

## Monitoring of the Lead Content in Agroecosystems of the Central Black Earth Region of Russia

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**Abstract**—Studies on the environmental assessment of the Pb content in agroecosystems were carried out in the forest–steppe zone of Belgorod oblast, which is located in the southwestern part of the Central Black Earth region. The soil cover was represented mainly by leached chernozems. As a result of these studies, it was established that in the 0- to 20-cm layer of arable soils, the average total content of Pb is 13.1, while the concentration of mobile forms is 1.09 mg/kg, which does not exceed the background values and is significantly below the APC and MAC levels. There were no significant differences in the content of Pb in the 0- to 20- and 21- to 40-cm soil layers. The excess of background concentrations of this element was established in the soils of roadside ecosystems. The main source of Pb ingress into the agroecosystems of Belgorod oblast is organic fertilizers, but this does not pose a hazard to pollution of soils and crop production. The average Pb contents in corn, barley, and winter wheat grains did not differ significantly and were 0.27, 0.28, and 0.29 mg/kg, respectively. The minimum amount of this element in the crops studied was contained in soybean grains (0.16 mg/kg), while the maximum amount was in sunflower seeds (0.34 mg/kg). The minimum amount of Pb in the perennial legume grasses was contained in clover hay (0.19 mg/kg), while the maximum amount was in esparcet hay (0.34 mg/kg). The MAC levels of Pb for food grains and the maximum residue levels of Pb in crop production were not exceeded.

**Keywords:** agroecological monitoring, clarke, lead, agricultural crops, heavy metals, chernozem, fertilizers

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### INTRODUCTION

Environmental contamination by lead and its compounds is acknowledged around the world to be one of the major ecological problems that significantly affects the health of the population. Among heavy metals (HMs), lead (Pb) is the most common and toxic element. It belongs to the first class of toxicity (highly hazardous substances) [1, 2]. This metal occurs in nature in the scattered state and as a constituent in more than 200 minerals. According to the estimates of different scientists, the clarke values of Pb in soil vary from 10 mg/kg [3] to 27 mg/kg [4]. The concentration in nonpolluted soil is determined by the geochemical features of the soil-forming rock. In turn, the Pb content in soil-forming rocks varies depending on their particle-size composition. As a rule, the

higher the content of physical clay in a soil-forming rock, the higher the total content of Pb [5].

This element enters the environment primarily upon combustion of petrol (60%) and production of nonferrous metals (22%), steel, and ferro-alloys (11%) [6]. Quite a high amount of Pb may be brought to the soil with sewage sludge (SS) [5].

Lead is found in all types of plants; however, its role in metabolism has not been determined accurately. The normal Pb concentration in plants that cause physiological disorders is within 0.5–10 mg/kg, while the toxic content is 30–300 mg/kg [2]. The lowest content of Pb is recorded in the reproductive organs of plants, which is associated with the activity of protective mechanisms impeding the entrance of HMs into these organs.

Due to the high toxicity of Pb compounds, the total content of this element in soils is normalized in many industrially developed countries of Europe, Canada, Australia [7], and China [8]. In Russia, the levels of approximate permissible concentrations (APC) were established for normalizing the total content of Pb in the soils with different particle-size compositions. For

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heavy loamy soils with  $\text{pH} < 5.5$ , Pb APC is 65, while for soils with  $\text{pH} > 5.5$ , it is 130 mg/kg. The maximum allowable concentration (MAC) for mobile forms of this HM is 6 mg/kg [9]. Since up to 85% of Pb comes into a human organism with food products, its MAC levels are determined in food products and animal foodstuff [1, 2]. For example, the MAC for grains used for food purposes is 0.5, while the MAC for animal feed is 5 mg/kg [10].

The Pb content in the main components of the agroecosystems is under the control of the agrochemical service of Russia in the framework of the State Program of agroecological monitoring.

The purpose of this work is to perform an ecological assessment of the Pb content in arable soils, fertilizers, and crop products.

### STUDY PROCEDURE

The major studies were conducted in 2016–2022 in the forest–steppe zone of Belgorod oblast located in the southwestern part of the Central Black Earth region (CBER). Among the most common soils in the forest–steppe zone are leached chernozems that occupy 37.2% in the plowed field structure [11].

The segment of the specially protected natural reservation (SPNR) Yamskaya Steppe of Belogorye Nature Reserve was selected as a background object. One cross section was made on a virgin segment soil, which is represented by leached chernozem. Twenty reference areas were segmented on arable leached chernozems in the forest–steppe zone. Soil sampling was done in accordance with the common procedure in the agrochemical service [12]. In the arable soils, 56.8% was the average content of physical clay in the 0- to 20-cm layer, 5.6% was the average content of organic matter according to the method of Tyurin, 5.3 was  $\text{pH}_{\text{KCl}}$ , while in the virgin soil, these values were 56.4, 9.7, and 5.3%, respectively.

The samples of soil, crop products, and fertilizers were analyzed in the certified testing laboratory. The total lead content (5 M  $\text{HNO}_3$  extragent) and the concentration of its mobile forms extracted by the ammonium-acetate buffer (AAB) solution with  $\text{pH} = 4.8$  were determined by the method of atomic-emission spectroscopy [13]. The element contents in the crop products and fertilizers were calculated using common procedures in the agrochemical service [13]. The samples of soils, fertilizers, and crop products were analyzed in the certified testing laboratory of Belgorod Center for the Agrochemical Service.

### RESULTS AND DISCUSSION

*Lead in soils.* The total Pb content in the upper part of the humus-accumulative horizon of virgin leached chernozem in the Yamskaya Steppe segment (background soil) was 13.0, while the concentration of

mobile forms of this element was 1.47 mg/kg (11.3% of the total content). The average total content of Pb in the 0- to 20-cm layer of arable leached chernozem was 13.1 mg/kg, which corresponded to its concentration level in the background soil. The content of mobile forms of Pb in arable soil (0–20 cm) was 1.09 mg/kg (8.3% of the total content), on average, which is even slightly lower than in the background soil. In the arable soil, the total content and concentration of mobile forms of the element did not differ significantly in the layers of 0–20 and 21–40 cm (Fig. 1). The total Pb contents in the arable soil layer (weighing 3000 t/ha) are 39.3 kg/ha, and the concentration of mobile forms is 4.4 kg/ha.

According to the generalized data, the total Pb content in the arable soils of the forest–steppe zone of CBER is within 8.2–14.5 mg/kg [14]. However, this index slightly characterizes the availability of this element for plants; therefore, it is necessary to determine the concentration of its mobile forms. The Pb compounds are most mobile in acid sandy soils and least mobile in heavy weakly alkaline soils [2]. In Lipetsk oblast, the contents of Pb mobile forms in the arable layer of leached chernozems with a weak acid medium reaction varied within 0.73–1.04 mg/kg, which is consistent with our data [15]. In Belgorod oblast, the leached chernozems with a weakly acid reaction of the medium contained 0.97–1.40 mg/kg of mobile Pb forms, while the typical chernozems with a medium reaction close to neutral had 0.25–0.59 mg/kg [14].

The numerous results of research indicate that the soils in the roadside ecosystems are contaminated with Pb. However, the level of soil contamination strongly varies depending on the land topography, traffic intensity, and duration of impact on the ecosystem. According to our studies of the impact made by highway transport exhaust emissions on the contamination of roadside ecosystems, the highest total content (163% to the background) and the concentration of mobile Pb forms (408% to the background) in the soils were recorded 5 m away from the roadbed. At an increase in the distance to 30 m, the lead content in the soil gradually decreased to the background values. The established levels of APC of total Pb and MAC of mobile forms of these metals in the soils [9] were not exceeded (Table 1). In addition, the roadsides of large highways are as a rule occupied by natural vegetation and tree belt areas and are not used in agriculture.

Comparable results were obtained in Altai krai. With a traffic intensity of 4000 vehicle/day, the largest content of mobile Pb forms that did not exceed MAC was recorded 50 m from the roadbed [16].

Despite the fact that it has been forbidden to use lead petrol since 2002, contamination of the roadside ecosystems with Pb is regularly detected, since those amounts of the element that have already been supplied will be deposited in the soil for a long time [17].

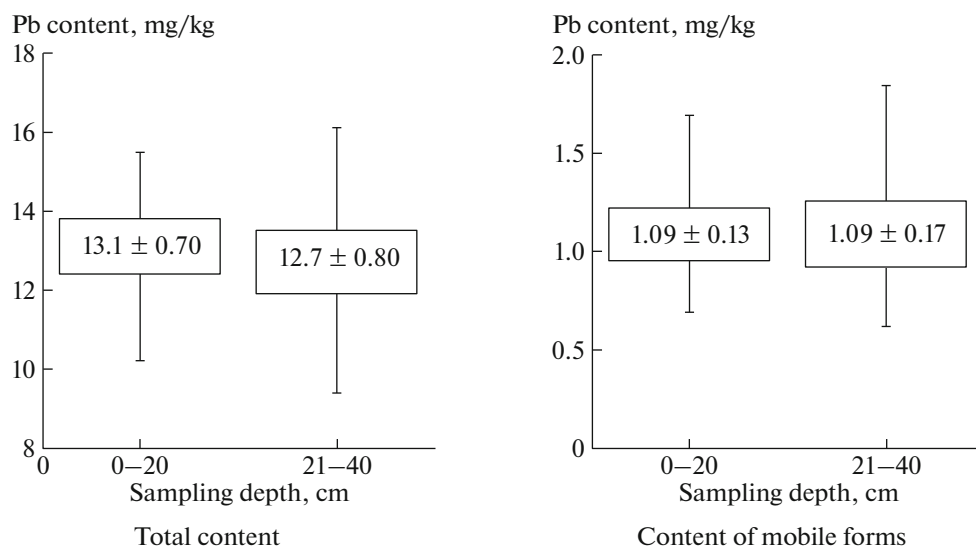


Fig. 1. Pb content in leached chernozems, mg/kg.

This element has extremely low migration capacity, and its half-life in soil is 740–5900 years [18].

**Lead in fertilizers and ameliorants.** Mineral fertilizers usually contain less Pb than soils; therefore, they are not considered to be a significant factor of agroecosystem contamination [2]. According to our data, the average Pb content in ammonium nitrate, the most common nitrogen fertilizer, is 0.16 mg/kg, while in the complex fertilizer nitrophoska, it is 0.24 mg/kg. Taking into account the usage doses of mineral fertilizers, 88.1–156.0 kg/ha, which were typical of CBER in the years 2016–2020, these Pb amounts do not pose a serious hazard to soil contamination.

The content and the ratio of different HMs in organic fertilizers vary strongly depending on the animal species and the technology of their feeding and management (Table 2). Pb comes into the soil in the amounts of 31.2 and 26.0, and 9.1 g/ha together with the large cattle manure doses that are recommended in the modern agrotechnologies (40 t/ha one time every 4–5 yr), straw-manure composts (20 t/ha one time every 4–5 yr), manurial discharges (70 t/ha one time every 2 yr), 31.2, 26.0 and 9.1 g/ha, respectively, which leads to an increase in the total reserves of this

metal in the arable layer by only 0.079, 0.066, and 0.023%. The Russian regions, in particular the regions comprising CBER, differ significantly in the level of using organic fertilizers. For example, for the period of 2016–2020, on average, the level of applying organic fertilizers in Belgorod oblast was 8.83, while in Tambov oblast, it was 0.23 t/ha of the cultivated area, in which case the average ingress of Pb (calculated as large cattle manure) was 6.9 and 0.2 g/ha a year, respectively.

Compared to organic fertilizers, quite a lot of Pb is contained in the defecation residues used widely for amelioration of acidic soil. However, the average doses of ameliorant addition to CBER are 8–12 t/ha, and the liming frequency is usually every ten years. Furthermore, liming of chernozems in CBER was conducted in a relatively small area of 132000 ha (1.5% of the cultivated area) over the years 2016–2020, on average. Therefore, Pb coming in the amount of 27.0–40.6 g/ha into the limed soils with defecation residues does not pose a hazard to soil contamination.

According to the published data, in the agroecosystems of Belgorod oblast, the largest ingress of this element occurs primarily with organic fertilizers, while

Table 1. Influence of the distance from the roadbed on the lead content in the soil (the 0- to 20-cm layer) of the roadside ecosystem (M2 Crimea highway, Belgorod oblast)

Index		Distance from the roadbed, m				
		5	10	15	20	30 (background)
Total content	mg/kg	22.0	20.6	19.9	19.3	13.5
	% to the background	163	153	147	143	100
Content of mobile forms	mg/kg	2.65	1.65	1.65	1.35	0.65
	% to the background	408	254	254	208	100

**Table 2.** Contents of lead in organic fertilizers and defecation residues, mg/kg

Kind of fertilizer	Total solids, %	Variation-statistical indices			
		<i>n</i>	$\bar{x} \pm t_{0.5} s \bar{x}$	lim	<i>V</i> , %
Manure discharges	2.22	48	0.13 ± 0.01	0.08–0.20	29.6
Straw–manure hay	56	36	1.30 ± 0.12	0.92–2.67	28.6
Large cattle manure	25	26	0.78 ± 0.09	0.45–1.27	29.3
Defecation residues	87	20	3.38 ± 0.52	1.42–4.74	29.8

**Table 3.** Contents of lead in the products of agricultural crops, mg/kg

Agricultural crops	Kind of product	Moisture content, %	Variation-statistical indices			
			<i>n</i>	$\bar{x} \pm t_{0.5} s \bar{x}$	lim	<i>V</i> , %
Winter wheat	Grain	14	66	0.29 ± 0.02	0.16–0.50	26.3
Barley	Grain	14	50	0.28 ± 0.02	0.14–0.46	29.1
Corn	Grain	14	73	0.27 ± 0.02	0.16–0.40	21.1
Soybeans	Grain	14	20	0.16 ± 0.01	0.13–0.21	14.7
Sunflower	Seeds	7	27	0.34 ± 0.03	0.20–0.43	21.6
Clover	Hay	16	22	0.19 ± 0.03	0.09–0.30	28.0
Lucerne	Hay	16	22	0.29 ± 0.04	0.11–0.41	29.8
Esparcet	Hay	16	22	0.34 ± 0.04	0.18–0.57	25.8

removal results from water erosion. The average annual losses of Pb with the eroded soil are estimated at 25.2 g/ha and significantly exceed the amounts of ingress of this element; therefore, the balance is negative [14]. By the estimates of several scientists, the real hazard of agroecosystem Pb contamination exists if the use of sewage sludge as unconventional organic fertilizers is not under control [5].

*Lead in agricultural crops.* The average contents of Pb in the grains of winter wheat (0.29 mg/kg), barley (0.28 mg/kg), and corn (0.27 mg/kg) did not differ significantly (Table 3). Sunflower seeds contained 0.34 mg/kg of Pb, which slightly exceeds the element concentration in the grains of barley and corn. The contents of this element in soybean grains (0.16 mg/kg) were much lower than in the grain crops and sunflower. The Pb contents in the grains and the seeds were below the MAC levels established for food products.

Among perennial legume grasses cultivated in CBER, clover is characterized by the lowest Pb content. The average content of the element was lower in clover hay than in the esparcet hay and the lucerne hay by a factor of 1.86 and 1.55, respectively. To evaluate the quality of coarse and succulent foods, the maximum residue level (MRL) of the Pb content was established equal to 5 mg/kg [19]. The average contents of the element in clover, lucerne, and esparcet hays were by a factor of 27.0, 17.5, and 14.5 below MRL.

In the period 2016–2020, the average yield of winter wheat in Belgorod oblast was 4.89; barley, 3.65;

corn, 7.04; sunflower seeds, 2.89; soya beans, 2.22; perennial grass hay, 3.0 t/ha; while the removal of Pb from the agroecosystems with these products was 1.4, 1.0, 1.9, 1.0, 0.3, and 0.8 g/ha, respectively.

In the studies conducted on the territory of the forest–steppe zone in CBER, the Pb contents were 0.22–0.37 mg/kg and 0.26–0.41 mg/kg in barley grain and winter wheat, respectively [20]. According to the generalized data from different countries of the world, the average content of Pb in grain crops is 0.47 mg/kg [4].

## CONCLUSIONS

Thereby, it was established that, in the 0- to 20-cm layer of the arable leached chernozem of the forest–steppe zone in CBER, the average total Pb content is 13.1, and the concentration of mobile forms is 1.09 mg/kg, which does not exceed the background values and is significantly below the APC and MAC levels. There were no significant differences in the contents of Pb in the 0- to 20- and 21- to 40-cm soil layers. The background concentrations of this element were exceeded in the soils of roadside ecosystems. The main source of Pb ingress into the agroecosystems of Belgorod oblast is organic fertilizers; however, this does not pose a hazard to contamination of soils and crop production. The average Pb contents in the corn, barley, and winter wheat grains did not differ significantly and were 0.27, 0.28, and 0.29 mg/kg, respectively. The minimum amount of this element in the studied cultures was contained in soybean grains

(0.16 mg/kg), while the maximum amount was in sunflower seeds (0.34 mg/kg). The minimum amounts of Pb in the perennial legume grasses were contained in clover hay (0.19 mg/kg), while the maximum amounts were in esparcet hay (0.34 mg/kg). The MAC levels of Pb for food grains and the maximum residue levels in crop production were not exceeded.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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