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Geochemical Anomalies of the Heavy Metals in the Industrial and Urban Agglomeration Soils

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ABSTRACT

The study of the soil cover of urban landscapes of the Mykolaiv industrial-urban agglomeration, which is a complex multifunctional system, was carried out. A sampling strategy was developed and the sources of pollution were analyzed, taking into account the areas of intensive bombing and ammunition explosions. The levels of contamination by heavy metals (Cr, Zn, Hg, Pb, Ni, Cu, Mn) at the positions of environmental safety were established, and the danger coefficient Ko and the integral danger index ($\sum K_o$ (1+2)) were applied for chemical elements of the I and II danger classes. A geochemical anomaly of military origin was identified with an excess of the maximum permissible levels for the following chemical elements: Hg (57.1) > Cr (20.6) > Ni (9.6) > Cu (9.2) > Zn (5.3) > Pb (1.5).

Keywords: heavy metals; danger coefficient; total pollution index; urban landscape; urban geosystem; industrial-urban agglomeration.

INTRODUCTION

The issue of sustainable development of territories is a priority in many EU Directors and Strategies, which are dedicated to nature protection, preservation of biodiversity, ensuring an adequate quality of life (Butler et al., 2016; Bezsonov et al., 2017; Mitryasova et al., 2018, 2020; Petrov et al., 2020; Przystupa et al., 2020). The road map for the development of territories includes environmental development priorities, which provide for monitoring, assessment of the state of modeling and forecasting of environmental objects (Pohrebennyk et al., 2016; Ishchenko et al., 2019; Mitryasova and Pohrebennyk, 2020; Jensen and Wu, 2018; Mitryasova et al., 2021).

Armed conflicts, the construction of military bases and the use of heavy transport damage soils and destroy vegetation. Each explosion of a projectile or missile is not only the release of a chemical cocktail into the environment, but also the complete destruction of all animals, plants and microorganisms in the radius of damage. Disturbed territories may not only not recover after the end of the conflict, but also become a source of pollution of the surrounding territories and the spread of invasive species. As a result of hostilities, the Mykolaiv Industrial-Urban Agglomeration (MIUA) suffered a lot of destructive actions as a result of intense attacks. The ground cover is subjected to an excessively high load. The physical destruction of the soil due to the bursting of projectiles, the formation of sinkholes with a radius of 10−12 m and a depth of up to 5−6 m is supplemented by excessive levels of pollution with heavy metals (HMs).

The classical understanding of HMs is reduced to approximately 40 chemical elements of the periodic table with an atomic mass of more than 40−50 a.u. and distinct metallic properties.

In the conditions of urbanized territories, the following sources of HMs entry into the soil cover are determined (Kucheryavii, 2001; Dolin et al., 2011; Pohrebennyk et al., 2019):

- contamination of the soil cover on the territory of industrial enterprises in places of unauthorized waste storage, as well as spontaneous landfills in the residential sector;
- leaching of HMs entering the atmosphere in solid and gaseous form as a result of the operation of enterprises, vehicle emissions, atmospheric precipitation from the atmosphere into the soil;
- deposition in the form of dust and aerosols − solid and liquid compounds in dry weather usually settle on the ground cover;
- with plant fall, HMs return to the soil; and the root system carries out selective concentration of individual metals.

HMs are fundamentally important polluters of industrial-urban agglomerations due to the concentric concentration of resource, industrial, energy, and population potential within urban agglomerations. Soil is a unique ecological indicator that is at the intersection of man-made pollution migration paths. Usually, HMs are present in the soil as natural impurities and create background concentrations. According to its properties, the soil is the main depositing (accumulating) environment of HMs, including from the atmosphere and the water environment. Pollutants that enter the soil or are in it undergo various processes: infiltration into groundwater, sorption, migration through lateral flows, transformation into soluble/insoluble forms, absorption by plants and inclusion in biogeochemical cycles, etc. (Mitryasova et al., 2017, 2021).

Contaminated soil acts are a source of secondary pollution of the surface layer of atmospheric air when it comes into direct contact with humans. HMs are conservative pollutants capable of migrating along trophic chains in any ecosystems and the danger of which is associated with mutagenic, toxic and carcinogenic effects on living organisms. Therefore, it is fundamentally important to ensure the ecological sustainability of the MIUA. In today's conditions and during the last year, a large-scale influence on the MIUA is exerted under the action of massive bombings, which obeys the objective historical processes of the development of MIUA. Based on the ecological approach, the MIUA, as a natural-territorial complex (geocomplex) together with a hierarchical structure − from the landscape to the facies, is formed in the cyclical interaction of connections between the elements that form it: "external", social and natural environment. Therefore, in view of the above, it is appropriate to apply the study of the state of urban landscapes of the city, focusing on the approach of superpositional interaction of a large number of factors in dynamic variations.

The spatio-temporal distribution of HMs of agglomerated territories has attracted the attention of scientists in recent years. Thus, the content of mobile forms of heavy metals in the city's soils was analyzed. The authors applied zonal functioning, the samples were taken in the following zones: residential zone with multi-story buildings, residential zone with mixed buildings, residential island zone, traffic load zone, city center zone, industrial and suburban zones. Exceeding the MPC levels for lead by 2−4 times, cadmium – by 2 times was established. Suggested recommendations for resolving the situation (Pylypenko, Skok, 2015).

A study of the levels of heavy metals (Cu, Pb, Zn) in the soils of the city of Uzhhorod was carried out and the areas of their accumulation in a large area with an excess of permissible levels of MPC were determined. The authors raise the problem of developing a strategy that will allow to promote the tendency to reduce their content in urban landscapes (Homonai et al., 2005). Systematization of spatial databases of geochemical parameters of soils of Kyiv was carried out and a territorial model of the distribution of heavy metals (Pb, Zn, Cu, Cr, Ni, Sn) was created using GIS technologies. The obtained results made it possible to identify the districts of the Kyiv city with the highest technogenic soil pollution, as well as to establish a spatial relationship with anthropogenic objects of load (Matsybora et al., 2014).

The main physical and chemical properties of Odessa city parks soils were studied, the indicators of the content of nutrients, humus, pH, granulometric composition of the soils were analyzed, and the levels of heavy metals Pb, Cd, Zn, Cu were determined. The composition of salts in soils, the concentration coefficients of chemical elements and the total index of pollution (K_c and Z_c) were determined. The level of chemical pollution of park areas was determined (Khokhryakova, Kulidzhanov, 2017). The regularities of the distribution of heavy metals in technogenic polluted soils were investigated. According to geochemical criteria, technogenic associations of heavy metals were determined: copper > lead > zinc > cobalt > chromium > vanadium > molybdenum > manganese > nickel. The main factors affecting the concentration levels and migration of heavy metals in the city's soils were analyzed (Fatieiev, Pashchenko, 2003; Splodytel et al., 2020).

The object is to determine the levels of heavy metal contamination of the soil cover of the MIUA in the locations of missile strikes by intensive bombing. The objectives of the research are: to develop a strategy for testing the MIUA soil cover; to estimate the level of HMs contamination (Cr, Zn, Hg, Pb, Ni, Cu, Mn) of the Mykolaiv industrial-urban agglomeration soil cover at the maximum permissible levels.

MATERIALS AND METHODS

The research methodology provides a strategy for choosing places for collecting samples on the territory of the urban agglomeration, which is based on the following basic principles:

- determining the location of sampling points with a step of 10−15 kilometers, taking into attention the distribution of bombing areas. The geomorphological nature of urban landscapes and the functional division of the city territory in accordance with the General plan of the city (General plan of Mykolaiv city, 2019) are also taken into account. At the same time, great attention is paid to the maximum consideration of the requirements for ecological and geological studies on scales from 1:50,000 to 1:25,000 (Smyrnova, Dolin, 2009);
- in the period from October to November 2022 (autumn season), soil sampling was carried out. For this, the envelope method was used, with the help of a plastic spatula, samples weighing no more than 200 g each were taken from the upper 5 cm of the surface. The collected samples were then pooled to ensure soil homogeneity, and large inclusions such as stones, glass, plant roots, etc. were manually removed. After processing, the collected samples were packed in a sealed glass vessel, placed in containers with a constant temperature of 3–5 °C and transported to the laboratory (ISO 10381-5:2009);
- in laboratory conditions, soil samples were dried in a temperature range of 40±5 °C, mixed in a centrifuge. Before analysis, the samples were crushed in a mortar and sieved through a sieve with a hole diameter of 1 mm;
- determination of the gross content of metals (Cr, Zn, Hg, Pb, Ni, Cu, Mn) in the samples was performed by extraction into an acid solution in a ratio of solid and liquid phases 1: 5 when heated and periodic stirring during the day. After leaching, the samples were filtered on a blue filter paper filter;
- to determine the chemical elements in the sample, the X-ray spectrometry method was used, namely the S2 PICOFOX Bruker X-ray spectrometer − detector type: silicon drift detector, high voltage generator: MNX 50P50/XCC, X-ray source, metal MCB50 with air cooling. -0.7G, X-ray optics: multilayer monochromator.

Statistical processing of experimental data was performed using the application package Microsoft Excel and Statistics 10.0. HMs were determined according to the indicators: $C_{i,av}$ − the weighted average indicator of HMs content at the studied points, C_{min} − the minimum concentration of HMs, $C_{i,max}$ − the maximum concentration of HMs. The assessment of the level of chemical pollution of the soil cover is carried out according to the indicator of the danger coefficient K_o, which is the ratio of the actual HMs content in the soil (C_i) in mg·kg^{-1} to the maximum permissible concentration of HMs (Dolin et al., 2011; Mitryasova et al., 2020), formula 1.

$$K_o = C_i / MPC_i \quad (1)$$

The danger of soil contamination is higher, the higher the danger class of the controlled HMs. The integrated danger indicator $\sum K_o(1+2)$, differentiated by the MPC of danger class 1 and 2 elements, the calculation formula has the form (Dolin et al., 2007) formula 2.

$$\sum K_o (1+2) = \sum C/MPC \quad (2)$$

When studying soil contamination with chemical substances, the assessment is carried out by categories (Dolin et al., 2007):

- acceptable (integral danger index < 16),
- moderately dangerous (integral indicator of danger in the interval 16−32),
- dangerous (integral indicator of danger in the interval 32−128),
- extremely dangerous (integral danger index > 128).

Soil condition can be assessed based on changes caused by natural and man-made processes, as well as on the level of pollution.

RESULTS AND DISCUSSION

The territory of the city of Mykolaiv is located in the zone of the southern steppe, and the soil cover in this city has different origins. Natural soils, soils that have changed under the influence of human activity, and urban soils can be distinguished (National report, 2021). The soil cover in urban areas has undergone serious changes. In large areas, especially under roads and buildings, it is actually destroyed. In recreational areas such as parks, squares and courtyards, it is prone to degradation, waste pollution and enrichment of heavy metals and other harmful substances from the atmosphere. The negative aspects of soils in urban areas include their over-compaction, insufficient moisture, loss of organic material and basic nutrients (Dolin et al., 2011; Smyrnova, 2013). In industrial and urban agglomerations, much attention is paid to studying how HMs get into the environment. In the soil cover of urban areas, harmful substances are an integral part due to man-made load. Pollution of HMs is associated with their wide use in industry and insufficiently efficient cleaning systems. Emissions of HMs into the atmosphere have the character of complexes, oxides and one-and-a-half oxides.

The soil cover is a depositing medium for HMs and is an indicator of man-made pollution. Deposition of HMs in the upper 0−10 cm soil layer is possible as a result of dry and wet deposition. The main mass of pollutants in the form of very fine aerosols and dust can be lifted by turbulent air flows into the higher layers of the troposphere and transported over long distances, which is characteristic of the steppe zone in the spring-autumn period. The peculiarity of the behavior of HMs within the MIUA is determined by the processes of diffusion (scattering), dissolution, sorption, sedimentation, disturbance, etc. Like every system, the MIUA strives to achieve equilibrium (homeostasis), primarily through self-recovery and leveling of pollutants.

The destructive impact of the man-made load caused after active hostilities on urban landscapes determines complex changes in geochemical, spatio-temporal and other conditions, which leads to a violation of the geochemical balance. In the classical version, two main factors of man-made load of HMs on urban landscapes are recognized – the activity of industrial facilities and the influence of motor vehicles. Emissions into the atmosphere in industrial zones are the most dangerous type of pollution with a direct environmental impact. Over time, dusty fractions are able to settle and accumulate in the near-surface layer of the soil, forming stable levels of pollution. Thus, in 2021, enterprises with an emission volume of more than 100 Mg, which accounted for 3.9% of the total number of registered enterprises, were classified as major polluters. The main polluters: OJSC "Mykolaivska CHP"; SE "Zorya"-"Mashproekt", "Black Sea Shipbuilding Plant", SE "Shipbuilding Plant named after 61 Communard (SZK), PJSC "Mykolaiv Shipbuilding Plant "Okean", LLC JE "Nibulon" (National report, 2021). These are enterprises of the energy, machine-building, river-transport and shipbuilding industries. The analysis of the situation proves that in the conditions of large-scale hostilities in the Mykolaiv region and directly on the territory of the city of Mykolaiv, it is necessary to state the practical reduction of the industrial load on the urban environment to a minimum, because up to 90% of enterprises have suspended their activities, including in conditions of an unsatisfactory state energy supply, limited industrial resources and a significant outflow of specialists from all fields of activity to other regions and abroad (Smyrnov et al., 2023).

Up to 60% of atmospheric pollution in agglomerations comes from transport infrastructure (Netrobchuk et al., 2020). The main sources of this pollution are motor vehicles, railways and aviation. However, it is important to note that during the hostilities, the airfield complex "Kulbakino", located on the southeastern outskirts of the city's international airport, was bombed on February 24, 2022 and is not functioning at full capacity today. For almost a year, the railway operated in a limited mode, carrying out irregular passenger transportation and limited volumes of cargo. Although motor vehicles remain the main source of pollution, it is important to consider that more than half of the city's residents have left for other regions of Ukraine and abroad, which has led to a significant reduction in the load from mobile sources on the atmosphere.

Moreover, during this period, the urban logistics system actually did not function due to low indicators. This indicates that transport communications practically did not work and still have limited functionality. This means that sales efficiency at the level of various enterprises and forms of ownership was low, and, accordingly, the level of emissions into the atmosphere remained low. So, in modern conditions and during the last year, the main negative factor that affects the soil pollution is the military factor by intensive bombing.

The research was conducted on the territory of the MIUA, which was heavily bombed during the war. The metals Cr, Zn, Hg, Pb, Ni, Cu, and Mn have the greatest ecological importance among HMs (Fig. 1 and Fig. 2). The choice of these elements is determined by the emissions of industrial enterprises, motor vehicles and the active hostilities influence.

Elements of the 1st danger class

Chromium (Cr) is a chemical element of the VI group of the periodic system of elements with atomic number 24, has an atomic mass of 51.996, content in the earth's crust (0.03%) (Kovalyova, Mozharivska, 2020; Menshov et al., 2020). On the area after active hostilities the content of the dust fraction of chromium in the studied area is in the range of 10.1−670 mg·kg^{-1}, the average indicator is 123. The maximum indicator of Cr pollution was determined 670 mg·kg^{-1} (K_o = 111.6) in the area of dislocation ss.13. This is a residential sector, a sleeping area, which for a long time was subject to prolonged bombing. The minimum level of chromium contamination was recorded near ss.5 (10.1 mg·kg^{-1}) (Table 1; Fig. 3a). The coefficient of concentration C_o, determined relative to the MPC (6 mg/kg) is in the range of 1.7−111.6. The average indicator (20.6. K_o(Cr) is represented in a decreasing series: ss.13 (111.6) > ss.12 (63) > ss.18 (48.8) > ss.19 (39.7) > ss.11 (20.1) > ss.14 (14.3) > ss.6 (14.2) > ss.7 (7.7) > ss.15 (7.5) > ss.3 (6.7) > ss.1; ss. 8 (6.2) > ss.9 (5.4) > ss.17 (5.3) > ss. 2 (4.8).

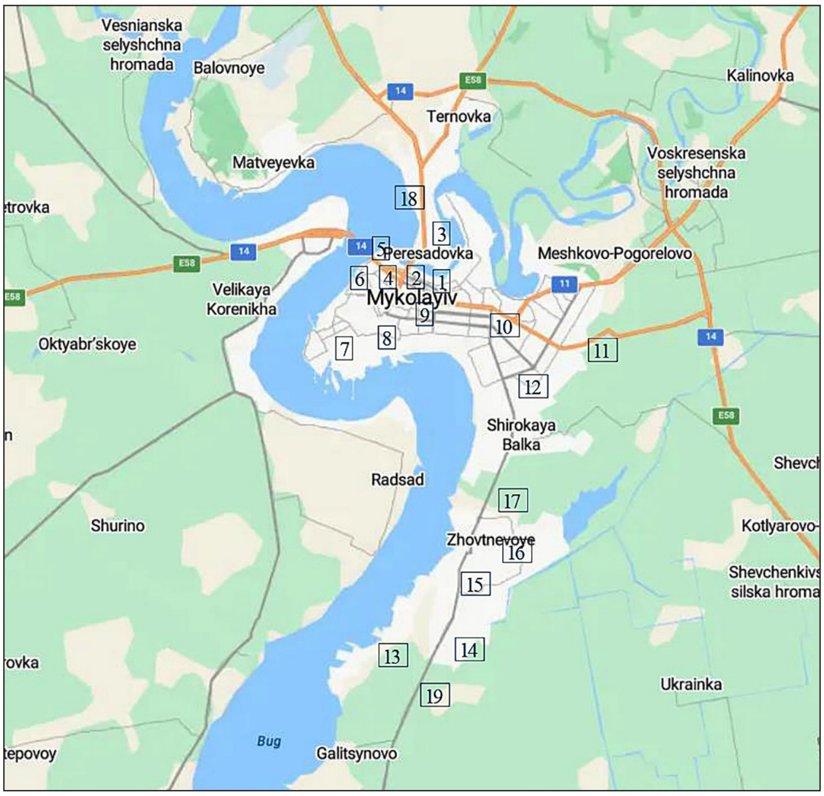


Figure 1. Sampling map of the MIUA; 1. PMBSNU (46.971846, 32.015536); 2. «Inhul» hotel (46.972471, 32.002948); 3. AMNUS (46.986888, 32.001258); 4. Mykola Arkas First Ukrainian Gymnasium (46.976937, 31.985766); 5. VSMNU (46.978614, 31.978792); 6. Hotel «Reikarts River Mykolaiv» (46.972578, 31.958026); 7. mcd. Lisky (40 Krylova St.) (46.956072, 31.960020); 8. Sports club «Equator» (46.958119, 31.980056); 9. «Mykolaiv» hotel (46.965298, 32.002379); 10. Mykolayiv Zoo, Kherson highway (46.961070, 32.035242); 11. Crossroads of 7th Povzdovzhnaya and st. Cosmonauts (46.950806, 32.063775); 12. Victory square (46.942112, 32.056533); 13. lane Aivazovsky St. 14 (46.852644, 32.000494);14. School № 48 (46.853513, 32.020967); 15. Palace of Culture (Korabelny district) (46.852735, 32.012770); 16. St. Yantarna, 77 (46.872278, 32.022909); 17. Glory Square, (Korabelny district) (46.887347, 32.028975); 18. Heroiv Ukrainy Ave., 91 (47.014911, 31.997199); 19. Crossroads of st. Ternopilska and st. Pschenichnya (Balabanovka microdistrict) (46.833951, 32.014944).

Zinc (Zn) in the earth's crust is $8.3 \cdot 10^{-3}$% (Zinc in nature). The content of zinc compounds within urban landscapes depends on the parent rock, the reaction of the soil solution, the content of organic matter, and anthropogenic factors. In natural conditions, pelites, as sedimentary clay rocks, are geochemically active sorbents and can influence the activity of zinc pollution. Fluctuations in zinc content at the level of up to 251.8 $mg \cdot kg^{-1}$, with an average value of 129.7, are observed within the influence of MIUA. The maximum exceedance of zinc permissible levels pollution was recorded in ss.13. The man-made and military factor led to the exceedance of the maximum permissible limit up to 17 times ($K_o = 16.9$), the concentration reached 670 $mg \cdot kg^{-1}$ in this point. It should also be noted two areas of excessive contamination with zinc compounds, where the MPC is exceeded by up to 11 times: ss.11; ss.17. Fighting took place in the area using explosive ammunition zinc pollution has not been recorded in the ss.13 area, that is, the level of pollution is limited by the capabilities of measuring equipment (Table 1; Fig. 3b). K_o(Zn) is represented in a decreasing series: ss.13 (16.9) > ss.11; ss.18 (10.9) > ss.10 (6.8) > ss.1; ss.8 (6.5) > ss.14 (6.2) > ss.6 (5.1) > ss.19 (5.0) ss.7 (3.6) > ss.9 (3.5) > ss.3 (2.9) > ss.16 (2.8) > ss.15 (2.5) > ss.5 (2.2) > ss. 17 (1.9) > ss. 2 (1.7) > ss. 12 (0.0).

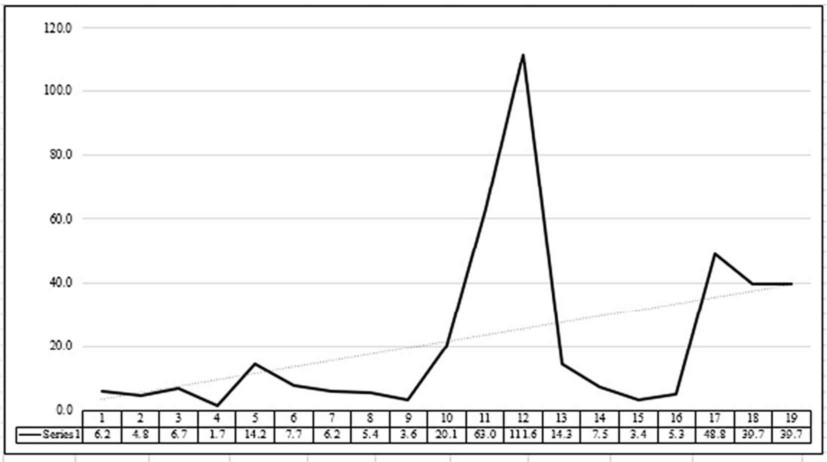
Figure 2. Example of the MIUA territory near 2nd point ("Inhul" hotel: 46.965298, 32.002379)

Mercury (Hg) is a liquid metal of the first class of danger, which is widely used in the electrical and instrumentation industry, laboratory and medical practice, and other fields. The potential danger lies in the fact that mercury has the property of easily evaporating into the atmosphere already at a temperature of 18 °C, this process begins to act intensively. Inhalation of Hg dust fractions contributes to its accumulation in the body through the respiratory organs and may have a carcinogenic effect (Safety data sheet, 2021). During the study, the content of the powdery fraction of mercury was measured in the studied areas. The results of the analyzes vary in the range of 0–319 $mg \cdot kg^{-1}$, the average indicator was 57.1. Critically high levels of the dusty fraction of mercury compounds in the

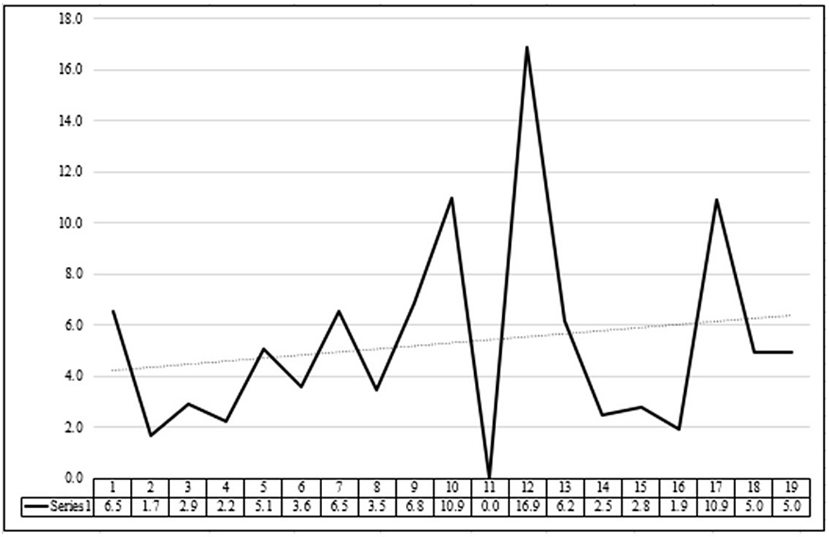
Table 1. Statistical characteristics of the danger coefficient according to the HMs content in the soil cover of the MIUA

Metal	Danger class						
	Cr	Zn	Hg	Pb	Ni	Cu	Mn
		I		II		III	
Contant, mg·kg-1	10.1-670 123.3	0-251.8 129.7	0-670 127	0-151.2 49.1	4.2-230 38.5	0-124 33.3	55.7-181668 11244.1
K_o	3.6-111.6 20.6	0-16.9 5.3	0-319 57.1	0-4.7 1.5	1-57.5 9.6	0-41.3 9.2	0-121.1 7.5
$\sum K_o$ (1+2)	23.6						

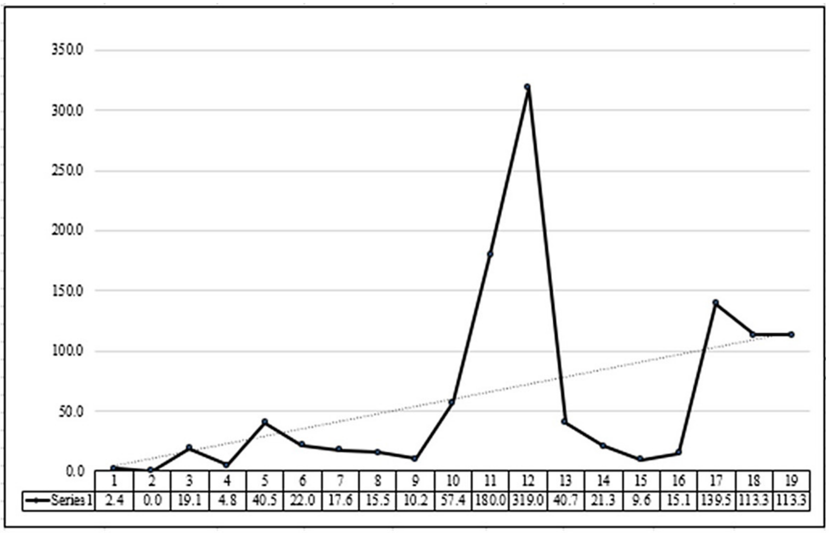
Note: *(1) The danger coefficient was determined in accordance with the Hygienic regulations on the permissible content of chemical substances in the soil (Order of the Ministry of Health of Ukraine, 2020); (2) The content of the element is given in mg/kg; in the numerator – limit definitions: C_{imax} – the minimum concentration of HMs, C_{imax} – the maximum concentration of HMs, in the denominator – C_{iav} – the average value of HMs at the studied points; (3) 0 – the concentration of pollutants, which is limited by the capabilities of the measuring technique (the sensitivity of the device), mg/kg.



a) Cr

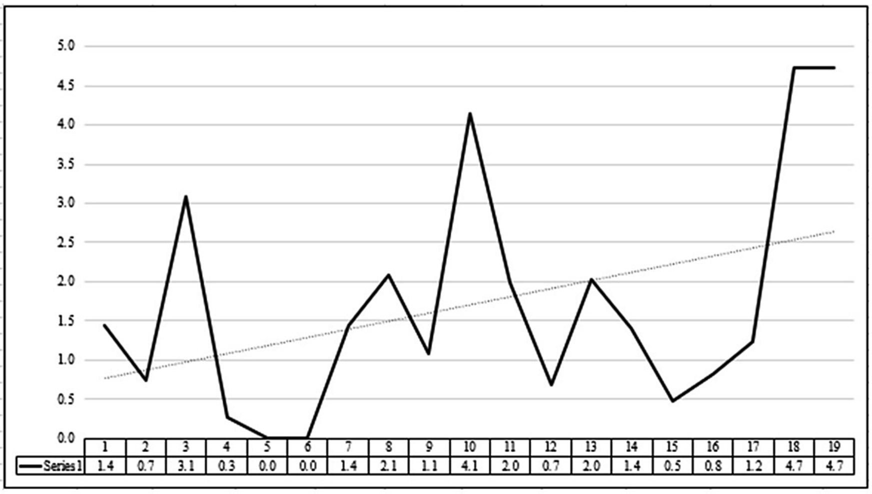


b) Zn

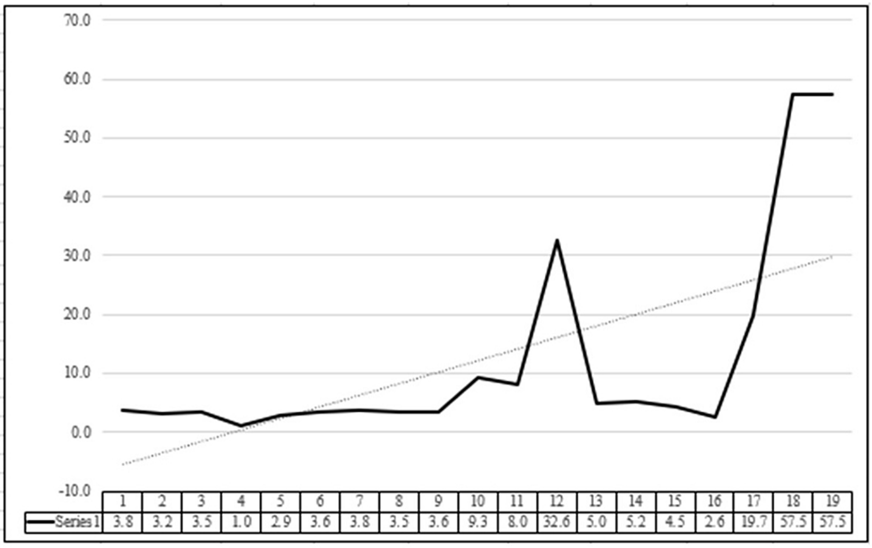


c) Hg

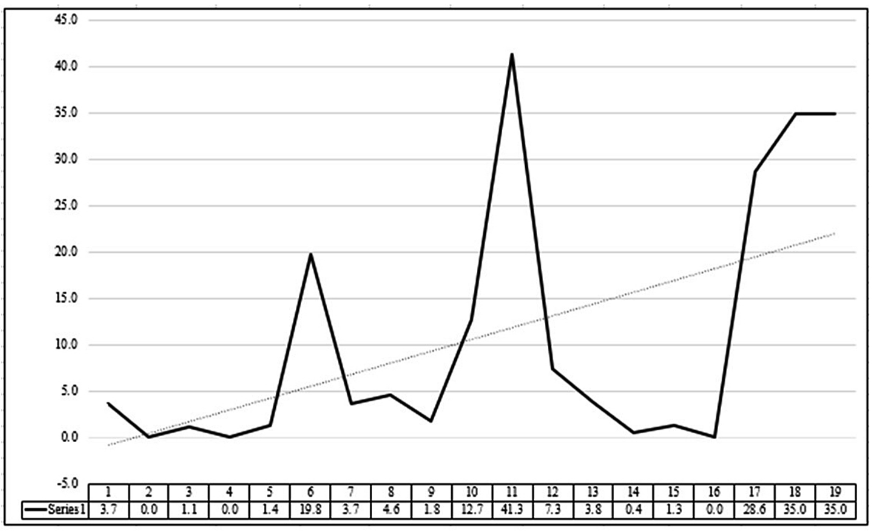
Figure 3. The danger coefficient of heavy metals: (a) chrome; (b) zinc; (c) mercury; Note: sampling points are marked on the Fig. 1; ss – serial number of soil sample



d)Pb

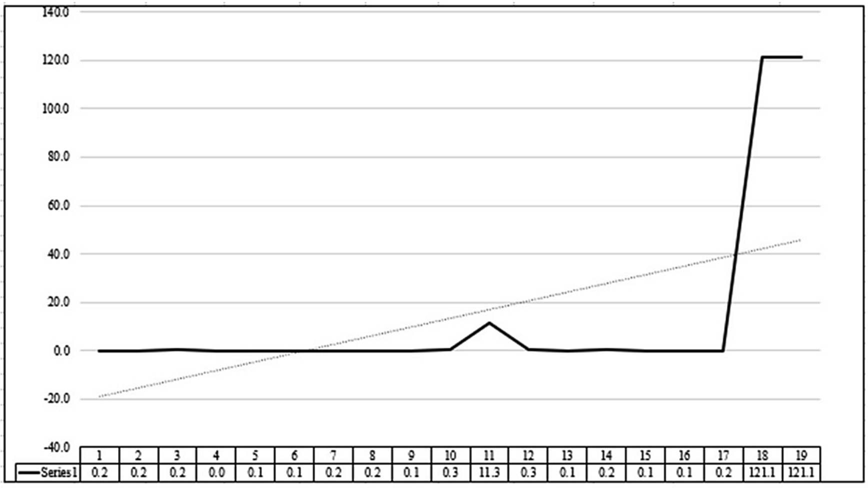


e) Ni



f) Cu

Figure 3. Cont. The danger coefficient of heavy metals: (d) lead; (e) nickel; (f) copper



g) Mn

Figure 3. Cont. The danger coefficient of heavy metals: g) manganese in the MIUA soil cover

MIUA soil cover were determined. Thus, abnormal levels exceeding the MPC, more than 100 times, are observed in the following samples: ss. 12 (K_o = 319); ss. 13 (K_o = 180); ss. 18 (K_o = 139.5); ss. 19 (K_o = 113.3) (Table 1; Fig. 3c). On the area after active hostilities the coefficient of concentration K_o, determined relative to the MPC (2.1 mg·kg^{-1}) is in the range of 0−319. The average indicator was 57.1. K_o(Hg) is represented in the decreasing series: ss.13 (319) > ss.12 (180) > ss.18 (139.5) > ss.19 (113.3) > ss.11 (57.4) > ss.14 (40.7) > ss.6 (40.5) > ss .7 (22) > ss.15 (21.3) > ss.3 (19.1) > ss.8 (17.6) > ss.9 (15.5) > ss.17 (15.1) > ss.10 (10.2) > ss. 16 (9.6) > ss.5 (4.8) > ss.1 (2.4) > ss.2 (0.0).

In the earth's crust, lead is contained at the level of 0.0016% by mass. It is a heavy, soft, malleable, gray metal with atomic number 82, belonging to the 14th group, 6th period of the periodic system of elements (Siegel, 1979; Roman-Vazquez et al., 2020). The average content of lead within MIUA is set at the level of 49.1 mg·kg^{-1}, with variation within the range of 0−151.2 mg·kg^{-1}. Fluctuation with increased lead content is more than 4 times observed in the areas: ss.11, where the concentration of lead pollution was recorded at the level of 132.6 mg·kg^{-1} (K_o = 4.1); ss.19 the pollution content was 151.2 mg·kg^{-1} (K_o = 4.7). Conditionally clean areas should be considered to be those where pollution does not exceed the MPC, namely: ss.6, ss.7 (concentration less than the maximum sensitivity of the device); ss.5 (K_o = 0.3); ss.16 (K_o = 0.5); ss.2, ss.13 (K_o = 0.7); ss.17 (K_o = 0.8) (Table 1; Fig. 3d). Fluctuations in the danger ratio are 0–4.7 with an average of 1.5. C_o(Pb) can be represented in a decreasing series: ss.19 (4.7) > ss.11 (4.1) > ss.3 (3.1) > ss.9 (2.1) > ss.12; ss.14 (2.0) > ss.1; ss. 8; ss.15 (1.4) > ss.18 (1.2) > ss.10 (1.1) > ss.17 (0.8) > ss.2; ss.13 (0.7) > ss.16 (0.5) > ss.5 (0.3) > ss.6; ss.7 (0.0).

Elements of 2-st danger class

Nickel (Ni) refers to scattered elements of the biosphere. Its average content in soils is 4.0·0^{-3}%. Content of the Nicol is 3.4·10^{-7}% in natural surface waters (Wuana, Okieimen, 2011; Modabberi et al., 2018). On average, the concentration of Nickel in the urban landscapes soil cover is 38.5 mg·kg^{-1}, which is 9 times higher than the MPC (4 mg·kg^{-1}). The spatial variation of Nicol in the studied areas is 4.2−230. The danger coefficient is determined at the level of 1−57.5 with an average statistical value of 9.6. Anomalous exceedances of MPC of Nickel content were recorded: ss.18, K_o = 19.7; ss.13, K_o = 32.6; ss.19, K_o = 57.5. The permissible level of pollution within the limits of the standard of the MPC is determined only within the limits of the selection in the park near the point of ss.5 (Table 1; Fig. 3e). K_o(Ni) is represented in a decreasing series: ss.19 (57.5) > ss.13 (32.6) > ss.18 (19.7) > ss.11 (9.3) > ss.12 (8.0) > ss.15 (5.2) > ss.14 (5.0) ss.16 (4.5) > ss.1; ss.8 (3.8) > ss.7; ss.10 (3.6) > ss.3; ss.9 (3.5) > ss.2 (3.2) > ss.6 (2.9) > ss.5 (1.0). Copper (Cu) is a rare chemical element with the atomic number 29. Its content in the earth's crust in the form of monovalent Cu(I) and divalent Cu(II) compounds is 3·10^{-3}% (Kobayashi, et al. 2015; Holden et. al. 2018). The content of copper in the MIUA soil cover varies in the range of 0−124 mg·kg^{-1}, the weighted average indicator is 33.3 mg·kg^{-1}. A significant rapid growth of the copper content was determined in the area of the point of ss.12. The concentration was determined at the level of 124 mg·kg^{-1}, K_o = 41.3. The indicator was 104.9 mg·kg^{-1}, which corresponds to K_o = 35 (ss.19), (Table 1; Fig. 3f). Accordingly, K_o is defined in the range of 0–41.3 with a weighted average indicator at the level of 9.2. K_o(Cu) can be represented in the decreasing series: ss.19 (35) > ss.18 (28.6) > ss.7 (19.8) > ss.11 (12.7) > ss.13 (7.3) > ss.9 (4.6) > ss.14 (3,8) > ss.1; ss.8 (3,7) > ss.10 (1,8) > ss.6 (1,4) > ss.16 (1,3) > ss.3 (1,1) > ss.5 (0 ,4) > ss.2; ss.5; ss.7 (0).

Elements of the 3rd class of danger

Manganese (Mn) is a chemical element with atomic number 25 in periodic table. It is contained in the earth's crust at the level of 0.1% by mass (Manganese Rocks and Ores, 2017). Mn varies in the range of 55.7–118668 g·kg^{-1} on the studied territory. The weighted average indicator is 11244.2 g·kg^{-1}. Accordingly, the weighted average K_o indicator is 7.5, the maximum value is 121 g·kg^{-1}. The results of the analyzes record an abnormally high concentration of 118668 g·kg^{-1} (ss. 19). The concentration exceeds the permissible level by 121 times. Rockets have been arriving in this neighborhood for a long time, it is an area of intense destruction. Attention should also be paid to the results of the analysis in the point of ss. 12, where the concentration reaches 16899.9 g·kg^{-1}. At this point, an 11-fold exceedance of the maximum permissible limit was recorded (Table 1, Fig. 3g). K_o(Mn) is represented in a decreasing series: ss.19 (121.1) > ss.12 (11.3) > ss.11; ss.13 (0.3) > ss.1; ss.2; ss.3; ss. 8; ss. 9; ss.15; ss.18 (0.2) > ss.6; ss.7; ss.10; ss.14; ss. 16; ss.17 (0.1) > ss.5 (0). So, within the urban landscapes of the MIUA, local geochemical anomalies were formed according to the K_o indicator, exceeding the MPC by 10 times, which can be presented in a decreasing order:

- ss.3: Hg (19.1);
- ss.6: Hg (40.5) > Cr (14.2);
- ss.7: Hg (22.0) > Cu (19.8);
- ss.8: Hg (17.6);
- ss.9: Hg (15.5);
- ss.10: Hg (10.2);
- ss.11: Hg (57.4) > Cr (20.1) > Cu (12.7) > Zn (10.9);
- ss.12: Hg (180.0) > Cr (6.03) > Cu (41,3);
- ss.13: Hg (319.0) > Cr (111.6) > Ni (32.6) > Zn (16.9);
- ss.14: Hg (40.7) > Cr (14.3);
- ss.15: Hg (21.3);
- ss.17: Hg (15.1);
- ss.18: Hg (139.5) > Cr (48.8) >Cu (28.6) > Ni (19.7) > Zn (10.9);
- ss.19: Hg (113.3) > Ni (57.5) > Cr (39.7) >Cu (35.0).

The integrated indicator of danger $\sum K_o(1+2)$, differentiated by the MPC of 1st and 2nd danger classes elements, on the territory of the MIUA is 23.6, which corresponds to the category of soil pollution "moderately dangerous" and indicates changes in the indicators of the health status of the population in pollution centers at the level of "increasing the level of general morbidity" (Table 1).

CONCLUSIONS

Soil pollution levels of the MIUA as a result of fighting took place in the area using explosive ammunition reach critical levels, affect the quality of the environment, and can cause a cumulative effect in the human body of the dusty fraction of highly toxic chemical elements of the I and II danger class. A geochemical anomaly of military origin was formed within the boundaries of the MIUA with exceeding the maximum permissible levels for the following chemical elements: Hg (57.1) > Cr (20.6) > Ni (9.6) > Cu (9.2) > Zn (5.3) > Pb (1.5). In 14 of 19 samples an excess of Hg in accordance with the MPC was found more than 10 times, and the range of K_o variation was determined in the interval (15.1–180.0). Contamination with copper compounds takes second place (7 samples out of 19) with fluctuations of K_o (14.2–111.6). It should be taken into account that today the active hostilities continue and increases man-made pressure caused by military aggression.

Therefore, the results of the heavy metals content study in soil cover are a basis for further research and the development of practical recommendations for soil restoration, the introduction of a monitoring system, and systematic observations in order to develop a system of measures to improve the environmental situation. In the future, research on the transformation of various forms of heavy metals in various types of plants is also relevant.

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