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ECOLOGICAL ESTIMATION OF CADMIUM CONTENT IN AGRICULTURAL CENOSIS OF THE CENTRAL CHERNOZEM REGION OF RUSSIA

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ABSTRACT

The content of cadmium in soil is the most important parameter in terms of sanitary and hygienic conditions. Plants absorb cadmium from the soil, accumulate it in their tissues, and are thus an intermediate link in the soil–plant–animal–human chain. The aim of this research was to carry out an ecological estimation of cadmium content in agricultural cenosis of the Central Chernozem region of Russia. The cadmium content in soils, fertilizers, and crops was determined by flameless atomic absorption spectrometry. To reveal the selectivity of absorption of chemical elements by plants, we used calculations of the coefficient of biological absorption. The total content of cadmium in the arable layer of chernozem in the forest-steppe zone was 0.23 mg kg^{-1}; for the steppe zone, this value was 0.35 mg kg^{-1}. In the profile of arable chernozem, the cadmium concentration decreased with depth. The maximum concentration of cadmium was observed in sunflower seeds (0.086 mg kg^{-1}), and the minimal concentration was in clover hay (0.014 mg kg^{-1}). The minimal values of the coefficient of biological absorption (less than 1.0) were characteristic of alfalfa and clover, and maximal values were revealed for soybean seeds (10.8). The bulk of cadmium (74.0% of the total supply) enters the soil with organic fertilizers. The economic balance of cadmium in the agrocenosis of Belgorod region is negative.

KEY WORDS: Belgorod region, Cadmium, Coefficient of biological absorption, Heavy metal, Percentage abundance.

INTRODUCTION

Current environmental conditions are aggravating both globally and regionally, so humanity is forced to seek effective measures for the sustainable development of the biosphere. One of the most powerful factors affecting the sustainability of agrocenosis is the entry of heavy metals (HMs) into them (Shcherbakov and Vasenev, 1996; Kabata-Pendias, 2011; Lukin, 2016). Cadmium is the most important representative of the group of HMs, and it is considered a highly dangerous element. Cadmium content is standardized both in soil and in food products (Chimitdorzhieva *et al*., 2012; Vodyanitskii, 2012; Jaiswal *et al*., 2018).

The content of cadmium in soil is the most important parameter in terms of sanitary and hygienic conditions, as its accumulation in excess concentrations constitutes a menace to the environmental safety of agricultural products. Plants absorb cadmium from the soil, accumulate it in their tissues, and are thus an intermediate link in the soil–plant–animal–human chain (Vinogradov, 1957; Il'in, 1991, Kabata-Pendias; 2011).

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Therefore, control of cadmium accumulation in agrocenosis is an important element of the state agro-environmental monitoring program, the results of which are used to develop environmentally-friendly systems for fertilizing crops (Antropova *et al.*, 2017; Chekmarev *et al.*, 2017; Kosova and Rudakova, 2018).

The aim of this research was to carry out an ecological assessment of cadmium content in agrocenosis of the Central Chernozem regions of Russia, specifically by the example of the Belgorod region.

MATERIALS AND METHODS

This paper used data from local agro-ecological monitoring, which is conducted annually on reference sites in the Belgorod region. These sites are laid on arable soil in 20 administrative districts of the region and represent a field or a part of a field with an area of 4–40 ha. The soil cover of the reference sites is represented by leached chernozem. From the plots, 20 samples of widely distributed agricultural crops (corn, soybean, sunflower, alfalfa, sainfoin, clover) were selected and analysed.

As a part of the investigation on the geographical patterns of HM distribution, 22 profiles of typical, heavy loamy chernozem in the Central Russian forest-steppe province and 22 profiles of typical chernozem in the Central Russian steppe province were analysed. The average content of physical clay in the Ap horizon of typical chernozem was 56.8% and in ordinary chernozem it was 72.5%. The average thickness of horizons of the soil profile, the content of soil organic matter, and pH_{H2O} values are presented in Table 1.

The cadmium content in soils, fertilizers, and crops was determined by flameless atomic absorption spectrometry. To extract the mobile forms of cadmium from the soil, ammonium acetate buffer solution with a pH of 4.8 was used.

To reveal the selectivity of absorption of chemical elements by plants, we used calculations of the coefficient of biological absorption (CBA), which is the quotient of dividing the amount of elements in the ash of plants by their total content in the soil. When calculating the CBA, it was taken into account that the ash content in the absolutely dry matter of corn grain and straw was 1.5% and 7.3%, respectively; in sunflower seeds and stems it was 2.5% and 5.1%, respectively; in beans and straw of soybean it was 5.2% and 5.6%, respectively; in alfalfa, sainfoin, clover, and steppe grasses the ash content was 8.8%, 5.6%, 8.5%, and 6.4%, respectively. The CBA for the steppe motley grass was calculated taking into account the total content of HM in the typical virgin chernozem of the Yamskaya Steppe site of the Belogorie Nature Reserve. During statistical processing of the obtained test results, the values of average ($\bar{x}$), maximum and minimum (lim) element concentrations, calculations of confidence intervals for mean values ($\pm t_{05}s$), and variation coefficients (V, %) were calculated. In the balance calculations, the data of the state statistics agencies in the Belgorod region on the application of organic and mineral fertilizers, ameliorants, acreage, and gross harvest of crops for 2010–2014 were used.

Table 1. Average content of organic matter and pH_{H2O} in profiles of typical and ordinary chernozem.

Genetic horizon	Average thickness of the horizon, cm	Content of organic matter, %	pH_{H2O}
Typical chernozem			
Ap	0–25	5.6	6.7
A	26–36	5.0	6.9
AB	37–90	3.6	7.5
B_{Ca}	91–111	2.1	8.0
BC_{Ca}	112–134	1.3	8.1
C_{Ca}	> 135	1.0	8.1
Ordinary chernozem			
Ap	0–25	5.2	7.8
A	26–43	4.8	7.9
AB	44–72	4.1	7.9
B_{Ca}	73–90	2.9	8.1
BC_{Ca}	91–124	1.9	8.3
C_{Ca}	> 125	1.6	8.3

RESULTS AND DISCUSSION

Cadmium in soils

During the determination of geographic regularities of the HM distribution in soils, it was established that the Ap horizon of typical chernozem contained, on average, 0.23 mg kg^{-1} of cadmium, and the C_{Ca} horizon contained 0.14 mg kg^{-1} (Table 2). In the arable horizon of ordinary chernozem, the gross content of cadmium was 0.35 mg kg^{-1}, and in the C_{Ca} horizon it was 0.27 mg kg^{-1} (Table 3). The observed significant decrease in the gross content of cadmium with depth is due to its biophilic accumulation in the humus horizon.

Table 2. Variation and statistical indicators of cadmium content in the profile of typical chernozem, mg kg^{-1}.

Genetic horizon	$\bar{x} + t_{0.5} s \bar{x}$	lim	v, %
Gross content			
Ap	0.23 ± 0.02	0.15–0.35	22.0
A	0.21 ± 0.03	0.13–0.37	29.0
AB	0.18 ± 0.02	0.12–0.27	20.6
B_{Ca}	0.16 ± 0.02	0.08–0.29	31.3
BC_{Ca}	0.15 ± 0.02	0.09–0.25	28.5
C_{Ca}	0.14 ± 0.02	0.07–0.23	30.0
Content of mobile forms			
Ap	0.05 ± 0.01	0.02–0.07	25.9
A	0.05 ± 0.01	0.03–0.07	25.6
AB	0.04 ± 0.01	0.03–0.07	23.5
B_{Ca}	0.07 ± 0.01	0.05–0.10	18.8
BC_{Ca}	0.07 ± 0.01	0.05–0.11	21.3
C_{Ca}	0.07 ± 0.01	0.04–0.10	26.3

Table 3. Variation and statistical indicators of cadmium content in the profile of ordinary chernozem, mg kg^{-1}.

Genetic horizon	$\bar{x} + t_{0.5} s \bar{x}$	lim	v, %
Gross content			
Ap	0.35 ± 0.02	0.27–0.41	10.4
A	0.32 ± 0.02	0.26–0.40	12.0
AB	0.29 ± 0.02	0.19–0.37	16.7
B_{Ca}	0.28 ± 0.02	0.20–0.35	15.2
BC_{Ca}	0.27 ± 0.02	0.18–0.34	16.3
C_{Ca}	0.27 ± 0.02	0.17–0.35	16.3
Content of mobile forms			
Ap	0.04 ± 0.01	0.03–0.06	16.2
A	0.05 ± 0.01	0.03–0.06	20.9
AB	0.05 ± 0.01	0.03–0.07	17.9
B_{Ca}	0.05 ± 0.01	0.02–0.08	33.4
BC_{Ca}	0.06 ± 0.01	0.03–0.10	34.6
C_{Ca}	0.06 ± 0.01	0.04–0.09	27.6

The content of mobile forms of cadmium in the arable layer of typical chernozem was 0.05 mg kg^{-1} (21.7% of the total content), and in ordinary chernozem it was 0.04 mg kg^{-1} (11.4%). In the studied soils with an increase in depth, there was a slight tendency towards an increase in the content of mobile forms of the element.

In the soils of the reference plots, the concentration of gross cadmium in the arable layer was 0.32 mg kg^{-1}, and the pattern of distribution through the layers of the soil profile was similar to that discussed above. The average content of mobile forms of cadmium through the soil profile of the reference plots did not significantly change and was in the range of 0.05–0.07 mg kg^{-1}.

In general, the gross cadmium content in arable soils of the forest-steppe zone was slightly lower than in arable land in the steppe zone. The increase in the concentration of the studied element to the southeast of the region was due to the heavier granulometric composition of the soil (Sokolov and Chernikov, 1999).

Cadmium in soils not subject to pollution is contained in quantities determined by its content in the parent rock. Among the soil-forming rocks, the highest content of cadmium is typical for clays, shale, and loess, and the lowest content is typical for sands and sandy loams.

The percentage of cadmium in the soil (average total content) was 0.5 mg kg^{-1} according to Vinogradov (1957) and 0.41 mg kg^{-1} according to Kabata-Pendias (2011). The background content of cadmium in the layer of 10–20 cm of the humus-accumulative horizon of virgin typical chernozem in the protected area of the Yamskaya Steppe was 0.35 mg kg^{-1}.

The results of surveys of arable soils in the Belgorod region show that the total content of cadmium there, as a whole, was lower than the percentage abundance and was determined according to Vinogradov's method. The contents of gross forms of cadmium in typical chernozem were lower than their concentrations in the Belogorie Reserve. The trends in the distribution of cadmium through the depth of the soil profile were the same for arable soils and the soils of the Yamskaya Steppe site in the Belogorie Reserve.

The data on the total content of cadmium made it possible to calculate its total stock in the arable layer of the soil. Cadmium reserves in different subtypes of chernozem were within 690–1,050 g ha^{-1}.

The approximate permissible concentration

(APC) of cadmium in heavy loamy soils with pH_{KCl} < 5.5 is 1 mg kg^{-1}. The APC for heavy loamy soils with pH_{KCl} > 5.5 is 2 times higher and amounts to 2 mg kg^{-1} for cadmium. The permissible content of mobile forms of cadmium in Russia is not established (Chernykh *et al*., 1999). The results of the study show that the content of cadmium in arable and virgin soils does not exceed the permissible concentrations.

Cadmium in plants

The content of cadmium in crops varies broadly depending on the biological peculiarities of the species and cultivar, the concentration of the element in the soil, used chemicalization means, etc. In the main product of grain crops, the average content of cadmium was estimated at 0.12 mg kg^{-1}, and for legumes this value was 0.33 mg kg^{-1} (Il'in, 1991; Rizwan *et al*., 2016). According to the summarized data, in barley plants the content of this element was 0.02–0.38 mg kg^{-1} of dry matter, and in corn plants it was 0.04–3.90 mg kg^{-1} (Dong *et al*., 2001).

The results of our studies showed that forage perennial grasses were characterized by low concentrations of cadmium: alfalfa contained 0.016 mg kg^{-1}, sainfoin contained 0.036 mg kg^{-1}, and clover contained 0.014 mg kg^{-1} (Table 4). For comparison, in natural biocenosis cadmium was contained in the amount of 0.053 mg kg^{-1}. Among grain and oil crops, the lowest concentrations of cadmium were found in corn grain (0.042 mg kg^{-1}), and maximum concentrations were in sunflower seeds (0.086 mg kg^{-1}). The highest content of this element in byproducts was registered in soybean straw (0.083 mg kg^{-1}). As a rule, cadmium accumulates most strongly in the byproducts of crops and not in their reproductive organs, which are associated with the activity of protective mechanisms that prevent the entry of HM into these organs. An exception is the content of cadmium in sunflowers, where an inverse relationship is noted.

For the ecological and toxicological assessment of coarse and succulent feed, approved temporary maximum allowable levels were used, for forage grains we used the technical regulations of the Customs Union 015/2011 "On grain safety". For food grains, the maximum permissible levels of toxic elements are set out in SanPiN 2.3.2.1078-01 "Hygienic requirements for the safety and nutritional value of food products". According to the data of the experiments, the concentration of cadmium in perennial grasses and the main and byproducts of cereals and oil crops did not exceed acceptable levels.

Absorption of elements by plants is not always directly proportional to their content in the soil. The intensity of the absorption of elements by plants is determined by their selectivity to identify which coefficient of biological absorption is used.

Values of CBA for HMs of agricultural and wild plants vary greatly. The maximum values of CBA of cadmium reached 10.8 (sunflower seeds). The minimum cadmium CBA (0.5–0.6) was characteristic for alfalfa and clover. For wild grasses, a relatively high CBA (2.4) value was characteristic.

Economic balance of cadmium

The economic balance of cadmium in the agrocenosis of Belgorod region, which is a part of the total biological circulation of substances, was calculated by comparing the amount of an element entering the soil with fertilizers and seeds of crops with its expenditure on crop production and losses

Table 4. Variation and statistical indicators of cadmium content in crops and steppe grasses (mg kg^{-1} of absolutely dry matter) and coefficients of CBA [(mg kg^{-1} plant ash)/(mg kg^{-1} soil)].

Crop		Variation and statistical indicators			CBA
		$\bar{x} + t_{0.5}s\,\bar{x}$	lim	v, %	
Corn	grain	0.042 ± 0.006	0.016–0.054	29.4	8.8
	straw	0.059 ± 0.005	0.051–0.088	16.7	2.5
Soybean	grain	0.072 ± 0.011	0.017–0.097	33.6	10.8
	straw	0.083 ± 0.010	0.033–0.106	25.6	4.3
Sunflower	seeds	0.086 ± 0.009	0.073–0.162	21.4	4.3
	stems	0.070 ± 0.003	0.060–0.079	8.4	4.6
Alfalfa	hay	0.016 ± 0.002	0.011–0.023	22.1	0.6
Sainfoin	hay	0.036 ± 0.008	0.013–0.063	47.2	2.0
Clover	hay	0.014 ± 0.001	0.010–0.020	19.3	0.5
Steppe motley grasses	hay	0.053 ± 0.001	0.048–0.059	5.4	2.4

due to water erosion.

The main sources of soil pollution with cadmium in the European Union are emissions of zinc-cadmium (60% of the total pollution) and copper-nickel (23%) smelteries and combustion of fuel (10%) and gasoline (3%). Other sources of pollution account for 4% (Pacyna *et al*., 1984). The element can accumulate in the soil at systematic introduction of high doses of organic fertilizers (Rao *et al*., 2018). In the Belgorod region, organic fertilizers are considered to be the main source of cadmium in the agrocenosis (Lukin, 2016). In a much smaller quantity, this element is introduced with mineral fertilizers, ameliorants, and seeds of agricultural crops used in agricultural production.

Ammonium nitrate and azophoska predominate in the structure of application of mineral fertilizers in the region and among the ameliorants there are defecates. According to our data, the content of cadmium was 0.04 mg kg^{-1} in ammonium nitrate, 0.1 mg kg^{-1} in azophoska, and 0.297 mg kg^{-1} in defecates (Table 5).

Organic fertilizers used in the region differ greatly in their content and ratio of chemical elements, which is a consequence of feeding and keeping of animals as well as the removal and storage of organic fertilizers. For example, the average nitrogen content in pig manure was 0.28%, in cattle manure it was 0.72%, and in composts from bird droppings it was 2.84%. To add a nitrogen dose of 100 kg ha^{-1} with organic fertilizers, about 35.7 t ha^{-1} of manure runoff, 13.9 t ha^{-1} of cattle manure, 3.5 t ha^{-1} of straw-dropping compost will be required, and with this amount of organic matter will be applied 0.29, 1.2, 0.53 g ha^{-1} of cadmium, respectively. Thus, with the same nitrogen dose in organic fertilizers, most cadmium is introduced into the soil with cattle manure.

During 2010–2014 in the territory of the Belgorod region, an average of 4.82 t ha^{-1} of organic fertilizers (cattle manure), 97.9 kg of active substances of mineral fertilizers, and 0.39 t ha^{-1} of ameliorants were applied. With this amount of agrochemicals, 0.40, 0.017, 0.116 g ha^{-1} of cadmium entered the soil (Table 6). A small contribution to the balance was made by seeds of cultivated crops. The share of cadmium taken with seeds was only 1.5% (0.008 g ha^{-1}).

Table 6. The economic balance of cadmium in the agrocenosis of the Belgorod region for 2010–2014.

Balance sheet item		Cadmium
Uptake, g ha^{-1}	organic fertilizers	0.400
	mineral fertilizers	0.017
	ameliorants	0.116
	seeds	0.008
	total	0.54
Consumption, g ha^{-1}	carrying-out with yield	0.22
	erosion losses of soil	0.61
	total	0.83
Balance, ± g ha^{-1}	-0.29	
Balance intensity, %	65.1	

The main expenditure item of the cadmium balance is the loss with soil being washed away as a result of water erosion. According to some estimates, 3,235,000 tons of soil (1.92 t ha^{-1}) are washed off annually in the region (Lukin and Khizhnyak, 2016). Thus, the amount of eluted cadmium with soil erosion losses is 0.61 g ha^{-1}.

A certain amount of elements trapped in the soil is used by plants and is alienated from the economically valuable part of the crop. However, this element is carried out much less with crop production compared with erosion losses.

Research results demonstrated that a negative economic balance was being formed for cadmium. The magnitude of the intensity of the balance (the ratio of the income part of the balance to the expenditure expressed as a percentage) of cadmium was 65.1%.

CONCLUSIONS

1. The total content of cadmium in the arable layer

Table 5. Variation and statistical indicators of the content of heavy metals in organic fertilizers and ameliorants, mg kg^{-1}.

Organic fertilizers	$x + t_{0.5} s\, x$	lim	v, %
Manure runoff(2.22% of dry matter)	0.008 ± 0.001	0.004–0.012	35.3
Straw-dropping manure (56% of dry matter)	0.151 ± 0.026	0.071–0.249	36.7
Cattle manure(25% of dry matter)	0.084 ± 0.014	0.035–0.139	36.3
Defecate(87% of dry matter)	0.297 ± 0.022	0.213–0.374	15.5

of typical heavy loamy chernozem in the forest-steppe zone was 0.23 mg kg^{-1}, and in the ordinary light clay chernozem of the steppe zone it was 0.35 mg kg^{-1}. In the profile of arable chernozem, a regular decrease in the concentration of cadmium with depth was observed, which is associated with the biophilic accumulation of this element in the humus horizon.

2. The maximum concentrations of cadmium were found in sunflower seeds (0.086 mg kg^{-1}), and minimum concentrations (0.014 mg kg^{-1}) were found in clover. In general, concentrations of the studied element in cultivated crops were at the level of its content in the natural vegetation of the Belogorye Reserve.
3. Minimum values of the CBA for cadmium (less than 1.0) were typical for alfalfa and clover, and the maximum was for soybean grain (10.8).
4. Organic fertilizers were quite different in chemical composition. When organic fertilizers were applied in the same nitrogen dose (100 kg ha^{-1}), the least amount of cadmium entered the soil with manure runoff, and the largest amount was applied with cattle manure.
5. Organic fertilizers introduce the main amount of cadmium in the soils of the region. With them, 74.0% of cadmium gets into the soil. Taking into account the large losses of the element with the soil being washed off as a result of water erosion and slight removal with the crop, the economic balance of cadmium in the agrocenosis of Belgorod region is negative.

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