HEAVY METALS ABUNDANCE IN THE SOILS OF THE PANTELIMON – BRĂNEŞTI AREA, ILFOV COUNTY: IRON, MANGANESE, NICKEL, LEAD, ZINC

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Abstract. More than 20 years later, a new research on heavy metals (iron, manganese, nickel, lead, zinc) contents in the soil cover of the Pantelimon – Brăneşti area located East of the Bucharest Municipality and exposed for several decades to the influence of industrial emissions from two non-ferrous metallurgy plants is presented. A 5,912.72 ha area was investigated, 544 samples taken by geometric horizons (0-20; 20-40; 40-60 cm) from 215 points have been analyzed. The dominant soils are: Preluvosols, Chernozems, and Phaeozems. The total manganese, nickel, and zinc contents of the analyzed soils are lower than their average contents in the lithosphere, while the lead content is 2.3 times higher. As compared to the average contents of the World’s soils the contents of the four heavy metals in the Pantelimon – Brăneşti area are much higher: 1.32 (zinc); 1.45 (manganese); 2.00 (nickel), and 2.43 (lead) times. The polluting chemical element of the area is lead. The iron and manganese contents frequency histograms are symmetric, while those of the nickel, lead, and zinc are asymmetric with right asymmetry. The tendency maps of the heavy metals distribution in the analyzed soils shows the insular character of the high contents generated by the polluting emissions nature, by the dominant winds direction, by the micro relief, and by the vegetation structure.

Introduction

In the Pantelimon-Brăneşti area, located in the Bucharest Municipality Eastern part, where the by-pass road meets the national highway 3 Bucharest – Fundulea – Lehliu, two industrial facilities functioned for many years with a non-ferrous metallurgy profile. One of them made auto accumulators and was also recovering

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lead from the disabled ones. The industrial emissions of these two plants contributed to environment pollution, including the soil in which higher heavy metals quantities accumulated.

Researches carried out by Răuță et al. (1978, 1980) highlighted the lead, zinc, and copper soil and cultivated plants pollution levels. Later Lăcătușu et al. (2000) established the surface distribution of total lead and copper contents in the 0-20 cm layer of the area, presented the statistical parameters of the area cadmium, cobalt, chromium, copper, manganese, nickel, lead, and zinc total contents, and tested this soil pollution at different fertilization levels effect on alfalfa, soybean, and salad plants growth.

The diminution of the two plants industrial activity after 1990, up to clearance, brought about the diminution of the polluting impact.

The present paper intends to highlight the content level of five heavy metals (iron, manganese, nickel, lead, and zinc) from the soils of the maximum pollution influenced area two decades after the activity diminution and the improvement of the emissions filtering system.

In a recent paper (Lăcătușu et al., 2011a) the abundance of other heavy metals (cadmium, cobalt, chromium, and copper) in the soils of the same area is presented.

1. Material and method

The investigated territory (Figure 1) is bordered by the Bucharest Municipality by-pass road to the West, by a line that would go through the Moara Domnească and Gâneasa localities to the South, by the Cozieni and Brănești localities Western limits to the north-East and East, by the A2 Highway to the South East, and by the 301 communal road to the South-West.

The investigated area has a 5,916.72 ha surface. Approximately 1/3 of the soil is dedicated to agriculture for field crops and 2/3 to forestry.

In order to determine the soil types pedology profiles have been made out of which soil samples were taken from genetic horizons, and to establish the heavy metals abundance soil samples were taken from geometric horizons (0-20; 20-40; and 40-60 cm). 544 soil samples were taken from 215 points (Figure 2). The samples were analyzed both from the general physical and chemical properties point of view and of the total heavy metals (cadmium, cobalt, chromium, and copper) contents. The latter were determined by atomic absorption spectrometry.

The analytical data were statistically computed, and the spreading (minimum value, maximum value, coefficient of variation, standard deviation) and grouping centre parameters (arithmetic mean, geometric mean, median, and module) were highlighted.

Tendency maps were drawn of the heavy metals distribution using the Surfer soft.
The values of the geochemical and pedo-geochemical indexes were computed after the Lăcătușu and Ghelase (1992) method.
2. Results and discussions

2.1. General characterization of the soil cover. Field and laboratory investigations lead to drawing up the soil map of the investigated territory (Figure 3). Soils of three taxonomic classes can be noticed: Chernisols, Luvisols, and Hydrosols. The first class comprises Cambic Chernozem, Argic Chernozem, and Phaeozioms, and the second one comprises red Mollic Preluvosols, Red Preluvosols, Vertic Preluvosols, and Planic, or Gleyic Stagnic Luvisols. Hydrosols occur on small areas and are represented by Mollic Gleysols and Vertic Luvic Stagnosols.

Some of the Chernozems and Preluvosols have a certain erosion degree. Red Preluvosols and Argic Chernozems are predominant.

The values of the main physical and chemical properties of the Pantelimon – Brânești area soils are presented in Table 1. Relatively close values can be noticed for the clay (< 2 µ) content in Preluvosols and Chernozems; the Vertic Stagnosol has higher clay content, namely 41.8%. All these values stand for a clay-loam texture.

The average values of the bulk density vary in a 1.46-1.78 g/cm³ interval, most of them between 1.46 and 1.52 g/cm³, which signifies a high and very high bulk density for the values over 1.59 g/cm³.

![PANTELIMON – BRĂNEŠTI AREA SOIL MAP](image_url)
Heavy metals abundance in the soils of the Pantelimon – Brânești area

Therefore, the soils of the Pantelimon – Brânești area have a clay-loam texture and a high and very high bulk density.

Tab. 1 – The main physical and chemical properties of the Pantelimon – Brânești area soils (0-60 cm)

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Localization</th>
<th>Clay &lt; 2 μm %</th>
<th>BD g/cm³</th>
<th>pH H₂O</th>
<th>Humus %</th>
<th>Ni %</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>mg·kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Preluvosol, slightly luvic</td>
<td>1 km W Brânești</td>
<td>26.9 – 35.5</td>
<td>1.30 – 1.62</td>
<td>4.7 – 5.9</td>
<td>0.80 – 3.70</td>
<td>0.072 – 0.373</td>
<td>38 – 49</td>
<td>105 – 130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.1</td>
<td>1.49</td>
<td>5.4</td>
<td>2.84</td>
<td>0.175</td>
<td>44</td>
<td>125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mollis Red Preluvosol</td>
<td>NW Cernica</td>
<td>31.1 – 37.0</td>
<td>1.31 – 1.57</td>
<td>6.3 – 6.7</td>
<td>1.60 – 2.40</td>
<td>0.125 – 0.137</td>
<td>4 – 13</td>
<td>130 – 159</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.0</td>
<td>1.46</td>
<td>6.5</td>
<td>2.07</td>
<td>0.131</td>
<td>9</td>
<td>146</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red Preluvosol</td>
<td>N Pantelimon</td>
<td>29.9 – 39.7</td>
<td>1.37 – 1.68</td>
<td>5.4 – 6.5</td>
<td>1.45 – 3.07</td>
<td>0.130 – 0.163</td>
<td>11 – 23</td>
<td>120 – 190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.6</td>
<td>1.51</td>
<td>5.8</td>
<td>2.33</td>
<td>0.150</td>
<td>17</td>
<td>130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stagnic Luvosol</td>
<td>E Pantelimon</td>
<td>29.0 – 41.1</td>
<td>1.45 – 1.65</td>
<td>5.7 – 6.1</td>
<td>0.90 – 2.28</td>
<td>0.061 – 0.119</td>
<td>9 – 14</td>
<td>94 – 148</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.1</td>
<td>1.59</td>
<td>5.8</td>
<td>2.33</td>
<td>0.092</td>
<td>12</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Luvic Vertic Stagnosol</td>
<td>E Pantelimon</td>
<td>30.4 – 49.5</td>
<td>1.70 – 1.82</td>
<td>6.1 – 7.2</td>
<td>1.00 – 2.20</td>
<td>0.074 – 0.104</td>
<td>40 – 63</td>
<td>140 – 161</td>
<td></td>
</tr>
<tr>
<td></td>
<td>41.8</td>
<td>1.78</td>
<td>6.7</td>
<td>1.42</td>
<td>0.085</td>
<td>52</td>
<td>156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambic Chernozem</td>
<td>N Cernica</td>
<td>36.1 – 48.0</td>
<td>1.42 – 1.62</td>
<td>7.3 – 7.8</td>
<td>1.40 – 4.10</td>
<td>0.199 – 0.280</td>
<td>83 – 172</td>
<td>259 – 374</td>
<td></td>
</tr>
<tr>
<td></td>
<td>36.9</td>
<td>1.52</td>
<td>7.5</td>
<td>3.50</td>
<td>0.204</td>
<td>129</td>
<td>222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argic Chernozem</td>
<td>N Brânești</td>
<td>36.0 – 39.0</td>
<td>1.41 – 1.84</td>
<td>6.2 – 7.1</td>
<td>2.20 – 4.00</td>
<td>0.146 – 0.211</td>
<td>30 – 58</td>
<td>304 – 355</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37.9</td>
<td>1.67</td>
<td>6.8</td>
<td>3.10</td>
<td>0.191</td>
<td>40</td>
<td>333</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values interval * Arithmetic mean

From the chemical point of view the fact is noticed that the Chernozems have a reaction interval relatively wide, from slightly acid to neutral, but the pH values specific to the neutral domain are predominant. Unlike the Chernozems, the Preluvosols, the Stagnic Luvosol, and the Vertic Luvosol reaction belongs to the moderate – slightly acid domain.

The humus content, assessed in dependence with the texture, is low both in Preluvosols and in Chernozems. The total nitrogen content is very low in Luvosol and Stagnosol, low and medium in Preluvosols, and medium in Chernozems. The phosphorus and potassium mobile forms supply depends on the mineral fertilization level. Thus, phosphorus supply is low in the Stagnic Luvosol and in some Preluvosols (Table 1), but high in another Red Preluvosol, in the Stagnosol, and in Chernozems. The mobile potassium, with values of 122-222 mg·kg⁻¹, oscillates in a large domain which also defines a various supply, from low to very high.

2.2. The iron, manganese, nickel, lead, and zinc abundance in the Pantelimon – Brânești area soils. The statistical parameters of the total heavy metals contents (Tables 2 and 3) highlight differences between the chemical elements as regards their accumulation in one studied horizon or another. Thus, the higher mobility of the elements with variable valence such as iron and manganese determines their accumulation at a bigger depth namely iron at 40-60 cm and manganese at 20-40 cm (Table 2). On the other hand, the other three analyzed
heavy metals (zinc, lead, and nickel) accumulated in the first geometric horizon, down to 20 cm depth.

The great content differences between the first and the third layers, namely 15.4 mg·kg⁻¹ for Zn and 22.4 mg·kg⁻¹ for lead, as compared to only 6.0 mg·kg⁻¹ for nickel, lead to the conclusion of an anthropic source presence contributing to the abundance of zinc and lead in the investigated area’s soils. The finding is consistent with the results of previous researches carried out by Răuță et al. (1978, 1980) and Lăcătușu et al. (2000) which highlighted the lead and zinc soil pollution around the two industrial units, on much smaller surface.

Tab. 2 – The statistical parameters of the total heavy metals (iron and manganese) total contents (mg·kg⁻¹) in the Pantelimon – Brănești area soils

<table>
<thead>
<tr>
<th>Depth, cm</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-20</td>
<td>20-40</td>
</tr>
<tr>
<td>n</td>
<td>224</td>
<td>103</td>
</tr>
<tr>
<td>x̄</td>
<td>12,385</td>
<td>20,296</td>
</tr>
<tr>
<td>x̅</td>
<td>46,434</td>
<td>30,387</td>
</tr>
<tr>
<td>σ</td>
<td>22,363</td>
<td>3,030</td>
</tr>
<tr>
<td>cv (%)</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>Me</td>
<td>22,350</td>
<td>22,090</td>
</tr>
<tr>
<td>Mo</td>
<td>22,090</td>
<td>25,755</td>
</tr>
</tbody>
</table>

Tab. 3 – The statistical parameters of the total heavy metals (chromium and copper) total contents (mg·kg⁻¹) in the Pantelimon – Brănești area soils

<table>
<thead>
<tr>
<th>Depth, cm</th>
<th>Zn</th>
<th>Pb</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-20</td>
<td>20-40</td>
<td>40-60</td>
</tr>
<tr>
<td>n</td>
<td>224</td>
<td>103</td>
<td>216</td>
</tr>
<tr>
<td>x̄</td>
<td>44.3</td>
<td>45.2</td>
<td>35.7</td>
</tr>
<tr>
<td>x̅</td>
<td>114.5</td>
<td>87.6</td>
<td>98.5</td>
</tr>
<tr>
<td>σ</td>
<td>11.4</td>
<td>8.7</td>
<td>8.6</td>
</tr>
<tr>
<td>cv (%)</td>
<td>15</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>Me</td>
<td>72.9</td>
<td>65.6</td>
<td>59.1</td>
</tr>
<tr>
<td>Mo</td>
<td>71.0</td>
<td>66.2</td>
<td>59.0</td>
</tr>
</tbody>
</table>

The frequency histograms of the heavy metals distribution (figures 4, 5, and 6) clearly highlight the symmetric iron and manganese distribution and the asymmetric distribution, with a right asymmetry, of nickel, lead, and zinc.

If the values of these heavy metals soil normal contents and the alarm threshold value for a land sensitive use are taken into account we find that most of
the manganese values are inferior to the normal soil contents and much lower than the alarm threshold for a land sensitive use (Figure 4). The same image is given by the zinc distribution frequency histograms (Figure 6). Therefore, the analyzed soils are not polluted with manganese or zinc.

![Figure 4](image1.png)

**Fig. 4** – The frequency histograms of the heavy metals (iron and manganese) distribution in the Pantelimon – Brânești area soils

- 0-20 cm;  - 20-40 cm;  - 40-60 cm;  - 0-60 cm
- normal content;  - Alarm threshold for a sensitive land use (MAPPM Order 756/1997)

![Figure 5](image2.png)

**Fig. 5** – The frequency histograms of the heavy metals (nickel and lead) distribution in the Pantelimon – Brânești area soils

- 0-20 cm;  - 20-40 cm;  - 40-60 cm;  - 0-60 cm
- normal content;  - Alarm threshold for a sensitive land use;  - Intervention threshold for a sensitive land use (MAPPM Order 756/1997)

The nickel analytical data range in the interval between the soil normal content value and the value of the alarm threshold for a sensitive land use. Only a few values exceed the alarm threshold value. These ones proceed from the soil
samples collected from around the industrial zone. Most of the points are ordered on curves placed in the half-interval close to the normal content domain.

As regards the lead, this chemical element reached the investigated area’s soils especially airborne, from the industrial emissions. The frequency histograms cover all the domains bounded both by the normal values and by those of the intervention threshold for a sensitive land use (Figure 5). Most of the values are ordered on both sides of the alarm threshold for a sensitive land use. Therefore, it can be stated that the polluting element of the area was lead.

2.3. The geochemical and pedo-geochemical abundance of manganese, nickel, lead, and zinc in the Pantelimon – Brânești area. The values of the geochemical abundance (IGA) and pedo-geochemical abundance (IPAg) indexes show the place of the analyzed chemical elements as compared to their general pedospheric and lithospheric abundance. The values higher than 1 of these indexes show that the soils of the investigated area have higher quantities of a certain chemical element than its average lithospheric or pedospheric content. The values lower than 1 show that the chemical element is to be found at lower content levels than those of the lithosphere or pedosphere.

Thus, the values of Table 4 show that the Pantelimon – Brânești area soils contain less manganese, nickel, and zinc than these chemical elements lithospheric concentration. Unlike them there is 2.28 times more lead in the analyzed soils than its average concentration in the lithosphere.

All the values higher than 1 of the pedo-geochemical abundance index of the four heavy metals show that the soils of the Pantelimon – Brânești area contain 1.45 more manganese, 2.0 times more nickel, 2.43 times more lead, and 1.32 times more zinc than these elements’ average contents in the World’s soils. The
The explanation is simple, the polluting impact of the two non-ferrous metallurgy units which functioned several decades in the area. The polluting emissions had different intensities from one chemical element to another. Besides the anthropogenic factor the geogenic factor significantly contributed to the general chemical elements abundance.

Tab. 4 – The geochemical and pedo-geochemical abundance indexes values (IGA and IPAg) of the total heavy metals from the Pantelimon – Brânești area soils

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGA</td>
<td>0.73</td>
<td>0.69</td>
<td>2.28</td>
<td>0.79</td>
</tr>
<tr>
<td>IPAg</td>
<td>1.45</td>
<td>2.00</td>
<td>2.43</td>
<td>1.32</td>
</tr>
</tbody>
</table>

2.4. The area distribution of the heavy metals. The tendency maps of the five heavy metals distribution (Figures 5, 6, 7, 8, and 9) clearly highlight the areas with the lowest or the highest chemical elements contents in the first soil horizon (0-20 cm).

The iron, with values of over 4,000 mg·kg\(^{-1}\), is to be found in the central-Southern part of the area, where hydrosols occur. In reduction conditions the iron mobility increases, and it passes from Fe\(^{3+}\) to Fe\(^{2+}\), and it migrates both vertically and horizontally. This explains the increased abundance in insular surfaces. The anthropic, industrial influence mustn’t be overlooked which could increase the iron content of the North-Western corner of the investigated surface (Figure 5).

The geochemical and pedo-geochemical behavior of the manganese is similar to the iron one as they both are chemical elements with variable valences. The arrangement of the insular surfaces with higher manganese concentrations, of over 800 mg·kg\(^{-1}\), could be linked to the hydrosols presence in the depression micro relief forms but also to the Luvosols presence on a significant surface (Figure 6).

Analyzing the zinc distribution map (Figure 7) it comes out that the focal points with values higher than 100 mg·kg\(^{-1}\) are placed near the industrial units locations. Therefore, a certain influence of the emissions proceeded from these units existed but at low values, below the maximum allowable limit (Kloke, 1980) or the alarm threshold for a land sensitive use.

The insular and random zinc distribution is maintained on the whole surface.

The lead tendency distribution map (Figure 8) clearly highlights the area around the industrial units stretching West in which the values are higher than the alert threshold for a sensitive land use. The insular character of the high
Fig. 5 – The tendency map of the total iron contents (mg·kg\(^{-1}\)) in the Pantelimon – Brânești area soils

Fig. 6 – The tendency map of the total manganese contents (mg·kg\(^{-1}\)) in the Pantelimon – Brânești area soils

(normal values (900 mg·kg\(^{-1}\), according to MAPPM Order No.756/1997)
Heavy metals abundance in the soils of the Pantelimon – Brânești area

Fig. 7 – The tendency map of the total zinc contents (mg·kg$^{-1}$) in the Pantelimon – Brânești area soils
- normal values (100 mg·kg$^{-1}$, according to MAPPM Order No.756/1997)

Fig. 8 - The tendency map of the total lead contents (mg·kg$^{-1}$) in the Pantelimon – Brânești area soils
- normal values (20 mg·kg$^{-1}$);
- alarm threshold for a land sensitive use (50 mg·kg$^{-1}$);
- intervention threshold for land sensitive use (100 mg·kg$^{-1}$); according to MAPPM Order No.756/1997
concentration (100 mg·kg⁻¹) surfaces is maintained on the whole area but with a higher frequency in the central zone stretching East.

The fact that the highest lead soil values are to be found in arable soils, as the map of Figure 8 shows, indicates that the forest constituted an obstacle in the way of lead loaded particles deposition on soil.

The nickel can also be considered a chemical element with anthropic collisions in its soil distribution (Figure 9) because its concentration surfaces are in the Eastern part of the polluting units’ location and in the North-Eastern part of the investigated area, beyond the forest’s Eastern limit. Therefore, as for the nickel, the forest constituted a barrier in the way of the polluting emissions which fall immediately after the forest ends. It can be assessed that the nickel outrunned the alarm threshold for a sensitive land use only punctiform, as the frequency histogram of its distribution showed (Figure 5).

**Conclusions**

The investigated area is located East of the Bucharest Municipality, between Pantelimon locality in the West and Brânești in the East. It has a total area of 5,916.72 ha.

The soil cover consists predominantly of Preluvosols and Chernozems associated with Phaeozioms along with Luvosols, and Hydrosols.
The Pantelimon – Brânești area soils have a clay-loam texture, a big and very big bulk density. The Chernozems are slightly acid up to neutral – slightly alkaline, and the Preluvosols are slightly-medium acid. The humus content is low, the total nitrogen one low up to medium, the phosphorus and potassium mobile forms supply is diverse, from low to high.

In the first 60 cm the iron, manganese, and zinc contents belong to the normal contents domain, while the nickel and lead concentrations are, on an average, 2, respectively 1.8 times higher than the normal values.

Some of the nickel (11) and lead (16) values, specific to the upper soil horizon (0-20 cm), outrun the maximum allowable limits values (50, respectively 100 mg·kg\(^{-1}\)) and those of the alarm thresholds for a sensitive land use.

The values of the geochemical abundance index show lower content levels of the manganese, nickel, and zinc than their average lithospheric content (clark value), while the lead content is 2.3 times higher than this indicator’s value.

As compared to the average content in the World’s soils in the soils of the Pantelimon – Brânești area the four heavy metals contents are higher 1.32 (zinc); 1.45 (manganese); 2.00 (nickel); and 2.43 (lead) times.

The frequency histograms of the iron and manganese contents have a symmetric tendency, while those of nickel, lead, and zinc are asymmetric, with right asymmetry.

The tendency maps of the heavy metals distribution in the Pantelimon – Brânești area soils show the insular character of the high contents generated by the polluting emissions nature, by the dominant winds direction, by the micro relief, and by the vegetation structure.

The tendency map of the lead distribution in the upper soil horizon (0-20 cm) clearly highlights this chemical element concentration at a polluting level in the pollutant emission source vicinity.

References:


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