

ANALYSIS OF AIR POLLUTION CAUSED BY PARTICLE MATTER EMISSION FROM THE COPPER SMELTER COMPLEX BOR (SERBIA)

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ABSTRACT

The main aim of this paper is to present analyses of temporal variations of particulate matter in Bor (Serbia) influenced by copper production at the Copper Smelter Complex Bor. Particulate emissions are of concern because the presence of fine particles (PM_{2.5} – particles with diameter less than 2.5 µm) and ultrafine particles (PM_{0.1} – particles with diameter less than 0.1 µm) assume higher risk for human health. Such particles can penetrate deeper into respiratory organs and, at the same time, a probability for such penetration and deposition in the respiratory system is greater. The analysis is based on comparison of SO₂ and PM measurements at several locations in the area of Bor town in the close vicinity of Copper Smelter. PM concentrations were highly correlated with sulfur dioxide and inversely correlated with local wind speed during pollution episodes. Presented results indicate that the dominant source of coarse and fine particles in Bor town is the Copper Smelting Complex Bor. The most significant factors for particulate matter distribution are meteorological parameters of wind speed and direction. It was found that exceeding of daily limit values of concentrations of PM₁₀ (50 µg/m³) usually occurs due to very high concentrations in a period of several hours during the day.

Key words: *sulfur dioxide, particulate matter (PM), respiratory particles, air pollution, monitoring*

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INTRODUCTION

The Municipality of Bor is located in a mountainous and forest area in the southeastern part of Serbia, close to the Bulgarian and Romanian borders (Figure 1). It has a total population of 65,000. The area has been the major centre for mining and processing of copper and other precious metals for almost a century. Air pollution is perceived as the main environmental problem in the Bor region. The main source of air pollution with SO₂ gas, heavy metals in PM and aero sediments is the Copper Smelter Plant within the RTB Bor Company (Copper Mining and Smelting Complex) which has been in operation for more than 100 years.

Figure 1. Map of the eastern Serbia with the location of the Bor Municipality area

A typical pyrometallurgical copper smelting process includes four steps: roasting, smelting, concentrating, and fire refining. Ore concentrate is roasted to reduce impurities, including sulfur, antimony, arsenic, and lead. Smelting of roasted ore concentrate produces matte, a molten mixture of copper sulfide (Cu₂S), iron sulfide (FeS) and some heavy metals. By converting of matte, the high-grade 'blister' copper of 98.5 to 99.5 % is recovered. Typically, blister copper is then fire-refined in an anode furnace, cast into 'anodes', and sent to the Electrolytic Refinery for further impurity elimination. Emissions from Copper Smelter are principally particulate matter and sulfur oxides (SO_x). Fugitive emissions are generated during material handling operations. Roasters, smelting furnaces, and converters are sources of both particulate matter and SO_x. Copper and iron oxides are the primary constituents of particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, mercury, and zinc, may be also present along with metallic sulfates and sulfuric acid mist. Fuel combustion products also contribute to the particulate emissions from multiple hearth roasters and reverberatory furnaces. Gas effluents from roasters usually are sent to the electrostatic precipitator (ESP) or spray chamber/ESP system or combined with the smelter furnace gas effluent before particulate collection. Overall, the hot ESP system removes only 20 to 80% of total particulate present in gas. Cold ESP system may remove more than 95 % of total particulate. Particulate collection systems for smelting furnaces are similar to those for roasters. In the standard Pierce-Smith converter (like in the Copper Smelter Bor), the off-gases are treated in ESP system to remove particulate matter, and in the Sulfuric Acid Plant to remove SO₂. Control of SO₂ from the Smelter Plant is commonly performed in the Sulfuric Acid Plant.

The technology for copper production in this Smelter Plant is outdated (classic pyrometallurgy with melting in furnaces and utilization of SO₂ gas in production of H₂SO₄ with relatively small degree of utilization <60%) which leads to the environmental pollution from higher concentrations of SO₂ and particulate matter [1] as well as aero sediments PM > PM₁₀. Ore melted in the Copper Smelter Plant in Bor is of chalcopyrite-pyrite type with the increased contents of arsenic which is found in the form of FeAsS and Cu₃AsS₄. The oxidation roasting and melting of such mineral forms results in increased heavy metals oxides and SO₂ gas which in certain quantities contaminate the environment [2]. Reportedly, 170000 to 250000 t of SO₂ and 1300 t of particulate contaminated with heavy metals and up to 1000 t of arsenic, 500 t of lead, 2500 t of zinc and 1.6 t of mercury are emitted to the atmosphere each year [1, 2].

In the Copper Smelter Plant in Bor there are two factory smokestacks (S1 and S2 as shown in Figure 2), the height of one is 120 m (D=3 m) for the Smelter Plant off-gasses with contents up to 1% SO₂ and, the

other of 150 m ($D=3.5$ m) for gasses when the Sulfuric Acid Plant is out of operation (gases resulting from the roasting procedure in fluo-solid reactor mixed with converter gases) with SO_2 content of 5–6% in the gas. The parameters that characterize the emissions from the Copper Smelter are given in Table 2. On the average, the Sulfuric Acid Plant is out of operation for about 3-6 months in a year. As a consequence, a large amount of sulfur dioxide is discharged directly into the atmosphere, together with toxic metals [2]. Both smokestacks are situated in the immediate vicinity of the urban settlement at a distance less than 500 m from the old urban center with numerous vital functions of the town. In addition, airborne dust resulting from the Open Pits and surrounding waste heaps which contain heavy metals, contributes to the air pollution of the area. Taking into account the location of the industrial complex and dominant wind directions, these pollutants are spread over Bor town and the surrounding area. Therefore, the inhabitants of Bor town are exposed to high levels of air pollution, which can pose serious risks to their health [3-6].

SO_2 is one of the most important pollutants of the environment and mostly originates from oxidation of sulfur compounds. Anthropogenic emission of SO_2 results from burning the fossil fuels (coal and heavy oils) or smelting of sulfide ore concentrates (most frequently Cu, Pb, and Zn ores). SO_2 is an irritant gas which causes breathing problems when people are exposed to its high concentrations. Although sulfur is useful for plants in small concentrations, atmosphere pollution with SO_2 gas due to its higher concentrations negatively affects plants and the impact size depends on its concentration. Smoke and particulate are nearly always associated with SO_2 and can cause difficulties in data interpretation and health risk assessments. Therefore, there is uncertainty associated with long term (24 hours plus) epidemiological studies. There is a possibility that the adverse effects of sulfur dioxide are really the effects of particulate or other associated substances. Due to the certain negative effect of SO_2 in the atmosphere, European Union limits its mass contents: limit per hour for protection of human health is $350 \mu\text{g}/\text{m}^3$, not to be exceeded more than 24 times per calendar year; daily limit for protection of human health is $125 \mu\text{g}/\text{m}^3$, not to be exceeded more than three times per calendar year; and annual limit for protection of ecosystems is $20 \mu\text{g}/\text{m}^3$ [7, 8].

Suspended particles are one of the most important ambient air pollutants which adversely affect human health. Prolonged exposure to PM particles often cause respiratory and cardiovascular diseases and increase mortality [3-6]. For the purpose of protection of human health EU has introduced two limitations for PM_{10} which should be implemented in two periods: the first one at the beginning of 2005 and the second one in 2010. The limit values for 2005 and 2010 are as follows: daily limit of $50 \mu\text{g}/\text{m}^3$ not to be exceeded more than 35 times per calendar year and annual limit of $40 \mu\text{g}/\text{m}^3$. The limits, which will be implemented after year 2010, are: daily limit of $50 \mu\text{g}/\text{m}^3$, not to be exceeded more than seven times per calendar year, and annual limit of $20 \mu\text{g}/\text{m}^3$ [7,8].

Figure 2. Map of the Bor Municipality area with measuring points (1. Park, 2. Jugopetrol, 3. Institute, 4. Brezonik, 5. Hospital) and location of the Copper Smelter smokestacks (S1, S2)

SAMPLING SITES

In the Mining and Metallurgy Institute Bor, Department for Chemical and Technical Control (CTC), there is a group for measuring the meteorology parameters and air quality control. The results presented in this paper

cover some experimental programs performed by CTC during 2004-2009 at 5 locations (locations 1-5 in Figure 2).

The monitoring of sulfur dioxide, particulate, and toxic metals has been carried out for many years in Bor. However, the methods and equipment are old and do not fully comply with the modern requirements for monitoring the atmospheric pollution. Since beginning of 2004, the new, suitable atmospheric monitoring equipment has been put into operation. The equipment, used during the experimental programs, consists of three fixed stations for measurement the ambient sulfur dioxide concentrations, one mobile station and two fixed station for measurement the ambient particulate (PM). The fixed stations were installed close to the Copper Smelter Complex in positions downwind from two prevailing wind directions (measuring points Park, Jugopetrol and Brezonik, as shown in Figure 2).

The prevailing winds are from west-northwest and therefore tend to carry away the pollution from the main population centers (the wind rose diagram in the time interval from 1998 to 2008 is also shown in Figure 2). During rainy periods, typical east or southeast winds are of more concern. Low or zero wind conditions occur regularly (more than 50% of time). Light and variable winds are likely to cause very high localized concentrations of pollutants.

Distances between measuring points and Copper Smelter Plant smokestacks are given in Table 1.

Measuring point 1 Park – Fixed station was placed downwind of the easterly prevailing wind. This location is within the Central Park in Bor. The site is located 650 m west from the Copper Smelter Plant. A dense population (mainly high-rise) is directly downwind from the Copper Smelter Plant during east winds. A large effect on the local environment is often noted at this location – burning eyes, throat, taste of sulfur dioxide is experienced. This station is also equipped with meteorological instrumentation.

Measuring point 2 Jugopetrol – Fixed station was placed downwind of northwesterly prevailing wind. The site is located 2 km south/southeast from the Copper Smelter Plant downwind during northwesterly winds. In the vicinity of the measuring point (1 km northeast) is the city dump. Although, the site appears to be in an area of low population density, some small villages are nearby (Ostrelj, Slatina, Brestovac), so there is an affected population.

Measuring point 3 Institute – Fixed station was placed downwind of northeasterly prevailing wind. The site is located about 2 km south/southwest from the Copper Smelter Plant downwind during northeasterly winds. In the vicinity of the measuring point is Foundry Castings of copper alloys, with the device for sanding. A dense population is directly downwind from the Copper Smelter Plant during northeasterly prevailing winds. This station is also equipped with meteorological instrumentation.

Measuring point 4 Brezonik – Fixed station was placed downwind of southeasterly prevailing wind. The site is located about 2 km north/northwest from the Copper Smelter Plant downwind during southeasterly winds. In the vicinity of the measuring point is Open Pit. Although the site appears to be in an area of low population density, some small villages are nearby (Veliki Krivelj, Brezonik), so there is an affected population.

Measuring point 5 Hospital – Fixed station was placed downwind of easterly prevailing wind. This location is within the town hospital. The site is located 1 km west from the Copper Smelter Plant. A dense population (mainly high-rise) is directly downwind from the Copper Smelter Plant during east winds. A large effect on

the local environment is often noted at this location – burning eyes, throat, taste of sulfur dioxide is experienced.

Table 1. The distances between measuring points and Copper Smelter Plant smokestacks S1 and S2

Table 2. The parameters that characterize the off-gases emissions from the Copper Smelter Plant

EXPERIMENTAL

The automatic measuring stations for real-time determination of SO₂ concentration have been installed at three measuring points (points 1, 2 and 4 in Figure 2). These instruments provide continuous and reliable measurement of SO₂ in ambient air. Data transfer from measuring stations to the control center in Mining and Metallurgy Institute Bor is carried out every 15 min. The content of SO₂ in the air is determined by UV-fluorescence after excitation to higher energy level and light emission measurement. This method enables automatic determination of SO₂ contents in ambient air according to ISO 10498 Standard. The reference method for sulfur dioxide measurement is that described in EN 14212:2005 'Ambient air quality - Standard method for measurement the sulfur dioxide concentration by ultraviolet fluorescence' [8]. Using UV-fluorescence method, the analyzers perform automatic measuring of SO₂ in ambient air in a concentration range from 0 to 10 000 µg/m³ with linearity of ±1% and minimum detectable limit (2σ) of 0.001ppm (< 3µg/m³). The analyzers were calibrated with standard gas mixtures (200 ppb) from certificated gas cylinders at least once in every three weeks. The calibration gas mixtures in cylinders are checked every year by an independent audit.

At two measuring points (points 2 and 5 in Figure 2) measurements were carried out using the standard UK 8-port samplers. Sulfur dioxide is measured by air passing through a dilute-acid solution of hydrogen peroxide (classical acidimetric method [9-12]). Sulfur dioxide reacts with hydrogen peroxide to form sulfuric acid, which is titrated with a standard alkaline solution, and sulfur dioxide concentration is calculated using the standard calculation (British Standard 1747 and ISO 9835 are reference documents for this technique). The limit of detection for the technique is less than 0.01 ppm. The results are comparable with those obtained by measurements of automatic analyzers carried out in parallel [13].

The reference method for sampling and measurement of PM₁₀ is that described in EN 12341:1999 'Air Quality - Determination of the PM₁₀ fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods'. The reference method for the sampling and measurement of PM_{2,5} is that described in EN 14907:2005 'Standard gravimetric measurement method for determination of PM_{2,5} mass fraction of suspended particulate matter'.

The concentrations of particulate matter presented in this paper were monitored using portable, direct reading, airborne particle analyzers OSIRIS (at measuring points 1,2,3 and 5 during 2004 - 2006) and GRIMM EDM180 (at measuring point 1 during 2009). These devices were designed for simultaneous real time measurement of PM (PM₁₀, PM_{2,5} and PM₁) according to the European Standards EN 12341 (for PM₁₀), and EN 14907 (for PM_{2,5}). Detection limit (2σ) for technique is less than 0.1 µg/m³ within particle size range (diameter) between 0.5 to 20µm. PM₁ values were also reported, although no EN standard currently exists. Also, the concentrations for PM₁₀ are monitored using BAM1020 ambient particulate concentrations analyzer

(measuring point 4 during 2007-2008). This analyzer is using beta ray attenuation method according to the U.S. EPA Designations PM₁₀: FEM (EQPM-0798-122), PM_{2.5}: Class III FEM, (EQPM-0308-170) with lower detection limit (2σ) less than 4.0 $\mu\text{g}/\text{m}^3$ and standard range between 0 to 1000 $\mu\text{g}/\text{m}^3$.

All analyzers have a possibility of automatic calibration (zero), definition of arbitrary interval sampling, averaging and saving the measured values, as with the local keyboard, and indirectly through the remote supervisory computer. The monitoring data from real time monitors have been available originally based on 15-min. averages. In order to provide necessary working conditions, the analyzers are placed within a closed container that is air-conditioned (18 to 20 °C) and has a stable power supply. The analyzers operate in accordance with the manual for the equipment. Maintenance schedules for replacement of consumable parts, diagnostic checks, and equipment fully follow the manufacturer recommendations. Routine and non-routine service visits are documented with detailed descriptions as well as the results of analyzer tests or calibrations performed during monitoring programs. Data validation was followed by checking in three-month intervals to ensure that they are reliable and consistent. For calculation of daily averages, minimum 80% of 15-min averages were required; otherwise the value was considered as missing. Any suspicious data in the original 'row' data set, such as large spikes or spurious high concentrations were fully investigated. Hourly and daily averages, used for statistical considerations, were calculated from 15-min averages. Sulfur dioxide and PM mass concentrations divided into annual, winter (October-March) and summer (April-September) averages are gathered in Table 3.

Table 3. Average daily concentration, standard deviation (SD) and ranges of SO₂, PM₁₀, PM_{2.5} and PM₁ at selected measuring locations during measuring periods

RESULTS AND DISCUSSION

Emissions from the Copper Smelter are principally particulate matter and sulfur oxides. As it was mentioned, smoke and particulate are nearly always associated with SO₂ and can cause difficulties in data interpretation. Measurements of concentration of sulfur dioxide and respiratory particles were carried out in the times when the Copper Smelter was in operation, as well as in the times when the Copper Smelter did not work continuously. Typical time series with mass concentrations of SO₂ and PM₁₀ during the time when the Copper Smelter was out of operation are presented in Figure 3 (measuring point 1 Park). Typical time series with mass concentrations of SO₂ and PM₁₀ during the time when the Copper Smelter was in operation were present in Figure 4, 5 and 6 (measuring point 1, 5 and 4 respectively).

Strong fluctuations of daily average mass concentrations can be observed. Especially SO₂ and PM₁₀ were characterized by strong amplitudes mostly related to changes in weather (wind speed and direction) conditions. This phenomenon is typical in conditions with the wind speed less than 2 m/s and such wind direction that air pollution can be detected at the measuring points (as shown in Figures 3-5.). Excursions over daily limit values of concentrations of SO₂ and PM₁₀ usually occurred due to very high concentrations in a period of several hours during the day (as shown in Figure 4).

According to the data present in Table 3, annual average values range from 44 to 228 $\mu\text{g}/\text{m}^3$ for SO_2 , 32.7 to 53.0 $\mu\text{g}/\text{m}^3$ for PM_{10} , 14.0 to 23.7 $\mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$ and 5.7 to 9.6 $\mu\text{g}/\text{m}^3$ for PM_1 . Variation of daily means can be demonstrated by variation coefficients, i.e. the standard deviation divided by the mean. The variability of SO_2 mass concentrations at measuring locations is very different, between 91 % and 212 %. The variability of PM mass concentrations at measuring locations changes between 57 % and 125 % for PM_{10} , between 51% and 105 % for $\text{PM}_{2.5}$ and between 72 % and 108 % for PM_1 .

Table 4. Production of sulfuric acid and copper cathodes in the Copper Smelter Plant (2004 – 2008)

Based on comparisons of these results with the data of sulfuric acid and copper cathodes production shown in Table 4, we made a conclusion that emissions of these pollutants from the Copper Smelter Bor were the dominant cause of air pollution episodes at almost all measuring points. However, the concentrations of SO_2 were clearly higher at locations 1, 2 and 5 compared to concentrations at locations 3 and 4. This can be explained by the fact that these measuring points are of the dominant wind direction relative to the Copper Smelter. Also, measuring points 1 and 5 are at half the distance from the Copper Smelter smokestacks relative to the other measuring points, and the values of SO_2 concentration at these measuring points are expected to be higher. The average annual concentrations of SO_2 measured at measuring points 1, 2, and 5 are the largest in the Republic of Serbia. These values are at least two times higher than those measured in Kostolac and Belgrade for the last few years.

The average annual concentrations of PM_{10} measured in Bor (32.7 to 53.0 $\mu\text{g}/\text{m}^3$) appear to be at the same level of PM_{10} concentrations measured in 2001 in selected European cities [14], or even lower [15, 16]. The average annual concentrations of PM_{10} were slightly higher at measuring points 2, 4 and 5 compared to concentrations at measuring points 1 and 3. At the measuring points 4 and 5, major seasonal changes in concentrations of PM_{10} can be detected relative to the other measuring points. The concentrations of PM_1 were very similar at all locations.

The changes in SO_2 and PM_{10} concentrations at measuring point 1 (Park) were simultaneous during almost the whole periods of SO_2 pollution episodes when the Copper Smelter Bor was in operation (as shown in Figure 4). The same conclusion can be made for changes of PM_{10} , $\text{PM}_{2.5}$ and PM_1 concentrations. Very little difference was found between the average concentrations for the summer and winter seasons. These results imply that the area in the vicinity of the measuring point 1 is influenced by the same source of pollution, in this case the Copper Smelter Bor.

The changes in SO_2 and PM_{10} concentrations at measuring point 2 (Jugopetrol) were simultaneous during almost the whole measuring period. This measuring point is more than 2 km away from the Metallurgy Complex, so the influence of other sources of pollution (such as the city dump and ore waste heap) in some periods is dominant. The same conclusion can be made for mass concentrations of $\text{PM}_{2.5}$ and PM_1 .

The changes in SO_2 and PM_{10} concentrations at measuring point 3 (Institute) are not so simultaneous as at the measuring points 1 and 2. Anomalies can be frequently seen in the second half of year. Very little difference was found between the average concentrations for the summer and winter seasons. This measuring point is not on the dominant direction of the wind from the Metallurgy Complex, which is the main source of SO_2

and particulate pollution, so the influence of other sources of pollution (such as traffic or Foundry Castings) in these periods is dominant. Mass concentrations of PM₁₀, PM_{2.5} and PM₁ have a similar trend.

The changes in SO₂ and PM₁₀ concentrations at measuring point 4 (Brezonik) do not have the same trend during the year, the trend is even inverted in some periods. This measuring point is not on the dominant direction of the wind from the Metallurgy Complex, so the influence of other pollution sources (such as traffic, ore waste heap or individual fireplaces) in these periods is dominant. This measuring point expressed strong influence on individual fireplace usage during the winter period, so that in this period, the measured concentrations were higher than those during the summer (relative change in PM₁₀ concentrations of 39% during 2007, and 33% during 2008). Nevertheless, the influence of the Metallurgy Complex on air pollution at this measuring point should not be neglected, since it is dominant in some periods.

The changes in SO₂ and PM₁₀ concentrations at measuring point 5 (Hospital) are proportional during the whole measuring period when the Copper Smelter Bor is in operation (as shown in Figure 5). The same conclusion can be made for mass concentrations of PM₁₀, PM_{2.5} and PM₁. The geographical position of this measuring point is such that, in winter, the winds that blow mostly from the north/northwest contribute to the reduction of PM pollution relative to the summer period when the frequency of winds from these directions is lower (relative change in PM₁₀ of 48%, in PM_{2.5} of 30% and in PM₁ concentrations of 14% during 2006). This measuring point is in the vicinity of the Copper Smelter Bor, hence it is the dominant source of air pollution.

Figure 3. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 1 (Park) in the time interval when the Copper Smelter Bor was out of operation

Figure 4. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 1 (Park) in the time interval when the Copper Smelter Bor was in operation

Figure 5. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 5 (Hospital) in the time interval when the Copper Smelter Bor was in operation

Figure 6. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 4 (Brezonik) during 2007 in the time interval when the Copper Smelter Bor was in operation

CONCLUSIONS

Monitoring of mass concentrations of PM is very important from the aspect of risk assessment to human health. Measurements of concentration of PM (PM₁₀, PM_{2.5} and PM₁) at the measuring sites in the urban area of Bor lead to the following conclusions:

- Presented results indicate that the dominant source of coarse particles in Bor town is the Copper Smelting Plant Bor. The most significant factors for the distribution of pollutants are meteorological parameters of wind speed and direction.
- Exceeding of daily limit values of PM₁₀ concentrations (50 µg/m³) usually occur due to very high concentrations in the period of several hours during the day. This is in good correlation with the

detected values of SO₂ concentrations. Therefore, while most of the particle pollution is below the limit value, large pollution intensity for a few hours, one or more times during the day, can lead to an exceedance of the daily average limit value.

- The share of PM₁₀ particles in TSP (Total Suspended Particles) is generally more than 70%, so that a PM₁₀ level exceeding the limit value is usually observed when the TSP pollution is above its limit value.

Very extensive research is ongoing in order to correlate PM results with meteorological parameters and find relationships among PM and other pollutants. Further work in this area should focus on prediction of sulfur dioxide and particles concentrations in real time, in order to provide short-term forecast of air quality.

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Table 1. Distances between measuring points and Copper Smelter Plant smokestacks S1 and S2

No.	Measuring location	Altitude [m]	Distances from smokestacks S1,S2	
			R1[m]	R2[m]
1	Park	370	650	650
2	Jugopetrol	382	2500	2500
3	Institute	386	2142	2032
4	Brezonik	400	2000	2000
5	Hospital	408	1000	1180

Table 2. Parameters that characterize the off-gases emissions from the Copper Smelter Plant

Smokestack S1			Smokestack S2		
Parameter	Min	Max	Parameter	Min	Max
Gas flow (m ³ /h)	90000	180000	Gas flow (m ³ /h)	0	300000
SO ₂ content (%)	0.1	0.9	SO ₂ content (%)	0.5	8
Temperature (°C)	150	300	Temperature (°C)	100	300
Dust content (g/m ³)	0.3	3	Dust content (g/m ³)	0.05	0.8

Table 3. Average daily concentration, standard deviation (SD) and ranges of SO₂, PM₁₀, PM_{2.5} and PM₁ at selected measuring locations during measuring periods

Measuring location	SO ₂ (µg/m ³)		PM ₁₀ (µg/m ³)		PM _{2.5} (µg/m ³)		PM ₁ (µg/m ³)	
	Mean (SD)	Max/Min	Mean (SD)	Max/Min	Mean (SD)	Max/Min	Mean (SD)	Max/Min
1. Park								
Year (2004)	86 (78)	914/11	41.1 (39.2)	204.5/2.8	22.7 (24.2)	123.7/1.4	9.6 (9.7)	89.8//0.6
Winter (2004)	68 (48)	892/11	40.7 (41.6)	204.5/2.8	23.0 (23.4)	88.9/1.4	9.9 (9.3)	36.6/0.6
Summer (2004)	103 (102)	914/11	36.6 (37.0)	138.1/12.5	22.4 (34.2)	123.7/7.7	7.5 (27.6)	89.8/2.9
Year (2006)	227 (292)	2441/10	32.7 (36.4)	204.3/1.9	14.0 (14.6)	68.5/1.2	5.7 (5.7)	27.2/0.4
Winter (2006)	255 (355)	2441/14	32.6 (47.5)	204.3/1.9	16.1 (18.1)	68.5/1.2	6.8 (7.0)	27.2/0.4
Summer (2006)	209 (246)	1370/10	41.7 (15.1)	77.7/17.7	10.6 (4.3)	49.3/4.6	3.5 (1.6)	6.9/1.0
Year (2009)	112 (157)	777/3	32.4 (16.3)	111.5/3.0	23.7 (13.5)	96.5/3.0		
Witer (2009)	160 (182)	777/4	36.1 (20.7)	111.5/3.0	29.2 (17.8)	96.5/3.0		
Summer (2009)	108 (128)	492/3	30.2 (12.5)	65.7/10.0	20.3 (8.3)	54.0/4.0		
2. Jugopetrol								
Year (2006)	178 (168)	1081/10	44.1 (29.4)	136.3/5.5	19.1 (17.7)	83.3/2.5	6.9 (7.3)	36.5/0.9
Winter (2006)	151 (150)	759/10	37.5 (28.4)	108.1/5.5	19.8 (22.6)	83.3/2.5	8.3 (10.3)	36.5/0.9
Summer (2006)	194 (177)	1081/10	48.5 (30.5)	136.3/14.4	19.4 (15.4)	62.7/4.0	6.3 (5.2)	23.3/1.1
3. Institute								
Year (2006)	62 (70)	589/10	38.3 (21.7)	116.7/9.8	16.0 (8.1)	49.3/2.0	6.7 (6.2)	22.9/0.9
Winter (2006)	66 (91)	589/10	37.3 (16.0)	72.7/9.8	19.5 (8.1)	49.3/2.0	9.7 (5.9)	22.9/1.9
Summer (2006)	59 (57)	422/10	39.4 (26.7)	116.7/12.5	10.3 (4.4)	46.2/3.3	3.6 (4.9)	21.2/0.9
4. Brezonik								
Year (2007)	44 (61)	328/5	42.5 (32.6)	293.6/8.8				
Winter (2007)	43 (64)	328/11	53.2 (41.5)	293.6/8.8				
Summer (2007)	45 (59)	217/5	32.4 (15.9)	111.0/10.3				
Year (2008)	68 (144)	1642/10	45.7 (29.9)	188.3/11				
Winter (2008)	92 (199)	1642/10	52.8 (34.9)	188.3/11				
Summer (2008)	45 (35)	196/10	35.2 (15.3)	84.9/14.7				
5. Hospital								
Year (2006)	228 (248)	1291/10	53.0 (66.5)	393.7/10	17.8 (18.7)	101.8/2.7	6.6 (7.1)	41.3/1.1
Winter (2006)	255 (290)	1291/14	34.2 (16.6)	73.5/12.7	14.2 (7.5)	30.1/3.8	6.0 (3.6)	14.1/1.3
Summer (2006)	210 (214)	843/10	65.9 (83.7)	393.7/10	20.2 (23.4)	101.8/2.7	7.0 (8.8)	41.3/1.1

Table 4. Production of sulfuric acid and copper cathodes in the Copper Smelter Plant (2004 – 2008)

Year	H₂ SO₄ production (t)	Cu production (t)
2004	49100	12000
2005	92900	21000
2006	71500	41000
2007	66500	31000
2008	70800	34000



Figure 1. Map of eastern Serbia with the location of the Bor Municipality area

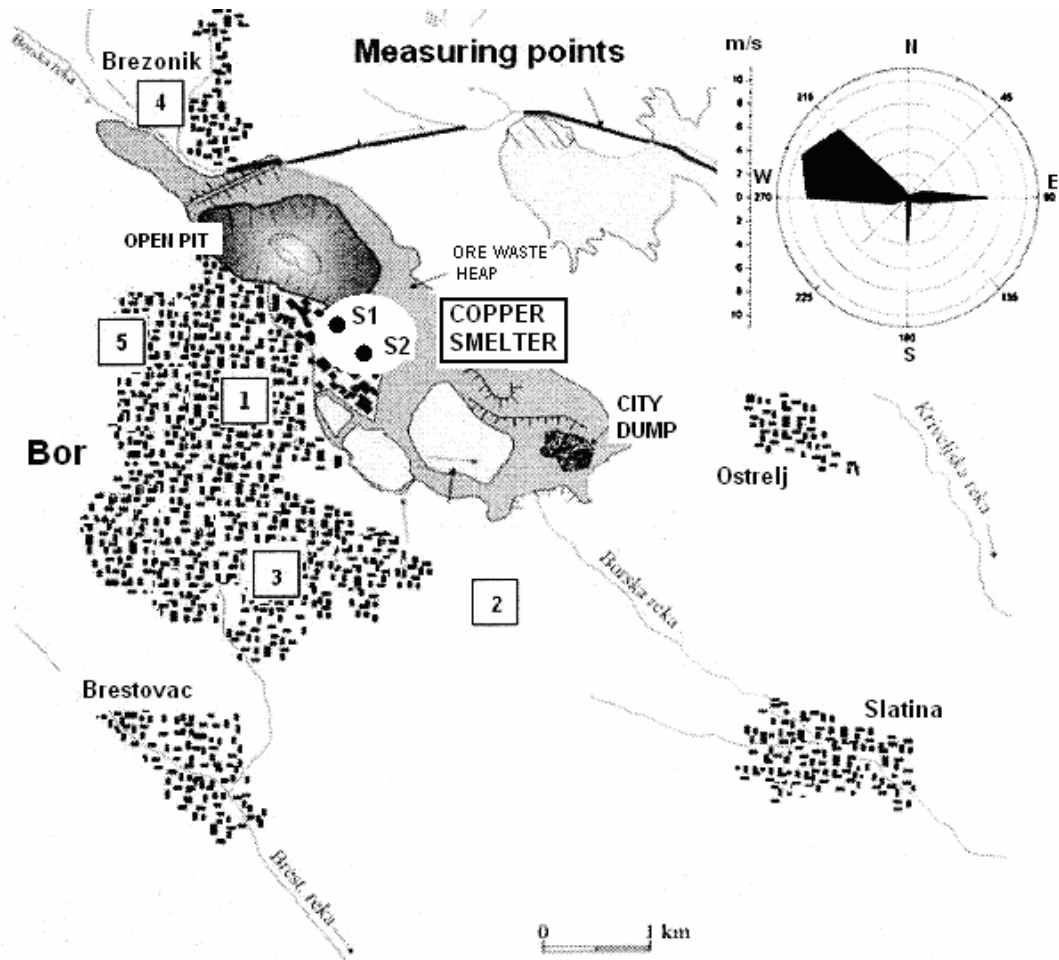


Figure 2. Map of the Bor Municipality area with measuring points (1. Park, 2. Jugopetrol, 3. Institute, 4. Brezonik, 5. Hospital) and location of the Copper Smelter smokestacks (S1, S2)

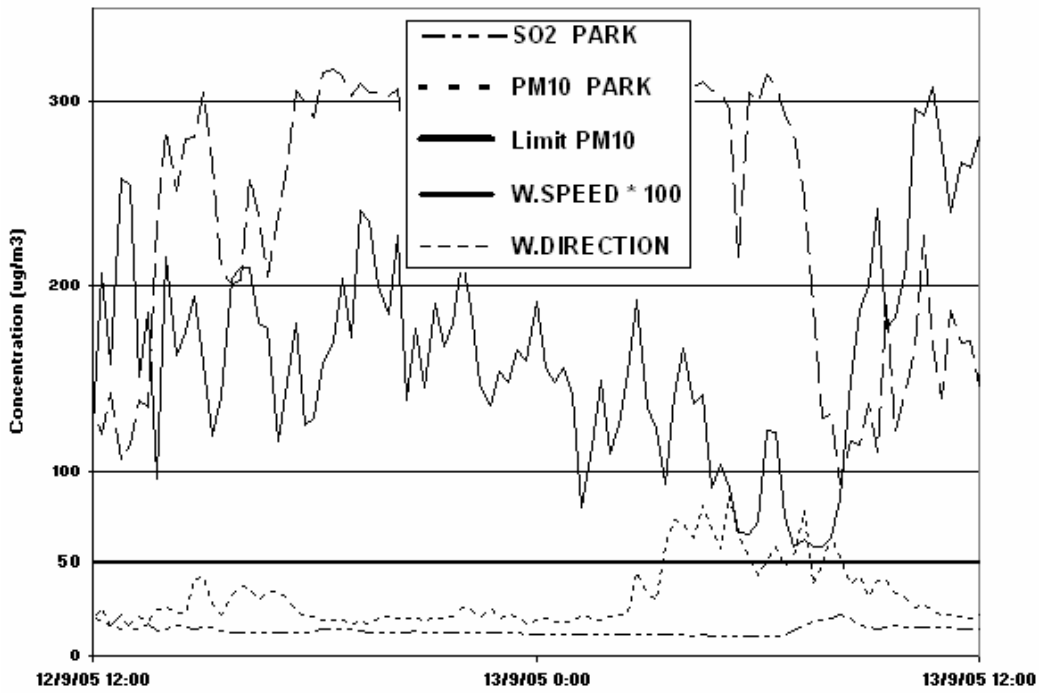


Figure 3. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 1 (Park) in the time interval when the Copper Smelter Bor was out of operation

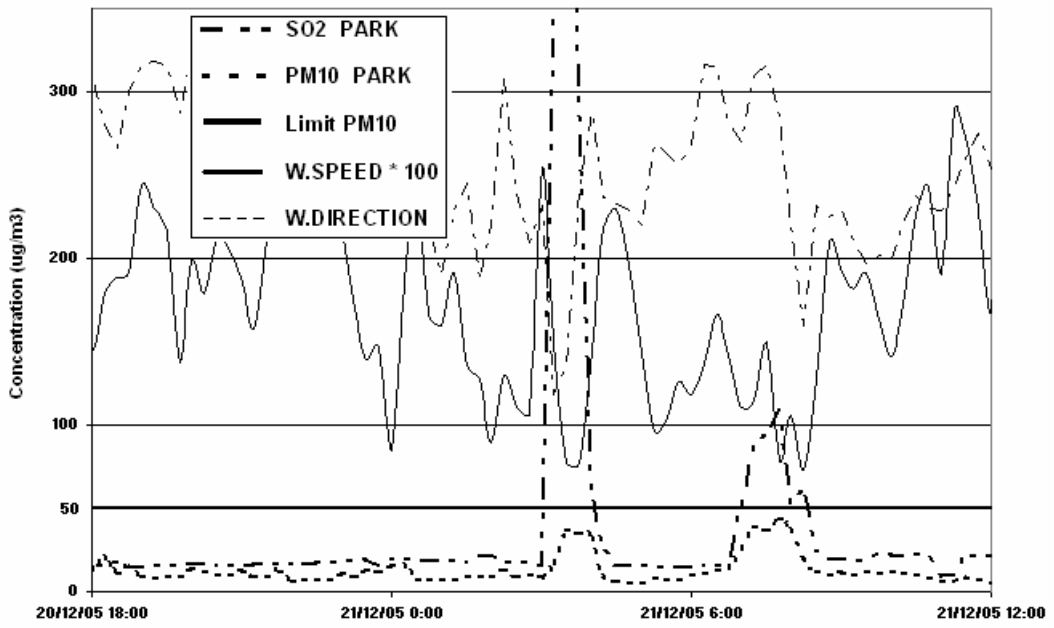


Figure 4. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 1 (Park) in the time interval when the Copper Smelter Bor was in operation

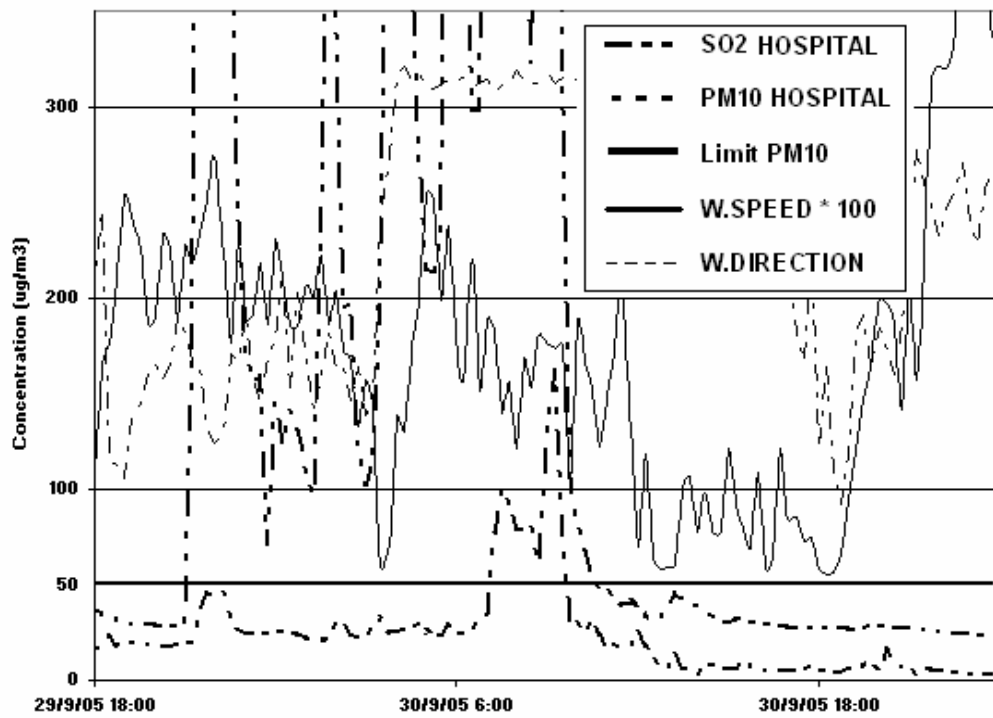


Figure 5. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 5 (Hospital) in the time interval when the Copper Smelter Bor was in operation

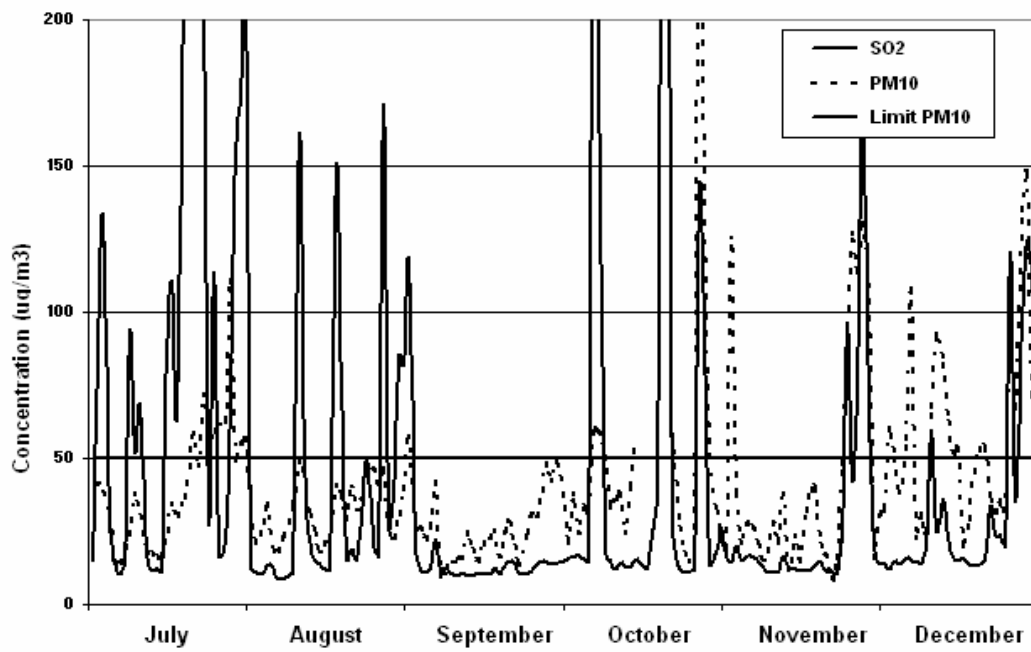


Figure 6. Time series of SO₂ and PM₁₀ mass concentrations at measuring point 4 (Brezonik) during 2007 in the time interval when the Copper Smelter Bor was in operation