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VARIATION CONCENTRATION OF SULFUR DIOXIDE AND CORRELATION WITH METEOROLOGICAL PARAMETERS

Ilić Predrag¹, Nešković Markić Dragana², Stojanović Bjelić Ljiljana³

¹ PSI Institute for protection and ecology of the Republic of Srpska, Banja Luka, Vidovdanska 43, 78000 Banja Luka, Republic of Srpska, Bosnia and Herzegovina, predrag.ilic@institutzei.net

² Public utility „DEP-OT“ Regional landfill Banja Luka, Republic of Srpska, Bosnia & Herzegovina

³ Pan-European University “APEIRON”, Banja Luka, Republic of Srpska, Bosnia & Herzegovina

ABSTRACT

Levels of SO₂ in air samples from urban zone of Banja Luka were determined at locality Center in Banja Luka (administrative center of the Republic of Srpska, in Bosnia and Herzegovina) which is highly populated area, with intensive traffic and industry. Through experimental measuring, daily and weekend variation of SO₂ concentration was determined. Daily variations are directly connected to regime and intensity of traffic and using fossil fuels. The paper presents measured average values of sulfur dioxide, together with max and min values and relationship between some parameters of air quality and meteorological parameters, i. e. for pollution modelling together with meteorological parameters.

Keywords: air pollution, Banja Luka, monitoring, sulfur dioxide, urban zone

INTRODUCTION

Eastern European and Balkan countries suffer the highest rate of the air contamination and air pollution related deaths throughout Europe. Bosnia and Herzegovina (B&H), Bulgaria, Albania and the Ukraine have the highest European mortality rates attributed to home and air pollution B&H is listed as the worst European performer and had European highest average of 55.1 µg particular matter per m³. B&H in 2012 registered nearly 231 deaths per 100,000 people and had European highest death rate [1]. The problem of air pollution is largely present in the Republic of Srpska, B&H. A small number of local community control of air pollution, and monitoring of emissions is not represented to the extent necessary [2]. Numerous studies have analysed the impact of meteorological parameters and air quality parameters [3,4,5,6,7,8], where the results were often uncoordinated or even opposed. For example, by examining the effect of air temperature on the concentration PM10, Kassomenos et al. [9] they get positive correlation values, and Giri et al. [10] they get negative correlation values. As an explanation for these differences may indicate different locations research studies, timing and so on.

The importance of air pollution prevention has been increasing in recent years, due to increasing knowledge of polluting sources and their pollution levels. Sulfur dioxide (SO₂) is one of the environmentally important air pollutants that has been closely associated with urban air quality problems during winters [11]. Sulfur dioxide is a colourless gas with a sharp, irritating odour. Sulfur dioxide is added to the atmosphere primarily as a by-product of combustion of coal, fuel oil, diesel

engine fuel; biological processes; sea spray; and to a lesser extent, the combustion of wood [12]. It smells like burnt matches. It can be oxidized to sulfur trioxide, which in the presence of water vapour is readily transformed to sulfuric acid mist. SO₂ can be oxidized to form acid aerosols. SO₂ is a precursor to sulphates, which are one of the main components of respirable particles in the atmosphere [13,14].

Sulfur dioxide is considered one of the indicators of air quality. It is formed primarily from the combustion of sulfur-containing fuels and can affect the health of people and have a negative impact on the environment. Modelling of environmental parameters is a basis for a better understanding and prevention of air pollution [15]. On concentration from 800 to 2600 mg/m³ it is possible to smell characteristic taste [16], which most of population smells on concentration of 1 ppm. Sulfur dioxide (SO₂), a major air pollutant with a strong disagreeable sulfurous odour, is both water-soluble and a strong respiratory irritant. In the atmosphere, SO₂ is a precursor to acid sulfates (including sulfuric acid), which are neutralized by ammonia, which is usually present. SO₂ and its reaction products have been steadily dropping in concentration in the atmosphere, mainly due to decreasing sulfur levels in fuels [12].

Decreasing of sulfur in atmosphere is result of lesser use fossil fuel for individual house heating [17]. Coal usage and the rise of newer industrial activities, such as the smelting of metal ores, produced acidic, odorous, and irritating sulfur-containing pollutants, which would have also contained toxic levels of metals such as lead and iron. The success of coal as a fuel and its widespread availability for industrial and domestic uses not only led to increasingly polluted air in outdoor and indoor environments, but it also served as the impetus that would eventually drive regulatory actions [12]. Sulfur dioxide concentration in atmosphere is varied for different places. Urban and industrial regions contains bigger concentration this pollution material. Rated concentration in urban area is 0.01-0.02 ppm. However, momentary concentration can be much bigger. Therefore, one-hour concentration can be bigger 4-7 times than rated annual concentration.

Despite the legal obligation, the state of monitoring is at a very low level and it is necessary to improve it in the Republic of Srpska [18,19], but there are significant research in the field of air pollution [20,21,22,23,24,25,13,26,18,19,20]. The present study aimed analysed concentration of SO₂ and investigate the relationship SO₂ with meteorological parameters, over the period from January – December 2016 in Banja Luka, Republic of Srpska, B&H.

MATERIALS AND METHODS

Location

Subject of the research is testing air pollution and meteorological parameters at locality Center in Banja Luka, with intensive traffic and high population. Banja Luka is the administrative center of the Republic of Srpska, in Bosnia and Herzegovina. It is located in the southern part of Europe. Banja Luka is located in Vrbas valley and is surrounded by hills 200-600 meters above sea level high. Banja Luka lies on a bank of the river Vrbas, which flows into Sava River, and later into Danube. It is the second largest city in Bosnia and Herzegovina, after Sarajevo, and as large industrial and financial centre with dense population and industry in the city itself and its surroundings, which are sources of air pollution. The largest sources of pollution are heating plants, traffic, foundries, metal-processing and chemical industry, and fireboxes in households, municipal waste, etc. It is necessary to take urgent measures in order to improve air quality in these and other areas, and in that way, to protect health of people living in urban areas [26].

Analytical procedure

Sulfur dioxide has been measured by equipment Teledyne Advanced Pollution Instrumentation, Inc. (TAPI) Sad Diego, California, United States. Monitoring of sulfur dioxides concentration was performed by the Model T 100 (*UV Fluorescence SO₂ Analyzer*). For the level of pollution by SO₂, *UV Fluorescence* method was used. Range 0-50 ppb / 0-20 ppm. For monitoring of sulfur dioxides, there

is BAS EN 14212 standard, as reference method for the measurement of sulfur dioxide [27]. The Model T100 uses the proven UV fluorescence principle, coupled with a state of the art user interface to provide easy, accurate, and dependable measurements of low level SO₂. Model T 100 is based on the principle that SO₂ molecules absorb ultraviolet (UV) light and become excited at one wavelength, then decay to a lower energy state emitting UV light at a different wavelength.



Pictures 1. SO₂ monitor

Simultaneously is supplied data on average temperature, air pressure, and relative humidity, speed and wind direction, recorded at the meteorological monitoring site at the outer rim of the inner city every day for the entire duration of the study. These results of concentration of polluting particles monitoring were compared in accordance with current law regulations regarding air quality, issues on pollution and air quality control. Based on both data and Regulation on air quality values [28], Directive 2008/50/EC on ambient air quality and cleaner air for Europe [29] and standards recommended by World Health Organization (WHO) and EU countries, an assessment of the current state will be given. It will be determined if the measured values satisfy recommended and limit values specified by the Law.

Statistical analysis

For statistical data processing while determining interdependence and relationship between some parameters of air quality and meteorological parameters, i. e. for pollution modelling together with meteorological parameters, were used EXCEL and SPSS statistical software tool. Descriptive statistical parameters like mean, Standard deviation (SD), minimum (min) and maximum (max) applied to the data.

RESULTS AND DISCUSSION

Measured average values of sulfur dioxide are shown in Table 1, together with max and min values. Research show that variation of SO₂ dominantly depend on both human activity during a day (Graph 1). For example, concentration of sulfur oxides in early hours without solar insolation and human activities is mostly constant. Daily variations are directly connected to regime and intensity of traffic and using fossil fuels. During a day, population activities such as traffic frequency increase, and this causes concentration of polluting substance sulfur dioxide to grow, but probably and sulfur trioxide and of sulfuric acid. Thus, under the right conditions SO₃ can lead to the formation of sulfuric acid, a strong irritant and corrosive agent. Ultimately, sulfuric acid is formed in water droplets from the interaction of SO₂ and hydroxyl radicals (OH•) [12].

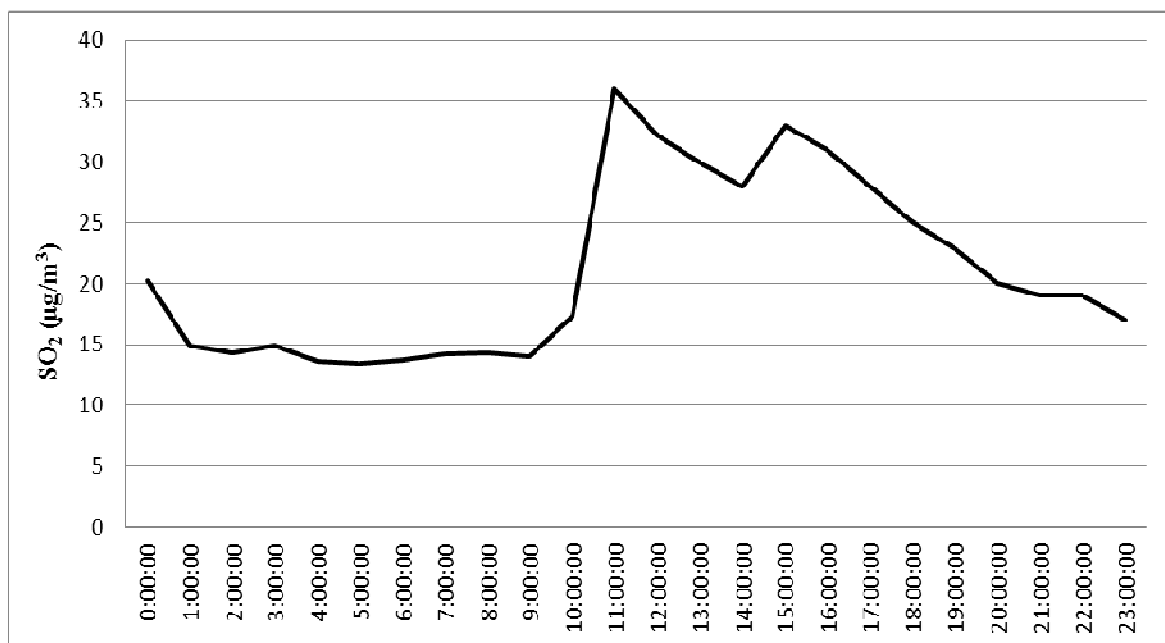
In combustion-generated plumes, a large number of other substances, organic and inorganic, surrounds SO₂ and the above reaction products. The result is the formation of particulate sulfates other than sulfuric acid (e.g., (NH₄)₂SO₄ and metal-containing sulfates). Sulfates contribute significantly to the fine particulate mass, PM_{2.5}, in regions that use fuels containing sulfur [12].

Mean annual value with the aim of protection of human health for sulfur dioxide, for sampling period of 1 hour is $350 \mu\text{g}/\text{m}^3$ and period of 24 hours is $125 \mu\text{g}/\text{m}^3$ [28], as prescribed and Directive 2008/50/EC [29]. In a research field, it is not exceeded and is $21.81 \mu\text{g}/\text{m}^3$ (Table 1) is lower than the value $39.35 \mu\text{g}/\text{m}^3$, which was measured during previous research [20]. Although high levels of sulfur dioxide have not been recorded during the investigated period, humidity during the analysed period of 66.40%, due to a number of chemical reactions in which sulfur dioxide is converted into sulfuric acid, can affect the increase in harmful effects caused by the action of sulfur dioxide. The presence of sulfur dioxide in the phenomenon of "temperature inversion" and in the absence of horizontal movement of the air it can lead to the appearance of acid smog, which usually occurs in the winter months, when concentrations of sulfur dioxide in the air are increased due to heating [28, 20].

Table 1. Statistical summary of SO_2 and meteorological parameters

		Mean	SD	Min	Max
SO_2		21.81	19.46	0.05	254.35
Meteorological parameters	VW (m/s)	0.33	0.0054	0	2.27
	DW (Å)	134.5	107.05	0.24	359.7
	P (Pa)	995.90	7.91	9710.93	1017.1
	T ($^{\circ}\text{C}$)	12.36	8.64	-8.39	34.57
	RH (%)	66.40	18.38	16.8	95.85

The Graph 1. shows the dependence of the concentration of SO_2 from the time of day during the measurement period. As can be seen from the graph the concentration of SO_2 is dependent on human activities. During the early morning hours (from 0:00 to 8:00) concentration of SO_2 was very low. Its maximum concentration was recorded in the period from 11 to 17 hours, and the values were reduced after 17 hours. Pollution by SO_2 in the area is believed to be dominated by road traffic [20, 22]. Sarigiannis et al. [31] SO_2 concentration starts to increase in the morning hours, reaching a morning peak ($2.3 \mu\text{g}/\text{m}^3$) from 11:00 until 20:00. A gradual increase of SO_2 concentration was noticeable, accompanied by the average hourly increase of trucks and buses.

Graph 1. Mean SO_2 values during 2016 at certain times of the day

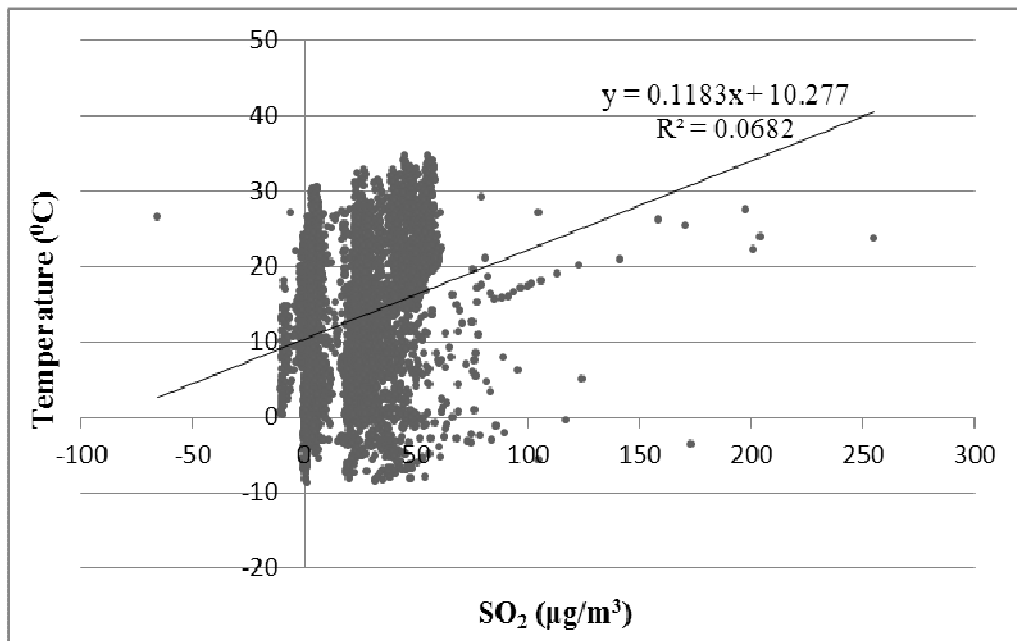
The relationship between SO_2 concentrations and other meteorological parameters in the study area was analysed using correlation analysis. The results of the correlation analysis between SO_2 concentration and meteorological parameters are shown in Table 2. Between the meteorological parameters of pressure and temperature there is a significant negative correlation ($r = -0.27$), respectively a significant negative correlation between the temperature and RH ($r = -0.56$). By

increasing the pressure, the temperature values were reduced, i.e. by reducing pressure, the temperature has grown. The increase in temperature has affected the reduction in value RH, i.e. the decrease in temperature has affected the increase RH.

Table 2. Pearson's correlation coefficients between SO₂ concentrations and meteorological parameters

	SO ₂ (µg/m ³)	VW (m/s)	DW (Å°)	P (Pa)	T (°C)	RH (%)
SO ₂ (µg/m ³)	1					
VW (m/s)	-0.14	1				
DW (Å°)	0.02	-0.07	1			
P (Pa)	-0.25	0.06	0.05	1		
T (°C)	0.26	0.13	0.09	-0.27	1	
RH (%)	-0.11	-0.18	-0.07	0.11	-0.56	1

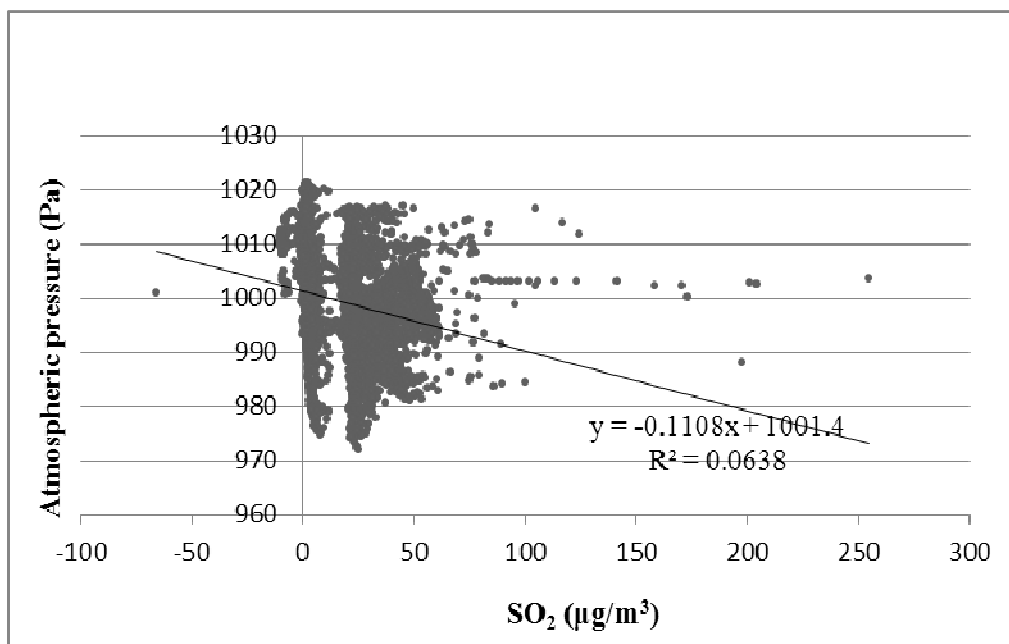
Correlation between SO₂ and temperature was positive and significant during the study period ($r=0.26$). With increase of temperature the SO₂ concentration increase, i.e., the decrease in temperature decreases the concentration SO₂. The Graph 2 shows the dependence of the concentration of SO₂ on the temperature, as well as the equation describing this dependence.



Graph 2. Correlation between SO₂ concentrations and temperature

Correlation between SO₂ and atmospheric pressure was negative and significant during the study period ($r=0.26$). With increase of atmospheric pressure the SO₂ concentration decrease, i.e. by decreasing atmospheric pressure, the concentration of SO₂ decreases. The Graph 3 shows the dependence of the concentration of SO₂ on the atmospheric pressure, as well as the equation describing this dependence.

24-hour average is recommended from World Health Organization (WHO) for sulfur dioxide is 125 µg/m³ [32], as well as in Republic of Srpska. In test area, average annual value is exceeded which is probably caused by combustion of liquid, solid and gas fuel and traffic frequency. In winter seasons on lower temperatures, fuel consumption is higher, great amounts of nitrogen dioxide, sulfur dioxide and particles that cause winter smog are created. Winter smog is created by mild airflow and temperature inversion that disables vertical airflow and diluting of pollution materials in lower layer of atmosphere [21]. High values of sulfur dioxide with presence of wind can contribute to transformation those contamination materials in sulfur, continuing in forming sulphate salt [33].



Graph 3. Correlation between SO₂ concentrations and atmospheric pressure

CONCLUSION

This paper presents results of simultaneous measurement of SO₂ and meteorological parameters at locality Centre in Banja Luka. Mean annual value for sulfur dioxide in a research field and is 21.81 µg/m³. The results obtained for SO₂ were below limits Regulation on air quality values. Concentration of SO₂ is dependent on human activities. Its maximum concentration was recorded in the period from 11 to 17 hours. Correlation between SO₂ and temperature was positive and significant during the study period ($r=0.26$). Correlation between SO₂ and atmospheric pressure was negative and significant during the study period ($r = -0.2$).

Statistical analysis confirms string of rolls, which shows directional connection between air pollution and meteorological parameters.

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