ASSESSMENT OF THE ECOLOGICAL STATE OF URBANOZEMS OF MEGAPOLIS BASED ON THE LEVEL OF HEAVY METALS AND PETROLEUM PRODUCTS AND INTEGRAL TOXICITY OF SOILS

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Abstract

This paper presents the results of an expert assessment of the soil cover of Nizhny Novgorod (Russia) of various degrees of transformation to determine the level of concentrations of the most mobile (water-soluble) fractions of heavy metals (zinc, cadmium, lead, and copper), as well as the total content of petroleum products, followed by the identification of the level of integral toxicity of urbanozems. The research was conducted in April 2019 based on the Ecological and Analytical Laboratory of Monitoring and Environmental Protection of Minin University. The soil cover of the park territories of 7 city districts closest to industrial zones and highway lanes was studied. The level of accumulation in the soil layer of 0-15 cm of easily mobile fractions of zinc – 0.2-2.8% of maximum permissible concentration, cadmium – 18-101% of approximate permissible concentration, lead – 3.1-8.1% of the maximum permissible concentration, and copper – 0.03-0.20% of maximum permissible concentration was established. The most common territorial variability of the element was found for zinc and copper, which, first of all, is due to the uneven contamination of the soil cover with these ecotoxicants. The effect of accumulation of water-soluble fractions of heavy metals in soils on the manifestation of their toxic properties on the territory of the Switzerland Recreation Park and Dubki Park was determined by the increased content of zinc and cadmium, and by the high content of zinc and lead on the territory of the Coulibin Park.

Keywords: heavy metals; petroleum products; integral toxicity of soils; easily mobile compounds of ecotoxicants; territorial differences; urbanozems, urban area

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1. Introduction

The soil cover is one of the main system environments, which has the function of mass deposition of pollutants [1,2]. According to the level of ecotoxicants in soils, the degree of anthropogenic impact is judged both when they come into direct contact with the soil cover and when gas-dust particles settle on its surface from atmospheric air. From the point of view of environmental monitoring, when examining the ecological state of anthropogenically transformed territories, urbanozems are given priority [3, 4]. On the one hand, their soil-absorbing complex, regardless of the granulometric composition of the day horizons and the content of organic matter in them, has a potential absorbing capacity, which is a criterion for the degree of accumulation of pollutants. On the other hand, the cumulative effect of urban soils concerning ecotoxicants is strongly prolonged in time, which serves as an indicator of the presence of chronic pollution of the area [5,6].

The territory of Nizhny Novgorod (Russia) is no exception in terms of the presence of long-term pollutants in the soil cover among large cities [7,8]. The reason for this is the highly developed machine-building, petrochemical, chemical and other industries, the heat and power sector, and road transport networks, the activities of which are inevitably accompanied by gas and dust emissions, sewage (including from urban storm sewers), and the formation of solid waste [9-11].

According to the principles of environmental regulation of pollutants in soils [12,13], the determination of the concentration level of their most mobile compounds refers to particularly significant indicators. Mass transfer and turnover of pollutants in adjacent environments of the ecotope-biotope system has a high intensity in the conditions of the washing and periodically washing water regime of the territory, due to the sufficiently high rate of migration of water-soluble forms of ecotoxicants into the underlying horizons of the soil body and into groundwater, as well as due to their significant accumulation in the phytomass of urban green spaces [14, 15].

Identification of territorial differences in the level of the most mobile compounds of priority pollutants in the urbanozems of Nizhny Novgorod with subsequent analysis of the integral toxicity of the soil cover.

2. Methods

The expert assessment was carried out concerning the soils of 7 city districts: Nizhegorodskiy (Coulibin Park), Sovetskiy (65th Victory Square), Priokskiy (Switzerland Recreation Park), Sormovskiy (Sormovo Park), Kanavinskiy (1st May Park), Leninskiy (Dubki Park), and Avtozavodskiy (Avtozavodsky Park).

The above-mentioned park zones are as close as possible to industrial enterprises and highways of the city. They were selected as the evaluated territories. The soil cover is represented by urbanozems of various degrees and depths of technogenesis, among which physical transformation with signs of both chemical contamination and the presence of soil-like neoplasms (replantozem) dominates [1,1,16].

To identify the greatest mobility of pollutants, soil samples were taken during the maximum amount of spring precipitation (the first half of April 2019), potentially affecting the solubility of substances in the upper horizons of soils. Soil sampling was carried out from four test sites (10×10 m), laid evenly across the territory of each park, using the envelope method (5 point samples → 1 combined sample) evenly from a depth of 0-15 cm. The territorial location of parks in the city and selection sites is shown in Fig. 1.

Soil samples were delivered to the Ecological and Analytical Laboratory of Monitoring and Environmental Protection of Minin University and analyzed by determining the concentrations of easily mobile compounds of heavy metals (Zn, Cd, Pb, and Cu) in the form of extraction of their compounds by water extraction [17, 18]. Also, the content of the total amount of petroleum products and integral toxicity were determined in the samples.

The content of heavy metals in soils was determined using the TA-Lab polarograph by the inversion-voltammetric method, the content of petroleum products was determined using the FLUORATE 02–4M luminescent analyzer, integral toxicity was determined using the genetically engineered bacterium

Escherichia coli M-17 on the BIOTOX toxicity analyzer by the 10th bioluminescent biotesting method [19]. Mathematical processing of the research results was performed using the method of variational analysis in the Microsoft Office Excel 2007 software.

3. Results

The data in Fig. 1 reflect the content of water-soluble zinc and cadmium compounds in the soils of Nizhny Novgorod. It was revealed that the level of zinc mobility in urban soils was quite small relative to the level of the maximum permissible concentration (MPC $_{Zn}$ = 23.0 mg/kg), and the absolute values of the content of water-soluble fractions of the element varied from 0.2% to 2.8% of the MPC.

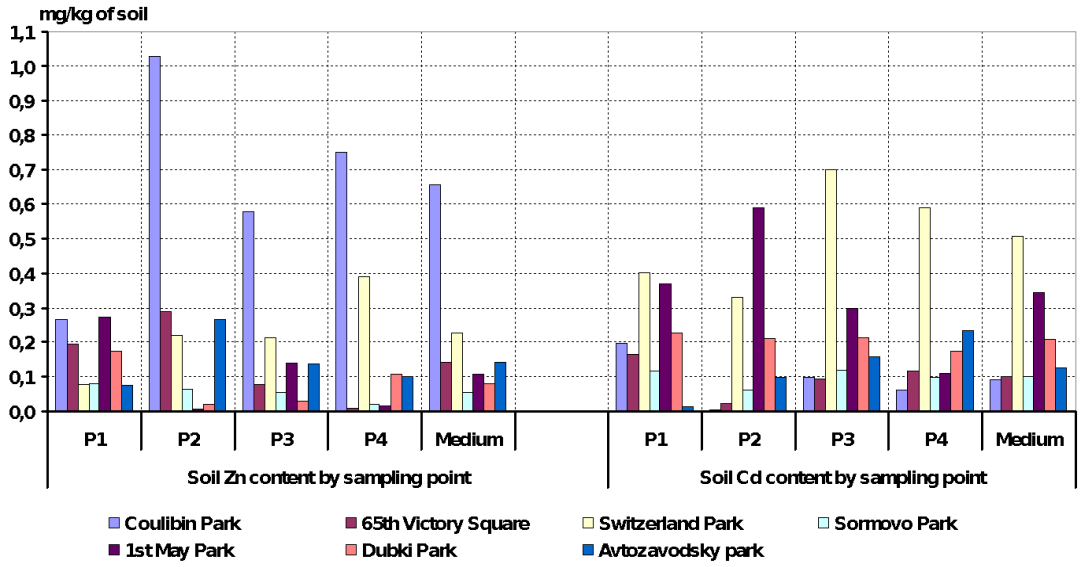

Fig. 1. Variability in the Concentration of Water-Soluble Compounds of Zinc (Zn) and Cadmium (Cd) in Urbanozems of Park Areas of the City of Nizhny Novgorod

Geographically, the smallest number of easily mobile zinc compounds was found in the urbanozems of Sormovskiy (Sormovo Park) and Leninskiy (Dubki Park) districts, and the largest – in the urbanozems of Nizhegorodskiy (Coulibin Park) and Priokskiy (Switzerland Recreation Park) districts. Inside, the territorial variation turned out to be maximal in the conditions of the 65th Victory Square, the Dubki Park, and 1st May Park, which, is due to the uneven contamination of territories, as well as the spatial heterogeneity of the soil cover.

The content of water-soluble forms of cadmium in the soils of the city turned out to be quite high – relative to the level of tentative permissible concentration $_{Cd}$ (0.5 mg/kg), its variability was in the range of 18% (Coulibin Park) up to 101% (Switzerland Recreation Park). The maximum accumulation of easily mobile forms of the element was established in the urbanozems of Priokskiy (Switzerland Recreation Park) and Kanavinskiy (1st May Park) districts; the smallest accumulation was detected in the soils of the Nizhegorodskiy, Sovetskiy, and Sormovskiy city districts. The variability of the indicator reached high values only in the territory of the Coulibin Park (up to 90%) and Avtozavodskiy Park (up to 74%), the V-indicator had more restrained values in other variants of the study.

Comparing the territorial accumulation of easily mobile compounds of lead and copper in urbanozems of the city (Fig. 2), first of all, it is necessary to point out the high variability of the copper content in soils relative to lead content. Thus, if the coefficient of variation was restrained concerning lead and took its maximum value once in the soil

cover of the territory of the 1st May Park (up to 80%), then concerning the accumulation of copper, the level of variation of the indicator across the territory turned out to be high and reached 83%-101% (Nizhegorodskiy, Priokskiy, Kanavinskiy, and Leninskiy districts).

With respect to sanitary and environmental standards (6.0 mg/kg by Pb; 3.0 mg/kg by Cu), the accumulation of water-soluble lead fractions in urbanozems of the city ranged from 3.1% (65th Victory Square) to 8.1% (Sormovo Park), and the accumulation of water-soluble copper fractions – from 0.03% (Avtozavodskiy Park) up to 0.20% (Square of the 65th anniversary of Victory and the Switzerland Recreation Park).

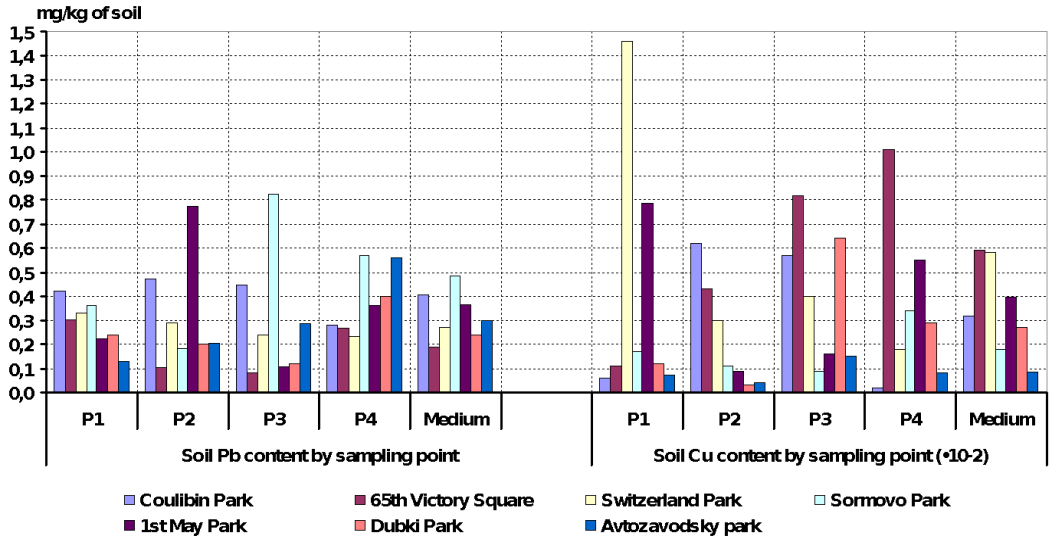

Fig. 2. Variability in the Concentration of Water-Soluble Compounds of Lead (Pb) and Copper (Cu) in Urbanozems of the Park Territories of the City of Nizhny Novgorod

The highest total content of petroleum products in urban soils, shown in Fig. 2, reached 19.13 mg/kg in the territory of the Dubki Park (Leninskiy district) and 15.81 mg/kg in the territory of the Switzerland Recreation Park (Priokskiy district).

The average concentration level of petroleum products in urbanozems (9.52 and 8.45 mg/kg) was established, respectively, on the territory of Coulibin Park and Avtozavodskiy Park. The minimum content of petroleum products was detected in the soils of the Sormovo Park (1.69 mg/kg), the 1st May Park (2.80 mg/kg), and the 65th Victory Square (4.36 mg/kg).

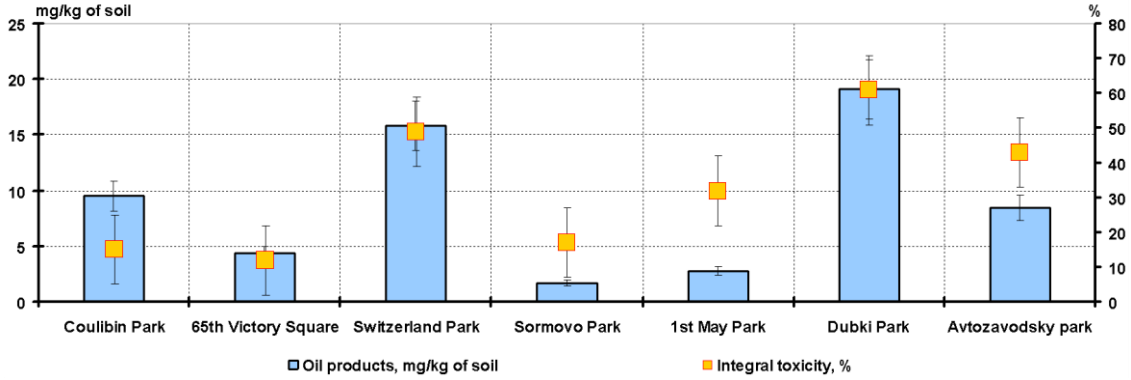

Fig. 3. Variability of the Concentration of Petroleum Products (Total) in Urbanozems of the City of Nizhny Novgorod and in Their Integral Toxicity

Regarding the integral toxicity of the city's soils (Fig. 3), first of all, it is necessary to indicate the presence of a trend of its dependence on the content of petroleum products in soils. In addition, the soils of the Dubki Park showed acute toxicity (group 3 of toxicity). The soils of the Switzerland Recreation Park, the 1st May Park, and the Avtozavodskiy Park showed medium toxicity (group 2), and the soils of the Coulibin Park, the 65th Victory Square, and the Sormovo Park – permissible toxicity (group 1).

4. Discussion

As indicated in modern studies [1,2,9,11], within the framework of regional environmental monitoring, the examination (reconnaissance assessment) of the soil cover for the presence of potential accumulation of easily mobile forms of pollutants is practically not carried out, as a result of which this issue is highly relevant and in demand for the subsequent identification of foci of vertical migration of ecotoxicants and their greatest chronic deposition, including in the form of insoluble matrices.

In general, it should be noted that of all the studied priority ecotoxicants of urban soils of Nizhny Novgorod, the content of easily mobile forms of copper turned out to be at the lowest level, which may be due to the relatively low content of the pool of copper-containing matrices in the initial soil cover [1,11]. Concerning lead compounds, it must be said that they are much slower than copper compounds, they pass into a water-soluble form and for the most part are acid-soluble forms for which sanitary and environmental standards of the federal level are established [12,20].

If we consider the effect of accumulation of water-soluble fractions of heavy metals in the soil cover on the manifestation of their toxic properties, then there is a possibility of such an influence on the territory of the Switzerland Recreation Park and Dubki Park from the increased content of zinc and cadmium, and increased content of zinc and lead on the territory of the Coulibin Park [21].

5. Conclusion

The examination of territorial differences in the level of concentrations of easily mobile forms of priority ecotoxicants, carried out in Nizhny Novgorod, showed the presence of relatively high content of water-soluble cadmium compounds – mainly in the mountainous part of the city, and lead – mainly in its riverine part.

The highest total content of petroleum products in urban soils was monitored in the Switzerland Recreation Park, located along one of the major highways (Gagarin Ave.), as well as in the Dubki Park, located in the industrial center and also experiencing man-made pressure in the form of gas and dust emissions from vehicles.

The integral toxicity of urbanozems, determined concerning the *Escherichia coli* M-17 biotest, is generally satisfactory, varies greatly across the city, and tends to depend on the number of accumulated petroleum products, as well as on the content of metals of the 1st class of toxicity – Zn, Cd, and Pb.

It is necessary to simultaneously monitor the degree of accumulation of mobile (acid-soluble) and gross forms of heavy metals to carry out a representative environmental assessment of the toxicity of Nizhny Novgorod urbanozems, as well as petroleum products, chlorides, sulfates, hydrogen sulfide, and acid-base state indicators in them. Such a set of indicators will allow not only identifying foci of soil contamination but also determining the functional dependence of integral toxicity on specific pollutants in certain soil differences.

6. Conflicts of interest

There are no conflicts to declare.

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