ISSN 1064-2293, Eurasian Soil Science, 2017, Vol. 50, No. 8, pp. 977–990. © Pleiades Publishing, Ltd., 2017.
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DEGRADATION, REMEDIATION, AND CONSERVATION OF SOILS

Long-Term Dynamics of Heavy Metals in the Upper Horizons of Soils in the Region of a Copper Smelter Impacts during the Period of Reduced Emission

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Received March 3, 2016

Abstract—The 23-year-long dynamics of actual acidity (pH_{water}) and acid-soluble heavy metals (Cu, Pb, Cd, Zn) in the forest litter and humus horizon of soils in spruce-fir forests were studied in the area subjected to the long-term (since 1940) pollution with atmospheric emissions from the Middle Ural Copper Smelter (Revda, Sverdlovsk oblast). For this purpose, 25 permanent sample plots were established on lower slopes at different distances from the enterprise (30, 7, 4, 2, and 1 km; 5 plots at each distance) in 1989. The emissions from the smelter have decreased since the early 1990s. In 2012, the emissions of sulfur dioxide and dust decreased by 100 and 40 times, respectively, as compared with the emissions in 1980. Samples of litter and humus horizons were collected on permanent plots in 1989, 1999, and 2012. The results indicate that the pH of the litter and humus horizons restored to the background level 10 and 23 years after the beginning of the reduction in emissions, respectively. However, these characteristics in the impact zone still somewhat differ from those in the background area. In 2012, the content of Cu in the litter decreased compared to 1989 on all the plots; the content of Cu in the humus horizon decreased only in the close vicinity of the smelter. The contents of other metals in the litter and humus horizons remain constant or increased (probably because of the pH-dependent decrease in migration capacity). The absence of pronounced removal of metals from soils results in the retention of high contamination risk and the conservation of the suppressed state of biota within the impact zone.

Keywords: industrial pollution, toxicity, soil remediation, soil recovery, metal mobility, ecosystem stability, resilience, Retisols

DOI: 10.1134/S1064229317080130

INTRODUCTION

Long-term atmospheric emissions from large metallurgical works form technogenic geochemical anomalies, in the epicenter of which the concentrations of heavy metals can exceed the background values by several orders of magnitude [47]. Such strong contamination has a harmful effect on biota and provokes radical changes in the structure and functioning of terrestrial ecosystems and their almost complete degradation on industrial barrens in the close vicinity of enterprises [56]. The high level of contamination near works is hazardous for humans not only due to the direst toxic effect but also because of the input of metals through food chains [40].

In the last decades, atmospheric emissions from metallurgical works decrease in many countries due to the reduction in production level (or the closure of enterprises) or the modification of technologies. The opportunity for studying the natural recovery of soils is an indirect result of this reduction. Along with the obvious practical aspects (e.g., related to remediation strategies), studies in this field are important in terms of fundamental ecology, because they allow analyzing the stability mechanisms of ecosystems in the impact region [9] (in our case, their resilience). Therefore, the analysis of biota dynamics during the period of emission reduction attracts interest [13, 21, 34, 52, 67].

In terms of the natural restoration of ecosystems, it is important to assess the rate of soil purification from pollutants, because this makes it possible to consider the changes in the toxic load on vegetation and soil biota in time. Such estimates are especially necessary for the upper soil horizons, because, first, they concentrate the major part of roots and active soil biota, and, second, the maximum concentrations of metals in the polluted areas are usually observed in the upper 20-cm-thick layer of soil profile [40]. Consequently, the processes occurring in these horizons largely determine the rate and character of restoration of the entire ecosystem.

An extremely low removal rate of heavy metals from the soil was demonstrated in the early studies of

† Deceased.

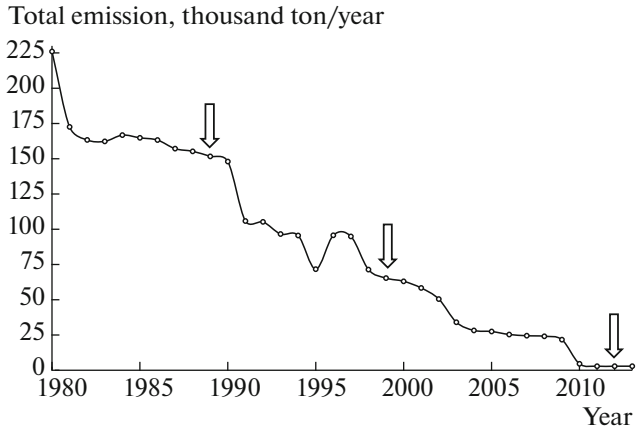

Fig. 1. Dynamics of total emission from the MUCS during the period of 1980–2013; arrows indicate the years of soil sampling for contamination assessing.

technogenic pollution consequences. Tyler [66] showed in laboratory experiments that even the partial unloading of soil requires hundreds of years. Similar estimates were obtained later in other laboratory [42] and field [16, 50] experiments, as well as from data on the removal of metals to the coupled soil horizons [49] or landscapes [20]. The increased concentrations of metals in the areas of metallurgical plants abandoned about 100 years ago [49] or even in the antic time [58] can be also evidence for the low mobility of metals.

Long-lasting (but generally not exceeding several tens of years) observations of metal dynamics in soils in the impact zones of large metallurgical plants are low in number, and their results are contradictory: a relatively rapid (within ten years) decrease in metal concentrations after the reduction of emission from the enterprise is reported [38, 45, 51, 62], as well as a constant contamination level [15, 17] or even its increase [25, 55].

The thesis about the extremely low mobility of heavy metals in the soil is frequently used to explain the stability of the suppressed state of biota after the reduction (or complete cessation) of emissions. In particular, this was made in the studies on the demography of birch [18] and bilberry [26], the diversity of the grass-subshrub layer [13, 34], and the abundance of soil fauna [10, 31], which demonstrated the absence of positive trends in biota dynamics. On the other hand, a relatively rapid biota restoration was also reported, including radial growth of trees [37, 54], the abundance of the grass-subshrub layer [38, 39] and lichens [64], and demographic parameters of birds [48]. Contradictory data are also available on changes of metal concentrations in plants and animals after the cessation of emissions: along with their decrease in organisms of small mammals [63], no changes in bird excrements are noted [43], which is attributed to the retention of high metal contents in the soil.

Thus, information on changes in the contents of metals and the state of biota in contaminated areas after the reduction of emissions is obviously insufficient.

The aim of this work was to analyze the long-term dynamics of heavy metal (Cu, Pb, Zn, Cd) concentrations and actual acidity in forest litter and the humus horizon of soils in the impact region of a large copper smelter during the period of a considerable reduction in its atmospheric emissions. Preliminary results on the contents of two elements (Cu and Pb) only in the humus horizon were reported earlier [34]. We tested the hypothesis that the contents of heavy metals and acidity in the upper soil horizons change little in the first decades after the reduction of emissions. Sampling was performed before the strong reduction of emissions, as well as 10 and 20 years later (Fig. 1).

Attention should be given to the following methodological aspect: the same plots should be considered for the analysis of metal dynamics under natural conditions, because otherwise the spatial variation could be mistaken for the change of parameters in time [13]. This is of special importance for the impact areas, because the spatial variation of metals and acidity under strong contamination is high at a scale of tens or hundreds of meters [7, 12]. Unfortunately, the use of the same sample plots in long-term studies in the impact regions is an exception rather than a rule. Our work belongs to such exceptions, because it is based on the survey of the same sample plots. However, even this scheme does not ensure the complete exclusion of some interfering factors, which can obscure the long-term dynamics. This is first true for the unavoidable micro-scale spatial heterogeneity (at a scale of tens of centimeters or few meters for sampling within a sample plot), as well as the seasonal and interannual variation. It is known that the seasonal variation can be manifested not only for mobile metal forms [27, 61], but also for their total content [61]: the maximum levels are observed in winter, early spring, and late fall, and the minimum levels are observed in summer. In our case, the effect of this factor can be ignored, because samples were collected at similar dates in different years. The contributions of interannual variation and micro-scale spatial heterogeneity are most probably insignificant [41].

OBJECTS AND METHODS

Studies were performed in the impact zone of atmospheric emissions from the Middle Ural Copper Smelter (MUCS) located on the periphery of the city of Revda, Sverdlovsk oblast (50 km to the west of Yekaterinburg). The smelter has operated since 1940; the main emission components are gaseous sulfur, fluorine, and nitrogen compounds, as well as dust particles with sorbed heavy metals (Cu, Pb, Zn, Cd, Fe, Hg, etc.) and metalloids (As). In the 1980s, the total MUCS emission reached 150000–225000 tons of pollutants annually, which made the enterprise one of the

Table 1. Dynamics of MUCS emissions during the period of 1980–2012, t/year

Component	Year of emission recording					
	1980	1989	1999	2005	2009	2012
SO_2	201450*	134089	57917	24272	19500	1730
Dust	21422*	16086	6395	2478	1560	485
HF	1943*	1015	32	20	no data	
NO_x	1214*	479	381	272	"	
Cu	4400	2610	402	45	13**	0.8**
Zn	no data	1753	810	225	168**	118**
As	943	640	116	18	6**	0.6**
Pb	1077	564	336	146	117**	66**

* Calculated indirectly from the known emission for the entire city of Revda and the MUCS/Revda ratio in 1986.

** Calculated indirectly from the known emission of dust and the element/dust ratio in 2005.

largest sources of technogenic pollution in the country. The emission gradually decreased since the early 1990s to 65000 t/year in 1999, 27000 t/year in 2005, and 3000–5000 t/year after the fundamental reconstruction in 2010 (Table 1).

The region under study is located to the west of the MUCS, in the southern taiga subzone, within the residual ridge of the axial Middle Urals and its western slope. According to the physicogeographical zoning of Sverdlovsk oblast, this area belongs to the natural region of the Middle-Ural low hills (with the predominance of dark coniferous forests) [22]; according to the soil-geographical zoning, it belongs to the Konovalovo and Kirgishan soil regions of the Middle-Ural soil province [14].

Spruce-fir forests with elements of nemoral floristic complex on gentle slopes of ridges were studied. When the distance from the emission source decreases, the woody layer is suppressed (the stand density, wood reserves, and crown closure decrease; the portion of dead trees increases) and the species richness and the abundance of the ground vegetation layer decrease. The manifestation of these processes varies among the load zones. The background zone characterizes the relatively undisturbed state subjected to only regional pollutant precipitation. In the buffer zone, structural reorganizations of ecosystems occur under the effect of local pollution; the elimination of sensitive species and groups is partially compensated by the development of more stable ones, and the intensity of production processes is decreased slightly. The degradation of ecosystems is most manifested in the impact zone, with extreme variants of the technogenic digression of communities, the structure and functioning of which radically differ from the background state: the wood stand remains as fragments of wilting and weakened trees; the species richness of the ground vegetation layer is reduced to 1–7 species; the monospecies moss cover composed of the pioneer species *Pohlia nutans* is developed [13]. No positive shifts in the state of ground vegetation layer were recorded in the impact zone during 20 years of reduced emissions, but an increase in diversity and abundance of vegetation was observed on other zones, which was related to the lighting of tree canopy (because of windfall in 1995) rather than to the decrease of pollution [13, 34].

Burozems and soddy-podzolic soils of heavy loamy texture with different degrees of manifestation of eluvial (podzolic) and gley processes prevail in the soil cover. Along with the accumulation of heavy metals and increase in acidity [2, 11], the technogenic transformation of soils is manifested in the enhancement of eluvial–gley process [19], the decrease in the content of exchangeable calcium and magnesium [19], the hampering of organic matter decomposition [4, 6, 24], the formation (because of the inhibition of large soil saprophages [8]) of thick peat-enriched forest litter [5] similar to the natural dry-peat litter [19], the degradation of soil aggregates, and the alteration of the humus status [24, 28]. Characterization of the studied soils (as on 2011), including their diagnostics according to [23] and [53], is given in Table 2.

Permanent sample plots were established in the background (at 30 km to the west of the smelter), buffer (at 4 and 7 km), and impact (at 1 and 2 km) zones of contamination on lower slopes characterizing the successive stages of technogenic digression of spruce-fir forests in 1989; a total of 25 sample plots of 25 × 25 m were established (5 plots at each distance). Sampling was performed in August 1989, July 1999, and July 2012. Thus, the observations cover a time period of 23 years, one part of which (till the early 1990s) corresponds to high emissions, and the other part (from the early 1990s to the present day) corresponds to their considerable reduction.

To estimate the content of heavy metals (Cu, Pb, Cd, Zn) and pH_{water} in forest litter and the upper (0- to 5-cm) layer of the humus horizon, one (in 1989) or five (in 1999 and 2012) mixed samples per sample plot

Table 2. Physical and chemical properties of soils at different distances from the MUCS in 2011

Soil diagnostics		Horizon	Depth, cm	C_{tot}, %	pH_{water}	$Ca^{2+}+Mg^{2+}$, cmeq/kg	Particle size distribution					
							physical clay, %	I	particles (μm), %			II
Russian classification, 2004 [23]	WRB, 2014 [53]								0–2	2–50	50–2000	
30 km (profile 30-1)												
Medium-humus, moderately fine, heavy loamy-clayey, unsaturated, typical soddy-podzolic soil	Albic Retisol (Cutanic)	O	0–1.5	34.95	5.1	45.90	–	–	–	–	–	–
		AY	1.5–15	4.40	4.5	7.99	54.9	LC	13.4	84.9	1.7	SL
		AYe	15–21	1.15	5.1	3.66	58.8	LC	19.4	78.2	2.4	SL
		EL	21–30	0.69	5.2	5.10	61.4	LC	20.6	78.2	1.2	SL
		BEL	30–43	0.47	5.5	13.43	76.7	MC	28.1	71.3	0.6	SCL
		BT1	43–56	0.44	5.7	18.19	70.4	MC	27.3	71.8	0.9	SCL
		BT2	56–...	0.45	5.5	11.56	69.6	MC	26.8	72.7	0.6	SL
7 km (profile 7-5)												
Chemically contaminated, podzolized, unsaturated, high-humus, medium skeletal, fine, heavy loamy burozem	Leptic Retisol (Toxic)	O	0–1.5	36.43	5.7	47.18	–	–	–	–	–	–
		AY	1.5–3.5	9.49	5.2	13.26	33.1	ML	7.2	70.2	22.6	SL
		AYe	3.5–13	3.55	4.8	4.42	49.3	HL	11.4	77.3	11.2	SL
		EL	13–21	0.97	5.2	2.55	51.3	LC	14.2	74.5	11.4	SL
		BEL	21–33	0.35	5.3	6.46	47.4	HL	14.3	74.9	10.8	SL
		BM	33–48	0.34	5.0	6.80	37.4	ML	9.2	75.1	15.7	SL
4 km (profile 4-2)												
Chemically contaminated, unsaturated, high-humus, slightly skeletal, clayey, heavy loamy, medium-fine, gleyic soddy-podzolic soil	Stagnic Retisol (Cutanic, Toxic)	O	0–4	38.77	5.5	43.35	–	–	–	–	–	–
		AY	4–15.5	6.33	5.0	9.86	52.0	LC	12.9	80.2	6.9	SL
		AYe	15.5–24	2.71	5.0	6.63	63.3	LC	20.0	72.7	7.3	SL
		EL	24–29	1.12	4.9	4.00	62.8	LC	19.1	71.2	9.8	SL
		BELg	29–41	0.68	5.0	10.03	60.0	LC	19.1	76.1	4.8	SL
		BT1g	41–54	0.51	4.8	13.43	57.1	LC	18.6	74.5	6.9	SL
		BTg2	54–...	0.36	5.2	33.66	56.3	LC	18.8	74.8	6.5	SL

Table 2. (Contd.)

Soil diagnostics		Horizon	Depth, cm	C_{tot}, %	pH_{water}	$Ca^{2+}+Mg^{2+}$, cmeq/kg	Particle size distribution					
							physical clay, %	I	particles (μm), %			II
Russian classification, 2004 [23]	WRB, 2014 [53]								0–2	2–50	50–2000	
2 km (profile 2-3)												
Cu-, Zn-, Pb-, and Cd-contaminated, unsaturated, high-humus, slightly skeletal, heavy, loamy-clayey, fine chemozem on gleyic soddy-podzolic soil	Stagnic Retisol (Cutanic, Toxic)	O	0–4	31.33	5.3	43.35	–	–	–	–	–	–
		AY	4–7	7.48	4.5	12.58	53.4	LC	16.9	76.9	6.1	SL
		AYe	7–13	4.06	4.6	7.65	58.9	LC	16.9	78.8	4.3	SL
		ELg	13–22	1.65	5.1	7.31	67.5	MC	25.4	70.6	4.0	SL
		BELg	22–35	0.89	5.0	9.18	66.8	MC	25.7	69.9	4.4	SL
		BT1	35–53	0.80	5.4	16.83	69.9	MC	24.8	72.2	2.9	SL
		BT2	53–...	0.78	5.0	16.83	73.9	MC	29.2	68.7	2.2	SCL
1 km (profile 1-1)												
Cu-, Zn-, Pb-, and Cd-contaminated, unsaturated, medium-humus, slightly skeletal, heavy loamy-clayey, fine chemozem on gleyic soddy-podzolic soil	Stagnic Retisol (Cutanic, Toxic)	O	0–4.5	33.30	4.9	20.40	–	–	–	–	–	–
		AY	4.5–11	4.25	4.9	10.54	54.2	LC	13.4	82.9	3.7	SL
		AYe	11–20	3.12	5.3	8.84	53.9	LC	13.3	82.4	4.3	SL
		ELg	20–28	1.48	5.3	5.61	57.8	LC	17.3	74.2	8.5	SL
		BELg	28–38	0.68	5.3	13.94	64.3	LC	20.7	74.7	4.6	SL
		BTg1	38–54	0.52	5.6	17.34	67.5	MC	23.8	73.1	3.1	SL
		BTg2	54–67	0.39	5.1	18.87	68.0	MC	24.4	73.0	2.6	SL

Diagnostics of soil texture according to Kachinskii (I): (ML) medium loam; (HL) heavy loam; (LC) light clay; (MC) medium clay; International classification (soil texture triangle) (II): (SL) silt loam; (SCL) silty clay loam.

were used for each horizon. Each mixed sample was composed of five individual samples situated on the envelope scheme (about 1 m in side) with the random location of sampling points on the plot. A total of 550 samples were analyzed.

Metals were extracted with 5% HNO_3 (substrate : extractant ratio 1 : 10, extraction time 24 h after the single shaking); the concentration was determined by atomic absorption on AAS-3 (1989 and 1999 samples) and AAS-6 Vario (2012 samples) flame ionization spectrometers (Analytik Jena, Germany). The values of pH_{water} were measured by ionometry (substrate : water ratio 1 : 5 for soil and 1 : 25 for litter). To reduce the analytical error, the samples of 1999 and the conserved samples of 1989 were analyzed in the same series. Special checking of results obtained with different spectrometers showed their good repeatability. All chemical analyses were performed in the Laboratory of Population and Community Ecotoxicology of the Institute of Plant and Animal Ecology, Ural Branch, Russian Academy of Sciences, accredited for technical competence in the RF System of Analytical Laboratories (certificate ROSS.RU0001.515630).

For the diagnosis of soils, full-profile soil pits were established in the close vicinity of sample plots in 2011 with sampling from genetic horizons. The content of total carbon was determined by high-temperature combustion in an oxygen stream with a Multi N/C 2100 analyzer (Analytik Jena, Germany); exchangeable calcium and magnesium were determined by the complexometric titration of soil extract with Trilon B (extractant 1 M KCl solution, soil : extractant ratio 1 : 50 for litter and 1 : 25 for mineral horizons; decantation was used for complete extraction). Particle size distribution was studied by laser diffraction with an Analysette 22 Nanotec analyzer (Fritsch, Germany), after sample dispersion with a 4% $Na_4P_2O_7$ solution, wet sieving, and determination of the sand fraction 250–2000 μm by gravimetry.

Along with the concentrations of metals, two pollution indices were considered: the contrast ratio (CR) of geochemical anomaly and the total pollution index (*Zc*). The former parameter is calculated for each element (in litter and humus horizon separately) as the ratio between its concentration on the sample plot and the mean concentration on the background area (at 30 km form the smelter) in the corresponding year. The latter parameter (only for the humus horizon) is the corrected sum of the excess of metal contents over the regional background level for all studied elements $Zc = \sum C_i/F_i - (n - 1)$, where C_i is the concentration of the ith element on the sample plot; F_i is the background concentration of the ith element (the same for all years); and n is the number of elements. Indicative background concentrations of metals were obtained for the main soil types in central Russia, among which clay and loamy soddy-podzolic soils are most similar to the studied area. Correspondingly, the following background values were taken for acid-soluble forms in calculations (mg/kg): 15 for Cu, 45 for Zn, 15 for Pb, and 0.12 for Cd [30]. When the *Zc* value is used, the level of soil pollution is usually estimated on the following indicative scale: <16, permissible; 16–32, moderately hazardous; 32–128, hazardous; >128, extremely hazardous [29]. Contrast ratios characterize the degree of manifestation of geochemical anomaly, and *Zc* characterizes the hazard of contamination for humans.

In statistical analysis, sample plots were taken as statistical units in all cases. Two-way ANOVA with repeated measures (separately for each of two periods 1989–1999 and 1999–2012) was used to assess the significance of differences in metal concentrations and pH between the load zones and the time periods; before analysis, logarithms of metal concentrations were taken. Multiple comparisons were performed using the Tukey test.

For characterizing the dynamics of MUCS emissions, information from all available sources was accumulated: annual state reports on the state of environment in Sverdlovsk oblast (for 1994–2012), archives of the enterprise and the Center of Ecological Monitoring and Control for Sverdlovsk oblast, and literature sources [57]. In some cases, target values were obtained by calculation from the emission ratio for the city of Revda [57] and the MUCS in the corresponding years or the known ratios between dust emissions and metals for other years.

RESULTS

Dynamics of emissions. The reduction of atmospheric emissions from the smelter involved both gaseous pollutants and dust particles (respectively, heavy metals). The emission of the major component (sulfur dioxide) in 2012 was reduced by more than two orders of magnitude compared to 1980; an analogous reduction was observed for hydrogen fluoride in 2005. The emission of dust in 2012 was reduced in 44 times compared to 1980. Among metals and metalloids, the most drastic reduction was observed for copper: in more than 3000 times in 2012 compared to 1989; the reduction of arsenic emission (in 1000 times) was slightly lower. For other elements, the reduction of emissions during this period was less considerable: in 15 timed for Zn and in 8 times for Pb. The metal ratio radically changed because of the difference in the reduction rate of their emissions: the contribution of Cu was more than 45% in 1989 and only 0.4% in 2012, while the share of Pb increased from 11 to 35% during this period.

Dynamics of acidity. The pH of forest litter in all zones increased from 1989 to 1999 (Table 3), although at different rates (the distance × time interaction was significant, Table 4). A significant increase (by 0.9–1.3 pH units) was observed in the background and buffer zones; therefore, the reached values (5.1–5.5) were

Table 3. Dynamics of pH_{water} and heavy metals (μg/g) in litter and humus horizon of soils in different load zones (mean ± SE, $n = 5$)

Element	Year	Load zone (distance from the smelter, km)				
		background (30)	buffer (7)	buffer (4)	impact (2)	impact (1)
Forest litter (O horizon)						
pH	1989	4.67 ± 0.15a	4.20 ± 0.07a	3.75 ± 0.05a	3.53 ± 0.11a	3.52 ± 0.04a
	1999	5.54 ± 0.13b	5.17 ± 0.13b	5.09 ± 0.05b	4.70 ± 0.10b	3.85 ± 0.17a
	2012	5.35 ± 0.09b	5.35 ± 0.05b	4.82 ± 0.08c	5.03 ± 0.10c	4.75 ± 0.05b
Cu	1989	98.5 ± 4.7a	1362.8 ± 140.2a	1617.5 ± 98.1a	3312.2 ± 269.5a	4156.1 ± 304.1ab
	1999	70.7 ± 7.4b	1139.1 ± 127.1a	1869.4 ± 237.1a	3881.7 ± 375.7a	5458.4 ± 459.7a
	2012	28.8 ± 0.8c	343.6 ± 35.6b	1166.9 ± 128.3a	2211.6 ± 160.3b	3042.5 ± 239.4b
Pb	1989	86.6 ± 2.2a	491.5 ± 30.0a	541.8 ± 44.1a	885.7 ± 62.5a	1058.7 ± 82.0a
	1999	96.8 ± 5.7a	515.5 ± 41.2a	743.2 ± 80.8ab	1370.8 ± 81.9b	2018.2 ± 161.3b
	2012	62.6 ± 4.1b	476.1 ± 52.5a	884.9 ± 99.6b	1715.8 ± 154.5b	1955.1 ± 93.7b
Cd	1989	4.0 ± 0.2a	11.3 ± 0.6a	6.3 ± 0.7a	6.1 ± 0.3a	7.8 ± 1.1a
	1999	3.7 ± 0.1a	14.7 ± 1.2a	10.0 ± 1.0a	10.8 ± 1.4b	10.3 ± 0.4a
	2012	2.3 ± 0.2b	11.1 ± 0.9a	8.0 ± 1.5a	22.1 ± 3.7 c	15.6 ± 1.0b
Zn	1989	296.1 ± 23.6a	610.4 ± 32.9a	349.4 ± 45.4a	430.6 ± 19.5a	502.0 ± 46.8a
	1999	223.2 ± 25.0b	734.6 ± 95.8a	427.4 ± 47.7a	555.1 ± 71.6a	459.8 ± 21.0a
	2012	190.5 ± 16.0b	636.6 ± 23.0a	347.4 ± 51.7a	922.0 ± 149.8b	607.4 ± 46.4a
Humus (AY) horizon						
pH	1989	4.53 ± 0.12a	4.33 ± 0.17a	4.04 ± 0.08a	4.29 ± 0.09ab	4.18 ± 0.13a
	1999	4.42 ± 0.08a	4.51 ± 0.19ab	4.01 ± 0.07a	4.04 ± 0.04a	3.87 ± 0.06a
	2012	4.89 ± 0.06b	5.03 ± 0.06b	4.55 ± 0.03b	4.63 ± 0.09b	4.60 ± 0.12b
Cu	1989	23.8 ± 2.2a	169.0 ± 13.4a	251.9 ± 29.9a	883.3 ± 105.7a	1567.8 ± 111.0ab
	1999	36.4 ± 3.8a	339.4 ± 52.8b	219.2 ± 23.8a	520.6 ± 40.8b	2038.2 ± 234.5a
	2012	52.2 ± 21.4a	424.1 ± 21.9b	366.7 ± 114.3a	1039.6 ± 146.9a	1084.4 ± 131.7b
Pb	1989	19.4 ± 1.3a	46.9 ± 5.6a	44.6 ± 9.1a	128.0 ± 22.1a	278.0 ± 33.4a
	1999	30.1 ± 2.2ab	101.3 ± 16.6b	47.9 ± 9.5a	60.4 ± 6.4b	288.4 ± 51.8a
	2012	65.9 ± 23.5b	215.0 ± 14.4c	135.0 ± 45.3a	317.1 ± 31.6c	378.7 ± 46.4a
Cd	1989	0.8 ± 0.1a	2.3 ± 0.3a	2.2 ± 0.2a	3.8 ± 0.4a	5.1 ± 1.0a
	1999	1.3 ± 0.2a	4.6 ± 0.8b	1.8 ± 0.1a	3.7 ± 0.3a	3.9 ± 0.4a
	2012	1.2 ± 0.3a	5.7 ± 0.4b	2.3 ± 0.5a	5.8 ± 1.0a	4.8 ± 0.3a
Zn	1989	36.4 ± 4.4a	100.4 ± 16.0a	90.0 ± 7.5a	167.2 ± 18.5ab	225.7 ± 32.7a
	1999	66.6 ± 7.9b	230.1 ± 64.1ab	82.7 ± 6.6a	147.4 ± 7.7a	153.1 ± 10.4a
	2012	80.0 ± 19.1b	257.0 ± 26.4b	107.7 ± 13.5a	203.2 ± 24.4b	185.1 ± 11.9a

Similar letters (within the group of three years for each element) indicate the absence of significant differences from the Tukey test (at a significance level of 5%).

close to the range typical for soddy-podzolic soils and burozems under the canopy of spruce-fir forests in the Middle Urals (5.1–6.0) [14, 36]. The litter pH at 2 km from the smelter also shifted by 1.2 units, but the difference from the background range was not exceeded because of the initially low level. In the close vicinity of the smelter, the litter pH did almost not change during this period; it remained on the low level (3.5–3.8), far from the background range. The pH of the humus horizon remained stable in all zones and varied by no more than 0.3 units from 1989 to 1999.

The litter pH in the background and buffer zones, as well as at 2 km from the smelter, did almost not change from 1999 to 2012 (the difference between years did not exceed 0.3 units); however, in the impact (1-km) zone, it increased by 0.9 units and almost reached background values. The pH of humus horizon in all zones increased by 0.5–0.7 units (to 4.6–5.0)

Table 4. Results of two-way ANOVA with repeated measures of differences in pH and heavy metal contents between the distances from the smelter and time periods (*F*-test and the significance level (in parentheses) are given)

Element	Period, years	Source of variation		
		distance ($df = 4$)	time ($df = 1$)	distance × time ($df = 4$)
Forest litter (O horizon)				
pH	1989–1999	59.7 (<0.001)	121.8 (<0.001)	3.5 (0.031)
	1999–2012	37.1 (<0.001)	9.1 (0.007)	10.9 (<0.001)
Cu	1989–1999	713.6 (<0.001)	0.0 (0.975)	4.3 (0.012)
	1999–2012	897.2 (<0.001)	117.4 (<0.001)	3.9 (0.017)
Pb	1989–1999	641.9 (<0.001)	41.8 (<0.001)	5.2 (0.006)
	1999–2012	546.2 (<0.001)	0.3 (0.583)	4.0 (0.015)
Cd	1989–1999	50.6 (<0.001)	27.9 (<0.001)	4.2 (0.014)
	1999–2012	60.5 (<0.001)	0.1 (0.774)	14.2 (<0.001)
Zn	1989–1999	24.4 (<0.001)	0.1 (0.720)	2.4 (0.089)
	1999–2012	30.0 (<0.001)	0.7 (0.407)	4.9 (0.006)
Humus (AY) horizon				
pH	1989–1999	6.6 (0.002)	2.2 (0.155)	1.2 (0.333)
	1999–2012	11.2 (<0.001)	137.5 (<0.001)	0.8 (0.528)
Cu	1989–1999	507.9 (<0.001)	3.3 (0.087)	8.4 (<0.001)
	1999–2012	123.1 (<0.001)	2.4 (0.133)	4.6 (0.008)
Pb	1989–1999	76.2 (<0.001)	0.7 (0.425)	6.8 (0.001)
	1999–2012	31.6 (<0.001)	63.2 (<0.001)	4.3 (0.011)
Cd	1989–1999	64.1 (<0.001)	2.8 (0.113)	4.5 (0.010)
	1999–2012	45.4 (<0.001)	4.1 (0.058)	0.8 (0.569)
Zn	1989–1999	28.7 (<0.001)	3.4 (0.079)	6.8 (0.001)
	1999–2012	25.7 (<0.001)	6.3 (0.021)	0.1 (0.970)

during this period and almost reached the values typical for soddy-podzolic soils and burozems in the Middle Urals (4.1–5.2) [14, 36]. Despite the positive trend for pH changes in the impact and buffer (4-km) zones, lower values than in the background area (by 0.2–0.4 units) remained there.

Dynamics of heavy metals. The concentrations of metals in forest litter changed differently from 1989 to 1999. The content of Cu in litter significantly decreased only in the background zone; it remained almost stable in the buffer zone and increased in the impact zone. The concentration of Pb increased in the impact zone and did not change in the other zones. The concentration of Cd remained on the initial level only in the background and buffer zones and also increased in the impact zones. A reliable decrease in the content of Zn was observed only in the background zone; its content in the other zones did not change.

In the background and buffer (7-km) zones, the concentration of Cu in the humus horizon increased rather than decreased, in contrast to litter. In the impact (1-km) zone, the concentration of Cu in the humus horizon also increased, as well as in the litter. The contents of other metals increased only in the background and buffer (7-km) zones and remained on the initial level in the other zones.

During the period from 1999 to 2012, the concentration dynamics of different metals in litter varied considerably: the content of Cu decreased significantly (in 1.5–3.0 times) in all zones; the content of Zn either remained on the initial level or increased (at 2 km); the content of Cd decreased only in the background and buffer zones and increased in the impact zone; the content of Pb decreased in the background zone and remained stable or increased in the other zones.

In the humus horizon, the concentrations of Pb, Zn, and Cd did not change or increased (especially for Pb). The content of Cu decreased only in the impact (1-km) zone and remained stable or increased in the other zones.

Dynamics of anomaly contrasts. At 7 km from the smelter, the contrast ratios were relatively stable during the entire period of observations, while dynamics was manifested on the other contaminated plots, opposite changes being observed in different horizons (Fig. 2). From 1989 to 2012, the anomaly contrast regularly increased for all elements in litter and decreased in the humus horizon. This tendency was most manifested

for Cu in the impact zone: the CR value increased from 42 in 1989 to 105 in 2012 in litter and decreased from 65 to 20 in the humus horizon. According to the exceeding of the background level, elements in all cases formed the series: Cu > Pb > Cd >Zn.

Changes in the risk of contamination. The total pollution index in all zones gradually increased from 1989 to 2012 (only at 1 km from the smelter, it slightly decreased in 2012 compared to 1999 because of Cu) (Fig. 3). In the background zone, the level of contamination was permissible throughout the observation period, although it came close to the moderately hazardous level in 2012. The level of contamination increased from moderate in 1989 to hazardous in 2012 in the buffer (7- and 4-km) zone and from hazardous to extremely hazardous in the impact (2-km) zone. In the close vicinity of the smelter (within 1 km), the level of contamination was extremely hazardous during all periods, despite some decrease in 2012.

DISCUSSION

Dynamics of acidity. The rate of pH recovery varies among the soil horizons and among the zones. At the low contamination level, the initial pH values were restored rapidly in litter (already during the first 10 years after the reduction of emissions), while this process took about 20 years on plots with initially high contamination levels. In contrast to the litter, the pH of humus horizons was restored only to the end of the period considered, regardless of the initial contamination level, although residual differences with the background level on the plots closest to the smelter remained up to now.

It is known that soil acidity is formed under the effect of incoming decomposition products of litterfall and the fallout of acidic or alkaline agents from the atmosphere. Atmospheric emissions from smelters usually include not only acid gases (sulfur dioxide, nitrogen compounds, etc.), which acidify the soil after hydration, but also dust containing Ca, Mg, and metal oxides. Ca and Mg compounds neutralize mineral acids or alkalize the soil, depending on their content, although usually only in the close vicinity of the emission source [15, 17], because the distance of dust transport is short. The emissions of sulfur dioxide and dust from the MUCS were reduced at similar rates (except for those in 2009–2012); therefore, the mechanism of neutralization could not considerably affect the acidity of soil compared to the multiple reduction of SO_2 emissions.

The effect of the second factor (litterfall decomposition products) on the recovery of pH could contribute only if the ratio between woody species shifted toward deciduous species or the input of herbaceous litterfall increased. The study of vegetation dynamics on the same plots during the period of 1989–2013 [13, 34] showed that a lighting of canopy occurred because of windfalls (hurricane in the early summer of 1995).

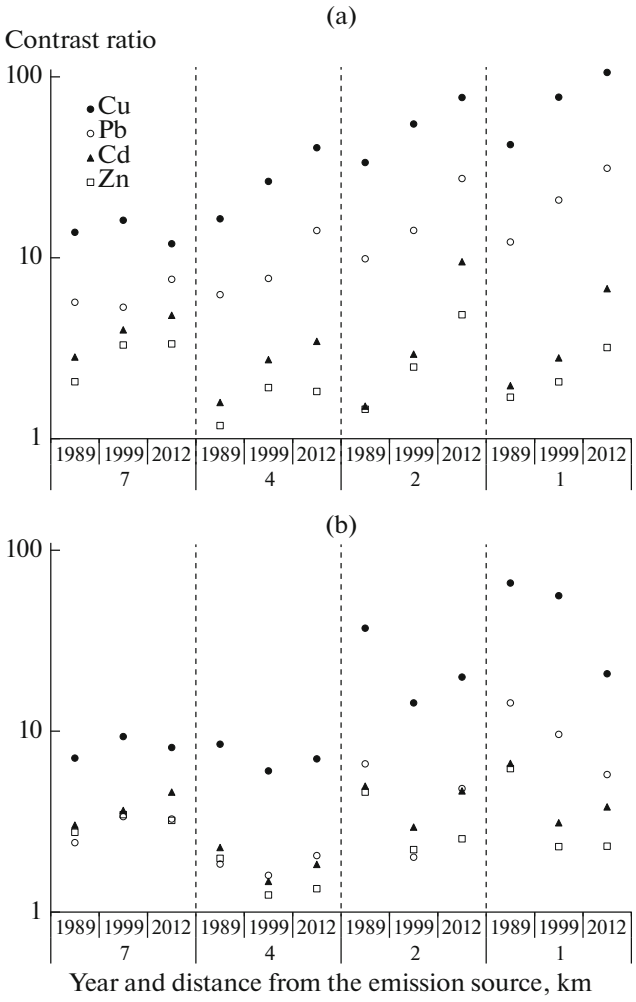

Fig. 2. Dynamics of contrast ratios in (a) litter and (b) humus horizon at different distances from the smelter; the value of 30 km is taken as 1.

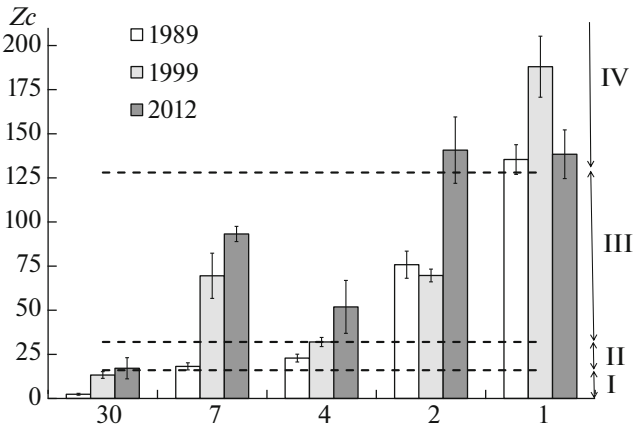

Fig. 3. Dynamics of total pollution index (*Zc*) at different distances from the smelter (mean ± SE, $n = 5$); contamination level limits: (I) permissible; (II) moderately hazardous; (III) hazardous; (IV) extremely hazardous.

This resulted in partial reforestation with deciduous species (birch, aspen) and an increase in abundance of the grass-subshrub layer. Later on, the soddy process was activated in the buffer (4-km) and impact zones, and the abundance of grasses increased [13]. Consequently, the restoration of pH in litter and humus horizon can be affected by changes in the litterfall structure; however, the relative contribution of this process is difficult to separate from multiple reduction in SO_2 emissions.

An obvious consequence of pH increase should be the decrease in mobility of heavy metals and, hence, their toxicity for soil biota and plants. Besides, an opposite tendency of increase in mobility with increasing pH is typical of arsenic [1] (not considered in this paper).

Dynamics of metals. The dynamics of heavy metals, as well as acidity dynamics, significantly varies among soil horizons and load zones; in addition, it is specific for each element. Positive consequences of emission reduction are detected only for litter and only for Cu. This well agrees with the dynamics of emission structure: Cu was the dominant metal, and the emission of Cu was reduced most considerably. The concentrations of other elements also decreased only in litter but only in the background area; on the other plots, they remained on the initial level or increased. In the humus horizon, the contents of most metals remained constant or even increased during 20 years. The only exception was the twofold decrease in the concentration of Cu in the close vicinity of the smelter. Thus, our hypothesis about the absence of manifested removal of metals from the soil in the contaminated area on the considered time scale (about 20 years) was largely confirmed.

This conclusion agrees with the dominant opinion about the longtime of metals retention by the soil (about 100–700 years), which ascends to the classical work by Tyler [66], whose conclusions were confirmed later in a similar laboratory experiment [42], a field experiment on the transfer of contaminated soil to the background area [16, 50], and a comparison of metal contents in coupled soil horizons [49]. The calculation of the time necessary for the complete unloading of technogenic anomaly in the MUCS region to the background level, which were based on the comparison of element pools in the entire soil profile and in the area runoff gave a value of about 1500–3000 years [20]. Our conclusion also coincides with the results of direct observations of metal dynamics in soils after the reduction (cessation) of emissions from several enterprises [15, 17, 25, 49, 55, 60].

On the other hand, some authors demonstrated multifold decrease of metal concentrations in strongly contaminated habitats during the similar periods after emission reduction [38, 51]. This can be related to both the methodological aspects (e.g., different points of sampling before and after the reduction of emissions at the obviously high spatial variation of concentrations) and the diversity of edaphic conditions. The conclusion about the extremely low rate of metal removal can be valid only for soils with relatively heavy texture, while a different situation can occur in other cases (e.g., loamy sandy soils). The work performed in the MUCS region, which demonstrated a faster recovery of mole range in light soils than in heavy soils [10], indirectly indicates that this factor can be decisive for the unloading of metals from the technogenic anomaly on weakly acid soils.

The unexpected increase in metal concentrations under the reduction of their atmospheric input deserves special discussion. A similar situation was described: after the reduction of emissions from a smelter in Poland, the concentrations of Cu in the soil almost doubled compared to the period of active functioning of the enterprise [55] (unfortunately, the authors found no unambiguous explanation to this fact).

The reduction of emissions from the MUCS was obviously not instantaneous, and the atmospheric input of metals continued through the years, although in significantly smaller volumes. However, the situation is most probably more complicated. Several mechanisms responsible for this phenomenon can be suggested (Fig. 4). First, the increase in pH plays the key role, which decreases the mobility of metals and, hence, increases their content in litter and humus horizon due to the lower removal beyond these horizons. Second, an additional amount of metals could income together with litterfall, into which they passed from the soil (both considered and lower horizons), and the activation of growth processes in plants (and the increase of primary production) because of the decrease in toxicity could be an additional factor. In other words, the turnover of elements acquires somewhat closed character under contamination. Third, the increase in the content of metals in litter can be related to the activation of destruction processes and the decrease in medium toxicity for soil biota because of increase in pH. Therefore, the reserve of litter decreases, which results in a peculiar concentrating of metals. Finally, the increase in the contents of all elements in the humus horizon (especially during the period 1999–2012) is most probably due to their gradual leaching from the litter, although the rate of this process is lower than during the period with lower pH values.

It is known that the migration mobility of metals in the soil profile depends not only on acidity, but also on texture and organic matter content [46], although pH plays the main role [44]. Among these three parameters, only pH is attributed to soil-moment [32]; consequently, manifested dynamics could be expected only for pH, as was observed. The content of fine particles is a very conservative parameter attributed to soil-memory [32]. This is also the case for the stable fractions of organic matter, which play the main role in the immobilization of heavy metals, in contrast to its labile fractions [44]. Consequently, we might consider only

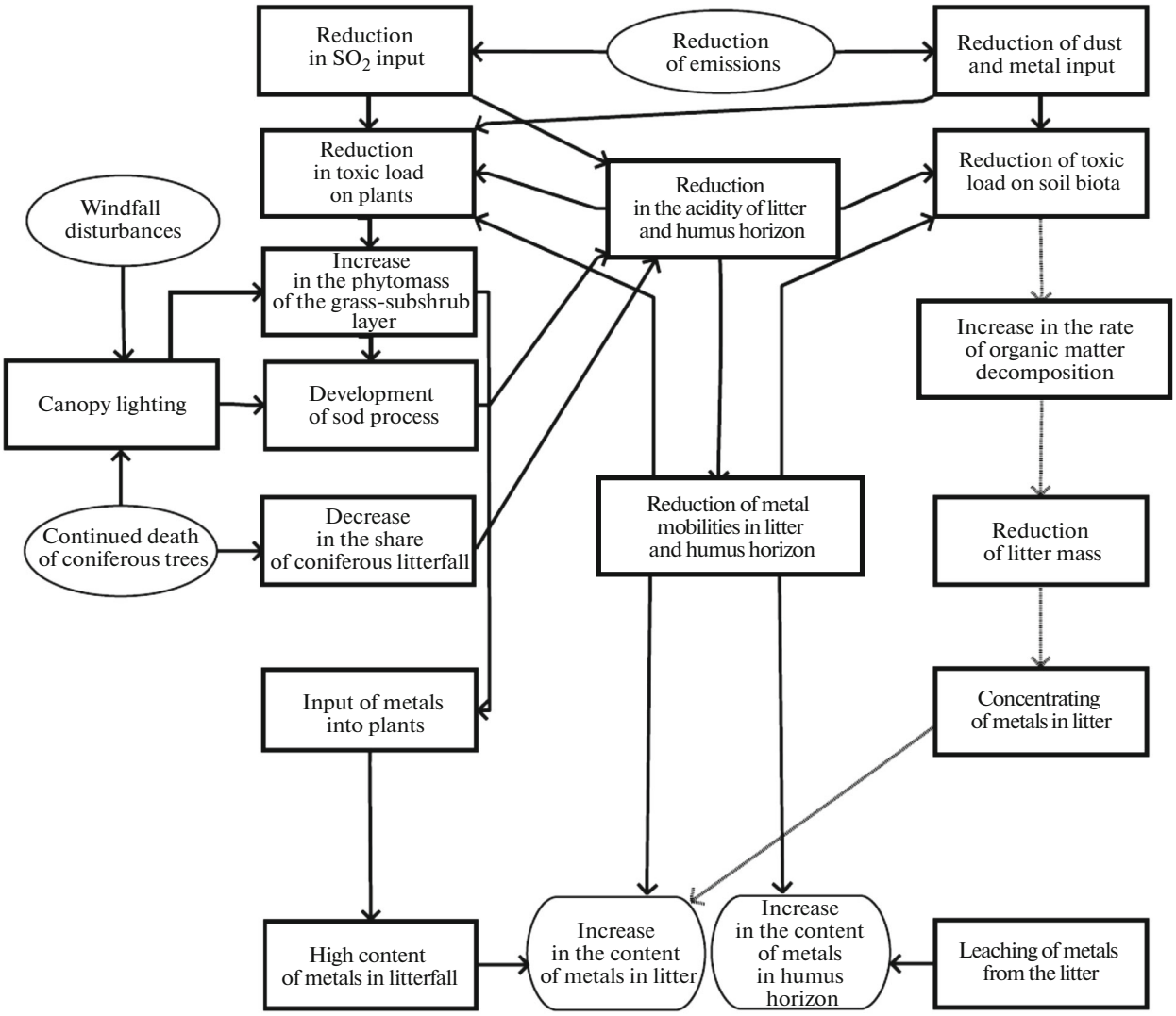

Fig. 4. Scheme of processes resulting in an increase in the content of heavy metals in forest litter and humus horizon under reduced emissions; (ovals) external reasons; (gray arrays) processes occurring only under low and moderate contamination.

the effect of pH in the analysis of dynamic of the migration mobility of metals, because the soil texture little varies among plots and the sorption of metals by clay minerals and humic substances is also controlled by pH [44, 59].

Differences in the behavior of the studied metals are related to their chemical properties, primarily to those determining the relationship between mobility and pH. Among the four considered metals, the mobilities of Zn and Cd most strongly depend on pH [44]. The concentrations of these elements in litter most increased from 1989 to 2012 in the impact (2-km) zone, where the increase in pH is most manifested. On the other hand, the concentrations of Zn and Cd in the humus horizon remained almost unchanged on all plots during this period; this well agrees with the stably low pH values determining the removal of these elements down the profile, which compensated their input. However, the thorough analysis of the specific behavior of different metals is far beyond this work, given that no data are available about the total metal contents and the proportions of different metal fractions.

Dynamics of pollution indices. The obvious nonstationarity of the 'metal deposition–metal content in litter–metal content in mineral horizon' system requires some correction of conventional approaches to assessing the contamination level of the area using different indices. Concentrations normalized to the local background values (i.e., the CRs of geochemical anomaly) are usually used as a measure of toxic load. However, multidirectional dynamics of this parameter for litter and humus horizon is observed in our case, which is related to the corresponding multidirectional changes in the background zone: the increase in local background concentrations in the humus horizon reduces the contrast, and their decrease in litter, on

the contrary, enhances the contrast. However, this dynamics of contrast cannot be considered as change in toxic load on biota. Consequently, the parameters of anomaly contrast for a single horizon should be used with reserve in nonstationary situations. For this purpose, it is advisable to use the initial local or regional background concentrations as the reference values. This also shows prospects of assessing soil contamination on the basis of data on the metals in some coupled horizons or the entire profile rather than in a single horizon [3].

The dynamics of the *Zc* value shows that, despite the reduction of emissions, the hazard of soil contamination for humans not only did not decrease, but appreciably increased in all load zones during the 20-year-long period. This coincides with the conclusion about the exceeding of environmental standards for the content of heavy metals in medical plants [33] and forest berries [35] in the impact region under consideration.

The assessment of the consequences of metal retention in terms of environmental protection is uncertain. On one hand, the long-lasting retention of pollutants in the upper horizons can be considered positive, because this prevents their migration down the profile and, hence, input into ground and surface water, which would pose a serious threat to humans due to the contamination of potable water sources. On the other hand, the retention of the high level of soil contamination hampers the recovery of biota. Conclusions about the stably suppressed state of vegetation near the smelter [13, 34], as well as analogous preliminary data for soil fauna [10], confirm this. In addition, the retention of metals in the soil because of the decrease in their mobility is the formation of a "chemical time bomb" [65], which can detonate at an abrupt shift of equilibrium in the future (e.g., because of acid fallouts) or slowly glows under gradual changes in soil acidity (e.g., because of the restoration of dark coniferous taiga on the place of secondary small-leaved forests or meadows).

CONCLUSIONS

The multifold reduction of atmospheric emissions from the copper smelter during 20 years resulted in the normalization of litter and humus-horizon acidity and the decrease in the content of Cu in litter of all contamination zones and in the humus horizon in the close vicinity of the enterprise. The contents of the other studied metals (Cd, Pb, and Zn) in litter and humus horizon remained stable or increased during the entire period. Consequently, the hypothesis about the stable contents of metals in soils of the impact region was confirmed.

The absence of the manifested removal of metals from the contaminated area implies that the toxic load on vegetation and soil biota not only did not decrease, but even increased during the analyzed period. This can be considered as one of the mechanisms responsible for the long-term conservation of biota in the impact region in the suppressed state and evidence for the concept of low resilience of ecosystems with respect to the industrial contamination with heavy metals.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 14-05-00686. The authors are thankful to Yu.N. Vodyanitskii, I.N. Korkina, and M.R. Trubina for discussion and commentaries to the manuscript; the anonymous reviewer for valuable remarks; T.Yu. Gabershtein for analyzing texture; I.A. Khlystov for measuring total carbon and exchangeable bases; and E.Kh. Akhundova and A.V. Shchepetkin for measuring metal concentrations.

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Translated by K. Pankratova