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Meteorological Parameters and Pollution Caused by Sulfur Dioxide and Their Influence on Construction Materials and Heritage

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Abstract: In work is presented research of presence Sulfur dioxide (SO2) on sample place where is intensive traffic and population density is high. Air quality monitoring was done with an automatic station. For the interpretation of the results are used monthly and annual patterns. On the basis of the detected pollutants during the air monitoring show the state of environmental conditions in terms of air pollution with Sulfur dioxide and influence of them on aero-pollution, structural materials and building heritage. Also is given evaluation of influence polluted air on building heritage. For statistical data processing and modeling of pollution along with meteorological parameters was used decision tree implementation of the analytical and statistical tool SPSS 17.

Keywords: Meteorological parameters, sulfur dioxide, air monitoring.

1 Introduction

Air pollution can damage materials, especially those used in buildings because of their long life. Damage to other objects tends to be less important: most cars, for instance, are replaced long before air pollution damage has become significant. The phenomena of the degradation of buildings are complex due to the numerous factors that intervene. There are factors of natural origin such as sun, rain, and the

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freeze/thaw cycle, in addition to manmade atmospheric pollution. It is often difficult to distinguish the share of each factor. However, there is a general consensus that manmade pollutants have greatly increased the degradation rate of buildings. Of particular importance are soiling caused by particles (especially soot) and corrosion or erosion caused by acid rain (especially due to SO2) [1]. SO2, along with nitrogen oxides, are the main precursors of acid rain. This contributes to the acidification of lakes and streams, accelerated corrosion of buildings and reduced visibility. SO2 also causes formation of microscopic acid aerosols, which have serious health implications as well as contributing to climate change.

Sulfur dioxide (SO2), as component of air, is a colourless gas. It smells like burnt matches. It can be oxidized to sulphur trioxide, which in the presence of water vapour is readily transformed to sulphuric 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.

Sulfur dioxide (SO2) is considered one of the indicators of air quality. It is formed primarily from the combustion of sulphur-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 [2]. On concentration from 800 to 2600 μg/m^3 it is possible to smell characteristic taste [3], which most of population smells on concentration of 1ppm. Emission of sulfur compound is significantly bigger in winter than in summer period, because of using fossil fuel. Winter smog appears most frequently in central, south and south-east Europe. Government in states in these regions led campaign to decrease use of vehicles in central city parts. Concentration of this pollution material in west European cities significant is decrease than 1970 years. Decreasing of sulfur in atmosphere is result of lesser use fossil fuel for individual house heating [4]. 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. But momentary concentration can be much bigger. So one-hour concentration can be bigger 4-7 times than rated annual concentration. Cities which have rated concentration from 0, 10 ppm can to expect concentration from 0.4-0.7 ppm in most adverse days and 1-2 ppm in most adverse hours [4]. Concentrations of sulfur dioxide from 1 ppm not results with visible reaction. Bigger concentration is irritable, and concentration more than 10 ppm can cause of eye conjunctivitis and seriously iritation of mucous tissues and respiratory organs. Concentrations from 400 to 500 ppm (accidental concentration) are very dangerous, and can be lethal. As maximal allowed concentration is 150 μg/m^3. The most present problem is the existence of synergism between sulfur and most of other pollution materials. [5]. In order to give the exact interpretation of the results regarding the presence of sulfur dioxide in the air, there has to be a minimum data scope obtained by continuous measurements of 90% [6], what is in case of examined place. Annual measurement shows significant seasonal varying concentration of Sulfur dioxide (which is characteristically for industrial and urban areas). With the biggest values in winter month and by total emission, dispersion and biological effects occupy lead position between air polutioners [5, 7].

Effects aero-pollution on different materials can be approved but general quantification can be difficult. A lot of documentation about effects of acid pollution material exists, especially about sulfur dioxide on decadence of marble [8–10]. Experiment has shown that metal corrosion in urban area, because of the presence of sulfur particle, is 4 times faster than air without sulfur particle. Big influence on corrosion has presence of SO2 in the air.

Increases in sulfur dioxide concentrations accelerate the corrosion of metals, probably through the formation of acids (eg. sulphuric acid (H2SO4)). (SO2 is a major precursor to acidic deposition usually known as acid rain.) Sulfur oxides may also damage stone and masonry, paint, various fibers, paper and leather [4]. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage. Particulate sulfate, much of which is derived from sulfur dioxide emissions, is a major component of the complex total suspended particulate mixture. SO2 also accelerates the decay of building materials and paints, which is even more intensive with the presence of ammonium in atmosphere. Larger amount of nitrogen oxide causes corrosion of tin metals. This is more noticeable when the air is humid. Corrosion of metals such as iron and sulfur oxides, together with other constituents of the atmosphere, is more intensive when air humidity is increased; when it is below 70%, corrosion is slower, but above than this value corrosion is much reported. Examines have shown that faster and more corrode metals in urban areas where air pollution is higher and bigger amount of sulfur oxide. Corrosion is more intensive in winter months when emission of sulfur is bigger. In 12-th control in Chicago is observed that on concentration Sulfur dioxide on 0,12 ppm corrosion is 50% bigger than in area which contain 0,03 ppm Sulfur dioxide Also is affirm that corrosion 1-5 times bigger in urban than in inurbane areas. Other ingredient of atmosphere influence on corrosion but sulfur dioxide has the biggest influence [4]. Most research has focused on the "traditional" pollutants: sulfur oxides, nitrogen oxides, and carbon dioxide. All are capable of dissolving in water to give an acidic solution, and so are capable of reacting with calcareous materials such as limestone, marble, and lime mortar. All are naturally occurring, but human activity has greatly increased the amounts that are to be found in urban areas. The effects of acidic pollutants on calcareous stones depend very much on the immediate environment of the stone. If the stone is in an exposed position where it is regularly washed by rain, the reaction products are washed away and the surface of the stone gradually recedes. If, however, the stone is in a relatively sheltered position, the reaction products accumulate and may form a dense black crust on the surface [11].

Illustrated example of sulfur dioxide influence is the fact that one of the two monuments ”Cleopatra’s Needle” that was transferred from Egypt to New York in 1880, was more damaged in the last 100 years that it was in the first 3000 years. It is similar with magnificient monuments in Athens, Rome, Venice and other cities-museums [5].

Particle pollution, also known as particulate matter (PM), includes the very fine dust, soot, smoke, and droplets that are formed from chemical reactions, and produced when fuels such as coal, wood or oil are burned. Particles also cause haze reducing visibility in places like national parks and wild areas that are known for their scenic vistas, and soot causes damages of stone and other construction materials, including monuments and statues.

Particles also make buildings, statues and other outdoor structures dirty. Trinity Church in downtown New York City was black until a few years ago, when cleaning off almost 200 years worth of soot brought the church’s stone walls back to their original light pink color. Particles can influence mterials mechanically and chemically. Chemical decomposition of materials, particles perform by being a nucleus for gases or strong acids which they carry with them or just by their corrosive activity. They speed corrosion of steel, iron and other metals. It is well known that metals are resistant to the influence of dry air, and even to humid air if it is clean. Inert dust and soot, without sulfur compounds, do not have high corrosive effects. Airborne particles speed up corrosion in two ways: if they are active (corrosive) and if they absorb active gases (eg SO2) or liquid from the air. Solid particles in the atmosphere negatively influence construction buildings too. They, soot especially, form a layer on walls, bricks, marbles, stones and glass, which is hardly washed out by rain, so that it influences esthetic appearance, besides this destroying effect. Acid rain on metal, stone, wood, cement and other building materials has a strong corrosive effect; the world has many ancient buildings and stone carving art corrosion damage by acid rain, such as Canadas parliament building, the Leshan Giant Buddha in China and so on. Negative influences of acid rainfall are present at tangible goods, causing corrosion of steel, iron, zinc and other materials, especially in urban areas with more rainfall. Increased rainfall acidity causes stone decay, which decreases life cycle of constructions and cultural monuments. This is how ancient heritage of Italy and Greece was damaged. Influence of acid rainfall on archaeological monuments in El Tajin, i. e. Veracruz, in Mexico, was researched through X-ray diffraction, and a significant influence of pollution on monuments decay was noticed. [12]. Many historical objects and buildings are influenced by air pollution, especially those built from marble, limestone materials and other materials subject to damage. Many objects are located in polluted areas and are subject to destruction. Here are the examples: Acropolis in Athens, Cologne Cathedral and entire cities, such as Krakow and Venice, which are among protected cultural monuments under protection of UNESCO:

Tajin and Maya archeological zones, in Veracruz, Tabasco, Campeche, Quintana Roo and Yucatan, Mexico, has a great cultural and historical value for mankind. However, there is a great concern on the potential effect of acidic deposition on these monuments because their building material is mainly calcium carbonate. It is known, also, these monuments are surrounded by atmospheric pollution sources (power electric plants, refineries, off and on shore oil exploitation, etc.). To know better the effects on the monuments, besides the pollution sources, it is fundamental to investigate the pathways of pollutants air parcels follow after these pollutants are emitted by the sources [12].

2 Research Objective

The aim of the research and this paper is to specify the condition of ecological conditions regarding air pollution caused by sulfur dioxide, based on detected pollutants during air monitoring performed by automatic monitoring station located in the city center of Banja Luka, and thus to show ecological condition with regard to air pollution caused by sulfur dioxide. Pollution modelling, together with meteorological parameters, would evaluate the impact of the air polluted by sulfur dioxide on construction heritage.

3 Methods

The subject of the research was to investigate the presence of sulfur dioxide in Centar locality in Banja Luka, near Institut of protection, ecology and informatics (Vidovdanska street 43), where traffic is intense and densely settled populations. Air quality was monitored using automatic station obtained by EU CARDS project "Support to air monitoring" in Bosnia and Herzegovina (Figure 1). For the interpretation of the results are used monthly and annual patterns. Values are expressed in $\mu g/m^3$.

For monitoring air pollution was used Measuring station LU3000. Sulfur dioxide was determined equipment Thermo Electron Corporation Environmental Instruments Environmental instruments 27 Forge Parkway Franklin Massachusetts [13].

Referential monitoring methods used for monitoring in accordance with air quality based on in daughter directive (99/30/EC, 00/69/EC & 02/3/EC). The same methods are recommended for monitoring EUROAIRNET [14].

Fig. 1. Measuring station.

SO2 is monitored in pulsed fluorescence SO2 analyzer, model 43C, UV fluorescence method, preset ranges 0-0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10, ppm. There is no CEN standard for this method yet, but tjhere is ISO/FDIS 10498 [15]. The Model 43C 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. The Gas Units screen shown below, defines how the SO2 concentration reading is expressed. The Thermo Environmental Instruments, Inc. Model 43C is designated by the United States Environmental Protection Agency (USEPA) as an Equivalent Method for the measurement of ambient concentrations of SO2 pursuant with the requirements defined in the Code of Federal Regulations, Title 40, Part 53.

For statistical data processing while determining interdependence and relationship between some parameters of air quality and meteorological parameters, i. e. for pollution modeling together with meteorological parameters, were used 'decision trees', which is the most frequently used statistical technique originated from artificial intelligence in the field of rules' generated from data - data mining. They are used to predict subject or object belonging to some of the categories of dependent variables based on measurements of one or more predictor variables. Analytical and statistical tool SPSS 17 was used for statistical data processing and decision trees generating.

4 Discussion

Results of measurements during the analyzed period show average annual value of 10,23 μg/m^3 at examined locality, which shows that this area is not polluted by sulfur dioxide, and its concentration is below the limited value, from 20 to 100 μg/m^3, which are the most frequent values in urban area [7].

The highest concentrations are in January (39,35 μg/m^3), and then in February and in December (18,10 μg/m^3 and 18,02 μg/m^3). Values of sulfur dioxide in the examined area in winter months are so high due to intensive traffic, because this pollutant is released as secondary product from cars and factory chimneys thus polluting the environment. In this period, fuels containing sulfur, such as coal, are being intensively used. Air quality is lower during heating season due to weather conditions with no wind because of emissions from individual boiler spaces and households, which shows that pollution was mainly caused by thermal sources in heating season - from city heating plant and household fireboxes, from several production entities in the city and from fuel combustion in cars.

Measured values SO2 shown in Figure 2.

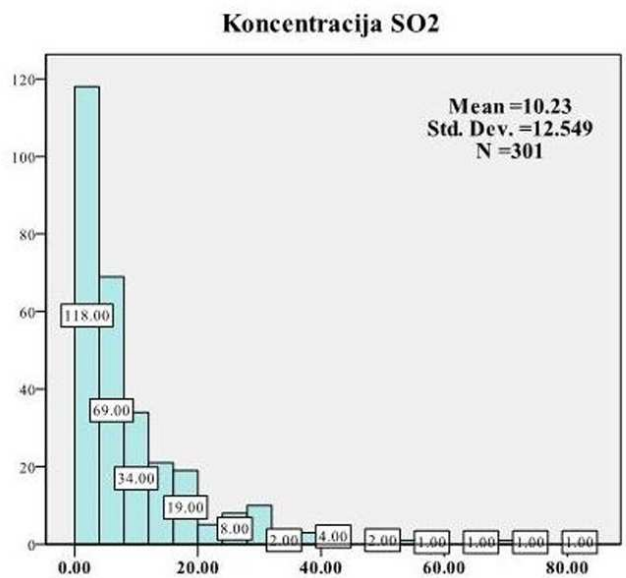

Fig. 2. Graphic review measured values of sulfur dioxide (SO2).

Considering sulfur dioxide, this area has slightly polluted and pure unpolluted air (1st Class air quality). This class of air quality has upper limit of pollution 3 to 5 times higher than natural level of harmful substances in the air, and no significant influence on people, flora, fauna, natural and human goods is noticed. Such air, evaluated according to this parameter, is considered to be slightly to moderately polluted, and can have influence on sensitive population.

High value was not exceeded during a year, as well as mean daily value with the aim to protect human health 125 μg/m^3. Maximum daily value was in January (81,66 μg/m^3), and minimum value was in June (0,01 μg/m^3) [7]. Limit values of

SO2 were exceeded four times (the value over 60 μg/m^3) (Figure 3). In Figure 3, review is given in right-angled diagram of SO2 value distribution.

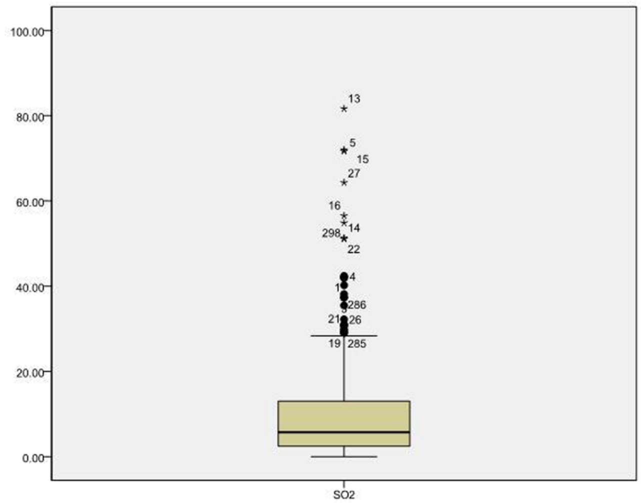

Fig. 3. Right-angled diagram of SO2 value distribution.

There can be seen eight points representing cases with extreme concentrations of SO2 (in the winter).

In Table 1 presents the target and exceeded limits SO2 depending on the meteorological parameters.

Figure 4 shows decision tree with appropriate variables.

It is clear that SO2 concentration depends on temperature - the highest average values of SO2 are present at lower temperatures. As temperature increases, concentration of SO2 decreases. Concentration of SO2 and temperature correlate and they represent combustion of fossil fuels and the effect of industry, which confirms previous research [6].

Modeling results show that, based on meteorological parameters, it is possible to clearly predict possible pollution by SO2.

Although high values of SO2 were not noticed during this research, high relative air humidity during this analyzed period (72,44%), due to several chemical reactions where SO2 is being transformed into sulfuric acid, can have influence on increase of harmful effects caused by impact of SO2 on construction materials and heritage. Presence of SO2, during temperature inversion and in the absence of horizontal movements of air results in acid smog, which is usually present in winter months, when concentrations of SO2 in the air are increased.

Table 1. Target and exceeded limits SO2 depending on the meteorological parameters

Target values		T	RV	BV	SV	P
Normal	N	297	297	297	297	145
	Minimum	−10.45	39.21	0.50	63.90	977.7
	Maximum	30.51	98.78	5.14	300.59	1019.8
	Range	40.96	59.57	4.64	236.69	42.1
	Median	12.4500	73.7500	1.0500	184.2600	999.500
	Mean	11.4307	72.5688	1.1513	187.0334	999.721
	Std. Dev.	8.31158	14.46379	0.49953	36.82234	7.8657
	Variance	69.082	209.201	0.250	1355.885	61.869
exceeded	N	4	4	4	4	
	Minimum	−12.37	63.99	0.82	131.81	
	Maximum	3.78	76.03	1.28	181.50	
	Range	16.15	12.04	0.46	49.69	
	Median	−3.3450	67.7850	0.9150	153.1700	
	Mean	−3.8200	68.8975	0.9825	154.9125	
	Std. Dev.	6.81552	5.75644	0.21014	20.92824	
	Variance	46.451	33.137	0.044	437.991	
Total	N	301	301	301	301	145
	Minimum	−12.37	39.21	0.50	63.90	977.7
	Maximum	30.51	98.78	5.14	300.59	1019.8
	Range	42.88	59.57	4.64	236.69	42.1
	Median	12.4000	73.4600	1.0500	183.8700	999.500
	Mean	11.2281	72.5200	1.1490	186.6066	999.721
	Std. Dev.	8.46674	14.38473	0.49701	36.82065	7.8657
	Variance	71.686	206.921	0.247	1355.760	61.869

5 Conclusion

Atmospheric pollution is an important factor in material deterioration including degradation of systems used for material protection. Due to pollution, the lifetime of technological products is shortened. Buildings, other structures, as well as objects of cultural heritage exposed to the atmosphere deteriorate more rapidly. The resulting physico-chemical and economic damage can be significant - not to mention the loss of unique parts of cultural heritage and hazards due to endangered reliability of complicated technological devices. Climate and pollution are acting together in a complex way, resulting in corrosion and degradation of materials. Even if the greatest effects of reducing air pollutants, regarding the degradation of materials, have already been observed in Europe, further reducing air pollutants is one of the more effective ways of compensating for increased risk of corrosion due to climate change. The effects of global climate change are closely related to

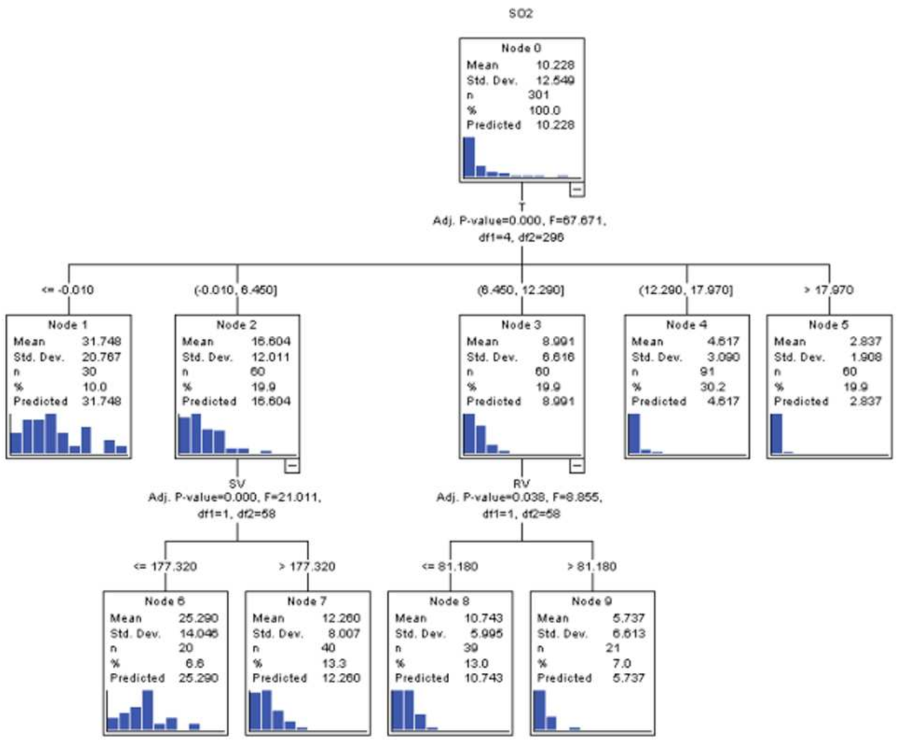

Fig. 4. Decision tree with appropriate variables.

local changes in air pollution trends. Future revisions and formulations of air quality directives aimed at the protection of cultural heritage and the built environment should consider this.

Bad condition of buildings belonging to cultural and historical heritage and monuments can be something that has to be avoided, at any expense. Materials cannot be expected to last forever. Restoring is necessary, together with primary protection measures, especially in areas with polluted air. Many objects which have been exposed to pollution for many years are in so bad condition that it is possible only to remove them and make their copies (replications), which is being done more and more frequently in the world. Different efforts to save something can be based on estimate of jeopardy of some object through appropriate taxes for air pollution, by which restoration of these objects would be financed.

Through monitoring of pollutants, monitoring of exceedings of set values is achieved. During analyzed period, pollution by SO2 was monitored at the researched area. For modelling of air pollution by SO2, decision trees were used, together with analytical and statistical tool SPSS 17. Results show that concentration of SO2 decreases as temperature increases. Concentration of SO2 and temperature correlate and they represent combustion of fossil fuels and the effect of industry, which confirms previous research. Results of modeling showed that, based on meteorological parameters, it is possible to clearly predict possible pollution by SO2 and future research should still be oriented towards interrelation between meteorological parameters and their mutual influence on construction materials and heritage.

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