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ANTHROPOGENIC EFFECTS ON THE AIR POLLUTION IN THE CITY OF SKOPJE, REPUBLIC OF MACEDONIA

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Abstract

Anthropogenic air pollution is a serious problem in urban areas. It modifies urban climate and deteriorates natural environment, economy and human health. The high concentration of industry and transportation causes large input of air pollution to urban atmosphere. Smog occurrence and high fallout of dust and soot are characteristic effects of that pollution.

Monitoring system with automated air monitoring stations was established in Skopje, Republic of Macedonia. Each station contains instruments for continuously measuring the concentration of CO, SO_2, NO, NO_2, suspended particular matters (SPM), O_3 in the air and at the same time, instruments for measurement of different meteorological parameters (temperature, humidity, wind speed, wind direction and solar radiation). It was found that the concentration of major pollutants (SO_2, NO_x, CO and SPM) increases remarkably during the heating season. These data are correlated with those obtained for stationary and mobile emission sources. High concentrations, especially in winter, are caused by additional pollution from heating facilities including home heaters, by geographical conditions peculiar for Skopje and by meteorological conditions which shows the tendency to form temperature inversion layers. On the basis of those data and data obtained from upper-layer meteorological data, atmospheric stability, which is an index expressing the relative difficulty of atmospheric dispersion, was determined. Data for heavy metals content in the SPM collected by high and low volume samplers in the city of Skopje are also given.

INTRODUCTION

Many of the cities in the Republic of Macedonia, including the capital, Skopje, are located in basins surrounded by mountains. The meteorological conditions unique to such basins are thus causing air pollution called "stagnation", due to gases emitted from factories, automobiles and households, often posing a serious problem to Macedonia [1-3]. Especially in some industrial cities, including Skopje, such air quality aggravation is serious especially in winter period when basin fogs generate. However, due to lack of an automatic monitoring method, there still exist many problems such as being unable to respond immediately to the aggravation in the concentration of air pollution.

Besides getting a better understanding of the present situation of air pollution, it is also important to make improvements in the monitoring system for the enactment of regulatory laws as well as assessments of improvements. Because of that, an air pollution monitoring system with four automatic monitoring stations in the city of Skopje was established [4-6]. Each station contains instruments for continuous measuring of the concentration of CO, SO_2, NO, NO_2, suspended particular matters (SPM) and O_3 (for one station) in the air, and instruments for the measurement of some meteorological parameters (temperature, humidity, wind speed and wind direction, and solar radiation for one station). All stations are connected with the central station for transferring data and for data processing. Starting 2003 this automatic air pollution monitoring system will be extended with stations in the cities of Kumanovo, Kocani, Kicevo and Bitola. In the city of Veles there are already 2 stations controlled by the "Zletovo" lead and zinc smelting plant.

In this paper the analysis of automatic continuous monitoring (AAM) results for meteorological as well as ambient air quality data was carried out for the period of April 1998 to March 1999 (non-heating season from April to September 1998, and the heating season between October 1998 and March 1999) is given. Those results are compared with those obtained for stationary (factories, heating facilities etc.) and mobile (mainly traffic) emission sources. Those results give many explanations about the air pollution in the region of the City of Skopje, distribution of the pollutants and the appearing of the "stagnation" phenomenon.

MATERIALS AND METHODS

On the basis of the meteorology and topographic conditions of emission sources, and preliminary investigation of distribution pattern of ambient air concentrations, the locations for four automated air monitoring stations was evaluated and installed: Station 1 (Gazi Baba), which is background concentration located on the top of the hill; Station 2 (Center), city area location in the central area of Skopje City; Station 3 (Karpoš), measuring point for measuring emission gases from automobiles located at the cross-junction of trunk road; Station 4 (Lisiče), measuring point located between industrial area and the new towns. The parameters being monitored and the monitoring instruments used are listed as bellow: SO_2 (Ultraviolet fluorescent method), NO_x (chemiluminiscence method), CO (non-dispersive infrared analyzer method), O_3 (Ultraviolet absorption method) and SPM (gravity balance method). Meteorological parameters are: temperature, humidity, wind speed, wind direction and solar radiation.

The monitoring altitude is set at a range of 3-4 m, taking into consideration the influence due rescattering of SPM. Auto-calibration method is used in the calibration of instruments. The monitored data is recorded in the data logger as well as the recorder and transmitted to the Central Station using the telemetric system. At the same time, this information is then sent out from the Central Station to the public information system set up in the town area. Each monitored station is well equipped with voltage regulators, UPS for data loggers, air-conditioners and security system for monitoring purposes.

Heavy metals determination in the SPM samples taken from the high volume and low volume samplers were carried out by the atomic absorption spectrometry and by x-ray fluorescence spectrometry.

RESULTS AND DISCUSSION

Meteorological Conditions

Surface Meteorology

Wind Direction and Speed. In observing the general trend, it was found that W and E winds have high frequencies while there are hardly any signs of an N wind. In addition, the wind velocity is weak and this is a characteristic of Skopje City. As for the variation of the monthly average wind velocity, there is a decreasing trend until June and gets slightly stronger in December.

Temperature and Humidity. The fluctuation in the daily average temperature and humidity are the same for every station. In addition, together with the temperature increase from May to August, humidity also decreased. In August, the highest daily temperature is about 30 °C while the humidity is about 40 %. The highest hourly value is about 40 °C. However, in the last half of December, approximately minus 10 degrees was recorded even in the daytime.

Solar Radiation. According to the data from Lisice Station, there is a significant increase in the solar radiation in summer. This is based on the monthly average temperature.

Appearance Frequency of Atmospheric Stability Classes. The atmospheric stability is an index for expressing the relative difficulty of atmospheric dispersion. When the atmosphere is unstable, dispersion of emitted pollutants in the air is accelerated. The pollutants emitted from a low stack are easily dispersed and the concentration level rapidly decreases. On the other hand, pollutants released by a tall stack are easily carried a long distance by advection, and a high concentration of pollutants occurs on the ground. When the atmosphere is stable, it is difficult to disperse pollutants. Pollutants emitted from a low stack are found the high concentration. Contrarily, pollutants released from a tall stack do not easily fall to the ground and the concentration of pollutants on the ground is low.

The investigated heating season, in particular the winter season, shows a tendency to be stable as compared to the non-heating season. In Skopje, the wind is often weak and there are many fair days in the summer season. The atmosphere is very unstable in this season when the solar radiation is high. The air pollutants are mixed and dispersed and hence unlike the winter season, the concentration does not get very high. On the other hand, during nighttime when there is no solar radiation, the atmospheric stability class is either neutral or shifting towards the stable side, and thus unlike the daytime, the mixing and dispersing of the atmosphere does not occur. As a result, the concentration of the air pollutants is often found higher at night than in the day, despite little traffic. In the case whereby the meteorological conditions in Skopje are being considered, the air pollutant concentration level and concentration variation obtained from this investigation is reasonable.

Upper-layer Meteorology

Using radiosondes and measuring temperature, wind direction and the vertical distribution of the wind velocity, additional survey of the upper layer meteorology was conducted. During the autumn season temperature inversion was found in the region of

400-1000 m above the ground. It was also found that the lower layers are unstable and the upper layers are stable. During the winter season (December-January) the inversion layer phenomenon occurs very frequently from about few hundred meters to 1000 m is 4°C/100 m). One of the reasons for this could be due to the geographical conditions whereby there are flat plains in the valley area. Under such meteorological conditions, emitted pollutants accumulate near the ground level without spreading to a wider region and severe air pollution occurred.

Ambient Air Quality

Sulfur Dioxide (SO_2)

In the non-heating season, SO_2 concentration level in the air neither exceeds the daily average value and hourly 98% value as well as maximum set by environmental standards (maximal mean daily concentration of 150 μg/m^3) for any of monitoring stations. When comparing the concentration level for each monitoring station, non-heating season shows low concentration and there is not any significant difference. In particular the winter season, very often the environmental standards are being exceeded and in some cases, extremely severe air pollution occurred continuously. Taking into the consideration the cases for combined pollution with SPM, from the period of the end of December to the start of January, the concentration of SO_2 exceed the limit for alarm in the First Stage.

Nitrogen oxides (NO, NO_2, NO_x)

During the heating season and in particular the winter season, the limit for the environmental standards are frequently being exceeded and like the case of SO_2, there are cases when the environmental standards are being continuously exceeded. When comparing the NO_2 concentration level for each monitoring station, Station 2, clearly shows the highest value. On the other hand, Station 1 tends to show low values as compared to the other monitoring stations. In addition, the highest 24-hour and hourly value for NO_2 and NO_x concentration sometimes is high in the case of Lisice. During the non-heating season, most of the time, the causes of NO_x can be considered to be due to automobile emission. While it is plausible to conclude that this is reflective of the surrounding areas near each monitoring stations. The ratio of NO_2 to NO_x (NO_2/NO_x) in the non-heating season and the heating season are shown in Table I.

Table I. Ratio of NO_2 to NO_x (April 1998 – March 1999)

Season	Station 1	Station 2	Station 3	Station 4
Non-heating season	0.7597	0.4882	0.5610	0.4323
Heating season	0.4968	0.2837	0.3597	0.2664

The NO_x formed by combustion normally takes the form of NO. Thus by analyzing the ration NO_2/NO_x, the emission source condition and oxidation mechanism can be clarified. The NO is oxidizing in the air and changes into NO_2 while influenced by the combined effect of solar radiation and O_3. The high value of Gazi Baba Station was thought to be the active NO_2 conversion-taking place because there is no NO_2 sources in the vicinity. As for Lisice Station, however, the influence of mobile sources on NO_2 conversion was thought significant. It was thought that solar radiation in the winter period was week and less influential on ratio of NO_2 to NO_x together with the heating plant effect.

Carbon monoxide (CO)

In the non-heating season the concentration level of CO in the air exceeds that required by the environmental standards in almost every case except Station 1. In the heating season the environmental standards were exceeded in all the cases for all the monitoring stations. The reason for this is that the standard values set are higher compared with that of Western standards. Among the four Monitoring Stations, like in the case for NO_x, the Center tends to show a slightly higher concentration level. As for the non-heating season, a high contribution was from automobiles and it was thought that high CO concentration of Station 2 and 4 being influence of such automobile emission that Station 1.

Suspended Particular Matter (SPM)

SPM concentration during the non-heating season exceeds the standard value in most cases in all monitoring stations. Aberrant hourly concentration such as 209 $\mu g/m^3$ in the 98 percentile is not merely resulted from stationary source and exhaust gas from vehicles. It can be resulted from suspended dust. It is known that in the cases of weak wind and dry air, like Skopje, the atmosphere tends to stay and SPM concentration level to increases. Moreover, the running car also effectuates the ground dust pick-up. During the heating season the environmental standards have been exceeded in all the cases at all the monitoring stations. In particular, the hourly value for Karpos station shows a high value (800 $\mu g/m^3$) and like the case of SO_2 causes severe air pollution.

Ozone (O_3)

The ozone concentration was monitored at Karpos and Lisice stations. The result of both stations resulted were almost identical but exceeded the standard from April to August. From September onwards and until mid-November, the concentration was observed to decrease, and after that, the level of concentration did not show much decrease, similar to that in the summer.

Appearance Frequency Distribution of Air Pollution Concentration

The appearance frequency distribution of air pollutant concentration provides strong support for the presumption that the pollutant source affects the characteristics of the air pollution phenomena at each monitoring station. There are significant differences observed between the heating and non-heating season such making it obvious that the air pollution in Skopje City is concentrated in the heating season. The figures of frequency distribution on each item reflect the characteristics of each point:

- As for NO_x in the non-heating season, 90 % of the frequency is within the range of 30 ppb concentration at Station 1. However, those at Station 2 and Station 4 are about 90 ppb. The value of 50 % frequency is about 10 ppb at Station 1, while those at the other points are at concentrations a few times higher than that at Station 1, where the characteristics of the monitoring points could be seen. As for NO_x in the heating season, 90 % of the frequency is within the range of 100 ppb at Station 1, and 230 ppb at Station 4. Concerning the other points, then are within that range.
- Comparing the monitored parameters, there are some differences in their pattern and it was noticed that their emission differs a little.
- Frequency of NO_x in the non-heating season appears higher at Station 2 and Station 4 and that of SO_2 at Station 1 and Station 2, and that of SPM at Station 2 and Station 3 are high. Each parameter always shows higher values at Station 2. However, the distribution of concentration differs, for example SPM appears to be high at Station 4 in the heating season.

Heavy metal content in suspended particular matters and dust

Two types of SPM samples were collected applying high volume sampler (tip, firma) and low volume sampler (Andersen type).

Using high volume sampler for 24 hours of sampling time, about 600 m^3 of air were passed through three filters collecting three types of SPM samples: >10 μm, between 2 μm and 10 μm and <2 μm. It was found that in all samples more that 95 % of SPM belongs to the fraction of <2 μm. This fraction as large amount of extracted SPM was prepared and analyzed using atomic absorption spectrometry for 11 elements including heavy and toxic metals (as, Pb, Cd, Zn, Mn, Cr, Cu etc.). Obtained data show that in heavy metal components, Pb (less than 0.4 $\mu g/m^3$) was not exceeded the environmental standard level (0.7 $\mu g/m^3$) except for some periods in winter were this concentration is over the limited value. In carbon components, the content of elemental carbon and of organic carbon are very high (between 20-30 % of each form of carbon from total mass of SPM). Data of some heavy metal analysis in SPM from high volume samplers for 4 sampling points in Skopje for the period April-August 1998 and February and March 1999 are given in Table 2.

Table 2. Results from metal analyses in dust collected from High Volume Samplers from the Stations (dust with particles below 2 μm)

Month/ Station	SPM, mg/m³	Element, μg/m³							
		Pb	Zn	Fe	Mn	Cr	Cu	Ni	Cd
April '98									
Gazi Baba	0.0406	0.0807	0.999	0.644	0.0178	0.0339	0.0084	0.0387	0.0054
Centar	0.0457	0.213	1.028	0.319	0.0139	0.0103	0.0071	0.0059	0.0061
Karpos	0.0372	0.138	1.083	0.347	0.0292	0.0194	0.0185	0.0038	0.0015
Lisice	0.0406								
May '98									
Gazi Baba	0.0194	0.343	0.516	0.324	0.0305	0.0077	0.0070	0.0032	0.0021
Centar	0.0221	0.197	0.535	0.297	0.0229	0.0090	0.0063	0.0	0.0019
Karpos	0.0224	0.152	0.479	0.324	0.0115	0.0088	0.0082	0.0	0.0019
Lisice	0.0238	0.255	0.506	0.328	0.0152	0.0256	0.0052	0.0058	0.0012
June '98									
Gazi Baba	0.0421	0.0763	0.416	0.221	0.0113	0.023	0.0275	0.0	0.0024
Centar	0.0425	0.152	0.252	0.263	0.0098	0.0048	0.0105	0.0063	0.0012
Karpos	0.0400	0.149	0.382	0.195	0.0065	0.0076	0.0098	0.0006	0.0009
Lisice	0.0402	0.190	0.231	0.313	0.0089	0.0170	0.0039	0.0033	0.0013
July '98									
Gazi Baba	0.0263	0.047	0.03	0.200	0.0104	0.0008	0.0024	0.0062	0.0010
Centar	0.0358	0.233	0.015	0.256	0.0109	0.0152	0.0081	0.0021	0.0015
Karpos	0.0224	0.191	0.01	0.179	0.0087	0.090	0.0095	0.0025	0.0012
Lisice	0.0380	0.298	0.015	0.271	0.0132	0.0024	0.0067	0.0045	0.0048
August '98									
Gazi Baba	0.0174	0.202	0.019	0.191	0.0365	0.0090	0.0027	0.0026	0.0020
Centar	0.0322	0.263	0.020	0.275	0.0196	0.0037	0.0079	0.0018	0.0035
Karpos	0.0380	0.286	0.058	0.122	0.0092	0.0032	0.0206	0.0014	0.0164
Lisice	0.0550	0.271	0.007	0.271	0.0166	0.0013	0.0087	0.0035	0.0001
February '99									
Gazi Baba									
Centar	0.0564	0.711	0.056	0.184	0.010	0.0028	0.0057	0.008	0.0020
Karpos	0.0702	0.572	0.130	0.243	0.0295	0.0059	0.0064	0.011	0.0027
Lisice	0.0840	0.362	0.088	0.494	0.0176	0.0088	0.0149	0.010	0.0034
March '99									
Gazi Baba									
Centar	0.0268	0.193	0.046	0.185	0.0056	0.0026	0.0054	0.003	0.0015
Karpos	0.0270	0.173	0.056	0.122	0.0049	0.0064	0.0058	0.003	0.0016
Lisice	0.0349	0.179	0.048	0.214	0.0078	0.0130	0.0060	0.006	0.0016

During the period of December 1997 through February 1998, supplemental measurement of fine particles concentration were conducted in Skopje using low volume sampler. SPM samples were collected by three sizes (PM2.5, PM5 and PM10) on three observation points in Skopje (2 in the more frequently part in the city and one near the Hydrometeorological Institute. Some of the samples from different sampling points were mixed and analyzed by AAS. The obtained results are given in Table 3.

Table 3. Results from metal analyses from mixed filter samples of SPM taken by Andersen-type Low-Volume Sampler

Month/ Station	Total mass, mg	Element, µg/mg							
		Pb	Zn	Fe	Mn	Cr	Cu	Ni	Cd
Sample 1	13.3	1.278	0.226	6.240	0.748	0.145	0.154	0.172	0.0375
Sample 2	8.25	1.273	0.1576	7.758	1.067	0.0958	0.091	0.201	0.071
Sample 3	9.44	1.006	0.1695	3.072	0.577	0.0095	0.159	0.147	0.0106
Sample 4	3.96	7.071	0.581	13.89	0.795	0.0417	0.53	0.303	0.0353
Sample 5	9.79	3.473	0.398	21.55	1.236	0.136	0.408	0.202	0.0215

Sample 1 (RHMZ, PM 10 µm): T1; T2; T8; T10 and T12
Sample 2 (RHMZ, PM 10 µm): T23; T45; T49; T51 and T53
Sample 3 (RHMZ, 2 samples 2.5 µm; 3 samples 5.0 µm): T4; T5; T7; T9 and T11
Sample 4 (Majcin Dom, PM 10 µm): T44; T50; T52; T54 and T60
Sample 5 (Railway Station, PM 10 µm): T61; T63; T64; T65 and T66

The results clearly showed the high content of all investigated heavy metals (Pb, Zn, Fe, Mn, Cu, Ni and Cd) in the samples 4 and 5 (near the Railway station) as compared the sample taken near the unurban area (Sample 1, 2 and 3). As for carbon, Railway station sample point show higher value of carbon in SPM (40-50 %).

Filters were also subjected to elemental analysis by X-Ray fluorescence spectrometry (XRF). From these analysis 12 elements (Al, Si, S, Cl, K, Ca, V, Mn, Fe, Zn, Br and Pb) were chosen for analysis of statistical technique - Principal Component Analysis (PCA). The matrix of linear coefficients for all 56 samples is given in Table 4. For n=56, correlation coefficient greeter than 0.35 in this matrix indicate a statistically significant (p=0.01) relationship. However, only coefficient value greater than 0.7 would indicate that at least 50 % of the variability can be explained by a linear association between the two elemental concentrations.

Table 4. Correlation matrix describing the correlation between the measured elements

	Al	Si	S	Cl	K	Ca	V	Mn	Fe	Zn	Br	Pb
Al	1.00	0.78	0.73	0.48	0.73	0.47	0.79	0.66	0.66	0.55	0.35	0.38
Si	0.78	1.00	0.74	0.47	0.80	0.47	0.58	0.61	0.58	0.55	0.18	0.22
S	0.73	0.74	1.00	0.89	0.98	0.89	0.75	0.62	0.86	0.63	0.59	0.59
Cl	0.48	0.47	0.89	1.00	0.90	0.99	0.55	0.34	0.85	0.54	0.72	0.70
K	0.73	0.80	0.98	0.90	1.00	0.90	0.69	0.56	0.86	0.63	0.57	0.58
Ca	0.47	0.47	0.89	0.99	0.90	1.00	0.55	0.36	0.84	0.52	0.69	0.68
V	0.79	0.58	0.75	0.55	0.69	0.55	1.00	0.61	0.74	0.51	0.53	0.54
Mn	0.66	0.61	0.62	0.34	0.56	0.36	0.61	1.00	0.60	0.49	0.38	0.38
Fe	0.66	0.58	0.86	0.85	0.86	0.84	0.74	0.60	1.00	0.71	0.87	0.87
Zn	0.55	0.55	0.63	0.54	0.63	0.52	0.51	0.49	0.71	1.00	0.57	0.70
Br	0.35	0.18	0.59	0.72	0.57	0.69	0.53	0.38	0.87	0.57	1.00	0.98
Pb	0.38	0.22	0.59	0.70	0.58	0.68	0.54	0.38	0.87	0.70	0.98	1.00

Good correlation is observed between S, Cl, K, Ca and Fe, suggesting that these elements were carried together in the same air mass, either because they arise from a single type of source, or because the spatial and temporal distributions of emissions from contributing source types are similar in Skopje. Particulate sulfur is expected to be preliminary the result of secondary sulfate, whose origin is SO_2 from the combustion of fuel oil. There is also good correlation between Al, Si, K, V, Mn and Fe.

Iron and manganese and potassium are all present in the aluminosilicate phase (crustal dust or rock).

Potassium is known to be more abundant in smoke from woodburning. These findings suggest that the correlation of S and K (Fig. 1) arise from stagnation conditions in cold weather, resulting in an accumulation in the atmosphere over Skopje of concentrations of heating source emissions over a long enough time period for some fraction of the SO_2 to oxidize to sulfate (one or two days). Ca and Fe are not commonly associated with heating sources, and thus represent another source of fine particles that accumulate during stagnation (probably cement manufacturing).

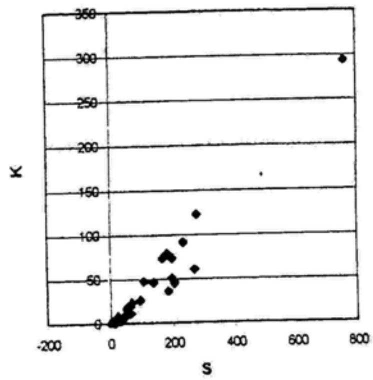

Fig. 1. K vs. S scatterplot

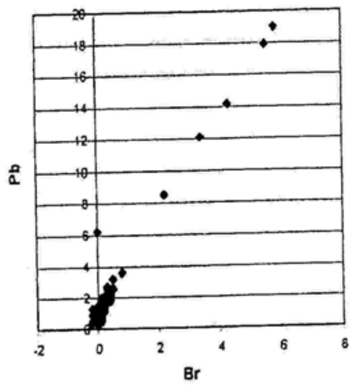

Fig. 1. Pb vs. Br scatterplot

Also, as expected, Br and Pb show a strong correlation, as both present in fixed ratios in the exhaust of vehicles fueled with leaded gasoline (Fig. 2).

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