

The Distribution of Heavy Metals Mobile Forms in the Industrial-Urban Agglomeration Soil

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ABSTRACT

The material is devoted to the distribution of heavy metals mobile forms in the ground cover urban landscapes of the Mykolaiv industrial urban agglomeration, which is a complex multifunctional system. The authors of the research collected soil samples from different places of agglomeration and measured the levels of heavy metals mobile forms in these samples. The purpose is a determination of the heavy metals migration levels in the missile strikes locations by the Russian aggressors. The objectives of the research are developing a strategy for testing the Mykolaiv Urban Industrial Agglomeration (MUIA) soil cover; estimating the migration level of heavy metals (HM) (Cr, Zn, Hg, Pb, Ni, Cu, Mn) of the MUIA soil cover according to the maximum permissible levels. The research data revealed that the HM concentration (Cr, Zn, Hg, Pb, Ni, Cu, Mn) is in three forms - ion exchange, available and fixed. The HM average concentration in the ion exchange form ranges from 0.9 mg/kg for Cr to 60.3 mg/kg for Mn. In available form, the HM average concentration varies from 0.4 mg/kg for Cr to 57.9 mg/kg for Hg. In fixed form, the HM average concentration ranges from 8.7 mg/kg for Cr to 582.9 mg/kg for Mn. The analysis of the study showed that the mobile forms content in soils agglomerations differs significantly depending on the place heavy metals of sampling. In some places, the content of heavy metals exceeds the permissible standards, which can harm on the ecosystem and human health.

Keywords: heavy metals, hazard ratio, total pollution index, urban landscape, urbogeosystem, industrial urban agglomeration.

INTRODUCTION

Geochemical provinces are territories with the same geochemical characteristics of rocks, which are determined on the basis of studies of the water chemical composition and rock samples. There are several geochemical provinces on the territory of Ukraine, among which the northern, central and southern provinces stand out. We focus on the geochemical province of southern Ukraine and its features.

The Southern Geochemical Province of Ukraine is located in the territory of the steppe zone and covers such regions as Zaporizhzhia,

Dnipropetrovsk, Mykolaiv, Kherson and Odesa regions [Dudka et al., 2011; Mykhailiuk et al., 2015; Salt et al., 1998]. This province is characterized by high levels of iron and manganese, as well as low concentrations of copper and lead. The most common rocks in this province are granites, gneisses, rhyolites and volcanic rocks [Kovalchuk et al., 2016; Pohrebennyk et al., 2016; Mitryasova et al., 2020].

The study of the geochemical province of southern Ukraine is important for understanding the geological history of this territory, as well as for the identification of various minerals and their placement. Research shows that the southern

geochemical province of Ukraine has many different minerals, including iron and manganese ores.

One of the most important areas of research in the southern geochemical province of Ukraine is the study of the environment state. Environmental pollution is a serious problem for the planet, and the study of geochemical characteristics of soils and water resources can help to detect pollution and develop effective methods of combating it [Dolin et al., 2007; Bernatska, et al., 2023, Mitryasova et al., 2021].

The study of the southern geochemical province of Ukraine is an important direction of scientific research, which allows studying the geological history of the region, identifying minerals and environmental pollution. The results of these studies can become the basis for the development of environmental protection effective methods, rational use of resources and improvement of the quality of life [Pohrebennyk et al., 2017; Reshetnyak & Pastuh, 2018; Shvets et al., 2018].

Although the southern geochemical province has great geological potential, its exploration is still a difficult task. One of the main challenges is the complexity of the geological structure of this region, as well as the lack of sufficient financial resources to conduct high-quality geochemical research. However, despite these limitations, research in the southern geochemical province of Ukraine continues. Recent studies of the geochemical composition of soils and water resources in the region allow for a more detailed study of its ecological situation and the development of effective methods of combating environmental pollution.

Also, the study of geochemical characteristics of mineral resources can help ensure rational use of these resources and reduce their harmful impact on the environment. For example, studying the characteristics of gypsum ores can help to develop more efficient technologies for their processing and reduce the amount of waste entering the environment. In addition to the potential for mining minerals and hydrocarbons, the southern geochemical province of Ukraine also has significant potential for studying environmental pollution. Environmental pollution is an important problem in many regions of the world, and conducting geochemical studies can help identify the sources of pollution and develop effective methods for its control.

In the southern geochemical province of Ukraine, environmental pollution can be associated with various sources, such as industrial

enterprises, road transport, agriculture and others. Pollution can have a negative impact on human health and the environment, it is important to identify its sources and take measures to reduce its impact.

To study environmental pollution in the south of Ukraine, various geochemical studies were conducted. For example, research was conducted on the various reservoirs water, in particular rivers and ponds, in order to determine the level of their pollution. Water research can provide information about the presence of various substances in it, such as heavy metals, nitrogen and phosphate compounds, pesticides etc. [Karpenko et al, 2017; Spivak et al, 2019; Ishchenko et al, 2019].

Such studies can be carried out using various methods, for example, atomic emission and atomic absorption spectroscopy. With their help, it is possible to determine the amount of various substances in the soil, as well as their concentrations. According to the results of geochemical research, it was found that the soil in the south of Ukraine may contain various heavy metals, such as lead, cadmium, copper and others. The presence of oil products and other toxic substances in the soil was also discovered. The most polluted areas are often associated with industrial enterprises, especially metal and chemical production. It is important to note that soil pollution can have serious consequences for human health and the environment. For example, high concentration of heavy metals in the soil can cause contamination of groundwater and sources used for drinking water. In addition, soil pollution can have a negative impact on flora and fauna, which can affect the ecosystem as a whole.

The Mykolaiv region is located in the south of Ukraine and has a diverse natural and geological history. From the point of view of geochemistry, the Mykolaiv region can be divided into several provinces depending on the soil chemical composition.

One of this province is the Western Black Sea Plain. The soils of the province contain low levels of heavy metals such as lead, cadmium and manganese, which are good indicators of the ecological stability of the area. However, the levels of carbon monoxide and carbonic acids in the province's soils can be quite high, which can cause soil acidity and affect the development of vegetation.

Another province of the Mykolaiv region is the Azov Range. Soils in the province have high levels of heavy metals such as lead, cadmium and

manganese, which may be related to industrial development and environmental pollution. Also, the province may have high levels of salts, which can cause increased acidity and soil pollution.

The third province is the Crimean platform, which consists of soils based on limestone and clay rocks. The soils of the province have high levels of calcium and magnesium, which ensure good soil fertility. However, this province can have high levels of aluminum, iron, and manganese, which can affect the development of vegetation and make soils less suitable for agricultural use.

The fourth province of the Mykolaiv region is the Southern Buh Basin. Soils in the province have high levels of nitrates, which may be related to the use of mineral fertilizers and sewage pollution. Also, the levels of heavy metals in the soil can be quite high, which may be related to the development of industry in this area [Salt et al., 1998; Dudka et al., 2011; Alloway, B.J. 2013].

The heavy metals content in the Mykolaiv geochemical province soil can vary significantly depending on the specific district and its industrial activity. For example, the heavy metals levels in soils can be higher in Mykolaiv district than in rural areas [Spivak et al, 2019; Pohrebennyk et al, 2019].

One of the most harmful heavy metals that can be found in soil is lead. Lead can accumulate in the soil as a result of its use in the manufacture of cars and other industrial applications. High levels of lead in soils can cause serious health problems in humans and animals that use these soils.

Another dangerous heavy metal that can be found in the soil is cadmium. Cadmium may be known as an element of industrial pollution because it is used in the production of batteries and other electronic devices. High levels of cadmium in soils can also cause serious health problems in humans and animals.

In addition to lead and cadmium, other heavy metals that can be found in the soil of Mykolaiv geochemical province include mercury, chromium, nickel and copper. High levels of these metals in soils can have serious effects on human and animal health, as well as on vegetation and the ecosystem.

The metals migration from the soil is the process by which metals from the soil enter the air, water, or plants. The process can cause environmental pollution and deterioration of human health. Soils play an important role in the circulation of heavy metals in the environment. They

are the key environment of terrestrial ecosystems, which has universal adsorption properties [Salt et al., 1998; Kroik, 2011; Bezsonov et al., 2017]. Undoubtedly, it is the soil that reflects the level of long-term anthropogenic influence on the environment as a whole. When the soil is saturated with chemical components, namely xenobiotics, the soil can become a source of secondary pollution for water, reservoirs, atmospheric air, animal feed and human food. Unlike other environments (for example, air, where dispersion processes prevail), soils do not have the possibility of their rapid purification. Chemical pollutants can be stored in it for many years and, being included in ecological chains, because the long-term effect of toxicants. This increases the risk of chronic intoxication. Therefore, soils require long-term ecological survey (monitoring).

One of the possible ways of metals migration from the soil is leaching into groundwater. When water passes through contaminated soil, metals can enter the groundwater and subsequently into aquatic ecosystems. This can cause deterioration of water quality and affect the life of animals and plants that depend on the aquatic environment.

Another way of metals migration from the soil is absorption by plants. Plants can absorb metals from the soil through their roots and leaves. This can cause metals to accumulate in plants and then be absorbed by animals that feed on those plants. If metals accumulate in the tissues of animals and humans, it can affect their health [Baker & Brooks, 1989; Chon et al., 1999; Khan et al., 2008]. Also, metals can enter the air through the processes of transport and industry. This can lead to air pollution and affect the health of people living in the area. In general, the migration of metals from soil is a serious problem of environmental pollution and can have a negative impact on human health and ecosystems. Therefore, it is necessary to conduct appropriate research and control the level of pollution in order to prevent negative consequences.

The metals migration from soil to water can occur through various mechanisms, such as:

- Leaching of metals from waste: Metals can enter the soil through waste such as mercury lamps, batteries and other waste containing heavy metals. These metals can then move from the soil to the water via water currents.
- Infiltration into the soil: Metals can enter the soil through a polluted atmosphere, contaminated groundwater, or other sources of

contamination. These metals can then move to the groundwater as a result of water infiltration into the soil.

- Deposition: metals can be deposited in the soil through deposition processes. This can happen due to a change in soil pH or other chemical reactions that contribute to the precipitation of metals in the soil. These metals can then move from soil to water through drainage channels or surface runoff.
- Soil erosion: metals can move from soil to water through soil erosion. This can happen as a result of climate change, high levels of rain, wind and other natural factors that contribute to soil erosion.

According to these mechanisms, metals can enter groundwater, rivers, lakes and other water sources, which can have a harmful effect on the environment. The metals content in the soil can affect their migration properties, that is, the speed and distribution of metals in the environment. Below we consider some of the factors that affect the migration properties of metals:

- Metals chemical properties: Chemical properties of metals, such as the size of the ion, its charge, degree of oxidation, solubility in water, and others, can affect their migration properties. For example, highly charged metals such as Cu^{2+} and Zn^{2+} tend to be more mobile in soil than less charged metals such as Fe^{2+} and Mn^{2+} .
- Level of soil contamination: The level of metal contamination in soil can affect their migration properties. A high level of pollution can promote the migration of metals in the soil and provide them with a path to water sources. On the other hand, a low level of pollution can contribute to the retention of metals in the soil.
- Soil type: Different soil types have different properties that can affect the migration properties of metals. For example, clay soils can retain metals better than sandy soils.
- Soil pH: Soil pH can affect the migration properties of metals. For example, metals that are bound to soil mineral particles may be more readily available for migration.

The purpose is a determination of the heavy metals' migration levels in the locations of missile strikes by the Russian aggressors.

The objectives of the research are developing a strategy for testing the Mykolaiv Urban Industrial Agglomeration (MUIA) soil cover;

estimating the migration level of HM (Cr, Zn, Hg, Pb, Ni, Cu, Mn) of the MUIA soil cover according to the maximum permissible levels.

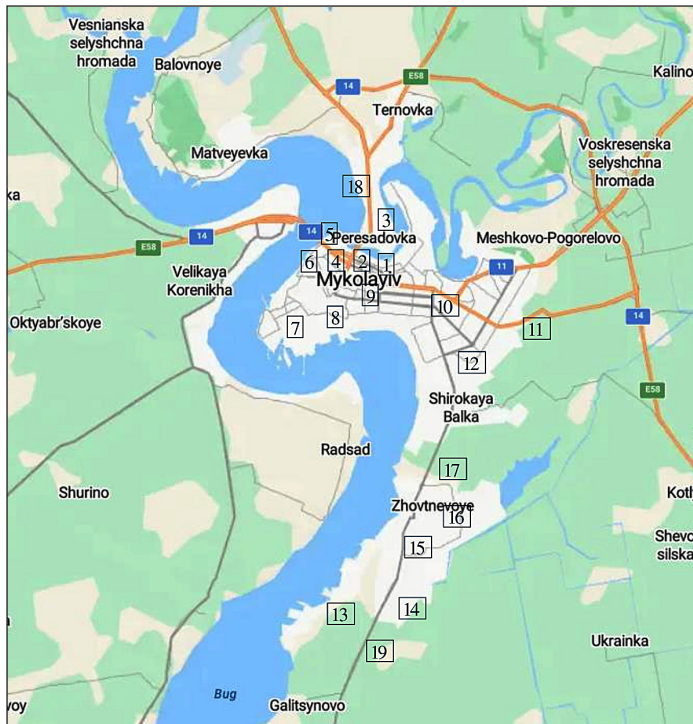
MATERIALS AND METHODS

The strategy of sampling on the territory of MUIA is based on the following principles: the location of sampling points with a step of 10–15 km, taking into account the scale of the localization of bombings. The geomorphological features of urban landscapes and the functional zoning of MUIA following the General Plan of the city (National Report on the State of the Natural Environment in the Mykolaiv Region in 2021, 2021; General plan of Mykolaiv city) are also taken with the maximum approximation to the regular one according to the “Requirements for ecological and geological studies on a scale of 1:50,000–1:25,000”; soil sampling was carried out during October–November 2022 (autumn section of data) (Figure 1).

With a plastic spatula, soil samples were taken from a depth of 0–5 cm weighing no more than 200 g each. The mass of the combined sample was about 1 kg and was mixed until the soil was homogeneous. Large inclusions (>2 mm) were removed manually: stones, glass, plant roots, etc. After the selection, the samples were packed in hermetic glass containers, placed in containers with a stationary temperature interval of 3–5°C and delivered to the laboratory. In laboratory conditions, soil samples were dried in a temperature range of 40±5°C, mixed in a centrifuge. Before analysis, the samples were crushed in a mortar and sieved through a sieve with a whole diameter of 1 mm (ISO 10381-5:2009). The content of chemical elements in a samples was determined using X-ray spectrometry (X-ray spectrometer S2 PICOFOX Bruker, a type of detector: silicon drift detector, high voltage generator: MNX 50P50/XCC, the source of X-rays: air-cooled metal MCB50. -0.7G, X-ray optics: multi-layer monochromator).

HM was determined according to the indicators: $C_{i_{av}}$ – the weighted average indicator of HM content at the studied points, $C_{i_{min}}$ – the minimum concentration of HM, $C_{i_{max}}$ – the maximum concentration of HM.

Separation of physical and chemical forms of heavy metals in soils was carried out by successive leaching. Leaching was carried out



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

Figure 1. Sampling map of the MIUA

during the day under normal conditions and occasional stirring. The ratio of solid and liquid phases is 1:5. The solution was separated from the residue on a paper filter “blue ribbon”; the filter residue was washed twice with distilled water (Figure 2).

Statistical processing of experimental data was performed using the application package Microsoft Excel and Statistics 10.0.

RESULTS AND DISCUSSION

The territory of the city of Mykolaiv is located in the southern steppe zone. Soil cover under the conditions of the city has a different genesis. Natural, surface-transformed soils and urban soils are distinguished [Petrychenko et al., 2019].

The soil cover of urban areas is undergoing radical transformation. On large areas, under highways and neighborhoods, it is physically destroyed, and in recreation areas - parks, squares, courtyards - it is prone to degradation, pollution by household waste, enriched with HM and harmful substances from the atmosphere. The negative indicators of soils in urban areas include overcompaction, an unfavorable degree of moisture saturation, a lack of humus and basic nutrients [Dudka et al., 2011; Rybalka et al., 2018; Shi et al., 2021].

In the conditions of industrial and urban agglomerations, great importance is attached to the study of the entry routes and forms of HM presence in the environment. In the soil cover of urban areas, HM are indispensable components, as factors of man-made load. HM pollution is associated

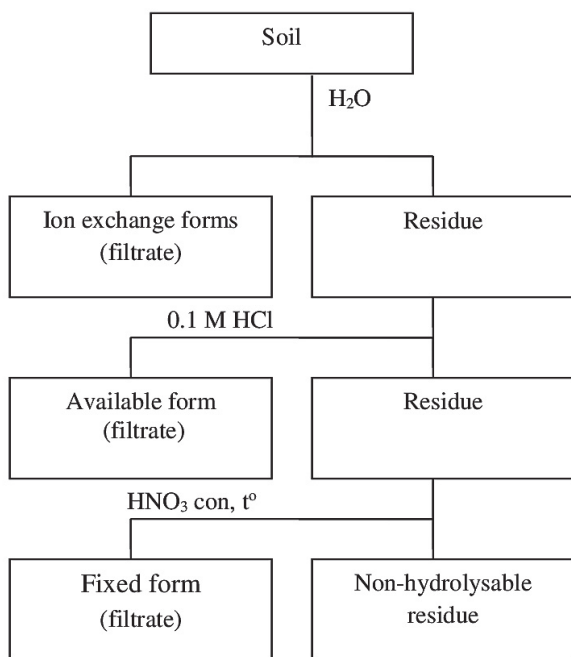


Figure 2. Scheme for separating the forms of heavy metals in soils

with their wide use in industrial production, significant entry into the ground cover along avenues of urban use, together with inefficient cleaning systems. The HM as part of emissions into urban landscapes occurs in the form of their complexes, oxides and one-and-a-half-oxides.

In the conditions of open military attacks, Russian terror should be considered as an effective militarized factor in the manifestation of the aggression of the Russian Federation. The analysis of the situation proves that under the conditions of large-scale hostilities in the Mykolaiv region and directly on the territory of the Mykolaiv city, it is practical to minimize the industrial load on the urban environment. After all, up to 90% of enterprises have stopped their activities, including under an unsatisfactory state of energy supply condition, limited industrial resources, and a significant outflow of specialists to other regions and abroad from all fields of activity.

Up to 60% of atmospheric pollution of agglomerations enters the atmosphere from the operation of transport infrastructure [Khan et al., 2008; Mitryasova et al., 2017]. Mobile sources have a direct impact: automobile, railway, aviation [Kabata-Pendias & Mukherjee, 2017; Wang et al., 2019; Ma et al., 2017]. However, in the context of hostilities, it can be stated that the airfield complex “Kulbakino” on the southeastern outskirts of the MUIA was bombed on February 24, 2022 and is not being operated at full capacity to this day. For almost a year, railway transport worked in asynchronous mode, carried out irregular passenger transportation and with limited capacities. Motor transport remains the main source of pollution, but considering that more than half of the city’s residents have left for other regions of Ukraine and abroad, it can be argued that the load from mobile sources on the atmosphere has been significantly reduced. Besides, in this period, the state of city logistics is characterized by low indicators, i.e., transport communications are not actively working until now. This means that there

is low sales efficiency at the level of enterprises of various forms of ownership, and therefore a low level of atmospheric emissions. Therefore, the dominant negative factor in the formation of the MUIA pollution field in modern conditions and during the last year can be considered the military factor of Russian aggression.

Distribution of heavy metals mobile forms in MUIA soils

Based on the analysis of numerous literary sources, in the research, mobile forms are considered as the sum of ion-exchangeable and available forms. The study is shown that the mobile form of heavy metals is associated mainly with finely dispersed fractions of organic matter and metal hydroxides [Pan et al., 2019; Li et al., 2020; Mitryasova et al., 2021]. The ratio of heavy metals forms in MUIA soils varies within limits and largely depends on the localization of pollution sources. Table 1 presents the lowest and highest values of metal concentrations at all sampling points. The average value was calculated by adding all metal concentration values and dividing by the number of samples.

Lead

The predominant concentration of lead in a fixed form is observed in the ground cover. The small amounts of soluble lead compounds obtained by treatment with ammonium acetate and hydrochloric acid solutions were found to be at the limit of detection and make up less than 0.01% of the total amount of lead in the soil. This indicates that lead in the soil is mostly bound to mineral components and organic substances that can act as sorbents of heavy metals. Such fixed forms of lead are not dangerous for the environment and human health, since they cannot easily change into a soluble form and accumulate in the bodies of living organisms.

Table 1. Distribution of the heavy metals content in the soil cover by forms

Metals	Danger class						
	Cr	Zn	Hg	Pb	Ni	Cu	Mn
	I			II			III
Ion exchange form, mg·kg ⁻¹	<u>0.9–60.3</u> 11.1	<u>0–17.6</u> 9.1	<u>0–14.1</u> 2.6	<u>0–0.01</u> 0.01	<u>0.08–4.6</u> 0.77	<u>0–0.01</u> 0.01	<u>17.8–58133</u> 3598
Available form, mg·kg ⁻¹	<u>0.4–26.8</u> 4.9	<u>0–57.9</u> 29.8	<u>0–44.9</u> 8.5	<u>0–0.01</u> 0.01	<u>0.67–36.8</u> 6.2	<u>0–0.01</u> 0.01	<u>10–32700</u> 2024
Fixed form, mg·kg ⁻¹	<u>8.7–582.9</u> 107.3	<u>0–176</u> 90.7	<u>0–611</u> 115	<u>0–151.2</u> 49.1	<u>3.4–188.6</u> 31.5	<u>0–123.8</u> 33.3	<u>27.8–90834</u> 5622

On the other hand, a small amount of soluble lead compounds in the soil may indicate the presence of a source of anthropogenic pollution, which can lead to an increase in the concentration of soluble compounds in the soil and water systems. Such pollution can occur as a result of industrial activity, transportation and storage of heavy metals and other sectors of the economy. Therefore, it is necessary to systematically monitor the level of soil pollution and take effective measures for their protection and restoration.

Zinc

As a result of the conducted research, it was found that more than 70% of zinc in the soil cover is contained in a fixed form, about 23% - in an available form, while only 7% of zinc is in an ion exchange form. It was found that the zinc mobility varies in the following order: ion exchange form < accessible form < fixed form.

The study revealed that the content of zinc mobile forms in the soil varies depending on the place of sampling. Some samples contained significantly more mobile forms of zinc, which can harm the ecosystem and human health. The reasons for such variation can be natural geochemical factors and anthropogenic activity, in particular industrial pollution. The results of the research are important for the development and implementation of environmental protection strategies, in particular for planning monitoring and reducing the content of heavy metals mobile forms in soils. In addition, the study emphasizes the importance of preserving the natural environment and reducing the impact of anthropogenic activities on the ecosystem.

Copper

According to the research results, there is an inversely proportional relationship between the gross content of copper and the content of its mobile forms in the soil cover. In particular, with an increase in the gross content of copper in the soil, there is a decrease in the content of its mobile forms. In general, it is determined that the mobility of copper in the soil depends on its physical and chemical properties, in particular, on the level of ion exchange availability and the degree of fixation. For this series of soils, it was established that the content of mobile forms of copper in them increases from the ion-exchangeable form to the fixed form.

This study provides important conclusions about the processes of changes in the content of mobile forms of copper in soils, which can occur both in natural and in anthropogenically modified ecosystems. According to the research data, an increase in the gross content of copper in the soil may indicate a decrease in its bioavailability for plants and other organisms. Therefore, the study confirms the importance of understanding the processes occurring in the soil cover and their impact on the environment. Knowledge about the mobile forms of copper and their distribution in soils can be useful for the development of effective strategies for preserving the soil resource and ensuring ecologically sustainable development.

Chrome

On average, more than 87% of chromium compounds are present in a fixed form, about 9% - in an ion-exchangeable form, while about 4% - in an available form (according to Table 1). According to the general trend, the share of mobile forms of chromium increases with a decrease in total Cr concentrations in the soil. The distribution of chromium in different forms can be described by a series: available < ion-exchangeable < fixed. This means that most of the chromium in the soil is in a stable fixed form, which is less available for dissolution and migration in the water environment. At the same time, a smaller part of chromium is present in the ion exchange form, which can change depending on the parameters of the environment, and in the available form, which is the most easily accessible to biological systems.

The results of the study indicate that the distribution of mobile forms of chromium in soils is related to the chemical and physical condition of the soil. For example, high levels of chromium fixation can be associated with the presence of oxidizing environments in the soil, which ensure the formation of stable chromium oxides. These data are important for understanding the processes of heavy metals interaction with soil and can be used to develop strategies for remediation of contaminated soils. In addition, they can form the basis for further research aimed at studying various aspects of ecotoxicology and bioremediation.

Nickel

According to the research results, the average share of fixed forms of nickel in MUIA soil is 82%, available forms – 16%, and ion exchange

forms - 2% (Table 1). The distribution of nickel by form shows significant fluctuations due to the location and type of man-made activity. Like other metals, there is a tendency to increase the mobility of nickel with a decrease in its total concentration. The Ni distribution according to the forms of its occurrence increases in the following order: ion exchange < available < fixed.

These results indicate that nickel in MUIA soil is mostly in a fixed form, which is, bound to solid soil particles. Available and ion-exchangeable forms of nickel make up a small fraction, which may be due to the low solubility of nickel in aqueous solutions. The specified distribution of nickel by forms can be related to various factors, such as the geological structure of the soil, climatic conditions, the type of man-made activity, etc. According to the research results, the nickel mobility in MUIA soil depends on its total concentration. When the total nickel concentration decreases, its mobility increases. This may be because that at lower concentrations of nickel in the soil, its binding to solid particles decreases and its availability for dissolution in aqueous solutions increases.

So, the indicated research results provide certain information about the distribution of various forms of nickel in the MUIA soil and the influence of various factors on its mobility. This information can be important for developing strategies for environmental protection and reducing the negative impact of man-made factors on soil cover.

Mercury

The MUIA soil cover is characterized by high concentrations of mercury, with the maximum value reaching $670 \text{ mg}\cdot\text{kg}^{-1}$. The average concentration of mercury in the soil is about $127 \text{ mg}\cdot\text{kg}^{-1}$, with more than 90% of mercury present in a fixed form (Table 1). The ion exchange form of mercury is only 2.1%, while the available form reaches 6.7%. The proportion of migratory forms of mercury increases in the order: ion exchange < accessible < fixed.

According to the above analysis, the MUIA soil cover is a significant source of heavy metals, particularly mercury. Although the relative proportion of mercury in its fixed form is quite high, the presence of accessible and ion-exchangeable forms can lead to their migration and contamination of aquatic and terrestrial ecosystems.

Increased concentrations of mercury can be the result of anthropogenic influence, in particular industrial pollution, as well as natural factors.

For example, the formation of mercury minerals in volcanic rocks, which are common in the investigated geochemical province, is possible. This analysis can serve as a basis for further research and development of environmental management and environmental protection strategies to reduce heavy metal pollution.

Manganese

According to the conducted research, it can be stated that manganese is the most migratory among the studied metals, while on average 50% of the manganese content in the soil is represented by mobile forms (according to Table 1). In addition, the share of ion exchange forms of manganese reaches 32%, with an average value of 15.6%, and the available form is 18%. These data indicate that manganese can easily move into soil and may be available to various biological systems, including plants. Such migration can be dangerous for the environment and human health, as manganese can be toxic at high concentrations. Also, from Table 1, it can be concluded that a significant proportion of manganese in the soil is in the form of mobile and ion-exchange forms, which can be easily accessible for various processes of migration and interaction with other elements.

In the general context, the research data can be useful for understanding the dynamics of manganese distribution in soil cover and development of strategies to reduce the impact of anthropogenic factors on the environment. In general, it can be stated that the increase in the mobility of heavy metals in the soil cover is associated with the following arrangement of metals in the order of increasing their concentrations: Lead (Pb) < Iron (Fe) < Chromium (Cr) < Nickel (Ni) < Copper (Cu) < Zinc (Zn) < Manganese (Mn), as shown in Fig. 2. The increase in the share of ion exchange forms in the composition of the soil reflects the following series of available metals: Lead (Pb) < Chromium (Cr) < Iron (Fe) < Copper (Cu) < Nickel (Ni) < Zinc (Zn) < Manganese (Mn).

This means that metals with less mobility, such as lead and iron, are usually held in more stable forms in soil, while metals with higher mobility, such as zinc and copper, can more quickly transition to mobile forms. In addition, an increase in the share of ion exchange forms may indicate greater availability of metals for biological and chemical interaction with other soil components. Therefore, the results of this study indicate a potential contamination hazard soil cover with heavy metals

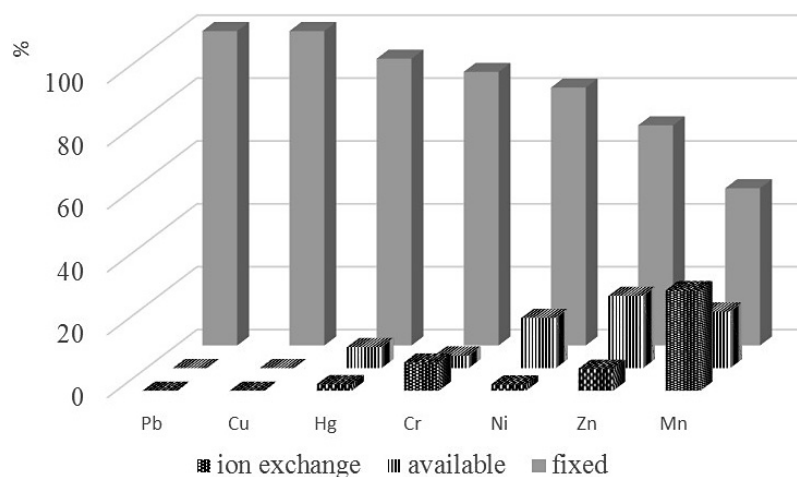


Figure 3. Forms of occurrence of heavy metals in the soil cover of the Mykolaiv industrial-urban agglomeration

in the geochemical province of Southern Ukraine (Fig. 3). To prevent the negative consequences of pollution and ensure environmental safety, it is recommended to take measures to control and manage the content of heavy metals in the soil, as well as to carry out monitoring studies.

CONCLUSIONS

The research data revealed that the concentration of heavy metals (Cr, Zn, Hg, Pb, Ni, Cu, Mn) is in three forms – ion exchange, available and fixed. According to the obtained data, the average concentration of heavy metals in the ion exchange form ranges from 0.9 mg/kg for Cr to 60.3 mg/kg for Mn. In available form, the average concentration of metals varies from 0.4 mg/kg for Cr to 57.9 mg/kg for Hg. In fixed form, the average concentration of metals ranges from 8.7 mg/kg for Cr to 582.9 mg/kg for Mn.

Natural processes aimed at preventing migration and slow dispersal of elements that are not characteristic of a given landscape may include various mechanisms that are components of natural bioregulation. Reducing the total amount of heavy metals in soils to normal values can increase their migration capacity. Depending on the type of heavy metal, its migration ability in the MPMA soil cover can increase in the following order: Mn (50%) < Zn (30%) < Ni (18%) < Cr (13%) < Hg (9%) < Cu (>1%) < Pb (>1%).

The heavy metals content in soils can depend on many factors, such as the type of soil, the presence of previous pollution, the level of anthropogenic influence and other factors. Studying such

factors can help identify risks to human health and the environment. One way to reduce the risks of heavy metal pollution is to use natural processes that help block the migration of these elements. For example, various microorganisms and plants can absorb heavy metals from the soil.

The study of the distribution of heavy metals mobile forms in the soil cover of the Mykolaiv industrial-urban agglomeration is a topical topic, since environmental pollution by heavy metals is a serious problem, especially as a result of military aggression. Research can be aimed at a more detailed analysis of the influence of various factors on the distribution of mobile forms of heavy metals, such as the type of soil, climatic conditions, the level of pollution of the territory, as well as the development of effective methods of cleaning the soil from heavy metals.

Research can also be aimed at studying the impact of heavy metal pollution on the state of the ecosystem and the health of the population, since heavy metals can negatively affect physiological processes in the human body and animals, as well as various ecosystem processes. Research can also be conducted in the field of phytoextraction and phytoremediation, which are promising methods of combating heavy metal pollution. Phytoextraction is the use of plants to remove heavy metals from the soil, and phytoremediation is the use of plants to clean contaminated soil of heavy metals. Therefore, further research in this field can be directed to the development of new methods of analysis and monitoring of soil pollution by heavy metals, to the development of effective methods of soil purification.

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