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GEOECOLOGY

Agroecological Assessment of Heavy Metals and Arsenic Content in Ordinary Chernozem in the Central Chernozem Region of Russia

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Abstract—Agroecological assessment of the contents of Mn, Zn, Ni, Cr, Cu, Pb, Co, As, Cd, and Hg in ordinary light-clay chernozems is carried out in the steppe zone of the Central Chernozem region. As a result of these studies, it has been found that the contents of the studied elements in the ordinary virgin chernozems was within the variation ranges of their concentrations in arable analogs or even lower. Only the gross content of Mn in the virgin soil was above the upper limit of variation in the content of this element in arable soils. By the average gross content in ordinary arable chernozems, the elements form the following descending series (mg/kg): Mn (397) > Zn (42.9) > Ni (33.1) > Cr (23.7) > Cu (15.8) > Pb (11.2) > Co (9.51) > As (5.48) > Cd (0.35) > Hg (0.023), and in terms of the average content of mobile forms, the dependence is slightly different: Mn (4.14) > Pb (0.75) > Ni (0.59) > Zn (0.36) > Cr (0.31) > Cu (0.1) > Co (0.09) > Cd (0.04). The APC and MAC of the studied elements did not exceed the established standards in the studied soils; therefore, it is safe to grow eco-friendly crop products. The contents of mobile forms of Mn, Zn, Cu, and Co correspond to a low abundance; therefore, these elements should be introduced into agrocenoses with trace fertilizers to increase the yield and quality of agricultural products.

Keywords: agroecological monitoring, clarke, biological absorption coefficient, soil, chernozem, background monitoring

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In the modern world, the anthropogenic impact on the agroecosystems increases steadily, including due to the input of some elements that are widely used in industry. Many of them (Mn, Zn, Cu, Co, Ni, Cr, Pb, Cd, and Hg) have an atomic weight of more than 40 amu, and the term "heavy metals" (HMs) is applied to them [1–3]. This group often comprises As, a metalloid [4]. Since the element distribution in the agroecosystems is characterized by high spatial variability determined by both natural and anthropogenic factors, the Program of State Agroecological Monitoring provides for periodic estimation of the gross content and concentration of mobile forms of many HMs in the agricultural soils [5, 6].

The physiological role for the plants of elements such as Mn, Zn, Cu, and Co was proved long ago; the influence of Ni and Cr on the biological processes has been studied less. However, these elements can be extremely toxic for plants and warm-blooded animals if their concentrations are high. The positive role of Pb, Cd, Hg, and As in vital processes has not yet been defined accurately, but their toxic action on humans has been studied well; therefore, the content of these elements is normalized in raw food and food products. In terms of the toxicity level, Pb, Cd, Hg, Zn, and As belong to the first class (highly hazardous substances); Cu, Co, Ni, and Cr, to the second class (moderately hazardous); and Mn, to the third class (low hazardous) [7, 8].

The agroecological estimation of HM contents in soils involves the comparison of particular monitoring results to the hygienic standards, which include the approximate permissible concentrations (APC) or the maximum allowable concentration (MAC), the clarke values of elements, and their regional background values [9, 10]. Furthermore, the content of mobile forms of necessary trace elements for the plants such as Mn, Zn, Cu, and Co in the soils was determined to be low; in this case, trace fertilizers with these elements are recommended [11].

The purpose of this work is to perform an agroecological estimation of the contents of Mn, Zn, Ni, Cr, Cu, Pb, Co, As, Cd, and Hg in ordinary chernozems

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Table 1. Contents of heavy metals and arsenic in ordinary virgin chernozem

Element	Gross content, mg/kg	Content of mobile forms	
		mg/kg	% of gross content
Mn	480.0	4.10	0.85
Zn	47.8	0.35	0.73
Ni	29.8	0.34	1.14
Cr	20.3	0.16	0.79
Cu	20.1	0.10	0.50
Pb	13.9	0.53	3.81
Co	9.60	0.07	0.73
As	5.60	no data	no data
Cd	0.40	0.032	8.0
Hg	0.026	no data	no data

in the steppe zones of the Central Chernozem Region (CCR).

STUDY PROCEDURE

In the CCR, ordinary chernozems are distributed in the steppe zone of Belgorod and Voronezh oblasts. In the plough land structure, they occupy 1 247 000 ha. These soils were formed approximately 9–12 ka under the influence of steppe vegetation [12].

The studies were conducted in 2016–2020 in Rovenskii district of Belgorod oblast. In arable soils, 22 sections of ordinary light-clay chernozems were made. In the specially protected area of Rovenskii Nature Park, two sections of light-clay virgin ordinary chernozem were made and 25 samples of miscellaneous steppe herbs represented primarily by mat grass, sheep fescue, fescue, etc., were collected. In the arable soils, the average content of physical clay in the 0–25 cm layer was 72.5%, C_{org} according to Tyurin was 3.02%, the pH of the aqueous extract (pH_{H_2O}) was 7.8, while in the virgin soil, they were 67.0%, 3.77%, and 7.1, respectively. The ash content in absolutely dry substance of the plant samples was 7.2%, on average.

The chemical analyses were conducted at a certified testing laboratory. The gross content of the elements (5 M HNO_3 extragent) and the concentration of their mobile forms in the soil extracted by an ammonium acetate buffer (AAB) solution with pH 4.8 were calculated using the atomic emission spectrometry method. The gross content of the elements in the plants was estimated using the procedures established in the agrochemical service [13].

To assess the intensity of accumulation of biophile elements in the soils, the biological absorption coefficient (BAC), which is the quotient of the amount of an element in the plant ash by its gross content in arable soil, was evaluated [5]. The statistical processing of the results of local monitoring conducted by using the Microsoft Excel program included the calculation of the confidence interval for the average values ($\bar{x} \pm t_{05} s\bar{x}$), the minimum and maximum values of the element concentration (*lim*), as well as the variation coefficient (*V*, %).

RESULTS

To assess the data of agroecological monitoring, it is important to obtain the results of background monitoring, which as a rule is performed on the soils of specially protected natural areas (SPNAs) that are not subject to significant anthropogenic action. By the gross content in the 0–25 cm layer of ordinary chernozem in Rovenskii Natural Park, the elements form the following descending series: Mn > Zn > Ni > Cr > Cu > Pb > Co > As > Cd > Hg. In addition to the total content in soils, for most elements, the concentration of their mobile forms available for the plants is determined. By this indicator, the elements form the following series: Mn > Pb > Zn > Ni > Cr > Cu > Co > Cd. Most of Cd (8%) and least of Cu (0.5%) occur in the mobile form in the total content of the elements in the soil (Table 1). The APC and MAC elements were not recorded to exceed the standards in the virgin soil. The background content of mobile forms of Mn, Zn, Cu, and Co in the agrochemical standards is estimated as low.

The HM content in the vegetation cover of a particular region is an important indicator of the environmental quality. To estimate the abundance more accurately and to characterize the translocation patterns of elements in the soil–plant system, their content in the miscellaneous herbs of the steppe is determined and the BAC is calculated. By the content in the miscellaneous herbs of the steppe, the elements form the following descending series: Mn > Zn > Cu > Ni > Cr > Pb > Co > As > Cd > Hg. By the BAC value, the elements form a slightly different descending series: Hg > Zn > Cu > Mn > Ni > Cr > Pb = Cd > As > Co. The highest values of BAC were established for the elements of the group of biological accumulation of Hg (2.65), Zn (1.76), and Cu (1.26). The remaining elements by the BAC value belong to the group of biological entrapment. The lowest values of BAC were typical of Co (0.05) and As (0.07) (Table 2).

The gross content of the elements in all soil samples studied was much lower than the APC or MAC levels. It is quite ordinary to estimate the element content by using the clarke values, but such estimates are quite approximate and conditional. According to the data of different authors, the clarke values vary strongly. According to the estimates of A.P. Vinogradov (1957) [14], for example, the Mn and Cr clarke values amount to 850 and 200 mg/kg, but according to the data of Kabata–Pendias (2011) [15], they are 488 and

Table 2. Content of heavy metals and arsenic in virgin miscellaneous herbs

Element	Variation-statistical indicators of element contents in miscellaneous herbs, mg/kg of absolutely dry substance			Average content in ash, mg/kg	Biological absorption coefficient (mg/kg of ash)/(mg/kg of soil)
	$\bar{x} \pm t_{05}s\bar{x}$	lim	V, %		
Mn	28.8 ± 2.9	11.2–44.2	24.3	400	0.83
Zn	6.06 ± 0.51	4.02–8.07	18.9	84.2	1.76
Cu	1.83 ± 0.34	0.95–3.79	29.5	25.4	1.26
Ni	1.41 ± 0.18	0.66–2.64	30.2	19.6	0.66
Cr	0.90 ± 0.09	0.49–1.68	25.4	12.5	0.62
Pb	0.48 ± 0.04	0.300–0.650	21.3	6.67	0.48
Co	0.035 ± 0.004	0.020–0.060	23.2	0.486	0.05
As	0.030 ± 0.005	0.014–0.054	37.3	0.417	0.07
Cd	0.014 ± 0.002	0.008–0.024	36.8	0.190	0.48
Hg	0.005 ± 0.001	0.003–0.008	38.2	0.069	2.65

Table 3. Gross content of heavy metals and arsenic in ordinary arable chermozem, mg/kg

Element	*APC	MAC	Clarke value in the soil		Variation-statistical indicators of the gross content of elements in the soil, mg/kg		
			Vinogradov, 1957 [14]	Kabata-Pendias, 2011 [15]	$\bar{x} \pm t_{05}s\bar{x}$	lim	V, %
Mn	–	1500	850	488	397 ± 18	311–463	10.2
Zn	220	–	50	70.0	42.9 ± 2.2	33.6–50.5	11.5
Ni	80	–	40	29.0	33.1 ± 2.2	24.6–41.3	14.1
Cr	not established		200	59.5	23.7±1.4	18.6–29.1	12.4
Cu	132	–	20	38.9	15.8 ± 0.5	12.6–17.5	7.6
Pb	130	–	10	27.0	11.2 ± 0.4	9.5–13.0	8.5
Co	not established		8	11.3	9.51±0.46	7.80–10.9	11.0
As	10	–	5	6.83	5.48 ± 0.34	4.10–7.13	14.2
Cd	2	–	0.5	0.41	0.350 ± 0.02	0.270–0.410	10.4
Hg	–	2.1	0.05	0.07	0.023 ± 0.002	0.015–0.035	23.4

* For clay loams and clayey soils with pH > 5.5.

59.5 mg/kg [14, 15]. The average gross content of Ni in the soil was higher than the clarke value of the element from [15], but below the clarke value from [14], while for Pb, Co, and As, the dependence was inverse. The average content of Mn, Zn, Cu, Cr, Cd, and Hg in the soil was lower than the clarke values according to both authors.

The average gross content of Co, As, Cd, and Hg in the arable soils almost fully corresponded to the content of these elements in the background soil. The average content of Ni and Cr in the virgin soil was slightly lower than in the arable soil, but it fit within the variation ranges of these indicators. The background gross content of Zn, Cu, and Pb was higher than in the ordinary arable chernozem, but it also fit within the variation ranges of these parameters in the plough land. The background concentration of Mn slightly exceeded the upper limit of variation in the element content in the arable soils (Table 3).

The content of mobile forms of HMs in ordinary arable chernozems was much lower than the MAC levels. The average concentration of mobile forms of Mn, Zn, Cu, and Co almost coincided with the background values that were established for the virgin soils, while for Ni, Cr, Pb, and Cd, it was slightly higher (Table 4). Moreover, in accordance with the agrochemical standards, the abundance of elements such as Mn, Zn, Cu, and Co in soils is low, which determines the need for using appropriate trace fertilizers in farming agrotechnology [11].

Table 4. Content of mobile forms of heavy metals in ordinary arable chernozem, mg/kg

Element	MAC	Level of low abundance	Variation-statistical indicators of content of mobile forms of elements in the soil, mg/kg		
			$\bar{x} \pm t_{05}s\bar{x}$	lim	V, %
Mn	140	<10	4.14 ± 0.70	1.48–7.16	37.9
Pb	6	not established	0.75 ± 0.04	0.57–0.90	11.1
Ni	4	not established	0.59 ± 0.03	0.53–0.73	9.2
Zn	23	<2	0.36 ± 0.04	0.23–0.60	25.0
Cr	6	not established	0.31 ± 0.02	0.24–0.42	14.7
Cu	3	<0.2	0.10 ± 0.01	0.06–0.16	24.3
Co	5	<0.15	0.09 ± 0.01	0.06–0.13	23.6
Cd	not established	not established	0.04 ± 0.01	0.03–0.06	16.2

DISCUSSION

This study confirms the conclusion that the ordinary chernozems of the steppe zone in the CCR are characterized by a higher gross content of HMs compared to the forest–steppe subtypes of chernozems (typical and leached). This is because the steppe chernozems are characterized by a higher content of physical clay and lower leaching of HMs from the topsoil [5, 16]. As a rule, the gross content of HMs in soils correlates directly with the content of physical clay. For example, the average gross content of Pb, As, and Cd in typical arable chernozems was lower by 0.9, 1.3, and 0.12 mg/kg, respectively, than in ordinary chernozems [8].

An important factor that affects the content of mobile forms of HMs in the soils and determines in many respects their uptake by plants is the soil acidity. As the acidity increases, HM mobility in the soils increases. Ordinary chernozems of the steppe zone are usually characterized by a neutral reaction of the environment, while chernozems of the forest–steppe subtypes are consistently acidified in agricultural exploitation [17, 18]. Therefore, despite the higher gross content of HMs, the concentration of their mobile forms in chernozems of the steppe zone is lower than in chernozems of the forest—steppe zone. For example, the content of Mn and Co mobile forms in ordinary virgin chernozem is lower than in typical chernozem in the protected area by a factor of 1.33 and 2.86, respectively [5]. The low content of mobile forms of some elements Mn, Zn, Cu, and Co in the soils of the natural ecosystems can be considered their genetic trait, which is propagated to arable chernozems of the CCR. For example, in Belgorod and Lipetsk oblasts, by the content of mobile forms of Mn, 38.6 and 19.0; Zn, 98.7 and 95.0; and Co, 99.3 and 23.0% of the studied arable soils, respectively, belong to the category of low abundant [5, 19].

According to the data of background monitoring, the HM content in miscellaneous herbs of the steppe that grow in the ordinary chernozem of the steppe zone is as a rule lower than in the SPNA vegetation cover located in the forest–steppe zone. For example, in the Yamskaya Step' forest–steppe SPNA where the topsoil is represented primarily by typical chernozems, the average contents of Zn, Cu, and Co in the miscellaneous herbs are higher than in Rovenskii Nature Park SPNA located in the steppe zone by a factor of 1.4, 2.32, and 2.57, respectively [7]. This pattern is determined by the lower content of mobile forms of HMs in ordinary chernozems compared to the chernozems of the forest–steppe zone. This study confirms the conclusion that the HM content in the ordinary chernozems is not dangerous for growing safe agricultural products [5, 7, 20].

CONCLUSIONS

According to the results of our studies, the contents of the studied elements in the ordinary virgin chernozem of the steppe zone in the CCR were within the variations of their concentrations in arable analogs or even lower. Only the gross content of Mn in the virgin soil exceeded the upper limit of this element content variation in the arable soils. By the average gross content in arable ordinary chernozems, the elements form the following descending series (mg/kg): Mn(397) > Zn(42.9) > Ni(33.1) > Cr(23.7) > Cu(15.8) > Pb(11.2) > Co(9.51) > As(5.48) > Cd(0.35) > Hg(0.023), and in terms of the average content of mobile forms, the dependence is slightly different: Mn(4.14) > Pb(0.75) > Ni(0.59) > Zn(0.36) > Cr(0.31) > Cu(0.1) > Co(0.09) > Cd(0.04). The APC and MAC of the elements studied did not exceed the established standards in the soils; therefore, it is safe to grow eco-friendly plant products. The contents of mobile forms of Mn, Zn, Cu, and Co correspond to a low abundance; therefore, these elements should be introduced into the agrocenoses with trace fertilizers to increase the yield and quality of agricultural products.

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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