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BIOMONITORING OF HEAVY METAL POLLUTION NEAR COPPER SMELTER IN BOR (SERBIA) USING ACACIA

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ABSTRACT
The correlations between sampling sites situated in the close vicinity of copper smelter (Bor, Serbia) based on heavy metal (Pb, Cu, Zn) content in plant parts and soil of acacia (Robinia pseudoacacia L.) were determined. Very strong correlations (R^2>0.9) were observed between the sites Town park and Hospital in the urban-industiral zone due to high air pollution in this sampling area. The performed cluster analysis confirmed these results by grouping the sites with high metal content in plant and soil material of Robinia pseudoacacia into the same clusters. Also, strong correlations were noted between less polluted sampling sites (Bor lake and Brestovac spa) with the control site (Sumrakovac).
Keywords: biomonitoring, Robinia pseudoacacia, heavy metals

1. INTRODUCTION
Air quality monitoring using biological material has been employed for more than a century. It represents a reliable way to relate long-term air pollution on large areas with the concepts of time and spatial variability at an acceptable cost [1,2]. Which species will be used for biomonitoring depends on how widely they are distributed throughout the region. The most often used higher plants are spruce [3], birch [4], pine [5], oak [6], etc. The main sources of trace elements in plants are their growth media. Although heavy metals are naturally present in soils, contamination comes from many local sources (industry, traffic, etc.). However, the bioavailability of trace elements from aerial sources through leaves also has a significant impact on plant contamination [7,8].
The aim of this paper was to determine the correlations between sampling sites in close vicinity of copper smelter based on heavy metal (Pb, Cu, Zn) content in plant parts and soil of acacia (*Robinia pseudoacacia* L.). *R. pseudoacacia* was selected as a biomonitor because it occurs from unpolluted areas to the ones with high levels of air pollution.

2. METHODOLOGY

2.1. The study area
The area studied in this paper, the territory of Bor (44°25' N latitude and 22°06' E longitude) and its surroundings is located in Eastern Serbia (Fig. 1a). The primary pollution source in Bor is pyrometallurgical production of copper from sulphide ores in The Mining and Smelting Complex Bor, which is located on the north-east border of the urban zone of the town. The first copper smelter started in 1906, and ever since has been a dominant source of air pollution with SO_2 and particulate matter with a high level of As and heavy metals. Open pits, ore and flotation waste heaps also represent air pollution sources, particulary during the dry season [9]. In Fig. 1b, a map of the town of Bor is shown with the position of sampling sites compared to the industrial area of the Mining and Smelting Complex Bor (RTB Bor) where it is a dominant source of air pollution, i.e. copper smelter.

2.2. The sampling sites

The sampling was carried out in the early autumn of 2008. The plant material and the soil samples of *R. pseudoacacia* were taken from ten selected sites distributed into five zones: urban-industrial (sampling sites Town park, Institute and Hospital), suburban (Jugopetrol and Brezonik), rural (Ostrelj and Krivelj), tourist (Bor lake and Brestovac spa) and control zone (Sumrakovac) located 25 km in SSW direction of Bor.

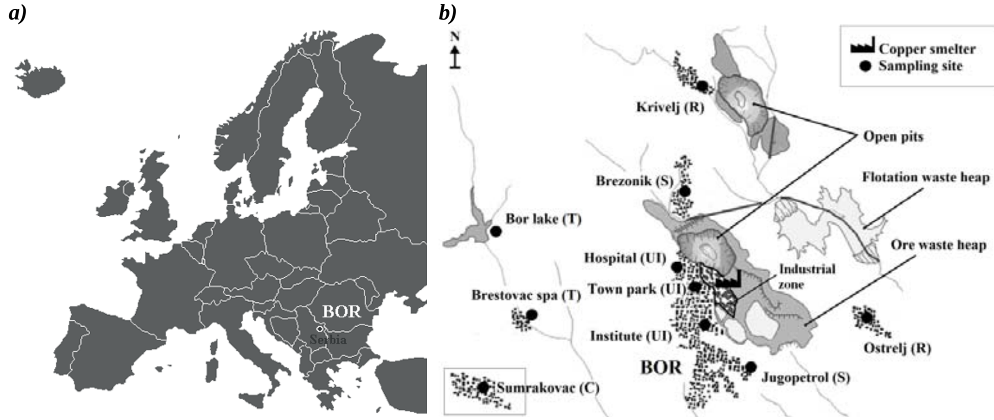

*Figure 1. **a)** Position of Bor; **b)** Sampling sites in the respect to the industrial zone of the RTB Bor (UI – urban-industrial zone, S – suburban zone, R – rural zone, T – tourist zone, C – control zone)*

2.3. Sample analysis

At each site samples of *R. pseudoacacia* were taken from three to five trees. Soil was taken in upper A-horizon, from which root samples were taken too. Root samples were thoroughly washed with tap water followed by distilled water for the purpose of removing soil particles. The leaves were separated from the branches at a laboratory and divided into two subsamples. One subsample was washed with distilled water for the purpose of removing atmospheric deposition, whereas the other one remained unwashed. All the samples were dried to a constant weight at room temperature during a period of fifteen days. The samples were then homogenized in a laboratory mill and griddled through 0.2-mm sieve. The samples were dissolved in HNO_3/H_2O_2 mixture and analysed by ICP-AES. All the results were calculated on a dry weight basis (μg g^{-1} dw) [10].

3. RESULTS AND DISCUSSION

3.1. The correlations between sampling sites

The correlations between the sampling sites based on average heavy metal concentrations (Cu, Zn, Pb) in washed/unwashed leaves, branches, root and soil of *R. pseudoacacia* are given in Fig. 2. Only the correlations between the sampling sites with determination coefficient (R^2) above 0.9 are shown in the figure.

At the sampling sites Town park and Hospital in UI zone, Cu and Zn are in very strong correlation due to high air pollution in this area [11], particularly Zn (R^2=0.995) (Fig. 2a and Fig. 2b). Zn and Pb are usual accompanying metals of copper sulphide ores, and they are constantly present in particulate matter and atmospheric depositions in Bor [11]. The correlations of Zn and Pb at the sites Town park and Hospital with the site Brezonik (Fig. 2c and Fig. 2d) are a consequence of unfavourable wind rose. The sites Jugopetrol and Institute are in strong correlation (Fig. 2e) because these sites are in the pathway of the pollutants originating from the copper smelter. Based on strong correlations of Cu, Zn and Pb at the sampling sites Bor lake and Brestovac spa (Fig. 2f-h), it can be concluded that the heavy metal content is the same in the tourist zone of the study area. Moderately to strong correlations of the sampling sites in the tourist zone with the control one (R^2=0.618-0.940; not shown in the Fig. 2.) suggest that tourist zone is less polluted. Weak correlations between the sampling sites in the urban-industrial (R^2=0.001-0.486), suburban (R^2=0.002-0.143) and rural (R^2=0.047-0.337) zone with the control one confirms higher level of pollution (not shown).

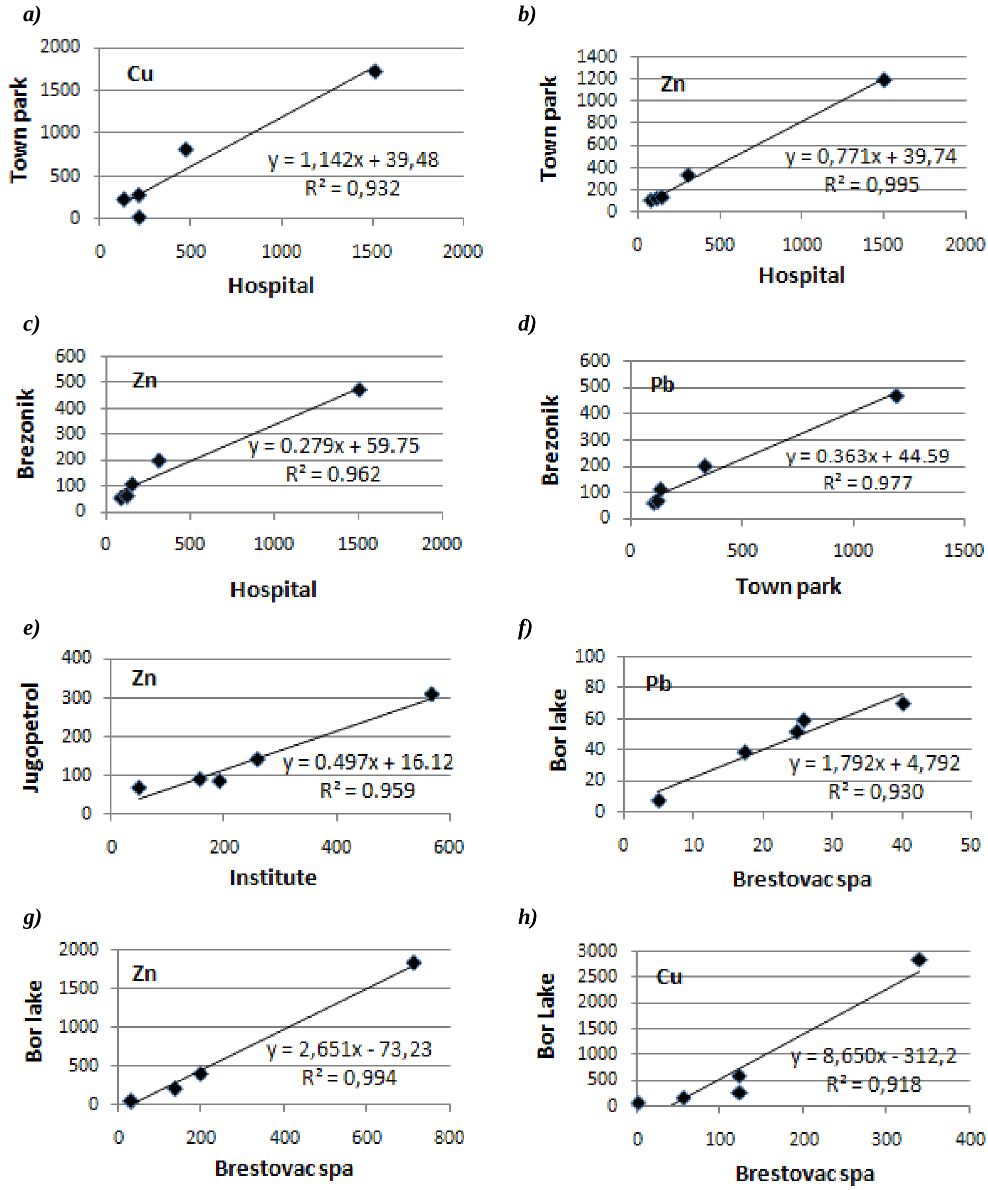

Figure 2. The correlations between the sampling sites based on the heavy metal content in plant parts and soil of R. pseudoacacia (R^2 - determination coefficient; R^2>0.9 strong correlation)

The cluster analysis of heavy metal content in washed/unwashed leaves, branches, root and soil of *R. pseudoacacia* at all the sampling sites was performed. Dendrogram in Fig. 3a represents the sampling sites in the urban-industrial and suburban zone. It can be seen that two clusters have been formed: cluster I consists of the sampling sites Hospital and Town park, which are the most polluted ones, whereas cluster II consists of the sites Institute, Jugopetrol and Brezonik. Dendrogram in Fig. 3b represents the sites in the rural, tourist and the control zone. Based on the strong correlations (R^2>0.9) among the sites Brestovac spa, Bor lake and Sumrakovac which form cluster I, it can be concluded that the sampling site Krivelj (cluster II) is more polluted compared to them. The main reason could be close vicinity of the other open pit – Veliki Krivelj, near the sampling area.

a)

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Rescaled Distance Cluster Combine using Average Linkage (Within Group)

C A S E        0         5        10        15        20        25
 Label         +---------+---------+---------+---------+---------+

 Hospital      -+-----------------------------------------------+
 Town park     -+                                               |
 Institute     -----+------+                                    |
 Jugopetrol    -----+      +------------------------------------+
 Brezonik      ------------+
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b)

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Rescaled Distance Cluster Combine using Average Linkage (Within Group)

C A S E        0         5        10        15        20        25
Label          +---------+---------+---------+---------+---------+

B.Spa          -+
Sumrakovac     -+-----+
Ostrelj        -+     +-----------------------------------------+
Bor lake       -------+                                         |
Krivelj        -------------------------------------------------+
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Figure 3. The dendrogram on heavy metal concentrations (Cu, Zn and Pb) in plant parts and soil of R. pseudoacacia ***a)*** *UI and S zone;* ***b)*** *R, T and C zone*

4. CONCLUSIONS

The major source of air pollution in Bor and its surroundings (Serbia) are the processes related to the processing of copper sulphide ores. Pb and Zn are usual accompanying metals of copper ores, and along with Cu they are continuously present in particulate matter and aero sediments in the air of Bor. The correlations and cluster analysis between the sampling sites based on average heavy metal concentrations (Cu, Zn and Pb) in washed/unwashed leaves, branches, root and soil of *R. pseudoacacia*, showed that the Town park and Hospital are the most polluted sites in the study area. These sites are in the closest vicinity of the copper smelter (<1.0 km). The results also showed that the tourist zone is less polluted, due to strong correlation, than the control zone.

5. ACKNOWLEDGMENTS

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