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DISTRIBUTION OF HEAVY METALS IN GRANULOMETRIC FRACTIONS AND ON SOIL PROFILES

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Abstract: Physico-chemical and granulometric studies of two soil types (anthrosol and eutricambosol) revealed heavy metal concentration variations and its distribution in the particle size fractions. The copper and lead contents in the anthropic soil, at both sampling depths exceed the alert thresholds. Zinc and cadmium contents exceed these thresholds only partially. Lead accumulates in the topsoil's coarse fraction, while Cu and Cd in the deeper fine fraction. In this soil type's topsoil, heavy metal distribution shows no dependence on particle size fraction. At higher depth, concentrations increase from silt and gravel to clay fraction. Heavy metals in the eutricambosol mainly have normal concentrations, or below the alert threshold, except for the clay fraction from all horizons where the alert and intervention thresholds can be exceeded. In this case, heavy metals accumulate mainly in the topsoil, and their concentration decreases with soil-profile depth.

Keywords: anthropic soil, eutricambosol, heavy metals, particle size distribution, physico-chemical properties.

1. INTRODUCTION

Heavy metals form an important group of the toxic pollutants found in soils. Determining the degree of anthropic heavy metal pollution in former or active industrial areas is most important to assess their negative effects. The origin of this pollution can be mainly linked to metallurgical industrial activities (Kabala & Singh 2001; Vaněk et al., 2005; Zong et al., 2016). The impact of potentially toxic heavy metal accumulation on population health was recently investigated (Nedelescu et al., 2017), while dendrochemical techniques for their determination and historical monitoring were also proposed (Marković et al., 2007). Most heavy metal concentration studies addressed only the topsoil (Damian et al., 2008; Paulette et al., 2017). It was also proven that heavy metal concentration distribution within a single soil profile depends drastically on its geochemical behavior (Damian et al., 2008). This way, Pb is retained in the topsoil horizons, while Zn can migrate into the deeper horizons.

Heavy metal sorption behavior exhibited by different granulometric fractions of different soil types was previously studied (Lair et al., 2007). Higher sorption properties were demonstrated in the fine granulometric fractions than in the coarse sand fraction, explained by bigger specific surfaces. But these results were challenged when high heavy metal concentrations were measured both in the coarsest and in the finest fractions (Zornoza et al., 2010). Increasing concentrations with decreasing size fractions were also observed in agricultural soils (Sarlak 2015). Sorption properties of synthetic nano-/microscale materials, like those that are naturally occurring in soils, are also of great interest (2008; Huang et al., 2011; Belyakova & Lyashenko 2014; Wang et al., 2016), demonstrating the importance of substrate physico-chemical properties, its dimensions and affinity towards heavy metals in forming supramolecular surface structures with the aimed toxic cations.

Accumulation of mining and metallurgical wastes results in a contamination of the natural resources: soils, surface and groundwater. The presence of heavy metals in soils represents a danger for vegetation, animals and humans (Khanum et al., 2017; Radovanović et al., 2017). This problem must be addressed from a convergent point of view, encompassing a study using a broad palette of diverse techniques. Therefore, the aim of this article is to present our results regarding the determination of heavy metals concentrations in different soil profiles, in each granulometric size fraction for two neighboring soil types polluted by the metallurgical activity.

2. MATERIALS AND METHODS

Anthropic and eutricambosol samples were collected near the lead smelter of Baia Mare, Romania, as can be seen from the map from Figure 1, which also contains the soil types from that area.

The anthropic soil has no structure. It is a mix of construction material fragments, industrial slag remains, sand, dust and soil fragments. Our sample originated from the immediate neighborhood of the lead smelter's gas-chimney. This area lacks vegetation. Soils with properties heavily modified by human intervention are categorized as anthrosols by the Soil Reference Group (Florea, & Munteanu 2012). There is no traceable limiting perimeter for this soil type in the area and it overlaps the native eutricambosol around the industrial plant.

The eutricambosol is at the beginning of soil formation heaving weakly differentiated pedogenetic horizons. But it is characterized by the presence of the Bv horizon, with high clay fraction content, formed from the alteration of the parental bedrock material (Florea, & Munteanu 2012). The parental material in our case is represented by andesitic and pyroclastic rocks. The sampled soil is at approximately 200m from the industrial plant. It has a typical Ao_1- Ao_2-Bv-C soil profile, as it can be seen from Figure 2. The Ao horizon, with a dark-brown color, has a granular structure, with a thickness of around 35 cm. The two subdivisions of this horizon are marked in the followings as Ao_1, down to a depth of 15 cm, and Ao_2 between 15-35cm. These can be differentiated by their color and humus content. The thickness of the Bv horizon is 47 cm thick, with a brown-yellow color and has clay texture. The C horizon has a thickness of approximately 50 cm, with a light-yellow color. Each pedogenetic horizon could be sampled for the eutricambosol.

For anthropic soils, the horizons are mixed and cannot be distinguished, so that two samples were taken from depths of 0-10 cm, and 20-40 cm, according to Romanian legislation (Order 184/1997). The eutricambosol samples from horizons Ao_1 and Ao_2 also approximately correspond to these two sampling depths, regulated by the above-mentioned law.

Each sample was separated in granulometric classes: gravel, sand, silt and clay. Wet separation and the 2mm and 0.05mm sieves were used. The clay fraction was separated from silt by repeated washing and decantation, until the supernatant was transparent to the eye. Each separate's Cu, Pb, Zn, Cd heavy metal content was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) in accordance with ISO 22036:2008 standard applied to the soil extract obtained with aqua regia in accordance with ISO 11466:1995.

3. RESULTS AND DISCUSSIONS

Sand and silt are prevalent in the anthropic soil, while gravel and clay fractions are present to a lower extent (Fig. 3. a.). The variations that can be observed between the granulometric distributions of the samples collected between 0-10cm and 20-40cm are insignificant. This is normal and explained by the presence in this soil type of slag and building material fragments.

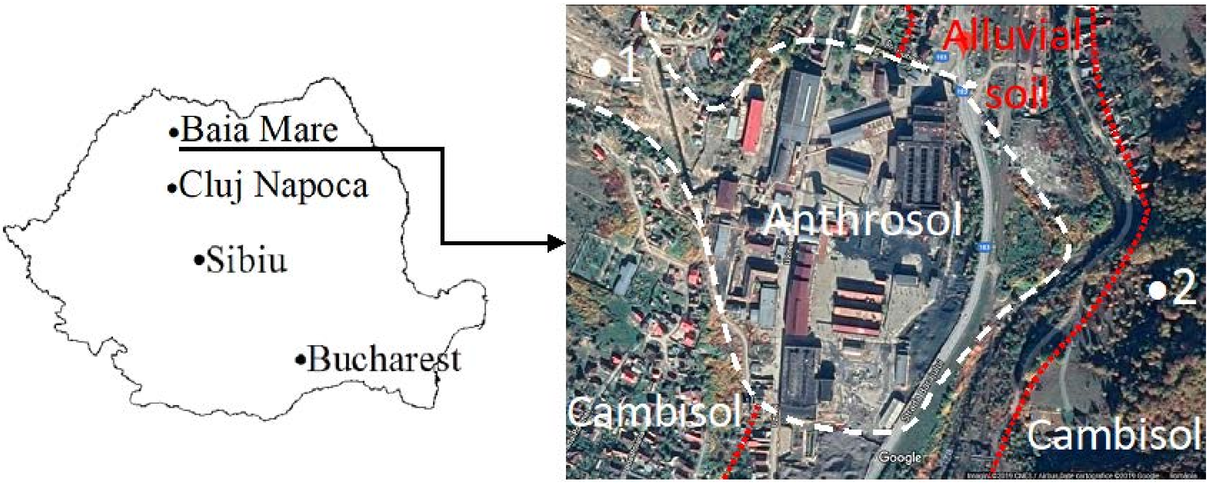

Figure 1. Map containing the sampling points and the soil types from the area of interest (Google map)

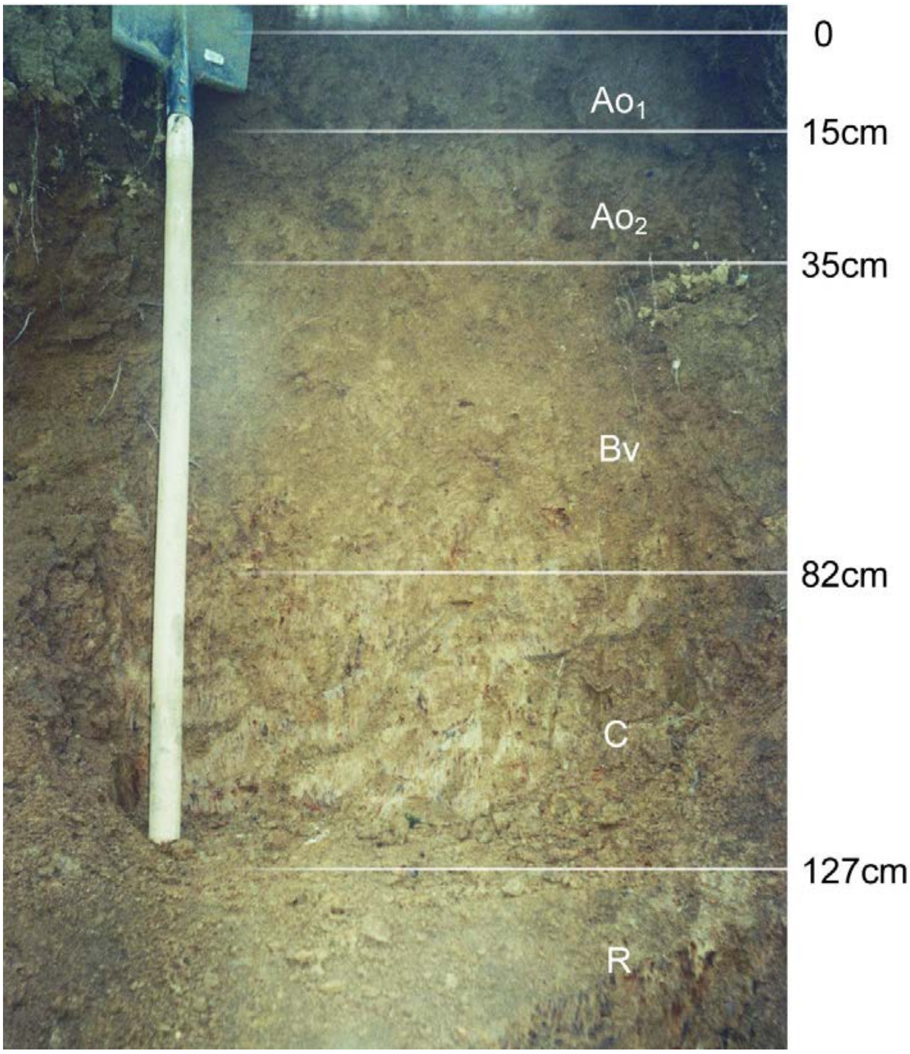

Figure 2. The pedogenetic horizons Ao_1- Ao_2-Bv-C on depth profiles for the sampled eutricambosol. The R horizon represent the bedrock

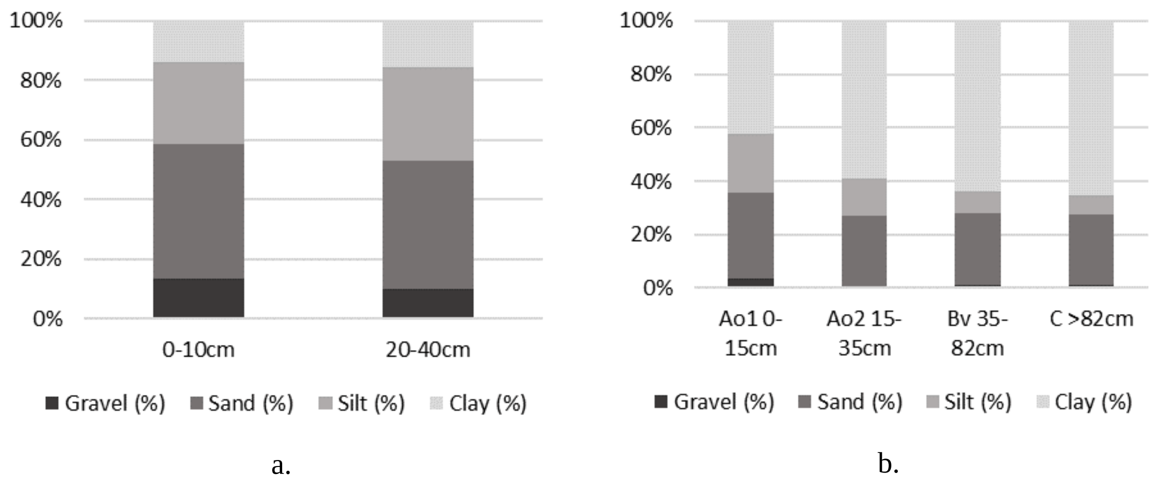

Figure 3. Particle size distribution in soil profiles. a. anthropic; b. eutricambosol

The clay fraction is prevalent in the eutricambosol (Fig. 3.b.). Its ratio increases with depth, from horizons Ao to Bv, while it remains constant in the deepest C horizon. This is according to the pedogenetic conditions and characterizes the soil type. But similar distributions were also communicated for other soil types (Kurt, 2018). Silicate alteration processes from horizon C resulted in accumulation of large clays quantities in the Bv and C horizons. Sand and especially silt fraction proportions decrease with profile depth in horizons Ao_1 and Ao_2, and, with a high rate, in Bv and C. The determined very low gravel ratio, only observable in the horizon Ao_1, is probably due to anthropic activities.

As a basis of comparison for the results of our heavy metal concentration measurements, the legal limits are presented in Table 1.

The graphical representation of the measured heavy metal concentrations, their distribution on different sampling depths/pedogenetic profiles, classified on granulometric size fractions, for both the anthropic and eutricambosol can be seen in the Figures 4 and 5, respectively. The measured values are also displayed as column labels to be directly comparable with the legally imposed limits.

In the anthropic soil, Cu concentrations display an inhomogeneous distribution, as can be seen in Figure 4. But at both sampling depths it exceeds intervention thresholds for sensitive soils, according to Romanian legislation (Order 756/1997). Also, the alert limit is exceeded for less sensitive soils, excepting for the sand fraction from 20-40 cm depth. Moreover, intervention limit for less-sensitive soils is exceeded for the clay and gravel size fraction for the 0-10 cm depths and for the clay, silt and gravel fraction sampled from 20-40 cm depth.

The alert limit is exceeded when considering both sensitive and less sensitive soils at both sampling depths for Pb. An exception is the sand fraction from 20-40 cm, where the alert threshold for less sensitive soils is not exceeded. The intervention threshold is exceeded for all size fractions in the topsoil and for the clay fraction from the deeper sample.

Table 1. Heavy metal contents on granulometric fractions and pedological horizons for the anthropic and eutricambosol

Threshold values from Order 756/1997 [23]	Heavy metal			
	Cu(ppm)	Pb(ppm)	Zn(ppm)	Cd(ppm)
Normal values	20	20	100	1
Alert threshold - Sensitive soil	100	50	300	3
Alert threshold - Less sensitive soil	250	250	700	5
Intervention threshold - Sensitive soil	200	100	600	5
Intervention threshold - Less sensitive soil	500	1000	1500	10

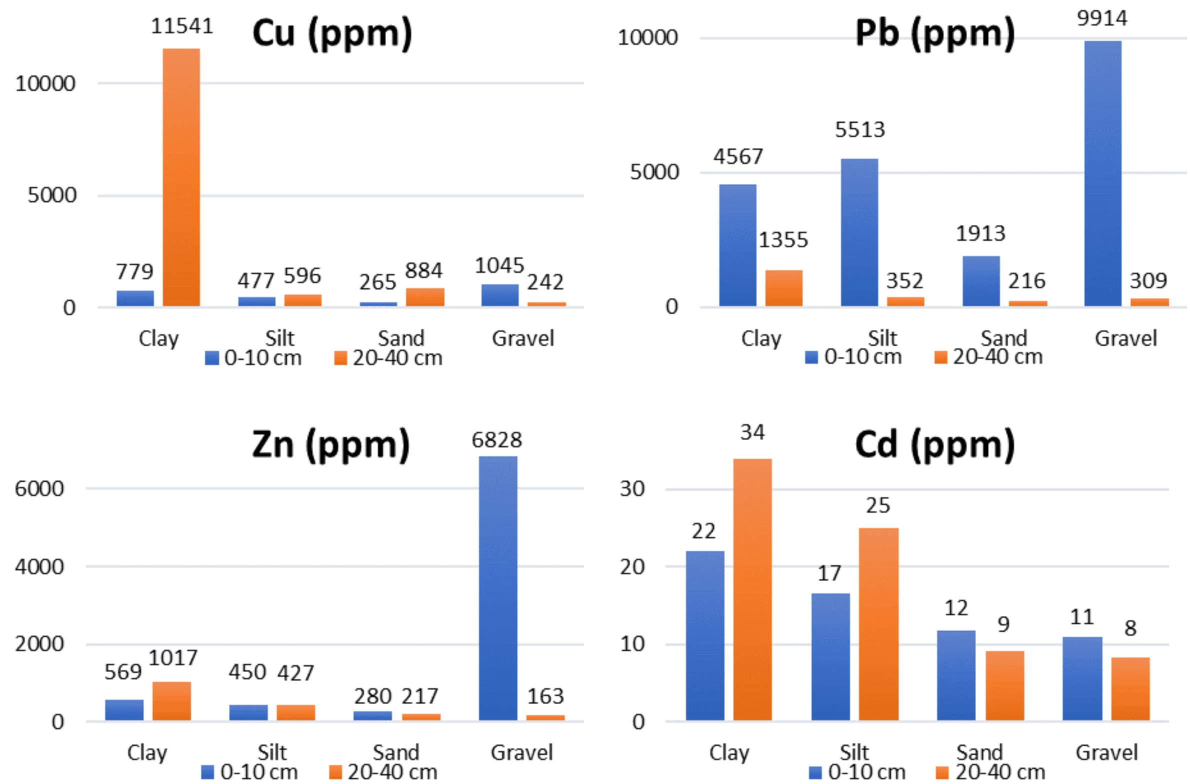

Figure 4. Heavy metal concentrations in anthropic soil

For Zn, the alert threshold for sensitive soils is exceeded excepting the topsoil's sand fraction, and sand and gravel fractions of the greater depth sample. When considering the less sensitive soil concentration limits, only the topsoil gravel fraction exceeds it. These concentrations are due to accumulation of slag resulting from industrial activity (Damian et al., 2008).

High concentrations of Cd, above the alert limit for less sensitive soils and intervention limits for sensitive soils, can be found in all size-fractions and at all depths. This is partially true when considering the less sensitive soil limits, excepting the sand and gravel fraction sampled at higher depts.

Exceeding the legal limits underlines the fact that these lands cannot be used for agricultural activities or residential area development. Although, according to previous studies, phytoremediation and stabilization could be applied, with the purpose of afforestation (Huang et al., 2011; Belyakova & Lyashenko 2014; Wang et al., 2016; Damian et al., 2013, 2018).

The measurements for the eutricambosol (Fig. 5) exhibit much lower heavy metal concentration values. Normal values for Cu were obtained in all size fractions from horizons Bv and C and in the silt from Ao_2. Exceptions can be found for the clay fraction from horizon Ao_1, where the alert threshold is exceeded, and in the clay fraction of horizon C. In this later case, the higher concentrations could have their origins in the parental material.

Normal values for Pb were obtained in the silt, sand and gravel size fractions of horizon Bv. But, the alert threshold for both sensitive and less-sensitive soils was exceeded in the upper horizon Ao and in the clay fraction of Bv. The alert threshold for sensitive soils is exceeded for the gravel size fraction from horizon C. The intervention threshold for sensitive soils is exceeded in the whole surface horizon Ao and in the clay fractions from the horizons Bv and C. The intervention threshold for less-sensitive soils is exceeded only in the clay fraction of horizon Ao.

The normal concentration values for Zn are exceeded in all size fractions excepting the sand from horizons Ao_2 and Bv. The alert threshold for sensitive soils are exceeded in horizon Ao_1 excepting the sand and clay fraction, in horizons Ao_2 and Bv. The alert threshold for less-sensitive soils is exceeded only in the clay fractions from horizons Ao_1 and Bv. Leeching can explain the reduced zinc content from the clay size fraction of horizon Ao_2.

Normal values of Cd can be found in horizons Ao_2, Bv and C. The alert threshold for less-sensitive soils is exceeded only in the clay size fraction from horizon Ao_1, while for sensitive soils in the silt and gravel fractions, also.

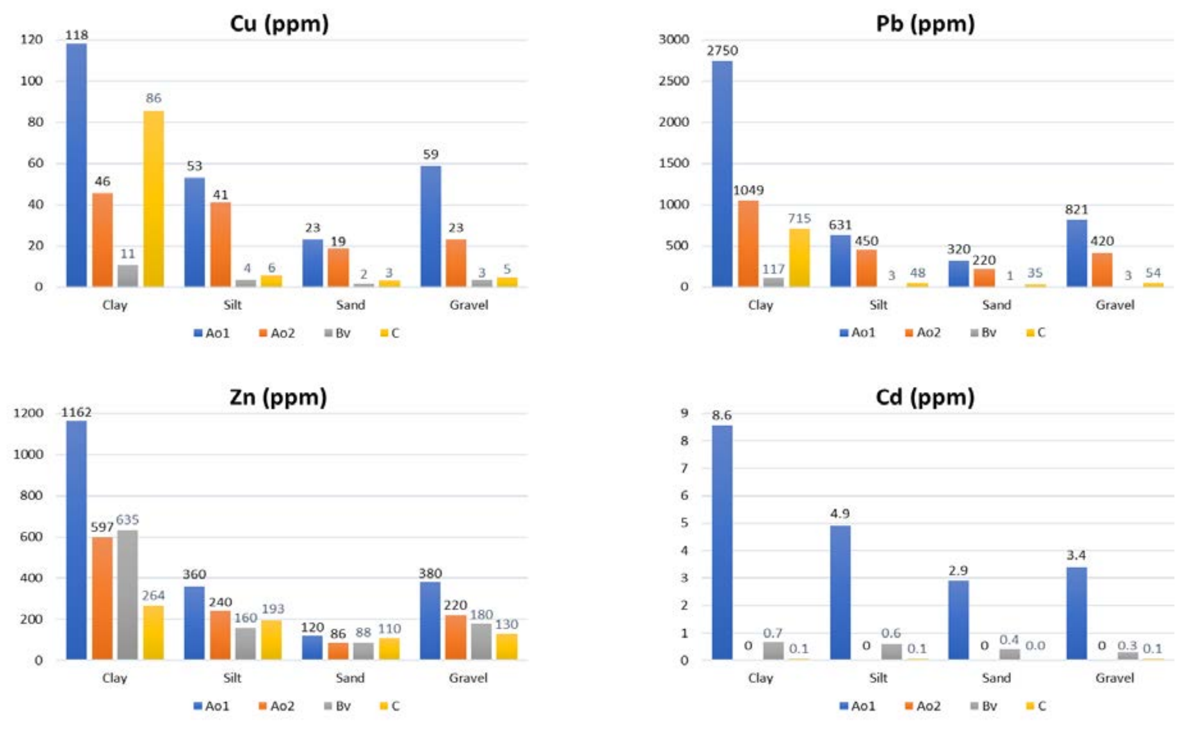

Figure 5. Heavy metal concentrations in each granulometric fraction from each pedogenetic horizons of eutricambosol

In the anthropic soil, Cu concentrations display an inhomogeneous distribution, as can be seen in Figure 4. It accumulates in the deeper clay fraction, because of its high vertical mobility. The mobility of metals in contaminated soils is significantly influenced by the total metal content (Kabala & Singh 2001). According to results about the presence of metals in different fractions, Cu could be found in this order: in the residual fraction, linked do organic matter, bound to Fe-Mn oxides, together with carbonates and in the exchangeable fraction (Liang et al., 2014). High concentrations are also found in the clay and gravel fractions of the topsoil that can be due to its high slag fragment concentrations (Damian et al., 2008). High topsoil Cu content is an indicative of anthropogenic contamination; however, it was demonstrated that Sulphur and copper contents in heavily contaminated soils can increase in the lower soil depths were the silt and clay contents gradually increase (Kříbek et al., 2010).

Lead can be found in high concentrations in the topsoil, mainly in the gravel fraction. Its presence in the coarse fractions can be explained by the same high slag contents, while, in the finer fractions, it could be due to the accumulation of the dust eliminated by the industrial activity (Damian et al., 2008). Although the concentrations remain above alert level at the 20-40 cm depths, the decrease can be explained by the lead's lower mobility in soils (Wieczorek et al., 2018).

Zinc has the highest concentrations at 0-10 cm in the coarse fraction due to the presence of the slag fragments. At 20-40cm, zinc amounts increase from gravel, sand to clay. It shows a patterned increase as the fraction gets finer, from gravel through sand, reaching highest concentrations in the clay fraction.

Cadmium accumulates predominantly in the finer, especially in the clay fractions, mainly at lower depths.

Heavy metal concentrations found in the eutricambosol are much lower than those found in the anthropic soil. The contents of Pb, Cu, Zn and Cd decrease from the top soil's Ao_1 horizon to the Bv horizon, as can be seen in Figure 5. They accumulate in the clay fractions in all horizons. Similar results were obtained for other soils contamined by anthropic activity (Kurt 2018). Higher concentrations are to be found in the top soil's gravel fraction than in its sand faction. This also can be explained by the presence of industrial slag. Concentration of Cu depends in a complex way on its interactions with the parent material, the soil's physico-chemical properties, extent of the industrial pollution and other anthropogenic sources (Ballabio 2018). The concentrations of Cu, Pb and Zn increase from the Bv to the C horizon. The heavy metals determined in this deepest soil horizon do not necessarily have an anthropic pollution origin. They could come from geogenic sources, originating from the component elements of the andesitic parental rock (Adriano, 2001).

The results of this article are comparable and should be correlated with previous studies. It was shown that heavy metal concentrations increase with the decreasing size of the sorbent particle (Mandzhieva et al., 2014; Yao et al., 2015). The finest nano-/micrometric clay fractions contain negative sites, favoring heavy metal attraction, sorption and retention, explaining this way the high toxic metal contents measured by us in this fraction (Huang et al., 2011; Belyakova & Lyashenko 2014; Wang et al., 2016; D'Souza et al., 2012). Another explanation for high heavy metal retention rates in the finest fractions is their increased sorption properties due to their high specific surface (Lair et al., 2007). Another factor resulting in high heavy metal sorption and retention rates in the clay fraction from the deepest horizons, is the lack of humus, determining free ion migration down to this depth. But, on the other hand, high concentrations from the first horizon Ao_1 could be due exactly to the presence of high humus contents (Damian et al., 2008).

The high Pb and Cu concentrations found in the first Ao_1 horizon of the eutricambosol can be explained by two mechanisms. Previous Cu and Pb sorption experiments on samples from the pedogenetic horizons of a luvisol profiles demonstrated higher affinity of lead towards organic components, than that of copper (Sipos 2010). The interaction of different factors on the sorption properties exhibited towards Cu, Pb, Zn and Cd in soils was also previously studied (Sipos et al., 2018). It was shown that for acid soils, like the ones described this article, important sorbent roles play the finest granulometric fraction and the humus content. It was also demonstrated that lead's affinity exhibited towards organic soil components is stronger than that of copper. The migration rate and bioaccumulation of potentially toxic metals from a mining area into plant organs was also studied (Damian et al., 2013, Andráš et al., 2017, Damian et al., 2018). It was proven that increasing the soil's organic matter content contributes in the immobilization of Pb, minimizing its absorption in plants, reducing this way its toxicity. Therefore, Pb can be mainly retained by the organic components found in the respective pedological horizons, while Cu could be captured by the nano-/microscale size fraction with high specific surface and high number of negatively charged sites.

Turning our attention to the anthropic soil, one can conclude that it cannot immobilize high heavy metal quantities as the eutricambosol because of its poor organic matter content. According to previous research, this capacity can be enhanced by augmenting this soil type using organic fertilizers, zeolite or organo-zeolite material (Andráš et al., 2017; Damian et al., 2018; Kwiatkowska-Malina 2018). This technique could also lower the toxicity levels determined in the eutricambosol.

4. CONCLUSIONS

The present article reports a correlated comparative study of Cu, Pb, Zn, and Cd heavy metal quantities measured in each granulometric fraction of each pedogenetic horizon, or respectively, at different sampling depths, for two neighboring, but different soil types (anthropic and eutricambosol). The sources for the presence for these toxic heavy metals are identified to be partially of geogenic origin and mainly industrial pollution from a former nearby lead smelter. Along with the sources, possible sorption and retention mechanism in each granulometric fraction and pedogenetic horizon are discussed. Conclusions are drawn on the utility of these soils, their potential toxic effects on life in general and possible measures for the stabilization and immobilization of the determined toxic metals. Augmenting the anthropogenic soil using organic fertilizers, zeolite or organo-zeolite material could lead to afforestation of this area, re-entering it in a sustainable development circuit. Increasing organic matter content in the eutricambosol's topmost horizon can lead to reduced Pb toxicity.

Granulometric study of the pedogenetic horizons for the eutricambosol reveals that the nano-/micrsocale clay fraction is predominant at each depth. But, in the case of the anthropic soil, sampled at two depths, according to legal requirements in Romania, sand and silt fractions are prevalent.

Our research demonstrated that the toxic heavy metal content of the anthropic soil is higher than what can be found in the neighboring eutricambosol. Copper contents in the anthropic soil exceed the intervention threshold for sensitive soils, and the alert threshold for less sensitive soils. Lead content exceeds the alert threshold in almost all size fractions for both sensitive and less sensitive soils. Zinc contents rarely exceed the alert threshold. Cadmium has high values in all granulometric fractions, at both sampling depths. The alert threshold is exceeded for less sensitive soils at the 0-10 cm sampling depth, and the intervention threshold in the fine fractions.

Regarding Cu contents of the eutricambosol, the conclusions are positive. Its concentrations do not exceed normal values but in the clay fraction from the topsoil horizon. The measured concentrations for Pb are normal in the Bv horizon, while exceeding the intervention limit for sensitive soils in all clay fractions. The concentrations of Zn exceed normal values in all cases, excepting the sand fractions of horizon Ao_2 and Bv. The alert thresholds are exceeded in the clay fractions. Cadmium has normal concentrations rarely exceeding the alert or intervention thresholds in the clay fractions. So, it can be observed that, for this soil type, above-normal values are measured mainly in the clay fractions.

Heavy metal distribution at different sampling depths differs in these two soil types. It shows an irregular distribution in the anthropic one, while concentrations decrease with depth for the weakly differentiated eutricambosol, down to the horizon Bv, excepting horizon C. Higher heavy metal contents were found in the clay fractions, which favor their accumulation and retention due to the presence of negatively charged sites, high specific surfaces and formation of supramolecular surface structures with organic substances. High concentrations of toxic metals from the gravel fractions of each soil type, especially in the topsoil, are due to anthropic intervention. Accumulation of Cu and Zn in the deeper horizons can be attributed to high ion mobility between soil profiles or are due to the parental andesitic material.

The exceeded alert or intervention level measured for the anthropic soil, and to a lesser degree for the eutricambosol, proves that it cannot be used for agricultural or residential development activities. These lands should be first reclaimed using phytoremediation, stabilized, then it is possible for them to be re-entered in foresting circuitry.

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