SOILS FROM THE BAIA MARE ZONE AND THE HEAVY METALS POLLUTION

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Abstract. The pollution of the soils with heavy metals, Pb, Cu, Zn and Cd, was studied on a surface over 20.53km² of Baia Mare. The total concentration of heavy metals was measured in the upper horizon for the entire surface of Baia Mare city and for each pedogenetical horizon within the soil profiles up to 1.20 m depth in the industrial zones. In both industrial areas Romplumb and Cuprom texture, pH, cation exchange capacity, base saturation, total carbon, the nutrient elements were determined for each horizon in the soil profile. The total contents of Pb, Zn and Cd are higher in the eutricambosols and aluviosols from Romplumb area than in the luvosols and aluviosols from Cuprom area. The total content of Cu is significantly for the luvosols and aluviosols in the organic horizon.

The highest concentrations of the heavy metals analysed in the upper horizon of the soils are present in the eastern side, the industrial zones and in the south-western part on the location of the tailing dump. The spatial distribution of Pb shows a high degree of variability. In some cases, on very small surfaces were found excessive concentrations of 40.375 ppm and maximum values that are higher than the maximum allowable limit up to 60 times, close to Romplumb (6565ppm) and Cuprom (982ppm) metallurgical smelter factories. The average concentration of Pb over 2417.71 ppm, for the entire investigated area corresponds with the state of high pollution. Maximum concentrations of Cu which indicate this high level of pollution are over 400ppm-5823ppm are specific for the Cuprom area on a big surface arounds the influence zone of gaseous emissions, associated with albic luvosol type. The maximum values determined for Cd (80-39ppm) in Cuprom area, 24.2-5.2ppm for Romplumb area and 15.13-3.05ppm in south-western part sustain the high pollution for the characteristic type of soils. The concentrations for Zn (6122-4513.2ppm) and Cuprom (982ppm) are related to the mobilization of metals within the soil profile. The maximum content of Cd is greater than the maximum allowable limit on the soil profile (3.17-21.5ppm). The maximum values for Zn (928ppm and 627ppm associated with maximum values for Cd: 50ppm and 40ppm) are related...
The total contents of heavy metals (Pb, Cu, Zn, Cd), their distribution and their mobility have been analyzed within the soil profiles close to Pb and Cu smelters (Romplumb area) and (Cuprom area). The physical and chemical properties of the soils, the humus content, pH, the cation exchange capacity, soil texture have been determined for each pedogenetic horizon. The knowledge of these factors is essential for the lability of heavy metals, (Iyengar et al., 1981, Sposito et al., 1982, Ma & Rao, 1997, Narwal & Singh, 1998, Karczewska et al., 1998).

The heavy metals concentration in the residential zone of the Baia Mare city has been determined at the level of the organic horizon of the soils. At this level for the
entire surface of Baia Mare city, we obtained the image of the spatial distribution of the analyzed metals, by using GIS technology (Arc View soft). It was obtained the distribution of heavy metals with implications in soil’s pollution according to the position and the distance from the pollution sources. In addition to gaseous emissions generated by these two metallurgical factories Romplumb (north-eastern) and Cuprom (south-western) the investigated surface includes even other sources of pollution for the city, represented by the tailing dump from the south-western part of the city. The effects of soil pollution with heavy metals on the vegetation of Baia Mare were studied by Lăcătușu et al., 1995, 1998, Râuță, et al., 1997.

2. MATERIALS AND METHODS

2.1. Site location

Investigated soils from Baia Mare are represented by various types, (Fig. 2). In the North part and north-eastern part of the city are predominated the regosol, eutrīcambosol, districambosol types and the andosols developed on volcanic deposits. In South part of the investigated the most common soils are: aluvisol, luvosol and stagnosol types.

The sampling of the soils was realised from the surface horizon at 0-10cm depth on a surface over 20.53km² that corresponds with the residential area from the center of Baia Mare city and from pedogenetic horizons within the soil profiles, which are located in the industrial zones (Romplumb north-eastern part, Cuprom south-eastern part).

The physic and chemical properties of the soils and total forms of heavy metals content were determinated in the laboratory of the Research Institute for Soil Science and Agrochemistry, Bucharest.

2.2. The Soil Type Description

The soils from Baia Mare were developed on the parental material represented by volcanic rocks, which are very specific to mountainous relief of northern part and north-eastern part and sedimentary rocks: clay, marls and alluvionic deposits like gravel and coarse-grained sand, very specific for the depresionary zone of Baia Mare (south-eastern and south–western part).

According to Romanian System of the soil’s Taxonomy (Florea & Munteanu 2003), in Baia Mare, have been identified seven types of soil: luvosol, aluvisol, eutrīcambosol, stagnosol, litosols, showed in (Fig. 2). In the Baia Mare industrial area the existing soil
types are: eutricambosols, aluviosols, luvosols, stagnosols.

Luvosols are formed on parental material represented by marls, in depression area with plane surfaces and low or less drained, with high humidity that percolates the soil and even generates the levigation of a notable part from colloidal complex. Are represented typical, gleic, albic subtypes of luvosols. Albic luvosols are overspread in the older part of Baia Mare city, at South and West from the municipal of Baia Mare. In the soil profile Ao-Ea-Bt-C, (Fig. 3) the horizons are clearly individualized. Horizon Ao has a thickness about 18 cm, gray colour and with a low content of humus, the structure is not well-developed and it has a sandy-clay texture. The E horizon has 10 cm with-gray colour, with a sandy texture. The Bt horizon is one of the most developed, with a thickness of 65 cm, brown-rusty colour and an aspect very well-defined.

![Fig. 3. BMC 5- Luvosol albic.](image)
![Fig. 4. BMR-4 Eutricambosol.](image)
![Fig. 5. BMC 2 Aluviosol.](image)

Eutricambosols appears in small areas, on the steep ridges of northern and eastern part of Baia Mare city. These soils have a medium level of acidity with small differentiation of the profile. The content of humus is relatively high in the organic horizon (2,76-4,44%) but decreases at the transition horizons (Table 1). The parental material is represented by marls, sandstones and delluvial deposits. The profile of eutricambosols is: Ao-Bv-C, (Fig. 4). The Ao horizon of dark brown colour has a granular structure and a thickness about 35 cm. The thickness of the Bv horizon varies between 47 cm (BMR-4) to 65 cm (BMR-2), with a brown-yellow colour. This horizon has a clay texture. The C horizon has a thickness of aproximatively 50 cm, and his colour is light yellow.

Aluviosols covers large areas along the rivers Săsar and Firiza. These soils are constituted of an Ao horizon about 30 cm thickness, gray or gray-brownish colour with a granular structure, moderate developed, having a direct disposal over alluvionary deposits represented by gravel and coarse-grained sand. Between the horizon A and C is present the transition horizon A/C with a thickness about 15-23 cm, (Fig. 5). In this horizon appears, frequently, fragments which are incorporated from parental material of C horizon.

The reaction of aluviosols is generally acid, with a little exception C horizon of which reaction is almost neuter. As regarding the supply with nutrients this differs on
the texture and humus quantity. Nitrogen, mobile phosphorus and mobile potassium supply is very low.

Stagnosols in Baia Mare zone appears on the right bank of Săsar river and on the western part of the city. They formed on pannonian clays. The effects of the water stagnation are observed on the inferior part of the Ao horizon and on the superior part of the Btw horizon. The investigated stagnosol presents a high content of humus in the upper horizon which decreases with depth. This soil’s reaction is acid and the pH increases with the depth, (Table 1). The soil profile is: Ao-E-Bt-C. The horizon Ao has a thickness of 23 cm, gray colour associated with stigmatic colours of reducing conditions, (Florea & Munteanu 2003) in the deeper part of this horizon. The E horizon is clearly individualized, with a thickness of 7 cm. The horizon Bt has a thickness of approximately 60 cm with a well-defined aspect and with frequent concretions aggregates and filaments of red colour which are overlapped over the reduction spots. Generally this horizon has a clay texture, is very plastic and adhesive in conditions of humidity. The C horizon is represented by pelitic material.

3. RESULTS AND DISCUSSION

3.1. Physical and chemical properties

Textural differentiation is very significant within the soil profiles on different types of soils. In all of these soil profiles for eutricambosols the sand decreases with depth, but in the clay it increases slowly in B horizons, and then the concentration is maintained at comparable quantities in transition horizons. In the luvosols, the sand decreases in E horizon and increases in Bt horizon, but in aluviosols the sand concentration increases with depth, (Table 1). In Bt horizon the clay content is larger than in the overlying horizon, caused by eluviation of fine clay particle. In aluviosols the clay is maintaining the same proportions in all horizons with a slowly decrease with depth. The studied texture class of the soil is predominantly clay loam, silty clay loam and silt loam. The cation exchange capacity is higher in eutricambosols than luvosols and aluviosols. Cation exchange capacity decreased with depth in eutricambosols and it increases with depth in luvosols and aluviosols. The increasing of cation exchange capacity with depth in luvosols is related to the enrichment in clay of Bt horizons by the illuviation process, (Meunier, 2005).

In general, the pH varies from strongly acid to moderate in soils from the investigated area. The low values of pH are specific to organics horizons. For all types of soil, in the profile’s deep horizons, the pH values tend to increase, (Table 1).

Within the soil profiles the humus content is generally highest in the surface horizons, with the migration in the lower parts of the soil profile, for luvosols, (Table 1). The base saturation varies according to the pH value. According to soil’s base saturation level from Baia Mare area, the soil corresponds to oligobasic (29.1-38.1%) and oligomesobasic (42.3-68.2%) and eubasic classes (92.2%). The studied soils are characterized by a low content in nutrients. The C/N ratio is high in the horizons rich in humus for all types of soil, from 10.8 to 12.7 in eutricambosols (Romplumb areal), from 12.2 to 22.1 in luvosols (Cuprom areal) and from 13.1 to 25.7 in aluviosols.
Table 1. The physical and chemical properties of pedogenetical horizons for eutricambosols, luvosols, stagnosols and aluviosols.

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<th>Texture type</th>
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<th>CEC (meq/100g sol)</th>
<th>Base Saturation (%)</th>
<th>C_eq (%)</th>
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BMR-Romplumb Baia Mare; BMC-Cuprom Baia Mare; Texture class: LL-clay loam; TP-silty clay loam; LP-silt loam.
This fact suggests the limitation of biological activity in soils and decreasing rate of humification, caused by the high concentration of heavy metal, (Khan & Scullion 2002).

3.2. The concentration of heavy metals

The concentrations in heavy metals from analyzed soils emphasised different grades of pollution with Pb, Cu, Cd and Zn in different type of soils. Heavy metals’ retaining mechanisms from soil are quite varied and are possible under the influence of the humus, pH, cation exchange capacity, (Mc Bride 1989, Kabata-Pendias 1993). Significant differences obtained on different types of metals from the analyzed contents for heavy metals were correlated with values limits which are specific to physic-chemical properties of soils.

Lead, is a persistent pollutant for the surface horizon of the soils. The excessive concentrations of Pb are distributed around the metallurgical factories from the industrial area. In the entire investigated zone the concentrations of Pb in total forms, ranged from 220 to 40375ppm with an average content of 2417.7ppm. The samples that exceed maximum allowable limit for the soil sensitive use, presents the higher frequency (Fig. 6).

![Fig. 6. The frequency diagram of the concentrations for Pb.](image)

![Fig. 7. The concentration of Pb within soil profile, and the humus content in eutricambosol.](image)

The high concentration of Pb in the surface horizons is related with the adsorption onto humic constituents of soil, (Angehrn et al., 1989, Bradl et al., 2005, Kabata-Pendias & Pendas, 1992). The values of Pb concentrations exceed the intervention threshold for sensitive soils, (Klobe 1980), and are between: 1429-6562ppm at the upper horizon of soil’s profiles from Romplumb area, and between 904-995ppm in Cuprom area. The high concentration of Pb in the surface horizons were determinated by the low mobility, as shown, by a decreasing content with depth in the soil profiles. Lead mobility with depth has a low value or is inexistent. The variation of Pb within the soil profile in relation with the humus content, for eutricambosols is showed in, (Fig. 7).

Specific processes of Pb concentration, in the horizon which are rich in humus, within the soil profiles are related with low values of pH which can vary between 3.77-4.40 in Romplumb area, (Fig. 8) and between 3.54-4.98 in Cuprom area.
Maximum concentration of Pb within the soil profiles in the surface horizons is related with the high values of cation exchange capacity, (19.70-36.12 meq/100g soil) in Romplumb area and (15.10-25.03 meq/100g soil) in Cuprom area. The immobilization of Pb in organic horizon is independent of the increasing concentration with depth of the cation exchange capacity from luvisols, (Cuprom area), (Fig. 9).

Copper is the heavy metal with implications regarding the soils’ pollution especially for luvisols from Cuprom area of Baia Mare. The maximum concentration is of 5823 ppm. The highest frequency is representative for those samples which have a content that varies between the maximum allowable limit and the intervention threshold, (Fig. 10). The concentrations which exceed the intervention threshold have lower frequency and are in relation with soils situated near the copper factory from south-western part of Baia Mare.

Within the soil profiles, copper concentration decreases from 286 ppm under the normal values of 20 ppm, due to the adsorption by organic matter (Bradl et al., 2005), in conditions of an acid pH. In acid soils were mentioned even other mechanisms to retain the copper from the Fe and Mn oxides, (Adriano, 2001). In Cuprom area the Fe and Mn oxides are presents in the deeper part of Ao horizon.

Cadmium is found in excessive contents in soils which are situated near these...
two metallurgical factories. This suggests that the source of Cd was the metallurgical industry, (Murray et al., 2004). In Cuprom area, in the surface horizons the content of Cd range from 80 to 39 ppm and from 11 to 24 ppm in Romplumb area.

The average concentration of Cd in the analyzed samples from the entire surface is of 8.3 ppm, it exceeds the intervention threshold values, (Klobe, 1980). The highly frequency is owned by samples of which contents varies between the normal values and warning threshold, (Fig. 11), followed by those between the warning threshold and intervention threshold. In case of cadmium, it is observed a mobility within the soil profiles. In transition horizons of soil’s profiles from Romplumb area the cadmium concentrations increased and it is related with decreased values of cation exchange capacity and with higher values of pH. In luvisols from Cuprom area the reaction is moderated acid of the organic horizons that favored the retention of the entire quantity of Cd which leaded to an accentuated pollution.

At the surface horizons the highest frequency has the samples which contain a concentration of Zn situated under the intervention threshold of 1500 ppm, (Fig. 12). The average concentration from samples of the entire surface is 483.73 ppm. The maximum concentrations of Zn range from 1511 to 6122 ppm and their frequency is low. These soil samples corresponds with the location of the tailing dump (south-western) and with the Romplumb area (north-eastern). The concentrations of Zn in soil’s profiles, varies between 3296-479 ppm at the surface horizon, in Romplumb area and between 536-252 ppm in Cuprom area.

In the transition horizons of the soil profiles the concentration of Zn is higher than in the surface horizon. The mobility of Zn within the soil profiles is influenced by several factors, as pH, cation exchange capacity, clay content and type of soil, (Bradl et al., 2005). In eutricambosols the content of Zn is maximum or sometimes aleatory in the transition horizons or in B horizons related with the high values of the cation exchange capacity, (Fig. 13).

4. SPATIAL DISTRIBUTION OF HEAVY METALS

The obtained results have been used in order to represents the variation in concentration of the heavy metals analysed between points of sampling. Applying GIS
Arc View technology, have been realized the maps with the distribution of the pollution of Pb, Cu, Zn, Cd for the entire surface of Baia Mare city. The high concentration of the heavy metal in soil from the vicinity smelters of Pb and Cu confirms the role of atmospheric gases deposition in soil’s pollution. Additionally the tailing dump from the South-Eastern part of Baia Mare city is an important source of heavy metal pollution for soil and groundwater. Heavy metals distribution in the upper horizon of soils in the investigated area is influenced by the predominantly direction of the atmospheric currents, with an important role in the dispersion of atmospheric emissions as a result of metallurgical activity.

In Baia Mare zone the air circulation had a local character determined by the influence of the orography of this zone and the presence of the atmospheric calm. These conditions favoured the high concentrations of heavy metals in soil near these two sources of emission, Romplumb and Cuprom. The spatial distribution of the heavy metals concentration in soils from Baia Mare zone in the organic horizon is higher near the smelters Romplumb (N-E) and Cuprom areas (S-E) and near the tailing dump from S-W, than in the central residential zone of the city. On the outside of these industrial areas the concentrations of heavy metals are lower and have a distribution relatively homogenous. The variation limits of the total forms of the heavy metals which were analysed, by comparison with the limits values for the sensitive soils (Klobe, 1980), sustain the spatial distribution of Pb, Cu, Zn, Cd for the area investigated. The maps of heavy metals distribution represents the relationship between concentrations in soils and the main factors associated with metal deposition.

Lead distribution in the soil’s upper horizon is characterized by decreasing values of the concentrations with the distance, from the sources of pollution. The Pb concentrations in entire this area aren’t under the maximum allowable limit, (Fig. 14). The values of Pb concentrations are excessive in north-eastern part, for a small area which sustains the accumulation capacity of Pb in soil’s surface. Gao et al., 1999, reported the high stability of complexes of Pb and Cu with humic acid.

For Cu the total concentrations values exceeded the limit of normal content and the maximum allowable limit for surfaces which are extending on long distances from the sources of pollution. The contrast that exists between these concentration and the maximum allowable limit for Cu is increased in NW-SE direction from Cuprom area, (Fig. 15). The intervention threshold is exceeded in Cuprom area with extension in luvosols from S-E part of the city and on small surfaces in S-W part of the city corresponds to the location of the tailing dump. In the Romplumb area the maximum concentrations are near the factory and its surroundings. The soils from the vicinity of Cuprom smelter have been exposed for a long period of time to relatively large emissions.

The image of Zn distribution in the soil’s upper horizon shows three small areas in which the contents exceeded the intervention threshold, (Fig. 16). These surfaces are overlaped with vicinity of Romplumb (N-E), and Cuprom (S-E) smelters and with the location of the tailing dump (S-W). The values of Zn concentrations are relatively decreased in the soil’s upper horizon which is a result of dispersion capacity of this metal confirmed by the concentrations that exceed the intervention threshold from the transition horizons of the soil profiles from Romplumb area.
Fig. 14. The map of Pb distribution in Baia Mare area on the 0-10 cm depth.

Fig. 15. The map of Cu distribution in Baia Mare zone on the 0-10 cm depth.

Fig. 16. The map of Zn distribution in Baia Mare zone on the 0-10 cm depth.

Fig. 17. The map of Cd distribution in Baia Mare zone on the 0-10 cm depth.
The distribution of Cd concentration in the upper horizon of soils is similar with those from Zn regarding the spreading of the high polluted areas, (Fig. 17). For Cd in surface horizon, the pollution is excessive for the industrial zones and is high in the tailing dump area. In Romplumb area from the total content of Cd, at the level of some soil’s profile, a percent of 63.77% is bound to the transition horizons in comparison with only 15.36% bound to the upper horizon.

The total concentrations between the warning threshold and intervention threshold for Cd are distributed on large areas, in the upper horizons of the soils, due the accentuated mobility of this metal. In the map of distribution of Cd and Zn, areas that exceed the maximum allowable limit present a greater spreading, than ones of Pb due the mobility of these two metals.

5. CONCLUSION

The GIS technology application emphasised the distribution of the Pb, Cu, Zn and Cd influenced by the anthropogenic source and the climate favorabil factors for atmospheric deposition in soils.

The interpolating maps used to estimate the polluted areas were made by using the concentrations of analysed heavy metals in total form Pb, Cu, Zn, Cd, for the sampling points from the upper soil horizons. The concentration level of the heavy metals and their mobility, related with the physic-chemical properties of soil, were studied in soil’s profiles in for industrial zones, (Romplumb and Cuprom areas). In the representation forms of the concentrations distribution for these four analyzed metals, the shape and size of surfaces from maps is the result of contents interpolation.

The soils from the industrial zones of Baia Mare, through the composition and physic-chemical properties influences the concentration level and heavy metals mobility of Pb, Cu, Zn, Cd. The total contents of Pb, Zn and Cd are higher in the eutricambosols and aluviosols from Romplumb area than in the luvosols and aluviosols from Cuprom area. The total content of Cu is significant for the organic horizon in the luvosols type. All the soil profiles from both industrial areas are characterised by high acidity with variation related with the soil type. The content of nutrients from the soils is decreased and the ratio C/N in the organic horizon is high. The Pb concentration decreases with the depth. The humus content and the low values of pH are the important factors for Pb binding and distribution, (Borůvka & Drábek, 2004). The contents of Zn and Cd increases with depth within the soil profile, their maximum concentrations are related with B horizon in luvosol type and with the transition horizons in eutricambosol type. For Cu we can clearly see the high concentration in the upper horizons which decreases with the depth. The high concentrations of Pb, Cu, Zn, Cd in the studied areas are related to anthropogenic sources represented by smelting and refining of lead, zinc, copper and flotation processes. In Romplumb area Pb, Zn and Cd pollution is excessive and in Cuprom area Cu has the highest level.

The pollution level of soils from Baia Mare city according to those four heavy metals which were analyzed, descrease with the increase of distance from the main sources of pollution. The maintenance of high level for Pb concentrations at different distances indicates the lead deposition from the atmospheric emissions, in time. The atmospheric local conditions favored the high concentrations of heavy metals in soil...
near these two sources of emission. Another source of pollution is located in south-western part of Baia Mare city which corresponds with the location of the processing wastes from nonmetallic ores.

The soils from these areas are vulnerable to heavy metal pollution because of the acid reaction, (Lăcătușu, et al. 1998). Generally in the industrial area the highest concentrations of Pb and Cu were bound to the surface horizon, rich in organic matter. In contrast for Cd and Zn is significant the mobility in surface and within the soil profiles.

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REFERENCES


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