Heavy Metal Contamination of Coal Mining Tailing Dumps: A Case Study of the Petrila Mining Site, Jiu Valley, Romania

Andrei Szollosi-Mota[1*], Maria Prodan[2], Vlad Mihai Pasculescu[3], Nicolae Ioan Vlasin[4], Gheorghe Daniel Florea[5], Vasilica Irina Nalboc[6], Niculina Sonia Suvar[7]

[1*] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; andrei.szolosi@insemex.ro; ORCID iD: 0009-0004-7948-4374,
[2] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; maria.prodan@insemex.ro; ORCID iD: 0000-0003-0112-0023,
[3] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; vlad.pasculescu@insemex.ro; ORCID iD: 0000-0002-6603-249X,
[4] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; nicolae.vlasin@insemex.ro; ORCID iD: 0000-0002-9313-3106,
[5] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; daniel.florea@insemex.ro; ORCID iD: 0009-0001-4488-9804,
[6] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; irina.nalboc@insemex.ro; ORCID iD: 0009-0000-9003-2257,
[7] National Institute for Research And Development for Mine Safety and Protection to Explosion -INSEMEX, Department of Safety Mineral Resources, 32-34 G-ral Vasile Milea, Petrosani, Romania; sonia.suvar@insemex.ro; ORCID iD: 0009-0009-0215-7742.

https://doi.org/10.29227/IM-2026-02-02-031

Submission date: *2026-07-04* | Review date: *2026-24-06*

Abstract

The increasing demand for metals and the depletion of primary mineral resources have led to a growing interest in alternative sources of raw materials. In this context, mining waste deposits are increasingly considered as potential secondary resources within the concept of urban mining and the circular economy. Historical mining activities have generated large quantities of waste rock that can contain significant concentrations of valuable metals. The Petrila mine tailings dump, located in the Jiu Valley coal basin (Hunedoara County, Romania), includes such a deposit, where millions of tons of mining waste have accumulated over decades of mining. The tailings dump occupies an area of approximately 225,201 m² and constitutes an important anthropogenic deposit with potential resource value. The objective of this study was to characterize the chemical composition of residual materials from the tailings dumps of the Petrila mine and to evaluate their potential as secondary resources for metal recovery potential, in urban mining zone. Sampling was carried out at several locations in the tailings heap, at depths of approximately 30 cm, 50 cm and 70 cm, to investigate the distribution of metals within the deposit of tailing dumps. Elemental concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). In addition, X-ray fluorescence (XRF) analysis was performed to determine the majority oxide composition of the samples and to support the geochemical characterization of the tailings material. XRF analyses show that the tailings material is dominated by silicate phases, with SiO_2 concentrations ranging from approximately 42 to 65 wt % and Al_2O_3 concentrations ranging from approximately 15 to 24 wt %. Iron oxides are also significant, with Fe_2O_3 values reaching up to about 17% by weight, while TiO_2 concentrations range between about 1.2 and 2.4% by weight. Trace metal concentrations determined by ICP-OES indicate the presence of several elements of economic interest, including chromium (up to ~137 mg/kg), nickel (up to ~90 mg/kg), copper (up to ~50 mg/kg), and zinc (up to ~105 mg/kg). The obtained results indicate that the Petrila mine tailings dump represents a potential secondary source of metals. Although the material is mainly composed of silicates and iron-bearing minerals, the presence of several base metals suggests possible opportunities for resource recovery through modern processing technologies. The study highlights the importance of geochemical investigations of historical mine waste deposits in the context of urban mining and sustainable resource management.

Keywords: *heavy metals, tailing dump, XRF, ICP-OES, Jiu Valley, coal mining*

1. Introduction

One of the most long-lasting effects of mining is coal tailing dumps [23]. For decades after the mine closes, they let heavy metals into the soil and water systems around them. [1] There are many such dumps in Romania, especially in old mining areas like the Jiu Valley, Maramures, and Hunedoara county [6,13]. Mostly, coal is made of carbon, but other geological materials can add small amounts of metals that could hurt the environment over time. It is important to systematically characterize and monitor these metals. Studies of Romanian coal tailing dumps consistently show that they contain elevated concentrations of lead(Pb), zinc (Zn), copper (Cu), cadmium (Cd), nickel (Ni), and iron (Fe). [10]

The main ways these metals get around are through acid mine drainage (AMD) and leaching, and they adversely affect soil, groundwater, and aquatic ecosystems. Many sites in Romania have not been fully remediated, which remains a major environmental concern. This means that there aren't enough seals, plants, or water treatment facilities, which means that a lot of contaminated material is left out in the open where it can be damaged by the weather and erosion. [8]

The current study focuses on Branch 4 of the Petrila mining waste dump in Hunedoara County (Fig. 1), which was one of the oldest coal mines in the Petrosani Basin and stopped working in 2015. The objectives of this study are: (i) to delineate the

geomorphological and geochemical characteristics of the waste dump; (ii) to quantify heavy metal concentrations via ICP-OES and XRF analysis; and (iii) to identify spatial contamination hotspots and assess the associated environmental risks and metal recovery.

Fig. 1. General view and geographical context of the Petrila mining waste dump - Branch 4.

2. Study Area

2.1 Geographical and Historical Context

The Petrila mine is located in the eastern part of the Jiu Valley coal basin, Hunedoara County, within the Petrosani Depression of the Southern Carpathians. The Jiu Valley coal field comprises 17 mining perimeters. The Petrila mining field extends approximately 3 km between the Lonea field to the east and the Petrosani–Dâlja field to the west, and is crossed by the Eastern (Transylvanian) Jiu River and its tributaries. Mining operations began in the year 1840 — the earliest in the Petrosani Basin — intensifying after 1859 and again after 1870. The mine was finally closed in 2015 under management by the National Company for Mine Closure Jiu Valley (SNIMVJ); assets including the waste dump were subsequently transferred to the Jiu Valley Energy Complex (CEVJ) [13].

2.2 Geology and Stratigraphy

Sixteen seams were identified in the Petrila mining field, of which ten were exploited (seams 3–9, 12, 13, and 14). Seam No. 3 is the main seam, with thickness ranging from 2 to 40 m and consisting of coal intercalated with clay shales and occasional spherosiderite lenses. The physico-chemical properties include: inherent moisture averaging 3.55%, hygroscopic humidity 2.47%, ash content 25.80%, and volatile substances 34.80%. Combustible sulphur — present mainly as pyrite — averages 2.83%, with a mean lower calorific value of 7,596 kcal/kg. The pyritic content is a critical factor driving acid mine drainage and metal mobilisation from the waste dump.

2.3 Waste Dump Location and Geomorphology

The Petrila mine waste dump is situated approximately 2,500 m from the Eastern Jiu River and 1,000 m from the nearest inhabited area (Minei Street, No. 2, Hunedoara County). Geomorphologically, the area displays a hilly landscape shaped by erosive watercourses along syncline flanks; the dump surface is crossed by temporary torrents active during precipitation. Rehabilitation measures provide partial sealing to limit infiltration, and stability analyses indicate the dump is stable at natural moisture content but potentially unstable at saturation — mitigated by the high water-draining capacity of deposited granular material.

3. Materials and Methods

3.1 Drone Survey and Geometric Characterisation

The geometric shape of Branch 4 was determined using LiDAR scanning with a DJI Matrice 350 RTK drone equipped with a DJI Zenmuse L2 LiDAR sensor. Point cloud data were processed using DJI Terra software in the WGS84 coordinate system. The slope areas of Branch 4 are covered with vegetation, a fact confirmed by the resulting 3D point cloud model. [22]

For the present study, Branch 4 of the Petrila Mining Exploitation waste dump was taken into consideration. The determination of its geometric shape was carried out by means of LiDAR scanning, utilizing the high-precision equipment mentioned above. The coordinate system used was WGS 84 (World Geodetic System 1984), and the coordinates of the reference control point are presented in the following table:

Tab. 1. The coordinates of the control point

Check Point Latitude (Y/N)	Check Point Longitude (X/E)	Check Point Altitude (Z/U)
45.4317566°	23.388586°	734 m

3.2 Sample Collection

A number of 12 soil samples were collected from four locations within and adjacent to Branch 4. Three locations (L1–L3) were positioned on the upper plateau of the waste dump, while location L4 outside the dump perimeter served as a geochemical control. From each location, three samples were collected at depths of 30 cm (P1, P4, P7, P10), 50 cm (P2, P5, P8, P11), and 70 cm (P3, P6, P9, P12) below the ground surface.

Tab. 2. Sampling locations and coordinates

Location	Samples	Latitude (N)	Longitude (E)
L1	P_1, P_2, P_3	45.4317566°	23.388586°
L2	P_4, P_5, P_6	45.4320459°	23.3940802°
L3	P_7, P_8, P_9	45.4323699°	23.4011366°
L4 (control)	P_{10}, P_{11}, P_{12}	45.4300583°	23.4070503°

3.3 ICP-OES Analysis

Elemental concentrations (As, Co, Cr, Cu, Fe, Mn, Ni, Ti, Zn) were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Solid samples were digested using aqua regia (HNO_3: HCl = 1:3), a standard procedure for releasing most elements from soil matrices. The resulting solutions were introduced into the plasma via a nebulizer system; dissolved solids exceeding 3% were managed using parallel-path nebulization and a wide-bore torch to prevent blockage. Results are expressed in mg/kg dry weight.

Solid sample digestion

Because solid samples cannot be introduced into the plasma directly, they must be either transferred into the plasma using a solid-sample accessory (e.g., electrothermal vaporization, laser ablation), or they must be dissolved or digested into a solution. The main techniques used to dissolve solids are acid digestion and fusion.

When using fusion for sample preparation, complete digestion takes place. It also results in high solid content. As a result, sample dilution is needed to bring the total dissolved solid content into the working range of the instrument, reducing the method detection limit.

Acid digestion usually involves the dissolution of a sample in a hot acid, or a mixture of hot acids. Heating acids is performed on a hot plate, or by using a microwave digestion system that employs pressurized vessels to produce even higher reaction temperatures.

3.4 X-Ray Fluorescence (XRF) Analysis

In X-ray Fluorescence the processes take place successively: the inner electrons of the sample atoms are expelled due to collisions with the X photons of the primary X-ray source; the electrons in the outer layers occupy the vacancies on the lower layers (K, L, M); as a result of the transitions that take place, energy quanta in the X-ray domain are released and leave the sample in all directions. The energy of the X-ray source is high between 5 and 100keV. Primary X-rays, as the radiation from the source is called, are directed towards the sample under analysis. Characteristic X-rays - specific to the elements of the sample and re-emitted by the sample - leave the sample, containing information that allows the chemical composition of the material (solid or solution) to be determined.

The X-ray Spectrometry method is widely used for the qualitative and quantitative determination of the elemental chemical composition of a sample, especially for inorganic substances (soils, minerals, different type of metals etc.) - mainly in industry. This method is based on the fact that the wavelength of X-radiation is of the same order of magnitude as the interatomic distances in crystal lattices; as a consequence of diffraction and interference, peaks in the intensity of the emerging rays occur.

Bulk elemental oxide composition was determined by X-ray Fluorescence spectrometry (XRF). Primary X-rays expel inner-shell electrons from sample atoms; characteristic secondary X-rays emitted during electronic relaxation are detected and quantified. The technique provides semi-quantitative to quantitative analysis of major and minor oxide fractions (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, MnO, Cr_2O_3, NiO, CuO, ZnO) expressed as weight percentages. XRF complements ICP-OES by providing bulk mineralogical context and detecting elements not easily quantified by wet chemistry. [5]

4. Results

4.1 ICP-OES Results — Trace Metal Concentrations

The results obtained by ICP-OES technique are given below in the Table 3.

Tab. 3. ICP-OES metal concentrations (mg/kg) across sampling points P1–P12. ND = not detected.

Metal (mg/kg)	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}
As	108.7	99.92	ND	4.196	68.53	89.77	6.86	73.91	6.618	48.87	26.74	32.24
Co	11.54	11.71	12.56	9.541	13.52	15.62	10.35	7.98	6.14	8.727	4.578	5.68
Cr	112.4	133.0	57.16	21.66	126.52	137.5	18.58	107.7	20.23	91.05	64.39	65.34
Cu	46.45	ND	27.73	17.62	46.5	46.81	30.58	50.90	18.27	27.68	5.015	6.054
Fe	27950	30100	25400	15180	28740	28070	17590	35050	15520	22960	13080	15190
Mn	471.5	544.3	654.2	412.2	481.1	454.5	68.34	518.9	349.9	220.5	125.4	349.7
Ni	81.73	77.23	90.0	56.70	83.93	85.86	68.34	83.8	48.19	27.62	81.73	14.29
Zn	85.01	85.86	69.71	56.70	75.78	79.82	68.83	90.56	105.5	53.18	85.01	45.22

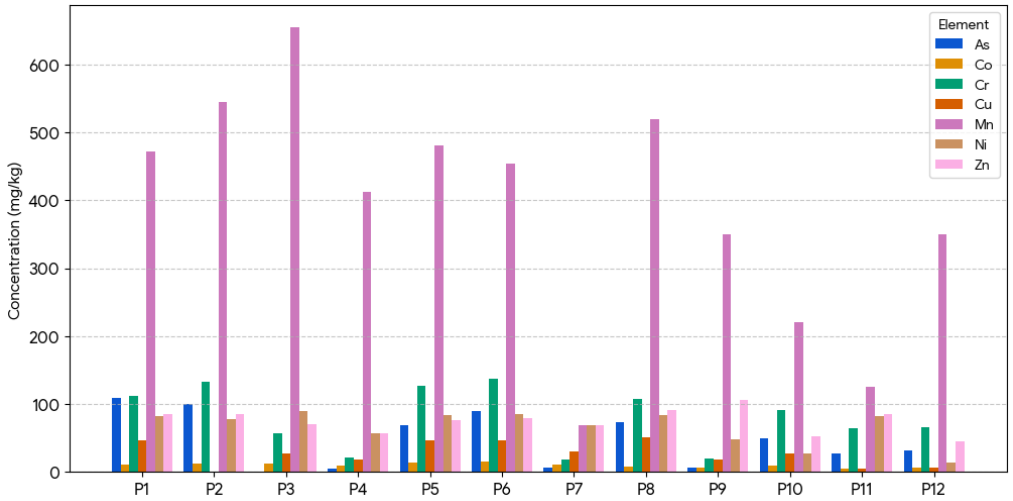

Fig. 2. Heavy metal distribution across sampling points (Excluding Fe)

4.2 XRF Results — Bulk Oxide Composition

XRF analysis reveals a distinct compositional divide between sampling groups. Samples P1–P9 (dump interior) show a stable profile characterised by moderate SiO_2 (42–49%), high Al_2O_3 (22–24%), and elevated Fe_2O_3 (11–17%). In contrast, samples P10–P12 (control zone) transition to a high-silica composition (SiO_2: 57–65%) with significantly reduced Al_2O_3 (15–17%) and Fe_2O_3 (7–13%). CaO is notably elevated in P5 (6.26%), and ZnO shows an anomalous peak in P10 (0.309%).

Tab. 4. XRF bulk oxide composition (wt%) across sampling points P1–P12. ND = not detected.

Oxide	P_1%	P_2%	P_3%	P_4%	P_5%	P_6%	P_7%	P_8%	P_9%	P_{10}%	P_{11}%	P_{12}%
Al_2O_3	23.4	23.2	22.0	22.6	21.9	24.0	23.6	23.4	22.1	17.1	15.3	15.2
SiO_2	44.7	47.0	45.8	43.1	42.7	49.1	45.8	44.6	42.3	57.5	64.3	65.3
Fe_2O_3	15.3	13.9	16.6	17.3	15.7	11.8	15.8	16.5	17.4	12.6	8.47	7.64
CaO	4.33	3.89	5.35	4.70	6.26	4.83	3.23	4.04	5.03	2.94	1.90	1.62
MgO	1.47	1.20	1.46	1.72	1.46	1.60	1.24	1.39	1.62	1.66	1.26	1.25
MnO	0.174	0.141	0.254	0.250	0.218	0.145	0.195	0.155	0.255	0.113	0.090	0.137
Cr_2O_3	0.095	0.141	0.080	0.086	0.143	0.094	0.075	0.070	0.083	0.069	0.099	0.057
NiO	0.049	0.050	0.049	0.056	0.042	0.043	0.036	0.034	0.055	0.022	ND	ND
ZnO	0.022	0.031	0.039	0.046	0.057	0.027	0.045	0.034	0.090	0.309	0.031	0.022

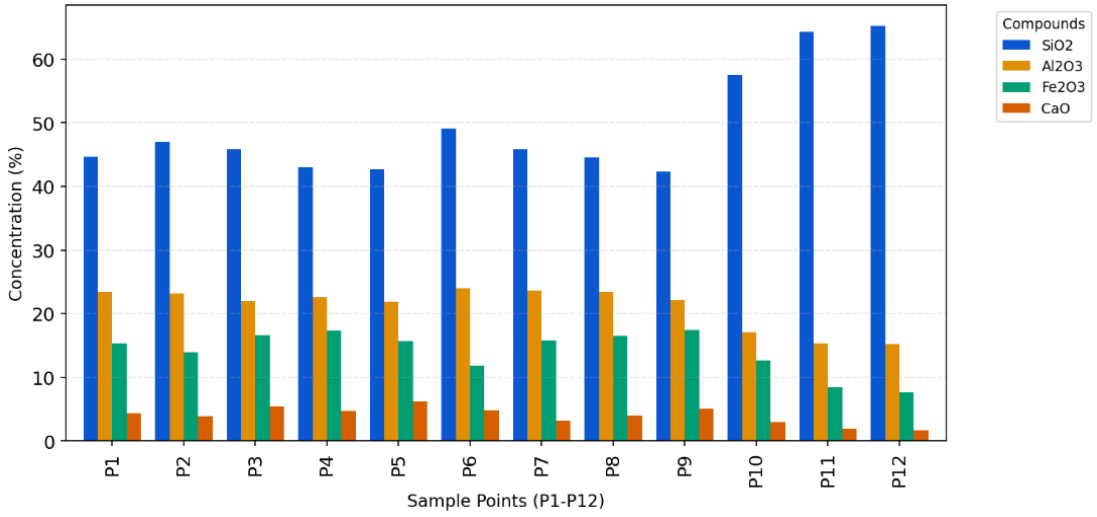

Fig. 3. Chemical composition analysis (Major oxides)

Iron (Fe) Dominance: Fe is the most abundant element across all samples, averaging 22,902 mg/kg. The highest concentrations are found in P8 (35,050 mg/kg) and P2 (30,100 mg/kg). While common in soil, these levels often indicate strong geological or industrial influence.

Manganese (Mn) & Chromium (Cr):

Mn peaks at P3 (654.2 mg/kg). There is a noticeable drop at P7 (68.34 mg/kg), which stands out as an anomaly. Cr shows significant levels in P6 (137.5 mg/kg) and P2 (133 mg/kg), following a similar distribution pattern to Iron in those specific points.

Arsenic (As) concerns: Arsenic levels are notably high in P1 (108.7 mg/kg) and P2 (99.92 mg/kg). These values are significantly higher than the overall average, which may suggest a localized source of contamination. Nickel (Ni) & Zinc (Zn): Both elements show a relatively stable distribution. Ni reaches its maximum in P3 (90 mg/kg), while Zn peaks in P9 (105.5 mg/kg).

Critical Sampling Points:

Hotspots: Samples P1, P2, and P6 are the most heavily loaded with toxic metals (As, Cr, Ni). Cleaner Areas: Samples P11 and P12 show the lowest overall concentrations, suggesting they are further from the contamination source.

5. Discussion

5.1 Interpretation of ICP-OES Results

Analysis of metal concentrations across twelve sampling points (P1–P12) in tailing dumps reveals substantial spatial heterogeneity in metal distribution, with Iron (Fe) constituting the dominant metal species across all locations. Critical hotspots of metal accumulation have been identified at specific sampling points, with point P8 exhibiting the highest overall metal load and elevated concentrations of multiple metals. The data indicates potential environmental and health risks associated with Arsenic (As) contamination at points P1 and P2, requiring immediate attention and remediation strategies.

Overall Metal Distribution Patterns

The analytical results demonstrate that metal concentrations in the tailing dumps vary significantly across the twelve sampling points. Iron dominates the metal composition throughout the site, with concentrations ranging from 13,080 mg/kg at point P11 to 35,050 mg/kg at point P8. The mean Iron concentration across all sampling points is 22,569 mg/kg, representing the primary metal constituent in the tailings.

Secondary metals present in substantial quantities include Manganese (Mn), Chromium (Cr total), and Arsenic (As), though their concentrations are orders of magnitude lower than Iron. The spatial distribution patterns suggest localized accumulation processes

influenced by historical dumping practices, weathering processes, or mineralogical variations within the tailings material.

Iron (Fe) – Dominant Metal

Iron exhibits the highest concentrations across all sampling points, with point P8 recording the maximum value of 35,050 mg/kg. Points P1, P2, P3, P5, and P6 also display elevated Iron concentrations exceeding 25,000 mg/kg. The lowest Iron concentration occurs at point P11 (13,080 mg/kg), which also demonstrates the lowest total metal load among all sampling locations. The consistent presence of elevated Iron levels indicates the ferrous nature of the original ore material processed at the site.

Arsenic concentrations present a critical concern, with points P1 and P2 exhibiting levels of 108.7 mg/kg and 99.92 mg/kg, respectively. Point P8 also records elevated Arsenic at 73.91 mg/kg. Notably, point P3 shows no detectable Arsenic (ND), indicating spatial variability in Arsenic distribution. The elevated Arsenic levels at P1 and P2 represent potential environmental and health hazards, as Arsenic is a known toxic metalloid with stringent regulatory limits in soil environments.

Manganese (Mn) – Moderate to High Levels Manganese concentrations are highest at point P3 (654.2 mg/kg), followed by points P2 (544.3 mg/kg) and P8 (518.9 mg/kg). The lowest Manganese concentration is observed at point P7 (68.34 mg/kg). The elevated Manganese at P3 suggests localized enrichment processes distinct from the Iron-dominated pattern observed elsewhere.

Chromium (Cr total) – Variable Distribution

Total Chromium displays considerable variability, with maximum concentrations at point P6 (137.5 mg/kg) and point P2 (133.0 mg/kg). Lower concentrations occur at points P4 (21.66 mg/kg), P7 (18.58 mg/kg), and P9 (20.23 mg/kg). This variability suggests heterogeneous source materials or differential weathering and leaching processes affecting Chromium mobility.

Nickel (Ni) – Significant Presence

Nickel reaches its maximum concentration at point P3 (90.0 mg/kg), with consistently elevated levels at points P1, P2, P5, P6, P8, and P11 (ranging from 77.23 to 85.86 mg/kg). The minimum Nickel concentration is recorded at point P12 (14.29 mg/kg), indicating spatial segregation of Nickel-bearing materials.

Other Metals (Co, Cu, Ti, Zn)

Cobalt (Co), Copper (Cu), Titanium (Ti), and Zinc (Zn) are present at lower concentrations compared to the metals discussed above. Copper shows non-detectable levels at point P2, while Titanium is not detected at points P3 and P9. These trace metals exhibit moderate spatial variability, with concentrations generally ranging from single digits to low hundreds of mg/kg.

The ICP-OES dataset reveals a multi-element contamination signature that is spatially heterogeneous and depth-dependent. Iron dominates the geochemical profile at all locations, consistent with the high pyritic content of Jiu Valley coal seams (average combustible sulphur 2.83%). Fe concentrations across the dump interior (15,180–35,050 mg/kg) significantly exceed background levels in uncontaminated Romanian soils (typically 15,000–25,000 mg/kg), indicating accumulation of pyrite oxidation products. The highest Fe value at P8 (35,050 mg/kg) coincides with elevated As (73.91 mg/kg), Cr (107.7 mg/kg), and Cu (50.90 mg/kg), suggesting this location represents a convergence point for multiple contamination pathways, possibly associated with preferential leaching or localised waste deposition.

Arsenic is the most toxicologically critical element identified. The maximum concentrations at P1 (108.7 mg/kg) and P2 (99.92 mg/kg) exceed the Romanian alert threshold for industrial soils (50 mg/kg, Order 756/1997) and approach or exceed European reference values for contaminated land. Arsenic in coal-associated wastes is typically bound to pyrite or arsenopyrite; upon oxidative weathering, it is released as arsenate or arsenite, both of which are highly mobile under mildly acidic to near-neutral conditions. The complete absence of detectable As at P3, despite elevated Ni and Mn at the same location, points to a lithological discontinuity or a reducing micro-environment that immobilises arsenic through co-precipitation with iron oxides or sulphides [5].

Chromium concentrations at P2 (133.0 mg/kg) and P6 (137.5 mg/kg) are also notable: these exceed Romanian background values (50–90 mg/kg) and warrant attention due to the potential presence of Cr (VI), a carcinogenic form produced under oxidising conditions. Nickel and cobalt show moderate but consistent elevation across dump locations relative to the control, reflecting their association with clay minerals and organic matter in coal shales. Manganese at P3 (654.2 mg/kg) is exceptionally high and not mirrored at adjacent locations, suggesting a discrete manganese-rich layer or inclusion within the sampled stratum. Zinc values, while not alarming in isolation (45–105 mg/kg), are consistently elevated above background across all dump locations, contributing to cumulative contamination load.

Comparison with the control samples (P10–P12) confirms that the dump material is geochemically distinct from surrounding natural soil. Control As values (26–49 mg/kg) are substantially lower than P1–P2, and Fe, Cr, Ni, Cu, and Co are all reduced, validating the sampling design. The depth gradient across the three sampling levels (30–70 cm) does not show a consistent increasing or decreasing trend, implying that contaminant distribution reflects heterogeneous waste composition rather than systematic downward leaching — though leachate-driven vertical transport cannot be excluded without pore water analysis.

5.2 Interpretation of XRF Results

The XRF compositional data furnish a crucial mineralogical framework for the interpretation of the ICP-OES trace metal results. The fact that SiO_2 (42–49%), Al_2O_3 (22–24%), and Fe_2O_3 (11–17%) are the most common minerals in dump samples P1–P9 shows that these are aluminosilicate-rich coal shale matrices with a lot of iron minerals. This composition aligns with the clay shale interbeddings documented in seams 3–14 of the Petrila field. The high Al_2O_3 content indicates a significant presence of kaolinite and illite minerals, which affects the ability of metals to be absorbed: aluminosilicate clay surfaces can absorb trace metals, making them less mobile, but they can also become a source of pollution if the pH changes. The Fe_2O_3 content in dump samples (11.8–17.4%) is much higher than in control samples (7.64–12.6%), and it also has a positive relationship with ICP-OES Fe concentrations. This confirms that iron enrichment is a defining feature of the waste material, attributable both to primary pyrite in the raw coal shale and to secondary goethite and ferrihydrite formed during oxidative weathering. Iron oxyhydroxide phases are known to sequester arsenic and other trace metals via surface adsorption and co-precipitation; the high Fe_2O_3 at P8 thus explains the concurrent elevation of As and other metals at this point as a consequence of enriched sorptive surfaces or partial dissolution of Fe-oxyhydroxide coatings under locally acidic conditions. The control group's move to high SiO_2 (57–65%) and low Al_2O_3 (15–17%) and Fe_2O_3 (7–13%) is similar to the geology of the Petrosani Basin, which is mostly made up of Paleocene–Eocene flysch sediments with more quartz. This stark difference confirms the geochemical boundary between waste material and native soil, and it also shows that the high levels of metals in dump samples come from people, not from natural lithogenic background [1].

The unusually high level of ZnO in P10 (0.309%) needs to be looked at more closely. P10 is outside the dump's perimeter and is considered a control. However, the Zn anomaly suggests that zinc-bearing leachate from the dump has moved sideways or that there was already a natural zinc enrichment in this area. Since the ZnO values in other control samples (P11: 0.031%, P12: 0.022%) are in

line with background levels, the P10 anomaly is more likely due to contamination moving from the dump, possibly through surface runoff that follows topographic gradients. This discovery highlights the necessity of monitoring beyond the immediate confines of the dump. The 6.26% CaO enrichment at P5 compared to the 3.2–5.4% average for the dump may be due to carbonate-rich material that came from calcite or siderite inclusions in certain coal seams or from using lime-based neutralization amendments in the past. High levels of CaO can help balance out acidity in the area and make metals less mobile. This might explain why the As concentrations at P5 are relatively low, even though P5 is close to P6, which is a high-Cr, high-Ti anomaly.

When stoichiometric conversion is used, the Cr_2O_3 XRF values and the ICP-OES Cr concentrations are mostly the same. This means that the two methods are valid and that chromium is mostly found in its trivalent, oxide-associated form.

5.3 Metal Recovery Potential from Tailing Dumps

The mining industry around the world has always made a lot of waste, which is kept in tailings dams and waste heaps (sterile dumps) [17]. These sites were once thought of as environmental liabilities, but they are now being looked at as "secondary resources." As high-quality primary ores run out, getting metals and coal out of waste is becoming a strategic need for long-term growth. [2] Aside from the environmental risk, the geochemical characterization presented here brings up an important question about resource valorization: is it possible to economically recover the metals found in the Petrila waste dump. The reprocessing of mine tailings and waste dumps for secondary metal recovery is a growing field, [10] driven by the rising demand for critical raw materials and advances in metallurgical technology [11,25]. International experience shows that coal-associated waste dumps can be a second source of iron, zinc, nickel, cobalt, chromium, and sometimes rare earth elements (REE), especially when the grades of primary ore are going down [5,16,19]. Iron is the most common metal that can be recovered at Petrila, with concentrations ranging from 13,080 to 35,050 mg/kg (1.3–3.5 wt%). These concentrations are lower than what is usually found in iron ore grades (about 50–65% Fe), but they are high enough to think about using magnetic separation of iron-bearing phases (magnetite, goethite) as a pre-concentration step [21], especially since Branch 4 has a lot of material. Magnetic separation has been successfully employed to extract iron from coal fly ash and mine tailings in various case studies, producing iron-enriched concentrates suitable for steelmaking or as pigments [20,24].

The concentrations of zinc (45–105 mg/kg) and nickel (14–90 mg/kg) at Petrila are within a range that makes hydrometallurgical extraction technically possible, especially if acid leaching is used to dissolve metal-bearing silicate and carbonate phases [12]. Using sulfuric acid, nitric acid, [15] or chelating agents like EDTA in acid leaching can get back a lot of metals [9,13] (more than 80%) from tailings with similar geochemical profiles [8]. The ICP-OES data show that the dump's interior (P1–P9) has a fairly even distribution of Zn, Ni, and Co. This suggests that these metals may be better suited for batch extraction than selective extraction [14]. After leaching, solvent extraction or ion exchange could be used to separate and concentrate certain metals from pregnant leach solutions [2] Arsenic poses a dual challenge: it is a contaminant requiring careful stabilization and management, although recovery may be technically feasible in specialized processing circuits [18].

More practically, the stabilization of arsenic through precipitation as ferric arsenate (scorodite) or co-precipitation with iron oxyhydroxides is a well-known method that turns mobile arsenic into a solid that doesn't leach easily [2]. Because the Petrila waste has a lot of iron in it, it might be possible to do in-situ geochemical stabilization using iron amendment and then lime addition to raise the pH at a low cost [17]. It is harder to get chromium back because Cr(III) is more common in aluminosilicate minerals, which need harsh digestion conditions to dissolve. The XRF Cr_2O_3 distribution suggests that Cr(VI) is present, which means that it is both a higher health risk and a resource that could be recovered. Electrokinetic remediation methods work especially well for moving Cr(VI) and other charged particles out of silty matrices with low permeability. They have also been shown to work on a small scale for both cleaning up and recovering metals at the same time. An integrated processing approach for the Petrila tailing dump might follow a sequential flowsheet: (1) physical pre-concentration by magnetic separation to recover iron-bearing phases; (2) acid leaching of the non-magnetic fraction to dissolve Zn, Ni, Co, and Cu; (3) selective precipitation or solvent extraction to recover individual metal fractions; (4) arsenic stabilisation and disposal of the As-bearing residue; and (5) neutralisation and revegetation of the detoxified tailings [3], European environmental policy's waste hierarchy principles and the EU Critical Raw Materials act both support this approach [25,4]. The EU Critical Raw Materials Act encourages getting strategic metals from secondary sources, like mining waste [7].

5.4 Spatial Contamination Hotspots and Remediation Priorities

Combining the ICP-OES and XRF datasets, a clear spatial prioritisation emerges. Point P8 is the main place where remediation and recovery happen. It has the most Fe, high As, Cr, and Cu, and high Fe_2O_3 by XRF, all of which show that the area has been heavily oxidized and metals have built up. Points P1 and P2 have the highest As risk and should be the first to be contained. Points P5 and P6 have the most Cr, so they need to be checked for Cr(VI) speciation. The control point anomaly at P10 (ZnO: 0.309%) suggests that contaminants have already moved beyond the dump's edge. This means that a downgradient monitoring network needs to be set up to check how leachate moves to groundwater and surface water bodies. The dump is only 2,500 meters from the Eastern Jiu River, so there is a real risk of metal export on a catchment scale. This needs to be looked at under the worst-case precipitation scenarios. Key thresholds for less sensitive soils (mg/kg dry matter): Key thresholds for less sensitive soils (mg/kg dry matter):

Tab. 5 Data provided for heavy metals

Metal	Normal value	Alert threshold	Intervention threshold
As	5	25	50
Co	15	100	250
Cr (total)	30	300	600
Cu	20	250	500
Mn	900	2000	4000
Ni	20	200	500
Zn	100	700	1500

Analysing the data provided for heavy metals

-Arsenic (As) – the only major issue: Severe exceedances (above intervention threshold 50 mg/kg): P1 (108.7), P2 (99.92), P6 (89.77).

- Exceeded alert threshold (25 mg/kg): P5 (68.53), P8 (73.91), P10 (48.87)

-Under alert: P4 (4.2), P7 (6.86), P9 (6.618), P11 (26.74 – slightly above alert), P12 (32.24 – above alert), P3 (ND).

- Chromium (Cr): Maximum 137.5mg/kg (P6) → no exceedances (below 300mg/kg alert and 600mg/kg intervention).
- Nickel (Ni): Maximum ~90mg/kg (P3, P5, P6) → no exceedances (below 200mg/kg alert).
- Copper (Cu): Maximum 50.9mg/kg (P8) → no exceedances (well below 250/500mg/kg).
- Cobalt (Co): Maximum 15.62mg/kg (P6) → no exceedances (below 100/250mg/kg).
- Manganese (Mn): Maximum 654.2mg/kg (P3) → no exceedances (below 2000/4000mg/kg).
- Zinc (Zn): Maximum 105.5mg/kg (P9) → no exceedances (below 700/1500mg/kg).
- Iron (Fe): Very high values (13.000–35.050 mg/kg), typical for mining waste, but without a regulated threshold.

Main problem: Arsenic (As) shows significant exceedances of the intervention threshold in samples P1, P2 and P6. These samples indicate a high risk of leaching and secondary contamination (infiltration waters, adjacent soils). The remaining metals (Cr, Ni, Cu, Co, Mn, Zn) are within acceptable limits for tailings dumps / less sensitive use. High-risk samples: P1, P2, P6 (and partly P5, P8 due to As).Relatively more acceptable samples: P4, P7, P9, P12 (low values for most metals).

Mandatory monitoring: Analysis of leachate (infiltration waters) and surrounding soils, especially in areas with high As. Management measures: Covering with vegetation, amendments (e.g. lime for stabilization), waterproofing the base of the dump or controlled recultivation, according to the extractive waste management plan.

Main problem: Arsenic (As) shows significant exceedances of the intervention threshold in samples P1, P2 and P6. These samples indicate a high risk of leaching and secondary contamination (infiltration waters, adjacent soils). The remaining metals (Cr, Ni, Cu, Co, Mn, Zn) are within acceptable limits for tailings dumps / less sensitive use. High-risk samples: P1, P2, P6 (and partly P5, P8 due to As). Relatively more acceptable samples: P4, P7, P9, P12 (low values for most metals).

Mandatory monitoring: Analysis of leachate (infiltration waters) and surrounding soils, especially in areas with high As. Management measures: Covering with vegetation, amendments (e.g. lime for stabilization), waterproofing the base of the dump or controlled recultivation, according to the extractive waste management plan.

6. Conclusion

This study characterised the heavy metal contamination profile of Branch 4 of the Petrila coal mine waste dump using ICP-OES and XRF analysis of twelve samples across four locations and three depths. The principal findings are as follows:

Iron is the predominant metal (13,080–35,050 mg/kg), directly reflecting pyrite-rich coal shale composition and confirming AMD-driven metal mobilisation. Arsenic poses the most critical contamination risk, with P1 and P2 exceeding Romanian industrial soil alert thresholds. Point P8 is the primary remediation hotspot, combining peak Fe, As, Cr, and Cu values. XRF data confirm a sharp geochemical boundary between dump material (high Al_2O_3, Fe_2O_3) and background soil (high SiO_2), validating the sampling design. The ZnO anomaly at control point P10 indicates lateral contaminant migration beyond the dump boundary, requiring extended monitoring. Spatial heterogeneity across the dump suggests discrete waste inputs, mandating site-specific rather than uniform remediation strategies.

From a resource perspective, the characterised dump contains recoverable quantities of iron, zinc, nickel, cobalt, and copper amenable to hydrometallurgical processing. An integrated sequential flowsheet — combining magnetic separation, acid leaching, solvent extraction, and As stabilisation — represents a technically viable approach that could partially offset remediation costs while recovering secondary metal resources in alignment with EU critical materials policy.

Despite the potential, several hurdles remain:

- Low Concentrations: The energy required to process large volumes of waste for small amounts of metal can be high;
- Chemical Complexity: Tailings often contain hazardous elements like arsenic or mercury that must be managed during recovery;
- Regulatory Frameworks: In many countries, waste heaps are legally classified as "waste," making it difficult to obtain mining permits for them.
-

Acknowledgments

This work was carried out through the “Nucleu” Program within the National Plan for Research, Development and Innovation 2022–2027, with the support of the Ministry of Education and Research – National Research Authority, project no. 23 32 02 01, as well as Installations and Special Objectives of National Interest – Research, Development and Testing Range for Explosive Materials, Flammable/Toxic Substances, Explosion-Proof Equipment, and Training of Intervention Personnel for Toxic/Explosive Environments (IOSIN PCDIEx).

References

1. Zhao P, Chen J, Liu T, Wang Q, Wu Z, Liang S (2023). Heavy metal pollution and risk assessment of tailings in one low grade copper sulfide mine. Front. Environ. Sci. 11:1132268. https://doi.org/10.3389/fenvs.2023.1132268
2. Escarré J, Lefèbvre C, Raboyeau S, et al. (2010). Heavy Metal Concentration Survey in Soils and Plants of the Les Malines Mining District (Southern France). Water Air Soil Pollut. https://doi.org/10.1007/s11270-010-0547-1
3. Weiquan L, Wang, Zhan Z, Luo J, Zhou D, Lei Y (2025). Extraction of valuable metals from acid mine drainage by an electrochemically activated limestone system. https://doi.org/10.1038/s41467-025-62045-w
4. Zhou T (2023). Remediation of metal mines heavy metal water pollution. Master thesis, University of British Columbia, Canada.
5. Remeteiová D, Ružicková S, Heželová M, Pikna L (2023). Utilization of Extraction Procedures for Evaluating Environmental Risk from Waste Materials. Toxics 11, 678. https://doi.org/10.3390/toxics11080678
6. Murarescu O, Radulescu C, Dulama ID, et al. (2022). Comprehensive Assessment of Tailing Dumps' Impact on Water Quality. Int. J. Environ. Res. Public Health 19, 14866. https://doi.org/10.3390/ijerph192214866.
7. Aburto-Hole J, Pincheira PBI, Acuna P, et al. (2026). Sustainable Metal Recovery from Untreated Mining Tailings by Direct Electrodeposition. Environments 13, 135.

References

8. Manea F, Ghicioi E, Suvar MC, Prodan M, Pupazan DG, Florea D, Simon-Marinica BA, Laszlo R, Ursut GA, Ilia G. Combustion Behavior of Flexible Polyurethane Foam in Oxygen-Enriched Atmosphere and Its Implications in the Development of a Fire in an ICU for COVID Patients—Case Study. Fire. 2026; 9(1):33. https://doi.org/10.3390/fire9010033
9. Araujo FSM, Taborda-Llano I, Nunes EB, Santos RM (2022). Recycling and Reuse of Mine Tailings: A Review. Geosciences 12, 319. https://doi.org/10.3390/geosciences12090319
10. Keskin T, Yilmaz E, Sari M, Tugrul K, Cao S (2026). Reuse and valorization practices of mine tailings: a review. Clean Technol. Environ. Policy 28:103.
11. Abbadi A, Mucsi G (2024). A review on complex utilization of mine tailings: Recovery of rare earth elements. J. Environ. Chem. Eng. 12, 113118.
12. Simon Marinica AB, Gaman GA, Pupazan D, Ghicioi E, Manea F, Suvar MC, Prodan M, Suvar NS, Florea GD, Laszlo R. Development of a Programmable System Used for the Preparation of a Mixture of Flammable/Explosive Gases. Automation. 2024; 5(3):246-258. https://doi.org/10.3390/automation5030015.
13. Dunca EC, Ioniță MF, Varga LA, et al. (2025). Assessment of Energy Recovery Potential of Biomass from Non-Productive Lands in the Jiu Valley. Sustainability 17, 9380.
14. Na H, Eom Y, Yoo K, Alorro RD (2024). A review on the reprocessing of sulfide tailings for resource recovery and AMD prevention. Minerals Engineering 218, 109025.
15. Grieco G, Sinojmeri A, Bussolesi M, et al. (2021). Environmental Impact Variability of Copper Tailing Dumps in Fushe Arrez (Northern Albania). Sustainability 13, 9643.
16. Faragan C, Grail BM, Johnson B (2017). New approaches for extracting and recovery metals from mine tailings. Minerals Engineering 106, 71–78.
17. A.B. Șimon-Marinică, E. Ghicioi, N. I. Vlasin, M. C. Șuvar, G. D. Florea, (2019). Visualization and record methods for the initiation of air-methane explosive atmospheres, The 19th International Multidisciplinary Scientific Geo Conference – SGEM 2019 Conference Proceedings, 1165- 1171.
18. Florea, G.D., Ghicioi, E., Vlasin, N.I. and Vass, Z., 2022. Release of overpressures in computational simulations of air-methane explosions. In MATEC Web of Conferences (Vol. 373, p. 00043). EDP Sciences.
19. Kursunoglu S (2025). A review on the recovery of critical metals from mine and mineral processing tailings. J. Sustainable Metallurgy.
20. Maltrana V, Morales J (2023). The Use of Acid Leaching to Recover Metals from Tailings: A Review. Metals 13, 1862.
21. Kim MJ, Kim TS (2011). Extraction of Arsenic and Heavy Metals from Contaminated Mine Tailings by Soil Washing. Soil Sediment Contam. 20(6), 631–648.
22. Point Zero – Ideogram Studio – Arheco Arhitectura Economică (2024). Development of the Urban Plan for Protected Built Areas and the Local Urban Regulation related to the Petrila Mine Area. Contract no. 9769/22.04.2024. Beneficiary: Hunedoara County Council.
23. Lottermoser, B. G. (2010). Mine Wastes: Characterization, Treatment and Environmental Impacts.
24. European Commission. (2023). Study on the Critical Raw Materials for the EU.