Investigation of heavy metal concentrations in the Kelmend tailings landfill and ecological assessment of pollution

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Abstract

Purpose. The research purpose is to determine the heavy metal concentrations in the Kelmend tailings landfill, an active landfill of Pb-Zn flotation waste from the Trepça mine located in the Stan Tërg district in northern Kosovo, as well as to assess the soil pollution level.

Methods. The data is based on two sampling profiles: profile P1 in the south-west of the tailings landfill with 7 samples and profile P2 in the north-east of the tailings landfill with 5 samples within the framework of the project “Environmental geochemical research of the tailings landfill in Kelmend”, funded by the Ministry of Education, Science, Technology and Innovation of the Republic of Kosovo. Each sample was taken according to standards and was analyzed to determine the Pb, Zn, and Mn concentration, as well as pH value. Chemical analyses were performed in the ECCAT-certified laboratory in Tirana, Albania, using atomic absorption spectroscopy (AAS) equipment.

Findings. The average concentrations of Pb, Zn and Mn in profile P1 were 1374.27, 564.7 and 1145.71 mg/kg, while in profile P2 – 796.68, 4510.0 and 14396.2 mg/kg. This significantly exceeds the limits of soil contamination according to Administrative Instruction (GRK), as well as the permissible limits for heavy metal content in soil by WHO and EU Directives. The studied samples clearly show a change in pH values in both profiles. In profile P1 the values are lower with an average value of 3.08 than in profile P2 with an average value of 6.48. This explains the importance and influence of pH on the mobility of heavy metals, especially in soil with acidic pH.

Originality. The originality of the research consists of taking 12 samples from two profiles in the Kelmend tailings landfill, chemical analyses to determine heavy metal concentrations in the ECCAT-certified laboratory in Tirana, Albania, and followed by the statistical interpretation of the results.

Practical implications. The tailings landfill in Kelmend is located near residential areas and is part of the amazing landscape of Shala of Bajgora. On a regional and local scale, the anthropogenic impact from this landfill remains may have already penetrated deeply into the natural material of the surrounding environment. This work highlights the importance of understanding the distribution and risk of toxic metals in sensitive ecosystems.

Keywords: tailings landfill in Kelmend, Pb-Zn mine, heavy metals, pollution

1. Introduction

The mining industry in Kosovo represents the main priority of Kosovo’s state institutions, as this sector is considered important to the country’s economy. The Republic of Kosovo has a varied geology that allows the exploitation of many natural mining resources, among which energy and non-ferrous metals are the most significant potential for economic development. According to the Mining Strategy of the Republic of Kosovo 2012-2025 [1], Kosovo’s coal mines (lignite) are the source of fuel for about 97% of Kosovo’s power. Nowadays, management of mineral resources containing lead, zinc, silver, gold, chrome, nickel, iron, cobalt, aluminium, copper, manganese etc., as well as a considerable number of non-metallic minerals and deposits of building raw materials is of paramount importance. Geochemical analyses have detected various rare earth elements and rare metals such as Sn, Sb, Nb, La, Ce, Sc, Zr, Mo, W, In, Re, etc. [1-3]. The Independent Commission for Mines and Minerals (ICMM) regulates Kosovo’s minerals sector, mining activities and ensures legislative compliance with international mining, environment and safety standards. The largest mining enterprises in Kosovo are Mining and Metallurgical Enterprise Trepça, Kosovo Energy Corporation (KEK JSC), NewCo Ferronikeli and Sharr Cem [1].

In Kosovo, the use of mineral resources is important not only today, in the future [3], but also in the perspective of long-term sustainable development. In addition to the sustainable conservation of mineral resources, the preservation of ecological ecosystems and human health must also be taken into consideration. Valorization and management of mineral resources requires comprehensive integration between the mining sector, government, society and environmental management authorities. Abandoned mining waste poses a serious environmental hazard. However, short-
long-term environmental monitoring strategies can help companies control and manage mining waste.

The threat to the environment in Kosovo from tailings landfills is a growing concern. The Trepça Pb-Zn mine, located in the northern part of Kosovo, has historically been associated with the generation of large volumes of solid waste, despite the significant contribution of this sector to the socio-economic development of the country. Definitely, this sector is still one of the pillars of the national development strategy, but the Kelmend tailings landfill belongs to landfills located near residential areas. Therefore, there is the possibility of the emergence and spread of toxic metals that are not of vital importance to humans, animals and plants, as well as useful metals for humans, animals and plants that are vital, but have high toxic concentrations.

More than 60 Mt of mining waste have accumulated in Kosovo. These volumes are distributed over 11 landfills in the vicinity of the mine and flotation concentrator [3]. The Kelmend tailings landfill is located in the village of Kelmend, northeast of the city of Mitrovica, in northern Kosovo (Fig. 1).

Mining waste is usually contaminated with potentially toxic elements such as heavy metals. The problems associated with mining wastes are being actively discussed today. Based on a significant number of studies, [9]-[12], the environment and people are constantly threatened by air, water, and soil pollution, especially when landfills are located near human settlements, rivers and exploitable land (Fig. 3 and 4). The nearest settlements to the Kelmend landfill are located only 500 m to the west and about 800 m to the south-east.

Of course, heavy metals are rock components and are therefore present in varying concentrations in all soils. However, the average content of these metals in rocks and soils can be significantly exceeded due to geochemical anomalies or anthropogenic impacts, as in the case of the Kelmend tailings landfill. Soil-forming processes (weathering, reactions, vertical or lateral transport) ultimately deplete and accumulate heavy metals in individual soil horizons [13]. In addition to the concentration, toxicity is also highly dependent on the pH and solubility of the metal, hence the form of metal binding [14].

This paper takes into account the anthropogenic accumulations of heavy metals that were and continue to be caused by mining activities at the Pb-Zn Trepça mine. It is necessary and imperative to study the increasing level of heavy metal concentrations in the Kelmend tailings landfill and conduct an environmental assessment of pollution to protect the environment and human health.
This research aims to determine the concentration of Pb, Zn and Mn in the study landfill area, as well as to identify the correlation between these metals based on pH and their mobility.

2. Materials and methods

2.1. Sample collection and handling

To assess heavy metal pollution of soil in the Kelmend tailings landfill (Fig. 5), a total of 12 samples from 2 profiles on opposite sides of the lake were taken within the framework of the project “Environmental Geochemical Research of Tailings Landfill in Kelmend”, funded by the Ministry of Education, Science, Technology and Innovation of the Republic of Kosovo.

2.2. Chemical analysis

The prepared samples were analyzed for heavy metals (Pb, Zn and Mn) using Atomic Absorption Spectrometry (AAS) according to standards: EPA Method 3050B [15] for Pb, Zn and Mn. The pH determination was based on the SH ISO 10390:2005 standard [16]. The adjustment and operating conditions of the instruments were performed in accordance with the manufacturers’ specifications, under the responsibility of the ECCAT laboratory.

2.3. Data analysis

The statistical evaluations and presentations in this paper include a description of each heavy metal and pH concentrations in the Kelmend tailings landfill using a numerical and
graphical representation. Soil pH is a key variable for heavy metal mobility. Concentration changes in P1 and P2 profiles, as well as over the entire sampling area were shown depending on the pH. Pearson correlation coefficient was calculated to assess the relationship between Pb, Zn and Mn concentrations.

For environmental assessment of pollution, the results of heavy metal concentration values in the landfill were compared with the maximum permissible values of heavy metal concentration limits in contaminated soil set by standard regulatory bodies such as Administrative Instruction (GRK – Government of the Republic of Kosovo), [17] EU Directives [18] and World Health Organization (WHO) [19], [20].

3. Results and discussion

In the absence of professional management, the tailings landfill in the village of Kelmend has an extremely negative impact on the attractive landscape of this area. On the other hand, the constant exposure of the deposited material to atmospheric precipitation and wind for nearly 50 years has undoubtedly caused toxic heavy metal pollution not only in Kelmend but also in other nearby villages.

3.1. pH value

pH is a key parameter influencing the mobility of heavy metals. Small changes in pH may cause significant changes in metals concentrations [21]. The pH values for both profiles (P1 and P2) are given in Figure 6. Based on these results, the statistical data are summarized in Table 1.

![Figure 6. pH distribution in profiles P1 and P2](image)

| Table 1. Statistical data on pH concentrations in landfill |
|----------------------------------|-------------|-------------|
| Parameter                        | Profile P1  | Profile P2  | Total  |
| (n = 7)                          | (n = 5)     | (n = 12)    |
| Minimum                          | 2.62        | 6.30        | 2.62   |
| Maximum                          | 3.45        | 6.80        | 6.80   |
| Average                          | 3.08        | 6.48        | 4.50   |
| Median                           | 3.07        | 6.40        | 3.43   |
| Standard deviation               | 0.29        | 0.21        | 1.76   |
| Coefficient of variation         | 0.0948      | 0.0321      | 0.3923 |

The results clearly show the pH change in the profiles. In samples M1–M7 from the south-west of the landfill, about 450 m from the industrial waste discharge site, pH values show a high concentration of H+ ions in the range of 2.62 to 3.45, which is clearly lower than pH values in samples M8–M12 from the north-east of the landfill, near the industrial waste discharge site, with pH values in the range of 6.3 and 6.8. The coefficient of variation has a low value in both profiles: 0.0948 for P1 and 0.0321 for P2, indicating that the data have a small distribution among themselves, making them closer to the average value.

Figure 6 shows the pH distribution in all samples of profiles P1 and P2. The soil acidity in the landfill is almost twice as high in profile P1, which increases the exposure time of the material from the mining waste. Here it can be concluded that geochemical processes, oxidation and reduction depending on the presence of oxygen, have caused the weathering of minerals, their solubility and mobility of heavy metals [9], [13] In profile P2, the pH value increases to a maximum value of 6.8 and corresponds to the exposure to industrial waste in a shorter time, as well as the proximity of the discharge site.

3.2. Lead

According to its geochemical character, lead is a chalcophile element and has an affinity for sulfur [22]. The most common mineral containing lead is galena. Galena is a naturally occurring mineral consisting of lead sulfide (PbS) and is the primary source of lead production. Other minerals that may be present in lead ore deposits include cerussite (PbCO3) and anglesite (PbSO4) [23]. Lead is a toxic metal that can cause serious health problems. Adverse effects of lead occur even at blood concentrations below 10μg/dl, especially in children, lowering IQ and creating learning disabilities [24]. Anthropogenic sources of lead in the environment include industrial activities, especially mining, smelting, battery manufacturing, etc. The lead content variability in the landfill soil samples shows a very high excess of permissible Pb value, which, according to Administrative Instruction (Kosovo) [17] is 200 mg/kg, according to EU Directives [18] – from 50 to 300 mg/kg, and according to WHO data [19] – 85 mg/kg. The highest analysis values were found in profile P1, ranging from 842.5 to 2218.0 mg/kg (Fig. 7). Noteworthy is the much lower Pb content in profile P2: with a minimum value of 597.1 mg/kg and a maximum value of 952.0 mg/kg. Profile P2 is located very close to the flotation tailings discharge site. Statistical data in Table 2 and in Figure 7 show that the Pb content in profile P1 changes significantly, while there are no significant changes in profile P2.

![Figure 7. Lead (Pb) distribution in profiles P1 and P2](image)

Table 2 shows the median values: for profile P1 – 1282.0 mg/kg, for profile P2 – 821.60 mg/kg, and for the total landfill – 935.70 mg/kg. The coefficient of variation for profile P1 is 0.3556, while for profile P2 – 0.1622, which is significantly higher in profile P1, reflecting the greater distribution of values from their average value in this profile. The coefficient of variation can also be used an indicator of the homogeneity of the samples [14]. Based on its value for the total landfill, equal to 0.4182, the samples show low heterogeneity of lead distribution.

<table>
<thead>
<tr>
<th>Table 2. Lead (Pb) distribution in profiles P1 and P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Profile P1</td>
</tr>
<tr>
<td>Profile P2</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Based on its value for the total landfill, equal to 0.4182, the samples show low heterogeneity of lead distribution.
Table 2. Statistical data on Lead (Pb) content in landfill

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Profile P1 (n = 7)</th>
<th>Profile P2 (n = 5)</th>
<th>Total (P1 + P2) (n = 12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum (mg/kg)</td>
<td>842.50</td>
<td>597.10</td>
<td>597.10</td>
</tr>
<tr>
<td>Maximum (mg/kg)</td>
<td>2218.00</td>
<td>952.00</td>
<td>2218.00</td>
</tr>
<tr>
<td>Average (mg/kg)</td>
<td>1374.27</td>
<td>796.68</td>
<td>1133.61</td>
</tr>
<tr>
<td>Median (mg/kg)</td>
<td>1282.00</td>
<td>821.60</td>
<td>935.70</td>
</tr>
<tr>
<td>Standard deviation (mg/kg)</td>
<td>488.67</td>
<td>129.21</td>
<td>474.11</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>0.3556</td>
<td>0.1622</td>
<td>0.4182</td>
</tr>
</tbody>
</table>

Apparently, the mobility of lead from profile P2 to profile P1 (Fig. 8) continues to increase, while the pH value decreases, which means that the correlation coefficient is also negative (-0.57).

Figure 8. Variation of lead content depending on pH in landfill profiles P1 and P2

Higher concentrations of lead are observed in profile P1, where the concentration of H+ ions predominates, that is, an acidic environment. A possible reason is, on the one hand the longer exposure of the material to atmospheric conditions and geochemical processes (oxidation and reduction), and, on the other hand, the type of chemical bonding of the metal. According to [13], [25], [26], lead is available as a free mobile cation Pb²⁺ with pH value of 5-6 of somewhere 80-90% and at lower values, especially bioavailable in high acidic environment, while at higher pH values, PbCO₃ and Pb(OH)₂ are the dominant species.

3.3. Zinc

Geochemically, it is a chalcophile element [22]. The most widespread sources of zinc are sulfide minerals: sphalerite (ZnS) and wurtzite ((Zn, Fe)S), and to a lesser extent smithsonite (ZnCO₃). Due to the same valence as Fe and Mg, zinc can replace these two elements in silicate networks. Zinc is usually accompanied by cadmium [23]. In a global perspective, the natural zinc cycle resulting from natural weathering and erosion processes is more important than the amount of zinc resulting from human activities. However, at the local level, anthropogenic inputs can be very high and toxic under certain conditions. In high concentrations, zinc causes disorders in the body, and in the environment it can have a negative impact on microbial growth [14].

Figure 9 shows that zinc is extremely present in profile P2, located in the north-east of the landfill, near the industrial waste discharge site, with a minimum value of 3839.0 mg/kg and a maximum of 5170.0 mg/kg, compared to the minimum value in profile P1, 281.40 mg/kg and the maximum value of 1192.0 mg/kg.

Figure 9. Zinc distribution in profiles P1 and P2

The statistical data in Table 3 show that the zinc content between the two profiles P1 and P2 varies greatly from one profile to another. The average value for profile P1 is 564.70 mg/kg, which is significantly lower than the average value in profile P2, 4510.0 mg/kg, indicating displacement and mobility of Zn in profile P1.

Table 3. Statistical data on zinc (Zn) content in landfill

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Profile P1 (n = 7)</th>
<th>Profile P2 (n = 5)</th>
<th>Total (P1 + P2) (n = 12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum (mg/kg)</td>
<td>281.40</td>
<td>3839.00</td>
<td>281.40</td>
</tr>
<tr>
<td>Maximum (mg/kg)</td>
<td>1192.00</td>
<td>5170.00</td>
<td>5170.00</td>
</tr>
<tr>
<td>Average (mg/kg)</td>
<td>564.70</td>
<td>4150.00</td>
<td>2208.58</td>
</tr>
<tr>
<td>Median (mg/kg)</td>
<td>498.60</td>
<td>4370.00</td>
<td>894.55</td>
</tr>
<tr>
<td>Standard deviation (mg/kg)</td>
<td>293.11</td>
<td>586.25</td>
<td>2073.41</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>0.5191</td>
<td>0.1300</td>
<td>0.9388</td>
</tr>
</tbody>
</table>

In all samples, except for sample M2 (281.4 mg/kg), there is a clear excess of the permissible value of Zn content, which according to Administrative Instruction (Kosovo) [17] is 300 mg/kg, according to the Directives of EU [18] – from 150 to 300 mg/kg, and according to WHO data [19] – 50 mg/kg. The highest analysis values were found in profile P2 and ranged from 3839.0 to 5170.0 mg/kg, indicating a high level of soil contamination. The coefficient of variation for profile P1 is 0.5191, while for profile P2 – 0.130, which is significantly higher in profile P1, reflecting the greater distribution of values from their average value in this profile. This is due to the high zinc concentration in the sample M1.

Based on its value for the total landfill, equal to 0.9388, the samples show an extremely high heterogeneity, but their content within profiles P1 and P2 can be considered homogeneous. The discrepancy between the data in profiles P1 and P2, as well as zinc mobility in profile P1 can be explained by the low pH in profile P1 [25] (Fig. 10).

The diagram shows a high agreement between these data with a correlation coefficient of 0.96. As pH increases from profile P1 to profile P2, the zinc content in the landfill also increases. In the highly acidic medium, in profile P1, the zinc content is very low with an average value of 564.7 mg/kg. In a weakly acidic medium with an alkaline tendency, the zinc content increases strongly from 3839.0 mg/kg in sample M9 to 5170.0 mg/kg in sample M10. As pH increases, the mobility of heavy metals decreases in the order Cd > Zn > Ni > Cu >Pb [26]. Zinc appears to be much more mobile in acidic medium compared to lead (Fig. 8).
3.4. Manganese

Geochemically, it is a lithophilic element, generally concentrated in rock-forming minerals [22]. In addition to silicates, such as nesosilicate Mn$_2$SiO$_4$ (tephroite), Mn$_3$Al$_2$(SiO$_4$)$_3$ (garnet-spressartine), etc., and manganese carbonate MnCO$_3$ (rhodochrosite), mainly manganese appears in oxides, such as MnO (manganosite), Mn$_2$O$_3$ (braunite), and Mn$_3$O$_4$ (hausmannite), etc. [27]. The causes of high anthropogenic inputs of manganese into the environment are: metallurgical industry, battery factories, and industrial plants emitting dust containing manganese [28]. Mining deposits and dumps are also the main carriers of high manganese distribution at the local level. High concentrations of manganese in plants cause great deformations in their growth [29]. Elevated levels can also lead to toxic effects on the nervous system, including speech impairment, loss of coordination skills and ultimately Parkinson’s-like disease, or so-called “manganism” [28].

Figure 11 shows clear differences in results of manganese content in profiles P1 and P2. Table 4 provides an overview of the statistical evaluation of the data for both profiles and the total landfill.

In profile P2, the manganese content is very high with a maximum value of 20420.0 mg/kg and a minimum value of 8661.0 mg/kg. In profile P1, manganese levels range from 616.1 to 2871.0 mg/kg. According to the coefficient of variation, for profile P1, with a value of 0.6940, for profile P2 of 0.3365 and the total landfill of 1.1168, it can be concluded that there is a significant change in the manganese distribution throughout the total landfill, especially in profile P2 (Fig. 11).

The high concentration of manganese in profile P2 significantly exceeds the maximum permissible level according to WHO data [20], [30], [31], which is 500 mg/kg, but ideally the manganese concentration in soil should not exceed 2000 mg/kg. Concentrations exceeding this value are considered high and toxic for plantations (Administrative Instruction (Kosovo) [17] and EU Directives [18], do not set a permissible limit for manganese in soil).

At pH value above 5, only a small amount of manganese enters the natural cycle, so it accumulates in the soil. On the other hand, increasing soil acidity leads to the release of manganese [26] and its transfer with flowing water [29]. Figure 12 shows that when manganese content changes in landfills depending on pH, the manganese concentration increases in accordance with pH increase and the correlation coefficient is 0.90.

In profile P2, the soil pollution is extremely high, while in profile P1, only sample M1 exceeds the maximum permissible manganese value of 2000 mg/kg. But since the high acidic medium dominates in profile P1, this means that manganese is transported from this profile to be chemically bound elsewhere in the environment, or to be used as nutrients by flora and fauna in the ecosystem. Oxygen demobilizes manganese and its mobility accelerates [26].

### Table 4. Statistical data on manganese (Mn) content in landfill

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Profile P1 (n = 7)</th>
<th>Profile P2 (n = 5)</th>
<th>Total (P1 + P2) (n = 12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum (mg/kg)</td>
<td>616.10</td>
<td>8661.00</td>
<td>616.10</td>
</tr>
<tr>
<td>Maximum (mg/kg)</td>
<td>2871.00</td>
<td>20420.00</td>
<td>20420.00</td>
</tr>
<tr>
<td>Average (mg/kg)</td>
<td>1145.71</td>
<td>14396.20</td>
<td>6666.75</td>
</tr>
<tr>
<td>Median (mg/kg)</td>
<td>856.20</td>
<td>15670.00</td>
<td>2059.50</td>
</tr>
<tr>
<td>Standard deviation (mg/kg)</td>
<td>796.19</td>
<td>4844.27</td>
<td>7445.35</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>0.6949</td>
<td>0.3365</td>
<td>1.1168</td>
</tr>
</tbody>
</table>

### Table 5. Correlation matrix for lead, zinc and manganese

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pb</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.62246</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Mn</td>
<td>-0.56516</td>
<td>0.96078</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 10. Variation of zinc content depending on pH in landfill profiles P1 and P2

Figure 11. Manganese distribution in profiles P1 and P2

Figure 12. Variation of manganese content depending on pH in landfill profiles P1 and P2
In profile P1 the content values of these two metals are at or very close to high suitability (Fig. 13), while in profile P2 there are slight variations in the measured values.

This can be explained by high mobility and much lower values of their concentration in acidic medium in profile P1 (Fig. 10 and 12). From this it can be concluded that in profile P2, in a neutral-alkaline medium, where the concentration of these two metals is high even with low mobility, these two metals continue to remain correlated with each other [32], but the correlation decreases compared to profile P1.

Lead in its two correlations, with manganese and zinc, shows negative values of compatibility and connection with these metals. The value of the correlation coefficient for lead/manganese is -0.56516 and for lead/zinc -0.62246 (-1 < ρ < 0). With manganese (Fig. 14) and zinc (Fig. 15) the correlation is strong, but this reflects a moderate negative relationship. As the lead content increases in profile P1 (in an acidic medium), manganese and zinc content decreases, while the opposite occurs in profile P2 (in a neutral-alkaline medium).

The result correlates with the mobility of lead as a function of pH (Fig. 8), where the correlation coefficient of lead and pH is -0.57. In both cases, the best correlations are observed in profile P2, as manganese and zinc are present in high concentrations, that is, less mobile, whereas in profile P1 they are very mobile. Conversely, lead in profile P1 is significantly less mobile compared to manganese and zinc.

The pH values decrease with distance from the north-east of the landfill, near the industrial waste discharge site (von Profile P2 to P1, Figure 6) and indicate that the soil ranges from alkaline to acidic in nature. pH influences the movement of heavy metals from soil to plants [32], especially Zn and Mn. Pearson correlation analysis for metals shows that the release potential of Mn and Zn occurs mainly in an acidic medium [29], [33]. The major conclusion of this research is that Zn and Mn, compared to Pb, are more liable to release and have a significant Pearson correlation of 0.96078 (0 < ρ < 1), indicating their co-existence and linear co-release. Thus, the mobility of metals followed in the order Mn > Zn > Pb. Lead shows lower mobility in acidic media, and Pearson correlation results confirm the statement that the order of the immobilization effect is Pb > Zn > Mn. Pb mobility is strongly negatively correlated with soil pH. Possible immobilization mechanisms are mainly ion exchange, complexation, bond action with clay minerals, humic substances, soil solutions, etc. [13], [23], [25], [26], [34]. It is likely that lead is not present as a pure phase but is integrated into other structures [26].

It is also clear that heavy metal concentrations varied spatially, with the highest average Mn and Zn concentrations occurring in the north-east of the landfill, near the industrial waste discharge site, in Profile P2, t which can be attributed to higher pH [25]. The high mobility of zinc and manganese in Profile P1 may pose a potential hazard to soil, surface water and groundwater near the landfill area, especially where leaching is not controlled [35]. After all, excess Mn is the most growth-limiting factor on acid soils worldwide [36]. In acidic medium (Profile P1), the average Mn concentration is 13 times lower than that in a neutral to alkaline medium (Profile P2). Similarly, Zn concentration in acidic medium is 8 times lower as compared to neutral to alkaline medium. In acidic medium, Mn and Zn appear in aqueous solutions as Zn+2 and Mn+2 ions [23]. In contrast, the mean Pb concentration is twice as high in acidic medium (Profile P1) than in neutral to alkaline medium (Profile P2). These data confirm the low mobility of Pb and high mobility of Mn and Zn in profile P1. Zinc ions, as highly mobile ions, are released rapidly at pH < 7. The extremely immobile lead only enters the aqueous phase at lower pH values (< 5) [26]. The total content and mobility conditions of Mn, Zn and Pb determined in the landfill area represent a potential burden on the soil, as well as bioaccumulation in the living system [37]. The risk of transfer of heavy metals Mn, Zn and Pb through soil should be described as high to very high.

In summary, the relationship between these heavy metals in environmental contexts can have significant implications for environmental health and human well-being [38], [39]. Increased heavy metal concentration caused by mobilization processes, can cause toxic effects on organisms and plant roots [11], [38], given the propensity of local people to cultivate food crops [10], [39]. Therefore, there is a need to monitor the concentrations of heavy metals [40], or remove those using different physical, chemical and biological modifications [41].
3.7. The prospects for future research

Prospects for future research are promising given the bio-accumulative nature of toxic and heavy metals, which underscore the need for government intervention to mitigate or eliminate their presence in soil and water. Renovating landfills and preventing further increases in heavy metal content are logical steps. Current research should focus on studying the long-term mobility of heavy metals, understanding redox processes and chemical forms of metal binding, as well as their transformations in soil-water and soil-plant systems. Additionally, there is a need to examine residential and agricultural areas for heavy metal contamination, study surface water flow and collection, conduct hydrogeochemical assessments of drinking and irrigation water, and survey surface water and soil ecosystems such as landfill lakes, streams, rivers, and surrounding flora and fauna for geochemical analysis. Furthermore, medical studies are necessary to determine the impact of heavy metals on populations, and geotechnical and technological measures should be implemented to manage tailings landfills, including vegetation techniques.

4. Conclusions

Statistical estimates show that heavy metals accumulate in landfills, posing a potential risks to both the environment and human health. Certainly, such an environmental assessment of pollution is possible only against the background of permissible limits of heavy metal content in the soil, set by national and international standards, such as Administrative Instruction (Kosovo), EU Directives and World Health Organization (WHO). The high concentration of heavy metals such as lead, zinc and manganese in tailings landfill in Kelmend due to anthropogenic influence does raise questions. All analyses clearly reflect that the metal content exceeds the permissible standard values and continues to cause environmental pollution.

The pH of the soil samples ranges from 2.62 to 6.80. The mobility and penetration affinity of heavy metals outside the landfill to nearby ecosystems increases under the influence of soil acidity. The significant increase in concentrations of these metals under anthropogenic influence casts doubt on the fact that if the content of these metals were simply geo-genetic or lithogenetic in nature, the proportions of heavy metals would not increase to such an extent. Although these metals occur naturally, their presence in the environment has increased significantly due to human activities.

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Conflicts of interests

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

References

Дослідення концентрації важких металів на полігоні хвостосховища у Кельменді та екологічна оцінка забруднення

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Мета. Визначення концентрації важких металів на Кельмендському хвостосховищі – діючому звалищі відходів свинцево-цинкового рудництва, розташованого в районі Стан-Терг на північ від Косова, в табл. 1 подано оцінка рівня забруднення грунту.

Методика. Дани були отримані в результаті аналізу проб, зібраних у різних точках хвостосховищ, розташованих в районі Стан-Терг. Для визначення концентрації важких металів в грунті були використані атомно-спектрометричні аналітичні методи.

Результати. Встановлено, що середнє значення концентрації Pb, Zn і Mn у грунті превищувало нормативи, встановлені для грунтів, які використовуються як індикатори грунтових відкладів. Середнє значення концентрації Pb, Zn і Mn у грунті превищувало нормативи, встановлені для грунтів, які використовуються як індикатори грунтових відкладів.

Наукова новизна. Отримані результати дослідження підкреслюють важливість вивчення токсичності важких металів у грунті, які можуть впливати на здоров'я людей та інших організмів.

Практична значимість. Відображена висока токсичність важких металів у грунті, які можуть впливати на здоров'я людей та інших організмів.

Ключові слова: хвостосховища у Кельменді, свинцево-цинковий рудник, важкі метали, забруднення

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