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GEOECOLOGY

Assessment of Zinc Content in Agroecosystems of the Central Chernozem Region of Russia

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Abstract—Studies were conducted in 2005–2024 in the forest-steppe zone of the Central Chernozem Region in the Belgorod and Voronezh regions where the soil cover is mainly represented by Haplic Chernozems and Luvic Chernozems. The purpose of the work was to conduct an agroecological assessment of zinc content in arable soils, fertilizers, and agricultural plants. During the research, based on local monitoring data, it was established that in the arable layer of chernozems the average content of acid-soluble forms of zinc is within 36.1–36.5 mg/kg. The results of continuous agroecological monitoring for the eighth and tenth cycles indicate that the weighted average content of mobile forms of zinc in the soils of the Belgorod Oblast is consistently low (0.50 mg/kg), and in the soils of the Voronezh Oblast it has decreased from 0.45 to 0.30 mg/kg. The low supply of mobile forms of zinc to arable soils is a significant factor limiting the productivity of agroecosystems. To eliminate the deficiency of this element, it is necessary to incorporate the use of microfertilizers in the technology of cultivation. Soils of roadside agroecosystems tend to accumulate this element. An important source of zinc in soils are organic fertilizers, especially in the Belgorod Oblast, where the average application doses reached 9.6 t/ha. The average zinc content in hay of perennial legumes was within 14.0–17.8; it was 26.5 to 43.5 in the main products of leguminous crops, and 17.6 to 28.6 mg/kg in grain crops. In sunflower seeds, the content of the element was 41.1, and in sugar beet roots it was 9.2 mg/kg. No exceedances of maximum permissible zinc concentrations in soils (including roadside agroecosystems) or maximum permissible levels of its content in feed products were recorded.

Keywords: agroecosystem, heavy metals, chernozem, organic fertilizers, defecation sludge, agricultural crops, maximum permissible concentration, maximum permissible level

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INTRODUCTION

One of the most hazardous man-made pollutants of agroecosystems are heavy metals (HM) which are widely used in industry [1, 2]. Along with Pb, Cd, Hg, and As, Zn belongs to the class of highly hazardous substances. This HM is toxic to living organisms only in high concentrations, while in small amounts it is an essential trace element that plays an important role in physiological processes by being incorporated into active enzyme groups and performing a catalytic function. As a rule, the natural Zn content in plants is within the range of 20–60 mg/kg, whereas the toxic level (at which a decrease in yield is observed) is more than 300 mg/kg of dry matter [3].

In the soils of Russia, the range of variations in the total content of this HM is from 11 to 100 mg/kg [3]. Loamy soils are significantly richer in zinc than sandy and loamy sand soils. The main anthropogenic sources of zinc input into agroecosystems are mining, nonferrous metallurgy, and fuel and energy industries, as well as motor transport. A fairly large amount of zinc enters soils through the use of high doses of organic fertilizers and particularly sewage sludge.

Given the high toxicity of HM, many countries worldwide regulate their content in soils [4]. In Russia, tentative permissible concentrations (TPC) have been established to regulate the total HM content in soils depending on their granulometric composition and acidity. For example, for clayey loam soils with a pH_{KCl} of more than 5.5, the Zn TPC is 220, and for soils with a pH_{KCl} of less than 5.5, it is 110 mg/kg. To regulate the content of mobile forms of Zn extracted with an ammonium acetate buffer solution with a

Table 1. Statistical frequency indicators of zinc content in arable soils at local monitoring reference sites, mg/kg

Content	n	$\bar{x} \pm t_{05}s\bar{x}$	lim	V, %
Haplic Chernozem				
Acid-soluble forms	23	36.5 ± 2.91	23.2–52.5	18.0
Mobile forms	23	0.39 ± 0.05	0.24–0.68	29.3
Luvic Chernozem				
Acid-soluble forms	23	36.1 ± 2.20	31.6–50.5	12.5
Mobile forms	23	0.44 ± 0.05	0.26–0.70	29.4

pH of 4.8, the maximum permissible concentration (MPC) is set at 23 mg/kg. In addition, the level of low mobile Zn content (less than 2 mg/kg) is regulated, and when this level is reached, it is recommended to apply this element to agroecosystems with microfertilizers [5, 6].

The Zn content in crop products used as food is not regulated, but its concentration in animal feed is. The maximum permissible levels (MPL) of Zn content for feed grain, roughage and green fodder are 50 mg/kg [7].

The continuous agroecological monitoring program in Russia, run by the agrochemical service, usually includes checking for mobile forms of zinc in soil. The local monitoring program includes determining the zinc content in fertilizers and crops at reference sites [3]. Based on the monitoring data, an agroecological assessment of the land is done, which consists of comparing the requirements of agricultural crops to growing conditions with the agroecological conditions of a specific area.

The objective of this study is to conduct an agroecological assessment of zinc content in arable soils, fertilizers, and agricultural crops in the Central Chernozem Region, using the Belgorod and Voronezh oblasts as examples.

RESEARCH METHODOLOGY AND CONDITIONS

The research was conducted in 2005–2024 in the forest-steppe zone of the Belgorod and Voronezh oblasts, where the predominant soils are leached chernozems (Luvic Chernozems) and typical chernozems (Haplic Chernozems). The paper analyzes the results of local monitoring conducted at reference sites on agricultural land typical for the region, ranging in size from 4 to 40 ha. Soil and crop samples are collected annually from these sites for analysis.

We used the results of continuous agroecological monitoring, where soil samples are taken from the arable layer (0–25 cm) from an area of 15–20 ha, following the standard methodology used by the agrochemical service [6]. Continuous surveys are conducted in cycles (4–5 years) across the entire cultivated area of the regions. In 2016–2020 the average total cultivated area was 1425 thousand hectares in the Belgorod Oblast and 2607 thousand hectares in the Voronezh Oblast.

As part of a background monitoring program, soil samples of Luvic and Haplic chernozems, as well as steppe grasslands, were collected in an area of natural ecosystem unaffected by farming (the Yamskaya Steppe section of the Belogorie Reserve).

The arable chernozems of the Luvic reference sites under local monitoring had 56.5% physical clay, 5.6% organic matter, and a pH_{KCl} of 5.3, while in the virgin soil the values were 56.4, 9.7, and 5.3%, respectively. In arable chernozems of Haplic reference sites, the physical clay content was 57.0%, organic matter 5.7%, pH_{KCl} 5.6, and in virgin soil, 56.4, 10.1, and 6.0%, respectively. In arable Haplic chernozems of roadside agroecosystems, the average physical clay content was 55.2%, organic matter content was 5.3%, and pH_{KCl} was 5.6.

The Zn content in soil samples, crop products, and fertilizers was determined using atomic emission spectrometry following conventional methodologies used in agrochemical services [8]. The extraction of acid-soluble and mobile forms of Zn from the soil was performed using 5 M HNO_3 and an ammonium acetate buffer solution with a pH of 4.8, respectively. Chemical analyses were performed at certified testing laboratories of the Belgorod and Voronezh branches of *Ros-Agrokhim* Service. Data was processed using the *Agroekolog Online* software [9].

RESULTS AND DISCUSSION

Zinc in soils. The background content of acid-soluble forms of Zn in the humus accumulative horizon of Haplic and Luvic virgin chernozems in the Belgorod Oblast is 45.7 and 44.7, respectively, and that of mobile forms is 0.79 and 0.75 mg/kg, respectively. The level of mobile forms, assessed as low, could be a genetic feature of chernozems. In the Lipetsk Oblast, the background mobile Zn content in virgin podzolized chernozems is also low [10].

The average content of acid-soluble and mobile forms of Zn in arable Haplic chernozems is 36.5 and 0.39 mg/kg, respectively, and in Luvic chernozems, it is 36.1 and 0.44 mg/kg, respectively. Based on these data, no significant differences were found between the studied subtypes of chernozems. The content of mobile forms is 1.07–1.22% of the acid-soluble forms (Table 1).

Based on continuous agroecological monitoring data, the weighted average content of mobile Zn forms in the Belgorod Oblast between the eighth (2005–2009) and tenth (2015–2018) survey cycles remained at a consistently low level of 0.50 mg/kg. In the Voronezh Oblast, in the eighth cycle (2006–2010), this parameter was 0.45 mg/kg, decreasing by a factor of 1.5 to 0.30 mg/kg by the tenth cycle (2016–2020).

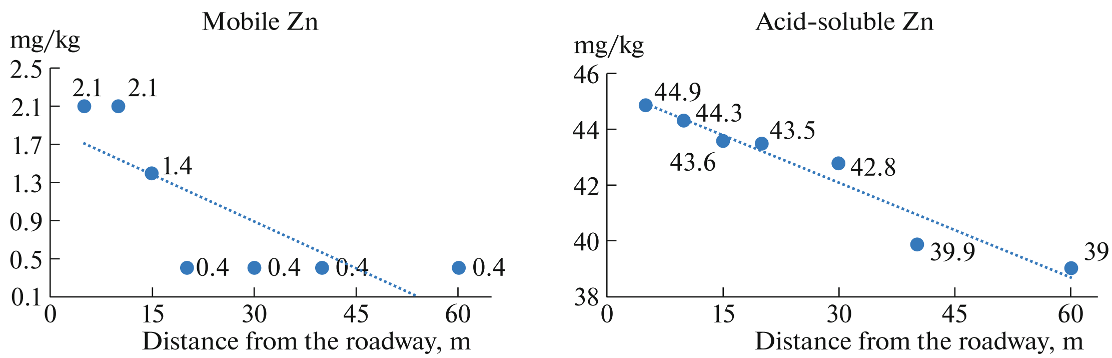

Fig. 1. Zinc content in the soil of the roadside agroecosystem (Belgorod District, M2 Crimea Highway).

As of January 1, 2021, the weighted average content of mobile Zn in arable soils in the Lipetsk, Kursk, and Tambov oblasts was 0.70, 0.59, and 0.48 mg/kg, respectively [3]. It appears that arable soils inherit low levels of this element from their virgin counterparts.

The main source of Zn in roadside agroecosystem soils is the wear and tear of galvanized car parts and tires [3, 11]. Important factors affecting the degree of soil contamination include landscape features, duration of exposure, and traffic intensity. Our research has shown that the highest content of acid-soluble (44.9 mg/kg) and mobile (2.10 mg/kg) forms of Zn was observed at a distance of five meters from the roadway. However, the acid-soluble Zn content as far as sixty meters away was at the level of uncontaminated soil (39.0 mg/kg). The concentrations of mobile forms at a distance of twenty meters were in line with the 0.40 mg/kg value typical for uncontaminated soil (Fig. 1).

The established patterns can be characterized by the following mathematical models:

Zn (a) = 45.5 – 0.113x (R^2 = 0.94);

Zn (m) = 1.87 – 0.033x (R^2 = 0.59), where Zn (a) is the acid-soluble Zn content (mg/kg), Zn (m) is the mobile Zn content (mg/kg), and x is the distance from the roadway (m).

No exceedances of the maximum permissible concentrations of this element in soils were found. However, the low availability of mobile forms of Zn in arable soils is a significant factor limiting the productivity of agroecosystems. To remedy this, microfertilizers with this element should be applied in crop cultivation.

Zinc in fertilizers and ameliorants. Mineral fertilizers produced domestically contain very small amounts of Zn. According to our data, the most common ammonium nitrate fertilizers contain an average of 5.9 mg/kg of Zn, and compound NPK fertilizers have on average 4.3 mg/kg of Zn. Thus, the use of basic mineral fertilizers is not seen as a major source of Zn in agroecosystems [12–14].

At high doses, a significant source of Zn input into agroecosystem soils are organic fertilizers [13, 15]. The content of macro- and microelements, and their ratios, vary greatly depending on the type of organic fertilizer and the techniques used to produce it. It is recommended to calculate the application rates of organic fertilizers based on their nitrogen content. For example, to apply 100 kg/ha of nitrogen with straw and manure compost, 3.3 t/ha of this organic fertilizer will be required, and 0.97 kg/ha of Zn will be added to the soil. To apply the same dose of nitrogen with cattle manure and manure slurry, 13.2 and 47.6 t/ha will be required, and the Zn input into the soil will be 0.26 and 2.56 kg/ha, respectively. In 2019–2023, the average application rates of organic fertilizers (recalculated to cattle manure) in the Belgorod and Voronezh oblasts were about 9.6 and 3.4 t/ha, and with them, 0.187 and 0.066 kg/ha of Zn entered the soil (Table 2).

In the Central Chernozem Region, defecation sludge (filtration sediment) is often used as a soil improver to chalk acidic soils, and it is also a source of zinc in the soil [16, 17]. Its average application rate is 8–12 t/ha, and it is applied once every ten years. The Zn input into the soil is estimated at 0.15–0.23 kg/ha. Between 2019 and 2023, liming in the Belgorod and Voronezh oblasts was carried out on a relatively small

Table 2. Statistical frequency indicators of Zn content in organic fertilizers and defecation sludge, mg/kg

Fertilizer (ameliorant)		Dry matter, %	*n*	$\bar{x} \pm t_{05}s\bar{x}$	lim	V, %
Fertilizer	Manure slurry	2.22	22	53.7 ± 6.7	30.4–78.2	28.4
	Straw and manure compost	56	20	294 ± 41	153–387	30.0
	Cattle manure	25	28	19.5 ± 2.1	12.4–32.7	28.0
Defecation sludge		87	18	19.2 ± 2.6	10.3–28.2	27.0

Table 3. Statistical frequency indicators of Zn content in crops at local monitoring reference sites, mg/kg of absolutely dry matter

Crops		*n*	$\overline{x} \pm t_{05}s\overline{x}$	lim	V, %
Winter wheat	grain	22	28.6 ± 1.6	26.4–34.0	11.6
	straw	22	10.4 ± 0.7	8.6–13.7	14.1
Barley	grain	25	25.4 ± 1.6	19.4–32.7	15.7
	straw	25	11.9 ± 1.3	7.8–18.2	26.1
Sugar beet	roots	20	9.2 ± 0.9	6.0–12.0	21.7
	tops	20	19.3 ± 2.4	12.0–26.7	26.1
Corn	grain	25	17.6 ± 0.9	13.0–20.6	12.1
	straw	25	14.0 ± 0.3	13.3–15.9	4.8
Soybeans	grain	22	35.6 ± 3.5	25.3–47.3	22.5
	straw	22	6.4 ± 0.6	4.5–8.5	20.7
Peas	grain	20	26.5 ± 1.5	17.3–30.9	12.6
	straw	20	3.5 ± 0.5	1.8–5.4	30.4
White lupin	grain	20	43.5 ± 1.9	36.5–51.1	9.4
	straw	20	9.0 ± 1.2	6.1–16.2	28.5
Sunflower	seeds	25	41.1 ± 1.3	34.1–45.7	7.4
	stalks	25	14.6 ± 0.8	13.0–19.3	12.5
Clover	hay	22	16.5 ± 0.8	13.0–19.2	11.0
Sainfoin	hay	22	17.8 ± 1.0	12.7–20.7	12.7
Alfalfa	hay	22	14.0 ± 1.8	6.9–19.8	29.3
Steppe grasses		20	27.7 ± 0.4	26.5–28.7	2.8

area of 44 100 ha/year (3.1% of the crop area) and 16 800 ha/year (0.6%), respectively [18].

The application of even water-soluble forms of Zn to chernozem soils (especially those with a *pH* close to neutral) with fertilizers does not always result in a noticeable increase in the content of mobile forms because of rapid formation of poorly soluble carbonates of this element. Therefore, in modern agronomic technologies, microfertilizers containing Zn are used not for direct application to the soil, but for seed treatment and foliar application.

Zinc in crops. Generally, the content of trace elements in crops varies significantly depending on the soil and climate conditions of the region and the biological properties of plant species. The average Zn content in natural grasslands on the chernozems of Central Siberia, which have low levels of mobile Zn, is 25.0 mg/kg [19]. Our research has shown that the Zn content in steppe grasses (feather grass, sheep fescue, crested hairgrass, etc.) of natural ecosystems averages 27.7 mg/kg, which correlates well with data obtained in Central Siberia.

The average Zn content in clover hay (Central Siberia) is 20.0 mg/kg [19]; our studies yielded very similar results (16.5 mg/kg). Of the perennial legumes cultivated in the forest-steppe agroecosystems of the Central Chernozem Region, the highest average zinc content was found in sainfoin hay (17.8 mg/kg), and the lowest in alfalfa (14.1 mg/kg) (Table 3).

In the agroecosystems of the Saratov Oblast, the average Zn content in legume crops is 31.2 mg/kg [1]. In our studies of legumes, the highest Zn content was found in the grain of white lupine (43.5 mg/kg); much less of this element accumulated in soybeans (35.6 mg/kg) and peas (26.5 mg/kg). The Zn content in the grain of white lupine, soybeans, and peas was higher than in straw by 4.83, 5.56, and 7.57 times, respectively.

In spring wheat and barley grains cultivated in Central Siberia, the element content is 28.5 and 25.3 mg/kg, respectively [19]. On the chernozems of the Saratov Oblast, the average Zn content in the main grain crops (rye, wheat, barley, and oats) ranges from 18.9 to 26.6 mg/kg [1]. In our studies, the highest Zn content among grain crops was found in winter wheat (28.6 mg/kg). The grain of barley and corn contained significantly lower amounts of this metal: 25.4 and 17.6 mg/kg, respectively. Zn accumulated in greater quantities in the grain of these crops than in by-products (straw), but the ratio was narrower than in legumes. For example, the Zn content in winter wheat, barley, and corn grain was 2.75, 2.13, and 1.26 times higher than in straw, respectively.

In experiments conducted in the Saratov Oblast, sunflowers were fairly high in Zn (35.0 mg/kg) in their main product. In the forest-steppe zone of Central Chernozem, the Zn content in sunflower seeds was also fairly high (41.1 mg/kg) compared to other crops studied. The content of this element in the by-products of this crop (stalks) was 2.82 times lower than in the seeds. In sugar beet roots, the average Zn content was 9.2 mg/kg, and in the tops, it was 19.3 mg/kg, which is 2.1 times higher.

No MPL exceedances were observed in the crop products studied.

In 2019–2023, the average yield of winter wheat (at 14% moisture content) in the Belgorod Oblast was 5.36, that of barley 3.96, corn 8.04, soybeans 2.24, sunflower seeds (at 7% moisture) 3.07, perennial grass hay (at 16% moisture) 2.9, sugar beet roots (at 75% moisture) 47.9 t/ha [16], while Zn removal from agroecosystems with the main production of these crops is estimated at 0.132, 0.087, 0.122, 0.069, 0.117, 0.039, and 0.110 kg/ha, respectively.

CONCLUSIONS

Thus, according to local monitoring data, it has been found that in the arable layer of chernozems in the forest-steppe zone of Central Chernozem Region, the average content of acid-soluble zinc forms ranges from 36.1 to 36.5 mg/kg. The results of continuous agroecological monitoring in the eighth and tenth cycles show that the weighted average content of zinc mobile forms in the soils of the Belgorod Oblast is at a consistently low level (0.5 mg/kg), while in the soils of the Voronezh Oblast, it has declined from 0.45 to 0.30 mg/kg. There is a tendency for this element to accumulate in the soils of roadside ecosystems. An important contributor of zinc to agroecosystems are organic fertilizers, especially manure slurry and straw and manure compost. The average zinc content in hay from perennial legumes ranged from 14.0 to 17.8 mg/kg, while in the main production of legumes it was 26.5 to 43.5 mg/kg, and in grain crops it was 17.6 to 28.6 mg/kg. The content of this element in sunflower seeds was 41.1 mg/kg, and in sugar beet roots, 9.2 mg/kg. In all crops studied, with the exception of sugar beet, the zinc content in the main product was higher than in the by-product. No exceedances of the maximum permissible concentrations of zinc in soils or maximum permissible levels in feed products were recorded.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflict of interest.

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