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Seasonal, Daily and Intradiurnal Variation of PM_{10}, NO_2, NO and O_3 in Residential Part of Zagreb, Croatia

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A B S T R A C T

Pollutants such as particulate matter, nitrogen oxides, carbon oxides, ground-level ozone, etc. are harmful to human health. Study of pollutant variation and its relationship with both dynamic and thermodynamic atmospheric boundary layer (ABL) structures is of importance not only for environmental protection but also for the public at large. The aim of this study was to analyze seasonal, daily and intradiurnal variation of PM_{10}, NO_2, NO and O_3 in a residential part of an urban area, and the effect of some meteorological parameters. The study was conducted from January 1 till December 31, 2004 in the City of Zagreb using following methods: beta radiation absorption, chemiluminescence and UV photometry. The results presented in this article, show the dependence of air pollution levels upon traffic density, seasons and meteorological conditions. Considering the level of air pollution relative to the regulated limit and tolerated values, the measured 24-hour concentrations of all study pollutants exceeded the borderline values and/or tolerated values, however, the number of days with such pollutant concentrations did not exceed the allowed frequency. This is a preliminary study with the main objectives to point to the possible identification of the source of pollution and to assess the level of air contamination according to the new national legislation coordinated with European regulations. Future measurements and studies should evaluate in detail the causes of the concentration levels detected.

***Key words**: air pollution, particulate matter (PM_{10}), nitrogen oxides, ozone, health risk, meteorological parameters*

Introduction

Air pollution is always a public concern, especially in urban areas. Air pollution is mainly caused by the sources of pollutant emission and by weather conditions such as the atmospheric boundary layer (ABL) stability, wind speed and direction, turbulence, temperature, precipitation, humidity, topography, etc[1]. Study of pollutant variation and its relationship with both dynamic and thermodynamic ABL structures is of importance not only for environmental protection but also for the public at large. It is well known that pollutants such as particulate matter, nitrogen oxides, carbon oxides, ground-level ozone, etc. are harmful to human health in different ways.

Airborne particulate matter (PM), a mixture of organic and inorganic substances, originates from a variety of sources such as power plants, industrial processes and diesel trucks, and is formed in the atmosphere by transformation of gaseous emissions. PM concentration measured as PM_{10} (which includes fine and coarse particles) originates not only directly from combustion processes but also from resuspension from street surfaces. In spring, after the snow has melted and streets dry out, particles from street surfaces are resuspended by traffic induced turbulence and wind[2,3]. In northern and Central European cities, resuspended particulate matter can have a substantial influence particularly on total suspended particles but also on PM_{10} concentrations[4,5]. Their chemical and physical composition depends on the location, time of year, and weather. Historically, the association between PM_{10} and mortality has been manifested in many air pollution episodes. Several studies demonstrated the

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relationship between low concentrations of PM_{10} and increase in daily mortality and morbidity[6–8], and between PM_{10} exposure and increase in bronchitis, chronic cough, and respiratory symptoms in persons with chronic obstructive pulmonary disease[9,10]. The term »nitrogen oxides» 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). 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. NO is not considered harmful at ambient concentrations. 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). It is also known that concentrations of NO_2 in ambient air and its potential mixtures can enhance the effects of other environmental pollutants and allergens. The health risks posed by nitrogen oxides may potentially result from NO_2 itself or its reaction products including O_3 and secondary PM. Additionally, NO_2 concentrations closely follow vehicle emissions in many situations so that NO_2 levels are generally a reasonable marker of exposure to traffic related emissions. Epidemiologic studies have provided some evidence that long-term NO_2 exposure may impair pulmonary function and increase the risk of respiratory symptoms. In most of these studies, NO_2 concentrations at the community level were correlated with PM and ozone[11–15]. Ozone is the most important photochemical oxidant in the troposphere. It is formed by photochemical reactions in the presence of precursor pollutants such as NO_x and volatile organic compounds. Ozone has harmful effects on vegetation and human health. There is evidence for a significant association between short-term peaks in ambient air concentrations of O_3 and lung epithelial damage[16]. Long-term effects of ozone on human health include an increased incidence of asthma and lung cancer, impaired pulmonary function, etc.[17].

In the present study, seasonal, daily and intradiurnal variation of PM_{10}, NO_2, NO and O_3 was analyzed in a residential part of an urban area. The effect of some meteorological parameters (temperature and precipitation) on these concentrations was also investigated.

Material and Methods

Measuring site and period

The study was conducted from January 1 till December 31, 2004 in the City of Zagreb with 779,145 inhabitants (as *per* 2001). Zagreb is situated on the southern hills of the Medvednica mountain (1000 m above the sea level), extending towards the Sava valley on the south. Air sampler was placed in the northern, residential part of the City of Zagreb (Gauss-Krüger coordinates: 050-76-794 N; 055-76-542 E; 175 m above the sea level), at >5 m distance from a street with moderate traffic intensity and 400 m distance from a crossing with high traffic intensity.

Sampling and measuring methods

Particulate matter PM_{10} was measured by the method of beta radiation absorption (Automated Equivalent Method: EQPM-0404-151) on an Environment S.A. Model MP101M PM_{10} Beta Gauge Monitor device[18]. NO_2 and NO were measured by the method of chemiluminescence (Automated Reference Method: RFNA-0795-104) on an Environment S.A. Model AC31M chemiluminescence nitrogen oxide analyzer[19]. O_3 was measured by the method of UV photometry (Automated Equivalent Method: EQOA-

TABLE 1
MONTHLY VARIATION OF 24-HOUR POLLUTANT CONCENTRATIONS IN ZAGREB-MIROGOJSKA, 2004

	Pollutant/24-hour concentrations (mgm^{-3})											
	Particulate matter (PM_{10})			Nitrogen dioxide (NO_2)			Nitrogen monoxide (NO)			Ozone (O_3)		
	Min.	Max.	$\overline{X}$	Min.	Max.	$\overline{X}$	Min.	Max.	$\overline{X}$	Min.	Max.	$\overline{X}$
Jan	12.81	59.94	31.54	4.96	73.09	34.93	4.19	57.76	26.23	4.44	49.36	25.11
Feb	16.47	76.63	28.50	8.26	70.42	38.77	2.99	114.26	22.88	5.67	70.42	38.77
Mar	11.66	45.23	28.88	10.26	56.85	29.22	2.92	34.74	12.13	31.74	93.59	57.27
Apr	12.70	49.96	23.52	5.09	35.84	23.74	2.92	22.04	11.11	42.52	83.82	61.88
May	12.83	40.49	19.49	6.83	44.02	19.24	2.20	16.63	8.42	48.61	104.64	73.89
Jun	12.52	28.5	18.56	8.00	28.68	15.50	2.40	12.12	5.88	47.17	113.96	71.33
Jul	11.51	34.01	21.42	3.87	25.14	15.23	1.76	15.08	5.93	45.47	112.28	75.34
Aug	11.94	33.21	21.06	5.23	27.05	13.66	2.11	11.03	5.34	49.56	91.39	70.27
Sep	16.19	45.85	30.48	5.55	33.22	18.14	2.20	38.86	11.36	24.41	93.12	50.37
Oct	15.16	62.89	35.33	6.99	35.75	23.79	4.70	57.90	23.90	6.11	39.97	22.51
Nov	13.30	108.66	41.31	2.16	50.32	26.39	2.73	128.10	29.28	2.27	56.93	23.94
Dec	16.93	84.18	42.59	13.57	45.32	28.29	7.32	65.53	31.86	3.74	44.16	17.02

-0206-148) on an Environment S.A. Model $O_3$42M UV ozone analyzer[20]. The values of air temperature were also recorded. Data on daily precipitation were provided by the Croatian Weather Bureau – Grič Observatory, located about 1 km from the measuring site. The ambient air quality was compared with the National Air Quality Standards[21] to be enacted in 2006.

Results

During 2004, the measured concentrations of airborne pollutants showed quite a regular pattern. During the winter, the highest 24-hour air concentrations were recorded for the following pollutants: PM_{10} (31.54–42.59 μgm^{-3}), NO_2 (28.29–38.77 μgm^{-3}) and NO (22.88–31.86 μgm^{-3}). In summer, these pollutants showed lowest 24-hour concentrations: PM_{10} 18.56 μgm^{-3}, NO_2 13.66 μgm^{-3}, and NO 5.34 μgm^{-3}. An inverse pattern was only observed for ozone (O_3), as lowest concentrations of this pollutant were recorded in winter (17.02–23.94 μgm^{-3}) and highest in summer (71.33–75.34 μgm^{-3}) (Table 1).

The effect of meteorological parameters, especially precipitation, on airborne pollutant concentrations was observable throughout the year. The concentration of pollutants decreased abruptly on days with precipitation (Figure 1).

According to the National Air Quality Standards, the concentration of PM_{10} exceeded the limit value (LV) of >50 μgm^{-3} on 17 occasions, and the margin of tolerance (tolerated value, TV) on 3 occasions during the calendar year. The concentrations of other pollutants (NO_2 and O_3) also were within the allowed limits of excess (Table 2).

TABLE 2
POLLUTANT EXCEEDENCE IN ZAGREB-MIROGOJSKA, 2004

	Pollutant					
	Particulate matter (PM_{10})		Nitrogen dioxide (NO_2)		Ozone (O_3)	
Values (24-hour average)	TV >75 μgm^{-3}	GV >50 μgm^{-3}	TV >120 μgm^{-3}	GV >80 μgm^{-3}	TV >110 μgm^{-3}	GV N/A
Number of days	3	17	0	1	3	
Range of conc. (mgm^{-3})	75.63–108.66	50.48–108.66	0	83,46	110.27–121.97	
Month	Feb, Nov, Dec	Jan, Feb, Oct, Nov, Dec	0	Feb	Jun, Jul	
Regulatory limit	Not to be exceeded more than 35 times a calendar year		Not to be exceeded more than 7 times a calendar year		Not to be exceeded more than 7 times a calendar year	

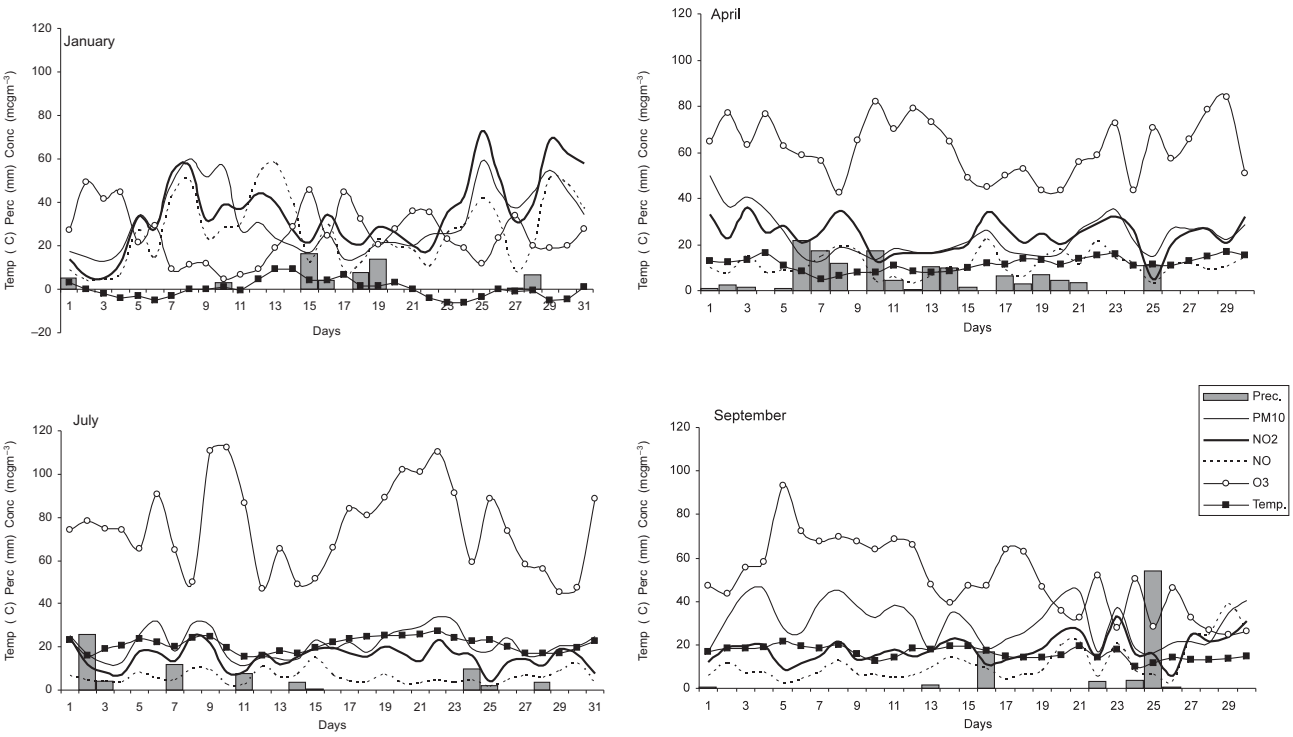

Fig. 1. Daily variation of 24-hour pollutant concentrations, mean temperature and precipitation during 2004 (Zagreb, Mirogojska 16).

The mean 24-hour PM_{10}, NO_2 and NO concentrations showed a rising tendency towards mid-week, with a peak on Wednesday (31.12 μgm^{-3}; 28.29 μgm^{-3}; and 19.84 μgm^{-3}) and minimal value on Sunday (24.11 μgm^{-3}; 17.89 μgm^{-3}; and 9.86 μgm^{-3}), whereas an inverse pattern was observed for O_3 (peak on Sunday, 72.23 μgm^{-3}, and minimal value on Wednesday, 45.62 μgm^{-3}). The same pattern was recorded in winter and summer, only the concentrations of PM_{10}, NO_2 and NO were lower and those of O_3 higher in summer (Figure 2). Intradiurnal curves of average hour concentrations of PM_{10}, NO_2 and NO were quite comparable, with two peaks (in the morning and in the afternoon) and lower values in summer. The only exception was the O_3 curve, showing one peak in the afternoon and higher values in summer. In winter, PM_{10} reached first peak concentration (43.3 μgm^{-3}) at 11.00 a.m. (in summer at 12.00 a.m.), and second peak concentration (46.7 μgm^{-3}) at 7.00 a.m. (in summer at 9.00 a.m.), whereas the lowest PM_{10} concentration was recorded at 5.00 a.m. The values of intradiurnal concentrations were lower in summer (April–September). NO_2 reached the first peak concentration at 10.00 a.m. in winter (36.0 μgm^{-3}) and at 9.00 a.m. in summer (39.1 μgm^{-3}); and second peak concentration at 6.00 p.m. in winter (39.1 μgm^{-3}) and at 9.00 p.m. in summer (25.0 μgm^{-3}). An identical pattern was observed for NO. The lowest concentrations of these pollutants were also recorded at 5.00 a.m. O_3 showed lowest concentrations at 8.00 a.m., to slowly rise until 4.00 p.m. (96.76 μgm^{-3} in summer and 43.83 μgm^{-3} in winter) and declining thereafter. The summer curve was characterized by an abrupt overnight increase to 58.43 μgm^{-3} at 1.00 a.m. and 80.74 μgm^{-3} at 2.00 a.m., followed by a decrease to 59.75 μgm^{-3} at 3.00 a.m. (Figure 3). The curves showed a similar pattern of intradiurnal distribution of the mean pollutant concentrations during work-days (Mon-Fri) and weekend (Sat-Sun) throughout 2004. Air concentrations of PM_{10}, NO_2 and NO were higher on workdays (most pronounced in NO and NO_2 curves), and those of O_3 on weekends (slight difference from work-days) (Figure 4).

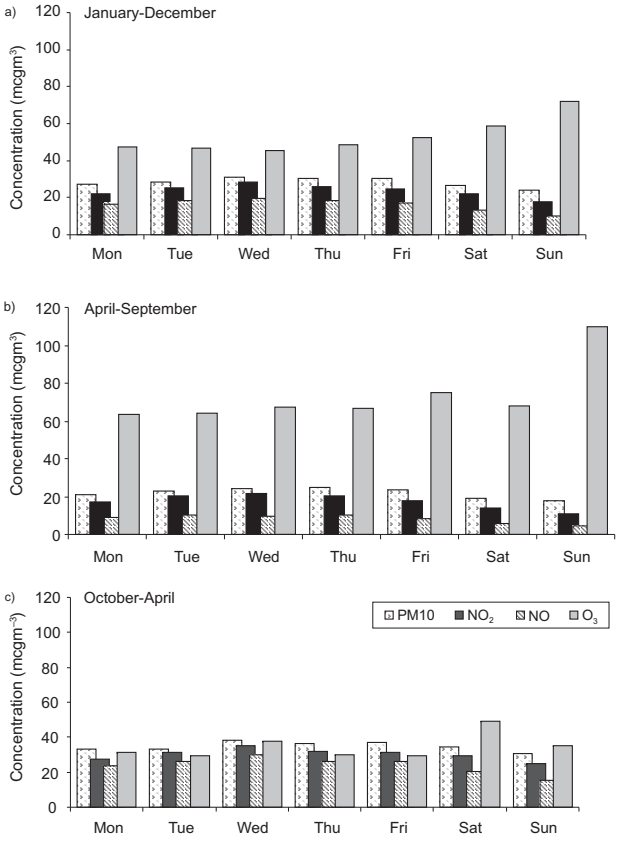

Fig. 2. Weekly variation of 24-hour pollutant concentrations a) annual, b) summer, c) winter.

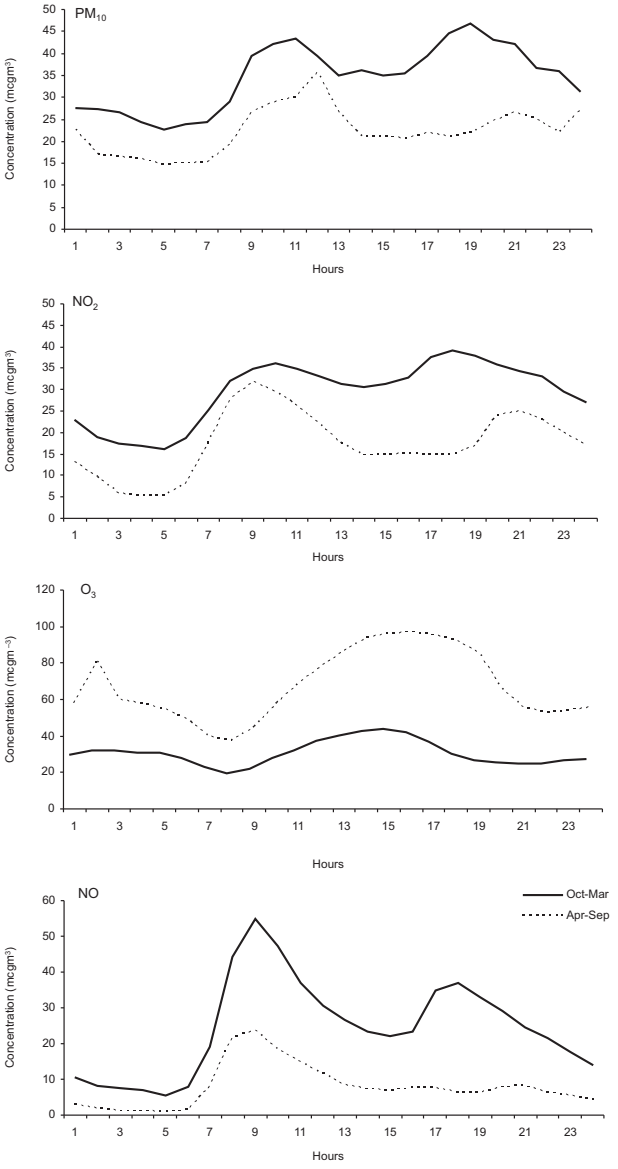

Fig. 3. Intradiurnal hourly concentrations of PM_{10}, NO_2, O_3 and NO during winter and summer (2004).

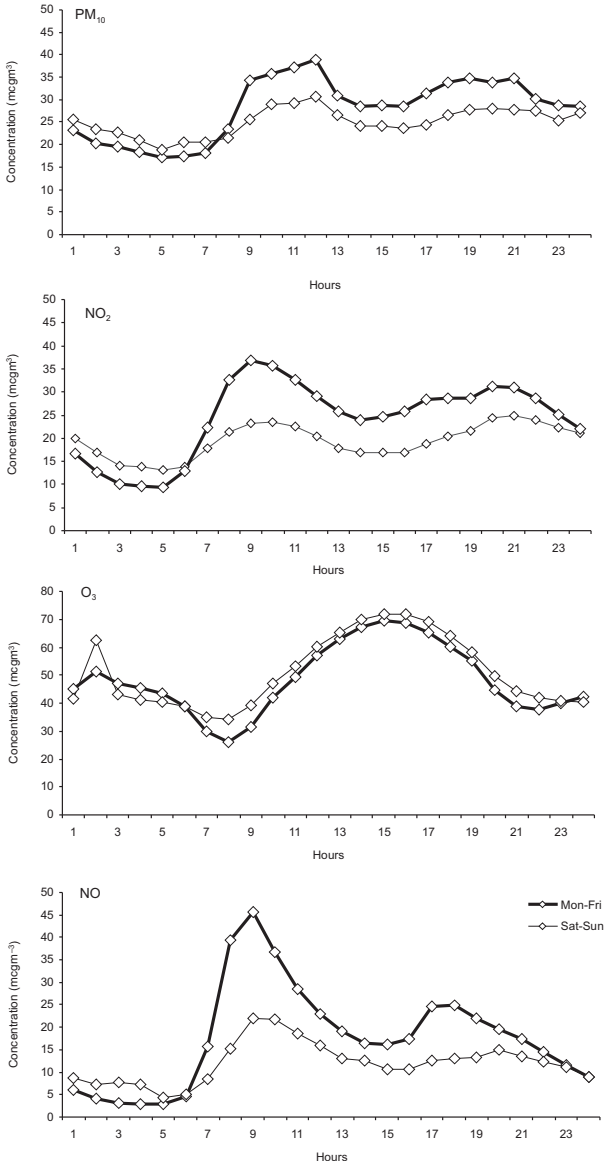

Fig. 4. Intradiurnal hourly concentrations of PM_{10}, NO_2, O_3 and NO during working and weekend days (2004).

Discussion

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 characteristic of the measuring site located in the residential area with moderate traffic intensity and a number of public institutions boiler-rooms of a medium size. A correlation of some meteorological parameters with variation in the concentration of the study pollutants was recorded in all seasons. In winter, the concentration of pollutants increased with temperature decline, especially on precipitation-free days. Similar results have been reported in a study of diurnal and seasonal variation of CO and NO_2 in Delhi[22]. The rise in PM_{10} concentration recorded in September was ascribed to the increased traffic intensity upon return of the majority of the Zagreb residents from their summer holiday and a small number of rainy days. The greater increase of PM_{10} concentration was probably consequential to the growing number of resuspended particles due to dry weather[4]. The regular diurnal pattern of 24-hour PM_{10} and NO_2 concentrations observed during the week, and of intradiurnal concentrations was directly related to traffic intensity. It was indicated by elevated concentrations towards mid-week and evident presence of two peak intradiurnal concentrations in the morning and in the afternoon. This phenomenon was especially pronounced in winter, characterized by higher traffic intensity[23] and more harmful operation of internal-combustion engines. Comparison of intradiurnal concentrations between summer and winter will be used in future studies to identify the rate of particular sources of pollution in the area.

Ozone is influenced by seasonal and diurnal variation. In our study, ozone concentration showed clear peaks in spring and summer, with the mean 24-hour concentrations in spring and summer twofold and threefold those measured in Vancouver, respectively, where annual peak was recorded in May (in Zagreb in July)[24]. The concentrations decreased towards autumn, to be lowest during winter. Also, higher levels of nitrogen oxides were associated with lower ozone concentrations. This situation reflected primary reactions involving ozone and ozone precursors in urban areas. A similar pattern has been reported from northern Europe, however, summer peak was not as clear[25]. The intradiurnal behavior during spring and summer (April-September) reflected sunshine and daily temperature, whereas during night the wind velocity was the most important driving force for the presence of ozone, i.e. when the mixing effect of the wind is low or diminished, the ozone is deposited into the vegetation due to its strong oxidizing potential[26]. Considering the level of air pollution relative to the regulated limit and tolerated values, the measured 24-hour concentrations of all study pollutants exceeded the borderline values and/or tolerated values, like those reported from Portuguese urban agglomerations however, the number of days with such pollutant concentrations did not exceed the allowed frequency[27]. In the present study, a part of the results collected during the first year of measurement at this site were processed, so it was a preliminary study with the main objectives to point to the possible identification of the source of pollution and to assess the level of air contamination according to the new national legislation coordinated with European regulations. Future measurements and studies should evaluate in detail the causes of the concentration levels detected.

Conclusions

1. 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.

2. The effect of meteorological parameters, especially precipitation, on airborne pollutant concentrations was observable throughout the year. The concentration of pollutants decreased abruptly on days with precipitation.

3. The mean 24-hour PM_{10}, NO_2 and NO concentrations showed a rising tendency towards mid-week, with a peak on Wednesday and minimal value on Sunday, whereas an inverse pattern was observed for O_3.

4. Intradiurnal curves of average hour concentrations of PM_{10}, NO_2 and NO were quite comparable, with two peaks (in the morning and in the afternoon) and lower values in summer. The only exception was the O_3 curve, showing one peak in the afternoon and higher values in summer.

5. The curves showed a similar pattern of intradiurnal distribution of the mean pollutant concentrations during workdays (Mon-Fri) and weekend (Sat-Sun). Air concentrations of PM_{10}, NO_2 and NO were higher on workdays, and those of O_3 on weekends.

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SEZONSKE, DNEVNE I INTRADIURNALNE VARIJACIJE PM_{10}, NO_2, NO I O_3 U STAMBENOJ ČETVRTI GRADA ZAGREBA, HRVATSKA

SAŽETAK

Onečišćujuće tvari kao što su lebdeće čestice, dušikovi oksidi, ugljikovi oksidi, prizemni ozon i dr. štetni su za ljudsko zdravlje. Svrha ovog rada je analizirati sezonske, dnevne i intradiurnalne varijacije PM_{10}, NO_2, NO i O_3 u stambenoj četvrti urbanog područja, kao i učinak nekih meteoroloških parametara na koncentraciju ovih onečišćujućih tvari. Istraživanje se provodilo u razdoblju od 1. siječnja do 31. studenoga 2004. godine u Gradu Zagrebu, a 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, sezonama i meteorološkim uvjetima. 24 satne koncentracije svih mjerenih onečišćujućih tvari u zraku prekoračuju granične i/ili tolerantne vrijednosti definirane zakonskom regulativom, ali broj dana s prekoračenjem koncentracija onečišćujućih tvari u granicama je dozvoljenih učestalosti. Ovaj rad predstavlja preliminarna istraživanja s ciljem identifikacije izvora onečišćenja kao i utvrđivanje razina onečišćenja prema novoj nacionalnoj legislativi koja je usklađena s Europskom regulativom.