Biogeochemical assessment of soils and plants in industrial, residential and recreational areas of Saint Petersburg

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Soils and plants of Saint Petersburg are under the constant technogenic stress caused by human activity in industrial, residential, and recreational landscapes of the city. To assess the transformed landscapes of various functional zones, we studied utility, housing, and park districts with a total area of over 7,000 hectares in the southern part of the city during the summer seasons of 2016-2018. Throughout the fieldwork period, 796 individual pairs of soil and plant samples were collected.

A complex of consequent laboratory studies performed in an accredited laboratory allowed the characterization of key biogeochemical patterns of urban regolith specimens and herbage samples of various grasses. Chemical analyses provided information on the concentrations of polluting metals in soils and plants of different land use zones.

Data interpretation and calculation of element accumulation factors revealed areas with the most unfavorable environmental conditions. We believe that a high pollution level in southern city districts has led to a significant degree of physical, chemical, and biological degradation of the soil and vegetation cover. As of today, approximately 10% of the Technosols in the study area have completely lost the ability to biological self-revitalization, which results in ecosystem malfunction and the urgent need for land remediation.

Key words: biogeochemical cycles; soil-plant interaction; urban ecosystem; environmental quality; urban ecology; urban zoning

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Introduction. Studying soil and vegetation covers of urbanized areas is essential for assessing the ecological state of a city [4,7,9,12,21,44,45,47]. Thanks to its physical and chemical properties, the soil within a city accumulates a wide range of pollutants, becoming one of the key biogeochemical barriers for most pollutants, capturing them on the way from the atmosphere to ground and surface waters [3,14,24,51]. Soils and plants are an integral indicator of environmental wellbeing and at the same time a potential source of secondary pollution of the natural environment [5,15,27,34,39,46].

In the major part of urbanized areas, technogenic factors predominate in pedogenesis, forming specific Technosols, in many cases characterized by a high pollution level [8,11,17,18]. As a consequence, at the maximum degree of chemical pollution, the soil completely loses its capacity for productivity and biological self-purification, which inevitably leads to a failure of its ecosystem functions [13,29,48,50,52].

Most urban soils lack the required amount of macro and micro components for favorable plant growth conditions [10,19,31,33,49,50]. At the same time, the amount of accumulated polluting substances, including heavy metals, increases annually [2,6,16,22,23,35]. Atmospheric emissions by vehicles, energy facilities, and industrial enterprises, as well as de-icing of roads in winter are the main sources of soil pollution. Metals are accumulated relatively quickly by the soil, being very slowly removed from it, which is due to biogeochemical barriers in the soil cover [13,25,30,36].

In recent years, more and more attention has been paid worldwide to assessing the quality of soils; this is not only because of the environmental situation at hand, but also for making decisions on urban zoning issues: how to puzzle out where industrial, cultural, and other districts are safest to be [20,26,32,40,42,48,53]?
Target setting. The problem of soil and vegetation degradation is absolutely relevant for Saint Petersburg, a city with a rich history of multi-industry development accompanied by research institutions and centers.

In order to improve the environmental situation in the Russia's Northern Capital, city administration significantly rose the number of high-quality young trees planted from various nurseries in recent years. However, a significant proportion of seedlings die. The main cause of young trees drying out is unfavorable soil conditions and poisoning with anti-icing agents near highways.

To date, the garden and park facilities of Saint Petersburg occupy 10 thousand hectares of public land, of which 3 thousand hectares are urban forests and groves and 7 thousand are urbanized lands that need rehabilitation. Periodic monitoring observations on permanent test sites are carried out at 100 points, which corresponds to no more than 8% of the total green space area.

Thus, the relevance of the work associated with conducting a comprehensive ecological and geochemical assessment of the quality of soil and vegetation cover in industrial, residential, and recreational landscapes is not in doubt.

Materials and Methods. The authors were carrying out the work aimed at assessing the degree of technogenic load on the soil of various landscape and functional zones of Saint Petersburg during the field seasons of 2016-2018. Industrial, residential, and park areas located in the Moskovsky District of Saint Petersburg, located in the south-west of the city and covering an area of more than 7,000 hectares, were chosen as a study object.

The soil assessment technique included several stages:
- reconnaissance of the study area and drawing up a map-scheme of the planned soil sampling;
- sampling and field sample preparation;
- specimen processing in the laboratory;
- chemical analysis by atomic absorption and X-ray fluorescence spectroscopy;
- interpretation of the data obtained.

During the reconnaissance work, we found that potential sources of pollution include enterprises that form the Southern Industrial Zone, extending from the Obvodny Canal to Kuznetsovskaya street, unauthorized dumps at wastelands along the railway, as well as automobile and railway transport. It is important to highlight that the main traffic load is related to the active functioning of two major road arteries in the study area, i.e. the Moskovskoe and Kievskoe highways.

Soil sampling was conducted following the guidelines of ISO 10381-5:2005 Soil quality – Sampling – Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination (GOST R 53123-2008, according to the Euro-Asian Council for Standardization, Metrology, and Certification). In order to avoid accidental errors associated with the determination of unreliable values, sampling from the surface was carried out using the so-called envelope method on sites of 2×2 m. In total, 796 samples were taken during the fieldwork, which covered 70% of the territory of the Moskovsky District of the city. Among them, 18% of samples were taken in parks and groves, 50% in housing areas, and 32% accounted for industrial zones. The combined soil samples were delivered to the Common Use Center of the Saint Petersburg Mining University, where they were processed to the air-dry state, thoroughly mixed and quartered until a homogeneous sample weighing 500 g was obtained. Further sample preparation was carried out in accordance with certified methods of quantitative chemical analysis. Prior to the chemical analysis, we measured humidity in each sample using the A&D Weighing MS-70 Moisture Content Tester.

In the course of monitoring lithochemical studies, the maximum attention was paid to a group of inorganic toxicants, with special regard to the heavy metals, potentially dangerous at high concentrations.

To assess the specific anthropogenic impact, a biogeochemical assessment of the accumulation of heavy metals by vegetation was carried out. In general, vegetation cover reflects the combined impact of environmental pollution sources, since one group of the substances enters the plant via
root absorption, while the second comes through the aerial gas exchange of plants [37, 41, 50]. To assess the ecological state of the study area, herbage samples of various grasses were taken. Vegetation sampling sites were consistent with the sampling points of the soil cover. A combined biogeochemical sample weighed at least 200 g of raw material. Each sample was marked and placed in a special bag for transportation to the laboratory and subsequent analysis. Preparation of the selected vegetation samples consisted of sequential execution of the following operations: drying, grinding, ignition, and dissolving in a mixture of acids.

The analyzed rasters were obtained by the method of atomic absorption with flame and electrothermal atomization with the use of the Shimadzu AA-7000 spectrophotometer.

**Results and Discussion.** As a result of the survey of the Technosols in industrial, residential, and recreational areas of the Moskovsky District of Saint Petersburg, it was found that lead, cadmium, and zinc are the priority pollutants among heavy metals. The table shows the distribution of metals by group depending on concentrations. These metals were particularly noted when exploring general patterns of migration and accumulation of chemical elements in residential landscapes [1]. First, this is due to the fact that their geochemical cycles are largely altered under a complex technogenic impact on urban soils. Secondly, lead, cadmium, and zinc pose a possible public health threat in urbanized areas since the intake of polluting elements by a human body occurs most intensively in these landscapes [28, 29, 32].

### Soil cover categorizing according to accumulation levels of the most common potentially hazardous heavy metals in the study area

| Element | Below the Maximal Permissible Concentration (MPC) | 1-2-fold exceedance over the MPC | 2-5-fold exceedance over the MPC | >5-fold exceedance over the MPC |
|---------|-----------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
|         | Number of samples | % | Number of samples | % | Number of samples | % | Number of samples | % |
| Pb      | Industrial area | 120 | 15 | 310 | 39 | 318 | 40 |
|         | Residential area | 294 | 37 | 318 | 40 | 72 | 9 |
|         | Recreational area | 223 | 28 | 191 | 24 | 48 | 6 |

To assess the uniformity of the area distribution of the studied metals in the soil, the coefficients of variation of the elements were calculated for the soils of certain land use zones, %:

| Element | Functional zone | Pb | Cd | Zn | Cu | Ni | As | Hg |
|---------|----------------|----|----|----|----|----|----|----|
| Pb      | Residential    | 81 | 77 | 54 | 51 | 74 | 90 | 215 |
|         | Industrial     | 105 | 99 | 125 | 92 | 64 | 91 | 240 |
|         | Recreational   | 74 | 76 | 47 | 53 | 66 | 76 | 170 |

The results of the analysis of the coefficients of variation showed that the distribution of the studied elements in the soil is extremely heterogeneous; therefore, local sources of technogenic impact are the main pollution contributors, not affecting the district as a whole.

Along with the evaluation of each considered metal, the distribution of chemical element associations was analyzed separately [1, 38, 43, 52]. An association of chemical elements should be understood as a group of elements found in the study object in an amount different from the criterion level. We applied the integrated chemical pollution index $Z_c$ to quantitatively measure and assess
the association. The results of the lithochemical survey showed that soil contamination in the studied part of the Moskovsky District does not exceed the values typical for urbanized territories. Thus, ca. 10% of the territory are characterized by the extremely dangerous level of pollution, 35% are dangerous, 39% are moderately dangerous, and at 16% of the area the level is acceptable (Figure).

The biological accumulation factor, which is the ratio of the pollutant concentration in a plant to its concentration in the soil, was used to characterize the uptake capacity of plants and evaluate the barrier function of root and aerial parts. Thus, in the case of active barrier functions, the factor value does not exceed 1. With the unhindered flow of metal ions into plant organs, the factor is greater than or equal to 1. The values of the biological accumulation factor of priority pollutants for the studied plant samples are given below:

| Element Factor | Pb  | Ni  | Cr  | Mo  | Cu  | Mn  | Co  | Fe  |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Maximum        | 0.62| 3.53| 0.54| 15.95|16.89| 7.95| 3.54| 0.75|
| Minimum        | 0.36| 0.70| 0.26| 2.47 | 7.43 | 1.20| 0.25| 0.20|
| Average        | 0.50| 2.01| 0.37| 7.82 |10.74| 3.14| 1.51| 0.36|

The values of the biological accumulation factor indicate that Cu, Mo, Mn, and Ni tend the most to be accumulated in the vegetation cover.

**Conclusion.** The conducted litho- and biogeochemical studies have shown that the soil cover of the Moskovsky District of Saint Petersburg is experiencing a huge technogenic load. The most unfavorable environmental situation is observed in the northern part of the district. The presence of numerous sources of harmful emissions into the milieu, strengthened by traffic intensity, creates a potential threat not only to the natural environment but also to the population of the city. Motor transport, fuel and energy complex enterprises, as well as the chemical industry, are among the priority pollution sources of urban landscapes. Taking into account the prevailing wind directions, it can be seen that polluted air flows come to the study area from the industrially developed Kirovsky District and enterprises situated in the north-west of the Admiralteysky District.

Technogenic pressure significantly transformed the physical, chemical, and biological characteristics of the soil and vegetation cover of the Moskovsky District. As shown by the study, at least one tenth of the soil cover of this territory has completely lost the ability to biological self-restoration, which led to the failure of its ecological functions and the urgent need for reclamation and remediation.

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