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HEAVY METALS CONCENTRATION OF THE SOILS AROUND ZLATNA AND COPŞA MICĂ SMELTERS ROMANIA

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Abstract. The concentration and distribution of Pb, Cu, Zn and Cd in the soils from Zlatna and Copşa Mică (Romania) highly polluted by metallurgical activity, have been studied in the soil profile for different types of soils related with the physical and chemical properties of the soils. In Zlatna area, there have been studied the Aluviosol, Dystricambosol and Alosol types and in Copşa Mică area the Aluviosol and Phaeozem types. Content of humus, pH, cation exchange capacity, base saturation, organic carbon, C/N ratio, nutrient elements, texture and the heavy metals concentration in total and mobile form were determined for each pedogenetic horizon. The heavy metals concentration varies within the soil profiles related with different properties of the soils and with the metal species. The highest concentrations of lead, of 245 ppm to763 ppm, are in relation with the organic horizons, in conditions of acid pH (3.12 – 3.85) of Dystricambosols and of Alosols from Zlatna zone, and of 561 ppm to 2768 ppm in Aluviosols and Phaeozems from Copşa Mică area, in conditions of alkaline pH. Lead contents decrease suddenly, under the maximum allowable limit in C horizons within the soil profiles. The affinity of Pb for surface horizons is emphasized by the excessive contents of global samples of 995 ppm in Z-T, 980 ppm in Z-2 and of 5000 ppm in CM-T. The copper contents of the soil profiles, close to the maximum allowable limit are specific for the surface horizon of Dystricambosols (73.8 ppm), for the global sample Z-T, (99.7ppm) and for the Aluviosols in Copşa Mică area (71.1 to 96.9 ppm). Copper concentrations of 1165 ppm from Zlatna area increase towards the site of smelter in the global sample Z-2. The copper concentration of Copşa Mică global sample, representative for Aluviosols type exceed maximum allowable limit, being of 199 ppm. In conditions of acid pH, Zn presents concentrations of 775 ppm and of 820 ppm at C and B horizons, rich in clay and with a higher content of Fe and Mn in Aluviosol and Dystricambosol types in Zlatna area. In conditions of neutral to alkaline pH (5.03, 7.10, 7.26) in the soils from Copşa Mică, Zn immobilization in quantities of 7500 ppm, 4900 ppm in Aluviosols, 684 ppm in the Phaeozem type and 8591ppm in global sample at the surface horizons it is associated with values of the humus content between 0.48-4.56 percent. The Cd contents of 5.05 ppm exceed the maximum allowable limit in the global sample Z-2. In Bv horizon of Dystricambosols, the content of Cd is of 2.87 ppm in comparison with the contents under 1 ppm from the surface horizons. The increase of Cd content with the depth is related with the increase of the clay content and with acid pH conditions (3.72-4.59). In soils from Copşa Mică, Cd represents a concentration in the surface horizons of the soil's profiles, between 100-400 ppm in Aluviosols and 17.99 ppm in Phaeozem type. The high concentrations of Cd (175ppm) and of As (1500ppm) are related with the organic horizon of the soils from the global sample in Copşa Mică area. In comparison with lead and copper, cadmium has mobility on the soil's profile because it maintains the contents over maximum allowable limit values and the intervention limit in the intermediate horizons of the soil's profiles.

Keywords: soil type, heavy metals, pollution, mobility, soil profile

1. INTRODUCTION

The pollution with heavy metals has been researched in adjacent soils of metallurgical factories from Zlatna and Copşa Mică, in Romania. Generally, soils nearby smelters, present high risk of pollution with heavy metals on long term (Kabala & Singh, 2001). High concentrations of Cu, Pb, Cd and Zn, have been reported in Poland (Pichtel et al. 1997), in Příbram region (Czech Republic) (Vaněk et al. 2005), Kola Peninsula, (Koptsik et al. 2005), in Finland, (Peltola & Åström, 2003), in Romania (Lăcătuşu et al. 1998, 1999, Damian et al. 2007). Pollution with heavy metals from the atmospheric emissions affects the ecological functions of soils (Koptsik et al. 2005). The urban soils from several cities in Europe are subject to heavy anthropogenic disturbance, (Lăcătuşu et al 2007, Biasioli et al. 2007).

Soils nearby those two cities cannot be used for agriculture, (Fig. 1a) forest field, (Fig. 1b) because of excessive pollution with heavy metals, being an affectation source for the population's health.

a b

Figure 1: a. Copşa Mică; b. Zlatna. Effects of pollution with heavy metals on soils

Unfortunately, the industrial activities that have place in Copşa Mică, (Fig. 2), are not correlated with research and development activities for environment protection, (Fekete 2006).

The negative effects of the atmospheric emissions on soils, vegetation, water and animals, from Zlatna and Copşa Mică areas, have been studied by Lăcătuşu et al. (1998, 1999), Har et al. (2004), Rusu et al. (2004) and Williamson et al. (2003).

Figure 2. Image in 2008 from Copşa Mică Pb-Zn smelter

The study of the behaviour of heavy metals in soils, from the two areas affected by the metallurgical industry, has had in view the following: investigation of the distribution of those four heavy metals, Pb, Cu, Zn and Cd in the soil's profiles, contamination rate and heavy metals mobility in relation with the physical-chemical properties of soils.

Generally, the soil, through its components and properties, controls solubility, mobilization and deposition of toxic metals, resulted from anthropogenic sources, (Narwal et al. 1999, Siegel 2002). The influence of the soil's properties over the relative distribution of the heavy metals, (Lăcătuşu 1998), is better observed in the soil profiles (Kabala & Singh 2001).

2. MATERIALS AND METHODS

2.1. Location of the studied areas

The two areas (Fig. 3) have been selected for this study because the soil's contamination with heavy metals has been caused by the mining and non-ferrous metallurgical activity.

Figure 3. Location of the studied area

Zlatna town is located in the Zlatna depression area from Apuseni Mountains, on the upper course of the Ampoi River, at an altitude of 450-500 m, at 38 km west of Alba Iulia town. The depression area is dominated by terraces, motion cones and alluvial formations in the meadow area. The annual atmospheric emissions have been of 150-450t of sulphur dioxide and of 3498t of dust loaded with heavy metal particles. Copşa Mică town is located in the central part of Transylvania, in the depression zone of the Târnava Mare River, surrounded by hills, at 43 km of Sibiu town, being dominated by hill formations and floodplains.

2.2. Soil Types Description

The identification of soil types from the adjacent areas of the two industrial plants has been achieved on the basis of soil profiles excavated up to 1.20 m depth. The description of the soils has been achieved, according to the Soil systematic, by the "Romanian System of Soil Taxonomy" (RSST-2000) (Florea & Munteanu, 2003).

The most representative soils of the investigated area from Zlatna are: Aluviosols, Alosols, Dystricambosols.

The Aluviosol type (AS) develops in the river Ampoi's meadow, on alluvial parental material, represented by gravel with coarse sand levels, and on the tributaries terraces. Gravels are formed, predominantly, of sedimentary, igneous and metamorphic rocks. The Ao horizons (Fig. 4) are found in the top 15-20 cm of the soil profiles. These horizons are composed of mineral materials with the brown colour and variable texture from sandy with little quantities of silt and clay, to loam. The humus content is low, of 1.02-1.56% and the pH is neutral to alkaline. The great quantity of potassium, of 251 ppm in profile Z-1 certifies the presence of clays of illite type. Under Ao horizon there is a C horizon. In the C horizon the sandy fraction prevails, and the silt and clay decrease, (Table 1). The C horizon consists of partially decomposed parental material represented by sand and gravel.

Z-1 Z-2

Figure 4. Profiles of the Aluviosols

Figure 5. Associated surfaces of the Dystricambosol and the soil profile Z-3

The Dystricambosol type (DC) occupies the biggest surface around Zlatna town. These soils are specific to hill and mountain areas. They were formed in delluvium deposits, from the fine sandstone in the slope areas of the right versant of Ampoi Valley. The soil's surface is eroded, (Fig. 5). Within the soil profile, the following horizons are distinguished: Ao–Bv-C. The Ao horizon has brown colour and has the high percentage of humus. The pH variation in the soil profile correlated with the depth is from 3.72 to 4.59. The textural differentiation is weak within the soil profile and skeletally moderated. In Bv horizon, the clay fraction that has been produced by weathering increases slightly, (Buol et al. 2003). The C horizon contains a high rate of parental material fragments, intensely weathered up to 56.65%. Base saturation is low and increases with the depth.

The Alosol type (AL) develops in the south-western part of the Zlatna area. These soils have formed in areas with slopes of 25-40°, on delluvial and colluvial sediments, represented by pyroclastic rocks, sandstone, clay, conglomerates resulted from Badenian formations, colour being predominantly red. The typical vegetation is that of deciduous forests (durmast, beech). The soil profile is well differentiated, including the horizons: Ao-El-E/B-Bt-C. The texture varies within profile from sand loamy to clay loamy with the depth. The content of humus is low of 1.38% in Ao horizon. The pH variation is low and maintains itself in the high acid domain. The base saturation is very low, of 8.24-3.66%. The Bt horizon is found from 62-112 cm, has a high quantities of clay, and contain the angular fragments in different degrees of weathering. The colour is yellow-brown, due to accumulations of iron oxyhydroxides. The colour of C horizon is yellowish. It is composed of disintegrated and weathered fragments of parental material and a high quantity of clay. The clay minerals are represented by smectite, kaolinite, illite.

Soils from Copşa Mică have been formed in varied conditions of relief with morphologic characteristics, which succeed on vertical, from mountains, hills, and depressions. In the bottom land area of Târnava Mare River are developing Aluviosols, and in the terrace and hill areas prevail Eutricambosol and Phaeozem types.

The Aluviosol type (AS) develops on the fluvial parental material, being represented by sands and gravel in alternation with centimetre levels of clay. The underground water level can be found at 2 m of soil profile and can influence its formation. Within the soil profile, the water drainage is very good.

Figure 6. Aluviosol CM-1

Figure 7. Aluviosol CM-2

Figure 8. Phaeozem CM-3

Aluviosols has a well-developed profile, (Fig. 6, Fig. 7) formed of the following horizons: Ao-C and Ao-C-bAo-bC. The Ao horizon with a thickness of 18 cm, has a black-grey colour due to pollution with carbon black. The content of humus is 2.2%, the pH is neutral and presents a high content of potassium. The texture is loamy. The C horizon is in progress of formation, unstructured, with low content of humus. The mineral material of this horizon is represented by quartz, illite, feldspars, kaolinite and smectites.

The Phaeozem type has a considerable development, especially in the inferior part of the hill and terrace areas, at north and south of Copşa Mică area. The relief is weakly inclined, 20-30°. The original vegetation is represented by durmast forest. The parental material is represented by marls, clays and Pannonian siltstone. The soil profile, CM-3, is typical for this type of soil, Am-Bv-C (Fig. 8). The Am horizon has a thickness of 24 cm, black colour, and with a high content of humus. The structure of this horizon is very well formed, prevailing granular soil aggregates related to the amount of organic matter, (Layton et al. 1993). The texture is clay-loam, with a high content of potassium and mobile phosphorus. The content of soluble salts is low. The mineral material of the soil is represented by illite and smectite, and fine quartz. The Bv horizon is predominantly clayey with a low content of carbonate. It is developed on a thickness of 70 cm with brown-yellowish colour due to accumulation of Fe oxyhydroxides. It is a very little structured horizon and has a low content of humus and low quantities of potassium and mobile phosphorus.

2.3. Sampling

There have been accomplished four soil profiles for copper smelter in Zlatna area and three profiles for Pb-Zn smelter in Copşa Mică area, on different types of soils and different distances from the smelters. The location of soil profiles had in view the ascertainment of soil's contamination with heavy metals for different uses, the forest field, and the arable field. The soil samples have been yielded from different depths, which correspond with the pedogenetic horizons in each soil profile up to 1.20 m deep.

The contamination rate of soils on a surface limited by soil profiles from the two areas has been checked by yielding some global samples from the depth of 0-20 cm, of 100 kg each. For Zlatna there have been yielded 2 global samples that correspond with the development area of Dystricambosols (Z-T) and with the development area of Aluviosols from the location area of metallurgical factory (Z-2T). For Copşa Mică, the global sample (CM-T) is representative for the Aluviosols nearby the factory.

2.4. Laboratory Analyses

Soil samples have been homogenized and dried in the air and sieved through 2 mm sieve. From each sample, there have been effectuated analyses for the concentrations in the total and mobile form of heavy metals as Pb, Cu, Zn, Cd, and for the physical-chemical properties of soils: pH, humus content, cation exchange capacity, C_{org}, base saturation, content of nutritive elements, C/N ratio, texture type.

The analyses have been effectuated at the Research Institute for Soil Science Agrochemistry and Environment Protection, Bucharest. Determination of pH has been accomplished in watery suspension in report with the soil: water of 1:2.5. The sum of basic cations of exchange has been achieved by the extraction with HCI 0.05 n, after

Kappen method (me/100 g soil). The hydrolytic acidity has been determined at equilibrium in solution of acetate of sodium 1 n, the soil report: solution of 1:2.5; by titration with NaOH, in presence of phenolphthalein of extracted acidity (me/100 g soil). The total cation exchange capacity has been determined through calculation: CEC= SB + Ah (me/100 g soil). Mobile content of heavy metals have been extracted in ammonium acetate 1 n and EDTA 0.01 m, the soil report: solution of 1:5 and dosing with the spectrophotometer with atomic absorption. Total contents of heavy metals have been obtained by wet mineralization with $HC1O_4$ and HNO_3 and dosing with the spectrophotometer with atomic absorption. The humus volumetrically has been determined used through the wet oxidation method (after Walkley-Black). The amount of total nitrogen has been obtained by Kjeldahl method. Phosphorous and potassium soluble has been determined in solution of ammonium acetate lactate of at pH = 3.7 (after Egner-Riehm-Domingo).

Particle size distribution has been determined by sieving and sedimentation. Determination of the content of clay and silt has been effectuated by sedimentation with the Kubien pipette method.

The X-ray diffraction analyses have been performed at the North University of Baia Mare using a Philips-Muller Diffractometer with PW 1050/25 goniometer and copper tube PW 1043/01 and the speed of registration of 1 degree per minute.

3. RESULTS AND DISCUSSION

3.1. Soil properties

Texture differentiation on soil profiles is low in both areas, and reflects the specific conditions of formation of soil types. In Zlatna, the Aluviosols with transition horizon, under the Ao horizon, the clay content decreases with the depth, and the sand content increases. In Dystricambosols and Alosols, the content of clay increases in Bv horizons towards Ao horizons, making a transition from sandy loam to loam. In Copşa Mică, within the soil profile the Aluviosols over the entire depth are sandy, poor in clay (6.6-13.7%), with the exception of Ao horizon from profile CM-1, where the content of clay is of 27.9%. In the Phaeozem type, the granulometric fractions are distributed in equal quantities between Am and Bv horizons (Tab. 1).

The cation exchange capacity is moderated in all A horizons (12.58-21.96 meq/100g soil) in Zlatna area and 16.65 meq/100g for Phaeozem type in Copşa Mică area. The increase of clay content from horizons B influences an increase of cation exchange capacity towards A horizons. The content of humus varies from low to moderate (1.02-3.12%) in surface horizons in the soils from Zlatna, and from very low to moderate (0.48-2.76%) in the soils from Copşa Mică. Generally, the content of humus decreases with the depth on soil profiles. In global samples, the content of humus varies from low (1.44%) in Z-2T (Zlatna) to high (4.38%) in Z-T Zlatna, and (4.56%) CM-T (Copşa Mică). After the values of pH, Aluviosols from both areas correspond to the class of neutral reaction to alkaline (6.39 – 8.16). The lower values of the pH are associated with the organic horizons, and the increase of pH with the depth is less than 1% in this type of soils.

Table 1. The physical and chemical properties of the soils from Zlatna and Copşa Mică areas

Soil Type/Horizon		Depth (cm)	pH	Humus	C_{org}	Nt	C/N	P	K	Sand	Silt	Clay	Texture class	CEC (meq/ 100gsol)	Base saturation, (%)
				%				ppm		%					
Aluviosol,															
Z-1	Ao	0-20	7.36	1.02	0.59	0.056	12.3	7.2	251	71.8	9.9	18.3	SG	-	-
	A/C	20-70	7.78	0.30	0.17	0.016	12.7	6.2	65	80.7	5.5	13.8	SG	-	-
Z-2	Ao	0-20	6.39	1.56	0.90	0.128	8.2	1.1	72	56.1	19.1	24.8	LL	21.96	20.51
	A/C	20-73	6.70	1.08	0.62	0.100	7.3	2.8	60	51	23.8	25.2	SL	22.33	21.34
Dystricambosol															
Z-3	Ao	0-20	3.72	3.12	1.81	0.124	17.0	5.0	39	64.2	18.7	17.1	SL	15.63	4.50
	Bv	20-47	3.90	0.78	0.45	0.060	8.8	-	40	59.9	21.0	19.1	SL	11.02	2.83
	C	47-97	4.59	0.42	0.24	0.108	2.6	-	93	62.6	10.5	26.9	LL	18.53	12.82
Alosol															
Z-4	Ao	0-20	3.85	1.38	0.80	0.070	13.3	0.8	49	53	27.1	19.9	SL	12.58	3.66
	E	20-45	3.98	0.66	0.38	0.038	11.7	3.8	61	46.5	26.4	27.1	LL	12.92	3.66
	Bt	45-90	4.13	0.48	0.27	0.036	9.0	-	81	45.7	22.1	32.2	LL	21.80	8.24
Z-T Global		0-20	3.49	4.38	2.54	0.180	16.5	34.1	39	65.61	16.4	18.05	SL	21.61	3.49
Z-2T Global		0-20	7.64	1.44	0.83	0.050	19.5	17.4	115	70.4	11.5	18.1	SM		
Aluviosol															
CM-1	Ao	0-18	7.26	2.22	1.28	0.16	9.3	6.3	232	54	18.1	27.9	LL	-	-
	A/C	18-47	7.96	0.54	0.31	0.014	26.1	10.3	53	88.3	2.3	9.4	UM	-	-
	C	47-73	8.16	0.30	0.17	0.016	12.7	7.2	39	84.7	5.9	9.4	UM	-	-
CM-2	Ao	0-25	7.10	0.48	0.27	0.028	11.6	13.4	84	84.9	5.2	9.9	UM	-	-
	C	25-32	8.02	0.42	0.24	0.022	12.9	8.7	81	90.7	2.7	6.6	UG	-	-
	bAo	32-49	7.55	1.56	0.90	0.062	17.0	79..3	149	84.4	6.0	8.6	UG	-	-
	bC	49-61	7.89	0.54	0.31	0.048	7.6	13.9	115	74.2	12.1	13.7	SM		
Phaeozem															
CM-	Am	0-24	5.03	2.76	1.60	0.11	15.8	38.3	237	63	13.3	23.7	LN	16.65	11.15
	Bv	24-74	5.94	0.96	0.55	0.076	8.5	8.5	74	62.8	13.8	23.4	LN	17.65	15.52
CM-T Global		0-20	6.94	4.56	2.64	0.140	22.0	20.4	170	65.1	12.7	22.2	LN	-	-

Z-1-4 soil profile Zlatna, CM-1-3, soil profile Copşa Mică; Texture class: SG-sandy loam, LL- loam; SL-sandy clay loam; UM-loamy sand; UG-sand; SM-sandy loam; LN-clay loam

The Dystricambosol and Alosol types from Zlatna have the pH on soil profiles between 3.72 to 4.59 and 3.85 to 4.13, corresponding to the class of acid strong reaction to acid moderate. Also, the soil of Phaeozem type from Copşa Mică, has acid weak reaction with variation of pH, from 5.03 to 5.94. In global samples from Zlatna, the pH is 3.49 in Z-T, proper to soil of Dystricambosols, and of 7.64 in soil from the location area of metallurgical factory (Z-2T). In global sample (CM-T) from Copşa Mică pH is 6.94. The base saturation rate increases with the depth in all soils from both areas. The quantity of C_{org} is, in general, very low $<2\%$ in soil profiles, the biggest values being specific to surface horizons of 0.592 to 1.810% in Zlatna, and between 0.27 to 1.60% in Copşa Mică area. In global samples, the content of C_{org} is moderated, 2.54% in Z-T and 2.65% in CM-T, and low in Z-2T, 0.835%.

The studied soils are poor in nutritive elements, (Tab. 1). The content of Nt varies from 0.056% to 0.128% in organic horizons of soil profiles from Zlatna, and from 0.028% to 0.16% in soils from Copşa Mică. The low content of nitrogen is the consequence of reducing the microbial activity of fixation of nitrogen caused by pollution with heavy metals, (Lorenz et al. 1992). The contents of potassium have low values, the highest values, of 237 to 152 ppm, are related with the organic horizons of soils, which had been treated with fertilizers, in Phaeozem and Aluviosol types (CM-1 soil profile in Copşa Mică area and in Z-1 soil profile from Zlatna area).

Generally, the content of phosphorus in the studied soils is low. Bigger contents of phosphorus have been determined in sandy and sandy loam soils, poor in clay fraction, which have determined the lower binding of phosphorus, (Zarcinas et al. 2003).

The mineralogical composition of the clay fractions (under 0.02 mm) in the soil global samples from both areas was determined by X-ray diffraction studies. The dominant clay types are: montmorillonite, illite, kaolinite. All the clay minerals present a poor crystallinity. The X-ray diffraction patterns of the clay particles indicate an amorphous phases.

3.2 Total concentration of heavy metals

The important anthropogenic sources, by which heavy metals are introduced into soil from both areas, have been represented by: gas emissions from the metallurgical factories with content of metallic particles, by dissolving under the effect of acid rains; leaching of heavy metals from the tailling dumps and from the metallurgical slag. Concentration in a total and mobile form (Tab. 2) of those four analyzed heavy metals, Pb, Cu, Zn and Cd in soil profiles and in the global samples of both areas, Zlatna and Copşa Mică, exceed maximum allowable limit for soils, according to the Romanian legislation.

Concentration in a total form of those four heavy metals in different types of soils reflects different rates of pollution on soil profiles depending on the metal species (Tab. 2). The concentration and distribution of heavy metals have been analyzed on soil profile in relation with certain physical-chemical properties of soils, which determined mobility and bioavailability in soils, (Jiemba 2005). In soil, heavy metals can be affected by processes of sorption/desorption, precipitation, dissolution, redox reaction, incorporation in the solid components of soil, (Koptsik et al. 2005).

Table 2. The total and mobile form of concentration of heavy metals in soil from Zlatna and Copşa Mică areas

Soil type/horizon/profile	Pb ppm		Cu ppm		Zn ppm		Cd ppm	
	total	mobile	total	mobile	total	mobile	total	mobile
Aluviosol **Z-1** Ao A/C	 66 57	 41.7 31.4	 45.2 24.2	 16.0 4.6	 102 207	 35.6 187	 0.95 1.01	 0.60 0.70
Z-2 Ao A/C	 48 39	 14.4 5.3	 19.2 12.4		 230 775	 63.0 69.1	 0.50 0.25	 0.63 0.19
Dystricambosol **Z-3** Ao Bv C	 763 39 39	 374 8.7 7.5	 73.8 20.1 13.7	 33.4 10.1 4.1	 150 161 830	 33.5 16.2 304	 0.35 0.35 2.87	 0.21 0.23 1.55
Alosol **Z-4** Ao E Bt	 245 48 30	 101 18.9 10.9	 38.8 27.9 24.7	 22.4 12.4 16.0	 105 82 93	 40.6 51.8 71.2	 0.35 0.28 0.45	 0.21 0.25 0.42
Aluviosol **CM-1** Ao A/C C	 2768 26 9	 1173 21.0 4.0	 96.9 5.1 1.0	 22.4 1.4 0.7	 7500 275 37	 2819 104 32.0	 400 2.79 0.45	 153 2.60 0.33
CM-2 Ao C bAo bC	 1429 61 182 21	 1313 48.0 89.0 9.8	 71.1 8.3 21.5 3.7	 23.3 3.0 8.7 1.3	 4900 1070 1808 54	 2974 489 306 35.6	 100 23.70 31.25 0.50	 74.4 23.18 25.24 0.34
Phaeozem **CM-3** Am Bv	 561 30	 498 12.1	 22.4 6.	 10.2 1.4	 648 513	 484 102	 17.99 1.60	 16.30 1.35
Z-T Global sample	995	876	99.7	40.7	127	26.4	0.50	0.34
Z-2T Global sample	980	378	1165	275	1377	170	5.05	2.90
CM-T Global sample	5000	2042	199	36.1	8591	2795	175	161
MAL	**100**		**100**		**300**		**3**	

MAL - maximum allowable limit; Z-1-4 soil profiles in Zlatna; CM-1-3 soil profiles in Copşa Mică.

3.2.1 Lead

The highest concentrations of lead are related with the organic horizons of Dystricambosols and of Alosols from Zlatna in conditions of acid pH, (Fig. 9) and in Aluviosols and Phaeozems from Copşa Mică in conditions of alkaline pH, (Fig. 10). Lead concentrations vary between 245 to 763 ppm in Zlatna, and between 561 to 2768 ppm in Copşa Mică. Lead contents decrease suddenly, under maximum allowable limit (MAL) in C and Bv horizons of the soil profiles, (Fig. 11) thus proving the Pb affinity for insoluble humic substances, (Angehrn-Bettinazzi et al. 1989).

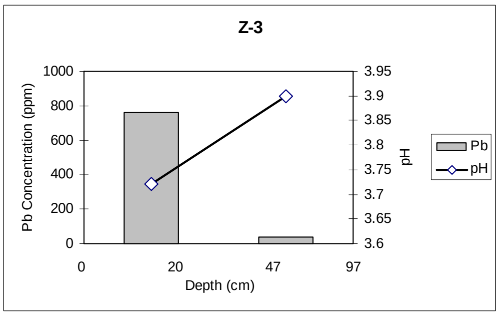

Figure 9. Distribution of Pb and the pH variation in soil profile Zlatna area

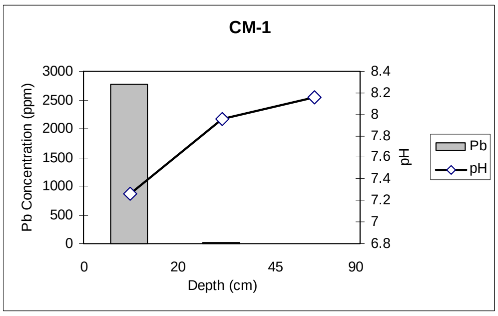

Figure 10. Distribution of Pb and the pH variation in soil profile Copşa Mică area

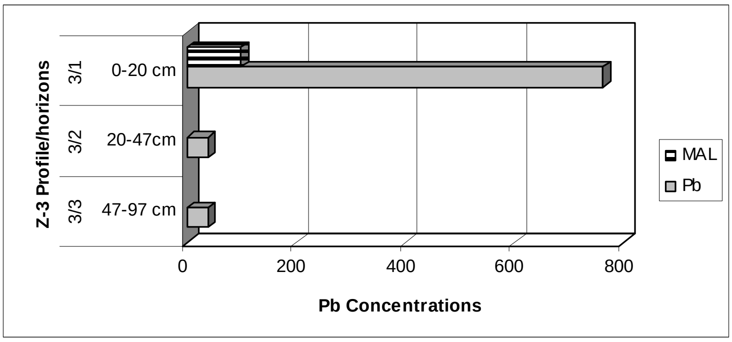

Figure 11. Distribution of Pb in soil profile and MAL of Pb

The bigger stability of complexes with humic acids of Pb and Cu (due to coordinative complexes) than that of complexes with Cu and Zn (due to reactions of ionic exchange) has been demonstrated by Pinheiro et al. (1994), Ladonin & Margolina (1997). For the excessive concentrations of Pb from Aluviosols and Phaeozems, in Copşa Mică, which have a content of humus from very low to medium (0.48 to 2.76%), it is possible that in retaining of lead through absorption mechanisms, an important role may be played by the clay fraction demonstrated by Sipos et al. (2003). The clay content in surface horizons of the CM-1 and CM-3 profiles is of 27.9% and 23.7%. Absorption might be favoured at near-neutral to alkaline pH values, (Voegelin et al. 2003), (pH of 5.03 in CM-3 and pH of 7.26 in CM-1) with a weak variation, (Bradl 2004) from surface horizons of soil profiles. An important role for biding through absorption of Pb, can be played by Fe oxides and of Mn, (Bradl et al. 2005), which are presented in great quantity in surface horizons of the soil profiles from Copşa Mică. Also, high pH could favour reactions of precipitation through which Pb is transformed in insoluble compounds in these soils of hydroxides Pb form that are, predominantly, between pH 6 and pH 10, (Bradl 2004). The immobility of Pb within the soil profiles is also emphasized by the percent concentrations of contents in mobile form of the total form contents. The percent of Pb in mobile form is higher in the upper horizon, and decreases with the depth on soil profiles of both areas. The affinity of Pb for surface horizons is emphasized by the excessive contents from global samples of 995 ppm in Z-T, 980 ppm in Z-2T, and 5000 ppm in CM-T.

3.2.2. Copper

Copper is the heavy metal, strongly bound of soil's phases, which determines a contamination on long term, (Koptsik et al. 2005), caused by formation of some constituents of soil of no exchangeable components, (Bradl et al. 2005).

Copper contents in studied soil profiles present low concentrations, under the maximum allowable limit of 100 ppm, but over the normal values. The contents close to maximum allowable limit are specific for Dystricambosols (73.8 ppm) profile and global sample Z-T (99.7 ppm) and for Aluviosols from Copşa Mică (71.1 to 96.9 ppm). Copper concentration from Copşa Mică global sample exceeds maximum allowable limit, being of (199 ppm), and the Cu content in global sample Z-2T exceeds this limit for 11.65 times. Association of bigger contents of copper with surface horizons of soil profiles (Tab. 2) and concentrations of the global samples sustains the role of organic material, in the form of humic and fulvic acids as mechanisms for Cu in soil retention, (Bradl et al. 2005). The repartition of Cu contents in quantities close to horizons, in the soil profiles of Dystricambosols and Aluvisols from Zlatna area, is related with Fe, Mn, and clay increases with depth. In these conditions, the weak mobility of Cu (in Z-4 soil profile) is associated with low values of pH (3.85, 4.13), which prevent the adsorption on clay fraction (Bradl et al. 2005). At bigger concentrations of Cu, it is obvious the bigger retention capacity of horizons rich in organic material of 68.58% in soil profiles for Dystricambosol and 94.07% in soil profile for Aluviosol type from Copşa Mică area. The mobility of Cu in soils from Copşa Mică was limited as shown by reduction in their concentration within the soil profiles in relation with decrease of humus content (Fig. 12). Association of Cu in high proportions (from 40 to 74%) with organic matter, Fe, Mn oxides and carbonate was demonstrated in sequential extraction by Ma & Rao (1997).

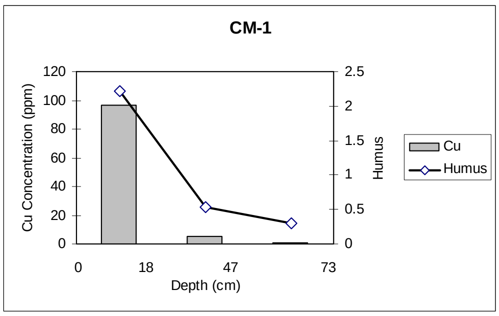

Figure 12. Distribution of Cu and the humus variation in soil profile from Copşa Mică area

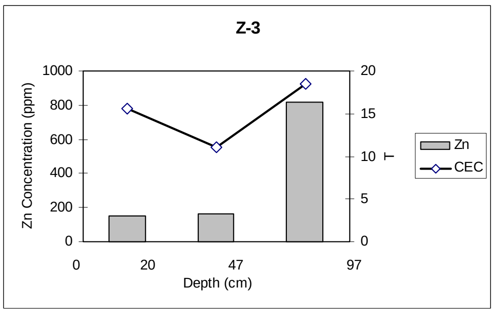

Figure 13. Distribution of Zn and CEC variation in soil profile from Zlatna area

The series of bivalent elements with affinity for the most stable complexes with humic acids is the following: Cu>Pb>Fe>Ni=Co=Zn>Mn=Ca, (Adriano 2001). The high percent of sand from soils of both areas could negatively influence the sorption of Cu, (Kabala & Singh 2001). The low concentrations of Cu from soil profiles of Zlatna area are due to losses from topsoil through erosion of flow that removed the fine part of the material from the surface. Concentrations of Cu from Zlatna area increase very much towards the site of smelter and near the tailing dump, in the lowest area of Aluviosols.

3.2.3. Zinc

The behaviour of Zn on soil profiles is different in the two areas, possible under the influence of pH values, (Catlett et al. 2002). In organic horizons of soils from Zlatna, where the pH varies from neutral to acid, Zn concentrations in total form do not represent significant values for pollution. The variation within the soil profile (Z-2 and Z-3) of the total content of zinc in relation with the content of humus and with the variation of pH, has emphasized the Zn concentration (775 ppm and 820 ppm) in quantities that exceed the maximum allowable limit of 300 ppm at C horizons rich in clay minerals, with high cation exchange capacity (CEC), (Fig. 13). Mobility on soil profiles in conditions of acid pH can be ensured by the ability of Zn to form complexes with mobile organic substances, with low molecular weight, (Angehrn-Bettinazzi et al. 1989). The role of the clay and of Fe and Mn oxides in Zn adsorption was demonstrated by Kuo et al. (1983), Narwal et al. (1999) and Bradl et al. (2005).

In conditions of neutral to alkaline pH (pH 5.03, 7.10, 7.26) in soils from Copşa Mică, the pollution with Zn is excessive at the surface horizons level of soil profiles. The immobilization effect of Zn in excessive quantities at surface horizons level, 7500 ppm, 4900 ppm, in Aluviosols and 684 ppm in Phaeozem type, is associated with values of humus content, between very low to moderate (from 0.48% to 2.27%). In presence of a relative low content of humus, through adsorption mechanisms, an important role in retention of Zn can be played by fine clay fractions that are 29% in Aluviosols and 23.75% in Phaeozem type. In alkaline soils Zn retention is due to the precipitation of Zn hydroxide or carbonates, (Adriano 2001).

The mobility of Zn is emphasized in all soil profiles from Copşa Mică, especially in profile CM-2, where the contamination rate with heavy metals is in relation with the development of soil under the influence of flooding. With all these, the biggest quantity of zinc is bounded to the surface horizons of soil, especially in the case of Aluviosols, also emphasized by the Zn content of global sample that is 8591 ppm, in conditions of alkaline pH, high content of humus, 4.56%, and of C_{org}, 2.64%.

3.2.4. Cadmium

Generally, on soil profiles of both areas, variation of Cd concentration is identical with that of Zn, and opposed to Pb and Cu. In Zlatna area, the content of 5.05 ppm for Cd exceeds the maximum allowable limit in global sample Z-2T. The concentration of Cd, increase within soil profiles, related with several soil properties with depth, including increased clay content, in conditions of acid pH from 3.72 to 4.59. The adsorption mechanisms for Cd specific to clay minerals, was demonstrated by Dudley et al. (1991). In Bv horizon of Dystricambosols, the content of Cd reaches 2.87 ppm in comparison with the content under 1 ppm of the surface horizon, (Fig. 14). Contents of Cd under 1 ppm of horizons rich in humus (from 1.02 to 12% in profiles and 4.38% in global sample Z-T) sustain the idea of low adsorption of Cd by the organic material at low pH.

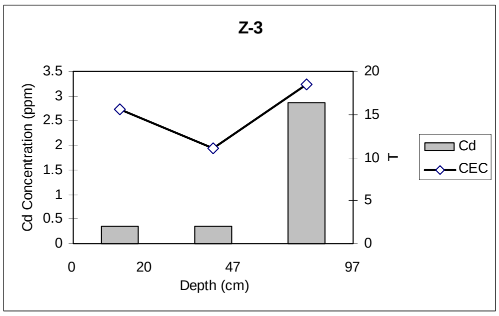

Figure 14. Distribution of Cd and CEC variation in soil profile from Zlatna area

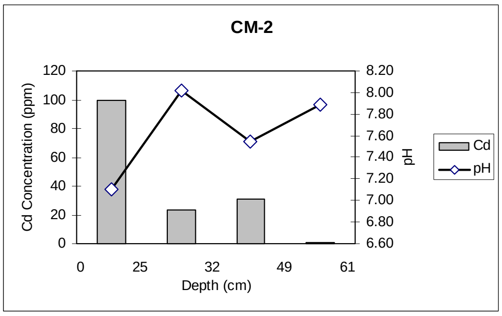

Figure 15. Distribution of Cd and pH variation in soil profile from Copşa Mică area

In soils from Copşa Mică area, the Cd content from surface horizons exceeds the intervention limit for 80 times. The retention of Cd in horizons rich in humus is due to the biding capacity of humic substances in conditions of high pH, (Reuter & Perdue 1997). In comparison with lead and copper, in the case of cadmium, it is observed mobility on soil profile in maintaining the contents over the maximum allowable limit values, and of intervention limit in intermediate horizons in the CM-2 profile, (Fig. 15). In conditions of high pH, (determined by the content of carbon introduced in soils from Copşa Mică by polluting with carbon black), there have been created conditions of precipitation of certain compounds of the analyzed heavy metals, which maintain the excessive rate of soil pollution at longer distances from the metallurgical factory. The sandy soils with a low content of organic material, with alkaline pH with high content of Cd, favours formation of $CdCO_3$, which controls solubility and concentration of Cd, (McBride 1980).

4. **CONCLUSIONS**

Distribution of heavy metals in studied soils within soil profiles is influenced by the soil's properties, determined by the pedogenetic processes and by the modifications under the influence of anthropogenic activities. The atmospheric emissions, with content of metallic particles and sulphur oxides, have determined the strong acidity of soil profiles in Dystricambosols and Alosols in Zlatna area (pH 3.72 to 4.59, 3.85 to 4.13). The same effects have been decreased in the case of Aluviosols from this area, which are situated in the floodable areas of rivers, where pH varies from 6.39 to 7.78 in soil profiles.

In Copşa Mică area, a severe impact on soils has had the emissions of black carbon, in a long period of time, simultaneously with the gas emissions from the metallurgical factories of Pb and Zn. In these soils, the reaction is neutral (pH from 5.3 to 5.94) (in Phaeozem type) to alkaline (pH 7.10, 7.26 in surface horizons with a light increase on soil profiles with depth) (in Aluviosol type). In these conditions, in Copşa Mică, soils have been produced a severe pollution with heavy metals in both surface horizons and soil profiles, over 1m deep.

Heavy metals concentrations determined in the studied soil types from both areas, Zlatna and Copşa Mică exceed the Romanian reference limits from the Order (756/1997). The great quantity of heavy metals from Copşa Mică is comparable with the excessive pollution of organic horizons due to the exceeding of maximum allowable limit for Pb of 5.61 up to 27.68 times, for Zn of 2.16 up to 25 times, and for Cd of 5.99 up to 133.3 times. For Zn and Cd the concentration in the total form exceeded of maximum allowable limit and an intervention threshold the clay-rich horizons at variable depths in both areas.

In global samples from Zlatna, concentrations of heavy metal exceed the maximum allowable limit for all four metals. The concentrations of Cu are the highest in global sample Z-2T, nearby the smelter and tailing dump, being of 1165 ppm. Copper is associated with Pb, 980 ppm, Zn 1377 ppm and Cd 5.05 ppm. Global sample Z-T, representative for the development area of Dystricambosols type, presents high concentrations of Pb, 995 ppm, and lower of Cu, 96.9 ppm, Zn 127 ppm and Cd 0.50. The migration of Zn and Cd in depth, observed in soil profile, is confirmed by the low content in the global sample.

The study on the heavy metals behaviour in soil profiles from nearby of those two smelters of copper (Zlatna) and of lead-zinc (Copşa Mică), has demonstrated the pH influence and that of the humus content from surface horizons on polluting these with Pb and Cu. The sudden decrease of Pb contents in soil profiles, under the horizon rich in humus, up to normal values, indicate high stability in surface horizons, determined by biding Pb to insoluble organic fractions (Angehrn-Bettinazzi et al. 1989).

Soils from Copşa Mică are characterised by excessive pollution with four heavy metals, Pb, Cu, Zn, Cd. Arsenic is added to these, being analyzed in the CM-T, global sample and its content is of 1500 ppm. The highest contents are related with the surface horizons of soil profiles.

Mobility on soil profiles has been observed for Zn and Cd in conditions of weak acid to neutral pH, in relation with the increase of clay fraction, and of Fe and Mn in Dystricambosols and Alosols, and with the increase of cation exchange capacity, in the soil profiles in Zlatna area. Distribution of Zn and Cd in soil profiles in both areas, from all types of soils, is variable with depth due to the high quantity of these metals in total form and of the high percent of mobile form at the level of horizons from the depth. In soils from Copşa Mică area, the conditions of neutral to alkaline pH are favourable to biding Zn under the form of secondary compounds with iron oxyhydroxides or under the form of anhydry silicates, which have been frequently identified in polluted soils by smelting processes, (Manceau et al. 2002, Kirpichtchikova et al. 2006). Retention of great quantities of Zn and Cd on surface horizons might be in relation with the contents of Fe and Mn from soil profiles, taking into consideration the moderate or reduced quantity of organic material from these horizons and alkaline pH. Mobility on soil profiles of Zn might be also determined by the formation of some compounds of Zn, which become soluble with the increase of pH with the depth. In Phaeozem type, repartition of Zn in comparable quantities, between horizon A and B, is associated with equal repartition of clay fraction in the two horizons.

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