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ASSESSMENT OF HEAVY METAL POLLUTION LEVELS IN SOILS OF SPECIFIC AREAS OF THE ODESA INDUSTRIAL-URBAN AGGLOMERATION

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Abstract. Unlike the more dynamic air basin and surface waters, where active self-purification processses occur, soil virtually lacks this capacity. The cleansing processes in soil are very slow, only through leaching, plant uptake, and water erosion, which poses an environmental hazard in urbanized areas over long periods. In the process of intensive urbanization, the soil cover has been influenced by many anthropogenic factors, resulting in changes to its physical and chemical properties and an increase in heavy metal concentrations. An analysis of previous research results shows that the most contaminated soils with specific heavy metals are found in industrial zones and areas adjacent to high-traffic roads. In contrast to these technogenically stressed areas, attention is drawn to park and square zones, where elevated background concentrations of lead and zinc have been recorded, whereas copper content in all areas was identified to be below background levels. However, the range of calculated geoaccumulation index values for these heavy metals corresponds to a low-to-moderate level of soil contamination which varies according to the distance from sources of technogenic pollution. According experimental results by biosensor bioluminescent analysis of soils from certain parks and squares of the Odesa agglomeration, no significant inhibition of luminescence levels of microbial cells-the basis of the sensor elements-was observed. This indicates the absence of substances which have toxic effect to soil microorganisms.

Keywords: heavy metals, soil cover, urbanized area, pollution.

1. Introduction

In the context of intensive anthropogenic contamination of the natural components of the environment in urbanized areas, particularly the soil cover, the assessment of soil contamination levels by various pollutants, including heavy metals, becomes especially relevant. It is known that HM is a conventional term for a group of chemical elements classified based on atomic mass, toxicity, density, and other criteria. In studies devoted to environmental pollution, HM typically refer to chemical elements with a mass exceeding 50 atomic units or a density greater than 8 g/cm³ (*Cr*, V*, Fe, Mn, Co, Cu, Ni, Zn, Mo, Sb, Cd, Hg, Sn, Pb, Bi,* etc.). A key factor in identifying these elements as heavy metals is their extremely toxicity to biological organisms at low concentrations, as well as their ability to bioaccumulate and biomagnify. Virtually all HM that fall under this definition (*Pb, Hg, Cd*, and *Bi*, whose biological roles remain unclear)

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actively participate in biological processes and are components of many enzymes (Filon, 2020). HMs are not only toxicants but also natural soil micronutrients, the content of which depends on the physicochemical properties of parent rocks and the specific nature of soil formation processes. Some HM, such as *Cu* and *Zn*, are essential micronutrients for soil fertility when present in optimal concentrations. Depending on their sources and properties, HMs in the soil are divided into those associated with parent rocks and those entering into the soil through anthropogenic activity. This leads to the destabilization of the soil's physicochemical properties, a decrease of number and diversity of soil organisms, and contamination with various pollutants, including HM. The background content of HM in the soil corresponds to their natural concentrations in soils of different soil-climatic zones, without significant anthropogenic impact.

Contamination with HM contributes to a reduction in soil porosity and negatively affects the circulation of air, water, and nutrients. The danger of HM pollution in soils also lies in the fact that it leads to deterioration in the quality of the rest of natural environmental components.

Determining the forms in which HM exist is a labor-intensive and analytically complex task, as they can be present in a wide variety of mineral and non-mineral compounds. The dominant methods for determining HM nowadays include atomic absorption spectrometry, mass spectrometry, and electrochemical techniques. The sensitivity of these methods and whether they detect total or mobile forms of the metals should be taken into account.

In urbanized areas, natural environmental components are affected by different anthropogenic factors which have led to the huge loss of their capacity for self-purification. Unlike the more dynamic air and surface water systems, which have active self-purification processes, the soil cover lacks such capabilities. Soils in urban areas are cleansed of HM very slowly, primarily through leaching, plant uptake, water erosion, and deflation. In polluted urban soils, organic matter content decreases, the natural *pH* balance of the topsoil is disrupted, and the cation exchange capacity declines, reducing the soil's buffering ability. Typically, in soils of technogenically polluted areas, the content of mobile forms of zinc, cobalt, nickel, copper, and lead (including water-soluble, easily exchangeable ions, and those soluble in mildly acidic environments) is higher compared to background levels and soils in recreational zones. Due to the heterogeneous composition of soils, even within a single land plot, their physicochemical properties can vary, therefore having an impact on HM concentrations.

The distribution and toxicity level of HM in soils depend on both natural local conditions and the particular element. For instance, *Hg*, *Pb*, and *Cd* tend to pile up in the upper layers of soil but their restricted ability of migration within the soil profile and their emissions beyond the soil are insignificant.

Monitoring soil conditions is extremely important, especially given the growing anthropogenic pressures each year. In the context of intensive urbanization, it is practically impossible to eliminate anthropogenic contributions to soil contamination. However, considering the ecological risks posed by the pollution of urban soils by heavy metal, assessing their content and distribution patterns remains a h ighly relevant issue. their content and distribution patterns remains a highly relevant issue.

The objective of this study is to evaluate heavy metal contamination level in the soils of specific areas within the Odesa industrial-urban agglomeration.

2. Materials and Methods

The work is based on pu blished information from foreign and domestic authors, including our own research materials. The geoaccumulation index (*Igeo*), pollution index, concentration coefficient, potential ecological risk index (Muller, 1969; Tomlinson et al., 1980; Kabata-Penddias, 2011; Kowalska et al., 2018; Shuangmei et al., 2020), and other indicators are commonly used to assess the level of soil contamination. The geoaccumulation index (*Igeo*) was applied in the given study, which serves as a geochemical criterion for identifying heavy metal contamination.

$$Igeo = \log_2(C_i/1.5\ GB), \quad (1)$$

where C_i is the content of heavy metals in the top humus horizon; *GB* is the background content of heavy metals for soils of the steppe zone of Ukraine (Fateev et al., 2003); *the coefficient 1.5* is used to detect minor anthropogenic impact. Depending on the geoaccumulation index value, the following categories are distinguished (Muller, 1969):

1) clean soils (< 0);
2) soils with low to moderate contamination (0–1);
3) soils with moderate contamination (1–2);

4) soils with moderate to high contamination (2–3);
5) soils with high contamination (3–4);
6) soils with very high contamination (4–5).

Additionally, samples of soil were collected in several parks around Odesa. The sampling conditions were the same. Samples were collected in the morning, before noon, almost at the same time. The samples were dry. Soil samples in Peremohy Park and Shevchenko Park were collected in accordance with the requirements of DSTU 4287:2004. Sampling was performed using an auger. The most common sampling method is the «envelope» method, which was used during the study. The dimensions of the “envelope” were as follows: width – 100 m, length – 300 m. The sampling depth was 0–25 cm (within the arable layer). The collected samples were represented by southern chernozem, low in humus, heavy loam on loess. From five point samples for each park, composite samples were formed (Peremohy Park – 3 composite samples, Shevchenko Park – 2 composite samples).

The study of the content of pollutants (in particular HMs) in soils (2 samples) using the water extraction method was conducted in the “Water Monitoring Laboratory of the Southern Region of Separate Unit of the Basin Water Resources Management of the Rivers of the Black Sea Region and Lower Danube Black Sea Center for Water Resources and Soils”.

Of particular interest are the empirical data from biosensor bioluminescent analysis of soils (3 samples) from specific sites within the Odesa industrial-urban agglomeration, which was carried out at the “F.D. Ovcharenko Institute of Biocolloid Chemistry of the National Academy of Sciences of Ukraine” (Rapid determination of the level of integral pollution and heavy metal…, 2012).

Analysis is based on recording changes in the intensity of bioluminescence of bacterial strains – components of the sensor element – under the influence of toxic substances present in the aqueous extract of the soil sample being analyzed, compared to a control, using a *Hidex bioluminometer* (Finland). A natural sod-podzolic soil (Pushcha-Vodytsia, Ukraine) served as the reference sample (control) for the content of hazardous substances.

When analyzing soil samples, considering the nature of their sensitivity to the content of heavy metals (HM), the following biosensor elements were used:

1) *BE1* – a biosensor element based on the *Vibrio fischeri* strain (natural luminescence);
2) *BE2* – a biosensor element based on the *Vibrio harveyi* strain (natural luminescence);
3) *BE3* – a biosensor element based on the *Photobacterium phosphoreum* strain (natural luminescence).

The bioluminescent test employed sensor elements manufactured in accordance with TU 21.2-05402714-005:2014 with Amendment No. 1 “Sensor elements for rapid biosensor analysis of the condition of agricultural soils by indicators of heavy metal contamination”.

The microbial strains *Vibrio fischeri (Aliivibrio fischeri)* F1, *Vibrio harveyi* Ms1, *Photobacterium phosphoreum* B 7071, used for the development of sensor elements, are deposited in the depository of the State Scientific Control Institute of Biotechnology and Strains of Microorganisms (SSCIBSM), Kyiv (Ukraine).

The strains are characterized by the ability to quench natural luminescence if a specific HM is involved. Bioluminescent bacteria contain the enzyme luciferase, which effectively converts the energy of chemical bonds of essential metabolites into a light signal at a level suitable for measurements. The ecotoxicity parameter, *E* is determined by formula (2) and reflects the level of integral pollution of the object, specifically HM, and is expressed as the ratio of the intensity of bacterial bioluminescence upon contact with the test sample (*Ip*) to the intensity of bacterial bioluminescence upon contact with the reference (control) sample (reference soils/water) (*Ie)*:

$$E = \frac{I_p}{I_e}. \quad (2)$$

Risk ranges depending on t he value of the environmental toxicity parameter (E) are as follows: *low* – from 0.6–0.9 to 1.1–1.5; *medium* – from 0.4–0.6 to 1.5–1.7; *high* – from 0.2–0.4 to 1.7–2.0.

3. Results and Discussion

The territory of the Odesa industrial-urban agglomeration is characterized by quite diverse soil-geochemical conditions (Khokhryakova & Kulidzhanov, 2018). During the process of intensive urbanization, the soil cover has been affected by numerous anthropogenic factors, as a result of which its physicochemical properties were changed leading to an increase in concentrations of hazardous substances, particularly HMs.

Analysis of previously conducted studies (Domuschy, 2023) shows that the most polluted soils are those of the industrial zone (0.5 – 1.7 mg/kg), where the content of mobile forms of cadmium (Cd) exceeds the maximum permissible concentrations (MPC) on 70 % of the territory. Among the most contaminated are the soils of Chornomorskoho Kozatstva Street – 10.5 mg/kg and the Luzanivka district – 150 mg/kg.

Among the motor transport highways, the most polluted are Balkivska, Serednifontanska, and Kanatna streets, where HM concentrations reach about 1 mg/kg. Within residential and recreational zones, the most polluted areas are Shevchenko Avenue, Dyukivskyi Garden, and Mykhailivskyi Park (0.92 mg/kg), where exceedances of normative HM values are approximately 4 % (Domuschy, 2023).

It is worth noting that the content of mobile forms of lead (Pb) in urban soils of various functional zones ranges from 1.5 to 202 mg/kg. Within areas of intensive transport influence, 80 % of the studied territory has *Pb* concentrations exceeding the MPC. It is deemed that the distance to motor highways determines the level of lead pollution in the soil cover of parks and squares (Domuschy, 2023).

Mobile forms of zinc's (*Zn*), like lead, in the urban soil cover varies over a very wide range: from 1.45 mg/kg to 240.0 mg/kg. Regarding the mobile forms of zinc's content, 50 % of the city's territory exceeds the standards. The industrial zone (over 8 mg/kg) and areas adjacent to highways (over 3 mg/kg) are the most contaminated by this metal (Domuschy, 2023).

Cobalt (*Co*) concentrations in the ground layer of Odesa also range broadly from 0.12 mg/kg to 22.15 mg/kg. The most polluted areas are Luzanivka (over 22.15 mg/kg), which exceeds the background content more than 50 t imes, and Balkivska Street (10 mg/kg) (Domuschy, 2023), i.e., technogenically stressed sites.

The highest pollution with copper (*Cu*) compounds is found on Liustdorfska Road – 17 mg/kg; Balkivska Street – 14 mg/kg; and Admiralsky Avenue – 9 mg/kg, exceeding MPC values by 3–5 times (Domuschy, 2023).

In the background of the technogenically stressed parts of the city, park and square areas hold a special place. According to (Khokhryakova & Mykhailiuk, 2021), in these zones, excess of the maximum permissible concentrations are observed only for copper. The zinc content exceeds the MPC values by 6 times, and the lead content – by 8 times.

MPC of mobile forms of heavy metals in soils, which serve as regulatory values for assessing the level of contamination, approved by the Resolution of the Cabinet of Ministers of Ukraine dated December 15, 2021, No. 1325 (On approval of standards..., 2021).

According to (Khokhryakova & Mykhailiuk, 2021), concerning the heavy metals' content in the soils of certain parks and squares of the Odesa industrial-urban agglomeration, the geoaccumulation index was calculated (Table 1). The calculation data for the main functional zones of the urbanized territory (Domuschy, 2023) are presented in Table 2.

Table 1

Heavy metal content and geoaccumulation index (*Igeo*) values in soils from selected parks and squares of the Odesa industrial-urban agglomeration

Sample No.	***The content of heavy metal, mg/kg of soil*** /*Igeo value*			Soil pollution level according to the *Igeo* value
	Pb/ *Igeo*	***Zn/*** *Igeo*	***Cu/*** *Igeo*	
1	4.54/−2.10	241.60/1.38	0.18/−7.81	clean (***Pb, Zn***), average ***(Zn)***
2	6.89/−1.50	13.22/−2.81	0.92/−5.46	clean (***Pb, Zn***, ***Cu***)
3	6.14/−1.67	15.02/−2.63	1.07/−5.24	clean (***Pb, Zn***, ***Cu***)
4	50.27/1.37	37.90/−1.30	1.32/−4.94	average ***(Pb)***, clean (***Zn***, ***Cu***)
5	37.79/0.95	18.38/−2.34	0.93/−5.44	weak-average ***(Pb)***, clean (***Zn***, ***Cu***)
6	2.66/−2.87	0.89/−6.71	1.36/−4.90	clean (***Pb, Zn***, ***Cu***)
7	4.53/−2.11	35.58/−1.39	0.49/−6.37	clean (***Pb, Zn***, ***Cu***)
8	9.74/−1.00	87.54/−0.09	1.33/−4.93	clean (***Pb, Zn***, ***Cu***)
9	48.32/1.31	25.10/−1.89	1.37/−4.89	average ***(Pb)***, clean (***Zn***, ***Cu***)
10	38.90/1.00	38.29/−1.28	1.58/−4.68	weak-average ***(Pb)***, clean (***Zn***, ***Cu***)
MPS	***6.0***	***23.0***	***3.0***	Maximum permissible concentrations, *mg/kg of soil*

1 – slopes near the Chkalov Sanatorium; 2 – square near the Odesa Regional Council (under the trees); 3 – square near the Odesa Regional Council (grass, lawn); 4 – "Dyukivsky Garden" (Rozkydailivska, 69); 5 – "Dyukivsky Garden" park; 6 – memorial of the 411th coastal battery;7 – "Aeroportivsky" park; 8 – Peremohy Park; 9 – Gorky Park; 10 – Shevchenko Park

Table 2

Content of heavy metals and values of the geoaccumulation index (*Igeo*)

The name of the functional zone	***The content of heavy metal, mg/kg of soil*** / *Igeo value*			Soil pollution level according to the *Igeo* value
	Pb/ *Igeo*	***Zn***/ *Igeo*	***Cu***/ *Igeo*	
Automotive	20.16/0.05	24.60/−1.92	11.02/−1.88	weak to moderate ***(Pb***), clean (***Zn***, ***Cu***)
Recreational	18.19/−0.10	23.07/−2.01	8.02/−2.34	clean (***Pb, Zn***, ***Cu***)
Industrial	61.16/1.65	82.66/−0.17	12.58/−1.69	weak to moderate ***(Pb***), clean (***Zn***, ***Cu***)
Residential	20.50/0.07	58.00/−0.68	1.16/−5.13	weak to moderate ***(Pb***), clean (***Zn***, ***Cu***)
MPS	***6.0***	***23.0***	***3.0***	Maximum permissible concentrations, *mg/kg of soil*

Table 3

Presents data on the content of heavy metals in the soils of individual parks and squares of the Odesa industrial-urban agglomeration based on the results of our own research

Sampling location	Soil sample weight	Units of measurement	***Cu***	***Cd***	***Zn***	***Ni***	***Pb***	***Hg***
Shevchenko Park	40 g	mg/dm³	0.020	0.001	–	–	0.020	–
		mg/kg	0.100	0.005	–	–	0.100	–
Peremohy Park	40 g	mg/dm³	0.015	0.004	–	–	0.012	–
		mg/kg	0.075	0.002	–	–	0.060	–

The differences in the results of HM analysis in soils from specific parks in Odesa, obtained by atomic absorption spectrophotometry (Tabls. 1, 2):

- ✓ DSTU 4770.2:2007, DSTU 4770.3:2007, DSTU 4770.6:2007, DSTU 4770.7:2007, DSTU 4770.9:2007
- ✓ (DSTU 4770.2:2007, DSTU 4770.3:2007, DSTU 4770.6:2007, DSTU 4770.7:2007 DSTU 4770.9:2007, 2009)

and water extraction (Table 3), are caused by the different principles of these methods. The atomic absorption spectrophotometry method involves thedissolution of a soil sample using acids and thus determines the content of mobile forms of HMs. One of the simplest and most commonly used approaches for assessing the mobile (water-soluble) forms of soil's heavy metals is the water extraction method. It is widely used in environmental monitoring because it enables the evaluation of the level of ecological hazard of soil contamination and the bioaccessibility of metals to plants, microorganisms, and humans. However, it should be mentioned that this method does not provide complete insights into total contamination, although it is valuable for ecotoxicological assessment and environmental risk evaluation. This method determines only the fraction of heavy metals that is mobile and potentially available for plant uptake (water-soluble, mobile forms).

According to the results of the ecological toxicity assessment of soil samples from certain parks in Odesa using an experimental biosensor bioluminescent analysis (Table 4), they were classified as having a low level of ecological toxicity.

Table 4

Assessment of the ecotoxicity level of soil samples from selected parks in Odesa based on experimental biosensor bioluminescent analysis

Sample No.	Sampling location	*BE1*	*BE2*	*BE3*	Environmental toxicity level
1	Shevchenko Park	1.24	1.34	1.27	low
2	Peremohy Park (point 1)	1.52	1.33	1.42	low
3	Peremohy Park (point 2)	1.40	1.45	1.47	low

4. Conclusions

1. High content of heavy metals in soils have been recorded in industrial areas and along highways with intense vehicle traffic.

2. Against the background of these technogenically stressed parts of the urbanized territory, park zones and squares occupy an important place. However, even in these areas, concentrations of certain heavy metals exceed the maximum allowable limits, except for copper content. Nevertheless, soils ranging from slightly to moderately polluted, as well as pure soils, have been found in the industrial zones and highway areas. For soils within certain parks and squares of the Odesa industrial-urban agglomeration adjacent to technogenically stressed zones, soils from slightly to moderately polluted have also been recorded, while other areas contain clean soils.

3. Based on the results of biosensor bioluminescent analysis of samples of soil taken from park zones of Odesa (Ukraine), it can be pointed out that no significant inhibition of the luminescence level of microbial cells – the basic sensing elements – was detected, indicating the absence of substances toxic to soil microorganisms. A slight stimulation of microbial cell luminescence – the basic sensing elements – was observed, which may be related to the increased content of organic components in the soil samples. Soil samples analized and collected from the park zones of Odesa (Ukraine) were assigned a low level of ecological toxicity; the contamination level by individual HM is low, corresponding to their pollution level pursuant to the geoaccumulation index values.

4. Heavy metals in soils undergo transformation; this process is complex and depends on a number of factors, primarily on the nature of the metal, the soil composition, and the state of the environment. Of particular interest is the identification of the transformation algorithm and its potential impact on the ecological condition of the soil.

5. It is advisable to continue studies on the level of HMs contamination of certain areas of the Odesa industrial-urban agglomeration using various methods to identify patterns of their spatial and temporal variability.

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