

Contamination of Soils with Heavy Metals in the Urban Ecosystem of the City of Rivne

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ABSTRACT

The paper analyzes the problem of soil cover contamination of the urban ecosystem with heavy metals. The work is based on the authors own long-term monitoring studies. The main sources of soil contamination are identified – industrial enterprises and motor transport. The content of total and mobile forms of Cu, Ni, Pb, Cr, and Zn in the soils of the city territory was found out. The concentration factors (C_f) of heavy metals and their total contamination indexes (TCI) were determined. The highest C_f values for the total form of heavy metals belong to zinc (up to 25.1). At 61.1% of the study sites, the C_f values of zinc are above 9.0. At 83.3% of the sites, the C_f values for the total form of copper content are in the range of 6.0–22.1. The results of the studies indicate high average C_f values for lead and chromium at the majority of the sites. The highest maximum and average C_f values for the mobile form for all heavy metals were found at test-site No. 4. As a result of the studies, it was found that the average values of the total contamination indexes for the total form of heavy metals exceed the permissible level by 1.6–2.7 times. For the mobile form of heavy metals, the average values of the TCI are within the permissible limits, except for test-site No.4, where an excess of 3.7 times is recorded. It is found that the soils of the northern and southern parts of the city are the most contaminated, the least contaminated are soils of the eastern part of the city.

Keywords: soil cover, urban ecosystem, heavy metals, test-site, contamination.

INTRODUCTION

Maintaining the environmental safety of urban eco-systems has recently become a problem of considerable importance due to the progressive increase in anthropogenic load. In this regard, it is important to prevent pollution of the urban ecosystem from solid waste disposal sites (Popovych et al., 2020, Voytovych et al., 2020), it is of great importance to ensure the environmental safety by proper municipal wastewater treatment (Malovanyy et al., 2016, Shmandiy et al., 2017), to introduce wastewater sludge utilization technologies (Tymchuk et al., 2020). An important

role is assigned to monitoring the condition of surface waters (Odnorih et al., 2020) and the processes of soil cover degradation which have recently increased in Ukraine; also, it should be noted that heavy metals rank next to pesticides in terms of the degree of danger of soil contamination. In high concentrations, heavy metals adversely affect the functions of natural ecosystems changing the soil biocoenosis and suppressing its activity (Breininger et al., 2022, Gryshko et al., 2012). Under the influence of stationary and mobile sources of pollutant emissions, local areas of soil contamination with heavy metals are formed (Achasova et al., 2003). The volumes of heavy

metals influx are ten times higher than their background concentrations in the soil.

The issue of contamination of soils in large cities with heavy metals and the assessment of their impact on soil processes is the subject of a number of studies (Grineva et al., 2021, Melnyk et al., 2010, Plyaskina et al., 2009). Accumulation and migration of trace elements in soils are described in the works of Ya.V. Genyk (Genyk., 1994), T.N. Myslyva, (Myslyva et al., 2009), O.H. Chaika (Chaika et al., 2018) and other authors (Shepelyuk et al., 2019).

The soil reflects the level of long-term anthropogenic influence, because it practically does not have the ability to quickly clean up. Heavy metals accumulate in the surface layer of the soil, are deposited and are characterized by low migration activity. Self-cleaning of the soil is a very slow process, and the soil contamination persists for decades (Makarenko et al., 2007, Myslyva et al., 2009).

Control over soil contamination with heavy metals is mainly carried out by 2 elements of toxicity class 1 (lead and zinc) and 3 metals of toxicity class 2 (nickel, chromium, copper) (Myroshnychenko et al., 2017). Identifying the degree of soil contamination with heavy metals is a difficult task. Heavy metals are found in soils in the form of various compounds that can transform and change from one form to another.

The natural soil cover of the territory of the city of Rivne is practically not preserved; during the long history of the city existence, the soil has been repeatedly transformed, drained or artificially filled up. In the floodplain of the Ustya River in the northern and southeastern outskirts of the city, as well as locally in the central part, there are eutrophic bogs.

The authors set the task of conducting an analysis of soil contamination with heavy metals based on the data of monitoring studies of the territory of the Rivne urban ecosystem.

MATERIAL AND METHODS

This paper is based on the analysis of the authors' own data obtained as a result of monitoring studies on the soil of the city of Rivne during the period 2002–2017. The study of the content of heavy metals was carried out in the areas of the city with different degrees of anthropogenic load. 230 soil samples were taken, 1,893 determinations of heavy metals were performed. A quantitative analysis of soil contamination was carried out as follows: Cu, Ni, Pb, Cr, Zn on the C115M-1 atomic sorption spectrophotometer with software calculation of measurement results in the accredited department of instrumental and laboratory control of the State Environmental Inspectorate in Rivne region. The study results characterize the total and mobile form of elements. The total form of heavy metals was extracted with 1 M HNO₃, the mobile form was extracted with an ammonium acetate buffer solution with pH = 4.8.

The level of soil contamination with heavy metals was determined according to the following criteria: the concentration factor of the chemical substance (C_f) and the total contamination index (TCI).

C_f is determined by the ratio of the actual content of heavy metals in the soil to the background content:

$$C_{fi} = C_i / C_{bi} \quad (1)$$

where: C_i – the actual content of the contaminant in the soil, mg/kg;

C_{bi} – the background content of the contaminant in the soil, mg/kg.

TCI is defined by the formula:

$$TCI_i = \sum_{i=1}^n C_{fi} k_i \quad (2)$$

Table 1. Determination of the coefficient by harm indexes

Characteristics of the contaminant	Coefficient by harm indexes
The content of chemicals in the soil exceeds the content of background forms, but not higher than the maximum permissible concentration (MPC)	k = 1.0
The content of chemicals in the soil exceeds their maximum permissible concentration according to the limiting general sanitary, migration water and migration air harm indexes, but is lower than the permissible level according to the translocation index	k = 1.1
The content of chemicals in the soil exceeds their maximum permissible concentration at a limiting translocation harm index	k = 1.2
The content of chemicals exceeds the maximum permissible concentration in the soil by all harm indexes	k = 1.3

where: n – the number of contaminants;
 C_{fi} – the concentration factor of each n -th component of contamination;
 $k_i = 1,0$ and is determined by the harm index, Table 1.

In the course of the study, field, laboratory, analytical, and calculation methods were applied. Processing and analysis of the obtained data was carried out by methods of mathematical statistics using modern application software.

RESULTS AND DISCUSSION

A prerequisite for determining the priority areas for monitoring the city’s soils was the availability of the results of analytical control of regional monitoring in the network of soil condition observations in the operating database “Region” of the Department of ecology and natural resources of the Rivne regional state administration. The entire territory of the city was conditionally divided by us into five experimental sites (test-sites) located in different parts of the city. Within each test-site, five plots were differentiated which are at different distances from the main sources of soil contamination (Methodological recommendations..., 2007).

When choosing plots for control, the following principles were followed:

- to survey all the soils of the city territory;
- to make maximum use of available informative material;
- to use the study results for further investigation of the Rivne urban ecosystem.

When studying the soil contamination with heavy metals in the city of Rivne, the territories of sanitary protection zones of the largest industrial enterprises of the city (flax-processing factory, radio plant, house-building plant, high-voltage equipment plant, reinforced concrete products plant, «Prometheus» enterprise, brick-making plant) were examined and analyzed. Also examined were right-of-ways for the railway, highways and the land for petrol-filling stations, the areas of public use and recreation – parks (Shevchenko park, Khimik park, and Hydropark), the minipark in Academician Demianchuk street, the Sonechko kindergarten, two schools – No.23 and No.14) and the agricultural land within the residential zone of the city, Figure 1.

At each plot, soil samples were taken at five points from a depth of 20 cm, quartered, and the required amount of soil sample was taken for analyzing in an accredited laboratory.

The methods according to which heavy metals were identified in the soil samples corresponded to the regulated “List of methods for measuring the composition and properties of samples of

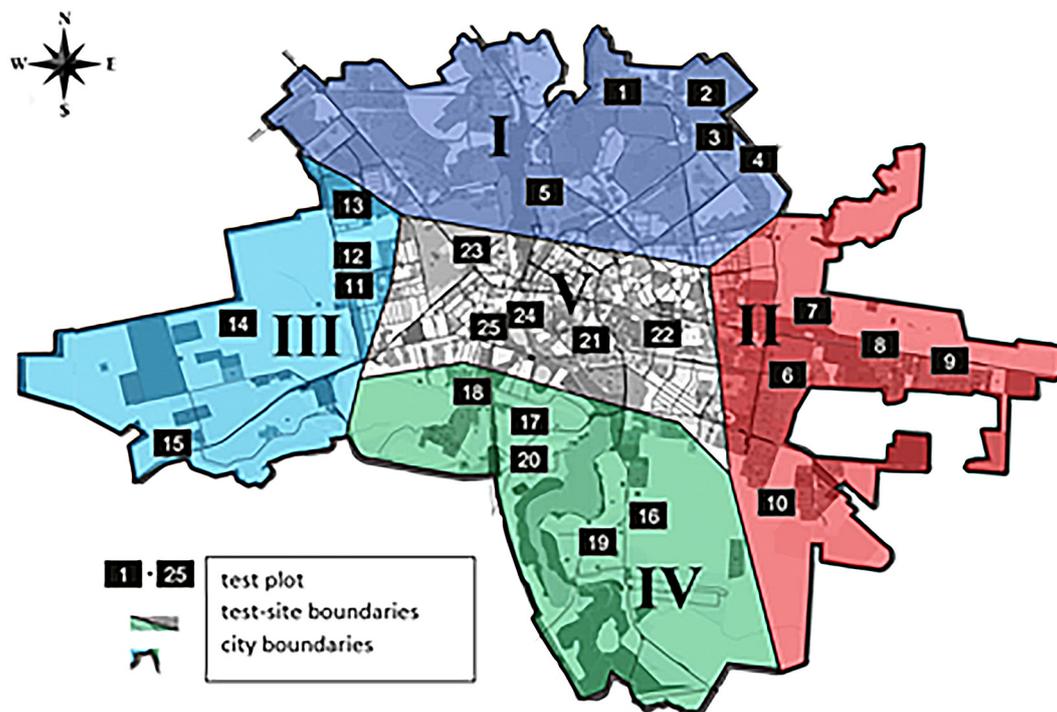


Figure 1. Schematic map of soil sampling points in the territory of the city of Rivne

Table 2. Average values of the background content of heavy metals in the soils of the urban ecosystem of the city of Rivne, mg/kg

Form of content	Cu	Ni	Pb	Cr	Zn
Total	1.2	2.7	2.8	1.9	3.0
Mobile	0.4	1.3	1.1	0.6	1.9

environmental objects temporarily approved for use by the State environmental inspectorate of Ukraine” (DSTU 4770.1-9:2007..., 2007).

The analysis of the obtained results of the study showed that the average values of heavy metals indexes of both total and mobile forms in the study territory of the Rivne urban ecosystem are generally significantly lower than the maximum permissible concentration. In our opinion, the most effective way to assess local soil contamination is to use background contamination indexes. That is why the level of soil contamination with heavy metals is determined by comparing the concentrations of certain heavy metals with the background concentrations determined in our study.

To find out the background content of heavy metals in the soil, the results of soil studies of recreational areas of the city, where there is no anthropogenic impact, were analyzed (Melnyk et al., 2010). We calculated and determined the

average background values of indexes for the total and mobile content of heavy metals, Table 2.

The value of indexes of the total form of the content of heavy metals in the soils of the Rivne urban ecosystem indicates mosaic patterns of contamination of the territory. Exceeding the background values was recorded for all average values of indexes of heavy metals under investigation. Thus, the average content of the total form of lead, zinc and copper exceeds the background forms by 17.3; 16.8 and 16.2 times, respectively. It should be noted that exceeding was recorded at all the study test-sites, Table 3.

A similar situation is observed in soil contamination by mobile forms of heavy metals. Exceeding the background values was recorded for all indexes of the four test-sites, except for test-site No.2. The highest average values of indexes were recorded at the test-site No.4, where the excess over the background values for copper was 19 times, for lead – 12 times, for chromium -10.6 times, for zinc – 8.5 times, Table 4.

It should be noted that the following patterns are observed in the contamination of the city’s soil with heavy metals:

- the highest degree of contamination with heavy metal is attributed to zinc, lead and copper;

Table 3. The content of total form of heavy metals in the soils of the Rivne urban ecosystem

Value	Heavy metal content, mg/kg of soil				
	Cu	Ni	Pb	Cr	Zn
Test-site No.1					
Maximum	22.60	19.40	27.18	13.88	114.00
Minimum	7.90	4.69	11.20	6.30	26.06
Average	15.9	12.3	17.4	10.9	50.8
Test-site No.2					
Maximum	10.3	9.7	13.4	8.5	41.3
Minimum	6.43	8.63	7.19	6.90	24.55
Average	9.5	11.8	10.3	7.8	38.4
Test-site No.3					
Maximum	21.6	14.9	192.3	9.8	125.3
Minimum	5.9	3.9	6.7	5.8	28.1
Average	12.7	8.9	48.7	7.5	50.4
Test-site No.4					
Maximum	24.5	19.0	33.8	15.4	76.0
Minimum	10.3	3.0	10.0	9.8	30.1
Average	14.0	10.2	17.9	11.9	49.9
Test-site No.5					
Maximum	61.4	26.9	107.7	11.4	121.0
Minimum	1.2	2.7	2.8	1.9	3.0
Average	19.1	9.0	26.7	5.8	43.1

Table 4. The content of the mobile form of heavy metals in the soils of the Rivne urban ecosystem

Value	Heavy metal content, mg/kg of soil				
	Cu	Ni	Pb	Cr	Zn
Test-site No.1					
Maximum	0.8	1.5	7.8	0.7	8.6
Minimum	0.7	0.6	1.1	0.3	2.0
Average	0.7	1.2	3.0	0.4	6.2
Test-site No.2					
Maximum	0.7	1.8	9.5	2.4	4.2
Minimum	0.2	0.1	0.7	0.2	1.1
Average	0.4	0.8	3.7	0.8	2.2
Test-site No.3					
Maximum	0.4	1.5	11.0	0.9	6.2
Minimum	0.3	0.2	0.3	0.2	1.2
Average	0.3	0.6	2.8	0.5	3.1
Test-site No.4					
Maximum	17.1	7.7	23.7	10.8	30.5
Minimum	0.5	0.7	0.8	0.5	2.9
Average	8.2	4.6	13.2	6.8	16.7
Test-site No.5					
Maximum	6.8	6.9	10.3	7.9	6.9
Minimum	0.4	1.3	0.6	0.6	1.9
Average	1.9	2.7	4.3	3.1	3.7

- the distribution of heavy metals in the soil cover coincides with the prevailing northwestern wind direction;
- the dispersion of heavy metals and the processes of their accumulation in soils are affected by: building density, the presence of open spaces and well-ventilated areas, microclimatic factors.

The level of soil contamination of the Rivne urban ecosystem with heavy metals was determined according to the following criteria: the concentration factor of the chemical substance and the total contamination index (Sternik, 2017, Fedorets et al., 2009). Analyzed were the results obtained from each test plot under study, also calculated were the concentration factors of each metal in the soil for both the total and mobile forms of their content.

The specific features of production processes of industrial enterprises in the city, emissions of various pollutants, and a dense network of motor ways affect the results of the studies.

For the total form of heavy metals, the highest values of the concentration factor (C_f) are characteristic of zinc ranging from 6.3 to 25.1, except for test plots No.22 and No.24, where the values

of C_f are recorded as 0.9 and 3.9, respectively. For 61.1% of the study sites, the C_f values of zinc are above 9.0, which poses a danger to soil biota.

The highest C_f values of copper are observed around the industrial enterprises of the city. In 83.3%, the values of C_f for the content of total form of copper are in the range of 6.0–22.1. Similar results for the average values of C_f of the total forms of zinc and copper are observed at all the study test-sites. At the same time, the study results indicate high average C_f values of lead (3.6–6.4) and chromium (2.6–6.7), which can be dangerous for soil biota, Table 5.

Local contamination spots in the study area are also observed for the C_f values of the mobile form of heavy metals. The highest values of C_f are found for copper, lead and zinc near the railway track and on the by-pass road (test plots No.16 and No.20). Here, the C_f of heavy metals is: for copper – 39.8; for lead – 21.0; for zinc – 28.7. At some test plots, a high level of C_f was also recorded for chromium, where the value reaches 13.8 (Table 6).

It should be noted that the highest average values of C_f for all the studied heavy metals were determined at test-site No.4 which is surrounded on all sides by a transport network, including a railway.

Table 5. Concentration factors of the total content of heavy metals in the soils of the Rivne urban ecosystem

Value	Concentration factor, C_f				
	Cu	Ni	Pb	Cr	Zn
Test-site No. 1					
Maximum	15.9	4.6	9.7	11.8	16.1
Minimum	6.7	1.7	4.0	3.4	6.3
Average	11.3	3.7	6.2	6.7	11.6
Test-site No. 2					
Maximum	8.8	3.6	4.8	5.6	13.7
Minimum	5.5	2.3	2.6	0.1	8.1
Average	7.0	3.2	3.6	3.7	10.3
Test-site No. 3					
Maximum	13.2	3.5	7.2	5.3	9.6
Minimum	4.9	1.4	2.4	3.1	6.3
Average	8.9	3.3	4.5	4.0	8.4
Test-site No. 4					
Maximum	20.7	7.0	10.6	8.3	25.1
Minimum	8.7	1.1	3.6	0.1	9.9
Average	11.9	3.8	6.4	3.8	16.5
Test-site No. 5					
Maximum	22.1	3.6	6.7	4.7	14.3
Minimum	0.7	1.4	2.7	0.1	0.9
Average	8.9	2.1	4.3	2.6	7.8

Table 6. Concentration factors of content of mobile form of heavy metals in the soils of the urban ecosystem of the city of Rivne

Value	Concentration factor, C_f				
	Cu	Ni	Pb	Cr	Zn
Test-site No.1					
Maximum	12.9	1.3	7.1	13.8	12.5
Minimum	1.5	0.5	1.0	0.2	1.9
Average	4.0	0.9	2.8	3.3	7.2
Test-site No.2					
Maximum	1.6	1.4	8.6	2.2	3.9
Minimum	0.5	0.1	0.4	0.3	1.0
Average	1.0	0.6	3.3	0.9	2.0
Test-site No.3					
Maximum	13.7	5.2	10.0	10.7	19.2
Minimum	0.7	0.1	0.1	0.3	1.1
Average	3.3	1.4	2.6	2.7	6.1
Test-site No.4					
Maximum	39.8	6.2	21.0	13.8	28.7
Minimum	1.1	0.5	0.7	0.8	2.8
Average	19.1	3.7	11.9	8.9	15.8
Test-site No.5					
Maximum	15.7	5.5	9.4	7.2	6.6
Minimum	0.9	1.0	0.6	0.5	1.9
Average	4.6	2.2	3.9	4.8	3.5

The total contamination index of both total and mobile forms of the content of heavy metals in the soils of the Rivne urban ecosystem shows different concentration factors of heavy metals in the soils of the city, Figs. 2, 3.

The analysis of the results obtained shows that the most contaminated areas are the territories of the northern and southern parts of the city (test-sites No.1 and No.4). The industrial enterprises that are concentrated in the northern part of the city are the main soil polluters (Sternik, 2017, Melnyk et al., 2010) [8, 13]. Soil contamination in the territory of the southern part of the city is the result of fugitive emissions from mobile pollution sources - motor vehicles and railway transport as well as industrial emissions from the brick-making plant.

The western and central parts of the city are characterized by moderate soil contamination. The density of high-rise buildings in the western part of the city, in combination with narrow driveways between the buildings, contribute to the slowing down of aeration processes and the settling of heavy metals within these test-sites. The main soil polluters here are motor vehicles.

The central part of the city has a lower location relative to the outskirts. The inflow of air masses from the outskirts to the central part due to the difference in temperature gradients of the central and suburban territories affects the content of heavy metals in soils. The dense network of highways and the railway line that crosses the city center, as well as the Rivne plant of high-voltage equipment, which is the largest polluter of the atmospheric air with heavy metals, – all this significantly contributes to soil contamination.

The eastern part of the city is the least polluted. This is facilitated by the radio plant that has been inactive for the past few years, the high efficiency of catalytic treatment of industrial emissions at the «Prometheus» enterprise, and a small number of petrol-filling stations.

CONCLUSIONS

As a result of monitoring studies on soil contamination in the territory of the Rivne urban ecosystem, the following conclusions can be drawn. The content of heavy metals in the soils of the study

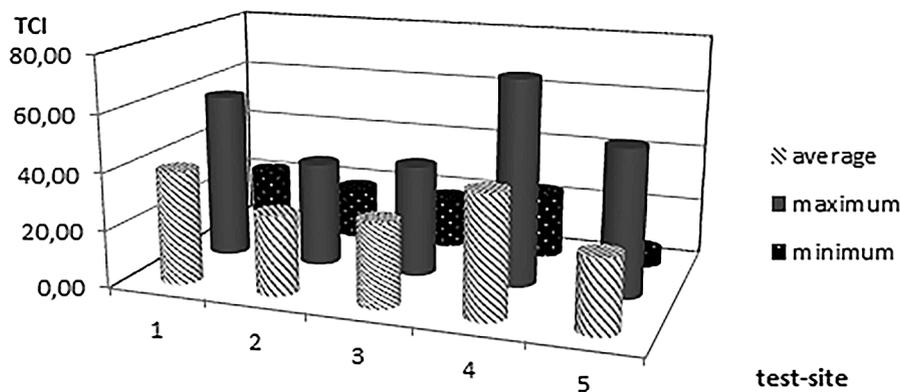


Figure 2. Values of TCI of the total content of heavy metals in the soils of the Rivne urban ecosystem

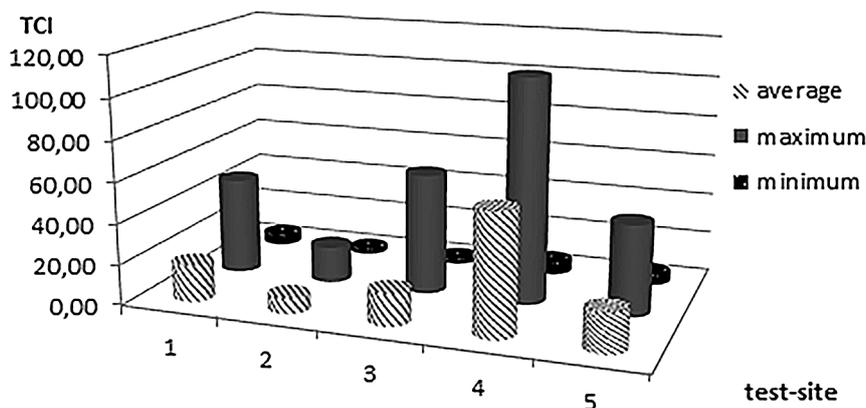


Figure 3. Values of TCI of the content of mobile form of heavy metals in the soils of the Rivne urban ecosystem

area is of a mosaic nature, which results in varying degrees of soil contamination in different parts of the city. The most contaminated are the soils of the northern and southern parts of the city, the least contaminated are the soils of the eastern part of the city. High average values of the concentration factors for total form of heavy metals are attributed to zinc, copper, lead and chromium at all the study test-sites. The highest average values of C_f for a mobile form for all the studied heavy metals were found for test-site No.4. The total contamination indexes for the total form of heavy metals are found to be within the range of 29.67–48.19. The highest total contamination index for the mobile form of heavy metals was recorded in the soil of test-site No. 4, which is 67.18, and the lowest - in the soil of test-site No. 2, which is 11.02 at the permissible level of 16. The results of the study will allow assessing environmental risks for biota and humans, they will make it possible to carry out ecological and social management of the territory of the city of Rivne on a scientific basis.

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