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DEGRADATION, REHABILITATION, AND CONSERVATION OF SOILS

Monitoring of Soil Contamination by Heavy Metals in the Impact Zone of Copper-Nickel Smelter on the Kola Peninsula

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Abstract—The results of landscape monitoring of the concentrations of acid-extractable Ni, Cu, Co, Mn, and Zn in soils of the local impact zone of the Severonikel industrial complex on the Kola Peninsula are discussed. The aim of monitoring studies was to reveal the spatial and temporal regularities of variation in the degree of soil contamination by heavy metals. In 2001–2011, the concentrations of acid-extractable compounds of the elements in the upper part of organic soil horizons around this plant exceeded their background concentrations by two orders of magnitude for Cu and Co and by three orders of magnitude for Ni. The degree of topsoil contamination with Ni, Cu, and Co generally corresponded to the distance of the plots from the contamination source and to the modern technogenic load. However, because of the long period of the emissions, their extreme amounts, and complex composition, indirect factors—the degree of technogenic soil degradation, the loss of soil organic matter, saturation of the surface soil layers by the contaminating metals, and competitive relationships between the elements—also affect soil contamination level. The concentrations of all the studied metals in the topsoil are characterized by considerable (1.5 to 7 times) variability in their long-term dynamics. The most important factors of this variability for Ni, Cu, and Co are the organic matter content of the samples and the amount of atmospheric precipitation in the year preceding the sampling. An inverse relationship between element concentrations in the soils and the amount of atmospheric precipitation attests to the dynamic nature and reversible character of the accumulation of heavy metals in the soils.

Keywords: heavy metals, long-term dynamics, spatial distribution pattern, ecological consequences

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INTRODUCTION

The Severonikel copper–nickel industrial complex (at present, the Monchegorsk division of the Kola Mining and Smelting Company) on the Kola Peninsula is one of the largest and long-term (more than 70 years) emission sources of SO_2 and heavy metals in the north of Europe. Set of polluting elements, the degree and the scale of the soil pollution by the emissions of this enterprise are well studied [1–3, 6–8, 12, 17, 18]. However, the main soil type in the region—podzols were only thoroughly examined, besides the areas near the Severonikel complex with the most disturbed ecosystems were only characterized by a few sampling sites. It should be also noted that a partial reconstruction of the enterprise resulted in a considerable reduction of the emissions. In 2001, the integrated soil and geobotanical monitoring was launched in the local impact zone of the Severonikel complex with the aim to update information on the nature of changes in the soil properties in relation to the reduction of the emissions in the preceding 15 years and the beginning of restoration of vegetation in this area and to trace the relationships between the soil properties and the state of ecosystems. All the main soil types of the region (Podzols, Gleyic Podzols, and Histosols [9]) arranged in catenas were studied. The chemical composition of atmospheric precipitation was specially studied to characterize recent technogenic loads [16]. In previous works, we characterized the morphology of studied soils and the content and composition of organic matter in them [5], their acidity status [4], and the distribution of total Ni, Cu, Co, Cd, Pb, Zn, and Mn in the soil profiles with the analysis of relationships between the degree of soil contamination and the state of ecosystems [3].

In this paper, data on the acid-extractable Ni, Cu, Co, Zn, and Mn determined in mixed samples from the topmost (0–3 cm) layer of the surface soil horizons on experimental plots in 2001, 2002, and 2005–2011 are discussed. The sampling system made it possible to characterize the spatial distribution patterns of the soil contamination by heavy metals (HMs) in three aspects: the geographical aspect (with due account for the position of the experimental plots in relation to the source of emissions), the landscape aspect (with due account for the catenary position of the experimental plots), and the within ecosystem aspect (in dependence on the degree of soil degradation of the separate

Table 1. General characteristics of monitoring plots and their location relation to the source of emissions

Catena	Plot	Distance	Direction	Height, m a.s.l.	Topography	Vegetation	
						tree layer	dwarf shrub layer
I	I-1	17.2	NNE	187	Hill top	Sparse young pines	Technogenic barren
	I-2	17.1	NNE	164	Footslope	Sparse young pines	Rare dwarf shrubs
	I-3	17.1	NNE	157	Local depression	Absent	Sedge and cotton grass
II	II-1	7.9	N	158	Flat summit of hill	Bushy birches	Technogenic barren
	II-2	7.7	N	145	Footslope	Sparse bushy birches	Technogenic barren
	II-3	7.6	N	136	Local depression	Absent	Cotton grass
III	III-2	7.6	NNW	157	Middle slope	Sparse young pines	Technogenic barren
	III-4	7.8	NNW	142	Local depression	Absent	Sedge
IV	IV-1	3.2	NNW	178	Hill top	Technogenic barren	Technogenic barren
	IV-2	3.3	W	154	Middle slope	Single pines, spruces, birches	Technogenic barren
	IV-3	3.4	NNW	128	Local depression	Absent	Cotton grass
V	V-2	3	E	230	Middle slope	Spruce with birch	Blueberry
	V-3	2.5	E	176	Lower part of slope	Dense young birch forest	Dwarf shrubs
	V-4	2	E	144	Local depression	Absent	Cotton grass

spots or presence of pioneer mosses within ecosystem). The long series of observations allowed us to trace the long-term variability in HM concentrations, and the complex character of monitoring works made it possible to identify the factors affecting this variability.

OBJECTS AND METHODS

The long-term dynamics of the concentration of contaminants was monitored in soils of five catenas (I, II, III, IV, and V) at distances from 1 to 17 km from the Severonikel plant (Table 1). Each catena was represented by two–four experimental plots (1–4) numbered from the upper elements of local topography (tops or upper parts of slopes of local hills or mounts) with Albic Podzols toward footslopes with Gleyic Podzols and local depressions with Histosols.

As element concentrations sharply decrease with the depth [2, 3], only data on the topmost layer (0–3 cm) were used to compare the degree of contamination of different soils. On most of the plots, several types of mixed samples (MS) were taken. Type MS-Oer[1] from plots I-1, I-2, II-1, II-2, III-2, and IV-2 characterized the areas, where the ground vegetation was absent, and the surface layer consisted of the remains of the eroded litter (O) horizon mixed with mineral particles from the deeper horizons.

Type MS-BFer from plots I-1, II-1, III-2, IV-1, and IV-2 characterized the areas with outcrops of the eroded illuvial horizon as a result of erosion or frost heaving. Other types of MS were taken from the top layer of the organic soil horizon. Type MS-shrub characterized the areas under sparse dwarf shrubs (crowberry, cowberry, bilberry, and ledum) on plots I-1 and I-2 and the areas with preserved dwarf shrubs at the background level (plots V-2 and V-3). Type MS-grass characterized the areas with grassy vegetation (cotton grass and/or sedge) of low moors in local depressions (plots I-3, II-3, III-4, IV-3, and V-4). Type MS-Moss characterized the areas under pioneer moss species on mineral soils (plots I-2, II-2, and III-2) or on peat soils (plots I-3 and III-4).

Mixed sampled were collected at the end of August in 2001, 2002, and 2005–till 2011.

The total emissions of Ni and Cu from the Severonikel plant [16] reached 50 000 t/yr by the beginning of the survey (2001). Maximum emissions were observed in the 1980s; they decreased by about six times by 2001 according to official data reaching 1258 and 829 t/yr for Ni and Cu, respectively. From 2001 to 2011, the emissions decreased by 3.6 times for Ni and almost twice for Cu. Despite the considerable decrease in the emissions, the HM content in atmospheric precipitation of the local zone remained very high during this period [16]. Data on the total concentration of Ni—the main metal-contaminant—in the snowmelt on the studied plots are given in Fig. 1a.

A specific feature of the local impact zone of the Severonikel industrial complex consists is that the current emission fluxes interact with the soils that were considerably transformed by the long-term impact of

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[1] The Oer and BFer horizons are designated O and B, respectively, according to the new classification system of Russian soils.

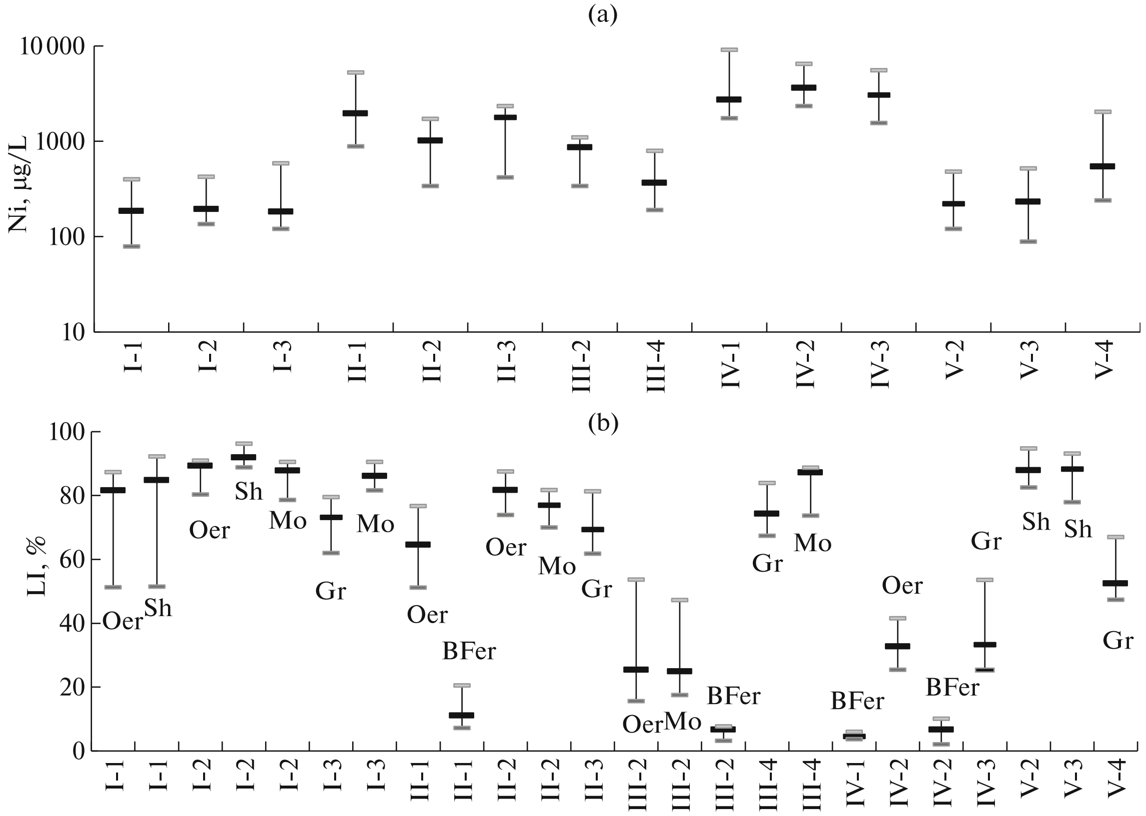

Fig. 1. Median and minimum–maximum of variation in the total Ni content in snowmelt water in 2005–2011 (a) and loss on ignition (b) in mixed samples (Sh is MS-shrub, Mo is MS-moss, and Gr is MS-grass) from the upper 3-cm-thick soil layer on monitoring plots in 2001, 2002, and 2005–2011.

emissions. By the beginning of the survey, the soils contained extremely high amounts of HMs [3]; on most of the plots, the soils were degraded and lost a considerable portion of their organic matter [5] with the high capacity to absorb and fix HMs. Each of the monitoring plots was characterized by the particular combination of technogenic load (Fig. 1a), the organic matter content (estimated as the loss on ignition (LI)) (Fig. 1b), and the contents of HMs (Table 2) in the upper soil layer. The highest concentrations of total Ni, Cu, and Co in the snow cover (i.e., current technogenic load) were typical of the plots or their parts, the soils of which were characterized by the significant (MS-Oer on plots II-1, III-2, and IV-2 and MS-Grass on plots IV-3 and V-4) or almost complete (MS-BFer on plots II-1, III-2, IV-1, and IV-2) loss of organic matter.

The background plot was not specifically chosen for this survey. To estimate the degree of contamination of podzols by HMs in the local impact zone, these data were compared with the median of data on the podzols of northern Finland [2, 3, 12, 17]. In these studies, the same sampling pattern and the same analytical procedures were used. Data on podzols can be also used for approximate assessment of the degree of contamination of other soil types.

The contents of Ni, Cu, Co, Mn, and Zn in the organic horizons were determined after the decomposition of the powdered sample in concentrated HNO_3. The samples from mineral horizons were decomposed by the mixture of concentrated HCl and HNO_3 (3 : 1). The contents of Ni, Cu, Co, Mn, and Zn in the obtained solutions was determined by atomic absorption on a Shimadzu 6800 spectrophotometer and a Kvant-Alfa spectrometer. All the analyses were made in a certified analytical laboratory of the Kola Geological Information Laboratory Center in Apatity.

The data treatment included the determination of the main statistical parameters (median, minimum, and maximum) of the content of acid-extractable forms of the elements for the main MS types and the construction of diagrams with the use of Microsoft Excel 2010. The reliability of differences between the compared data sets was assessed by the Mann–Whitney U-test (http://www.psychol_ok.ru/statistics/mann_whitney).

Table 2. Variations in the concentrations (median above the line and minimum–maximum under the line) of acid-extractable forms (HNO_{3conc} for organic horizons and 3 : 1 mixture of HCl_{conc} and HNO_{3conc} for mineral horizons) of contaminants in mixed soil samples on monitoring plots (data on 2001, 2002, 2005–2011) and under background conditions of the northern Finland (according to [2, 12, 17])

Plot	Mixed sample	*n*	Ni	Cu	Co	Zn	Mn
I-1	Oer	9	1270 390–2985	1034 277–1949	49 12–74	40 26–79	84 54–148
	Shrub	9	1323 806–2613	1004 550–1744	42 30–72	39 33–69	147 107–229
I-2	Oer	9	1758 1438–2776	1399 961–1951	65 47–90	54 26–79	68 55–121
	Shrub	8	1661 1099–2612	1212 943–2056	57 37–68	50 25–57	115 96–235
	Moss	9	1874 1338–2788	862 320–1297	70 51–90	39 25–103	52 34–76
I-3	Grass	5	961 716–1575	353 318–570	34 25–43	31 21–38	33 25–43
	Moss	9	1434 691–1941	610 255–774	42 21–63	36 18–105	48 33–66
II-1	Oer	7	6830 4120–13064	4880 4248–7016	239 138–310	64 39–109	92 72–157
	BFer	5	275 170–720	304 157–666	17 11.4–33	24 18.8–115	159 106–303
II-2	Oer	8	7002 2856–11026	5395 2588–8100	241 91–333	56 40–95	67 55–92
	Moss	9	7435 5213–10486	4763 3319–5880	255 170–319	73 39–151	73 45–105
II-3	Grass	9	10250 4873–13977	5508 4010–6751	402 149–523	76 32–134	740 182–1081
III-2	Oer	9	1781 685–3325	1285 433–2839	63 28–90	40 19–93	136 41–229
	BFer	5	217 124–288	132 76–177	11 8.0–15	21 9.9–82	146 104–201
	Moss	9	1438 1016–2601	1126 782–1858	51 38–87	35 21–62	139 74–254
III-4	Moss	8	2640 1570–4303	981 555–2023	73 47–146	28 18–76	48 36–76
	Grass	6	2754 1733–4416	1325 595–1858	82 59–122	34 17–86	39 29–56
IV-1	BFer	6	614 314–1073	206 144–607	22 12–35	24 19–115	131 64–259
IV-2	Oer	7	10 274 5597–17 160	3228 2965–4477	329 181–512	57 42–116	149 72–220
	BFer	7	812 781–1905	626 325–892	31 26–57	24 19–101	145 70–204

Table 2. (Contd.)

Plot	Mixed sample	*n*	Ni	Cu	Co	Zn	Mn
IV-3	Grass	7	6485 1620–10 308	4529 2133–7452	184 93–337	59 32–118	163 129–262
V-2	Shrub	8	3417 1538–4814	2674 1676–3283	116 69–213	54 40–99	389 343–711
V-3	Shrub	6	2203 1922–2876	2215 1579–4086	78 75–150	75 57–113	442 185–1350
V-4	Grass	9	3183 2080–5456	2862 1791–5834	109 14–220	51 40–141	157 102–324
Background	O horizon	177	5.5 2.0–17.4	6.7 2.7–24	1.14 0.3–8.8	48.2 12.7–103	122 19–1210
	BHF horizon	445	16.3 1.4–142	9.6 0.9–126	5.5 0.1–20.9	24.7 3.7–209	94.9 23.8–1450

RESULTS AND DISCUSSION

The contents of HMs on test plots and their comparison with background values. The lowest contents of acid-extractable compounds of the main contaminating metals (Ni, Cu, and Co), were found in the top layer of the organic horizon of soils on catena I, the most remote from the emission source (17 km to the north); the same regularity was established for the bulk contents of these metals [3]. On plot I-1, the median concentration of acid-extractable compounds in the MS-Oer exceeded the background value by 230 times for Ni, 150 times for Cu, and 40 times for Co (Fig. 2). The highest contents of acid-extractable Ni and Co were determined in the MS-Oer of the eroded podzol on plot IV-2 (3 km to the north-northwest of the emissions source). The median content of metals in the MS-Oer from this plot exceeded the background value by almost 2000 times for Ni and 300 times for Co. The highest acid-extractable Cu content was determined in the top part of the organic horizon of catena II (8 km from the plant). The median Cu content in the MS-Oer from plot II-1 exceeded the background value by more than 700 times.

The contents of acid-extractable compounds of the main contaminating metals (Ni, Cu, and Co) in the eroded illuvial horizon of podzols (MS-BFer) were significantly lower than those in the top organic horizon. The lowest contents of these elements in the MS-BFer were determined on plot III-2. Here, the median content of metals exceeded the background value by 13 times for Ni and Cu and twice for Co. The highest content of all the studied HMs in the MS-BFer was found for plot IV-2. The median exceeded the background value by 50 times for Ni, 65 times for Cu, and more than 6 times for Co.

The bulk contents of metals in the snow of monitoring plots exceeded the background value by 7 (plot II-3) to 38 (plot IV-1) times for Zn and from 15 (plot V-3) to 190 (plot IV-1) times for Mn. In contrast to the atmospheric precipitation, the concentrations of acid-extractable Zn and Mn compounds in the MS-Oer and MS-BFer from the studied plots were within the limits of their natural variation in the corresponding horizons of background podzols.

The balances calculated for small catchments in summer low-water period on the basis of median concentrations of soluble forms of elements [2] confirmed a significant Mn and Zn mobility in landscapes in comparison with the main contaminating metals. For example, the leaching of HMs with the surface water beyond the catchment in the impact zone of the Severonikel industrial complex comprised 40% for Ni, 2% for Cu, and 8% for Co with respect to their input with the atmospheric precipitation. The removal of Mn considerably exceeded its input with precipitation. The loss of Zn was about 10% of the metal input. The high mobility of Zn in the northern taiga landscapes is confirmed by sharp occasional rises in its concentrations in the surface water not only in the local impact zone but also under the background conditions beyond the impact zone [13].

The absence of an increase or a decrease in the concentrations of Zn and Mn in the top organic horizon of podzols in the local impact zone in response to their higher input with atmospheric precipitation may be explained by their competitive relationships with the predominant Ca and Mg cations rather than with the main contaminants (Ni and Cu), because the equivalent concentrations of Ca and Mg in the atmospheric precipitation and in the soils are significantly higher than those of Ni and Cu [2, 3].

Long-term dynamics of acid-extractable forms of HMs. The content of acid-extractable forms of HMs significantly varied from year to year in all the types of

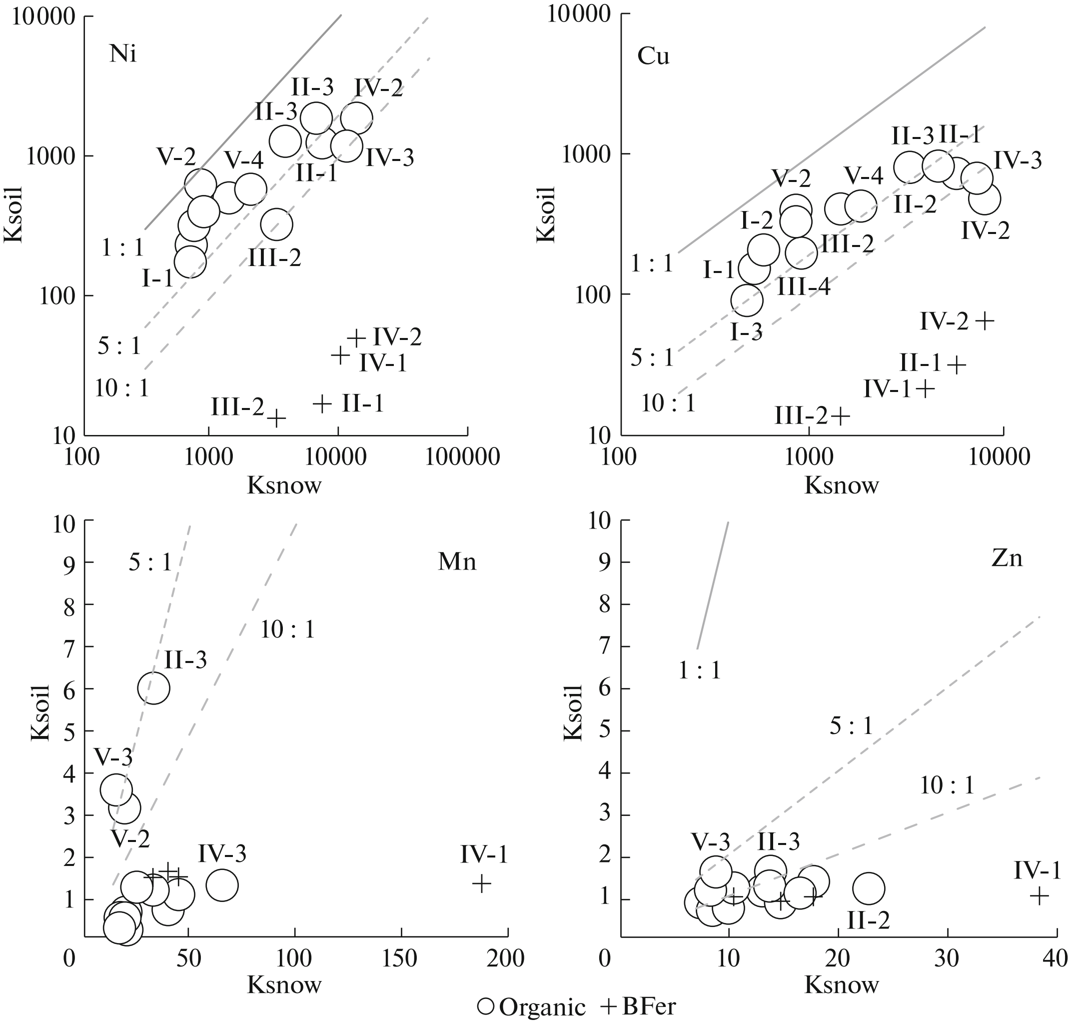

Fig. 2. Median concentrations of the total Ni, Cu, Zn, and Mn in snowmelt water on monitoring plots relative to their background concentrations (Ksnow) versus median concentrations of acid-extractable Ni, Cu, Mn, and Zn in mixed soil samples on monitoring plots relative to their background concentrations (Ksoil); data of 2005–2011.

MS (Fig. 3). The ratio between the maximum and minimum contents of HMs in the upper soil layer varied from 1.5 in the MS-shrub on plot V-3 to 7.6 in the MS-Oer on plot I-1 for Ni; from 1.5 in the MS-Oer on plot IV-2 to 7 in the MS-Oer on plot I-1 for Cu; and from 1.7 in the MS-grass on plots I-3 to 15.6 in the MS-Grass on plot V-4 for Co. Variations in the concentrations of accompanying contaminants (Zn and Mn) were of the same order.

Precipitation in the year preceding the sampling was one of the factors controlling the contents of exchangeable Ca and Mg (as well as the content of exchangeable hydrogen and the cation exchange capacity) in the upper soil layer within the local impact zone [4]. The highest content of the main contaminants (Ni, Cu, and Co) in most of the MS, as well as the exchangeable cations, was found in 2008. In the year from August 2007 to August 2008, the precipitation was the smallest (402 mm) of all the years of the monitoring. On the contrary, the minimum contents of Ni, Cu, and Co in the most disturbed soils were observed in August 2007. Note that the precipitation from May 15 to August 28 (the date of sampling) in 2007 reached 325 mm with 82% (265 mm) in the form of long heavy rains.

The analysis of data on 2005–2011 has shown a negative correlation between the concentrations of HMs and the annual precipitation for most of the MS. For the most degraded soils that lost a large part of their organic matter, this correlation was reliable. Thus, for Ni in the MS-Oer, the correlation coefficient *r* was –0.87 at $P = 0.99$; for Ni in the MS-moss, *r* was–0.84 at $P = 0.95$) on plot III-2 and for Cu in the MS-grass on plot IV-3 ($r = –0.94$, P = 0.95). Nevertheless, when this dependence is plotted on a diagram (Figs. 4a and 4b for Ni and Cu, respectively), it can be seen that the correlation is only caused by the agreement of a few extreme values.

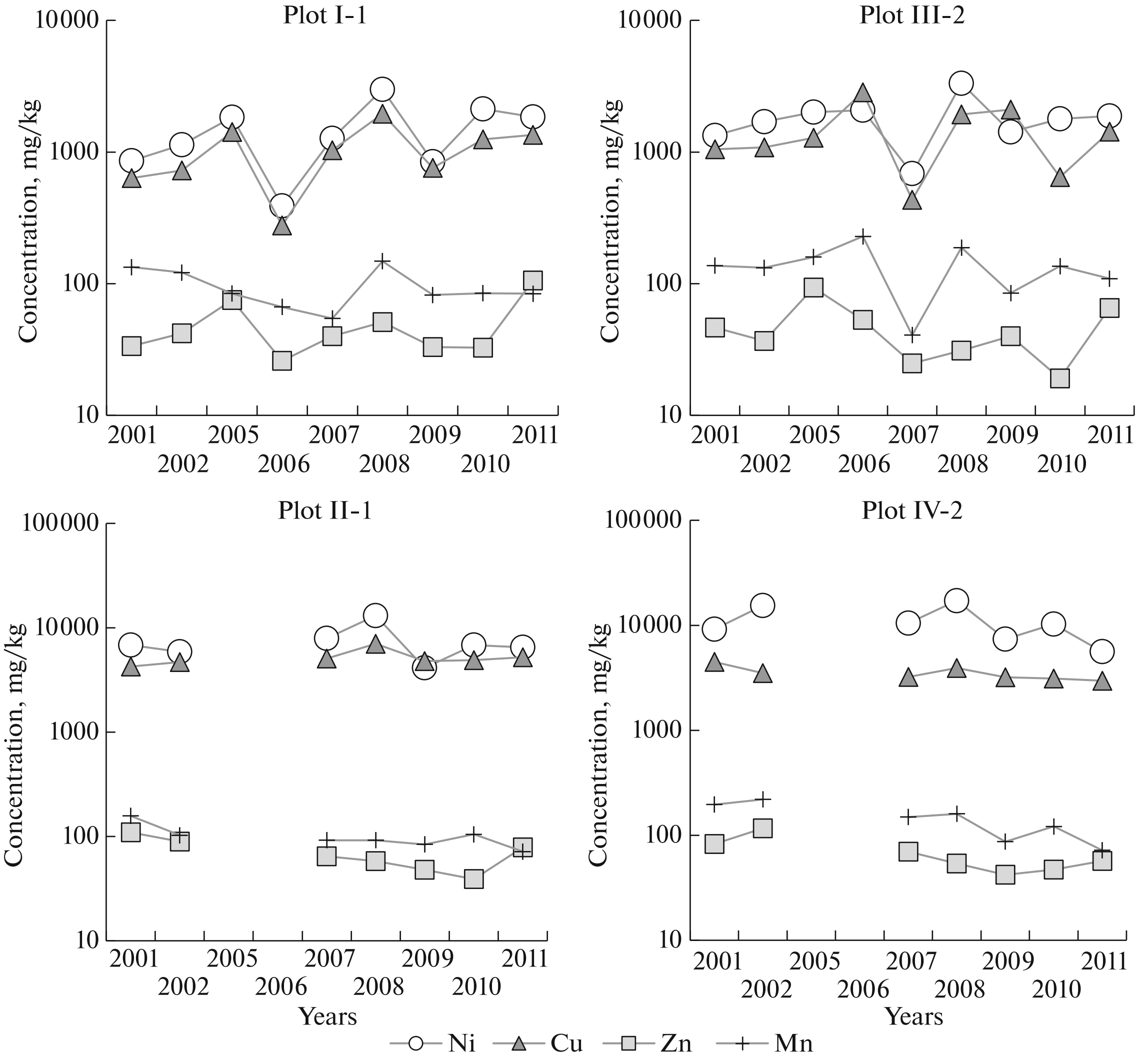

Fig. 3. Long-term dynamics of the concentrations of acid-extractable Ni, Cu, Mn, and Zn in mixed Oer samples on plots I-1, II-1, III-2, and IV-2 (data of 2001, 2002, and 2005–2011).

At the same time, the fact that the concentrations of HMs were high in 2008 with extremely low atmospheric precipitation and low in 2007 with extremely high precipitation suggests that the accumulation of HMs in soils is dynamic and may be reversible. The previously adsorbed HMs may be partially leached from the topsoil by the subsequent less concentrated atmospheric precipitation.

According to [11], first portions of precipitation are more concentrated than subsequent ones. The maximum bulk Ni concentration exceeded the minimum concentration of this element in rainwater on monitoring plots by 270 times (catena I) to 400 times (catena V); for Cu, the difference between its maximum and minimum concentrations in rainwater was somewhat smaller: 20 times (catena II) to 320 times (catena III) [16]. Variations in the content of contaminants in the snow cover on monitoring plots in the local impact zone from year to year were less significant: 3–8 times for Ni, 2–6 times for Cu, 2–14 times for Co, 7–48 times for Zn, and 3–170 times for Mn. However, most contaminants were removed from the snow with the first portions of snowmelt [15], which also resulted in the alternation of strongly and slightly contaminated solutions entering the soil.

The effect of atmospheric precipitations on the contents of HMs in the upper soil layer may be also related to the combination of different intensities and distances of lateral and radial migration of contaminants. It should be noted that HMs can migrate down the soil profile not only in ionic forms and compounds with organic matter but also as dust particles, because the size of technogenic dust (10–30 μm [14]) is comparable to pore sizes of sandy soils (10–100 μm [10]).

The content of organic matter with the high capacity for accumulation of many contaminants may be

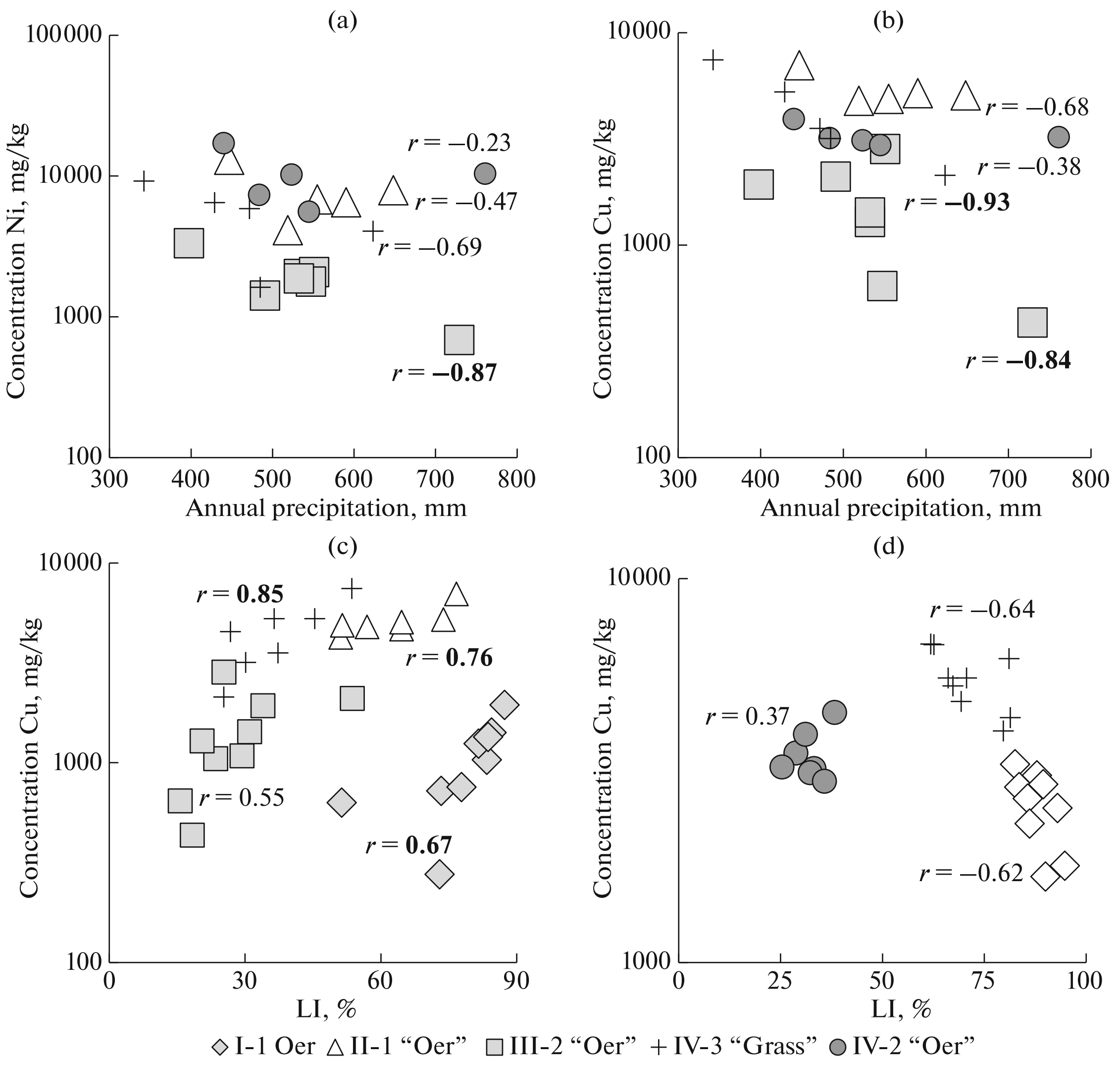

Fig. 4. The ratios between annual atmospheric precipitation and the concentrations of acid-extractable (a) Ni and (b) Cu and between the loss on ignition (LI) and the concentration of acid-extractable Cu (c, d) in mixed samples from monitoring plots (data of 2005–2011). Correlation coefficients reliable at significance level of 99% are given in bold type.

another factor responsible for the variation in the HM contents in the samples. The most considerable difference in the organic matter content was seen in the MS characterizing the most disturbed soils—eroded podzols (Fig. 1b). For example, the loss on ignition in the MS-Oer and MS-BFer varied by 1.6 and 4.8 times, respectively, on plot IV-2 and by 3.4 times in the MS-Oer on plot III-2. Such a considerable variation in the organic matter content in the MS-Oer may be explained by the high spatial unevenness in the residual thickness of the eroded organic horizon and variable portion of mineral admixture in it. Therefore, the MS-Oer in eroded podzols (plots I-1, II-1, III-2, and IV-2) included various combinations of organic matter and mineral admixture in different years. On plots I-1, II-1, and III-2, the contents of Cu (Fig. 4c), Ni, and Co in the MS-Oer were characterized by a pronounced positive correlation with the organic matter content.

The correlation between the content of the main contaminating metals and the organic matter in the MS-Oer of the most contaminated plot IV-2 is weaker (Fig. 4d). Thus is due to the fact that the sorption in the top organic horizon on this plot has reached its saturation limit, and the metals are accumulated due to the mechanical fixation of technogenic dust [3]. Its content is largely determined by the ratio between dust input with atmospheric precipitation and transportation down the slope or into deeper horizons.

A positive correlation between the organic matter content and the amount of Cu (r = 0.85, P = 0.95) and Ni (r = 0.49) was also revealed in the MS-grass on plot IV-3. The organic matter content in the top soil layer of this plot was determined by the ratio between the input of mineral particles with the surface lateral flow from the above-located eroded slope and their leaching to deeper peat layers by the radial flow. As the difference between the Mn and Zn contents in the organic and mineral horizons was not large, the effect of the ratio between the organic and mineral material in the MS on the concentration of these elements was not revealed.

Less disturbed plots at the foot of the slope (plots I-2 and II-2 with gleyic podzols under semihydromorphic conditions) were characterized by the greater organic matter content in the top organic horizon in comparison with eroded podzols of automorphic landscape positions. The MS-Oer from these plots was specified by less significant variations in the organic matter content (Fig. 1b) and in the contents of Ni, Cu, and Co in their long-term dynamics in comparison with the automorphic podzols. The correlation between the loss on ignition and the contents of HMs was absent.

On the plots with well-preserved vegetation (mountain ecosystem on plot V-2 and low moors (except for plot IV-3)), the correlation between the contents of HMs and organic matter in their long-term dynamics, on the contrary, becomes negative. This correlation is reliable for Ni and Co in the MS-shrub on plot V-2 ($r = -0.84$ and -0.87, respectively; $P = 0.99$). The negative correlation of Ni and Co contents with the loss on ignition is also reliable for the MS-grass on plot II-3 ($r = -0.91$, $P = 0.99$ for both elements). The correlation of Cu with the loss on ignition is insignificant, though it is well seen on the diagram (Fig. 4d). A decrease in the contents of Ni, Cu, and Co with an increase in the organic matter contents explained by the fact that different quantities of fresh litterfall participate in the MS on these plots every year. Fresh litterfall are characterized by the high organic matter content and a relatively low content of HMs in comparison with the top organic soil horizon. For example, fresh litterfall on plot V-2 are mainly represented by birch and bilberry leaves with the median loss on ignition of 96.4 and 95.9%, respectively, and the Ni content of 68 and 46 mg/kg, respectively. At the same time, the median loss on ignition in the MS-shrub is 88%, and the Ni content is 3417 mg/kg. The difference between the organic matter and HM amounts in the MS-grass and leaves of cotton grass (the main suppliers of fresh litterfall) on plot II-3 is even more considerable. The median values of the loss on ignition on this plot are 69.3 and 95.6%, for the MS-grass and leaves of cotton grass, respectively, and the Ni concentration is 10 250 and 67 mg/kg, respectively.

The content of HMs in top soil layers may be also influenced by the modern HM input with atmospheric precipitation, which remains very high and varies from year to year. This is especially the case for the plots near the contamination source. For example, at the median Ni content in the MS-Oer about 10 g/kg on plot IV-2, its fallout in the winder varied from 0.4 (2009) to 1.3 g/m^2 (2007) [16].

Thus, several factors affect the contents of HMs in the top soil layers of the local impact zone. These factors may act in somewhat different directions, and their combination and, hence, summary effect may be specific for each plot. For example, in 2007, a large amount of atmospheric precipitation was accompanied by the high Ni and Cu content in the snow on most of the plots. However, on plots I-2, I-3, and II-1, the high precipitation coincided with the smallest deposition of these elements in the winter. For the MS-grass on plots I-3, II-3, and III-4 and for the MS-Oer on plot III-2 and IV-2, the negative effect of the high precipitation in 2007 was enhanced by the low content of organic matter. In 2008, the lowest atmospheric precipitation coincided with the low HM concentrations in it on most of the most plots. For the MS-Oer on plots I-1, II-1, II-2, and III-2, the positive effect of the dry year was enhanced by the high organic matter content.

Spatial distribution pattern of soil contamination by HMs. The distribution patterns of the main contaminating metals (Ni, Cu, and Co) in the upper soil layer within the local impact zone generally correspond to the distribution patterns of these metals in the snow cover. However, as seen from Fig. 2, the ratios between element concentrations in the soils and in the snow cover are variable; for some plots, the proportionality between them is absent. As for the accompanying contaminants (Zn and Mn), the correlation between their concentrations in the upper soil layer and in the snow is absent.

Distance from the source of emissions. For the assessment of the effect of the distance from the source of emissions on the concentration of HMs in the upper soil layer, we compared data on the MS-Oer taken from podzols on the summits and slopes of the studied catenas: MS-Oer from plots. I-1, II-1, III-2, and IV-2; the MS-shrub sample characterized plot V-2. These plots may be arranged in certain sequences according to the following parameters:

(a) distance from the source of emissions—IV-2 = V-2 > II-1 > III-2 > I-1;

(b) median of Ni, Cu, and Co concentrations in the snow—IV-2 > II-1 > III-2 > V-2 > I-1;

(c) median of Ni and Co concentrations in the MS—IV-2 > II-1 > V-2 > III-2 > I-1; and

(d) median of Cu concentrations in the MS—II-1 > IV-2 > V-2 > III-2 ≥ I-1.

They testify that the distance of the plot from the source of emissions and the level of technogenic load on it not always determine the degree of contamination of the upper soil layer with HMs. Changes in the position of plot V-2 in the sequences characterizing HM concentrations in the snow and soils as dependent on the distance from the emission source are related to the location of this plot beyond the major directions of the local wind rose and above the emission flare. As a result of the low content of organic carbon in the MS-Oer, plot III-2 is shifted to the end of the sequence characterizing Ni and Cu concentrations. A higher amount of Cu in the upper soil layer on plot II-1 in comparison with plot IV-2 located closer to the source of emissions and generally stronger contaminated, is explained by several reasons: a narrow Ni to Cu ratio in the atmospheric precipitation [16], a higher organic matter content in soils of plot II-1 (Fig. 1b), and a stronger affinity of Cu to the soil organic matter.

The Mann–Whitney U-test shows that the differences between the plots at different distances from the source of emissions (except for plots I-1 and III-2) with respect to the contents and major contaminants (Ni, Cu, and Co) in the MSs are significant. The differences between the plots in the degree of contamination of the upper soil layer with HMs in different years may be considerable: thus. Ni concentration in the MS-Oer from plot I-1 (the least contaminated) differed from that in the MS-Oer from plot IV-2 (the most contaminated) by four times in 2002 and by 15 times in 2011.

Differences between the plots in Zn concentration in the MSs were no greater than three times and were statistically insignificant. The distribution of Zn in the analyzed samples did not depend on the distance from the source of emissions and on the atmospheric fallout of Zn in the winter season.

The concentrations of Mn in the MS-shrub of plot V-2 was significantly (according to Mann–Whitney U-test) higher in comparison with all the other plots. Its low amount in the snow on this plot testifies that the increase in the Mn concentration in the upper soil layer is not related to the emissions. Under these particular conditions, it may be related to the influence of the trees and dwarf shrubs preserved on this plot, as their falloff is rich in Mn. The differences between other plots in the Mn concentrations in the upper top soil layer were less significant (from 1.1 to 3.6 times) and depended neither on the distance from the source of emissions nor on the precipitation in the winter season.

Intraecosystem differences. The comparison of data on HM concentrations in different MSs taken on one plot (under conditions of the same technogenic load) makes it possible to evaluate the effect of the degree of technogenic degradation of the plot or the appearance of pioneer mosses on the concentrations of HMs in the upper soil layer. The content of organic matter and the concentrations of Ni, Cu, and Co are significantly (according to the Mann–Whitney U-test) lower on the spots with the exposure of the illuvial horizon to the surface (MS-BFer on plots II-1, III-2, and IV-2) in comparison with the spots, where fragments of organic horizon are preserved (MS-Oer). For example, Ni concentration in the MS-Oer on plot IV-2 was from 4 (2009) to 21 times (2008) higher in comparison with that in the MS-BFer.

The differences between the plots with suppressed dwarf shrubs in the Ni, Cu, and Co concentrations in the MS-shrub (spots with a small annual input of fresh littrfall) and MS-Oer (areas without fresh plant littrfall for a long period) on plots I-1 and I-2 were insignificant according to the Mann Whitney U-criterion.

The spots with very small (1–2 mm) pioneer mosses on plots I-2, III-2, and II-2 also did not exert a significant impact on the organic matter content and HM concentrations in the upper soil layer.

The MS-moss on bogs of plots I-3 and III-4 under hydrophytic pioneer mosses differed from the MS-grass in a higher organic matter content, loose consistence, and shorter period of interaction with technogenic flows (mosses appeared after the decrease in emissions). However, the differences in HM concentration between these two MS were insignificant according to the Mann–Whitney U-test.

Contrary to the other elements, the concentration of Mn in the samples greatly depended on the presence of dwarf shrubs. For example, the Mn concentration in the MS-shrub on plots I-1 and I-2 was significantly (according to the Mann–Whitney U-test) higher in comparison with that in the MS-Oer. It may be concluded that even a small amount of fresh litterfall with a higher Mn content (the median of Mn content in leaves within the local impact zone was 348 mg/kg for birch, 704 mg/kg for cowberry, and 1215 mg/kg for bilberry) exerts a considerable influence on the concentration of Mn in the upper soil horizon under dwarf shrubs. The high content of Mn in the upper soil horizon on plots. V-2 and V-3 with well preserved trees and dwarf shrubs confirms the possible impact of fresh litterfall on the Mn concentration in the upper soil layer.

The Mann–Whitney U-test did not show significant differences in the Zn contents between the studied MS types. This is explained by a small difference in the amount of acid-extractable Zn forms between the organic and mineral horizons and between soils and vegetation (medians of Zn concentration in the leaves is 52 mg/kg for birch, 241 mg/kg for cowberry, 22 mg/kg for bilberry, and 31 mg/kg for cotton grass) and also by considerable variations in the Zn content of the upper soil layer in the long-term dynamics.

Differences between the plots of the same catenas. The comparison of data on concentrations of HMs in the MSs from the plots occupying different landscape positions is very important for studying the regularities of the spatial distribution of soil contamination under conditions of the rugged topography. The plots on the catenas were located at distances of 100–500 m from one another. The differences in technogenic loads on them (as judged from data on HM contents in the snow) were insignificant according to the Mann–Whitney U-test (Fig. 1a). The only exception was represented by catena V, where plot V-4 was found closer to the source of emissions and was characterized by significantly higher contents of Ni and Cu in the snow in comparison with plots V-2 and V-3 on the slope. The complicated topography favored the redistribution of HMs in the landscape with their higher accumulation in the soils of subordinate positions.

The effect of the distance from the source of emissions was analyzed only for one soil type—podzols—occupying local tops and slopes. At the same time, technogenic fluxes of HMs interact with different types of soils along the catenas: podzols on tops and slopes, gleyic podzols on footslopes, and Histosols in the local depressions. The organic matter content (Fig. 1b), the thickness of the upper organic horizon, and the redox conditions in the upper soil layer along the catena may considerably differ in dependence on the soil type and the degree of soil degradation. In some cases, the difference in organic matter content is statistically significant according to the Mann–Whitney U-test.

Despite significant differences in the soil conditions along the catenas, our data do not show any definite regularities in the distribution of HM concentrations in the upper soil layer in dependence on the landscape position of particular plots. In most cases, distribution patterns of HMs content in the MSs were individual for each catena, each element, and each particular year.

CONCLUSIONS

The concentrations of acid-extractable forms of major contaminating HMs in the upper soil layer within the local impact zone of the Severonikel industrial complex in 2001–2011 were hundreds (for Cu and Co) and thousands (for Ni) of times higher than those in the background soils. The concentrations of acid-extractable Mn and Zn in the upper organic soil layers and in illuvial horizons exposed to the surface did not exceeds their background concentrations.

The differences between minimum and maximum concentrations of acid-extractable HMs in the soil samples varied from 1.5 to 6–7 times during the survey period. The organic matter content in the sample exerted the most considerable effect on the concentrations of Ni, Cu, and Co: the relationships between the organic matter content and the concentrations of these HMs depended on the degree of degradation of vegetation and soils on the particular plots.

At the same time, the high concentrations of HMs in the upper soil layer in 2008 with extremely small atmospheric precipitation and their low concentrations in 2007 with the highest atmospheric precipitation suggest that the processes of HM accumulation in the soils are dynamic and may be reversible. Heavy metals not only enter the soils with atmospheric precipitation; some part of HMs previously accumulated in the soil may be leached off from the upper soil layer by the subsequent less concentrations portions of atmospheric precipitation.

Other factors may also affect the variation in the concentrations of HMs in the soils: the intensity of atmospheric precipitation, the level of recent fallout of HMs with atmospheric precipitation, and the presence and quantity of fresh litterfall (i.e., the state of the local ecosystems).

The distribution patterns of Ni, Cu, and Co in the upper soil layer on the examined plots do not always correspond to the distance from the source of emissions and the degree of contamination of the snow cover. This is related to the fact that the sorption capacity of the upper soil layer becomes smaller in the most considerably contaminated and degraded ecosystems because of the significant loss of organic matter and the approaching of the soil to the saturation limits with the major contaminants (Ni and Cu).

Within a given ecosystem, the concentrations of acid-extractable Ni, Cu, and Co in the samples from the illuvial horizon exposed to the surface are much lower than those in the soils with the preserved organic horizons. Therefore, from the ecological point of view, the complete destruction of forest litter and the exposure of the illuvial horizon to the surface may be considered the processes favoring self-purification of the soils and creation of more favorable conditions for pioneer plants. This is confirmed by the allocation of seedlings of trees and mosses to the areas with the strongly disturbed or completely removed forest litter.

The participation of dwarf shrubs results in a significantly higher content of acid-extractable Mn in upper soil layer under the shrubs. The low content of this important for plants microelement in soils of heavily disturbed ecosystems may be related not only to the competition with the main cations as was supposed earlier [2, 3] but also to the destruction of vegetation by the emissions, so that the soil does not receive fresh litterfall with the high concentration of this element.

Despite considerable differences in soil conditions, we failed to find some general regularities in the distribution of HMs in the upper soil layer in dependence on the catenary position of the plots. The absence of significant variations in the concentrations of acid-extractable forms of the main contaminating metals (Ni and Cu) in the upper soil layer along the catenas confirms the conclusion [3] that the improvement of the state of ecosystems from the tops of the hills (with the most degraded ecosystems) toward their footslopes and local depressions with eutrophic bogs is not related to the level of the of HMs in the soils.

The objective assessment of the degree of soil contamination by HMs cannot be based on data of one sampling because of the great variations in the contents of HMs and their long-term dynamics. The data of long-term monitoring studies are required for this purpose. The spatial nonuniformity of the degradation rate and the presence of vegetation should be taken into consideration in the design of sampling patterns on monitoring plots.

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