____ AGRICULTURAL CHEMISTRY _ AND SOIL FERTILITY =

Ecological Assessment of Concentrations of Heavy Metals and Arsenic in Soils and Crops of the Central Chernozemic Region

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Abstract—The ecological assessment of the contents of Cr, Pb, Cd, Hg, and As in arable soils and crops grown in the central chernozemic region of Russia was carried out by the example of Belgorod oblast. It was found that average bulk contents of Cr, Pb, As, Cd, and Hg in leached arable chernozem were 19.8, 10.0, 4.15, 0.22, and 0.021 mg/kg; in typical arable chernozems, 20.0, 10.3, 4.18, 0.23, and 0.022 mg/kg; and in ordinary chernozems 20.9, 11.2, 5.48, 0.35, and 0.023 mg/kg, respectively. The average contents of mobile forms of Pb, Cr, and Cd were 0.52, 0.14, and 0.06 mg/kg in leached arable chernozems; 0.46, 0.13, and 0.05 mg/ka in typical arable chernozems; and 0.55, 0.13, and 0.04 mg/kg in ordinary chernozems, respectively. These elements did not exceed the established maximum permissible concentrations (MPCs) and tentative permissible concentrations (TPCs) for the studied soils. Organic fertilizers were found to be the main source of heavy metals in the arable soils of Belgorod oblast. Average concentrations of Cr, Pb, As, Cd, and Hg in cattle manure were 0.90, 0.78, 0.277, 0.060, and 0.0084 mg/kg, respectively. Among studied crops, sunflower seeds had the highest concentrations of Cd, Pb, and Cr, while winter wheat grains had the highest concentrations of Hg and As. Soybeans contained the lowest average contents of Pb, Hg, and As, and the corn grain had the lowest average contents of Cr, Cd, and As. In the grains of winter wheat, corn, soybeans, and sunflower seeds, the contents of Pb, Cd, Hg, and As did not exceed MPCs established for products intended for food purposes, and the concentration of Cr did not exceed the MPC established for feed.

Keywords: monitoring, chernozem, fertilizers, cadmium, lead, chromium, mercury, content of mobile forms of element

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INTRODUCTION

Human impact on agroecosystems, including soil contamination with elements widely used in industry, such as Cr, Pb, Cd, Hg, and As is steadily increasing [1, 22, 29]. In accordance with Russian legislation, Pb, Cd, Hg, and As fall into the first class (highly hazardous substances) of toxicity, and Cr belongs to the second (moderately hazardous) class [1, 4, 7].

The term heavy metals (**HMs**) is often used for the elements Pb, Cd, Hg, and Cr. The metalloid As is often considered together with this group [1, 5, 7]. The contents of HMs and As in components of agroecosystems are characterized by high spatial variations, caused by both natural and anthropogenic factors. Even average abundances (clarkes) of these elements in soils determined by different authors differ significantly. For example, the clarkes of Pb and Cr according to [3] reach 10 and 200 mg/kg and according to [24], 27.0 and 59.5 mg/kg, respectively. Within the framework of the government program of agroecological monitoring of agricultural lands carried out by the

Agrochemical Service of Russia, provision is made for periodical determination of the contents of major HMs in soils, fertilizers, and agricultural products [25, 26].

Taking into account high toxicity of As and HMs, their concentrations in soil are regulated in many countries of the world [23, 30]. The levels of tentative permissible concentration (TPC) were established in Russia to standardize the bulk contents of As and major HMs in soils depending on their texture and acidity. For example, TPCs for Pb, As, and Cd are 130, 10, and 2 mg/kg, respectively, for heavy loamy soils with $pH_{KCl} > 5.5$. The maximum permissible concentration (MPC) of 2.1 mg/kg was established for the total content of Hg in soils. Additionally to the total contents, there are also MPCs for the concentrations of mobile forms of some HMs in Russia. For example, MPC of 6 mg/kg was established for mobile forms of Cr and Pb extracted by an ammonium acetate buffer solution with pH 4.8 [14].

The compounds of Pb, Cd, Hg, and As possess high toxicity for warm-blooded animals, including

humans, so their contents in products intended for food and in fodder for farm animals is standardized [17]. Maximum permissible level (**MPL**) of Cr content is regulated for feed products [2].

This work was aimed at ecological assessment of Cr, Pb, As, Cd, and Hg contents in arable soils and crops in the central chernozemic region of Russia.

OBJECTS AND METHODS

The study was carried out in Belgorod oblast, in the southwestern part of the Central Chernozem Economic region of Russia. Long-time annual average Selyaninov hydrothermal coefficient (HTC), which is calculated as the proportion between precipitation (mm) over the period with air temperature above 10°C and accumulated temperatures over the same time decreased 10 times, ranges within 0.9–1.2. The soil cover in the forest-steppe zone of the oblast is dominated by typical chernozems (Haplic Chernozems) (44.8% of the total arable area) and leached chernozems (Luvic Chernozems) (25.7%); in the steppe zone, by ordinary chernozems (Haplic Chernozems) (13.0%) [16].

Average crop area in Belgorod oblast in 2016-2020 constituted 1425 thousand hectares. The structure of the area under crops was dominated by winter wheat (26.8% of the area under crops), soybeans (16.6%), sunflower (10.3%), and grain corn (9.2%) [35].

Background soil monitoring has been carried out at the Yamskaya Step site of the Belogor'e State Reserve in the forest-steppe zone, in Gubkin City municipal district and in the Rovenskii National Park in the steppe zone, in Roven'skii municipal district. The contents of physical clay (particles <0.01 mm) and C_{org} and pH_{H₂O} in the upper part of the humus horizon (10–20 cm) constitute 56.4, 5.63%, and 6.3 in the virgin leached chernozem; 57.3, 5.86%, and 7.0 in the typical chernozem; 67.0, 3.77%, and 7.1 in the ordinary chernozem, respectively.

The materials of local agroecological monitoring carried out by the Agrochemical Service of Russia in 2016–2022 were used in the work. This type of monitoring is carried out on arable lands of the oblast using specially established reference objects (field plots of 4-40 ha in area), from which soil is s sampled for complete agrochemical analysis; every year, before the beginning of harvesting, the main products and byproducts of agricultural crops are sampled [8]. The average content of physical clay (particles <0.01 mm) in the plow layer (0-25 cm) of leached and typical chernozems of reference objects in the forest-steppe zone is 56.2 and 56.8%; the Corg content, 3.13 and 3.25%; and $pH_{\rm H_{2}O},~6.3$ and 6.7, respectively. Crop products are sampled at reference fields for chemical analysis. The average yield of the studied crops reaches 5.0 t/ha for of winter wheat grains, 3.7 t/ha for barley grains, 7.0 t/ha for corn grains, 2.2 t/ha for soybeans 2.2, and 3.0 t/ha for sunflower seeds. The average content of physical clay in the plow horizon of reference arable soils in the steppe zone is 72.5%; the C_{org} content 3.02%, and $pH_{H,O}$ 7.8.

All analytical measurements for this study were carried out in accredited testing laboratory. The content of acid-soluble forms of HMs (extractant 5 M HNO₃) and mobile forms extracted with an ammonium acetate buffer solution with pH 4.8 were determined by atomic emission spectrometry. The contents of HMs in mineral and organic fertilizers and crop products were determined by atomic absorption spectrometry method according to procedures commonly accepted in the agrochemical service. The content of As in the soil, crop, and fertilizer samples was determined by the photometric method [9].

Statistical treatment of the data of local monitoring included calculation of confidence interval for the mean ($\overline{x} \pm t_{05}s\overline{x}$) and coefficient of variation (*V*). It was carried out automatically, using the Agroecologist Online GIS software package [6, 28].

RESULTS AND DISCUSSION

Contents of the elements in soils. The background contents of acid-soluble forms of Cr, Pb, As, Cd, and Hg in the virgin leached chernozem reach 19.8, 10.1, 4.45, 0.21, and 0.020 mg/kg; in the typical chernozem,19.9, 10.6, 4.41, 0.22, and 0.018 mg/kg; and in the ordinary chernozem, 20.3, 13.9, 5.60, 0.40, and 0.026 mg/kg, respectively. Average values of this indicator for Cr, Pb, As, Cd, and Hg in arable soils constitute, respectively, 19.8, 10.0, 4.15, 0.22, and 0.021 mg/kg in leached chernozems; 20.0, 10.3, 4.18, 0.23, and 0.022 mg/kg in typical chernozems; and 20.9, 11.2, 5.48, 0.35, and 0.023 mg/kg in ordinary chernozems (Table 1, Fig. 1). The contents of acidsoluble forms of As and Cd in arable ordinary chernozems are significantly higher than in leached and typical chernozems. At the same time, there are no significant differences in the contents of Cr, Pb, and Hg between the studied soils, though a tendency for their higher contents in ordinary chernozems in comparison with leached and typical chernozems can be traced. The differences in the contents of the studied HMs between leached and typical chernozems of the forest-steppe zone and ordinary chernozems of the steppe zone is mainly due to a heavier texture of the latter. The contents of Cr, Pb, As, Cd, and Hg are below clarke values for world's soils, which constitute 59.5, 27.0, 6.83, 0.41, and 0.07 mg/kg, respectively [24].

The stocks of acid-soluble forms of Cr, Pb, As, Cd, and Hg in the plow layer (of mass 3000 t/ha) in leached chernozems average 59.4, 30.0, 12.45, 0.66, and 0.063 kg/ha; in typical chernozems, 60.0, 30.9, 12.5, 0.69, and 0.066 kg/ha; and in ordinary chernozems 62.7, 33.6, 16.4, 1.05, and 0.069 kg/ha, respectively.

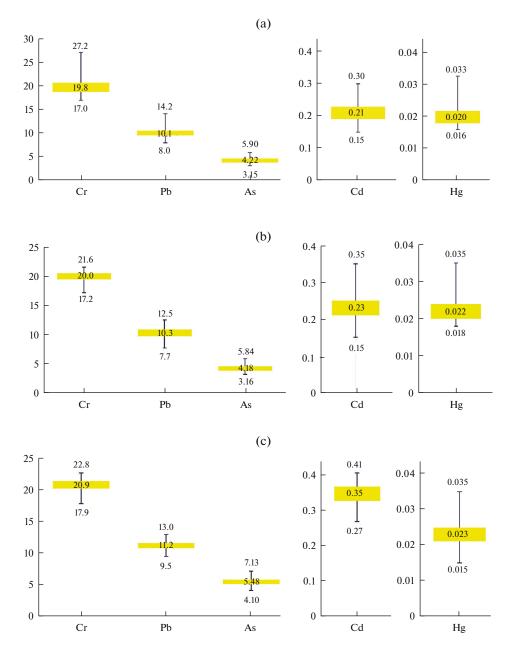


Fig. 1. Contents of acid-soluble forms of elements in (a) leached, (b) typical, and (c) ordinary (c) chernozems, mg/kg.

The established levels of the content of studied HMs are in agreement with the results obtained in other steppe and forest-steppe regions of Russia. For example, the average contents of acid-soluble Pb, As, Cd, and Hg in the plow layer of chernozems in Saratov oblast are 14.7, 4.5, 0.39, and 0.022 mg/kg, respectively [7]. The Hg content ranges within 0.019–0.029 in different subtypes of chernozems in Central Siberia and within 0.02–0.03 mg/kg in chernozems of Lipetsk oblast [10, 13]. The Cr content in leached chernozems of the Krasnoyarsk region averages 25.7 mg/kg and ranges from 19.8 to 33.4 mg/kg [11].

EURASIAN SOIL SCIENCE Vol. 57 No. 10 2024

The total content of elements does not characterize their availability for plants. Therefore, for Cr, Pb, and Cd, the concentration of their mobile forms is determined in soil. At the same time, during agroecological monitoring, the mobile forms of As and Hg are not determined. The background content of mobile forms of Pb, Cr, and Cd in virgin leached chernozem is 0.70, 0.14, and 0.06 mg/kg; in typical chernozem, 0.62, 0.15, and 0.05 mg/kg; and in ordinary chernozem, 0.53, 0.16, and 0.03 mg/kg, respectively. These values are within the limits of variation of determined for arable analogues of virgin soil. The average content of

| F 1 | Mean content | Sta | atistical measures of H | M contents in arable so | oils |
|------------|----------------|--------|-------------------------|--|------|
| Element | in virgin soil | п | lim | $\overline{x} \pm t_{05} s \overline{x}$ | V, % |
| | | Leach | ed chernozem | | |
| Pb | 0.70 | 21 | 0.31-0.73 | 0.52 ± 0.06 | 23.5 |
| Cr | 0.14 | 21 | 0.12-0.21 | 0.14 ± 0.01 | 19.8 |
| Cd | 0.06 | 21 | 0.03-0.08 | 0.06 ± 0.01 | 26.1 |
| | | Typic | al chernozem | · · · | |
| Pb | 0.62 | 22 | 0.28-0.63 | 0.46 ± 0.05 | 20.1 |
| Cr | 0.15 | 22 | 0.11-0.18 | 0.13 ± 0.01 | 14.5 |
| Cd | 0.05 | 22 | 0.02-0.07 | 0.05 ± 0.01 | 25.9 |
| | | Ordina | ary chernozem | · · · | |
| Pb | 0.53 | 22 | 0.37-0.70 | 0.55 ± 0.05 | 17.1 |
| Cr | 0.16 | 22 | 0.09-0.17 | 0.13 ± 0.01 | 19.4 |
| Cd | 0.03 | 22 | 0.03-0.06 | 0.04 ± 0.01 | 16.2 |

Table 1. Contents of the mobile forms of heavy metals in studied soils, mg/kg

mobile forms of Pb, Cr, and Cd in arable soils is 0.52, 0.14, and 0.06 mg/kg in leached chernozems; 0.46, 0.13, and 0.05 mg/kg in typical chernozems; and 0.55, 0.13, and 0.04 mg/kg in ordinary chernozems, respectively. There are no significant differences in these indicators between the studied soils. However, there is a tendency for a higher content of mobile forms of Cd in leached chernozems in comparison with ordinary chernozems, and this apparently is related to a less acid reaction (pH) in the latter soil. In arable soils, the mobile forms of Cr, Pb, and Cd constitute 0.62–0.71, 4.23-5.20, and 11.4-7.3% of the content of their acidsoluble forms, respectively. Exceedance of Russian standards for the maximum permissible concentration (MPC) and tentatively permissible concentration (TPC) has not been observed in our study and in previous comprehensive environmental and toxicological soil surveys. ecological-toxicological survey performed earlier.

The average content of mobile forms of Cr in leached chernozems of the Krasnoyarsk region is slightly higher (0.2 mg/kg) than that in the soils of Belgorod oblast [11]. The average contents of mobile forms of Cr and Pb in soils of Saratov oblast are 0.70 and 0.82 mg/kg, respectively [7], and this is significantly higher than in the soils of Belgorod oblast. In arable leached chernozems of Lipetsk oblast, the mobile Cd content is within the range of 0.03–0.08 mg/kg; in ordinary chernozems of Saratov oblast, 0.03–0.07 mg/kg [7, 13], and these data agree well with our data for Belgorod oblast.

Numerous studies attest to soil contamination in roadside ecosystems with Cd as a result of wear of car tires and with Pb, which polluted these ecosystems before 2002, when the use of leaded gasoline was allowed [20, 34]. A significant excess of background

contents of Pb and Cd was observed in soils of roadside ecosystems in Belgorod oblast at distances up to 50 m from the road surface of large highways. However, these areas are usually occupied by natural vegetation and are separated from agrocenoses by protective forest belts [25, 26].

Contents of the elements in fertilizers. Mineral fertilizers, taking into account their chemical composition and the rates of application, are not considered as important source of soil contamination with HMs in agroecosystems of Russia [19, 21, 22]. However, it is known that Cd contained in phosphorous fertilizers is a significant source of soil contamination in some foreign countries; particularly, in Australia and China [24]. Average contents of Cr, As, Pb, Cd, and Hg in the most common mineral fertilizers applied in Russia are 1.13, 0.34, 0.16, 0.04, and 0.005 mg/kg in ammonium nitrate and 1.32, 0.94, 0.24, 0.10, and 0.01 mg/kg in azophosphate (16:16:16), respectively. The average of application of mineral fertilizers accounted for in Belgorod oblast in 2019–2022 was 114.4 kg of active substance/ha; nitrogen, phosphorus, and potassium constituted 64.8, 17.3, 17.9% of the total fertilizer nutrients, respectively. Calculations demonstrate that Cr, As, Pb, Cd, and Hg are annually added to the soil with this dose of fertilizers in amounts of 0.34, 0.18, 0.06, 0.02, and 0.002 g/ha, respectively.

An important source of the considered elements in soils of agrocenoses is organic fertilizers applied at high rates [31, 32]. Depending on the type of animal, feeding ration, technology of livestock keeping, and quantity and quality of litter, the contents and ratio of different elements in organic fertilizers vary significantly. Different technological procedures of litter removal and storage affect significantly the chemical composition of organic fertilizers. Average contents of

| Element | | Statistical | measures | |
|---------|----|---------------|--|------|
| Element | п | lim | $\overline{x} \pm t_{05} s \overline{x}$ | V, % |
| Cr | 20 | 0.56-1.25 | 0.90 ± 0.14 | 28.1 |
| Pb | 26 | 0.45-1.27 | 0.78 ± 0.09 | 29.3 |
| As | 22 | 0.111-0.394 | 0.277 ± 0.036 | 29.5 |
| Cd | 28 | 0.04-0.09 | 0.060 ± 0.006 | 27.1 |
| Hg | 26 | 0.0044-0.0125 | 0.0084 ± 0.0010 | 29.8 |

Table 2. Contents of the elements in cattle manure (25% dry matter), mg/kg

Cr, Pb, As, Cd, and Hg in cattle manure constitute 0.90, 0.78, 0.277, 0.060, and 0.0084 mg/kg respectively (Table 2).

The average rate of application of organic fertilizers in Belgorod oblast reaches 9.6 t/ha per year. The annual input of Cr, Pb, As, Cd, and Hg with organic fertilizers is estimated at 8.64, 7.49, 2.66, 0.58, and 0.08 g/ha, respectively. Thus, it is 25, 125, 15, 29, and 40 times higher, respectively, than the input with mineral fertilizers. The total stores of Cr, Pb, As, Cd, and Hg in the plow layer of typical chernozems predominating in Belgorod oblast increase due to application of organic fertilizers by 0.014, 0.024, 0.021, 0.084, and 0.12% per year, respectively (without taking into account the removal of these elements with harvested crops and due to erosion).

According to various estimates, the balance of the studied elements in agriculture of Belgorod oblast is negative. The removal of elements with yield and their loss with eroded soil exceed the total input from various sources [15, 18].

Contents of the elements in agricultural crops. Specific chemical composition of plants is largely determined by the agroecological properties of soils in the areas, where the particular species was formed. Therefore, the content and proportions between HMs in different plant species are likely fixed in the course of evolution and keep the signs of the chemical composition of the environment in the place of their origin [27].

Lead is an obligate element for all agricultural crops, but its functional role in metabolism remains poorly studied. The concentrations of Pb in plants within 0.5-10 mg/kg are considered normal (not leading to physiological disturbances); when lead concentrations in plants reach 30-300 mg/kg, various toxic symptoms may be manifested [24]. The lowest Pb content is usually observed in the reproductive organs, which is explained by the functioning of protective mechanisms preventing the entry of this toxicant into them.

A generalization of data obtained in different countries shows that the average Pb content of Pb in cereal grains is 0.47 mg/kg [24]. In the central chernozemic region of Russia, the Pb content in barley grains ranges

EURASIAN SOIL SCIENCE Vol. 57 No. 10 2024

within 0.22-0.37 mg/kg; in grains of winter wheat, within 0.26-0.41 mg/kg [15].

According to the data obtained, the average content of Pb in winter wheat grains is 34 mg/kg, and it does not differ significantly from the Pb content in corn grains (0.31 mg/kg). The Pb content in sunflower seeds (0.36 mg/kg) is close to its content of in cereal grains. The minimum content of Pb was found in soybean (0.18 mg/kg). The content of Pb in by-products of winter wheat, corn, soybean, and sunflower is 1.44, 1.77, 1.22, and 1.61 times higher than in the main products, respectively (Table 3).

In the studied crop products, the Pb content is below the MPC level, which is set at 0.5 mg/kg for grain used for food and 1.0 mg/kg for sunflower seeds [17].

Cadmium in plants accumulates mostly in the roots, its contents in the aboveground and especially generative organs are significantly lower. The role of Cd in physiological processes is studied insufficiently. Most of the works are focused mostly on the study of the negative influence of high content of this element on crop yields [1, 7].

In the territory of Central Siberia, the Cd content in spring wheat grain ranges within 0.020–0.023 mg/kg; in the hay of perennial legumes, 0.028–0.110 mg/kg [12]. Generalized data from different countries suggest that the Cd content in wheat grain is in the range of 0.02–0.07 mg/kg, and the average content of this element in sunflower seeds is 0.14 mg/kg [24].

The results of this study demonstrate that maximum average content of Cd (0.090 mg/kg) is in sunflower seeds. There is no significant difference in the Cd contents in the winter wheat and corn grains: 0.045–0.048 mg/kg, which is almost two times lower that the Cd content in sunflower seeds. The average content of Cd in soybean is 0.072 mg/kg, and this is 1.25 times lower than in sunflower seeds and 1.50– 1.67 times higher than in the main products of grain crops..

The Cd content in by-products of winter wheat, corn, and soybean is 1.25, 1.29, and 1.15 times higher than in the main products. In sunflower seeds, it is 1.29 times higher than in sunflower by-products,

| Table 3. 5 | Statistical parame | sters of the conter | Table 3. Statistical parameters of the contents of elements in agricultural crops, mg/kg abs. dry matter | agricultural crop: | s, mg/kg abs. dry | matter | | | |
|------------|---|---------------------|--|--------------------|-------------------|--------------------|-------------------|--------------------|-----------------|
| Flement | Statistical | Winter | Winter wheat | Corn | irn | Soybean | ean | Sunf | Sunflower |
| TIMIN | measures | grains | straw | grains | straw | grains | straw | seeds | stems |
| | и | 9 | 66 | 73 | 3 | 20 | 0 | 27 | 2 |
| d d | $\overline{x} \pm t_{0.5} s \overline{x}$ | 0.34 ± 0.02 | 0.49 ± 0.04 | 0.31 ± 0.02 | 0.55 ± 0.05 | 0.18 ± 0.01 | 0.22 ± 0.02 | 0.36 ± 0.03 | 0.58 ± 0.05 |
| 10 | lim | 0.19-0.59 | 0.27-0.77 | 0.18 - 0.46 | 0.34 - 0.89 | 0.15 - 0.24 | 0.18 - 0.29 | 0.21 - 0.46 | 0.35-0.95 |
| | V, % | 26.3 | 25.4 | 21.1 | 24.1 | 14.7 | 16.5 | 21.6 | 25.2 |
| | и | 9 | 69 | 73 | 3 | 42 | 2 | 2 | 25 |
| τU | $\overline{x} \pm t_{0.5} s \overline{x}$ | 0.048 ± 0.003 | 0.060 ± 0.004 | 0.045 ± 0.003 | 0.058 ± 0.004 | 0.072 ± 0.005 | 0.083 ± 0.005 | 0.090 ± 0.009 | 0.070 ± 0.003 |
| | lim | 0.025 - 0.079 | 0.022-0.095 | 0.022-0.062 | 0.049 - 0.088 | 0.017-0.097 | 0.033 - 0.106 | 0.073-0.162 | 0.060 - 0.079 |
| | V, % | 29.0 | 29.3 | 26.1 | 16.3 | 25.7 | 19.8 | 21.4 | 8.4 |
| | и | L | 20 | 23 | 3 | 42 | 2 | 2 | 22 |
| ~ | $\overline{x} \pm t_{0.5} s \overline{x}$ | 0.023 ± 0.002 | 0.029 ± 0.002 | 0.019 ± 0.001 | 0.024 ± 0.001 | 0.019 ± 0.001 | 0.026 ± 0.001 | 0.021 ± 0.001 | 0.025 ± 0.001 |
| SK . | lim | 0.011 - 0.048 | 0.019-0.060 | 0.016 - 0.024 | 0.021 - 0.027 | 0.012-0.033 | 0.021 - 0.034 | 0.018 - 0.024 | 0.023 - 0.028 |
| | V, % | 29.3 | 29.7 | 11.7 | 7.0 | 22.8 | 9.1 | 9.5 | 6.9 |
| | и | 41 | 1 | 22 | 2 | 21 | 1 | 2 | 23 |
| Цç | $\overline{x} \pm t_{0.5} s \overline{x}$ | 0.008 ± 0.001 | 0.011 ± 0.001 | 0.004 ± 0.001 | 0.010 ± 0.001 | 0.003 ± 0.0004 | 0.009 ± 0.001 | 0.004 ± 0.0003 | 0.010 ± 0.001 |
| າ11 ກ | lim | 0.004-0.010 | 0.007 - 0.018 | 0.002-0.005 | 0.009-0.012 | 0.001 - 0.005 | 0.008 - 0.011 | 0.002 - 0.005 | 0.008 - 0.012 |
| | V, % | 24.9 | 23.5 | 29.9 | 11.0 | 26.5 | 11.5 | 19.7 | 14.1 |
| | и | 2 | 20 | 20 | 0 | 22 | 2 | 2 | 22 |
| ŗ. | $\overline{x} \pm t_{0.5} \overline{x}$ | 0.41 ± 0.02 | 0.51 ± 0.02 | 0.22 ± 0.01 | 0.36 ± 0.02 | 0.41 ± 0.01 | 0.39 ± 0.03 | 0.45 ± 0.02 | 0.42 ± 0.02 |
| 5 | lim | 0.33 - 0.46 | 0.45 - 0.59 | 0.17 - 0.29 | 0.23 - 0.50 | 0.37-0.45 | 0.31 - 0.43 | 0.39-0.51 | 0.34 - 0.50 |
| | V, % | 8.3 | 9.1 | 11.9 | 14.8 | 5.6 | 14.9 | 8.5 | 9.1 |

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EURASIAN SOIL SCIENCE Vol. 57 No. 10

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which is probably related to the biological features of this crop.

The MPC of Cd for food grains is 0.1 mg/kg; for sunflower seeds used for food, 0.2 mg/kg [17]. The exceedance of these standards was not found in this study.

Arsenic is accumulated mostly in straw and stems, but not in grains or seeds of agricultural crops. According to generalized data, the content of this metalloid in corn by-products is 1.3 times higher than in corn grain; for soybean, this difference reaches 1.4 times [12, 33]. The average content of As in plant products produced in Russia ranges from 0.020 to 0.046 mg/kg [12].

It was found that the average content of As in winter wheat grain and sunflower seeds is 0.023 and 0.021 mg/kg, respectively. There is no significant difference in this indicator between these crops. In corn grain and soybean, the As content is significantly lower and averages 0.019 mg/kg. The contents of As in the by-products of winter wheat, corn, soybean, and sunflower are higher than in the main products by 1.26, 1.26, 1.37, and 1.19 times, respectively.

The MPC of As for wheat, barley, and corn grains used for food is 0.2 mg/kg; for sunflower seeds and soybean, 0.3 mg/kg [17]. In the present study, no excess of the MPC has been observed.

Mercury in the crops is accumulated to a lesser extent in generative organs of plants. For example, the Hg content in by-products of corn and soybean is 2.9 higher than in the main products [12, 33]. Average contents of Hg in agrocenoses of Central Siberia constitutes 0.0016 mg/kg in wheat grains, 0.002 mg/kg in barley, and 0.004 mg/kg in hay of perennial grasses [12]. The average Hg content in plant products grown in different federal districts of Russia varies from 0.0005 to 0.010 mg/kg [12].

The maximum average content of this metal was found in winter wheat grain (0.008 mg/kg). The content of Hg is significantly lower in sunflower seeds (0.004 mg/kg), corn grain (0.004 mg/kg), and soybean (0.003 mg/kg). The content of Hg in by-products of these crops is higher than in the main products by 1.38 times for winter wheat, 2.5 times for corn, 3.0 times for soybean, and 2.5 times for sunflower.

The MPC of Hg is 0.03 mg/kg for wheat, barley, and corn grains and 0.05 mg/kg for sunflower seeds and soybean [17]. Actually determined concentrations of Hg in the studied crops are significantly lower than the MPC.

Chromium is a less toxic element in comparison with other studied HMs [18, 19]. According to generalized data, its safe concentration not leading to disturbance of physiological processes in plants is 0.1-0.5 mg/kg, and toxic concentration is 5-30 mg/kg [22, 24]. In the Krasnoyarsk region, the content of Cr in spring wheat grain is within 0.10-0.20 mg/kg and in barley grain, 0.18-0.22 mg/kg [12].

The maximum content of Cr was found in sunflower seeds (0.45 mg/kg). Its content in winter wheat grain and soybean was somewhat lower (0.41 mg/kg). The content of Cr in corn grain (0.22 mg/kg) was more than two times lower than in sunflower seeds. In the by-products of winter wheat and corn, the Cr content in was 1.24 and 1.64 times higher than in the main products, respectively. The contents of Cr in the main products and by-products of soybean and sunflower did not differ significantly.

In Russia, Cr concentration is only regulated for products intended for cattle feed products. The maximum permissible level of this element for feed grain is 0.5 mg/kg [2]. In our study, the Cr content in crop products and by-products remained below this value.

CONCLUSIONS

It was found that the content of acid-extractable forms of As and Cd in arable ordinary chernozems is significantly higher than in leached and typical chernozems. At the same time, no significant differences between the soils were not found for the contents of Cr. Pb. and Hg. However, there was a tendency for their higher contents in ordinary chernozems in comparison with leached and typical chernozems, which may be due to a heavier texture of ordinary chernozems in Belgorod oblast. There were no significant differences between the studied soils with respect to the content of mobile forms of Pb, Cr, and Cd, though a tendency for a higher content of mobile forms of Cd in leached chernozems in comparison with ordinary chernozems could be traced; this may be related to a higher pH in the ordinary chernozems. In none of the soils, the contents of studied HMs exceeded the existing maximum permissible and tentative permissible concentrations.

Organic fertilizers are the main source of the input of studied elements to arable soils in Belgorod oblast. The input of Cr, Pb, As, Cd, and Hg with organic fertilizers is 25, 125, 15, 29, and 40 times higher than their input with mineral fertilizers, respectively.

Maximum concentrations of Cd, Pb, and Cr were found in sunflower seeds and reached 0.09, 0.36, and 0.45 mg/kg, respectively; maximum concentrations of Hg and As were found in winter wheat grain: 0.008 and 0.023 mg/kg, respectively. Minimum average concentrations of Pb, Hg, and As were found in soybean (0.18, 0.003, and 0.019 mg/kg, respectively), whereas Cr, Cd, and As had minimum concentrations (0.22, 0.045, and 0.019 mg/kg, respectively) in corn grain. As a rule, the concentrations of considered elements were higher in by-products than in the main crop products. However, the Cd concentration in sunflower seeds was 1.29 times higher than in stems. The concentrations of Cr in the main products and by-products of sunflower and soybean did not differ significantly. The concentrations of HMs in grains of winter wheat and corn,

soybean, and sunflower seeds did not exceed the MPC values for food products, and the Cr concentration did not exceed the maximum permissible level established for forage.

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ETHICS APPROVAL AND CONSENT TO PARTICIPATE

This work does not contain any studies involving human and animal subjects.

CONFLICT OF INTEREST

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

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EURASIAN SOIL SCIENCE Vol. 57 2024 No. 10

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