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Associations of heavy metals in the development of environmentally dependent diseases of the population of Bashkortostan

Asocijacije teških metala u razvoju bolesti izazvanih ekološkim faktorima stanovništva Baškortostana

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Abstract: The analysis of the microelement composition of soils in the background and transformed territories made it possible to assess the intensity of heavy metal pollution of the environment, feed resources and agricultural products. The accumulation of heavy metals - Cu, Zn, Ni, Pb, Cd in the soil of large industrial cities of the Republic of Bashkortostan, where pollution occurs by emissions from machine-building, oil refineries and petrochemical plants, has been studied. For comparison, the results on the content of heavy metals in the soil cover of small towns of the republic are presented. The analysis of the structure and trends of diseases of the population of these cities is also given. The scale of emissions of pollutants into the atmosphere from stationary and mobile sources and the degree of contamination of the soil cover of urban areas are shown. The morbidity of the population of the cities of Blagoveshchensk and Meleuz exceeded the national average by 20 and 25%, Kumertau by 42%. Comparison of the scale of emissions of pollutants into the atmosphere from stationary and mobile sources, the degree of contamination of the soil cover of urban areas and the incidence of the population indicates a tense situation requiring improvement of soil conditions and environmental protection.

Keywords: heavy metals, morbidity, soil, pollution, emissions, atmosphere, petrochemical plants, Republic of Bashkortostan.

Sažetak: Analiza mikroelementnog sastava zemljišta u transformisanim teritorijama omogućila je procenu intenziteta zagađenja teškim metalima životne sredine, stočne hrane i poljoprivrednih proizvoda. Proučavana je akumulacija teških metala - Cu, Zn, Ni, Pb, Cd u zemljištu velikih industrijskih gradova Republike Baškortostan, gde zagađenja nastaju kao rezultat emisija iz mašinogradnje, rafinerija nafte i petrohemijskih postrojenja. Poređenja radi, prikazani su rezultati o sadržaju teških metala u zemljišnom pokrivaču malih gradova republike. Takođe je data analiza strukture i trendova oboljenja stanovništva ovih gradova. Prikazane su razmere emisije zagađujućih materija u atmosferu iz stacionarnih i mobilnih izvora i stepen kontaminacije zemljišnog pokrivača urbanih područja. Morbiditet stanovništva gradova Blagovešćenska i Meleuza premašio je nacionalni prosek za 20 i 25%, Kumertaua za 42%. Poređenje obima emisija zagađujućih materija u atmosferu iz stacionarnih i mobilnih je područja i incidencija stanovništva ukazuje na napetu situaciju koja zagađenosti zemljišnog pokrivača urbanih područja i incidencija stanovništva ukazuje na napetu situaciju koja zahteva preduzimanje mera za poboljšanje stanja zemljišta i zaštitu životne sredine.

Ključne reči: teški metali, morbiditet, zemljište, zagađenje, emisije, atmosfera, petrohemijska postrojenja, Republika Baškortostan.

INTRODUCTION

It is known that trace elements play an important role in the processes of growth and development of organisms, but some of them are dangerous environmental pollutants. These are heavy metals (HM) - copper, zinc, nickel, lead, cadmium, cobalt, chromium, molybdenum and mercury (Ermakov et al., 2012; Saet et al., 1990). At the same time, the ecological and biogeochemical problem of the imbalance of chemical elements (CE) is becoming more and more urgent all over the world, including in the Russian Federation (RF). Depending on the nature of environmental pollution, various systems of the human body are affected, which leads to the development of diseases (Kovalsky, Andrianova, 1974; MU, 1999). The number of ecologically unfavorable biogeochemical provinces includes the South Ural region of the biosphere, its natural environments are characterized by a high content of copper, zinc and other CE (Kuramshina, Imashev, 2013; Kuramshina et al., 2014). Their sources are numerous geochemical anomalies of natural and man-made origin, which are characteristic of the territory of the Republic of Bashkortostan of the Russian Federation, where the oil, metallurgical and mining industries are developed (Yearbook, 2020; State Report, 2021).

1. MATERIALS AND METHODS

The work investigated soil contamination with heavy metals in cities with developed oil refining, petrochemical and machine-building production -Ufa, Sterlitamak, Salavat, Ishimbai, Meleuz, Blagoveshchensk. The pollution of the soil cover of small towns - Beloretsk, Baymak, Kumertau, Birsk, Dyurtyuli, Davlekanovo, where small enterprises of the metallurgical and manufacturing industries were studied.

Technogenic emissions polluting the soil cover through the atmosphere are mostly concentrated in the upper surface layers of the soil, therefore sampling was carried out from the surface horizon, according to State standard 17.4.3.01-2017. Soil samples were taken in the zone of intense exposure to the source of pollution within a radius of 1 km (12 samples), 5 km around the source (25 samples) and in the central part of the city (5 samples). Soil sampling in the city was carried out in a zone with a radius of 0 - 1 km around the source of pollution and in the urban area. Soil sampling in Sterlitamak was carried out in a zone with a radius of 0 - 1 km around the source of pollution - Company "Caustic" and in the urban area, and in Salavat - 0 - 5 km from Company "Salavatnefteorgsintez". In the cities of Birsk, Dyurtyuli, Davlekanovo, soil samples were taken in the city center. In the cities of Meleuz, sampling in a zone with a radius of 0 - 1 km around the source of pollution - Company "Meleuz mineral fertilizers". In Ishimbai – 0 - 1 km from the plant of transport engineering, and in Blagoveshchensk and and Kumertau on the territory of the city.

The gross content of heavy metals was determined on an atomic adsorption spectrophotometer "AAS-3", extracts were carried out with nitric acid. The total indicator of soil pollution

$$Z_{c} = \Sigma (C_{i}/C_{bi}) - (n-1),$$

where C_i is the content of the element in the sample under study; C_{bi} is the background content of the element; *n* is the number of summable elements (Saet et al., 1990). The indicators of TM content in the soils of the corresponding territory are taken as background values.

2. RESULTS AND DISCUSSION

The main content of elements such as Cu, Zn, Ni, Pb, Cd in the soils of cities with metallurgical production occurs through atmospheric pollution. It is shown that the level of such pollution in such cities ranges from 0,2 to 3,2 t/h. Gross emissions of pollutants into the atmosphere from stationary and mobile sources amounted to 318,8 thousand t/year (4,50 t/h). The contribution of vehicles to total emissions was 64%. The economy of the large cities of Bashkortostan (Sterlitamak, Salavat) is represented by enterprises of the chemical and petrochemical industry with large gross emissions into the atmosphere. So, pollutants from stationary and mobile sources are 19,50 t/h and 5,71 t/h, respectively (Table 1).

The economy of medium-sized cities of Bashkortostan with a population of up to 70 thousand people (the cities of Meleuz, Ishimbai, Blagoveshchensk) is represented by enterprises of the chemical, food industry and transport engineering. Gross emissions of pollutants into the atmosphere from stationary and mobile sources in cities amounted to 3,24, 0,98, 1,86 t/h. The contribution of motor transport to total emissions was 91, 94, 51 %, respectively. The economy of small towns of Bashkortostan with a population of 20 to 60 thousand people - Kumertau, Birsk, Dyurtyuli, Davlekanovo is represented by enterprises of mechanical engineering, light and food industries. The volumes of gross emissions of pollutants from these industries by cities were: 1,25, 1,27, 2,97, 1,49 t/h, respectively (Table 1). The contribution of vehicles to total emissions reaches 64%.

The soils are mainly dark gray forest, as well as leached chernozems. The content of most HM in Sterlitamak soils exceeds background concentrations by 1,2 - 2,5 times, the maximum values are char-

acteristic of lead. Indicators of soil contamination of HM (Z_c) in the kilometer zone around Company "Caustic" and on the territory of the city had not high values of $Z_c - 8,1$; 5,5, respectively. HM concentr-

ations in the soil of the industrial zone and urban area are higher than the background ones. The indicators of Z_c varied from 5,5 to 4,6 and corresponded to the permissible level of pollution (Table 2).

 Table 1 - Characteristics of the population, soil type and gross emissions of pollutants into the atmosphere in the cities of Bashkortostan

	Population		Air emissions			
City	ity size Soil types		Thousand t/year	t/h		
Cities with metallurg	jical and manufac	turing industries				
Baymak	17223	Southern chernozems	0,166	0,732		
Beloretsk	66939	Grey Mountain forests	0,187	3,207		
Kumertau	61943	Leached chernozems	0,342	0,209		
Large and medium-	sized cities of the	Republic of Bashkortostan				
Ufa	1096702	Leached chernozems	318,8	4,49		
Sterlitamak	277048	Dark gray forest soils	103,1	9,50		
Salavat	154593	Leached chernozems	60,5	5,71		
Meleuz	59994	Leached and typical chernozems	10,3	3,24		
Ishimbai	66177	Leached and typical chernozems	10,1	0,98		
Kumertau	61943	Leached, loamy chernozems	21,2	1,25		
Small towns of the Republic of Bashkortostan						
Blagoveshchensk	32989	Dark gray forest soils	12,0	1,86		
Birsk	39992	Grey and dark grey forest soils 8,9		1,27		
Dyurtyuli	29984	Leached and typical chernozems 7,4		2,97		
Davlekanovo	23860	Typical chernozems 6,1		1,50		

Table 2 - Heavy metal content (gross) in large and medium-sized cities of Bashkortostan

C:4.	The content of HM in the soil of the urban area, mg/kg						
City	Cu, M±m	Zn, M±m Ni, M±m		Pb, M±m	Cd, M±m	l±m Z _c	
Ufa, 0-1 km	83±12	79±13	87±15	39±8	0,43±0,13	8,1	
0-5 km	61±9	72±13	81±16	30±7	0,29±0,11	5,5	
Background	23	66	54	11	0,20		
Sterlitamak, 0-1 km	36±5	40±10	93±16	45±10	0,23±0,08	5,5	
Urban area	26±6	73±16	84±17	37 ±11	0,15±0,13	4,6	
Background	17	34	56	18	0,11		
Salavat, 0-1 km	31±12	82±16	91±17	32±12	0,20±0,06	2,8	
Urban area	26±8	79±17	81±21	25±7	0,16±0,04	1,9	
Background	25	63	69	21	0,13		
Meleuz, 0-1 km	27±4	102±22	129±45	46±6	0,14±0,03	4,2	
Background	15	49	102	29	0,10		
Ishimbai, 0-1 km	35±6	98±17	92±22	32±5	0,31±0,10	5,6	
Background	22	87	50	14	0,12		
Blagoveshchensk	56±7	98±17	82±15	33±5	0,57±1,23	13,8	
Background	22	32	13	15	0,33		

The content of Cu, Zn, Ni, Pb, Cd in Meleuz soils exceeded background concentrations by 1,3 - 2,1times, the maximum value is typical for zinc. The concentration of TM in the soils of Ishimbai is 1,3 - 2,6 times higher than the background values, the maximum value is characteristic of cadmium. The content of Cu, Zn, Ni, Pb, Cd in the soils of the urban area of Blagoveshchensk is 1,7 - 8,3 times higher than the background values, the maximum value is typical for nickel. Indicators of HM soil contamination in the kilometer zone in Meleuz and Ishimbai corresponded to the permissible level. Soil contamination of the HM of the urban territory of Blagoveshchensk corresponded to $Z_c - 13,8$ (Table 2).

The soils of the near one-kilometer zone around machine-building enterprises are the most contaminated with HM. The excess of background concentrations of Cu, Zn, Ni, Pb, Cd by 1,3 - 3,6 times was found everywhere. The highest values in the cities of Blagoveshchensk, Baymak, Beloretsk, Kumertau, Ufa $- Z_c$: 13.8 - 9.6 - 9.5 - 8.6 - 8.2, accordingly (Table 3).

In the soils of the city of Kumertau, the content of Cu, Zn, Ni, Pb, Cd exceeded the background values by 2.0 - 3.2 times. Elevated concentrations of copper and lead were found, the maximum value is typical for cadmium. The content of HM in the soils of Birsk is also 1.2 - 2.5 times higher than the background ones; Dyurtyuli - 1.1 - 1.7 times; Davlekanovo - 1.6 - 2.5 times. The content of copper, zinc and lead is increased, but the maximum values are characteristic of lead. Indicators of soil pollution of the urban area (Z_c) varied in the range 2.0 - 6.2 (Table 4).

	HM enterprise in the soil of the urban area, mg/kg					
City	Cu, M±m	Zn, M±m	Ni, M±m	Pb, M±m	Cd, M±m	Zc
Baimak, 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
The territory of the city	373±76	347±86	141±34	93±18	3,8±1,2	5,2
Background	134	244	100	52	2,10	
Beloretsk, 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
The territory of the city	59±8	232±48	61±13	125±22	0,59±0,21	4,4
Background	44	122	35	51	0,33	

Table 3 - Heavy metal content (gro	ss) in cities with metallur	pical and manufacturing industries
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Table 4 - Heavy metal content of small towns of Bashkortostan

City	Concentration of HM in the soil of the urban area, mg/kg						
City	Cu, M±m	Zn, M±m	Ni, M±m	Pb, M±m	Cd, M±m	Z _c	
Kumertau	38±7	76±19	141±35	32±8	0,67±1,61	06	
Background	16	38	67	11	0,21	8,6	
Birsk	42±9	96±28	87±21	89±18	0,30±0,10	E E	
Background	17	62	73	41	0,14	5,5	
Dyurtyuli	25±7	67±15	88±19	27±8	0,42±0,14	2.0	
Background	23	61	78	16	0,41	2,0	
Davlekanovo	33±8	71±18	162±33	25±7	0,13±0,04	6,2	
Background	17	34	76	10	0,08	0,2	

The analysis of the general morbidity in the zone of influence of metallurgical enterprises showed a change in the indicator from 78723 to 98363 per 100 thousand population. In the city of Beloretsk, the indicator exceeded the national average by 15%. Respiratory diseases occupy the first place in the structure of the general morbidity and account for about 36%. At the same time, the incidence of malignant neoplasms varied from 166,2 (Baymak) to 314,7 (Beloretsk). For Beloretsk, the excess of the republican indicator was 13% (Table 5). Analysis of static data on the general morbidity in large cities of Bashkortostan with developed machine-building, oil refining and petrochemical production showed an increase in the indicator in the series: Salavat, Ufa, Sterlitamak (71648, 85742, 95316 per 100 thousand population). It should be noted that for all cities there was an excess of the republican indicator by about 9 - 13% (Table 5).

Table 5 - Indicator of total soil pollution, general and oncological morbidity in the cities of Bashkortostan

City	7	Morbidity rate per 100 thousand population						
City	Z _c	General	Oncological					
Cities with metallurgi	Cities with metallurgical and manufacturing industries							
Baimak	9,6	80187	166,2					
Beloretsk	9,5	98364	314,7					
Large and medium-s	ized cities of the Republic	of Bashkortostan						
Ufa	8,2	85742	312,9					
Sterlitamak	5,5	95316	304,1					
Salavat	2,8	71648	313,2					
Meleuz	4,8	107452	264,8					
Ishimbai	5,6	80187	230,3					
Blagoveshchensk	13,8	102908	263,2					
Small towns of the Republic of Bashkortostan								
Kumertau	8,6	105203	394,8					
Birsk	5,5	98364	233,0					
Dyurtyuli	2,0	93820	231,9					
Davlekanovo	6,2	71098	248,3					

A general assessment of the health status of the population in the studied cities showed that the general morbidity of the population of medium-sized cities of the republic increased in a row: Ishimbai, Blagoveshchensk, Meleuz. The morbidity rates of the population of the cities of Blagoveshchensk and Meleuz exceeded the national average by 20 and 25%. The incidence of malignant neoplasms varied from 230,3 - Ishimbai to 263,2 - Blagoveshchensk and 264,8 - Meleuz (per 100 thousand population). Analysis of static data on the general morbidity of the population of small towns of Bashkortostan showed a change in the indicator from 71098 to 105203 per 100 thousand. It should be noted that for Kumertau, the republican indicator was exceeded by 42% (Table 3) (State Report, 2021).

CONCLUSION

The paper presents comprehensive studies of heavy metals pollution of Cu, Zn, Ni, Pb, Cd urban soils of Bashkortostan under the influence of metallurgical industries, oil refineries, petrochemical enterprises in the central part of the republic and in small towns, where the main source of pollution is road transport. Assessment of soil contamination with metallurgical production in the cities of Baymak, Beloretsk showed that concentrations of copper, lead, exceed background values by 2,2 - 4,3 times. The study of the content of HM in the soil of the territory of Ufa, the capital of Bashkortostan, and the large cities of Sterlitamak and Salavat, showed an excess of background values for HM by 1,3 -,.6 times. The degree of pollution of the territory adjacent to machine-building, oil refining and petrochemical industries in the cities of Salavat, Sterlitamak, Ishimbai corresponded to the permissible level - $Z_c = 1,9 - 5,6$. The soils in Ufa, Blagoveshchensk were characterized by a HM pollution index by Z_c in the range of 8,1 - 13,8.

Emissions into the atmosphere of small cities of Bashkortostan by small enterprises of mechanical engineering, light and food industries, motor transport pollute the territories and the content of HM on their soils is 1,6 - 3,2 times higher than background values. Soil pollution in Kumertau corresponded to a weak level, and Birsk, Dyurtyuli, Davlekanovo acceptable.

In the zone of influence of mining deposits and metallurgical enterprises, there was a slight excess of the republican indicator of general morbidity (Beloretsk, 13%) and the incidence of malignant tumors (Beloretsk, 15%). In large cities of Bashkortostan with developed machine-building, oil refining and petrochemical production, a lower level of morbidity of the population was noted. However, for medium and small cities of the republic, the republican level of the general morbidity of the population has already been significantly exceeded: Blagoveshchensk - 20%; Meleuz - 25%; Kumertau - 22%. Incidence of malignant neoplasms in Kumertau.

Comparison of the scale of emissions of pollutants into the atmosphere from stationary and mobile sources, the degree of contamination of the soil cover of urban areas and the incidence of the population indicates a tense situation requiring improvement of soil conditions and environmental protection.

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