

Heavy metal compounds in a soil of technogenic zone as indicate of its ecological state

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Abstract

The emissions from the Novocherkassk power station comprise 1% of the total volume in the Russian Federation and up to 58% of the emissions in the Rostov oblast. The aim of this work was to assess the regularities of heavy metals accumulation and transformation in soils subjected to aerosol emissions from the power station on the basis of the fractional composition of their compounds. Studies have been conducted on the soils of monitoring plots distances from the power station (1.0–20.0 km) during 15 years. The monitoring plots located on fallow areas. Soil samples for the determination of soil properties and the contents of heavy metals compounds were taken from a depth of 0–20 cm. The soil cover in the region under study consisted of ordinary chernozems, meadow-chernozemic soils, and alluvial meadow soils. The total amount of heavy metals in soils was determined by X-ray fluorescence. Metals in soil extracts were determined by atomic absorption spectroscopy. The fractional composition of heavy metals was determined using combined fractionation. A combined approach for fractioning metal compounds in soils on the basis of and parallel extractions (1 N NH₄Ac, pH 8; 1% EDTA in NH₄Ac; and 1 N HCl) was used. Aerosol emissions from the power station are the major agents of technogenic impact on the soils under study in the Rostov oblast. The highest degree of contamination with metals (mg/kg: Ni - 64, Cd - 1.3, Cr - 145 and As - 12) was observed for soils located within a radius of 5 km from the power station along the predominant wind direction. It was marked the rise of metals mobility in the polluted soils and predominant participation of Cr and Ni organic-mineral complexes among their mobile species. The increasing of Cd mobility was provided predominantly by exchangeable forms and specifically sorbed by Fe-Mn (hydr)oxides. The environmental contamination hazard increases with the decreasing metal-buffering capacity of soils.

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Introduction

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 heavy metals (HM). The emissions from the NPS comprise 1% of the total volume in the Russian Federation and up to 58% of the emissions in Rostov oblast,

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where the city of Novocherkassk and its suburbs are the predominant sources of emission (99%) (On the State of..., 1998; Kurdyumov et al., 2010; Belousova, 2001).

The identification of the 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, revealing the mechanisms of the adverse environmental effects of the technogenic factors, and evaluating the resistance of the soil system to these factors (Fateev and Samokhvalova, 2002).

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. They allowed answering some ecologically important questions and revealing the understudied problems. At least two aspects of the problem of characterizing the fractional composition of the HM compounds in soils are topical. One of them is connected with the improvement of the methods of their determination, and the other one concern the evidence of the information capacity of the parameters indicative of HM compounds obtained with these methods for the assessment and forecasting of the ecological status of soils. The capability of these methods to reveal the regional particularities of the studied soils is important. We can consider that the ecological importance of the processes of the HM compounds formation and transformation in the soils of natural and technogenic landscapes is confirmed.

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 HMs 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 (Ladonin, 2002; Ladonin and Karpukhin, 2011; Minkina et al., 2010).

These facts determined the goals of our work: to study the regularities of the formation and transformation of the Cr, Ni, and Cd compounds in the soils of the NPS environs, and to determine the factors affecting these processes.

Material and Methods

Studies were conducted on the soils of monitoring plots subjected to NPS emissions. This research allowed two problems to be solved: (1) to assess the status of metals in the soils and (2) to assess the information values of two methods for determining the group composition of metal compounds in soils (parallel extraction of metal compounds and their combined fractionation). In 2000, monitoring plots were established at different distances from the NPS (1.0–20.0 km). They coincided with the air sampling sites for the ecological certificate of the plant (plots 1, 2, 3, 5, 6, 7) (Figure 1). The most attention was paid to the main wind direction from the contamination source to the northwest through the residential areas of Novocherkassk (zones 4, 8, 9, 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 ordinary chernozems. Plot 2 is occupied by an alluvial meadow sandy soil, and plot 3, which is situated on the floodplain only 300 m away from plot two, by a light clay meadow-chernozemic soil. The soils in plots 6 and 8 are heavy loamy meadow-chernozemic 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 and meadow chernozemic soils developed on loess-like loams were heavy loamy, and the alluvial meadow soil on alluvial deposits had a light texture. The light clayey meadow chernozemic soil on the alluvial deposits had maximal contents of physical clay and clay. The content of humus in these soils did not strongly vary (4.2–4.8%), except for the alluvial meadow calcareous sandy soil (2.9%). They were also characterized by low a cation exchange capacity (CEC), namely, 10 mmol (+) / 100 g soil.

The total contents of HM in the soils were determined with the X-ray fluorescence method. The parameters of the fractional-group composition of the HM in the studied soils were investigated using combined scheme for fractionating the HM compounds (Minkina et al., 2008). 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.

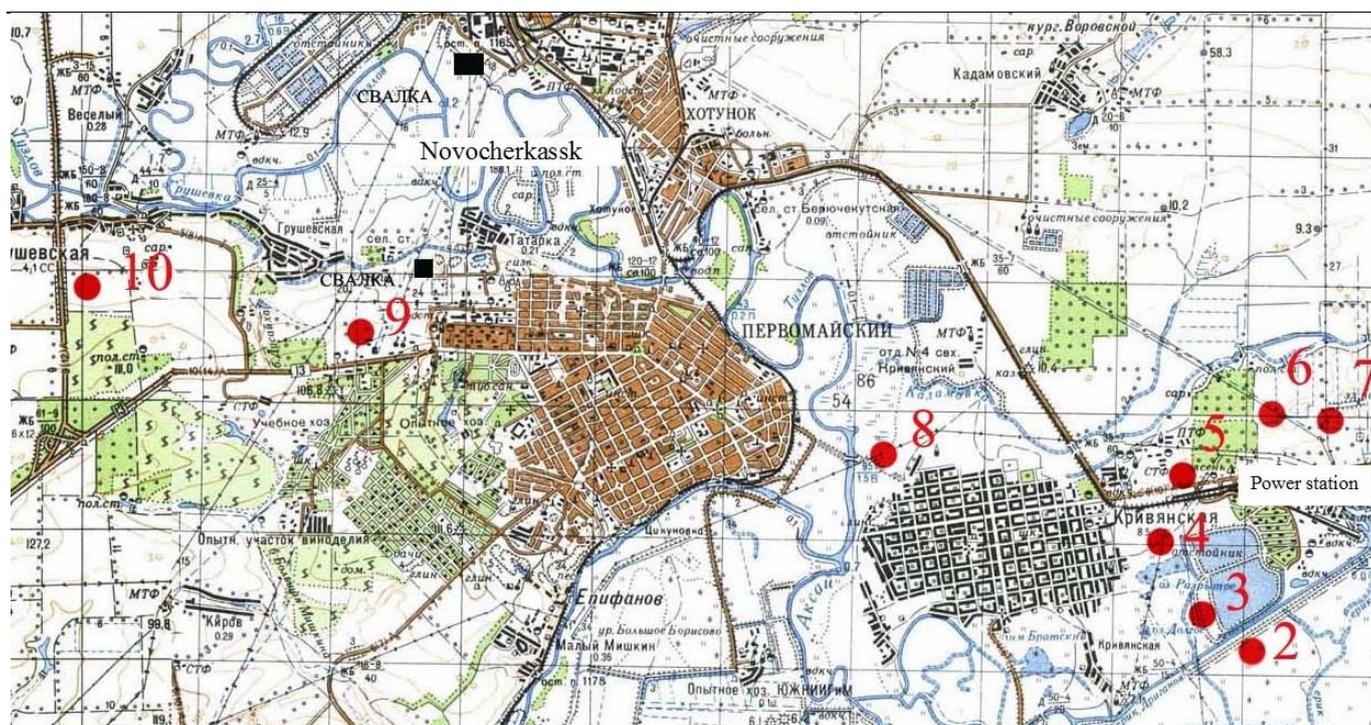


Figure 1. Schematic map of the allocation of the monitoring plots in the impact zone of the NPS. The direction and distance of the plots from the NPS:

- (1) 1 km to the NE; (2) 3 km to the SW; (3) 2.7 km to the SW; (4) 1.6 km to the NW; (5) 1.2 km to the NW; (6) 2.0 km to the NNW; (7) 1.5 km to the N; (8) 5 km to the NW; (9) 15 km to the NW; (10) 20 km to the NW

The HM compounds classified as loosely bound were transferred to solution by means of parallel extractions using the following reagents ([Methodological Guidelines...](#), 1992; [Minkina et al., 2009](#)):

1. A 1 N ammonium acetate buffer (NH_4Ac) pH 4,8 (soil : solution ratio 1 : 10, extraction time 18 h) capable of solubilizing the exchangeable forms of metals characterizing their “actual” mobility.
2. A 1% EDTA solution in NH_4Ac with pH 4.8 (soil : solution ratio 1 : 10, extraction time 18 h), which supposedly solubilizes the relatively unstable complex compounds of metals together with their exchangeable forms ([McLaren and Crawford, 1973](#)). The concentrations of the metals in the complex compounds were calculated by the difference between the metal concentrations in extracts 2 and 1 ([Nosovskaya et al., 2001](#); [Protasova and Gorbunova, 2006](#)).
3. The acid-soluble metal compounds extracted with 1 N HCl (soil : solution ratio 1 : 10, extraction time 1 h) characterize the reserve of the mobile metal compounds in the soil. They are supposedly represented by the metal ions capable of exchange and by the specifically absorbed compounds including the Fe and Mn retained by the amorphous oxides and carbonates. The amount of specifically absorbed metal compounds was calculated by the difference between the metal concentrations in the HCl and NH_4Ac extracts ([Minkina et al., 2009](#)). The additivity of the extracts was shown by experiments ([Minkina et al., 2008](#)).

The metal concentrations in the soil extracts were determined with atomic absorption spectrophotometry (AAS).

The parallel extraction of the metal compounds from the studied soils was combined with their successive extraction according to the Tessier method ([Tessier et al., 1979](#)). 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 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).

Table 1. Combined fractionation of metal compounds in the soil (Minkina et al., 2008)

Parameter	Method of determination	
	Experimental	Calculation (from the difference between the HM contents in extracts)
1. Content of exchangeable metal:		
– Total	1 N NH ₄ Ac, pH 4.8	
– Easily exchangeable	1 M MgCl ₂	
– Difficulty exchangeable		Difference 1 N NH ₄ Ac - 1 M MgCl ₂
2. Content of metal bound to carbonates and that in the form of separate phases:		
– Total	No method	
– LB (specifically sorbed)	1M NaCH ₃ COO, pH 5	
– SB (coprecipitated, occluded, chemisorbed, insoluble HM compounds)	No method	
3. Content of metal bound to nonsilicate Fe, Al and Mn compounds:		
– Total	0.04 M NH ₂ OH.HCl	
– LB (specifically sorbed)		Difference (1 N HCl - 1 N NH ₄ Ac) - 1 M NaCH ₃ COO
– SB (occluded) (except Mn oxides)		Difference 0.04 M NH ₂ OH.HCl - ((1 N HCl - 1 N NH ₄ Ac) - 1 M NaCH ₃ COO)
4. Content of metal bound to organic matter:		
– Total	30% H ₂ O ₂	
– LB (complex)		Difference 1% EDTA in 1 N NH ₄ Ac - 1 N NH ₄ Ac
– SB (chelates)		Difference (30% H ₂ O ₂ - 1% EDTA) - 1 N NH ₄ Ac
5. Content of metal SB to silicates	Extraction with HF + HClO ₄ from the residual soil fraction	Difference between the total element content in the soil and the total content of all fractions (except the residual fraction)

Results and Discussion

The total content of Ni and Cd in the soils of plots 9 and 10 (38–39 and 0.2–0.3 mg/kg, respectively) (Table 2) 15–20 km away from the source of the pollution was close to their clarkes by Vinogradov (1957) (40 and 0.5 mg/kg, respectively) and to the regional background (32 and 0.3 mg/kg, respectively) levels (Agafonov, 1994; Akimtsev et al., 1962; Ecology of Novochoerkassk..., 2001). The Cr concentrations in the soils of plots 9 and 10 (620–650 and 104–106 mg/kg, respectively) were below their clarkes by Vinogradov (1957) (850 and 200 mg/kg, respectively) and close to their regional background (624 and 110 mg/kg, respectively) concentrations (Agafonov, 1994; Akimtsev et al., 1962; Ecology of Novochoerkassk..., 2001). Such are the regional biogeochemical features of the soil microelement composition in Rostov oblast and of the mineralogical composition of the parent rocks.

The data on the total contents of the Ni, Cd, and Cr obtained with the X-ray fluorescence method were close to the sum of the fractions of these metals calculated using the data of their fractional-group composition (Table 2).

The distance of the points of the sampling and the wind direction are the main factors of the formation of the total HM content in the soils around the Novochoerkassk 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). The concentrations of Ni, and Cr in the soils sampled 1.2–1.6 km away from the source of the pollution in the other directions were 1.4–1.5 times higher and even smaller when the soils were 5 km away. All the studied soils located 1–5 km away from the NPS were classified as contaminated ones, and the total contents of the HM in these soils significantly exceeded their concentrations in the uncontaminated soils.

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

Plot number; distance (km) and direction from the NPS	Total content, mg/kg	Sum total fraction s, g/kg	LB/FB	Loosely bound compounds, % of the concentration in the group				Firmly bound compounds, % of the concentration in the group			
				exchangeable, MgCl ₂	complex	specifically sorbed on		Organic substances	Fe (hydro)oxides	silicates	
						carbonates	Fe and Mn (hydro)oxides				
Cr											
1. 1,0 NE	129	124	20/80	12	16	29	43	18	13	69	
2. 3,0 SW	85	72	22/78	8	5	33	54	4	28	68	
3. 2,7 SW	112	117	14/86	7	17	41	35	19	12	69	
4. 1,6 NW	137	152	26/74	15	16	35	34	18	14	68	
5. 1,2 NW	146	149	25/75	15	16	43	26	14	17	69	
6. 2,0 NNW	130	137	20/82	8	18	35	39	19	16	65	
7. 1,5 N	135	122	21/79	11	16	31	42	19	11	70	
8. 5,0 NW	128	118	19/81	9	10	21	60	18	7	75	
9. 15,0 NW	104	98	13/87	10	14	36	40	14	15	71	
10. 20,0 NW	106	103	13/87	8	14	25	53	12	14	74	
Ni											
1. 1,0 NE	59	56	26/74	3	10	63	24	13	14	73	
2. 3,0 SW	36	39	29/71	7	7	57	29	10	16	74	
3. 2,7 SW	48	52	20/80	6	11	53	30	19	12	69	
4. 1,6 NW	74	66	33/67	5	12	53	30	17	14	69	
5. 1,2 NW	64	67	33/67	5	12	46	37	16	17	67	
6. 2,0 NNW	59	62	32/68	9	9	55	27	18	15	67	
7. 1,5 N	55	49	26/74	5	12	35	48	15	16	69	
8. 5,0 NW	50	56	20/80	0	12	45	43	19	8	73	
9. 15,0 NW	39	42	8/92	0	6	44	50	15	11	74	
10. 20,0 NW	38	40	10/90	0	8	38	54	18	10	72	
Cd											
1. 1,0 NE	0,6	0,5	41/59	9	4	65	22	6	30	64	
2. 3,0 SW	0,4	0,5	42/58	10	0	85	5	7	57	36	
3. 2,7 SW	0,5	0,5	33/67	6	6	82	6	6	36	58	
4. 1,6 NW	1,0	1,0	47/53	22	4	54	20	10	25	65	
5. 1,2 NW	1,3	1,2	48/52	29	5	45	21	11	27	62	
6. 2,0 NNW	1,0	1,0	44/56	22	7	53	18	16	26	58	
7. 1,5 N	0,7	0,6	42/58	8	4	80	8	8	22	70	
8. 5,0 NW	0,6	0,4	31/69	0	7	72	21	6	45	49	
9. 15,0 NW	0,3	0,3	7/93	0	0	50	50	8	23	69	
10. 20,0 NW	0,3	0,2	10/90	0	0	50	50	11	17	72	

The compounds of Ni, Cd, and Cr in the uncontaminated soils were obviously dominated by the firmly bound ones, the portion of which comprised 85–89% of the total content for all the metals (Table 2). This was determined mostly by the metals fixed within the structures of the silicates (their portion comprised 69–74% of the total reserve of the firmly bound compounds of the HM 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 HM compounds was observed in the soils with the maximum technogenic loads (plots 4 and 5). The metals formed a decreasing series ($Cd > Ni > Cr$) according to the increase of the concentrations of their mobile compounds owing to the pollution. The portion of the loosely bound Cd forms increased maximally (up to 48%) in the contaminated soils of plots 4 and 5 (1.2–1.6 km away to the northwest from the source of the pollution) 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 slightly lower (up to 48%) in the soils 1.2–1.6 km away from the source of the pollution irrespectively of the direction, and it was even lower in the soils 5 km away from the NPS (up to 31%).

The portion of the loosely bound forms of Ni increased to a relatively lesser degree (up to 21–29%) in the soils of plots 1, 2, 3, 6, and 7 (they were less than 3 km away from the source) and by up to 20% in the soils 5 km away.

A specific feature of the Cr behavior consists of the fact that the portion of its loosely bound forms changed to a lesser degree than that of the other elements against the background of the increasing mobility in the contaminated soils. Their concentrations increased by 25–26% in the soils of the most polluted plots (4 and 5) and only by 19% in the least contaminated (plot 8) soils (Table 2).

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. An obvious domination of silicates is recorded among the firmly bound compounds in the case of the soil contamination with Cr, and Ni. 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.

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 and Ni.

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.

The composition of the loosely bound metal compounds in the uncontaminated soils is dominated by the specifically absorbed forms; their portion for Ni, and Cd exceeded 90%. It was lower for Cd and comprised 76–78% of the content of the loosely bound compounds. 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. A significant increase of the portion of the exchangeable compounds (almost up to 10 times) was typical for Ni. Hence, the HMs form the following decreasing sequence according to their danger of passing into the adjacent media (by reference to the changes in the composition and content of their loosely bound compounds owing to the contamination): $Cd > Ni > Cr$.

The soil properties play an important role in the accumulation and retention of metals. The difference in the ecological resistance of the soils relative to the metals was especially obvious when comparing the two monitoring plots near the emission source represented by soils with different sorption capacities. Lesser

amounts of metals were accumulated in the alluvial sandy soil (plot 2) than in the light clay meadow-chnozemic soil (plot 3), and they were fixed less firmly. This was suggested based on the increase as the result of the contamination of the portion of loosely bound compounds of metals in the sandy soil and their higher content in the exchangeable form. The portion of the loosely bound compounds of Cd was 48% in the alluvial soil of plot 2 and 42% in the meadow-chnozemic soil of plot 3; the portion of these forms of Ni comprised 34% in the alluvial soil against 24% in the meadow-chnozemic soil. The difference in the concentrations of the loosely bound compounds of Cr was less pronounced: 19 and 15%. The portions of the exchangeable compounds of metals in the group of loosely bound compounds comprised 15% Cr, 15% Ni, and 14% Cd in the alluvial meadow soil and was 3–7% lower in the meadow-chnozemic soil.

The insignificant amount of metals in the form of complex compounds and their tight fixing by Fe (hydro)oxides was related to the low content of organic matter in the alluvial soil (humus content of 2.9%). On the contrary, the organic matter (humus content of 4.0–4.7%) in the meadow-chnozemic soils (plots 3, 6, and 8) interacts actively with the HMs, and the concentrations of the complex compounds of the metals loosely and firmly bound with the organic matter were maximal in these soils. The soil in plot 3 differed from the other soils not only in the greater humus content but also in the clay (37%) and physical clay (63%) contents and, hence, in its higher CEC (42%). All these factors affected the fixation of the metals. Plot 8 situated at a greater distance from the emission source and occupied (similar to plot 3) by a meadow-chnozemic soil had close physicochemical properties. However, it had lesser amounts of mobile metal compounds.

Three zones of the risk of soil contamination with metals were outlined around the NPS on the basis of the revealed regularities of the formation and transformation of the Cr, Ni, and Cd compounds in the soils. The zone of the maximal risk of contamination with HMs was typical for the soils 1.6 km away in the northwestern direction from the NPS (plots 4 and 5). The total contents of Ni, Cr, and Cd increased in these soils in comparison with the background soils (by 1.3–4.3 times), and the portion of their loosely bound compounds (by 2–7 times) under the influence of the emissions of the NPS. The zone of moderate risk fell on the soils approximately at the same distance from the NPS to the N, NNW, and NE (plots 1, 6, and 7). The total concentrations of the metals in the soils of this zone increased by 1.2–2.3 times, and the portions of the loosely bound compounds increased by 1.5–6.0 times. The zone of low risk of contamination was 5 km away to the NW and about 3 km away to the SW from the NPS (plots 2, 3, and 8). The total contents of the metals in the soils of this zone increased by 2 times, and the portion of the loosely bound compounds of the metals increased by no more than 4.7 times.

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 Ni, Cr, and Cd compounds formation in the uncontaminated soils around the NPS, their transformation in the course of the soil contamination with the emissions, the effects of the different factors on the transformation of the metal compounds in the soils, and the ecological assessment of these factors.

The firmly bound forms predominately in the silicates predominate among the Ni, Cd, and Cr compounds in the uncontaminated soils. The loosely bound compounds of metals were dominated by the least mobile specifically absorbed forms. Carbonates played the most significant role in the formation of the specifically absorbed metal compounds' reserves.

The total contents of Ni, Cr, and 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 soil contamination with Cd was especially dangerous; the portion of its loosely bound compounds increased by 6 times and reached almost 50% of the total content of this metal. A relatively smaller increase of the mobility was observed for Cr. The portion of its most mobile fraction increased in the reserve of the loosely bound metal compounds. The portion of the exchangeable compounds of Cd (within this group of metal compounds) increased up to 30 times, and Ni by almost 10 times. The increase of the Cr by the increase of its forms loosely bound with carbonates. The studied metals formed the following decreasing sequence according to the ecological danger of the soil contamination: Cd > Ni > Cr.

The accumulation and tightness of the metal retention was higher in the light clay meadow-chnozemic soil than in the sandy alluvial meadow soil under the same technogenic load. According to the buffering capacity with respect to HMs, the soils in the vicinity of the NPS form the following increasing sequence: silty clayey

meadow-chernozemic soil < clay loamy meadow-chernozemic soil < clay loamy ordinary chernozem < sandy alluvial meadow soil.

Three zones of risk of the soil contamination with metals were determined in the studied territory: the zone of high risk, up to 1.6 km to the NW (the dominating direction of the wind); the zone of medium risk of contamination, a similar distance to the N, NNW, and NE; and the zone of low risk of contamination, more than 5 km to the NW and more than 3 km to the SW from the NPS.

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