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# Chemical Content of Landfill Neoreliefs in the Territory of the Subcarpathia Forestry District of Ukraine

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#### ABSTRACT

The tourism industry is concentrated within the boundaries of the Subcarpathia Forestry District of Ukraine. These are mostly resort complexes with recreation houses, hotels and restaurants. Since the issue of solid household waste processing has not been resolved in Ukraine, landfills are emerging near recreation facilities. Undoubtedly, such a situation contradicts the improvement processes, because landfills are objects of detonation of dangerous substances and compounds infiltrating into all components of the environment due to geochemical flows. The object of the conducted research was determination of chemical elements in the newly formed substrates on the surface of the following landfills, i.e. Bronytskyi, Stryiskyi, Boryslavskyi, which are located not far from the border with Poland within the tourist and recreational complex of the Lviv region of Ukraine, geographically belonging to the Subcarpathia Forestry District of Ukraine. It was established that the chemical elements of the toxic group and biogenic elements accumulate. The traces of individual elements were also determined. The Bronytskyi landfill is the most polluted with the following chemical elements: Pb (3.56–4.06 mg/kg), Zn (2.84–3.67 mg/kg), Gd (0.021–0.033 mg/kg), P (457.3–609.7 mg/kg), K (9.7–14.6 mg/kg), Ca (174.7–237.7 mg/kg), Ga (3.58–5,98 mg/kg), La (1.09-1.24 mg/kg), Y (0.013-0.014 mg/kg), Cd (0.15-0.176 mg/kg), Sn (0.013-0.018 mg/kg), Nd (0.029–0.046 mg/kg), Eu (0.022–0.036 mg/kg) and Th (0.05–0.078 mg/kg). The site of the Boryslav landfill is most polluted in the western side - Fe (16.06–19.72 mg/kg), Cu (0.37–0.43 mg/kg), Gd (0.003 mg/kg), Si (43–58.2 mg/kg), P (782.4–995.5 mg/kg), Ca (88.6–104.7 mg/kg), Mn (1.7–2.7 mg/kg), Sc (0.009 mg/kg), Cr (1.069–1.255 mg/kg), Y (0.015–0.016 mg/kg), Nd (0.016–0.018 mg/kg). In the eastern side of the Stryi landfill the presence of the following elements is most evident - Fe (18.98–27.97 mg/kg), Ni (0.09–0.21 mg/kg), Zn (0.14–0.19 mg/ kg), Pb (0.05–0.1 mg/kg), Al (1.6–2.0 mg/kg), P (718.1–652.5 mg/kg), Mn (2.5–3.5 mg/kg), Ga (0.01 mg/kg), La (0.02–0.04 mg/kg), Cr (0.009–0.013 mg/kg), Ge (0.214–0.551 mg/ kg), Cd (0.014–0.02 mg/kg), Nd (0.017–0.037 mg/kg), Th (0.009–0.016 mg/kg). Such a detailed chemical analysis for the presented research objects was carried out for the first time. Determining of the chemical content of the newly formed substrate is important from the point of view of environmental protection solutions implementation.

Keywords: landfill, heavy metals, neo-relief, environmental safety, phytomelioration.

### INTRODUCTION

Landfills of solid household waste, regardless of the formation and operation conditions, are a natural and technogenic ecosystem, characterized by anthropogenic and natural conditions of interaction. Abandoned landfills, where household waste is not dumped any more, over time turn into objects with a peculiar ecotope, characterized by a specific ecosystem. Formation of the landfill ecosystem is based on soil-forming processes on their surface. It can be notionally named like that from the point of view of the renaturalization approach. In general, neorelief formation processes under the influence of microorganisms (in particular, micromycetes) take place here.

The determination of the chemical content in the landfill neorelief is an important issue of environmental safety. Since landfills are a center of chemical and radiation pollution, it is interesting for the researchers to find out the degree of pollution of this "layer of life" (according to Vernadskyi, 1926) and the peculiarities of the migration of chemical elements into other components of the environment (air, water bodies, adjacent soils).

A lot of research of the chemical content has been done, in particular in terms of heavy metals content in the territory of devastated landscapes, among which it is worth noting the studies that revealed significant differences in the toxicological composition of devastated landscapes in different places. In order to prevent the occurrence of waste water accumulations that are dangerous for the ecological state, it is necessary to use natural resources rationally, to carry out demineralization, reclamation and phytomelioration of disturbed lands in a timely manner (Bosak P. et al., 2021).

According to (Zeng D. et al., 2021), arsenic is the most common heavy metal in landfills, both in the leachate and in the soil. The presence of the toxic metal in landfill leachate threatens the quality of soils and plants near landfills, and can significantly pollute surface and groundwater. It is important to regularly monitor the quality of the leachate to ensure the effectiveness and suitability of the treatment. The soil exposed to waste/leachate in spontaneous landfills is highly saturated with heavy metals. At natural landfills, it is extremely important to carry out cleaning and install an isolated barrier under the waste (Zeng D. et al., 2021).

According to monitoring data (Yaoa J. et al., 2019), groundwater is heavily polluted near solid waste dumps. The main pollutant is nitrate, which contributes to groundwater pollution, followed by heavy metals, including As and Cr<sup>6+</sup>. Precipitation increases the factors contributing to leaching from the upper layer of the soil; however, a minimal amount of nitrates and Pb penetrates into groundwater (Yaoa J. et al., 2019).

The research (Xu S. et al., 2021) comprehensively revealed the variety, abundance and expression of heavy metals in waste from a conventional landfill. The process of waste degradation can reduce excess heavy metals and in the meantime change the profile. Heavy metals in waste can undergo uncontrolled migration to the bottom of a landfill or downslope into the environment. The litter degradation process can reduce ~10% of heavy metals over 10 years, which may not be enough to fully reduce the potential risks.

After the end of technogenic impact due to emergency situations, soil contamination decreases during the first 3 years. Reduction of substrate pollution the by oil products depends on the depth. In the surface layers, it happens faster: in the soil – it reaches the background values after 4–6 years; at great depths, near bedrock, after 7–9 years or more (Karabyn V. et al., 2019).

Joint burial of various wastes changes the characteristics of the leachate and the leaching of heavy metals. The leaching behavior of Mn and Cr as well as the contents of Zn and Cu are related to pH. Heavy metal migration depends not only on waste content and heavy metal species, but also on leachate characteristics such as pH, organic matter and chloride content (Wang Q. et al., 2021).

The authors (Wang P. et al., 2021) claim that the operation of landfills endangers the quality of groundwater and the aquifer, as evidenced by the presence of a wide range of chemical compounds, including pollutants, in the leachate plume. This poses a serious risk to health, which will lead to a ban on the use of groundwater for human needs in the area affected by landfills. The influence of specific factors (such as the age of the waste, the date of closure of the landfill and the season) on the chemical composition of groundwater was studied (Wang P. et al., 2021). The authors (Wang P. et al., 2021) note that the investigation of seasonal influence is significant only in combination with the status of the landfill. A number of specific factors can make it difficult to compare results, if the data are obtained from multiple landfills with different lifetimes, as it is commonly practiced (Wang P. et al., 2021).

Antibiotics, heavy metals and antibiotic resistance in several landfill systems were comprehensively investigated in (Wang P. et al., 2019). The results showed that antibiotics, heavy metals and antibiotic resistance genes are widespread in landfill systems. Among them, most antibiotics in waste showed relatively decreasing trends with landfill age, while opposite results were observed for most heavy metals (Wang P. et al., 2019).

The risk of technogenic pollution of the soil with heavy metals consists in the fact that it may not manifest itself for a long time, due to the buffering properties of soils, as well as consistute a significant factor in negative transformations of both the soil and its individual components (Popovych, V. et al., 2021). Mining voids, proposed to be filled with non-toxic substances, are a danger to the environment (Petlovanyi M. et al., 2021).

Evaluation of reactor performance for ammonia removal from landfill leachate is quite important. The removal efficiency of ammonia can reach 72.5%, 98.5%, and 98.6%, respectively, at an applied voltage of 10 V. This experiment was

conducted under temperature and non-temperature conditions (Wang P. et al., 2019).

The combined use of various granular reactive media allows the removal of heavy metals contained in the filtrate, which can be safely processed in treatment facilities (Bilardi S. et al., 2018). This leachate pretreatment methodology could be cost-effective for using excess sludge through composting rather than landfilling, which in turn could significantly reduce the cost of sludge disposal. The methodology can be used as an on-site technology for leachate pretreatment (Bilardi S. et al., 2018).

The main mechanism of absorption of heavy metals occurs on a homogeneous layer of biosorbent, which is well described by Langmuir isotherms. After desorption, this biosorbent can be reused, the process was carried out in an acidic media and under optimal conditions in landfill leachate (Souza W. et al., 2018).

The choice of bentonite for geoecological applications determines the need to use its mineralogical and physicochemical properties. Moreover, the emission of heavy metals over a long period of time can cause the damage that affects its adsorption capacity and hydraulic behavior (Ray S. et al., 2021).

Health risk assessment shows that heavy metals in soils pose non-carcinogenic and carcinogenic health risks to both adults and children. On the basis of the health risks of these indicators, children are more vulnerable to heavy metals than adults in polluted areas. The physicochemical properties of the soils are generally suitable for agriculture, but the concentrations of Hg, Zn, Pb and As exceed the MAC recommended for agricultural soils in some or all zones. Therefore, it is recommended to carry out the research to determine the toxicity of the heavy metals effects on plants, since some investigations have shown a non-linear relationship between heavy metals in the soil and their amount absorbed by plants (Liu S. et al., 2019).

The analysis of the microbial diversity of old landfills indicates a diversity and abundance of bacteria that is significantly higher than bacteria in a newly created landfill. Common microbial communities can be effectively regulated by adjusting the relevant organic matter and heavy metals in landfill leachates. Thus, components and microbial activity interact, which plays an important role in waste degradation processes (Li R. et al., 2021). Filtrate pretreatment is necessary when the metal content is higher than the norm for draining into the sewer. The main sediments formed in the reactor are amorphous iron sulfide and aragonite. The influence of substances on the structure of dissolved metals is summarized by modeling over a wide range of filtrate concentrations (Hassana A. et al., 2020).

Fungi exhibit various attributes of tolerance. The highest removal efficiency for the most metals (Mn 71%, As 77%, Cu 52%, Cr 60%) is observed in the soil treated for metal removal. The results obtained in the study (Francisca F.M. et al., 2019) are useful in the design and application of a fungal formula for the treatment of metals in contaminated soils.

Converter slag can be used as a building material for permeable reactive barriers due to the high acid content with neutralizing ability in the treatment of acid mine drainage (Esfahani A. et al., 2021).

The improved removal of the investigated heavy metals in the solutions of synthetic metal ions using a UV membrane laminated with a matte fiber compared to an unmodified membrane can be explained by the complexation of metal ions with carboxylate ions from the fiber. Metal removal efficiency is generally higher in landfill leachates (Ray S. et al., 2021).

The authors (Deng M. et al., 2018) investigated that the heavy metals concentrations in wastewater were within the limits of official discharge standards. Basic biological treatment plays a secondary role (Argun M. et al., 2020). During the study of leachates, landfills are characterized as sources of intense pollution, including a high concentration of macro- and micro-pollutants (Adelopo A. et al., 2020).

Concentrations of heavy metals in closed landfills are significantly higher than the concentrations from active landfills for 11 of the 15 heavy metals studied. The differences are caused by the difference in the age of landfill use. The landfill poses a great risk to human health with a carcinogenic effect. Electronic waste can be the main source of these elements (Abiriga D. et al., 2020).

Exploitation of groundwater from landfills poses serious risks to human health. It is worth noting that the investigation of the seasonal effect turned out to be important only in combination with the status of the landfill. A number of sitespecific factors can make it difficult to compare results if data are obtained from multiple landfills with different lifetimes, as it is commonly practiced. The ideal approach is a long-term singlesite study (Calabrò P. et al., 2018).

The statistical differences between the concentration of leachate collected during municipal solid waste emission and after recirculation were calculated in (Alam R. et al., 2019). Only the average concentration of Pb during the pre-recirculation period was statistically higher compared to the post-recirculation period (Alam R. et al., 2019).

The concentration and distribution of metals in water, soil and plants within the buffer zone of the landfill can affect human health by entering the food chain. Due to leachate migration, the adjacent reservoir is responsible for the accumulation of heavy metals in the water. The average absorption of heavy metals by the soil is within the permissible limit, some areas remain at the level of high risk. In general, the environmental state is unsatisfactory for landfills. The authors (Bakhshoodeha R. et al., 2020) declare that waste management, sustainable development and stable environmental monitoring of toxic metals in landfills will prevent excessive accumulation of hazardous substances in the food chain.

According to monitoring data (Hussein M. et al., 2019), groundwater is highly polluted near solid waste landfills, which indicates that groundwater pollution was caused by point pollution. Environmental pollution around landfills can come from both natural and anthropogenic sources of pollution. Landfills are a potential source of groundwater pollution. Although the sandy and loamy top layer of the soil with high permeability is favorable for infiltration (Hussein M. et al., 2019).

Thus, after analyzing a number of cross-border studies of the physical and chemical composition of landfill substrates and leachates, it can be stated that constant monitoring of their content is extremely relevant.

### MATERIALS AND METHODS

The Lviv region is located in the western part of Ukraine. The region occupies the southwestern edge of the Eastern European Plain and the western part of the northern macroslope of the Ukrainian Carpathians. Lviv region borders Poland to the west, the Volyn region to the north, the Rivne region to the northeast, the Ternopil region to the east, the Ivano-Frankivsk region to the southeast, and the Zakarpattia region to the south. The territory of the Lviv region is 21.8 thousand km<sup>2</sup> (3.6% of the territory of Ukraine), divided into 7 districts, each of which is divided into territorial communities (Gensyruk S. et al., 1981).

The Bronytsya landfill is located in the Drohobych district of the Lviv region, near the Bronytsya village. Its geographic coordinates are 49.429954, 23.435612. It occupies the area of 3.48 hectares. The entrance is equipped with a road, a bypass ditch for leachate is partially built; there is no fence and system for collecting and removing leachate. It has been closed since 2018. There is no accumulation of waste. Reclamation works are not carried out. In this area, south-easterly winds prevail, and north-westerly winds are somewhat rarer. The temperature distribution shows the predominance of above-zero daytime temperatures during the sampling (+10 - +25), which alternated on certain days with nighttime chills (-2 - +5). The spread of the wind is more concentrated in the eastern side, which carried the residues of substances into the surrounding forest massif.

The Boryslav landfill is located in the Drohobych district of the Lviv region, near the city of Boryslav. Its geographic coordinates are 49.308329, 23.424374. The occupied area is 3 hectares. The entrance is complicated, the road is unsurfaced, there is no fence, there is no checkpoint and scales at the entrance. It requires the installation of a biogas collection and extraction system and eliminating of waste. Despite their small scale, solid household waste is imported from neighboring cities and tourist complexes (Drohobych, Boryslav, Truskavets, Skhidnytsia, Medenichi, and others). According to the 2030 Waste Management Strategy in the Lviv region, this landfill is subject to reclamation by 2024. This is the only functioning landfill on the territory of the Drohobych district. The direction of the prevailing winds and the daily distribution of the temperature regime during the period of research here are similar to the previous object, due to the small distance between them, i.e. 25 km. In this area, the predominant wind directions are southeasterly, somewhat less often are north-westerly winds, which, accordingly, have an effect on the geomorphological topography of the landfill.

The Stryi landfill is located in the southwestern part of the city of Stryi, Stryi district, Lviv region. Household waste is brought here from the cities of Stryi, Morshyn, Skole, and the village of Slavske. Its geographic coordinates are 49.276430, 23.826540. The area of the landfill is 22.5 hectares. The entrance is equipped with an unsurfaced road, there is a control checkpoint, scales for weighing cars and a control disinfection zone. There is also an existing hydrotechnical structure for flood preventing, a partially constructed bypass ditch for leachate. The problem is the lack of a stationary fence, the lack of a system for filtrate collection and discharge, as well as the biogas extraction system. The problem and, accordingly, growing danger, is the presence of places of stay of numerous homeless people who spontaneously stay at this landfill. The location of these investigated objects is given below (Fig. 1).

The aim of this research was to determine the chemical content of samples of landfill substrates that may affect the environment and public health.

The object of the conducted research is the chemical content of the newly formed substrates on the surface of three landfills, i.e. Bronytsya, Stryi, Boryslav, which are located within the tourist and recreational complex of the Lviv region of Ukraine, not far from the border with Poland, which geographically belongs to the Subcarpathia Forestry District of Ukraine.

In order to determine the contamination by heavy metals in the territory of the landfills in the autumn period (September 10, 2021), 24 samples of the substrate were taken. The samples were taken from 4 sides of the horizon of three landfills. Sampling was carried out according to the standard methodology of the "Program of the State Hydrometeorological Service" (Program of the State Hydrometeorological Service of the Ministry of Mines and Resources of Ukraine, 2004). The sample was prepared by using the envelope method, at an average temperature of +13 - +23 °C. The sampling depth was 10 and 20 cm. The samples were appropriately dried, crushed and marked.

The research was conducted in the research laboratory of the Freiberg Mining Academy (Germany, Saxony), during the academic mobility training in the frame of the program: "Scientific cooperation with universities of developing countries" of the international project "EcoMining: development of an integrated postgraduate program for sustainable mining and environmental protection activities" in the period from September 20 to October 20, 2021.

Determination of the heavy metals content in landfill substrates was carried out using inductively coupled plasma mass spectrometry (ICP -MS). It covers the entire necessary concentration range of measurements. They are used to carry out routine analyses in laboratories with a large flow of samples and require maximum performance and reliability of the device. The pre-prepared samples are injected into the plasma in the form of solutions.



Figure 1. Location of investigated landfills

### **RESULTS AND DISCUSSION**

From the results, the following data were obtained. The elements were divided into toxic, biogenic and those that contained traces and did not affect the growth and development of plants (Table 1).

# Chemical parameters of the substrates of the Bronytsya landfill

The data on the content of toxic, biogenic and trace elements were obtained from the investigated samples of the substrate taken from all sides of the horizons in sections of 0–10 cm and 0–20 cm (Fig. 2–8):

In the considered case, in the 0-20 cm horizon, the highest Fe content of 70 mg/kg and 81.01 mg/kg (0.2 m) was observed on the southern side of the Bronytsya landfill. It does not exceed the allowable concentration (MAC for Fe - 3500 mg/kg) [3]. The highest Ni content of 0.4 mg/kg (0.1 m) and 0.51 mg/kg (0.2 m) was observed on the

 
 Table 1. Assessment of heavy metal contamination of the landfill's soil cover

Hazard degree	Elements
Toxic	Fe, Co, Ni, Cu, Zn, Cd, Pb
Biogenic	Mg, Al, Si, P, K, Ca, Mn, Ga, As, La, U
Traces	Sc, Cr, Ge, Y, Sn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th

eastern side of the Bronytsya, which does not exceed the allowable concentration. The MAC for Ni in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 4.1 mg/kg for soils (Fig. 2).

The Co content from the eastern side of the Bronytsya landfill was 0.08 mg/kg (0.1 m) and 0.13 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Co in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 5.1 mg/kg in soil. The highest Cu content was observed on the eastern side of the Bronytsya landfill and was estimated at 0.88 mg/kg (0.1 m) and 0.9 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Cu in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 3.2 mg/kg for soils. As for Pb, its highest content was observed on the western side of the Bronytsya landfill and was estimated at 3.98 mg/kg (0.1 m) and 3.94 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Pb in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 6 mg/kg for soils. The highest Zn content was observed on the eastern side of the Bronytskyi landfill and was estimated at 2.84 mg/kg (0.1 m) and 2.67 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Zn in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 23.2 mg/kg in soil. For Cd, the highest content was observed on the



Figure 2. The content of toxic elements Ni, Fe in the substrate of the Bronytsya landfill in the 0.1 and 0.2 m horizon



Figure 3. The content of toxic elements Co, Cu, Pb, Zn, Cd in the substrate of the Bronytsya landfill in the horizon of 0.1 and 0.2 m

eastern side of the Bronytsya landfill and was estimated at 0.021 mg/kg (0.1 m) and 0.033 mg/ kg (0.2 m), which does not exceed the allowable concentration. The MAC for Cd in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 0.74 mg/kg for soils.

The research results indicate that the morphological analysis of the soils of the investigated territory did not reveal any visible signs of their anthropogenic change or disturbance. The content of chemical elements (toxic) does not exceed the MAC (Fig. 3). In terms of the indicators of biogenic elements, the highest content of Mg was observed on the eastern side of the Bronytsya landfill – 2.3 mg/kg (0.1 m) and 3.9 mg/kg (0.2 m). This indicates a low content in the substrates, as Clark proved that it reaches 1.98% (by mass) in the Earth's crust. The highest P content was observed on the eastern side of the Bronytsya landfill – 9.1 mg/kg (0.1 m) and 14.6 mg/kg (0.2 m). The highest content of Mn was observed on the western side of the Bronytsya landfill and was estimated at 3.53 mg/kg (0.1 m) and 5.98 mg/kg (0.2 m),



Figure 4. The content of biogenic elements Mg, P, Mn in the substrate of the Bronytsya landfill in the 0.1 and 0.2 m horizon



Figure 5. The content of biogenic elements Al, Si, K in the substrate of the Bronytskyi landfill in the 0.1 and 0.2 m horizon

which does not exceed the allowable concentration. The MAC for Mn in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 1500 mg/kg in soil (Fig. 4).

The highest Al content of 23.4 mg/kg (0.1 m) and 36.1 mg/kg (0.2 m) was observed on the eastern side of the Bronytsya landfill. As for Si, in our case, its highest content of 457.3 mg/kg (0.1 m) and 609.7 mg/kg (0.2 m) was observed on the eastern side of the Bronytsya landfill. The highest K content of 174.7 mg/kg (0.1 m) and 237.7 mg/kg (0.2 m) was observed on the eastern side of the Bronytsya landfill.

In the considered case, the highest Ga content of 0.9 mg/kg (0.1 m) and 0.13 mg/kg (0.2 m) was observed on the eastern side of the Bronytsya landfill. The highest La content of 0.12 mg/kg (0.1 m) and 0.19 mg/kg (0.2 m) was observed on the eastern side of the Bronytsya landfill. The content of U, as a biogenic element, was mostly observed from all sides of the Bronytsya landfill and was estimated at 0.3 mg/kg (0.1 m) and 0.4 mg/kg (0.2 m) (Fig. 6). Thus, biogenic elements in the substrates of the Bronytsya landfill do not have a high content.



Figure 6. The content of biogenic elements Ga, La, U in the substrate of the Bronytsya landfill in the 0.1 and 0.2 m horizon

Regarding the determined traces of a number of chemical elements, Sc was observed throughout the territory of the Bronytsya landfill and was estimated at 0.003 mg/kg (0.1 m) and 0.004 mg/kg (0.2 m). In the considered case, the highest content of Sn was observed in the entire territory of the Bronytsya landfill and was estimated at 0.001 mg/kg (0.1 m) and 0.003 mg/kg (0.2 m). Traces of Sn were observed throughout the Bronytsya landfill and were estimated at 0.003 mg/kg (0.1 m) and 0.005 mg/kg (0.2 m). In the considered case, the traces of Tb were observed throughout the Bronytsya landfill and were estimated at 0.003 mg/ kg (0.1 m) and 0.004 mg/kg (0.2 m). The highest content of Ho was observed on the eastern side of the Bronytsya landfill and was estimated at 0.003 mg/kg (0.1 m) and 0.004 mg/kg (0.2 m). For Er, traces of 0.007 mg/kg (0.1 m) and 0.01 mg/kg (0.2 m) were observed throughout the Bronytsya landfill. In the considered case, the traces of Tm were observed throughout the Bronytsya landfill and were estimated at 0.00012 mg/kg (0.1 m) and 0.0014 mg/kg (0.2 m). Lu was observed throughout the Bronytsya landfill and was estimated at 0.001 mg/kg (0.1 m) and 0.0012 mg/kg (0.2 m). Traces of Ge were observed throughout the Bronytsya landfill and were estimated at 0.013 mg/kg. The content of Yb traces was observed throughout the Bronytsya landfill and were estimated at 0.008 mg/kg. MAC for Yb in soils was not determined (Fig. 7).

As for the content of Y traces, they were most observed on the eastern side of the Bronytsya landfill in the amount of 0.15 mg/kg. The traces of Cr were observed on the western side of the Bronytsya landfill and were estimated at 1.064 mg/kg (0.1 m) and 1.114 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Cr in accordance with [3] is 6 mg/kg in soil. In the considered case, the traces of Ge were observed the most from the northern side of the Bronytsya landfill and were estimated at 0.21 mg/kg (0.1 m) and 0.29 mg/kg (0.2 m). The Nd content was observed the most from the northern side of the Bronytsya landfill and was estimated at 0.098 mg/kg (0.1 m) and 0.133 mg/kg (0.2 m). In the considered case, the traces of Cd were observed most on the western side of the Bronytsya landfill and were estimated at 0.089 mg/kg, which does not exceed the allowable concentration. The MAC for the chemical element Cd in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 0.74 mg/kg in soil. Traces of Th were observed most from the northern side of the Bronytsya landfill and were estimated at 0.044 mg/kg (0.1 m) and 0.073 mg/kg (0.2 m). The traces of Pr were observed the most from the northern side of the Bronytsya landfill and were estimated at 0.025 mg/kg (0.1 m) and 0.026 mg/ kg (0.2 m). In the considered case, the traces of Sm were observed most from the northern side of the Bronytsya landfill and were estimated at 0.02 mg/kg (0.1 m) and 0.026 mg/kg (0.2 m).Traces of Dy were observed the most from the northern side of the Bronytsya landfill and were estimated at 0.016 mg/kg (0.1 m) and 0.021 mg/ kg (0.2 m) (Fig. 8).

The research results show that the morphological composition of the substrates of the Bronytsya landfill did not reveal any visible signs of their anthropogenic change or disturbance.



Figure 7. Content of trace elements Sc, Sn, Eu, Tb, Ho, Er, Tm, Lu, Ge, Yb in the substrate of the Bronytsya landfill in the 0.1 and 0.2 m horizon



Figure 8. Content of trace elements Y, Cr, Ce, Nd, Cd, Th, Pr, Sm, Dy in the substrate of the Bronytsya landfill in the 0.1 and 0.2 m horizon

From the results obtained from the Stryi landfill, the following data were obtained, which were divided into toxic, biogenic and those that contained traces that do not affect plant growth (Table 1).

### Chemical content of the substrates of the Stryi landfill

From the analysis of samples taken from all sides of the horizon in sections of 0.1 and 0.2 meters at Stryi landfill, the following data were obtained for toxic, biogenic and trace elements (Figures 8–14): in the considered case, the highest content of Fe was observed from the southern side of the Stryi landfill and was estimated at

27.97 mg/kg (0.1 m) and 18.98 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Fe in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 3500 mg/kg in soil. The highest Ni content of 0.09 mg/kg (0.1 m) and 0.11 mg/kg (0.2 m) was observed on the eastern side of the Stryi land-fill and it does not exceed the allowable concentration. The MAC for Ni in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 4.1 mg/kg in soil (Fig. 9).

The highest Co content of 0.01 mg/kg (0.1 m)and 0.03 mg/kg (0.2 m) was observed from all sides of the horizon of the Stryi landfill. It does not exceed the allowable concentration. The MAC for Co in accordance with [3] is 5.1 mg/kg



Figure 9. The content of toxic elements Ni, Fe in the substrate of the Stryi landfill in the horizon of 0.1 and 0.2 m

in soil. Regarding the Cu content, the highest content was observed on the eastern side of the Stryi landfill and was estimated at 0.04 mg/kg (0.1 m) and 0.03 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Cu in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 3.2 mg/kg in soil. The Pb content of 0.05 mg/kg (0.1 m) and 0.12mg/kg (0.2 m) was observed on the southern side of the Stryi landfill, which does not exceed the allowable concentration. The MAC for Pb in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 6 mg/kg in soil. The highest Zn content of 0.19 mg/kg (0.1 m) and 0.14 mg/kg (0.2 m) was observed on the eastern side of the Stryi landfill, which does not exceed the allowable concentration. The MAC for Zn in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 23.2 mg/kg in soil. In the considered case, the highest Cd content of 0.008 mg/kg (0.1 m) and 0.004 mg/kg (0.2 m) was observed on the eastern side of the Stryi landfill, which does not exceed the allowable concentration. The MAC for Cd in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 0.74 mg/kg in soil. The results of the research show that the morphological analysis of the substrates of the Stryi landfill did not reveal any visible signs of their anthropogenic change or disturbance (Fig. 10).

With regard to biogenic elements, the data were present below. The highest content of the biogenic element Mg was observed on the western side of the Stryi landfill and was estimated at 1.7 mg/kg (0.1 m) and 2.2 mg/kg (0.2 m). This testifies to the low content of this biogenic metal in the substrates. The highest P content of 2.3 mg/ kg (0.1 m) and 2.2 mg/kg (0.2 m) was observed on the western side of the Stryi landfill. As for Ca, the highest values of 3.6 mg/kg (0.1 m) and 4.6 mg/kg (0.2 m) were observed on the western side of the Stryi landfill. The amount does not exceed the allowable concentration. In the considered case, the highest Mn content of 3.41 mg/kg (0.1 m) and 1.41 mg/kg (0.2 m) was observed on the western side of the Stryi landfill. The amount does not exceed the allowable concentration. The MAC for Mn in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 1500 mg/kg in soil (Fig. 11).

The highest Al content of 72.2 mg/kg (0.1 m) and 72.8 mg/kg (0.2 m) was observed on the western side of the Stryi landfill. In the considered case, the highest Si content of 1081 mg/kg was observed on the western side of the Stryi landfill. Regarding potassium, its highest content of 90 mg/kg (0.1 m) and 95.4 mg/kg (0.2 m) was observed on the western side of the Stryi landfill (Fig. 12).

Ga was observed on the western side of the Stryi landfill and was estimated of 0.02 mg/kg. The highest content of As of 0.01 mg/kg (0.1 m) and 0.03 mg/kg (0.2 m) was observed on the western side of the Stryi landfill. Its amount does not exceed the allowable concentration. The MAC for the chemical element As in accordance with



Figure 10. The content of toxic elements Co, Cu, Pb, Zn, Cd in the substrate of the Stryi landfill in the horizon of 0.1 and 0.2 m







Figure 12. The content of biogenic elements Al, Si, K in the substrate of the Stryi landfill in the horizon of 0.1 and 0.2 m

[3] is 2 mg/kg in soil. The highest La content of 0.06 mg/kg (0.1 m) and 0.02 mg/kg (0.2 m) was observed on the western side of the Stryi landfill. The U content of 0.007 mg/kg (0.1 m) and 0.006 mg/kg (0.2 m) was observed on the western side of the Stryi landfill (Fig. 13).

Similarly, traces of some of chemical elements were found at the Stryi landfill. In the considered case, the Ge content was observed the most from the western side of the Stryi landfill and was estimated at 0.0035 mg/kg (0.1 m) and 0.0027 mg/ kg (0.2 m). The MAC for the Ge in soils is not determined. In the considered case, the Cd content was observed most on the eastern side of the Stryi landfill and was estimated at 0.0016 mg/kg. It does not exceed the allowable concentration. The MAC for Cd in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 0.74 mg/kg in soil. The highest content of Sn of 0.0008 mg/kg (0.1 m) and 0.0017 mg/kg (0.2 m) was observed on the western side of the Stryi land-fill. As for Er, the highest content of 0.002 mg/kg (0.1 m) and 0.0031 mg/kg (0.2 m) was observed on the southern side of the Stryi landfill. The traces of Yb were observed from the western side of the Stryi landfill and were estimated t 0.0026 mg/kg (0.1 m) and 0.0036 mg/kg (0.2 m). As for the highest content of Ho, it was observed from the southern side of the Stryi landfill and was estimated at 0.0009 mg/kg (0.1 m) as well as 0.001



**Figure 13.** The content of biogenic elements Ga, As, La, U in the substrate of the Stryi landfill in the 0.1 and 0.2 m horizon





mg/kg (0.2 m). Tm was observed throughout the territory of the Stryi landfill and was estimated of 0.0003 mg/kg (0.1 m) and 0.0004 mg/kg (0.2 m). Lu was observed throughout the territory of the Stryi landfill and was estimated at 0.0003 mg/kg (0.1 m) and 0.0005 mg/kg (0.2 m). The traces of Eu were observed on the western side of the Stryi landfill and were estimated at 0.0015 mg/kg (0.1 m) as well as 0.0012 mg/kg (0.2 m). The traces of Tb were observed on the western side of the Stryi landfill and were estimated at 0.0011 mg/kg (0.1 m) as well as 0.0006 mg/kg (0.2 m) (Fig. 14).

The highest content of Cr was observed on the eastern side of the Stryi landfill and was estimated at 0.214 mg/kg (0.1 m) and 0.551 mg/kg (0.2 m), which does not exceed the allowable concentration. The MAC for Cr in accordance with [3] is

6 mg/kg in soil. Regarding the traces of Y, they were observed most on the western side of the Stryi landfill and were estimated at 0.026 mg/kg (0.1 m) as well as 0.024 mg/kg (0.2 m). Ge was observed on the west side of the Stryi landfill and was estimated at 0.12 mg/kg (0.1 m) and 0.05 mg/kgkg (0.2 m). The MAC for Ge in soil was not determined. Traces of Nd were observed most from the western side of the Stryi landfill and were estimated at 0.055 mg/kg (0.1 m) as well as 0.02 mg/ kg (0.2 m). In the considered case, the traces of Th were observed the most from the western side of the Stryi landfill and were estimated at 0.0305 mg/kg (0.1 m) and 0.0112 mg/kg (0.2 m). Trace amounts of Sc were observed on the west side of the Stryi landfill and were estimated at 0.0097 mg/kg (0.1 m) as well as 0.0152 mg/kg (0.2 m).



Figure 15. Content of trace elements Cr, Y, Ce, Nd, Th, Sc, Pr, Sm, D in the substrate of the Stryi landfill in the 0.1 and 0.2 m horizon

The traces of Pr were observed the most from the western side of the Stryi landfill and were estimated at 0.0146 mg/kg (0.1 m) as well as 0.00054 mg/kg (0.2 m). The traces of Sm were observed the most from the western side of the Stryi landfill and were estimated at 0.0098 mg/kg (0.1 m) as well as 0.004 mg/kg (0.2 m). In the considered case, the content of Dy was observed most from the western side of the Stryi landfill and was estimated at 0.0059 mg/kg (0.1 m) as well as 0.0039 mg/kg (0.2 m) (Fig. 15).

The research results indicate that the morphological composition of the substrates of the Stryi landfill did not reveal any visible signs of their anthropogenic change or disturbance. The determination of the chemical composition of landfill substrates is important from the point of view of selecting the vegetation species for the biological stage of reclamation.

From the obtained results from the Boryslav landfill, the following data were obtained for the site, which were divided into toxic, biogenic and trace elements that do not affect plant growth (Table 1).

### Chemical content of the substrates of the Boryslav landfill

From the soil samples taken from all sides of the Boryslav landfill at the horizon in sections of 0.1 and 0.2 meters, the following data were obtained for toxic, biogenic and trace elements (Figures 15–22): the highest Fe content of 16.06 mg/ kg (0.1 m) and 19.72 mg/kg (0.2 m) was observed from the southern side of the Boryslav landfill. Its

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content does not exceed the allowable concentration. The MAC for Fe in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 3500 mg/kg in soil. Ni content was most observed on the eastern side of the Boryslav landfill and was estimated at 0.37 mg/kg (0.1 m) as well as 0.43 mg/kg (0.2 m). The content does not exceed the allowable concentration. The MAC for Ni in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 4.1 mg/kg in soil (Fig. 16).

The content of Co from the western side of the horizon of the Boryslav landfill was 0.02 mg/kg, which does not exceed the allowable concentration. The MAC for Co is 5.1 mg/kg for soil [3]. In the considered case, the highest Cu content of 0.03 mg/kg and 0.04 mg/kg was observed on the eastern and western sides of the Boryslav landfill. It does not exceed the allowable concentration. The MAC for Cu in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 3.2 mg/kg in soil. As for Pb, its highest content of 0.12 mg/ kg (0.1 m) and 0.05 mg/kg (0.2 m) was observed on the western side of the Boryslav landfill. It does not exceed the allowable concentration. The MAC for Pb in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 6 mg/kg in soil. The highest Zn content of 0.06 mg/kg (0.1 m)and 0.09 mg/kg (0.2 m) was observed on the eastern side of the Boryslav landfill. It does not exceed the allowable concentration. The MAC for Zn in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 23.2 mg/kg in soil. For Cd, the highest content of 0.002 mg/kg (0.1 m)and 0.003 mg/kg (0.2 m) was observed from all



Figure 16. The content of toxic elements Ni, Fe in the substrate of Boryslav landfill in the horizon of 0.1 and 0.2 m



Figure 17. The content of toxic elements Co, Cu, Pb, Zn, Cd in the substrate of the Boryslav landfill in the 0.1 and 0.2 m horizon

sides of the Boryslav landfill and it does not exceed the allowable concentration. The MAC for Cd in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 0.74 mg/kg in soil (Fig. 17).

The research results indicate that the morphological analysis of the soils of the investigated area did not reveal any visible signs of their anthropogenic change or disturbance. The content of chemical elements (toxic) does not exceed the MAC.

As far as the indicators of biogenic elements are concerned, the highest content of Mg was observed on the western side of the Boryslav landfill -1.2 mg/kg (0.1 m) and 1.6 mg/kg (0.2 m). This testifies to its low content in the substrates. The highest P content of 1.8 mg/kg (0.1 m) and 2.1 mg/kg (0.2 m) was observed on the western side of the Boryslav landfill. The Ca content of 1.7 mg/kg (0.1 m) and 2.7 mg/kg (0.2 m) was observed on the western side of the Boryslav landfill and it does not exceed the allowable concentration. In the considered case, the highest Mn content of 1.13 mg/kg (0.1 m) and 1.26 mg/kg (0.2 m) was observed on the eastern side of the Boryslav landfill. It does not exceed the allowable concentration. The MAC for Mn in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 1500 mg/kg in soil (Fig. 18).



Sampling site

Figure 18. The content of biogenic elements Mg, P, Ca, Mn in the substrate of the Boryslav landfill in the 0.1 and 0.2 m horizon



Sampling site

Figure 19. The content of biogenic elements Al, Si, K in the substrate of Boryslav landfill in the horizon of 0.1 and 0.2 m

The highest content of Al, a biogenic element, was observed on the western side of the Boryslav landfill. Its amount reaches 43 mg/kg (0.1 m) and 58.2 mg/kg (0.2 m). As for Si, the highest content of this biogenic element of 782.4 mg/kg (0.1 m) and 995.5 mg/kg (0.2 m) was observed on the western side of the Boryslav landfill. The highest K content of as a biogenic element was observed on the western side of the Boryslav landfill. It reaches 88.6 mg/kg (0.1 m) and 104.7 mg/kg (0.2 m) (Fig. 19).

In the considered case, the highest content of the biogenic element Ga was observed from all sides of the Boryslav landfill and it was estimated to be 0.01 mg/kg. In the considered case, the highest content of biogenic element As was observed on the southern side of the Boryslav landfill and it was estimated to be 0.01 mg/kg (0.1 m) as well as 0.02 mg/kg (0.2 m), which does not exceed the allowable concentration. Just as the MAC for the chemical element As in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 2 mg/kg in soil. The highest content of La as a biogenic element was observed on the western side of the Boryslav landfill and it was estimated to be 0.02 mg/kg. The U content of 0.004 mg/kg was observed the most on the western side of the Boryslav landfill (Fig. 20).



Figure 20. The content of biogenic elements Ga, As, La, U in the substrate of the Boryslav landfill in the 0.1 and 0.2 m horizon



Figure 21. Content of trace elements Sc, Ge, Cd, Pr, Sm, Eu, Yb, Dy, Th, Er in the substrate of the Boryslav landfill in the 0.1 and 0.2 m horizon

In the considered case, the content of Sc was observed on the western side of the Boryslav landfill and was estimated of 0.009 mg/kg. The content of Ge was observed the most from the western side of the Boryslav landfill and was estimated at 0.002 mg/kg (0.1 m) as well as 0.003 mg/kg (0.2 m). Traces of Cd were observed from all sides of the horizon of the Boryslav landfill and were estimated of 0.001 mg/kg (0.1 m) as well as 0.002 mg/kg (0.2 m), which does not exceed the allowable concentration. Since, the MAC for the chemical element Cd in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 0.74 mg/kg in soil. Pr was observed the most from the western side of the Boryslav landfill and was estimated of 0.005 mg/kg. The content of Sm was observed the most from the western side of the Boryslav landfill and was estimated of 0.004 mg/kg (0.1 m) and 0.003 mg/kg (0.2 m). Traces of Eu were observed throughout the territory of the Boryslav landfill and were estimated at 0.001 mg/kg. In the considered case, the content of Yb was observed throughout the territory of the Boryslav landfill and was estimated at 0.001 mg/kg (0.1 m) as well as 0.002 mg/kg (0.2 m). The content of Dy was observed the most on the western side of the Boryslav landfill and was estimated at 0.003 mg/kg. Traces of Th were observed most from the southern side of the Boryslav landfill and were estimated at 0.01 mg/kg (0.1 m) as well as 0.006 mg/kg(0.2 m). Er was observed throughout the territory of the Boryslav landfill and was estimated at 0.01 mg/ kg (0.1 m) as well as 0.02 mg/kg (0.2 m) (Fig. 21).

In the considered case, the highest content of Cr traces was observed on the northern side of the Boryslav landfill and was estimated at 1.855 mg/kg (0.1 m) as well as 0.838 mg/kg (0.2 m), which does not exceed the allowable concentration. Since, the MAC for Cr in accordance with (Order of the Ministry of Health dated of Ukraine ..., 2004) is 6 mg/kg in soil. Regarding the content of traces of Y, they were observed most on the western side of the Boryslav landfill and were estimated at 0.015 mg/kg. The highest content of Sn was observed on the southern side of the Boryslav landfill and was estimated at 0.032 mg/kg (0.1 m). In the considered case, the traces of Ce were observed on the western side of the Boryslav landfill and were estimated at 0.04 mg/kg. Regarding the content of Nd, it was most observed on the western side of the Boryslav landfill and was estimated at 0.018 mg/kg (Fig. 22).

The research results indicate that the morphological analysis of the soils of the investigated area did not reveal any visible signs of their anthropogenic change or disturbance.

Traces of Tb were observed on the western side of the Boryslav landfill and were estimated at 0.0005 mg/kg. The traces of Ho were observed on the western side of the Boryslav landfill and were estimated at 0.0006 mg/kg. In the considered case, the traces of Tm were observed on the western side of the Boryslav landfill and were estimated at 0.0003 mg/kg. The highest content of Lu was observed on the western side of the Boryslav landfill and was estimated at 0.0004 mg/kg (0.1 m) and 0.0003 mg/kg (0.2 m) (Fig. 23).

The research results indicate that the morphological analysis of the soils of the investigated area did not reveal any visible signs of their anthropogenic change or disturbance.





Figure 22. Content of trace elements Cr, Y, Sn, Ce, Nd in the substrate of the Boryslav landfill in the 0.1 and 0.2 m horizon





### CONCLUSIONS

The article presents the results of determination of the content of 37 chemical elements in the horizons of 0-0.1 m and 0-0.2 m of the substrates of the Bronytsya, Stryi, and Boryslav landfills in the territory of the Lviv region of Ukraine.

It was established that the most chemically polluted area is the eastern side of the Bronytsya landfill, though the MAC level is not exceeded. Among the toxic elements, it is possible to single out the greatest presence of Pb (3.56–4.06 mg/kg), Zn (2.84-3.67 mg/kg) and Gd (0.021-0.033 mg/ kg) with a significant difference with other sides of the landfill. As for biogenic elements, P (457.3 - 609.7 mg/kg), K (9.7 - 14.6 mg/kg), Ca (174.7 - 237.7 mg/kg), Ga (3.58 - 5.98 mg/kg) and La (1.09 - 1.24 mg/kg) were detected at the eastern side. The traces of the following chemical elements were determined: Y (0.013-0.014 mg/kg), Cd (0.15–0.176 mg/kg), Sn (0.013–0.018 mg/kg), Nd (0.029-0.046 mg/kg), Eu (0.022-0.036 mg/ kg) and Th (0.05-0.078 mg/kg), which indicates that this landfill is most loaded with chemical compounds and heavy metals from the eastern side.

The most polluted area of the Boryslav landfill is from the west. The presence of a large number of toxic elements was determined - Fe (16.06–19.72 mg/kg), Cu (0.37–0.43 mg/kg), Gd (0.003 mg/kg). The higher content of biogenic elements was determined at the western side, i.e. Si (43–58.2 mg/kg), P (782.4–995.5), Ca (88.6– 104.7 mg/kg), Mn (1.7–2.7 mg/kg). The presence of traces of Sc (0.009 mg/kg), Cr (1.069–1.255 mg/kg), Y (0.015–0.016 mg/kg), Nd (0.016 – 0.018 mg/kg) in the substrates of the western side landfills was identified.

The eastern side of the Stryi landfill provides the greatest results regarding the presence of heavy metals in samples of the obtained substrates. The presence of the following elements is pronounced – Fe (18.98–27.97 mg/kg), Ni (0.09–0.21 mg/kg), Zn (0.14–0.19 mg/kg), Pb (0.05–0.1 mg/kg), Al (1.6–2 mg/kg), P (652.5–718.1 mg/kg), Mn (2.5–3.5 mg/kg), Ga (0.01 mg/kg), La (0.02–0.04 mg/kg), Cr (0.009–0.013 mg/kg), Ge (0.214–0.551 mg/kg), Cd (0.014–0.02 mg/kg), Nd (0.017–0.037 mg/kg), Th (0.009–0.016 mg/kg). Such a detailed chemical analysis for the presented research objects has been carried out for the first time.

The determination of the chemical content is important for the renaturalization approach, based on the return of the territory for the humanity needs by means of reclamation (phytomelioration) and phytoremediation.

Further research will be aimed at determination of the chemical content of the pioneer vegetation that begins to develop on the newly formed substrate. The data obtained in the future will make it possible to draw the conclusions about the physiological stability of the selected species and their phytoremediation properties.

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