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Ecological risk of contamination of urban soils with heavy metals using the example of Dnipro city (Ukraine)

Tetiana Yakovyshyna*

Prydniprovska State Academy of Civil Engineering and Architecture, Faculty of Environmental Engineering and Ecology, Department of Ecology and Environmental Protection, Architector Oleg Petrov St., Dnipro, UKRAINE
*Corresponding author: t_yakovyshyna@ukr.net

Abstract. Identifying interrelation between the ecological risk of urban soils contamination with heavy metals and health indicators solves the essential task of forecasting environmental threat to the population. The research was conducted using the example of the urban ecosystem of the city of Dnipro, where a network of key soil sampling areas was formed by applying a grid of 2 km × 2 km. The area of sampling was about 200 m^2. The gross content of metals in the soil was measured after its acid treatment on an atomic absorption spectrophotometer. In the study, the data on soil contamination with heavy metals (Cu, Zn, Pb, Cd, Ni) and statistical measures of public health was used. The ecological risk due to element and polyelement contamination of the soils of the Dnipro urban ecosystem with heavy metals was identified, considering the three ways of their intake (by swallowing, inhalation, through the skin). It was found that the greatest environmental threat is caused by soil contamination with lead, so the ecological risk was unacceptable and mostly high throughout the city of Dnipro. Taking into account the polyelement nature of the pollution, the ecological risk was identified as unacceptable, mostly average, and in some cases as high. The correlation between the state of health of the population and the quality of the environment of the Dnipro urban ecosystem under technology-driven stress was established on the basis of correlation coefficients between the values of ecological risk, mortality rate and the number of cases of cancer.

Key words: ecological risk, heavy metals, environmental pollution, environmental hazard, soil, urban ecosystem.

Introduction

The principles of the European Green Deal, aimed at sustainable development of cities, condition the preservation of the proper quality of the urban ecosystem as a human habitat, while intensifying economic growth. An increase in technology-driven stress within urban ecosystems affects the human body causing harm to health. The interrelation between the environment and human health is of increasing concern, particularly in urbanized areas, where health vulnerability is differentiated relative to different levels of pollution. Therefore, among the set of conditions and characteristics that create and sustain the level of environmental safety for the population, a particular attention in urban ecosystems under technology-driven stress is required for the quality of the environment, the share of which, according to the estimates by the WHO and various authors (Bolshakov et al., 1999; Barbashova, 2014; Krcmar et al., 2018), varies from 17 to 20% of the total health impact.

Risk assessment is a relevant tool for assessing and quantifying the possible side effects of pollutants on human health and the environment (Mari et al., 2009; Krcmar et al., 2018). Kiseliov (2001) suggests using infant mortality, general morbidity and mortality of adults as the most indicative characteristics of the anthropogenic impact on public health (Kiselev, 2001). Currently, the adverse effect of excess amount of heavy metals on the human body has been proven, namely: Cu – affects the intestines, liver, stomach, leads to skin cancer, angiosarcoma, peripheral neuropathy and vascular diseases (Gaetke & Chow 2003; Hartley & Lepp, 2008; Harmanescu et al., 2011; Rahman et al., 2014; Jia et al., 2018); Zn – contributes to the occurrence of anaemia, gastrointestinal disorders, coronary disease (Bolshakov et al., 1999); Pb – can cause hypertension, damage the skeleton, immune system, endocrine system, reduce intellectual potential in children (Ekong et al., 2006; Navas-Acien et al., 2007; Nieboer et al., 2013); Cd – causes osteotoxicity and nephrotoxicity, lung adeno-carcinomas, proliferative lesions of the prostate gland, lung adenocarcinomas and immune perturbations (Klaassen et al., 2009; Lin et al., 2013); Ni is associated with renal irritation, damage to cardiovascular system, and vision impairment (Bolshakov et al., 1999). However, among the above effects of the heavy metals on the human body, oncological diseases predominate (Bolshakov et al., 1999). The share of cancer diseases as a cause of death in the population of the Dnipropetrovsk region was higher than in Ukraine until 2020 (Fig. 1) (BNCRU, 2014-2020). Therefore, it is quite important to establish an environmental hazard rate for the contamination of urban soils with heavy metals, which would indicate their adverse effect on the health of the people residing in urban ecosystems under technology-driven stress, which, in turn, will allow taking the necessary measures to minimize undesirable effects, such as early mortality and cancer incidences. Identifying the above regularities between the ecological carcinogenic risk of urban soils contamination with heavy metals and vitals allows solving the essential scientific and practical task of forecasting environmental threat to the people living in urban ecosystems.

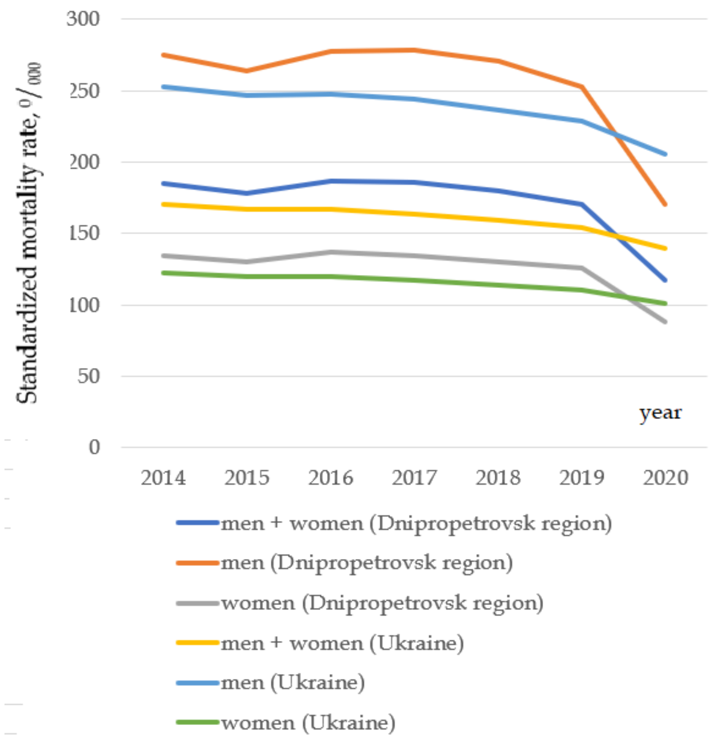

Fig. 1. Standardized mortality rate of Ukraine and Dnipropetrovsk region, (BNCRU, 2014-2020).

The purpose of the study was to assess the ecological carcinogenic risk of soil contamination of urban ecosystems with heavy metals (Cu, Zn, Pb, Cd, Ni) using the example of the city of Dnipro in order to discover possible patterns of impact on the health of the adults in the areas experiencing technology-driven stress in terms of mortality and cancer incidence.

Materials and Methods

The Dnipro city is located in the temperate continental climate zone, the degree of continentality of which is 38.1%. The frequency of tropical and arctic air varies between 14-15%. Quite often there is air of temperate latitudes over the study area and, unlike the continental, the sea air is less frequent and weakens due to the elimination of fronts from the west associated with the intense activity of cyclones in Europe (Pavlov et al., 2000).

The Dnipro city is located on the edge of the Ukrainian crystalline massif and the Dnipro-Donets depression, in the middle course of the Dnipro River on the northern bend of the great Dnipro twist at the point of confluence of the Samara River with the coordinates of the center of lat. 48°27′ N, long. 35°02′ E. The Dnipro River crosses the city and divides it into two parts: the left-bank and the right-bank areas. The width of the river valley within the urban ecosystem reaches 20 km, but the streambed occupies only the small deepest part of the valley bottom of 0.7-1.0 km (Pasechny et al., 1998). The relief of the urban ecosystem of the Dnipro city is characterized by heterogeneity and structural complexity, which, in turn, contributes to the diversity of the urban landscape, as well as engineering geological and environmental conditions for development planning. The surface of the city area is characterized by deep (120-134 m) and massive (0.8-0.9 km/km^2) erosion within the Dnipro River with a gradual decrease in intensity as distance increases (Hrytsan et al., 1998). The consequence of anthropogenic activity in the city is the man-made forms of relief, namely: planned surfaces of terraced slopes, excavations, ditches, embankments, dams, quarries and dumps of various sizes and configurations.

The area of the city is 390.8 km^2, of which 55.0% is the built-up area, 30.0% are the landscape and recreational areas, 15.0% - water and other surfaces (Pavlov et al., 2000). Its length is 22 km from north to south, and 33 km from east to west. The population is 968 thousand people as of January 01, 2022, with a density of 2,811 people per km^2. Among all urban areas, the following groups are distinguished: private sector, high-rise building, industrial, and green zones.

The database of the content of heavy metals (Zn, Pb, Cu, Cd, Ni) in soils selected from 65 key sites from different districts of the city of Dnipro was used to calculate the ecological carcinogenic risk of pollution (Table 1). The network of key soil sampling sites was generated by applying a grid of 2 km × 2 km on the territory of the city. The size of the grid was determined by the area and population of the city (Baluk et al., 2004). The area of sampling was about 200 m^2. The sampling sites were allocated uniformly, under the conditions of avoiding atypical microrelief (pits, ditches, rain rills), fires, piles of garbage, visually heterogeneous in terms of composition and color spots. Soil sampling was carried out by the envelope method from a depth of 0-10 cm, a representative sample included 25 individual samples (State standard of Ukraine, 2019). Soil samples were taken and prepared for analysis in compliance with the requirements of the current standards (State standard, 1984; 1994). The gross content of metals in the soil was measured after its acid treatment on an atomic absorption spectrophotometer (Baluk et al., 2004).

Cd, Pb, Zn, Cu and Ni, which are priority pollutants of the urban ecosystem of Dnipro (Kharitonov et al., 2014; Yakovyshyna, 2019), were investigated in the monitoring system. In the city of Dnipro, there are 237 industrial enterprises of various sectors of the national economy, such as rocket and space construction, power industry, metallurgy, engineering, construction industry, utilities, which, in turn, produce a number of emissions into the atmosphere, of which as many as 74 enterprises emit heavy metals. According to the location, they can be grouped into 5 industrial zones. Annually, the industrial enterprises of Dnipro city emit heavy metals (oxides, salts) in a total amount of about 102.3 tons (data for 2012-2022). According to the data of the Main Department of Statistics in the Dnipropetrovsk region, on average 5 kg of copper, 11 kg of zinc, 5 kg of lead, 1 kg of cadmium, 4 kg of nickel enter each square kilometer of soil of the Dnipro urban ecosystem annually, and these may also leak and leach into the groundwater, as well as enter the surface layer of atmospheric air with the dust. As is generally known, a share of heavy metal cations and soil components form tightly bound compounds, while other cations remain capable of migrating in the plant-animal-human trophic chain and to a great extent pause environmental threat for the people dwelling in urban ecosystem.

Table. 1. Distribution of soil sampling sites on the territory of Dnipro city.

District	Area, hectares	Population, thousands of people	Total sampling sites	Characteristics of sampling sites			
				Industrial zone	High-rise building	Private sector	Green zone
AmurNyzhniodniprovskyi	7162.6	154.4	13	1	-	9	3
Indystrialnyi	3267.9	132.7	5	2	2	1	-
Novokodatskyi	8870.2	151.7	12	-	4	4	4
Samarskyi	6683.4	77.9	8	1	-	4	3
Sobornyi	4409.3	169.5	8	-	3	1	4
Tsentralnyi	1040,3	67.2	3	-	2	-	1
Chechelivskyi	3589.7	120.6	9	4	-	5	-
Shevchenkivskyi	2679.4	152.0	7	1	2	2	2
Left Bank	19300.7	438.8	26	4	2	14	6
Right Bank	18402.1	587.2	39	5	11	12	11

A quantitative assessment of the ecological carcinogenic risk of adverse effects on adult health caused by the contamination of soils of Dnipro urban ecosystem with heavy metals was carried out based on USEPA protocol (USEPA, 1991; 2007; 2011), considering the three main ways of their intake (ingestion, inhalation, skin penetration). Ecological carcinogenic risk rationing was carried out according to the recommendations (Zvyagintseva & Averin, 2006) and Ashby acceptance criteria: > 10^{-3} – high; 10^{-3} – 10^{-4} – average; 10^{-4} – 10^{-6} – low; <10^{-6} – minimum (acceptable). Assessment of the impact of contamination of soils of Dnipro urban ecosystem with heavy metals on the health of adult population (cancer, mortality) according to the data of the Main Department of Statistics in the Dnipropetrovsk region was carried out using correlation analysis.

Results

Among the analyzed pollutants, the greatest ecological carcinogenic risk to the health of the population of Dnipro urban ecosystem was caused by lead, and the least - by nickel, the level of which was acceptable in a quarter of the city area. The statistical analysis of the samples showed that the largest range between the maximum and minimum values of the ecological carcinogenic risk was for Pb contamination, which is due to the significant variability caused by the processes of deconcentrating at the urban ecosystem development and long-term soil pollution as a result of emissions of industrial enterprises and exhaust gases of motor vehicles under the conditions of busy traffic (Table 2). The average value of ecological carcinogenic risk for Cu, Zn, Pb, however, as well as polyelement pollution in general, exceeded the median, which indicated a large-scale progressive environmental threat caused by pollution of the city of Dnipro area with the specified metals. Positive values of kurtosis for all series of ecological carcinogenic risk conditioned the peaked distribution, which, under slight right-sided asymmetry in (< 5.5) according to Tarasova (2008), except for Cu, indicated an intensive technology-driven stress due to contamination of soils with heavy metals throughout the Dnipro city. Significant shift in the curve of the distribution of the ecological carcinogenic risk of Cu pollution highlighted small but powerful hot spots against a fairly uniform urbanized geochemical background.

Table 2. Characteristics of ecological carcinogenic risk from soil element and polyelement pollution by heavy metals for Dnipro urban ecosystem

Index	Ecological carcinogenic risk					
	Element pollution					Polyelement pollution
	Cu	Zn	Pb	Cd	Ni	
Minimum	2.37×10^{-6}	1.64×10^{-6}	5.04×10^{-5}	4.51×10^{-5}	4.01×10^{-6}	1.18×10^{-4}
Maximum	2.73×10^{-4}	1.03×10^{-4}	3.21×10^{-3}	5.58×10^{-4}	3.35×10^{-5}	3.51×10^{-3}
Average	2.18×10^{-5}	3.13×10^{-5}	4.93×10^{-4}	1.99×10^{-4}	1.37×10^{-5}	7.59×10^{-4}
Median	1.57×10^{-5}	2.32×10^{-5}	2.77×10^{-4}	2.00×10^{-4}	1.40×10^{-5}	5.16×10^{-4}
Excess	45.31	0.11	7.70	2.20	2.05	5.97
Asymmetry	6.28	0.99	2.90	1.04	0.87	2.56
Dispersion	1.19×10^{-9}	6.58×10^{-10}	4.60×10^{-7}	9.31×10^{-9}	2.97×10^{-11}	5.66×10^{-7}
Standard deviation	3.44×10^{-5}	2.57×10^{-5}	6.79×10^{-4}	9.65×10^{-5}	5.45×10^{-6}	7.52×10^{-4}
Extend	2.70×10^{-4}	1.02×10^{-4}	3.16×10^{-3}	5.13×10^{-4}	2.95×10^{-5}	3.40×10^{-3}

Table 3. Ecological carcinogenic risk assessment from soil polyelement pollution by heavy metals for urban ecosystem of Dnipro

District/City	Level of ecological carcinogenic risk	
	high	average
Amur-Nyzhniodniprovskyi	3.32×10^{-3} / 1	4.63×10^{-4} (1.32×10^{-4} – 8.76×10^{-4}) / 12
Indystrialnyi		4.81×10^{-4} (1.70×10^{-4} – 9.08×10^{-4}) / 5
Novokodatskyi	2.85×10^{-3} (2.83×10^{-3} – 2.87×10^{-3}) / 2	5.89×10^{-4} (2.84×10^{-4} – 9.49×10^{-4}) / 10
Samarskyi	1.50×10^{-3} / 1	3.98×10^{-4} (1.67×10^{-4} – 5.18×10^{-4}) / 7
Sobornyi		4.49×10^{-4} (1.18×10^{-4} – 6.20×10^{-4}) / 8
Tsentralnyi	3.04×10^{-3} / 1	5.38×10^{-4} (5.15×10^{-4} – 6.05×10^{-4}) / 2
Chechelivskyi	1.62×10^{-3} (1.32×10^{-3} – 1.92×10^{-3}) / 2	6.49×10^{-4} (4.80×10^{-4} – 8.56×10^{-4}) / 7
Shevchenkivskyi	3.51×10^{-3} / 1	5.48×10^{-4} (3.67×10^{-4} – 6.86×10^{-4}) / 6
Left Bank	2.41×10^{-3} (1.50×10^{-3} – 3.32×10^{-3}) / 2	4.48×10^{-4} (1.32×10^{-4} – 9.08×10^{-4}) / 24
Right Bank	2.58×10^{-3} (1.32×10^{-3} – 3.51×10^{-3}) / 6	5.57×10^{-4} (1.18×10^{-4} – 9.49×10^{-4}) / 33
Dnipro city	2.54×10^{-3} (1.32×10^{-3} – 3.51×10^{-3}) / 8	5.11×10^{-4} (1.18×10^{-4} – 9.49×10^{-4}) / 12

Note: numerator – average value, in parentheses – fluctuations limit of ecological carcinogenic risk value; the denominator – number of key soil sampling sites.

As to the routes of entry for all the studied elements, the greatest danger was caused by the risks of absorption of dust particles containing heavy metals when breathing and during contact through the skin, rather than when swallowed.

The value of the ecological carcinogenic risk due to polyelement heavy metal contamination of soils of the Dnipro urban ecosystem was average, and in some cases, high. As a result of environmentally unsound location of enterprises in the Dnipro city, namely the inclusion of industrial zones in residential areas in the almost complete absence of sanitary protection zones, and there are no areas of acceptable ecological carcinogenic risk in the city. According to Table 3, the highest level of environmental threat was observed in the Amur-Nyzhniodniprovskyi, Samarskyi, Novokodatskyi, Tsentralnyi, Chechelivskyi and Shevchenkivskyi districts, mainly on the right bank, rather than on the left bank part of Dnipro urban ecosystem (Fig. 2).

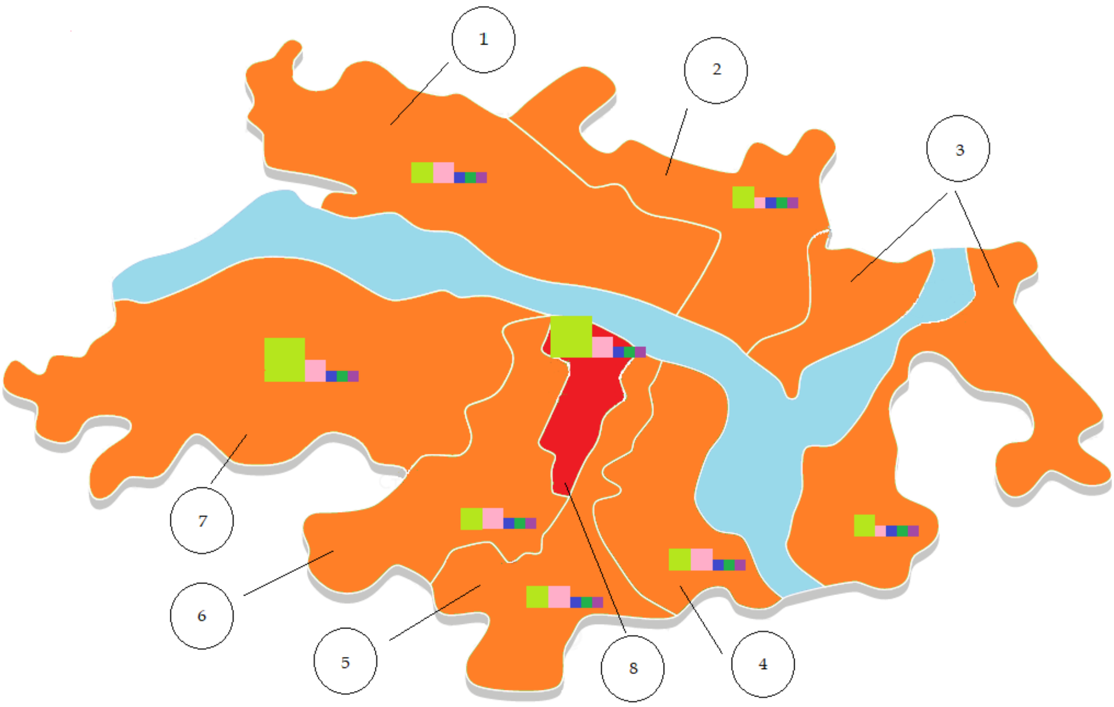

Fig. 2. Ecological carcinogenic risk from soil element and polyelement pollution by heavy metals for district of Dnipro city

Note: 1 – Amur-Nyzhniodniprovskyi district; 2 – Indystrialnyi district; 3 – Samarskyi district; 4 – Sobornyi district; 5 – Shevchenkivskyi district; 6 – Chechelivskyi district; 7 – Novokodatskyi district; 8 – Tsentralnyi district.

- high level of ecological carcinogenic risk from soil element pollution;
- average level of ecological carcinogenic risk from soil element pollution;
- low level of ecological carcinogenic risk from soil element pollution;
- high level of ecological carcinogenic risk from soil polyelement pollution;
- high level of ecological carcinogenic risk from soil polyelement pollution;
- Pb;
- Cd;
- Zn;
- Cu;
- Ni.

Discussion

When establishing the degree of environmental hazard, in our case of contamination of urban ecosystem soils with heavy metals, the question arises on how accurately the ecological carcinogenic risk value reflects the identified threat to human health. Currently, a large number of studies have been carried out to assess the ecological carcinogenic risk of heavy metals contamination of soils using the methodology (Li et al., 2014; Diami et al., 2016), the outcome of which is mainly a statement of the fact of ecological carcinogenic risk and a comparison of its values in individual sites of the study area. This comparison, firstly, allows identification of environmentally safe and environmentally hazardous sites in a single area, and secondly, identification of heavy metals as priority pollutants contributing to the risk magnitude (Yang & Wang, 2020). The factorial analysis helps to identify the causes of soil contamination of industrial agglomerations under technology-driven stress (Bolshakov et al., 1999). Usually, for urban ecosystems, such causes are industrial enterprises and motor vehicles. Currently, the studies are generally focused on the analysis of spatial correlation of risks between different heavy metals due to urban ecosystems soil pollution (Barbashova, 2014). In our case, close correlation dependence was not found, although it was directly proportional for all elements, which was caused, firstly, by a rather distinct difference in the composition of emissions of enterprises of various industries, and, secondly, by the presence of 5 industrial zones within the city, and therefore by the variety of pollution. The highest coefficient of correlation between the ecological carcinogenic risk values was found between Cd and Ni (r=0.670) - the metals included in the emissions of industrial enterprises of all 5 industrial zones, albeit in small quantities. The increased coefficient of correlation between Pb and Zn (r=0.419) against the values for other heavy metals indicated the pile-up of traffic emissions and pollution spots formed as a result of the deposition of pollutants from industrial enterprises. Unfortunately, the literary sources do not discuss the topic of assessing ecological carcinogenic risk in relation to the manifestation of undesirable effects on human health. The focus is on determining the most dangerous pathway of exposure to the human body (Yang & Wang, 2020). In our case, these are inhalational and dermal ways, where the latter slightly predominates. However, it may differ among different authors (Li et al., 2014; Diami et al., 2016; Pan et al., 2016) and depends on the choice of dermal absorption coefficients, therefore it needs to be clarified in order to unify the methodological approach. Based on the concept of "ecological risk", it would be desirable to find out how well it describes the danger to human health, the more so as to date, medical investigations have proven the relationship between certain diseases and excessive content of heavy metals (Gaetke & Chow 2003; Ekong et al., 2006; Navas-Acien et al., 2007; Hartley & Lepp, 2008; Klaassen et al., 2009; Harmanescu et al., 2011; Lin et al., 2013; Nieboer et al., 2013; Rahman et al., 2014; Jia et al., 2018).

Correlation analysis of the values of ecological carcinogenic risk by average figures for the city districts and by mortality and cancer rates showed a direct proportional dependence of 0.329 and 0.379 for the adult population. However, this approach is not correct, because it requires the exclusion of extreme points – the Tsentralnyi and Sobornyi districts, as there are no industrial enterprises on their territory and they are quite small in area, which, in turn, causes intercity migration of the population during the working week. With the specified areas excluded, the correlation coefficient r increased almost twice and was 0.618 and 0.654, which confirmed the relation between the state of health of the population and the quality of the environment and thus indicated soil contamination with dangerous metal compounds as one of the significant causes of cancer in Dnipro.

Conclusion

The ecological carcinogenic risk due to element and polyelement contamination of soils of the Dnipro urban ecosystem with heavy metals (Cu, Zn, Pb, Cd, Ni) was identified, considering the three main ways of their intake (by swallowing, inhalation, through the skin). Risks to the health of adult population due to heavy metal contamination of soil ranged from low to high. By routes of intake, the greatest hazard is the risk of breathing in and skin contact. It was found that the greatest environmental threat is caused by soil contamination with lead, so the ecological carcinogenic risk was unacceptable and mostly high throughout the city of Dnipro. Taking into account the polyelement nature of the pollution, the ecological carcinogenic risk was identified as unacceptable, mostly average, and high in some cases. The correlation between the state of health of the population and the quality of the environment of the urban ecosystem of Dnipro under technology-driven stress was established on the basis of coefficients of correlation between the values of ecological carcinogenic risk, mortality rate and the number of cases of cancer. It has been substantially proven that environmental pollution with heavy metals is a significant cause of cancer cases among the citizens of Dnipro. The results of the research may be used to justify the inclusion of an ecological carcinogenic risk indicator in the program of integrated monitoring of urban ecosystems, as it determines the environmental threat to human health due to the contamination of urban soils with heavy metals.

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