EXAMINATION OF SOIL COMPOSITION IN "WILD" LANDFILL IN THE CITY OF LESKOVAC AND POTENTIAL ECOLOGICAL RISKS

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(SHORT COMMUNICATIONS)
UDC: 631.4:628.4
DOI: DOI: 10.5937/savteh2401067E

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The wild landfills management is a major environmental problem and cause for concern as solid waste is disposed of in an unregulated manner resulting in the creation of illegal landfills. Such illegal disposal of waste can lead to damage to the environment, contamination of the soil, and creation of leachate, which affects people's health. On the territory of the Jablanica district, there are currently 81 registered, unorganized, wild landfills. This paper analyses the soil contamination at the closed landfill on the territory of the city of Leskovac. The aim is to determine the quality of the soil, detect possible contamination, and identify potentially harmful materials in the examined samples. An increased concentration of aromatic hydrocarbons and polycyclic aromatic hydrocarbons was detected in the tested samples. It was established that the measured concentrations of various metals in the analyzed samples exceeded the maximum permissible values. This work provides useful information on further planning of remediation measures, closed landfill management, and environmental protection.

Keywords: landfill, contamination, soil analysis

Introduction

In addition to being illegal, waste disposal at places not intended for disposal is also a serious environmental problem [1]. Waste at the biggest wild landfill on the territory of the city of Leskovac, whose soil quality is being tested, contains a wide variety of waste like furniture, batteries, plastics waste, glass, electronic waste, paper and organic fractions, industrial and biomedical waste. That type of waste is often burned, which is an even bigger problem because the melting of the material leads to additional contamination and soil degradation. This waste contains harmful and hazardous substances like pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and heavy metals which directly or indirectly leads to serious degradation of ecosystems [2].

The huge negative impact of pesticides on the environment is well-known. Accumulation of pesticides in the soil negatively affects macro and micro-organisms in the soil. By washing pesticides out of the soil, they get into the leachate and then into the underground water, which can also be used as drinking water. Excessive amounts have long-term effects on the quality and fertility of the soil [3].

Polychlorinated biphenyls are an organochlorine compound [4]. They are toxic and dangerous for the environment, animals, and humans. Once in soil or water, they remain for 10 years or more. Combustion of polychlorinated biphenyls produces the highly toxic compound dioxin (2,3,7,8-tetrachloro-dibenzo-dioxide), if there is an accidental burning of landfill waste, greater soil contamination can occur. Since it has been shown that they do more harm than good, today polychlorinated biphenyls are banned in most countries of the world [5].

Polycyclic aromatic hydrocarbons are obtained as a by-product of incomplete combustion of fossil fuels. When they reach the soil, they have the characteristic of staying in it for a long time. There are over 100 units that belong to this group of pollutants, but the impact of about 40 of them is most often researched. The United States Environmental Protection Agency (USEPA) has placed 16 compounds from this list on the list of priority pollutants [6]. The paper examines the influence of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene.

The toxicity of heavy metals, in quantity in the soil, is a growing problem. Accumulation of these metals and their further interaction in the soil represents a potential danger to the living world. Purification of soil of

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The manuscript received: 19.09.2023.
Paper accepted: 11.05.2024.

heavy metals is one of the most significant challenges of environmental protection [7].

In this paper, after sampling the soil from the illegal landfill at the territory of the city of Leskovac, the quality of the soil was examined. The content of pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and heavy metals was identified. The obtained results were then analyzed in relation to the maximum permissible and remediation values of polluting, harmful, and hazardous substances in the soil given in the Regulation on maximum permissible values of polluting substances in the soil [29]. After analyzing the obtained results, a possible ecological risk and soil degradation were pointed out.

Material and methods

This research was carried out in the territory of the city of Leskovac, the largest city of the Jablanica district. Apart from Leskovac, the towns of Bojnik, Vlasotince, Lebane, Medveđa, and Crna Trava are also located in the Jablanica district. On the territory of the Jablanica district, there are currently 81 registered, unorganized, mixed landfills. The landfill whose soil quality is tested is the largest in the territory of the city. It was created in the middle of a settlement. Near the landfill, there is a school and a kindergarten. Also, merely 2 km from the landfill there is a river, the quality of which could deteriorate due to leachate and acid rain, considering that waste at the landfill often burns and emits pollutants into the air. At the landfill, three places were determined for soil sampling, where the largest amount of the most diverse waste was found. Figure 1 shows a satellite view of the sampling sites location while Table 1 shows the sample's GPS coordinates.

Figure 1. Satellite view of sampling points

Table 1. Sample tags and GPS coordinates.

sample label	GPS coordinates N	GPS coordinates E
01	42.985942	21.965853
02	42.985317	21.966131
03	42.985100	21.966181

The soil sampling, transport, and storage procedure was done according to criteria applicable in the Republic of Serbia and standard ISO 18400 together with ISO 18400-101, ISO 18400-102, ISO 18400-105, ISO 18400-107, ISO 18400-202, ISO 18400-203 and ISO 18400-206. Sampling of the soil was carried out by first cleaning the surface of the soil from plant remains, then a pit was opened in the surface layer of the soil in the shape of a square. First, a 2-3 cm thin layer of soil was cut. The lateral pieces of the plants were removed with a knife so that a 4.6 cm wide soil sampling site was prepared. After preparation, the soil was removed for sampling at a depth of 50 cm. The individual samples thus obtained are placed in a glass container, where they are later crushed and homogenized. The necessary requirements according to the sampling plan and standards at the specified location are shown in Figure 2.

Laboratory analyses of soil samples

Laboratory analyses of soil samples were carried out using the accredited methods given in Table 2.

Figure 2. Sampling Site

Table 2. List of methods used for soil analysis

Parameter	Methods
pH	SRPS ISO 10390
moisture content	ISO 11465
organic matter content	EN TC WI:2003
granulometric composition	SRPS EN ISO 17892-4
Mineral oils C_{10}-C_{40}	BS ISO 16703
Metals: cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), arsenic (As), barium (Ba); cobalt (Co) molybdenum (Mo), antimony (Sb)	EPA 3051A/ EPA 6010c
Mercury (Hg)	EPA 3051A:2007/ SRPS EN ISO 12846:2013
Polychlorinated biphenyls (PCBs): PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180, PCB	ISO 10382
Aromatic hydrocarbons (BTEX): Benzene, Ethylbenzene, Toluene, Xylene, Styrene	EPA 5021
Polycyclic aromatic hydrocarbons: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a, h)anthracene, benzo(g,h,i)perylene	ISO 18287
Pesticides	ISO 10382

Granulometric composition of soil

The fraction, that is, the presence of grains of certain sizes in the soil, is determined in the laboratory, by determining the granulometric soil composition [9]. Paper presents the method of sieving with the help of a sieve system according to SRPS EN ISO 17892-4 which was used to determine the granulometric soil composition. The standard represents a set of methods for determining the particle size distribution of soil samples. By knowing the particle size distribution, we can describe soils and divide them into classes. By using the Sieve System, that is, by sifting, we can determine the size of each class [10]. First, the stone and gravel fractions are separated from the fine soil fractions. The stone fraction is separated on a sieve with an opening of 20 mm, and the gravel on a sieve with an opening of 2 mm. Fine soil made up of fractions (coarse and fine sand, powder, and clay) passes through a sieve with a 2 mm opening.

Organic matter content

The plants' most important source of nutrients is organic matter. In the surface layer of the soil, organic matter contains 3-8 $t\ N\cdot ha^{-1}$ and 2-5 $t\ P\cdot ha^{-1}$, while soils rich in humus contain more than 20 $t\ N\cdot ha^{-1}$. By adding organic matter to the soil, erosion is reduced, while soil aeration, drainage, and water capacity of the soil are increased [11]. In this paper content of nitrogen was determined using the standard Klejdach method, and according to the EN TC WI: 2003 standard [12].

pH value

Soil acidity represents the soil's ability to release protons, i.e. hydrogen ions (H^+-ions). H^+-ions in the soil are a result of the existence of carbon dioxide that reaches the soil with aqueous atmospheric precipitation [13]. In this work, the standard method SRPS ISO 10390 is used to determine the pH value of the aqueous suspension [14].

Moisture content

An important factor of soil quality is moisture content. Moisture content affects plant growth and quality. The soil is a natural reservoir for storing water until the next irrigation or rain so that the plants have available water for development. The conditions for measuring humidity in the field are complex. Determining the moisture content can be done by different methods [15]. In this work, an accredited gravimetric method according to the ISO 11465 standard was used to determine the moisture content. The examined sample of soil was dried at 105 °C, then the difference in soil mass before and after the drying process was calculated [16].

Soil hardness and $CaCO_3$ content

$CaCO_3$ has a favourable effect on the pH value of the soil because it causes a slightly alkaline reaction. Migration process of $CaCO_3$ is very slow in our climate region with relatively little precipitation and has been going on for hundreds of years, so its content in the soil does not change during the season. In this work, the $CaCO_3$ content was determined quantitatively using an apparatus that measures the volume of released CO_2 (Scheibler's calcimeter) [17].

Mineral oils C_{10}-C_{40}

The content of mineral oils in this paper was determined according to the ISO 16703:2004 standard using gas chromatography. This method is used to determine hydrocarbons that have a boiling range of 175 °C to 525 °C [18].

Metals

One of the causes of long-term negative consequences for the soil is heavy metals. It can lead to significant health and environmental disturbances. The metal content shows which metals are present in a given tested sample. In this work the test methods EPA 3051A/ EPA 6010c and EPA 3051A:2007/ SRPS EN ISO 12846:2013 were applied [19, 20].

Polychlorinated biphenyls

The presence of polychlorinated biphenyls (PCB) in the soil is a sure sign of soil contamination because they are the result of human activity only. Due to the large negative effect, PCB production is maximum permissible and strictly controlled [21]. The presence of PCBs in the work was tested using the accredited ISO 10382 method [22].

The soil sample (5 g) is extracted with n-hexane after treatment. The concentrated extract is passed through a column filled with aluminium oxide. Compounds are separated using a capillary column with a low polarity stationary phase. Detection occurs using an electron capture detector (ECD). Polychlorinated biphenyls (PCBs) are quantified by comparing relative retention times and relative peak heights (or peak areas) to the corresponding variables of an external standard solution. Programmable temperature vaporizer (PTV) injection system was used for sample injection 1 μL 0.1 min at 40 °C, 300 °C min^{-1} to 250 °C, 5 min at 250 °C cooling down with 50 °C min^{-1} to 40 °C. Column HT 8 50 m, 0.22 mm inner diameter, 0.25 μm film thickness. Oven program 2 min at 50 °C, with 12 °C min^{-1} to 190 °C, with 7 °C min^{-1} to 270 °C, with 20 °C min^{-1} to 320 °C, 20 min at 320 °C [27].

Aromatic hydrocarbons and polycyclic aromatic hydrocarbons

Aromatic hydrocarbons (BTEX) are compounds that have a benzene ring in their structure. Their presence in the samples was tested using the EPA 5021 method [23]. Polycyclic aromatic hydrocarbons (PAHs) are compounds that originate from the process of incomplete combustion, or perfusion at more than 700 °C, of organic matter that in their structure have carbon and hydrogen. PAHs have a long half-life and a permanent negative impact on the environment [24]. With the help of the ISO 18287 standard method, the presence of PAHs in soil samples was examined [25].

Pesticides

As modern agricultural production cannot be imagined without the use of pesticides, their presence in the country is inevitable. Due to frequent, excessive, and improper use, their negative impact on the environment is great [26]. The paper analyzed the existence of pesticides in the examined samples with the help of the accredited ISO 10382 method, the same procedure that was used in PCB detection [22, 27].

Legislative framework of the Republic of Serbia

The Republic of Serbia is a signatory to the Stockholm Convention on Persistent Organic Pollutants. The National Assembly of the Republic of Serbia assumes the Law on the Ratification of the Stockholm Convention, while the Ministry of Agriculture and Environmental Protection, as the competent authority for the management of chemicals in the Republic of Serbia, monitors and harmonizes the EU legislation from these areas. One of the earliest documents to introduce the term "persistent organic pollutants (POPs)" is the Regulation on POPs substances, methods, and procedures for managing POPs. It defines the list of polluting compounds, ways and procedures for managing waste that has been in contact with these compounds, as well as maximum permissible values for these polluting substances [8]. Maximum permissible values (SWsb) represent the amount of toxic or harmful substances to which the human organism, animal, or plant organisms can be exposed without harmful consequences and for a long time [38]. In 2012 the Republic of Serbia defined the priority organic polluting compounds that are controlled in sediment, when the Government of the Republic of Serbia adopted the Regulation on maximum permissible values of pollutants. The Regulation defines maximum permissible values for priority organic pollutant compounds in sediment, their target, and both maximum permissible value (SWsb) and remediation value. Remediation value (IWsb) is the threshold value for the concentration of the pollutant in the sediment above which there is an unacceptable risk to the aquatic ecosystem, soil, and human and animal health [39]. As a result of the harmonization of the Serbian with the legislation of the European Union in 2014, the Regulation on maximum permissible values of priority and priority hazardous substances was adopted [8].

The regulation on systematic monitoring of soil condition and quality determines the content of the Soil Monitoring Program, the methodology for systematic monitoring of soil quality and condition, criteria for determining the number and arrangement of measuring points, a list of parameters for specific soil type, list of methods and standards used for soil sampling, sample analysis, and data processing, scope and frequency of measurements, indicators for soil degradation risk assessment, deadlines and method of data submission. The soil monitoring program examines the mechanical composition of the soil; soil acidity, $CaCO_3$ content, capacity of exchangeable cations, degree of base saturation, content of organic material, total heavy metals, and potentially toxic elements. Depending on the method of land use in the local network, soil physical properties like dry soil density, solid phase density, total porosity, water retention at different pressures, accessible water, water permeability rate, structure, and hardness are also examined. If necessary, chemical properties of the soil like hydrolytic acidity of the soil, total nitrogen and sulphur, content of accessible micro and macro elements in the soil, accessible heavy metals and potentially toxic elements, electrical conductivity, chemical composition of groundwater, anions and cations in the soil, hydrocarbons of petroleum origin (fractions C_6-C_{40}), polycyclic aromatic hydrocarbons (PAH), pesticide residues, polychlorinated biphenyls (PCB), chlorophenols, volatile halogenated hydrocarbons, volatile aromatic hydrocarbons are also examined [28].

The Regulation on the maximum permissible values of polluting, harmful, and hazardous substances in the soil establishes the maximum permissible values of polluting, harmful, and hazardous substances in the soil. Maximum permissible values of polluting, harmful, and hazardous substances in the soil are determined by measurement and/or calculation based on the measurement results. In the case of exceeding the maximum permissible values from and maximum permissible concentrations of pollutants in groundwater determined by a special regulation, additional research is carried out at contaminated locations to determine the degree of soil pollution and develop remediation and recultivation projects [29].

Pollutants Indices

The content of pollutants was compared with the corrected maximum permissible and remediation values given in the "Official Gazette of RS", no. 30/2018 and 64/2019"[29]. Corrected maximum permissible and remediation values for metals and arsenic, with the exception of antimony, molybdenum, selenium, tellurium, thallium, and silver, depend on the content of clay and organic matter in the soil according to the "Official Gazette of RS", no. 30/2018 and 64/2019" [29]. The measured content of metals was compared to corrected maximum permissible and remediation values [29]. When determining the type and properties of the soil, the values from the "Official Gazette of RS", no. 30/2018 and 64/2019" are corrected to the values applicable to the actual soil, based on the measured content of organic matter and clay content. For pollutants, the following correction formula (1) is used, depending on the soil type, based on which the correction is performed [29]:

$$SWb, IWb = SWsb, IWsb \times \frac{A + B \times \%clay + (C \times \%OM)}{A + B \times 25 + C \times 10} \quad (1)$$

where SWb, IWb are the corrected maximum permissible and remediation values for a specific soil; SWsb, IWsb are the maximum permissible and remediation values given in the "Official Gazette of RS", no. 30/2018 and 64/2019"[29]; % clay is the content of clay in a specific soil (<2 μm); % *OM* is the content of organic matter in a specific soil; A, B, C - cost depends on the elements according to the "Official Gazette of RS", no. 30/2018 and 64/2019" [29].

Maximum permissible values and remediation values for organic compounds and PAHs depend on the content of organic matter in the soil. For organic compounds, except for polycyclic aromatic hydrocarbons, the following correction formula (2) is used [29]:

$$SWb, IWb = SWsb, IWsb \times \frac{\%OM}{10} \quad (2)$$

For soils with an organic matter content above 30%, as well as for soils with an organic matter content below 2%, the maximum permissible values and remediation values for organic compounds are corrected by taking these two values for % of organic matter in the calculation [29].

For soils with an organic matter content of up to 10%, the maximum permissible and remediation values of polycyclic aromatic hydrocarbons are not corrected. For soils with an organic matter content of 10-30%, a correction formula is used [29].

Results and discussion

Laboratory results are presented in Tables 3, 4, 5, and 6.

Table 3. Results of testing samples for the content of polychlorinated biphenyls, polycyclic aromatic hydrocarbons, BTEX and mineral oils

Parameter Polychlorinated biphenyls, mg·kg^{-1}	**01**	**02**	**03**	**Maximum permissible value, mg·kg^{-1}**
PCB 28	<0.003	<0.003	<0.003	0.010
PCB 52	<0.003	<0.003	<0.003	0.010
PCB 101	<0.003	<0.003	<0.003	0.010
PCB 138	<0.002	<0.002	<0.002	0.010
PCB 153	<0.002	<0.002	<0.002	0.010
PCB 180	<0.002	<0.002	<0.002	0.010
$PCBs_{total}$	<0.015	<0.015	<0.0015	0.010
Polycyclic aromatic hydrocarbons, mg·kg^{-1}				
Naphthalene	<0.001	<0.001	<0.001	70.000
Acenaphthylene	<0.003	<0.003	<0.003	70.000
Acenaphthene	<0.003	<0.003	<0.003	70.000
Fluorene	0.007	<0.003	<0.003	1.000
Phenanthrene	0.039	0.006	0.005	5.000
Anthracene	0.048	0.003	<0.001	5.000
Fluoranten	0.13	0.005	0.003	1.000
Pyrene	0.15	0.003	0.002	0,200
Chrysene	0.092	0.007	0.007	1.000
Benzo(a)anthracene	0.045	0.003	0.003	0.500
Benzo(b)fluoranthene	0.080	<0.003	<0.003	0.050
Benzo(k)fluoranthene	0.024	<0.003	<0.003	0.050
Benzo(a)pyrene	0.019	<0.003	<0.003	0.050
Indeno(1.2.3-c,d)pyrene	0.006	<0.003	<0.003	0.050
Dibenzo(a,h)anthracene	<0.003	<0.003	<0.003	0.500
Benzo(g,h,i)perylene	0.007	<0.003	<0.003	0.050
PAH_{total}	0.65	<0.05	<0.05	1.000
Aromatic hydrocarbons (BTEX), µg·kg^{-1}				
Benzene	0.053	0.084	0.054	0.010
Toluene	0.12	0.23	0.13	0.010
Ethylbenzene	0.011	0.020	0.014	0.030
Styrene	0.058	0.13	0.064	0.300
Xylene	0.076	0.081	0.052	0.100
$BTEX_{total}$	0.32	0.54	0.31	0.020
Mineral oils, mg·kg^{-1}	8.6	0.75	6.2	50.000

Concentrations of polychlorinated biphenyls, polycyclic aromatic hydrocarbons, BTEX, and mineral oils based on the obtained soil test results shown in Table 3. were detected in the tested samples. The concentration of polychlorinated biphenyls was detected at the lowest level and was approximately the same in all analyzed samples. As for Polycyclic aromatic hydrocarbons, the highest concentration was detected in sample 1 where the highest concentration is Fluoranthene and Pyrene; Sample 2 and 3 have a lower concentration of pollutants. In sample 2, the highest presence of BTEX was detected, concentration of Benzene is 0.084 µg·kg^{-1} and for Xylene 0.081 µg·kg^{-1}. Mineral oils were detected in all samples, the highest concentration has sample no.1. (8, 6), and the lowest concentration has sample no.3. Even though, the obtained values of these parameters do not exceed the maximum permissible values these pollutant concentrations can have a negative impact on the environment. Because PAHs are resistant to biodegradation, they are persistent organic pollutants. They have a strong adsorption power on solid soil particles and sediments, which can lead to their dissemination in different parts of the environment on a global level [30].

Table 4. Results of testing samples for pesticide content

Pesticides, mg·kg^{-1}	**01**	**02**	**03**	**Maximum permissible value, mg·kg^{-1}**
DDT/ DDD/ DDE (total)	<0.0003	<0.0003	<0.0003	0.01000
Drins (sum: aldrin, dieldrin, endrin)	<0.0003	<0.0003	<0.0003	0.00500
Aldrin	<0.0001	<0.0001	<0.0001	0.00006
Dieldrin	<0.0001	<0.0001	<0.0001	0.00050
Endrin	<0.0001	<0.0001	<0.0001	0.00004
α–HCH	<0.0001	<0.0001	<0.0001	0.00300
β–HCH	<0.0001	<0.0001	<0.0001	0.00900
γ–HCH	<0.0001	<0.0001	<0.0001	0.00005
HCH total	<0.0003	<0.0003	<0.0003	0.01000
Chlordane	<0.0001	<0.0001	<0.0001	0.00003
Endosulfan	<0.0001	<0.0001	<0.0001	0.00001
Heptachlor	<0.0001	<0.0001	<0.0001	0.00070
Heptachlorepoxide	<0.0001	<0.0001	<0.0001	0.0000002
HCB (Hexachlorobenzene)	<0,001	<0,001	<0,001	0.00001
Pentachlorobenzene	<0,001	<0,001	<0,001	0.00200
Endosulfan sulfat	<0.0001	<0.0001	<0.0001	0.00200

In all of the analyzed samples shown in Table 4, the concentrations of polychlorinated biphenyls and pesticides were detected. Pentachlorobenzene and hexachlorobenzene were detected in the highest concentration in the tested samples. All three samples have the same concentration of the mentioned pollutant. Although the concentration of these pollutants does not exceed the maximum permissible and remediation values, these pollutants have a long half-life and slow natural degradation in water and soil. These pesticides can get into living organisms with high toxicity [31].

Table 5. Analysis results - granulometric composition, organic matter content, pH value, moisture content and $CaCO_3$ content

Parameter	01	02	03
Granulometric composition			
Clay, % 1	2.6	8.2	10.2
Sand, % 4	5.9	71.3	72.2
Powder, % 4	1.5	20.5	17.6
Content of organic matter, %	4.4	2.2	2.4
pH	6.9	6.8	6.5
Moisture content, %	16.2	13.8	13.7
$CaCO_3$, %	2.5	3.4	0.84
Soil hardness, MPa	0.22	0.25	0.34

Based on the obtained soil test results shown in Table 5. soil samples have a relatively high sand content, while the clay content ranges in a range of 8.2% to 12.6%. The content of organic matter is low in all samples, and the pH indicates a slightly acidic soil. Soil hardness ranges from 0.22 to 0.34 MPa, which indicates relatively soft soil.

Table 6. Results of testing samples for the content of heavy metals

Metals, $mg \cdot kg^{-1}$	01	02	03
Antimony (Sb)	**3.2**	1.7	1.6
Arsenic (As)	18	12	10
Copper (Cu)	**47**	**25**	15
Barium (Ba)	**127**	**96**	70
Zinc (Zn)	**133**	51	52
Chromium (Cr)	58	42	36
Cadmium (Cd)	**1.3**	**0.71**	**0.67**
Cobalt (Co)	**11**	**8.1**	**7.1**
Nickel (Ni)	**30**	**20**	**23**
Molybdenum (Mo)	0.52	1.7	0.46
Lead (Pb)	35	11	17
Mercury (Hg)	0.057	0.031	0.037

Table 6 presents the results of heavy metals analysis of soil samples. The concentrations of cadmium, cobalt, and nickel exceeding the maximum permissible value were observed in all samples. The most contaminated soil sample is sample 1, which, in addition to the increased concentration of cadmium and cobalt, has an increased concentration of antimony, copper, barium, and zinc. In sample 2, an increased concentration of copper and barium was also observed. Contamination of soil with heavy metals leads to a negative impact on soil characteristics and limits the production and ecological functions. Heavy metals affect the number, diversity, and microbial activity of microorganisms in the soil. They not only have toxicity to living organisms inhabiting the soil but also get inside various organic and inorganic colloids, in an immobilized form where they can persist for a long time before being available again to living organisms including plants [32].

Corrected maximum permissible / remediation value of harmful and hazardous substances in the soil

Based on the Regulation on maximum permissible values of polluting substances, harmful and hazardous substances in the soil [29], corrected maximum permissible and remediation values for metals are shown in Table 7. Corrected maximum permissible and remediation values, which may indicate significant contamination for metals and arsenic, except for antimony and molybdenum, is carried out.

Table 7. Corrected maximum permissible and remediation values for metals depending on clay and organic matter

Sample No.		(Sb)	(As)	(Cu)	(Ba)	(Zn)	(Cr)	(Cd)	(Co)	(Ni)	(Mo)	(Pb)	(Hg)
01	SWb	3	22	25	96	94	75	0.59	6	23	3	67	0.25
	IWb	15	41	133	375	485	286	8.88	147	136	200	418	8.29
02	SWb	3	19	21	73	78	66	0.51	4	18	3	60	0.23
	IWb	15	36	112	286	401	252	7.7	115	109	200	377	7.67
03	SWb	3	20	23	84	84	70.4	0.53	5	20.2	3	63	0.24
	IWb	15	38	119	327	433	268	7.98	129	121.2	200	390	7.91

SWb - corrected maximum permissible value ($mg \cdot kg^{-1}$), IWb - corrected remediation value ($mg \cdot kg^{-1}$)

Analysis of the samples for the content of heavy metals showed that:

- The content of antimony and zinc exceeds the maximum permissible value in sample 1.
- The measured concentration of copper and barium exceeds the maximum permissible value in samples 1 and 2.
- The measured concentration of zinc exceeds the maximum permissible value in sample 1.
- In all analyzed samples, the measured concentrations of cadmium, cobalt, and nickel exceed the maximum permissible values.
- In all analyzed samples, no metal concentrations were detected in values exceeding the remedia-

tion value.

Soils enriched with heavy metals may represent a potential threat to human health by investigation of soil. Traditional human health risk assessment calculations are most often based on total (or pseudo-total) concentrations, implying that the entire ingested contaminant is available for uptake into the bloodstream [33]. When metals reach the environment and pollute it, they remain in the soil for a long time, depending on the type of metal and the soil, therefore the dependence of the remediation speed depends on the amount of metals that have reached the soil, the composition of the soil and the amount of semisolids. Remediation processes used for soil remediation can be in-situ or ex-situ, on-site or off-site, and biological, physical, and chemical. Often these techniques are combined for a more economical and efficient remediation of the contaminated site [34].

Soil test results of concentrations of aromatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and pesticides are presented in Table 8.

Table 8. Maximum permissible/remediation values for aromatic hydrocarbons and polychlorinated biphenyls

Aromatic hydrocarbons, μg·kg^{-1}	**SWsb**	**IWsb**
Benzene	10	1000
Toluene	10	130000
Ethylbenzene	30	50000
Styrene	30	100000
Xylene	100	25000
PAH_{total}	1	40
$PCBs_{total}$ *, mg·kg^{-1}	0.02	1

SWsb - maximum permissible value, IWsb- remediation value

*Sum of: Anthracene, benzo (a) anthracene, benzo (k) fluoranthene, benzo (a)pyrene, chrysene, phenanthrene, indeno (1,2,3-cd)pyrene, fluorescents, naphthalene, benzo (g, h, i)perylene

Concentrations of aromatic hydrocarbons and polycyclic aromatic hydrocarbons were detected in the tested samples. Although the concentration of these pollutants does not exceed the maximum permissible and remediation values, the pollutants are stable, resistant to biodegradation and as a result accumulate in the environment leading to the toxicity of these pollutants. Soil contamination can directly affect human health. It is high time to adopt effective measures to remediate contaminated sites and control other sites from contamination. There are a number of physical, chemical, and biological methods used to remediate a contaminated site. The choice of method and treatment depends on the type of pollutant, the type of soil, the interferences present, and the analysis of the risks associated with the techniques. Although physical and chemical methods are effective, most of them are energy, cost, or chemical intensive. Considering the limitations associated with physicochemical treatment, biological methods are gaining popularity due to their ecological nature and bioconversion of toxic pollutants into harmless/non-toxic chemical species [35].

Soil test results of concentrations of mineral oils and corrected maximum permissible/remediation values for mineral oils are demonstrated in Table 9.

Table 9. Corrected maximum permissible /remediation values for mineral oils

Sample No.	**SWb, mg·l^{-1}**	**IWb, mg·l^{-1}**
01	22	2200
02	11	1100
03	12	1200

Based on the laboratory results, the concentration of mineral oils does not exceed the maximum permissible values. Although the concentration does not exceed the maximum permissible values, contaminated soil often lacks organic matter and has low microbial activity. That is why it is necessary to remediate the land so that pollutants do not reach the surrounding river or harm people's health in the future. Bioremediation is an attractive approach to cleaning mineral oils because it is easy to maintain, applicable to large areas, cost-effective and leads to the complete destruction of pollutants [36].

Soil is by definition a renewable resource, however, after testing the quality of this soil, its regeneration is impossible through natural means. The existence of the mentioned pollutants in the soil leads to deterioration of the quality of the soil, underground water, and leachate. It can have a big negative impact on the living world and people's health [37]. The first step in protecting soil and preserving its natural roles and preventing degradation processes is monitoring the condition and noticing changes in soil characteristics in the form of establishing a monitoring system, i.e. permanent soil monitoring. This implies continuous monitoring of certain soil parameters for the purpose of collecting information on changes in the condition and characteristics of the soil, and identification of the form and degree of degradation. After determining soil contamination, it is necessary to remediate the soil in accordance with the type of pollution, efficiency, effectiveness, and economy of the remediation process.

Conclusion

Based on the test results, in accordance with the Regulation on maximum permissible values of polluting substances (Official Gazette of the RS, no. 30-2018 RS, no. 30-2018 and 64-2019), it was determined that the concentrations of various metals were measured in the analyzed soil samples exceeded the maximum permissible values. The analysis results show that concentrations of aromatic hydrocarbons and polycyclic aromatic hydrocarbons were detected in the tested samples. However, the obtained values of these parameters do not exceed the maximum permissible values. Concentrations of polychlorinated biphenyls and pesticides were detected in all analyzed samples but concentrations do not exceed the maximum permissible and remediation values. All samples have a relatively high sand content. The content of organic matter is low in all samples. Although the content of $CaCO_3$ has increased, this amount is not enough to reduce the acidity of the soil, pH value indicates slightly acid soil. Soil hardness ranges indicate a relatively soft soil. Analysis of soil samples at the closed landfill showed that there are concentrations of various metals that exceed the maximum permissible values prescribed by the Regulation. This pollution can have a negative impact on the environment. Further monitoring is needed to prevent further spread of pollution and to carry out soil remediation.

Acknowledgment

Republic of Serbia- Ministry of Science, Technological Development and Innovation, Program for financing scientific research No. 451-03-66/2024-03/200133.

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Izvod

ISPITIVANJE SASTAVA ZEMLJIŠTA „DIVLJE“ DEPONIJE U GRADU LESKOVCU I POTENCIJALNI EKOLOŠKI RIZICI

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Upravljanje divljim deponijama predstavlja veliki ekološki problem i izaziva zabrinutost jer se čvrsti otpad odlaže na nepropisan način čime dolazi do stvaranja divljih deponija. Ovakvo nelegalno odlaganje otpada može dovesti do narušavanja životne sredine. Može doći do kontaminacije zemljišta, stvaranja procednih voda što negativno utiče na zdravlje ljudi. Ovaj rad predstavlja rezultate analize uzoraka zemljišta na zatvorenom smetlištu na teritoriji grada Leskovca i ima za cilj određivanje kvaliteta zemljišta, detektovanje moguće kontaminacije i identifikaciju potencijalno štetnih materija u uzorcima zemljišta. Rezultati analize pokazali su da su u ispitivanim uzorcima detektovane koncentracije aromatičnih ugljovodonika i policikličnih aromatičnih ugljovodonika. Utvrđeno je da su u analiziranim uzorcima zemljišta izmerene koncentracije različitih metala premašile granične vrednosti. Ovaj rad će pružiti korisne informacije za dalje planiranje mera sanacije, upravljanje zatvorenim smetlištem i zaštitu životne sredine.

Ključne reči: deponija, kontaminacija, analiza zemljišta