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ZONE DISTRIBUTION OF ATMOSPHERIC ARSENIC

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ABSTRACT
Measurements of air quality in the territory of Bor and its surroundings (Serbia) were performed at the measuring sites in the urban and rural zones during the 2005–2007 period. The major source of air pollution is the copper smelter which is situated in the close vicinity of the urban zone of Bor. Average annual As concentrations from 2005 to 2007 exceeded the limit value at almost all the measuring sites in the urban and rural zones. The most endangered areas are the ones around the measuring sites which are in the westward wind direction (Jugopetrol, Slatina, Oštrelj), as well as in the close vicinity of the pollution source (Town park, Hospital, Brezonik). If distribution of As is compared in the two zones, it can be concluded that average annual As concentrations are higher at the measuring sites in the urban than in the rural zone.
Keywords: arsenic, air pollution, zone distribution

1. INTRODUCTION

Particulate matter (PM) represents a complex mixture of components with different chemical and physical characteristics. PM can be very variable in size, formation mechanism and origin. In addition, its concentration is also a function of sources, atmospheric reactions and meteorological conditions [1].

Arsenic (As) in particulate matter represents a major threat to human health. The International Agency for Research on Cancer (IARC), has classified As and its compounds in Group 1 of human carcinogens according to numerous epidemiological evidences [2]. One of the major anthropogenic sources of As in PM is copper smelting of non-ferrous metals [3].

2. METHODOLOGY

2.1. The study area

The study area is the town of Bor and its surroundings (60,000 inhabitants), which is located in the Eastern Serbia on the Balkan Peninsula (geographic coordinates of Bor are 44°25'N latitude and 22°06'E longitude). The area is predominantly hilly and mountainous and covers an area of 856 km^2. Approximately 70% of the inhabitants live in Bor, while the rest of them live in thirteen rural settlements (Fig. 1): Zlot, Brestovac, Šarbanovac, Metovnica. Krivelj, Gornjane, Brestovačka banja, Slatina, Donja Bela Reka, Luka, Bučje, Oštrelj and Tanda [4].

The climate of the study area is moderately continental. Bor and its surroundings are located in the area of high wind frequency with moderate intensity. The dominant winds, during the study period from 2005 to 2007, were in the directions of: WNW (9.9%), W (8.2%) and NW (7.7%), E (7.6%). Less frequent wind is in S direction (4.4%), as shown in Figure 2 [5].

2.2. Brief environmental history

The primary pollution sources in Bor are mining of copper ores and metallurgy (pyrometallurgical production of copper from copper sulphide ores: chalcopyrite-$CuFeS_2$, chalcozine-Cu_2S and coveline-CuS). Besides production and processing of copper ores, pollution is also caused by ore waste heaps, as well as the flotation tailing ponds, which represents a serious source of dust, particularly during a dry season. The first copper smelter started in 1906, and ever since has been a dominant source of air pollution with sulphur dioxide and particulates (PM and atmospheric depositions). In spite of dust removal from waste gases, which takes place in several stages, PM with high arsenic and heavy metal content is discharged into the atmosphere. The usual minor constituents of copper sulphide ores are: Fe, Pb, As, Cd, Ni, Hg, Zn, Mn, as well as noble metals. Arsenic is present in copper ores in the form of mineral arsenopyrite (FeAsS) [4]. It should be noted that, the industrial zone of The Mining and Smelting Complex borders with the urban zone of the town.

2.3. The measuring sites

Air quality monitoring in Bor and its surroundings was performed in accordance with The Law on Environmental Protection of the Republic of Serbia and The Regulation about limit values, methods of concentration measurements, criteria for determining the measuring sites and data records [6]. The most frequent measurements were performed at the measuring sites (Fig. 1, Tab. 1): **Town park**-which is located in the urban area 0.5 km WSW of the mining and smelting complex; **Institute**-located 2.0 km SSW of the complex in the urban area; **Jugopetrol**-located 3.3 km SSE of the complex in the urban area; **Hospital**-located 1.0 km WNW of the complex in the urban area; **Brezonik**-located 2.0 km WNW in the urban area. Less frequent measurements were performed at the sites in the rural settlements: **Slatina -** located in SE direction of the complex, **Oštrelj -** located in ESE direction of the complex and **Krivelj -** located in N direction of the complex. In the tourist areas of Bor Lake (WNW) and Brestovačka banja (WSW), the measurement were rare, since the obtained concentrations of the polluting substances were within the permitted limit values [6].

2.4. Sample analysis

Measurements of the PM_{10} concentrations were performed using a mobile analyzer (OSIRIS Dust Monitor AGL Air Industries, GB) and the sampling apparatus (M-TYPE Sampler AGL Air Industries, GB). Arsenic concentration from the PM sample is determined by the graphite furnace atomic absorption spectroscopy (AAS, Perkin Elmer, model 1100B) in The Mining and Metallurgy Institute Bor.

3. RESULTS AND DISCUSSION

Table 1 shows the annual mean concentrations of As at the measuring sites in the urban (U) and rural (R) zone in Bor and its surraundings from 2005 to 2007. The highest number of air quality measurements during the three-year period was performed at the measuring sites Town park, Institute and Jugopetrol (N≥30), Hospital, Brezonik and Oštrelj (N≥15), while in Krivelj and Slatina measurements were performed very rarely (N≥5).

Table 1. Arsenic concentrations at the measuring sites in the urban (U) and rural (R) zone during the period 2005-2007

Zone	Measuring site	Index	**2005**	**2006**	**2007**	N
Urban (U)	Hospital	U11	30.2	59.3	19.2	14
	Brezonik	U12	19.5	4.7	10.3	15
	Town park	U10	29.3	38.9	25.0	30
	Institute	U3	12.0	15.5	21.0	30
	Jugopetrol	U5	30.7	41.3	31.8	29
Rural (R)	Krivelj	R6	8.0	7.0	82.3	3
	Slatina	R11	20.4	5.3	37.9	5
	Oštrelj	R5	5.7	20.6	6.5	11

**all values expressed as ng m^{-3}*
N – number of measurements

Figure 1 shows the three-year average As concentrations in the local districts (LD) and rural settlements (R) in Bor and its surroundings. It can be concluded that the most polluted LDs in the urban zone were: Sever (measuring site Hospital), Sloga (Jugopetrol) and Stari centar (Town Park), Mladost (Institute) and Brezonik (Brezonik). Regarding the rural zone, air monitoring data exist only for the settlements Krivelj, Slatina and Oštrelj. The average As concentration decreases at these measuring sites in that order. However, during the study period, in Krivelj and Slatina only a few measurements were performed, which is not enough for more accurate conclusions. However, the recorded concentrations were above the LV for As at the annual level, amounting to 6 ng m^{-3} [6]. In the tourist zone (Bor Lake), during the study period, only one measurement was done, which showed no air contamination with arsenic (not shown in Fig. 1). In the remaining LDs and the rural settlements, measurements of air quality were not performed, which does not mean that there is no air pollution.

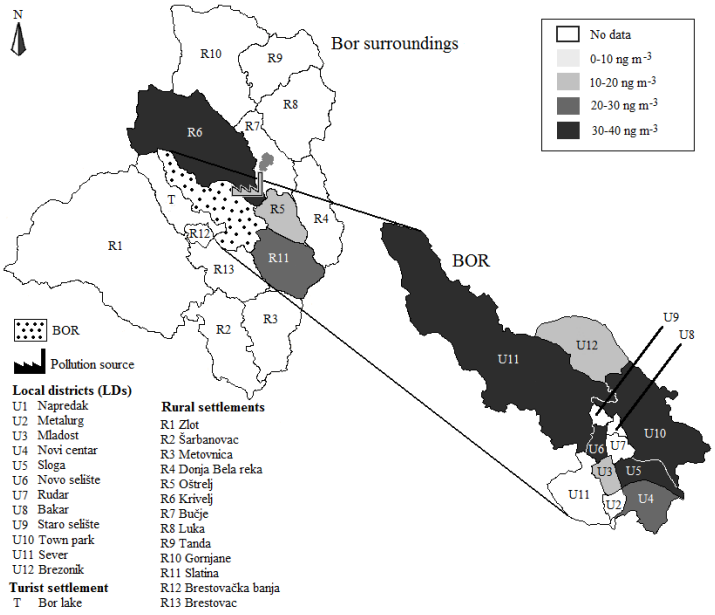

Figure 1. Zone distribution of As in Bor and its surroundings during the 2005-2007 period

In Figure 2 the annual wind rose (%) diagrams from 2005 to 2007 in the Bor area are shown [5].

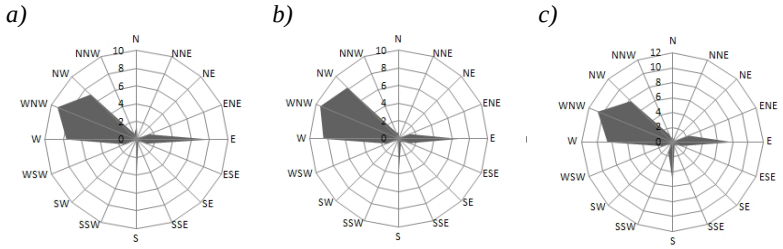

Figure 2. Wind rose diagrams (%) in Bor for a) 2005; b) 2006; c) 2007

As already mentioned in the section 2.1., the dominant winds were in W directions. Different authors showed that the wind direction is an important factor affecting the dispersion of pollutants from pollution sources on large areas [7]. Vicinity of pollution sources is also important [8]. The increased As concentrations at the measuring site Jugopetrol are due to the influence of the dominant wind direction. At the other measuring sites, vicinity of pollution sources is crucial. Rural settlements

Slatina and Oštrelj were under the influence of westward wind, while at the Krivelj site there are additional sources of pollution (open pit and flotation tailing ponds).
At the measuring sites Town Park, Institute and Jugopetrol, where air quality was regularly performed, none of the annual average As concentrations since 1994 until 2008 (Tab. 2) were within the LV [9]. Moreover, some of the mean monthly As concentrations were over 100 times higher than the allowed value [9].

Table 2. As concentrations at the three measuring sites during the period 1994-2008 [9]

Measuring site	Range	Mean	Min	Max	SD
Town park	304.1	131.4	18.9	323.0	99.1
Institute	133.0	51.3	12.0	145.0	36.5
Jugopetrol	202.3	93.7	30.7	233.0	55.8

**all values expressed as ng m^{-3}; SD – standard deviation*

Arsenic in PM poses a great threat to human health. In the WHO Air Quality Guidelines, it is indicated that there is no safe level of inhalation exposure to As which can be recommended [10].

4. CONCLUSIONS

The major source of environmental pollution in Bor and its surroundings are processes related to the processing of copper ores. Arsenic, which is a carcinogenic substance, as a part of PM is on a daily basis emitted into the atmosphere of Bor. According to the air quality monitoring data, it can be concluded that there is a great health risk for the inhabitants. Mean annual concentrations of As, from 2005 to 2007, exceeded the LV in almost all the measuring sites in the urban and rural zone. Concentrations of As were within the range 4.7-59.3 ng m^{-3} in the urban and in the range of 5.3-82.3 ng m^{-3} in the rural zone. The most endangered areas are around the measuring sites that are in the dominant westward wind directions (Jugopetrol, Slatina, Oštrelj) and in the vicinity of the copper smelter (Town Park, Hospital, Brezonik). Comparing As zonal concentrations, it can be concluded that the annual mean concentrations were higher at the measuring sites in the urban than the in rural zone. However, the insufficient number of measuring the air quality and the limited number of measuring sites does not give accurate access of airborne arsenic pollution in Bor and its surroundings.

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