CHAPTER «BIOLOGICAL SCIENCES»

METHODOLOGICAL APPROACHES TO DIAGNOSTIC AND MONITORING OF SOIL POLLUTION IN URBANIZED TERRITORIES

Oleksii Krainiukov[1]
Ivetta Kryvytska[2]

DOI: https://doi.org/10.30525/978-9934-26-406-1-5

Abstract. Observation of the content of heavy metals in herbaceous vegetation growing on monitoring sites confirms the expediency of conducting regular bioindication for the purpose of prompt forecasting of trends in the development of man-made soil pollution processes. The combination of soil and plant diagnostics of pollution will contribute to greater objectivity of land monitoring in urbanized areas and the adoption of timely preventive measures. **The purpose** is to scientifically substantiate the improvement of monitoring of heavy metal contamination of soils of urban areas using a complex of chemical-analytical and biodiagnostic methods. **Methodology** of the study is based on spatio-temporal analysis of man-made soil pollution indicators within urbanized areas. The following methods were used to solve the problems: field research, chemical-analytical, biotesting, mathematical-statistical. **Results.** For the soils of urban urban landscapes, which are under the cumulative effect of various pollutants, it is not enough to assess the level of pollution only by the excess of the content of heavy metals, and it is necessary to supplement the methods of chemical and analytical research with biodiagnostic methods, in particular phytotoxicity. This increases the objectivity of diagnosing pollution, provides an integral assessment of its impact on plants, and increases the level of reliability of

[1] DSc (Geography), Professor,
Professor of the Department of Environmental Safety and Environmental Education,
V.N. Karazin Kharkiv National University, Ukraine
[2] Ph.D (Biology), Associate Professor,
Associate Professor of the Department of Environmental Safety and Environmental Education,
V.N. Karazin Kharkiv National University, Ukraine

© Oleksii Krainiukov, Ivetta Kryvytska

soil monitoring in urban landscapes. It is necessary to implement the latest methodical approaches to the organization of soil monitoring in urbanized areas, which will include: taking into account the local geochemical background, functional purpose of land, different buffering properties of soils, multicomponent nature of pollution and its phytotoxic effect, assessment of the degree of geomorphological and lithological homogeneity, priority selection of observation sites in geochemical subordinate elements of the landscape in places with open ground cover, differentiated periodicity of indicator measurements, combining data of chemical-analytical control and biodiagnostics. **Practical implications.** Methodical approaches to the monitoring of soil pollution in populated areas have been implemented in the work of the Ministry of Ecology and Natural Resources of Ukraine to ensure the proper functioning and improvement of the land and soil monitoring system within the framework of the National Action Plan to Combat Land Degradation and Desertification, approved by the Cabinet of Ministers of Ukraine dated 30.03. 2016 No. 271-r (letter No. 5/4.1-16/9645-19 dated August 29, 2019). The results of research on the improvement of biotesting methods have been implemented in the work practice of the laboratory of biological research and biotesting of the National State University "Ukrainian Scientific Research Institute of Environmental Problems" and the communal enterprise "Regional Center of Natural Resources and Ecology" of the Kharkiv Regional Council in determining the phytotoxicity of soils in urbanized areas. **Value/originality.** The obtained factual materials on the assessment of man-made soil pollution and the developed methods of their biotesting are included in the educational process of teaching environmental disciplines at Taras Shevchenko Kyiv National University, V. N. Karazin Kharkiv National University, and G. S. Skovoroda Kharkiv National Pedagogical University.

1. Introduction

The increase in the world's population is inevitably accompanied by the expansion of the area of built-up land, which entails the deepening of environmental problems related to the quality of the urban environment. Negative changes in urban ecosystems are largely due to the fact that the soil in them increasingly loses its functions as a habitat and a means of food production, instead it serves mainly as a base for urban infrastructure facilities and a depository of various pollutants. According to FAO experts, soil sealing (shielding with road and other coverings) is becoming the most threatening phenomenon in Europe, where the annual alienation of land under urban territory reached 1000 km^2 in the last decade of the 20th century and has a tendency to increase. The state of urban soils, which remain unsealed, is complicated by pollution, over-compaction, violation of the integrity of the soil cover, changes in the water and salt regime, etc.

In accordance with the global goals of sustainable development until 2030 declared by the UN General Assembly Resolution No. 70/1 of September 25, 2015, the Decree of the President of Ukraine No. 722/2019 of September 30, 2019 recognized one of the goals of Ukraine's sustainable development as one of the goals of sustainable development of Ukraine ecological sustainability of cities and other settlements (item 11). The high level of urbanization and man-made load inherent in many cities of Ukraine lead to the pollution of the soil cover, the deterioration of the ecological condition of the soil and the living conditions of the soil biota, flora and fauna up to their death.

2. Sources of soil pollution of urban and man-made landscapes

Urban soils are one of the anthropogenic sources of heavy metal dispersion, as they are under the constant influence of industrial and economic activity, and the transport system and sewage disposal are the main factors in changing the area of contaminated land [1].

Man-made pollution is an indispensable companion of industrial cities, the soil cover of which is under the combined influence of gas and dust emissions from industrial enterprises, motor vehicles, thermal power facilities, residential and communal spheres, etc. These emissions form a kind of urbanized background, on which local centers of pollution are superimposed around separate sources of pollutant emissions. In suburban and working villages around factories founded in the first half of the 20th century or even earlier, the soils retain the effects of man-made pollution for a very long time after the liquidation of the enterprises themselves. The average term for the formation of a permanent man-made anomaly is estimated at 20-50 years, and the minimum at 5-10 years. A characteristic feature of the soils of the technogenic pollution zone is the technogenicaccumulative type of profile distribution of heavy metals, which differs from the natural distribution by their accumulation in the upper layer.

The assessment of the danger of soil pollution, as a rule, is a component of the organization of ecological monitoring and comprehensive assessment of the state of the environment of cities. Systematic monitoring makes it possible to make a predictive assessment of the dynamics of the development of man-made pollution processes in urban landscapes and to take the necessary measures to stop them in a timely manner.

The aggravation of environmental problems in cities stimulates the interest of local self-government bodies in obtaining objective information about the state of the soil cover and projected risks for the population. First of all, this is a question of valuation of lands taking into account their ecological condition, as well as long-term planning of urban infrastructure, greening of the territory, control of environmental safety, etc. However, the method of urban soil monitoring is far from perfect. As V. B. Ilyin convincingly showed, the issue of correct selection of the soil background and establishment of the association of polluting elements is a particular difficulty for monitoring heavy metals in large industrial cities. Since an assessment of the local background content of heavy metals is necessary for an adequate assessment of the level of pollution and the organization of its monitoring, for this purpose it is suggested to use data on the soil cover of large parks or regional parameters differentiated for groups of soils with different granulometric composition. Differentiation of the background indicators of the content of heavy metals in soils, as well as the level of their permissible contamination, is a forced but necessary measure, since the natural variation of the elemental composition and buffer properties of soils reaches ten or more times. In addition, the monitoring of soil pollution by heavy metals should take into account the types of specialized purpose of functional urban zones, which differ significantly in terms of sources, levels and composition of pollution, which corresponds to the modern European practice of monitoring heavy metals in the urban environment [2; 3].

The highest level of technogenic pollution was recorded in the soils of large industrial centers with a long history of industrial development. For example, the Scottish city of Glasgow until the 60s of the last century was a world center for chrome ore processing and steel smelting, as well as a poorly developed machine-building industry. As a result of a detailed study by the British Geological Survey based on the analysis of 1,381 samples, it was established that the average content of Cd, Cr, Ni and Zn in the upper layer of soils is 2-3 times higher than in the country as a whole, and Cu and Pb are 5 times higher – 7 times [4]. On the other hand, in cities with an insignificant level of man-made load, as well as in green zones of cities on their outskirts, the accumulation of chemical elements in the soil often does not differ significantly from the background values.

Roads and railways are also a source of heavy metal emissions in cities, leading to aerial redistribution and contamination of homegrown vegetable and horticultural produce. Studies in the urban agroecosystems of the Italian city of Bologna showed a 1.5-fold increase in the content of heavy metals on the surface of vegetables grown at a distance 10 м from the road compared to a distance of 60 м. The total share of heavy metals on the surface of lettuce leaves reached 160 mg/kg of dry weight, basil – 210 mg/kg [5]. Despite the fact that the use of lead as an anti-detonator in gasoline was banned many years ago, the contribution of car exhaust to soil pollution is still noticeable due to the low mobility of this element [6]. This regularity persists regardless of the continent and the history of the development of the urban area. For example, in the Libyan city of Misurata, the level of soil contamination by heavy metals in the industrial area was higher than in residential streets, but the highest concentrations of lead were found at the entrance to the gas station and near the main roads [7]. The concentration of lead and copper in the soils of the parks of Prague, which is considered a mainly residential city, was found to be higher than in Ostrava, which is mainly an industrial city with a developed steel industry. Cadmium, on the other hand, is a typical pollutant around metallurgical enterprises [8].

According to the assessment of Ukrainian researchers, as a result of long-term use of etiolated gasoline in the soils near gas stations, there is an excess of the MPC by 2-3 times [9]. In the city of Kherson, the main zones of soil contamination with heavy metals (up to 2-4 MPC for Pb, 2 MPC for Cd) were found in places of mass accumulation of cars, intensive development of transport infrastructure facilities and industrial enterprises [9]. A similar situation has developed in the city of Kharkiv, where, along with motor vehicles, the main soil polluters are the thermal power plant and the waste incineration plant located in the city [10].

An apparent increase in lead content in the soils of commercial and residential areas was also found in Hong Kong [11]. One of the reasons for the increased concentration of lead in residential quarters of cities is considered to be the widespread use of paints based on this metal in the mid-90s of the last century [12]. A significant accumulation of As, Cd, Cu, and Zn in soils in areas where fruits and vegetables are grown for a long time is also noted [11].

A significant, but specific source of soil pollution is the production of construction materials. A. I. Fateev and Y. V. Pashchenko established that in the radius from 4 km the Zmiivskaya TPP and the Balakliya Cement and Slate Plant, about 0.18 tons of zinc and 0.15 tons of lead per year reach the soil surface, and at a distance of up to 5-6 km, this value increases 20 times. However, man-made dust from enterprises producing building materials mostly has an alkaline reaction, which reduces the mobility of heavy metals. Ukrainian researchers also note the trend of changes in the acid-base properties of urban soils towards alkalization, especially near enterprises of the machine-building complex, production of building materials, energy industry, which are sources of carbonate dust emission [13].

The above shows that the soil cover of urbanized areas is under the combined influence of various pollutants, which gradually form a special "urbanized background" of elements, which determines the difference in the chemical and physicochemical properties of urban soils and increases their spatial heterogeneity.

Landscapes of all urbanized areas are always characterized by a certain anomaly, which is usually heterogeneous and distributed over a number of small anomalies tied to current or former sources of emission of chemical elements. The soils of urbanized areas are characterized by a much greater variability of chemical composition than the soils of agricultural lands, because intense migration flows associated with atmospheric deposition, the presence of a solid urban surface, and the release of waste are added to the natural variability [4]. Such elements as As, Ba, Cd, Cr, Cu, Ga, Ge, Mo, Ni, Pb, Sb, Se, Sn, W, Y and Zn are actively redistributed along the profile.

Researchers of the problem of migration of heavy metals emphasize that soils are not only an environment for growing plants and a reservoir for burying waste, but also a powerful source of many pollutants entering surface and underground waters, the atmosphere, and human food [11].

Heavy metals are relatively immobile and non-uniformly distributed on roadsides, especially through drainage ditches. Soils adjacent to the road surface, as a rule, contain their largest mass [14]. Elevated concentrations in grass vegetation can be observed within 5–8 m of the road, although high levels of lead have been detected in soil up to 25 m [15]. Elevated concentrations of lead were detected in the tissues of several species of small mammals in a narrow zone near roads [16].

In the Netherlands, roadsides 5–15 m wide with traffic volumes of 11,000–124,000 vehicles/day had slightly higher accumulations of heavy metals on the downwind side, but no correlation with traffic volume was found. All mean levels of Pb, Cd, Zn, Cr, Ni and As in grass clippings (hay) from these roadsides were below the Dutch maximum acceptable levels for livestock feed and 'clean compost'. Only Zn in some studied roadsides exceeded the maximum for "very clean compost" [15].

It was established that the transfer of heavy metals from landscapes located hypsometrically higher than the residential areas of the city led to an increase in the content of Pb by 4.5 times, Sr by 1.7, Ag by 2.2, Cu by 1.7, Zn – by 2.5, Ga – by 1.5, Sn – by 1.6, and Yb – by 1.5 times [17].

On the territory of the city of Luhansk, located in similar soil and climatic conditions, atmospheric precipitation brings Cd – 1.12 mg/m^2 per year, Cu – 41.9, Cr – 20.6, Pb – 60.4, Ni – 89.9 mg/m 2 per year, and the dispersion areas of Cd, Ni, and Cu are local and confined to the sources of these elements, while Zn and Pb spread over a greater distance from the sources of pollution [18].

It is known that the reaction of the environment also directly affects the mobility of chemical elements. In an acidic environment, most cationic elements (Cd, Hg, Pb, Ni, Co, Mn, Zn, Cu, etc.) migrate easily, and an increase in pH leads to a sharp decrease in the intensity of migration processes due to the formation of poorly soluble compounds of these elements. Thanks to this feature, it is possible to predict the emergence of centers of the greatest danger of migration of potential toxicants to water supply sources within the city territory [19].

Another important factor influencing the migration of heavy metals is redox conditions. According to leading experts, they have the lowest mobility in strongly reducing conditions (for Eh ≈ 50-150 mV), and the highest for Co, Cd, Mn, Fe, Ni, Zn is for Eh values of about 400 mV, for

Cu –700-800 mV. Unfortunately, due to the rapid variability of redox potential values, quite a few studies in this direction are conducted in Ukraine. However, the comparison of Eh of soil suspensions from Cherkasy soil samples showed a significant difference between the park zone (350-500 mV) and residential and industrial areas (160-245 mV) [13].

A comparison of soil lead concentrations in two Florida cities showed a significant excess of residential and commercial areas over park areas. Specifically, in Miami, soils are divided into two groups: commercial and residential areas with high lead concentrations, where detoxification is primarily required to reach a level of 500 mg/kg, and public buildings and public parks with low lead concentrations. It was also established that in the territory covered with woody vegetation, the content of heavy metals in the soil is higher than on an open surface, due to the interception of aerosols by leaves and subsequent washing away by rains or with tree litter [20].

Thus, the migration of heavy metals in the zones of man-made pollution significantly affects the course of the ecological situation and depends on the functional structure of the city, relief, vegetation, acid-base and reduction-oxidation conditions. At the same time, it is difficult to quantitatively assess the contribution of migration processes to the accumulation or dispersion of heavy metals in the soil cover due to their slow course, which is the task of organizing long-term monitoring.

3. Principles and methods of diagnosis and monitoring of heavy metals in the soil

The traditional method of assessing the pollution of soils that are under cumulative technogenic influence is the determination of the so-called total pollution index (Z) proposed by Yu. Yu. Sayet, which is calculated by adding the n-th number of so-called concentration coefficients (K_c), i.e. excess content of chemical elements in the soil above their background values, and later established in GOST 17.4.3.06 as an "integral indicator of polyelement soil pollution". The basis of this method is the ratio of the actual content of a potentially dangerous element (or substance) to its natural content (or standardized value, for example, MPC). A similar approach is provided for in the national standard DSTU 7243, intended for man-made polluted lands that are in agricultural use [21].

Until now, the vast majority of scientific research and all practical activities on man-made soil pollution control are based on the above methodical approach. For example, the determination of the total indicators of the concentration of heavy metals in the soils of the city of Dniprodzerzhinsk (now the city of Kamianske) made it possible to rank the sources of emissions according to the reduction of man-made pressure on the soil cover of the territory from the Dnipro metallurgical plant (value 135.3) to the thermal power plant (value 43.7), which reflects the efficiency of dust and gas cleaning equipment of these industrial enterprises.

Environmental-geochemical methodology is most often used to study soil cover pollution in urban areas, the leader of which in Ukraine was E. Ya. Zhovynskyi and his students, who determined the geochemical parameters of soils according to 13 classes of geochemical landscapes of Ukraine, especially in the eastern part of Ukraine. Environmental and geochemical research (surveying) carried out by the enterprise "Donbas Geology" involved taking soil samples along a spatial network with a certain step, from to 0,5 km and 2 km linking the results both to geological maps and to man-made sources of emission of chemical elements [22]. Ecological and geochemical studies of agrolandscapes are more focused on the relationship between soils and vegetation and surface and groundwater, which determines the balance of microelement composition for the nutrition of plants and animals [23]. Since the components of agrolandscapes and urbanscapes are often very closely related within urbanized areas, researchers are inevitably forced to combine geochemical approaches with agrochemical [24] and ecotoxicological ones [25; 26].

Thus, the modern development of the ecological-geochemical approach to the study of the soils of urban areas consists in involving a complex of methods from the field of soil science, geoinformatics, mineralogy, biodiagnostics, statistical analysis, etc. The practical application of these methods in domestic research is well tested on the example of the city of Mariupol, which occupies the leading positions in the list of cities with the most stressful ecological situation. The results of research into the forms of heavy metals in the soils, bottom sediments and vegetation of the city of Mariupol, which are under the technogenic load of ferrous metallurgy enterprises, made it possible to identify areas with their anomalous values and propose measures to improve the situation [27]. The characteristic elements of soils around metallurgical enterprises are the so-called siderophilic geochemical class of elements – iron, manganese, titanium [23]. However, according to research by M. N. Zhukov and others., the geochemical association of heavy metals in the soils of Mariupol is represented by the following elements: Pb > Cu > Zn > Cr > Mn (in layer 0-5 cm) and Pb > Cu > Cr > Mn > V (in layer 5-10 cm) [28].

The reason for such discrepancies may be the diversity of soil conditions, which is especially large in cities, the overlap of haloes of pollution from different sources, as well as different ways of the entry of pollutants into the soil. The generalization of the geochemical features of the soils of the cities of Ukraine, carried out in the 90s of the last century with the help of factor analysis, showed that although Mn takes an active part in technogenesis, due to its chemical properties, this element is not included in the pyrogenic association of elements Zn-Cu-Ni-Pb-Cd-F.

An important aspect of urban soil pollution monitoring is taking into account the location of observation sites in the geochemical landscape. As noted by A. O. Timely soil cover monitoring should be based on landscape-geochemical principles, and it is advisable to place control sites at transeluvial positions, and sites for assessing the degree of pollution – in the zone of accumulation of substances [29]. The scheme of geochemical urban landscapes, which is the basis of the monitoring network in the city of Novorossiysk, provides for the selection of industrial areas and wastelands, and the division of residential areas into one-story, 2-5-story, and 5-10-story. The subordinate unit is the location in the geochemical category: on steep slopes (transeluvial elements), in the lower part of inclined slopes (transaccumulative elements) and in the upper part of the slopes (trans-superaquatic elements) [17].

In contrast to the traditional assessment of soil pollution, based on the comparison of monitoring results with threshold values, the use of hierarchical cluster analysis and the method of principal components allows to separate areas of high risk and build pollution profiles. The application of such a methodical approach in the area of Burgas (Bulgaria) helped to identify four main sources of heavy metal emissions associated with industry and agriculture, and most importantly, to reliably separate the effects of pollution for the two different types of soils prevailing in this seaside city [30]. It was established that the lowest concentration of

As, but the highest concentration of Cd, is observed in the cluster with the predominance of soils under forest and vegetables. Urban soils in built-up areas, on the contrary, have three times higher lead content than soils in agricultural areas. Factor analysis is used to identify relationships between factors that determine the behavior of heavy metals in soils. In particular, a comparative analysis of the accumulation of acid-soluble forms of heavy metals in Czech cities showed that 39.5% of the variability reflects the relationship between organic carbon and Cu, Pb, As, and Zn, 27.6% is a dependence on pH and humus quality, and 12.3% is the content of physical clay and cadmium [21].

In Western Europe, the geoaccumulation index proposed by G. Muller about 50 years ago is quite often used to assess soil and sediment pollution [31]:

$$I_{geo} = \log_2 (C_n / 1.5B_n), \qquad (1)$$

where I_{geo} – geoaccumulation index;

C_n – element concentration in the soil, mg/kg;

In $_n$ is the geochemical background of the element, mg/kg.

There are seven geoaccumulation index classes. Soils of class 0 (Igeo = 0), moderately polluted from 1 to 2, strongly from 3 to 4 and extremely strongly above 5 are considered uncontaminated.

An ecological-geochemical approach to the assessment of pollution was developed in the works of Yu. M. Dmytruk, who calculated migration indices based on the accumulation of heavy metals in genetic horizons and proposed to calculate indices of soil saturation with chemical elements as the geometric mean of their concentration coefficients [32]. According to the scientist, the most correct approach to determining background concentrations is the study of soils of different ages, both the modern daytime surface and those buried under archaeological monuments [33].

It was established that the polyelemental background of cities with a population of more than 700,000 is significantly different from the elemental composition of cities with an average and small number of inhabitants. The latest generalization of the chemical composition of the soils of large cities, carried out by G. Li et al., shows that the content of heavy metals in them decreases in the following order: Zn > Cr, Pb, Cu > Ni > As > Cd, Hg, and the distribution of lead in the largest to some extent related to human activity [34]. In V. B. Ilyin's opinion, it is the lack of information about the background content and polyelemental nature of pollution that are the main difficulties that prevent monitoring of heavy metals in large industrial cities. Conversely, as demonstrated by this famous scientist, the correct calculation of the local background is the key to an adequate assessment of the real danger.

Thus, the study of the pollution of urban areas should take into account not only the chemical composition of man-made emissions and the ways of their arrival, but also the natural heterogeneity of the soil cover, the location in the geochemical landscape, the functional purpose of the territory, the background content of chemical elements and the resistance of soils to pollution. Ignoring any of the listed influencing factors can lead to an incomplete, inaccurate, or even false assessment of the real danger.

With the development of civilization and the increase of anthropogenic pressure on the soil, the ecological functions of the soil cover become more and more important, the preservation of which is on the agenda in all large cities. As Ukrainian ecologists emphasize, understanding the role of soil in urban ecosystems is an important component of sustainable management of the urban economy in general [35].

Currently, environmental protection measures to regulate and limit the introduction of environmentally hazardous substances and compounds into the natural environment are, as a rule, based on the comparison of the actual values of their content with the established maximum limit values of these substances for the corresponding component of the natural environment. But at the same time, the use of only information on exceeding the MPC of individual chemicals is not enough to assess the ecological state of the territory, since the impact of the combined action of multicomponent chemical compounds on the biotic component of ecosystems is not taken into account. This is due to the fact that the MPC provides for the normalization of the isolated exposure of chemical substances to the relevant test organisms, which are used during the establishment of the MPC, while in real conditions the influence is exerted by complex mixtures of substances, as a result of which the combined effect of exposure – additivity can be manifested, synergism, antagonism [36].

Most of the attempts used to standardize soil contamination by pollutants are limited to determining the maximum permissible concentration of the substance in the soil. However, due to objective reasons, such as the multifunctionality and heterogeneity of the soil, the variety of its types, the variety of pollutants, the phenomena of synergism and antagonism between them, the ability of living organisms to adapt, and the soil to self – purify, the use of MPC of pollutants to assess the level of pollution is insufficient indicator.

The expediency of using biological methods for assessing the quality of landscape components, in particular, soils, is emphasized in numerous works by domestic and foreign authors [37; 38]. In particular, in the work of M. O. Klymenko, when determining the list of indicators for assessing the quality of environmental components under conditions of anthropogenic load, it is recommended to use biological methods along with other: "...Bioindication and biotesting, in contrast to known analytical methods of monitoring the state of the environment, are indispensable in determining the toxicity and harmfulness of factors for living organisms, because these characteristics are biological, and therefore determine the biological quality (or poor quality) of the environment" [39]. The above is confirmed by the results of establishing a correlation dependence between the assessment of water toxicity levels and the values of the coefficients of its pollution by individual chemical substances, which was 0.06 [40].

According to the scientists of the Institute of Microbiology and Virology of the National Academy of Sciences of Ukraine, bioindication of soils contaminated with heavy metals should be carried out at different levels of structural organization, namely: pre-cellular (enzyme activity), cellular, population and cenotic.

In order to speed up the diagnosis of contamination by the bioindication method, it is suggested to use species with a high intensity of reproduction, for example, duckweed (*Lemna minor* L.), and to choose the number of chloroplasts in the epistrophic position and the number of dead cells as criteria. Along with this, due to the high buffering capacity of chernozems and the tolerance of higher plants to certain heavy metals, low levels of pollution can even stimulate the germination and growth of sprouts, for example, winter wheat on ordinary chernozem at 1 MPC of Cu, Zn, Cd, Hg, Pb. A similar effect can be observed with the enzymatic indication of pollution due to the absorption of heavy metals by the components of the agro-technogeochemical background, the presence of easily accessible organic and mineral substances in the composition of the pollution, optimization of pH and gas regime of the soil, etc.

It was established that the influence of many pollutants, including and heavy metals on living organisms of the soil is manifested up to a certain limit in the stimulation of both test functions and the productivity of entire ecosystems, and only with a further increase in the dose does suppression begin. The high mosaicity of the soil cover of cities is a key to the preservation of many types of soil bacteria and fungi, that is, the maintenance of biodiversity [35]. Along with this, as a result of technogenic pollution, soil biogeocenoses undergo significant changes, and their biodiversity decreases. For example, the study of edaphotopes of the urban ecosystems of the city of Mariupol showed that although the taxonomic structure of algal communities in urban soils generally preserves the features of natural soils of the steppe zone, in the sanitary-protective transport and settlement zone, the species composition of algae and the composition of dominants are markedly depleted [41]. Phytotoxicity is a very common phenomenon on man-made soils formed as a result of the mining industry, where edapho-ecological restrictions approach the minimum and maximum [42].

It is noted that at the initial stages of heavy metal contamination of chernozem soils, biological indicators such as the activity of symbiotic activity, carbon dioxide release, cellulolytic and nitrifying activity, the number of nitrifiers, actinomycetes and fungi are the criteria for the response of the microbial system. However, biotesting indicators determined by different test systems never match completely, which is due to their unequal sensitivity to each pollutant. In connection with the unequal reaction of the root system, aerial part and seeds to increased concentrations of heavy metals, it is advisable not to replace chemical analyzes with biotesting, but to use both methods in a complex. A similar approach regarding the combination of chemical-analytical monitoring in time and space with observations of biological test objects is also successfully applied to adjacent environments, for example, in the case of pollution of sea water and bottom sediments along the coastline of the oil refinery complex in Venezuela [43].

Despite the existing differences in the estimation of pollution by different methods, most researchers believe that the assessment of bioavailability of pollutants in the urban environment can explain the complex relationship between urban soils, the impact of pollutants and the state of health of the population [34; 44].

In general, the results of studies of the soil cover of urbanized areas and its contamination by various substances are intended not only to attract the attention of state institutions and local authorities, but are actual source material for further planning of the development of the urban area. As summarized by V. I. Vasenev and co-authors, the assessment of ecosystem services of soils in urbanized areas provides an opportunity to bring soil science research to a new level of practical use and to take an active part in the ecological management of cities [45]. In Great Britain, work is being done to adjust soil guideline values (SGV), exceeding which indicates the need for special studies on detoxification. In particular, Glasgow was found to exceed such standards by 20% for Cr and 5% for Pb, which is the basis for re-evaluating the quality of land resources in this city [4].

Soils are considered the most informative and stable component of the landscape, the structure of which has a significant impact on adjacent components. Among the three structural elements of the biosphere (atmosphere, hydrosphere, lithosphere), the central link is the soil, which plays a decisive role in their formation and significantly affects the redistribution of matter and energy in other components of the natural environment. Control of soil degradation and reproduction processes should be carried out during comprehensive monitoring as a system of observing the ecological state of soils for the purpose of their rational use and protection. Today, it is necessary to create a system of soil and ecological monitoring adapted to the conditions of complex anthropogenic influence on soils. Reliable diagnosis and assessment of the ecological state of soils will only be possible if the most complete information is available about changes in the structure of the soil cover, land transformation, and changes in ecological and biogeochemical characteristics.

The analysis of publications shows that the diagnosis and monitoring of soil pollution by heavy metals in urbanized landscapes is a complex scientific and practical task, the solution of which requires a comprehensive approach involving soil science, geochemical, biodiagnostic and statistical methods. The key issues that need to be resolved during monitoring are the consideration of natural and anthropogenic soil heterogeneity, the objective determination of the background content of chemical elements, and the combination of chemical-diagnostic and biodiagnostic methods.

4. Methodical approaches to the organization of complex soil monitoring of urban areas

First of all, at the stage of preparatory work, it is necessary to assess the degree of geomorphological and lithological homogeneity of the territory, which is reflected in the complexity of the soil cover and the geochemical characteristics of the soil. In our opinion, in the presence (which is most likely) of superaquatic landscapes in the studied territory, it is advisable to place monitoring sites precisely on them, since it is in the geochemically subordinate elements of the landscape that the majority of pollutants accumulate in the first place, and due to the proximity of groundwater, the danger of downward migration is the largest In addition, the determination of the homogeneity of the territory and the establishment of the most typical geomorphological and lithological (primarily – in terms of granulometry and mineralogy) conditions are necessary for the correct selection of places for determining the geochemical background in the territory adjacent to the city.

Basic information for the correct organization of monitoring can be obtained only during the basic survey. At the same time, it should be held both on the territory of the settlement and outside its borders. Sampling of soil samples formed under similar conditions of soil formation, but at a distance of at least 15-20 km from the main centers of man-made emission of pollutants, allows to form a sample for determining their background content. It should be noted that at this time, in accordance with the Decree of the Cabinet of Ministers of Ukraine dated January 20, 2016 No. 94-r "On recognition of acts of sanitary legislation as having lost their validity and as not applicable on the territory of Ukraine" and the decision of the State Regulatory of the Service of Ukraine dated 07/15/2014 No. 33, in Ukraine, as of January 1, 2017, acts of sanitary legislation, which approved the MPC of pollutants in the soil, were suspended. Under these circumstances, the only way to establish the facts of man-made soil pollution is a comparison with the background values of the content of individual chemicals.

In our opinion, it is best to conduct a basic survey of the soil cover of a settlement using a network that is as close to uniform as possible, with the location of test sites in places with open soil cover and a functional purpose that prevails within this cell of the network. This allows, firstly, to proportionally display the ratio of lands with different functional purposes, and secondly, to display the general urbanized background inherent in the settlement as objectively as possible. In addition, based on the data of the basic survey, it is possible to easily identify zones with the highest level of man-made soil pollution, as well as those where the accumulation of pollutants in the soil is minimal.

In order to increase the objectivity of the evaluation of the condition of the soils of urbanized areas, biotesting should be started already at the stage of the basic survey. In addition, in soil samples, it is important to determine the main indicators that determine their buffering capacity against pollution, namely: aqueous or saline pH, the content of physical clay particles or the granulometric composition in general, the content of humus (organic carbon). Another reason for the desirability of conducting biotesting on all sites of the baseline survey is the usefulness of this information for planning green spaces in the urban economy. In the case of detection of a significant phytotoxic effect, it is advisable to find its cause (heavy metals, salts, pH or other) and recommend appropriate soil detoxification measures.

Regarding the content of heavy metals in soils, we consider the best form of determination to be mobile (acetate-ammonium buffer solution with pH 4.8), since the degree of extraction of acid-soluble (strongly bound) forms strongly depends on pH and the content of carbonates, and for hazard assessment pollution by the gross amount of chemical elements requires a more in-depth study of the buffering capacity of soils. As our research has shown, the soils of urbanized areas are characterized by polyelemental pollution with heavy metals, so even their limited amount reflects to some extent the general level of man-made load on the soil cover in general. It is clear that one should try to determine the largest possible number of elements, but in the case of a limited material and technical base, it is possible to get by with four or five elements in the first approximation.

Having received the data of the basic survey of the soil cover, we can proceed to the design of the monitoring network. Based on the results of our dissertation research, for proper representativeness, the monitoring network should:

– more or less uniformly display the lands of industrial, residential, recreational and administrative and cultural zones;

– to represent soils with different buffering capacity to pollution, but to give preference to soils of subordinate geochemical landscapes;

– be tied to the main sources of emissions of pollutants, with the advantage of being located on the leeward side or on the line of the predominant linear flow from them;

– make up at least 10-15% of the number of test sites of the basic survey, but not less than 5 sites for each type of functional zones, taking into account the probability of removing these places for development, new transport routes and other objects.

The area of the monitoring sites may be different, but not too small, which impairs the representativeness and identification of boundaries in cases where there are no clear reference points for reference on the terrain. On the other hand, too large an area of monitoring sites creates problems regarding the reproducibility of the results of repeated measurements, because the probability of the influence of random factors increases. Taking this into account, we consider the best area of the monitoring site to be the interval from 50 to 250 m^2. Due to the complex configuration of the urban planning of the territory, the shape of the plot may be different, but it is very appropriate to tie its extreme points to certain landmarks with a fixed location: roads, houses, etc.

We believe it is best to map the monitoring areas in the coordinate system at their center, which is defined as the middle of the axis line along the longest length.

A very important issue is the number of individual soil samples that make up a representative mixed soil sample. The results of our research show that during the basic survey, the selection of 12-15 individual samples on the plots located on the lands of industrial enterprises and adjacent territories, in accordance with the methodology of soil and geochemical surveys of urban areas, does not ensure reliable data reproducibility. It is necessary either to immediately increase the number of individual samples by at least two times, or to re-take samples from the areas designated as monitoring, with a density of 20-40 individual samples to make up a mixed sample.

Our observations during the period of the dissertation research show that due to numerous influencing factors, the number of which is higher within urbanized territories than on adjacent agricultural, forestry or other purpose land, it is better to conduct more detailed studies on a wide range of indicators than to make annual measurements of several indicators on a limited number of sites. There are many reasons for this, namely: the slow nature of changes in soil properties due to its buffering, the high probability of accidental soil contamination from mobile sources, the disturbance of the soil profile in most open areas within the industrial, residential, and cultural-administrative zones of cities, the variety of pollutants and their predominant concentration in the upper five-centimeter soil layer, etc. Due to these circumstances, we believe that the periodicity of soil monitoring in the city should be differentiated: observation of the most dynamic indicators (pH, content of water-soluble salts and mobile forms of priority pollutants determined during the basic survey) should be carried out once every five years, and for the entire list of monitoring indicators – once every ten years.

5. Conclusions

For the soils of urban urban landscapes, which are under the cumulative effect of various pollutants, it is not enough to assess the level of pollution only by the excess of the content of heavy metals, and it is necessary to supplement the methods of chemical and analytical research with biodiagnostic methods, in particular phytotoxicity. This increases the objectivity of diagnosing pollution, provides an integral assessment of its impact on plants, and increases the level of reliability of soil monitoring in urban landscapes.

It is necessary to implement the latest methodical approaches to the organization of soil monitoring in urbanized areas, which will include: taking into account the local geochemical background, functional purpose of land, different buffering properties of soils, multicomponent nature of pollution and its phytotoxic effect, assessment of the degree of geomorphological and lithological homogeneity, priority selection of observation sites in geochemical subordinate elements of the landscape in places with open ground cover, differentiated periodicity of indicator measurements, combining data of chemical-analytical control and biodiagnostics.

The need for the simultaneous use of chemical and biological methods (in particular, the biotesting method) for a comprehensive assessment of the impact of pollution on the ecological state of the natural environment is due to the diversity and variability of pollutants, the absence of established standards for most of them, the impossibility of taking into account the ecological danger of their combined action. The legality of this approach is confirmed by the identified discrepancies in the assessment of the ecological state of the natural environment based on chemical and toxicological indicators.

In order to objectively assess the degree of danger of man-made pollution, it is necessary to determine the phytotoxic properties of the soil for higher plants. For this, a methodical approach was developed, which made it possible to make a generalized assessment using two test crops, namely: corn Zea mays L. as a representative of monocotyledonous cereals, and seed radish Raphanus sativus L. as a representative of dicotyledonous (eudicot) broad-leaved plants. In connection with the possible imbalance of growth processes in the early stages of plant development under the influence of pollution, which is expressed in the violation of the ratio of roots and sprouts, the degree of growth imbalance is taken into account in the general assessment of soil phytotoxicity.

References:

1. Arora Sh., Jain C. K., Lokhande R. S. (2015). Review of Heavy Metal Contamination in Soil. *International Journal of Environmental Science and Natural Resources*, vol. 3, pp. 1–6.

2. Linde M., Bengtsson H., Öborn I. (2001). Concentrations and pools of heavy metals in urban soils in Stockholm, Sweden. *Water, Air, and Soil Pollution*, vol. 1, pp. 83–101.

3. Marjanović A., Vukčević B. (2009). Antonović Heavy metals concentration in soils from parks and green areas in Belgrade. *Journal of Serbian Chemical Society*, vol. 74(6), pp. 697–706.

4. Urban Soil Geochemistry of Glasgow – Main Report (2012). Edinburg: British Geological Survey, 374 p.

5. Antisari L. V., Orsini F., Vitanello G., Gianquinto G. (2015). Heavy metal accumulation in vegetables grown in urban gardens. *Agronomy of sustainable Development,* vol. 35, pp. 1139–1147.

6. Chirenje T., Ma L. Q., Reeves M. (2004). Lead distribution in near-surface of two Florida cities: Gainesville and Miami. *Geoderma,* vol. 119, pp. 113–120.

7. Elbagermi M. A., Edwards H. G. M., Alajtal A. I. (2013). Monitoring of Heavy Metals Content in Soil Collected from City Centre and Industrail of Misurata, Libya. *International Journal of Analytical Chemistry.* Article ID 312581. 5 p.

8. Galuśhkova I., Borúvka L., Drábek O. (2011). Urban Soil Contamination by Potentially Risk Elements. *Soil and Water Research*, vol. 6(2), pp. 55–60. (in Ukrainian)

9. Pylypenko Yu. V., Skok S. V. (2015). Otsinka rivnia zabrudnennia gruntu vazhkymy metalamy v mezhakh miskoi systemy (na prykladi m. Kherson) [Assessment of the level of soil contamination by heavy metals within the urban system (on the example of the city of Kherson)] *Biolohiia ta Valeolohiia.*

Zb. naukovykh prats Kharkivskoho natsionalnoho pedahohichnoho universytetu imeni H. S. Skovorody – Biology and Valeology. Coll. of scientific works of Kharkiv National Pedagogical University named after H. S. Skovoroda, vol. 17, pp. 138–145. (in Ukrainian)

10. Krainiuk O. V., Buts Yu. V. (2007). Tekhnohenne zabrudnennia spolukamy svyntsiu gruntiv mista Kharkova [Man-made contamination of soil with lead compounds in the city of Kharkiv]. *Problemy nadzvychainykh sytuatsii – Problems of emergency situations,* vol. 6, pp. 79–86. (in Ukrainian)

11. Chen T. B., Wong J. W. C., Zhou H. Y. (1997). Assessment of trace metal distribution and contamination in surface soils of Hong Kong. *Environmental Pollution,* vol. 96 (1), pp. 61–68.

12. Brinkmann R. (1994). Lead pollution in soils adjacent to homes in Tampa, Florida. *Environmental Geochemistry and Health*, vol. 16 (2), pp. 59–64.

13. Honcharenko T. P., Zhytska L. I. (2014). Doslidzhennia yakosti miskykh gruntiv (m. Cherkasy) [Study of the quality of urban soils (Cherkasy)]. *Visnyk Cherkaskoho derzhavnoho tekhnichnoho universytetu – Bulletin of the Cherkasy State Technical University*, vol. 4, pp. 89–94. (in Ukrainian)

14. Wust W., Kern U., Hermann R. (1994). Street wash-off behavior of heavy metals, polyaromatic hydrocarbons and nitrophenols. *Sci. Total Environ.,* vol. 147, pp. 457–463.

15. Dienst Wegen Waterbouwkunde (1994). The Chemical Quality of Verge Grass in The Netherlands. *DWW Wijzer 62. Delft, Netherlands,* p. 4.

16. Getz L.L., Verner L., Prather M. (1977). Lead concentrations in small mammals living near highways. *Environ. Pollut,* vol. 13, pp. 151–57.

17. Alekseenko A. V., Pashkevich M. A. (2016) Novorossiysk agglomeration landscapes and cement production: geochemical impact assessment. *IOP Conference. Series: Earth and Environmental Science,* vol. 43, pp. 234–248.

18. Sytina O. M. (2010). *Mihratsiia vazhkykh metaliv u systemi grunt-roslyna tekhnohennykh landshaftiv (na prykladi m. Luhanska)* [Migration of heavy metals in the soil-plant system of technogenic landscapes (on the example of the city of Luhansk)]: dys. ... kand. biol. nauk. Kharkiv. (in Ukrainian)

19. Titenko H. V., Klieshch A. A. (2015). Osoblyvosti heokhimichnoi mihratsii elementiv ta spoluk u pryrodnykh ta pryrodno-antropohennykh kompleksakh richkovoi dolyny r. Lopan [Peculiarities of geochemical migration of elements and compounds in natural and natural-anthropogenic complexes of the Lopan river valley]. *Liudyna ta dovkillia. Problemy neoekolohii – Man and environment. Problems of neoecology,* vol. 1–2, pp. 3–45. (in Ukrainian)

20. Galuśhkova I., Borúvka L., Drábek O. (2011). Urban Soil Contamination by Potentially Risk Elements. *Soil and Water Research*, vol. 6(2), pp. 55–60.

21. DSTU 7243:2011 Iakist gruntu. Zemli tekhnohenno zabrudneni. Obstezhennia ta vykorystannia [Soil quality. Lands are man-made polluted. Examination and use], 25 p. (in Ukrainian)

22. Volkova T. P., Snizhok I. S. (2012). Analiz ta otsinka vplyvu metalurhiinykh pidpryiemstv na zabrudnennia gruntiv Donetskoi oblasti [Analysis and assessment of the impact of metallurgical enterprises on soil pollution in the Donetsk region]

Naukovi pratsi DonTU. Ser. "Hirnycho-heolohichna" – Scientific works of DonTU. Ser. "Mining and geological", vol. 16(206), pp. 73–78. (in Ukrainian)

23. Yehorova T. M. (2015). *Naukovi osnovy ekoloho-heokhimichnykh protsesiv v ahrolandshaftakh Ukrainy* [Scientific basis of ecological-geochemical processes in agrolandscapes of Ukraine]: dys. ... dokt. s.-h. nauk. Kyiv. (in Ukrainian)

24. Myslyva T. M. (2012). *Ekotoksykolohichna otsinka komponentiv ahro- ta urbolandshaftiv Zhytomyrskoho Polissia za vmistom riadu vazhkykh metaliv* [Ecotoxicological assessment of the components of agro- and urban landscapes of Zhytomyr Polissia by the content of a number of heavy metals]: dys. ... d-ra s.-h. nauk. Kyiv. (in Ukrainian)

25. Miroshnychenko M. M., Fatieiev A. I. (2007). Ahroheokhimiia mikroelementiv v gruntakh Ukrainy [Agrogeochemistry of trace elements in the soils of Ukraine]. *Ahrokhimiia i gruntoznavstvo – Agrochemistry and soil science*, vol. 2, pp. 98–107. (in Ukrainian)

26. Krainiukov, O., Nekos, A., Kochanov, E., Buts, Yu., Miroshnychenko, I. (2020). Biomonitoring of soil quality within the limits of the oil refining enterprise. *14th International Scientific Conference Monitoring of Geological Processes and Ecological Condition of the Environment,* 10-13 November 2020. Kyiv, pp. 49–51.

27. Karmazynenko S. P., Kuraieva I. V., Samchuk A. I. (2014). *Vazhki metaly u komponentakh navkolyshnoho seredovyshcha m. Mariupol (ekoloho-heokhimichni aspekty)* [Heavy metals in environmental components of Mariupol (ecological-geochemical aspects)]. Kyiv: Interservis, 168 p. (in Ukrainian)

28. Zhukov M. N., Kuraieva I. V., Voitiuk Yu. Yu. (2015). Kompleksna otsinka stanu zabrudnennia gruntiv m. Mariupol metodom holovnykh komponent [Comprehensive assessment of the state of soil pollution in the city of Mariupol by the method of principal components]. *Geoinformatika – Geoinformatika*, vol. 3, pp. 60–67. (in Ukrainian)

29. Achasova A. O. (2003). *Hruntovo-ekolohichni umovy formuvannia prostorovoi neodnoridnosti vmistu vazhkykh metaliv u gruntakh Livoberezhnoho Lisostepu Ukrainy* [Soil and ecological conditions of the formation of spatial heterogeneity of the content of heavy metals in the soils of the Left Bank Forest Steppe of Ukraine]: dys. ... kand. biol. nauk. Kharkiv, 20 p. (in Ukrainian)

30. Astel A. M., Chepanova L., Simeonov V. (2011). Soil contamination interpretation by the Use of Monitoring Data Analysis. *Water and Air Pollution,* vol. 216, pp. 375–390.

31. Muller G. (1969). Inlex of geo-accumulation in srediments of the Rhine River. *Geo Journal,* vol. 24, no. 2, pp. 108–118.

32. Dmytruk Yu. M. (2006). *Ekoloho-heokhimichnyi analiz gruntovoho pokryvu ahroekosystem* [Ecological and geochemical analysis of the soil cover of agroecosystems]. Chernivtsi: Ruta, 328 p. (in Ukrainian)

33. Dmytruk Yu. M. (2012). *Fonovyi vmist mikroelementiv u hruntakh: monohrafiia* [Background content of trace elements in soils]. Chernivtsi: Chernivetskyi natsionalnyi universytet, 220 p. (in Ukrainian)

34. Li G., Sun G.-X., Ren Y. (2018). Urban soil and human health: a review. *European journal of Soil Science*, vol. 69, pp. 196–215.

35. Lykholat Yu. V. (2003). *Ekoloho-fiziolohichni osnovy formuvannia dernovykh pokryviv v umovakh stepovoi zony Ukrainy (stiikist, dynamika, teikhnohenez)* [Ecological and physiological basis of the formation of turf covers in the conditions of the steppe zone of Ukraine (stability, dynamics, teichnogenesis)]: dys. ... d-ra biol. nauk: 03.00.16. Chernivtsi, 42 p. (in Ukrainian)

36. Krainiukov O. M., Kryvytska I. A. (2018). Udoskonalennia sposobu vyznachennia stupenia zabrudnenosti gruntiv metodom biotestuvannia [Improvement of the method of determining the degree of soil contamination by biotesting]. *Visnyk ZHU. Biolohichni nauky – Bulletin of ZSU. Biological sciences,* vol. 1, pp. 83–90. (in Ukrainian)

37. Manual for the Evaluation of Laboratories Performing Aquatic Toxicity Tests. U. S. Environmental Protection Agency, Office of Research and Development. EPA/600/4-90/031. Cincinnati, 1991. 108 p.

38. Steinhauser K. G., Hansen P. D. (1992). Biologische Testverfahren. Stutgart: Gustav-Fisher Verlad, 884 p.

39. Klymenko M. O., Trusheva S. S., Hrokhovska Yu. R. (2004). *Vidnovna hidroekolohiia porushenykh richkovykh ta ozernykh system (hidrokhimiia, hidrobiolohiia, hidrolohiia, ekolohiia, upravlinnia)* [Restorative hydroecology of disturbed river and lake systems (hydrochemistry, hydrobiology, hydrology, ecology, management)]. Rivne: t. III, 211 p. (in Ukrainian)

40. Vprovadzhennia rezultativ toksykolohichnoho monitorynhu v systemu ekolohichnoho menedzhmentu baseinu r. Dnipro [Implementation of the results of toxicological monitoring in the ecological management system of the Dnipro river basin]. Zvit na proekt № 9112 dlia Mizhnarodnoho tsentru rozvytku naukovykh doslidzhen. Ukrainskyi naukovo-doslidnyi instytut ekolohichnykh problem. Kharkiv, 1999. 61 p. (in Ukrainian)

41. Shekhovtsova O. H. (2016). *Ekoloho-biolohichna otsinka edafotopov urboekosystem mista Mariupolia* [Ecological and biological assessment of edaphotops of urban ecosystems of the city of Mariupol]: dys. ... kand. biol. nauk. Dnipro. (in Ukrainian)

42. Masyuk A. N., Gorban V. A. (2017). Specific features of accumulation of humus in technozems under poplar plantations in the conditions of the Western Donbass. *Gruntoznavstvo,* vol. 18, pp. 57–66.

43. Croquer A., Bone D., Bastidas C. (2016). Monitoring coastal pollution associated with the largest oil refinery complex of Venezuela. *Peer J.*, vol. 4, p. 2171.

44. Zimova M., Duris M., Spevackova V. (2001). Health risk of urban contaminated by heavy metals. *International Journal of Occupational Medicine and Environmental Health*, vol. 14, pp. 231–234.

45. Vasenev V. I., Van Oudenhoven A. P., Romzaykina O. N. (2018). The ecological functions and ecosystem services of urban and technogenic soils: from theory to ptactice (a review). *Eurasian Soil Science*, vol. 51, pp. 1119–1132.