

Original article

Studies and Research on Soil Quality Evaluation in S.C. Romplumb S.A. Baia Mare to Address Remediation of Polluted Sites

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Abstract

Mining activity practiced in Romania for centuries resulted in extended soil polluted areas, having negative effects on the environment and an increased risk for human health. Heavy metal density inside Romplumb Baia Mare was measured to a depth of 100 cm. Spatial distribution of heavy metals in soil layers is extremely varied. In some cases, there has been an excessive concentration of 27770 mg/kg and values 60 times higher than the accepted limit. In 2010 as compared to 2005, experimental results indicate that heavy metal concentration dropped at 0 - 10 cm depth – because this layer consists of filling material; in 2010 compared to 2005, heavy metal concentration increased between 75 - 100 cm depth, because pollutants migrated in time, leading to massive pollution.

Keywords: heavy metals, soil, pollution, assessment

1. Introduction

Nowadays, heavy metal soil pollution is a great issue in Baia Mare, threatening both human health and the environment. High heavy metals concentration is determined by human activities, mining and metallurgical industry.

In Baia Mare, the high concentration of heavy metals in soil is related to high levels of Pb, Cu, Zn, and Cd. The excessive amount of heavy metals present in soil inhibits plant growth and negatively influences nitrogen attachment by microorganisms.

Slag covers most of the surfaces inside the company. In time, the industrial waste covered different areas of the society surface. This has led to current situation in which the first 30 cm of soil has an average metal density of over 30 % (iron being the main constituent) [2].

Therefore, most soil samples taken from shallow layer is not soil itself, but filling material composed of technological waste and building materials remains [2].

2. Material and Method

Soil sampling was conducted under STAS 7184/1-75, within the company precinct, near the fence. Three samples were taken for each depth, from the buildings proximity [4].

In 2005, preparation and analysis of the soil samples was carried out by SC Prospeciuni SA, Bucharest, Geological Laboratory Division –

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Physico - Chemical Analysis Department, accredited RENAR, method of analysis SR EN 1483/2003 [3].

In 2010, the entire heavy metal content was analyzed in laboratories at the Institute for Analytical Instrumentation Research, IAIR Cluj-Napoca, by extracting from soil soluble microelements into nitromuriatic acid (aqua regia). The method used was spectrometry of atomic emission in plasma induction clutch, ICP-AES, with SpectoFlame FMD 07 Spectometre.

3. Results and Discussions

3.1. pH variation

Generally, pH varies from strongly to moderately acid in the investigated soil. Low pH values are specific to organic level, being lower in 2010 than in 2005. In soil layers, pH values tend to increase with depth (fig. 1).

3.2. Variation of heavy metal concentration

Variation limits of heavy metals were analyzed by comparison to values for less sensitive

soils, according to Order no 756/1997, about environmental pollution assessment [3].

Heavy metal concentrations in the analyzed soil proved varying levels of pollution with Pb, Cu, Zn and Cd for both 2005 and 2010. The assessed values are presented in table 1 by comparison to reference inputs.

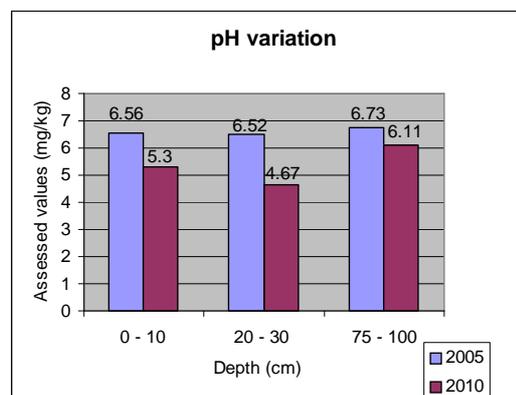


Figure 1. pH variation in the soil layers in 2005 and 2010

Table 1. Concentration of heavy metals the in soil layer in 2005 and 2010

| Metal | Assessed values (mg/kg) | | | Reference input according to Order 756/1997 (for less sensitive use soil) | | |
|-------|-------------------------|-------|---------|--|----------------|-------------|
| | Depth (cm) | 2005 | 2010 | Normal values | Critical value | Usage value |
| Pb | 0 - 10 | 4238 | 499 | 20 | 250 | 1000 |
| | 20 - 30 | 14930 | 27660 | | | |
| | 75 - 100 | 885 | 22320 | | | |
| Cu | 0 - 10 | 1172 | < 96.8 | 20 | 250 | 500 |
| | 20 - 30 | 3491 | 5590 | | | |
| | 75 - 100 | 187 | 7520 | | | |
| Zn | 0 - 10 | 3872 | < 117.7 | 100 | 700 | 1500 |
| | 20 - 30 | 9196 | 2199 | | | |
| | 75 - 100 | 816 | 7760 | | | |
| Cd | 0 - 10 | 15 | 4.32 | 1 | 5 | 10 |
| | 20 - 30 | 31 | 11.68 | | | |
| | 75 - 100 | 9 | 67.4 | | | |
| Cr | 0 - 10 | 63 | 38.67 | 30 | 300 | 600 |
| | 20 - 30 | 93 | 146 | | | |
| | 75 - 100 | 19 | 132 | | | |
| Mn | 0 - 10 | 1840 | 314.4 | 900 | 2000 | 4000 |
| | 20 - 30 | 1750 | 8250 | | | |
| | 75 - 100 | 950 | 7360 | | | |
| As | 0 - 10 | 27.6 | 58.6 | 5 | 25 | 50 |
| | 20 - 30 | 63.5 | 1957 | | | |
| | 75 - 100 | 15.7 | 1770 | | | |
| Fe | 0 - 10 | 57600 | 1540 | | Unnormalized | |
| | 20 - 30 | 78300 | 99500 | | | |
| | 75 - 100 | 47600 | 77200 | | | |

The histogram analysis of pollutants' variation compared to depth highlights a general trend of decreasing concentrations of all elements for samples taken in 2005.

Instead, for 2010, only lead maintains its slight tendency to decrease, while copper, cadmium and zinc show increasing values with depth.

Lead is distributed to all depths of sampling as main pollutant [1]. In all investigated soil, concentration of lead exceeds the critical values for both 2005 and 2010 (fig.2).

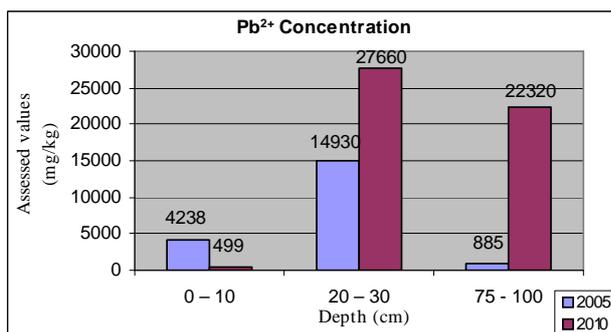


Figure 2. Lead variation in the soil layers in 2005 and 2010

In the entire studied area, the concentrations of lead ranged between 499 - 27660 mg/kg. Considering the critical value (250 mg/kg), in 2005, lead concentration was 17 times higher for depth level between 0 - 10 cm, 60 times higher for 20 - 30 cm level and 4 times for 70 - 100 cm level.

Considering the same critical value, in 2010, lead concentration was 110 times higher in the 20 - 30 cm level and 90 times higher in 75 - 100 cm. Nowadays, in the level between 0 - 10 cm, the lead concentration is only twice higher than the critical value as compared to 2005 when it was 17 times higher. The concentration decrease is due to the filling material brought here in the last 4 - 5 years.

Graphic analysis (fig. 2) shows a low lead mobility. In both 2005 and 2010, the highest density is registered in the 20 - 30 cm layer; occasionally, the concentration here is even 27 times higher than the usage value (1000 mg/kg).

Copper distribution in soil (fig. 3) is characterized by surface attachment, but at high concentrations it can go deeper [4]. Exceeding the usage value (500 mg/kg) is less frequent in deeper soil layers of 0 - 10 cm (2010) and 75 - 100 cm (2005). At 75 - 100 cm deep, copper concentration is 15 times higher than the usage value and 30 times higher than the critical value.

Zinc is a widespread metal in nature and it usually occurs in small quantities in the Earth's

crust. High concentration of Zn in soil, forming small solid particles, is due to metallurgical industry [1]. Zinc concentration (fig.4) exceeds the critical value (700 mg/kg) at all sampling levels, except for the 0 - 10 cm level in 2010. In this case, zinc concentration was slightly higher than the normal value of 100 mg/kg.

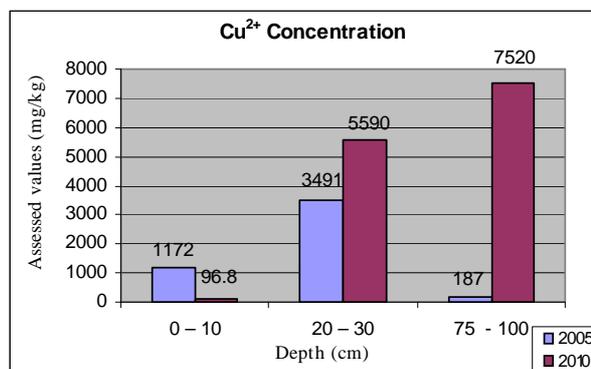


Figure 3. Cooper variation in the soil layers in 2005 and 2010

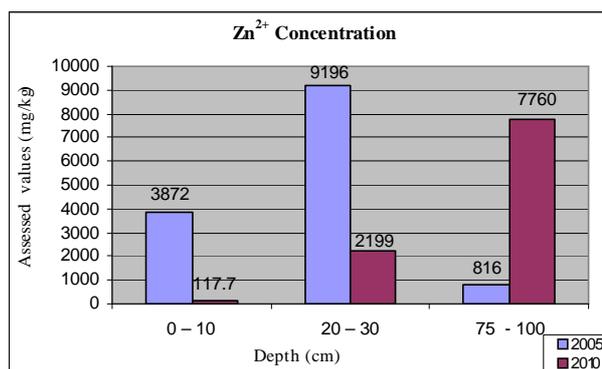


Figure 4. Zinc variation in the soil layers in 2005 and 2010

Cadmium is more stable in soil than in air and water. Cadmium attachment, absorption and distribution in soil depend on: pH, soluble organic matter content, metal oxide content, clay type and content [1].

Cadmium is a heavy metal found in soil, with normal concentrations higher than 1 mg/kg.

As its toxicity is 2 - 20 times higher than in the case of other heavy metals, it is not essential for life. In soil samples taken from the site we studied, cadmium concentration is very high, exceeding critical value (5 mg/kg) at all sampling levels, except for the 0 - 10 cm layer in 2010, where the concentration is lower than the critical value (fig. 5).

In 2005, cadmium concentration samples indicate a decrease in depth, while samples in 2010 show an increase in depth, being 13.5 times higher

than the critical value and 7 times higher than the usage value (10 mg/kg).

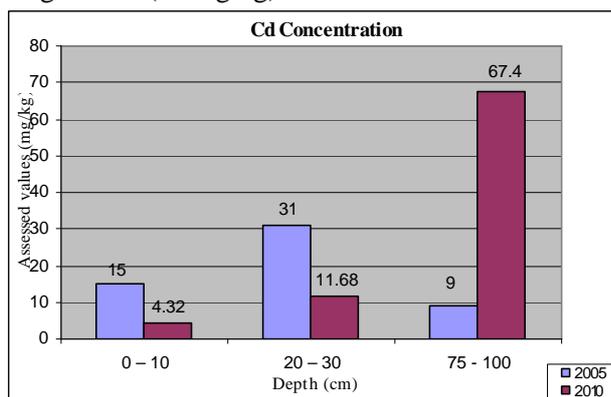


Figure 5. Cadmium variation in the soil layers in 2005 and 2010

Chromium is classified as heavy metal, and even if it appears in larger amounts in the soil, it is rarely a problem. It is toxic to plants only when it appears as oxidized anion (hexavalent chromium). This only occurs under certain conditions of pH and low potential, which are not persistent in soil [1]. Chromium distribution of in soil is characterized by a concentration below critical value (300 mg/kg) for all studied samples (fig.6).

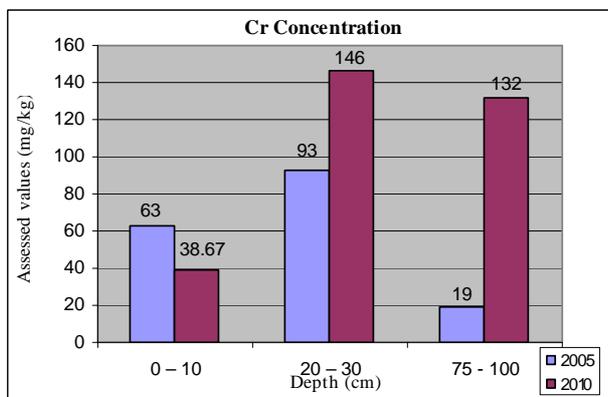


Figure 6. Chromium variation in the soil layers in 2005 and 2010

In 2005, **manganese** level in soil is generally constant at all levels of sampling, while in 2010 the concentration is twice the critical value for the 20 - 100 cm depth level (fig.7).

In the case of **arsenic**, the usage value (50 mg/kg) is exceeded in all samples, with one exception. In 2005, at a depth of 75 - 100 cm, it was below the critical value (25 mg/kg), but three times higher than the normal value (fig. 8).

Iron is the metal found in all soil types, being a fixed element in clay minerals. It can be found in all sampling levels of soil in high concentrations, except the layer between 0 - 10 cm in 2010 (fig. 9).

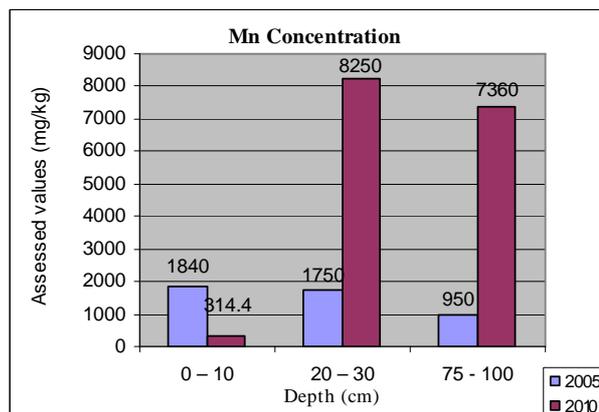


Figure 7. Manganese variation in the soil layers in 2005 and 2010

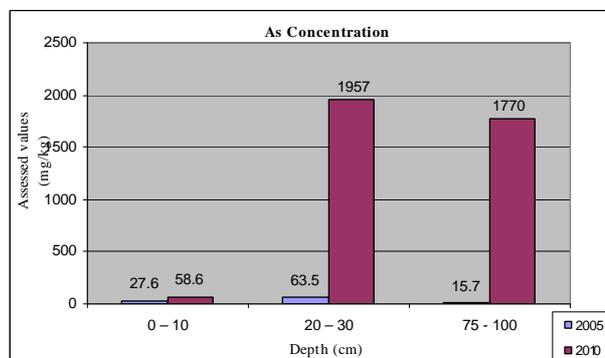


Figure 8. Arsenic variation in the soil layers in 2005 and 2010

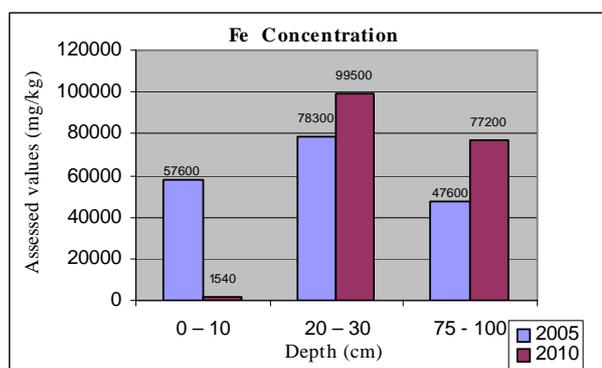


Figure 9. Iron variation in the soil layers in 2005 and 2010

4. Conclusions

Current state of soil pollution inside Romplumb Company is the result of 150 years of processing lead zinc concentrates, in which technologies have excessively polluted the environment. Consequently, this sampling site is one of the historically polluted areas along with Zlatna and Copsa Mica.

In 2005, variation of pollutants' concentration highlights a general descending trend along depth. Instead, in 2010 there is an increasing concentration tendency with depth. Determinations carried out on soil quality analysis concerning pollution with Pb, Cd, Zn, Cu, As, Mn and Fe put in an alarming exceeding of critical and usage values for all samples. There is though, one exception: for 75 - 100 cm depth in 2005 and 0 - 10 cm depth in 2010.

For 2010 soil samples, lead concentration is 27 times higher than the usage value, cadmium level is 7 times higher, copper 15 times higher and zinc 5 times higher than regular usage values. The main conclusion that emerges from the study shows drastic heavy metals soil pollution, at 0 - 100 cm depth, requiring complex remediation solutions.

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