



## Multi-criteria analysis of soil pollution by heavy metals in the vicinity of the Copper Smelting Plant in Bor (Serbia)

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**Abstract:** This study highlights the consequences on soil pollution of one hundred years of manufacturing in the Copper Mining and Smelting Complex RTB-Bor (Serbia). Soil sediments were taken *via* a probe from the surface layer of the soil at twelve different measuring points. The measuring points were all within 20 km of the smelting plant, which included both urban and rural zones. Soil sampling was performed using a soil core sampler in such way that a core of a soil of radius 5 cm and depth of 30 cm was removed. Subsequently, the samples were analyzed for pH and heavy metal concentrations (Cu, Pb, As, Cd, Mn, Ni and Hg) using different spectrometric methods. The obtained results for the heavy metal contents in the samples show high values: 2,540 mg kg<sup>-1</sup> Cu; 230 mg kg<sup>-1</sup> Pb; 6 mg kg<sup>-1</sup> Cd; 530 mg kg<sup>-1</sup> Ni; 1,300 mg kg<sup>-1</sup> Mn; 260 mg kg<sup>-1</sup> As and 0.3 mg kg<sup>-1</sup> Hg. In this study, critical zones of polluted soil were identified and ranked according to their metal contents by the multi-criteria decision method Preference Organization Method for Enrichment Evaluation/Geometrical Analysis for Interactive Assistance – PROMETHEE/GAIA, which is the preferred multivariate method commonly used in chemometric studies. The ranking results clearly showed that the most polluted zones are at locations holding the vital functions of the town. Therefore, due to the high bioavailability of heavy metals through complex reactions with organic species in the sediments, consequences for human health could drastically emerge if these metals enter the food chain.

**Keywords:** heavy metals; soil; pollution; multi-criteria; PROMETHEE /GAIA.

### INTRODUCTION

At the onset of the new millennium, more and more attention is being devoted to the quality of air and soil in urban and rural areas in Europe.<sup>1–4</sup> Nume-

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rous studies provide various data about the content of heavy metals such as: Cu, Pb, Zn, As, Cd and Hg in air and soil in the vicinity of non-ferrous metal smelters, especially copper smelting plants which are a significant source of environmental pollution.<sup>5–13</sup> In studies of this type, high concentrations of heavy metals have been reported. These metals are discharged with the smelting gases in the form of airborne particles (PM<sub>10</sub>), their concentrations decreasing as distance from the smelter plant chimney increases. Soil contamination has sometimes been detected at locations at a long distance from the smelter. For example, in the case of the Canadian smelting plant Flin Flon, the maximum distance on which contamination with copper was registered is 33 km and in the case of zinc, 217 km.<sup>14</sup>

The size of the contaminated area, distance from the copper smelter plant and the period of soil exposure to heavy metals contamination, as well as their concentration, depend on numerous factors, such as: direction and speed of the wind, terrain configuration, dimensions of the airborne particles, concentration of the airborne particles at the smelter plant chimney, height of the stack, *etc.* Copper smelter plants discharge with their gasses heavy metal particles (Cu, Pb, As Cd, Ni, Mn, Hg and other toxic elements). These air-born pollutants have detrimental effects on human health. In addition, the precipitation of these particles onto the soil over a long period increases its pollution, which causes contamination of crops with heavy metals, making them hazardous for animal and human health.<sup>15–18</sup>

Due to increasing urbanization and the development of non-ferrous metallurgy in Europe, a special EU Commission was formed which regulates threshold values for heavy metals and gases within industrial, urban and rural zones. Special international regulations oblige many countries to protect particular regions from pollution. For instance, the Danube countries through which the Danube River flows are determined to protect this river from all kinds of pollution. Representatives of the Serbian government have also signed several such legal acts.

In this paper, the results of a study of the content of heavy metals in the soil in the vicinity of the Copper Smelting Plant in Bor after a centenary-long production of copper are presented. During the period 1970–1980, this smelting plant was one of the largest copper smelting plants in Europe according to its capacity.<sup>19</sup> The locations from which soil samples were taken were located in the urban zone of the town, which has a population of more than 40,000. In addition to the urban zones, the nearby rural zones are also considerably inhabited, with more than 20,000 residents living within a range of approximately 20 km from the smelter (the source of air pollution).<sup>20</sup> The following fact should be emphasized: 200,000 t of SO<sub>2</sub> are discharged annually, *i.e.*, approximately 3.33 t per resident on average, as a result of company operations.<sup>21</sup> Furthermore, approximately 2.25 kg of dust is discharged per ton of processed raw material, which lead to annual emission of 5.3–19.6 kg As, 4.86–7.99 kg Zn and 6.27–25.11 kg

Pb per resident, and these already high values are frequently exceeded, presenting extremely large numbers if compared to other industrial zones in Europe.<sup>22</sup> These facts indicate that this is highly polluted region, which, besides endangering human health in the region, represent a particular threat for a broad region of southeastern Europe as well. Regardless of the size of this region, the attitude of the company's management towards pollution should be based on a global approach for solving this problem concerning the results obtained during investigations of soil, air and water pollution on the local scale.<sup>23,24</sup> The authors of this paper believe that the results of the investigations presented herein could be useful for achieving such a goal.

The objective of this study was to indicate the potential threats from increased content of heavy metals in the soil within a rather wide area around the Bor Copper Smelting Plant, which is showing a tendency to expand while utilizing the same smelting technology. Simultaneously, this zone is defined as one of the most polluted zones in Serbia, which, therefore, represents a zone of great threat to human health in this part of Europe. The influence of heavy metals in food chains in this region has not been studied specifically but, on the other hand, increased contents of As, Cu and Pb in some plants and increased contents of As and Pb in the organisms of the employees of the RTB-Bor Company and citizens of Bor have been registered.<sup>22</sup> According to this report, waste gases from the smelter plant have destroyed to various extents the soil in almost all villages around Bor. The total affected surface of damaged soil in the Municipality of Bor is estimated at some 25,500 ha, which constitutes 60 % of all agricultural soils.<sup>22</sup> The high extent of damaged soil in the Bor area has both economical and health-related consequences, such as decreased agricultural production, production of lower-quality food, further impoverishment of farmers, higher food prices on the local market with a consequential drop in living standards and inadequate nutrition, affecting growth and development of children, and health in general. For example, copper is an essential element for the growth of plants but the high copper content in the soil around Bor is toxic for plants as it reduces the growth of their roots. High As concentrations also have an adverse impact on the growth of plants.

## EXPERIMENTAL

### *Study area*

The Municipality of Bor encompasses an area of 856 km<sup>2</sup> in the central part of Eastern Serbia; around 100 km from the Romanian and 30 km from the Bulgarian border (Fig. 1). The population density of the Municipality is 67.2 inhabitants per km<sup>2</sup>. The altitude of the town Bor, 378 m, is low compared with the surrounding high mountains (Stol 1156 m, Veliki Krs 1146 m and Crni Vrh 1043 m). Bor is located in the valley of the Homonym River. Wood soil covers 45 % of the area of the Municipality of Bor; the remainder is 49 % agricultural soil and 6 % infertile soil. The climate is moderate continental. The average mean annual rainfall is

around  $469.2 \text{ mm m}^{-2}$ , snow coverage lasts about 60 days and the annual average temperature is  $11.7 \text{ }^\circ\text{C}$ . The annual average mean relative air humidity is 73 %, while the average atmospheric pressure is 971 mbar. The prevailing wind is WNW with an average velocity of  $0.5 \text{ m s}^{-1}$ ; the wind still period is over 50 %.

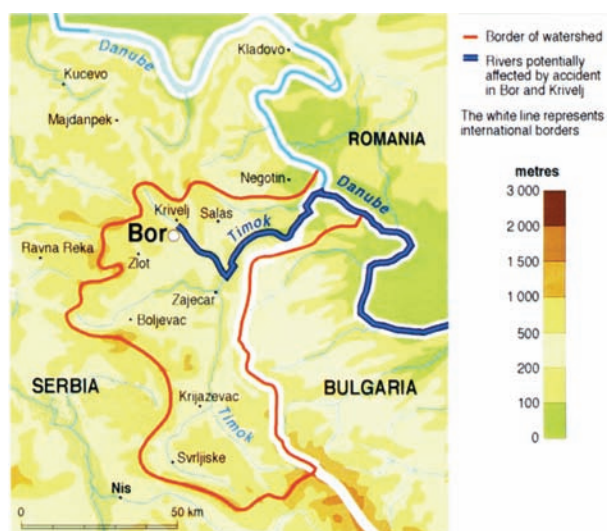


Fig. 1. Map of the studied area in the surroundings of the Copper Smelter Bor, Serbia.

The RTB Bor Copper Smelting Plant, a part of the RTB Mining and Smelting Complex, is located in the town Bor. Production in Bor commenced in 1903 by underground mining. The mine is located on the north-eastern rim of the town; the open pit, the metallurgical-smelting complex and the flotation tailings pond make a boundary between the urban and the industrial zone. Due to the fact that the town was built in the near vicinity of the mine, as well as near the location of the copper smelting plant and two further mines close by, the town itself represents a serious environmental hot spot of Serbia and Europe.<sup>25</sup> The Bor River (industrial river), representing one of the most polluted rivers in the world, flows into the Timok River, a tributary of the Danube River (Fig. 1).

In addition to industrial practice, this region has considerable tourist potentials which are located near Bor. Certainly the most remarkable natural and tourist region is the National Nature Park “Djerdap” to the northeast on the banks of the Danube. Closer to Bor are the Bor Lake and the mountain complex “Homoljske Mountains” to the WNW. All these areas have preserved nature and considerable flora and fauna species with some endemic characteristics. All are endangered with the technology currently employed for copper production in the RTB Bor.

#### *The technology process employed in the RTB Bor Copper Smelting Plant*

Degradation of a huge soil area, a huge volume of the soil waste and pollution of underground and surface water are the main attribute for most activate or closed mines and copper smelting plants. The technology used for copper production in the Smelting Plant in Bor is outdated.<sup>26</sup> This technology is based on classical pyrometallurgy,<sup>27</sup> with smelting in reverberatory furnaces and a relatively low degree of  $\text{SO}_2$  gas utilization ( $< 50 \%$ ) for the pro-

duction of sulfuric acid. The technical limitations of such technology leads to pollution of the environment with large concentrations of  $\text{SO}_2$  and airborne particles of  $\text{PM}_{10}$  dust, as well as aero-sediments even larger than the  $\text{PM}_{10}$  particles.<sup>20</sup> The ores used in this process are of the chalcopyrite and pyrite type with an increased content of As, which is found in the form of  $\text{FeAsS}$  and  $\text{Cu}_3\text{AsS}_4$ . During oxidative roasting and smelting of these minerals, heavy metal oxides, As and  $\text{SO}_2$  gas are formed which exit through the chimneys of the smelter plant and pollute the environment.<sup>28–29</sup> The geographical ranges with a concentration level of  $\text{SO}_2$  lower than the approved maximum value are 15 km from the factory chimney. Copper ore smelting in Bor with high sulfur dioxide emissions has caused erosion, high acidity of soils and destruction of the vegetation in the nearby areas. Acid soil affects fertility and also increases the mobility of heavy metals that could reach vegetation. Around the mining and metallurgical industrial complex, the acidity values of the agricultural soils are the highest. Sulfur dioxide damages plant and tree leaves in either an acute or chronic manner. Acute damages are caused by a short impact of very high sulfur dioxide concentrations and are manifested by damage to cells and/or the drying of leaves. Chronic damages occur after longer exposure of plants to lower sulfur dioxide concentrations, and this causes a decrease in organic growth.<sup>22</sup>

Contamination by  $\text{PM}_{10}$  particles is present up to 15 km from the smelter smokestack which emits the harmful substances. The concentration of  $\text{SO}_2$  gas and heavy metals in the  $\text{PM}_{10}$  are largely above the threshold concentrations regulated by EU directives.<sup>20,25,30,31</sup> The concentrations are also above the limits prescribed by the local Serbian Regulatory that defines the maximum allowed heavy metal content in the air.<sup>22</sup>

The main reason for such a situation is the failed opportunity for implementation of new technology at a time when it was financially feasible (during 1980s). At that point, this should be considered as the most important step in the life cycle of the company.<sup>32</sup> During 2003, a continuous operational real-time monitoring system (CORTMS) for tracking air pollution was installed in Bor. This system enables the continuous measurement of the  $\text{SO}_2$  concentration in air (values are read at 15 min intervals) and the cumulative measurement of the heavy metals content in airborne particles at two measuring points in the urban part of the city of Bor. In addition, a mobile station is operational, which allows the measurement of the  $\text{PM}_{10}$  content and aero-sediments at 15 different locations.<sup>20</sup>

#### *Sampling*

Soil samples were taken from the locations indicated in Fig. 2, between July and August 2008. These locations were not farmed; therefore, contamination of the ground through the use of agricultural measures was excluded. Ten samples were taken from each location. The soil samples were taken *via* a soil core sampler in such a way that a core of a soil was removed of radius 5 cm and depth 30 cm. A 5-cm surface layer of the core was stripped off and the rest of the sample was dried at 50 °C for 2 h and its weight measured. In the next step soil, the samples were ground and homogenized until the required size was obtained and then the pH and heavy metals contents were determined. The obtained reproducibility for the metals contents in the samples were relatively high (0.87–0.95).

#### *Chemical analysis*

The pH value of the samples was realized using a pH–conductivity/°C meter,  $\text{PC}_{10}$ /EUTECH Instrument. For determination of the heavy metals contents in the soil, each sample was dissolved in an acidic mixture consisting of  $\text{HF}+\text{HClO}_4$ , while HCl was used for filling up to the volume of the flask. The contents of Cu, Pb, Cd, Ni and Mn content were determined by atomic adsorption spectrophotometry (AAS),<sup>33</sup> using a Perkin Elmer model 2380 instru-

ment. The As content was determined by inductively coupled plasma atomic emission spectrophotometry (ICP–AES) employing an ARL 3410 instrument, while mercury content in the samples was determined by flameless atomic adsorption spectrophotometry–mercury analyzer (A–Hg) using a Perkin Elmer FIMS-100 instrument. All chemical analyses were performed in a certified chemical laboratory of the Institute for Mining and Metallurgy in Bor.

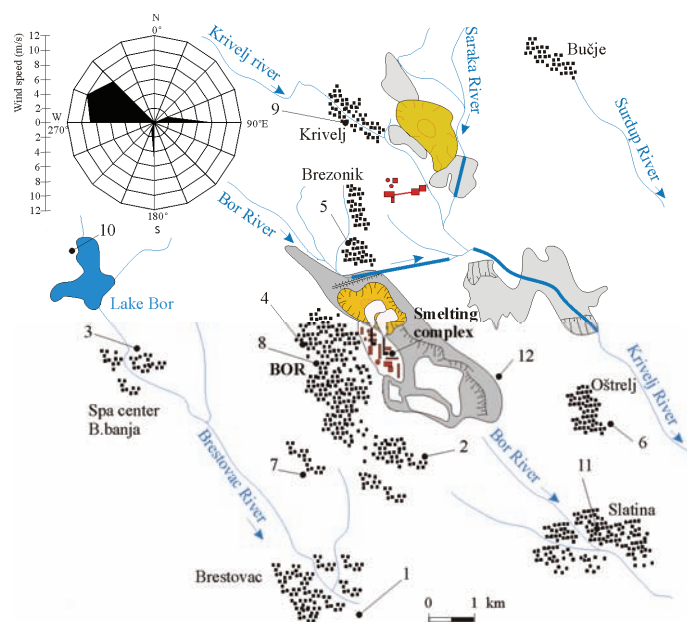


Fig. 2. Map of sites from which the samples were taken (1 – Village of Brestovac; 2 – Industrial zone “Elektroistok”; 3 – Spa center “B. banja”; 4 – Hospital; 5 – Village of Brezonik; 6 – Village of Ostrelj; 7 – Suburban area “Bor 2”; 8 – City location “Šumska sekcija”; 9 – Village of Krivelj; 10 – Lake Bor; 11 – Village of Slatina; 12 – Zone behind the industrial waste-yard).

#### Data analysis

There are many statistical methods used in chemometric studies.<sup>34,35</sup> For the purpose of ranking the zones of the studied region (Fig. 2) according to the soil contamination, it was decided to use the method of multi-criteria decision making, MCDM.<sup>36</sup> Many authors use MCDM for analyzing the problem of air and soil pollution.<sup>37–40</sup> In this study, the PROMETHEE method was used for ranking the locations from which the soil samples were taken in accordance with the heavy metals contents, while GAIA plane was used for graphical interpretation of the PROMETHEE results. In other words, GAIA plane provides a clear picture of a decision making problem by visualization of the PROMETHEE ranking.<sup>41</sup> The GAIA visual modeling method provides the decision maker with information about the conflicting character of the criteria and the impact of the weights of the criteria on the final results. The GAIA plane is defined by corresponding unit eigenvectors  $u$  and  $v$ , resulting from a unicriterion net flows covariance matrix, obtained using principal components analysis (PCA). Using PCA, it is possible to define a plane having the minimal amount of information lost by projection ( $\Delta$ ).<sup>42</sup> Main reason for implementing PROMETHEE/GAIA for processing the acquired data was the



specific advantages of this method in regards to other MCDM methods. These advantages are mostly attributable to the way of structuring the problem; high quantity of data which can be processed; ability to quantify qualitative values, good software support and presentation of processed data.<sup>20,43,44</sup>

The PROMETHEE method presents an outranking method for a fixed set of alternatives.<sup>45</sup> For the application of this method, it is necessary to define a specific preference function and to assign a weight of significance (weight coefficient) to each criterion. The preference function defines the rank of one option with respect to another and translates deviation between two parallel alternatives into a unique parameter which is associated with the degree of preference. The degree of preference presents a growing deviation function, whereby, in case of small deviation, it refers to a weak preference and in the case of large deviation, it represents a strong preference associated with a reference alternative. The PROMETHEE method has at its disposal six possible shapes of preferential functions (usual, U-shape, V-shape, level, linear and gaussian), whereby every shape depends on two thresholds ( $Q$  and  $P$ ). The indifference threshold ( $Q$ ) represents the maximum deviation which the decision maker considers as unimportant, while the preference threshold ( $P$ ) represents the minimum deviation which is considered to be decisive for the decision maker, where  $P$  is not allowed to be smaller than  $Q$ . The Gaussian threshold ( $S$ ) represents a mean value between the thresholds  $P$  and  $Q$ .<sup>45-49</sup>

The PROMETHEE method is based on determining the positive ( $\Phi^+$ ) and the negative flow ( $\Phi^-$ ) for each alternative towards outranking relations and in correlation with the acquired weight coefficients for each criterion-attribute. In the case of the investigations presented in this paper, the alternatives were the investigated locations, while the criterions were the heavy metals content detected at the locations. The positive preference flow expresses how much an alternative dominates over the others; therefore, the greater the value ( $\Phi^+ \rightarrow 1$ ), the more significant is the alternative. The negative preference flow expresses the preference of all the other alternatives compared to the analyzed one. An alternative is more important if the value of the output flow is smaller ( $\Phi^- \rightarrow 0$ ). The complete ranking of PROMETHEE II is based on the calculation of a net outranking flow value ( $\Phi$ ) that represents the balance between the positive and the negative outranking flows. The higher the net flow is, the better the alternative.<sup>42,50,51</sup> Accordingly, if the alternative has a greater positive ( $\Phi^+$ ) and a lower negative flow ( $\Phi^-$ ), then the net outranking flow ( $\Phi$ ) for this alternative is higher. For the investigations presented in this paper, this would mean that such a location (alternative) has a larger significance compared to the other, which means that this location is less contaminated with heavy metals (criterions) compared to the other investigated locations.<sup>20</sup>

## RESULTS AND DISCUSSION

### *Chemical analysis*

The obtained results for the heavy metals contents in the samples taken from the urban zones of town site Bor and surroundings are presented in Table I for 12 locations in total, the positions of which are shown in Fig. 2. Maybe the most important finding that should be considered by the local authorities and stakeholders is a fact that according to legislation,<sup>52</sup> 100 % of the analyzed samples were contaminated with copper (maximum allowed concentration for copper in soil is 36 mg kg<sup>-1</sup>); 100 % of the samples were contaminated with cadmium (maximum allowed concentration for cadmium in soil is 0.8 mg kg<sup>-1</sup>);<sup>52</sup> 58.3 %

of the samples were contaminated with arsenic (maximum allowed concentration for arsenic in soil is  $29 \text{ mg kg}^{-1}$ )<sup>52</sup> and 25 % of the samples were contaminated with lead (maximum allowed concentration for lead in soil is  $85 \text{ mg kg}^{-1}$ ).<sup>52</sup>

The highest contents of some heavy metals were found in the samples taken from the locations near to the town center (Table I). The wind “rose” (Fig. 2) for the period 2005–2008 indicates that the WNW (west–northwest) wind direction is prevalent during the year (approximately 30 %) which led to the highest degree of air pollution in this part of the town (measuring points 4 and 8 – City Hospital and the city location “Šumska sekcija – Forest Section”, respectively). The following objects are located in this part of the town: the old town center, a hotel, the town market, the town hall building, the faculty campus, an elementary school and the city hospital. With increasing distance from the plant stacks, the soil pollution decreased and it is minimal was at a distance of 20 km (measuring point 10 – Lake Bor); however the influence of pollution was still apparent.

TABLE I. Evaluation table. Heavy metals concentrations ( $\text{mg kg}^{-1}$ ) in the soil at 12 locations in the urban area of the town Bor and its surroundings, with given preference function and respective thresholds for each criterion

Alternatives	Criteria-metal concentrations in sediments							
	pH	Cu	Pb	Cd	Ni	Mn	As	Hg
Analytic method	pH-Meter	AAS	AAS	AAS	AAS	AAS	ICP–AES	A–Hg
Minimum/Maximum	–	Min	Min	Min	Min	Min	Min	Min
Preference Function	–	Linear	Linear	Linear	Linear	Linear	Linear	Linear
Indifference threshold ( $Q$ )	–	116	10	0	2	42	12	0.0101
Preference threshold ( $P$ )	–	696	57	1	12	252	73	0.0603
Location 1	7.7	530	70	2	45	1100	17	< 0.1
Location 2	7.6	1050	100	4	33	880	68	0.1
Location 3	7.5	550	60	2	33	1300	52	0.1
Location 4	7.4	2540	180	6	49	1200	260	0.3
Location 5	7.9	770	80	2	12	1200	33	0.1
Location 6	7.8	390	40	2	41	1200	15	< 0.1
Location 7	6	1000	40	< 2	37	1200	23	< 0.1
Location 8	7.2	2140	230	5	53	1100	140	0.3
Location 9	6	580	60	2	16	1200	25	0.1
Location 10	7.5	220	50	3	37	460	19	< 0.1
Location 11	7.7	930	80	3	49	900	41	0.1
Location 12	7.7	260	50	< 2	37	1100	16	0.1
Max. value		2540	230	6	53	1300	260	0.3
Average value		913.33	86.67	2.92	36.83	1070	59.08	0.133
Min. value		220	40	< 2	12	460	15	< 0.1
Limit values according to the soil quality standard of the Netherlands <sup>52</sup>		< 36	< 85	< 0.8	< 35	–	< 29	< 0.3
Limit values according to the National Legislation of the Republic of Serbia <sup>53</sup>		< 100	< 100	< 3	< 50	– <sup>a</sup>	< 25	< 2

<sup>a</sup>Manganese limit value is not regulated in the National Legislation of the Republic of Serbia



The heavy metals found in the analyzed soils from these sampling locations are in such concentrations that they can only be explained to be the result of atmospheric precipitations of airborne particles and aero-sediments from gases produced by the Copper Smelting Plant located in Bor. To confirm this assumption, soil samples from five locations which are more than 20 kilometers from the Copper Smelting Plant were analyzed. Three of the five samples contained copper but less than the limiting value of  $100 \text{ mg kg}^{-1}$ . The presence of As and the other investigated heavy metals was not registered at a significant level at any of the locations. The contents of the heavy metals at the investigated locations presented in Table I are much higher compared to these more distant locations, which corroborated the assumption that atmospheric precipitations of airborne particles and aero-sediments from the Copper Smelting Plant stacks in Bor was responsible for the high levels of pollutants found in the near vicinity of the plant.

On settling at pH values between 6 and 8 over many years, these materials became mineralized. However, as their concentrations were not high enough for classical mineralogical analysis, possible mineralogical forms of the heavy metals in the analyzed soils were determined utilizing the HSC Chemistry 4.0 software package (chemical reaction and equilibrium software) by analyzing the areas of stability for the possible phases in the *Eh*-pH equilibrium diagram calculated for room temperature. The stability field diagrams calculated the presence of a range of metal oxide, hydroxide and sulfate minerals in the analyzed soil: Cu (CuO; Cu<sub>2</sub>O; Cu); As (H<sub>2</sub>AsO<sub>4</sub>; HAsO<sub>4</sub>; AsO<sub>4</sub>; HAsO<sub>3</sub>); Cd (Cd<sup>2+</sup>; Cd(OH)<sub>2</sub>; CdSO<sub>4</sub>·2.67H<sub>2</sub>O; CdS; Cd); Pb (PbO<sub>2</sub>; Pb<sub>4</sub>(OH)<sub>4</sub>; Pb<sub>6</sub>(OH)<sub>8</sub>; PbSO<sub>4</sub>; PbO·PbSO<sub>4</sub>; Pb); Hg (Hg; HgO); Ni (Ni(OH)<sub>3</sub>; NiO; Ni; NiHO<sub>0.68</sub>; NiSO<sub>4</sub>·4H<sub>2</sub>O); Mn (MnO<sub>4</sub>; MnO<sub>2</sub>; Mn<sub>2</sub>O<sub>3</sub>; Mn<sub>3</sub>O<sub>4</sub>; Mn(OH)<sub>2</sub>; Mn<sup>2+</sup>; Mn; MnSO<sub>4</sub>; MnS). In addition, presence of Cu<sub>2</sub>S, CdS and FeS is possible. The presence of oxides, hydroxides and sulfates of heavy metals in the contaminated soil indicates a large probability of their transition into ground waters and the human food chain.<sup>17</sup>

Also, the determined values of the heavy metals contents in the surface layer cannot originate from primary mineralization of the ore deposit in this region because minerals of the heavy metals are found at depths deeper than 100 m, from where the ore deposit exploited by the Copper Smelting Plant is obtained.

When comparing the values given in Table I with the values at other urban regions in the surroundings of industrial zones, Sophia (Bulgaria):<sup>12,54</sup> Cu,  $40 \text{ mg kg}^{-1}$ ; Pb,  $32 \text{ mg kg}^{-1}$  and Cd,  $0.4 \text{ mg kg}^{-1}$ , Palermo (Italy):<sup>55</sup> Pb,  $202 \text{ mg kg}^{-1}$ ; Cu,  $63 \text{ mg kg}^{-1}$  and Hg,  $0.68 \text{ mg kg}^{-1}$ , Manresa (Spain):<sup>56</sup> Cu,  $20.3 \text{ mg kg}^{-1}$ ; Cd,  $0.28 \text{ mg kg}^{-1}$  and Pb,  $0.18 \text{ mg kg}^{-1}$ , Port Kembra (Australia):<sup>8</sup> Cu,  $49 \text{ mg kg}^{-1}$ ; As,  $3.2 \text{ mg kg}^{-1}$  and Pb,  $20 \text{ mg kg}^{-1}$ , the present results indicate that the soil pollution in the studied zone is very high. Continuing the operation of the Copper Smelting Plant in the present manner is cumulatively increasing the heavy metal

content in the soil and presents a severe threat to human health in this part of Europe.

#### *PROMETHEE and GAIA ranking analysis*

The obtained values of the heavy metals Cu, Pb, Cd, Ni, Mn, As and Hg contents in the soil in the examined urban zone of the town of Bor and its surroundings (20 km in diameter from plant smokestacks) are given in Table I for 12 locations, the positions of which are shown in Fig. 2. These results represent the average values of heavy metal contents in 10 samples obtained from each location. Additionally, data was provided regarding chosen preference functions and indifference and preference thresholds which are necessary for multi-criteria ranking of locations by the degree of contamination with heavy metals using the PROMETHEE/GAIA method. The model implies the ranking of the best alternatives – locations with the lowest presence of heavy metals according to given set of preference functions and weight criteria. In all cases a linear function is used as the preferential one. The reason for such a consideration results from the fact that the heavy metal content in the soil decreases with increasing distance from the factory chimney in the direction of wind flow. The simplest mathematical expression that can explain this pattern is a linear function.

Consequently, the locations were ranked according to their degree of contamination with heavy metals in the studied area using the aforementioned PROMETHEE/GAIA method. Considering that the data in Table I have a quantitative character, a linear function was chosen for the preference function, Fig. 3. (example for Cu), for all the defined criteria with indifference and preference thresholds ( $Q$  and  $P$ ) in the 5 and 30 % zones, respectively.<sup>45</sup>

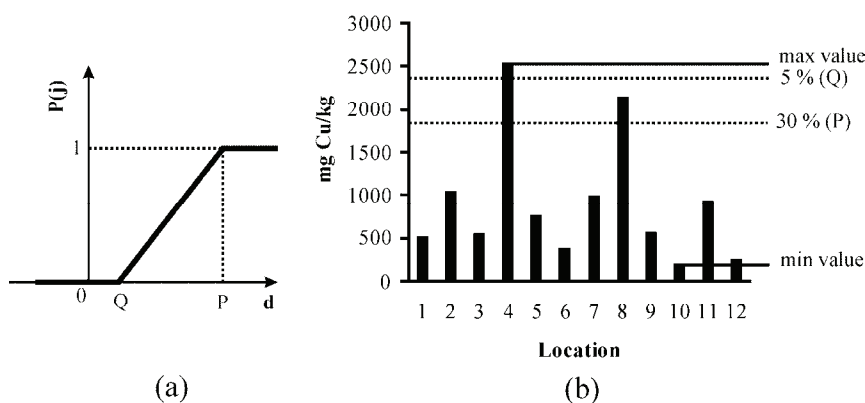


Fig. 3. a) Determination of the preference function values based on the indifference and preference thresholds for a linear preference function; b) defining the indifference and preference thresholds zones for the copper concentration as a criterion.

For the purpose of defining the weight coefficients, it was taken into account that the heavy metals do not have the same significance, *i.e.*, each of them has a different effect on human health and the environment, which is defined in Table II. The weight of significance assigned to each metal was determined considering the reference dose of exposure, toxicity and damage to human health. By utilizing the Decision Lab 2000 software package, with the PROMETHEE/GAIA method, based on the data in Tables I and II, values were acquired for the positive ( $\Phi^+$ ) and negative ( $\Phi^-$ ) flows, (Table III).

TABLE II. Given weights for each criterion

Criteria-dangerous metal	Weight	Influence on health
Pb	22.5	I Category, retained in the human organism and is carcinogenic
Cd	22.5	I Category, retained in the human organism and is carcinogenic
As	15	I Category, easily removed from the organism within 3–5 days
Hg	10	Poisonous, not carcinogenic, removed from the organism with in 1 month
Ni	15	Carcinogenic
Mn	10	Influence on the nervous system
Cu	5	Harmful, but removable
$\Sigma = 100$		

TABLE III. Preference flows for case scenario

Location	$\Phi^+$	$\Phi^-$	$\Phi$
1	0.2575	0.1338	0.1237
2	0.2794	0.4138	-0.1344
3	0.2910	0.1295	0.1615
4	0.0225	0.8536	-0.8310
5	0.3445	0.1025	0.2421
6	0.3222	0.0862	0.2360
7	0.3203	0.0889	0.2314
8	0.0516	0.8402	-0.7886
9	0.3692	0.0510	0.3183
10	0.3813	0.1475	0.2338
11	0.2382	0.3131	-0.0749
12	0.3387	0.0565	0.2822

The PROMETHEE II method provided a complete ranking spanning from the best to the worst location, based on the heavy metal content in the soil (Fig. 4), where the “best” locations were those with the lowest concentrations of heavy metals and the “worst” were those with the highest concentrations. The obtained results showed that the most polluted locations were: Hospital (Location 4) and city location “Šumska sekcija – Forest Section” (Location 8), and the least pol-

luted locations were found on the territory of the village Krivelj (Location 9) and the sampling location “Iza planira” (Location 12).

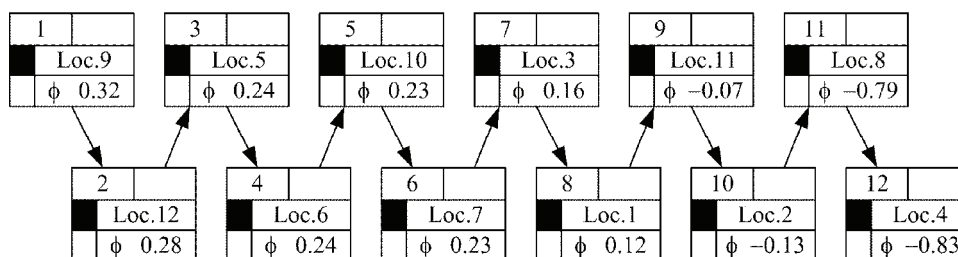


Fig. 4. PROMETHEE II Ranking of locations (sampling locations were ranked from left to right, which is from the best to the worst location).

Advantages of Decision Lab software package can be found within implementation of geometrical analysis for interactive assistance (GAIA). Considering that the value of the delta parameter ( $\Delta$ ) was rather large (85.15 %), the validity of this tool should be taken into account. This means that only 14.85 % of the total information is lost in the projection. In real world applications, the value of  $\Delta$  should always be larger than 60 % and in most cases larger than 80 %. This means that even when the number of criteria is large, the GAIA plane still provides reliable information.<sup>42</sup>

Based on the position of the criterion in GAIA plan (squares), Fig. 5, conformity or conflict between individual criteria can be determined. Thus, one conformable group of criteria consists of Hg, Pb, As and Cu, a second conformable group consists of Ni and Cd, while Mn does not concur with any of the given criteria. Likewise, the positions of the alternatives (triangles) determine the strength and weakness with respect to the criteria. Alternatives present the investigated locations from which the soil samples were taken. The closer it is to the orientation of the individual criterion axis, the better the individual alternative is, judging by that criterion. Thus, the contamination level of specific location is lower if it is closer to a particular heavy metal in the GAIA plane.

Within Cluster A, locations Hospital (Location 4) and “Šumska sekcija – Forest Section” (Location 8) can be found, having the largest percentage of heavy metals in the soil, apparently not being ranked as good by any criterion and as such being orientated in an opposite direction with respect to the decision axis ( $pi$ ), which defines a compromising solution in accordance with the given weight criteria. As opposed to them, the location group B (Cluster B) represents a better solution by a greater number of criteria, among which Location 12 sets itself apart as the closest to the decision axis ( $pi$ ), as well as location Village of Krivelj (Location 9), which was judged the best in terms of the content of Ni and Cd. These ranking results were also determined with PROMETHEE II complete ranking.

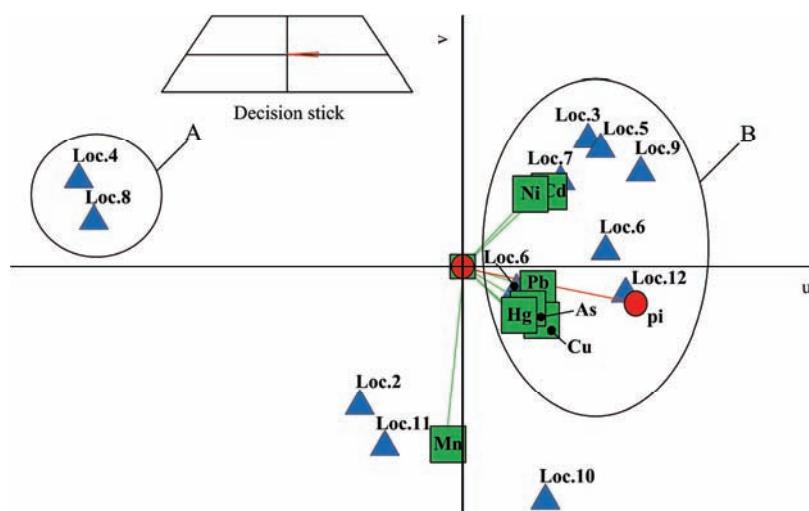


Fig. 5. GAIA plane analysis for the defined model of heavy metal soil contamination.

The ranking results in this study indicate certain correlation with the results of a similar model used for air pollution in same area.<sup>20</sup> The reason for such coincidence is the fact that the soil pollution is caused by the temporal atmospheric distribution and fallout of heavy metal emissions from the Copper Smelting Plant in Bor, as well as meteorological and geographical conditions and the distance from the point sources. This means that the employed multi-criteria model represents a reliable way for analyzing and solving ecological problems, because it is possible to determine the distribution and impact of all pollutants simultaneously around the emission source, and to define the relations among them regarding the locations.

#### CONCLUSIONS

The determined contents of heavy metals in the layer of soil down to 30 cm in depth do not originate from ore mineralization in this region because the heavy metals exist at much deeper levels – on the contrary they are the consequence of precipitation of airborne particles and aero-sediments from the air over many years, which originated from the oxidation roasting and smelting of the copper concentrate containing heavy metals. This was proved after analyzing the soil samples obtained at greater distances from the smelting plant.

Through ranking of obtained results with the PROMETHEE/GAIA method, the most polluted zones are on the locations Hospital (Location 4) and the city location “Šumska sekcija – Forest Section” (Location 8), which have vital functions for the town, therefore representing a risk for human health. The determined heavy metal contents (Cu, Pb, Ni, Mn, As and Hg) in the soil in the studied area of the Bor region indicate a large degree of soil degradation, with the potential

danger of heavy metals entering the animal and human food chains with the associated severe consequences.<sup>17</sup>

Some of these consequences were already reported.<sup>22</sup> The contents of As and heavy metals in food supplies from four villages around Bor were determined. The results revealed that the Cu and As contents in the food supplies from the village Krivelj (Location 9 in Fig. 2) were much higher than in the other 3 villages (Oštrelj, Zlot and Šarbanovac), which are more distant from the Copper Smelter Plant and do not lie in the path of the prevailing wind direction. As discussed above, this location was ranked the best compared to other urban areas in Bor; nevertheless, it is more polluted compared to other more distant villages. Higher than allowed concentrations of As and heavy metals were found in fruits, grapes, vegetables and eggs.

Research has also been conducted on lead and As content in blood and urine of children in Bor and village Zlot (outside metallurgical smoke range). This research showed that children from Bor have considerably higher contents of these metals. This means that there is a continued risk of lead and As input into the organisms of children from Bor, especially if they spend their whole life in polluted surroundings. By studying the impact of pollution on health, growth and development of children in Bor and Sokobanja (unpolluted region 100 km from Bor), it was found that the hemoglobin content was 1.1 % lower and number of red blood cells in general was 400,000 lower for the children from Bor than the children from Sokobanja. The same study showed that children from Bor are more liable to diseases of the respiratory organs: blocked nose, enlarged tonsils, swollen pharynx and swollen gland secretion in bronchi. For these reasons, children in Bor are more liable to allergy diseases, particularly to bronchial asthma.<sup>22</sup>

The shortage of food supplies caused by soil contamination has resulted in the need for people to obtain food from elsewhere, which results in higher prices and a further reduction in living standards. Consequently, the people in Bor buy cheap but not varied food, which affects child growth and development and human health in general. Due to the existing situation, village farmers are unwilling to invest in agricultural development, with some choosing instead to go to the town to search for employment. This, in turn, leads to neglect of their farms and consequentially a further decrease in agricultural production.

After obtaining the very alarming results presented in this paper, the authors believe that the further strategy for the environmental protection of this region should include a wider methodological approach, such as the Ecological Risk Assessment (ERA) methodology.<sup>57,58</sup> This kind of methodology enables a detailed identification of situations dangerous for humans under conditions of this kind.

In addition, the facts described in this paper imply the necessity for urgent intervention at the source of the emissions of sulfur dioxide, As and heavy metals airborne particles, and for the modernization and reconstruction of the Copper



Smelting Plant in Bor, as well as urgent restoration of the already degraded soil. Continued operation of the smelting plant under the existing conditions will increase the heavy metal content in the soil resulting from their precipitation from the air.

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## ИЗВОД

## ВИШЕКРИТЕРИЈУМСКА АНАЛИЗА ЗАГАЂЕНОСТИ ЗЕМЉИШТА ТЕШКИМ МЕТАЛИМА У ШИРОЈ ОКОЛИНИ ТОПИОНИЦЕ БАКРА У БОРУ

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У овом раду предочене су последице стогодишње производње у топионици бакра у Бору на загађење земљишта. У ту сврху, извршено је површинско узорковање земљишта на дванаест различитих мерних локација. Све мерне локације се налазе у пречнику од 20 километара од извора загађења, у урбаним и руралним деловима града Бора. Узорак земљишта је узиман сондом на тај начин да је вађено језгро земљишта пречника 5 cm и дубине 30 cm. Након тога, извршена је анализа рН вредности узорка и саржаја тешких метала (Cu, Pb, As, Cd, Mn, Ni и Hg) коришћењем различитих метода спектрофотометрије. Резултати анализе садржаја тешких метала у узорцима земљишта показали су високе вредности: 2,540 mg kg<sup>-1</sup> Cu; 230 mg kg<sup>-1</sup> Pb; 6 mg kg<sup>-1</sup> Cd; 530 mg kg<sup>-1</sup> Ni; 1,300 mg kg<sup>-1</sup> Mn; 260 mg kg<sup>-1</sup> As и 0,3 mg kg<sup>-1</sup> Hg. За идентификовање и рангирање критичних зона загађеног земљишта на основу присуства тешких метала у њима, у овом раду је коришћена PROMETHEE/GAIA метода, која се често користи у хеометријским студијама. Резултати рангирања јасно указују да се најзагађеније зоне налазе на виталним локацијама у самом центру града. Због тога, услед повећане биодоступности тешких метала и њихових комплексних реакција са органским врстама у земљишту, последице по људско здравље се могу драстично увећати уколико ови тешки метали доспеју у ланце исхране.

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