ISSN 1995-4255, Contemporary Problems of Ecology, 2013, Vol. 6, No. 2, pp. 213–222. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © T.V. Zhuykova, V.S. Bezel, V.A. Zhuykova, O.V. Chankina, K.P. Kutsenogy, 2013, published in Sibirskii Ekologicheskii Zhurnal, 2013, No. 2, pp. 271–282.

Chemical Elements in the Mineralization of Plant Residues under Soil Pollution with Heavy Metals

T. V. Zhuykova[a], V. S. Bezel[b], V. A. Zhuykova[a], O. V. Chankina[c], and K. P. Kutsenogy[c]

[a] *Nizhnii Tagil State Social Pedagogical Academy, ul. Krasnogvardeiskaya 57, Nizhnii Tagil, 622031 Russia*
e-mail: hbfnt@rambler.ru
[b] *Institute of Plant and Animal Ecology, Ural Branch, Russian Academy of Sciences,*
ul. Vos'mogo Marta 202, Yekaterinburg, 620144 Russia
[c] *Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences,*
ul. Institutskaya 3, Novosibirsk, 630090 Russia

Abstract—Mineralization processes of plant residues in background and anthropogenically affected areas are analyzed. The multielement composition of plant residues before and after their exposure in soil is provided with the help of synchrotron radiation (XPA SR). It is demonstrated that the destruction process is accompanied by changes in the chemical composition of plant residues. Chemical elements with concentrations increasing as they are filtrated from soil into the exposed samples are determined. Agrobotanical groups of plants with the highest infiltration rate are revealed.

Keywords: destruction, plant residues, chemical elements, chemical pollution

DOI: 10.1134/S1995425513020169

The stability of natural biocenosises is determined by the biogenic turnover of chemical elements, which depends on their being absorbed from soil by plants and the further decay of plant residues. The intensity to which chemical elements are involved in the biogenic turnover and the rate of destruction are two major indicators of the ecosystem state. Thus, many publications are devoted to this problem. Great emphasis is placed on studying how various natural and anthropogenic factors influence the processes of organic-matter mineralization. The destruction of mortmass is significantly determined by the ratio between C, N, and P. In addition, one should consider the integrated effect of the following factors: weather and climate conditions; seasonal conditions; the acidity of soils; the content of toxic agents; and other characteristics that determine the state and the abundance of soil destructors, which are mainly microbial communities and micromycetes directly influencing the rate of organic-matter destruction [1–6 et al.].

As a rule, the rate of destruction is judged either by changes in the mass of cellulose samples and plant residues or by a decrease in the thickness of litter [7–9].

The destruction of plant residues is accompanied by the release of mineral components. As a result, it is the content of chemical elements in the destructing phytomass and soil that serves as an indicator of biogenic turnover intensity. The latter is of special interest in the case of the chemical pollution of soils. According to most researchers, the excess of chemical elements (first and foremost heavy metals) can inhibit the activity of microbial communities and slow the destruction of mortmass. Most works demonstrate the suppression of organic matter destruction in soils polluted by heavy metals and sulfur compounds [10–15 et al.]. At the same time, a reverse effect is sometimes observed. For example, the experiments made it possible to learn that technogenically polluted agricultural ecosystems demonstrate more intensive mineralization accompanied by the emissions of CO_2 and nitrogen oxides [16, 17].

This work considers changes in the chemical composition of plant residues in a gradient of soil pollution with heavy metals.

MATERIAL AND METHODS

In nature, the mineralization of an organic substrate is determined by the species composition of communities, physical and chemical conditions, and the activity of meso- and microfauna associated with them [2]. During our experiment, three agrobotanical groups (legumes, cereals, and herbs) were singled out. The plant samples were exposed to soils with different contents of metals, nitrogen, and carbon oxides that are transmitted by air.

The material was obtained in the Middle Ural region (taiga zone and southern taiga subzone). The industrial complex in the area under study (Sverdlovsk oblast, Nizhnii Tagil, 60° E, 58° N) is represented by iron works. The total annual emission of industrial pollutants was 641.4 thousand tons. The emissions from stationary sources fell to 200000 tons starting in 1994. The main pollutant is polymetallic dust in the form of oxides (Cr, Ni, Fe, Cu, Zn, Cd, Pb, etc.) [18].

At different distances from the source of industrial emissions (the Nizhniy Tagil Iron and Steel Works), five test plots were established. The phytocenosises where the plant material was collected and the field works were carried out are represented by secondary herb–cereal and cereal–herb meadow communities that developed on deposits and copper-ore mining dumps [19]. The initial soil type in background areas is soddy podzolic soil, one soil variant is loamy clay with various degrees of podzolization. During a long period of aerogenic pollution with chemicals, the soil type becomes significantly different from the initial soddy podzolic soil. For example, this is clearly seen from changes in pH. According to the acidity degree, the soils under study are characterized as alkaline or strongly alkaline soils. Their pH varies from 7.10 to 8.47. Soil alkalization in all the plots is the result of metallurgical production, gray iron foundry, coke and by-product processes (fertilizer manufacturing), and a refractory plant and a cement plant (each producing emissions with high concentrations of Ca and Mg). Under these conditions, the solubility and the mobility of cations are low. Thus, the latter are accumulated in the upper horizons of soil. In anthropogenically affected areas, the fractions that are 5.0–10.00 mm in size are dominant. They make up 24–67% of the cover (coarse-grained soils). This is typical for immature and initial soil, which is not common for typical zonal soils, because it develops in deposits and copper-ore mining dumps that are over 45 years old [19]. Over this period, a stable and grass-covered soil layer developed. The thickness of the humus-accumulating layer is 2–7 cm. The content of hygroscopic moisture decreases with a growth in the technogenic load in the plots (from 6.6 to 2.3%).

In order to perform the analysis, 2 g of dry substrate were bolted using a sieve (egg diameter 1 mm). The metals were extracted with 5% HNO_3, the ratio between substrate and extracting agent was 1 : 10, and the extraction period was 24 h. The contents of Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in acid extracts from soil and plants were measured on a PerkinElmer AAS 300 atomic absorption spectrophotometer [22]. The concentrations of mobile metals in the plots under study varied in the following way, μg/g: zinc from 18 to 901, copper from 12 to 950, lead from 8 to 421.41, cadmium from 0.05 to 2.85, cobalt from 7 to 124, manganese from 237 to 2365, iron from 6.62 to 6247.89, chrome from 4.31 to 87.26, and nickel from 4.51 to 188.84. The total level of chemical pollution was expressed through the summarized toxic load (S_i), which was estimated based on the content of Zn, Cu, Pb, Cd, Co, Ni, Cr, Fe, and Mn in soil. In our case, S_i varied from 1 to 30 relative units (rel. units) [19, 23]. According to the level of summarized toxic load, the plots were divided into three zones: the background zone (S_i = 1.0 and 3.33 rel. units), buffer zone (S_i = 6.19 rel. units), and impact zone (S_i = 22.78 and 30.0 rel. units). The nomenclature of plants is given according to the United Nations Environment Program (UNEP) [24].

In order to determine the actual destruction rate of plant residues, we used the aboveground and belowground phytomass of three agrobotanical groups (legumes, cereals, and herbs) as an exposed material. The phytomass was collected in two background and three technogenically polluted areas. Herbs were composed of the following species: lady's mantle (*Alchemilla vulgaris* L.), upright bedstraw (*Galium mollugo* L.), coltsfoot (*Tussilago farfara* L.), common dandelion (*Taraxacum officinale* Wigg. s.l.), burnet saxifrage (*Pimpinella saxifraga* L.), common sowthistle (*Sonchus oleraceum* L.), meadow buttercup (*Ranunculus acris* L.), broadleaf plantain (*Plantago major* L.), common wormwood (*Artemisia vulgaris* L.), etc. Among cereals, the dominants were fowl blue grass (*Poa palustris* L.), meadow fescue (*Festuca pratensis* Huds.), awnless brome (*Bromus inermis* (Leyss.) Holub.), smooth meadow grass (*Poa pratensis* L.), and wood small-reed (*Calamagrostis epigeios* (L.) Roth.); legumes were represented by meadow vetchling (*Lathyrus pratensis* L.), red clover (*Trifolium pratense* L.), zigzag clover (*T. medium* L.), tufted vetch (*Vicia cracca* L.), bush vetch (*Vicia sepium* L.), etc.

The composition of the agrobotanical groups changed in the gradient of chemical pollution [25]. Since the plant samples represented the total phytomass of the plots, this work covers some integral processes of destruction for different agrobotanical groups, regardless of their species composition.

The plant samples dried to the air-dry state were put in 5 × 10 cm bags made of fosta nylon (egg size 0.5 cm). The initial mass of the sample was (2.001 ± 0.009) g. The bags were laid in the upper soil layer (depth 3–4 cm) of the plots from which the phytomass had been collected. During laying, we made slight cuts on the timer to minimize the destruction of ground vegetation. Sequentially, three layings (10 bags of legumes, cereals, and herbs) were made in the transect. The distance between the samples was 30 cm. In all, 150 samples were used for the experiment. The field experiment lasted for 4 months.

When taken out of soil, the bags were prepared for further analysis according to the methodology described in [26]: soil particles and tin roots were removed with scalpel or brush and then dried in a cabinet dryer to an absolutely dry state at 105°C for 24 h. The samples were weighted using digital analytic balance (Denver Instrument Compony AA-200) within an accuracy of 0.001 g. The rate of destruction of the exposed material was estimated according to a decrease in the mass of sample (%).

Then the chemical composition of three agrobotanical groups was studied before and after their exposure using X-ray fluorescence analysis with the help of synchrotron radiation (XPA SR). The measurement was carried out in the Station of Chemical Analysis, Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences (VEPP–3 accumulator). Due to the high intensity of synchrotron radiation, this method makes it possible to determine trace concentrations in the light samples without destroying them. In order to prepare the samples for analysis and measure the concentrations of chemical elements in them, we followed the methodology described in [27]. In all, 65 samples were analyzed; 1365 analyses of chemical composition were carried out.

The significance of differences between the concentrations of chemical elements in the plant residues before and after their exposure, as well as between the samples exposed in the background and polluted zones, were assessed with the help of Wilcoxon's *U* criterion (Mann–Whitney test) under $p < 0.05$. The differences in destruction rate between three agrobotanical groups exposed within the limits of one and the same plot were determined by means of the one-way ANOVA test; the *F* criterion was calculated. A comparison of the destruction rates of the agrobotanical groups from plots with different pollution was done with the help of Scheffe's multiple-comparison approach (*S* method). The dependence between the destruction rate of plant residues and their toxic load was assessed using Spearman's rank correlation coefficient (R_s). A statistical analysis was performed in Statistica 6.0 (StatSoft, Inc. 1984–2001).

RESULTS

It can be assumed that the mineralization rate of plant residues in soils, as well as the intensity to which chemical elements are involved in the biogenic turnover, are determined by the following factors: the chemical and biochemical composition of plant material, the physical and chemical characteristics of soil (pH, concentration of mobile micro- and macroelements), the activity of soil biota, and weather and climate conditions [2, 5, 6, 28, 29, et al.].

In our case the main pollutants are heavy metals. The mobile variants of the latter are given in Table 1.

Table 1. Average concentrations of mobile variants of the major pollutants in soils, μg/g ($M \pm m$)

Polluted area	Content of metals		
	Cu^{2+}	Zn^{2+}	Pb^{2+}
Background	14.43 ± 0.28	19.79 ± 0.89	7.94 ± 2.33
Buffer	101.57 ± 11.13	150.37 ± 12.21	56.12 ± 4.91
Impact	951.49 ± 236.10	620.68 ± 63.62	193.85 ± 18.34

The chemical composition of three agrobotanical groups of meadow plants, which were collected under various chemical pollutions to their exposure in soils, is given in Table 2. Obviously the concentration of metals increases as the pollution of the soil becomes higher.

As a result of long-term exposure in the background and pollution soils, the concentration of many chemical elements in the plant residues changed (Table 3). The statistical significance of these differences before and after exposure is provided in Table 4. It should be emphasized that the concentrations of some chemical elements in the samples, which had been exposed in the polluted area, exceeded background values (Ca, Cr, Mn, Cu, Zn, As, Se, Mo, and Pb) (Fig. 1). The concentration of other elements was beyond the background one (K, Ni, Br, Rb, Sr, and Nb).

Legumes. In the background zone, concentrations of most chemical elements increased in the exposed samples of legumes. The concentration of Ti, Cr, Zr, and Nb in the exposed material increased 20–27 times. At the same time, the content of K, Rb, and Br decreased. Differences in the concentrations of such elements as Ti, V, Cr, Mn, Fe, Co, Cu, Y, Zr, Nb in the exposed elements before and after exposure are statistically significant (see Table 4). Those chemical elements that function as pollutants are most interesting (see Table 4). In contrast to the background samples, the samples exposed in polluted areas demonstrate a significant increase in the concentrations of Zn; Pb; and, especially, Cu (in 2.6, 3.2, and 12.0 times, respectively). This fact corresponds to data on pollution of soil with these elements (see Table 1).

Cereals. Concentrations of the chemical elements under study were found to change in the exposed samples of cereals. In the background plots, cereals are characterized by an increased content of Ca, Mn, Cr, and V (0.2–15.7 times), as well as, especially, Fe and Ti (70.1–82.0 times). The concentrations of K and Br are reduced. This effect is not as prominent in the polluted plots after exposure (Table 2, 3). Like in legumes, the content of Cu, Zn, and Pb increased 3–25 times.

Herbs. The above-described trend is sustained. The concentrations of K, Br, and Rb in the herb residues gradually become lower as they are exposed in the background zone and the impact zone. The concentrations of other elements in the exposed samples of herbs grows, but to a lesser degree than in legumes and cereals. This is also applicable to the concentrations of pollutants (Cu and Zn). Their content in herbs exposed in anthropogenically affected areas increased 10 and 2.3 times, respectively. The concentration of Pb became 2.5 times higher.

The submitted data offer clear evidence that mineralization is accompanied by changes in the concentrations of chemical elements within the plant residues. This fact is indicative of a complex relationship

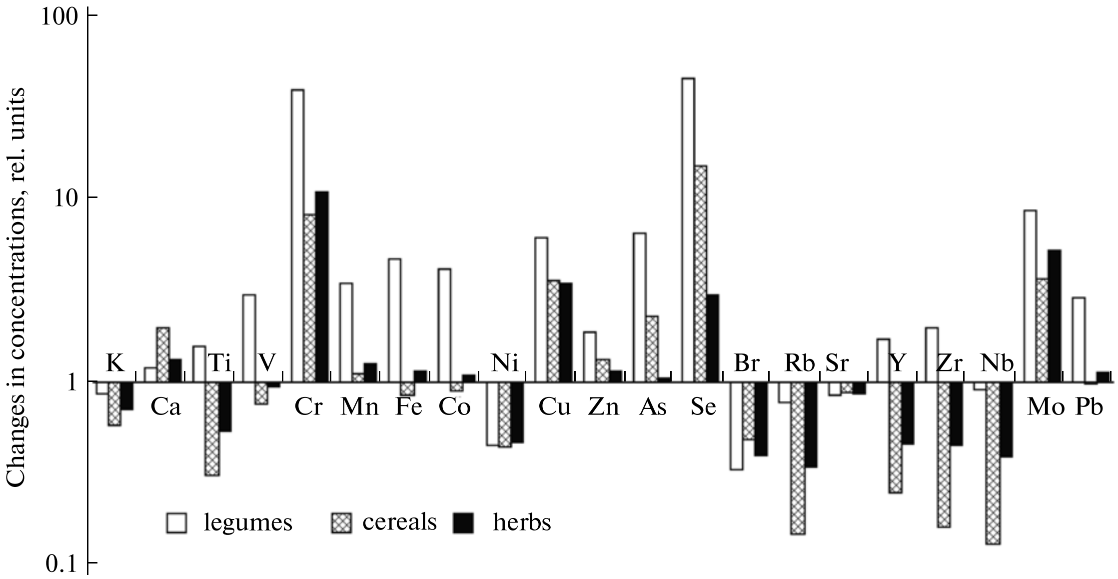

Fig. 1. Changes in the concentrations of chemical elements in agrobotanical groups exposed in the impact area compared against the background values (after their exposure in soil).

between the chemical composition of plants and the mineral background of soil structures. During the exposure process in the three agrobotanical groups under study, the concentration of most chemical elements increased.

It can be assumed that the increase in the concentrations of chemical elements in the plant residues occurs because their ash content grows over the process of mineralization. In this case, the concentration calculated by us would be suitable only for a smaller number of samples. It was to be expected that a statistical "adjustment" of the chemical concentrations in plant samples taken from polluted areas should have been identical for all the chemical elements under study. What is probably meant here is that mobile variants of chemical elements undergo infiltration in the gradient of chemical concentrations from the higher ones in soils to the lower ones in plant residues. This concerns, for example, elements such as Ca, Ti, V, Cr, Mn, and Fe and, especially, Cu, Zn, and Pb. A reverse transport is also possible, when the destruction of plant residues is accompanied by the partial wash out of chemical elements (K, Br, and Rb).

Let us introduce some average concentration factors, which are equal to the ratio between the content of chemical elements in the plant samples after and before they are exposed. In this case, all chemical elements under consideration can be divided into three groups (Table 5). The first group consists of K, Br, and Rb. It is always characterized by low concentrations after plant samples have been put in soil. The second group (Mo, Ca, Sr, Zn, Ni, Mn, V, Nb, and Pb) is characterized by average concentration factors. The highest values are observed for Zr, Co, Ti, Cu, Fe, Cr, and Y.

In the unpolluted plots, the average concentration factors of chemical elements in decaying plant residues are higher than the ones in the anthropogenically affected plots. In the first and the second groups there are no statistically important differences between the concentration factors of the samples exposed in the background and polluted zone ($U = 0.22–0.65$; $n = 3$; $p = 0.51–0.83$). This demonstrates that most nonpollutants have a common mineral background in all plots under study. As a result of the exposure of plant residues, almost equal and, in our case, critical concentrations are obtained. This does not include pollutants (the third group); their content in the samples taken from the anthropogenically affected plots after exposure is significantly higher than the background values ($U = 1.96$; $n = 3$; $p = 0.05$).

The maximum concentration of chemical elements was revealed in the samples of cereals. The exposed samples of legumes and herbs contained equal concentrations of chemical elements.

The influence of chemical pollution on the rate of mineralization can be assessed by means of the integral assessment of the toxic load produced by pollutants (Cu, Zn, and Pb). The integral assessment of this load is based on the following index:

$$S_n = \frac{1}{n}\sum_{i}^{n}\frac{C_i}{C_f} \text{ rel. units,}$$

where C_i and C_f are concentrations of only those elements that are considered toxic agents in anthropogenically affected and background plots, respectively; n is the number of chemical elements that are pollutants. This index can be used to assess the general level

Table 2. Concentrations of chemical elements in the agrobotanical groups to their exposure in soil, μg/g

Chemical element	Polluted zone								
	background			buffer			impact		
	Legumes	Cereals	Herbs	Legumes	Cereals	Herbs	Legumes	Cereals	Herbs
K	17712 ± 1134	14294 ± 683	21499 ± 389	12175 ± 974	12642 ± 1691	23834 ± 3272	12327 ± 804	9940 ± 926	20418 ± 437
Ca	16946 ± 1156	3729 ±235	14330 ± 1726	23274 ± 2493	5128 ± 843	21497 ± 2297	19906 ± 1827	3428± 108	23180 ± 1374
Ti	6.4 ± 2.2	5.2 ± 2.3	12.1 ± 3.3	8.5 ± 2.2	6.5 ± 0.8	9.3± 1.7	20.3± 2.3	6.0 ± 0.5	17.6 ± 1.4
V	0.19 ± 0.02	0.20 ± 0.04	0.41 ± 0.03	0.26 ± 0.12	0.21 ± 0.04	0.38 ± 0.05	0.62 ± 0.06	0.26 ± 0.05	0.65 ± 0.07
Cr	4.4 ± 1.7	25.1 ± 16.7	4	8.1 ± 2.7	14.2 ± 3.68	13.3 ± 5.5	152 ± 22.3	43.8 ± 9.1	159 ± 11
Mn	37 ± 1.4	228 ± 26	70 ± 6.3	52 ± 2.6	80 ± 27	70 ± 19	75 ± 2.1	78.5± 5.1	95.2 ± 9.3
Fe	107 ± 13	78 ± 14	157 ± 13	380 ± 53	171 ± 10	477 ± 105	690 ± 27	187 ± 9	610 ± 39
Co	0.04 ± 0.01	0.02 ± 0.01	0.05 ± 0.001	0.09 ± 0.01	0.05 ± 0.01	0.11 ± 0.02	0.14 ± 0.001	0.05 ± 0.01	0.13 ± 0.001
Ni	16.3 ± 0.6	2.4 ± 0.4	12.9 ± 2.2	3.6 ± 1.6	1.7 ± 0.4	1.99 ± 0.59	2.81 ± 0.35	1.39 ± 0.11	1.68 ± 0.17
Cu	9.5 ± 0.37	4.29 ± 0.03	5.92 ± 1.17	7.07 ± 0.20	3.87 ± 0.45	5.83 ± 0.61	6.47 ± 0.32	2.82 ± 0.08	6.33 ± 0.55
Zn	27.7 ± 3.05	23.3 ± 1.3	44 ± 5.2	61 ± 11	32 ± 4	72 ± 9	34 ± 1.8	20 ± 1.5	40.5 ± 3.4
As	0.14 ± 0.04	0.17	0.40	0.40 ± 0.10	0.20 ± 0.06	0.32 ± 0.07	0.13 ± 0.07	0.14 ± 0.10	0.28 ± 0.09
Se	0.16	0.02	0.03	0.07	0.09 ± 0.04	0.16 ± 0.08	0.17 ± 0.06	0.23 ± 0.05	0.28 ± 0.05
Br	4.5 ± 0.01	7.5 ±0.26	10.8± 0.72	3.10 ± 1.01	5.16 ± 2.84	9 ± 1.02	1.56 ± 0.39	1.88 ± 0.32	5.96 ± 1.9
Rb	16.5 ± 0.51	6.9 ±0.08	22.9 ± 2.84	10.32 ± 3.59	8.91 ± 2.12	11.48 ± 1.26	8.96 ± 0.81	5.47 ± 0.15	10.78 ± 1.02
Sr	113 ± 15	25.9 ± 0.25	96.6 ± 11.25	89.4 ± 5.40	27 ± 3.66	105 ± 7.01	73 ± 3.14	24.5 ± 1.06	98.8 ± 14.8
Y	2.20 ± 1.01	0.73 ± 0.02	1.24 ± 0.46	0.88 ± 0.28	0.20 ± 0.10	0.38 ± 0.13	0.59 ± 0.21	0.47 ± 0.15	0.78 ± 0.13
Zr	2.14 ± 1.19	0.74 ± 0.17	1.33 ± 0.18	2.70 ± 0.33	0.77 ± 0.32	2.26 ± 0.18	9.48 ± 5.57	1.37 ± 0.32	4.92 ± 0.56
Nb	0.99 ± 0.13	1.61 ± 0.51	0.26	0.39 ± 0.09	1.74 ± 0.47	0.58 ± 0.01	2.11 ± 0.46	1.41 ± 0.13	1.250 ± 0.30
Mo	0.41 ± 0.06	0.08 ± 0.01	0.28 ± 0.01	0.88 ± 0.44	0.66 ± 0.30	0.52 ± 0.23	5.05 ± 1.79	0.86 ± 0.06	1.0630 ± 0.07
Pb	1.94 ± 0.37	2.63 ± 0.70	3.11 ± 0.05	3.29 ± 0.42	2.76 ± 0.63	4.50 ± 0.34	3.78 ± 0.16	1.93 ± 0.32	5.27 ± 0.39

Table 3. Concentration of chemical elements in plant residues after their exposure in soils, μg/g

Chemical element				Polluted zone					
	background			buffer			impact		
	Legumes	Cereals	Herbs	Legumes	Cereals	Herbs	Legumes	Cereals	Herbs
K	3186 ± 963	2432 ± 440	3258 ± 189	2989 ± 276	2136 ± 652	3233 ± 238	2452 ± 946	2084 ± 1243	1647 ± 634
Ca	22594 ± 3926	11202 ± 1182	29620 ± 2254	22214 ± 7325	8454 ± 1857	29698 ± 2715	30505 ± 5112	26888 ± 20202	30496 ± 22279
Ti	171.1 ± 23.0	424.7 ± 149.4	489.7 ± 39.2	305.7 ± 127.6	330.1 ± 227.4	485.4 ± 126.5	260.0 ± 131.2	207.8 ± 108.0	124.2 ± 29.0
V	1.20 ± 0.14	3.13 ± 1.07	3.95 ± 0.03	3.00 ± 1.20	3.22 ± 2.15	5.88 ± 1.38	3.97 ± 2.02	3.14 ± 1.45	2.33 ± 1.02
Cr	87.8 ± 20.08	264.7 ±107.0	246.7 ± 61.0	202.3 ± 69.4	282.7 ± 57.1	553.8 ± 69.4	3869.8 ± 4280.5	3118.5 ± 3486.6	1321.8 ± 1486.2
Mn	88.9 ± 9.7	234.9 ±52.1	228.6 ±20.4	213.7 ± 65.4	235.4 ± 110.2	300.7 ± 47.9	295.4 ± 56.0	289.2 ± 58.4	268.3 ± 30.4
Fe	2154 ± 185	5503 ± 1671	5932 ± 648	8220 ± 2989	8821 ± 5331	14354 ± 2788	9378 ± 2597	7590 ± 3376	4796 ± 1127
Co	0.42 ± 0.04	1.05 ± 0.22	1.10 ± 0.12	1.28 ± 0.42	1.39 ± 0.71	2.26 ± 0.42	1.65 ± 0.11	1.35 ± 0.59	1.01 ± 0.23
Ni	17.17 ± 4.30	11.18 ± 1.91	23.12 ± 4.08	5.22 ± 1.80	5.19 ± 3.64	8.93 ± 2.62	11.6 ± 12.5	6.3 ± 6.9	3.9 ± 4.1
Cu	14.36 ± 1.37	11.19 ± 1.04	14.72 ± 2.90	22.04 ± 2.54	16.48 ± 5.23	35.66 ± 3.47	77.16 ± 65.90	70.14 ± 78.69	61.10 ± 64.78
Zn	46 ± 7	53 ± 5	88 ± 11	100 ± 21	62 ± 7	176 ± 34	88 ± 14	83 ± 28	91 ± 50
As	0.46 ± 0.25	0.49 ± 0.32	1.28 ± 0.12	1.51 ± 0.30	1.53 ± 0.28	2.59 ± 0.64	1.57 ± 0.18	2.64 ± 2.68	1.49 ± 0.41
Se	0.01 ± 0.01	0.04	0.25	0.42 ± 0.07	0.27 ± 0.001	1.04 ± 0.23	0.47 ± 0.46	0.62 ± 0.02	0.65 ± 0.08
Br	3.43 ± 0.58	5.17 ± 0.51	6.10 ± 0.20	2.38 ± 0.32	2.27 ± 0.70	6.60 ± 1.18	1.18 ± 0.31	2.20 ± 2.33	2.55 ± 1.62
Rb	6.54 ± 0.69	15.96 ± 5.34	16.42 ± 2.68	7.18 ± 2.70	7.10 ± 5.48	11.46 ± 4.18	4.19 ± 0.54	4.17 ± 3.21	2.63 ± 0.83
Sr	119.91 ± 7.08	79.20 ± 13.73	164.40 ± 11.14	99.91 ± 9.24	65.61 ± 27.98	155.82 ± 27.12	117.16 ± 20.07	86.06 ± 37.96	104.17 ± 58.95
Y	15.04 ± 0.99	39.79 ± 11.42	42.50 ± 2.57	22.36 ± 7.98	23.17 ± 15.19	43.62 ± 12.11	18.35 ± 4.78	20.21 ± 13.95	11.82 ± 3.22
Zr	58.00 ± 0.77	336.21 ± 120.86	304.54 ± 86.44	98.45 ± 41.23	100.44 ± 80.72	196.75 ± 66.15	117.62 ± 86.58	96.13 ± 57.60	53.54 ± 23.69
Nb	22.78 ± 1.52	74.92 ± 27.12	77.94 ± 18.14	24.00 ± 13.36	26.12 ± 24.64	36.71 ± 14.56	21.65 ± 17.13	16.74 ± 10.96	10.32 ± 3.82
Mo	0.62 ± 0.001	0.46 ± 0.09	0.84 ± 0.01	2.89 ± 1.81	0.68 ± 0.45	1.54 ± 0.56	5.64 ± 3.07	3.49 ± 3.79	2.41 ± 1.51
Pb	3.99 ± 0.48	9.85 ± 0.32	12.87 ± 0.82	8.54 ± 0.95	8.15 ± 2.00	25.62 ± 6.92	11.99 ± 4.32	10.34 ± 3.63	12.97 ± 5.17

Table 4. Differences in the concentrations of chemical elements exposed in various plots with samples before and after their exposure in soil (Mann–Whitney test)

Chemical element	Legumes		Cereals		Herbs	
	Polluted zone					
	background	impact	background	impact	background	impact
K	+	+	+	+	+	+
Ca	–	+	+	+	–	–
Ti	+	+	+	+	+	+
V	+	+	+	+	+	+
Cr	+	–	+	–	+	–
Mn	+	+	–	+	+	+
Fe	+	+	+	+	+	+
Co	+	+	+	+	+	+
Ni	–	–	+	–	–	–
Cu	+	+	+	+	+	+
Zn	–	+	+	+	–	+
As	–	–	–	–	–	+
Se	–	–	–	–	–	–
Br	–	–	–	–	+	–
Rb	–	+	–	–	–	+
Sr	–	+	+	+	–	–
Y	+	+	+	–	+	+
Zr	+	+	+	+	+	+
Nb	+	+	+	+	+	+
Mo	–	–	+	+	–	–
Pb	–	+	+	+	+	+

Note: "+" is the statistical significance of differences; $p < 0.05$; "–" is no differences.

Table 5. Average concentration coefficients of chemical elements during the mineralization of various agrobotanical groups

Chemical elements	Background areas			Polluted areas		
	Legumes	Cereals	Herbs	Legumes	Cereals	Herbs
K, Br, Rb	0.53	0.84	0.46	0.51	0.64	0.35
Mo, Ca, Sr, Zn, Ni, Mn, V, Nb, Pb	3.90	5.68	3.29	3.55	4.74	3.98
Zr, Co, Ti, Cu, Fe, Cr, Y	31.60	123.10	58.3	18.60	27.2	18.57

of soil pollution and for determining the toxic load on decaying samples [25].

The values of S_n calculated in such way demonstrate that, after having been exposed in the background soil, the toxic load on herb samples increases 7.6 times. During the same period, the load on this group in polluted plots increases 13.3 times. Accordingly, cereals demonstrate the following values: 11.5 (background zone) and 22.9 rel. units (impact). The indices of legumes are 6.3 and 19.3 rel. units.

In order to find out to what degree the toxic load in the decaying samples influences the processes of destruction, the share of destructed phytomass was investigated for the exposure period in soils. Based on an ANOVA analysis of variance, we found that the destruction rate of legumes, cereals, and herbs in the backgound area vary (Table 6). The factor of "agrobotanical groups" contributed 32.4% to the total variability of the characteristic under study. The highest mineralization rate is common for herbs ((39.4 ± 1.1) %), the lowest one was registered in legumes ((29.6 ± 1.3) %).

Table 6. Results of the one-way ANOVA test (*F* criterion) of the destruction rate of agrobotanical groups

Polluted zone	*F*	*df*	*p*	Factor impact in the total variability, %
Background	5.99	2; 25	0.008	32.4
Buffer	48.54	2; 13	0.000001	88.2
Impact	47.18	2; 24	⩽0.001	80.0

Translating these results into the daily rate of destruction results in values ranging from 0.25 (legumes) to 0.54% a day (herbs), which coincides with data obtained by other researchers [2, 6, 30]. Nevertheless, in contrast to many other studies, our results demonstrate that the mineralization rate of organic matter in the polluted areas is higher than in the background zone. Thus, the rate of destruction during the exposure in polluted areas is 61.00–65.10% (for herbs), 35.14–45.69% (for legumes), and 32.54–45.67% (for cereals) (Fig. 2). Statistically important values (herbs: $F = 32.9$; legumes: $F = 20.81$; cereals: $F = 10.90$; $df = 4; 46$; $p = 0.001$) were obtained as a result of comparing the destruction rates between three agrobotanical groups within the anthropogenically affected areas ($S_i = 6.19$–30.0 rel. units) and other variants ($S_i = 1.0$–3.33 rel. units) using Scheffe's multiple-comparison approach (*S*–method).

It is known that the intensity of mineralization depends on soil biota, the activity of which, according to most researchers, can be depressed by introducing toxic concentrations of heavy metals in soil. This is associated with the possible elimination of the most sensitive microorganisms and micromycetes, as well as the depression of their activity. In our case, high contents of metals in soils and agrobotanical groups lead to a rise in the destruction rate of samples taken from the anthropologically affected areas. The pollution levels under study are probably not sufficient for the critical concentration of metals when the activity of soil biota is depressed. It is also possible that some defense mechanisms of microbiota make up for the toxic effect of heavy metals [2, 13, 31, 32].

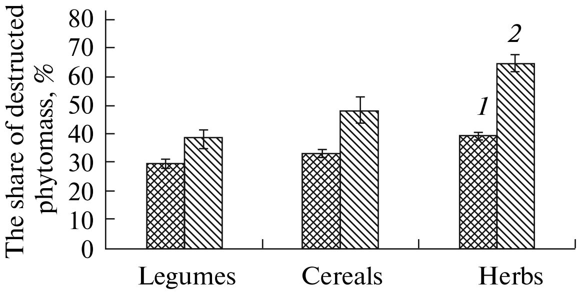

Fig. 2. Changes in the mass of plant residues during the mineralization in (*1*) the background and (*2*) impact zones.

On the other hand, the more rapid destruction of plant residues in the meadow communities in the gradient of increasing chemical pollution can be evidence of some stimuli for microbiota development in soil. This fact should be associated with nitrates in the aerogenic emissions of iron and steel works that influence soil biota. Such a stimulation of destructors was registered by many researchers who studied the mineralization of plant residues in agricultural lands rich in nitrogenous compounds [4], as well as occurring due to potassium-containing dust pollution [33] or nitrogen-containing compounds [34].

CONCLUSIONS

(1) The destruction intensity of plant residues varies in the gradient of soil pollution with heavy metals. The highest rate of mineralization was registered in the anthropologically affected areas, %: herbs, 61.0–65.1 (over the exposure period); legumes, 35.1–45.7; and cereals, 32.5–45.7.

(2) During the mineralization of plant residues, the concentration of chemical elements varies. The content of Ca, Cr, Mn, Cu, Zn, As, Se, Mo, Pb in the anthropogenically affected areas is higher than in the background areas. The concentration of K, Ni, Br, Rb, Sr, Nb is lower than the background concentrations.

(3) Based on the value of concentration factors, three groups of chemical elements were singled out: this index decreases in all the agrobotanical groups for K, Br, Rb. The moderate values are typical for Mo, Ca, Sr, Zn, Ni, Mn, V, Nb, Pb. The maximum values were registered for Zr, Co, Ti, Cu, Fe, Cr, Y.

(4) The largest accumulations of pollutants (Zn, Cu, Pb) in the impact zone were found in the plant residuals of cereals (by 3–25 times). Regardless of the species composition of legumes and herbs, the content of these elements gets higher almost to the same degree (from 2 to 12 times).

(5) The calculated toxic load on the samples of herbs increases 7.6 times after exposure and 13.3 times in the anthropogenically affected area. For cereals, these values are 11.5 and 22.9 rel. units, respectively. For legumes, they are 6.3 and 19.3 rel. units.

The registered changes in chemical composition of plant residuals during their mineralization are directly associated with urgent problems such as the formation of biogenic cycles of chemical elements in background zones and polluted environments.

ACKNOWLEDGMENTS

The work was financially supported by the Ministry of Education and Science of the Russian Federation (state assignment in 2008–2011, no. 1.1.08, in 2012 no. 5.5329.2011); the Development Program of Leading Science Schools (NSh-5325.2012.4); Programs of the Presidium of the Russian Academy of Sciences, Ural Branch (project no. 12-I-4-2051); and the Russian Foundation for Basic Research (project no. 10-04-00146-a).

REFERENCES

1. Marfenina, O.E., *Antropogennaya ekologiya pochvennykh gribov* (Anthopogenic Ecology of the Soil Fungi), Moscow: Meditsina dlya Vsekh, 2005.
2. Vorobeichik, E.L., Seasonal Changes in the Spatial Distribution of Cellulolytic Activity of Soil Microflora under Conditions of Atmospheric Pollution, *Russ. J. Ecol.*, 2007, vol. 38, no. 6, pp. 398–407.
3. Parshina, E.K., Decomposition of the Plant Matter in Forest-Tundra, *Sib. Ekol. Zh.*, 2007, no. 5, pp. 781–787.
4. Ponazkina, L.V., General Assessment of the Effect of Technogenic Pollution and Climatic Factors on Agricultural Systems of Baikal Nature Region, *Uspekhi Sovrem. Biol.*, 2011, vol. 131, no. 3, pp. 194–203.
5. Swift, M.J., Heat, O.W., and Anderson, J.M., *Decomposition in Terrestrial Ecosystem*, Oxford: Blackwell Sci. Publ., 1979.
6. Fischer, Z., Niewinna, M., and Yasulbutaeva, I., Intensity of Organic Matter Decomposition in Landscapes of Caucasus (Dagestan), *Pol. J. Ecology,* 2006, vol. 54, no. 1, pp. 105–116.
7. Nikonov, V.V. and Lukina, N.V., Technogeneous Transformation of Forest Floor Reserves in the Fir Biogeocenosises of the Polar Regions, in *Degradatsiya i vosstanovlenie lesnykh pochv* (Degradation and Recultivation of the Forest Soils), Moscow, 1991, pp. 174–184.
8. Vorobeichik, E.L., Alteration of the Forest Floor Capacity at the Chemical Pollution, *Ekologiya,* 1995, no. 4, pp. 278–284.
9. Tyler, G., The Impact of Heavy Metal Pollution on Forests: A Case Study of Gusum, Sweden, *Ambio*, 1984, vol. 13, no. 1, pp. 18–24.
10. Vorobeichik, E.L., Changes in the Spatial Structure of the Destruction Process under the Conditions of Atmospheric Pollution of Forest Ecosystems, *Biol. Bull.*, 2002, vol. 29, no. 3, pp. 300–310.
11. Vorobeichik, E.L., Reaction of the Forest Floor on the Toxic Pollution and Its Relationship with Biota, *Lesovedenie,* 2003, no. 2, pp. 32–42.
12. Freedman, B. and Hutchinson, T.C., Effect of Smelter Pollutants on Forest Leaf Litter Decomposition Near a Nickel-Copper Smelter at Sudbury Ontario, *Can. J. Botany*, 1980, vol. 58, no. 15, pp. 1722–1736.
13. Baath, E., Effect of Heavy Metals in Soil on Microbialprocesses and Populations (a Review), *Water, Air, Soil Pollut.*, 1989, vol. 47, nos. 3–4, pp. 335–379.
14. Berg, M.P., Ekbohm, G., Soderstrom, B., and Staaf, H., Reduction of Decomposition Rate of Scots Pineneedle Litter Due to Heavy-Metal Pollution, *Water, Air, Soil Pollut.*, 1991, vol. 59, pp. 165–177.
15. Chew, I., Obbard, J.P., and Stanforth, R.R., Microbial Cellulose Decomposition in Soils from a Rifle Range Contaminated with Heavy Metals, *Environ. Pollut.,* 2001, vol. 111, no. 3, pp. 367–375.
16. Ponazkina, L.V., Kotova, L.G., and Lubnina, E.V., *Biogeokhimicheskii monitoring i otsenka rezhimov funktsionirovaniya agroekosistem na tekhnogenno-zagryaznennykh pochvakh* (Biogeochemical Monitoring and Assessment of Functional Regimes of Agricultural Ecosystems on Technogenically Polluted Soils), Novosibirsk: Nauka, 1999.
17. Ponazkina, L.V., Kotova, L.G., Lubnina, E.V., et al., *Ustoichivost' agroekosistem k tekhnogennomu zagryazneniyu ftoridami* (Resistance of Agricultural Ecosystems to Technogeneous Pollution by Fluorides), Irkutsk: Sib. Otd., Ross. Akad. Nauk, 2004.
18. *O sostoyanii okruzhayushchei prirodnoi sredy i vliyanii faktorov sredy obitaniya na zdorov'e naseleniya Sverdlovskoi oblasti v 2009 godu: Gos. doklad* (The State Report on the Condition of Environment and Influence of Habitat Conditions on the Human Health in Sverdlovsk Oblast in 2009), Yekaterinburg: Ministerstvo Prirod. Resursov Sverdlovsk. Obl., 2010.
19. Zhuikova, T.V., Reaction of Cenopopulations and Herbaceous Communities on Chemical Pollution of Environment, *Extended Abstract of Doctoral (Biol.) Dissertation,* Yekaterinburg, 2009.
20. *Metodicheskie rekomendatsii po provedeniyu polevykh i laboratornykh issledovanii pochv pri kontrole zagryaznenii okruzhayushchei sredy* (Practical Recommendations for the Field and Laboratory Study of Soil and Plants during Monitoring of Environmental Pollution), Zyrin, N.G., et al., Eds., Moscow: Gidrometeoizdat, 1981.
21. *Metodicheskie rekomendatsii po opredeleniyu tyazhelykh metallov v pochvakh sel'zhozugodii i produktsii rastenievodstva, 2-e izd.* (Practical Recommendations for Determination of Heavy Metals in Soil of Farms and Agricultural Plant Products, 2nd Edition), Moscow: TsINAO, 1992.
22. Khavezov, I. and Tsalev, D., *Atomno-absorbtsionnyi analiz* (Atomic Absorption Analysis), Leningrad: Khimiya, 1983.
23. Zhuikova, T.V., Bezel', V.S., and Mordvina, E.S., Phytocenosises of Thechnogenically Destroyed Territories and Their Role in Biogenic Cycles of Chemical Elements, in *Uchenye zapiski NTGSPA/Nizhnetagil. gos. sotsial.-ped. akad.* (Scientific Bulletin of Nizhnii Tagil State Social-Pedagogic Academy), Nizhnii Tagil, 2006, pp. 31–73.
24. *Global Environmental Monitoring System (GEMS) SCOPE Rep. 3*, Canada, 1973.
25. Bezel', V.S. and Zhuikova, T.V., A Role of Herbaceous Communities in Formation of Biogenic Cycles of Chemical Elements, *Povolzhsk. Ekol. Zh.*, 2010, no. 3, pp. 219–229.
26. *Ekologicheskaya toksikologiya: Uchebnoe posobie* (Ecological Toxicology: Study Manual), Bezel', V.S.., Ed., Yekaterinburg: Ural. Univ., 2001.

27. Kutsenogyi, K.P., Makarikova, R.P., Milyutin, L.I., Naumova, N.B., Tarakanov, V.V., and Chankina, O.V., The Use of X-Ray Fluorescent Analysis with Synchrotron Radiation to Measure Element Composition of Phytomass and Soils, *Nucl. Instr. Meth.*, 2007, vol. A575, pp. 214–217.
28. Vorobeichik, E.L., A Shift of Cellulose Decomposition Intensity Caused by Technogeneous Burden, *Ekologiya,* 1991, no. 6, pp. 73–75.
29. Berg, M.P., Kniese, J.P., Zoomer, R., and Verhoef, H.A., Long-Term Decomposition of Successive Organic Strata in a Nitrogen Saturated Scots Pine Forest Soil, *Forest Ecol. Manage.*, 1998, vol. 107, nos. 1–3, pp. 235–244.
30. Bienkowski, P., Cellulose Decomposition as Bioenergetic Indicator of Soil Degradation, *Pol. Ecol. Stud.*, 1990, vol. 16, nos. 3–4, pp. 235–244.
31. Gadd, G.M., Interaction of Fungi with Toxic Metals, *New Phytol.,* 1993, vol. 124, pp. 25–60.
32. Giller, K.E., Witter, E., and McGrath, S.P., Toxicity of Heavy Metals to Microorganisms and Microbial Processes in Agricultural Soils: A Review, *Soil Biol. Biochem.,* 1998, vol. 30, pp. 1389–1414.
33. Volkova, V.G. and Davydova, N.D., *Tekhnogenez i transformatsiya landshaftov* (Technological Progress and Transformation of Landscapes), Novosibirsk, 1987.
34. Fenn, M., Increased Site Fertility and Litter Decomposition Rate in High-Pollution Site in the San Bernandino Mountains, *Forest Science,* 1991, vol. 37, no. 4, pp. 1163–1181.