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Analysis of the occurrence of heavy metals in the landfills at the former dye industry plant "Boruta" in Zgierz

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Abstract

The paper aims to analyse the occurrence of heavy metals (HMs) in the vicinity of a post-production waste landfill. The detection of HMs was based on the analysis of soil samples collected around the waste landfill in the Zgierz municipality. The research included soil analysis for HMs content using the atomic absorption spectrometry (AAS) method. Samples were collected in summer and winter. Soil samples were tested for physico-chemical properties. All soil samples were collected from locations accessible to residents near the former "Boruta" Dye Industry Plant in Zgierz, currently located in the Zgierz Boruta Industrial Park. The plant's activities greatly impacted the current landscape, leaving behind landfills that were a 'ticking bomb' in Zgierz. Products manufactured include dyes, acids, chemicals for the military, textile, pharmaceutical and food industries, furniture and agriculture.

Keywords: heavy metals, AAS method, hazardous waste, Boruta Zgierz

1 Introduction

The growing city of Lodz, famous for its textile industry, weaving and substantial trade deals, contributed to the dynamic development of the city of Zgierz and the neighbouring municipalities and villages. The development of civilization and the first migrations to cities contributed to increased pollution of rivers, soil and air. The public's life in the inconvenient conditions of the developing city contributed to an increase in the number of sick and disabled people. Polluted rivers, waters, soil and air contributed to the development of diseases (City of Lodz, 2024). The development of the textile industry in 19th- and 20th-century Lodz contributed significantly to environmental pollution. Massive production of various types of textile materials characterized the former areas surrounding the current capital of Lodz province. The materials from which everyday products will be created in the first preparation stage should be dyed with specialized chemical dyes. The residue from the dyeing of textiles was usually dumped

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into rivers or settling ponds. No one thought about the harmfulness of such products and their further decomposition and shuffling in the environment. Irresponsible handling of dye residues - washings is associated with substantial environmental contamination: pollution of soils, waters and air. One of the plants producing "colours" for fabrics was the "Boruta" Dyeing Industry Plant in Zgierz. The production of synthetic dyes involves the use of heavy metals such as cadmium (Cd), mercury (Hg), and lead (Pb) (Marchewka, 2009).

Human activities, along with economic growth, lead to waste generation. Their generation poses a powerful environmental challenge due to their significant generation from materials unknown to nature, such as plastics, glass, metals, and chemicals. Depositing waste in landfills has been the most widely used option for eliminating a nuisance. Leachate, unpleasant odour, scattered debris around the landfill, and the spread of rodents and birds are among the dangers lurking after the landfill's operation (Wiercik and Szymańska - Pulikowska, 2010)

HMs in the human body can be toxic, where the body's reaction is immediate or occurs shortly after absorbing a given dose of the contaminant. Still, they can also accumulate in the body in specific organs. HMs can be absorbed into the human body through the respiratory, digestive, and skin systems. Human exposure to HMs can occur in the work environment, at sites where metal ore was mined years ago, where pesticides were used before synthetic substitutes were used, at former industrial sites, and as a result of exposure to fumes and vapours from existing industrial plants. Some elements, such as zinc (Zn) and copper (Cu) are essential for the proper functioning of the body and are harmful to human health only in excessive amounts. The second group of HMs are elements that are entirely unnecessary to humans and do not take part in human life processes; they include mercury (Hg), cadmium (Cd), and lead (Pb) (Kondej, 2007). The HMs have adverse effects on the human body, including allergies, changes in the nervous, skeletal, circulatory, digestive and respiratory systems, reproductive disorders and pregnancy complications. Some HMs are carcinogenic and mutagenic (Golinska and Bany, 2000).

The purpose of the study was to determine the presence of HMs in the vicinity of the landfill, which could pose a threat to the environment. Due to the possibility of hazardous substances associated with the site, it was decided to carry out an environmental impact study.

2 Research methodology and location

The first and oldest landfill in the study area is called "Behind the Bzura". Lush vegetation (shrubs and trees) covers the top of the landfill as well as the slopes. The area occupied by the waste is directly adjacent to the Bzura River from the south. The period of operation dates back to the 80s and 90s and ended in 1995. The landfilled waste was not recorded until 1990 when an average of 270 Mg/year of waste was observed until the end of the operation.

The second study area is a landfill for non-hazardous and inert waste. The southern part of the site was used for the storage of bottom ash and gypsum from 1960 to 1986, and is referred to as a "dry landfill." The operation lasted until 1996, during which time gypsum and calcium salt for the production of 2,7-naphthalene-sulfonic acid and gypsum from H-acid production were exported to the top for a decade.

Since 1990, when the weight of waste started to be recorded, the average amount has been 1,500 Mg/year. The dumping of hazardous and non-hazardous waste started in the northern part of the site, near Miroszewska Street. The period of waste disposal is 1995-2015, and post-production waste was collected in containers, barrels, and bins. The waste mentioned above was covered with ash, sand or rubble, and with the help of municipal waste, it was covered with layers of ash and gypsum. By 2016, the landfill had received 40027.746 Mg of waste, about 3640 Mg per year. The top of the landfill is covered with low vegetation and grasses, with mixed municipal waste, ash and debris visible in some places. Illegally stored, unsecured asbestos waste was observed in the area. As a result of the different origins of the materials stored, fires frequently occur under the top layer of the landfill, causing smoke to rise and sinkholes to form after the fires.

The third study site is a landfill for non-hazardous and inert waste near the wastewater treatment plant. The owner of this area is "Wodociągi i Kanalizacja - Zgierz" Sp. z o.o. The storage of hazardous waste in the landfill area is prohibited, as indicated by a sign in front of one of the entrance gates to the landfill (NIK, 2020).

Samples were taken along the hazardous waste and non-hazardous and inert waste landfills and around the "old landfill" (Fig. 1). No permits were required to enter the study area. Samples were taken along Miroszewska Street, Łukasińskiego Street and Aleksandrowska Street.

The AAS technique is based on measuring the absorption of light of a specific wavelength by atoms and ions of particular elements present in the samples. The HMs content of the soil samples was determined using appropriate

cavity cathode tubes assigned to specific elements (García and Báez, 2012). The HMs concentrations were determined using the AAS flame technique on a Thermo Scientific iCE 3300 series atomic absorption spectrometer.



Figure 1. Location of soil sampling points (Google Earth, 2024).

Legend:

- 1 landfill "behind the Bzura" ("old landfill")
- 2 sewage treatment plant in Zgierz
- 3 landfill of non-hazardous and inert waste
- 4 hazardous and non-hazardous waste landfill and "dry landfill"
- 5 settling tank number 3
- 6 S14 expressway

Based on the study of the granulometric composition of the soil, the percentage of each fraction in the total weight of the soil tested was determined. The soil samples' grain size distribution was determined using a sieve and aerometric (PN-B-02480:1986, PN-EN ISO 14688-1:2006). The HMs content in the soil samples was determined by atomic absorption spectrometry (AAS).

3 Discussion

In the first series of sampling, which took place at the end of summer 2023, based on the PN-86/B-02480 standard, the soils were classified as clayey sand (Pg), sandy clay (Gp) and sandy silt (π p). The average content of the gravel

and cobbles fraction was 1.6%, sand 76.9%, silt 16.3% and clay 5.2%. Based on EN ISO 14688, the soils were classified as sand with silt (siSa), two samples were silt with sand (saSi), one sample was sand with clay (clSa) and one sample was fine sand (FSa). The average gravel and cobble fraction content was 1.6%, sand 71.2%, silt 22%, and clay 5.2%.

The second series of soil samples was taken in the late winter of 2023. The soil classification according to PN-86/B-02480 shows that the soil around the landfills was mainly clayey sand (Pg), while sample number 2 was sandy loam (Gp). The average fraction of gravel and cobbles was 1.7%, sand 75.9%, silt 16.3% and clay 6.2%. The soil types determined from EN ISO 14688 were mostly sand with silt (siSa), sample number 2 was clay with silt and sand (sasiCl), and sample number 9 was sand with clay (clSa). The average fraction of gravel and cobbles was 1.7%, sand 68.9%, silt 23.2% and clay 6.2%. The results were given in Table 1.

No.	Fraction according to PN-86/B-02480 [%]								Fraction according to PN-EN ISO 14688							
	Gravel and cobbles		Sand		Silt		Clay		Gravel and cobbles		Sand		Silt		Clay	
	Sampling															
	I	П	I	II	I	II	I	II	I	II	I	II	I	II	I	II
1	0.5	8.2	76.8	65.4	15.8	19.1	6.9	7.3	0.5	8.2	74.8	57.2	17.8	27.3	6.9	7.3
2	2.1	0.9	63.7	64.6	28.3	23.6	5.9	10.8	2.1	0.9	55.9	55.8	36.2	32.5	5.9	10.8
3	3.8	1.1	63.8	75.7	18.1	16.4	14.3	6.8	3.8	1.1	58.1	68.9	23.8	23.2	14.3	6.8
4	2.3	1.2	77.3	69.7	17.5	20.4	2.9	8.8	2.3	1.2	72.5	59.9	22.3	30.1	2.9	8.8
5	0.1	0.7	86.0	81.5	12.0	14.8	2.0	3.0	0.1	0.7	81.0	75.6	17.0	20.7	2.0	3.0
6	0.0	0.5	88.1	85.7	9.0	10.9	3.0	3.0	0.0	0.5	85.1	78.8	11.9	17.8	3.0	3.0
7	0.1	0.0	87.0	87.1	9.0	8.9	4.0	4.0	0.1	0.0	82.0	84.1	13.9	11.9	4.0	4.0
8	0.5	0.2	86.6	80.0	9.9	14.9	3.0	5.0	0.5	0.2	79.7	75.1	16.9	19.8	3.0	5.0
9	6.0	0.9	69.9	73.4	15.7	15.8	8.3	9.9	6.0	0.9	66.2	66.5	19.4	22.7	8.3	9.9
10	2.0	2.9	75.9	72.3	17.3	18.1	4.8	6.7	2.0	2.9	67.2	62.8	26.0	27.6	4.8	6.7
11	0.4	1.0	78.8	74.6	16.9	18.5	4.0	5.9	0.4	1.0	70.9	68.7	24.8	24.4	4.0	5.9
12	1.8	3.3	81.7	77.6	12.6	13.4	3.9	5.7	1.8	3.3	77.8	69.0	16.5	22.0	3.9	5.7
13	1.1	0.7	63.8	78.7	30.2	16.7	4.9	3.9	1.1	0.7	55.1	73.8	39.0	21.6	4.9	3.9
Average	1.6	1.7	76.9	75.9	16.3	16.3	5.2	6.2	1.6	1.7	71.2	68.9	22.0	23.2	5.2	6.2

 Table 1. Results of soil granulometry analysis.

Following the Regulation of the Minister of the Environment of September 1, 2016, on the method of assessing land surface pollution (Journal of Laws of 2016, item 1395), a group of soils (I - IV) was defined depending on the type of land use, taking into account the local spatial development plan. The area marked with the symbols "P" and "O" belongs to soil group IV and includes soil samples numbered 1-9 and 13, and the area marked with the symbol "Z" belongs to soil group III and includes soil samples numbered 10-12. As a result of assigning specific areas to specific soil groups, threshold concentrations have been identified that may cause significant risk to the environment. Soil samples analysed using the AAS method showed specific concentrations compared with applicable standards.

Regarding the content of HMs in the soils, the highest concentrations of zinc (Zn) were recorded in samples no. 10, 11, 12 (Fig. 2).



Figure 2. Zinc concentrations in individual soil samples from two collections.

These samples were above the permissible standard set by the regulation, which is 1000 mg Zn/kg dry matter (DM) of soil for green areas. This does not change the permissible value for industrial areas, which was also exceeded by 2000 mg Zn/kg dry matter. The remaining samples are within acceptable limits. The range of Zn concentrations in the soil samples from the first collection was 26.75 - 3735.2 mg/kg with a range between the extremes of the results of 3708.45 mg/kg and from the second collection 23.96 - 4422.6 mg/kg with a range of 4398.64 mg/kg. The mean concentration of all samples from the first and second replicates was 798.98 mg/kg. At the landfill in Štěpánovice in the Czech Republic, Zn concentrations in the soils were lower than those investigated in this work. The range of concentration values obtained during the investigation of eight soil samples was 83-519 mg/kg (Vaverkova et al., 2018). The maximum value obtained was almost four times lower than the permissible concentrations in the soil around landfills, the example of a study carried out around a landfill near Thessaloniki in Greece can be used. The study area was degraded by the mining, metallurgical and tanning industries. The research used the same method - atomic spectrometry - but the sampling depth was greater and varied (2.5-17.5 m). The Zn content of the soil ranged from 6.38 to 343.75 mg/kg (Kassassi et al., 2008). These values were below the standards applicable in Poland and much lower than those tested at Zgierz.



Cadmium (Cd) concentrations in samples numbered 1-8 and 13 were below the detection limit (Fig. 3).

Figure 3. Cadmium concentrations in individual soil samples from two collections.

In samples 10 and 11, the limit value for Cd in green areas of 10 mg/kg DM was exceeded. Sample 9 showed values exceeding the permissible concentration standard in industrial regions of 15 mg/kg DM. Additionally, sample 12 in the second sampling exceeded the value of both permissible standards, although it is in green areas. The maximum value detected in the first sampling around landfills was 15.05 mg/kg DM, while the lowest was 3.2 mg/kg DM; in the second sampling, the maximum concentration was recorded at 26.3 mg/kg DM, and the lowest was 12.37 mg/kg DM. Comparing the maximum values tested around the landfills that once belonged to the Boruta plant with the data obtained in work examining HMs in the area of the Łubna landfill near Warsaw, the concentration values of the Zgierz samples exceed the results of measurements near Warsaw by twenty times. The concentrations obtained around the Łubna landfill range from 0.8 to 1.3 mg/kg DM (Gworek et al., 2016).

The contents of Cu consistent with the standard were observed in samples numbered 1-10 and in samples: 11 in the first sampling and 13 in the second sampling (Fig. 4).



Figure 4. Copper concentrations in individual soil samples from two collections.

Sample number 12 exceeded the limit values for green areas in the second sampling and the limit values for industrial areas in the first sampling. The Cu concentration in sample number 13 in the first sampling was exceeded for industrial areas. The highest Cu concentration value was recorded in the first sampling, sample 12 (41587.7 mg/kg DM), while the lowest value was in sample number 8, which had a concentration of 4.39 mg/kg DM. The range of Cu content in the soil in the first sampling is high and amounts to 41583.31 mg/kg DM. The second sampling was characterised by a smaller concentration range of 6.88 - 377.57 mg/kg DM. A literature review showed the concentration of HMs in a closed landfill in the village of Likeng in Guangzhou, China, ranging from 0.023 to 0.31 mg/kg DM (Xie et al., 2009). The levels found in the Middle Kingdom are deficient and more than ten times lower than the minimum values recorded at the Zgierz landfills.

Nickel (Ni) concentrations in the areas around the landfills were not exceeded in any soil sample (Fig. 5). The Ni content in the first sampling ranged from 4.29 to 89.99 mg/kg DM. For the second sampling, the minimum value was 7.82 mg/kg DM, and the maximum was 40.22 mg/kg DM. When comparing the Ni content in soils, one can cite research on the landfill near Bydgoszcz. The Ni concentrations in nearby soils range from 4.45 to 17.98 mg/kg (Matuszczak et al., 2016). The order of concentration values was similar to the samples tested in this work, but the extreme values differed by more than five times.



Figure 5. Nickel concentrations in individual soil samples from two collections.

Concentrations exceeding the permissible lead (Pb) values were observed in samples no. 10-12 located at the oldest landfill (Fig. 6).



Figure 6. Lead concentrations in individual soil samples from two collections.

The remaining concentrations were within the specified standards of 500 mg/kg DM for green areas and 600 mg/kg DM for industrial areas. The Pb concentration for the first sampling was 9.28 mg/kg DM for sample number 1 and 2340.84 mg/kg DM for sample number 12, and the difference between the extremes was 2331.56 mg/kg DM. The second sampling was characterised by a more significant difference between the minimum concentration value of 19.66 mg/kg DM in sample number 2 and the maximum value of 3034.26 mg/kg DM in sample number 12. At the Jebel Chakir landfill in Tunis, Tunisia, the Pb concentration values were much lower than those tested in this work. The range of concentration values obtained during the investigation of twenty-four soil samples was 5.6 - 16.1 mg/kg (Bouzayani et al., 2014).

4 Conclusions

Waste that ends up in landfills is a mixture of different components, including HMs. These toxic metals are released from the waste and contaminate soil near landfills. It is important to remember that the landfill base and cover layers must be adequately sealed to minimise the risk of these substances being released. The HMs such as Pb,

Cu, Ni, Cd and Zn can disrupt the natural biological balance and inhibit self-purification processes. It is, therefore, essential to monitor and control these pollutants to protect the natural environment and people living near contaminated areas, especially those where economic activities involving harmful substances occurred years ago. In conclusion, every human activity generates a threat to the environment. Everyone feels the consequences because the natural cycle is closed and cannot be stopped. However, pollution can be prevented and controlled by properly designed landfills and by monitoring their changes.

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