Migration of Zinc and Cadmium in the System Soil–Plant Near the Karazhyra Coal Mining Company (Kazakhstan)

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Abstract

Features of the spatial distribution of the total content and the forms of zinc and cadmium compounds in the industrially polluted soil cover are investigated. It is established that the maximal accumulation of chemical elements in soil is distributed in the northern and north-western directions at a distance of 250 m from the boundaries of the open-pit mine, while the minimal one is in the east at a distance of 5000 m. A close connection between the concentrations of zinc and cadmium in *Artemisia marschaliana* sp. and the accumulation of these elements in the soil cover at the Karazhyra coal deposit is discovered. According to concentrating in the top part and in the roots of plants, zinc is characterized by the basipetal distribution and cadmium by the acropetal one.

INTRODUCTION

At present, mining industry relates to the major pollution sources of the biosphere. Intense development of coal deposits using powerful excavators and extractive equipment leads to the formation of vast areas with industry-affected relief and to disturbance of the natural landscapes [1]. However, along with the direct disturbance of the earth's surface, mining causes also pollution of the adjacent territories; erosion nuclei arise, the soil layer is affected by physical, mechanical and chemical action. Migration geochemical fluxes characterized by high concentrations of heavy metals (HM) spread outside the open pit [2]. Therefore, it is necessary to carry out quantitative estimations of soil pollution, which is an integral component of complex ecological and geochemical investigations that make up the basis for planning the measures aimed at the reduction of negative consequences of the development of coal mining deposits.

The goal of the work was to reveal the basic regularities of the spatial distribution of zinc and cadmium in the system soil–plant around the territory of a Coal Mining Company.

OBJECTS AND METHODS OF INVESTIGATION

The Karazhyra coal deposit founded in 1991 is situated at a distance of 130 km to the southwest from Semipalatinsk (East Kazakhstan Region) in the land of the former Semipalatinsk test site. The area of the deposit is 21.4 km^2. The wells remaining from nuclear tests are situated in the immediate proximity to the open pit.

The construction of the experimental-industrial open pit started in 1996 at the deposit. The productivity of the mine with respect to access way is 7.0 mln m^3. The year of the development of planned productive capacity was 1998. As a mean, the mined amount is 3.6 mln t/year.

The set of sources polluting the environment includes: mining and tripping in the open pit mine; rock dump located near the pit wall at a distance of 1 km to the north; pit-wall coal storage grounds (to be consumed and the reserve) situated to the south-east from the existing open pit mine near the exit trench; coal storage yard at the railway station situated at a distance of 45 km to the north-west from the pit, and the boiler house supplying heat to the workers' camp.

The technological operations connected with mining and processing of the coal at the Karazhyra pit are accompanied by environmental pollution. As the results of investigations (2001–2005) show, emissions include coal dust, rock dust, gas components etc. As a mean, 592.63 t of pollutants are annually emitted into the atmosphere at the pit, while the maximal allowed emission is 665.4 t/year.

The average ash value of the coal from this deposit is 15.7 %, the ash value of the rock mass is 25.7 % varying from 18.7 to 30.2 %. The amount of dust precipitation varies in the region under consideration from 19.5 to 82.5 kg/(km^2 · day), background precipitation is 25 kg/(km^2 · day).

The region under investigation is represented by the soil of light chestnut subzone: light chestnut shallow (17.1 % of the total area), light chestnut average (42.9 %), shallow light chestnut solonetz (28.6 %), meadow light chestnut (2.9 %). The soil is formed on eluvial-dealluvial and dealluvial deposits and on tertiary clays.

According to the agrochemical indices, the soil has low humus content (1.45 %), high physical clay content (15.2 %); the pH of soil is close to the neutral value (6.6). The buffer capacity index calculated by us on the basis of V. B. Il'in's system [3] is characterized by medium values.

The species composition of the plant cover on this ground is poor and represented by the wormwood species.

To achieve the formulated goal, we collected 280 soil samples taken at different distances from the open pit mine in accordance with the wind rose radially along the eight route directions: north (separated into two directions 1 and 01, because the dump of the access way is located there and loading works are performed in this direction, too), south, west, east, north-west, south-west, north-east, south-east – at a distance of 250 to 5000 m from the pollution source. The background soil samples were collected at the opposite side of the wind rose (east) at a distance of 60 km from the open pit contour. Since the numerous literature data suggest (for example, [2, 4]) that HM get accumulated under the industry-related pollution in the upper layer of soil, we took soil samples at a depth of 0–10 cm. Sampling was carried out strictly in agreement with the standard procedures [5].

In conjugation with soil sampling, plant samples of *Artemisia marschaliana* (Compositae family) at the end of the vegetation period were collected (95 samples). The test grounds were arranged in agreement with the procedures accepted in phytocenology and modified for biogeochemical investigations [6].

Zinc and cadmium were chosen for investigation on purpose: these elements are the pollutants of priority in the East Kazakhstan Region.

Total HM content was determined in soil, along with the forms of their compounds: acid-soluble (extracted with 1 M HCl solution), exchangeable (extracted with the ammonium acetate buffer (CH_3COONH_4) with pH 4.8) and water-soluble (extracted with twice distilled water).

The concentrations of HM in soil and in plant samples were determined using the photocolorimetric chemical dithizone method proposed by G. Ya. Rinkis [7]. The method is based on measuring the optical density of coloured extract with the KFK-3 photoelectrocolorimeter. The experiments were repeated three times.

The entire set of experimental data was treated using the variation statistical methods described in the guides by N. A. Plokhinskiy [8] and B. A. Dospekhov [9]. The main indices used to estimate the degree of pollution were concentration coefficients (K_c) indicating the level of anomaly in element content, and danger coefficients (K_d) indicating the level of danger caused by soil pollution. These indices are defined by the expressions $K_c = C/C_b$ and $K_d = C/\text{MPC}$ where C is the concentration of a chemical element in soil (plant); C_b is the geochemical background showing the average value of the natural variation of a chemical element in the soil of the territory under investigation; MPC is the maximum permissible concentration of an element in soil.

To characterize the distribution of the elements between the living matter and the abiotic medium, we calculated the coefficient of biological absorption (CBA) which represents the ratio of the concentration of a chemical element in a living organism (plant) to the concentration of the element in the environment (lithosphere) [10].

TABLE 1

Total content of zinc and cadmium in the soil of the Karazhyra coal deposit depending on distance

Element	Distance from the pit edge, m							Background,
	250	500	750	1000	1500	3000	5000	mg/kg
Zn	153.6 − 165.2 / 159.4 ± 5.8 (5.1)	55.2 − 137.8 / 98.5 ± 10.4 (31.2)	70.2 − 133.6 / 98.8 ± 11.5 (27.8)	59.2 − 125.4 / 88.4 ± 11.9 (32.4)	31.5 − 112.8 / 66.7 ± 11.1 (43.2)	27.6 − 84.3 / 44.8 ± 8.5 (45.6)	28.1 − 36.2 / 32.2 ± 4.1 (17.7)	27.4
Cd	4.18 − 4.86 / 4.52 ± 0.35 (24.5)	0.68 − 4.53 / 2.40 ± 0.43 (14.4)	1.10 − 4.41 / 2.58 ± 0.53 (21.0)	0.78 − 3.66 / 1.97 ± 0.52 (20.1)	0.65 − 3.05 / 1.42 ± 0.35 (13.1)	0.67 − 1.94 / 1.09 ± 0.19 (7.9)	0.62 − 0.79 / 0.71 ± 0.09 (5.9)	0.67

Note. Here and in Tables 3, 5: numerator shows the range of variation, mg/kg; denominator shows the arithmetic mean and its error, mg/kg; variation coefficient is given in parentheses, %.

RESULTS AND DISCUSSION

The concentrations of zinc and cadmium (belonging to especially toxic elements [11]) in the Karazhyra coal pit are shown in Table 1.

It was established that the overall content (in mg/kg) of zinc in the soil within the sanitary protective zone (SPZ, 250–750 m from the pit boundary) varied within the range 55.2–165.2 (118.9 as a mean), cadmium 0.68–4.86 (3.16 as a mean).

The average overall concentration of zinc in soil at a distance of 250 m from the pollution source exceeded the background value by a factor of 5.8, cadmium by a factor of 6.7; at a distance of 500 m the corresponding excess values were 3.6 and 3.6 times; at a distance of 750 m − 3.6 and 3.3 times; 1000 m − 3.2 and 3.0 times; 1500 m − 2.4 and 2.1 times, respectively. At a larger distance (3000 and 5000 m) the concentrations of heavy metals reached the background values. The average excess of zinc in the soil of the SPZ was 4.3 times above the background, while for cadmium 4.3.

Zinc concentration in the soil cover of the SPZ (250–750 m) of the coal deposit decreased by 33.4 %, cadmium by 17.7 %. At a distance of 1000 to 5000 m along the perimeter from the pollution source, we observed a regular decrease in the level of zinc by 22 %, cadmium by 17.0 %.

The maximal level of the chemical elements is distributed in the soil in the north and northwest direction, the minimal level in the east (Fig. 1). Predominant pollution of soil in the north is explained by the fact that the coal-loading ramp and the north dump of the open pit are situated in that direction. In addition, the distribution of the elevated HM concentrations corresponds to the rate and frequency of the prevailing air flows, that is, the wind rose. The topography of soil pollution with HM is also determined by the relief regions formed under the action of industry.

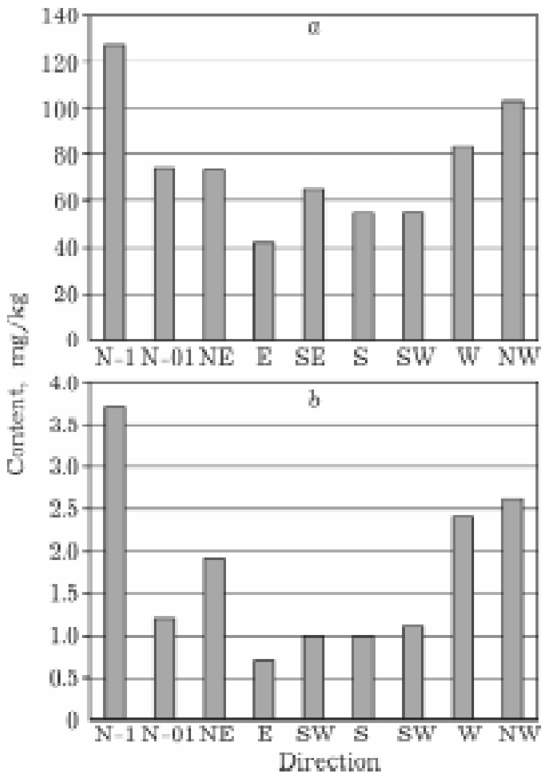

Fig. 1. Zinc (*a*) and cadmium (*b*) content in soil depending on the direction from the Karazhyra coal pit.

TABLE 2

Main geochemical parameters of the chemical elements under investigation

Metal	Our data, mg/kg	Soils of the world, mg/kg [12]	K_{lit}	K_c	MPC, mg/kg [Kloke, 1979]	TPC, mg/kg [13]
Zn	$\frac{27.6 \pm 165.1}{82.3}$	50	83	$\frac{0.3 \pm 2.0}{1.1}$	300	220
Cd	$\frac{0.62 \pm 4.86}{2.0}$	0.5	0.13	$\frac{4.8 \pm 37.4}{15.4}$	3	2

Changes of concentrations and the distance are accompanied also by the changes of the variation coefficient (K_v). Thus, K_v for zinc increases by a factor of 9 with a decrease in its concentration in soil and the accompanying increase in the distance from the coal open-pit mine. Quite contrary, the K_v coefficient for cadmium decreases by a factor of 4 with respect to these parameters (see Table 1). Such a character of element variations is due to the convection of airflows. In addition, it was noted that the average K_v value for zinc (29 %) is two times larger than the given K_v value for cadmium (15.3 %).

Comparing the HM content in the soils of the region under investigation with the clarke values in the soil over the world (Table 2) it is necessary to note that the average zinc content in the soil of Karazhyra deposit is 1.6 times higher than the average content of this element in soil over the world, while the corresponding value for cadmium is 4.0 times higher.

When comparing the total content of elements in the soil of the deposit under investigation with their clarke in the lithosphere (K_{lit} is the average content in the lithosphere), we calculated the clarke of element concentration (C_c), which is a formalized general index of the relative abundance of chemical elements in natural objects; this index is used rather widely. The comparative analysis of C_c promotes the accumulation of local information in combination with the regional and global ones. Calculations showed the following: the soil samples under investigation, taken at a distance of 5000 m from the deposit, are distinguished by the excess cadmium content (by a factor of 288); however, within the SPZz boundaries (average C_c = 20.8) this index decreases and the excess is by a factor of 160. It is necessary to stress that zinc does not form soil anomalies substantial in intensity and contrast in comparison with the clarke.

For the ecological characterization of the soil cover, integral indices are the values of tentative permissible concentrations (TPC) of chemical elements in the soils of different physicochemical composition. For example, the average zinc content in SPZ soil (related to neutral loam soil) does not exceed TPC. Fort he average content of cadmium in the soil samples from the sanitary zone, the TPC is exceeded by a factor of 1.6, while the maximal content (4.86 mg/kg) in the sample taken at a distance of 250 m to the north exceeds the TPC by a factor of 2.4.

The state of soil in the region was characterized from the ecological and geochemical viewpoint by the concentrating factor (K_c is an increase in the element content in the investigated soil in comparison with the background) and danger coefficient (K_d is an increase in the element content in the soil in comparison with the MPC). It was discovered that the average total content K_c for cadmium exceeds the background value by a factor of 4.5; no excess was detected for zinc. For K_d of the metals investigated, no excess over the MPC was observed:

Metal	K_c	K_d
Zn	[illegible] ± [illegible] / [illegible]	$\frac{0.09 \pm 1.3}{0.27}$
Cd	[illegible] ± [illegible] / [illegible]	$\frac{0.21 \pm 1.62}{0.67}$

The ecologically acceptable amount of HM in soil is directly dependent on the buffer ability of the soil. For the soil of the region under investigation, with its average buffer value of 22.5 points, the maximum permissible level (MPL) according to V. B. Il'in [14] will be the range from 7 to 10 background amounts. So, the MPL for the total zinc content in the vicinity of the Karazhyra coal deposit is equal to 274, for cadmium 6.7. Concentrations exceeding the MPL calculated by us for zinc and cadmium in the soil cover are not observed.

The data on the mobility of heavy metals, that is, on their ability to pass from the solid phase of the soil into the liquid one, become extremely important when investigating heavy metals in soil. When the chemical elements become mobile, they become able to migrate over the soil profile till the ground water and to pass into the form more available for assimilation by plants, which is an extremely urgent aspect. The main reserve is the ions present in the soil water which are in the exchange state in the soil absorbing complex. It is quite evident that the occurrence of the excess amount of this form in the soil is fraught with negative consequences: pollution of plant products and ground water.

However, the information important for practical purposes is also that dealing with less mobile elements which may become mobile and therefore more available for plants as a result of changes in the soil conditions, mainly the acid-base situation. The set of these compounds is usually considered as a near reserve in feeding the ion flux from soil to the plants [3].

A unique importance of the mobile compounds of the chemical elements of soil is comprised by the fact that they provide the performance of ecological functions of the soil. The small biological cycle and to a large extent the large geological cycle of chemical substances are connected with this group of compounds [15]. The formation and redistribution of mobile compounds of type-morphic elements in the soil profile is the main essence of elementary soil-forming processes; their migration in the soil profile provides its differentiation and the natural variety of soils. The biogenic elements included in

TABLE 3

Content of the mobile forms of heavy metals in the soil of the Karazhyra coal pit depending on distance

Metal	Form	Distance from the pit edge, m							Background, mg/kg
		250	500	750	1000	1500	3000	5000	
Zn	Acid-soluble	5.8 − 6.1 5.9 ± 0.16 (11.2)	1.9 − 5.3 3.6 ± 0.94 (44.2)	2.4 − 4.8 3.5 ± 0.42 (16.6)	2.1 − 4.4 3.1 ± 0.43 (17.1)	1.4 − 4.1 2.4 ± 0.39 (14.5)	1.1 − 3.2 1.7 ± 0.32 (13)	1.0 − 1.2 1.1 ± 0.1 (7.1)	1.1
	Exchangeable	2.0 − 2.4 2.2 ± 0.2 (14.4)	0.9 − 2.1 1.5 ± 0.14 (4.6)	0.9 − 2.0 1.4 ± 0.16 (6.6)	0.8 − 1.8 1.2 ± 0.16 (6.6)	0.5 − 1.4 0.9 ± 0.11 (4.4)	0.5 − 1.2 0.7 ± 0.11 (4.4)	0.4 − 0.6 0.5 ± 0.1 (7)	0.5
	Water-soluble	1.3 − 1.5 1.4 ± 0.1 (7.1)	0.4 − 1.3 0.9 ± 0.09 (3.1)	0.6 − 1.1 0.9 ± 0.08 (3.2)	0.5 − 1.0 0.8 ± 0.1 (3.9)	0.3 − 0.9 0.6 ± 0.08 (3.3)	0.3 − 0.7 0.5 ± 0.06 (2.7)	0.2 − 0.4 0.3 ± 0.1 (7.1)	0.3
Cd	Acid-soluble	0.75 − 0.85 0.8 ± 0.06 (4.7)	0.13 − 0.8 0.44 ± 0.07 (2.6)	0.29 − 0.76 0.47 ± 0.08 (34)	0.12 − 0.64 0.34 ± 0.09 (35)	0.1 − 0.57 0.25 ± 0.07 (27)	0.12 − 0.34 0.19 ± 0.04 (1.5)	0.1 − 0.14 0.12 ± 0.02 (1.4)	0.11
	Exchangeable	0.47 − 0.53 0.5 ± 0.02 (2.1)	0.08 − 0.5 0.27 ± 0.04 (1.6)	0.17 − 0.46 0.29 ± 0.05 (2)	0.12 − 0.41 0.23 ± 0.05 (2.2)	0.06 − 0.33 0.15 ± 0.03 (1.7)	0.07 − 0.21 0.13 ± 0.02 (0.97)	0.06 − 0.09 0.08 ± 0.01 (1.1)	0.07
	Water-soluble	0.029 − 0.034 0.032 ± 0.003 (02)	0.005 − 0.031 0.017 ± 0.003 (0.1)	0.01 − 0.031 0.018 ± 0.01 (0.24)	0.006 − 0.026 0.02 ± 0.003 (0.14)	0.005 − 0.021 0.01 ± 0.002 (0.1)	0.005 − 0.014 0.01 ± 0.001 (0.1)	0.004 − 0.006 0.005 ± 0.001 (0.1)	0.004

the mobile compounds provide plant nutrition and thus the fertility of soil.

The analysis of the experimental data characterizing the mobility of metals in soil, revelation of their connection with the soil properties fort he estimation and prediction of the ecological state of soil under its pollution was one of the goals of the present investigation.

The variation statistical indices of the concentrations of the forms of metal compounds in the soil of the coal-mining complex under investigation are shown in Table 3.

Acid-soluble form, or the near reserve

Thus extractable mobile form includes HM bound with various soil particles: clay minerals, humic compounds, and the oxides of iron, manganese, aluminium, and primary minerals. They are characterized by different migration abilities.

It was established that the content (in mg/kg) of the acid-soluble form of zinc within the PSZ boundaries varied from 1.9 to 6.1, cadmium from 0.13 to 0.85. The mean concentration of this mobile form of zinc (4.3) exceeded the background by a factor of 3.9, cadmium (0.57) by a factor of 5.2. The average accumulation of zinc in the samples of soil cover out of the protective zone decreased (2.1 mg/kg); the background was exceeded by a factor of 1.9. The average cadmium content at a distance from 1000 to 5000 m off the open-pit boundary was 0.23 mg/kg, which exceeds the background by a factor of 2.1.

Depending on the distance from the pit boundary, that is, from 250 to 5000 m, the concentration of this form of zinc decreased by a factor of 6.1, cadmium by a factor of 8.5 (Fig. 2).

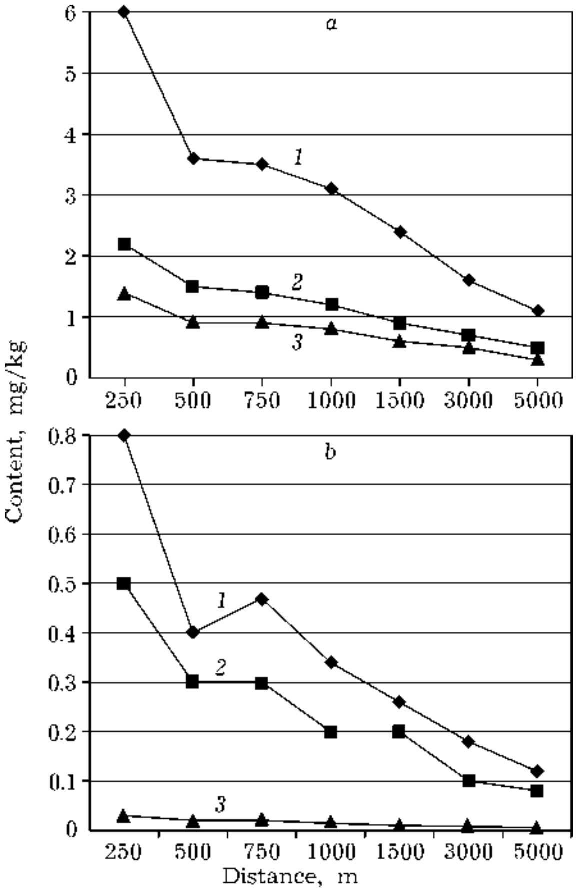

Fig. 2. Content of mobile forms of zinc (*a*) and cadmium (*b*) in the soil of Karazhyra coal pit: *1* – acid-soluble form, *2* – exchangeable, *3* – water-soluble.

The fraction of the acid-soluble form of zinc of its total content was 3.2 to 4.4 %, cadmium form 15.4 to 22.7 %.

To estimate the degree of soil pollution with the mobile HM forms at the Karazhyra coal deposit, similarly to the case of total accumu-

TABLE 4

Average values of concentration coefficients and danger coefficients for the mobile forms of zinc and cadmium in soil of the Karazhyra coal pit

Metal	K_c, mg/kg			K_d, mg/kg			MPC, mg/kg [12]
	Acid-soluble	Exchangeable	Water-soluble	Acid-soluble	Exchangeable	Water-soluble	
Zn	1.1 ± 5.5 / 3.0	1.0 ± 4.8 / 2.6	0.5 ± 5.0 / 2.7	0.04 ± 0.27 / 0.14	0.01 ± 0.10 / 0.06	0.01 ± 0.08 / 0.04	23
Cd	0.62 ± 7.73 / 3.7	0.6 ± 7.6 / 3.6	0.7 ± 8.5 / 4.1	0.08 ± 0.85 / 0.41	0.04 ± 0.53 / 0.25	0.003 ± 0.034 / 0.016	1

lation, we used the concentrating factor and the danger coefficient (Table 4). Calculations showed that the average content K_c of the acid-soluble form of zinc exceeded the background concentration by a factor of 2.7, cadmium 33.6. For the average values K_d of this mobile form of the metals under investigation, no excess was revealed.

To estimate the contribution from the industry-related component into the total HM content of soil, we used the extraction criterion which is the ratio of HM content in acid extracts to their total content, expressed in per cent. In the case under consideration, the extraction criterion for zinc is 3.6 % as a mean, while that for cadmium is 17.6 %.

Exchangeable form

The treatment of soil with the buffer solution causes partial desorption of HM ions from the weakest sorption centres, dissolution of some HM compounds, extraction of HM ions from the soil absorping complex due to the acid reaction and destruction of some HM complexes due to the complexing ability of the reagent used. It is assumed that the compounds weakly held by the slid phases of soil pass into the extract. These compounds are the potential soil resource of mobile compounds available for plants [16].

It was revealed that the average concentration of the exchangeable form of zinc (in mg/kg) in the soil is 1.2, with a variation from 0.4 to 2.4; for cadmium it is 0.22 with a variation from 0.06 to 0.53. The average content of the mobile form of zinc exceeds the background level by a factor of 2.4, cadmium 3.1. An insignificant excess over the background level was observed for the soil of the protective zone: by a factor 3.4 with the average accumulation of the exchangeable form 1.7 mg/kg for zinc, by a factor of 5 with the average of 0.35 mg/kg for cadmium (see Table 3).

With an increase in the distance from the pollution source, the amount of zinc extracted with the acetate ammonium buffer solution decreases by a factor of 6.0, cadmium by a factor of 8.8 (see Fig. 2).

The exchangeable form of zinc accounts for 1.1 to 1.8 %, cadmium 9.7 to 16.4 % of the total amounts of these elements.

Judging from the concentrating factor and danger coefficient (see Table 4), the mean content K_c of a given mobile form of zinc exceeds the background level by a factor of 5.2 and cadmium by a factor of 51.4. For K_c of the exchangeable form of HM no excess of MPC was detected.

Water-soluble form

One of the indices of the availability (mobility) of pollutants is their amount in the aqueous extracts from soil. This index characterizes the actual mobility of chemical substances. An aqueous extract is most close in composition to the soil water [13]. Three groups of compounds are included in this fraction: 1) readily soluble HM compounds; 2) difficultly soluble compounds dissolved in water in agreement with their solubility products; 3) water-soluble complex compounds with various organic and inorganic ligands [17].

It was established that the content (in mg/kg) of water-soluble form of zinc in soil was 0.2 to 1.5 (0.7 mg/kg as a mean), cadmium 0.004 to 0.034 (0.014 mg/kg as a mean). The excess over the background was observed for the mean concentration of zinc in this available form by a factor of 2.3, cadmium 3.5. Within the SPZ boundaries, the excess of zinc over the background in soil was almost the same as its excess at more remote distances, while for water-soluble cadmium it increased up to 5.6 times (see Table 3).

With an increase in the distance from the deposit (from 250 to 5000 m), zinc concentration in the aqueous extract decreased by a factor of 7.5, cadmium by a factor of 8.5 (see Fig. 2).

The fraction of water-soluble form of zinc was 0.9 % on average, cadmium 0.72 % of their total content.

The average content K_c of the given mobile form of zinc exceeded the background level by a factor of 9.0, cadmium by a factor of 102.5. The K_d factor of the water-soluble form of the investigated metals did not exceed MPC (see Table 4).

The variation coefficient K_v of the acid-soluble form of zinc in soil varies from 7.1 % at a distance of 5000 m from the coal deposit to 44.2 % at a distance of 500 m; for the exchangeable form, K_v decreases from 14.4 to 4.4 % depending on the distance; however, at a distance of 5000 m an increase to 7 % occurs; for water-soluble zinc form, the situation similar to that for the exchangeable form is observed: a decrease by a factor of 2.6 and a sharp increase up to 7.1 % at a distance of 5000 m. The K_v coefficient for cadmium has a trend to decrease for all the mobile forms as cadmium concentrations in the soil cover decrease with an increase in the distance from the coal pit, which is also due to permanent changes of airflows.

To solve practical problems of nature conservation, some authors [18, 19] propose to express the main forms of pollutants as the bioavailability factor (BF). Its value is determined by the ratio of all the concentrations of mobile forms to the total concentration of an element and generally shows the part of its total concentration that can be assimilated by plants. No substantial variations were revealed for the BF of zinc in soil *versus* the distance; as an average, this factor is equal to 6 %, while the BF for cadmium is equal to 29.7 %.

The maximal accumulation of acid-soluble, exchangeable and water-soluble forms of zinc and cadmium is distributed in he soil samples of the northern direction at a distance of 250 m from the pollution source; the minimal one is observed in the eastern direction at a distance of 5000 m, which corresponds to the wind rose of the territory under investigation and to the distribution of overall concentrations of these metals in the soil of the coal-mining region.

A plant as a self-adjusting system possesses a powerful adaptive potential and can be an active component in the system soil–plant, with the interrelations appearing as a complicated problem. Plant roots permanently synthesize and release various organic compounds (amino acids, low-molecular organic acids, carbohydrates, enzymes, hormones *etc.*) [20]; these compounds are able to bind HM ions into complex compounds thus decreasing their toxicity [21]. Determination of microelements in the plants of industry-related landscapes, such as the coal deposit Karazhyra, is an integral part of ecological and biogeochemical monitoring.

The subject of investigation was the predominant plant species of the region under examination – wormwood, or *Artemisia marschaliana*. The zinc and cadmium content of

TABLE 5

Heavy metal content in wormwood *Artemisia Marschaliana* depending on the distance from the Karazhyra coal deposit

Metal	Plant parts	Distance from pit edge, m							Background, mg/kg
		250	500	750	1000	1500	3000	5000	
Zn	Top	97.6 – 82.3 81.0 ± 1.4 (23)	21.5 – 82.0 53.5 ± 8.1 (42.8)	43.9 – 70.8 62.9 ± 4.2 (16.1)	33.5 – 71.4 52.8 ± 6.4 (26.7)	24.0 – 59.8 40.1 ± 6.8 (37.8)	18.2 – 48.1 31.3 ± 5.3 (37.5)	17.2 – 20.2 18.7 ± 1.5 (11.3)	18.5
	Roots	65.5 – 76.8 71.2 ± 5.7 (11.2)	16.8 – 74.3 36.1 ± 6.5 (50.3)	24.3 – 75.9 55.1 ± 7.8 (34.1)	23.1 – 52.5 32.5 ± 5.5 (37.2)	15.5 – 60.3 34.8 ± 7.5 (46.9)	14.4 – 42.7 24.9 ± 5.2 (46.3)	12.1 – 15.4 13.7 ± 1.6 (16.9)	14.2
Cd	Top	0.93 – 1.44 1.2 ± 0.2 (18)	1.3 – 3.5 2.0 ± 0.3 (9.7)	1.2 – 3.5 2.4 ± 0.3 (14.3)	1.0 – 2.7 2.0 ± 0.3 (15.8)	1.0 – 2.9 1.5 ± 0.4 (17.0)	0.8 – 1.8 1.2 ± 0.2 (10.0)	0.6 – 1.0 0.8 ± 0.2 (14.1)	0.03
	Roots	1.57 – 2.03 1.8 ± 0.2 (15.8)	2.8 – 7.2 4.8 ± 0.5 (18.6)	3.2 – 7.5 5.1 ± 0.6 (25.9)	2.2 – 4.8 3.2 ± 0.4 (20.2)	1.8 – 5.1 3.0 ± 0.6 (28.3)	1.8 – 3.0 2.2 ± 0.2 (8.9)	1.8 – 2.1 1.9 ± 0.2 (22.3)	0.07

plant samples varied within a broad range (Table 5), which is explained by the effect of the physicochemical properties of the elements, their physiological role in metabolic processes, biological features of the plant and, which is most important, by the direct influence of the industry-related load.

Analysis of the data obtained provides evidence that the minimal accumulation of chemical elements in wormwood was detected in the east and the maximal one in the north. Such a distribution of HM in wormwood almost exactly repeats the distribution of the metals in the soil of the coal deposit (Fig. 3).

It was established that the average concentration of zinc in wormwood at a distance of 250 m from the pit edge exceeds the background value in the top part by a factor of 4.4, in roots by a factor of 5.0; for cadmium, 39.6 and 25.7 times, respectively; at a distance of 500 m: zinc 3.3 and 2.8 times, cadmium 12.3 and 11.4 times; at a distance of 750 m: zinc 3.3 and 3.8 times, cadmium 12.0 and 10.8 times; at a distance of 1000 m: zinc 2.8 and 2.3 times, cadmium 11.6 and 7.1 times; at a distance of 1500 m: zinc 2.0 and 2.2 times, cadmium 6.3 and 5.0 times, respectively, and at a distance of 3000 and 5000 m from the pit edge the metal concentration reached the background level. Within the SPZ

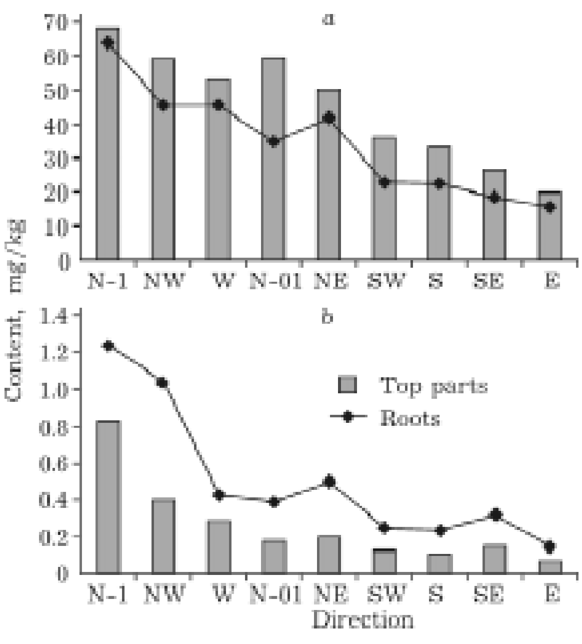

Fig. 3. Average zinc (*a*) and cadmium (*b*) content in wormwood depending on the direction from the Karazhyra coal pit ($n = 95$).

boundaries (250 to 750 m), the average zinc content in the top parts of the plants (65.8 mg/kg) exceeded the background limit by a factor of 3.6, in roots (54.1 mg/kg) by a factor of 3.8; the average cadmium content in the top organs of wormwood (1.87 mg/kg) was larger than the background by a factor of 62.3, in roots (3.9 mg/kg) by a factor of 55.7. The highest concentrations of cadmium were observed in roots, which confirm numerous investigations (for example, [22, 23]) concerning the protective capacity of the root system of plants, a kind of the physiological barrier for the admission of HM from soil into the top organs. In the case under consideration, zinc is an exception: its highest accumulation was observed to occur in the top parts of plants, which may be explained by the effect of extra root penetration. The conclusion that the mechanisms preventing the transport into the top parts are most active towards cadmium and much weaker expressed for zinc has also been made by A. Lurie and coworkers (1995) who investigated the translocation of zinc and cadmium from roots into the top part of plants. In addition, these mechanisms are exhibited for cadmium at any level of its content in soil [24].

When calculating the coefficient of biological absorption (CBA), it is more correct to use the mean concentration of the elements in the lithosphere but not their content in a given soil, because the chemical composition of plants is first of all determined not by the substrate but by the systematic position: family, genus and species to which a given plant belongs. During the time of species formation, separate individuals were growing on different substrates, so the chemical composition of the ash depicts mainly not the composition of the soil on which a plant was growing but the average composition of all the soil kinds on which the previous generations of this species had been growing. Calculation shows (Table 6) that zinc, according to Perelman's classification, judging from CBA values for the top parts of wormwood belongs to the elements of vigorous accumulation and in roots to the elements of strong accumulation, while cadmium belongs to the elements of vigorous accumulation both for top parts and for roots.

TABLE 6

Average values of the coefficient of biological absorption (CBA) and accumulation (K_a) for zinc and cadmium in wormwood of *Atremisia Marschaliana* sp.

Metal	Parts of plant	CBA	K_a		
			Acid-soluble	Exchangeable	Water-soluble
Zn	Top	10.5	17.5	41.1	70.2
	Roots	4.9	13.2	32.1	53.2
Cd	Top	43.1	0.8	1.2	18.5
	Roots	48.2	1.5	2.3	35.8

A quantitative index of the transition of chemical elements from soil into plants, that is, the ratio of HM concentration in the air-dry mass of wormwood (in mg/kg) to the concentration of the mobile forms of HM compounds in soil (in mg/kg), is the accumulation coefficient (K_a). The calculated K_a values for zinc and cadmium entering from soil; wormwood of *Artemisia marschaliana* sp. was characterized by the elevated zinc accumulation (see Table 6) both in the top and in underground parts of plants. Active zinc concentrating in wormwood can be explained by the fact that this metal is an element accumulated in the soil of a coal-mining region. In addition, according to the results of investigations performed by V. B. Il'in and M. D. Stepanova [25], wormwood is capable of accumulating zinc with the higher intensity, which is connected with the participation of this element in metabolic processes.

Studying the effect of total content and the concentrations of mobile forms of HM in the soil of the region under investigation on their accumulation in plants we calculated the correlation coefficients (K_{cor}) (Table 7). Literature data confirm the dependence between HM content in soil and in plants [26]. Our investigation also showed that there exists a direct correlation between the content of HM in soil and in plants.

CONCLUSIONS

1. Average concentrations of the investigated HM in the soil cover of the SPZ and outside it do not exceed MPC. An excess over the background level was established in SPZ soil for zinc by a factor of 4.3, for cadmium by a factor of 4.7. At a distance from 1000 to 5000 m off the

TABLE 7

Correlation between zinc and cadmium content in wormwood of *Artemisia Marschaliana* sp. and their content in soil

Metal	Parts of plant	K_{cor}			
		of total content	Acid-soluble	Exchangeable	Water-soluble
Zn	Top	$\frac{0.90 \pm 0.08}{11.3}$	$\frac{0.90 \pm 0.08}{11.2}$	$\frac{0.91 \pm 0.07}{13.0}$	$\frac{0.93 \pm 0.06}{15.5}$
	Roots	$\frac{0.87 \pm 0.09}{9.7}$	$\frac{0.88 \pm 0.08}{11.0}$	$\frac{0.89 \pm 0.08}{11.1}$	$\frac{0.89 \pm 0.08}{11.1}$
Cd	Top	$\frac{0.89 \pm 0.08}{11.1}$	$\frac{0.87 \pm 0.09}{9.6}$	$\frac{0.86 \pm 0.09}{9.5}$	$\frac{0.89 \pm 0.08}{11.1}$
	Roots	$\frac{0.94 \pm 0.06}{15.7}$	$\frac{0.93 \pm 0.07}{13.2}$	$\frac{0.89 \pm 0.08}{11.1}$	$\frac{0.94 \pm 0.06}{15.6}$

pollution source, zinc content decreases by 22 %, cadmium by 17 %.

2. Among the mobile forms of zinc and cadmium, the largest percentage of the total content is observed for the acid-soluble form (10.8 as a mean), a smaller one for the exchangeable form (6.5 %) and water-soluble one (0.8 %).

3. The maximal accumulation of the total content and mobile forms of HM was detected in soil samples taken at a distance of 250 m from the pit edge; with an increase in the distance from the source, the concentrations of the metals under investigation decreased and approached the background at a distance of 5000 m. The maximum of zinc and cadmium in soil is distributed in soil in the northern direction, the minimum is in the east, which corresponds to the velocity and frequency of the prevailing air flows (wind rose) and is mainly determined by the features of the relief formed under the effect of industrial activities.

4. Accumulation of chemical elements in wormwood of *Artemisia Marschaliana* sp. is in close connection with the amount of metals in soil. The mobile forms of HM compounds reveal an intense connection with their content in plants; water-soluble form is the most available one in soil for plants, judging from the correlation coefficient value.

5. For concentrating in the top parts and in roots, zinc is characterized by the basipetal distribution while cadmium is characterized by the acropetal one. The accumulation of chemical elements in wormwood almost repeats the picture of the pollution of soil cover of the territory of the Karazhyra coal deposit.

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