Toxic elements in the soils of urban ecosystems and technogenic sources of pollution

GORELOVA S.V.[1], GORBUNOV A.V.[2], FRONTASYEVA M.V.[3], SYLINA A.K.[1]

[1]Natural Science Institute, Department of Biology [2] Laboratory of Chemical Analytical Research
[3] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,
[1]Tula State University [2] Geological Institute of the Russian Academy of Sciences (GIN RAS) [3] JINR
[1] Lenin Av., 92, Tula, Tula region.,300012, [2] Pyzhevsky per., 7s1, Moscow, 119017,
[3] 141980, Moscow Region, Dubna, JINR
RUSSIAN FEDERATION

Abstract: Using physicochemical methods of analysis (XRF and AAS), the elemental composition of urban soils of large urban ecosystems of one of the industrially developed regions of Russia was studied. It was revealed that most of the soils of urban ecosystems have technogenic anomalies in a number of heavy metals and metalloids: As, Co, Ni, Pb, Zn, Cr. An abnormally high iron content in the soils of the region was established compared with the world level and clarke of element in the soils. Without exception, all studied urbanozems are characterized by a high S content. Territories with a moderately hazardous and dangerous pollution level, which amounted to 20% of the studied urban ecosystems, respectively, were identified by the total pollution index. Sources of toxic elements in urban soils are metallurgical, defense, metalworking and chemical industries. The industrial production and toxicant-polluted urban soils considered in the article are a potential source of pollution of natural waters and surface layers of the atmosphere. The soils of cities and sanitary protection zones of industrial enterprises with geochemical anomalies require bioremediation.

Key-Words: soils, technogenic pollution, urban ecosystems, sanitary protection zones of industrial enterprises, toxic elements, heavy metals (HM), XRF, AAS

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1 Introduction

Recently, in connection with the development of industry and an increase in the number of vehicles, anthropogenic impact on soils has intensified, accompanied by their transformation and loss of buffer properties, as well as the accumulation of toxic elements in them, aggravation of biogeochemical cycles, transmission of them and increase in the concentration of toxicants in food chains.

If these processes are accompanied by an increase in soil acidity, nutrients are removed from its upper horizons, and the availability of toxicants for plants increases.

These processes lead to deformation of the original plant and microbial communities, degradation of the vegetation cover, decreased photosynthetic activity and productivity of plants due to defoliation and death of sensitive species, destruction of the photosynthetic apparatus and manifestation of necrotic changes [1-12]. The smallest soil particles during soil erosion during weathering can rise into the surface layers of the atmosphere, entering the human lungs and penetrating the alveolar barrier to accumulate in the body, causing a number of toxic effects, one of which is a debilitation of the immune system, which is especially dangerous during a pandemic.

In addition, cross-border transport of toxic components by airflow is possible.

All this leads to disruption of ecosystem sustainability and exacerbation of global environmental problems.

A necessary component of environmental pollution control is monitoring the state of soils, identifying geochemical anomalies and developing methods for their elimination.

2 Problem Formulation

Model region of the study was Tula region urban ecosystems and the city of Tula. The model region is characterized by well-developed industry: mechanical engineering and metalworking, chemical industry; defense industry, ferrous metallurgy; construction materials; light industry, food industry. Districts of Tula region are characterized by varying degrees of anthropogenic impact. Tula industry (ferrous metallurgy and mechanical engineering) and Novomoskovsk (chemistry) account for more than 2/3 of the regional production.

A great contribution to the pollution of the region make the chemical industry centers Schekino, Efremov, Aleksin and the center of the electricity Suvorov. The remaining 20 districts of the region account for 10% of industrial production.

According to the concentration of industrial enterprises, the Tula region is the second only to Moscow and it is among the five most ecologically unfavorable regions of Russia, 10 times exceeding the amount of emissions to the atmosphere neighboring the Kaluga and Oryol regions. 94% of all emissions are due the city of Tula and Aleksinsky, Suvorovsky, Efremovsky, Novomoskovsky, Uzlovsky, Schekinsky districts where the largest number of industrial enterprises in the region are allocated. 52% of pollutants in the atmosphere falls to the share of industrial enterprises.

The regional center - the city of Tula locates180 km south of Moscow. This ecosystem includes the city area of 154 sq. km and a population more than 500 thousand; it represents an area with developed metallurgical, chemical, engineering and defense industries with the city's infrastructure and network of roads with heavy traffic.

Comparative retrospective analysis of the content of elements in the atmosphere of the region (2000 - 2015 years), obtained by passive briomonitoring method (ENAA of moss samples) showed an increase in air pollution Fe, Cr, Co, As, Cd, Sr and Sm in the past 10 years. In comparison with the other regions of Russia, the air of Tula region is polluted by such elements as: V, Fe, Co, As, Sr, La, Ce, Tb, Hf, Ta, Th, U, Sm [13].

These are the elements of technogenic origin associated with the activity of the enterprises of metallurgical, metalworking, defense, coal mining of the region. These elements can be transferred by air masses in neighboring areas.

Compared with passive biomonitoring data for Republic Belarus, Ukraine, UK and EU the air of the region contains 1.5-7 times higher V, Cr, Fe, Zn, As, Cd [14-16].

Elements from the air masses fall into the soil with atmospheric precipitation. There they accumulate, being adsorbed by the soil-absorbing complex and the organic component of the soil, create geochemical anomalies, and have a toxic effect on biota. Monitoring soil pollution, identifying the components of technogenic emissions of urbanized ecosystems, where most of the population lives, is not only a fundamental task, but also aims to help solve the problem by selecting plants and microorganisms for phytoremediation.

2.1 Sampling and sample preparation

Sampling was carried out in urbanized ecosystems and the sanitary protection zone (SPZ) of highways and industrial enterprises in the most polluted areas of the region, the soils of which according to previous studies were characterized by extremely high and high levels of pollution. Sampling points were consistent with maps of atmospheric deposition of the region for the most toxic components. Soils on the territory of the of L.N. Tolstoy museum-estate "Yasnaya Polyana". Soil sampling of the regional center was based on data from previous projects and was carried out from sites whose soils were previously classified as moderately hazardous and dangerous.

Samples were taken according to standard methods [17, 18]. by the "envelope" method by averaging the material of at least 5 private samples from five points with an area of 10x10 m^2. Sampling depth - 0-20 cm.

A total of 61 medium soil samples were taken. Samples were dried to an air-dry state at a temperature of 40 °C, ground and sieved through a sieve with a hole diameter of 1 mm^2. For subsequent x-ray spectral analysis, the samples were pelletized.

2.2 Analysis

X-ray spectral analysis (XRF) of soil samples was carried out in the laboratory of chemical and analytical studies of the Geological Institute of the Russian Academy of Sciences (GIN RAS) using a Bruker AXS S4 Pioneer sequential wave XRF spectrometer [19,20].

Processing of the obtained results was carried out using the S4 Spectra Plus software package. Using the RFA, the concentration of Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Ba, Pb, Th in the soil was determined .

As reference samples, standard composition samples were used: SCT-1.2, IAEA Soil-7. GBW-07404, 07405.

An objective assessment of the soil pollution level was carried out with the calculation of the

concentration coefficient Cc (formula 1) and the total pollution index Zc (formula 2).
The concentration coefficient of the chemical substance Cc was determined by the ratio of the actual content of the analyte in the soil (Ci) in mg / kg of soil to the regional background (Cphi):
$C_C = C_I / C_{bgl}$ (formula 1).
The total pollution index is equal to the sum of the concentration coefficients of chemical elements - pollutants and is expressed by the formula:
$Z_C = SUM (C_{ci} + ... + C_{CN}) - (n - 1)$ (formula 2),
where n is the number of determined summed substances; Cci is the concentration coefficient of the i-th component of the pollution [25, 26].

3 Problem Solution

During the study, the elemental composition of urban soils of 10 urban ecosystems of the region with varying degrees of anthropogenic pollution and the level of industrial development was studied.
As a background zone, the content of elements in forest and meadow ecosystems of a specially protected natural area - L.N. Tolstoy the Museum-Reserve "Yasnaya Polyana".
An XRF analysis of the studied urbanozems of the regional centers showed that in the soils of urban ecosystems with varying degrees of technogenic impact, geochemical anomalies are observed for elements such as As, Co, Ni, Pb, Zn, whose concentrations in soils often exceed the MPC. The content of non-normalizable elements is very high: Fe and Cr – the chromium content in soils exceeds critical concentrations for the multifunctional use of the RF lands (Bashkin, 2004) in 80% of the studied urbanized ecosystems.
The most burdened geochemical anomalies should be considered the soils of the regional center - the city of Tula (high Fe content, excess of MPC (AEC) for As, Co, Cu, Pb, Zn); Novomoskovsk (high content in the soils of Fe, S, Cu, Zn, Sr, Hg), Uzlovaya (excess of MPC (MPC) by Co, Pb, S, Sr); Kireyevsk (excess MPC (OEC) for As, Co, Cr, Ni, S, V, Zn); Efremova (excess MPC (UEC) by As, Co, Ni, S, V) (Table 1).
The soils of all cities without exception have geochemical anomalies. In the soils noted earlier on the maps of the regional centers located in the clean zone (Odoev) an excess of the standards for Co, S, Zn was found.
The average value for all studied urbanozems shows geochemical anomalies in As, Co, Pb, S, and Zn (Table 1).

Table 1

The content of elements in the soils of urbanized ecosystems with varying degrees of technogenic load, mg / kg

MPC [21-23]	**Content in clay and loamy soils	*Critical concentrations of HM	background zone	Urbanozems	Odoev	Schekino	Chern	Efremov	Aleksin	Novomoskovsk	Kireevsk	Yasnogorsk	Uzlovaya	Tula	Elements
5	2,4-16,3/ 5-30		5.1±1.7	5.0±1.1	4.47	5.9	5.1	6.6	2.4	5.3	6.3	4.6	4.4	5.3	As
5.00	4-58	>1	9.1±1.7	11.2±1.1	10.07	9.90	13.7	17.5	8.6	10.8	14.1	4.5	9.5	13.1	Co
	4-200	90/ 50-130	116±13	113±8	122	77	91	114	71	129	152	147	115	109	Cr
66	16-70/4-21	55/ 20-70	29±3	54±14	30	44	38	46	19	47	45	23	55	189	Cu
40	13-104	85/ 10-60	41±5	35±2	35	35	33	43	21	39	42	26	34	41	Ni
65	1.5-52	32/ 30-85	28.3±0.2	63±8	51.7	47.8	91.0	44.4	29.4	42.9	48.8	67.2	93.7	114	Pb
160			247±11	760±94	543	897	382	399	527	757	1049	693	1351	999	S
150	15-330/34-210		65±9	53±4	56	46	51	68	34	65	69	26	57	62	V
110	31-177/ 9-77	100/ 50-150	53±5	110±21	117	91	78	78	60	86	151	45	106	290	Zn

* Critical concentrations of HM under multifunctional land use, mg / kg RF / EU [24]
** Content in clay and loamy soils of the world / USSR [25, 32, 33]

We have studied the content of toxic elements in the sanitary protection zone (SPZ) of regional enterprises, which can be sources of technogenic pollution of air, soil and natural waters. The results of the study are presented in Table 2. According to the data obtained, the technogenic source of such elements as Co, Cr, Cu, Ni, Pb, S, Zn, and Fe are the enterprise of the defense industry; Co, Ni, Zn, Fe, Mn, V represent ferrous metallurgy enterprises; As, Co, Cu, Ni, S, Zn are associated with enterprises of the chemical industry. Without exception, all industries pollute the environment and soil in particular with sulfur.

Table 2

The content of elements in the soils of sanitary protection zones of industrial enterprises, mg / kg

Elements	As	Co	Cr	Cu	Ni	Pb	S	V	Zn	Fe	Mn	Hg
Tula metallurgical Plants	7,8	13,1	125	41	45	50,5	451	94	140	57744	3275	0,116
Heavy industrial fittings	6,1	41	174	96	48	48,6	569	56	185	25996	665	0,074
Weapon Plant	13	11	1260	1188	285	185	983	91	4579	68306	1259	0,352
Plastic	7,1	11,3	139	40	44	40	1124	76	125	28177	604	0,143
Machine-building Plant Uzlovaya	0,6	5,2	119	26	19	21,5	547	28	32	8171	189	0,018
Nedex	7,7	15,2	167	45	47	44,6	905	63	98	22354	692	0,056
IEK metal-plast	4,3	12,7	155	42	43	97,9	627	64	86	22718	716	0,042
Chemical enterprises Novomoskovsk	35	19,6	126	234	48	65,1	763	75	149	27785	615	0,086
Novomoskovsk basalt plastic	4,9	12,9	153	93	47	26,6	294	77	93	26918	676	0,065
Knauf gypsum	3	17,5	129	48	44	27	429	75	73	27296	639	0,111
Aleksin chemical Plant	4,5	11,6	71	31	29	34,8	758	46	117	17706	416	0,125
Efremov Synthetic rubber Plant	5,5	15	125	39	46	39,4	454	68	109	25968	600	0,084
Kargil	4,9	12,9	104	49	47	32,5	468	72	194	27226	620	0,035
SchekinoAzot	4,7	7,3	98	75	41	45,9	978	31	102	16161	845	0,082
MPC [21-23]	5	5		66	40	65	160	150	110		1500	2,1

4 Discussion

According to the data of Sayet and Nesvizhskaya [25], the permissible total content of heavy metals in soils, based on general hygienic restrictions, is 23 mg / kg for Cu, 150 mg / kg for Zn, and 35 mg / kg for Pb and Ni. As can be seen from the data presented in Table 1, it is violated for 80% of the soils of the studied cities for Cu; the excess of the general hygienic limits for Zn was found only in the most industrially developed regional center - the city of Tula; for 90% of the cities the hygienic standards for Pb were exceeded, in 30% of the studied urban soils - by Ni.

According to the series of toxicity of elements for mammals, it decreases in the series: Hg, Cd> Cu, Pb, Co,> Mn, Zn, Ni, Fe, Cr [29].

The average content of elements of the first hazard class in urban soils was: Pb - 63 mg / kg, taking into account the standard deviation, this value lies within the threshold values of MPC. At the same time, the MPC for the element was exceeded in 30% of the studied urban ecosystems in urban soils (Table 1).

In the first place among the sources of Pb contamination are emissions from vehicles followed by metallurgical production, onwards machine building, metalworking, construction, chemical industry, municipal solid waste and sewage sludge.

The mortality rate of people living along highways from cardiovascular and pulmonary diseases is 9-13% higher than the average [30].

The average content of As, the element of the hazard class 1, in the urban soils of the Tula region is 5 mg / kg, that corresponds to the average values in the soils of the world, but in 60% of cities an excess of the MPC for the element in urban soils is noted (Table 1). Arsenic is a highly technogenic element close to Pb and Zn in technogenicity and it enters the environment during coal combustion, motor vehicles, cement production, coal coking, and metallurgical and chemical industrial enterprises.

Once in the human body, it accumulates in the tissues of the kidneys and liver, binds to hemoglobin of erythrocytes, and affects the central nervous system [30].

The content of Zn, the element of the hazard class 1, in the studied urbanozems was 110 mg / kg (Table 1) and exceeded the average values in the soils of the world by more than 2 times [31] and was on the border of the MPC for the element, and was also higher than the concentrations for functional use of soils.

At the same time, an excess of MPC for an element was observed in 30% of the studied cities and it was the maximal 290 mg / kg in the regional industrial center - the city of Tula (Table 1).

The average content of Cu, the element of the hazard class 2, in the soils of urban ecosystems of the Tula region was 54 mg / kg, that is 2 times higher than the average values of the element for soils in the USA and 2.7 times higher than the average values in soils of the world, although it does not exceed the upper limits of these concentrations [32].

An excess of the MPC for the element by 3 times was detected only in the soils of the regional center - the city of Tula (189 mg / kg), that is associated with the transfer of the element from the emission sources - the metallurgical and defense enterprises of the city with aerosol particles (previously, an excess of one-time MPC for Cu in the atmospheric air of the city [34]).

The average content of Cr, the element of the hazard class 2, in the soils of cities was 116 mg / kg and exceeded the MPC in soils of 30% of the studied urban ecosystems (Table 1). At the same time, the content of the element in the soils of cities did not exceed the upper limits of the value of the content of the element in the soils of the world (200 mg / kg) [24, 29], but it was higher than the critical concentrations for the functional use of soils in the Russian Federation and 2.2 times higher than the average values for the element in the soils of the United States [24, 33].

Chromium is contained in the dust of steel-making furnaces, machine-building industries, and gas emissions from thermal power plants.

In humans, an excess of Cr can cause various diseases and syndromes: decreased glucose tolerance, poor carbohydrate metabolism, increased blood cholesterol levels and the formation of cholesterol plaques from blood vessels, impaired activity of the nervous system and decreased sperm fertility, chromium dermatoses [29].

In 90% of the studied urban soils, including the soils of the conditionally clean zone, the content of Co, a highly toxic element of hazard class 2, 2-3 times exceeded the MPC (Table 1). The average value of the content of the element in the studied urban soils was 11.2 mg / kg, that is 25% higher than the average values for soils in the USA and 40% higher than the average values for soils in the world [29].

An excess of cobalt can reduce the ability of the thyroid gland to accumulate iodine [29], that leads to the development of hypothyroidism; this is exacerbated by a lack of iodine in water and food products of the region and is a serious problem.

The sources of cobalt in the environment are metallurgical and battery industries, coal ash, production of nitric acid, dyes, sewage sludge and solid waste incineration.

The average content of V, a highly toxic element of hazard class 3, in urban soils of urban ecosystems is 53 mg / kg. This value fits into the world data for large industrial cities. The MPC for an element was exceeded in 40% of the studied urban ecosystems in urban soils.

The source of vanadium in the study region is the processing of vanadium-containing ores and ferrous metallurgy (EVRAZ Vanadiy Tula, PJSC Tulachermet).

The source of the element can also be waste from thermal power plants operating on coal, machine-building enterprises. It is an element that falls out with aerosol deposition and can be transported by air masses; it is a pollutant of atmospheric air of the region [15, 16].

As shown by the research results, the soils of all sanitary protection zones (SPZ) of industrial territories are contaminated with sulfur, the content of which in the SPZ of industrial enterprises is in the range of 451-1124 mg / kg, exceeding the MPC by 3-7 times (Table 2). Apparently, this element enters the soil in the form of an anion of sulfuric acid associated with cations - components of industrial emissions, or in the form of atmospheric deposition from sulfur oxides emitted during production.

The content of Co in the soils of the SPZ of industrial enterprises is in the range of 5.2-19.6 mg / kg in most of the studied soils, exceeding the MPC by 1.5-4 times (Table 2). The largest contribution to environmental pollution is made by chemical enterprises in Novomoskovsk, plants in the Yasnogorsk region: IEK metal-layer and chemical plant Nedex; JSC Heavy industrial fittings Aleksin, metallurgical industry of Tula: PJSC Kosogorsky metallurgical enterprises (KME), PJSC Tulachermet, JSC Polema, "EVRAZ Vanadium Tula"; Efremov Synthetic Rubber Plant.

Chemical enterprises in Novomoskovsk, the defense (Weapon Plant) and metallurgical industry in Tula, the Nedex chemical plant make the largest contribution to arsenic environmental pollution; the As content in the soils of the SPZ zones of these industries is 34.8; 12.5; 7.8 mg / kg, respectively, and is 1.5-5 times higher than the MPC limits (Table 2). Arsenic belongs to the elements of hazard class 1 and, according to the WHO, can cause lung cancer, skin diseases, hematological effects, including anemia, and it also suppresses the functioning of the immune system.

Copper pollution is caused by the activities of such enterprises as JSC Heavy industrial fittings, chemical enterprises of Novomoskovsk, the Weapon Plant, in the SPZ soils of which the copper content is in the range of 93-234-1188 mg / kg and it exceeds the MPC for the element (Table 2).

The data obtained correlate with the data on the contamination with this element in aerosol deposition in the regional center [34]. Copper is a substance of hazard class 2 and in excessive concentrations has a toxic effect on both plants and the human body, accumulating in the liver, as a result of which cirrhosis of the liver, hemolysis (increased destruction of red blood cells), anemia, and the formation of kidney stones can develop.

Excessive copper content in the body leads to the development of diabete, vascular aneurysm, and atherosclerosis. A variety of behavioral disorders (attention disorders, hyperactivity, emotional instability) are common among young people [29].

A high content of nickel and lead was noted for the soils of the sanitary protection zones of the Weapon Plant, where their content is 285 and 185 mg / kg, respectively (Table 2). Since the deposition pattern of lead is 3-10 km, the greatest contamination of the element from the plant's emissions falls on a part of the Zarechensky and Proletarsky districts of Tula [34].

The content of V in the soils of the SPZ of industrial enterprises is within the limits of the MPC, however, a multiple excess of the MPC to 9 times for this element in the sludge collector of PJSC Tulachermet was noted.

The Zn content in the soils of the industrial SPZ exceeded the limit standards only in 50% of cases. At the same time, abnormally high concentrations of Zn in the soil 40 times higher than the MPC are observed in the SPZ of the Weapon Plant from the side of the Proletarsky bridge (Table 2). Exceeding the limits of the MPC was also detected in the soils of the SPZ of metallurgical enterprises in Tula, JSC Heavy industrial fittings (Aleksin), soils of the SPZ of chemical enterprises in the city Novomoskovsk, chemical plant (Aleksin), Kargil plant (Efremov). Thus, enterprises of the metallurgical, chemical and defense industries make the greatest contribution with Zn to the soil pollution of industrial cities.

The most polluted by the whole complex of TM SPZ near the defense industry enterprise is the Weapon Plant (Tula). Due to the fact that near the sampling site there is also a machine-building plant and a road junction with a busy transport traffic bridge, as well as a bus station, the contribution of motor vehicle emissions and emissions from the machine-building plant is not excluded.

The content of iron, which is an unstandardized element in the soils of SPZ enterprises, is abnormally high and ranges from 8171 mg / kg to 68306 mg / kg (Table 2). The content of the element in the soils of metallurgical enterprises of the regional center and enterprise of the defense industry exceeds the clarke of the element for soils by 1.6-1.9 times, respectively. They are the main sources of urban soil pollution.

Iron can enter the atmosphere in the form of dust particles when working in ore quarries, its source is the enterprises of processing iron ore and ferrous metallurgy, the metalworking industry, iron foundry, which concentrates, in addition to iron, Pb, Zn, W, Mo, Co, Cu, Ni, Cr, and Mn and is their source in the atmosphere and soils [29].

The Mn content exceeded the MPC only in the soils of metallurgical enterprises by more than 2 times. The main source of the element in the urban environment is the production of ferromanganese

(PJSC KME). In the rest of the soil samples, no excess of the MPC for the element was found (Table 2).

At the same time, an abnormally high content of Cr (1260 mg / kg), Cu (1188 mg / kg), Ni (285 mg / kg), Pb (185 mg / kg), Zn (4579 mg / kg) is observed in the urban soils of the sanitary protection zone of the industrial zone of the Weapon Plant and the highway. Thus, a multicomponent geochemical anomaly formed at a given sampling point can contribute not only to an increase in the incidence of human diseases, but also enter the soil solution and be carried out into the runoff of the Upa River, causing HM pollution of natural waters.

The soils of the sanitary protection zones of metallurgical enterprises in Tula also have a high degree of soil pollution with toxic elements: PJSC Tulachermet, PJSC KME, JSC Heavy industrial fittings of Aleksinsky district, chemical industry enterprises in Novomoskovsk, which contribute to air and soil pollution with As, Co, Ni, Pb, and Zn. Most pristine of all the studied industries is the Uzlovaya Machine-Building Plant.

The calculation of the concentration coefficients of elements in the soils of urban ecosystems in comparison with the background (Yasnaya Polyana forest) showed that all urban soils are characterized by a high degree of pollution S from 2 to 5.4 times compared to the background values (Fig. 1, 2). Urbanozems Uzlovaya> Kireyevsk> Shchekino, Tula differed in the decreasing maximum sulfur values. For most urban soils, Cu and Zn accumulation was noted compared to the background from 2 to 8.6 times for Cu and from 2 to 3.7 for Zn. The most unfavorable situation for pollution of Cu soils is observed in the cities of Tula> Novomoskovsk> Aleksin. According to monitoring data (Fig. 1), the situation with Zn has been aggravated by a factor of 5 in the regional center over the past 6 years; for Cu - 2.2 times, which should be associated with the intensification of the activities of enterprises in the defense, metalworking, metallurgy and machine-building, as well as chemical industries. Zinc and copper are necessary for the human body elements that regulate biochemical processes, but their excessive ingestion and accumulation can cause a number of toxic effects. Thus, the intake of zinc in the body at a dosage above 150 mg can cause a decrease in immunity due to the development of anemia (zinc is a copper antagonist that regulates hematopoiesis during absorption in the small intestine) or neutropenia. Zinc in excessive concentration affects the functioning of T-lymphocytes, causing a decrease in the body's immune response to bacteria and viruses. In this regard, its high concentrations in the environment, in particular in soils, are a threat to public health, especially during periods of pandemics.

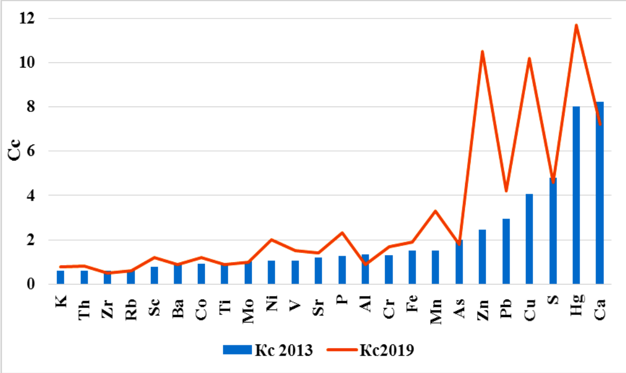

Figure 1. The concentration coefficients of elements in the soils of Tula (background zone Yasnaya Polyana) comparison by years 2013-2019

Noteworthy is the high Hg concentration coefficient in the cities of Aleksin, Novomoskovsk, Tula, which exceeds the background by 8.5–9 and 11.7 times, respectively (Fig. 1, 2). Sources of mercury in the environment can include chemical industry, non-ferrous metallurgy, machine building and metalworking industries with heat treatment of metals, waste from metallurgical industries, waste water and municipal solid waste. Mercury is an element of the first hazard class and, due to its chemical properties, is a serious threat to the population.

According to WHO, the main selective effects of mercury on the body are: effects on the nervous system, including short-term memory; impaired sensory functions and coordination, renal failure, mutagenic processes, genetic changes in the cells of the body, harmful effects on the development of the fetus, the development of birth defects. Possible sources of the element in the environment in the above urban ecosystems may include such enterprises as Polema JSC, EVRAZ Vanadiy Tula, Tulachermet PJSC, Metal Rolling Plant LLC, Elektromash JSC, Aleksinsky Experimental Mechanical Plant JSC , Aleksinsky factory of heavy industrial valves, OJSC Novomoskovskogneupor, Novomoskovsk plant of metal structures, Novomoskovsk electrical installation plant, Pervomaisky plant of reinforced concrete products.

The concentration coefficient of Pb in most cities of the region is from 2 to 4 and is maximum in the regional center (Fig. 1, 2).

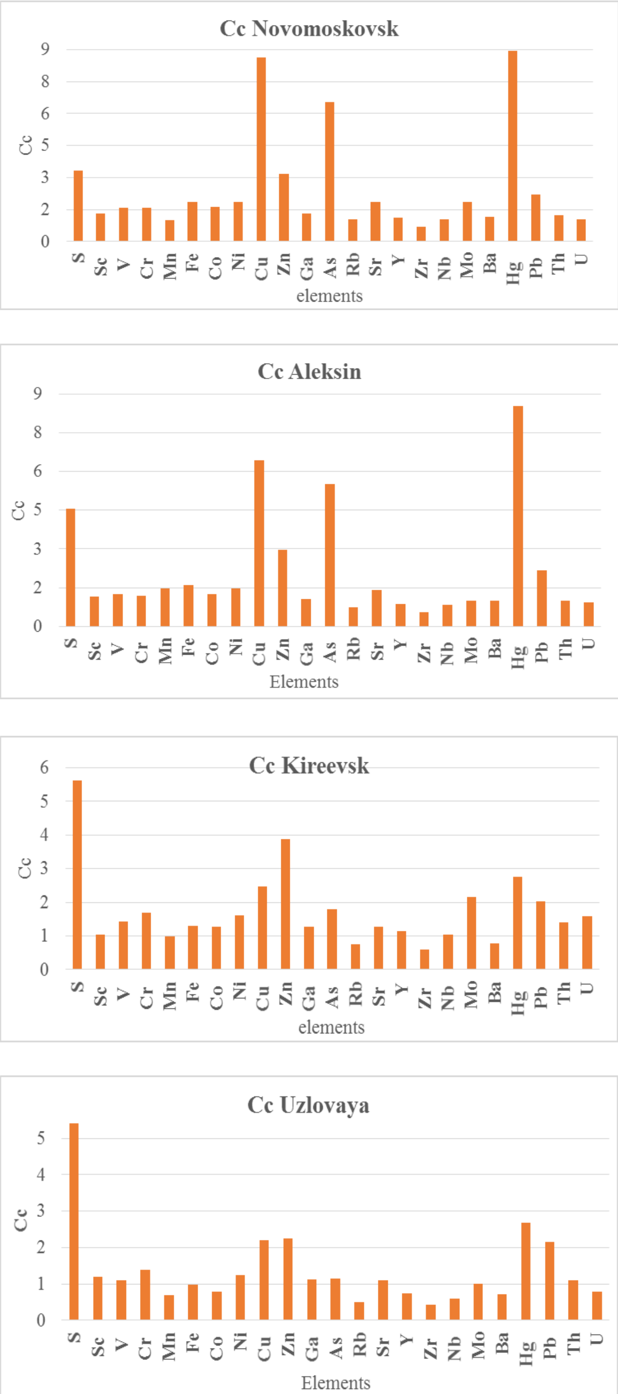

Figure 2. The concentration coefficients of elements in the soils of Tula region cities (background zone Yasnaya Polyana)

Lead is an element of the first hazard class. Its potential effects on the human body are: violation of blood formation processes; damage to the liver and kidneys; neurological effects, mutagenic processes, genetic changes in the cells of the body, weakened immunity. The source of the element in the environment is the enterprises of ferrous and non-ferrous metallurgy, machine building and the metalworking industry, municipal solid waste, wastewater and motor emissions. Due to the high traffic load in urban ecosystems, which is increasing every year, the obtained coefficients are logical.

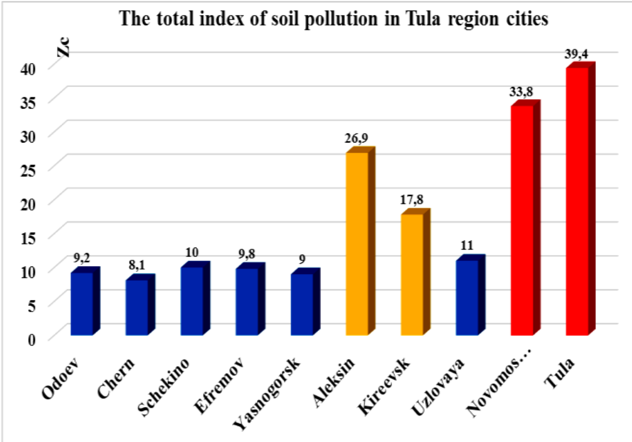

Figure 3. The total index of soil pollution (Zc) of Tula region cities

The calculation of the total index of soil pollution in the regional center - the city of Tula, showed that over the past 6 years it has increased more than 2 times - from 16.4 to 39 (fig. 3). Urban soils of two of the studied urban ecosystems - Tula and Novomoskovsk are classified as dangerous; two - Aleksin and Kireevsk - are classified as moderately dangerous. According to the geochemical gradation, a moderately hazardous category of soils (Zc = 16 ... 32) can lead to an increase in the general morbidity of the population, hazardous (Zc = 32 ... 128) - to an increase in the general morbidity, the number of frequently ill children, children with chronic diseases, impaired functional state of the cardiovascular system [25, 26]. 40% Urbanozems of the studied cities in the region pose a threat to the health status of the population and require the selection of plants for their phytoremediation and remediation measures.

A statistical analysis of the results of the study of urban soils of the most polluted of the studied cities of the regional center, revealed pair correlations for the elements presented in Table 3.

Noteworthy is the high correlation coefficient between the main element-pollutants of soil: Co-Cr, Cu-Mn, Zn-Mn, As-Zr, As-Nb, Hg-Sr, which can be associated in complexes.

Table 3
Correlation value of elements in the soil of Tula

Correlated pair of elements	R - correlation coefficient	P- error probability
Co-Cr	0,775	<0,001
Cu-Mn	0,986	<0,001
Zn-Mn	0,642	<0,001
Cu-Zn	0,676	<0,001
Ga-Mn	0,934	<0,001
Ga-Cu	0,931	<0,001
Ga-Zn	0,811	<0,001
Fe-Rb	0,546	0,003
As-Zr	0,853	<0,001
As-Nb	0,575	0,005
Zr-Nb	0,806	<0,001
Zr-Sr	0,743	<0,001
Nb-Sr	0,881	<0,001
Hg-Rb	0,547	0,003
Hg-Sr	0,657	0,001
Hg-Zr	0,556	0,003

4 Conclusion

Monitoring data on technogenic pollution of the soil cover of urban ecosystems using an example of an industrially developed model region of the Russian Federation showed a high level of pollution of Fe, Cr, As, Co, Ni, Pb, Zn, which form geochemical anomalies of the urabanozems. The accumulation of these elements in soils is associated with the activities of metalworking, metallurgical, defense, engineering, and chemical industries and their air transport from pollution sources. In 40% of the studied urbanized systems, moderately hazardous and hazardous soil categories were identified by the total pollution index. Living in such cities can lead to an increase in the overall incidence, the number of frequently ill children, children with chronic diseases; disorders of the functional state of the cardiovascular system. This is confirmed by the general increase in the incidence of the population in cities with geochemical anomalies of the soil cover in recent years (by an average of 9%) [27, 28]. Over the past 6 years, the level of technogenic pollution of a large industrial urbanized ecosystem has more than doubled, which requires further monitoring of the state of the soil cover, development of methods to reduce the technogenic load, as well as phytoremediation of soils with geochemical anomalies from toxic elements.

References:

[1] Baath E. Effects of heavy metals in soil on microbial processes and population: a review *Water Air Soil Pollut.*, 47: 1989, pp. 335-379.
[2] Lukina N.V., Nikonov V.V. Biogeohimicheskie cikly v lesah Severa v usloviyah aerotekhnogennogo zagryazneniya. V 2-h ch. Apatity: Izd-vo Kol'skogo nauchnogo centra RAN, 1996. Ch. 1. 213 s. CH. 2. 192 p.
[3] Lukina N.V., Nikonov V.V. Pitatel'nyj rezhim lesov severnoj tajgi: prirodnye i tekhnogennye aspekty. Apatity: Izd-vo Kol'skogo nauchnogo centra RAN, 1998. 316 p.
[4] Alekseeva-Popova N.V. Toksicheskoe dejstvie svinca na vysshie rasteniya // Ustojchivost' k tyazhelym metallam dikorastushchih vidov. L.: Nauka, 1991.
[5] T.V. CHernen'kova, A.M. Stepanov. Vozdejstvie tyazhelyh metallov na rastitel'nye organizmy. Metodicheskoe posobie. M.: Izd-vo MISiS. 2001. 163 p.
[6] Chernen'kova T.V. Reakciya lesnoj rastitel'nosti na promyshlennoe zagryaznenie // Pod red. A.S.Isaeva. M.: Nauka. 2002. 190 p.
[7] Alekseenko V.A. Himicheskie elementy v gorodskih pochvah/ V.A. Alekseenko, A.V. Alekseenko. – M.: Logos, 2014.
[8] Buharina I.L., Povarnickaya T.M., Vedernikov K.E. Ekologo-biologicheskie osobennosti drevesnyh rastenij v urbanizirovannoj srede: monografiya / I.L. Buharina, T.M. Povarnicina, K.E. Vedernikov. – Izhevsk: FGOUVPO Izhevskaya GSKHA, 2007. – 216 p.
[9] Gorelova S.V., Frontasyeva, M. V.; Yurukova, L.; Coskun, M.; Pantelica, A.; Saitanis, C. J.; Tomasevic, M.; Anicic, M.. Revitalization of urban ecosystems through vascular plants: preliminary results from the BSEC-PDF project. AGROCHIMICA, 2011, 55 (2): 65-84
[10] S.V. Gorelova, M.V. Frontasyeva, S.M. Lyapunov, A.V. Gorbunov, O.I. Okina. BIOINDICATION AND MONITORING OF ATMOSPHERIC DEPOSITION USING TREES AND SHRUBS //Materials of 27th Task Force Meeting of the UNECE ICP Vegetation. France, Paris, January 28-29, 2014. P.63
[11] Gorelova S., Frontasyeva M., Gorbunov A., Lyapunov S., Mochalova E., Okina O. The biogeochemical activity of exotic gimnosperm species in indastrial urbanised ecosystems // Bulletin of I. Kant Baltic Federal University - Kaliningrad, 2015 – P. 92-106
[12] Gorelova S.V., Garifzyanov A.R., Lyapunov S.M., Gorbunov A.V., Okina O.I., Frontas'eva

M.V. Ocenka vozmozhnosti ispol'zovaniya drevesnyh rastenij dlya bioindikacii i biomonitoringa vybrosov predpriyatij metallurgicheskoj promyshlennosti / A.R. Garifzyanov, S.M. Lyapunov, A.V. Gorbunov, O.I. Okina., M.V. Frontas'eva // Problemy biogeohimii i geohimicheskoj ekologii, 2010, №1 (12) – pp.155-163.

[13] Gorelova S.V., Frontasyeva M.V., Vergel K.N., Babicheva D.E., Ignatova T.Yu. Biomonitoring in Central Russia: Tula Region Case Study // ICP Vegetation 30th Task Force Meeting 14th – 17th February 2017 Poznan, Poland. Programme & Abstracts. – 2017. P.63.

[14] Gorelova S.V., Frontasyeva M.V., Vergel K.N., Babicheva D.E., Volkova E.V. Atmospheric Deposition of Trace Elements in Central Russia: Tula Region Case Study. Comparison of Different Moss Species for Biomonitoring // Environmental Science, 1, 2016, P. 220-229. ID: 73703-145/

[15] Gorelova S.V., Frontasyeva M.V., Babicheva D.E., Ignatova T.Yu., Vergel K.N. Temporal Trends Of Heavy Metalls Contamination Of Tula Region Air (Moss Monitoring). // The 8th International Workshop on Biomonitoring of Atmospheric Pollution (BIOMAP 8) (Dubna, July 2–7, 2018): Programme and Abstracts. — Dubna: JINR, 2018. P. 63.

[16] Gorelova S.V., Frontasyeva M.V., Vergel K.N., Babicheva D.E., Tula region // Marina Frontasyeva, Harry Harmens, Alexander Uzhinskiy, Omar Chaligava and participants of the moss survey Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond. 2020. pp.219-221.

[17] GOST R 53123-2008 Kachestvo pochvy. Otbor prob

[18] GOST 28168-89. Pochvy. Otbor prob

[19] Chirkin L.A. Rentgenofluorescentnyj analiz ob"ektov okruzhayushchej sredy: Uchebn. posobie. – Vladimir: Izd-vo Vladimirskogo gos. un-ta, 2009. – 57 s.

[20] Sbornik metodik po opredeleniyu tyazhelyh metallov v pochvah, teplichnyh gruntah i produkcii rastenievodstva. Izd. Minsel'hozprod RF, Moskva, 1998. – S. 27-82.

[21] GN 2.1.7.020-94. Orientirovochno dopustimye koncentracii (ODK) tyazhelyh metallov i mysh'yaka v pochvah. (dopolnenie №1 k perechnyu PDK i ODK № 6229-91).

[22] GN 2.1.7. 2041-06. Predel'no dopustimye koncentracii (PDK) himicheskih veshchestv v pochve.

[23] Predel'no-dopustimye koncentracii (PDK) himicheskih veshchestv v pochve: Gigienicheskie normativy. – M.: Federal'nyj centr gigieny i epidemiologii Rospotrebnadzora, 2006. – 15 s.Bashkin V.N. Biogeochimia. – M.: Nauchniy Mir, 2004.- pp.512-513.

[24] Kabata-Pendias, A., Pendias H. Mikroelementy v pochvah i rasteniyah. – M.: Mir, 1989. S. 440.

[25] Saet YU.E., Revich B.A., YAnin E.P. Geohimiya okruzhayushchej sredy. M.: Nedra, 1990. – 335 s.

[26] MU 2.1.7.730-99. Gigienicheskaya ocenka kachestva pochvy naselennyh mest. Metodicheskie ukazaniya.

[27] O sostoyanii sanitarno-epidemiologicheskogo blagopoluchiya naseleniya v Tul'skoj oblasti v 2016 godu: Gosudarstvennyj doklad. – Tula: Upravlenie Federal'noj sluzhby po nadzoru v sfere zashchity prav potrebitelej i blagopoluchiya cheloveka po Tul'skoj oblasti, 2017. – 209 s.

[28] Polousova, G.YU. Statisticheskij analiz vliyaniya ekologicheskih faktorov na zdorov'e naseleniya Tul'skoj oblasti. // Avtoreferat dissertacii na soiskanie uchenoj stepeni kandidata ekonomicheskih nauk. Moskva, 2003. – 21 s.

[29] Ivanov V.V. Ekologicheskaya geohimiya elementov. Spravochnik v 6 knigah. M.: nedra, 1995. – Kniga 4.: glavnye d- elementy. – 416 s.

[30] Ivanov V.V. Ekologicheskaya geohimiya elementov. Spravochnik v 6 knigah. M.: nedra, 1996. – Kniga 3.: redkie p- elementy. – 352 s.

[31] Vinogradov A.P. Geohimiya redkih i rasseyannyh elementov v pochvah. M. Izd-vo AN SSSR. 1957. 238 s.

[32] Dobrovol'skij V.V. Geografiya mikroelementov: Global'noe rasseyanie. M. Mysl'. 1983. 272 s.

[33] Dobrovol'skij V.V. Osnovy biogeohimii. – M.: Izdatel'skij centr «Akademiya», 2003. – S. 22-23, 155-156.

[34] S.V. Gorelova, A.V. Gorbunov, S.M. Lyapunov, O.I. Okina, M.V. Frontasyeva, S.A. Kozlov. Assessment of the impact of industrial agglomeration on soil and air pollution of urban ecosystem with toxic elements (on the example of the Tula city) // Ecology of urbanized areas. N 2, 2020. - P. 6-20.