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Patterns of spreading of heavy metals in soils of urbanized landscapes (on the example of Brovary city)

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Abstract. Results of the study about pollutants content in soils of urbanized landscapes are presented. Patterns of their migration and accumulation in main soil types of Brovary are grounded. Correlation relationships between the individual components of ecological-geochemical system of urbanized territory were analyzed. Dependences of landscape resistance to technogenic pollution on the level of conservation of natural geochemical parameters of soils, degree of their anthropogenic transformation and level of heavy metals were determined. According to geochemical criteria technogenic associations of heavy metals in soils are determined, which are represented by the following elements: Cu>Pb>Zn>Co>Cr>V>Mo>Mn>Ni. Level of gross content of chemical elements compounds in soils of different zones of the city is heterogeneous. City zones with the highest polyelement contamination of soil have been identified. Maximum technogenic load is recorded in urban areas of transport infrastructure zone and zone of production and communal-warehouse facilities. Ecological and geochemical assessment on the total index of pollution by using methods of Y.E. Saeta, is shown. Value of this topsoil parameter in Brovary (0-10 cm) ranges from 30 to 106, the average is 65, which corresponds to hazardous level of soil pollution. According to the total indicator of technogenic pollution, Brovary belongs to cities with high pollution level. Soils in all parts of the city, except for residential areas, are classified as hazardous. Studied soils of the city are characterized by plumbum geochemical specialization. High levels of zinc, manganese, cobalt and chromium were also found (the maximal permissible concentrations in soil exceeds by 1.7-4.7 times). Especial attention is paid to the patterns, mechanisms of pollutants influence on the complex of soil properties and processes that determine the ecological condition of soils and their resistance to anthropogenic flows. Soil contamination by pollutants leads to changes in their physical and chemical properties (cation exchange capacity pH, organic matter content) which causes a low buffering capacity of soil cover of the city.

Keywords: heavy metals, gross content, mobile forms, urban soil, migration, spreading patterns

Закономірності розподілу важких металів у ґрунтах урбанізованих ландшафтів (на прикладі м. Бровари)

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Анотація. Наведено результати дослідження вмісту забруднюючих речовин у ґрунтах урбанізованих ландшафтів. Обґрунтовано закономірності їх міграції та акумуляції в основних типах грунтів м. Бровари. Проаналізовано кореляційні зв'язки між окремими компонентами еколого-геохімічної системи урбанізованої території. Встановлено залежності стійкості ландшафтів до техногенних забруднень від рівня збереження природних геохімічних параметрів ґрунтів, ступеня їхньої антропогенної перетвореності та рівня надходження важких металів. За геохімічними критеріями визначено техногенні асоціації важких металів у ґрунтах, які представлені такими елементами: Cu>Pb>Zn>Co>Cr>V>Mo>Mn>Ni. Рівень валового вмісту сполук хімічних елементів в ґрунтах різних зон міста різнорідний. Виявлено зони міста з максимальним поліелементним забрудненням ґрунтів. Максимум техногенного навантаження зафіксовано в урбаноземах зони транспортної інфраструктури та зони виробничих та комунально-складських об'єктів. Наведено еколого-геохімічну оцінку за сумарним показником забруднення з використанням методик Ю.Є. Саєта. Значення цього показника поверхневого шару ґрунту м. Бровари (0-10 см) коливається від 30 до 106, середній показник – 65, що відповідає небезпечному рівню забруднення ґрунтового покриву. За сумарним показником техногенного забруднення м. Бровари відноситься до міст з високим рівнем забруднення. Ґрунти всіх зон міста, за винятком житлової, віднесені до категорії небезпечних. Досліджувані ґрунти міста характеризуються свинцевою геохімічною спеціалізацією. Встановлено також досить високі рівні цинку, мангану, кобальту та хрому (перевищення ГДК у ґрунті в

1,7-4,7 рази). Окрему увагу приділено закономірностям, механізмам впливу забруднюючих речовин на комплекс ґрунтових властивостей і процесів, що визначають екологічний стан грунтів і їх стійкість до техногенних потоків. Забрудненість грунтів полютантами призводить до змін їх фізико-хімічних властивостей (катіонно-обмінна ємкість, рН, вміст органічної речовини), що зумовлює низьку буферну здатністю ґрунтового покриву міста.

Ключові слова: важкі метали, валовий вміст, рухомі форми, урбанеземи, міграція, закономірності розподілу

Introduction. Methodological component of the ecological-geochemical assessment of urbanized territories is landscape-geochemical analysis of the environment conditions. An important area of such analysis is studyi of pollutants migration, transformation of technogenic flows and accumulation of pollutants in individual components of the landscape, taking into account the natural conditions and reactions of natural landscape systems to anthropogenic impact.

Intensive development of industry and increase of economic activity types of society are the reason and consequence of urbanization processes growth. In Ukraine, there is a steady upward trend in the share of urban population. Presently, the urbanization rate is 67%, but according to the UN forecasts the proportion of urban population in Ukraine will reach 79.0% in 2050. Constantly growing pollution of natural systems, as a result of anthropogenic activities and low efficiency of methods for extraction of pollutants pose a threat to the human health and the environment as a whole.

Under the influence of urbanization-technogenic processes, geochemical transformation of soils takes place, which leads to the violation of their properties and structure. The most significant geochemical changes in soils are confined to the top soil horizons, into which a significant amount of dust and aerosols containing pollutants comes from the atmosphere. In particular, small dust fractions, humus substances increase the absorption capacity of urban soils and carbonate dust falling leads to an increase in the pH of the top layer soil horizons. Topsoil burdened by the accumulation of pollutants, including heavy metals (HM) and radionuclides. The most common pollutants found in the soil of cities are: plumb on the example of the city of Brovary, Kyiv region (Pb), mercury (Hg), chromium (Cr), cuprum (Cu), nickel (Ni) and zinc (Zn) content (Zhovinskiy et al., 2002; Zhovynskyi et al., 2012). Technogenic geochemical anomalies in the topsoil of cities are more stable than in adjacent environments. Therefore, degree of contamination of soil cover is the main environmental and geochemical criterion for characterizing anthropogenic impacts.

The purpose of this work is ecological-geochemical assessment of urban areas; establishment of the degree of contamination by HM of individual components of urban landscapes, revealing patterns of their behavior in topsoil.

Theoretical basis of the modern ecological-geochemical studies of urban areas is the basic scientific concepts of geochemistry of landscapes (Polynov, 1952, 1956; Hlazovska, 1972, 1976; Perelman, 1975, 1979, 1999; Kasymov, 1982, 1995, 2004, 2013). The studies of B.F. Mitskevycha (1971, 1981), E.Ia. Zhovynskoho (1976, 1979, 1980, 1981, 1991, 1992, 2005, 2012), A.I. Samchuka (1982, 1993, 1998, 2002, 2005, 2006, 2012), I.V. Kuraievoi (1996, 2014, 2002, 2010, 2011, 2012, 2013, 2015, 2019), L.L. Malyshevoi (1997, 2000), H.M. Bondarenka (2000, 2002, 2004), V.O. Yemelianova (2004), V.V. Dolina (2004, 2011, 2011b, 2011), H.V. Lysychenka (2009), O.Iu. Mytropolskoho (2004, 2006), V.M. Shestopalova (2011) including other scientists have made a significant contribution to ecological-geochemical studies of individual components of the landscape in Ukraine. Studying of the content of toxic elements in the topsoil cover of urban areas is devoted to the following works: S.S. Voloshchynskoi (2008, 2012), Y.V. Henyka (1994, 1996), P.P. Nadtochii (2012), M.V. Pelypets (2000), T.K. Klymenko (2005), V.S. Homicha (1996, 1997, 2004, 2005, 2013), A. Greinert (1995, 1998, 1999), C. Ferguson (1999), P. *Wieczorkowski (2002, 2005*)*,* Wang KY, Han P, Zhang SZ. (2012), Stockmann, U. (2015), Schneider, A.R. (2016) including other researchers. However, most of the studied urban agglomerations did not lend themselves to the complex landscape-geochemical analysis.

The current study focuses not only on the determination of HM in urban landscapes within the areas of impact of man-made objects, but also on the analysis of the conditions of their lateral migration in the soil cover of the urban environment.

Materials and methods of the study. The sdudy object is the landscape complexes of Brovary, located within areas of influence of large industrial enterprises and municipal-warehouse facilities.

Research was performed using analytical, cartographic, statistical methods, as well as methods of landscape-geochemical researches with the use of GIS-analysis tools. Basic information on the landscape-geochemical structure of the territory is supplemented by detailed geochemical studies of landscapes in key areas.

Methodology of soil-geochemical survey provided for the selection of pooled soil samples (for each field and soil sections, respectively) according to the current DSTU (State Standards of Ukraine) 4287: 2004, DSTU (ISO) 10381-2: 2004; study of particle size distribution of soils - DSTU 4730: 2007; determination of total soil humus - DSTU 4289: 2004; soil pH – GOST (All Union State standard) 2621291. Methods for determining composition and properties of soils; pH of the water extract - GOST 17.5.4.01-84. Soil sampling was carried out according to the regular network of key sites, taking into account the features of the functional zoning of Brovary. 1674 soil samples from 7 zones of the city were selected and analyzed in total.

To determine the geochemical parameters the following modern physicochemical methods were used: emission spectral analysis, atomic absorption, potentiometric, etc. For all key areas of the study, total technogenic contamination (Zc) was calculated using the formula (Saet, 1990):

$$Zc = \sum Kn_{si} - \ldots(n-1),$$

where *n* is the number of anomalous elements;

Soil samples determined their basic physicochemical properties and total trace element content. The particle size distribution was determined by the Casa-grandex isometric method, the pH potentiometrically in a suspension of 1 mol dm^3 of HCl solution. Hydrolytic acidity and exchange cations – Ca^{2+}, Mg^{2+}, K^+, Na^+ are determined by the Kappen method.

Content of HM was determined by mass spectral (ICP-MS) and atomic emission methods (ICP-AES) with inductively coupled plasma on Elan-6100 devices and Optima-4300 DV (Perkin-Elmer, USA) also ICP–MS analyzer ELEMENT-2 (Germany) at the Institute of Geology of the Polish Academy of Sciences and the Institute of Geochemistry, Mineralogy and Ore Formation of the NAS of Ukraine named after M.P. Semenenko.

Correlation coefficients were calculated for the statistical evaluation of test results. These coefficients and content of HM in the soil samples were compared with the values that determine the geochemical background of soils according to the National Science Center "*Institute of soil sciences named after Sokolovsky*" as well as the normative indexes of the GDK values of gross content and GDK of mobile forms of pollutants in soils (Dobrovolskiy, 1983; Fatieiev et al., 2003). To assess soil contamination, Kc concentration coefficient was calculated using the formula: Kc = C / Sf, where: C is the actual content of the contamination; SF is the background content.

Results and discussion. Content and distribution of HM in soil profiles is determined by the amount of organic matter, physical and chemical properties of soils and the course of the soil-forming processes. The natural content of trace elements in the soil depends primarily on the type of parent rock, which is their main source of genesis (Kabata-Pendias, 1989; Samonova et al., 1998; Vorobyova et al., 1980 Zhovinskiy et al., 2002).

Typical features of urban soils are neutral or alkaline reaction, increased bulk weight, reduced moisture and compaction. This complicates an ability to identify the dependence of physicochemical changes occurring in soil cover and contributes to the fixation of pollutant elements.

Territory of the city is polluted with elements of I-III class of hazardous - plumbum, zinc, cobalt, cuprum, etc. Plane pollution exceeds background values and some man-made fields have indicators in excess of MPC. The study was allocated to areas with a high content of chemical elements that form the plane and pinpoint anomalies (Table 1).

During the landscape-geochemical study of the territory of Brovary, special attention was paid to the territories under the influence of enterprises, characterized by high level of air emissions: State-owned powder metallurgy plant, CJSC "Brovarskyy zavod plastmass", JV "BROVARSKYI FACTORY AUCTION ENGINEER, CO", Municipal Enterprise "KZASK LTD", "Polymer Color LLC".

Plumbum. The Earth's crust plumbum accumulates almost exclusively as Pb^{2+}, sporadically Pb^{4+}. In igneous rocks, Pb is present in dispersed form, mainly in feldspars and biotites. Plumbum has high sulphide tendencies, which are appeared in the formation of sulphide minerals. It is highly dispersed in sulfide liquids and is converted to residual sulfide products. It shows high geochemical affinity with zinc, forming common geochemical anomalies (Avessalomova I.A., 1978; Kabata-Pendias A., 1989).

The presence of a plumbum in city soils is directly related to the mineralogical and granulometric composition of soil rocks. Plumbum, due to the poor solubility of minerals, migrates in the soil less intensively than Cadmium and Zinc. Elevated levels of plumbum in the topsoil layers are largely associated with anthropogenic influence production and communication of emissions. Acidic reaction of soils, their poor absorption capacity and low humus content increase the absorption of plumbum by plants (Alloway, 1995; Avessalomova, 1978; Bakker et al., 1997; Samonova, 1998; Vorobyova et al., 1980).

Plumbum compounds from anthropogenic sources accumulate in the surface soil layer of

Table 1. Coefficients of HM concentration by functional zones of Brovary (calculated based on results of own research)

Chemical element	Public area	Residential area	Land-scape and recre-ational area	Area of transport infra-structure	Area of engineering infrastructure	Area of pro-duction and municipal-warehouse facilities	Special pur-pose area	Regional background values (by A.I. Fateev)
Mn	**400**	**380**	**220**	**760**	**670**	**910**	**830**	395
Kc	1.01	0.9	0.5	1.9	1.7	2.3	2.1	
Ni	**9.4**	**8.3**	**8.1**	**10**	**7.5**	**11**	**10**	12
Kc	0.7	0.69	0.67	0.83	0.6	0.9	0.8	
Co	**5.6**	**4.7**	**4.1**	**6.4**	**32**	**52**	**44**	10
Kc	0.56	0.47	0.4	0.64	3.2	5.2	4.4	
V	**14**	**9.5**	**11**	**10**	**32**	**43**	**29**	16
Kc	0.87	0.59	0.68	0.62	2	2.6	1.8	
Cr	**42**	**55**	**28**	**82**	**110**	**138**	**102**	39
Kc	1.07	1.4	0.7	2.1	2.8	3.5	2.6	
Mo	**2.1**	**1.9**	**1.7**	**4.2**	**5.1**	**6.4**	**4.5**	2.4
Kc	0.87	0.79	0.7	1.7	2.1	2.6	1.8	
Cu	**31**	**43**	**38**	**115**	**340**	**540**	**490**	8
Kc	3.8	5.3	4.7	14.3	42.5	67.5	61	
Pb	**55**	**18**	**16**	**82**	**76**	**78**	**62**	11
Kc	5	1.6	1.4	5.8	6.9	7	5.6	
Zn	**35**	**55**	**32**	**110**	**165**	**230**	**170**	42
Kc	0.8	1.3	0.76	2.6	3.9	5.4	4	

urban areas. Dispersion of plumbum in all surface environments is associated with its widespread use in the production of batteries and gasolines with the addition of its compounds. A part of the plumbum accumulated in the soil is formed by the incineration of waste. Its compounds are used for the production of paints, pesticides, plastic stabilizers and metallic lead in accumulators, alloys and pipes receiving sewage channels after production (Kabata-Pendias, 1989).

High coefficients of plumbum variation within the city indicate the sporadic nature of spreading of the pollutant, which is a consequence of anthropogenic origin. Gross content of plumbum (Pb) in urban soils of all functional zones of Brovary exceeds its background content (25-28 mg / kg). The low level of gross Pb content is characterized by soils of landscape-recreational and residential zones (16-21 mg / kg) while in the soils of transport and engineering infrastructure zones (80-400 mg / kg) its content varies from medium to very high. In 58% of the city soils, the gross plumbum content is 1.1-3.2 MAC. Excess of the maximumal permissible concentration of plumbum by 1.2-3.5 times is observed in 70% of the territory of industrial and municipal-warehouse facility zones and by 1.1-2.0 times in 39% of the residential territory.

The highest concentrations of plumbum (348, 400 mg / kg) were recorded along Gagarin Street and within the engineering corridor along Onikienko street. Very high level of soil pollution (more than 400 mg / kg) was found in 2% of the city territory (urban soils of the public zone) by 9% (urban soils of the transport infrastructure zone) - medium and high (250-370 mg / kg) and only 15% - low (80-120 mg / kg), which is associated with the high transport loads in the suburban area of Kiev.

Cuprum. In soils, cuprum is found in various forms, usually creating sedentary compounds in the form of precipitation of carbonate and sulfate. Cuprum is highly sorbed by organic substances and clay minerals. Absorption of cuprum connected inversely with the reaction soil acidity; decrease in pH increases the availability of this element, with increase in soil pH, level of absorption of the element decreases (Avessalomova, 1978; Kabata-Pendias, 1989; Vorobyova et al., 1980 Vinohradov, 1957).

Cuprum is widely used in electrical engineering, decorative products both in pure form and in alloys (bronze and brass). Cuprum compounds are also used in the manufacture of plastics, plant protection products, fertilizers, paints, pharmaceuticals and other industries (Kabata-Pendias, 1989).

Soils of the city are characterized by increased cuprum content. In most tested samples, concentration limits exceed the background (8 mg / kg) and MPC (33 mg / kg) by a factor of ten. The maximum cuprum content (1000 mg / kg) was fixed in the sample No 231, taken from the lawn around Peronna street. Data on the gross content of cuprum (Cu) in the soils of production and municipal-warehouse facilities zone (600-1000 mg / kg) and residential zone (80-100 mg / kg), public zone (400-600 mg / kg) can be united into a single generalized unity. It is characterized by an increased and high level of the content of this metal, while in the soils of the landscape-recreational zone (30-50 mg / kg) the cuprum content is relatively low. In 90% of soil samples taken in different parts of Brovary, MPC is exceeded by gross cuprum content by 30 times; this is primarily typical for urban soils in the production and municipal-warehouse facilities and special-purpose zones.

A similar situation is observed for the gross ***vanadium*** content. The level of this metal in the soils of the public zone is assessed as average (10-18 mg / kg), whereas in soils of production and municipal storage facility zones their excess amount is (> 40 mg / kg) and in 20% of the studied territories the MPC exceeds by 3.1 types in average and makes 150 mg / kg.

Nickel and cobalt. Soil cover of the territory plays a decisive role in the spreading of nickel and cobalt, content of which depends on their amount in the parent rock. The maximum values of Ni and Co are confined to the humus horizons of soil. In gley horizons, at high concentrations of iron, noticeable decrease in pollutants occurs compared to ungleened (Vorobyova et al., 1980; Vinohradov, 1957; Zhovinskiy et al., 2002; Zhovynskyi et al., 2012.).

Analysis of the studies shows the clear trend in uniform distribution of pollutants in the soils of the city. Nickel and cobalt content does not exceed the upper limit of permissible concentrations in the surface horizons of the soil (Ni - 8-10 mg / kg, Co - 4-6 mg / kg). Only in the area of Metallurgov, Schelkovskaya and Onikienko streets, their content exceeds the MPC by 2-4 times (reaching 100 mg / kg).

Zinc. Pollutants accumulate in top layer horizons, where it is sorbed by organic matter and clay particles. Interacting with humus forms stable compounds, and the adsorption level depends on pH. In alkaline environment zinc is absorbed by the mechanism of chemisorption, and in the acidic environment of the ion adsorption Zn weakens due to competition with other ions, which leads to the desorption from the solid phase into the soil solution and leaching Zn. Proportion of mobile zinc increases with increasing of acidity (Alloway, 1995; Samonova et al., 1998).

Soils of the city are characterized by contrast distribution of zinc: from 60 to 1000 mg / kg. In most samples zinc content does not exceed 120 mg / kg, with a regional background value of 42 mg / kg. Zinc is one of the most heavily used non-ferrous metals. In general (more than 90%), it is used in metal state and is used to coat steel sheets and metal caster for corrosion protection (for example, in automobiles, construction). Alloys (bronze, brass) are widely used for the manufacture of machine parts and accessories. Dispersion of zinc in metal form is small, but its compounds are easier to migrate, which are used in the manufacture of rubber, plant protection products, fertilizers, pharmaceuticals and cosmetics. An important source of soil zinc pollution is paint production, coal burning, tire detrition, sewage discharges, as well as leaching from landfills (Vorobyova et al., 1980; Samonova et al., 1998).

Increased content of zinc in soils is observed mainly in the northeast and northwest of the region - within the territory of most industrial and adjacent to the main roads. The highest concentration of zinc was observed in soils located on Lisova, Bandery, Fialkovskoho, Symonenka streets. The maximum content of zinc (1050 mg / kg) was found near the “KZASK LTD” plant.

Very high zinc content (530-827 mg / kg) is typical for soils nearby the enterprises: CJSC “Brovarskyy zavod plastmass”, JV “BROVARSKYI FACTORY AUCTION ENGINEER, CO”. Content of 347 mg / kg of zinc was also found on Pereyaslav Shlyakh and Stepana Bandery streets.

Mangan. Significant accumulation of manganese in the top layer horizons of soil cover is associated with the fixation of this element with humic substances (Alloway, 1995; Avessalomova, 1978). Manganese compounds are well soluble, especially during the acidic reaction of the environment.

Soil cover of the territory contains relatively high manganese content, but the concentration coefficient in soils does not exceed 6 in average, and more than 40% of the surveyed areas contains from 360 to 540 mg / kg of this element. The maximum manganese content was recorded in the area of industrial and municipal storage facilities (2300 mg / kg). Moreover, the concentration within the city varies from 320 to 1900 mg / kg. Manganese soil pollution is especially significant near the enterprises: State-owned powder metallurgy plant (1910 mg / kg) and OJSC “Building constructions plant”.

Chromium. Chromium content in soils is mainly determined by its content in the parent rock [1]. The main part of chromium in soils is in trivalent form. In acidic soils, chromium compounds are almost station-

Table 2. HM concentration coefficients by functional zones of Brovary (Calculated according to our own research results)

Chemical element	Public area	Residential area	Landscape and recreational area	Area of transport infrastructure	Area of engineering infrastructure	Area of production and municipal-warehouse facilities	Special purpose area	Regional background values (by A.I. Fateev)
Mn	**400**	**380**	**220**	**760**	**670**	**910**	**830**	395
Kc	1.01	0.9	0.5	1.9	1.7	2.3	2.1	
Ni	**9.4**	**8.3**	**8.1**	**10**	**7.5**	**11**	**10**	12
Kc	0.7	0.69	0.67	0.83	0.6	0.9	0.8	
Co	**5.6**	**4.7**	**4.1**	**6.4**	**32**	**52**	**44**	10
Kc	0.56	0.47	0.4	0.64	3.2	5.2	4.4	
V	**14**	**9.5**	**11**	**10**	**32**	**43**	**29**	16
Kc	0.87	0.59	0.68	0.62	2	2.6	1.8	
Cr	**42**	**55**	**28**	**82**	**110**	**138**	**102**	39
Kc	1.07	1.4	0.7	2.1	2.8	3.5	2.6	
Mo	**2.1**	**1.9**	**1.7**	**4.2**	**5.1**	**6.4**	**4.5**	2,4
Kc	0.87	0.79	0.7	1.7	2.1	2.6	1.8	
Cu	**31**	**43**	**38**	**115**	**340**	**540**	**490**	8
Kc	3.8	5.3	4.7	14.3	42.5	67.5	61	
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Kc	5	1.6	1.4	5.8	6.9	7	5.6	
Zn	**35**	**55**	**32**	**110**	**165**	**230**	**170**	42
Kc	0.8	1.3	0.76	2.6	3.9	5.4	4	

Notes. Kc is the concentration coefficient

ary and at pH 5.5 precipitate (Avessalomova, 1978). The main man-made sources of chromium include the chemical industry (Vorobyova et al., 1980; Vinohradov, 1957; Zhovynskyi et al., 2012.).

Pollutant enters the soil from ore dumps, scrap metal and household chromium-containing waste.

Regional background value of chromium for city soils is 39 mg / kg. The average content in sandy and clay soils is 37 mg / kg. It is proved that the average content of gross forms of Cr in soils of the city, in particular in soddy-low-podzolized sandy and sub-sandy, is 32-42 mg / kg. Little fluctuations of Cr content in some soils were detected and more of these elements correspond to light gray, clay loamy and alluvial sandy loam soils - 60-80 mg / kg of soil. Maximal values are fixed for special purpose areas (102 mg / kg) and engineering infrastructure (110 mg / kg). High chromium content (92-140 mg / kg) is also typical for the soils of production and municipal storage facility zones.

In residential area of Brovary the accumulation of HM in soils occurs similarly to nutrients in a concentric type. This is due not only to the type of parent rocks, but also to temporary differences in the development of these territories.

Local technological anomalies, taking into account regional characteristics, allow to identify the concentration coefficients we calculated (Table 2). HM content in the soils of Brovary is increased (Ks> 1.0) compared to the background territories that do not experience significant anthropogenic impact.

According to the values of this coefficient in the city soils there is an increased gross content of HM in comparison with the background values. Content of Cu, Pb, Zn is increased (Kc>3) in zones of engineering infrastructure and production and municipal-warehouse facilities; Pb, Zn, Co – in area of engineering infrastructure; Pb and Cu in public area; Zn, Ni, Pb i Cu – in area of transport infrastructure.

For gray soils - Pb, Cu; for sod-podzolic soils – Pb i Cu; for sod-podzolic silt and meadow soils – Cu i Zn; for urban soils the main pollutants are Cu, Zn, Pb (Kc> 4.0);

In general, Brovary has found the presence of polyelement contamination of urban soils. In soils of technogenic and anthropogenic zones of the city the main pollutants are: Cu, Pb та Zn. Ranges of accumulation of the gross forms of HM in accordance with the Kc in the functioning of the city are as follows:

Public area:
Pb>Cu>Cr>Mn>V>Mo>Zn>Ni>Co;
Residential area:
Cu>Pb>Cr>Mn>Zn>Mo>Ni>V>Co;
Landscape Recreation Area:
Cu>Zn>Pb>Mo>Cr>Mn>V>Ni>Co;
Transport infrastructure area:
Cu>Pb>Zn>Cr>Mn>Mo>Ni>Co>V;
Engineering Infrastructure Area:
Cu>Pb>Zn>Co>Cr>Mo>V>Mn>Ni;
Area of production and municipal-warehouse facilities: Cu>Pb>Zn>Co>Cr>V>Mo>Mn>Ni;
Special Purpose Area:
Cu>Pb>Co>Zn>Cr>Mn>V>Mo>Ni.

Soils of landscape and recreation zone are characterized by the lowest content of heavy metals: for many elements Kc <1, accumulation is observed only for Cu and Pb. One of the highest concentrations of pollutants in the city has been identified in the area of production and municipal l-warehouse facilities and special purpose area. Pb, Zn (Kc = 5.8 i 2.6) as well Cr, Mo, Ni (0.8-2.1) usually accumulate near major highways. V (0.62) was found in lower concentrations. Localization of HM anomalies is recorded in the urban industrial area and near highways.

In residential area of the city soils of one-apartment buildings and zones of multi-apartment small and medium-sized buildings are different. The processes of accumulation and scattering of HM in soils of private buildings are less intense than multi-apartment, despite their significant emission. Areas of single-family buildings are characterized by a weak geochemical transformation of soil curve: for most elements Kc <1,0, except Zn, Pb. In the area of multi apartment building higher concentrations of pollutants were found: for Cr and Cu (Kc = 1.4 i 5.3 relatively). In the background soils and in the landscape and recreational zone of the city, except for the association of Cu>Zn>Pb>Mo>Cr>Mn>V>Ni>Co the association Cu>Pb>Cr>Mn>Zn>Mo>Ni>V>Co is observed. Composition of associations in soils of private building areas is close to the background values and values of the landscape and recreational area.

When comparing the background and urban areas anthropogenic association is highlighted: Cu>Pb>Zn>Co>Cr>V>Mo>Mn>Ni. It is dated to production and municipal-warehouse objects and zones of special purpose, investigated HM are characterized by high technophilicity.

The mobile forms of HM are in the particular content in the estimation of the ecological-geochemical state of soils is, which are able to pass from solid phases to soil solutions and be absorbed by living organisms. That is why we have evaluated the content of mobile forms of HM both in soils of main functional zones of the city and in main types of soils within the city of Brovary.

Unlike the gross content, a concentration of mobile forms of plumbum in soils of all studied functional zones of the city does not exceed the MPC. Exceedance of sanitary and hygienic indicators is also not noted for cobalt and nickel. Unlike the gross content of HM in soils, which shows a clear difference between anthropogenic and man-made areas of the city the series of accumulations of HM by Kc for all functional zones of the city are similar. The most dangerous pollutants are the mobile forms of Zn and Pb (Table 3).

The content of mobile forms of zinc in soddy-slightly podzolic sandy and sandy loamy soils is within acceptable values, while the soils of production and municipal storage facility zone are beyong the MPC. 58% of the territory of the special zone and transport infrastructure zone of mobile zinc in the soil exceeds the MPC by 1.1-2.7 times. Soil of all functional zones of Brovary exceeds the MPC in terms of the

Table 3. Content of mobile forms of HM in functional zones of Brovary (according to our own research)

Functional area	Ni	Co	Cr	Cu	Pb	Zn
Public area	0.59	0.27	0.26	2.8	0.61	4.10
Residential area	0.29	0.31	0.21	5.7	0.34	4.30
Landscape and recreational area	0.31	0.33	0.32	2.9	0.58	3.88
Area of transport infrastructure	0.56	0.50	0.41	4.30	1.03	4.90
Area of engineering infrastructure	0.42	0.72	0.38	3.87	0.93	5.60
Area of production and municipal -warehouse facilities	0.68	0.81	0.49	6.80	0.88	6.80
Special purpose area	0.52	0.58	0.51	9.70	0.94	6.60
MPC of mobile forms Kysel V.I., 1997 (acetate-ammonium buffer, pH 4.8)	4	3	6	3	2	23

content of movable cuprum. In 90% of the territories of production and municipal storage facility zone objects and special purpose zone, regardless of the soil type, content of movable cuprum reaches 1.4-3.2 MPC, in 32% of the residential zone (urban soil) - up to 1.1-2, 3 MPC. In soddy viscous sandy loam soils 34% and in light gray soils 19% there is an excess of MAC for mobile copper, which is 1.2-3.4 MAC and 1.1-1.6 MAC, respectively.

The content of mobile forms of iron in the soils of residential and public areas of the city is within the normal range (0.24 mg / kg), and in the soils of the landscape-recreational zone there is a sharp increase in its content (0.52 mg / kg). Accumulation of iron in these soils can be associated both with the features of parent rocks and with destruction of glandular compounds entering the soil with well-preserved plant residues.

We have identified the following associations of accumulation of mobile forms of heavy metals, typical for various functional zones of the city:

Public area: Zn>Cu>Pb>Ni>Co>Cr;

Residential area: Zn>Cu>Pb>Co>Ni>Cr;

Landscape and recreational area: Zn>Cu>Pb>Co>Cr>Ni;

Area of transport infrastructure: Zn>Cu>Pb>Ni>Co>Cr;

Area of engineering infrastructure: Zn>Cu>Pb>Co>Ni>Cr;

Area of production and municipal-warehouse facilities: Zn>Cu>Pb>Co>Ni>Cr;

Special purpose area: Cu>Zn>Pb>Co>Ni>Cr.

Natural background soils by the content and degree of contamination of mobile forms of heavy metals have low content of Ni, Co, Cr and average – Cu, Pb and Zn (Table 4).

7% of the public and residential area soils and 32% of the landscape and recreation area soils are poorly polluted with Cu, 11% territory of the engineering infrastructure zone and 21% of the city areas occupied by light gray loamy soils have a high degree of soil contamination by this pollutant.

Background soils of the city accumulate mobile forms of HM in the following order of declining:

Light gray sandy: Cu>Zn>Ni>Pb>Cr>Co;

Light gray loam: Zn>Cu>Ni>Pb>Co>Cr;

Turfy slimy slightly saline light-loamy: Zn>Cu>Pb>Ni>Co>Cr;

Turfy -slightlypodzolic sandy-loamy: Zn>Cu>Ni>Co>Pb>Cr;

Alluvial layered sandy loam: Zn>Cu>Co>Pb>Ni>Cr.

According to the summed indicator of the soil pollution by mobile forms of heavy metals, the studied functional zones of the city experience a moderately hazardous technogenic load.

Comparing values of Zc in gross content of HM with content of their mobile forms, it can be assumed that in the soils of production and municipal storage facility zone, most of the HM is in a form readily available to plants. While the soils of residential and landscape recreational areas are characterized by opposite tendency, the metals here accumulate mainly in fixed, stationary forms. In turfy - slightlypodzolic sandy-loamy and turfy loam soils of the background areas of the city no significant fluctuations in gross contents of Cr, Ni and Co are observed along the soil profile. Compared to urban soils, the accumulation of heavy metal compounds from deep soil horizons is observed in the soils of background territories. Obviously, this is due to a significantly lower level of technogenic load and increased acidity of top layer horizons of natural soils, compared to urban soils. Under such conditions solubility of compounds of the most HM increases and their migratory capacity increases. Low content of HM in top layer humus horizon and overwhelming accumulation of them in the lower soil horizons is also explained by the absence of woody vegetation forms in the background. Obviously, this prevents the movement of HM from parent rocks to the top layer horizons of the soil and land. In this case, a low contrast biogeochemical barrier associated with the formation of plant biomass is observed. The only exception is zinc, whiches content in the top layer soil horizon is slightly higher. Urban soils are heavily polluted by HM compared to natural background soils. Maximum concentrations of contaminant elements in most cases are confined to the top layer organogenic horizon, where the process of humus creation is intensively taking place, which contributes to the binding of HM and their accumulation.

Other horizons of the studied soils are characterized by low humus content (up to 0.4%), reaction of soil solution medium changes and soil density increases with depth. These properties lead to a decrease in the microbiological activity of soils and mobility of heavy metals. Spreading of the part of HM (Pb, Zn, Cu) in soils of functional zones of the city is subject to general trends: in soils of natural and anthropogenic zones along the profile of HM they are distributed evenly, as in soils of the background territory with a small accumulation in the top layer horizon. For technogenic and anthropogenic zones of the city, regardless of soil type, there is a clear accumulation of metals in the top layer soil horizon.

Table 4. Content of gross and mobile forms of HM in the background soils of Brovary, mg / kg (according to the results of own research)

№	Soil	Ni	Cr	Zn	Co	Cu	Pb
1	Light gray sandy	15	21	45	4	11	32
		1.6	0.26	2.1	0.18	2	0.38
2	Light gray loam	20	34	55	6	23	38
		1.5	0.36	1.9	0.38	3.1	0.43
3	Turfy slimy slightly saline light-loamy	12	29	38	8	34	35
		0.49	0.32	4.52	0.37	2.37	0.47
4	Turfy -slightlypodzolic sandy-loamy	19	21	58	8	32	24
		1.3	0.27	3.42	0.9	3.18	0.33
5	Alluvial layered sandy loam	11	19	34	6	26	20
		0.26	0.24	2.1	0.53	1.12	0.29
	MPC of mobile forms Kysel V.I., 1997 (acetate-ammonium buffer, pH 4.8)	4	6	23	3	3	2

This is primarily due to the aerotechnogenic nature of the pollution of these soils. The accumulation of these metals is also affected by the sorption barrier, which manifests itself in the fixation of metals by organic matter and clay components. For example, Cu and Zn, being trace elements, can accumulate in the upper horizon and due to biogenic accumulation (Avessalomova, 1978; Bakker et al., 1997).

Spreading of Ni, Mn, and V has its own characteristics. In the background territories soil accumulation of Ni, Mn, humus eluvial at a depth of 8-10 cm, and V accumulates in the transition to the soil-forming rock horizon, at a depth of 28 cm.

Similar patterns are typical for Ni in the soils of all technogenic and anthropogenic zones of the city for Mn - in soils of industrial and municipal - warehouse facilities zone, for V - in soils of both engineering infrastructure zone and landscape and recreation zone. In soils of residential and public zones, Mn and V accumulate in the top layer humus horizon.

Thus, accumulation of HM in soils of the city is affected by degree of man-made and anthropogenic load, features of polluting element itself and biogeochemical barriers. In the spreading of mobile forms of HM along the profile of urban soils, regardless of their type, general patterns could not be identified. Obviously, they are largely associated with the physicochemical composition of soils. Most migration capacity of mobile forms of Pb is observed in soils of transport infrastructure area and the area of industrial and municipal storage facilities, where the holding capacity of HM varies with a reduced content of organic carbon and depending on the absorption capacity of soils. In soils of residential and public areas, the maximal accumulation of Pb was recorded in transition horizon to soil-forming rock, since pH level, which is maximal in it, plays a decisive role. In most territories of natural and anthropogenic zones of the city, Pb accumulation is observed in illuvial-humus horizon. Spreading of mobile Zn forms along the soil profile of background soils and soils of residential and landscape-recreational zones is uniform also for light gray sandy loamy soils is a similar pattern of spreading of its gross forms. In soils of production and municipal storage facilities zone, two maximums of zinc mobile forms accumulation are observed: in top layer horizon, most enriched in humus and in the lower, where the pH of soil solution increases. Accumulation of mobile forms of Cu and Co in urban soils and soils of the background territory is approximately similar in profile, with the exception of soils of the special-purpose zone, where two accumulation maximals are observed in Cu, as in Zn and in Co - one in the illuvial-humus horizon with signs of urban pathogenesis.

The pH of the soil solution also affects the accumulation of Ni in the transition to the soil-forming rocks horizon of the zone of production and municipal-warehouse facilities. In the soils of the residential zone and landscape-recreational zone, Ni accumulation occurs in top layer horizons and decreases down the profile and in gray forest loamy soils, as a rule, two accumulation maxima are observed.

Based on the values of concentration coefficients, the total pollution index Zc (65) was calculated, which reflects the total content of HM in soils, both for the main functional zones of the city and for the main types of city soils (Fig.1).

According to the total indicator of technogenic pollution, residential zone of the city belongs to a moderately hazardous category of soil pollution. While all the functional areas of the city can be classified as hazardous.

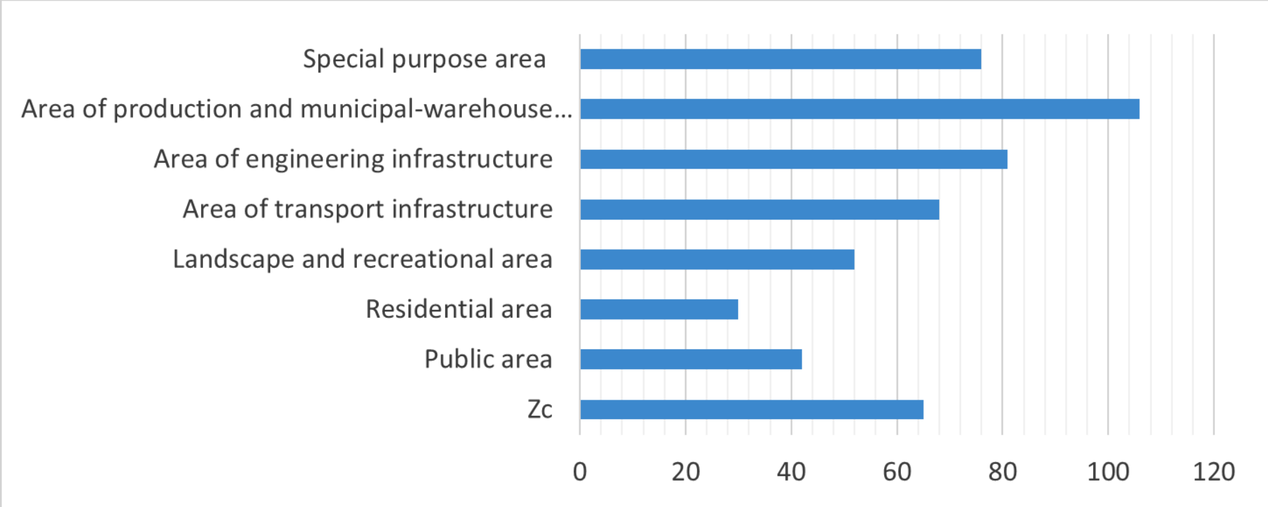

Fig. 1. The total pollution factor of Brovary

According to the gross content of HM in the soils of technogenic and anthropogenic zones of the city, main pollutants are Cu and Pb. While the most dangerous soil pollutants of all functional zones of the city are mobile forms of Zn and Ni.

Spreading of metals on the soil profile of natural and natural-anthropogenic zones of the city has similar trends. Pollution of HM of various types of soils of Brovary by humus-accumulative nature, that is, the maximum accumulation is noted in the top layer horizon. It is primarily associated with their aerotechnogenic input, strong fixation on biogeochemical sorption barriers by binding to soil humic substances and due to biological accumulation.

The determining factor in the distribution of HM in the city is the content of humus, that is, the activity of biogeochemical barrier. In slightly humus soils (<0.6%), the content of HM increases with increasing of pH. In soils with a higher humus content (0.7-1.0%), HM are fixed by clay particles, especially the level of pollution increases in the range of their content from 11.2 to 15.2%. In soils with a relatively high (>1%) humus content, the accumulation of HM is determined by the amount of physical clay and carbonates. Maximal content of pollution in the city is confined to soils with a light particle size distribution and a high content of carbonates. In soils with a physical clay content of > 13%, pollution index increases at pH < 7.5, which may be due to the combined effect of sorption barrier and transition of individual pollutants during acidification of medium into non-mobile forms (Mo).

Pollution level of 38% of the territory is moderate - these are landscapes of almost the entire landscape-recreational and residential zone and individual sections of public zone. Moderate pollution is typical for transport infrastructure zones territory, engineering infrastructure and special purpose zones. Area of production and municipal-warehouse facilities has a high level of pollution (Zc> 46). Anomalous concentrations of Zn, Cu, Ni, as well as an increased content of other HM were found in soils in the area of production and communal storage facilities and the sphere of its influence in soils. In residential area, Pb, Cu, as well as Cr, Zn accumulates. Local anomalies increase the variability of concentrations of HM in urban soils creates a high spatial heterogeneity associated with the discreteness of pollution sources. Ni, Co, Cr is characterized by an increased content in soils of production and municipal storage facilities zone, due to activities of construction enterprises.

Conclusions. It was established that polyelement pollution of the soil cover is present in Brovary. According to the gross content of HM in the soils of technogenic and anthropogenic zones of the city, main pollutants are Cu and Pb. Concentrations of gross and mobile forms of HM exceed background values and MAC values by 17-28 times.

Modern urbanized soils of the city are characterized by the following technogenic geochemical association of heavy metals: Cu>Pb>Zn>Co>Cr>V>Mo>Mn>Ni. Dominant association is distributed throughout the city mosaic, forming geochemical anomalies depending on the source of pollution. The maximum of technogenic load was recorded in the urban soils of transport infrastructure zone and production and municipal storage facility zone. Soil contamination with pollutants leads to changes in their physicochemical properties (cation-exchange capacity, pH, organic matter content) which cause a low buffering capacity of the soil cover of the city.

According to the total index of technogenic pollution, Brovary refers to cities with a high level of pollution. Soils of all areas of the city, with the exception of residential area, are classified as hazardous.

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