

Soil and Vegetation Pollution from an Abandoned Mining Area Situated in Hunedoara County, Romania

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The soils situated near the abandoned mines are highly polluted with metals due to the discharge and dispersion of mine waste into nearby air, water (surface and groundwater) and soil. Heavy metals may be transferred to humans through ingestion, inhalation or dermal absorption and can produce serious health problems affect the nervous, endocrine and immune systems, hematopoietic function and cellular metabolism. This paper investigates the presence of metallic elements from fourteen soil samples (seven sampling points) and thirty-six vegetation samples (different types of leaves, plants, roots and tree barks). The samples were collected from six different sites located in an abandoned mining area and from a point (blank sample) located 5 km in the SV direction of the quarry. The results obtained for soil samples show an overrun of the alert and / or intervention threshold for the following metals: arsenic, cadmium, cobalt, copper, manganese, nickel, lead and zinc. The analytical investigation for vegetation samples indicated that concentration for calcium, magnesium, cadmium, chromium, manganese, nickel, lead, zinc were situated over the normal range in some samples. The analytical investigations were performed by optical emission spectrometry (ICP-OES). The study's conclusion indicates that, as result of soil acidic pH and high mobility of some metals, metallic elements migrate from soil to vegetation.

Keywords: metals, mining site, pollution, soil, vegetation

Pollution caused by environmental contamination with heavy metals has now become a global issue. Due to their properties, heavy metals may cause adverse effects on environmental components. These elements do not decompose but *bio-accumulate* in plants, animals and the environment, which makes toxins level to grow in these organisms over time, along with the toxicity and risk for local ecosystems [1-3].

Mining exploitations represent areas of potential risk of environmental pollution by toxic metals, both by accidental spillage of mine waters, acidic waters with high content of metals, as well as mining waste deposits where there may be infiltrations to groundwater and / or surface water. Even in the case when mining is closed for a long time, metal pollution can continue [4-6].

Soil pollution with heavy metals is a problem both at national and international level, affecting a large number of sites but also soils from mining areas in the vicinity of mines are heavily polluted with heavy metals. The soil characteristics (composition, texture, pH) in the adjacent area to mining are very important. A clay soil will retain the metals, embedding them in its structure, while sandy soil will allow their migration to the underground water. Soil pH also has a decisive role, as a basic soil will immobilize the metals, while an acidic pH soil will allow their mobility [7-10].

In soil, metals can be found as metallic ions bound in soluble inorganic form, they can form soluble metal complex combinations or with organic compounds, precipitates or insoluble compounds such as oxides, carbonates or hydroxides, or they can form silicates. Anthropogenic activities, such as mining activities, can generate contamination on extended areas of soil, surface water, groundwater, and implicit vegetation [11, 12].

Heavy metals accumulation in plants is dependent on the heavy metals content in soil and water, with serious effects on human health. Many plant species absorb contaminants from soil such as lead, cadmium, chromium, arsenic [13, 14].

Based on this property of plants to bioaccumulate the essential metals necessary for growth (iron, manganese, zinc, copper, magnesium, molybdenum, nickel), phyto-extraction, representing a phytoremediation procedure, can be used to remove heavy metals from polluted soil. However, essential nutrients for plants can become toxic at high concentrations. At the same time, metals which do not have a known biological function (cadmium, chromium, lead, cobalt, silver, mercury) and which prove to be toxic by bioaccumulation can also accumulate [15].

Contamination of soil, water and vegetation with metals can affect human health due to penetration into the food chain (terrestrial and aquatic flora and fauna). Effects on human health mainly include allergies, but can also severely affect the kidneys, the heart, the reproductive system [16-19]. Arsenic can be dangerous for humans and animals when ingested in fine particles or when consumed in contaminated waters [20, 21].

The purpose of this paper is to present the impact of a decommissioned mining area, strongly polluted with metals, located in the Certej Valley, Hunedoara County, Romania, on the vegetation and the soil located in the immediate vicinity of an abandoned mining quarry and of sterile mining waste dumps. Soil samples and vegetation samples were collected and the content of metals (Al, As, Ca, Cd, Cr, Co, Cu, Fe, Mn, Mg, Ni, Pb, Zn) was determined by inductively coupled atomic emission spectrometry.

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Table 1
GPS COORDINATES OF SOIL AND VEGETATION SAMPLING POINTS

Nr. crt.	GPS Coordinates	Sample type / sample indicative	Observations
1	45° 59.431' 023° 00.835'	soil (S1) S1/1: 0-10cm S1/2: 30-40cm vegetation (V1a + V1d)	- Sampling point situated at about 100 m from the Coranda pit in the southern direction
2	45° 59.410' 023° 00.697'	soil (S2) S2/1: 0-10cm S2/2: 30-40cm vegetation (V2a + V2g)	- Sampling point situated at about 50 m from the South Dump in the eastern direction
3	45° 59.523' 023° 00.219'	soil (S3) S3/1: 0-10cm S3/2: 30-40cm vegetation (V3a + V3d)	- Sampling point located in the immediate vicinity of Coranda pit at about 50 m in the western direction
4	45° 59.752' 023° 00.515'	soil (S4) S4/1: 0-10cm S4/2: 30-40cm vegetation (V4a + V4d)	- Sampling point situated in the immediate vicinity of North dump at about 50 m in the western direction
5	45° 59.600' 023° 00.880'	soil (S5) S5/1: 0-10cm S5/2: 30-40cm vegetation (V5a + V5f)	- Sampling point situated at about 50 m from the Coranda pit in the eastern direction
6	45° 59.410' 022° 59.722'	soil (S6) S6/1: 0-10cm S6/2: 30-40cm vegetation (V6a + V6f)	- Sampling point on Baiaga Spring situated upstream of the confluence with Ciongani Spring and downstream of the confluence with career water;
7	45° 57.263' 022° 57.863'	soil (M) SM/1 : 0 -10 cm SM/2 : 30-40 cm vegetation (Vm1 + Vm5)	- Blank sample, sampling point situated at 5 km from Coranda pit the in the south-western direction

Experimental part

Sample collection and preparation

Soil and vegetation samples were taken from the Certej Basin (Hunedoara County). Seven (6 samples and a control sample) soil samples were collected, each on 2 depths (0-10 cm and 30-40 cm), as well as 36 vegetation samples, from 7 harvest points. The location of harvesting points is shown in figure 1, while GPS coordinates and sample indices are shown in table 1.

Soil samples were collected according to the standards in force [22].

In order to assess the soil pollution, seven pedological profiles were established on two depths: 0-10 cm and 30-40 cm. The blank sample was selected at a distance of about 5 km in the direction of SV of Coranda quarry, being

located in a sufficiently remote area, considered unpolluted by the mining activity carried out for decades in the selected area. Sampling was performed with the Buerkle soil sampling device.

Vegetation samples were collected from the immediate vicinity of the soil sampling point, aiming at harvesting various species (leaves; root plants, stems and leaves; tree bark, buds). All vegetation (except the tree bark and a species of *Milium effusum*) was young, freshly bred. The collected samples were stored in plastic bags. At the receipt of the samples in the laboratory, the vegetation was sorted based on species and parts of the plants.

The separation on species was done with the support of two botanical specialists who established the Latin name of the samples (table 2).

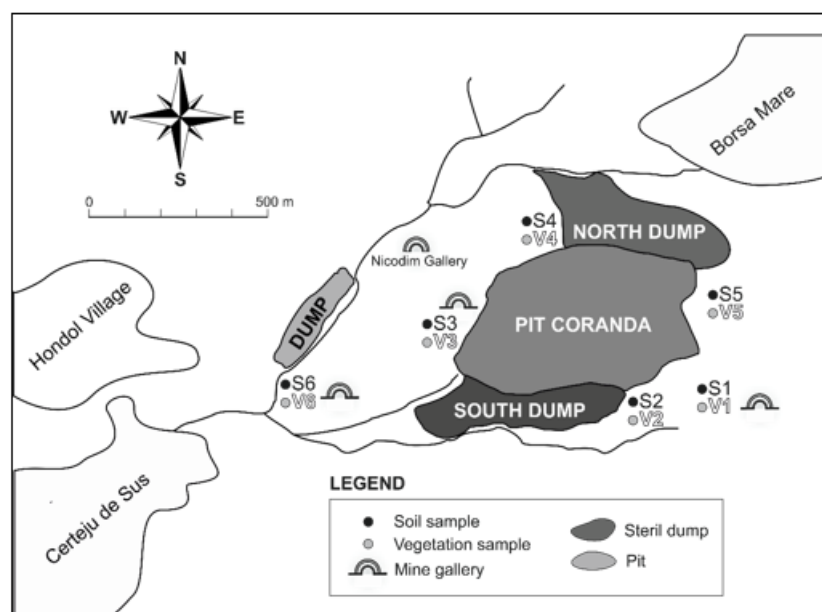


Fig. 1. Location of soil and vegetation sampling points

No	Flora Species	Sample type	Vegetation code sample
1	Apple tree (<i>Malus domestica</i>)	leaves, buds, bark	Vm1 (leaves, buds) Vm5 (bark) V5f (leaves)
2	Ash tree (<i>Fraxinus excelsior</i>)	branch, leaves	Vm2 (branch, leaves)
3	Birch tree (<i>Betula sp.</i>)	bark	V3c
4	Beech tree (<i>Fagus sp.</i>)	leaves, twigs, buds, bark	V3b, V4d, V5c (leaves) V5b (buds) V5e (bark)
5	Clover (<i>Trifolium</i>)	leaves	V2f
6	Cypress spurge (<i>Euphorbia cyparissias</i>)	roots, stem, leaves	V2c
7	Couch grass (<i>Elymus repens</i>)	whole plant	Vm4
8	Dandelion plant (<i>Taraxacum officinale</i>)	stem, flowers	V2a
9	Dry vegetation		V5d
10	Grass (<i>Poaceae sp.</i>)	whole plant	V1b, V6a
11	Hornbeam tree (<i>Carpinus betulus</i>)	leaves, bark	V1d, V2g, V4c (bark) V2b, V4a, V6c (leaves)
12	Maple tree (<i>Acer sp.</i>)	leaves, bark	V6b (leaves) V6e (bark)
13	Millet grass (<i>Milium effusum</i>)	whole plant	V3a, V5a
14	Moss (<i>Hypnum cupressiforme</i>)	whole plant	V3d, V4b
15	Patience dock (<i>Rumex patientia</i>)	leaves	V1a
16	Raspberry plant (<i>Rubus idaeus</i>)	leaves	V6f
17	Small spikenard (<i>Aralia racemose</i>)	branch, fruits	Vm3
18	Stinging Nettle (<i>Urtica dioica</i>)	whole plant	V6d
19	Strawberry plant (<i>Fragaria ananassa</i>)	stem, leaves, roots	V2e
20	Thyme plant (<i>Thymus vulgaris</i>)	roots, leaves, stem	V2d, V1c

Table 2
SPECIES AND PARTS
OF SAMPLED
VEGETATION

Analytical procedures

Soil samples

For the determination of the metals total content, the soil samples were air-dried, milled, sieved and homogenized, retaining the fraction of less than 150 μm for analysis. About 2 g of soil were weighed in Berzelius beakers, a mixture of 7 mL HNO_3 and 21 mL water was added and it was mineralized in open system until the remaining liquid had cleared. The mixture was filtered, washed with distilled water and the obtained filtrate was collected in a 50 mL volumetric flask [23]. The solution thus obtained was used for the determination of metals by inductively coupled plasma optical emission spectrometry.

Vegetation samples

Vegetation samples were dried at room temperature for 2 weeks in an environment protected from contamination. After drying, the samples were finely milled and about 1 g was weighed for metal analysis. Over the vegetation sample placed in a 100 mL Berzelius beaker, 10 mL of HNO_3 and 2 mL of H_2O_2 - ultra-pure reagents were added. The beakers covered with watch glasses were

left for 16 h at room temperature in order to destroy organic matter (cold mineralization). The next step consisted of hot mineralization; the samples were mineralized on a sand bath until the remaining liquid became clear. The samples were filtered and brought to a 25 mL volumetric flask, the remaining residue was washed with ultra-pure water and the resulting water was collected in the volumetric flask.

The vegetation metal content was determined by inductively coupled plasma optical emission spectrometry using ICP-EOS Optima 5300 DV Perkin Elmer equipment.

Determination of metal contents

In the case of vegetation samples, 13 metallic elements were analyzed, namely As, Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, metals for which literature studies indicate normal ranges of concentration. In the soil samples, 10 metals were analyzed: As, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb and Zn. The Al, Ca and Mg content was not determined because they exist in high concentrations in the natural soil structure (e.g. aluminosilicates).

Indicator	Blank sample			Reference values for soils with sensitive uses			Toxic soil for plants [28]
	UM	SM/1	SM/2	NV	AT	IT	
pH	pH units	4.81	4.68	-	-	-	-
As	mg/kg	7.69	6.59	5	15	25	20
Cd	mg/kg	1.27	1.19	1	3	5	3 ÷ 8
Cr	mg/kg	29.07	32.16	30	100	300	75 ÷ 100
Co	mg/kg	8.74	8.87	15	30	50	25 ÷ 50
Cu	mg/kg	70.48	68.74	20	100	200	60 ÷ 125
Fe	mg/kg	11584	11046	-	-	-	-
Mn	mg/kg	1044	871	900	1500	2500	1500 ÷ 3000
Ni	mg/kg	26.23	29.75	20	75	150	100
Pb	mg/kg	52.65	48.80	20	50	100	100 ÷ 400
Zn	mg/kg	105.8	98.12	100	300	600	70 ÷ 400

NV: Normal Value; AT: Alert threshold; IT: Intervention threshold

Table 3
RESULTS OF PHYSICO-CHEMICAL ANALYZES FOR THE BLANK SAMPLE

Table 4
PHYSICO-CHEMICAL CHARACTERIZATION OF S1-S6 SOLID PROFILES

Dm	UM	S1/1	S1/2	S2/1	S2/2	S3/1	S3/2	S4/1	S4/2	S5/1	S5/2	S6/1	S6/2
pH	pH units	7.06	6.86	4.03	3.89	3.62	3.74	5.61	5.79	3.65	3.72	7.04	7.00
As	mg/kg dm	16.1	15.1	24.5	5.54	121	119	77.9	86.1	35.6	38.7	51.7	43.1
Cd	mg/kg dm	1.56	1.35	1.91	1.76	4.21	3.89	3.49	3.33	1.04	0.53	11.4	6.53
Cr	mg/kg dm	45.9	31.9	39.2	54.9	73.6	62.2	17.3	17.8	5.44	4.51	25.4	26.2
Co	mg/kg dm	18.9	14.8	12.8	33.4	25.6	19.4	3.61	4.36	0.86	0.82	69.8	79.7
Cu	mg/kg dm	44.9	37.8	44.8	14.8	91.9	88.2	20.4	14.9	15.3	10.5	378	305
Fe	mg/kg dm	18629	16232	16277	16515	21862	19970	13663	12516	8494	8403	23439	22635
Mn	mg/kg dm	1771	1475	1459	1404	1628	1571	143	266	288	282	6218	3167
Ni	mg/kg dm	40.3	18.3	59.6	50.4	610	565	11.3	12.2	3.13	2.20	75.6	57.3
Pb	mg/kg dm	166	146	208	214	888	769	120	110	332	330	527	435
Zn	mg/kg dm	198	188	246	247	575	524	193	175	156	101	2202	1807

Results and discussions

The concentrations of metals and the pH of blank soil samples collected on two depths (0-10 cm and 30-40 cm) are presented in table 3.

It can be seen that the control samples show acidic pH on both depth levels, recording a Pb value (in bold letters) above the soil sensitivity alert threshold for agricultural area according to the Romanian legislation in force [24].

The results obtained for the metal content (As, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb and Zn) in soil samples, on two depths (0-10 cm and 30-40 cm) and the pH value are presented in table 4.

Each soil sample was collected on two depths, interpreting the results by taking into account the values of the metal concentrations obtained in both samples. From the experimental data obtained it can be noticed that the pH of the analyzed soils is in the acidic pH range, as is the case with the blank soil samples, as well as in the neutral range of pH.

The results of the metal content were compared with the reference values for *sensitive uses soils* according to Romanian Order no. 756/1997 [24].

The soil with the highest content of metals is S6 (both profiles), in which concentrations of As, Cd, Co, Cu, Mn, Pb, Zn above the intervention threshold for sensitive use have been obtained. In the same soil, on the first depth, a Ni value above the alert limit (75 mg/kg dm) was determined.

The Pb content is 1.2 to 9 times higher than the intervention threshold (100 mg/kg dm) in all analyzed samples, on both depths. The intervention threshold for Ni (150 mg/kg dm) is exceeded only in S3 profile, at both depths. As regards the As content, values above the alert threshold (15 mg/kg dm) in S1 profile (both depths) and S2 profile (surface sample) were determined and the intervention threshold (25 mg/kg dm) was exceeded in samples S3, S4, S5 at both depth levels, with values ranging from: 36 ÷ 121 mg/kg dm.

Regarding the Mn content, concentrations above the alert threshold (1500 mg/kg dm) were found in S1 samples (first level) and S3 samples (both depths). Cd contents above the alert threshold (3 mg/kg dm) were determined in S3 and S4 samples, at both depths.

With the exception of the S6 profile, the content of Cr, Co, Cu, and Zn in all analyzed samples is within the normal limits for soil quality.

In the vegetation samples 13 metallic elements were determined, namely: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn. For these metals literature studies indicate the normal content and toxic concentration in plants (table 5) [25-28].

From each location of the 7 sampling points, several vegetation samples were collected so that, in total, 36 samples were analyzed. The analyzed plants are mostly plant leaves, tree leaves, grass, buds and a smaller proportion of tree bark. The sampling was done in early spring, when the vegetation was in the budding period.

The analyzed vegetal blank samples Vm1 ÷ Vm5 (*Fraxinus excelsior*, branch, leaves; *Aralia racemose*, branch, fruits; *Elymus repens*, whole plant; *Malus domestica*, leaves, buds) indicate a Ni pollution. These plant samples show Ca and Mg contents over normal ranges, which are also found in the other analyzed plants, with few exceptions.

The Cr content in all vegetation samples is situated within normal range (0.32 mg/kg ÷ 17.9 mg/kg) (table 5). The chromium content in the soil is relatively low, standing around the normal limits for soil. This is reflected in the low chromium content of the sampled vegetation.

The Cu content of all sampled vegetation types is situated in the normal value range (table 5) by the recorded values (1.86 mg/kg ÷ 15.6 mg/kg). Even though in soil samples collected from the S6 profile the copper concentrations were 1.5 to 2 times higher than the intervention threshold for sensitive land use, the metal is

Metallic element	Normal concentration range (mg/kg)	Metallic element	Normal concentration range (mg/kg)
Aluminium	200 – 1000	Iron	640 – 2486
Arsenic	5	Magnesium	0.73 – 1.41
Cadmium	2	Manganese	15 – 100
Calcium	1830 – 2042.5	Nickel	0.1 – 3.7
Cobalt	0.1 – 10	Lead	3
Chromium	0.006 – 18	Zinc	1 – 70
Copper	0.4 – 45.8		

Table 5
CONCENTRATION RANGES FOR METALS CONTENT IN PLANTS

bound to the soil structure and is not available to vegetation, the values ranging from 5.3 mg/kg in the V6e sample (*Acer sp*, bark) to 14.3 mg/kg in V6a sample (*Poaceae sp*, whole plant).

The Co content recorded very low values in vegetation, being below the quantification limit of the method (0.02 mg/kg) or reaching values of maximum 1 mg/kg. This low content correlates with low cobalt values obtained in soil samples, with the exception of the S6 profile, where the contents of 70 mg/kg and 80 mg/kg respectively were recorded. This behavior, also seen in the case of Cr and Cu, can be explained by the fact that the pH of this profile is neutral, the metals being bound in compounds not available for leaching in soil and groundwater.

Regarding the Fe content of the vegetation samples, recorded values were in the normal concentration range, except for the V4c sample (*Carpinus betulus*, bark) in which 2600 mg/kg Fe was determined.

The concentration of Ni in the analyzed vegetation samples was found to be within the normal concentration range in 11 of the 36 analyzed samples (V1a, V1b, V1c, V1d, V2a, V2c, V2e, V2f, V2g, V4b, V5e), these values being correlated to the Ni concentrations in the corresponding soil profiles (S1, S2, S4 and S5) where the Ni contents were around the normal value.

For the other 25 vegetation samples, including blank samples, the nickel was above the normal range of concentrations, the values being in the range of 4.23 mg/kg ÷ 10.8 mg/kg. The highest concentration of Ni was found in the sample V3a (10.8 mg/kg, *Milium effusum*), correlated with both the acidic pH and the Ni values of the soils collected in the S3 profile, which exceeded 4 times the threshold intervention for soils with sensitive use.

Concerning the Pb content, only 7 of the 36 vegetation samples recorded values above the acceptable threshold (3 mg/kg). Thus, samples of V3c (16.2 mg/kg, *Betula sp*, bark) and V3d (32 mg/kg, *Hypnum cupressiforme*, whole plant) collected from soil recorded a content approximately

9 times higher than the intervention threshold. Correlated with the acidic pH of this profile, the content found in plants confirms the mobility of lead from soil to vegetation. The highest concentration of Pb was found in sample V4c (66.6 mg/kg, *Carpinus betulus*, bark), as the sample was collected from a soil profile with Pb values above the intervention threshold and acidic pH. This concentration is the result of accumulation over time in the bark of the tree planted in such a polluted area. The V5a vegetation samples (10 mg/kg, *Milium effusum*, whole plant), V5d (4.33 mg/kg, dry vegetation) and V5f (14.2 mg/kg, *Malus domestica*, leaves) which recorded high Pb values accumulated it from the S5 soil profile, where Pb values were about 3 times higher than the intervention threshold for sensitive use soils. The S5 profile records a strongly acidic pH (table 4), which favors metal migration to vegetation and groundwater.

Manganese content in most vegetation samples is above the normal concentration range, the upper limit being 100 mg/kg (fig. 2). Very high Mn values were recorded in V2b samples (927 mg/kg, *Carpinus betulus*, leaves), V3b (693 mg/kg, *Fagus sp.*, Leaves), V4a (1929 mg/kg, *Carpinus betulus*, leaves), V4d (1345 mg/kg, *Fagus sp*, leaves), V5c (572 mg/kg, *Fagus sp*, leaves) - samples of leaves collected from beech and hornbeam trees grown on acid pH soils. The accumulation was mainly due to leaching from Mn rich acidic soil (S2 and S3 profiles), but also due to accumulation over time, both for samples V4a and V4d (max. 270 mg/kg dm Mn in soil) as well as V5c sample (280 mg/kg Mn in soil). Although the Mn content in the S1 profile exceeds the alert threshold, the neutral pH of this profile does not facilitate the leaching of Mn to vegetation, the V1a ÷ V1d vegetation samples having Mn contents in the range of 35 ÷ 60 mg/kg. As for the S6 soil profile, the Mn content was 2.5 times higher (table 4) than the intervention threshold (S6 /1), but vegetation samples V6a ÷ V6f had Mn values in a range close to the normal limit due to the neutral pH of soil samples.

The As values determined in 34 vegetation samples were included in the range of 0.14 mg/kg to 3.08 mg/kg, values

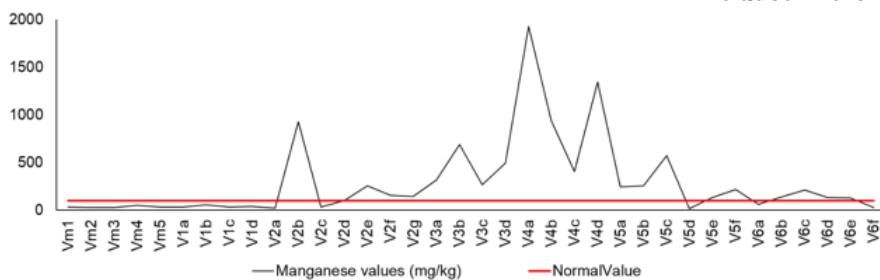


Fig. 2. Manganese values recorded in vegetation samples

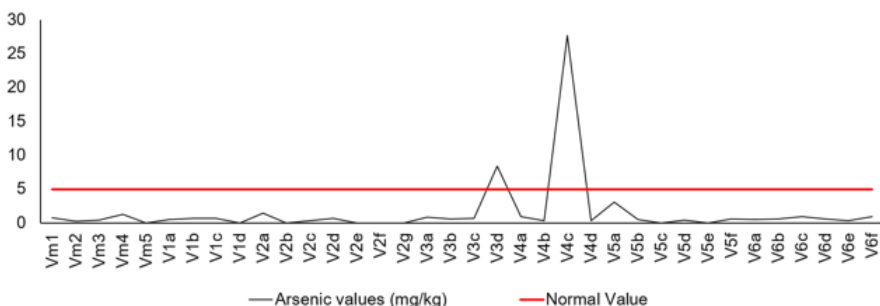


Fig. 3. Arsenic values recorded in vegetation samples

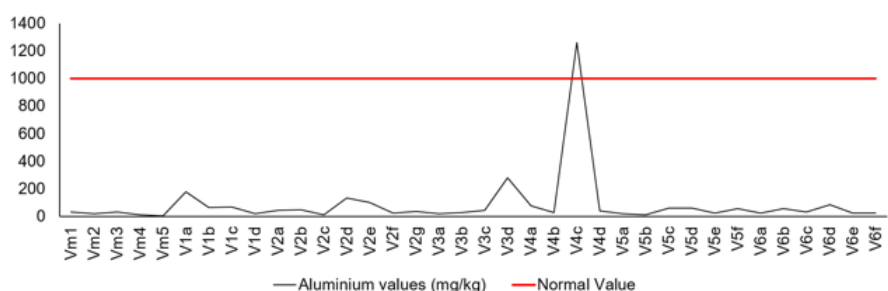


Fig. 4. Aluminium values recorded in vegetation samples

Fig. 6. Cadmium values recorded in vegetation samples

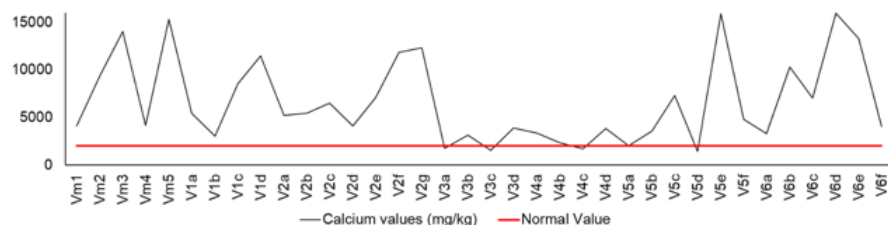


Fig. 5. Calcium values recorded in vegetation samples

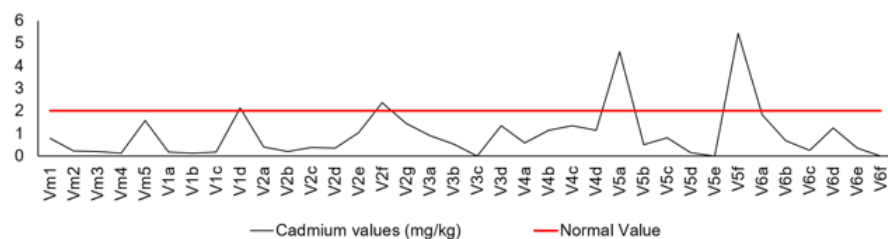


Fig. 7. Magnesium values recorded in vegetation samples

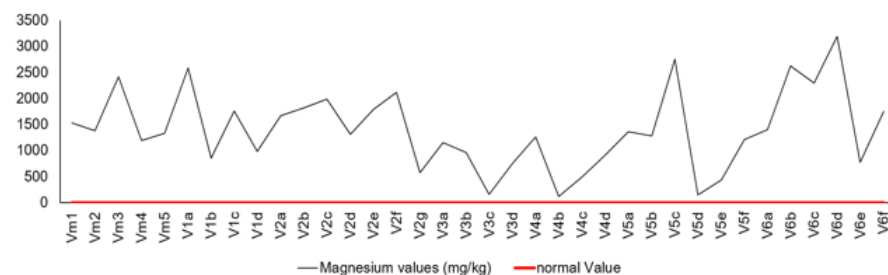
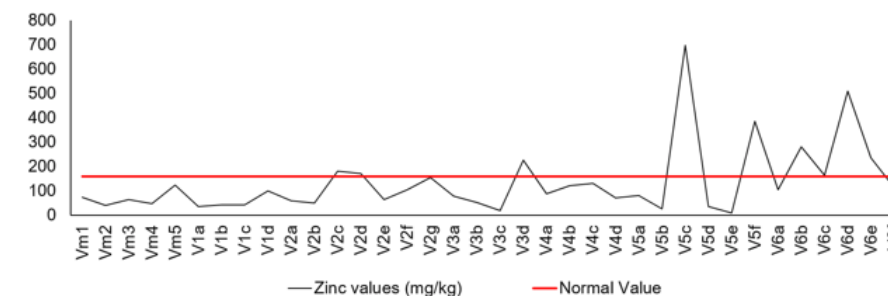


Fig. 8. Zinc values recorded in vegetation samples



below the vegetation normal limit (fig. 3). A value of 8.38 mg/kg (V3d, *Hypnum cupressiforme*, whole plant) was recorded in a S3 profile sample, where the As content is 5 times higher than the intervention threshold for sensitive use soils. The soil also has an acidic pH, which explains the leaching of As in the moss plant sample. The highest As concentration was found in the sample V4c (27.7 mg/kg, *Carpinus betulus*, bark) due to As accumulation in the bark over time, from the acid pH soil having an As content 3.5 times higher than the intervention threshold.

The Al content is situated below the normal concentration value (1000 mg/kg) in all analyzed samples, except for sample V4c (1263 mg/kg, *Carpinus betulus*, bark) (fig. 4).

As regards the Ca content, V3a samples (1757 mg/kg, *Milium effusum*), V3c (1543 mg/kg, *Betula sp.*, Bark), V4c (1710 mg/kg, *Carpinus betulus*, bark) and V5d (1447 mg/kg, dry vegetation) were below the upper limit of the normal concentration range for Ca in plants (fig. 5). All other species and parts of vegetation analyzed had higher values than the normal concentration range for Ca, including all control samples, of which Vm3 sample (14019 mg/kg, *Aralia racemose*, branch, fruits) and Vm5 sample (15323 mg/kg, *Malus domestica*, bark) had about 5 times higher concentrations. The highest contents were recorded in: V1c (8537 mg/kg, *Thymus vulgaris*, roots, leaves, stem), V1d (11459 mg/kg, *Carpinus betulus*, bark), V2f (11848 mg/kg, *Trifolium*, leaves), V2g (12316 mg/kg, *Carpinus betulus*, bark), V5e (15889 mg/kg, *Fagus sp.*, bark) and V6e (13270 mg/kg, *Acer sp.*, bark).

The Cd content exceeds the normal value of 2 mg/kg in several samples: V1d (2.15 mg/kg, *Carpinus betulus*, bark), V2f (2.37 mg/kg, *Trifolium*, leaves), V5a (4.62 mg/kg, *Milium effusum*, whole plant) and V5f (5.43 mg/kg, *Malus domestica*, leaves). Even though S2 and S5 soil samples contain Cd in normal concentration limits for sensitive use soils, cadmium leaching in vegetation is due to acidic pH. All other analyzed samples of vegetation show a cadmium concentration below the normal value.

The normal Mg concentration in vegetation was exceeded in all 36 analyzed samples (including control samples), with values ranging from 119 ÷ 3194 mg/kg. The highest magnesium content was recorded in Vm3 samples (2415 mg/kg, *Aralia racemosa*, branch, fruits), V2f (2117 mg/kg, *Trifolium*, leaves), V5c (2760 mg/kg, *Fagus sp.*), V6b (2626 mg/kg, *Acer sp.*, leaves), V6d (3194 mg/kg, *Urtica dioica*, whole plant).

Zn concentration had values above the upper limit of the normal concentration range in V2c samples (181 mg/kg, *Euphorbia cyparissias*, roots, stem, leaves), V2d (170 mg/kg, *Thymus vulgaris*, roots, stem, leaves), V3d (226 mg/kg, *Hypnum cupressiforme*, whole plant), V5c (697 mg/kg, *Fagus sp.*, leaves), V5f (386 mg/kg, *Malus domestica*, leaves), V6b (281 mg/kg, *Acer sp.*, leaves), V6c (165 mg/kg, *Carpinus betulus*, leaves), V6d (509 mg/kg, *Urtica dioica*, whole plant) and V6e (235 mg/kg, *Acer sp.*, bark). While in the S2 and S5 profiles the Zn content is below the alert threshold, the acid pH favors zinc migration to the plants (roots, stem, leaves). The S3 profile recorded values close to the intervention threshold for Zn and acid pH, so the V3d vegetation sample accumulated Zn by

absorbing it from the soil. The soils collected for the S6 profile are 3.5 times above the intervention threshold, so zinc is accumulated both in the bark and in the leaves.

Similar studies have demonstrated the mobility of metals in soils with acid pH to vegetation for metals such as Cu, Cd, Fe, Mn, Ni, Pb, Zn [29-32].

Conclusions

The experimental study conducted in the polluted mining site situated in the Certej area, Deva, included the analysis of 14 soil samples and 36 vegetation samples, collected around the soil profiles. The content of the analyzed metals was compared to the maximum allowed limits in the legislation for soil quality (sensitive use), i.e. the normal content of metals in plants.

Regarding the soil component of the environment, for the 7 analyzed profiles including the control sample, the highest metals concentrations were found in S3 and S6 samples. In the case of the S3 profile, there is a significant pollution induced by Ni, Pb and As whose concentrations exceed the intervention threshold for sensitive uses of soils. On both sampling levels of the S3 profile, it is noticeable that the Cd and Mn quality indicators exceed the alert threshold for sensitive uses soils, causing a potentially significant pollution. The presence of analyzed metals in high concentrations in this profile is due to a primary cumulative effect given by the Coranda pit and the Nicodim gallery and also to a side effect given by the Northern tailings dumps.

The most polluted profile, where pollution is reflected on both sampling levels, is the S6 profile. Most part of the analyzed metals in this profile (Cd, Co, Cu, Mn, Pb, Zn and As) induce significant pollution by their presence in quantities exceeding the intervention threshold for sensitive uses soils. The presence of high concentrations for most of the analyzed indicators in this profile is due to the cumulative effect generated by the presence of Coranda pit, tailings dumps and Nicodim gallery, both through the contribution of surface waters and percolation waters loaded with metals that infiltrate the soil.

By correlating the metals content determined in the plants with that existing in the soil samples it can be asserted that due to the acidic pH of the analyzed profiles, Cd, Mn, Ni, Pb and Zn contents were found above the normal values of these metals in the vegetation collected early in spring.

99% of the analyzed vegetation samples showed Ca and Mg content above the normal concentration ranges both in the samples of the polluted area and in the control sample taken from 5 km in South-West direction from the study area.

For 61% of the vegetation samples, the manganese content is above the upper limit of the normal concentration range, Mn being the most abundant metal.

In spite of the fact that the S6 profile was the most polluted with metals, the neutral pH of the area made the metals above the alert threshold, respectively intervention threshold for sensitive uses of soil not to be found in concentrations above the normal values in the vegetation samples. The exception is zinc, due to the accumulation process over time in a soil with Zn content 3 times higher than the intervention threshold.

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