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Technogenic geochemical abnormalities in the soils and bottom sediments of Voronezh

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Abstract.- Environmental pollution in large industrialized cities has become an urgent global problem. On the territory of the Russian Federation, a tense ecological situation is developing in almost all cities with a population of over one million and in large administrative centers. The creation of a quality urban environment is a national priority, a complex and financially costly task, the solution of which cannot be postponed any longer. The main sources of problems in the territories occupied by cities lie in the concentration of production capacities, the steady growth of the population, and as a result, the amount of transport. Due to production, industrial cities concentrate substances of natural and man-made origin forming local and even regional geochemical anomalies in various landscapes. Among all the interrelated components, a special place belongs to the depositing (accumulating) media–soils and bottom sediments. Based on the results of geochemical studies of 2018–2020, the indicators of the quality of the soils of Voronezh were determined, the levels of the content of pollutants of I-III hazard classes in the soils of urban and peripheral areas of Voronezh (benzo(a)pyrene and heavy metals) were established. The authors provide an assessment of the accumulation of pollutants in the bottom sediments of the Voronezh water reservoir, which is located on the territory of the urban district.

Keywords: urban environment; degradation; load; functional areas; pollutants; concentration and accumulation factors; total pollution index.

Anomalías Tecnogénicas Geoquímicas en Suelos y Sedimentos de Fondo en Voronezh

Resumen.- La contaminación del medio ambiente de ciudades grandes industrializadas es un problema global de actualidad. En Rusia se ve una situación difícil medioambiental casi en todas las ciudades con más de un millón de habitantes y en centros administrativos mayores. La creación de un entorno urbano de alta calidad es una tarea nacional compleja prioritaria que requiere costes materiales intensivos y la solución más urgente posible. Los orígenes de los problemas de territorios urbanizados se hallan en la concentración de capacidades de producción, un crecimiento constante de población y, con ello, la cantidad de vehículos de transporte en uso. Las sustancias de origen natural y tecnogénico concentradas por ciudades industrializadas a través de capacidades productivas forman anomalías geoquímicas locales y hasta regionales en varios paisajes. Una posición distinta entre todos los componentes interrelacionados pertenece a suelos depositantes (acumuladores) y sedimentos del fondo. Los resultados de las pruebas geoquímicas conducidas en 2018-2020 se usan para medir los índices de calidad de los suelos de la localidad. También se determinan los contenidos en el suelo de contaminantes de los clases de peligro I a III (benzopirenos y metales pesados). Se evalúa la acumulación de sustancias contaminantes en los depósitos de fondo del la represa de Voronezh que se halla por completo en el territorio del distrito urbano.

Palabras clave: medio urbano; degradación; carga; zonas funcionales; contaminantes; coeficientes de concentración y acumulación; indicador acumulativo de contaminación.

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1. Introduction

The problems of the landscape-geochemical organization of the territory of the city of Voronezh lie in its complex historical past. During the Great Patriotic War, fierce battles took place in the city. From July 1942 to January 1943, the right bank of the Voronezh river was occupied and the buildings and infrastructure were destroyed in the course of intense hostilities. By the time of liberation, no more than five percent of the buildings remained intact in this part of the city.

The echo of the war sounds in Voronezh until now. Post-war cinder block buildings make up a significant part of the city's dilapidated housing stock. The urban landscape of the right bank is actually formed on the ruins and remains of buildings. As a result of the functional transformation of industrial areas, the foundations and parts of residential buildings, plants, and factories that existed in the pre-war period are exposed.

Landscaping of the territory of Voronezh and its suburbs with rapidly growing balsam poplars (*Populus balsamifera*) is also a result of the post-war period. Replacing green spaces with new sustainable and low maintenance plants is a long-term process that requires carefully considered decisions and investments [1]. The growth of the urban area has led to the occupying of large areas of adjacent forestry. Thus, the following recreational areas appeared in the city: Severny Lesopark, Figurnaya Roscha, Malaya Roshcha, Treugolnaya Roshcha, Pridonskaya Roscha, and Peschany Log.

In 1967, the "rehabilitation of the Voronezh River" was carried out within the city limits and the Voronezh water reservoir was created. The filling of the reservoir coincided with several dry years. The floodplains of the river by this time were very swampy, and the channel needed to be cleaned not only from the polluting runoff but also from the construction waste left after the restoration of the city.

The result of the improvement of the floodplain of the Voronezh River was the creation of a shallow multipurpose water reservoir. Its aquatic and terrestrial ecosystems turned out to be unstable, which contributed to the further development of imbalance in the "reservoir-environment" system.

The operation of the reservoir as a transport artery between the cities of Voronezh and Lipetsk has been completely stopped. The fishery is represented only by sportfishing.

Despite the reduction in water consumption by industry and agriculture, the reservoir has become shallow and overgrows with duckweed regularly in the warm season.

A vivid example of the degradation of the reservoir is the Maslovsky Zaton area - the place where the river flows into the Tavrovka river reservoir. The river, surrounded by buildings and asphalt, eventually turned into a temporary watercourse. Lack of runoff led to stagnation and intensive development of blue-green algae in the warm season.

The only right decision was the ecological rehabilitation of the territory with the reclamation of land and the formation of the river bed. The work was completed in November 2019, but it was not enough to completely solve the problems of the reservoir. Residents of the city still complain about the putrid smell from the reservoir.

At present, Voronezh, in terms of the urban environment quality index, ranks only twelfth among the fifteen cities with a population of over one million in Russia, significantly inferior to the leader (Moscow) in terms of the quality of landscaping and the development of the road network. This assessment was given by the Ministry of Construction and Housing and Utilities (Ministry of Construction of Russia) according to the Decree of the President of the Russian Federation of May 7, 2018, No. 204 "On national goals and strategic objectives of the development of the Russian Federation for the period up to 2024" and the national project "Housing and urban environment".

Work on environmental impact assessment in Voronezh is carried out regularly for new construction projects and reconstruction. All relationships between natural and man-made systems are regulated by regulatory documents. A mandatory stage of engineering and environmental surveys is to obtain reliable data on the ecological and geochemical state of the environment. The condition for the reliability of the materials obtained is information on the sources of pollution, factual data on the regional background values of the most common harmful substances.

Information about stationary sources and the mass of emissions of pollutants is accumulated by the Federal Service for Supervision of Natural Resource Usage (Rosprirodnadzor) and the Federal Service for Supervision of Consumer Rights Protection and Human Welfare (Rospotrebnadzor).

Background concentrations of substances in the air of the city of Voronezh are registered by the Federal Service of the Russian Federation for Hydrometeorology and Environmental Monitoring (Roshydromet).

The Federal Agency for Water Resources collects data for measures for the protection of water bodies and the use of water resources to ensure potable and utility water supply.

The purpose of the study was to control the pollution of soils in urban areas and bottom sediments by discharges, and emissions from various enterprises, transport and the general anthropogenic load.

2. Materials and methods

Voronezh is a complex research object in the modern landscape and functional structure of which anthropogenic (technogenic) components prevail, combined with natural systems. The territory of the city is a set of functional areas formed over a long historical period [2, 3, 4, 5, 6].

Various types of soils of urbanized landscapes have been formed on the territory of the city. The natural soil cover of the left-bank part of the city is represented by soddy forest, sandy, and sandy loam soils. Chernozems prevail on the right bank of the city. The territory of the city is characterized by a significant change in the soil cover and the formation of urban soils [7, 8, 9, 10].

The terrain of the city consists of contrasting elements. The right-bank part is located on a hilly plateau, and the left-bank part is located in a low flat area, which gradually turns into a river terrace.

The choice of objects of observation (functional areas and territories) is determined by the economic-geographical and physical-geographical characteristics of the survey area [5], materials of previous surveys [11, 12], and data from the public cadastral map.

Particular attention was paid to the following sources of pollution:

- industrial and transport enterprises;
- power supply enterprises;
- enterprises for storage and transportation of oil products;
- residential areas;
- production and domestic wastes generation areas;
- recreation areas;
- road transport network.

Soil sampling was carried out per GOST 17.4.3.01-2017 according to a previously planned and adjusted in situ scheme using a uniform grid during route trips. To neutralize the local features of the distribution of pollutants, mixed samples were taken from 5 point samples from test plots of 25 m^2. The sampling depth of point and mixed samples was 0–20 cm.

Bottom sediment samples were taken per GOST 17.1.5.01-80. The standard applies to bottom sediments of water bodies flowing into the sea and establishes general requirements for sampling bottom sediments of water bodies for analysis of contamination by chemical indicators.

The assessment of the state of bottom sediments of the water reservoir was carried out per regulatory document RD 52.24.609-2013 “Organization and carrying out of observations of the content of pollutants in bottom sediments of water bodies”.

Observations of the quality of the soil of the city were carried out by guidelines MU 2.1.7.730-99 “Hygienic assessment of the quality of soil in populated areas”. The list of the studied indicators includes chemical substances of various hazard classes from the list of indicators of Sanitary

Regulations and Norms SanPiN 2.1.7.1287-03 "Sanitary and epidemiological requirements for soil quality" (Table 1).

The fertility of the soil was assessed by an indirect indicator - the content of ammonium nitrogen. For plants, exchangeable ammonium is available, as well as ammonium of water-soluble salts, contained in small quantities. These two forms are extracted from the soil with a 2 % solution of potassium chloride. Since the ammonium of water-soluble salts is only a small part of nitrogen, GOST 26489-85 is considered a method for determining exchangeable ammonium.

A titrimetric method was used to determine chlorides. Their content was used to determine the degree of salinization of urban soils.

The effect of sulfur compounds in emissions from fossil fuel combustion is indirectly characterized by the content of mobile sulfur, determined by the turbidimetric method.

The extraction of 3,4-benzo(a)pyrene was carried out by liquid extraction, n-hexane is used as the extractant. The extraction was analyzed by high performance liquid chromatography (HPLC) with spectrofluorimetric detection using Fluorat-02-2M device. The determination of benzo(a)pyrene content was carried out in the branch of the Center for laboratory analysis and technical measurements (TsLATI) in the Voronezh region and the testing laboratory center of the Federal State Budgetary Institution "Center for Hygiene and Epidemiology in the Voronezh Region".

Following the requirements of environmental surveys, the assessment of the acid-base properties of soils is carried out in any work on the study of the state of the environment. To assess soil acidity, two groups of indicators are used: pH of aqueous and salt extracts. Based on the requirements of GOST 17.5.4.01-84, the actual soil acidity (pH of the aqueous extract) was measured.

At present, exchangeable soil acidity is understood as the total number of acidic components that are retained on the surface of colloidal particles mainly by electrostatic forces [13]. Exchangeable acidity is a more harmful form of soil acidity for plants [4]; it was determined in pH units of salt extract (1M KCl) according to GOST 26489–85.

At the same time, the soil samples were examined for the content of technogenic pollution indicators - heavy metals (HM). The preparation of soil extracts for the determination of the gross metal content was carried out according to generally accepted methods, followed by instrumental analysis on the "SPEKTR-4" atomic absorption spectrometer [4].

Acid-soluble forms of heavy metals were determined on the "Spektr-5-4" atomic absorption spectrometer with flame atomization in the accredited laboratory of the branch of the Center for laboratory analysis and technical measurements (TsLATI) in the Voronezh region of the TsLATI in the Central Federal District, as well as by stripping voltammetry on the TA-4 analyzer in the ecological analytical laboratory of the Faculty of Geography, Geo-ecology, and Tourism of Voronezh State University. The error varied from 15 to 30 % in all measurement ranges.

The degree of soil pollution was estimated by the accumulation coefficient (Ko) relative to MPC (APC). For bottom sediments, the concentration factor of the chemical substance (Kc) was used, calculated as the excess of the concentrations relative to the background concentrations [14].

The identification of anomalies was carried out according to the calculations of the total indicators of pollution (Zc).

The interpretation of the data obtained and their mathematical processing was carried out using computer technology. The selection of contours of soils of various degrees of pollution and mapping was performed using the MapInfoPro program at the Faculty of Geography, Geo-ecology, and Tourism of Voronezh State University.

3. Results and discussions

One of the main indicators of the state of soils is their acidity. The values of the indicator directly depend on the quality and quantity of anti-icing agents used, the presence of construction waste, the composition of dust, and atmospheric precipitation.

In recent years, numerous research results have been obtained on the problems of changes in the

Table 1: Main indicators for assessing the state of soils in the city of Voronezh depending on their functional purpose

No.	Indicator	Research method
1	Ammonium nitrogen, (mg/kg)	GOST 26489-85 Soils. Determination of exchangeable ammonium by the method of Central Research Institute of Agrochemical Services for Agriculture (TsINAO)
2	Chlorides, (mg/kg)	GOST 26425-85 Soils. Methods for the determination of chloride ions in aqueous extract
3	Hydrogen index of aqueous extract, (pH)	GOST 26423-85 Soils. Methods for determination of electrical conductivity, pH and solid residue of aqueous extract.
4	Hydrogen index of salt extract, (pH)	GOST 26483-85 Soils. Preparation of a salt extract and determination of its pH by the method of Central Research Institute of Agrochemical Services for Agriculture (TsINAO)
5	Sulfur compounds, (mg/kg)	GOST 26490-85 Soils. Determination of mobile sulfur by the method of Central Research Institute of Agrochemical Services for Agriculture (TsINAO)
6	Heavy metals, (mg/kg)	Regulatory document RD 52.18.191-89 Methodological guidelines. Methods for measuring the mass fraction of acid-soluble forms of metals (copper, lead, zinc, nickel, cadmium) in soil samples by atomic absorption analysis. Environmental regulations PND F 16.1:2:2.2:3.48-06 Methods for measuring the mass concentration of zinc, cadmium, lead, copper, manganese, arsenic and mercury in soils, greenhouse grounds, sapropels, silts, bottom sediments, solid waste by stripping voltametry using TA-type analyzers.
7	Benz(a)pyrene, (mg/kg)	Environmental regulations PND F 16.1:2:2.2:3.39-03 Quantitative chemical analysis of soils. Methods for measuring the mass fraction of benzo(a)pyrene in samples of soils, grounds, solid waste, and bottom sediments by the method of high-performance liquid chromatography using "Lyumakhrom" liquid chromatograph

acidity of the soil cover of Voronezh [15, 4]. It was found that changes in the actual acidity are associated not only with the type of soil but also with the levels of technogenic load on the territory. The high level of anthropogenic impact on the soil of the city has led to significant geochemical transformation and a change in the nature of the functioning of the soil.

The excess of alkalinity in the soils of the city, on average, reached three pH units in comparison with the background territories for the actual acidity level and four pH units for exchangeable acidity (Figures 1, and 2). By the reaction, the soil pH can be classified as weakly acidic, neutral, and slightly alkaline. The values vary over a wide range, which significantly differs across functional areas.

For the developed industrial areas, regardless of location, slightly alkaline or neutral pH values are characteristic. The acidity value is influenced by powerful technogenic factors (Table 2). As a result, the values of the indicator in these areas are the highest ($pH_{aq.} > 7$).

The obtained results of the values of the hydrogen index coincide with the data of other authors on the increased alkalinity of the soils of Voronezh and the dependence on the degree of atmospheric pollution [15, 6, 9]. The shift in the reaction is due to the impact of technogenic emissions on the soil, which contains a large number of alkaline components.

The study revealed, for the city of Voronezh, statistically significant correlation coefficients of the pH values and the atmospheric pollution indicator [15]. With approaching the administrative boundaries of the city and weakening of the traffic load, the pH values of the aqueous and salt extracts become neutral and slightly acidic in the forests of recreational functional areas.

The pH value of the salt extract of soils is in direct correlation with the content of mobile sulfur. For functional areas, the following values were calculated: $r = +0{,}59$ in the recreational area, $r = +0{,}53$ in the residential and $r = +0{,}4$ in the industrial area.

In the recreational functional areas, the average degree of linear dependence of the pH of the salt extract on the accumulation of mobile sulfur and exchangeable ammonium in the soil was established (+0,59 and +0,69). When calculating the correlation coefficient between the measured values of the pH of the aqueous extract and mobile sulfur in the soils of industrial and recreational functional areas, a slight degree of linear dependence was revealed (+0,47 and +0,39, respectively). Thus, the concentrations of nitrogen and sulfur compounds identified in the soil within

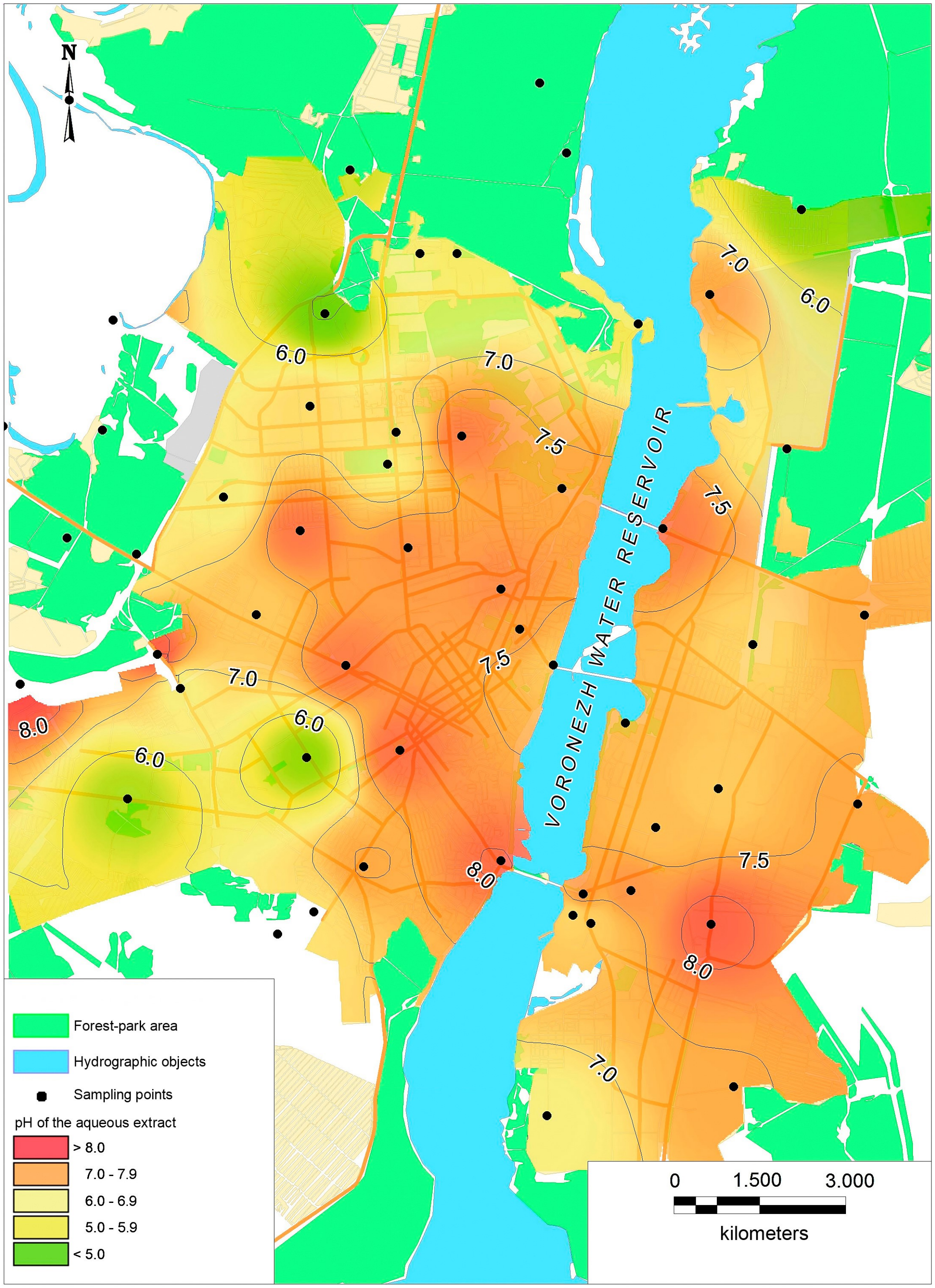

Figure 1: Distribution of the pH values of the aqueous extract in the surface soils of Voronezh

the territory of the city affect the pH value and occur due to transport, industrial, and “atmospheric” sources.

The soil cover of the city of transport functional areas has been formed under special conditions. In the selected areas, neutral indicators of the average pH values of the aqueous and salt extracts have been established. This greatly contributes to the active accumulation of readily soluble salts, strong fragmentation of the soil surface layer, and the development of degradation processes.

Water-soluble chlorides play a significant role

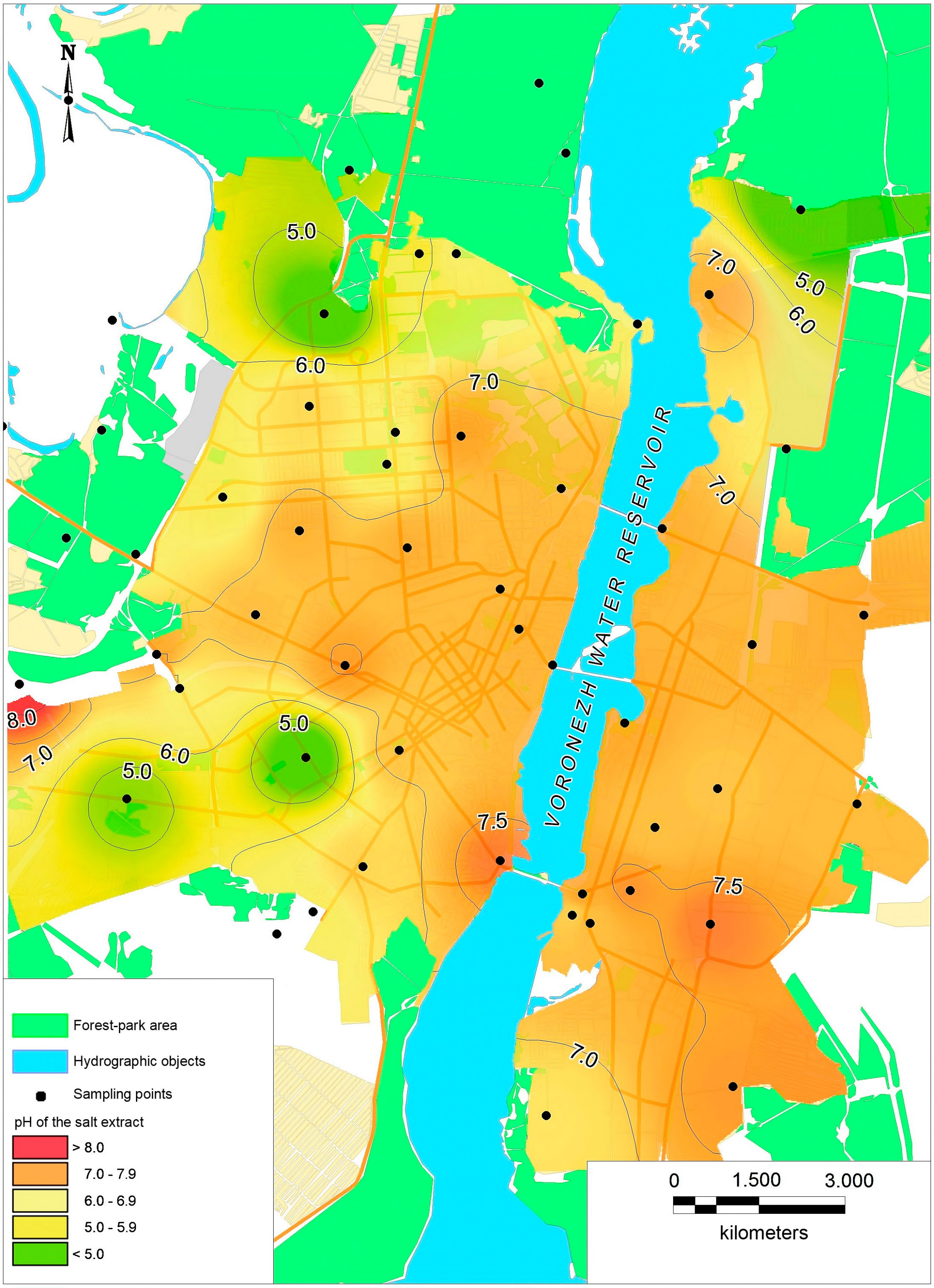

Figure 2: Distribution of the pH values of the salt extract in the surface soils of Voronezh

in technogenic urban flows. As the most mobile compounds, migrating further than other salts, and can significantly increase the impact zone (Figure 3).

In the soils adjacent to traffic intersections and highways, a slight direct correlation was found between the pHsalt indicators and the concentration of oil products (r = +0,41). Studies carried out earlier for the city territory [14, 16, 17, 5, 9] have revealed stable correlations in the "source

Table 2: Physical and chemical properties of the surface soil layer (0–20 cm) in various functional areas of the city of Voronezh

Areas	Indicator	$pH_{aq.}$	pH_{salt}	Chlorides (mg/kg)	Mobile sulfur (mg/kg)	Exchangeable ammonium (mg/kg)
Background areas	Average	6,74	6,55	75,97	15,56	6,21
Industrial functional areas	Average	7,49	7,29	92,75	28,35	9,78
	Min	6,65	6,68	67,45	2,00	2,50
	Max	8,15	7,66	118,04	53,60	23,66
	Max-Min	1,50	0,98	50,59	51,60	21,16
Transport functional areas	Average	7,39	7,12	95,87	31,82	9,59
	Min	6,12	6,24	67,45	14,81	2,50
	Max	8,33	8,14	181,32	54,47	27,86
	Max-Min	2,21	1,90	113,87	39,66	25,36
Recreational functional areas	Average	6,01	5,73	73,8	33,83	9,13
	Min	5,2	4,21	67,45	24,51	2,49
	Max	7,21	7,17	84,31	43,16	15,28
	Max-Min	2,01	2,96	16,86	18,65	12,8
Residential functional areas	Average	6,5	6,02	92,73	31,93	9,88
	Min	5,0	3,86	50,59	12,5	2,5
	Max	7,86	7,49	118,04	52,2	26,9
	Max-Min	2,86	3,63	67,45	39,7	24,4

of pollution - soil" system. Strong positive correlations between concentrations and car traffic intensity have been reliably established.

Compared to the background areas, urban soils are rich in plant nutrients. Extremely high or low content of nutrients in soils determines the resistance of plants.

The signs of critical parameters of soil indexes are the suppression of plant associations for each key object [18].

Urban soils are not used for agricultural production, and the main removal of nutrients occurs during the annual harvesting of fallen leaves. The loss of nutrients leads to the destruction of mineral and organic components and worsens soil fertility.

The need for cleaning activities in the city is determined by the functional purpose of landscaping objects. Thus, in the changeable climate of the Voronezh region, lawns not cleared of autumn leaves are less enduring in the winter season and quickly degrade. In city parks, boulevards, and central streets, foliage harvesting is important not only for aesthetic but also for environmental reasons: all urban green spaces during the growing season receive a complex set of pollutants from the air, including compounds of heavy metals, benzo(a)pyrene, sulfur, etc.

The territory of Voronezh city is distinguished by a high content of mobile sulfur. High contents were found in various functional areas of the city, which are characterized by natural soil formation. Historical and landscape parks, green spaces of departmental territories, forests, and forest parks have preserved areas with natural soil formation and foliage harvesting is not advisable here. The soils of these territories accumulate the nutrient element (mobile sulfur) better than others.

The highest concentrations of mobile sulfur (over 16 mg/kg) are found in the forest-park and park area, as well as in the area of the Peschany Log memorial. Among the industrial functional areas, the territories adjacent to the combined heat and power production plant feature high concentrations of mobile sulfur. In the recent historical past, heat and power supply enterprises used coal. As a "legacy" from this period, the city has got "ash dumps" on the banks of the Voronezh water reservoir.

Urban soils, sandy loam, and meadow soils of the left bank of the city are insufficiently supplied with mobile sulfur (the content is less than 6 mg/kg). These soils make less than 14 % of all studied soil samples.

The content of exchangeable ammonium is a relative indicator characterizing the fertility of the

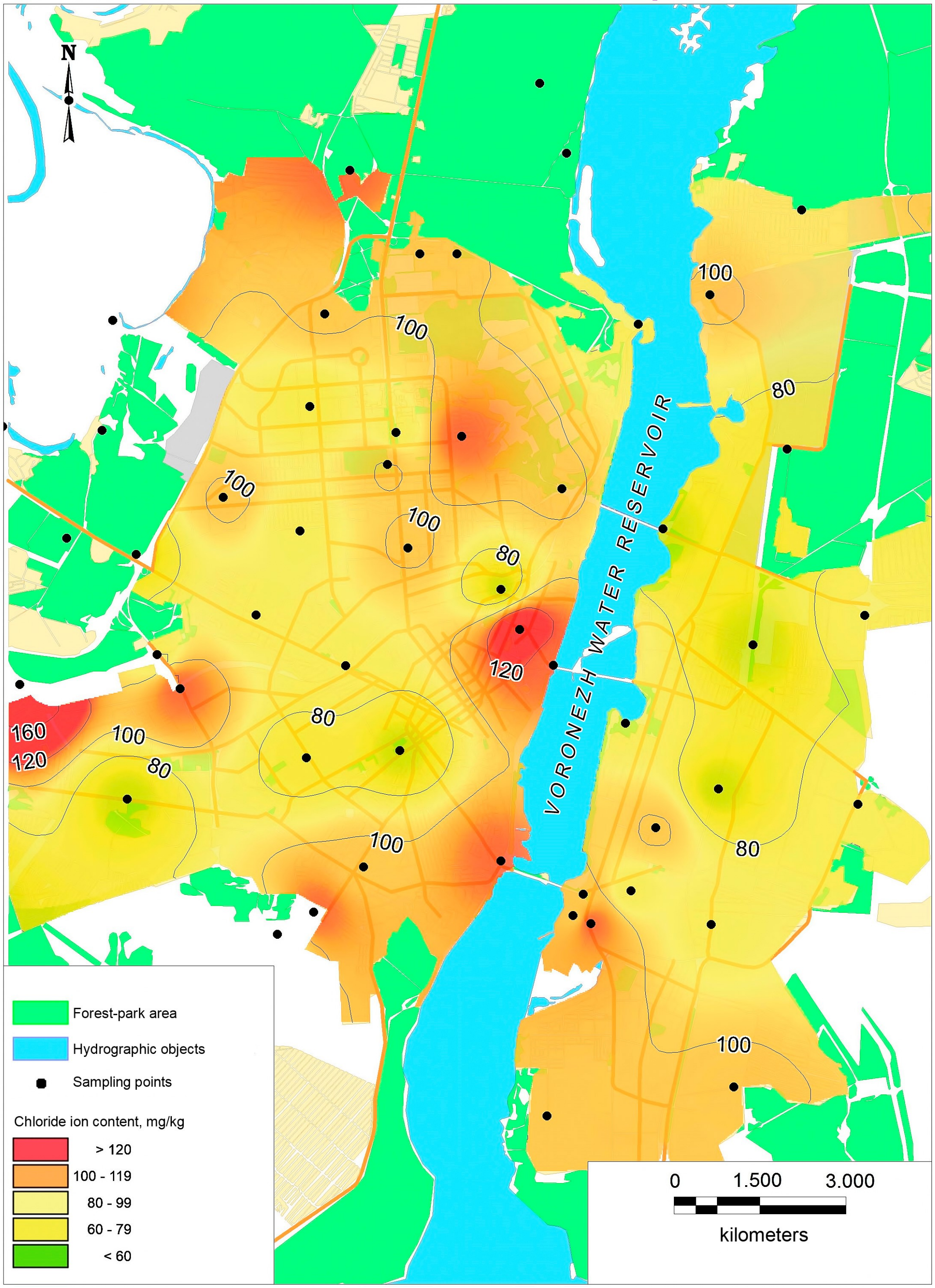

Figure 3: Distribution of chloride ion in the surface layers of soils in Voronezh

soil surface layer (Table 2). According to the level of exchangeable ammonium content, the functional areas of the city form a series: residential area (1,92 Kc)> industrial area (1,90 Kc)> transport area (1,86 Kc)> recreational area (1,77 Kc).

Under the influence of alkalization, urban soils are transformed, the soil absorbing elements are saturated, the migration capacity of many heavy metals decreases and leads to their accumulation (Table 3).

One of the main processes affecting migration in soils is the fixation with the humic matter. It occurs

Table 3: The content of heavy metals and benzo(a)pyrene (mg/kg) in the surface soil layer (0-20 cm) of the city of Voronezh

	Indicator	Lead	Cadmium	Copper	Zinc	Benz(a)pyrene
Maximum permissible concentrations [19]	MPC (maximum permissible concentration) / APC (approximate permissible concentration)	32	0,5	33	55	0,02
Industrial functional areas	Average	69,21	1,27	23,83	14,37	0,050
	min	3,04	0,12	2,96	0,38	< 0,005
	max	453,00	8,02	93,02	123,80	0,170
	max - min	449,96	7,90	90,06	123,42	0,17
Transport functional areas	Average	25,9	0,20	21,24	98,75	0,028
	min	0,79	0,01	4,13	0,61	< 0,005
	max	134,7	1,29	94,7	499,98	0,360
	max - min	133,91	1,28	90,57	499,37	0,355
Recreational functional areas	Average	7,7	0,06	6,39	11,01	< 0,005
	min	0,59	0,02	0,42	0,26	< 0,005
	max	18,73	0,15	14,02	36,86	< 0,005
	max - min	18,14	0,13	0,19	0,2	0,00
Residential functional areas	Average	14,52	0,18	11,83	6,15	< 0,005
	min	0,00	0,00	3,32	1,98	< 0,005
	max	40,50	0,44	26,70	10,42	< 0,005
	max - min	40,50	0,44	23,38	8,44	0,00

due to the formation of salts with organic acids by metals, the adsorption of ions on the surface of organic colloidal systems, or the creation of complexes with humic acids.

The studied parameters are distributed in different ways in urban soils. Heavy metals are widespread in industrial and transport functional areas of the city. According to the present research, the soil adjacent to the railway tracks leading to the production areas is under maximum stress. Thus, on the left bank of the city in the area of the railway bridge (Otrozhka station) and the production base of the locomotive depot, lead concentrations exceed the MPC by 4,5 times, and in the area of the Pridacha railway station on the border with the aircraft building plant, the MPC is exceeded 14,2 times.

The industrial areas of the city have a high content of lead and cadmium. The average concentrations in soils exceed the MPC of lead and cadmium by more than 2 times. Within the industrial territories, the excess of MPC of lead was found in 42 % of the samples taken, cadmium in 25 %, and copper in 16,7 %.

In general, the soils of the Voronezh region are characterized by a deficiency of microelements - copper and zinc. Revealing their high concentrations makes it possible to speak about their technogenic sources in the industrial areas of the city, such as the chemical and mechanical processes of metal processing and the processes of burning organic fuel.

Transport functional areas throughout the city concentrate heavy metals. On sections of streets with the maximum traffic intensity, pollutants of the 1st and 2nd hazard classes are accumulated. The values of the total pollution indicator for transport areas vary in the range from permissible to moderately hazardous values.

In smooth and sloped sections of transport functional areas, pollutants are accumulated in different ways. The actual accumulation of heavy metals in the upper and middle parts of the slopes of 3 to 5 degrees was established for the territory of the city. On the soils of the slightly sloping areas of the Voronezh River embankments, pollutants are practically not accumulated ($Zc < 16$). This is due to leaching and the light texture of the soil.

High concentrations of benzo(a)pyrene are characteristic of anthropogenically transformed soils of industrial areas, as shown Figure 4.

For the areas of the left bank, the content of benzo(a)pyrene varies in the range from 0,05 to 0,08 mg/kg, for the areas of the right bank from

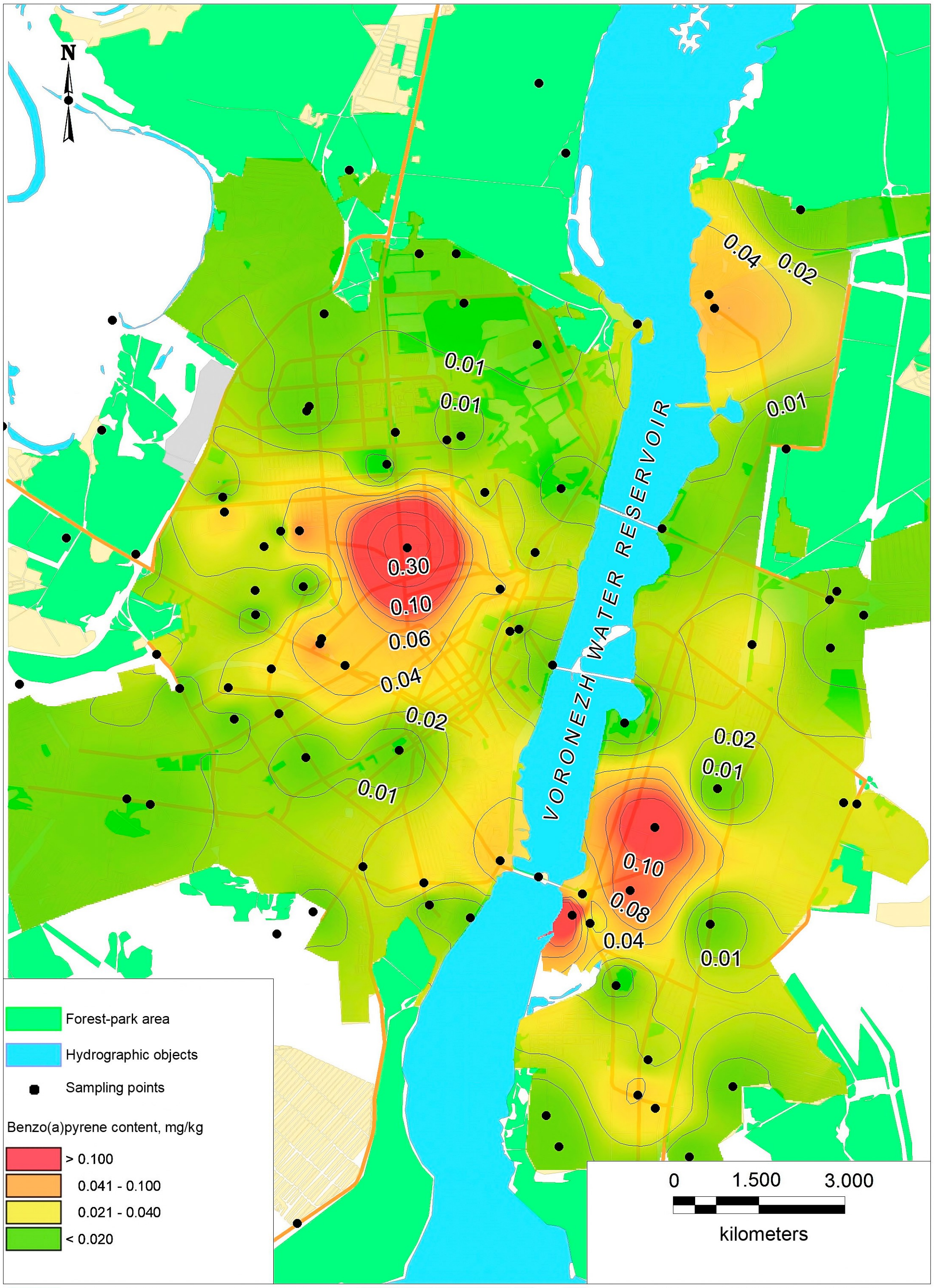

Figure 4: Accumulation of benzo(a)pyrene in the surface layers of soils in Voronezh

0,05 to 0,17 mg/kg. The soils of recreational and residential areas in the city do not contain PAHs.

On the territory of the city, the excess of MPC for benzo(a)pyrene was found in every second sample of soil from industrial areas and in every third sample from transport functional areas.

At the intersection of sanitary protection zones of enterprises with road and rail transport interchanges, the maximum concentration of benzo(a)pyrene is reached. Specification of the boundaries of "polluted" areas and identification of facilities of negative impact at the moment is not possible. These enterprises are classified as highly hazardous industrial facilities with limited access to the territory.

When comparing the average concentrations of benzo(a)pyrene in the soils of the functional areas of the city with the MPC (0,02 mg/kg), the coefficient of environmental hazard (Ko) was calculated. The excess of the standard in the soils of the industrial areas of the city is quite high and averages 5 MPC for the left-bank part of the city and 2,5 MPC for the right-bank part. The maximum values (Ko $= 8,5$) are noted in the urban soils of the industrial area of the left bank near the Combined heat and power production plant 1.

The concentration coefficient (Kc) shows a strong degree of soil pollution in the industrial areas of the city. Particularly dangerous is the territory of the transport area in the central part of the city at the intersection of a busy road junction of motor transport (Zastava square), railway transport (Plekhanovskaya station), and the production area of the refrigeration plant (Ko = 18). By calculating the total indicator of soil pollution (Zc), these territories were classified in this study as “hazardous” in terms of the degree of pollution (32 < Zc < 128).

Most of the city is categorized as an area with an acceptable pollution level ($Zc < 16$). These territories can be used without restrictions for housing construction, developing areas of cultural leisure, and business buildings.

Moderately hazardous soil pollution ($16 < Zc < 32$) with heavy metals and benzo(a)pyrene was revealed in areas adjacent to the steep slopes of the right bank of the Voronezh water reservoir. Sloped surfaces, rainsheet, and linear erosion facilitate the migration of pollutants from the soil into the water reservoir. A significant amount of man-made compounds and suspended substances from the entire urban area enter the water of the reservoir with the runoff from the storm sewer network and treatment facilities of the left bank, as shown in Table 4.

Above the water area of the reservoir, special climatic conditions are created with changes in the speed and direction of the wind during the day. These movements are permanent and affect the transport of substances along the entire bank line.

Analysis of the granulometric composition of the bottom sediments of the Voronezh water reservoir revealed the predominance of fractions of physical sand. In total, coarse, medium, and fine sand make up more than 60 % of the sample mass. Clay fractions, including silts, make on average about 30 % of the mass in all studied samples.

The chemical composition of the bottom sediments of the water reservoir is characterized by great diversity and is a consequence of long-term anthropogenic impact. Comparison of different parts of the reservoir was carried out in the present study according to the concentration coefficient (Kc) of each pollutant in comparison with the background indicator, as shown in Table 4.

As the background concentration of the pollutant, the bottom sediments were used, the anthropogenic impact on which is minimal. These are the sediments at the site in the north of the urban agglomeration, above the M-4 highway at the influx of the Voronezh River in the reservoir.

Long-term observations of the bottom sediments of the Voronezh water reservoir make it possible to identify the most "polluted" parts of the reservoir and to determine the periods during which the reservoir experienced the greatest technogenic loads.

The highest concentration coefficients of heavy metals (Kc) are typical for 2008 - 2010. The Kc coefficient values increase from north to south, in the direction of water flow. The greatest pollution of bottom sediments of the reservoir on the territory of the city is typical for the area below the outlet from the treatment facilities of the left bank.

The levels of pollution of bottom sediments with heavy metals increase in the following order: lead<cadmium<copper<zinc. Thus, the main heavy metals polluting the water body are zinc and copper.

4. Conclusions

Based on the results of the study, the following conclusions can be made:

In the surface layers of Voronezh soils, the pH value changes. Alkalization of the soil occurs,

Table 4: Accumulation coefficient (Ko) of heavy metals in the bottom sediments of the Voronezh water reservoir

No.	Sampling spot	Year	Lead	Cadmium	Zinc	Copper
1	Water reservoir 500 m downstream the railway bridge	2008	1,7	3,3	6,5	15,7
		2010	1,9	1,0	7,5	8,2
		2018	1,4	1,0	8,0	3,8
		2019	1,9	1,0	5,4	3,0
		2020	1,2	1,0	4,2	3,0
2	Water reservoir 500 m downstream the North bridge	2008	5,6	1,7	5,7	5,7
		2010	5,5	3,7	38,6	43,2
		2018	1,1	1,0	3,5	3,7
		2019	1,6	1,0	2,6	2,5
		2020	1,1	1,0	1,8	2,3
3	Water reservoir 500 m downstream the Chernavsky bridge	2008	9,4	0,9	13,9	5,7
		2010	1,1	1,0	6,4	6,2
		2018	1,8	3,0	4,9	2,0
		2019	1,3	1,0	2,7	2,3
		2020	1,2	1,0	1,9	2,4
4	Water reservoir between the dam of the Chernavsky bridge and the Pridachenskaya dam	2008	2,2	1,7	11,7	1,0
		2010	1,8	1,0	2,4	5,4
		2018	2,3	1,0	4,6	4,2
		2019	0,4	1,0	2,0	1,8
		2020	1,2	1,2	1,9	1,7
5	Water reservoir in the Petrovskaya embankment area	2008	8,9	0,1	17,4	8,6
		2010	8,1	3,0	37,7	34,1
		2018	1,7	1,0	4,2	2,7
		2019	1,4	1,0	3,8	2,5
		2020	1,2	0,9	2,5	2,6
6	Water reservoir 500 m downstream the bridge of Voronezh State District Power Plant	2008	16,7	1,8	44,8	25,7
		2010	12,9	7,6	27,1	81,8
		2018	1,4	3,0	8,4	4,5
		2019	2,2	5,2	6,5	2,8
		2020	2,0	3,8	5,9	3,1
7	Water reservoir 500 m downstream the outlet of “Levoberezhnye wastewater treatment facilities”	2008	3,3	19,2	28,7	60,4
		2010	33,1	180,1	235,5	81,8
		2018	7,2	16,0	22,4	46,7
		2019	10,1	22,3	16,1	24,4
		2020	12,4	20,5	15,9	22,5
8	Water reservoir 500 m upstream the waterworks	2008	1,1	0,1	2,2	0,9
		2010	4,5	2,2	25,0	43,2
		2018	1,7	1,0	12,7	18,0
		2019	2,0	1,0	8,4	9,0
		2020	1,2	1,2	7,5	6,9

which in turn affects the solubility of heavy metals and their concentration in the soil.

High levels of soil pollution are typical for the centers of geochemical abnormalities in industrial and transport functional areas.

The soil cover in Voronezh contains excessive concentrations of metals, which makes it possible to identify areas that are polluted by man-made sources.

Certain geochemical abnormalities have a diverse pattern, which often does not reflect a real assessment of the state of the environment. The distribution of elements is largely determined by landscape and geochemical conditions. Metal content abnormalities are most evident on the windward side of pollutant emission sources. They are intensely accumulated in temporary drying up streams and in the troughs of untreated rainwater and meltwater.

The process of accumulation of zinc and copper in the bottom sediments of the reservoir is facilitated by the processes of degradation of the urban soil surface layer, which is deficient in these biogenic elements.

Landscape-geochemical conditions and functional organization of urban areas are important factors that determine the level of anthropogenic impact on the soil and bottom sediments.

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