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# Concentrations of particulate matter and arsenic in Bor (Serbia)

S.M. Šerbula[a,*], M.M. Antonijević[a], N.M. Milošević[b], S.M. Milić[a], A.A. Ilić[a]

[a] University of Belgrade, Technical Faculty, P.O. Box 50, 19210 Bor, Serbia
[b] The Mining and Metallurgy Institute, Zeleni Bulevar 35, 19210 Bor, Serbia

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ABSTRACT

Measurements of air quality in the territory of Bor (Serbia) were performed at the sampling sites in the urban-industrial, suburban and rural area during the 2003–2008 period. A high level of arsenic (As) concentration in suspended particulate matter (PM) is of a predominantly industrial origin. The major source of pollution is the copper smelter which is situated in the close vicinity of the urban area of Bor. The ambient level of PM and As is influenced by meteorological parameters as well as the remoteness from the copper smelter. Continual exceedances of the annual limit value (LV) for As (6 ng $m^{-3}$) were recorded at the sampling sites in the urban-industrial and suburban area. Maximum annual As concentrations were recorded at Town Park (46.5 ng $m^{-3}$) in 2004, Institute (95.4 ng $m^{-3}$) in 2004 and Jugopetrol (74.5 ng $m^{-3}$) in 2003. In the past 15 years not a single mean annual As concentration recorded at the sampling sites Town Park, Institute and Jugopetrol has been within the LV. When the average annual and maximum monthly As concentrations are compared, it can be concluded that the level of pollution is higher in the urban-industrial and suburban areas than in the rural area.



## 1. Introduction

The International Agency for Research on Cancer (IARC) has classified arsenic and its compounds as Group 1 human carcinogens, based on a great deal of epidemiological evidence [1]. Elemental arsenic and its compounds have been classified as dangerous substances for the environment by the European Union [2]. Besides being toxic, arsenic forms stable compounds that are characterized by their ability to bioaccumulate in the living organisms, due to which fact it is included in the PBT list (Persistant, Bioaccumulative and Toxic) of the US Environmental Protection Agency [3].

Arsenic gets into the atmosphere from natural and anthropogenic sources. The greatest natural emission sources of arsenic are active volcanoes, whereas a small amount comes from vegetation and wind-driven dust. The greatest anthropogenic arsenic emission results from pyrometallurgical operations in the production of non-ferrous metals, combustion of fossil fuels and the use of pesticides. It has been estimated that anthropogenic emission is three times higher than the natural [4].

In the atmosphere, arsenic exists predominantly absorbed on particulate matter (PM) and is usually present as a mixture of arsenite As(III) and As(V) arsenate [5]. One of the main anthropogenic sources of arsenic in PM (usually present in the form of a sulphide) is copper smelting [6]. The level of arsenic pollution depending on the location can be shown in the following order: remote < rural < urban < traffic < certain industrial locations [7]. Typical arsenic levels for the European region are between 0.2 and 1.5 ng $m^{-3}$ in the rural, 0.5 and 3.0 ng $m^{-3}$ in the urban and lower than 50 ng $m^{-3}$ in the industrial areas [7]. Several factors having the greatest influence on As levels in the atmosphere are: the type of industrial facility, the type of flue gas cleaning, the type of the process involved, as well as the distance and the position of a sampling site in relation to the facility [7].

Arsenic in particulate matter poses a great threat to human health. In the second edition of the Air Quality Guidelines for Europe of the World Health Organization (WHO) published in 2000, it is indicated that a safe level of inhalation exposure cannot be recommended [4]. Three population groups are at a higher risk of exposure to arsenic: the occupationally exposed, people drinking water with abnormally high concentrations of arsenic, and people living in the close vicinity of copper smelters [4]. Several incidents of air pollution caused by arsenic from copper smelters have been described in detail around the world [5]. On entering the respiratory system, the particulate matter in the atmosphere is reported to cause a wide range of health effects including cancer and heart failures [8]. Epidemiological research shows a causal connection between the human exposure to inorganic arsenic and the occurrence of serious diseases such as cancer [9–11]. Chronic effects in humans are related to the organs involved in absorption, accumulation and/or excretion of arsenic from the organism [12].

This paper presents the results of monitoring concentrations 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

* Corresponding author. Tel.: +381 30 424 555; fax: +381 30 421 078.
*E-mail address:* ssherbula@tf.bor.ac.rs (S.M. Šerbula).

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it is under the influence of various polluting substances such as sulphur dioxide and suspended particulate matter with a high content of Cu, Zn, As, Pb, Cd, Hg, Mn and Ni [13]. The copper smelter, which is part of the Mining and Smelting Complex, is the major pollution source apart from the open pit, flotation waste heap and ore waste heap [14]. The greatest and most frequent annual exceedances of the ambient limit value (LV) are recorded for arsenic, which is why the As concentrations in the urban-industrial, suburban and rural area are analyzed in this paper. The influence of meteorological parameters (wind direction) on the pollution level around the sam-

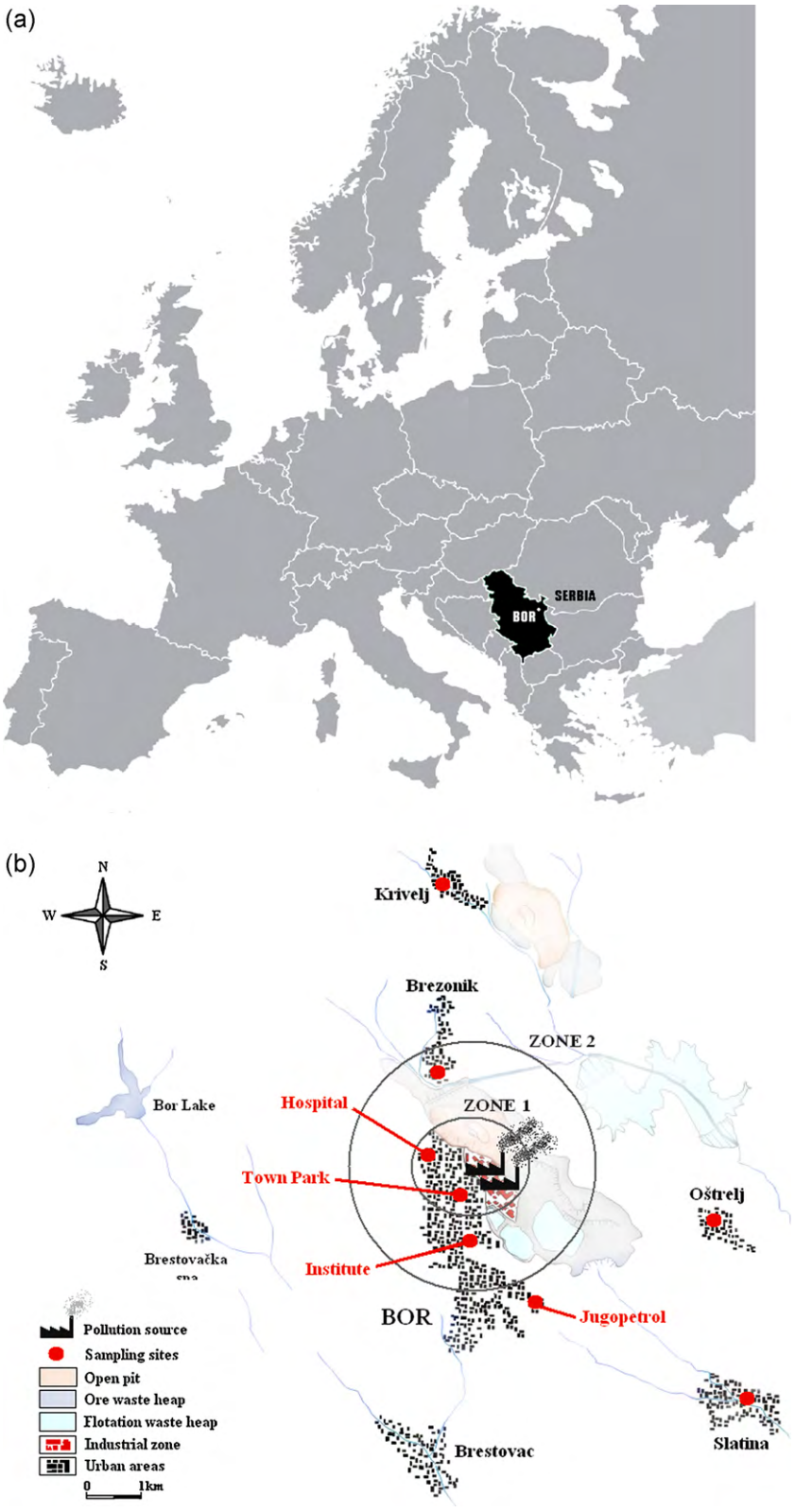


**Fig. 1.** (a) Location of Bor (Eastern Serbia) and (b) map of the study area showing sampling sites in Bor and its surroundings.

pling sites was analyzed as well as the influence of the remoteness of the sampling sites from the major pollution source.

## 2. Methodology

### 2.1. The study area

The area studied in this paper, the territory of Bor and its surroundings (60 000 inhabitants), is located in the central part of East Serbia (Fig. 1a). Approximately 40 000 inhabitants live in the town (Fig. 1b), whereas the remaining 20 000 live in 13 surrounding rural settlements [14]. This region belongs to the Danube river basin. Geographic coordinates of the town of Bor are 44°25′ N latitude and 22°06′ E longitude. The territory of Bor and its surroundings is predominantly hilly and mountainous and covers an area of 856 km$^2$. The population density is 67.2 inhabitants per square kilometre, which is below Serbian average amounting to 100 inhabitants/km$^2$.

The climate of the study area is moderately continental. The mean annual values of meteorological parameters of the study area are given in Table 1. As it can be seen, there are no significant inter-annual variations of meteorological parameters in Bor. As for the distribution of the polluting substances from the pollution source to other areas, wind is one of the more significant meteorological parameters. The Bor region is characterized by high wind frequency; however, these winds are of moderate intensity. The predominant winds in the study area are WNW (comprising 9.4–11.2% of the wind activity, including the wind calm period), NW (6.5–10.7%) and W (6.1–8.6%), as well as the E wind (6.8–8.1%), whereas the S wind is less frequent (Fig. 2).

Meteorology is an important but ancillary subject in the assessment of atmospheric pollution. Meteorological data is essential for modeling atmospheric pollution sources. Wind speed [15] and direction indicate environmental risk areas affected by major pollution sources. A good correlation has been observed for arsenic concentration with wind velocity, temperature and relative humidity [16].

### 2.2. Environmental history

The primary pollution sources in Bor are mining (surface and underground mining of copper ore) and pyrometallurgical production of copper from sulphide ores chalcopyrite ($CuFeS_2$), chalcozine ($Cu_2S$) and coveline (CuS). Besides production and processing of copper ore, pollution is also caused by ore waste heap from the open pit as well as the flotation tailings resulting from the process of copper ore benefication. Secondary pollution is caused by burning of fossil fuels and it stems from two sources. The first one is traffic, whose emissions continually contaminate the air, whereas the second source is the town heating plant, whose coal burning emissions contaminate the air during the heating season [17].

Mining in Bor started in 1902 when rich copper ore deposits, which are among the largest ones in Europe, were discovered in this region. The first smelting plant started its operation back in 1906. The present smelting plant was built during the 1961–1968 period and it is the biggest source of $SO_2$ and PM emissions in Serbia [13,18,19].

**Table 1**
Average annual meteorological data for the Bor region in the period 2003–2008.

| | 2003 | 2004 | 2005 | 2006 | 2007 | 2008[a] |
|---|---|---|---|---|---|---|
| Temperature (°C) | 10.6 | 10.8 | 10.0 | 11.7 | 11.7 | 13.2 |
| Relative humidity (%) | 71 | 74 | 75 | 73 | 68 | 64 |
| Atmospheric pressure (mbar) | 973.2 | 972.3 | 971.9 | 971.0 | 971.6 | 969.8 |
| Wind calm (%) | 62.3 | 51.7 | 54.3 | 53.6 | 49.8 | 46.9 |

[a] Monitoring conducted from January to September 2008.

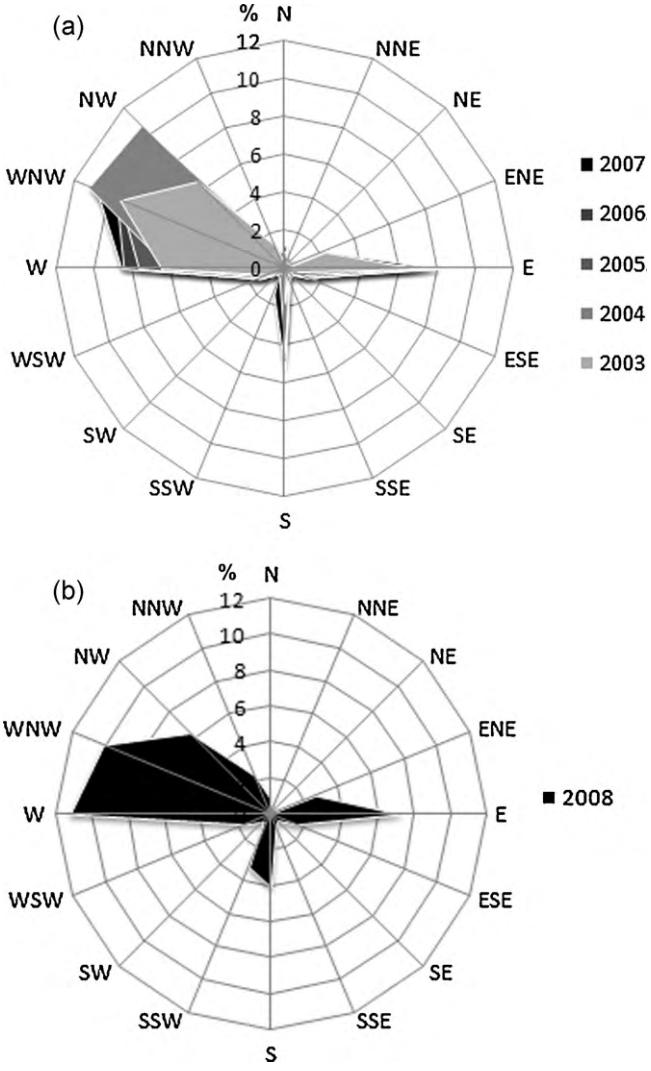


**Fig. 2.** (a) Wind rose diagram and wind frequency (%) for the period 2003–2007 and (b) wind rose diagram and wind frequency (%) for the period January–September 2008.

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 1996. 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. 3). 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 part of the Mining and Smelting Complex, was built in order to prevent air contamination with waste gases from the smelting plant. These gases contain from 3 to 7% $SO_2$ which is converted to $H_2SO_4$ in the sulphuric acid plant. The plant capacity enables treatment of less than 60% of waste gases, whereas the remaining 40% is discharged untreated into the atmosphere. In spite of dust removal from flue gases, which takes place in several stages, PM with high As and heavy metal content is discharged into the atmosphere together with $SO_2$. Apart from Cu, the usual minor constituents of sulphide ores are Fe, Pb, As, Cd, Ni, Zn, Mn as well as precious metals. Every year the copper smelter emits 5–8 kg of Zn, 6–25 kg of Pb and 5–20 kg of As per inhabitant of the Bor region. The amount of metals emitted in the atmosphere depends upon the production volume as well as upon their content

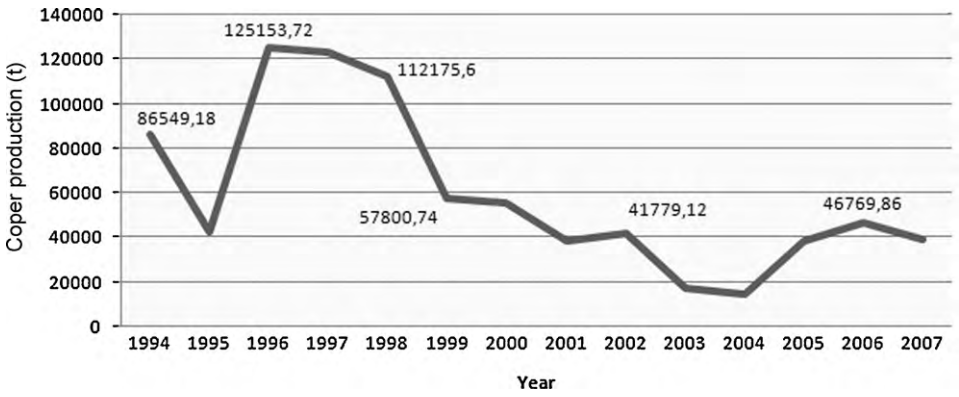


**Fig. 3.** Anode copper production from 1994 to 2007 in the Mining and Smelting Complex in Bor.

in the starting raw materials. Arsenic is present in copper ore in the form of sulphide mineral arsenopyrite (FeAsS). The ore waste heaps from open-pit operations and flotation tailings ponds represent a serious source of dust, particularly during a dry season. Wind lifts up between 1.1 and 4.5 kg $s^{-1}$ of dust from waste heaps and tailings ponds and it can be transported up to 5 km [14].

The effects of massive long-term pollution represent a regional problem and are felt in East Europe, West and Central Balkans as well as in the Danube basin.

### 2.3. Sampling sites

The sampling sites measuring pollutant concentration are unevenly arranged, depending on the following factors: type of settlement (position and number of residential units), distribution of the main traffic flows, meteorological and topographic factors of the region, industrial facilities, as well as the emission volume and type (height and speed of emission, the temperature of the emitted gases, etc.).

Air quality monitoring in the territory of Bor and its surroundings was performed continuously 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 (Fig. 1b):

*Site 1* The Town Park, located in the urban-industrial area, 800 m southwest 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. The urban-industrial area of Bor includes the old town core in the close vicinity of the industrial area and the Mining and Smelting Complex itself.
*Site 2* The Mining and Metallurgy Institute (the Institute), located 1900 m south of the urban-industrial area. The sampling site is located in a densely populated residential part of the town. In the close vicinity of the sampling site there are several schools and a recreational sports centre.
*Site 3* Jugopetrol warehouse (Jugopetrol), located 2500 m southeast of the pollution source in the suburban industrial area. The area surrounding this sampling site is poorly populated and is characterized by the highest frequency winds.
*Site 4* The Hospital is 1300 m away from the pollution source in the west–northwest direction.The site is located in the urban-industrial area next to the town hospital.
*Site 5* Brezonik, located 2000 m north of the pollution source in the suburban area.

Less frequent measurements are performed in the rural settlements of Slatina, Oštrelj and Krivelj, whereas they are rarely performed in the tourist areas of Brestovačka Spa (9 km west of Bor) and Bor Lake (17 km west–northwest of Bor) because the registered concentrations are usually within the permitted limits.

Based on the performed measurements, the paper presents typical results of the monitoring of polluting substances in the air of Bor and its surroundings. In order to demonstrate the influence of wind direction on the distribution of polluting substances, we presented the results of air monitoring for July 2006 at the sampling sites Hospital, Town Park, Jugopetrol, Krivelj and Oštrelj. A mobile sampling station was installed at the following sites for 7 days during July, except for the sampling site Oštrelj, where measurements were performed for 5 days:

- 1st–7th July 2006 at the sampling site Hospital (urban-industrial area);
- 7th–14th July 2006 at the sampling site Town Park (urban-industrial area);
- 14th–21st July 2006 at the sampling site Jugopetrol (suburban area);
- 21st–27th July 2006 at the sampling site Krivelj (rural area);
- 27th–31st July 2006 at the sampling site Oštrelj (rural area).

In order to demonstrate the influence of the remoteness of a sampling site from the pollution source on the pollution levels, monthly results were presented for 2007 at the sampling sites divided into two zones: The Town Park and Hospital (Zone 1), and Brezonik and the Institute (Zone 2), which is explained in more detail in Section 3.2. Measurements were taken during the months of March–August 2007 at the sampling sites Town Park and Hospital in Zone 1, and during January, March, May, July, September and October 2007 at the sampling sites Brezonik and the Institute in Zone 2. The sampling period was not the same for Zones 1 and 2. A comparison was made between the values of As concentration in the months during which a mobile sampling station was installed at both sampling sites in Zones 1 and 2 during 2007 (March, May and July).

### 2.4. Extraction procedure and analysis

Air quality monitoring in Bor is performed by the Mining and Metallurgy Institute in Bor in accordance with The Law on Environmental Protection of the Republic of Serbia [20]. The Mining and Metallurgy Institute issues monthly reports that combine atmospheric monitoring data with meteorological data. The reports include daily data for wind speed/direction, temperature, humidity, atmospheric pressure as well as the atmospheric contaminant data.

Measurements of the PM concentration are performed using a mobile analyzer (OSIRIS Dust Monitor AGL Air Industries, GB) and

the sampling apparatus (M-TYPE Sampler AGL Air Industries, GB). Air quality measurements are performed over 24-h periods for 7 days in a month at a particular sampling site, whereupon the mobile analyzer is moved to another location. The mobile analyzer is an optical device simultaneously measuring TSP, $PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations in the air. The mobile apparatus for suspended particle analysis consists of a sample inlet, a photometer, a collection medium and a flow regulated pump. A photometer uses the light scattering technique to determine the concentration of particulates in the 0.4–20 μm size range [13]. The air-flow rate for the OSIRIS dust monitor is 0.7 $m^3$/24 h, whereas the time resolution is 15 min. The M-TYPE Sampler collects PM on a collection medium that can be used for determining heavy metal content in the air. The air-flow rate for the M-TYPE sampler is 25–30 $m^3$/24 h. Prior to the installation of a sampling station at a particular site, a clean filtration medium is weighed on analytical scales (model "Mettler", with a precision of 0.00001 g), which enables determining the net mass of a sample. The filtration medium used for PM collection was a membrane filter "Sartorius", type 13400. 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 amount of the solution depends upon the amount of the sample. The vessel containing a subsample is further transferred to a sand bath and heated to the boiling point (until nitrogen oxide is completely removed). Then distilled water is poured into the vessel and the suspension is put back to boil. After cooling the subsample is prepared in a 100 ml flask. Next, the prepared subsample is analyzed by atomic absorption spectrometer (AAS Perkin Elmer, model 1100B). Arsenic concentration in the sample is determined by the graphite furnace technique from a working curve obtained by instrument calibration with standard solution of known concentration. The detection limit for determining arsenic by the AAS method is 2 ng $m^{-3}$. During the sampling process, the filtration medium is changed daily so that seven 24-h samples are collected after 7 days of sampling. Based on the chemical analysis of the samples, a mean monthly arsenic concentration in suspended particles is determined for a particular sampling site.

## 3. Results and discussion

Pursuant to the Law on Environmental Protection of the Republic of Serbia the ambient limit value (LV) represents the maximum permitted level of pollutant concentration in the air during a 24-h measurement or on an annual level. According to the Law, the 24-h mean limit value of the total suspended particles (TSP) for populated areas is 120 μg $m^{-3}$ [20]. Since the Law does not specify the limit value for $PM_{10}$ particles, the TSP limit value is applied. The daily mean limit value for arsenic (As) for populated areas is 6 ng $m^{-3}$, which is also applied at a monthly and an annual level [20].

The European Union has set the permitted mean annual $PM_{10}$ concentration at 40 μg $m^{-3}$, whereas the permitted daily limit value is set at 50 μg $m^{-3}$ and cannot be exceeded over 35 times during the year [21]. Furthermore, according to Directive 2008/50/EC the annual limit value for $PM_{2.5}$ particles is set at 25 μg $m^{-3}$ to be met in 2015 (target value from 2010) [21]. The European Union limit values for As concentration amount to 6 ng $m^{-3}$ on an annual level [22]. The mean annual $PM_{10}$ concentration stipulated in the WHO guidelines is 70 and 150 μg $m^{-3}$ on a 24-h level. The permitted daily and annual particulate matter concentrations for smaller size particles (up to 2.5 μm) are also defined by the WHO and amount to 35 and 75 μg $m^{-3}$, respectively [23].

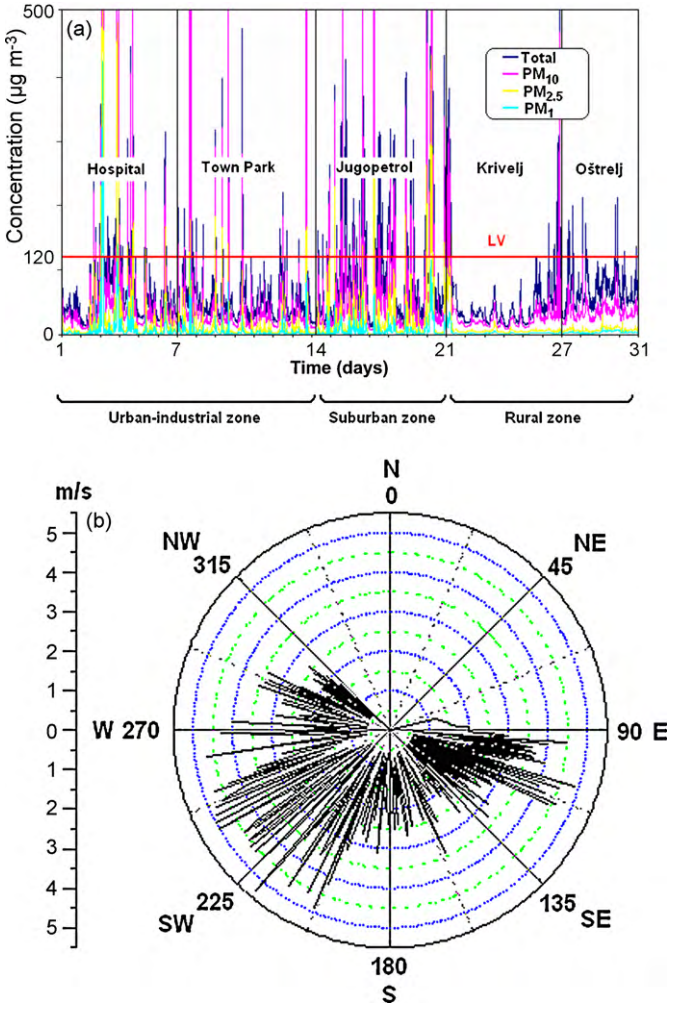


**Fig. 4.** (a) 15-min concentrations of the total suspended particulate matter and $PM_1$, $PM_{2.5}$ and $PM_{10}$ during July 2006 at the sampling sites in the urban-industrial, suburban and rural area (LV-limit value) and (b) wind rose diagram for the study period based on 15-min measurements.

### 3.1. The influence of wind direction on pollutant distribution

Fig. 4a shows concentrations of total suspended particulate matter and $PM_1$, $PM_{2.5}$ and $PM_{10}$ at five sampling sites in Bor and its surroundings during July 2006.

From Fig. 4a it can be seen that in short time intervals concentrations of the total suspended particulate matter exceeded 120 μg $m^{-3}$ at the sampling sites Hospital, Town Park, Jugopetrol, Krivelj and Oštrelj. The most frequent 15-min exceedance of the TSP daily limit value was recorded at the sampling site Jugopetrol, whereas less frequent exceedances were recorded at the sampling sites Town Park and Hospital. There were several exceedances of the limit value at the village of Oštrelj during the month of July and there was no significant air pollution at the village of Krivelj. There were several instances of increased $PM_{2.5}$ concentrations in short time intervals at the sampling sites in the urban-industrial and suburban area, unlike the rural area in which no exceedances of the limit value were recorded. The smallest size fraction in the total suspended particulate matter is comprised of the particles of diameter less than 1 μm ($PM_1$), which are present to a small extent in the total suspended particulate matter. Increased values of these particles during the month of July were recorded only at the sampling site Hospital and only during a short time interval. Since the Law on Environmental Protection of the Republic of Serbia does not set the limit values for different size fractions of ambient PM (only

**Table 2**
Average monthly concentrations of arsenic in $PM_{10}$ during July 2006 at the sampling sites in the urban-industrial, suburban and rural area in the Bor region compared with the current air quality standards.

| | Hospital | Town Park | Jugopetrol | Krivelj | Oštrelj |
|---|---|---|---|---|---|
| 2006 | 14.8 | 30.2 | 59.8 | 7.0 | 10.2 |
| LV[a,b] | 6 | | | | |
| EC[a,c] | 6 | | | | |

Results expressed as ng $m^{-3}$.
[a] Air quality standards.
[b] Regulation on limit values, methods of concentration measurements, criteria for determining the measuring sites and data records, the Official Gazette of the Republic of Serbia, 19/06.
[c] EU: Council directive 2004/107/EC.

for the TSP) the above mentioned values cannot be compared with the limit values set by law.

A one-month study shows a direct influence of the wind direction on the pollutant transport to the particular sampling sites. Fig. 4b shows the wind rose for a one-month study period, created on the basis of 15-min measurements of wind speed and direction. During the month of July, the E and ESE winds transported pollution towards the sampling sites Hospital and Town Park. Similarly, the NW and WNW winds contributed to high concentration levels at the sampling sites Jugopetrol and Oštrelj. The less frequent S wind had no considerable effect on pollutant transport towards the village of Krivelj.

A chemical analysis of the suspended particles showed an increased concentration of arsenic in the sample taken in July 2006. As shown in Table 2, the annual limit value was exceeded at all sampling sites. The highest exceedance was recorded at the sampling site Jugopetrol, then at the sampling site Town Park and at the sampling site Hospital. In the rural areas of Krivelj and Oštrelj a smaller exceedance of the daily LV for $PM_{10}$ and the annual LV for As was recorded.

The influence of wind direction on pollutant distribution from industrial facilities to populated areas has been shown in many research results [24–29]. According to the estimates of the WHO for Europe, arsenic concentrations range from 1 to 10 ng $m^{-3}$ in rural areas to 30 ng $m^{-3}$ in urban areas. Near emission sources, such as non-ferrous metal smelters and power plants burning arsenic-rich coal, concentrations of airborne arsenic can exceed 1 μg $m^{-3}$ [4]. According to the data presented in Table 2, the mean monthly As concentrations in the rural area of Bor are within the WHO guideline values, whereas the As concentration at the sampling sites Town Park and Jugopetrol is higher than the WHO estimate due to the unfavorable influence of the wind direction.

### 3.2. The influence of the remoteness of sampling sites from the pollution source on arsenic concentration

The influence of the remoteness of sampling sites from the pollution source on airborne arsenic concentrations was studied on a monthly level during 2007. The sampling sites were divided into two zones based on their remoteness from the Mining and Smelting Complex as a dominant pollution source in Bor (Fig. 1b). Zone 1 comprises the sampling sites that are about 1000 m away from the complex: Town Park (800 m) and Hospital (1300 m). Zone 2 includes the sampling sites located about 2000 m away from the complex: Brezonik (2000 m) and the Institute (1900 m). A similar division of sampling sites into zones was made by Beceiro-Gonzalez et al. [30].

#### 3.2.1. Zone 1

The mean monthly As concentrations in Zone 1 are shown in Fig. 5. During the study period the As limit value was exceeded in 5 months at the sampling site Town Park, whereas only in July the As concentration was within the limit value. In the same period exceedances of the limit value were recorded for 3 months at the sampling site Hospital. In May, the As concentration equaled the LV, whereas it was below the LV in July and August.

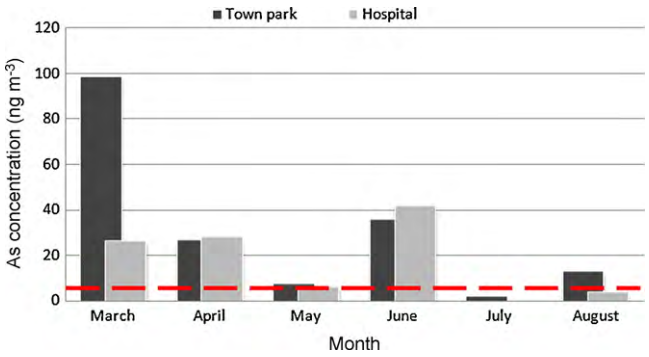


**Fig. 5.** Average monthly As concentrations during 2007 at the sampling sites in Zone 1 (dashed line-limit value).

#### 3.2.2. Zone 2

The mean monthly values of As concentration in suspended particles at the sampling sites Brezonik and Institute in Zone 2 are shown in Fig. 6. Throughout all 6 months of measurements, the As concentration values at the sampling site Institute were above the limit value in January, March, May, July, Septembar, October, whereas an increased emission was detected at Brezonik during four months in January, March, July, October. In May and September the As concentration was within the legal limit.

When the exceedances of the LV are compared in Zone 1, 8 out of 12 mean monthly arsenic concentration values were above the annual limit value, whereas at the sampling sites in Zone 2 as many as 10 out of 12 arsenic concentration values were above the annual limit value. However, since the measurements were not performed simultaneously, more precise comparisons can be made on the basis of measurements performed during March, May and July 2007 at the sampling sites in Zones 1 and 2. The average As concentrations for these three months in Zone 1 amounted to 33.8 ng $m^{-3}$ (Town Park) and 16.6 ng $m^{-3}$ (Hospital), whereas in Zone 2 their values were 14.7 ng $m^{-3}$ (Institute) and 8.9 ng $m^{-3}$ (Brezonik). Based on a 3-month average, it can be concluded that the highest As air pollution levels were recorded in the near vicinity of the Mining and Smelting Complex, that is, at the sampling sites Town Park and Hospital followed by the sampling site Institute, whereas the lowest As air pollution levels were recorded at the sampling site Brezonik. Although the sampling sites Brezonik and Hospital are located opposite to the prevailing wind direction, the As concentration was almost double at the sampling site Hospital,

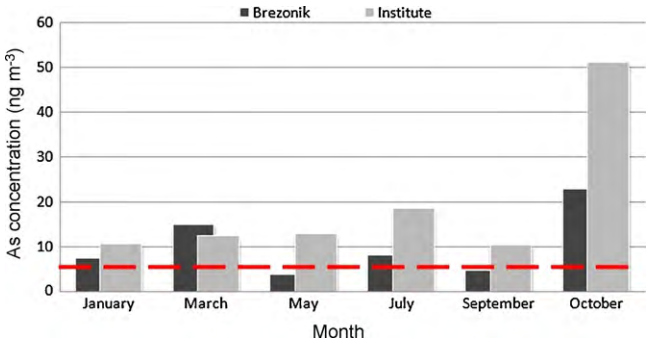


**Fig. 6.** Average monthly As concentrations during 2007 at the sampling sites in Zone 2 (dashed line-limit value).

**Table 3**
Mean annual and minimum and maximum monthly As concentrations measured at the sampling sites in the urban-industrial and suburban areas from 1994 to 2008 compared with the current air quality standards.

| | Town Park | | | Institute | | | Jugopetrol | | |
|---|---|---|---|---|---|---|---|---|---|
| | Min | Mean | Max | Min | Mean | Max | Min | Mean | Max |
| 1994 | 30.7 | 116 | 343 | 5.7 | 33.9 | 78.2 | 20.4 | 101 | 364 |
| 1995 | 15.5 | 172 | 372 | 6.4 | 51 | 104 | <2 | 75.2 | 216 |
| 1996 | 69.3 | 255 | 464 | 8.4 | 57.9 | 108 | 30.3 | 233 | 670 |
| 1997 | 39.7 | 163 | 410 | <2 | 57.2 | 124 | 26.4 | 123 | 254 |
| 1998 | 58.2 | 176 | 351 | <2 | 46.8 | 98.7 | 32.9 | 137 | 282 |
| 1999 | 5.2 | 107 | 327 | <2 | 36 | 85.3 | 3.4 | 48.3 | 106 |
| 2000 | 105 | 272 | 529 | 28.6 | 96.6 | 210 | 20 | 109 | 244 |
| 2001 | 31 | 183 | 399 | <2 | 44.6 | 96.9 | 24.3 | 154 | 414 |
| 2002 | 99.4 | 323 | 669 | 41.2 | 145 | 292 | 48.8 | 132 | 247 |
| 2003 | <2 | 44.6 | 91.2 | 10.3 | 41.4 | 71.6 | <2 | 74.5 | 137 |
| 2004 | <2 | 46.5 | 162 | <2 | 95.4 | 356 | <2 | 64.4 | 189 |
| 2005 | <2 | 29.3 | 149 | 1.9 | 12 | 36.1 | <2 | 30.7 | 94.2 |
| 2006 | <2 | 38.9 | 170 | <2 | 15.5 | 75.7 | <2 | 41.3 | 148 |
| 2007 | 1.6 | 25 | 98.8 | 4.8 | 21 | 51.1 | 7.8 | 31.8 | 71.3 |
| 2008[a] | <2 | 18.9 | 33.6 | 3.8 | 14.8 | 32.9 | <2 | 50.9 | 179 |
| LV[b,c] | 6 | | | | | | | | |
| EU[b,d] | 6 | | | | | | | | |

Results expressed as ng m$^{-3}$.
[a] Monitoring performed from January to September 2008.
[b] Air quality standards.
[c] Regulation on the limit values, methods of concentration measurements, criteria for determining the sampling sites and data records, the Official Gazette of Republic Serbia, 19/06.
[d] EU: Council directive 2004/107/EC.

which is closer to the pollution source. Although the sampling sites Town Park and Institute are both exposed to low intensity winds the As concentrations recorded at the sampling site closer to the pollution source (Town Park) were considerably higher than the ones recorded at the sampling site Institute.

There have been considerable exceedances of the annual LV for arsenic in the territory of Bor for many years. Table 3 shows data for the mean annual as well as the minimum and maximum monthly values of As concentration at the sampling sites Town Park, Institute and Jugopetrol obtained from the annual reports on monitoring of polluting subtances in the air of Bor during the 1994–2008 period [18]. In the past 15 years not a single mean annual arsenic concentration recorded at the sampling sites Town Park, Institute and Jugopetrol has been within the LV (6 ng m$^{-3}$). Two maximum monthly As concentrations were measured at the sampling sites Town Park in 2002 (669 ng m$^{-3}$) and Jugopetrol during 1996 (670 ng m$^{-3}$).

During the study period, from January 2003 to September 2008, in the urban-industrial and suburban areas, the monthly As concentrations in the Town Park ranged from below detection limit (<2 ng m$^{-3}$, recorded in the 2003–2006 period and 2008) to a maximum of 170 ng m$^{-3}$ (2006). The monthly As concentrations at the Institute were in the range from <2 ng m$^{-3}$ (during 2004 and 2006) to a maximum of 356 ng m$^{-3}$ (2004). The monthly As concentrations at the sampling site Jugopetrol were in the range from <2 ng m$^{-3}$ (during the 2003–2006 period and 2008) to a maximum of 189 ng m$^{-3}$ (2004).

In addition to monitoring air quality at the sampling sites in the urban-industrial and suburban area, air monitoring was also performed in rural areas from 2003 to 2008. During the observed period, the mean annual As concentrations at the sampling sites Slatina, Oštrelj and Krivelj were within the LV. However, increased As concentrations were recorded for certain months in the villages of Slatina (37.9 ng m$^{-3}$) in February 2007, Oštrelj (43.8 ng m$^{-3}$) in November 2006, and Krivelj (82.3 ng m$^{-3}$) in February 2007. By comparing the average annual and maximum monthly As concentration in the urban-industrial and suburban area (shown in Table 3) with the rural concentration values (not shown), a conclusion can be drawn that the pollution levels are higher in the urban-industrial and suburban area, i.e. sampling sites Town Park, Institute and Jugopetrol.

Fig. 7 shows the mean annual concentrations for arsenic at the sampling sites Town Park, Institute and Jugopetrol during the period 1994–2008. The highest mean annual value amounting to 323 ng m$^{-3}$ at the sampling site Town Park was recorded in 2002. It represents the maximum recorded value in Bor for the last 15 years. At the sampling site Institute a maximum concentration of 145 ng m$^{-3}$ was also recorded in 2002, whereas the highest limit value exceedance at the sampling site Jugopetrol amounting to 233 ng m$^{-3}$ was detected in 1996.

The Town Park sampling site is located in a densely populated area with high traffic volume. However, since 2002, when the highest arsenic concentration was recorded, up to now there has been an obvious falling trend in annual concentration values. During the 1994–2002 period ore production and treatment reached the highest point, after which comes a period of production decline. Consequently, there has been a drop in the emission of polluting substances, which is not sufficient as the arsenic concentration is still 4–7 times higher than the limit value. The As levels are comparable to the values observed in Santiago (Chile) in the period 1997–2003 showing a clear decrease in concentrations with time, which seems highly consistent with the decontamination plan hav-

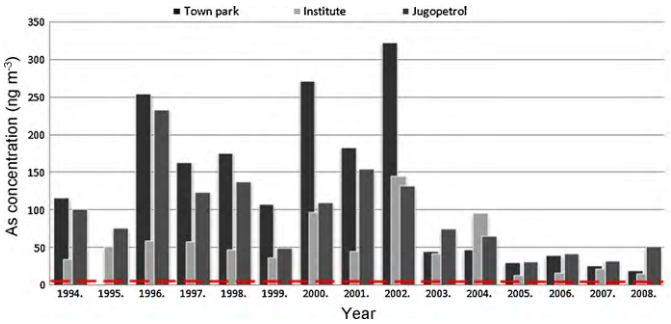


**Fig. 7.** Mean annual arsenic concentrations recorded at sampling sites Town Park, Institute and Jugopetrol from 1994 to 2008 in the urban-industrial and suburban area (dashed line-limit value).

ing been implemented in Central Chile since 1998 [31,32]. The Institute sampling site is located at the most densely populated residential area of the town. The mean annual As concentrations at this site are the lowest compared to the sampling sites Town Park and Jugopetrol but they are still above the limit value. The area around the sampling site Jugopetrol is poorly populated but it is significant because of the fact that it is exposed to high-frequency winds (WNW and NW). The 15-year average As concentrations at the sampling sites Town Park, Institute and Jugopetrol amount to 131.4, 51.3 and 93.7 ng $m^{-3}$, respectively. The immediate vicinity of the sampling site Town Park to the pollution source and the position of the sampling site Jugopetrol along the prevailing wind direction can account for high levels of As air pollution at these sampling sites as compared to the ones recorded at the sampling site Institute. The wind being the most significant means of pollutant transport plays a crucial role in the distribution of arsenic in suspended particles [33]. In addition, the distance from the facility emitting polluting substances into the atmosphere plays a decisive role. Generally, concentration levels are highest in the immediate vicinity of the facility, with near background levels being reached 2–3 km apart [7].

## 4. Conclusion

Situated in the close vicinity of the urban area of the town of Bor, the Mining and Smelting Complex is the major pollution source, emitting particulate matter and sulphur dioxide into the atmosphere of Bor and its surroundings. Air quality measurements were taken at the sampling sites in the urban-industrial, suburban and rural area, from 2003 to 2008.

The predominance of a particular wind direction determines the distribution of PM and As. A one-month data analysis shows a direct influence of the wind direction on the pollutant transport to the particular sampling sites. Due to unfavorable wind conditions, the areas around the sampling sites Town Park and Hospital (E and ESE wind direction) are considered pollution risk areas. As far as suburban settlements are concerned, the area around the sampling site Jugopetrol is an endangered area and among the rural settlements within the municipality, the village of Oštrelj is especially endangered by pollution. The village of Krivelj is located in the direction of a less frequent S wind, which accounts for a lower pollution level in this area.

The influence of the remoteness of sampling sites from the pollution source was studied on a monthly level during 2007. The sampling sites were divided into two zones based on their remoteness from the Mining and Smelting Complex. Although more frequent exceedances of the limit value were observed in Zone 2, the mean 3-month arsenic concentrations recorded at the sampling sites Brezonik and Institute in Zone 2 were lower than the mean arsenic concentrations at the sampling sites Town Park and Hospital in Zone 1.

During the last 15 years not a single mean annual As concentration at the sampling sites Town Park, Institute and Jugopetrol in Bor has been within the annual limit value. The maximum arsenic concentrations in the period 1994–2008 were recorded in 1996 and 2002 at the sampling site Jugopetrol and Town Park, respectively. The recorded values were more than 100 times higher than the limit value. The immediate vicinity of the sampling site Town Park to the pollution source as well as the position of the sampling site Jugopetrol along the prevailing wind direction caused high As air pollution levels, as compared to the sampling site Institute. When average annual and maximum monthly As concentrations are compared, it can be concluded that the level of pollution in urban-industrial and suburban areas is higher than the level of pollution in rural area. In toxicological risk assessment it should be taken into consideration that the inhabitants of Bor are simultaneously exposed to other types of pollutants, which also increases the health risk. High concentrations of sulphur dioxide, heavy metals and their compounds in suspended particles are constantly present in the atmosphere of Bor [18,19].

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