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The Study of Heavy Metal Impacts on Biotic Processes in the Soils of the Urban Ecosystem of the City of Rivne (Ukraine)

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ABSTRACT

The paper deals with investigating the impact of heavy metals on biotic processes in the soils of the urban ecosystem of the city of Rivne. The territories of the northern part of the city, where the main industrial enterprises are concentrated, and the southern part of the city, with a significant impact of fugitive emissions from the railway and road transport, are characterized by the highest level of soil contamination. The soils are assigned to class III of hazard of contamination with heavy metals with "medium impact level" on biological processes, soil contamination category is "hazardous". The western and central parts of the city are marked by a significant level of contamination, the soils belong to class IV of hazard with "moderate impact level" on biological processes, the soil contamination category is "moderately hazardous". The eastern part of the city is the least contaminated and is assigned to class V of hazard. The contamination level is "low", the soil contamination category is "permissible".

Keywords: heavy metal hazard level, soil biotic activity, monitoring.

INTRODUCTION

Urbanized territories are natural and anthropogenic systems and hold a special place in terms of the environmental problems acuteness, since they concentrate the maximum human impact on all components of the environment (Vovk, 2001). Significant anthropogenic pressure is exerted on water resources, the atmosphere, and soils. This requires the need to apply advanced technologies for municipal wastewater treatment (Malovanyy et al., 2016; Shmandiy et al., 2017), disposal of household and industrial waste (Tymchuk et al., 2020; Voytovych et al., 2020), treatment of hazardous industrial effluents (Malovanyy et al., 2019; Malovanyy et al., 2020), protection of the atmosphere (Lazaruk et al., 2020; Vaskina et al., 2020). But soil contamination in urbanized areas is of particular concern. The analysis of scientific literature shows that a significant number of works by foreign authors address the problem of comprehensive assessment of the condition of urban soils: Solgi et al. (2017), Vlad et al. (2016), Toth et al. (2013), as well as works of Ukrainian scientists: Pylypenko et al. (2015), Melnyk et.al. (2010, Melnyk et.al. (2015), Chornyi (2018) and others.

Thus, in the scientific literature of the United States, when assessing, three conditional categories of soil quality indicators are distinguished: chemical, physical, and biological. At the same time, American scientists insist on an integrative analysis of soil quality measurement data (Pankhurst et al., 1997). Great importance is attached to biological indicators which give an idea of the condition of the living component of the soil. According to the researchers' evaluations, biological indicators are the most informative parameters of soil functions. They dynamically respond to external anthropogenic and natural processes and show real-time changes in the soil. Among the biological indicators, the enzymatic activity of soils is also proposed (Pankhurst et al., 1997). Since the source of enzymes is the entire set of living organisms, the activity of enzymes indicates the intensity and orientation of biochemical processes in the soil and can be an indicator of the condition of its biota (Dick, 1994; Filina, 1999).

In the specialized literature (Pankhurst et al., 1997) the authors distinguish between the concepts of "soil quality" and "soil health" (Toth, 2008). Indicators of "soil health" characterize the general ecological and ecosystem functions of the soil, while indicators of "soil quality" reflect the parameters of soil fertility.

British scientists considered that the most important functions, which should be taken into account in comprehensive assessments of soil pollution, are the interaction of soil with the environment, the production of food and fiber, and the maintenance of biodiversity, etc. For 11 specified criteria that form the basis of soil assessment (these criteria may change), priority is given to the existing laboratory base and established methods for determining soil properties. According to the authors, the assessment indicators should be easily integrated into the national environmental monitoring system (The development…, 2006).

An analysis of the publications of European scientists shows a common understanding of the concept of soil quality assessment with American colleagues (Blum, 2005). Thus, the scientific basis of soil use in Europe was prepared and approaches were proposed for determining quality parameters related to soil functions, which are outlined in the "Thematic Strategy for the Protection of Soils of the European Union" (Thematic Strategy..., 2006). The authors of the Thematic Strategy for assessment identified the main seven functions of the soil which fall within the area of "production of food and other types of biomass – creation of habitats and storage of the gene pool of living organisms, physical and cultural environment for humanity" (Van-Camp et al., 2006). Most of these functions are interdependent, but the line "soil is a source of raw materials" can be traced, which raises concerns about the reduced ability of soils to perform their functions.

According to French scientists, the concept of soil quality depends on the ability of certain soils to perform their ecosystem and production functions and has no unambiguous definition (Jolivet at al., 2006). An important criterion for soils quality is their ability to adapt to modern climate change. The ecological assessment criteria, determined by French scientists regarding soil well-being indicators, include: the content of heavy metals (Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn) and the biological criteria of the national monitoring system (the numbers of certain groups of bacteria and fungi and representatives of soil fauna).

In Ukraine, modern approaches to solving the problem of soil contamination with heavy metals are covered in the works of Vovk (2001), Zhuk (2004), Sternik et al. (2016), Rybalova and Korobkina (2017), Malovanyy et al. (2022). The issues of accumulation and migration of trace elements in soils and plants are highlighted in the work of Myslyva et al. (2009). The main factors influencing soil contamination are described in the articles of Yelda (2015), Popovych et al. (2020), Bosak et al. (2022) and others.

Despite the fact that the number of proposed methods for assessing soil condition is significant, the issue is still problematic and requires a comprehensive study of the soil cover. The scale of difficulties in solving this issue is evidenced by the fact that there is not a single legal document in Ukraine that would legally approve this or that method of assessing the condition of urban soil cover and recommend it for general use in work. The aim of the paper is to find out, by means of monitoring studies, the degree of danger of heavy metals influence on biotic processes in soils.

MATERIAL AND METHODS

Determining the degree of danger of soil contamination with heavy metals in the city of Rivne was the result of a comprehensive monitoring study conducted at 25 sites in the city with different levels of anthropogenic load on the soil. (Malovanyy et al., 2022) provides data on the monitoring studies of soil contamination in the Rivne urban ecosystem, the studies address the issue of assessing the degree of danger of heavy metal impact on biotic processes in soils. The localization of soil sampling points and their substantiation in the territory of the city of Rivne is given in Table 1. Soil samples for determination of all parameters were taken from a depth of 0–20 cm at the same sites during the period 2014–2015 in accordance with our monitoring program (Malovanyy et al., 2022). Also used were materials on soil contamination with heavy metals from the operating database "Region". The study results describe the mobile form of heavy metals which were extracted with an ammonium acetate buffer solution with pH = 4.8. In total, we determined the content of eight heavy metals in 50 soil samples in key areas, of which 138 cellulase determinations were carried out in 46 samples. In 67 soil samples, 552 determinations of the catalase enzyme were performed. The cellulosic activity of the soil was determined by the percentage of mass loss of a linen fabric flap which was placed along the soil profile (Fedorets et al., 2009). For the determination, a flap of linen fabric measuring 10×30 cm was used (Fig. 1).

Table 1. Substantiation of soil sampling points in the territory of the city of Rivne

Test-site No.	Study areas	Substantiation of site localization
	Test-site No.1 (the northern part of the city of Rivne)	
1	House-building plant, Budivelnyky St., sanitary-hygienic zone	Production of concrete slabs, impact of industrial emissions of the enterprise
2	Flax-processing factory, sanitary-hygienic zone	Processing and converting flax, the impact of industrial emissions of the enterprise
3	High-voltage electric transmission line (ETL), Fabrychna St.	Influence of the electromagnetic field
4	OKKO petrol-filling station No.2, 18 Gagarin St., exit road to the city of Sarny	Impact of fugitive emissions of the petrol-filling station
5	Reinforced concrete products plant, Budivelnyky St.	Concrete production, impact of fugitive emissions
	Test-site No.2 (the eastern part of the city of Rivne)	
6	Radio plant, 25 D.Galytsky St., sanitary-hygienic zone	Impact of industrial emissions of the enterprise
7	Flowerbed in the eastern part of the city, 4 Academician S. Demianchuk St.	Impact of motor transport emissions
8	OLAS petrol-filling station No.1, 108 Kyivska St.	Impact of fugitive emissions of the petrol-filling station
9	Prometheus enterprise, 25A D.Galytsky St., sanitary-hygienic zone	Production of copper-enamel wire, impact of the enterprise emissions
10	Vegetable garden plots, Vidinska St., within the sanitary-hygienic zone of the radio plant	Impact of industrial emissions of the radio plant
	Test-site No.3 (the western part of the city of Rivne)	
11	School No.23, the territory along Yuvileyna St.	The territory of the school, the impact of motor transport emissions
12	Khimik park, Kniaz Ostrozhky St.	Public recreational area
13	OLAS petrol-filling station No.2, 18 Mlynivska St.	Impact of fugitive emissions of the petrol-filling station
14	Vegetable gardens near Makarov St. (Yuvileyne settlement)	Impact of motor transport emissions
15	Roadside, 20m from the road, exit from the city to the airport	Impact of motor transport emissions
	Test-site No.4 (the southern part of the city of Rivne)	
16	Detour to Basiv Kut, 30 m from the road	Impact of motor transport emissions
17	Secondary school No.14, 34 Zaliznychna St.; Basiv Kut district	The school territory
18	Territory of brick-making plant No.2, Dvoretska St.	Brick production, impact of industrial emissions
19	Vegetable bed of the residential sector, Fedin St.	Territory of one's own household (vegetable bed)
20	Railway right-of-way land, Zdolbunivska St., 50 m from the railway track	Impact of railway transport emissions
	Test-site No.5 (the central part of the city of Rivne)	
21	The Sonechko kindergarten No.3, 54 16-th Lypnia St.	The territory of the kindergarten
22	Taras Shevchenko Park, relaxation area	Recreational area, background site, rest area for people
23	Rivne high-voltage equipment plant, 16 Bila St., sanitary-hygienic zone	Impact of industrial emissions of the enterprise
24	The territory of the hydropark, the city center	Recreational area
25	Railway right-of-way land, Dvoretska station, 50 m from the railway track	Impact of railway transport emissions

The determinations were performed in three-fold repeatability. The degree of decomposition of the linen cloth was determined after 30 days, and the intensity of the decomposition process was estimated according to Table 2. The activity of soil catalase was determined by the gasometric method based on the amount of molecular oxygen which was released during the decomposition of hydrogen peroxide in the process of its interaction with the soil. The determination was carried out according to the standard method (Fedorets et al., 2009) under conditions close to natural ones ($CaCO_3$ was not added to the sample during titration). The assessment of the degree of soil enrichment with the enzyme is set according to the scale of Table 2. The level of soil contamination with heavy metals was determined according to the following criteria: the concentration factors (C_f) of the chemical substance and the total contamination index (TCI) by the formulas $C_{fi} = C_i / C_{fi\ and\ TCI\ =} \sum C_{fi} \cdot k_i$ (Malovanyy et al., 2022).

The assessment of the hazard level of soil contamination with a complex of metals in terms of TCI was carried out according to the assessment scale developed and tested by the authors of the article (Table 3). The following methods were used in the course of the study: field, laboratory, analytical, calculation, graphical). The processing and analysis of the obtained data was carried out by methods of mathematical statistics (correlation and regression analysis) using modern computer programs. Correlation relationships were

Fig. 1. Specimens of linen cloth after 30 days of exposure in the soil

Table 2. Scale for assessing soil enrichment with enzymes

Cellulase enzyme		Catalase enzyme	
The extent of the cellulose decomposition process, %	Intensity of the cellulose decomposition process	Catalase, ml O_2/g per min.	Degree of soil enrichment with enzyme
<10	Very low	Less than 1	Very poor enrichment
10–30	Low	1–3	Poor enrichment
30–50	Medium	3–10	Medium-level enrichment
50–80	High	10–30	Enriched
> 80	Very high	More than 30	High-level enrichment

Table 3. Classification of urboedaphotopes according to the consequences of contamination with heavy metals

Hazard classes	TCI value	Level of impact on biological processes,%	Assessment of the impact level and condition of urboedaphotopes	Soil contamination category
I	>128	> 60	Very high level of impact, low soil biological activity	Catastrophic
II	76–128	31–60	High impact level	High hazard level
III	33–75	26–30	Medium impact level	Hazardous
IV	17–32	10–25	Moderate impact level	Moderately hazardous
V	< 16	< 10%	Low impact level, soil biological activity is high, minor contamination with heavy metals	Permissible

identified between soil contamination with heavy metals and soil biotic parameters, and correlation and determination coefficients were determined. Student's t-test was applied to check the permissible values of experimental errors.

RESULTS AND DISCUSSION

Control over soil contamination with heavy metals of the city was carried out for 3 elements of hazard class I (cadmium, lead, zinc), 4 elements of hazard class II (cobalt, copper, nickel, chromium) and for 1 element of hazard class III (manganese). The study on the intensity of the cellulose decomposition process and the determination of the degree of soil enrichment with the cellulase enzyme were carried out in each of the 25 specified sites (Table 4). Catalase is known to be the most sensitive of all the enzymes studied, that is why its activity was used as a criterion for assessing the recovery of soil functions, Table 5.

The level of soil contamination is determined by the value of the concentration factor (C_f), the assessment of the soil contamination level is carried out by the total contamination index (TCI) (Fig. 2). The study was conducted in 2 stages. At the first stage, soil contamination with heavy metals was monitored (Malovanyy et al., 2022). The second stage of monitoring consisted in examining the biological component of the soil. To study the biotic activity of the soil, we proposed a set of indicators that are representative for conducting monitoring studies. Practice has shown that there is no need to determine an unreasonably large number of indicators, but it is sufficient to determine the most informative ones, characterizing the biotic activity of the soil and

Table 4. Cellulosic activity in Rivne soils

Value	Cellulosic activity, %	Assessment of cellulosic activity of the soil	
		Degree of soil enrichment with enzyme	Intensity of cellulose decomposition process
Test-site No.1			
Maximum	22.57 ± 2.42	Very poor enrichment	Low
Minimum	8.37 ± 0.8	Very poor enrichment	Very low
Test-site No. 2			
Maximum	31.87 ± 2.47	Poor enrichment	Medium
Minimum	7.3 ± 0.66	Very poor enrichment	Very low
Test-site No. 3			
Maximum	34.87 ±2.1	Poor enrichment	Medium
Minimum	6.87 ± 0.85	Very poor enrichment	Very low
Test-site No. 4			
Maximum	45.8 ± 5.67*	Medium-level enrichment	Medium
Minimum	11.27 ± 1.33	Very poor enrichment	Low
Test-site No. 5			
Maximum	42.6 ± 1.2	Medium-level enrichment	Medium
Minimum	14.47 ± 0.9	Very poor enrichment	Low

Table 5. Values of catalase activity in urboedaphotopes of the city of Rivne

City area under study	Catalase activity, ml O_2/g/min			Degree of soil enrichment with enzyme (average values)
	Maximum values	Minimum values	Average values	
Test-site No.1	4.17 ± 0.06	1.60 ± 0.2	2.62 ± 0.18	Poor enrichment
Test-site No.2	5.63 ± 0.21	1.63 ± 0.06	3.12 ± 0.20	Medium-level enrichment
Test-site No.3	4.93 ± 0.61	1.53 ± 0.06	2.84 ± 0.22	Poor enrichment
Test-site No.4	4.27 ± 0.7	1.37 ± 0.15	2.55 ± 0.33	Poor enrichment
Test-site No.5	3.30 ± 0.03	1.57 ± 0.06	3.16 ± 0.18	Medium-level enrichment

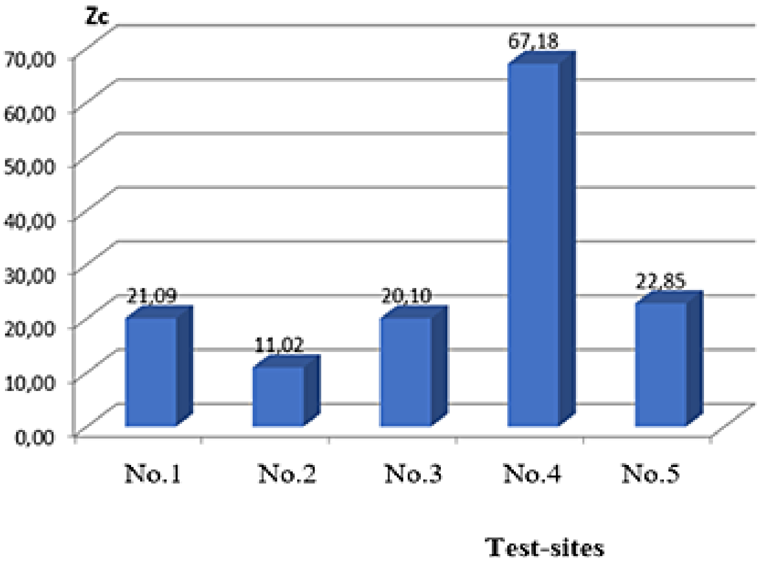

Fig. 2. Average values of the total contamination index for mobile form of heavy metals in urboedaphotopes of the city of Rivne

its toxicity. In our opinion, such indicators are: cellulose activity and catalase activity as well as determination of soil toxicity. They complement each other in soil monitoring studies.

When choosing test-sites for conducting studies, the following categories of land use in the city of Rivne were taken into account:

- urban and private development land – residential area;
- public land – industrial zone;
- land of the natural and recreational zone;
- agricultural land;
- reserve land

The main criteria for selecting indicators for monitoring were as follows:

- informative value of the indicator (correlation between the indicator and anthropogenic
- factor;
- high sensitivity of the indicator and good reproducibility of results;
- simplicity, low labor costs and high speed of determination;
- prevalence of research methods in Ukraine and abroad.

The results of the study show that the degree of soil enrichment with the cellulase enzyme in 76% of the cases is defined as “very poor” with “very low” and “low” intensity of the decomposition process. Thus, in 28% of the studied samples, the intensity of cellulose decomposition was defined as “very low”, in 48% – “low” and in 24% – medium”. Analyzing the obtained data on the average values of cellulosic activity of the city’s soil, it should be noted that the anthropogenic impact of industrial enterprises is confirmed by the results of the studies (Fig. 3).

Test-sites No. 2 and No. 5 were found to be the least contaminated, the values of the indicators of cellulosic activity of the soil being 23.3% and 22.55%, respectively. The most polluted are test-sites No. 1 and No. 4, where the degree of decomposition of linen cloth was half as much: 10.05±3.4–11.08±1.25%, respectively. In the conditionally background control territory of the city, the indicator of cellulosic activity of the soil was 42.6 ± 1.2%, the decomposition process was assessed as “medium”, and the degree of soil enrichment with the enzyme was “enriched”. The difference between the main and control groups of values was 2.776 and is statistically reliable, with an error value of no more than 5% ($P \leq 0.05$).

According to ecotoxicological standards, the level of pollution impact on biological processes is to be determined by the deviation in the activity of biological processes (Fedorets et al., 2009). In the study territory of the city of Rivne, we established such deviations within 19.30–32.55% of the background values (Table 6).

The biological role of the catalase enzyme is to protect organisms from the harmful effects of peroxide compounds formed during intracellular oxidation. The toxic effect of heavy metals on the soil microflora leads to inhibition of the enzyme activity. It was found that the activity of catalase

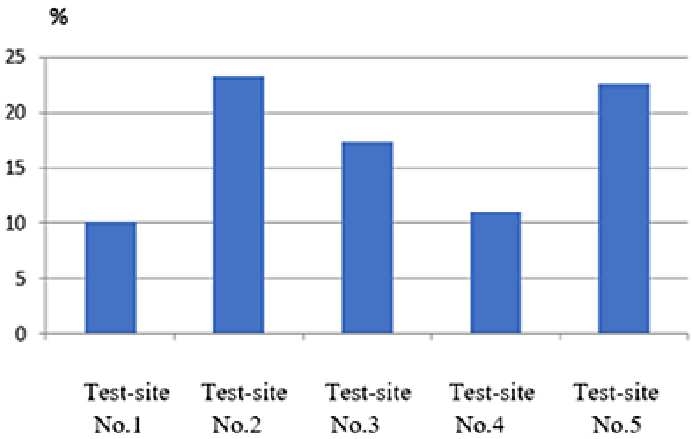

Fig. 3. Average values of cellulosic activity of urboedaphotopes in the city of Rivne

Table 6. Deviations in the activity of biological processes of the cellulase enzyme in urboedaphotopes of the city of Rivne

City area under study	Cellulosic activity of the soil, %	Deviations in the activity of biological processes, %	Level of anthropogenic load impact
Test-site No.1	10.05 ± 3.4	32.55	Hazardous
Test-site No.2	23.3 ± 5.1	19.30	Moderately hazardous
Test-site No.3	17.33 ± 6.42	25. 27	Hazardous
Test-site No.4	11.08 ± 1.25	31.52	Hazardous
Test-site No.5	22.55 ± 5.12	29.05	Hazardous

in the soil in the territory of the city in 60% of the study sites is from 1.33±0.14 ml O_2/g/min. up to 2.63±0.06 ml O_2 /g/min., and the degree of soil enrichment with the enzyme is described as "poor", and in 40% – "medium" (Fig. 4).

Based on the results of the study, the deviations of biological processes in the soil were calculated and the level of anthropogenic load impact was determined by the average values of catalase activity indicators, Table 7.

Thus, deviations in the activity of the catalase enzyme in soils at test-sites No. 2 and No. 5 are within 48% with a "hazardous" level of impact. The "high hazard level" of anthropogenic impact on the activity of the catalase enzyme was found out at test-sites No. 1, No. 3, and No. 4; the deviation in the activity of biological processes in soils significantly exceeds 50%. In the conditions of the city of Rivne, emissions from individual industrial enterprises containing heavy metal compounds significantly affect the activity of soil enzymes. This fact is confirmed by the results of the analyses, according to which the lowest values of enzymes with the

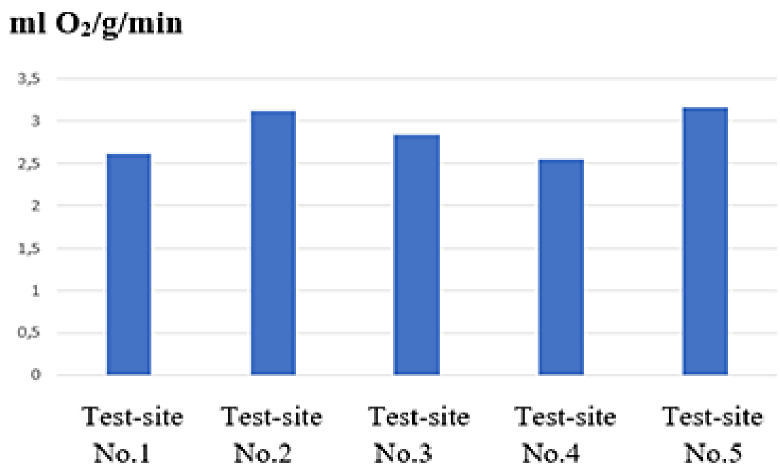

Fig. 4. Average values of catalase activity of urboedaphotopes in Rivne

Table 7. Deviation of the activity of biological processes of the catalase enzyme in urboedaphotopes in the city of Rivne

City area under study	Catalase activity, ml O_2/g/min	Deviation in the activity of biological processes, %	Level of anthropogenic load impact
Test-site No.1	2.62 ± 0.18	56.8	High hazard level
Test-site No.2	3.12 ± 0.20	48.6	Hazardous
Test-site No.3	2.84 ± 0.22	53.2	High hazard level
Test-site No.4	2.55 ± 0.33	58.0	High hazard level
Test-site No.5	3.16 ± 0.18	47.9	Hazardous

highest values of deviations in biological processes were recorded in the urboedaphotopes of test-sites No. 1, No. 3, and No. 4.

For a complete picture, the relationship between soil contamination with heavy metals and indicators of the biotic functions of the soil in the city of Rivne was investigated. The analysis of the dependence shows a close correlation between the total contamination index for mobile forms of heavy metals and the activity of cellulase and catalase of the soil. The correlation between the values of soil cellulosic activity and the total contamination index is close R = -0.808. The dependence is described by the equation of a 3rd-order polynomial with a coefficient of determination of 0.8583 (Fig. 5).

For the total contamination index of the mobile form of heavy metals with catalase activity in the soil, the correlation coefficient is R = -0.799. The dependence is described by the equation of a 3rd-order polynomial with a coefficient of determination of 0.7509 (Fig. 6). It was found that the highest total contamination index for the mobile form of heavy metals was recorded in the soil of

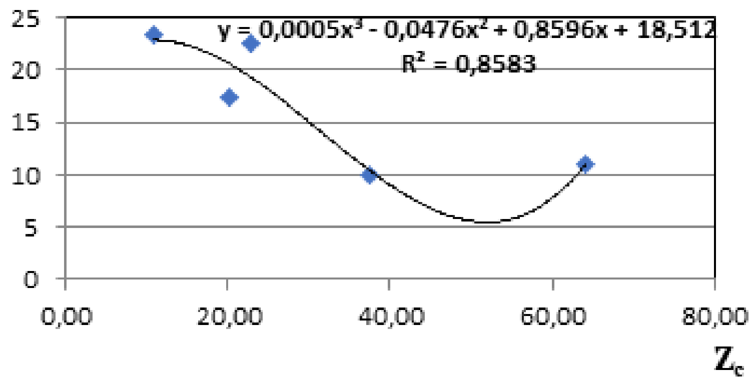

Fig. 5. Dependence of the indicator of cellulosic activity of the soil on the total contamination index for the mobile form of heavy metals

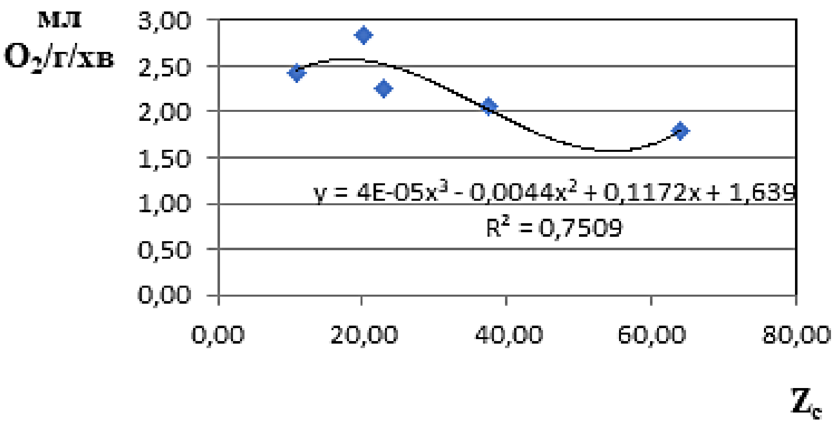

Fig. 6. Dependence of the indicator of soil catalase activity on the total contamination index for the mobile form of heavy metals

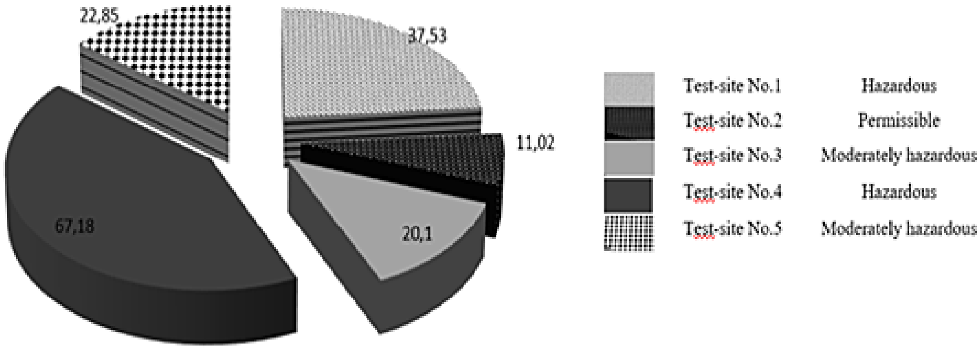

Fig. 7. Hazard level of heavy metal-contaminated soils in the city of Rivne

test-site No. 4, which is 67.2, and the lowest index is in the soil of test-site No. 2, which is 11.0, with a permissible limit of 16. The hazard level of soil contamination in the city with a mobile form of heavy metals is characterized from “permissible” to “hazardous” (Fig. 7).

Based on the conducted monitoring studies, the hazard classes of urban soil contamination were determined (Table 3). It was found that the soils are within the range of hazard classes III–V of heavy metal contamination with “medium”, “moderate” and “low” levels of impact. The soil contamination category ranges from “hazardous” to “permissible” at the studied test-sites. The results of the study can be used to develop recommendations and additional environmental protection techniques to minimize harmful effects on soils as a supplement to the functioning Regional Program for the Development of Land Relations in the city of Rivne for the period 2016–2025.

CONCLUSIONS

As a result of the studies, it was found that the most representative indicators for conducting comprehensive monitoring of urboedaphotopes in the city of Rivne are as follows: cellulosic activity, catalase enzyme activity, and soil toxicity. The degree of soil enrichment with the cellulase enzyme in 76% of the study sites is “very poor enrichment” with “very low” and “low” intensities of the cellulose decomposition process. Deviation in the activity of biological processes is within 19.3–32.6% of the background values with a close correlation between the values of cellulosic activity and the heavy metal concentration factor, R = -0.808. The degree of soil enrichment with catalase enzyme in 60% of the samples is defined as «poor enrichment», in 40% – «medium-level enrichment». The deviation of the biological processes of catalase activity is found to be in the range of 48–58%, the level of anthropogenic load impact is “hazardous” and “high hazard level”. The correlation between the values of catalase activity indicators and the concentration factor of heavy metals is close, R = -0.799.

The danger level of soil contamination in the city of Rivne with heavy metals is found to be: test-sites No. 1 and No. 4 – hazard class III, “medium-level impact” on biological processes in the soil, category of soil contamination – “hazardous”; test-sites No. 3 and No. 5 – hazard class IV, “moderate-level impact” on biological processes in the soil, category of soil contamination – “moderately hazardous”; test-site No. 2 – hazard class V, “low-level impact” on biological processes, soil contamination category – “permissible”. Based on the results of the monitoring studies, a classification of soils according to the consequences of contamination with heavy metals was proposed.

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