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**FORMS OF CADMIUM COMPOUNDS IN SOILS CONTAMINATED BY EMISSIONS FROM  
NOVOCHERKASSK POWER STATION**

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**INTRODUCTION**

The identification of the heavy metals (HM) compounds in the soil and their bonds with different soil components is the basic tool for studying the small geochemical cycles of elements in landscapes of technogenic zones [3, 6]. There is available published information by now about the concentrations of different HM compounds in soils obtained mostly using the methods of their extraction fractionating [11]. They allowed answering some ecologically important questions and revealing the understudied problems. The capability of these methods to reveal the regional particularities of the studied soils is important. However, the information about the importance of particular soil components in the HMs retention is insufficiently complete. The integration of the available literature data on the soil absorbing capacity relative to the HM is difficult particularly because of the diversity of the methods used for their extracting and the difference between the properties of the studied soils, including their regional features [4, 7].

The soils of the Lower Don Region (Russia) are especially noteworthy because of the complex anthropogenic impact on them. The region is the country's biggest producer of agricultural products and an industrial juggernaut. The enterprises of the mining and processing industry, the power industry, and the metallurgy industry are active sources of environmental pollution with HM. The emissions of the Novochoerkassk power station (NPS) comprise up to 1 % of the total pollutant emissions to the atmospheric air of Russia and up to 99 % of the aerosol emissions in Rostov oblast. The atmospheric emissions contain soot (more than 30 t/year), vanadium pentoxide (about 8 t/year), iron oxides (more than 5 t/year), chromic anhydride (about 0.1 t/year), etc. The concentrations of Cd in Novochoerkassk city air exceed the allowable levels of these metals [2].

These facts determined the goals of our work: to study the regularities of the formation and transformation of Cd compounds in the soils of the NPS environs.

## MATERIALS AND METHODS

The studied objects were represented by the soils of monitoring plots subjected to the influence of the NPS emissions. The monitoring plots were established at different distances from the NPS (1.0 – 20.0 km) in 2000 (Fig. 1). A relatively greater number of plots were arranged in the “main direction” from the NPS according to the wind direction to the north-west of the pollution source through the residential areas of the city of Novocherkassk (plots 4, 5, 6, 8, 9, and 10).

The plots for monitoring the observations are situated on virgin lands or fallow lands, and the soil cover of these plots is mostly composed of Chernozems Calcic. Plot 2 is occupied by a sandy Fluvisols Umbric, and plot 3, which is situated on the floodplain only 300 m away from plot two, by a light clay Phaeozems Calcaric. The soils in plots 6 and 8 are heavy loamy Phaeozems Calcaric ones. The soil samples for studying the soil properties and the concentrations of the HM compounds were taken yearly from the depth of 0–20 cm. The soil reaction was slightly alkaline (pH 7.2–7.7), and the carbonate concentrations made up 0.2–0.7 %. The studied soils differed in their particle-size composition. The chernozems Calcic and Phaeozems Calcaric developed on loess-like loams were heavy loamy, and the Fluvisols Umbric on alluvial deposits had a light texture. The light clayey Phaeozems Calcaric soil on the alluvial deposits had maximal contents of clay and silt. The content of humus in these soils did not strongly vary (4.2–4.8 %), except for the sandy Fluvisols Umbric (2.9 %). They were also characterized by low a cation exchange capacity (CEC), namely, 10 mmol (+) / 100 g soil.

According to the bonding strength, two groups of HM compounds in the soils under study were singled out: HMs strongly bound to the soil (SB) and those LB to the soil (LB). However, the metal compounds in each of these groups are dissimilar as well, because they are retained by soil components by means of different binding mechanisms. The parameters of the fractional-group composition of the HM in the studied soils were investigated using combined scheme for fractioning the HM compounds [10]. When analyzing them, we focused on the proportion between the metal compounds firmly and loosely bound with the soil components, which determined the ecological consequences of the soil contamination with metals.

The application of a combined fractionating procedure allows determining the heterogeneous composition of the metal compounds firmly and loosely bound with the soil components. They are retained by these components through different mechanisms and represent different fractions. The metal concentrations in these fractions were found with analytical methods and by calculation (Table 1). The metal concentrations in the soil extracts were determined with atomic absorption spectrophotometry (AAS). The total content of the metals loosely bound with the soil components was found as the sum of the exchangeable, complex, and absorbed specifically by the carbonates and iron (hydro) oxides fractions; the content of the firmly bound compounds was found as the sum of the metals firmly retained by the organic substances, iron (hydro) oxides, and silicates. The proportions were calculated between the fractions of the metals that represented the groups of firmly and loosely bound compounds and between the loosely and firmly bound metals in the soil as a whole (LB/FB).

## RESULTS AND DISCUSSION

The total content of Cd in the soils of plots 9 and 10 (0.2–0.3 mg/kg) (Table 2) 15–20 km away from the source of the pollution was close to its Clarkes by Vinogradov [8] (0.5 mg/kg) and to the regional background (0.3 mg/kg) levels [1, 2].

The distance of the points of the sampling and the wind direction are the main factors of the formation of the Cd content in the soils around the Novocherkassk Power Station. The total content of Cd in plots 4 and 5 (1.2–1.6 km to the northwest of the source of the pollution) was the most increased (5 – 6 times) in comparison with the background soils (Table 2). All the studied soils located 1–5 km away from the NPS were classified as contaminated ones, and the total contents of the Cd in these soils significantly exceeded their concentrations in the uncontaminated soils.

The compounds of Cd in the uncontaminated soils were obviously dominated by the firmly bound ones, the portion of which comprised 90–93 % of the total content the metal (Table 2). This was determined mostly by the Cd fixed within the structures of the silicates (the metal portion comprised 69–72 % of the total reserve of the firmly bound compounds of Cd in the soil). The concentrations of the loosely bound metal compounds sharply increase in the contaminated soils, and the absolute concentrations increased more pronouncedly than the relative values.

An especially high increase of the concentrations of the loosely bound metal compounds was observed in the soils with the maximum technogenic loads (plots 4 and 5). The portion of the loosely bound Cd forms increased maximally (up to 48 %) in the contaminated soils of plots 4 and 5 and even slightly exceeded the concentrations of the firmly retained metal compounds. The increase of the relative content of the loosely bound Cd forms was even lower in the soils 5 km away from the NPS (up to 31 %).

The fractional-group composition of the HM compounds demonstrated which fractions of the HM soil contamination were responsible for the increase of the HM concentrations in every group of the loosely and firmly bound compounds. The participation of silicates in the formation of the firmly bound compounds of the Cd was weak, and their portion decreased in some soils to 36 – 49 % of the firmly retained metals.

Table 1. Combined fractionation of metal compounds in the soil

Parameter	Determination method	
	experimental	calculation (from the difference between the HM contents in extracts)
1. Exchangeable metal compounds:		
Total	1 N NH <sub>4</sub> Ac, pH 4.8	
Easily exchangeable	1 M MgCl <sub>2</sub>	
Difficultly exchangeable		Difference 1 N NH <sub>4</sub> Ac – 1 M MgCl <sub>2</sub>
2. Metals bound to carbonates and occurring as separate phases:		
Total	No method	
Loosely bound (specifically sorbed)	1M NaCH <sub>3</sub> COO, pH 5	
Firmly bound (coprecipitated, occluded, chemisorbed, precipitates of low-soluble HM compounds)	No method	
3. Metals bound to Fe, Al, and Mn nonsilicate compounds:		
Total	0.04 M NH <sub>2</sub> OH·HCl	
Loosely bound (specifically sorbed)		Difference (1 N HCl – 1 N NH <sub>4</sub> Ac) – 1 M NaCH <sub>3</sub> COO
Firmly bound (occluded) (except Mn oxides)		Difference 0.04 M NH <sub>2</sub> OH · HCl – (1 N HCl – 1 N NH <sub>4</sub> Ac – 1 M NaCH <sub>3</sub> COO)
4. Metals bound to organic matter:		
Total	30 % H <sub>2</sub> O <sub>2</sub>	
Loosely bound (complexes)		Difference (1 % EDTA in 1 N NH <sub>4</sub> Ac) – 1 N NH <sub>4</sub> Ac
Firmly bound (chelates)		Difference 30 % H <sub>2</sub> O <sub>2</sub> – 1 % EDTA
5. Metals strongly bound to silicates	HF + HClO <sub>4</sub> extract from the residual soil fraction (after all extractions)	Difference between the total element content in the soil and the total content of all fractions (except the residual fraction)

Iron (hydro) oxides were the most active in the tight retention of the Cd in the contaminated soils, their participation increased in particular cases (plots 2 and 8) by more than two times in comparison with the uncontaminated soils. The participation of organic substances in the Cd retention practically did not change in the course of the soil contamination. The contributions of the Fe (hydro) oxides and organic matter were practically equal for Cr.

As for the fractional composition of the metal compounds loosely bound with the soil components, the data of Table 2 confirmed the regularity found for the changes of the LB/FB ratio of the HM compounds caused by the soil contamination. The soil contamination with metals proved to be accompanied by the increasing contribution to the formation of the loosely bound compounds, which are characterized by higher mobility.

Table 2. Total content and fractional-group composition of the Cd in the soils of the monitoring plots

Plot number; distance (km) and direction from the NPS	Total content, mg/kg	LB*FB*	LB, % of the concentration in the group				FB, % of the concentration in the group		
			exchangeable	complex	specifically sorbed on carbonates	Fe and Mn (hydro) oxides	Organic substances	Fe (hydro) oxides	silicates
1. 1.0 NE	0,6	41/59	9	4	65	22	6	30	64
2. 3.0 SW	0,4	42/58	10	0	85	5	7	57	36
3. 2.7 SW	0,5	33/67	6	6	82	6	6	36	58
4. 1.6 NW	1,0	47/53	22	4	54	20	10	25	65
5. 1.2 NW	1,3	48/52	29	5	45	21	11	27	62
6. 2.0 NNW	1,0	44/56	22	7	53	18	16	26	58
7. 1.5 N	0,7	42/58	8	4	80	8	8	22	70
8. 5.0 NW	0,6	31/69	0	7	72	21	6	45	49
9. 15.0 NW	0,3	7/93	0	0	50	50	8	23	69
10. 20.0 NW	0,3	10/90	0	0	50	50	11	17	72

\*Group of the loosely bound compounds; \*\*Group of the firmly bound compounds

The composition of the loosely bound metal compounds in the uncontaminated soils is dominated by the specifically absorbed forms; their portion for Cd exceeded 78 %. The carbonates had the maximum effect on the formation of the specifically absorbed Cd compounds reserves: the portion of Cd retained by the carbonates was in some cases almost an order of magnitude (7 times) higher than the fraction of the metal loosely bound with the iron (hydro) oxides.

The sharp increase in the contaminated soil of the content of exchangeable Cd is worth noting. The share of the exchangeable Cd compounds in the formation of the group of loosely bound compounds in the most contaminated soil increased almost by 30 times. Ecologically dangerous consequences of the soil contamination with Cr can be connected with the increase of its loosely bound with the carbonated forms in the contaminated soils.

### CONCLUSION

The information capacity was proved of the results of the combined fractionation method of the metal compounds in soils. The obtained results allowed revealing the regularities of the Cd compounds formation in the uncontaminated soils around the NPC. The firmly bound forms predominately in the silicates predominate among the Cd compounds in the uncontaminated soils. The loosely bound compounds of metal were dominated by the least mobile specifically absorbed forms. The total contents of Cd increased in the soils contaminated with the emissions of the NPS by 1.4–6 times, and this increase was accompanied by a sharp increase of their mobility. The portion of its loosely bound compounds increased by 6 times and reached almost 50 % of the total content of this metal.

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