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Chapter 9

Assessment of Soil Pollution with Heavy Metals in Romania

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1. Introduction

Human activities, industry, erosion and the continuous spread of urbanization can induce soil pollution in various ways. The pollution of soil can be dangerous for human health because the toxic substances can enter the crops and the ground water. The soil, due to its properties and structure, plays the role of a filter that can retain and be a deposit for toxic substances. The most frequent contaminants of soil in Europe are heavy metals and mineral oil. The group ‘heavy metals’ for the purpose of discussing health risks or impacts generally includes: Arsenic (As), Lead (Pb), Cadmium (Cd), Chromium (Cr) (although only the form Cr(VI) is toxic), Copper (Cu), Mercury (Hg), Nickel (Ni), Zinc (Zn).

Several of these elements are necessary for human health and are beneficial when taken into the body in foods or as supplements at appropriate, low levels. Conversely, cadmium, lead and mercury have no known biological function and are toxic to humans.

The sources of heavy metals that pollute the soil can be human activities like metalliferous mining (As, Cd, Cu, Ni, Pb, Zn), smelters (As, Cd, Pb), metallurgy, electronic industry (where metals are used in batteries, semiconductors, circuits), rolling (Ni, Cd, Pb, Hg, Se), dyes and paints industry (Pb, Cr, As, Se, Mo, Cd, Co, Ba, Zn), plastics industry (Cd, Zn, Pb, Sn are used as polymer stabilizers), chemical industry (using Pb, Ni, Nb, Hg, Pt, Ru as electrode catalysts), wood industry (As, Cr and Cu). In the vicinity of furniture factories and wood-processing, these elements were often identified as soil and water pollutants [1, 2, 3, 4, 5, 6, 7, 8, 9].

Also, by storing municipal waste, special and hazardous waste, the soil may be contaminated with various heavy metals.
The combustion of fossil fuels leads to the presence of Cd, Zn, As, Se, Cu, Mn, V, in the ashes and particulates of combustion. Some heavy metals (Se, Te, Pb, Mo, Li) are added to fuels and lubricants to improve their properties. [1, 2, 3, 4, 5, 6, 7, 8, 9].

Corrosion of metals contained in various materials (Cu, Pb pipes and roofs, Cr, Ni, Co in stainless steel, Cr, Pb painting) can cause soil pollution. Agro-livestock activities can also cause soil pollution (As, Cu, Zn can be added to feed pigs and poultry, Cd, As, Pb, Mn, Cu, Zn can be present in phosphate fertilizers and pesticides). [1, 2, 3, 4, 5, 6, 7, 8, 9].

Pollution by heavy metals and many organic contaminants is practically irreversible (European Commission, 2012).

Excess heavy metal accumulation in soils is toxic to humans and other animals.

Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer. Acute (immediate) poisoning from heavy metals is rare, but possible, through ingestion or dermal contact. Chronic problems associated with long-term heavy metal exposures are [10, 11, 12, 13, 14, 15, 16, 17, 18, 19] for:

1. Lead [20-60] – is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys. Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead poisoning severe enough to cause evident illness is now very rare. Lead can be harmful after uptake from food, air, water or contaminated dust. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, as well as entire food chains.

2. Cadmium – affects kidney, liver, and GI tract [28, 30, 61, 62, 63].

3. Arsenic – is associated with skin damage, increased risk of cancer and problems with circulatory system, affects kidneys and the central nervous system [64, 65, 66, 67, 68, 69].

4. Chromium is associated with allergic dermatitis in humans [70, 71].

5. Mercury is associated with kidney damage [72, 73, 74, 75].

6. The most common problem caused by cationic metals (metallic elements whose forms in soil are positively charged cations e.g., Pb2+) are mercury, cadmium, lead, nickel, copper, zinc, chromium and manganese. The most common anionic compounds (elements whose forms in soil are combined with oxygen and are negatively charged e.g., MoO42-) are arsenic, molybdenum, selenium, and boron.

1.1. The aim of the study

This study tried to assess the level of soil contamination with heavy metals (lead, cadmium, mercury, manganese, nickel, total chromium, zinc, cobalt, copper and arsenic) in 34 counties in Romania. No previous data exists as a reference level of soil pollution.
2. Material and methodology

Sampling was done in 2012, in the fall (September – October). Soil samples were taken from max 20 cm deep, from areas around children’s units like nurseries, kindergartens, schools or playgrounds for children. The samples were taken in county capital cities. Also, soil samples were taken from areas of land used for agricultural purposes like farmlands and gardens.

For metal analysis, 0.2 g of ground soil were digested with aqua regia using microwave digestion (EN 13346:02) followed by filtration and adjusting the volume in a volumetric flask. Concentrations of Pb, Cd, Cu, Cr were measured using the electrothermal atomic absorption spectrometry (ISO 11464:2006, SR ISO 11047/1999, EPA 6020). Concentrations of Zn, Mn, Co, Ni, Cr were measured using flame AAS (atomic absorption spectrometry) and concentrations of Hg and As were measured using atomic absorption spectrometry with cold vapour (HVG-AAS) and SR EN 1485/2007. [76, 77]

Despite the importance of soil pollution for our society, there is no EU legislation specifically targeting the protection of soil [78, 79]. A regulation regarding the soil pollution exists in Romania (Order nr. 756, November, the 3th, 1997). In this Order [80], the following definitions are of importance: environmental impact, types of land uses that require a certain soil quality, soil characterized by a maximum acceptable level of pollutants - sensitive and less sensitive soil, remediation targets, potentially significant pollution, significant pollution, threshold alert – (concentrations of pollutants in air, water, soil or emissions / discharges, which are designed to alert the competent authorities of a potential impact on the environment and determines the triggering of additional monitoring and / or reduction of concentrations of pollutants in emissions / evacuations), intervention threshold, reference sample [80].

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Reference threshold for sensitive soil</th>
<th>Alert thresholds - sensitive soil</th>
<th>Alert thresholds - soil less sensitive</th>
<th>Action levels - soil sensitive</th>
<th>Action levels – soil less sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>5</td>
<td>15</td>
<td>25</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>15</td>
<td>30</td>
<td>100</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>Chromium (Cr) :  Total Chromium total</td>
<td>30</td>
<td>100</td>
<td>300</td>
<td>300</td>
<td>600</td>
</tr>
<tr>
<td>Hexavalent Chromium</td>
<td>1</td>
<td>4</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>20</td>
<td>100</td>
<td>250</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>900</td>
<td>1500</td>
<td>2000</td>
<td>2500</td>
<td>4000</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.1</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>20</td>
<td>75</td>
<td>200</td>
<td>150</td>
<td>500</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>20</td>
<td>50</td>
<td>250</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>100</td>
<td>300</td>
<td>700</td>
<td>600</td>
<td>1500</td>
</tr>
</tbody>
</table>

*Table 1. Reference values for traces of heavy metals in soil - Heavy metals (mg/kg dry substance). Values are stipulated in Order 756/1997 for the approval of the Regulation on the assessment of environmental pollution [80].*
3. Results and discussions

Cadmium in the soil registered levels that ranged from 0 and 0.86 mg/kg, in the urban areas and in the rural areas. Compared to the threshold value it can be seen that the levels of cadmium in soil, in both urban and rural areas, have not exceeded the threshold value (1 mg/kg). It can be seen that the level of cadmium in soil is slightly higher in rural areas compared to urban areas.

Lead in soil, registered levels that ranged from 0 and 96.11 mg/kg in the urban areas and from 0 to 147.67 mg/kg in rural areas. It can be seen that, both in the urban and rural areas, the lead levels in soil exceeded the threshold value (20 mg/kg). The alert threshold for sensitive soil (50 mg/kg) was exceeded in both the urban and rural areas.

Figure 1. Lead levels in soil in urban areas

Figure 2. Lead levels in soil in rural areas

Comparing the two charts it can be seen that, in the same area (Constanța county), the level of lead in soil is over the alert threshold in the urban and in the rural area. In other two counties...
(Buzău and Ialomița) the levels of lead in soil are exceeding the threshold limit both in the urban area and in the rural area. There are other two counties beside Constanța, where the levels of lead are exceeding the alert threshold in urban areas (Olt and Sibiu). In rural areas it can be seen that the number of counties where lead levels in soil exceed the threshold is higher than in urban areas.

**Copper** in soil registered levels that ranged from 0 and 128.5 mg/kg in the urban areas and from 0 to 80.43 mg/kg in rural areas. It can be seen that the levels identified in soil exceeded, both in the urban and rural areas, the threshold value (20 mg/kg). Also, the alert threshold for sensitive soil (100 mg/kg) was exceeded in a single urban area. In rural areas a slightly higher level of copper in the soil was observed.
The alert threshold was exceeded in a single county in urban areas. The number of counties where was found levels of copper in soil, in rural areas, that exceeded the threshold was double in comparison with urban areas.

**Nickel** in soil registered levels that ranged from 0 and 44 mg/kg in the urban areas and from 0 to 41.6 mg/kg in rural areas. The levels of nickel found in soil samples exceeded the threshold value (20 mg/kg), in the urban and rural areas. Nickel recorded slightly higher levels in the soil of rural areas, but, also, were found peaks in urban soil. The alert threshold for sensitive soil (75 mg/kg) was not exceeded in either urban or rural area.

![Figure 5. Nickel levels in soil in urban areas](image1)

![Figure 6. Nickel levels in soil in rural areas](image2)

As it can be seen in the charts above, the soil pollution with nickel is similar in the urban and rural areas, regarding the number of counties affected.
Manganese in soil registered levels that ranged from 0 and 1256.57 mg/kg in the urban areas and in rural areas the levels ranged from 0 to 1072.62 mg/kg. Compared to the threshold value, the levels of manganese found in soil exceeded the threshold, both in the urban and rural areas (900 mg/kg). Alert threshold (1500 mg/kg) was not exceeded in neither rural areas nor urban areas.

Concerning the levels of total chromium in soil, values are similar, in urban and rural areas. The levels found in soil were between 0 and 40.81 mg/kg in urban areas and between 0 and
57.23 mg/kg in rural areas. Only the threshold (30 mg/kg) was exceeded in the urban and rural areas and not the alert threshold (100 mg/kg).

![Figure 9. Total chromium levels in soil in urban areas](image)

![Figure 10. Total chromium levels in soil in rural areas](image)

The total chromium levels registered in soil exceeded the threshold in a small number of counties. Only in one county (Mureș), levels of chromium exceeding the threshold were found in both the urban and rural areas.

Cobalt levels were higher in rural areas compared to urban areas. The highest value was found in the soil of a farmland in Covasna county, where the level of cobalt was equal to 20.23 mg/kg, exceeding the threshold value (15 mg/kg) but not the alert threshold (30 mg/kg).
From the charts, it can be seen that it is only one hot spot where the levels of cobalt in soil exceeded the threshold.

**Zinc levels** ranged between 0 and 275.35 mg/kg in the soil of urban areas and between 0 – 131.79 mg/kg in the soil of rural areas. The levels recorded were similar in urban and rural areas. One single higher value was found in Sibiu county.
A similar situation with zinc pollution of the soil was found in the urban and in the rural areas of Romania as number of counties affected.

**Mercury** levels in the soil ranged between 0 and 0.265 mg/kg in the soil of urban areas and between 0 – 0.305 mg/kg in the soil of rural areas. The threshold value is equal to 0.1 mg/kg and was exceeded in urban and rural areas, but the alert threshold is equal to 1 mg/kg and was not exceeded in neither urban nor in rural areas. Special mention must be made for district Ferneziu of the town Baia Mare where there is a historical pollution of the environment. The level of mercury found in this area was equal to 0.265 mg/kg.
For the situation of soil pollution with mercury it must be stressed that, in the area of Maramureş there is a historical pollution due to a non-ferrous industry existing for a long period of time.

Arsenic levels in soil were between 0 and 8.22 mg/kg in urban areas and 0 and 9.59 mg/kg soil. Arsenic concentrations were higher in rural areas compared to urban soil. The reference
threshold is equal to 5 mg/kg and the alert threshold is equal to 15 mg/kg. The threshold value was exceeded but the not the alert threshold.

Comparing the two maps, it can be seen that, levels of pollution exceeding the threshold were found in the Sibiu and Mureș County, in the middle of the country, in both urban and rural areas.

Figure 17. Arsenic levels in soil in urban areas

Figure 18. Arsenic levels in soil in rural areas
4. Conclusions

This study is the first study that tried to assess the situation of soil pollution with heavy metals in Romania.

After assessment of the soil contamination with heavy metals in 34 counties in Romania, it can be concluded that for all investigated metals except cadmium the threshold values were exceeded.

Alert thresholds were exceeded for lead and copper, both in urban and rural areas, especially in two counties: Maramureș county and Sibiu county. Areas like Maramureș county or Sibiu county have a historic pollution due to the industry present since 1844 in Baia Mare, Maramures county and 1936 in Copșa Mică, Sibiu county.

A national screening program was performed in the years 2008-2010 in Maramureș county (Baia Mare city and especially Ferneziu district) to see the impact on human health in connection with lead pollution. In the years 2008 and 2009 a group of 91 children was investigated [81, 82].

The results showed the following situation:

<table>
<thead>
<tr>
<th>Year of study</th>
<th>Lead in blood up to 10 μg/dl</th>
<th>Lead in blood up to 20 μg/dl</th>
<th>Lead in blood up to 30 μg/dl</th>
<th>Lead in blood up to 35 μg/dl</th>
<th>Lead in blood &gt; 35 μg/dl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>95.4</td>
<td>97.8</td>
<td>97.8</td>
<td>97.8</td>
<td>2.2</td>
</tr>
<tr>
<td>2009</td>
<td>58.70</td>
<td>71.74</td>
<td>84.06</td>
<td>89.13</td>
<td>10.87</td>
</tr>
</tbody>
</table>

Table 2. Lead levels in blood in city Baia Mare, Maramureș county in 2008 and 2009.

A special situation had the children living near the factory that processes lead in the district Ferneziu in Baia Mare county.

During the year 2010, the study group was made of 94 pregnant women and 94 new born babies. The blood was taken from the new born cord in the case of children [83].

<table>
<thead>
<tr>
<th>Level of lead in blood of pregnant women</th>
<th>0-10 μg/dl</th>
<th>10-20 μg/dl</th>
<th>20-30 μg/dl</th>
<th>&gt; 35 μg/dl</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of the study group</td>
<td>94.7</td>
<td>1.06</td>
<td>2.12</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Table 3. Lead levels in blood in the group of pregnant women, in city Baia Mare, Maramureș county, in 2010.
### Table 4. Lead levels in blood in the cord of new born babies, in city Baia Mare, Maramureș county, in 2010

<table>
<thead>
<tr>
<th>Level of lead in blood of cord of new born babies</th>
<th>0-10 μg/dl</th>
<th>10-20 μg/dl</th>
<th>20-30 μg/dl</th>
<th>&gt; 35 μg/dl</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of the study group</td>
<td>93.6</td>
<td>1.06</td>
<td>-</td>
<td>5.34</td>
</tr>
</tbody>
</table>

For copper, alert thresholds was exceeded, both in urban and rural areas. In Suceava county, copper mining was performed since 1922. In this area, there were taken rehabilitation measures in the period between 1999-2005. Still, some of the effects of the ancient pollution situation can be seen today.

All the other investigated metals in the soil, both in residential areas and agricultural areas (which both can be classified as sensitive lands), do not exceed the alert threshold for sensitive lands.

For cadmium, nickel, manganese, cobalt and arsenic higher levels were recorded in the soil of rural areas than in the soil of urban areas.

For total chromium, zinc and mercury similar levels were recorded in the soil of urban and rural areas.

It must be stressed that in the areas where the alert thresholds were exceeded, pollution with impact on the environment can be present. The situation can be labelled as “potentially significant pollution”. In this case, the competent authorities can take action to reduce the pollutants emissions in the air or to take measures to diminish the possibilities to contaminate the soil directly or through water.

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