



# Heavy Metals Contamination of Soil in Urban Areas of Southern Ural Region of Russia

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## Abstract

We studied the influence of mining, refining and petrochemical enterprises to the soil contamination by heavy metal of the Southern Urals and adjacent territories. It is established that the highest values of soil contamination study area with heavy metals (pollution degree  $Z_c = 17,4; 20,4$ ) was observed in the zone of influence of the mining and processing plant. The area adjacent to the machine-building, oil refining and petrochemical industries in major cities of Bashkortostan, was characterized by valid ( $Z_c = 1.9$  to  $5.5$ ) or weak impurity ( $Z_c = 8,1; 13,8$ ). In the operation level is set to contamination of urban soils by heavy metals under the influence of the mining and metallurgical industries of the Southern Urals of emissions from machine-building enterprises, oil-refining and petrochemical companies, operating in large, medium and small cities of Bashkortostan.

**Keywords:** Southern Urals, Bashkortostan, soil, heavy metals (copper, zinc, nickel, lead, cadmium), incidence.

## 1. Introduction

The Republic of Bashkortostan (Russia) is located on the border of Europe and Asia and is a part of the Eastern border of the East European plain (the Urals region), mountain zone and the elevated plains of the Southern Urals. The length of the territory from West to East is 420 km and from West to East reaches 540 km (Fig. 1). On the territory of the Republic there are about 200 oil and gas condensate fields, more than 15 deposits of copper and iron ore, 10 deposits of brown coal. Information on the annual number of industrial emissions in urban areas in the zone of influence of existing facilities is presented in Table 1.

Analysis of biogeochemical provinces with regard to the level and duration of exposure, area distribution showed that the number of ecologically unfavorable parts of the South-Ural sub-region of the biosphere, the components of which are characterized by high content of copper and zinc [1]. Their sources are numerous geochemical anomalies and copper-pyrite ore. It is known that trace elements play an important role in the growth and development of plants. However, some of them are dangerous environmental pollutants [2, 3]. This is heavy metals: copper, zinc, nickel, lead, cadmium, cobalt, chromium, molybdenum and mercury. Analysis of the trace element content of soils on the background and technogenically transformed areas allows us to estimate the intensity of heavy metal pollution of the environment, food resources and agricultural products [4, 5].

This work is devoted to study the accumulation of heavy metals (Cu, Zn, Ni, Pb, Cd) in the soil of urban areas of the Republic of Bashkortostan in the zone of influence of mining ore and metallurgical industries of the Southern Urals. Also studied soil pollution of large cities emissions of existing engineering companies, refineries and petrochemical plants in the central part of the region. For comparison presents the results of the content of heavy metals in the soil cover of the small towns of the Republic.

## 2. Materials and methods

In the work investigated the contamination of soil cover the territory of Bashkortostan from the functioning of enterprises of the mining and manufacturing industries of the Southern Urals (Uchaly, Sibay, Baimak, Beloretsk). Of particular interest is the assessment of the degree of soil pollution with heavy metals in cities with developed oil refining, petrochemical and engineering production (Ufa, Sterlitamak, Salavat, Ishimbay, Meleuz, Blagoveshchensk). For comparison, studied the condition of the soil on the territory of small towns in Bashkortostan (Kumertau, Birsik, Dyurtyuli, Davlekanovo) (Picture).

Information on the annual number of industrial emissions in urban areas in the zone of influence of existing facilities is presented in Table 1. Anthropogenic emissions of polluting the soil cover through the atmosphere, mostly concentrated in the upper surface layers of the soil, so the sampling was made from the surface horizon.



The name of cities: 1 – Dyuptyuli; 2 – Birsik; 3 – Blagoveshchensk; 4 – Ufa; 5 – Uchaly; the level of statistical significance  $P < 0,056$  – Davlekanovo; 7 – Beloretsk; 8 – Sterlitamak; 9 – Salavat; 10 – Ishimbay; 11 – Meleuz; 12 – Kumertau; 13 – Sibay; 14 – Baimak

**Figure 1:** The degree of soil contamination in urban areas of Bashkortostan by heavy metals.

Soil samples were collected on-site in the zone of intensive exposure to the pollution source within 1 km (12 samples); 5 km around the source (25 samples) and in the Central part of the city (5 samples). A total content of heavy metals in samples was determined by atomic-absorption spectral analysis [6]. Mathematical processing of the results included the calculation of statistical parameters of trace elements in soils (arithmetic mean  $M$ , standard deviation  $S$ , the level of statistical significance  $P < 0,05$ ).

The calculation of the aggregate indicator of soil contamination  $ZC$  was performed according to the formula:  $ZC = \sum(C_i / CB_i) - (n-1)$ , where  $C_i$  is the content of the element in the sample;  $CB_i$  – background content of the element;  $n$  is the number of summed elements [7]. As background values adopted the average of the indicators of the content of HM in soils ecologically clean part of the territory.

Used in the work estimated the scale of the danger of contamination of soils by the cumulative indicator  $ZC$ , which has the follow-

ing form: allowable pollution ( $ZC = 1-8$ ), weak ( $ZC = 8-16$ ), average ( $ZC = 16-32$ ), strong ( $ZC = 32-64$ ), very strong ( $ZC = 64-128$ ), extremely dangerous ( $ZC > 128$ ) [6].

### 3. Results and Discussions

The results of the study of heavy metals (Cu, Zn, Ni, Pb, Cd) in the soil of urban areas in the zone of influence of mining ore and metallurgical industries of the southern Urals showed that the main pollutants in the region are: Uchalinsky GOK (UGOK, Uchaly) and its subsidiary (UGOK, Sibay), Baimak foundry-mechanical plant (BLMZ), Beloretsk metallurgical plant (BMK). Grosse missions of pollutants from stationary and mobile sources was 2.9-12.5 thousand tons/year (0,21-3.21 t/ha) (Table 1). The contribution of road transport in total emissions amounted to 81-96%.

**Table 1:** The urban population, soil type urban area and gross emissions of pollutants per year

City	The population of the city	Types of soil	Emissions into the atmosphere	
			Thousand tons/year	Ton/hectare
Uchaly	40145	Mountain forest sod-podzolic soils	8.4	1.81
Sibay	60144	Southern chernozem	11.3	0.73
Baimak	17223	Southern chernozem	2.9	0.21
Beloretsk	66939	Grey mountain-forest soils	12.5	3.21
Ufa	1096702	Chernozem leached and typical	318.8	4.49
Sterlitamak	277048	Dark-grey forest soils	103.1	9.50
Salavat	154593	Chernozem leached	60.5	5.71
Meleuz	59994	Chernozem leached and typical	10.3	3.24
Ishimbay	66177	Chernozem leached and typical	10.1	0.98
Blagoeshchensk	32 989	Dark-grey forest soils	12.0	1.86
Kumertau	61 943	Chernozem leached, loamy	21.2	1.25
Birsk	39 992	Gray and dark-gray forest soils	8.9	1.27
Dyurtyuli	29 984	Chernozem leached and typical	7.4	2.97
Davlekanovo	23 860	Black and typical chernozem	6.1	1.50

Soils in the northern part of the investigated region presents mountain forest sod-podzolic and gray mountain-forest soils, passing in the southern black and black leached loamy. It is established that soils with a high content of HM were within one kilometer zone from the pollution source. Everywhere were found to have elevated concentrations of copper, lead, exceeding background values in the range of 2,2-4,3 times. The maximum value is exceeded typical background concentrations for cadmium and reached 16,3 (Uchaly) and 11.5 times (Cibay) (Table 2).

Indicators of soil pollution with heavy metals ( $Z_c$ ) in one kilometer zone around the enterprises of UGOK had a fairly high values:  $Z_c = 20,4$  (Uchaly);  $Z_c = 17,4$  (Cibay) and testified about the average level of contamination (Table 2). The area adjacent to the foundry-mechanical production of Baymak (BLMZ) and Beloretsk (BMK) was characterized by a weak impurity ( $Z_c = 9,5-9,6$ ) (Table 2).

**Table 2:** Heavy metal concentration and the general indicator of soil pollution ( $Z_c$ ) in the cities of Bashkortostan with the mining and Manufacturing industry

Name of the city	The concentration of heavy metals in the soil of the urban area, mg/kg (M±m)					$Z_c^*$
	Cu	Zn	Ni	Pb	Cd	
Uchaly, UGOC, 0-1 km	532±120	487±98	101±14	177±32	2.62±1.13	20.1
City center	234±46	382±58	143±32	101±24	1.45±0.11	11.8
All territory	380±87	320±92	98±19	130±28	1.52±0.63	11.5
Background	181	315	94	67	0.16	
Sibay,	510±54	121±23	77±17	81±21	4.94±1.83	17.4

UGOC, 0-1 km						
City center	151±31	67±15	57±12	46±9	2.49±0.11	2.6
All territory	323±58	96±18	87±17	64±12	3.38±1.21	6.1
Background	150	64	42	35	1.33	
Baymak, Mechanical plant, 0-1 km	570±135	470±98	170±42	140±34	6.2±2.2	9.6
City center	350±64	372±78	134±26	73±7	4.1±0.8	4.8
All territory	373±76	347±86	141±34	93±18	3.8±1.2	5.2
Background	134	244	100	52	2.10	
Beloretsk, BMC, 0-1 km	98±17	270±70	67±14	194±47	1.12±0.43	9.5
City center	47±11	240±51	50±9	100±24	0.64±0.24	3.7
All territory	59±8	232±48	61±13	125±22	0.59±0.21	4.4
Background	44	122	35	51	0.33	

The analysis of static data on the overall incidence in the zone of influence of mining deposits and metallurgical enterprises of the Southern Urals showed a change in the rate from 78723 to 98363 per 100 thousand populations. Exceeding indicator Beloretsk on the average value (85890/100 thousand population) was about 15%. In the overall morbidity of respiratory diseases take the first place and is about 36%. However, the incidence of malignancy was changed from 166,2 (Baimak) to 314,7 (Beloretsk) per 100 thousand population. It should be noted that only for Beloretsk exceeded the national rate (278,5 /100 thousand population) approximately 13% (Table 3).

**Table 3:** The total contamination of soil, the overall incidence and incidence of malignant neoplasms

Name of city	Total contamination index, $Z_c$	The incidence per 100 thousand population	
		Total incidence	Malignant neoplasms
The centres of the mining and manufacturing industries			
Uchaly	20.4	97 820	213.1
Sibay	17.4	71 648	237.7
Baimak	9.6	80 187	166.2
Beloretsk	9.5	98 364	314.7
The complex of oil refining, petrochemical and engineering			
Ufa	8.1	85 742	312.9
Sterlitamak	5.5	95 316	304.1
Salavat	2.8	71 648	313.2
Meleuz	4.8	107 452	264.8
Ishimbay	5.6	80 187	230.3
Blagoveshchensk	13.8	102 908	263.2
Small towns			
Kumertau	8.6	105 203	394.8
Birsk	5.5	93 364	233.0
Dyurtyuli	2.0	93 820	231.9
Davlekanovo	6.2	71 098	248.3

Study the content of HM in the soil of the territory, Ufa, capital of Bashkortostan, showed that the main pollutants are: Ufa production engineering (UMPO), Ufa group of refineries, petrochemical plants and electric power companies. Gross emissions of pollutants from stationary and mobile sources was 318,8 thousand tons/year (4,5 t/ha) (Table 1). The contribution of road transport in total emissions amounted to 64%. Sampling was carried out in an area with a radius of 0-5 km around the source of pollution – UMPO. The examined soils are mainly presented as chernozem leached and typical. Soil near one kilometer zone around UMPO most contaminated with heavy metals. Everywhere found to exceed 1.3-3.6 times the background concentrations of HM (Cu, Zn, Ni, Pb, Cd), the maximum value belongs to the copper. Indicators of soil contamination HM ( $Z_c$ ) in one kilometer zone around UMPO had high values ( $Z_c = 5,5; 8,1$ ) and was responsible for a weak level of contamination (Table 4).

**Table 4:** Heavy metal concentration and the general indicator of soil pollution in the cities of Bashkortostan with the developed machine-building, oil refining and petrochemical production

City, company	The concentration of heavy metals in the soil of the urban area, mg/kg (M±m)					Zc*
	Cu	Zn	Ni	Pb	Cd	
Ufa, UMPO, 0-1 km	83±1 2	79±13	87±15	39±8	0.43±0.1 3	8.1
0-5 km	61±9	72±13	81±16	30±7	0.29±0.1 1	5.5
Background	23	66	54	11	0.20	
Sterlitamak, "Caustic", 0-1 km	36±5	40±10	93±16	45±1 0	0.23±0.0 8	5.5
Territory of the city	26±6	73±16	84±17	37±1 1	0.15±0.1 3	4.6
Background	17	34	56	18	0.11	
Salavat, "Salavatnefteorgsintez", 0-5 km	31±1 2	82±16	91±17	32±1 2	0.20±0.0 6	2.8
Territory of the city	26±8	79±17	81±21	25±7	0.16±0.0 4	1.9
Background	25	63	69	21	0.13	
Meleuz, Mineral fertilizers, 0-1 km	27±4 2	102±2	129±4 5	46±6	0.14±0.0 3	4.2
Background	15	49	102	29	0.10	
Ishimbay "Vityaz", 0-1 km	35±6	98±17	92±22	32±5	0.31±0.1 0	5.6
Background	22	87	50	14	0.12	
Blagoveshchensk, territory of city	56±7	98±17	82±15	33±5	0.57±1.2 3	13.8
Background	22	32	13	15	0.33	

Economics major cities of Bashkortostan with a population of over 150 thousand people (Sterlitamak, Salavat) is represented by the enterprises of chemical and petrochemical industry. Gross emissions of pollutants from stationary and mobile sources was up 103.1 thousand tons/year (9,50 t/ha) and 60.5 thousand tons/year (5,71 t/ha) (Table.1). The contribution of road transport in total emissions amounted to 39, and 40%, accordingly. The soils sampling, Sterlitamak conducted in the area of the 0-1 km radius around the source of pollution – JSC "Caustic" and, Salavat – in 0-5 km from JSC "Salavatnefteorgsintez" in the urban area. Surveyed soil predominantly dark-gray forest and leached chernozem. The content of most of HM in soils Sterlitamak (JSC "Caustic") exceeds the corresponding background concentrations of 1.2-2.5 times, the maximum value of the characteristic for lead. Indicators of soil contamination HM (ZC) in one kilometer zone around JSC "Caustic" and the urban areas had not high values (ZC = 8,1; and 5,5, respectively) and corresponded to low levels of contamination (Table 4). The concentration of HM in the soil of industrial areas (JSC "Salavatnefteorgsintez") and the urban area was slightly higher than the corresponding background values. Indicators ZC was changed from 5.5 to 4.6 and consistent with acceptable levels of contamination (Table 4).

The analysis of static data on the overall incidence in the major cities of Bashkortostan with the developed machine-building, oil refining and petrochemical production showed a growth rate in the series: Salavat, Ufa, Sterlitamak (71648, 85742, 95316 per 100 thousand population). However, only the incidence, Sterlitamak exceeded the national average is 11%. The incidence of malignant neoplasms was changed from 304,1 (Sterlitamak) to 313,7 (Salavat) per 100 thousand population. It should be noted that for all cities exceeded the national rate (278,5/100 thousand population) approximately 9-13% (Table 3). Economy medium-sized cities of Bashkortostan with a population of 70 thousand people (Meleuz, Ishimbay, Blagoveshchensk) represented by the chemical industry, food industry and transport engineering. Grosse missions of pollutants from stationary and mobile sources in the cities represented 10,3; 10,1; 12,0 thousand tons/year (3,24; 0,98; 1,86 t/ha) (Table 1). The contribution of road transport in total emissions amounted to 91, 94, 51%, respectively. The soil sampling Meleuz produced in the zone of the 0-1 km radius around the

source of pollution - JSC "Meleuz mineral fertilizers, in, Ishimbay - in 0-1 km from the plant transport engineering (JSC IC "Vityaz") and in the urban area, Blagoveshchensk. The study site is predominantly based on leached Chernozem and typical, as well as dark-gray forest soils.

The HM content (Cu, Zn, Ni, Pb, Cd) in soils, Meleuz (JSC "MMU") above the respective background concentrations of 1.3-2.1 times, the maximum value is typical for zinc (Table 4). The concentration of HM in soils, Ishimbay (JSC IC "Vityaz") above the respective background values 1.3-2.6 times, the maximum value of the characteristic for cadmium (Table 4). The HM content (Cu, Zn, Ni, Pb, Cd) in soils, Blagoveshchensk (urban area) exceeded the corresponding background concentrations of 1.7-8.3 times, the maximum value is typical for nickel (Table 4). The rate of soil contamination HM (ZC) in one kilometer zone around OJSC "MMU" (Meleuz) and JSC IC "Vityaz" (Ishimbay) had not high values (ZC = 4,2; 5,6) and consistent with acceptable levels of pollution. Indicators of soil pollution the urban area of Blagoveshchensk ZC = 13.8 and corresponded to a weak level of contamination (Table 4). General morbidity of the population of medium-sized cities of the Republic grew in number: Ishimbay, Blagoveshchensk, Meleuz (80187, 102908, 107452 per 100 thousand population). Morbidity in urban populations Blagoveshchensk and Meleuz exceeded the average national value by 20 and 25%. The incidence of malignant neoplasms is changed from 230,3 (Ishimbay) to 263,2 (Blagoveshchensk) and 264,8 (Meleuz) per 100 thousand population. It should be noted that the indicator for all cities excess of the national rate (278,5/100 thousand population).

The economy of small towns in Bashkortostan with a population of from 20 to 60 thousand people (Kumertau, Birsk, Dyurtyuli, Davlekanovo) is represented by the enterprises of machine-building, light and food industries. Grossemissions of pollutants from stationary and mobile sources in the cities amounted to 21,2; 8,9; 7,4; 6,1 thousand tons/year (1,25; 1,27; 2,97; 1,49 t/ha) (Table 1). The contribution of road transport in total emissions amounted to 38, 95, 64, 84%, respectively.

The soil sampling, Kumertau produced in the centre of the urban area. The surveyed areas are predominantly leached chernozem loam and dark gray forest soils. The HM content (Cu, Zn, Ni, Pb, Cd) in soils, Kumertau exceeded the corresponding background concentration of 2.0-3.2 times. Detected elevated concentrations of copper, lead, maximum value is characteristic for cadmium. Indicators of soil pollution the urban area Kumertau (ZC = 8,6) corresponded to a weak level of contamination (Table 5).

**Table 5:** Heavy metal concentration and the general indicator of soil pollution in small towns of Bashkortostan

Name of the city	The concentration of heavy metals in the soil of the urban area, mg/kg (M±m)					Zc*
	Cu	Zn	Ni	Pb	Cd	
Kumertau, City center	38±7	76±19	141±35	32±8	0.67±1.61	8.6
background	16	38	67	11	0.21	
Birsk, City center	42±9	96±28	87±21	89±18	0.30±0.10	5.5
background	17	62	73	41	0.14	
Dyurtyuli, City center	25±7	67±15	88±19	27±8	0.42±0.14	2.0
background	17	34	76	10	0.08	
Davlekanovo, City center	33±8	71±18	162±33	25±7	0.13±0.04	6.2
background	17	34	76	10	0.08	

The soil sampling in, Birsk, Dyurtyuli, Davlekanovo produced in the centre of the urban area. Surveyed plots are represented respectively by the following types of soils: dark grey forest, chernozem leached typical and typical chernozems. The content of HM (Cu, Zn, Ni, Pb, Cd) in soils, Birsk exceeded the corresponding background concentrations of 1.2-2.5 times; Dyurtyuli – 1.1-1.7 times; Davlekanovo – 1.6-2.5 times. Detected elevated con-

centrations of copper, zinc and lead, the maximum value is characteristic for lead. Indicators of soil pollution in urban areas (ZC) are changed in the range of 2.0 to 6.2 and consistent with acceptable levels of contamination (Table 5).

The analysis of static data on general morbidity of the population in the small towns of Bashkortostan showed a change in the rate from 71098 to 105203 per 100 thousand populations [4]. Data of Kumertau on the overall incidence significantly (22%) more than the average national level (85890/100 thousand population). While the incidence of malignant neoplasms was changed from 231,9 223 (Dyurtyuli), 233,0 (Birsk) to 394,8 (Kumertau) per 100 thousand population. It should be noted that only Kumertau exceeded the national indicator (278,5 /100 thousand population) on the ~ 42% (Table 3).

#### 4. Conclusion

The first comprehensive studies held of the risk of heavy metal (Cu, Zn, Ni, Pb, Cd) contamination of urban soils of Bashkortostan under the influence of the mining and metallurgical industries of the Southern Urals (4 cities; oil refining, petrochemical enterprises in the central part of the Republic (6 cities) and in small towns (4 cities), where the main source of pollution is road transport.

In the study of soil contamination under the influence of the mining and metallurgical industries (Uchaly, Sibay, Baimak, Beloretsk) generally were found to have elevated concentrations of copper, lead, exceeding background values in the range of 2,2-4,3 times. The indicators (Zc) were changed in the range of 17,4-20,4 and testified about the average level of contamination.

The study of the content of HM in the soil of the territory of Ufa, capital of Bashkortostan, and two large cities (Sterlitamak, Salavat) showed values above background concentrations of HM in 1.3-3.6 times. The degree of pollution of the territory adjacent to the machine-building, oil refining and petrochemical industries (Salavat, Sterlitamak, Ishimbay) conforms to the valid levels ( $Z_c = 1,9-5,6$ ), and the soil Ufa, Blagoveshchensk were characterized by a weak contamination ( $Z_c = 8,1; 13,8$ ).

Emissions into the atmosphere of the small towns of Bashkortostan small enterprises of machine-building, light and food industry, road transport leads to contamination. Content of HM in urban soils exceeded the corresponding background concentrations of 1.6-3.2 times. Indicators of soil contamination Kumertau ( $ZC = 8,6$ ) corresponded to a weak level of pollution, and for the cities of Birsk, Dyurtyuli, Davlekanovo ( $ZC = 2,0-6,2$ ) corresponded to acceptable levels of pollution.

The mapping scale emissions of pollutants from stationary and mobile sources, extent of soil contamination in urban areas with statistical data on the overall incidence and incidence of malignant tumors did not reveal an unambiguous communication. In the zone of influence of mining deposits and metallurgical enterprises of the southern Urals there was a slight excess of the average national indicator overall morbidity (Beloretsk, 13%) and the incidence of malignancy neoplasms (Beloretsk, 15%). In the major cities of Bashkortostan with the developed machine-building, oil refining and petrochemical production marked lower level of morbidity. However it is not typical for medium-sized and small towns of the Republic, in which have been significantly exceeded the national performance rate of morbidity (Blagoveshchensk – 20; Meleuz – 25; Kumertau – 22%) and the incidence of malignant neoplasms (Kumertau ~ 42%).

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