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Special Aspects Of Heavy Metals Accumulation In Chernozem Soils.

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ABSTRACT

A particular danger for agrobiocenoses is represented by heavy metals that tend to accumulate in and poison living organisms. The study aimed to reveal the features of heavy metals (Cd, Pb, Zn, Cu, Co, and Mn) accumulation in the soils of the Samara Trans-Volga region. The experiments were conducted in 2012-2014. The objects of the study were leached chernozem, modal chernozem, and southern chernozem. The results of the experiments established that the greatest number of total forms of Cd, Pb, Zn, Mn, and Cu in the conditions of the Samara Trans-Volga region is accumulated in leached chernozem and that of Co is accumulated in modal chernozem. The maximum level of localization of mobile forms of Cd, Pb, Cu, and Co also accounts for leached chernozem. The content of total forms of heavy metals in the soil is largely determined by the presence of clay and silt fractions (r = 0.71-0.92 and r = 0.64-0.92, respectively) and also by the content of humus (r = 0.53-0.98), especially Cd, Pb, Zn, and Cu (r = 0.85-0.98). The presence of mobile Cd, Pb, Cu, and Co is associated with soil dispersity and the presence of P_2O_5 (r = 0.58-0.91) in the soil, and the presence of Mn is associated with humus (r = 0.51). In the years of research, the level of concentration of total and mobile forms of heavy metals in all studied subtypes of chernozems was close to the background values and did not exceed the maximum allowable concentrations (MAC).

Keywords: Heavy metals, chernozem, soil, humus, accumulation, cultivated lands, cadmium, lead, copper.

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INTRODUCTION

Under conditions of increasing human anthropogenic impact on the biosphere, a particular danger for agrobiocenoses is represented by heavy metals, the accumulation of which is increasing every increasing every year in cultivated soils [1, 2]. The heavy metals enter the soil and plants, accumulate in agrosystems, and are included in the metabolic cycles of living organisms, forming highly toxic carcinogenic–organometallic compounds that are not biochemically decomposed and are heavily removed (the half-removal period of zinc from the soil is 500 years, that of cadmium is 1100 years, and that of lead is up to 5000 years) [3]. The contamination of soil by heavy metals through food chains leads to the violation of all components of the ecosystem and the degradation of human society as a whole.

In this context, studies aimed at analyzing the features of accumulation and migration of heavy metals in agrobiological objects, as well as the search for technological methods that would reduce their entry into biological circulation, are of particular relevance [4, 5].

The study aimed to identify the special aspects of the heavy metals accumulation (Cd, Pb, Zn, Cu, Co, and Mn) in the soils of the Samara Trans-Volga region.

MATERIALS AND METHODS

The experiments were performed on the left-bank territory of the Samara region, located in the middle reaches of the Volga River. The climate of the region is continental, with a pronounced unstable humidity, which is insufficient on the southern borders. The average temperature of the warmest month (July) is +19°C - 22°C, whereas that of the coldest (January) is 13.5°C–14.0°C. The sum of effective temperatures (above +10) varies from 2200°C in the north of the region to 2600°C in the south. Atmospheric precipitation is distributed unevenly, both over the years and for individual periods of the year, from 200 to 600 mm. Most of the precipitation occurs in the warm season. The relief is represented by asymmetrically constructed watersheds, with the predominance of open steppe plains flatlands at an altitude of 75–100 m above sea level, sloping toward the rivers. In some places, they intersect with hollows and ravines [6, 7].

To solve the tasks set, in 2012–2014, cultivated lands that best reflect the zonal natural features of the Samara Trans-Volga region in relief, type of soil, soil-forming material, chemistry of groundwater, as well as by type of agricultural use (crop rotation, tillage, predecessors, crops, etc.,), were investigated in Kamyshlinsky area in the northern zone, Kinelsky area in the central zone, and Bolsheglushitsky municipal area in the south zone. In these cultivated lands, the elementary landscapes were determined, and stationary test sites for taking the soil samples were identified in these landscapes. The study objects were leached chernozem, modal chernozem, and southern chernozem soils.

The experiments were performed in accordance with the existing methodological guidelines [8, 9]. Soil samples for analysis were taken using the standard methods [10]. From each sampling site, located at three equidistant points (the vertices of an isosceles triangle), samples weighing up to 1 kg were taken from the upper (0–10 cm) soil horizon using an entrenching shovel; the samples from the three sites were mixed thoroughly, and an average sample weighing 300–400 g was selected using the envelope method. The three samples were again poured together, mixed, and a 500 g sample was also selected using the envelope method and placed in a marked paper bag. The process was repeated for samples taken from the middle (10–20 cm) and lower horizons (20–30 cm). The soil samples in the bags were delivered to the laboratory of the Federal State Institution of Samara Agrochemical Service Station, which has an accreditation certificate of a testing laboratory № POCC RU. 0001.510565 (valid until 25.04.2020).

The soil samples were prepared using the traditional method to determine the total content of heavy metals in them. The soil was air–dried. Then, the average soil sample was ground in a porcelain mortar and sieved through a nylon sieve having a sieve size of 1 mm, and 2 g of soil was weighed and placed into a marked parchment paper bag. For determining the total forms of heavy metals in soils and plant samples, preliminary preparation of samples was carried out by the method of dry mineralization at 575°C. The mobile forms of the compounds were recovered by an acetate–ammonium buffer (AAB) solution (pH 4.8.). The final determination of the elements was carried out using flame and electrothermal atomic absorption spectrophotometer Spectr

5-4 in acetylene–air flame. At the same time, a blank analysis was performed, including all the stages except soil sampling. The arithmetic mean of two parallel determinations was considered as the final test result.

In addition to determining the presence of heavy metals in soils, the following were also determined: humus content by the Tyurin method, pH of aqueous extract; content of mobile phosphorus in neutral soils according to Chirikov method and that in carbonate soils according to Machigin method; content of exchangeable potassium in neutral soils according to Chirikov method and that in carbonate soils according to Machigin method; and content of easy hydrolysable nitrogen in the acid (0.5 N H_2SO_4) extract by the method suggested by Tyurin and Kononova and modified by Kudeyarov [11, 12].

The content of mobile phosphorus and exchangeable potassium was determined using different methods in order to ensure comparability; the results of laboratory analysis using Machigin method were obtained, and they were recalculated using the Chirikov method. Mathematical processing of the experimental material was performed at the computer center of the Federal State Budgetary Educational Institution of Higher Education Samara State Agricultural Academy.

RESULTS AND DISCUSSION

A study of the dynamics of the heavy metals accumulation in soils of different geographical regions was conducted by many researchers [13, 14, 15, 16] who pointed out that the volume of toxicants' localization in the arable layer is largely determined by the physical, mechanical, and agrochemical properties of soils. Analysis of soil samples in our experiments revealed that the chernozem subtypes under study have significant differences in a number of parameters——accumulative capacity of the soil and the level of its fertility—depending on the heavy metal. Thus, leached chernozem has a comparatively high specific gravity in the structure of aggregates of finely dispersed clay (<0.01 m) of 57% and silt particles (<0.001 mm) of 44%, which result in high sorption capacity. In modal chernozem, the quantity of the particles did not exceed 53% (7.5% less than the control index) and 35% (25.7% less than the control index) on average, and in southern chernozem, their amount did not exceed 47% (21.3% less than the control index) and 31% (41.9% less than the control index). The differences in the content of humus can also be clearly traced. In the upper horizon of leached chernozem (0–10 cm), humus concentration was 6.3%, and in the average for the arable profile (0–30 cm), it was 6.2%, which was 18.8%–19.6% higher than the indices of modal chernozem and 61.5%–63.1% higher than those of southern chernozem. The reaction of the soil medium and the amount of exchange bases changed with southing. In the leached chernozem, pH of the aqueous extract varies within the range of 6.0–6.2, with a total of exchange bases of 370–460 to mg eq/kg of soil. At the same time, Ca accounts for 78.0%–87.0% of the total volume. The reaction of modal chernozem solution is slightly shifted toward the alkaline side (pH 6.6–6.9), and the sum of the exchange bases is 373–410 mg/eq/kg. This is 8.8%–12.2% less than the indices of the first subtype. In addition, the presence of Na in the lower horizon (20–30 cm) can be traced, and the specific gravity of Mg increases to 16.6%–22.1%.

The southern chernozem has an alkaline reaction in the 0–20 cm layer (pH 7.2–7.3) and in the 20–30 cm layer (pH 7.5). The amount of exchangeable bases was decreased to 380 mg/eq/kg (0–20 cm layer) and – 300 mg/eq/kg (20–30 cm layer). The presence of Na^+ ions is noted throughout the soil profile. The fraction of Ca^{2+} ions accounts for 71.7%–82.4% of the total sum of absorbed bases.

Analysis of control indices of the presence of mobile forms of P_2O_5 and K_2O revealed that leached chernozem is richest in these biogenic elements (P_2O_5on average 211 mg/kg and K_2O, 213 mg/kg of soil) compared with modal and southern chernozem. The maximum concentration of P_2O_5 and K_2O were observed in the upper horizon of the soil (0–20 cm). The reserves of P_2O_5 and K_2O in modal chernozem decreased, on average, to 191 and 201 mg/kg, or by 10.5% and 6.0%, respectively; in the southern chernozem, they decreased to 180 and 197 mg/kg, or by 17.2% and 8.1%, respectively.

The studies revealed that all subtypes of chernozem had Cd, Pb, Zn, Cu, Co, and Mn. However, their total volumes do not exceed the MAC; however, leached chernozem accumulates the greatest amount of heavy metals. Thus, the level of accumulation of Cd (0.44 mg/kg) in leached chernozem was 1.22 times higher than that in modal chernozem (0.36 mg/kg) and 1.69 times that in southern chernozem (0.26 mg/kg). Similar patterns can also be observed for Pb: 18.7 mg/kg (leached chernozem, 1.68 times) versus 11.1 mg/kg (modal chernozem) and 7.86 mg/kg (southern chernozem, 2.37 times). The accumulation volumes of Zn were approximately equal and amounted to about 40.0 mg/kg in the steppe zone and 44.0 mg/kg in the forest-steppe zone. The concentration of Cu in leached chernozem was, on average, 19.9 mg/kg, exceeding the indices of modal chernozem and southern chernozem by 24.8% and 89.0%, respectively. The Co content in the soils of the northern and central zones was approximately equal, showing a slight variation of 9.17–9.92 mg/kg. In the steppe zone, the concentration of Co in the arable layer did not exceed an average of 6.31–6.56 mg/kg, or it was lower by 45.3%–51.2%. Zonal features were also observed with respect to Mn. In the north of the Samara region, in leached chernozem, the quantity of Mn in the arable layer averaged 707 mg/kg; in the center, in the modal chernozem, it was 612 mg/kg; and in the south, in the southern chernozem, it was 464 mg/kg.

Thus, in terms of the quantitative content of the total forms of Cd, Pb, Zn, Cu, Co, and Mn, the soils of the Samara Trans-Volga region form a decreasing series, such that leached chernozem > modal chernozem > southern chernozem.

The increased level of metal accumulation in the chernozem of the northern forest-steppe, along with the changes in the physical and chemical properties of the soil and the complex, natural climatic conditions, is apparently caused by man-made impact on agrobiocenoses.

Certain regularities were also traced in terms of the distribution of chemical elements along the profile of the arable horizon. In all subtypes of chernozems, the largest amount of chemical elements was concentrated in the upper humus horizon (0–10 cm), which is due to the large absorption capacity of the organic and mineral part of this soil layer. At a depth of 10–20 cm, the content decreased by an average of 1.5%–5.6%. In the lower horizon (20–30cm), it increased again to average values. Apparently, these variations are caused by the washing out of heavy metals by atmospheric precipitation from the upper and middle layers of the soil and by their displacement to the illuvial horizon where they are absorbed by clay and silt soil particles.

An analysis of the quantitative composition of accumulants showed that in all the subtypes of chernozems assessed in this study, Mn occupies the largest part of the total volume, which, on average, is 87.6%–88.7%, followed by Zn (5.5%–7.6%), then Cu (2.1%–2.6%), Pb (1.5%–2.3%), Co (1.2%–1.4%), and Cd (0.04%–0.05%).

For a more objective estimation of the volumes of accumulation of metal toxicants and determination of the level of their biological hazard, we compared the results obtained with the MAC indices and the background values. The calculations showed that in the northern forest-steppe, despite a relatively small total amount, Co, which is 0.65 MAC, is closer to the threshold parameter, followed by Pb (0.62 MAC), Mn (0.47 MAC), Zn (0.44 MAC), Cu (0.36 MAC), and Cd (0.15 MAC). With respect to the background value, heavy metals form the following series: Mn>Pb>Zn>Cu>Co>Cd. The accumulation levels of Mn, Pb, Zn, and Cu were 44.0%, 38.0%, 34.0%, and 10.0%, respectively, above the background value.

Certain regularities were also traced on modal chernozem. The highest MAC index of 0.69 was also noted for Co. The toxicity levels of Mn and Zn were approximately the same, at 0.41 and 0.40 MAC, respectively. Accumulation of Pb did not exceed 0.37 MAC, and that of Cu was 0.30 MAC, which is, respectively, 67.5% and 20.0% lower than the parameters of leached chernozem. The minimum value of 0.12 MAC was found in Cd. With respect to the background level of accumulation, the elements are arranged in the following order: Mn > Zn > Cu > Pb > Co > Cd. In this case, the excess of the background value was noted only in Mn and Zn (by 16.0% and 15.0%, respectively).
The accumulation amount of toxicants in the southern chernozem was significantly lower than that in the northern and central zones. However, even in this case, Co was 0.45 MAC, which was closer to the limit index, followed by Zn(0.40 MAC) and Mn (0.21 MAC). The amount of Pb and Cu did not exceed 0.26 MAC and 0.20 MAC, respectively, and Cd was 0.08 MAC. During the years of research, prevalence over the background indicator was noted only in Zn, which was by 16.0%. With respect to this parameter, the metals under study could be arranged in the following decreasing series: Zn>Mn>Cu>Pb>Co>Cd.

An important criterion characterizing the degree of accumulation of heavy metals in agrocenoses is their reserve in the root zone (0–30 cm), expressed in kg/ha. Calculations showed that the number of total forms of elements in leached chernozem can vary from 1.32 kg/ha in Cd to 2121 kg/ha in Mn. The arable horizon of the northern zone contained relatively large amount of Zn, Cu, and Pb - 132.0, 59.7, and 56.1 kg/ha, respectively. The volume of accumulation of Co was 28.2 kg/ha. The total weight of the metal toxicants studied per hectare was 2398 kg. In accordance with the patterns revealed previously, modal chernozem contained Cd 0.24 kg less per 1 hectare, Pb 22.8 kg less, Zn 10.8 kg less, Cu 10.2 kg less, and Mn 285 kg less; on the contrary, Co was 0.9 kg more per hectare. The accumulation level of Cd, Zn, Cu, and Co in the southern chernozem was 1.09 – 1.82 times less, and that of Pb was 2.37 times less than that in the soil cover of the northern zone, and 1.02 – 1.51 times less than that in the central zone. The total weight of heavy metals per hectare was 1589 kg, which is 809 kg less than that the northern zone and 481 kg less that than the southern zone.

According to several researchers [17, 18, 19, 20], the greatest danger to biological objects is not the total forms of metals, but their mobile forms. The experiments that were conducted showed that the volume of heavy metals involved in the biological circulation and their mobility in the cultivated lands of the Samara Trans-Volga region is largely determined by the zonal features of the soil environment. Analyses revealed that the mobility of Cd with displacement from north to south decreases, on average, from 26.5% in leached chernozem to 20.4% in modal chernozem and 11.5% in southern chernozem. At the same time, the potentially dangerous amount of toxicant per hectare is decreased from 0.35 kg in the north to 0.22 kg in the center and 0.09 kg in the south (Table 1)

Table 1: Content of total and mobile forms of heavy metals in soil, 2012–2014.

Soil	Indices	Elements					
		Cd	Pb	Zn	Cu	Co	Mn
leached chernozem	total form, kg/ha	1.32	56.1	132.0	59.7	28.2	2121
	mobile form, kg/ha	0.35	2.07	1.02	1.89	1.35	111.9
	% mobility	26.5	3.7	0.8	3.2	4.8	5.2
modal chernozem	total form, kg/ha	1.08	33.3	121.2	49.5	29.1	1836
	mobile form, kg/ha	0.22	1.53	1.74	0.42	0.36	159.9
	% mobility	20.4	4.6	1.4	0.8	1.2	8.7
southern chernozem	total form, kg/ha	0.78	23.6	120.9	32.7	19.2	1392
	mobile form, kg/ha	0.09	1.50	1.26	0.30	0.89	76.8
	% mobility	11.5	6.3	1.0	0.9	4.6	5.5

In relation to Pb, the inverse relationship was traced during the years of research. Its highest mobility (5.2% - 7.5%) was observed in southern chernozem, whereas the lowest (3.5% - 3.8%) was observed in leached chernozem. Mobility of the toxicant in modal chernozem was equal to an average of 4.6%, and its available volumes in the arable layer (0–30 cm) averaged 1.53 kg/ha, which is 35.3% less than in leached chernozem (2.07 kg/ha). The reserves of available Pb in southern chernozem were equal to an average of 1.50 kg/ha.

The mobility of Zn was more pronounced in modal chernozem and reached an average of 1.4%. In leached chernozem, it was 0.8%, and in southern chernozem, it was 1.0%. Obviously, low migration of Zn in the years of research is due to the arid type of weather conditions and the lack of moisture in the soil profile. It has been established that in the soils of the northern zone, about 1.02 kg of Zn potentially accessible to plants per hectare is accumulated, in the central zone it is 1.74 kg/ha, and in the southern zone it is 1.26 kg/ha.
The mobility of Cu was more pronounced in leached chernozem and varied from 2.8% to 3.6%. The volume of biologically active Cu was equal to 1.89 kg/ha. In the modal and southern chernozems, its mobility did not exceed 0.8%–0.9%, and its bioavailability was 0.42 and 0.30 kg/ha, respectively, which is 4.6 and 6.3 times less than that in the soil of the northern zone.

Leached chernozem also conditioned relatively high mobility of Co(4.3%–5.3%). With the transition of values to modal chernozem, the absorption of Co increased, and mobility decreased to 1.0%–1.5%. Again it increased to 4.1%–4.8% in the southern chernozem. The content of mobile Co in the studied subtypes of soils (leached, modal, and southern chernozems) was 1.35 kg/ha, 0.36 kg/ha, and 0.84 kg/ha, respectively.

Mn, on the contrary, showed great biological activity in modal chernozem, achieving mobility of 8.5%–8.8%. The content of mobile forms in the arable horizon averaged 159.9 kg/ha. In the soil of the northern zone, the mobility of Mn ranged from 5.0% to 5.4%, and its reserves in the upper soil layer (0–30 cm) were 111.9

kg/ha. In southern chernozem, the volume of accumulated Mn was within 76.8 kg/ha, or 5.5% of the total content.

A mathematical analysis of the results obtained revealed a close relationship between the content of total forms of heavy metals and the presence of clay and silt fractions in the soil. Correlation coefficients were r = 0.71 – 0.92, 0.64 – 0.92, respectively, and with humus content r = 0.53 – 0.98) (Table 5). The concentration of Cd, Pb, Zn, and Cu was determined to a greater extent by the presence of organic matter in the soil (r = 0.85 – 0.98). A clear dependence of Pb to the volume of absorbed bases and, in particular, the content of mobile forms of P_2O_5 (r = 0.72, 0.88) in the soil was traced.

A similar dependence was also observed for Cd, Zn, Mn, and Co (r = 0.62 – 0.85). The analysis revealed that the level of concentration of both total and mobile forms of metals in the soil during the years of research was practically independent of the pH of the soil medium. Obviously, the limits of its variation in the cultivated lands of the Samara Trans-Volga region are relatively small and do not have a significant effect on the processes of metal accumulation in the soil. The calculations established a close relationship of mobile Cd, Pb, Cu, and Co with the soil dispersity and the presence of P_2O_5 in it (r = 0.58 – 0.91). The presence of mobile Mn correlated, on average, with the presence of humus (r = 0.51), clay fractions (r = 0.32), and saturation with absorbed bases (r = 0.32). Zn was determined to a certain extent by the reaction of the soil medium (r = 0.34).

Thus, in terms of mobility of heavy metals in soils, the following series can be constructed. leached chernozem–: Cd>Mn>Co>Pb>Cu>Zn; modal chernozem –: Cd>Mn>Pb>Zn>Co>Cu; and southern chernozem–: Cd>Pb>Mn>Co>Zn>Cu.

A comparative analysis of the obtained results and MAC indices for mobile forms of metal toxicants revealed that the level of accumulation of chemical elements in the soils of the forest-steppe and steppe zones of the Samara Trans-Volga region is significantly lower than the control indices and does not exceed 0.37, 0.23, and 0.21 MAC, respectively, in leached chernozem on Mn, Ca, and C (Table 2).

Table 2: Content of mobile forms of heavy metals (relative to MAC), 2012–2014

Soil	Elements					
	Cd	Pb	Zn	Cu	Co	Mn
leached chernozem	0.23	0.11	0.02	0.21	0.09	0.37
modal chernozem	0.15	0.09	0.03	0.05	0.02	0.53
southern chernozem	0.07	0.08	0.02	0.03	0.06	0.27
MAC	0.5	6.0	23.0	3.0	5.0	100.0

The concentration of Pb, Co, and Zn was even smaller and was equal to 0.11, 0.09, and 0.02 MAC, respectively. Similar patterns were observed in modal and southern chernozems. In the soil of the central zone, the metals were located in the following descending series: Mn > Cd > Pb > Cu > Zn > Co; in the south zone, they were in the following descending series: Mn > Pb > Cd > Co > Cu > Zn.

CONCLUSIONS

On the basis of the results of the studies, it can be concluded that the largest number of total forms of Cd, Pb, Zn, Mn, and Cu under conditions of the Samara Trans-Volga region is accumulated in leached chernozem, and that of Co is accumulated in modal chernozem. The maximum level of localization of mobile forms of Cd, Pb, Cu, and Co also accounts for leached chernozem, and that of mobile forms of Zn and Mn accounts for modal chernozem. The content of total forms of heavy metals in the soil is largely determined by the presence of clay and silt fractions (r = 0.71 – 0.92 and r = 0.64 – 0.92) and also by the content of humus (r = 0.53 – 0.98), especially for Cd, Pb, Zn, and Cu (r = 0.85 – 0.98). The presence of mobile Cd, Pb, Cu, and Co is associated with soil dispersity and the presence of P_2O_5 (r = 0.58 – 0.91) in it, and the presence of Mn is associated with humus (r = 0.51). During the study period, the level of concentration of total and mobile forms of metal toxicants in all chernozem subtypes studied was close to the background values and did not exceed the MACs.

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