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Tekući račun Saveza inženjera i tehničara Srbije broj: 170-260-10 kod Unicredit banke Beograd
PIB 100289838, Maticni broj 07009909

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U FINANSIRANJU IZDAVANJA ČASOPISA "TEHNIKA" UČESTVUJE MINISTARSTVO PROSVETE, NAUKI I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

CIP – Kataloziacija u pUBLIKACiji
Narodna biblioteka Srbije, Beograd
62
Dvomesečno. - Ima podzbirke: Novi materijali = ISSN 0354-2300, Naše građevinarstvo = ISSN 0350-2619, Rudarstvo, geologija i metalurgija = ISSN 0350-2627, Mašinostroj = ISSN 0461-2531, Elektrotehnika (Beograd) = ISSN 0013-5836, Saobraćaj = ISSN 0558-6208, Menadžment = ISSN 1450-9911, Kvalitet, standardizacija i metrologija = ISSN 2334-7368, ISSN 0040-2176 = Tehnika (Beograd)
COBISS.SR-ID 2527490
Takođe se obrađuju za inostrane baze podataka: SAIDC-el (ISKRA, SL), SAIDC-gr (CTK, SL), INSPEC (IEEE, UK), METADEX (M. I., UK), CASEARCH (CA, USA)
Rukopisi i criteži se ne vraćaju.

Kompjuterski slog:
Savez inženjera i tehničara Srbije
Telefon: (011) 32 35 891

Štampa: Graficki atelje "Dunav", Zemun
Tiraž: 280 primeraka
TEHNIKA

NOVI MATERIJALI

New Material – Nouveaux matériaux
– Neue Materialien – Новые материалы

GODINA 24 – 2015.

BROJ 3

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Several industrial pollution sources at the territory of the Republic of Macedonia, were studied, one Pb-Zn mine with mill, one copper mine with mill and copper leaching facility, as well as one former Pb-Zn smelting facility near the city of Veles and one Fe-Ni smelting facility near the city of Kavadarci. The concentrations of heavy metals at Veles hot-spot were in the range: 20÷1823 mg kg\(^{-1}\)Pb, 29÷2395 mg kg\(^{-1}\)Zn, 28÷65 mg kg\(^{-1}\)Cd, 27÷82 mg kg\(^{-1}\)Cu, 39÷164 mg kg\(^{-1}\)Ni, 508÷938 mg kg\(^{-1}\)Mn and 1.6÷3.8% Fe, all of them being above Dutch standard optimal values. The vicinity of the Feni plant displayed concentrations of heavy metals as follows: 16÷31 mg kg\(^{-1}\)Pb, 117÷286 mg kg\(^{-1}\)Zn, 13÷24 mg kg\(^{-1}\)Co, 42÷119 mg kg\(^{-1}\)Cu, 158÷292 mg kg\(^{-1}\)Ni, 119÷236 mg kg\(^{-1}\)Cr and 2.24÷3.79% Fe. Airborne dust measurements around the Zletovo mine displayed multiplexed above standard values, with an exception of nickel, there enrichment factors ranged from mediate ones such were those for copper of 20.8, cadmium of 28.7, arsenic of 32.5 up to high ones for zinc with 341.7 and lead 925. Soil samples around the Zletovo mine displayed: 19.3-76.9 g kg\(^{-1}\)Fe, 643-28000 mg kg\(^{-1}\)Mn, 42.3-529.66 mg kg\(^{-1}\)Pb and 138-3240 mg kg\(^{-1}\)Zn. Finally around the Bucim copper mine the results displayed the following findings: 13.1÷225 mg kg\(^{-1}\)As, 0.67÷17.9 mg kg\(^{-1}\) Cd, 30.1÷171 mg kg\(^{-1}\)Cr, 17.8÷1734 mg kg\(^{-1}\)Cu, 9.8÷69.4 mg kg\(^{-1}\)Ni, 46÷3456 mg kg\(^{-1}\)Pb, 88÷3438 mg kg\(^{-1}\)Zn, 169÷998 mg kg\(^{-1}\)Mn, 0.73÷5.02% Fe.

**Keywords:** heavy metals, contamination, mines, anthropogenic, R. Macedonia.

**INTRODUCTION**

As major polluted localities, confirmed even with our latest results, are the areas around the former Pb-Zn smelting plant located at the Veles city limits, active ferro-nickel plant located in the well known wine region of Kavadarci, active lead and zinc mines with their respective tailing dams in Eastern Macedonia (Zletovo) and active open pit of the Buchim copper mine with large waste dump and tailing dam (Figure 1).

Preventive measures are a must where mine and mine related plant are processing and produce significant environmental influx, so understanding the environmental impact of these processes is crucial. Metal mining has traditionally been an important part of the economy of the Republic of Macedonia and recently increased in importance due to governmental efforts to stimulate mining through renewed exploration and development, though the country relies on its agriculture and must safeguard its soil and water resources. Pollution from active and past mining related processing represents significant problem in some parts of the country.

The problem continuously is solved at active mines/plants while the problem is harder to solve at those with ceased production (Veles former Pb-Zn smelting plant etc.).

**MATERIAL AND METHODS**

The process of sampling was carried out over a prolonged period (2004-2014). Soil surface samples (0-5 cm depth) were collected at several localities pointed earlier as potential so-called “hot spots” in regards to heavy metal pollution (Figure 1). Samples were located using the Global Positioning System.
System, topographic maps (1:25 000) and TrackMaker software. Each sample represents composite material collected at the central sampling point accompanied with at least four points collected around a central one within radius of 1 m towards N, E, S and W directions. Each sample (~0.5 kg) was prepared for analysis and analyzed using emission spectrometry with inductively coupled plasma (ICP-AES) at the Institute of Chemistry, Faculty of Natural Sciences, University “Sts.Cyril and Methodius” Skopje, R. Macedonia. Random order of samples and standards submission to laboratory assured unbiased treatment and precision less than 5%.

Results and discussion

**The Veles smelting plant:** It used to be the largest Pb-Zn facility in former Yugoslavia with capacity for producing 65000 t of zinc and 45000 t of lead annually and entire production was exported. The anthropogenic impact in that particular part of the Veles basin has been studied at two regions around former Pb-Zn smelting plant during the 2008, Bashino Selo (village to the north of the smelting plant) and area to south of the smelting plant close to the city. Within the first area were sampled two parallel sections and one section normal to them while at the second area were sampled only two parallel sections (30 m distances between each sample, Figure 2). Concentrations of elements were: 20±1823 mg kg⁻¹ Pb, 29±2395 mg kg⁻¹ Zn, 28±65 mg kg⁻¹ Cd, 27±82 mg kg⁻¹ Cu, 39±164 mg kg⁻¹ Ni, 508±938 mg kg⁻¹ Mn and 1.6±3.8% Fe. All of them being quite above the reference values (Table 1 and Figure 3). If an average of Pb in World soils is 35 mg kg⁻¹ [1], in European topsoil 33 mg kg⁻¹ [2] and in topsoil for entire study area 220 mg kg⁻¹ [3], it was found that in studied area the Pb average is 34-times higher than in the World, 36.1-times higher than European and 5.41-times higher than Macedonian (this region) averages.

In regards to zinc where the average in World soils is 90 mg kg⁻¹ [3], European topsoil 68 mg kg⁻¹ [2] and an average in topsoil for the study area is 280 mg kg⁻¹ [3], it was found that in the studied area an average concentration of Zn is 19.7-times higher than World average, 26.1-times higher than European and 6.35-times higher than Macedonian average (for this region).

![Fig. 2. Spatial distribution of profile lines and sampling points along them](image)

Similar to the previous two heavy metals (Pb, Zn) we analyzed cadmium geochemistry (World average 0.35 mg kg⁻¹ Cd [1], European average 0.12 mg kg⁻¹ Cd [2], an average for the entire study area 7.7 mg kg⁻¹ Cd [3]), and we found that an average concentration of Cd was 120-times higher than the World average, 350-times higher than the European average and higher than Macedonian average (for this region) for 5.45-times.

In the very same manner copper had 2-times higher concentration than the World average of 30 mg kg⁻¹ Cu, 3.53-times higher than European average (17 mg kg⁻¹ Cu) and 1.36-times higher than Macedonian average (44 mg kg⁻¹ Cu), which matches findings by other researchers that very same year [3]. The group that comprises of Cd, Pb and Zn, as chemical elements that have been introduced into the environment through the anthropogenic activities [4], have shown the highest values in soils around the Veles smelting plant. That was expected even at the beginning of the study, but tremendously high values exceeded expectations. These findings illustratively are displayed at Figure 3.

Table 1. Concentrations of metals in soil samples around the former smelting plant in the vicinity of Veles.

<table>
<thead>
<tr>
<th>Element</th>
<th>n</th>
<th>Median</th>
<th>min</th>
<th>max</th>
<th>Dutch list standard</th>
<th>Dutch list standard</th>
<th>above standard</th>
<th>below standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (mg kg⁻¹)</td>
<td>15</td>
<td>1190</td>
<td>20</td>
<td>1823</td>
<td>Std. Optimal: 85</td>
<td>Std. Action: 530</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>Zn (mg kg⁻¹)</td>
<td>15</td>
<td>1778</td>
<td>29</td>
<td>2395</td>
<td>Std. Optimal: 140</td>
<td>Std. Action: 720</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>Cd (mg kg⁻¹)</td>
<td>15</td>
<td>42</td>
<td>26</td>
<td>65</td>
<td>Std. Optimal: 0,8</td>
<td>Std. Action: 12</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Cu (mg kg⁻¹)</td>
<td>15</td>
<td>60</td>
<td>27</td>
<td>82</td>
<td>Std. Optimal: 36</td>
<td>Std. Action: 190</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>Ni (mg kg⁻¹)</td>
<td>15</td>
<td>116</td>
<td>39</td>
<td>164</td>
<td>Std. Optimal: 35</td>
<td>Std. Action: 210</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>15</td>
<td>3,2</td>
<td>1,6</td>
<td>3,8</td>
<td>Std. Optimal: 1,8</td>
<td>Std. Action: -</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>Mn (mg kg⁻¹)</td>
<td>15</td>
<td>841</td>
<td>508</td>
<td>938</td>
<td>Std. Optimal:</td>
<td>Std. Action:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Also, after detailed study it was determined that values from respective sampling points were spatially dependent. Namely, as can be seen from the plots and sampling location map, the lowest
values were determined at topographically higher places than those for lower ones.

![Fig. 3. Measured concentrations of Pb, Zn vs. standard values around former smelting plant near the Veles, Macedonia. (Note: Plots a and b have logarithmic vertical scale)](image)

This clarifies the correlation between pollution and smoke dust produced by the activity of former smelting plant in Veles.

**The FENI smelting plant:** The major source of anthropogenic environmental impact in the Tikvesh basin should be the FENI Industries’s smelting plant (Figure 4), where environmental concern intensified due to fact that it is located in the hearth of the well-known wine producing Tikveš region. Plant has been operational since 1982 (produced ~5000 t of nickel metal annually), in 2005 it was acquired by Cunico Resources and steadily increased production to 16000 t per year. Soil sampling programme around the FENI plant took place at two separate localities, one on the NW of the smelting plant and the other one on the S-SE of the smelting plant. In both cases samples were taken along two parallel profiles and one perpendicular to them (Figure 4). Samples were analyzed to a standard array of heavy elements: Pb, Zn, Cu, Ni, Fe, Cr, Co and Mn (Table 2). Their concentrations were in the range as follows: 16÷31 mg·kg⁻¹ Pb, 117÷286 mg·kg⁻¹ Zn, 13÷24 mg·kg⁻¹ Co, 42÷119 mg·kg⁻¹ Cu, 158÷292 mg·kg⁻¹ Ni, 119÷236 mg·kg⁻¹ Cr and 2.24÷3.79% Fe.

![Fig. 4. Sampling locations around the FENI Industries smelting plant, small inset at the right upper corner gives the satellite position of the area.](image)

All of them were significantly above the reference values (Figure 5). Also, the calculated enrichment ratio (measured values over the reference value) speaks itself regarding the level of contamination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>Median</th>
<th>min</th>
<th>max</th>
<th>Dutch list standard optim.</th>
<th>Dutch list standard action</th>
<th>above standard</th>
<th>below standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (mg kg⁻¹)</td>
<td>24</td>
<td>22</td>
<td>16</td>
<td>31</td>
<td>85</td>
<td>530</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>Zn (mg kg⁻¹)</td>
<td>24</td>
<td>141</td>
<td>117</td>
<td>286</td>
<td>140</td>
<td>720</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>Cu (mg kg⁻¹)</td>
<td>24</td>
<td>63.5</td>
<td>42</td>
<td>119</td>
<td>36</td>
<td>190</td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>Ni (mg kg⁻¹)</td>
<td>24</td>
<td>219.5</td>
<td>158</td>
<td>292</td>
<td>35</td>
<td>210</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>Fe %</td>
<td>24</td>
<td>3.46</td>
<td>2.24</td>
<td>3.79</td>
<td>1.8</td>
<td>-</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>Ba (mg kg⁻¹)</td>
<td>24</td>
<td>151.5</td>
<td>0</td>
<td>223</td>
<td>160</td>
<td>625</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>V (mg kg⁻¹)</td>
<td>24</td>
<td>47</td>
<td>24</td>
<td>75</td>
<td>42</td>
<td>250</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>Cr (mg kg⁻¹)</td>
<td>24</td>
<td>187</td>
<td>119</td>
<td>236</td>
<td>100</td>
<td>380</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>Co (mg kg⁻¹)</td>
<td>24</td>
<td>18</td>
<td>13</td>
<td>24</td>
<td>9</td>
<td>240</td>
<td>0</td>
<td>24</td>
</tr>
</tbody>
</table>

Namely, the enrichment ratios ranged from relatively low 1.873 for Fe, 2.188 for Mn and 3.801 for Cu, through the medium 16.987 for Ni and 3.225 for Zn up to high 1.471 for Pb and the highest 2.823 for Co and 5.0124 for Cr. These increased concentrations, bearing in mind the findings of [5, 6], probably can not be attributed solely to the...
anthropogenic input, since they were increased already due to geological composition.

![Graph of Ni vs. standard values](image)

**Fig. 5.** Measured concentrations of Ni vs. standard values around the Feni-industries’s smelting plant

It is probable that the FENI Industry plant, beside certain environmental impact, has not contributed extremely to measured values [5, 6, 7, 8].

**The Zletovo Pb-Zn Deposit:** Study of environmental impact of the Zletovo mine we have started with airborne dust produced during the primary crushing of ore, when it is released significant amount of dust that poses serious threat to the environment [8, 9, 10]. Analyzes displaying heavy metal concentrations in the dust averaged: 169 mg kg\(^{-1}\) As, 86 mg kg\(^{-1}\) Cd, 354 mg kg\(^{-1}\) Cu, 10 mg kg\(^{-1}\) Ni, 14800 mg kg\(^{-1}\) Pb and 16400 mg kg\(^{-1}\) Zn. All the measured values multiplexed above standard values, except nickel. Enrichment factors ranged from mediate ones such as those for copper of 20.8, cadmium of 28.7, arsenic of 32.5 up to high ones for zinc with 341.7 and lead 925. High concentration levels of heavy metals introduced by deposition from airborne dust and dispersion by wind, pose serious threat to an adjacent environment.

Soil sampling around the Zletovo mine was performed by other researchers but without any systematics and due to it was very hard to prepare complete review, which would reflect real situation regarding soil pollution [11]. We have decided to strengthen that knowledge and performed additional sampling (24 samples) in the vicinity of the Zletovo Pb-Zn mine. Namely, it was determined that representative elements are lead, zinc, iron and manganese and they are given in more details within this paper (Table 6), while elements such Cr, V, Ni, Co have not displayed elevated concentrations (Table 3, Figure 6). An average amount of Pb in the world’s soils is 35 mg kg\(^{-1}\) [1], in the European topsoil is 33 mg kg\(^{-1}\) [2], in Macedonia (studied part) is 26 mg kg\(^{-1}\) [12]. As it is obvious from Table 3, lead values ranged from the 42.30±529.66 mg·kg\(^{-1}\) Pb, while the lowest values were determined near the Zletovo village the highest ones were determined in samples from localities Koritnica, Kiselica and Strmos.

In the main polluted area the average concentration of Pb is 8.6-times higher than the European Pb average and Macedonian average for 10.9-times. Although the average content of lead in the topsoil for the entire study area was found to be about 284.36 mg kg\(^{-1}\), there are areas with increased concentration up to 529.66 mg kg\(^{-1}\), although even such values were not above action values by the Dutch list (Table 3; Figure 6).

The average amount of Zn in the world’s soils is 90 mg kg\(^{-1}\) [1], in the European topsoil is 68 mg kg\(^{-1}\) [2], in Macedonia (studied part) is 55 mg kg\(^{-1}\) [12]. The highest concentrations of zinc were determined near the Koritnica, Kiselica and Ziganci while the whole range was quite wide starting from 138 mg·kg\(^{-1}\) Zn and ending up to 3240 mg·kg\(^{-1}\)Zn. For the main polluted area, the average concentration of Zn is 19.2-times higher than the European Zn average and Macedonian average for 23.7-times. Similarly to the findings for lead, although the average content of zinc in the topsoil for the entire study area was found to be about 1303.5 mg kg\(^{-1}\), there are areas with very high level of contamination (Table 3; Figure 6).

**Table 3. Concentrations of particular heavy metals in soil samples from the vicinity of the Zletovo Mine, Macedonia**

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>min</th>
<th>max</th>
<th>average</th>
<th>Dutch list (Optimum)</th>
<th>Dutch list (Action)</th>
<th>Above optimum</th>
<th>Above action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (mg kg(^{-1}))</td>
<td>24</td>
<td>42.3</td>
<td>529.66</td>
<td>266,5442</td>
<td>85</td>
<td>530</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Zn (mg kg(^{-1}))</td>
<td>24</td>
<td>138</td>
<td>3240</td>
<td>1180,333</td>
<td>140</td>
<td>720</td>
<td>23</td>
<td>14</td>
</tr>
<tr>
<td>Fe (g kg(^{-1}))</td>
<td>24</td>
<td>19.3</td>
<td>76.9</td>
<td>38.70</td>
<td>18</td>
<td>72</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>Mn (mg kg(^{-1}))</td>
<td>24</td>
<td>643</td>
<td>28000</td>
<td>6707,583</td>
<td>33</td>
<td>330</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

The average amount of Fe in the world’s soils is 35 g kg\(^{-1}\) [1], in the European topsoil is 21.7 g kg\(^{-1}\) [2], in Macedonia in the considered area is 33 g kg\(^{-1}\) [12]. As it is obvious from the table above (Table 3), we would like to stress out that iron values ranged from the 19.3±76.9 g·kg\(^{-1}\) Fe.
Either the iron haven’t shown significantly increased values, the highest ones were recorded for the locations such as Kiselica, Koritnica and Strmос. In the main polluted area the average concentration of Fe is 1.9-times higher than the European Fe average and Macedonian average for 1.2-times. Although the average content of iron in the topsoil for the entire study area was found to be about 40.67 g kg\(^{-1}\), there are areas with increased concentration up to 76.9 g kg\(^{-1}\), although only one value was above action value by the Dutch list.

On the World scale, the range of Mn average contents was calculated at 488 mg kg\(^{-1}\), while for the US soils it is 495 mg/kg [13], in European topsoil is 382 mg kg\(^{-1}\) [2], and in Macedonia in the considered area is averages 650 mg kg\(^{-1}\) [12]. Manganese analyses around the Zletovo mine area have shown the highest concentrations among analyzed elements, ranging from 643 up to 28000 mg kg\(^{-1}\) Mn. In the main polluted area the average concentration of Mn is 14.9-times higher than the European Pb average and Macedonian average for 11.9-times. Although the average content of Mn in the the entire study area was found to be about 7791.75 mg kg\(^{-1}\), there are areas with increased concentration up to 28000 mg kg\(^{-1}\), however all the measured values were above action value by the Dutch list (Table 3).

Here we are dealing with anthropogenic input in soils around the Zletovo mine, which clearly indicates their connection with the processing of lead-zinc ore from the mine.

**The Buchim Cu Deposit:** The only one active copper mine within the Macedonia was enclosed in ours environmental study. Considering airborne dust pollution we would like to stress out that the studies on this subject already exists [14, 15, 16], so we used them as representative ones, while interesting Cu and other elements anomalies in soils were given by [8, 17]. Our results, performed on 25 samples from 25 locations including minimal, maximal, average and referent values according to the New Dutch list ([www.contaminatedland.co.uk/standards/dutch-1.htm](http://www.contaminatedland.co.uk/standards/dutch-1.htm)) are shown at Table 4. Distribution of some pollutants is shown at Figure 7a, b. These results are in agreement with those obtained by [18] from the study of soil pollution in the wider region of Radoviš and its environ where As, Cu, Pb, V and Zn were determined as anthropogenic elements due to the mining and ore processing at the Buchim plant. That is especially accentuated in the eastern and southwestern parts of the main polluted area around flotation.

High contents of Cu and Pb are not only due to mining works, but also the town works, traffic, industry and developed technological processes which emitted higher amounts of these heavy metals in air [14, 15, 16, 18, 19, 20, 21]. An average amount of arsenic in the World’s soils of 5 mg kg\(^{-1}\) [1], and European of 12 mg kg\(^{-1}\) [2] has been overcome within entire study area, ranging 13.1–225 mg kg\(^{-1}\) (average 63.904 mg kg\(^{-1}\); Table 4 and Figure 7a).

In several anomalous areas it could be seen that the highest values are in the area closest to the outflow of flotation dam (from 51 to 225 mg kg\(^{-1}\)) and so-called Buchim Lake and dry riverbed draining open pit mine and in the south-western part of the area (67.4–82.8 mg kg\(^{-1}\)).
According to this, it is evident that the source of high arsenic in this region is directly related to processing of copper ores in the Buchim Mine.

During the processing of ore, probably one part of that arsenic have been released and distributed into the adjacent environment.

Table 4. Statistical data from the soil samples around the Buchim copper mine

<table>
<thead>
<tr>
<th>Element</th>
<th>n</th>
<th>min</th>
<th>max</th>
<th>Average</th>
<th>Optimum (Dutch list)</th>
<th>Action (Dutch list)</th>
<th>Above optimum</th>
<th>Above action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (%)</td>
<td>25</td>
<td>0.72</td>
<td>5.90</td>
<td>2.89</td>
<td>4.7</td>
<td>-</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>25</td>
<td>0.73</td>
<td>5.02</td>
<td>3.15</td>
<td>1.8</td>
<td>-</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>As (mg kg⁻¹)</td>
<td>25</td>
<td>13.1</td>
<td>225</td>
<td>63.9</td>
<td>29</td>
<td>55</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Cd (mg kg⁻¹)</td>
<td>25</td>
<td>0.67</td>
<td>17.9</td>
<td>2.19</td>
<td>0.8</td>
<td>12</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>Co (mg kg⁻¹)</td>
<td>25</td>
<td>3.62</td>
<td>22.3</td>
<td>12.4</td>
<td>9</td>
<td>240</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>Cr (mg kg⁻¹)</td>
<td>25</td>
<td>30.1</td>
<td>171</td>
<td>80.7</td>
<td>100</td>
<td>380</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Cu (mg kg⁻¹)</td>
<td>25</td>
<td>17.8</td>
<td>1734</td>
<td>129</td>
<td>36</td>
<td>190</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td>Mn (mg kg⁻¹)</td>
<td>25</td>
<td>165</td>
<td>998</td>
<td>552</td>
<td>33</td>
<td>-</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Ni (mg kg⁻¹)</td>
<td>25</td>
<td>9.8</td>
<td>69.4</td>
<td>29.5</td>
<td>35</td>
<td>210</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Pb (mg kg⁻¹)</td>
<td>25</td>
<td>46</td>
<td>3465</td>
<td>288</td>
<td>85</td>
<td>530</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>Sr (mg kg⁻¹)</td>
<td>25</td>
<td>17.6</td>
<td>132</td>
<td>75.8</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V (mg kg⁻¹)</td>
<td>25</td>
<td>14</td>
<td>144</td>
<td>83.6</td>
<td>42</td>
<td>250</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>Zn (mg kg⁻¹)</td>
<td>25</td>
<td>88</td>
<td>3438</td>
<td>320</td>
<td>140</td>
<td>720</td>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

The cadmium range of 0.67–17.9 mg kg⁻¹ (averaging 2.19 mg kg⁻¹) in the topsoil for the entire study area significantly overcome Cd in soils in the World of 0.35 mg kg⁻¹ [1] and in European topsoil of 0.12 mg kg⁻¹ [2]. The average concentration of Cd is more than 18-times higher than the European cadmium average and up to 7.5-13 times more than Macedonian average of 0.16 mg kg⁻¹ (study in 2002, see [22]) and 0.29 mg kg⁻¹ (study in 2005, see [23]). Cadmium concentrations were very high in the topsoils from the copper mine facilities and flotation dam vicinity. These higher contents are the result of anthropogenic origin where cadmium was introduced by mine industrial complexes as it was confirmed elsewhere [24].

Soil contamination by Cu compounds displayed the highest increased levels around Cu mines and smelters [25]. As Cu is only slightly mobile under most soil conditions elevated contents may persist for a long time. The average amount of Cu in the world’s soils is 30 mg kg⁻¹ [1], in the European topsoil is 17 mg kg⁻¹ [2] and in Macedonia is 31.8 mg kg⁻¹ [19]. The average amount of Cu in the topsoil for the entire study area is 129.064 mg kg⁻¹, with a range of 17.8–1734 mg kg⁻¹ (Table 4; Figure 7b). In the main polluted area, the average concentration of Cu exceeds the European Cu average by a factor of 15.3 and Macedonian average for 8.2-times. The highest content of copper is present in topsoils from areas of the copper mine drainage dry riverbed close to the mine.

The average amount of Pb in the world’s soils of 35 mg kg⁻¹ [1], in European topsoil is 33 mg kg⁻¹ [2] and in Macedonia is 44.3 mg kg⁻¹ [19] was overcome for the entire study area with an average of 288 mg/kg (range of 46–3465 mg kg⁻¹, Table 4).
The average amount of Zn in the world’s soils is 90 mg kg⁻¹ [1, 13], in the European topsoil is 68 mg kg⁻¹ [2] and in Macedonia is 31.8 mg kg⁻¹ [19]. The average Zn amount in the topsoil for the entire study area is 319.8 mg kg⁻¹, with a range of 88–3438 mg kg⁻¹ (Table 4). Similarly to the findings for lead, there are areas with very high level of contamination (Table 4), although all high Cu and Pb contents can not be attributed to mining works, but also can be due to traffic, industry and other processes which aloud emission of higher amounts of these heavy metals [6, 14, 15, 16, 20, 21].

5. CONCLUSION:

The results of this study have shown that at all the localities are characterized by increased values of pollutant heavy metals in soil, which can be attributed to the anthropogenic influx around the aforementioned mines and related processing facilities. Pollution halo around them sometimes reaches over 20 km. Along common pollutants (Pb, Zn, Cd) around Zletovo mine at lead-zinc and Veles and smelting were determined increased concentrations of As, Ag, W, Ni, Co etc., while around the FENI concentrations along to Fe and Ni were determined increased values of Cr, V, Co, Mn etc. Increased concentrations, as expected, of Cu, As, Pb, Zn and Cd were determined around the Buchim mine.

REFERENCES:
REZIME

INDUSTRIJSKA KONTAMINACIJA ZEMLJIŠTA POVEZANA SA NEKIM AKTIVNIM I ZATVORENIM RUDNIČKIM POSTROJEJIMA U REPUBLICI MAKEDONIJI

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Nekoliko industrijskih izvora kontaminacije na teritoriji Republike Makedonije, su proučeni, jedan rudnik olova i cinka sa flotacijom, jedan rudnik bakra sa flotacijom i postrojenjem za luženje za luženje bakra, kao i jedno staro Pb-Zn topioničko postrojenje u blizini Velesa i jedno Fe-Ni topioničko postrojenje u blizini Kavadara. Koncentracije teških metala u “vrručoj tački” Veles su bili opseg: 20÷1823 mg kg\(^{-1}\) Pb, 29÷2395 mg kg\(^{-1}\) Zn, 28÷65 mg kg\(^{-1}\) Cd, 27÷82 mg kg\(^{-1}\) Cu, 39÷164 mg kg\(^{-1}\) Ni, 508÷938 mg kg\(^{-1}\) Mn i 1.6÷3.8% Fe, pri čemu su svi bili iznad optimalnih vrednosti prema Holandskom standardu. U blizini fabrike Feni koncentracije teških metala su bile kao što je prikazano: 16÷31 mg kg\(^{-1}\) Pb, 117÷286 mg kg\(^{-1}\) Zn, 13÷24 mg kg\(^{-1}\) Co, 42÷119 mg kg\(^{-1}\) Cu, 158÷292 mg kg\(^{-1}\) Ni, 119÷236 mg kg\(^{-1}\) Cr i 2.24÷3.79% Fe. Merenja prašine u vazduhu oko rudnika Zletovo su pokazala povećane vrednosti, nekoliko puta iznad standardnih, osim nikla, a faktori obogaćivanja su se kretali od srednjih, kao što su bili oni za bakar od 20.8, kadmijum 28.7, arsen od 32.5 pa sve do visokih za cink od 341.7 i 138 mg kg\(^{-1}\). Uzorci zemljišta iz okoline rudnika Zletovo su pokazali sledeće koncentracije: 19.3÷76.9 g kg\(^{-1}\) Fe, 643÷2800 mg kg\(^{-1}\) Mn, 42.3÷529.66 mg kg\(^{-1}\) Pb i 138÷3240 mg kg\(^{-1}\) Zn. Na kraju u okolini rudnika bakra Bučim rezultati su pokazali sledeće koncentracije: 13.1÷225 mg kg\(^{-1}\) As, 0.67÷17.9 mg kg\(^{-1}\) Cd, 30.1÷171 mg kg\(^{-1}\) Cr, 17.8÷1734 mg kg\(^{-1}\) Cu, 9.8÷69.4 mg kg\(^{-1}\) Ni, 46÷3456 mg kg\(^{-1}\) Pb, 88÷3438 mg kg\(^{-1}\) Zn, 169÷998 mg kg\(^{-1}\) Mn i 0.73÷5.02% Fe.

Ključne reči: teški metali, kontaminacija, rudnici, anthropogeno, R. Makedonija.