Assessment of Heavy Metals Concentration in Soil and Plants from Baia Mare Area, NW Romania

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Abstract

The results showed diverse patterns of Pb, Cd, Zn, Co, Cu, Ni, Mn, Cr and Sn, in case of Pb in all areas exceeded the M.L.A (average 32.59 mg/kg while M.L.A. = 20 mg/kg), other elements shows high concentration that exceed the M.L.A. for Ferneziu and Săsar area. In the case of plant material also records exceedances of the M.L.A for Ferneziu and Săsar area, but in the Dura area there were no overtaking of M.L.A.

Keywords: contaminated soil, soil pollution, heavy metals

Introduction

The town of Baia Mare used to be an important nonferrous metallurgical centre where heavy metals like Pb and Cd have been extracted and processed from centuries. Due to the aerial emissions form a metallurgical plant ”Romplumb” that has been processing lead, located in the Ferneziu district, as well as from ”Cuprom” plant that has been processing copper, located in the eastern part of the city, the soil in Baia Mare area is highly polluted with heavy metals: Pb, Cd, Cu, Zn, (Mihaly *et al.*, 2013).

The main soil pollution sources are: mine entraces (mine openings), one processing factories, metallurgical factories (a Pb and Cu smelter), and tailing ponds. The Pb smelter was closed in January 2012, after more than 150 years of production, and Cu smelter has been closed in 2018 afther more than 80 years of production. Currently the mining and metallurgical industry has reduced the activity by closing or diminishing the production capacity, however Baia Mare is facing the historical contamination of soil with heavy metals (Levei *et al.*, 2009).

The present study aimed to assess the actual state of soil pollution taking into account the sources of soil pollution and the most exposed areas Ferneziu and Săsar district. The Ferneziu area has been impacted by the presence of the Pb smelter that is located in close poximity to the residential zones. The Săsar district is located along the Săsar River and is exposed to the dominant East to West wind. The paper aims to investigate the contents of heavy metals in soils and plants in Baia Mare area (47° 39’ N, 23° 34’ E).

Materials and methods

The sampling of soil and plant material was carried out during the vegetation period in May 2017. The study includes the sampling of the soil at the depth of 0-30 cm from Ferneziu, Săsar and Dura areas. In the same time, there has been collected plants growing in the same same location from where the soil samples had been drawn. They were collected Bentgrass (*Agrostis sp.*), Clover (*Trifolium repens*) and Nettle (*Urtica dioica*) from spontaneous flora.

The soil samples were dried, homogenized and then passed through a 20-mesh sieve to obtain very fine particles. The method for microwave digestion using a Milestone START D Microwave Digestion System, was optimized in a previous work (Bora *et al.*, 2018): 0.25 g soil, 9 mL of 65% HNO_3, 3 mL concentrate HF and 2 mL of concentrated HCl were placed in a clean Teflon digestion vessel. A total of 144 soils and 162 material samples were analysed, samples originated from Ferneziu, Săsar and Dura areas. The plant material samples (100 g per sample, hand-picked) were thoroughly washed with tap water followed by ultra-pure water using (Milli-Q Integral ultrapure water-Type 1), after washing was oven dried at 80 °C to constant weight using a (FD 53 Binder). The method for microwave digestion using a Milestone START D Microwave Digestion System using plant material was optimized in a previous work (Bora *et al.*, 2015): 1 g sample of plant material, 7 mL of 65% HNO_3 and 2 mL of 30% H_2O_2 were placed in a clean Teflon digestion vessel.

The analysis was made using multielement analysis and ICP-MS (iCAP Q Thermo Scientific) technique, after an appropriate dilution, using external standard calibration method. The determination methods for elements concentration from soils was optimized in a previous work (Bora *et al.*, 2018).

Results and discussions

The element concentration in investigated soils varied among samples, but it is noticeable that examined elemental may considerably surpassed the M.A.L (Maximum Admissible Limit), this is particularly obvious in the case of Pb, Cd, Zn, Cu, Ni and Cr. The highest concentrations were obtained in the Ferneziu and Săsar area for all metals, at the opposite pole there was the Dura area, which recorded the lowest heavy metals concentration. In the case of Dura area it can be seen that the concentration of Pb and Cd also exceeds the M.A.L. [32.59±1.47 mg/kg average value (M.L.A. = 20 mg/kg Pb)], with regard to Cd concentration, this limits was exceeds only in the surface from 0-5 cm (1.16±0.12 mg/kg) and 5-10 cm (1.07±0.12 mg/kg) (Tab. 1).

The highest concentration of metals from soil, was obtained by Mn (593.33±5.13 mg/kg average value) > Cu (408.41±1.83 mg/kg average value) > Pb (104.42±4.37 mg/kg average value) > Zn (57.46±2.58 mg/kg average value) > Cr (29.39±0.53 mg/kg average value) > Co (11.60±0.18 mg/kg average value) > Cd (10.43±0.66 mg/kg average value) > Ni (9.82±0.65 mg/kg average value) > Sn (4.72±0.23 mg/kg average value). The highest concentrations of heavy metals can be assumed that are coming from antropogenic ativities (Cd, Pb, Cu and Zn mining and non-ferrous metallurgy) and Co, Cr, Mn and also Ni are rather related to their natural occurrence in soil. The results obtained are comparable to those obtained by Mihaly *et al.* (2013) 115.00-19.195 [Pb (mg/kg)], 0.15-113.00 [Cd (mg/kg)], 100.000-3791.00 [Zn (mg/kg)], 0.20-23.50 [Co (mg/kg)], 6.50-1730.00 [Cu (mg/kg)], 0.20-29.30 [Ni (mg/kg)], 4.25-2124.00 [Mn (mg/kg)], 0.20-50.50 [Cr (mg/kg)] and 1.30-21.40 [Sn (mg/kg)].

Concerning the concentration of metals in plants, it can be seen that Pb, Cd, Zn and Cu they exceeded the M.A.L. for Ferneziu and Săsar area. Bentgrass (*Agrostis sp.*) has recorded high concentration at Pb, Zn, Ni (Ferneziu), Clover (*Trifolium repens*) has recorded high concentration at Cd, Co and Sn (Ferneziu) and Nettle (*Urtica dioica*) has recorded high concentration at Zn, Co and Sn (Săsar) (Tab. 2). In case of Dura area, all the elemental studied were under the maximum limit admitted. The highest concentration of metals from plants, was obtained by Mn (116.68±2.89 mg/kg average value) > Zn (84.45±0.31 mg/kg average value) > Cu (32.74±1.32 mg/kg average value) > Pb (23.83±1.08 mg/kg average value) > Cd (2.25±0.14 mg/kg average value) > Cr (2.22±0.11 mg/kg average value) > Ni (1.71±0.13 mg/kg average value) > Co (0.65±0.04 mg/kg average value) >Sn (0.25±0.03 mg/kg average value). The results obtained are comparable to those obtained by Mihaly et al. (2013) 1.04-255.00 [Pb (mg/kg)], 0.02-4.81 [Cd (mg/kg)], 30.10-199.00 [Zn (mg/kg)], 0.03-0.46 [Co (mg/kg)], 0.35-33.60 [Cu (mg/

Table 1. Variation of the elemental content in soils (mg/kg DW) (Mean ± standard deviation)(n = 12)

Areas	Type of soil	Depth (cm)	Total metal concentration								
			Pb	Cd	Zn	Co	Cu	Ni	Mn	Cr	Sn
			M.A.L.**	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.
Normal Values			20 mg/kg	1 mg/kg	100 mg/kg	15 mg/kg	20 mg/kg	20 mg/kg	900 mg/kg	30 mg/kg	20 mg/kg
Alert threshold	Susceptible		50 mg/kg	3 mg/kg	300 mg/kg	30 mg/kg	100 mg/kg	75 mg/kg	1.500 mg/kg	100 mg/kg	35 mg/kg
	Less Susceptible		250 mg/kg	5 mg/kg	700 mg/kg	100 mg/kg	250 mg/kg	200 mg/kg	2.000 mg/kg	300 mg/kg	100 mg/kg
Intervention threshold	Susceptible		100 mg/kg	5 mg/kg	600 mg/kg	50 mg/kg	200 mg/kg	150 mg/kg	2.500 mg/kg	300 mg/kg	50 mg/kg
	Less Susceptible		1.000 mg/kg	10 mg/kg	1.500 mg/kg	250 mg/kg	500 mg/kg	500 mg/kg	4.000 mg/kg	600 mg/kg	300 mg/kg
Ferneziu (polluted area)	Aluviosol	0-5	224.16±2.37 bβ	23.61±1.48 a α	86.79±6.32 c γ	16.08±1.45 a α	586.76±8.23 d γ	13.78±1.75 a α	899.73±22.96 bβ	33.46±1.56 c δ	8.72±1.06 a α
		5-10	269.71±18.60 aα	20.21±3.02 b α	108.41±5.57 a α	13.62±0.96 b β	643.20±10.09 ab α	14.27±2.58 a α	921.41±4.56 a α	40.76±1.35 a α	8.41±1.24 a α
		10-15	137.52±2.63 cγ	16.82±2.46 c γ	97.89±8.02 b β	13.76±0.88 b β	622.73±9.87 c β	10.05±0.34 bc γ	834.81±9.82 d δ	38.93±0.55 a β	8.16±0.54 a α
		15-30	139.82±1.35 cγ	17.01±1.33 c β	105.51±3.21 ab α	13.45±0.99 b β	546.33±16.96 e δ	11.41±0.72 b β	855.58±9.96 c γ	36.47±1.47 b γ	6.71±0.64 b β
		Average	192.80±8.26	18.79±0.81	99.65±2.00 β	14.23±0.26	599.75±3.87	12.38±1.01	877.88±7.84	37.40±0.46	8.00±0.33
Săsar (polluted area)	Luvosol	0-5	97.72±12.20 d β	13.04±2.25 d α	55.23±9.50 d β	12.46±0.85 b α	643.70±10.67 abβ	11.34±1.02 b α	739.75±6.64 e α	30.58±2.07 d β	5.57±0.58 bc α
		5-10	107.36±4.19 d α	11.17±0.89 de β	61.89±5.51 d α	12.65±0.70 b α	650.31±7.88 a α	10.04±0.33 bc β	541.31±5.46 g γ	31.35±1.15 cd α	5.38±0.85 c α
		10-15	71.31±8.63 e γ	10.73±1.40 de β	42.11±2.40 e β	10.75±0.71 c β	631.45±10.23 bcβγ	10.57±1.44 bc β	520.15±13.27 h δ	30.51±1.51 d β	5.48±1.17 bc α
		15-30	73.63±6.65 eγ	8.75±0.32 e γ	45.48±1.38 e β	12.66±0.51 b α	531.75±10.28 e δ	9.00±0.58 cd γ	567.76±19.45 f β	30.39±0.81 d β	5.52±0.45 bc α
		Average	87.87±3.39	10.92±0.82	51.30±3.65	12.13±0.14	641.31±1.27	10.24±0.49	592.43±6.48	30.71±0.54	5.49±0.32
Dura (background area)	Stagnosol	0-5	41.02±1.36 f α	1.16±0.12 f α	26.5±5.56 f α	8.37±0.42 d α	11.41±1.17 f β	6.09±0.55 e β	320.95±5.14 i β	19.53±0.85 e β	0.68±0.11 d β
		5-10	36.76±0.62 f β	1.07±0.12 f α	22.65±1.45 fg β	7.89±0.58 d β	9.36±0.50 f γ	6.22±1.49 e β	325.26±7.16 i α	20.68±1.81 e α	0.60±0.17 d γ
		10-15	28.96±2.13 f γ	0.80±0.21 fδ	20.18±1.96 fg β	8.65±0.54 d α	11.23±1.00 f β	7.23±0.58 de α	297.19±6.58 j γ	19.37±0.40 e β	0.71±0.14 d α
		15-30	23.61±4.61 f γ	0.84±0.17 f γ	16.55±0.95 g γ	8.88±0.24 d α	12.70±0.47 f α	7.81±0.69 de α	295.18±5.05 j γ	20.69±0.75 e α	0.70±0.05 d α
		Average	32.59±1.47 f β	0.97±0.04 β	21.43±2.09 β	8.45±0.15	11.18±0.35	6.84±0.45	309.67±1.05	20.07±0.60	0.67±0.05
Average			104.42±4.37	10.43±0.66	57.46±2.58	11.60±0.18	408.41±1.83	9.82±0.65	593.33±5.13	29.39±0.53	4.72±0.23
Minumum Values			23.61±4.61	0.80±0.21	16.55±0.95	7.89±0.58	9.36±0.50	6.09±0.55	295.18±5.05	19.37±0.40	0.60±0.17
Maximum Values			269.71±18.60	23.61±1.48	108.41±5.57	16.08±1.45	650.31±7.88	14.27±2.58	921.41±4.56	40.76±1.35	8.72±1.06
F			327.223	57.346	136.836	32.728	3335.881	15.031	1468.749	105.262	61.392
Sig.			***	***	***	***	***	***	***	***	***
Areas Sig.		F	1426.589	297.861	719.623	161.726	18066.695	65.107	7655.708	550.053	330.490
		***	***	***	***	***	***	***	***	***	
Depth Sig.		F	142.777	7.230	7.790	3.975	110.187	1.939	138.448	8.641	1.492
		***	**	**	*	**	in	***	***	in	
Areas x Depth Sig.		F	52.991	2.232	7.097	4.105	38.457	4.885	71.084	5.310	1.642
		***	in	***	*	**	**	***	**	in	
Mihali et al., 2013			115.00-19.195	0.15-113.00	100.00-3791.00	0.20-23.50	6.50-1730.00	0.20-29.30	4.25-2124.00	0.20-50.50	1.30-21.40

Average value ± standard deviation (n = 12). Romans letters represent the significance of the variety difference (*$p \le 0.05$*). Greek letters represent the significance of the depth difference (*$p \le 0.05$*). The difference between any two values, followed by at least one common letter, is insignificant. *Order of the Ministry of Waters, Forests and Environmental Protection No. 756/3 November 1997, approving the regulation on the assessment of environmental pollution, Bucharest, Romania; 1997. **M.A.L (Maximum Admissible Limit) = Normal Values. in = insignificant. S.A.T. = Susceptible Alert Threshold.

Table 2. Variation of the elemental content in plant materials (mg/kg DW) (Mean ± standard deviation)(n = 12)

Areas	Plant Materials Pb M.A.L.**		Total metal concentration								
			Cd	Zn	Co	Cu	Ni	Mn	Cr	Sn	
			M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	M.A.L.	
Normal Values			3 mg/kg	0.5 mg/kg	50 mg/kg	-	50 mg/kg	-	-	-	-
Ferneziu (polluted area)	Bentgrass (*Agrostis sp.*)		42.13±3.12 aα	3.91±0.34 b β	122.65±3.03 b α	0.57±0.09 b γ	54.43±9.65 a β	1.81±0.43 b α	81.08±1.36 d α	0.70±0.13 c β	0.17±0.06 ab β
	Clover (*Trifolium repens*)		25.89±4.98 d γ	4.59±0.39 a α	113.46±1.57 c γ	0.71±0.03 b α	40.64±4.57 b γ	1.29±0.33 bcd β	80.23±5.13 d β	0.61±0.13 c γ	0.19±0.06 ab γ
	Nettle(*Urtica dioica*)		35.70±4.83 bc β	3.73±0.10 b β	114.96±2.46 c β	0.67±0.11 b β	58.89±5.13 a α	0.77±0.18 d γ	82.89±2.89 d α	0.77±0.10 c α	0.18±0.04 ab α
	Average		34.57±1.03	4.08±0.15	117.02±0.04	0.65±0.04	51.32±2.78	1.29±0.12	81.40±1.90 d	0.69±0.02	0.18±0.01
Săsar (polluted area)	Bentgrass (*Agrostis sp.*)		34.36±2.72 bc β	3.96±0.61 b α	130.74±1.89 a β	0.93±0.13 a γ	52.35±2.78 a α	1.56±0.29 bc α	84.20±8.86 α	0.27±0.05 c γ	0.25±0.07 ab γ
	Clover (*Trifolium repens*)		40.19±2.15 ab α	2.51±0.47 c β	100.12±1.90 d γ	1.04±0.17 a β	31.47±1.61 c γ	0.95±0.07 cd γ	59.35±2.84 e γ	0.31±0.02 c β	0.32±0.10 ab β
	Nettle(*Urtica dioica*)		32.58±6.10 c γ	1.15±0.14 d γ	131.03±2.14 a α	1.21±0.17 a α	40.16±3.11 b β	1.06±0.14 cd β	62.62±5.53 e β	0.64±0.09 c α	0.34±0.08 a α
	Average		35.71±2.14	2.54±0.24	120.36±0.14	1.00±0.03	41.33±0.79	1.19±0.11	67.60±3.01 β	0.41±0.03	0.30±0.02
Dura (background area)	Bentgrass (*Agrostis sp.*)		1.32±0.26 e α	0.11±0.02 e γ	16.37±1.17 e α	0.33±0.04 c β	6.51±0.97 d α	2.68±0.50 a β	166.84±9.64 c	6.67±0.41 a α	0.18±0.04 ab γ
	Clover (*Trifolium repens*)		1.34±0.10 e α	0.12±0.01 e β	16.46±1.21 e α	0.19±0.06 c γ	6.22±0.95 d β	2.72±0.29 a α	243.79±10.68 a	6.15±0.95 a β	0.32±0.16 ab β
	Nettle(*Urtica dioica*)		0.92±0.12 e β	0.19±0.04 e α	14.31±1.11 e β	0.35±0.16 c α	4.01±0.31 d γ	2.55±0.61 a γ	192.45±3.72 b	3.78±0.63 b γ	0.33±0.09 a α
	Average		1.19±0.09	0.14±0.02	15.71±0.05	0.29±0.06	5.58±0.37	2.65±0.16	201.03±3.76	5.57±0.27	0.27±0.06
Average			23.83±1.08	2.25±0.14	84.45±0.31	0.65±0.04	32.74±1.32	1.71±0.13	116.68±2.89	2.22±0.11	0.25±0.03
Minumum Values			0.92±0.12	0.11±0.02	14.31±1.11	0.19±0.06	5.58±0.37	0.77±0.18	59.35±2.84	0.27±0.05	0.17±0.06
Maximum Values			40.19±2.15	4.59±0.39	131.03±2.14	1.21±0.17	54.43±9.65	2.68±0.50	243.79±10.68	6.67±0.41 a	0.34±0.08
F			77.809	106.257	2213.944	21.175	80.632	14.289	321.357	122.706	2.212
Sig.			***	***	***	***	***	***	***	***	***
Areas		F	354.156	423.261	147.126	785.032	412.036	102.155	89.145	450.066	147.126
Sig.		***	***	***	***	***	***	***	***	***	
Plant materials		F	23.184	47.546	132.004	15.236	1745.166	12.261	145.162	132.165	14.156
Sig.		***	***	***	***	***	***	***	***	***	
Areas x Plant materials		F	57.162	12.326	17.581	23.265	145.162	348.561	156.165	164.261	187.566
Sig.		***	***	***	***	***	***	***	***	***	
Mihali et al., 2013			1.04-255.00	0.02-4.81	30.10-199.00	0.03-0.46	0.35-33.60	0.21-3.22	0.20-260.00	0.15-2.85	0.02-0.15

Average value ± standard deviation (n = 12). Romans letters represent the significance of the variety difference ($p \le 0.05$). Greek letters represent the significance of the depth difference ($p \le 0.05$). The difference between any two values, followed by at least one common letter, is insignificant. *Maximum allowable level in dehydrated vegetables and fruits (food), mg/kg DW (Order no 975/1998). **M.A.L (Maximum Admissible Limit) = Normal Values.

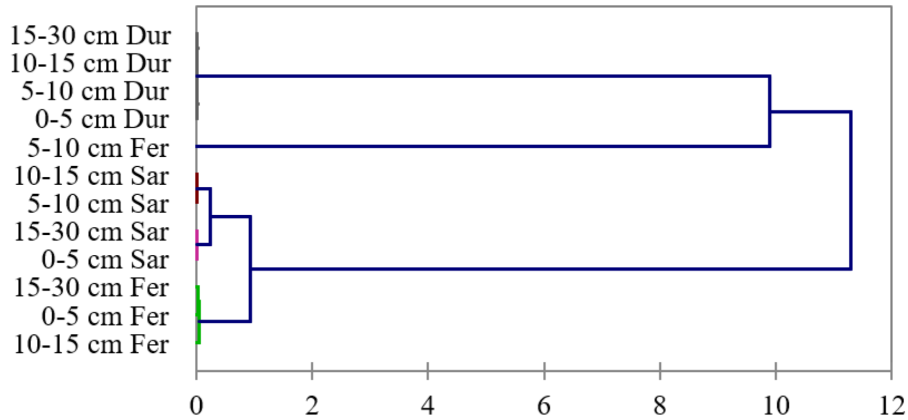

Figure 1. Hierarchical dendrogram for pollut areas based on heavy metals content in soils

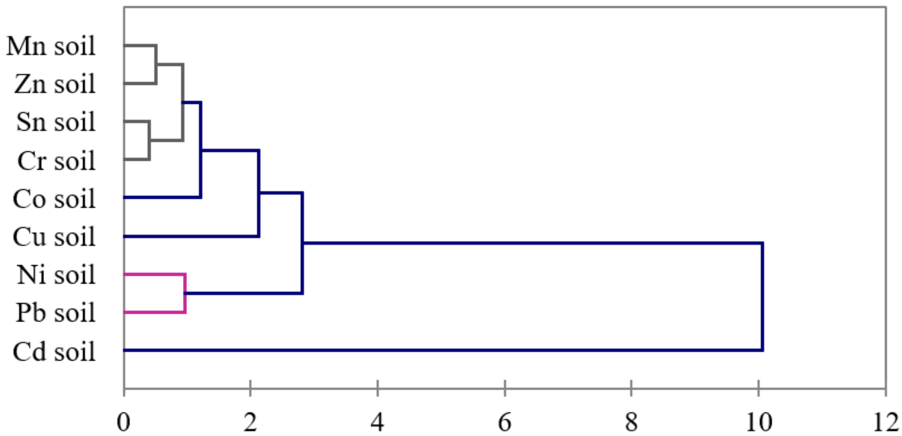

Figure 2. Hierarchical dendrogram for heavy metals in soils

kg)], 0.21-3.22 [Ni (mg/kg)], 0.20-260.00 [Mn (mg/kg)], 0.15-2.85 [Cr (mg/kg)] and 0.02-0.15 [Sn (mg/kg)].

The hierarchical dendrogram for polluted areas based on heavy metals content in sol material (Fig. 1) shown the contaminated locations are group in two primary clusters. The first cluster is formed of the sites which are located in Dura area, while the second one is formed of the sites of Ferneziu and Săsar. In terms of measure interval, the difference between these two-primary cluster is significant, which suggests that the level of soil pollution is significant higher in Ferneziu and Săsar area. Both primary cluster are further divide into several new subclusters. The position of an isolated subcluster which belongs to the Dura area, suggests that this area does not show severe pollution with heavy metals.

The dendrogram from heavy metals in soil (Fig. 2) shows the grouping of the elements in to main cluster: one isolated for Cd and other for the rest of elements, as numerous different subclusters. It terms of measure interval the difference between these two primary clusters is significant, which confirms that the source of Cd content in soils is simple, geology, whereas the contents of other metals in soils under the influence of atmospheric pollution. The largest influence of this pollution is reflected on the content of Cu, Pb and Zn.

Conclusions

In soils, the results showed diverse patterns of Pb, Cd, Zn, Co, Cu, Ni, Mn, Cr and Sn, in case of Pb in all areas exceeded the M.L.A (average 32.59 mg/kg while M.L.A. = 20 mg/kg), other elements shows high concentration that exceed the M.L.A. for Ferneziu and Săsar area. In the case of plant material also records exceedances of the M.L.A for Ferneziu and Săsar area, but in the Dura area there were no overtaking of M.L.A. The hierarchical dendrogram for polluted areas shown that the

Ferneziu and Săsar shows the highest trace of heavy metals pollution while the Dura area does not show severe pollution with heavy metals. The dendrogram from heavy metals in soil shows the Cd content in soils is simple, geology, and the largest influence of this pollution is reflected on the content of Cu, Pb and Zn.

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