https://doi.org/10.17221/95/2020-SWR

Soil pollution status of urban soils in St. Petersburg city, North-west of Russia

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Citation: Polyakov V., Kozlov A., Suleymanov A., Abakumov E. (2021): Soil pollution status of urban soils in St. Petersburg city, North-west of Russia. Soil & Water Res., 16: 164–173.

Abstract: The intensive urbanisation of terrestrial environments and industrial activity have an effect on the accumulation of risky metals in the soil and increase the toxicological risk to the terrestrial ecosystems and human health. Ninety-six topsoil samples from of St. Petersburg Russia as the source of the content of seven key risky metals (As, Cd, Pb, Zn, Ni, Cu, Hg) and polycyclic aromatic hydrocarbons (PAHs) have been investigated. To identify the spatial distribution of the risky metals and PAHs, GIS technologies have been used. Based on the data obtained, interactive maps of urban soil pollution were made. The spatial distribution of seven metals and their metalloids greatly varied from the local anthropic inputs. The results indicate that the highest concentrations of copper, mercury and lead were found in the urban environment. The most polluted areas were located in the city centre and the areas adjacent to industrial zones. The topsoil in this area represents an environmental pollution risk with regards to the elements Cu > Pb > As > Zn > Ni > Hg > Cd. The contents of the risk-type elements in the industrial area were higher than those in other land-use types in the north of city, indicating a considerable risk of metal migration and accumulation to the Neva River, the Gulf of Finland and the groundwater.

Keywords: artificial alluvial landscapes; benzo(a)pyrene; risk elements; soil pollution

The urban macro landscape of St. Petersburg is located in the most important part of the Baltic region. The urban landscape is associated with the Neva lowland, known as the region most anthropogenically modified in the northwest region of Russia and Scandinavia.

A characteristic feature of the modern period of human development is the rapid rate of urbanisation. It changes or destroys the natural environment both from a quantitative aspect (new land consumption) and from a qualitative one (environmental degradation). Rapidly progressing urbanisation, an increase in the area of cities and settlements leads to the fact that the urban environment is constantly exposed to the effects of internal and external factors. In the process of urbanisation, an urban ecosystem is formed, a natural-urban system consists of fragments of natural ecosystems surrounded by houses, industrial zones, roads, etc. The urban ecosystem is characterised by the creation of new types of artificially

Supported by Grant of Saint-Petersburg State University "Urbanized ecosystems of the Russian Arctic: dynamics, state and sustainable development" (field research, 50%) and Project of Russian Science Foundation No. 17-16-01030 (laboratory research, 50%). The chemical analysis was performed in the Chemical Analyses and Materials Research Center of Saint Petersburg State University.

https://doi.org/10.17221/95/2020-SWR

created geosystems as a result of the degradation, destruction and (or) replacement of natural systems (Chasovskaya 2007; Hu et al. 2014).

Urban soils, as a depositing component of the urban landscape, accumulate many risky elements, including risky metals and metalloids, as well as organic compounds that are toxic for living organisms. Technogenic territories are characterised by a regressive-accumulative type of distribution of risky elements in the profile: risky elements accumulate in the upper humus horizon and decrease their concentration in the underlying horizons. Due to the obvious non-degradability and latency of risky soil elements, they are difficult to detect and have a long incubation period before the danger and toxicity of excessive metals in the soil can be realised (Cui et al. 2005; Fernandez-Luqueno et al. 2013; Zhang et al. 2020). Once in the soil, risky elements can pass from one environment to another, thus accumulating in the water area of the city, living organisms and in the form of dust in the atmosphere (Mamat et al. 2014). The study of the soil cover of cities and urban agglomerations, such as St. Petersburg, must be carried out taking all the features and a wide range of influencing factors on soil formation processes into account. The concentration of risky elements in the soil is an important indicator for assessing the quality and state of the environment (Liu et al. 2015). The long-term accumulation of risky elements in the soil represents a great threat to human health and the sustainable development of the ecological environment (Qing et al. 2015; Dong et al. 2018).

Three main types of soil prevail on the territory of St. Petersburg: grounds, created by using transported land for the construction of landscaped facilities; natural cultivated, which are mainly located in forest parks and parks of urban suburbs, and alluvial, created by washing of the sands and sandy loams materials on the coast from the bottom of the Gulf of Finland. The ecological state of urban soils is not uniform and is determined not only by their initial heterogeneity and the impact of anthropogenic factors, but also by the natural features of the terrain and the conditions of exploiting green spaces (Kapelkina 1994). The active transport of industrial products, the gas exhaust, waste water, household waste, as well as the application of fertilisers and pesticides to the soil are the main sources of risky elements. Determining the sources of the spatial distribution of risky elements in the soil, especially in industrial and agricultural areas, are essential for effective management measures to control the pollution levels and improve the soil quality (Qing et al. 2015; Dong et al. 2018).

Remote sensing data are a useful tool in soil research (Mulder et al. 2011). Multi- and hyperspectral images from unmanned aerial vehicles, aircraft and space satellites are used for different scientific tasks. The active use of satellite data in the last years has been facilitated by improved image quality (spatial resolution), a large data set (multi-year image archives), and a short interval between the images, free access to satellite images (Sentinel, Landsat, and others). Remote research methods are operational, more cost-effective and allow you to cover larger areas. The above-mentioned advantages allow the use of effective space data for mapping urban areas within large megacities. GIS technology in combination with statistical methods allows a comprehensive study of the characteristics of pollution and the identification of potential sources of the input of risky elements into the soil (Lado et al. 2008; Sun et al. 2013; Hou et al. 2017).

Thus, the aim of this work is to provide the pollution status of the city. To achieve this goal, the following objectives were formulated:
– to evaluate the degree of soil contamination in the city by risky elements, petroleum products and benzo(a)pyrene by comparing the measured values with the threshold concentrations;
– provide geochemical maps based on the concentration of the pollutants in the soils of Saint Petersburg.

MATERIAL AND METHODS

Study area. The studies were conducted in the city of St. Petersburg in Russia, within the Prinevskaya lowland. The city covers an area of 1 439 km^2 with a population of about 5.4 million people. The historical centre of the city is located on Litorin marine sediments of various compositions (sands, loams, clays); the northern part of the city is located on limno-glacial deposits of the second Baltic glacial lake. The climate is temperate, transitional from temperate continental to temperate marine. The average annual temperature is +5.8 °C. The annual precipitation is 662 mm. There are about 62 sunny days in a year.

Sampling methodology. Field studies were conducted in the summer of 2018. The study areas belong to different functional zones of the city (port, recreational, industrial and residential) in areas free from asphalt. The soils were selected from the upper horizons (0–20 cm). The sample preparation was carried out according to the standard procedure. The air dry samples were sieved through a 2 mm sieve. Ninety-six soil samples were taken from various functional areas of the city. They include both alluvial territories and soils associated with postlithogenic soil formation. The sampling points are shown in Figure 1.

Data analysis. To establish the pollution status of the soils and create interactive maps of the city pollution by the risky elements and polycyclic aromatic hydrocarbons (PAHs), the following indicators were studied: benzo(a)pyrene, petroleum products (PP), pH, Zn, Cu, As, Pb, Ni, Hg, Cd. The chemical analysis of the soils was carried out in the certified laboratory of industrial sanitation and ecology "LiK" and in the Department of Applied Ecology, SPBU. The determination of the content of (Zn, Cu, Pb, Ni, Cd) and metalloids (As) in the soil was carried out in accordance with the inversion voltammetry method on TA analysers (ISO 11047:1998). The pH of the salt extract was determined by a potentiometric method with a glass electrode using a Multitest IPL-301 instrument (Semico, Russia) according to the method of GOST 26483-85. The benzo(a)pyrene content was determined on a Fluorat-02 liquid chromatograph (PND F 16.1:2:2.2:2.3:3.39-2003). The content of the PP in the soil was made in accordance with the method of PND F 16.1: 2.21-98 on a Fluorat 02-3M fluorometric detector (Lumex, Russia). The assessment of the risky elements, benzo(a)pyrene and PP pollution was carried out by comparing the obtained data with the existing hygienic standards and background contents. The maximum permissible concentrations (MPC), i.e., the threshold concentration, were used from the Russian Federation Hygiene Code (TAC 6229-91). The geochemical background was used for St. Petersburg according to Lodygin et al. (2008) and Ufimtseva et al. (2011).

Satellite data. Cloud-free Sentinel-2A satellite images from 18.07.2018 were download from the Copernicus Open Access Hub (https://scihub.copernicus.eu/dhus/#/home). The satellite data contain 13 spectral channels with spatial resolution from 10 to 60 m. The 11-8-4 channel sequence (SWIR-NIR-RED) was used to create the urbanisation map (Figure 2). The interpolation maps were created by inverse distance weighted (IDW) methods. The satellite data processing and cartographic materials creation was carried out in the QGIS 3.6.0 geographic information system. The atmospheric correction of the space data was performed using the "Semi-Automatic Classification Plugin" module.

Statistical analyses. The statistical data processing and Spearmen's correlation analysis were performed in the Python programming language, in the Jupyter Notebook web-based interactive computational environment using the pandas, matplotlib, numpy, seaborn, sklearn libraries.

Figure 1. Map of Saint Petersburg

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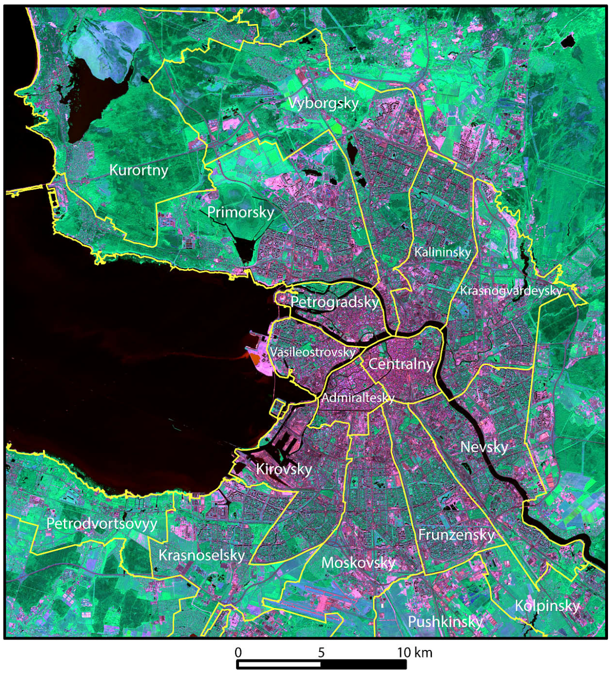

Figure 2. Urban city map created using data from Sentinel 2A purple – urbanised territory, green – natural areas, black – water objects, yellow lines – district borders

RESULT AND DISCUSSION

Monitoring of the benzo(a)pyrene and petroleum product in the soils of the alluvial territories of St. Petersburg. The results obtained for the content of the PP, benzo(a)pyrene and pH are presented in Figure 3. A high degree of soil contamination by benzo(a)pyrene has been noted in the industrial area of the city. In most of the studied soils of the city, the MPC was exceeded several times (Table 1). The highest benzo(a) pyrene content is observed in the south of the city (Moskovsky, Kirovsky and Frunzensky districts). The largest plants in the city are located here, which are sources of anthropogenic load. The cleanest zone is located in the Vyborgsky district of the city, many parks and green zones are located in the district, where the concentration of benzo(a)pyrene is below the detection limit. This is primarily due to the long range of the Vyborgsky district from major traffic intersections and with the wind front that goes from the Gulf of Finland to the city, which prevents the sedimentation of dust and exhaust from cars. An additional source of PAHs is fresh organic material (peat). Due to its introduction in the green zone of the city, heavy polyarenes can pass into the soils and lead to the secondary pollution of the soil. A large technogenic load is the cause of significant environmental tensions in the city. High levels of PAH contamination are point clusters confined to a number of industrial zones in the city. The high PP content can be noted in the Petrogradsky, Centralny and Nevsky districts. The source of the PP in the soils is often fuel spills as well as the activity of vehicles in the urban environment.

The medium values of benzo(a)pyrene content in the soils are noted in the area of the ports of St. Petersburg and its major highways. The automobile activity and ship activities are the source of PAHs formed from the product of incomplete gasoline combustion and pass into the soil along with the exhaust gases (Chukov et al. 2006; Lodygin et al. 2008; Dymov et al. 2013; Shamilishvily et al. 2018).

According to the pH distribution, a neutral reaction of the soil in the city can be observed. It is associ-

Table 1. Descriptive statistics of the risky element concentrations in the soil samples

	pH	B[a]P	PP	Cu	Zn	Pb	Cd	Ni	Hg	As
		(mg/kg)								
N	75	84	84	96	96	96	96	96	90	78
Mean	6.7	0.4	751	215	207	561	0.4	17.7	0.34	3.3
Min	4.1	0.004	4.5	1	4	0.1	0.09	0.09	0.01	0.09
Max	8.6	5.47	9 901	10 095	3 808	45 507	4	342	2.4	19.77
SD	1.18	0.81	1 760	1 089	483	4638	0.5	37.9	0.49	3.63
MPC	–	0.005	-	55	100	30	0.5	85	2.1	2
Geochemical background	4.5–5.5	–	–	1	15	19.1	0.1	1.4	0.03	1.4
SD	1.18	0.81	1 760	1 089	483	4 638	0.5	37.9	0.49	3.63
CV (%)	18	213	234	507	233	825	137	214	151	110

B[a]P – benzo(a)pyrene; PP – petroleum product; MPC – maximum permissible concentrations; SD – standard deviation; *CV* – coefficient of variance

https://doi.org/10.17221/95/2020-SWR

ated with alkalisation due to building activities and calcareous materials, which are used in construction.

Content of risky elements in the soils of St. Petersburg. According to the obtained data, the extremely high soil pollution with risky elements was noted. From the geochemical maps (Figure 4), the coastal zones of the city are more polluted with risky elements, except for Cu and Hg, whose excess Cu and Hg concentrations are noted throughout the city. Most of the coastal zones are alluvial territories. The alluvial territories of St. Petersburg are young formations. The alluvial territories formed as a result of a washing of alluvial materials from the bottom of the Gulf of Finland. Presumably, before the washing of the material, it could be exposed by anthropogenic impacts and contaminated with risky elements, since the Gulf of Finland is a major maritime artery of the region. Sandy loam material has a high absorption capacity and responds well to the accumulation of pollutants. Thus, the technogenic impact from industrial complexes also acts on artificial soils from the bottom of the Gulf of Finland.

Seven elements (Cu, Zn, Pb, Cd, Ni, Hg, As) were analysed in the soils of the study area (Figure 4). All the soils except for the urban beaches have varying degrees of pollution. According to the content of copper in the soil, a 10× excess of this element was noted in the soils of the port area the Petrogradsky, Vasileostrovsky and Kirovsky districts. In this region, there is a similar excess of zinc, the content of this element exceeds the standard value by 19 times. The content of lead in the soils also indicated different degrees of pollution, there is practically no pollution in the residential area and on the beaches, the value of the standards is exceeded by a maximum of 2 times. The industrial zone is characterised by a high degree of pollution, the excess reaches 11 times the standard value. The residential area is characterised by pollution from the surface, which is associated with the air transport of pollutants from motor vehicles and

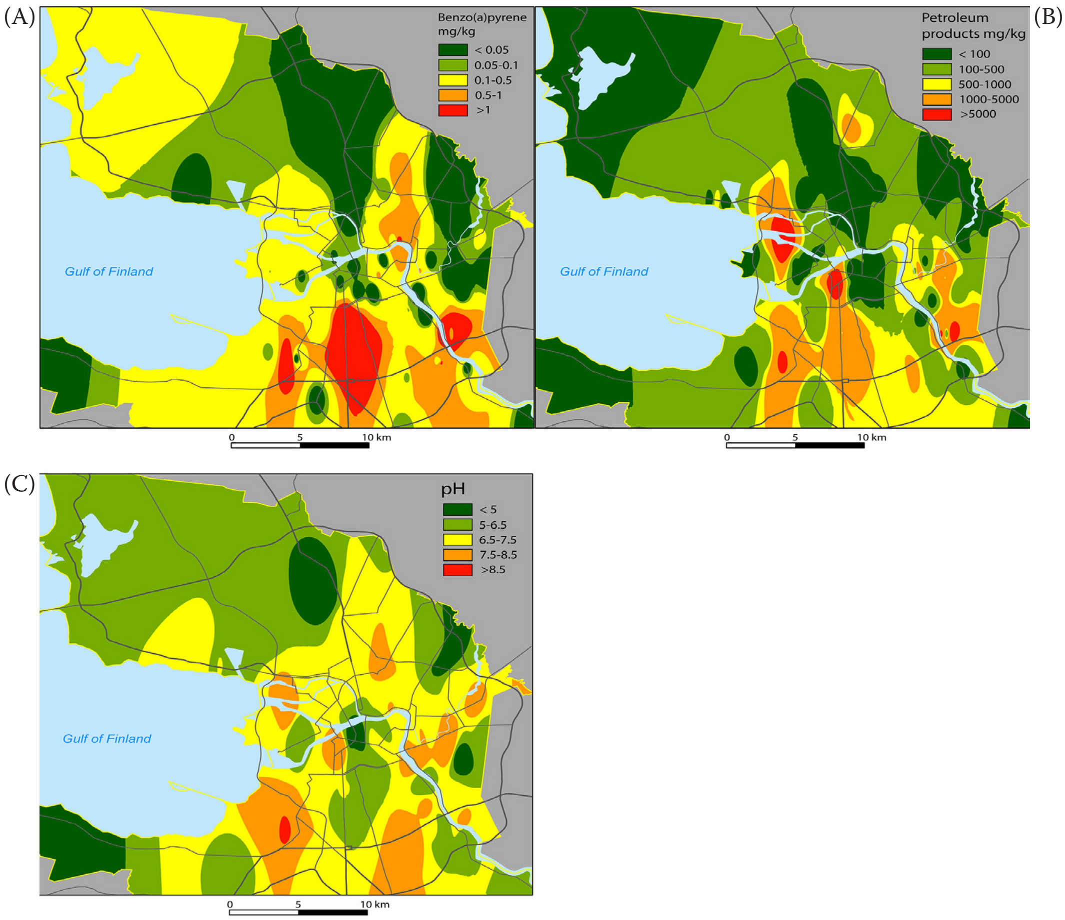

Figure 3. Geochemical maps of the benzo(a)pyrene, petroleum products and pH: benzo(a)pyrene (A); petroleum products (B); pH values (C); the content of the studied indicators is presented in Table S1 in the Electronic Supplementary Material

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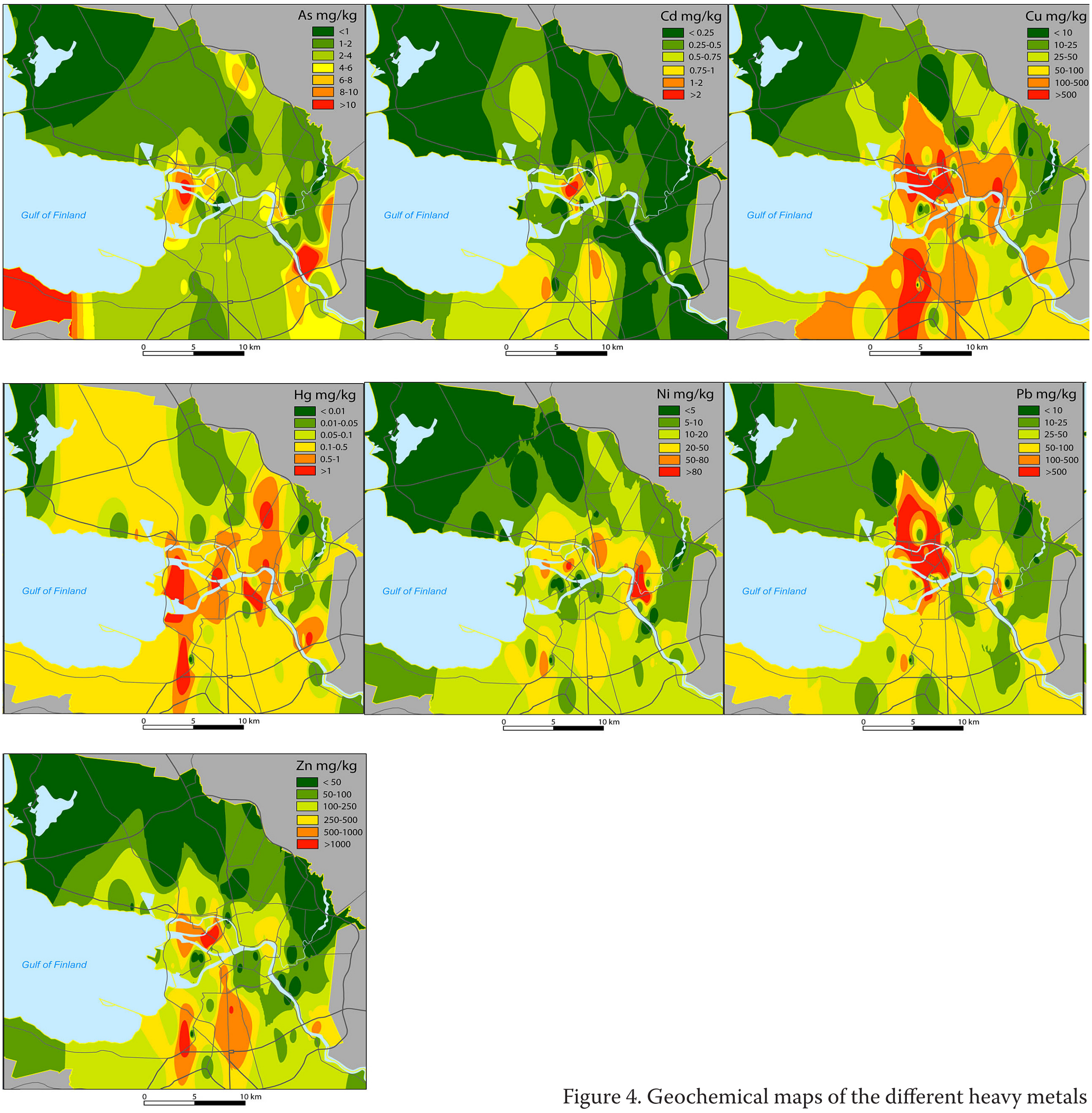

Figure 4. Geochemical maps of the different heavy metals

fuel and energy facilities. Whereas for the industrial zone, it is inherent in the pollution throughout the soil profile, this is due to the constant anthropogenic impact on this territory. The content of cadmium showed a significant amount of pollution only in the port area. On the content of nickel and mercury, only single excesses were noted. A significant excess in the arsenic content was detected in the port area only.

Cu, Hg and Pb are the most common risky elements in the urban environment of St. Petersburg. High levels of mercury and lead pollution are associated with exhaust gases from vehicles, furnaces, boiler houses and other industries. From the graphs obtained, it can be seen that the most polluted areas of the city are the historical centre of the city, while on the periphery of the city, the pollution level is much lower. Due to the climatic features, especially frequent winds, and the geographical location of the city, part of the toxic substances have been removed from the city, part of the risky elements interact with water vapour and form compounds that enter and accumulate in the urban soil cover.

The content of PAHs in the soils and grounds is extremely high. A high degree of urbanisation (hyper-urbanisation), a large man-made load, is the cause of significant environmental tensions in the

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area. The regularity of the spatial distribution of PAHs is determined by the proximity to highways and the presence of introduced peat (Gennadiyev et al. 1990, 2004; Gabov et al. 2004, 2007; Kogut et al. 2006; Lodygin et al. 2008; Abakumov et al. 2017).

Other scientists in different countries occupy evaluations of the soil pollution and the development of various standards to monitor the soil's condition. Depending on the goals and objectives of the research, they use different approaches and different methods of assessment and valuation. This usually results in incompatible data. In different countries of Europe, these data may vary significantly. Thus, the background pollution of the land with risky elements in Central Europe, taking into account that they set standards there, is significantly higher than in Russia. This is one of the reasons for the different levels of regulation. For example, in Germany and Russia in the soils of the reserves, the content of risky elements (in mg/kg) is: lead – 100 and 11, copper – 200 and 20, nickel – 200 and 47, zinc – 500 and 52, respectively. A similar difference can be noted for other pollutants (Cappuyns & Swennen 2007; Chernova & Beketskaya 2011; Kryatov et al. 2012; Suleymanov et al. 2020).

In Europe, a similar system of rationing the soil is used – soil screening value (SVs). It is divided into three levels of risk: insignificant (target value) – the concentration at which a substance or element does not affect the natural properties of the soil. An unacceptable (intervention value) – the maximum possible concentration that allows the use of soil for a particular type of economic activity. A medium or cautionary risk (middle, trigger value) – the average concentration between target and intervention, at which it is necessary to study the possibility of using the soil. In most European countries, these levels have different estimates depending on the natural conditions and geochemical background values. The levels of the SVs of the Netherlands are taken as the basis. The most similar level of risk of pollution in relation to Russia is the trigger value, it is similar to the MPC levels in Russia (Chernova & Beketskaya 2011; Kryatov et al. 2012; Huot et al. 2013).

The increased content of PAHs is characteristic of the soils near major streets, where, under conditions of a large flow of cars, there is a maximum supply and accumulation of PAHs in the upper soil layer. Prolonged exposure to a source of pollution, as well as the fact that PAHs are carried by air currents, has led to an increase in PAHs in the studied soils (Gennadiyev et al. 1990, 2004; Chukov et al. 2006; Lodygin et al. 2008; Abakumov et al. 2015; Abdel-Shafy & Mansour 2016).

The main sources of soil pollution for risky elements are emissions of pollutants into the atmosphere by transport, energy facilities and industrial enterprises. Metals accumulate relatively quickly in the soil and are very slowly removed from it (Khan et al. 2008; Ufimtseva et al. 2011; Abakumov & Maksimova 2012;

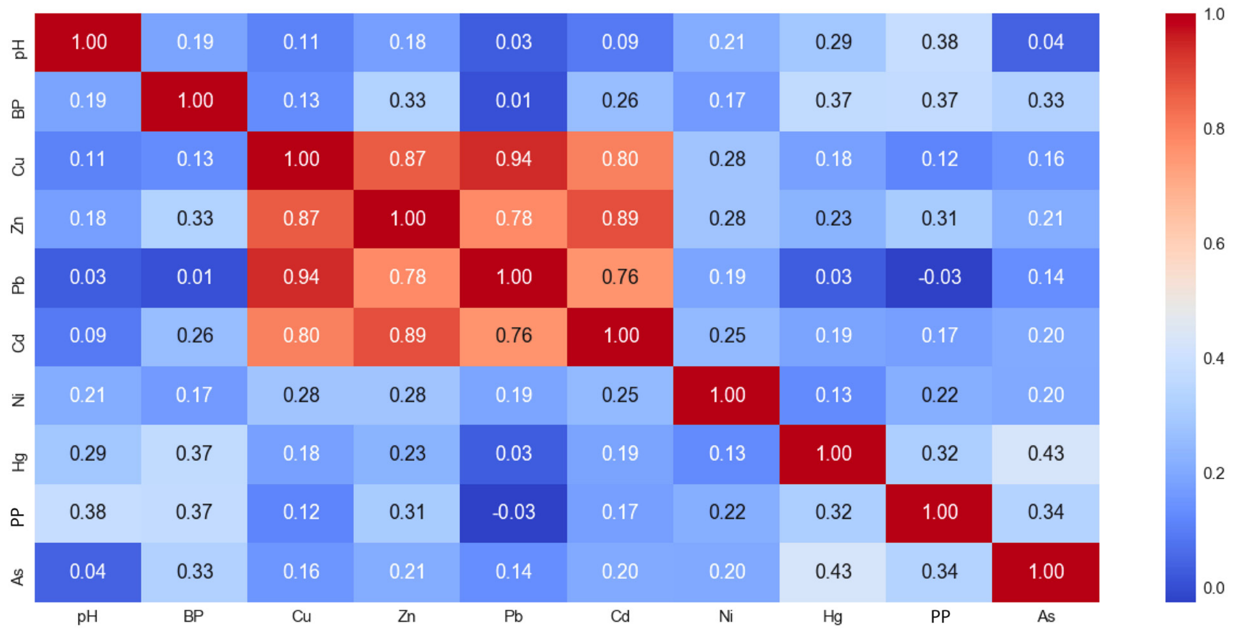

Figure 5. Spearmen's correlation diagram of the heavy metals, benzo(a)pyrene (BP), petroleum products (PP) and pH

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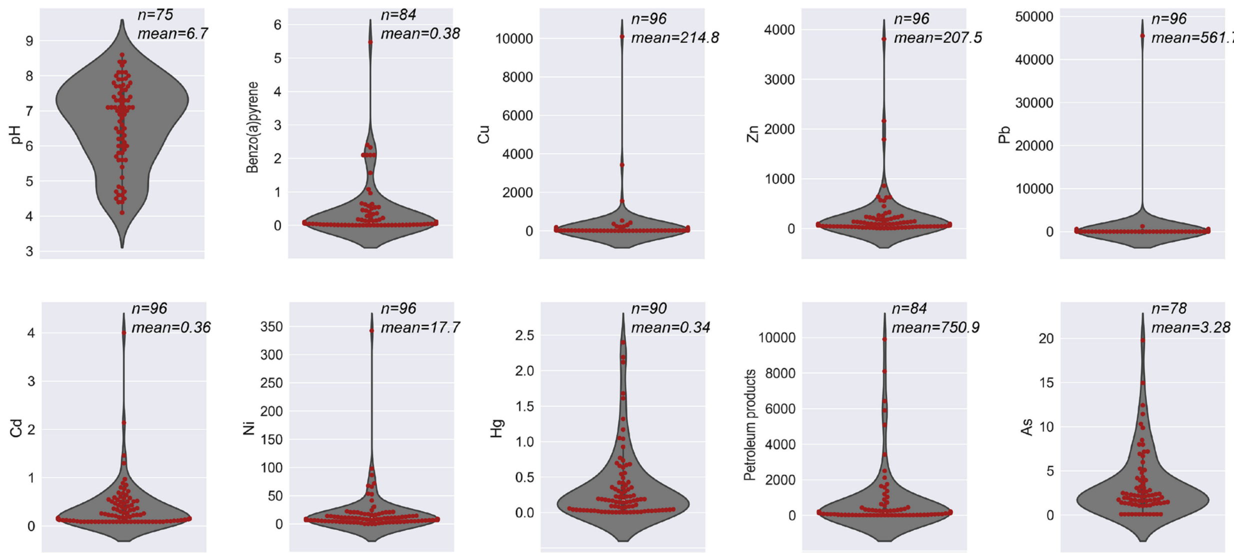

Figure 6. Violin plots of the pH, heavy metals, petroleum products and benzo(a)pyrene

Bogdanov 2014; Adama et al. 2016; Abakumov et al. 2019). The main pollutants of the city's soils are zinc, lead, copper, and chromium. The content and pattern of distribution of risky elements in the soils is related to their location, life duration, method of operation and their relative position to the roads, traffic intensity, and physical and chemical properties of the soils (Vodyanitsky 2010; Dymov et al. 2013; Kapelkina 2010; Bi et al. 2006; Li et al. 2014; Suleymanov et al. 2018).

Contamination of the soil by risky elements is carried out through their technogenic dispersion: with gas and dust emissions into the atmosphere during high-temperature technological processes (metallurgy, roasting of cement raw materials), as well as during the combustion of mineral fuels (coal, oil). The mass of risky elements very quickly reaches the surface of the soil. A significant part of them is included in the soil-forming process, a certain amount is absorbed by the vegetation and taken out with the surface groundwater runoff. As a result, technogenic geochemical anomalies of risky metals are formed, characterised by a rapid decrease in the concentration of metals from the source of pollution to the periphery (Vodyanitsky 1998; Wei & Yang 2010; Vodyanitsky & Yakovlev 2011; Vodyanitsky et al. 2012; Ji et al. 2019; Chen et al. 2005).

Statistical data. For the statistical data processing, we used a Spearmen's correlation diagram and violin plots (Figures 5 and 6). From the correlation diagram, a high relationship is observed between Cu and Pb (R = 0.94), Zn and Cd (R = 0.89) and Cu and Zn (R = 0.87). The descriptive statistics of the risky element concentrations are presented in Table 1.

This distribution is associated with homogeneous sources of input of these elements into the soil cover. Copper and zinc are quite common metals in the urban environment of large Russian cities, this is due to the use of these metals in metallurgy and the production of household goods based on them.

CONCLUSIONS

The impact of risky elements, benzo(a)pyrene and petroleum products to the soil pollution status of the urban soils in Saint Petersburg has been investigated. From the data obtained, it results that most of the soils in the districts of St. Petersburg are intensively influenced by risky elements, benzo(a)pyrene and petroleum products. Based on this, geochemical maps of the city's pollution were obtained. A high anthropogenic load and active rates of urbanisation negatively affect the soil pollution status of the city. A high excess of the permissible level of soil pollution by such risky elements such as Cu, Zn, Ni and Pb was revealed. The main sources of pollution in the urbanised area are exhaust gases, the industrial activities, construction work, as well as the use of contaminated soils for landscaping the city. Therefore, urban soils have a high risk to the health and life of its citizens. In relation to implementing effective reclamation measures, the use of a hydrodynamic method of cleaning with water or a reagent solu-

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tion, followed by drainage and purification of the wastewater can be recommended. In forest-park areas and on wastelands, it is recommended to use the phyto-extraction of pollutants by specialised plants. The data obtained could be used for further elaboration on environmental management systems in the highly urbanised ecosystem of Saint Petersburg, located near the Russian-Finland trans-border region.

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Received: July 14, 2020
Accepted: March 15, 2021
Published online: April 29, 2021