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Variation of PM_{10}, NO_2, NO and O_3 in City of Mostar, Bosnia and Herzegovina

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Abstract: Pollutants such as particulate matter PM, nitrogen oxides and troposferic ozone are harmful to a human health. Study of pollutant variation and its relationship is of importance not only for environmental protection but also for the benefit of public at large. The aim of this study was to analyze seasonal and daily variation of PM_{10}, NO_2, NO and O_3 in a residential part of an urban area. The study was conducted from January 1 till December 31, 2011 in the City of Mostar using the following methods: absorption of beta radiation, chemiluminescence and UV photometry. The results presented in this article, show the dependence of air pollution levels upon traffic density and seasons. Considering the level of air pollution relative to the regulated limited and tolerated values, the measured 24-hour concentrations of all studied pollutants did not exceeded the limited values and tolerated values.

INTRODUCTION

Air pollution is the introduction of chemicals, particulate matter, or biological materials that cause harm or discomfort to humans or other living organisms, or cause damage to the natural or built environment, into the atmosphere. According to the WHO (*World Health Organization*) air pollution is a significant risk factor for multiple health conditions including respiratory infections, heart disease, and lung cancer. Air pollution is always a public concern, especially in urban areas. Study of pollutant variation is of importance not only for environmental protection but also for the public at large. Air pollution can be natural or human-made.

Particulate matter is the term for solid or liquid particles found in the air. Because particles originate from a variety of mobile and stationary sources (traffic, industrial processes, combustion plants, *etc*.), their chemical and physical compositions widely vary. In 1987., EPA (*Environmental Protection Agency*) replaced the earlier Total Suspended Particulate (TSP) air quality standard with the PM_{10} standard.

The PM_{10} standard includes particles with a diameter of 10 micrometers or less. Because of their small size, particles PM_{10} can penetrate the deepest part of the lungs such as the bronchioles or alveoli. Larger particles are generally filtered in the nose and throat via cilia and mucus, but particulate matter smaller than about 10 micrometers, referred to as PM_{10}, can settle in the bronchi and lungs and cause health problems. Major concerns for human health from exposure to PM_{10} include: effects on breathing and respiratory systems, damage to lung tissue, cancer, and premature death (Li-Shun Lu et al. 2006).

The term »nitrogen oxides» NO_X refers to a group of oxides formed in the combustion process, the principal constituents of which are nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are among the common atmospheric pollution. The principal sources of NO_X are motor vehicles and fuel combustion process and local heating. The majority of nitrogen oxides emitted from vehicle exhausts are in the form of NO. This gas can react with unburned hydrocarbonates, also present in the exhaust, to form NO_2. Nitric oxide is not considered harmful at ambient concentrations. Nitric dioxide ,NO_2 is a reactive pollutant

formed by oxidation of atmospheric nitrogen during fuel combustion at high temperature and a key component for the rise of secondary toxic pollutant (nitric acid, the nitrate part of secondary inorganic aerosols and photo-oxidants including ozone). Oxides of nitrogen have adverse effects on human beings, plants and animals. For human beings, NO_X can, at high concentrations (10-30 ppm), cause nose and eye irritation, pulmonary edema, bronchitis and even pneumonia. Fortunately, the levels even in the polluted areas are not quite that high. The effects on plants are more severe (necrosis and growth retardation) (Yuan Gao *et al.* 2011). In addition to potentially damaging human health, nitrogen oxides are precursors to ozone (O_3) formation, which can harm human health and vegetation. Finally, nitrogen oxides contribute to acid deposition, which damages vegetation and aquatic ecosystems (Hariri M.H., 1994; Lelieveld J. and Dentener F. J., 2000).

Ozone is the most important photochemical oxidant in the troposphere and it is the key ingredient of so-called summer smog, the main pollution problem in almost all big cities worldwide. It is a secondary pollutant since it is not emitted directly. The majority of tropospheric ozone formation occurs when nitrogen oxides (NO_X), carbon monoxide (CO) and volatile organic compounds (VOCs), react in the atmosphere in the presence of sunlight. NO_X, CO, and VOCs are called ozone precursors. Motor vehicle exhaust, industrial emissions, and chemical solvents are the major anthropogenic sources of these chemicals. Ozone has harmful effects on vegetation and human health. Long-term effects of ozone on human health include an increased incidence of asthma and lung cancer, impaired pulmonary function, *etc*. In addition, ozone is a significant greenhouse gas, particularly in the cold upper troposphere (Logan,1985).

Table 1. Limit and tolerance values of air pollutants – National Standards

Pollutant	Limit value c, μg m^{-3}	Maximum margin of tolerance c, μg m^{-3}	Averaging period	Permitted exceedences each year
NO_2	200	225	1 h	18
NO_2	85	125	24 h	/
PM_{10}	50	75	24 h	35
O_3	120	/	8 h	25*

* Averaged over 3 years

The European Union has developed an extensive body of legislation which establishes health based standards (limited and tolerated values) and objectives for a number of pollutants in air. These standards for measured pollutants in this study are summarized in the Table 1.

In the present study, seasonal and daily variation of PM_{10}, NO_2, NO and O_3 was analyzed in a residential part of an urban area.

EXPERIMENTAL

Measuring site and period

The study was conducted from January 1 till December 31, 2011 in the City of Mostar with 111 116 inhabitants (evaluation as per 2008). Station for monitoring (tracking) air quality Mostar-1 is placed in the western, residential part of the City of Mostar (coordinates: N 43° 20´ 42,6´´ i E 017° 45´ 34,7´´; 64 m above the sea level), at >6 m distance from a main street with high traffic intensity.

Sampling and measuring methods

Particulate matter PM_{10} was measured by the method of beta radiation absorption on a Verewa Beta-Dust Monitor F-701-20. The Beta Dust Meter measures the dust concentration in μg dust/cubic meters of gas. The sample gas is drawn through a glass fiber filter tape and the volumetric flow of the gas is recorded by the system. The dust particles are then trapped on the filter tape and radiometrically measured. The radiometric measurement is achieved using a Betaemitter (C-14) and a Geiger-Müller counter.

NO_2 and NO were measured by the method of chemiluminescence on NO_X–Analyzer, Horiba Model APNA–370. The APNA-370 uses a combination of the dual cross flow modulation type chemiluminescence principle and the referential calculation method. This gives it the advantages of the single-detector method plus the ability to do continuous measurements of NOx, NO, and NO_2. The design gives great stability and extremely high sensitivity.

O_3 was measured by the method of UV photometry on O_3– Analyzer Horiba Model APOA–370. The APOA–370 is using the non-dispersive ultraviolet absorption (NDUV) method as its operating principle. The ultra-violet-absorption method works on the principle that ozone absorbs ultra-violet rays in the area of 254 nm.

RESULTS AND DISCUSSION

During 2011, the measured concentrations of airborne pollutants showed quite a regular pattern. During the winter period (Oct-Mar), the highest average 24-hour a month air concentrations were recorded for the following pollutants: PM_{10} (17.21 – 29.99 μg m^{-3}), NO_2 (14.24 – 21.51 μg m^{-3}) and NO (2.38 – 10.90 μg m^{-3}).

In the summer period (Apr-Sep), these pollutants showed lowest 24- hour concentrations: PM_{10} (12.60 – 23.08 μg m^{-3}) NO_2 (7.70 – 14.96 μg m^{-3}), and NO (0.12 – 1.16 μg m^{-3}).

The results of seasonal variation in 24-hour concentrations of PM_{10}, NO_2 and NO, indicating higher values in winter, could be explained by air pollution from two emission sources: higher traffic intensity and a number of public institutions boiler-rooms. The higher values of PM_{10} concentration in the summer period was probably consequential to the growing number of resuspended particles due to dry weather and wildfires in this areas *(*Toth I. *et al*. 2011).

An inverse pattern was only observed for ozone (O_3), as lowest concentrations of this pollutant were recorded in the winter period (41.79 – 74.43 μg m^{-3}) and highest in the summer (85.28 – 94.53μg m^{-3}) (Table 2.).

In Figure 1 are presented the 24-hour concentrations of pollutants during 2011. The pollutants showed maximum values in late autumn and winter: PM_{10} (max value 61.83 μg m^{-3}, peak on 03/12/2011), NO_2 (max value 50.55 μg m^{-3}, peak on 12/02/2011) and NO (max value 47.78 μg m^{-3}, peak on 14/01/2011), while O_3 reach its maximum in spring and summer (max value 121.94 μg m^{-3}, peak on 28/09/2011).

Table 2. Monthly variation of 24-hour pollutant concentrations in Mostar, 2011.

	Pollutant/24-hour concentrations (μg m^{-3})					
	Particullate matter PM_{10}			Nitrogen dioxide NO_2		
	Min.	Max.	$\overline{X}$	Min.	Max.	$\overline{X}$
Jan	4.26	61.13	**24.58**	7.63	50.55	**20.64**
Feb	10.50	55.83	**29.99**	7.69	47.61	**21.51**
Mar	5.67	58.75	**23.79**	5.96	38.58	**18.52**
Apr	9.67	39.71	**17.86**	5.97	27.01	**14.96**
May	5.29	26.76	**15.47**	4.39	24.14	**10.28**
Jun	8.13	37.98	**17.65**	4.57	16.79	**9.28**
Jul	5.62	29.47	**12.60**	4.52	15.04	**8.75**
Aug	6.95	24.00	**22.08**	4.69	14.67	**7.70**
Sep	7.77	37.30	**23.08**	7.02	21.33	**12.93**
Oct	4.18	35.28	**17.21**	3.65	32.54	**14.24**
Nov	11.88	46.65	**23.60**	6.15	35.55	**20.24**
Dec	4.17	61.83	**17.80**	3.78	44.39	**18.21**

	Nitrogen monoxide NO			**Ozone O_3**		
	Min.	Max.	$\overline{X}$	Min.	Max.	$\overline{X}$
Jan	0.42	44.78	**10.90**	7.98	82.81	**43.69**
Feb	0.04	21.87	**4.92**	17.84	92.37	**63.55**
Mar	0.03	13.10	**2.38**	34.82	99.96	**74.43**
Apr	0.06	6.54	**0.90**	46.67	114.38	**85.28**
May	0.02	1.15	**0.12**	54.23	115.02	**92.54**
Jun	0.03	1.08	**0.52**	73.41	115.94	**94.53**
Jul	0.46	1.64	**0.97**	59.59	117.13	**90.23**
Aug	0.56	1.67	**1.04**	63.31	108.97	**90.90**
Sep	0.58	2.72	**1.16**	40.92	121.94	**91.30**
Oct	0.69	21.13	**4.60**	15.25	105.14	**54.73**
Nov	0.76	17.79	**7.06**	23.24	75.77	**44.06**
Dec	0.60	43.57	**10.31**	5.69	71.41	**41.79**

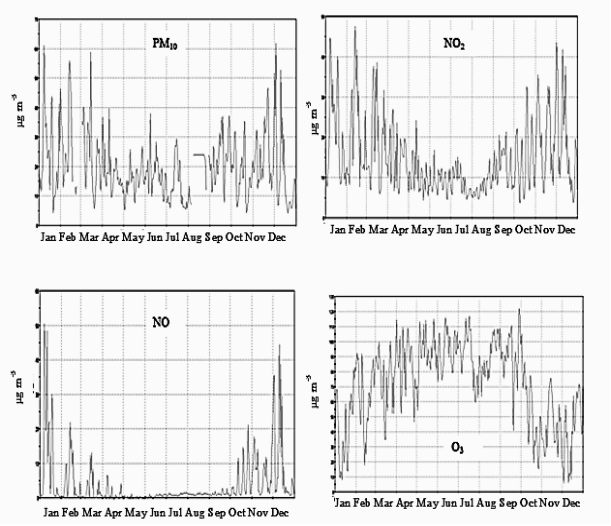

Figure 1. Variation of 24-hour pollutant concentrations during 2011.

In Figure 2 the curves showed a similar pattern of intra diurnal distribution of the mean pollutant concentrations PM_{10}, NO_2 and NO during work-days (Mon-Fri) and weekend (Sat- Sun) throughout 2011. Air concentrations of pollutants were higher on workdays.

The regular diurnal pattern of 24-hour PM_{10}, NO_2 and NO concentrations observed during the week and of intradiurnal concentrations was directly related to traffic intensity. It was indicated by elevated concentrations towards working days and lower values at weekends (WBG 1998).

Ozone is influenced by seasonal and intra diurnal variation. The concentrations decreased towards autumn, to be lowest during winter. Also, higher levels of nitrogen oxides were associated with lower ozone concentrations and *vice versa* because ozone is formed primarly by nitrogen oxides in the presence of sunlight (Figure 3).

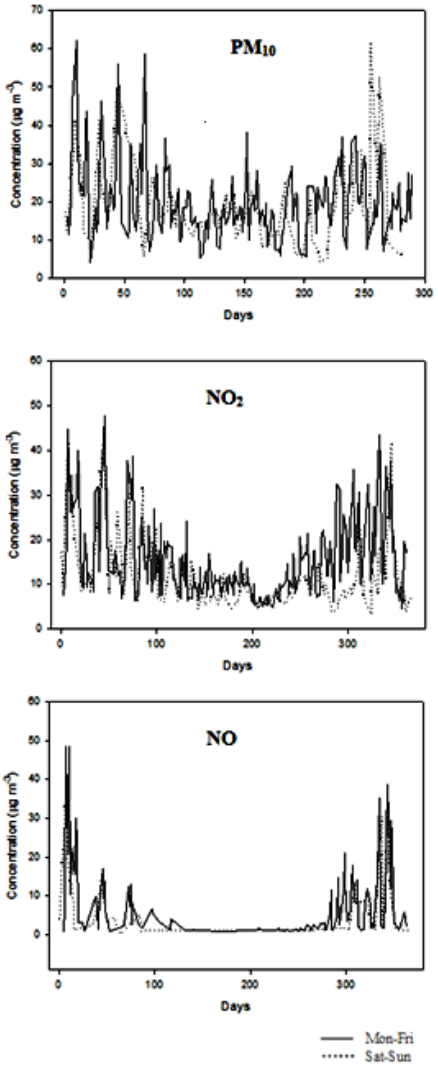

Figure 2. Intradiurnal hourly concentrations of PM_{10}, NO_2, NO and during working and weekend days (2011).

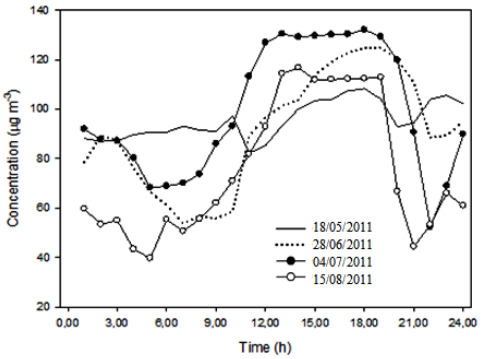

Figure 3. Hourly concentrations of O_3 (2011).

In Figure 4. can be seen that lower ozone concentrations were observed during early morning hours and high ozone levels were typically found in the afternoon. Those days were randomly chosen during summer time to see intradiurnal behavior variation in concentration of O_3.

Similar results have been reported in other study (Yuan Gao *et al.*, 2011, Lelieveld J. and Dentener F. J., 2000).

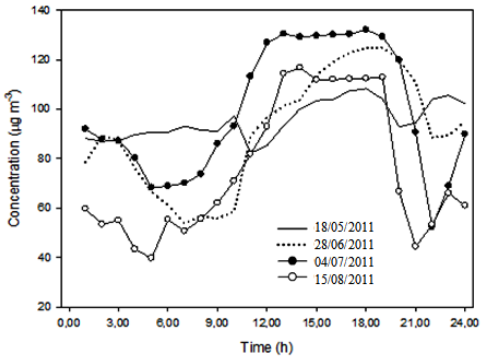

Figure 4. Hourly concentrations of NO_2 and O_3 (2011).

CONCLUSIONS

During the winter, the highest 24-hour air concentrations were recorded for the following pollutants: PM_{10}, NO_2 and NO. An inverse pattern was observed for ozone O_3.

The curves showed a distribution of the mean pollutant PM_{10}, NO_2 and NO concentrations during workdays (Mon-Fri: highest peaks) and weekend (Sat-Sun:lowest peaks). Air concentrations were higher on workdays.

Lower ozone concentrations were generally observed in winter and during early morning hours, while high ozone levels were typically found in summer and in the afternoon.

In the urban area in the City of Mostar the air quality is relatively good with occasionally higher concentration of ozone in the summer time, which did not exceeded limited and tolerated values.

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Summary/Sažetak

Zagađujuće tvari kao što su lebdeće čestice, dušikovi oksidi i prizemni ozon štetni su za ljudsko zdravlje. Svrha ovog rada je analizirati sezonske , dnevne i satne varijacije PM_{10}, NO_2, NO i O_3 na urbanom području grada Mostara. Istraživanje se provodilo u razdoblju od 1. siječnja do 31. prosinca 2011. godine u Gradu Mostaru. Koristile su se sljedeće metode: apsorpcija beta radijacije, kemiluminiscencija i UV fotometrija. Rezultati prezentirani u ovom radu pokazuju povezanost razina onečišćujućih tvari s gustoćom prometa i sezonskim uvjetima. 24 satne koncentracije svih mjerenih onečišćujućih tvari u zraku nisu prekoračile granične i tolerantne vrijednosti definirane zakonskom regulativom.