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Analysis of SO_2 Concentrations in the Urban Areas near Copper Mining and Smelting Complex Bor, Serbia

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Monitoring of SO_2 mass concentrations is very important from the aspect of human health risk assessment, having in mind the negative effects of elevated levels of SO_2 in ambient air on human health. The aim of this study was to analyse ambient air pollution with SO_2 in the urban areas near the copper smelter in the Bor town, Republic of Serbia. The results of measurements of SO_2 levels in the period 2001-2010 at four measuring points in Bor and its surroundings were analysed. The analysis has shown that SO_2 concentrations exceeded the corresponding Serbian and European Union (EU) air quality standards. The lowest levels of SO_2 were observed at Brezonik and Institute that is the least impacted by the SO_2 emissions from the Copper Mining and Smelting Complex Bor. The average annual SO_2 concentrations observed at Park and Jugopetrol are the greatest in the Republic of Serbia and in Europe as well. The copper smelter activities during the unfavourable meteo conditions for dispersion of air pollutants lead to high SO_2 concentrations in the ambient air in Bor and its surroundings. The presence of very high SO_2 concentration in the period of several hours during the day often causes the exceeding of SO_2 daily limit. That was also the main reason for the absence of clear seasonal changes in SO_2 concentrations at all measuring points.

1. Introduction

Air pollution has both acute and chronic effects on human health, affecting a number of different systems and organs. It ranges from minor upper respiratory irritation to chronic respiratory and heart disease, or even lung cancer (Kampa et al., 2008). SO_2 is one of the most important environment polluter. It mostly originates from oxidation of sulphur compounds. Anthropogenic emission of SO_2 results from burning the fossil fuels (coal and heavy oils) or smelting of sulphide ore concentrates (most frequently Cu, Pb, and Zn ores). Volcanoes and oceans are its major natural sources. It is known that high concentrations of air pollutants cause adverse health effects including increased morbidity or mortality (Pope et al., 2007). The SO_2 as well as all SO_x gases can react with other compounds in the atmosphere to form small particles. These particles penetrate deeply into sensitive parts of the lungs and can cause or worsen respiratory disease, such as emphysema and bronchitis, and can aggravate existing heart disease, leading to increased hospital admissions and premature death. Because of the certain negative effect of SO_2 in the atmosphere, the EU issued limits of its mass contents:

- Limit value per hour for protection of human health is 350 μg/m^3, not to be exceeded more than 24 times per calendar year;
- Daily limit for protection of human health is 125 μg/m^3, not to be exceeded more than three times per calendar year;
- Annual limit for protection of ecosystems is 20 μg/m^3.

The Municipality of Bor is located in the eastern part of the Republic of Serbia, less than 50 km far from Bulgarian and less than 100 km far from Romanian border. The main source of air pollution with SO_2 is the copper smelter which operates within the RTB Bor Company (Copper Mining and Smelting Complex Bor).

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Emissions from copper smelter are mostly particulate matter and sulphur oxides (SO_x). Fugitive emissions are generated during material handling operations. Copper and iron oxides are the primary constituents of solid particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, mercury, and zinc, may be also present along with metallic sulphates and sulphuric acid mist (Tasić et al., 2010). The technology of copper production in the copper smelter in Bor is outdated (classic pyrometallurgy with melting in furnaces and utilization of SO_2 gas in production of H_2SO_4 with relatively small degree of utilization < 60 %) which leads to the environmental pollution of higher concentrations of SO_2 (Nikolić et al., 2010). The copper smelter is situated in the immediate vicinity of the urban settlement at a distance about 500 m from the old urban centre. Taking into account the location of the copper smelter and dominant wind directions, the inhabitants of Bor are exposed to high levels of SO_2 which can pose serious risks to their health (Dimitrijević et al., 2009). The main objective of the study was analysis of all available data about ambient air pollution with SO_2 in the time interval from 2001 to 2010 in order to better determine seasonal and diurnal changes in SO_2 concentrations at observed measuring points.

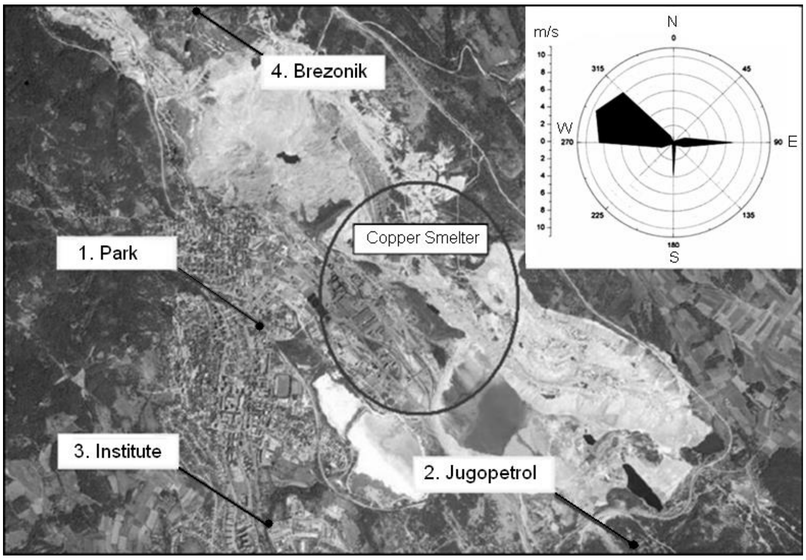

Figure 1: Map of the Bor town with locations of the automatic air quality monitoring stations (1.Park, 2.Jugopetrol, 3.Institute and 4.Brezonik) and wind rose in the time interval from 1998 to 2010

2. Methodology

Monitoring of SO_2 and soot in the Bor town has started in 1976, while monitoring of meteorological parameters has started in 1980. As time passed by, the methods and measuring equipment became obsolete and had not been fully complied with the modern requirements for monitoring the atmospheric pollution. So that, in the beginning of 2004, new atmospheric monitoring equipment has been put into the operation (Tasić et al., 2013). The results presented in this paper refer to the regular measurements conducted by the Mining and Metallurgy Institute Bor, in the time interval from 2001 to 2010.

2.1 Sampling procedures and equipment

In the time interval from 2001 to 2004 measurements of SO_2 levels were carried out by using the standard UK 8-port samplers at all sampling sites (ISO4219, 1979). The SO_2 level in ambient air was measured so that sampled air passes through a dilute-acid solution of hydrogen peroxide. The detection limit for such method was less than 0.01 ppm. Two automatic analyzers for real-time determination of SO_2 mass concentrations has been installed in Bor during 2003 (sampling sites Park and Jugopetrol, as shown in Figure 1) as part of the UNOPS project: ″YUG 00-R71 Clean-Up of Environmental Hotspots.″ The locations for installation the real time air quality monitoring equipment was determined based on air pollution modelling (Vairo et al., 2014). Nowadays, Serbian Environmental Protection Agency (SEPA) performs monitoring of air pollution at 37 Automatic Monitoring Stations (AMS) at the entire territory of the Republic of Serbia. Three of them have been installed in Bor in the time interval from 2007 to 2010. The reference method used for SO_2 measurement is described in (EN 14212, 2005). By using the UV-fluorescence method, the analyzers perform automatic measuring of SO_2 in ambient air in a concentration range from zero to 10,000 μg/m^3 with linearity of ±1 % and minimum detectable limit (2σ) < 3 μg/m^3 (Ioana and Popescu, 2010).

3. Results and discussion

The measurements of SO_2 mass concentrations were carried out when the copper smelter was in operation, as well as when the copper smelter did not work continuously. Typical time series with daily mean concentrations of SO_2 are shown in Figure 2. Strong fluctuations of daily mean SO_2 concentrations were mostly related to changes in weather conditions. High SO_2 concentrations has been detected during such weather conditions with wind speed less than 2-3 m/s and wind direction that lead spreading of air pollution toward the certain measuring point (Tasić et al., 2010). Exceeding the daily limits had occurred due to presence of very high concentrations in a period of several hours during the day. At measuring points Park and Jugopetrol a large number of days with SO_2 concentrations above the daily limit value were observed. According to Table 1, in the time interval from 2001 to 2010 exceeding of the daily limit value for SO_2 had occurred at all sites, sometimes over 150 d/y. The copper smelter point sources were the major sources of SO_2 emissions in Bor. By the examination of hourly mean SO_2 concentrations in the time intervals when the copper smelter was out of operation that fact has proved. Figures 3 and 4 illustrate that situation. When the copper smelter was out of operation there was no significant air pollution with SO_2 regardless of season (heating or non-heating season). SO_2 concentrations measured in the period from 2001 to 2010 were divided into annual, summer (April-September) and winter (October-March) averages and analyzed.

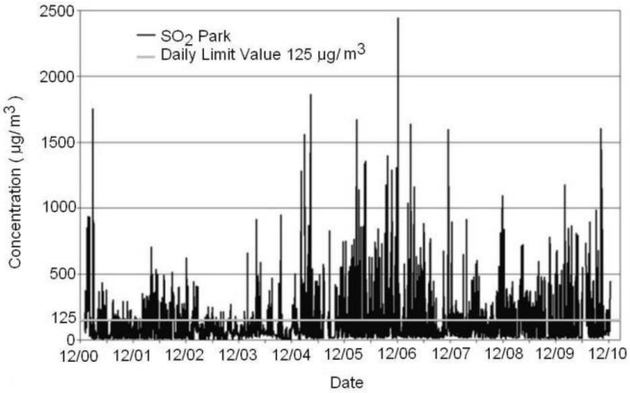

Figure 2: Time series of the daily mean SO_2 concentrations at the measuring point Park (2001 - 2010)

Table 1: Number of days with SO_2 concentrations above the daily limit value (- no data)

Year	Park	Jugopetrol	Institute	Brezonik
2001	142	89	-	-
2002	123	40	5	-
2003	39	28	28	-
2004	67	84	9	-
2005	119	155	21	8
2006	132	144	25	32
2007	109	150	20	51
2008	69	126	22	36
2009	36	83	-	18
2010	34	77	60	44

At Park, annual mean of SO_2 concentrations range from 76.0 to 225.4 μg/m^3. The variation of the daily means could be demonstrated by variation coefficients, i.e. the standard deviation (SD) divided by the mean. The variability of annual mean of SO_2 concentrations at Park was very different, between 90 % and 148 %. The variability of SO_2 concentrations in summer was between 83 % and 190 %, and in winter between 81 % and 169 %. SO_2 concentrations were higher in winter than in the summer, about 26 % in average, in seven of 10 years observed. At Jugopetrol annual mean of SO_2 concentrations range from 61.6 to 223.6 μg/m^3. The variability of annual mean of SO_2 concentrations at Jugopetrol was very different, between 92 % and 150 %. The variability of summer mean of SO_2 concentrations was between 76 % and 137 %, and between 77 % and 168 % in winter. Geographical position of measuring point Jugopetrol is such (as shown in Figure 1) that in winter winds mostly blows from the north/northwest directions. This fact explains increase of SO_2 concentrations at Jugopetrol in winter relative to summer period, when the frequency of winds from north/northwest directions was lower. SO_2 concentrations were higher in winter than in summer in average 25.8 %, in eight of 10 y observed.

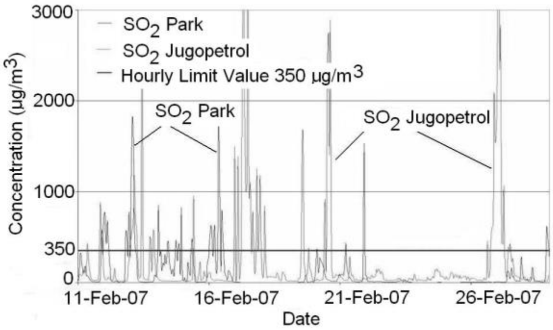

Figure 3: SO_2 concentrations in the time intervals when the copper smelter was in operation (from 11.02. to 22.02.2007) and when it was out of operation (from 22.02. to 26.02.2007), during heating season

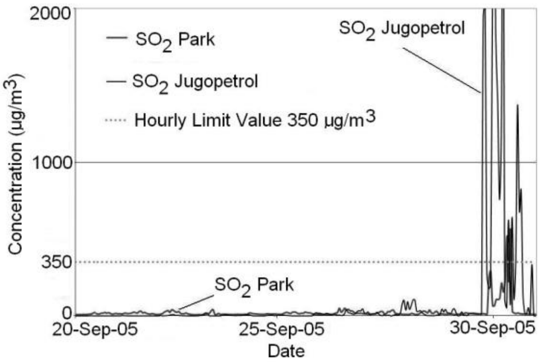

Figure 4: SO_2 concentrations when the copper smelter was out of operation (from 20.09. to 29.09.2005), and when it was in operation (from 29.09. to 30.09.2005), during non-heating season

At Institute annual mean of SO_2 concentrations range from 14.1 to 110.2 $\mu g/m^3$. The variability of annual mean of SO_2 concentrations was very different, between 61 % and 133 % (in the time interval from 2001 to 2003 SO_2 concentrations were excluded from the analyses). The variability of SO_2 concentrations in summer is between 25 % and 139 %, and between 47 % and 156 % in winter. At Institute the smaller difference between the SO_2 concentrations in summer and winter was observed, in average 15 %. At Brezonik, annual mean of SO_2 concentrations range from 48.2 to 100.0 $\mu g/m^3$. The variability of annual mean of SO_2 concentrations was very different, between 74 % and 155 % (in the time interval from 2004 to 2010). The variability of SO_2 concentrations in summer is between 42 % and 121 %, and in winter between 25 % and 227 %. At Brezonik winds blows mostly from the south/southwest directions in summer. This fact explains increase of SO_2 concentrations at Brezonik in summer, relative to winter period, when the frequency of winds from the south/southwest directions was lower. SO_2 concentrations were higher in summer than in winter in average 34 %, in six of 7 y observed. Based on the facts mentioned above, it was clear that SO_2 concentrations were higher at Park and Jugopetrol, compared to SO_2 concentrations measured at Institute and Brezonik. The ten-year average of daily mean SO_2 concentrations at Park, for period from 2001 to 2010, was 140.7 $\mu g/m^3$. Almost identical value of 141.5 $\mu g/m^3$ was calculated for Jugopetrol in the same period. At Institute and Brezonik, ten-year averages of daily mean SO_2 concentrations were 48.4 $\mu g/m^3$ and 70.2 $\mu g/m^3$. Such differences in SO_2 concentrations could be explained by the fact that Park and Jugopetrol were on the dominant wind direction relative to the copper smelter. In addition, measuring point Park is at half the distance from the copper smelter smokestacks relative to the other measuring points. Thus, SO_2 concentrations at Park is expected to be higher compared to other measuring points. Diurnal SO_2 concentration pattern was driven by the emission characteristics of the dominant sources and meteorological conditions (mostly by the wind speed and wind direction). Average daily patterns of SO_2 concentrations at Park have been very similar for all seasons, as shown in Figure 5. The same conclusion also stands for all other measuring points, as shown in Figures 6-8. SO_2 concentrations at Jugopetrol were minimal in time interval from 10:00 AM to 6:00 PM, as shown in Figure 6. This period has been followed by a very pronounced midnight maximum. SO_2 concentrations at Institute reached their minimums in time interval from 11:00 AM to 8:00 PM regardless of seasons, as shown in Figure 7. This period was followed by very pronounced early morning maximum. Compared to Jugopetrol and Institute, a maximum of SO_2 concentrations at Brezonik occurred in time interval from 7:00 AM to 4:00 PM, as shown in Figure 8. This period was preceded and followed by the periods of uniform changes in SO_2 concentrations.

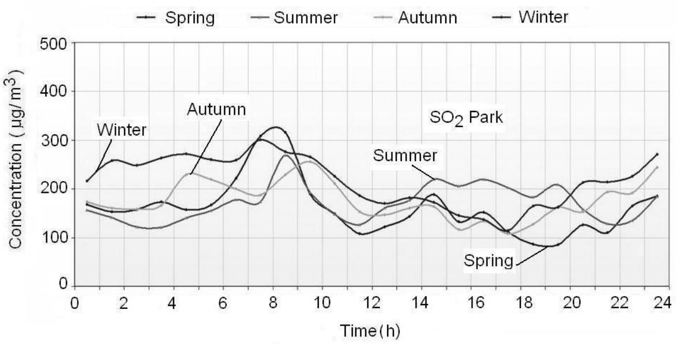

Figure 5: Diurnal time pattern of SO_2 concentrations at Park (2004-2010)

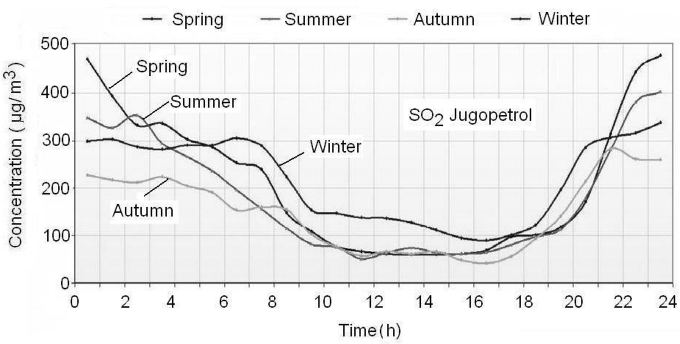

Figure 6: Diurnal time pattern of SO_2 concentrations at Jugopetrol (2004-2010)

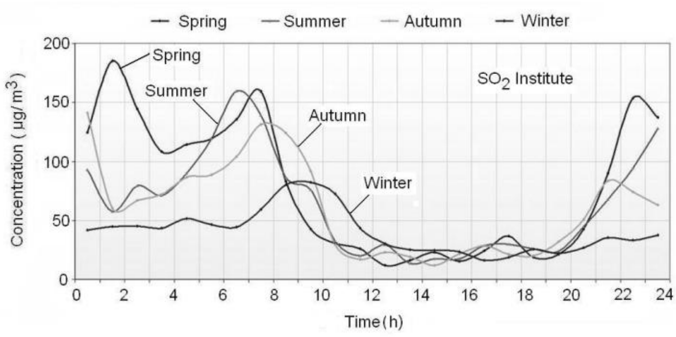

Figure 7. Diurnal time pattern of SO_2 concentrations at Institute (2010)

4. Conclusions

The aim of this study was to analyze ambient air pollution with SO_2 in the urban areas near the copper smelter in the Bor town, Republic of Serbia. According to the results shown, it could be noted that the citizens of Bor were exposed to the high concentrations of SO_2 in the time interval from 2001 to 2010. The SO_2 concentration levels at all measuring points exceeded the corresponding Serbian and EU air quality standards. The lowest SO_2 levels were observed at sites Brezonik and Institute that was the least impacted by SO_2 emissions from the copper smelter facilities. The annual average SO_2 concentrations observed at Park and Jugopetrol were the greatest in the Republic of Serbia and in Europe as well. It was confirmed that there were no clear seasonal changes in SO_2 concentrations throughout the years. The differences between diurnal concentration patterns between sampling sites was observed, that were driven by the emission characteristics of the dominant sources and meteorological conditions. The strong fluctuations of the hourly mean SO_2 levels were mostly related to changes in the weather conditions (wind speed and direction). This phenomenon is typical for the wind speed less than 2 m/s and as well as for the wind direction changes. To reduce the air pollution, and to solve the problem of SO_2 emissions from the copper smelter in Bor, the introduction of the new technologies for the copper smelting is necessary. The Serbian Government, in fully respecting the ecological standards of European Union, invests a notable means in building of the new copper smelter and sulfuric acid factory in Bor. So, in the near future, the citizens of Bor will no longer be the hostages of the present mode of the copper production.

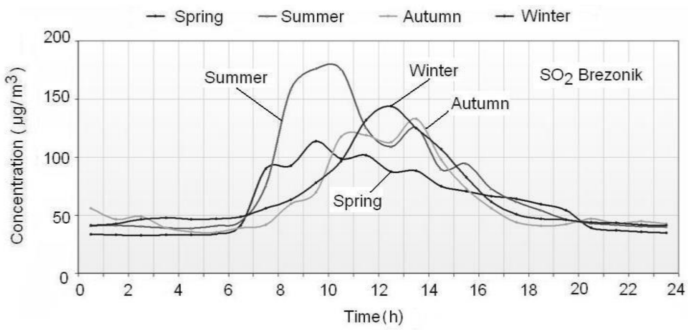

Figure 8. Diurnal time pattern of SO_2 concentrations at Brezonik (2007-2010)

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