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# HAZARDOUS MATERIALS IN A MINING-METALLURGICAL PRODUCTION PROCESS

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**ABSTRACT**
*The mining-metallurgical operations are major sources of airborne pollutants, and they present a risk for nearby ecosystem. The Mining-metallurgical Complex Bor (Eastern Serbia) exploits sulphide copper ore, emitting acid sulphur gases and suspended particles with high content of As, Pb, Cu, Zn, Cd etc. The annual concentrations of $SO_2$ in the atmosphere of Bor, in the period of 13 years considerably exceeded the limit value at the sites in the urban-industrial and suburban zones. The presented box plots of Pb, Cd, Cu and As concentrations showed that over 50% of the As concentrations at all the sites far exceeded the LV, while the other concentrations were within permited values. According to cluster analysis, heavy metals grouped into one cluster, while arsenic and sulphur dioxide formed separate clusters, due to their high concentrations.*
**Keywords:** Air pollution, Havy Metals, $SO_2$.

## 1. INTRODUCTION

The two most important artificial sources of sulphur dioxide are burning of fossil fuels and smelting of ores containing sulphur. The moisture and sulphur dioxide in the air combine in a photochemical reaction to form sulphurous or sulphuric acid, which are constituents of acid rain. In the Air Quality Guidelines of the WHO the proposed 24-hour mean limit value for $SO_2$ is 20 µg $m^{-3}$ [1]. The 24-hour limit value for $SO_2$ defined by the EU Directive is 125 µg $m^{-3}$ and should not be exceeded more than three times a year [2]. According to the Serbian Regulation, the daily limit value for $SO_2$ in residential areas is 150 µg $m^{-3}$, whereas the annual limit value is set at 50 µg $m^{-3}$ [3].
This paper presents the monitoring results of the polluting substances in the air of Bor and its surroundings. The inhabitants of the study area are exposed to a great health risk since it is under the influence of sulphur dioxide and suspended particulate matter with a high content of Cu, Zn, As, Pb, Cd, Hg, Mn and Ni [4]. The greatest and most frequent annual exceedances of the limit value (LV) are recorded for As [5] and $SO_2$ which are why the As concentrations in the urban-industrial, suburban and rural zone are analysed in this paper.

## 2. METHODOLOGY

### 2.1. The study area

The study area is the Bor town and its surroundings (60,000 inhabitants), which is located in Eastern Serbia. Approximately 40,000 inhabitants live in the town, whereas the remaining 20,000 live in 13 surrounding rural settlements [4]. The territory of Bor and its surroundings is predominantly hilly and mountainous and covers an area of 856km$^2$.

### 2.3. Sampling sites

Air quality monitoring in the territory of Bor and its surroundings was performed continuously by fixed and mobile measuring stations. Concentrations of $SO_2$ in the air were measured using fixed stations on four locations (Town park, Institute, Jugopetrol and Brezonik). Monitoring stations for determining sulphur dioxide concentrations were measured automatically by the "Environment S.A" AF22M analyser. Determining PM, heavy metals and As was conducted for 7–8 days in a month in the period from the beginning of 2003 to September 2008. A mobile sampling station was installed at the following sampling sites:

- Site 1 Town park, located in the urban-industrial area, 0.5 km SW of the Mining and Smelting Complex as the major pollution source. It is the oldest and most densely populated part of the town where the main business, commercial and administrative buildings are located.
- Site 2 Institute, located 2.0 km S of the urban-industrial area. The sampling site is located in a densely populated residential part of the town.
- Site 3 Jugopetrol, located 2.3 km SE of the pollution source in the suburban industrial area. This sampling site is in the direction of the highest frequency winds.
- Site 4 Hospital, 1.0 km away from the pollution source in the WNW direction. The site is located in the urban-industrial area next to the town hospital.

**2.4. Sample analysis**

At the completion of a 24-h sampling period a representative sample of circular cross-section is obtained on the filtration medium. Depending upon the required chemical analyses, the sample is divided into a number of subsamples (2, 4 or more). One subsample is transferred to a glass vessel and diluted with a 1:1 nitric acid. The vessel containing a subsample is further transferred to a sand bath and heated to the boiling point (until nitrogen oxide is completely removed). The prepared subsample is analyzed by atomic absorption spectrometer (AAS Perkin Elmer, model 1100B). Arsenic and heavy metal concentrations in the sample are determined by the graphite furnace technique from a working curve obtained by instrument calibration with standard solution of a known concentration.

**3. RESULTS AND DISCUSSION**

The average annual production of anode copper and average annual concentrations of $SO_2$ (3 measuring sites) in the period from 1994-2006, are shown in Figure 1.

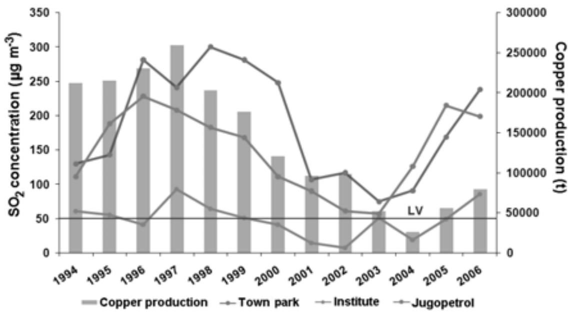


*Figure 1. Average annual $SO_2$ concentrations recorded at the sampling sites Town park, Institute and Jugopetrol from 1994 to 2006 (LV-limit value)*

From 1994 to 1998 the copper smelter produced on average 98,000 t of anode copper annually. A peak production of 125,000 t was achieved in the course of 1997. The subsequent years saw a steady drop in annual production, so that in the period 1999–2007 the average annual production of anode copper amounted to 39,000 t (Fig. 1). The average annual production of cathode copper in the electrolytic plant amounted to 82,000 t in the period 1994–2000. Since 2002 cathode copper production has considerably dropped, amounting to 13,500 t annually. The sulphuric acid plant, which is a part of the Mining-metallurgical Complex, was built in order to prevent air contamination with waste gases from the smelting plant. The plant capacity enables treatment of less than 60% of waste gases, whereas the remaining 40% is discharged untreated into the atmosphere. The annual concentrations of $SO_2$ in the atmosphere of Bor, in the period of 13 years considerably exceeded LV [3] at the sites Town park and Jugopetrol, whereas the concentrations at Institute were around the allowed value. From Figure 1, it can be seen that the level of copper production is one of the factors which can influence the level of air pollution with sulphur dioxide. The other factors are meteorological conditions and the distance of measuring sites from the copper smelter.

In Fig. 2 average monthly concentrations of lead, cadmium, copper and arsenic, respectivelly are presented in the period from 2005 to 2008 at three measuring sites. The concentrations of lead (Fig.2a) in the observed period were in the range of the LV. However, concentrations which were indicated as extreme points did not exceed the LV. Concentrations of cadmium (Fig. 2b) exceded the LV at the measuring sites Town park and Institute in October 2006, and also at Jugopetrol in December, whereas in November the same year the concentration was on the LV. At the box plot for average monthly concentrations of copper (Fig. 2c), three atypical points can be noticed. Arsenic, which is a cancerogenic matter (Fig. 2d) was at all the measuring sites in the examined period, in the concentrations which far exceeded the LV. More than 50% of arsenic concentration was above the LV at all three measuring sites. Being up to 200 ng $m^{-3}$, concentrations of arsenic were indicated as atypical and extreme points when compared to the LV (6 ng $m^{-3}$). Besides the industrial complex, the power plant also has its influence on the increased concentrations of Pb, Cd, Cu and As in suspended particles, since higher concentrations of heavy metals appear mainly during the winter season.

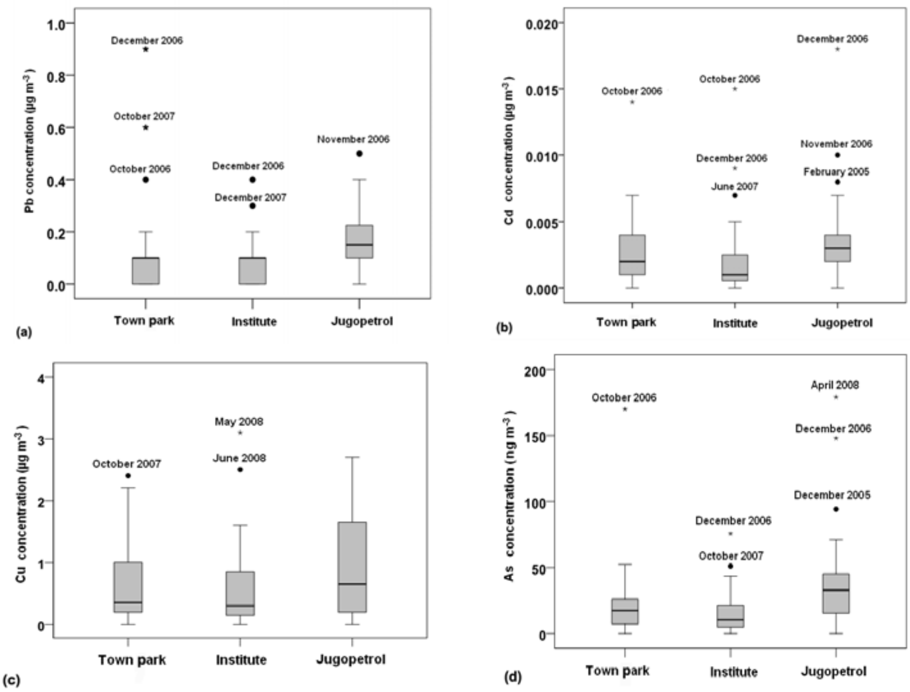


*Figure 2. Average monthly concentrations of: (a) Lead, (b) Cadmium, (c) Copper and (d) Arsenic in the period 2005-2008 at the sampling sites Town park, Institute and Jugopetrol*

Fig. 3. shows a dendrogram of pollutant concentrations in the period from 2005 to 2007. As Fig. 3 presents, three clusters have formed. In the first cluster heavy metals have grouped at four measuring sites. The second cluster consists of arsenic at all the measuring sites and the third one consists of sulphur dioxide at the measuring sites Institute, Town park and Jugopetrol. The reason for grouping of heavy metals into the same clusters is probably due to the concentration of heavy metals in the same fractions, while As and $SO_2$ group into separate clusters due to the high concentrations in the air at four measuring sites.

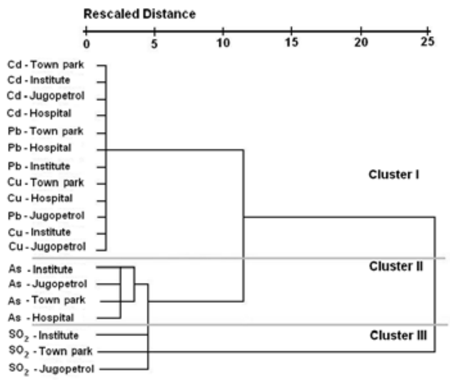


*Figure 3. Dendrogram of heavy metals, arsenic and sulphur-dioxide concentrations in the period from 2005 to 2007 at the sampling sites Town park, Institute Jugopetrol and Hospital*

## 4. CONCLUSIONS

Air pollution with sulphur dioxide in Bor has been present from the very beginning after the copper smelter started working, which was about 100 years ago. The annual concentrations of $SO_2$ in the atmosphere of Bor, in the period of 13 years considerably exceeded LV at the sites the Town park and Jugopetrol, whereas the concentrations at the Institute were around the allowed value. The average annual copper production is one of the influential factors on the level of air pollution with sulphur dioxide. The other factors are meteorological conditions and the distance of the sampling sites from the smelter. Box plot presents atypical and extreme concentrations of Pb, Cd, Cu and As. Cadmium is separated as a carcinogenic matter whose extreme values are dangerous for the environment. Over 50% of the arsenic concentration value at all the sites in the examined period far exceeded the LV. Arsenic is also a carcinogenic matter, so that this state of matter is troublesome.

According to cluster analysis, heavy metals in PM arranged into one cluster. Arsenic and sulphur dioxide formed separate clusters, due to their high concentrations. It can be concluded that the industrial complex influences air pollution in Bor and its surroundings most of all, and that the influence of other antropogene factors, such as the power plant and the traffic, are minor polluters.

The mining-metallurgical production as an emitter of dangerous matter, which are precursors of acid rains, pose a risk for ecosystem located in the vicinity or very close to the place of production.

## 5. ACKNOWLEDGMENTS

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