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GEOECOLOGY

Assessment of the Content of Arsenic and Mercury in the Agroecosystems of the Central Chernozem Region of Russia

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Abstract—The results of state agroecological monitoring of soils conducted in the southwestern part of the forest–steppe zone of the Central Chernozem Region are analyzed. It was found that in the Aar layer of the arable chernozem in a typical forest–steppe zone of the Central Chernozem Region, the mean total contents of As and Hg are 4.18 and 0.022 mg/kg, respectively. In the parent rock (C), the content of As is 1.38 times higher, and Hg is 2.22 times lower than in the Aar layer. Organic fertilizers are the main source of As and Hg in the agroecosystems of the Belgorod region, but this does not pose a danger to soil pollution or crop production. The highest mean As content (0.020 mg/kg) was found in winter wheat, peas, and sunflower seeds, and the lowest (0.016 mg/kg) was in corn and soybeans. The highest Hg content was found in barley (0.006 mg/kg) and winter wheat (0.007 mg/kg), while the lowest content of this element (0.002 mg/kg) was found in sainfoin hay. No evidence of exceeding the maximum allowable concentration of As and Hg in food grains and the maximum allowable level in feed products was revealed in this study.

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INTRODUCTION

Arsenic and mercury belong to the class of highly hazardous substances. Clarks of As and Hg in soils, according to A.P. Vinogradov, are 5.0 and 0.05 [1], and according to the data of A. Kabata-Pendias, 6.8 and 0.07 mg/kg [2], respectively.

As and Hg are part of the pesticides that were widely used in agriculture in the last century. Hg is a component of ethylmercuric chloride and ethylmercurophosphate, which are the most common active ingredients in many fungicides used for seed dressing. Arsenic is found in arsenic anhydride, sodium arsenate, and other compounds used in some insecticides, fungicides, and acaricides. Dumps of sulfide ores are important sources of As contamination of soils. Significant sources of these elements entering the biosphere are gas and dust emissions from various industrial enterprises, combustion of fossil fuels and municipal solid waste, and the use of sewage sludge (SS) as fertilizers [3–5].

Taking into account the high toxicity of As and Hg, their total content is standardized in the soils of many countries of the world [6, 7]. In Russia, the approximate permissible concentrations (APC) of this element have been developed to normalize the total content of As in soils, which are 2 mg/kg in sandy and sandy loamy soils, 5 mg/kg in acidic heavy loamy soils, and 10 mg/kg in neutral heavy loamy soils. To normalize the gross content of Hg in soils, the level of its maximum permissible concentration (MPC) was set equal to 2.1 mg/kg [8].

Since MPC of Hg is 42 times higher than the clarke of the element according to A.P. Vinogradov, and the APC of As in acidic heavy loamy soils corresponds to the clarke values, scientists and practitioners have many questions about the scientific validity of domestic standards [9]. The MPCs have not been developed for the content of mobile forms of As and Hg in soils; therefore, these indicators are not determined in the agroecological monitoring program.

Taking into account the high toxicity of As and Hg compounds for warm-blooded animals, their content in products intended for food purposes and in feed for farm animals is standardized [10, 11].

The goal of this work is to conduct an environmental assessment of the content of arsenic and mercury in arable soils, fertilizers, and crop products.

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Table 1. Organic matter content and pH_{H_2O} value in the soil profile of typical arable chernozem soils

Indicator	Statistical characteristics	Layer/Depth, cm					
		Aar 0–25	A 26–36	AB 37–90	Bca 91–111	BCca 112–134	Cca >135
pH_{H_2O}	$\bar{x} \pm t_{05}s\bar{x}$	6.6 ± 0.3	6.8 ± 0.3	7.5 ± 0.3	7.9 ± 0.2	8.1 ± 0.2	8.1 ± 0.2
	lim	5.8–7.9	5.9–8.1	6.2–8.1	6.4–8.5	6.9–8.5	6.7–8.5
	V, %	8.7	9.9	7.7	6.5	4.0	4.5
Content of organic matter, %	$\bar{x} \pm t_{05}s\bar{x}$	5.6 ± 0.2	5.0 ± 0.2	3.5 ± 0.2	2.1 ± 0.3	1.2 ± 0.1	0.9 ± 0.1
	lim	4.6–6.3	3.9–6.1	2.4–4.4	0.8–2.8	0.6–1.7	0.5–1.5
	V, %	7.9	11.6	13.8	25.8	23.2	29.6

METHODS OF RESEARCH

The studies were carried out in the southwestern part of the forest-steppe zone of the Central Chernozem Region (CCR) on the territory of the Belgorod region in the years 2016–2022. Typical chernozems are among the most common soils in this zone. Background monitoring was carried out at the Yamskaya steppe site of the Belogorye State Reserve, where a soil section was excavated and samples of typical virgin chernozem were taken. Twenty-two sections were laid in the watershed arable areas of the Prokhorovskii district, the soil cover of which is represented by typical chernozems.

In a typical virgin chernozem, in the 10- to 20-cm layer of the humus-accumulative layer (A), the content of organic matter (according to the Tyurin method) and the pH value of the water extract (pH_{H_2O}) are 10.1% and 7.0, while in the 121–165 cm layer of the parent rock (layer C), they are 1.1 and 8.2%, respectively. The values of these parameters for typical arable chernozems are presented in Table 1.

Sampling of soil, fertilizers, and crop products (in the phase of technological maturity) was carried out in accordance with the method generally accepted in the agrochemical service [12]. In the selected samples, the As content was determined by the photometric method and Hg was determined by the atomic absorption method according to the methods generally accepted in the agrochemical service [13]. All chemical analyses were performed in an accredited testing laboratory of the Federal State Budgetary Institution Belgorod Center of Agronomical Service.

RESULTS AND DISCUSSION

Arsenic and mercury in soils. According to background monitoring data, the total contents of As and Hg in the 10- to 20-cm depth of the humus-accumulative layer (layer A) of typical virgin chernozem are 3.12 and 0.030 mg/kg, and in the 150- to 160-cm layer of the parent rock (layer C), they are 3.65 and 0.015 mg/kg, respectively. Thus, the As concentration in the C layer is 1.17 times higher than in the A layer, while the Hg content, on the contrary, is two times lower. In layer A of the podzolized virgin chernozem of the Lipetsk region, the total contents of As and Hg are 2.7 and 0.02 mg/kg, and those in gray forest soil are 4.1 and 0.03 mg/kg, respectively [14].

In the arable layer of the typical chernozem, the mean As content is 4.18 mg/kg, and in layer C, the value of this parameter increases by a factor of 1.38 (Fig. 1). Reverse regularity is typical for the distribution of Hg along the profile of the given soil.

In the arable layer, the Hg concentration is 0.022 mg/kg, which is 2.44 times higher than in the C layer. The noted patterns are largely due to the peculiarities of the biogenic migration of these elements, the quantitative indicator of which is the biological absorption coefficient (BAC). This coefficient is calculated as the ratio of the element content in plant ash (mg/kg ash) to its content in the soil (mg/kg soil) [15]. The value of the BAC in natural virgin vegetation is 0.14 for As and 6.60 for Hg [16, 17]. According to the value of this parameter, Hg belongs to the elements of strong biological accumulation and, as a rule, it is characterized by accumulation in the humus layer, while As is related to the elements of medium biological capture. Therefore, it is characterized by a higher content in the parent rock.

The mean gross reserves of As and Hg in the arable soil layer (weighing 3000 t) of typical chernozem are 12.5 and 0.066 kg/ha, respectively. No evidence of exceeding the levels of APC for As (10 mg/kg) and MPC for Hg was found.

In the arable layer of ordinary chernozems in the Saratov region, the total content of As and Hg was within 3.80–4.54 and 0.018–0.039 mg/kg [18], and in the Belgorod region, 4.10–7.13 and 0.015–0.035 mg/kg, respectively [16]. In various subtypes of chernozems of Central Siberia, the mean content of Hg was in the range of 0.019–0.029 mg/kg [5].

Arsenic and mercury in fertilizers and ameliorants. Mineral fertilizers are not considered an important source of As and Hg soil pollution in agroecosystems. According to our data, the mean contents of As and

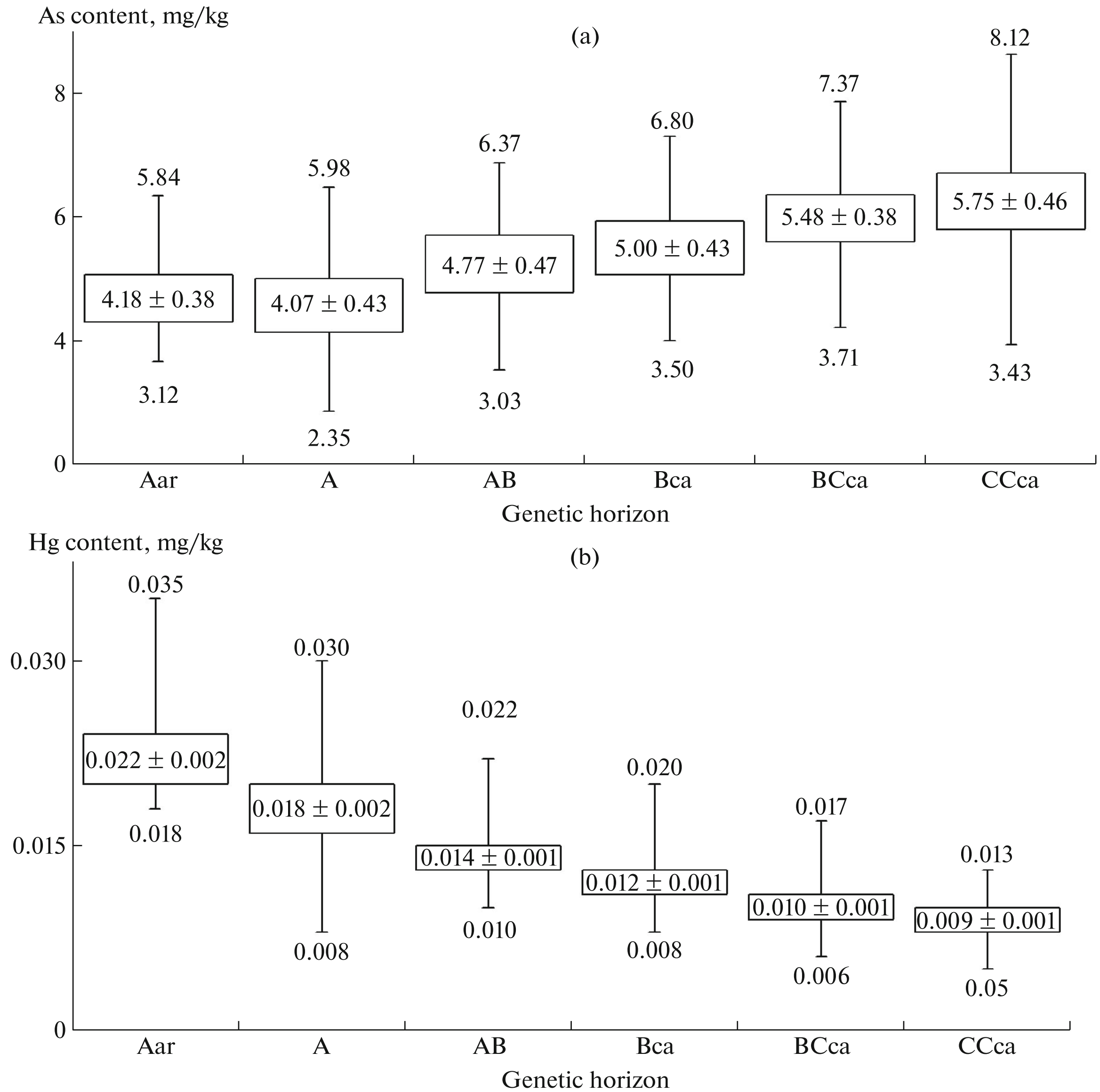

Fig. 1. Total content of (a) As and (b) Hg in the profile of the typical chernozem, mg/kg.

Hg in ammonium nitrate are 0.34 and 0.005 mg/kg and in azophoska, 0.94 and 0.010 mg/kg, respectively, which is lower than the total content of these elements in soils. In the period 2016–2020, 88–156 kg of active ingredient/ha of mineral fertilizers were applied to CCR on average per year, in which As and Hg introduced in the soil amounted to 0.13–0.23 and 0.002–0.003 g/ha, respectively. In this case, the stocks of As in the arable soil layer would increase by only 0.001–0.002%, and those of Hg, by 0.003–0.005%.

Organic fertilizers are an important source of these elements in the soil of agroecosystems. In modern crop cultivation technologies used in CCR, cattle manure and straw manure composts are recommended to be applied once every 4–5 years, and manure runoff once every two years. With the introduction of the recommended doses of 40 t/ha of cattle manure, straw manure compost 20 t/ha, and manure runoff 70 t/ha, the entry of As into the soil would include 11.08, 1.76, and 0.35 g.ha, while the entry of Hg would be 0.336, 0.082, and 0.070 g/ha, respectively (Table 2).

However, the level of application of organic fertilizers is quite low in the CCR with the exception of the Belgorod region. For example, in the years 2016–2020, the average doses of their introduction (in terms of cattle manure) in the Tambov region amounted to 0.23, and in the Belgorod region, 8.83 t/ha. With this amount of organic fertilizers, 0.06 and 0.002 As and Hg would enter the soils of the Tambov region and 2.45 and 0.074 g/ha, respectively, in the Belgorod region. At the same time, the increase in the gross

Table 2. Content of arsenic and mercury in organic fertilizers and defecation, mg/kg

Variation-statistical indicators	Type of fertilizer			
	manure runoff (2.22% of dry matter)	straw manure compost (56% of dry matter)	cattle manure (25% of dry matter)	defecation (87% of dry matter)
		As		
n	52	42	22	20
$\bar{x} \pm t_{05}s\bar{x}$	0.005 ± 0.001	0.088 ± 0.008	0.277 ± 0.036	2.00 ± 0.23
lim	0.003–0.008	0.045–0.139	0.111–0.394	1.10 ± 2.93
V, %	29.6	28.0	29.5	25.5
		Hg		
n	64	32	26	20
$\bar{x} \pm t_{05}s\bar{x}$	0.0010 ± 0.0001	0.0041 ± 0.0004	0.0084 ± 0.0010	0.014 ± 0.002
lim	0.0006–0.0018	0.0021–0.0060	0.0044–0.0125	0.005 ± 0.020
V, %	28.0	27.9	29.8	33.2

reserves of As and Hg in the soils of the Tambov region would be 0.0005 and 0.003%, and those in the Belgorod region, 0.02 and 0.112%, respectively.

The content of As and Hg in defecation, which is widely used for melioration of acidic soils, is significantly higher than in organic fertilizers. In CCR, the average application rates of this ameliorant are 8–12 t/ha, and the frequency is once every ten years. On average in the years 2016–2020, liming in CCR was carried out on a relatively small area, 132000 ha/year (1.5% of the sown area) [19]. Therefore, the entry into agroecosystems with defecation of As and Hg in amounts of 16.0–24.0 and 0.109–0.163 g/ha does not pose a threat to soil pollution.

According to some authors, the annual losses of As and Hg with washed soil as a result of the development of erosion processes in the agroecosystems of the Belgorod region are estimated at 7.20 and 0.044 g/ha, respectively, and the balance of these elements is negative [16].

Arsenic and mercury in agricultural crops. In agricultural plants, As and Hg accumulate to the greatest extent in by-products (straw, stems) and not in the main product (grain, seeds). For example, the content of As and Hg in by-products of corn is 1.3 and 2.9 times higher than in the corn, and that of soybeans is 1.4 and 2.9 times, respectively [4, 5].

The mean content of As in sunflower seeds, winter wheat, and peas was 0.020 and in barley, 0.019 mg/kg. There were no significant differences in this indicator between these cultures. In corn and soybeans, the As content was significantly lower than in the crops noted above and averaged 0.016 mg/kg. In clover and alfalfa hay, the average content of the element was 0.018 mg/kg, which did not differ significantly from its content in sainfoin (Table 3).

The MPC for grains of wheat, barley, and corn used for food purposes is set at 0.2 mg/kg, and for sunflower seeds, soybeans, and peas, 0.3 mg/kg [10]. To assess the quality of rough and succulent fodder (including hay), the maximum allowable level (MAL) of the As content was set equal to 0.5 mg/kg [11]. In our studies, no excess of MPC and MAL of the studied elements was observed. The average As content in crop products produced in Russia varies from 0.020 to 0.046 mg/kg [20].

In corn, peas, and soybeans, clover, and alfalfa hay, the mean content of Hg is 0.003, while in sunflower seeds it is 0.004 mg/kg. The content of this element is significantly higher in barley (0.006 mg/kg) and winter wheat (0.007 mg/kg). The lowest average Hg content was found in sainfoin hay (0.002 mg/kg).

The MPC of Hg was set at 0.03 for food grains of wheat, barley, and corn; for peas, 0.02; and for sunflower seeds and soybeans, 0.05 mg/kg [10]. The MRL for the Hg content in hay is 0.05 mg/kg [11]. In the agrocenoses of Central Siberia, the mean content of Hg in wheat grain is 0.0016; in barley, 0.002; and in hay of perennial grasses, 0.004 mg/kg [5]. The mean content of mercury in crop products in different federal districts of Russia varies from 0.0005 to 0.010 mg/kg [20].

In the years 2016–2020 in the Belgorod region, the average yield of winter wheat was 4.89; corn, 7.04; sunflower, 2.89; soybeans, 2.22; perennial grass hay, 3.0; and the alienation of As and Hg from agroecosystems with the main production of these crops was 0.10 and 0.034, 0.11 and 0.021, 0.06 and 0.012, 0.04 and 0.007, and 0.05 and 0.009 g/ha, respectively.

CONCLUSIONS

Thus, it has been established that in the Aar layer of the arable chernozem of the typical CCR forest—steppe zone, the mean total content of As and Hg is 4.18 and 0.022 mg/kg, respectively. In the parent rock (C),

Table 3. Content of arsenic and mercury in agricultural products, mg/kg

Product type (humidity, %)	Agricultural culture	*n*	$\overline{x} \pm t_{05}s\overline{x}$	lim	*V*, %
			As		
Seeds (7%)	sunflower	22	0.020 ± 0.001	0.017–0.022	9.5
Grain (14%)	winter wheat	70	0.020 ± 0.002	0.009–0.041	29.3
	barley	80	0.019 ± 0.001	0.011–0.034	28.4
	corn	23	0.016 ± 0.001	0.014–0.021	11.7
	peas	22	0.020 ± 0.002	0.013–0.028	20.6
	soybeans	42	0.016 ± 0.001	0.010–0.028	22.8
Hay (16%)	clover	22	0.018 ± 0.001	0.014–0.023	14.8
	alfalfa	22	0.018 ± 0.001	0.015–0.021	11.8
	sainfoin	22	0.017 ± 0.001	0.014–0.020	10.9
			Hg		
Seeds (7%)	sunflower	22	0.004 ± 0.0003	0.002–0.005	19.7
Grain (14%)	winter wheat	41	0.007 ± 0.001	0.003–0.009	24.9
	barley	45	0.006 ± 0.001	0.003–0.009	28.3
	corn	22	0.003 ± 0.001	0.002–0.004	29.9
	peas	22	0.003 ± 0.0002	0.002–0.004	20.6
	soybeans	21	0.003 ± 0.0003	0.001–0.004	26.5
Hay (16%)	clover	22	0.003 ± 0.0004	0.001–0.006	28.3
	alfalfa	22	0.003 ± 0.0003	0.002–0.004	19.0
	sainfoin	22	0.002 ± 0.0004	0.001–0.005	30.0

the content of As is 1.38 times higher, and Hg is 2.22 times lower than in the Aar. In the agroecosystems of the Belgorod region, organic fertilizers are the main source of As and Hg, but this does not pose a danger to soil pollution and crop production. The highest mean As content (0.020 mg/kg) was found in winter wheat, peas, and sunflower seeds, and the lowest (0.016 mg/kg) was in corn and soybeans. The highest Hg content was found in barley (0.006 mg/kg) and winter wheat (0.007 mg/kg), while sainfoin hay had the lowest content of this element (0.002 mg/kg). No exceeding of the levels of As and Hg MPC for food grains and MRL for feed products was revealed in the studies; however, this does not eliminate the need to monitor the quality of crop products.

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CONFLICT OF INTEREST

The author of this work declares that he has no conflicts of interest.

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