain features, the vehicle traffic rate, and the duration of impact on the ecosystem. According to our research results obtained in the course of the study of the Cd content in a typical chernozem of the roadside ecosystem, the highest total Cd (1.22 mg/kg) and mobile forms (0.42 mg/kg) in the soil layer of 0–20 cm are observed at a distance of 5 m from the roadway. As the distance increases to 60 m, Cd decreases linearly to the level of uncontaminated soil (Fig. 2).

This pattern is described with high accuracy by the following mathematical models:

$$\mathrm{Cd}(\mathrm{tot.}) = -0.015x + 1.30\ (R^2 = 0.94);$$

$$\mathrm{Cd}(\mathrm{mob.}) = -0.007x + 0.45\ (R^2 = 0.91),$$

where Cd(tot.) is the total Cd content (mg/kg), Cd(mob.) is the content of mobile Cd forms (mg/kg), and x is a distance from the roadway (m).

The AAC of total Cd in soils (2 mg/kg) was not exceeded. In addition, the roadsides of federal highways, such as M2, are usually occupied by natural vegetation and forest belts, and they are not used in agricultural production.

Cd in fertilizers and ameliorants. In some foreign countries, in particular, Australia and China, Cd contained in phosphate fertilizers is a major source of soil contamination [15]. The Russian ore raw materials used for the production of phosphate fertilizers are among the highest-quality in the world and are characterized by relatively low Cd. Therefore, the use of Russian mineral fertilizers should not be considered as an important source of Cd soil contamination [4]. According to our data, the average Cd is 0.04 mg/kg in ammonium nitrate and 0.10 mg/kg in a nitrogen–phosphorus–potassium fertilizer. With the average application rates of mineral fertilizers at 88–156 kg/ha of active substance (a.s.), which was recorded in the Central Black Earth Region in 2016–2020, the Cd supply is estimated at 0.09–0.16 g/ha. According to the estimates of other authors, when applying 100–200 kg a.s./ha of mineral fertilizers, the Cd content is in the range of 0.20–0.30 g/ha [4].

Organic fertilizers make a significant contribution to the Cd supply into agrocenoses. Based on modern agricultural technologies, it is recommended to apply cattle manure and straw manure composts once every 4–5 years and manure runoff, no more than once every two years. When applying the average cattle manure of 40 t/ha, straw manure compost of 20 t/ha, and manure runoff of 70 t/ha, the Cd supply into the soil is 2.40, 2.80, and 0.56 g/ha, respectively. As a result, total Cd in the arable layer increases only by 0.25, 0.29, and 0.06% (Table 1). However, in Russia as a whole, the application level of organic fertilizer is relatively low. For example, the average fertilizer application (in terms of cattle manure) in the Central Black Earth Region ranged from 0.23 t/ha (Tambov region) to 8.83 t/ha (Belgorod region) in 2016–2020. Hence, fertilizers bring 0.01 and 0.53 g/ha Cd, respectively, into the soil.

Compared to traditional organic fertilizers, total Cd is relatively high in compost often used in reclamation of acidic soil. In the Central Black Earth Region, the average application rate of this ameliorant is 8–12 t/ha and the frequency is once every ten years. In 2016–2020, liming in the CBER region was carried out over a relatively small area, 132 000 ha/year (1.5% of the sown area), on average [16]. Therefore,

Table 1. Cd content in fertilizers and ameliorants, mg/kg

Fertilizer type	Dry matter content, %	Variation–statistical indicators			
		n	$\bar{x} \pm t_{05}s\bar{x}$	lim	*V*, %
Manure runoff	2.22	56	0.008 ± 0.001	0.004–0.012	28.7
Straw manure compost	56	30	0.14 ± 0.02	0.08–0.24	28.3
Cattle manure	25	28	0.06 ± 0.006	0.04–0.09	27.1
Compost	87	20	0.30 ± 0.02	0.21 ± 0.37	15.5

Table 2. Cd content in agricultural products, mg/kg

Agricultural crop	Product type	Water content, %	Variation–statistical indicators			
			n	$\bar{x} \pm t_{05}s\bar{x}$	lim	*V*, %
Winter wheat	Grain	14	69	0.042 ± 0.003	0.022–0.068	29.0
Barley	Grain	14	63	0.037 ± 0.003	0.020–0.060	29.6
Corn	Grain	14	73	0.039 ± 0.003	0.010–0.053	26.1
Soy	Grain	14	55	0.062 ± 0.004	0.015–0.083	25.7
Peas	Grain	14	20	0.034 ± 0.004	0.015–0.050	28.5
White lupine	Grain	14	20	0.011 ± 0.002	0.005–0.016	26.9
Sunflower	Hay	7	25	0.086 ± 0.010	0.071–0.155	29.6
Sugar beet	Root crop	75	20	0.011 ± 0.002	0.006–0.018	30.3
Corn	Silage	70	22	0.012 ± 0.002	0.007–0.019	29.0
Clover	Hay	16	20	0.012 ± 0.001	0.008–0.017	19.3
Alfalfa	Hay	16	20	0.013 ± 0.002	0.009–0.019	22.1
Yamskaya Steppe forbs	Hay	16	20	0.045 ± 0.001	0.040–0.050	5.4

Cd brought into the calcareous soils with 3.0–3.6 g/ha of compost does not pose a serious danger of contamination to the soil.

According to the data in the scientific literature, the average annual Cd losses with soil washed away as a result of erosion in the Belgorod agroecosystems are estimated at 0.61 g/ha. This value exceeds the Cd input, and, therefore, the balance of this element is negative [17].

Cd in agricultural crops. In plants, Cd is the highest in the roots and much less in the aboveground and especially generative organs. For example, the Cd content is 1.4 and 1.2 times higher in sunflower and soybean by-products, respectively, than in the main product (seeds and grains) [17].

In our studies, sunflower seeds are characterized by the highest average Cd content (0.086 mg/kg) (Table 2). No significant differences in contents of this HM were found in winter wheat, barley, and corn. On average, grains of these crops contained 0.037–0.042 mg/kg Cd, which is more than two times less than sunflower seeds. Among leguminous crops, the highest Cd was determined in soybeans (0.062 mg/kg), and its concentration was much lower in peas (0.034 mg/kg) and white lupine (0.011 mg/kg). The Cd MACs were specified at the level of 0.1 and 0.2 mg/kg for grains and sunflower seeds, respectively [8]. In our studies, MAC was not exceeded.

Perennial legumes accumulated approximately the same amount of 0.012–0.013 mg/kg Cd. In the virgin steppe forbs of the Yamskaya Steppe site, the average Cd was 0.045 mg/kg, which is more than 3.5 times higher than in legumes. Cd averaged 0.012 mg/kg in corn silage. To assess the quality of rough and succulent fodder and root crops, the maximum allowable level (MAL) of Cd was specified as 0.3 mg/kg [9]. The average Cd in sugar beet roots, corn silage, clover, and alfalfa hay was 23–27 times lower than the MAL. The regularities revealed in the Cd content were mainly due to the biological characteristics of the crops studied.

In 2016–2020, in the Belgorod region, the average yield of winter wheat was 4.89 t/ha at 3.65 of barley, 7.04 of corn, 2.89 of sunflower, 2.22 of soybean, 3.0 of perennial grass hay, and 44.8 t/ha of sugar beet [17], while Cd extraction from agroecosystems with main products of these crops was 0.21, 0.14, 0.27, 0.25, 0.14, 0.04, and 0.49 g/ha, respectively.

In the studies carried out in Central Siberia, Cd was in the range of 0.020–0.023 in spring wheat grains, 0.028–0.110 in perennial legumes hay, and 0.026–0.140 mg/kg in hay of natural lands [18]. According to the generalized data from different countries of the world, Cd was in the range of 0.02–0.07 mg/kg in wheat [2]. The average content of this element in sunflower seeds was 0.14 mg/kg [1].

CONCLUSIONS

Hence, it can be concluded that the arable chernozem layer of 0–20 cm in the leached forest–steppe zone of the Central Black Earth Region contains 0.32 mg/kg Cd, and its mobile forms reach 0.08 mg/kg. These data correspond to the background values and are much lower than the AAC. Cd is almost the same in the arable soil layers of 0–20 and 21–40 cm. The background concentrations of this element are excessive in the soils of roadside ecosystems at a distance of up to 60 m from the roadway. Most Cd is brought into the agroecosystems of the Belgorod region with organic fertilizers, which do not pose any contamination danger to soil and crop products. Out of the crops studied, Cd is minimum in white lupine grains (0.011 mg/kg) and maximum in sunflower seeds (0.086 mg/kg). The average Cd contents were not drastically different in the grains of corn, barley, and winter wheat (0.037–0.042 mg/kg). The average Cd was almost the same in clover and alfalfa hay (0.012–0.013 mg/kg) and much lower than in natural forbs (0.045 mg/kg). In the crop products studied, the Cd MAC of food grains and MAL of feed were not exceeded.

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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