

# Distribution of different forms of manganese in coal mining waste: A case study of the Vizeyska mine, Ukraine

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**Abstract.** This study assesses the ecological hazards posed by the Vizeyska mine in the Lviv-Volyn coal basin, focusing on manganese distribution in mine waste and its environmental impact. The spoil heap, formed from mining operations between 1960 and 2009, covers 225,000 m<sup>2</sup> and contains approximately 5.1 million m<sup>3</sup> of waste rock, with a heterogeneous composition of burnt and unburnt mudstones, siltstones, sandstones, and coal. Sampling and analyses were conducted to quantify manganese in bulk, acid-soluble, and bioavailable forms using standardized methods. The results revealed high variability in manganese concentrations, with bulk forms ranging from 119 mg/kg to 3850 mg/kg, highest in burnt siltstones and lowest in sandstones. Acid-soluble manganese concentrations were highest in unburnt coal (218 mg/kg) and lowest in burnt mudstones (10 mg/kg). Bioavailable manganese, extracted using ammonium acetate, displayed a different trend, being highest in burnt siltstones (95 mg/kg). Water-soluble manganese concentrations were minimal, reflecting its limited mobility in this environment. The combustion process significantly alters manganese distribution by increasing bulk concentrations through the burning of organic matter, while simultaneously reducing the presence of mobile forms. Soil samples showed manganese levels below regional thresholds, indicating minimal ecological risk. However, elevated manganese in water-soluble forms during specific processes highlights the potential for localized contamination. The study concludes that spoil heap materials can be used in construction with minimal environmental risk. Yet, the dynamic behavior of manganese in different forms necessitates ongoing monitoring and further research to mitigate potential long-term ecological impacts.

## 1. Introduction and analysis of previous studies

The presence of increased concentrations of heavy metals in soils, rocks and coal mining wastes has the potential to disrupt ecological equilibrium in certain areas of the geological environment [1, 2]. In such cases, mobile forms of heavy metals, which can be washed out from coal mining wastes and enter the soil, surface and underground water resources, as well as absorbed by plants, are of particular concern [3-4]. Among the various heavy metals, manganese is of particular interest due to its significant bioavailability and substantial variability in its content across different environmental components. Manganese is one of the most abundant trace

elements in the lithosphere, with an average content of 1000 mg/kg in the Earth's crust and ranging from 350 to 2000 mg/kg in rocks. Globally, the manganese content in soils varies from 10 to 9000 mg/kg, with the maximum on the curve of its distribution falling in the interval 200-800 mg/kg [5]. Approximately 250 minerals are recognised in which Mn is the primary component, including pyrolusite ( $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ ), brownite ( $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ ), manganite ( $\text{MnO}(\text{OH})$ ), rhodochrosite ( $\text{MnCO}_3$ ), and others. The most prevalent oxidation state of Mn in rock-forming silicate minerals is +2. The  $\text{Mn}^{2+}$  cation has the ability to substitute divalent cations (e.g.  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ) of certain elements (e.g. Si, Al) in silicates and oxides [5]. Consequently, manganese is concentrated in soil horizons enriched with iron oxides and hydroxides. Due to its high biophilicity, Mn is also accumulated in the upper soil layer as a result of its fixation by organic matter.

The global mean value for manganese in soils is 545 mg/kg, while in urban soils it is 729 mg/kg [4, 5]. The regional mean values for manganese in soils in Ukraine: Steppe 670 (from 200 to 1600), Forest-steppe 735 (from 240 to 3000), Carpathians: foothills 676 (from 150 to 1575), mountainous areas 924 (from 500 to 1500) [5].

The behaviour of manganese in surface sediments is an extremely complex phenomenon that is dependent on various factors. Of these, the pH and Eh of the medium are of the greatest importance [5, 6]. The greatest mobility of Mn has been observed in conditions of reductive acidic environment, where ions in the form of  $\text{Mn}^{2+}$  are present as oxide salts of chlorides, sulfates, and bicarbonates.

The highest concentrations of mobile manganese forms have been observed in sod-podzolic soils, ranging from 50 to 150 mg/kg. In contrast, lower concentrations of manganese have been observed in chernozems (1–75 mg/kg), grey soils (1.5–125 mg/kg), and chestnut and brown soils (1.5–75 mg/kg). The least amount of mobile forms of manganese is observed in carbonate and humus-carbonate soils. The content of Mn in plants varies from 0.0001 to 0.02% [5].

The significance of soluble forms of manganese in relation to ecological significance is highlighted by the dependence of its content in plants on its solubility in soils. In well-drained soils, the solubility of manganese (Mn) invariably increases with rising soil acidity. However, the ability of manganese to form anionic complexes and complexes with organic ligands can lead to an increase in its solubility in alkaline media [5].

The primary impediments to the movement of manganese in soil include an alkaline environment, carbonates, and elevated levels of humus. In aerobic conditions, manganese is characterised by low solubility. However, within an alkaline environment, solubility can be reduced due to the formation of hydroxides. Manganese forms amorphous structures within humic substances, maintaining its solubility and plant availability while mitigating rapid leaching into groundwater [7].

The absorption of manganese (Mn) by plants is a consequence of metabolic processes, with the transport of Mn in plants most likely occurring as  $\text{Mn}^{2+}$ . In general, manganese is actively absorbed and rapidly transported by plants. Studies [8] indicate that manganese uptake is enhanced when associated with organic chelating agents such as artificial humic substances, which increase its bioavailability. The bioassay results show that manganese primarily exists in the +2 oxidation state within an amorphous matrix, facilitating its absorption by plants. Additionally, the presence of humic substances in the soil can aid in the transport of manganese, ensuring its availability to plants while mitigating potential leaching into groundwater. The role

of humic substances extends beyond manganese mobility, as they also improve soil structure and water retention, creating favorable conditions for plant growth [7].

It is imperative to acknowledge that the manganese content in plants is contingent not solely on their intrinsic nature, but also on the prevailing total quantity of manganese in the soil matrix, a factor that is predominantly dictated by the inherent properties of the soil. The highest concentrations of manganese that are readily available to plants are typically observed in acidic and flooded soils. Its concentration in plants is characterised by a negative correlation with soil pH and a positive correlation with the content of organic matter [6].

It is evident that all plants have a specific need for manganese, and probably its most important function is participation in redox reactions. Manganese is involved in the oxygen-forming system of photosynthesis and also plays a major role in the electron transport of the photosynthetic system. In conditions of deficiency of this element, the production of photosynthetic oxygen is the first process to be affected, while the content of chlorophyll and leaf dry mass changes insignificantly. Disturbance of photosynthesis is accompanied by a sharp decrease in the content of hydrocarbons in plants, especially in roots [9]. Additionally, manganese deficiency can reduce a plant's tolerance to environmental stressors such as low temperatures, further demonstrating its critical role in plant metabolism [7].

Coals are characterised by lower concentrations of manganese compared to crustal rocks and soils. According to M.P. Ketris & Y. E. Yudovich, , the average content of manganese in brown coals is 100 g/t, and in hard coals, it is 70 g/t [10].

The concentration of manganese in coal can exhibit significant variability, even within a single deposit. For instance, the Mn content in coal from the Moatize deposit in Mozambique ranges from 32.6 to 259 mg/kg [11].

*The objective* of the present study is to evaluate the ecological hazards posed to the environment by the Vizeyska mine in the Lviv-Volynsk coal basin. The investigation focuses on the distribution of manganese in the rocks of mine slag heaps and its subsequent impact on the surrounding ecosystem.

*The object* of research is waste rock and soils in the zone of influence of Vizeyska mine, which belongs to Chervonograd mining-industrial district of Lviv-Volyn coal basin. The mine commenced operations in 1960, with an annual production capacity of 0.25 million tonnes of coal, and ceased operations in 2009. The process of coal mining resulted in the accumulation of a substantial quantity of waste rock on the surface. The terricon are located 250 m northeast of the mine on alluvial deposits of the Rata River. The atmospheric precipitation from the spoil heap is directly absorbed into the Rata River [12], emphasising the necessity for the determination of the concentration of mobile forms of heavy metals. The base area of the Vizeyska mine heap measures 225,000 m<sup>2</sup>, with a height ranging from 10 to 40 m and a slope angle varying from 25 to 47°. The terricon has accumulated 5,100,000 m<sup>3</sup> of rock. The terricon is heterogeneous in structure and consists of two interconnected parts: the western and eastern regions. The western part of the terricon is composed primarily of burned rocks, forming a truncated cone, while the eastern part consists of unburned rocks that have been formed into a flat dump. On the slopes, the spoil heap has been partially reclaimed by filling a layer of sand and loam with a thickness of 0.5-0.7 m, which is overgrown with grass [12].

*The subject* of research are the factors of ecological hazard of the environment in the zone of influence of Vizeyska mine caused by the presence of various forms of manganese in the rocks of mine heaps. The assessment of environmental hazard factors is an urgent task, especially in the zone of influence of objects of increased technogenic danger, potential sources of pollution of

drinking water, and so on [13]. It is also noteworthy that the Lviv region is characterised by a high specific density of high-hazard objects, with 38.5 objects per thousand km<sup>2</sup>, which underscores the necessity for more detailed environmental assessments and continuous monitoring of such objects [14 - 16].

## **2. Research Methodology**

The sampling of rocks was conducted in accordance with GOST 17.4.4.02.84, with the rocks being obtained directly from the heap. A total of 20 rock samples were collected from various locations across the heap. A macroscopic description of the rocks was conducted, and their quantitative ratios were established. The rocks were then meticulously arranged according to their lithological composition. Additionally, 10 soil samples were collected at distances of 50 and 200 meters from the foot of the spoil heap. Subsequent to collection, all samples were dried and pulverised. Rock extracts were then prepared from the pooled samples. Samples of unburnt mudstones, burnt mudstones, unburnt siltstones, burnt siltstones, burnt sandstones, unburnt coal, and soils at distances of 50 and 200 m from the heap were then combined.

The preparation of solutions of extracts from rocks and soils was carried out in accordance with GOST 4770.9: 2007. The bulk form of manganese was determined after rubbing the rock with 1 N HNO<sub>3</sub> in the presence of H<sub>2</sub>O<sub>2</sub>. The acid-soluble form of manganese was determined in the extract of 0.1 n HCl solution, mobile forms from acetate-ammonium buffer solution (AABS) with pH 4.8, and aqueous extract using distilled water. Individual native sample suspensions were used in the preparation of extracts. The rock-solution mass ratio of 1:10 was observed. During sample preparation, possible contamination and losses were controlled, ensuring consistency in extraction and digestion steps.

AABS extracts primarily chemical elements in ion-exchange form, which are the most bioavailable for plants, and thus the amounts of metals removed by AABS are termed bioavailable. It is noteworthy that ammonium acetate extract, in addition to its role in the removal of exchangeable forms, facilitates the extraction of metals from organic substances, oxides, and hydroxides [17, 18].

The concentration of manganese in the samples under study was determined by atomic absorption method using AAS-115-M-1 spectrometer. The relative error of measurement for this instrument does not exceed 2-5%, according to the manufacturer's specifications. Calibration of the spectrometer was performed before each measurement cycle using certified reference materials to account for instrumental drift. Additionally, each sample was analyzed in triplicate, and the mean value was reported to minimize random errors. The reproducibility of results was further verified by comparing measured concentrations with known standards, confirming the reliability of the obtained data.

## **3. Research results**

### *3.1 Lithological and mineral composition of rocks*

The lithological and mineral composition of the rocks. The lithological composition of the rocks present at the Vizeyska mine heap is dominated by burnt and unburnt mudstones, siltstones, sandstones, and coal, with a ratio of 55:25:15:2 [12].

### 3.2 Variability of the content of bulk forms of manganese

The mean content of manganese in coals from the Lviv-Volyn basin is 164.0 mg/kg, whereas in coals from the Vizeyska mine it is 163.7 mg/kg [12]. That is, the rocks of the Vizeyska mine dump are typical for the basin rocks in terms of Mn content. This is 2.3 times greater than the mean content of manganese in hard coals worldwide.

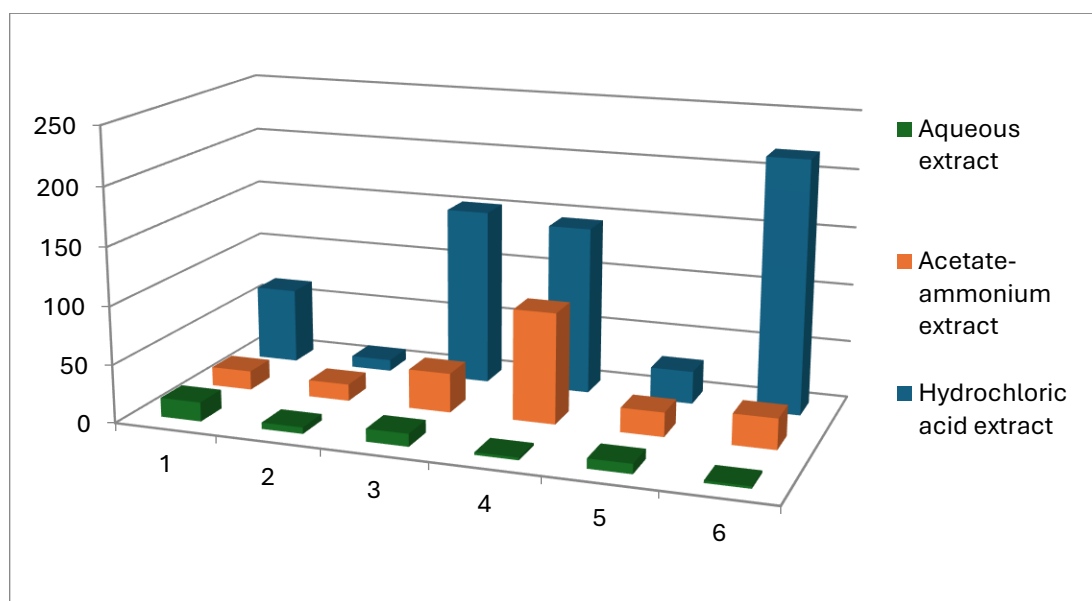
For data [12, 19] the most variable is the concentration of manganese in sandstone, which ranges from 1350 to 2037 mg/kg. In siltstone, the Mn content ranges from 1089 to 1751, and in mudstone from 1632 to 2062 mg/kg. It is noteworthy that there is an absence of a uniform pattern of manganese concentration in rocks of different lithological composition. In particular, the concentration of manganese increases in a number of siltstone-sandstone-argillite on the spoil heaps of Vizeyska and Mezhirichanska mines and in a number of argillite-siltstone-sandstone on the spoil heap of Chervonogradska mine.

The concentration of the bulk form of manganese in the rocks of the Vizeyska mine spoil heaps varies from 118 mg/kg to 3850 mg/kg, with an average of 1181 mg/kg. The highest concentrations of manganese were found in burned siltstones, while the lowest concentrations were found in sandstones. The manganese concentration coefficients in non-burnt rock varieties relative to clark in sedimentary rocks are as follows: coal (2.0), siltstone (0.9), mudstone (0.7); in burned samples: siltstone (5.8), mudstone (1.0), sandstone (0.2).

In the soils sampled in the zone of influence of the Vizeyska mine spoil heap, the content of bulk forms of manganese was found to be 8.0 mg/kg at a distance of 50 m and 10.6 mg/kg at a distance of 200 m from the spoil heap.

### 3.3 Variability of manganese content in hydrochloric acid and ammonium acetate extracts

According to the data presented in Fig. 1, the highest concentration of manganese in acid-soluble extract was found in unburnt coal (218 mg/kg), the lowest in unburnt siltstones (153 mg/kg), burned siltstones (145 mg/kg) and the lowest in burned mudstones (10 mg/kg) in the Vizeyska mine dump.



**Figure 1.** Distribution of manganese in extracts from rocks of the Vizeyska mine waste heaps (mg/kg): 1 – unburnt argillite, 2 – burned argillite, 3 – unburnt siltstone, 4 – burned siltstone, 5 – burned sandstone, 6 – unburnt coal.

The decrease of manganese content in acetate-ammonium extract is somewhat different: burned siltstone (95 mg/kg) - unburnt siltstone (34 mg/kg) - coal (27 mg/kg) - sandstones (21 mg/kg) - unburnt and burned mudstones (17 and 15 mg/kg).

Soils in the vicinity of the Vizeyska mine slag heap contain manganese extracted by hydrochloric acid extract in the amount of 7.5 mg/kg and 9.1 mg/kg, in ammonium acetate extract - 2.7 mg/kg and 2.5 mg/kg at a distance of 50 and 200 m, respectively.

### *3.4 Variability of the content of water-soluble forms of manganese*

Water-soluble forms of heavy metals are directly involved in the water cycle, and therefore control of their distribution is very important for assessing the environmental safety of the territory. In the rocks of the Vizeyska mine spoil heap, the highest concentration of manganese was found in unburnt mudstone (17 mg/kg), the lowest in unburnt siltstone (11 mg/kg), and the lowest in unburnt coal (2 mg/kg). In the soils located at a distance of 50 and 200 m from the spoil heap, no manganese was detected in the water extract.

## **4. Discussion of research results**

The concentration of mobile forms of heavy metals is the primary determinant of environmental hazards related to heavy metal pollution. This is due to the fact that they are bioavailable and, having a high migration capacity, can pollute water, including drinking water. Concurrently, the concentration of bulk and acid The terminology employed -soluble forms of heavy metals provides insights into the accumulation of these elements, as under conditions of hypergenesis, bulk and acid-soluble forms can eventually transition into mobile forms. Most available data focus on the bulk forms of heavy metals in rocks and soils [20-24]. For example research on the leaching of manganese from coal fly ash in India revealed significant environmental concerns. Short-term and long-term leaching studies on various types of ash from thermal power plants indicated that the leachate from fly ash had a manganese concentration of 0.2001 mg/L. Field investigations at an abandoned open cast mine filled with pond ash showed that the concentration of manganese in groundwater beneath the ash-filled mine reached up to 6.0 mg/L. This indicates a higher potential for manganese migration into groundwater systems in certain conditions [24].

It is crucial to conduct more detailed studies on mobile and bioavailable Mn forms to better understand their role in environmental risks. It is therefore vital to understand the relationship between the concentrations of chemical elements in different forms, as this will allow us to predict the concentrations of mobile element forms, given their concentrations in the bulk form. Manganese distribution in coal seams is significantly influenced by its affinity for carbonate minerals and its interaction with sulfide phases. Studies indicate that increased carbonization reduces manganese content due to the breakdown of metal-organic compounds, while dia-and epigenetic mineralization processes enhance manganese accumulation in specific zones. Furthermore, vertical profiling of coal seams reveals variability in manganese concentration, reflecting differences in mineralogical associations and depositional environments [25].

### *4.1 Patterns of variability of concentrations of different forms of manganese in rocks and soils*

The results of studies of distribution of various forms of Mn in the technogenesis zone of coal mine spoil heaps are very few. This paucity of research is primarily attributable to the elevated

labour intensity and financial cost associated with conducting such studies. Conversely, the acid-soluble, bioavailable, mobile form of Mn is of paramount importance for the assessment of environmental safety and migration forecasting. A challenge that pervades the comparison of research results is that analytical determinations are not always carried out by the same methods.

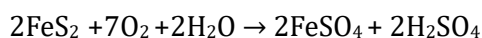
To better understand the mobility of manganese in mining environments, a comparison with spoil heaps in other regions provides insight into the broader environmental behavior of manganese. A relevant study conducted by Herndon et al. [26] in a reforested coal mine spoil heap in the Appalachian region highlights key differences and similarities in manganese distribution and mobility. The study by Herndon et al. employs an extraction methodology, focusing on exchangeable Mn ( $\text{MgCl}_2$ -extracted), reducible Mn (associated with Fe-Mn oxides), and oxidizable Mn (linked to organic matter and sulfides). Despite these differences, some parallels can be drawn: the exchangeable Mn fraction in Herndon's study, extracted using  $\text{MgCl}_2$ , is comparable to the ammonium acetate-extractable Mn in this study, as both target weakly bound Mn forms with high bioavailability. In both studies, weakly bound Mn forms contribute to Mn mobility, albeit to different extents depending on soil composition and extraction conditions. The study by Herndon et al. [26] emphasizes the dominance of reducible Mn, bound mainly to Fe-Mn oxides, which act as major Mn reservoirs under oxic conditions, while exchangeable Mn, which is weakly bound to soil particles, forms only a minor fraction of total Mn in soils. The exchangeable Mn fraction in Appalachian coal mine spoils, extracted using  $\text{MgCl}_2$ , ranged from 5 to 45 mg/kg, with a mean value of 23 mg/kg. In comparison, our study found that ammonium acetate-extractable Mn in Vizeyska spoil heaps ranged from 15 to 95 mg/kg, indicating significantly higher bioavailable Mn concentrations in our study area. Additionally, while Herndon et al. observed a dominant fraction of Mn bound to Fe-Mn oxides (60-80% of total Mn), our results suggest a higher proportion of acid-soluble Mn, emphasizing a greater potential for manganese mobilization in the Vizeyska mine environment.

The rocks of the Vizeyska mine dump are distinguished by highly variable coefficients of transitions between different forms of manganese. The bulk form concentration coefficients of manganese in hydrochloric acid extracts range from 0.014 to 0.242 in rocks and from 0.86 to 0.94 in soils. In ammonium acetate extracts, the range is from 0.02 to 0.177 in rocks and from 0.23 to 0.34 in soils. In aqueous extracts, the range is from 0.0005 to 0.072 in rocks. The largest coefficients of manganese transfer from native samples into hydrochloric acid extracts are characterised by soils, less by unburnt siltstone, burned sandstone and unburnt coal, and the smallest by burned siltstone and burned mudstone. In the acetate-ammonium extract, the largest indices are characterised by soils and sandstone, the smallest by argillites, siltstones, and unburnt coal. In the aqueous extract, the largest transition coefficients are characterised by sandstone, the smallest by unburnt argillite, and the smallest by burned-out argillite, siltstone and unburnt coal.

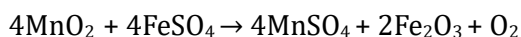
It is noteworthy that the content of bulk acid-dissolved forms of manganese increases in the soil with distance from the heap. This phenomenon may be attributed to the high migration capacity of this metal in a reducing environment, which is known to form in areas of intensive oxidation of organic compounds, and the subsequent fixation of manganese in the transition of a reducing environment to an oxidising one.

The primary source of the mobile form of  $\text{Mn}^{2+}$  may be the interaction between ferum (III) sulfate and pyrolusite, which undergoes the following stages [27]:

Stage I. The sum equation of the multistage process of conversion of pyrite (ferum (III) persulfide) to ferum (III) sulfate:



Stage II. The interaction of  $\text{FeSO}_4$  with pyrolusite (the most significant manganese ore) at elevated temperatures is of particular interest, given its occurrence in conjunction with iron and copper ore deposits.



Stage III. The dissociation of  $\text{MnSO}_4$  is well soluble, resulting in migration from the heap into the soil and water bodies.



#### *4.2 Patterns of changes in manganese concentrations due to thermal weathering of rocks*

According to [12], the burned rocks of the Vizeyska mine slope exhibit a higher concentration of manganese in bulk form, with a coefficient of 2.15 in comparison with non-burned rocks. In other mines, the burned rocks of the slag heap of the Mezhrichanska mine concentrate manganese with a coefficient of 0.7. This indicates that burning rocks results in a decrease in the concentration of this element.

The results of our studies indicate that burned mudstones and siltstones of the Vizeyska mine spoil heap exhibit higher concentrations of bulk forms of manganese compared to their unburned analogues. However, the concentration of other forms of this element changes primarily in the opposite direction following rock burning.

It has been established that the increase in the concentration of bulk forms of manganese in burned-out rocks is directly proportional to the increase in the granulometric composition of rocks. Concurrently, the intensity of reduction of water-soluble concentrations of manganese in burned-out rocks is found to increase with the granulometric composition of rocks.

The elevated bulk concentrations of manganese in burned-out rocks in comparison with non-burned-out rocks can be explained by the concentration of the mineral skeleton of the rock due to the burning of its organic part. Recent findings demonstrate that calcination under 600–750°C significantly enhances the availability of manganese by converting its insoluble fractions into soluble metal oxides and carbonates. Sequential extraction techniques indicate a recovery potential of up to 90%, underscoring the importance of thermal processes in modifying manganese distribution and mobility. Calcination facilitates the decomposition of manganese-bearing minerals, which are otherwise encapsulated in coal refuse, enabling their transition to bioavailable forms. This process not only impacts manganese's ecological distribution but also suggests pathways for resource recovery [28]. Studies on bottom sediments reveal that manganese extraction rates are highly dependent on the sample preparation method. Microwave-assisted treatments using a combination of nitric and hydrochloric acids achieve the highest manganese recovery, with content levels reaching up to 2,000 mg/kg. These findings underscore the need for methodological consistency to accurately assess manganese distribution in environmental matrices [29].

During the process of combustion, mobile forms, particularly water-soluble ones, are extracted from rocks. Consequently, their concentration in burned-out rocks is considerably lower.

The findings from this study highlight the importance of monitoring manganese mobility in coal mining waste to prevent potential groundwater contamination. The observed variability in manganese solubility suggests that site-specific assessments are necessary when considering spoil heap materials for reuse in construction or land rehabilitation. Future research should



focus on developing stabilization techniques to minimize leaching risks and ensure the safe utilization of waste materials.

## 5. Conclusions

5.1 The Vizeyska mine is located within the Lviv-Volyn coal basin, with the composition of its spoil heap comprising burnt and unburnt mudstones, siltstones, sandstones, and coal in a ratio of 55: 25: 15: 2. The content of bulk forms of manganese in the rocks of the Vizeyska mine spoil heaps ranges from 118.61 mg/kg to 3849.61 mg/kg, with an average of 1181.14 mg/kg. The highest concentrations of manganese were found in siltstones, while the lowest concentrations were found in sandstones. In the soils sampled in the area influenced by the spoil heap, the content of bulk forms of manganese was found to be 7.99 mg/kg at a distance of 50 m and 10.57 mg/kg at a distance of 200 m from the spoil heap. Concentration coefficients of manganese in non-burnt rock varieties relative to the clark in sedimentary rocks are as follows, decreasing in the row: coal - siltstone - mudstone -; in burned-out samples: siltstone - mudstone - sandstone.

5.2 In the acid-soluble extract, the manganese concentration decreases in the following sequence: unburned coal – unburned and burned siltstone – unburned mudstone – sandstone – burned mudstone. Conversely, the manganese content in the acetate-ammonium extract exhibits a divergent trend, with the sequence being: unburned and unburned siltstone - coal - sandstones - unburned and unburned mudstone. In the aqueous extract, manganese concentrations decrease in the sequence: burned mudstone - non-burned siltstone - sandstone - burned mudstone - burned siltstone. With respect to the bulk form, the concentration ratios of manganese in the hydrochloric acid extract range from 0.014 to 0.239 in rocks and from 0.86 to 0.94 in soils; in the ammonium acetate extract, the range is from 0.020 to 0.177 in rocks and from 0.23 to 0.34 in soils; and in the aqueous extract, the range is from 0.0005 to 0.072 in rocks. The increase in the concentration of bulk forms of manganese in burned rocks is directly proportional to the granulometric composition of the rocks. Furthermore, the intensity of the decrease in water-soluble concentrations of manganese in the burned-out rocks increases with the increase in the granulometric composition of rocks.

5.3 Concentrations of various forms of manganese in the studied rocks and soils do not exceed regional clarks and, in this respect, cannot adversely affect the ecological state of the environment, and the rocks can be used in construction. The low mobility of manganese in burned rocks suggests their potential for use as fill material in infrastructure projects, which could reduce the demand for natural aggregates. However, additional environmental assessments should be conducted to confirm the long-term stability of these materials in construction applications.

5.4 These findings underscore the need for further research to comprehensively understand the long-term impact of these spoil heaps on the surrounding water resources and ecosystems. Continued monitoring and more comprehensive assessments are crucial to ensure the environmental safety of the region. Regular testing of soil and water in the vicinity of spoil heaps can help detect any gradual increase in manganese mobility due to changing environmental conditions. Additionally, further studies should explore the feasibility of manganese recovery from mining waste, particularly through thermal treatment or hydrometallurgical processing, to support resource efficiency and sustainable waste management strategies.

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