Evaluation of the Bioavailability and Pollution Indexes of Some Toxic Metals in Polluted Soils from an Abandoned Mining Area

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The paper presents soil quality assessment using pollution and bioavailability indexes in order to highlight possible pollution generated by a decommissioned mining area in Certej, Deva County, Romania. Metals such as Cd, Cr, Cu, Ni, Pb and Zn were analyzed in pseudo-total and mobile form and the results were correlated with the content found in the vegetation collected from the same points during a previous study. The research shows a high mobility for Ni, Pb and Zn, respectively, a moderate mobility for Cd.

Keywords: bioavailability index, metals, mining site, pollution indexes, soil

Soil is a non-regenerative resource that fulfills several vital functions including: food/biomass production; storage, filtration and conversion of certain substances; is a source of biodiversity, habitats, species and genes; serves as a platform/physical environment for people and human activities; is a source of raw materials; is a geological and archaeological heritage etc. Among the forms of soil pollution, the most serious is the pollution of the soil by its destruction on large surfaces due to pollution from mining and industrial exploitations [1].

Soil pH can be highlighted as an important characteristic. Nutrients and pollutants mobility (availability) is directly dependent on the *p*H value [2]. The activity of soil organisms, the degradation of organic substances, the release of iron, manganese and aluminum also depend on pH level . The solubility of metals increases at low *p*H and decreases at high pH [3]. It is known that metals adsorption is directly proportional to the soil *p*H, this fact being observed in many adsorbent components of the soil as well as in different soil types [4]. The effects that pH generates on soil solubility can also be observed in precipitation-dissolution reactions. Acid rains have a pH of less than 5.6, this pH being due to inorganic (sulfuric, nitric) and organic (formic, acetic, carbonic) acids resulting from complex atmospheric reactions [5].

Soils from industrialized and urban areas accumulate metallic trace elements, affecting the ecosystems and the human health [6-8] and posing serious risks to biota. Many researches pointed out that mining activity can be considered a main source of heavy metals contamination of vicinity soils and sediments [7].

Classically, soil pollution risk evaluations focus on total trace metal concentrations, but trace metal bioavailability based on their physical chemical fractions seem to be more relevant, providing a more accurate estimate of the environmental impact [4].

Evaluation of the bioavailability processes in soils and sediments should use different methods, including - besides usual measurements of total content - the calculation of specific indexes as tools for risk assessment [6].

Assessing soil contamination levels of heavy metals by applying different techniques may result in discrepancies, thus it is important to compare results obtained using different relevant factors and indexes such as contamination factor [7], enrichment factor [9], pollution, bioavailability and geoaccumulation indexes [9] or to sum different individual risks in order to estimate the total pollution risk [10].

The paper presents the assessment of soil quality in a polluted mining area located in Deva County, Romania, using pollution indexes. In this area, a complex study was carried out, which aimed to assess the quality of all environmental factors, namely surface water and sediment [11], soil, vegetation [12].

Experimental part

Sample collection and preparation

Soil samples were taken from the Certej Basin (Hunedoara County). Soil samples (10 samples and a control sample) were collected, each on 2 depths (0-10 cm and 30-40 cm), from 11 harvest points.

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 die to the mining activity carried out for decades in the selected area.

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 from sensitive use areas, vegetated soils situated outside the area that was used in mining activities. Soil samples were collected according to the standards in force [13]. Sampling was performed with the Buerkle soil sampling device.

Analytical procedures

Pseudo-total metal content

For the determination of the pseudo-total content (Cd, Cr, Cu, Fe, Ni, Pb, Zn), 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 HCl 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 [14]. The solution thus obtained was used for the determination of metals by

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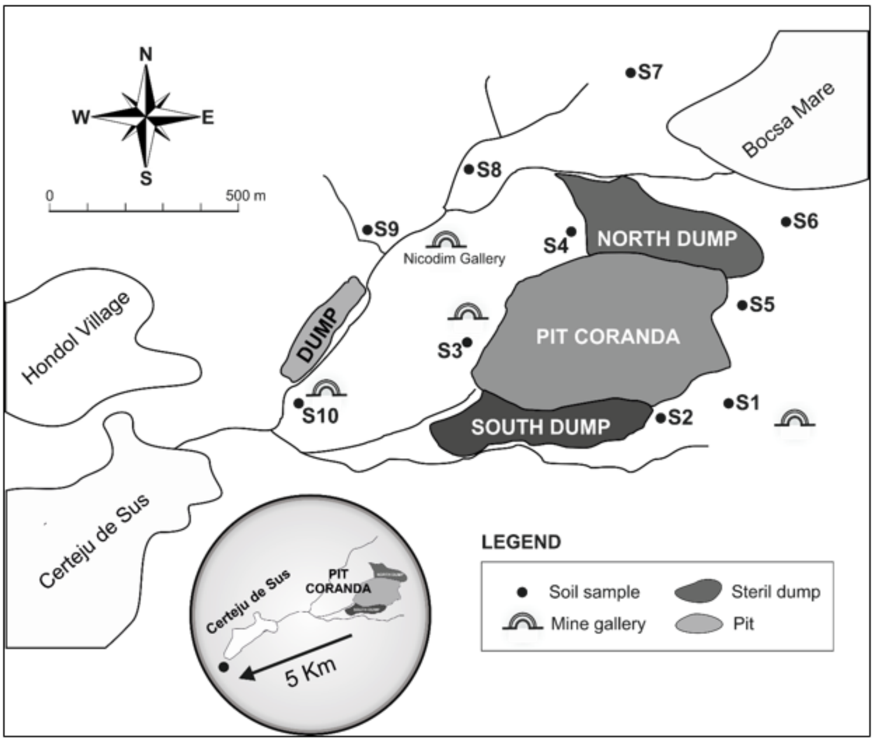


Fig. 1. Map of soil sampling points, Certej Area

Table 1

GPS COORDINATES OF SOIL SAMPLING POINTS

Crt. No.	GPS Coordinates	Sample type / sample indicative	Observations
1	45^{0} 59.431’ 023^{0} 00.835’	soil (S1)	Sampling point situated at about 100 m from the Coranda pit in the southern direction
2	45^{0} 59.410’ 023^{0} 00.697’	soil (S2)	Sampling point situated at about 50 m from the South Dump in the eastern direction
3	45^{0} 59.523’ 023^{0} 00.219’	soil (S3)	Sampling point located in the immediate vicinity of Coranda pit at about 50 m in the western direction
4	45^{0} 59.752’ 023^{0} 00.515’	soil (S4)	Sampling point situated in the immediate vicinity of North dump at about 50 m in the western direction
5	45^{0} 59.600’ 023^{0} 00.880’	soil (S5)	Sampling point situated at about 50 m from the Coranda pit in the eastern direction
6	45^{0} 59.762’ 023^{0} 01.021’	soil (S6)	Sampling point situated in the immediate vicinity of North dump at about 100 m in the eastern direction
7	46^{0} 00.026‘ 023^{0} 00.824’	soil (S7)	Sampling point situated in the immediate vicinity of North dump at about 250 m the northern direction
8	N45^{0}59.843’ E023^{0}00.259’	soil (S8)	Sampling point situated upstream to Coranda river
9	45^{0}59.677’ 022^{0}59.966’	soil (S9)	Sampling point situated on Baiaga river downstream from the confluence with water from the Nicodim gallery;
10	45^{0}59.410’ 022^{0}59.722’	soil (S10)	Sampling point situated on Baiaga river downstream from the confluence with pit water and upstream to the confluence with Ciongani river;
11	45^{0} 57.263’ 022^{0} 57.863’	soil (M)	Blank sample, sampling point situated at 5 km from Coranda pit the in the south-western direction

inductively coupled plasma optical emission spectrometry on an Optima 5300 DV Perkin Elmer equipment.

Mobile fraction

For mobility tests, three simple chemical extraction methods were used, using different chemical reagents and soil-to-extractant ratios. Both weak extractants (e.g. CH_3COONH_4, NH_4NO_3) and strong complexing agents (chelating agents), such as EDTA, or a mixture of them [15, 6] were used:

Method I: NF X 31 – 120/2003 Standard: 0.01 M EDTA + 1 M CH_3COONH_4, $pH = 7\pm0.002$, soil/extraction solution ratio = 1:10, stirring time: 2 h at 40 rotations/min; [16].

Method II: ISO 19730:2008 Standard : 1M NH_4NO_3, pH 7±0.002, soil/extraction solution ratio = 1:2.5, stirring time: 2 h at 40 rotations/min; [17].

Method III: ONORM L 1094-2/2016 Standard: CH_3COONH_4, $pH = 7\pm0.002$, soil/extraction solution ratio = 1:10, stirring time: 2 h at 40 rotations/min ; [18].

Pre-treated soil samples were used according to ISO 11464 [14], following the same procedure as for the pseudo-total content. From each sample, a sub-sample (5 g) was weighed and transferred into a 100 mL iodine flask. A separate part of these samples was used to determine the water content. 50 mL of extraction solution (method I and III), respectively 12.5mL (method II) was added. The containers were sealed and shaken for 2 h (20 ± 2 ° C) using a shaker. The extracts were decanted into centrifuge vials and centrifuged for 10 min at 3000 rpm. The supernatant obtained from each sample was filtered using a membrane filter with a porosity of 0.45 μm.

The content of Cd, Cr, Cu, Ni, Pb, Zn was determined using inductively coupled plasma optical emission spectrometry.

Estimation of pollution index and bioavailability index

Interpretation of the obtained analytical results was achieved both by reference to the indicators' values for the reference samples (control samples) and by reference to the limits stipulated in the MAPPM Order No. nr. 756/1997 - *Regulations on environmental pollution assessment* which introduces the notions of *normal value*, *alert value* (PA) and *intervention value* (PI).

As reported in literature, numerous factors / indexes can be used in order to estimate soil quality [9, 19, 7]. Pollution index for the soil can be quantified in terms of *contamination factor* (C_f), calculated as the ratio of average metal concentration in the soil samples to the baseline reference concentration in the earth crust [20], as summarised in the following formula [21].

$$C_f = \frac{C_i}{C_e} \qquad (1)$$

where, C_i represent the mean concentration of the metal in the examined samples, respectively C_e - the normal value of the metal in the earth crust.

As for the interpretation of contamination factor values, higher value indicate lower retention time of the element in the soil and thus a higher risk to the environment [22].

The degree of contamination, C_d, which is an overall indicator of contamination, is estimated by summing the contamination factors (C_f) of each pollutant.

$$C_d = \sum_{i=1}^{n} Cf \qquad (2)$$

where *n* is the number of analyzed elements, *i* represents the pollutant, while C_f signifies the contamination factor.

C_d is determined also as the ratio of metal concentration in soil to the metal's background values.

The modified degree of contamination (mC_d) is calculated as the sum of all the contamination factors divided by the number of analyzed pollutants. This index averages the contamination of all elements at a particular site through a single value and is determined using the following formula [10]:

$$mC_d = \frac{\sum_{i=1}^{n} Cf}{n} \qquad (3)$$

The level of contamination using the C_d index is shown in table 2.

Table 2

MODIFIED DEGREE OF CONTAMINATION AND ITS EFFECTS

mC_d levels	Contamination status
$mC_d < 1.5$	Very low degree of contamination
$1.5 \leq mC_d < 2$	Low degree of contamination
$2 \leq mC_d < 4$	Moderate degree of contamination
$4 \leq mC_d < 8$	High degree of contamination
$8 \leq mC_d < 16$	Very high degree of contamination
$16 \leq mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

Another relevant index is the *Geoaccumulation index* (I_{geo}), which compares the current concentration in the soil with the pre-industrial pollution, being defined by the mathematical relation:

$$I_{geo} = \log_2(C_n/1.5B_n) \qquad (4)$$

where C_n is the metal concentration, while B_n represents the background of the element [17].

I_{geo} is classified into seven classes [7] as shown in Table 3.

Table 3

THE CLASSES OF THE VALUE OF I_{geo}

I_{geo}	Class	Soil quality
$I_{geo} \leq 0$	1	Practically unpolluted
$0 < I_{geo} < 1$	2	Unpolluted to moderately polluted
$1 < I_{geo} < 2$	3	Moderately polluted
$2 < I_{geo} < 3$	4	Moderately to strongly
$3 < I_{geo} < 4$	5	Strongly polluted
$4 < I_{geo} < 5$	6	Strongly to very strong
$5 < I_{geo}$	7	Very strong pollution

To evaluate the soil contamination rate, Enrichment *Factor* (EF) can be also applied. Enrichment factor can be evaluated considering the differences between the natural and the anthropogenic contribution of the metals in soil [8], according to the next formula:

$$EF = \left[\frac{X}{Fe}\right]_{sample} / \left[\frac{X}{Fe}\right]_{crust} \qquad (5)$$

where $\left[\frac{X}{Fe}\right]_{sample}$ and $\left[\frac{X}{Fe}\right]_{crust}$ represent the ratio of average concentrations of the target metal and Fe in the studied sample and earth crust, respectively.

In this case Fe is used as a reference element. The most common reference elements are Sc, Mn, Al and Fe.

EF is classified in five contamination categories, as appears in table 4.

Table 4

THE CLASSES OF THE VALUE OF EF

EF<2	Depletion to minimal enrichment
2<EF<5	Moderate enrichment
5<EF<20	Significant enrichment
20<EF<40	Very high enrichment
EF> 40	Extremely high enrichment

The ability to transfer metals from the soil to the environment is estimated by calculating the *Index of Bioavailability* (I_{bio}) using the following formula:

$$I_{bio}\,(\%) = \frac{Cmobil * 100}{Ctotal} \qquad (6)$$

where C_{mobil} is the content of metal from exchangeable form, water soluble and weak acid soluble fraction (carbonates), while C_{total} represents the total concentration of metal in the soil sample.

Results and discussions

Distribution of the metals

Table 5 lists the minimum, maximum, average, and median values for the pseudo-total and mobile metal content of the 20 samples, collected from 10 sampling points, 2 depths.

The pseudo-total content is used in the evaluation of different pollution indexes (EF, C_f, mCd, I_{geo}), highlighting the degree of pollution within the studied area, contaminated by past mining activities. Even if the area was shut down for mining activities, the pollution generated in the past continues to rise environmental concerns. The tabulated data show that there are exceedances of intervention limits for Cd, Cu, Ni, Pb and Zn, the recorded exceedances being 2.3 times higher in the case of Cd; 1.9 times higher for Cu; 4 times higher for Ni; 8.9 times higher for Pb, 3.7 times higher for Zn.

The values of the mobile fraction obtained by applying the three extraction methods were reported. By comparing the results, it can be observed that methods using ammonium acetate in a mixture with EDTA (method I) or ammonium acetate only (method III) extract high amounts of metals into the mobile form. By comparing the bioavailability indexes (I_{bio}) evaluated for each metal and

			Cd	Cr	Cu	Ni	Pb	Zn
		Min	0.05	3.95	9.45	2.2	13.4	56.3
Total		Max	**11.4**	73.6	**378**	**610**	**888**	**2202**
		Mean	1.25	27.2	61.9	84.6	224	369
		Median	2.27	22.6	25.8	23.8	133	182
Exchangeable Method I		Min	0,05	0.08	1.87	0.62	2.67	26.3
		Max	**8.16**	16.5	**264**	**180**	**193**	**1309**
		Mean	1.24	5.82	36.9	28.3	49.1	198
		Median	0.73	7.14	12.5	12.6	23.3	84.7
Exchangeable Method II		Min	0,05	0.05	0.08	0.07	0.01	10.3
		Max	3.02	2.13	87.6	**153**	29.4	**781**
		Mean	0.48	0.30	8.74	18.5	3.19	101
		Median	0.14	0.06	0.73	7.2	0.68	24.7
Exchangeable Method III		Min	0,05	0.33	1.04	0.11	3.64	16.3
		Max	**7.20**	11.6	164	126	**209**	**1323**
		Mean	1.00	5.82	18.3	18.4	43.9	154
		Median	0.57	7.69	4.92	7.99	20.5	42.8
Normal value			1	30	20	20	20	100
Alert value (PA)			3	100	100	75	50	300
Intervention value (PI)			5	300	200	150	100	600

Table 5
STATISTICAL DISTRIBUTION OF PARAMETERS FOR SELECTED METALS (mg/kg) iN BOTH FRACTIONS OF ALL SOIL SAMPLES, PSEUDO-TOTAL AND MOBILE CONTENT

method, Method I was selected as the optimal single chemical extraction method for the investigated soil.

Evaluation of soil quality using pollution indexes

Modified degree of contamination index

The contamination factor has been calculated in two ways, either by reference to the terrestrial crust reference value C_f c [20] or by reference to the normal soil value according to the Romanian legislation in force [23], C_f n.

Overall degree of contamination (C_d), which sums the individual factors of contamination, has a value of 24.4 when the normal soil value is used as reference value [23], respectively a value of 31.9 when the normal value in earth crust is used as the reference value [20].

In terms of modified degree of contamination index [10], both approaches indicates a high degree of contamination of the analyzed soils ($4 \le mC_d \le 8$).

Enrichment factor

During the calculation of the enrichment factor, reference values in the terrestrial crust were used [20], the normalization being based on the iron content. Factors for all collected samples were calculated, as well as the average value for each element and the standard deviation. Table 8 lists the enrichment factors (minimum, maximum and average values; standard deviation).

	Cd	Cr	Cu	Ni	Pb	Zn
Ci	1.25	27.2	61.9	84.6	224	369
Cn*	1.00	30.0	20.0	20.0	20.0	100
C_f n	1.25	0.91	3.10	4.23	**11.2**	3.69
$C_d = \Sigma C_f$ n	**24.4**		$mC_d = C_d/6$		**4.06**	

*Cn, Normal value according to Romanian Soil Order [23]

Table 6
CONTAMINATION FACTOR USING PSEUDO-TOTAL CONTENT REPORTED TO THE NORMAL VALUES OF METAL IN SOIL

	Cd	Cr	Cu	Ni	Pb	Zn
Ci	1.25	27.2	61.9	84.6	224	369
Cn crust*	0.15	102	60.0	84.0	14.0	70.0
C_f c	**8.33**	0.27	1.03	1.01	**16.0**	5.27
$C_d = \Sigma C_f$ c	**31.9**		$mC_d = C_d/6$		**5.32**	

Cn crust* [20]

Table 7
CONTAMINATION FACTOR USING PSEUDO-TOTAL CONTENT REPORTED TO REFERENCE VALUES OF METAL IN TERRESTRIAL CRUST

		Cd	Cr	Cu	Ni	Pb	Zn
EF	Min	1.37	0.16	0.65	0.18	3.93	3.37
	Max	**182**	1.86	15.1	19.0	**163**	**75.6**
	Mean	**47.8**	0.88	2.98	2.90	**55.9**	15.6
	SD	45.6	0.57	3.86	5.51	58.3	19.4

The highest values of EF were recorded for Cd and Pb.

Table 8
STATISTICAL DATA FOR ENRICHMENT FACTOR (EF)

Regarding the Cd content, 45% of the samples fall in the *extremely high enrichment* range (EF> 40), 30% being included in the *very high enrichment* range (20 <EF <40), while the average value of all factors is higher than the maximum value of 40. Very high values of EF indexes were found in soils S2, S3, S4, S5 and S10. The highest value was recorded in S10 sample (first level), where EF is 182.

For Pb, 40% of the samples are in the *extremely high enrichment* range, with 20% being in the *moderate*, *significant* to *very high enrichment* ranges. Samples that have high EF values are S2, S3, S5 and S10. In the case of Pb, the mean EF value for all soil samples is higher than the maximum value of 40, corresponding to an *extremely high enrichment* (55.9). The highest values were determined in S3, respectively S5 soil samples (values higher than 150).

As regards chromium, all EF values are below 2, indicating *depletion to minimal enrichment*.

For copper, S10 soil samples (both levels) show *significant enrichment*, while S1, S2 and S3 soil samples show *moderate enrichment*, the average EF value on all analyzed samples ranging from 2 to 5.

Regarding the Ni content, the S3 sample indicates *significant enrichment* (10%), while only 20% of the samples (S2, S7, S10) were in the *moderate enrichment* range, with insignificant contribution of the rest of the samples.

For the zinc content, 10% show *extremely high enrichment* (S10 samples), 10% *very high enrichment* (S3 samples), and most samples (50%) being classified as *significant enrichment*. Also, the average value of these samples is very close to the upper threshold of the significant enrichment range. The highest values in the S10 sample are above the value of the EF index (64).

Overall, samples showing enrichment indexes falling in the *extremely high enrichment* range are S2 (Cd, Pb), S3 (Cd, Pb), S4 (Cd), S5 (Cd, Pb), S10 (Cd, Pb, Zn) samples.

Geoaccumulation index

When evaluating the geoaccumulation index, the normal value in soil according to the Romanian legislation in force was taken as the reference value (table 5) and the pseudo-total metal concentrations were used. Similar reports for I_{geo} calculations were recorded in the soils collected from an area adjacent to a copper mine in China [7], where ground metal concentrations in the Jiangxi province in China was considered as background.

The geoaccumulation index indicates very high values for Pb in S3, S5 and S10 samples, respectively for Ni (S3 samples), Cu (S10 samples) and Zn (S10 samples).

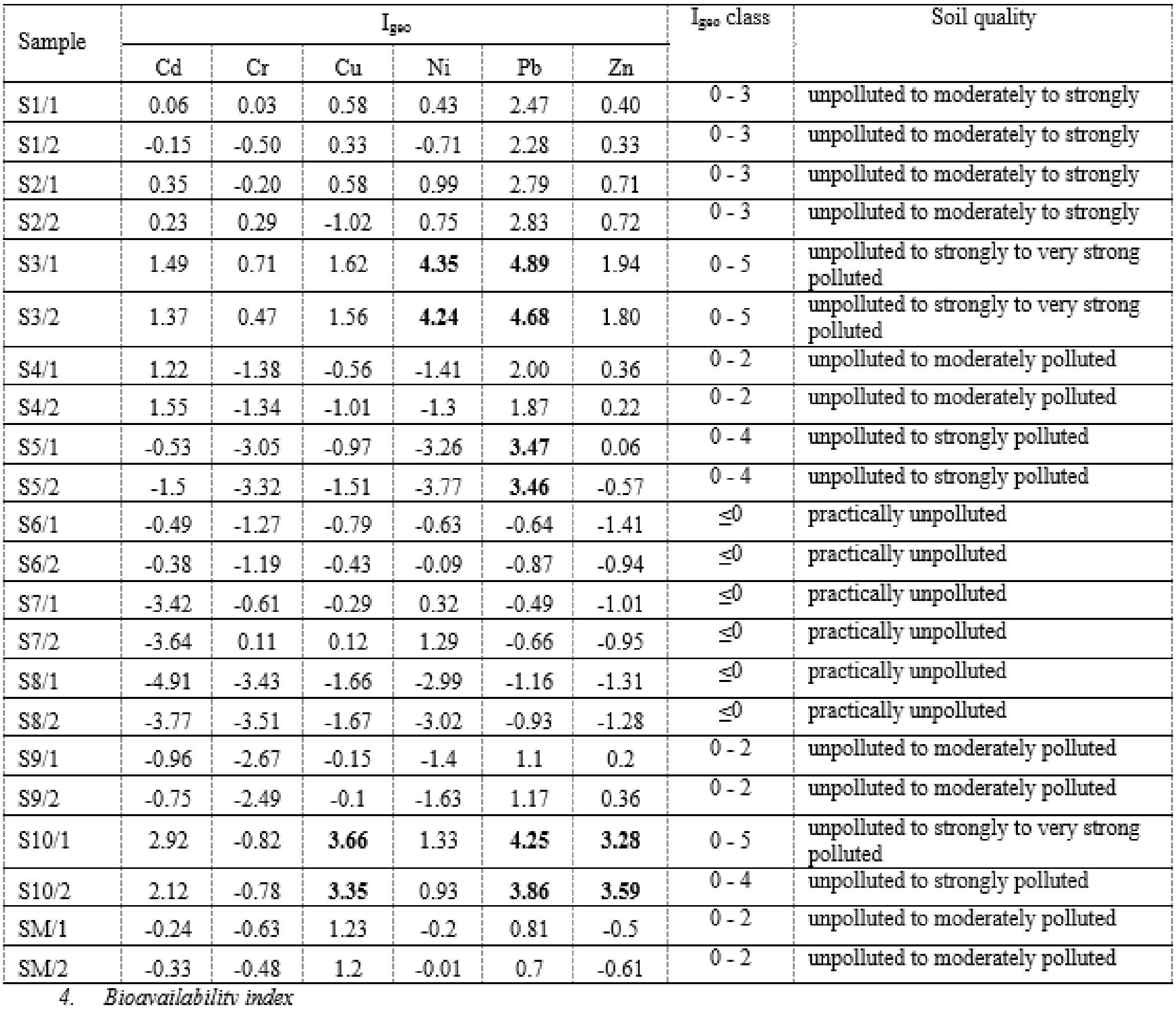
Moderate to strong pollution from Pb in S1 and S2 samples, respectively from Cd in S10 samples was also noted.

Bioavailability index

In S1 samples it can be observed that the bioavailability index I_{bio} is very high for Cd, Cu, Ni and Zn (> 70%), even if the *p*H of the soil is neutral, which implies the leaching of these metals to the vegetation and the groundwater (table 10). It should be noted that for an I_{bio} value of 45% for lead, due to the high pseudo-total metal content, the mobile fraction exceeds the alert threshold for sensitive uses land.

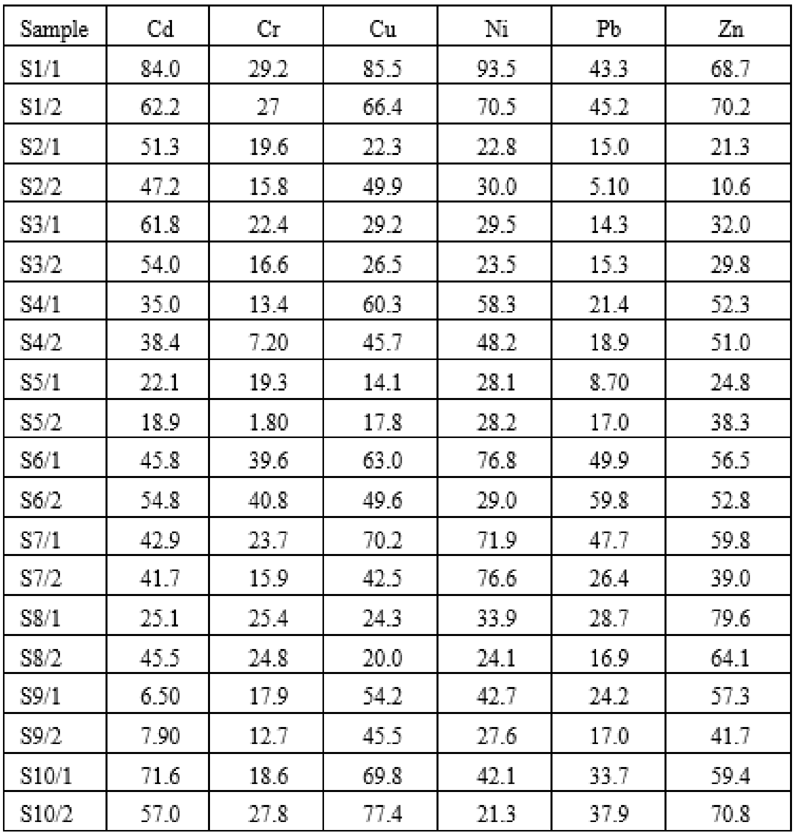
Table 9

INDEX OF GEOACCUMULATION (IGEO) IN SOIL SAMPLES



Sample	I_{geo}						I_{geo} class	Soil quality
	Cd	Cr	Cu	Ni	Pb	Zn		
S1/1	0.06	0.03	0.58	0.43	2.47	0.40	0 - 3	unpolluted to moderately to strongly
S1/2	-0.15	-0.50	0.33	-0.71	2.28	0.33	0 - 3	unpolluted to moderately to strongly
S2/1	0.35	-0.20	0.58	0.99	2.79	0.71	0 - 3	unpolluted to moderately to strongly
S2/2	0.23	0.29	-1.02	0.75	2.83	0.72	0 - 3	unpolluted to moderately to strongly
S3/1	1.49	0.71	1.62	**4.35**	**4.89**	1.94	0 - 5	unpolluted to strongly to very strong polluted
S3/2	1.37	0.47	1.56	**4.24**	**4.68**	1.80	0 - 5	unpolluted to strongly to very strong polluted
S4/1	1.22	-1.38	-0.56	-1.41	2.00	0.36	0 - 2	unpolluted to moderately polluted
S4/2	1.55	-1.34	-1.01	-1.3	1.87	0.22	0 - 2	unpolluted to moderately polluted
S5/1	-0.53	-3.05	-0.97	-3.26	**3.47**	0.06	0 - 4	unpolluted to strongly polluted
S5/2	-1.5	-3.32	-1.51	-3.77	**3.46**	-0.57	0 - 4	unpolluted to strongly polluted
S6/1	-0.49	-1.27	-0.79	-0.63	-0.64	-1.41	≤0	practically unpolluted
S6/2	-0.38	-1.19	-0.43	-0.09	-0.87	-0.94	≤0	practically unpolluted
S7/1	-3.42	-0.61	-0.29	0.32	-0.49	-1.01	≤0	practically unpolluted
S7/2	-3.64	0.11	0.12	1.29	-0.66	-0.95	≤0	practically unpolluted
S8/1	-4.91	-3.43	-1.66	-2.99	-1.16	-1.31	≤0	practically unpolluted
S8/2	-3.77	-3.51	-1.67	-3.02	-0.93	-1.28	≤0	practically unpolluted
S9/1	-0.96	-2.67	-0.15	-1.4	1.1	0.2	0 - 2	unpolluted to moderately polluted
S9/2	-0.75	-2.49	-0.1	-1.63	1.17	0.36	0 - 2	unpolluted to moderately polluted
S10/1	2.92	-0.82	**3.66**	1.33	**4.25**	**3.28**	0 - 5	unpolluted to strongly to very strong polluted
S10/2	2.12	-0.78	**3.35**	0.93	**3.86**	**3.59**	0 - 4	unpolluted to strongly polluted
SM/1	-0.24	-0.63	1.23	-0.2	0.81	-0.5	0 - 2	unpolluted to moderately polluted
SM/2	-0.33	-0.48	1.2	-0.01	0.7	-0.61	0 - 2	unpolluted to moderately polluted

4. *Bioavailability index*



Sample	Cd	Cr	Cu	Ni	Pb	Zn
S1/1	84.0	29.2	85.5	93.5	43.3	68.7
S1/2	62.2	27	66.4	70.5	45.2	70.2
S2/1	51.3	19.6	22.3	22.8	15.0	21.3
S2/2	47.2	15.8	49.9	30.0	5.10	10.6
S3/1	61.8	22.4	29.2	29.5	14.3	32.0
S3/2	54.0	16.6	26.5	23.5	15.3	29.8
S4/1	35.0	13.4	60.3	58.3	21.4	52.3
S4/2	38.4	7.20	45.7	48.2	18.9	51.0
S5/1	22.1	19.3	14.1	28.1	8.70	24.8
S5/2	18.9	1.80	17.8	28.2	17.0	38.3
S6/1	45.8	39.6	63.0	76.8	49.9	56.5
S6/2	54.8	40.8	49.6	29.0	59.8	52.8
S7/1	42.9	23.7	70.2	71.9	47.7	59.8
S7/2	41.7	15.9	42.5	76.6	26.4	39.0
S8/1	25.1	25.4	24.3	33.9	28.7	79.6
S8/2	45.5	24.8	20.0	24.1	16.9	64.1
S9/1	6.50	17.9	54.2	42.7	24.2	57.3
S9/2	7.90	12.7	45.5	27.6	17.0	41.7
S10/1	71.6	18.6	69.8	42.1	33.7	59.4
S10/2	57.0	27.8	77.4	21.3	37.9	70.8

Table 10
BIOAVAILABILITY INDEXES ACCORDING TO METHOD I (I_{bio})

The other metal contents in the mobile form fall around the normal soil value, except for lead.

In the case of S2 acid *p*H samples (*p*H = 4), it can be noted that although the Pb values exceed the intervention threshold, the mobile content (I_{bio} = 5 ÷ 15%) is low, standing around the normal value. The other metals in the mobile form do not exceed the concentrations of the normal values in the soil. Regarding S3 samples, which are highly polluted and show a *p*H in the acid range (*p*H = 3.6), the mobile fraction is above the intervention threshold for Pb and Ni even if I_{bio} is in the 15 ÷ 30% range. Cd is bioavailable in a percentage of 60%, but the obtained values are below the alert threshold.

In the case of S4 samples (*p*H = 5.7), the total metal contents are either low (Cr, Cu, Ni and Zn) or the bioavailability percentage is low (Pb, Cd) which makes the mobile fraction values to fall in the normal range concentration.

For the S5 samples (*p*H = 3.6), low percentages of bioavailability (2 ÷ 38%) are recorded, so that all mobile values (except for Pb in the depth layer where the alert threshold is exceeded) are lower than normal values. The S6 samples (neutral *p*H) show very high bioavailability (30% ÷ 77%), but low metal content in pseudo-total concentration leads to mobile contents below normal levels.

A similar situation with S6 occurs in S7, S8 and S9 samples, but having the *p*H in the acid range (S7, *p*H = 3.7; S8, *p*H = 5.5 and *p*H = 5.2 in S9).

In the case of S10 samples, although the pH is neutral, because of the high metal content and also because of the bioavailability rates falling in the 22 ÷ 77% range, the Cd (first depth), Cu, Pb and Zn mobile metals are above the intervention threshold value, posing a danger to both vegetation and groundwater and surface water pollution.

Metal values in the mobile fraction for the control sample (*p*H = 4.8) are below or around the normal value.

As mentioned in our previous study [12], which investigated the quality of early spring collected vegetation in the Certej area, significant amounts of Cd, Ni, Pb and Zn were detected in the vegetation samples. Thus, both leaves and roots have accumulated levels above normal values for Ni (70% of the collected samples), correlated with either elevated I_{bio} indices or acidic pH. A low percentage of 19% of vegetation samples [12] showed Pb values above the maximum limit allowed, despite the very high lead content in the soil, but correlated with the relative low mobility of this metal. There was an accumulation over time of Pb content in the bark of some trees (*Carpinus betulus*).

With regard to the Cr and Cu content, in all 36 collected samples of vegetation, they fall into the normal concentration range, either due to their low pseudo-total content (Cr, Cu) or because of their low mobility (Cu).

A low percentage of 11% of vegetation samples contain Cd above the maximum admissible level in both leaves and bark (*Carpinus betulus*). In terms of zinc content, 25% of the vegetation samples contain Zn above the admissible content, found in the root, bark, leaves. The highest concentrations are found in the vegetation samples collected at points S3 and S10, correlated with both high zinc content and high percentage of I_{bio}.

Conclusions

The study in the Certej mining area, which aimed to characterize the soil quality, complements the previous studies undertaken in this area where the quality of vegetation, surface water and sediment was investigated. Thus, it creates an overview of the decommissioned and heavily polluted mining area, establishing correlations between the environmental factors.

The mC_d, EF, I_{geo} pollution indexes evaluated based on the pseudo-total metal content provide only partial information on the environmental pollution potential, a bioavailability study of the metal in the soil being necessary.

Thus, three single chemical extraction methods were tested, selecting the method using EDTA and CH_3COONH_4 as the optimal method for mobility assessment.

The study highlighted the transfer of metals from the soil to the vegetation, as metal content was found in all the analyzed vegetation types (root, leaf, bark, stem).

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