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Original Scientific Paper

Analysis of Summer 2006 Ozone Pollution in Zagreb*,**

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Abstract: In the summer of 2006, ozone concentrations were measured at three sites in the Zagreb area. Stations Velika Gorica (VG), Dugave (DUG), and Institute for Medical Research and Occupational Health (IMI) were located at the same elevation along a 15-km stretch from the Zagreb Airport in the south (VG) to about 2.5 km north from the city centre (IMI). At all three sites, ozone volume fractions showed pronounced diurnal variations, peaking between 15 h and 18 h (VG) and between 13 h and 16 h (DUG, IMI) local time (CEST). Average ozone volume fractions measured in the northern and southern residential part of the town (IMI and DUG) were similar and also showed similar daily pattern. In VG daily variations were more pronounced. The analysis of summer 2006 ozone data clearly shows the highest ozone concentrations at the southernmost point (VG). Because the comparison of diurnal variations at all three stations neither confirms nor disproves the transport of ozone precursors to the VG station, it is possible that the source of these high ozone levels at the VG station is local or further south. The wind rose shows there is a low probability of transport from VG station into the city.

Keywords: airport, daily variations, meteorological parameters, photochemical pollution

INTRODUCTION

The capital of Croatia, Zagreb, has one of the longest histories of surface ozone measurements in Europe. The first measurements in 1889−1900[1] were done by Andrija Mohorovičić, the discoverer of the Moho discontinuity (between the Earth's crust and mantle), who used Schönbein's method. In the 20th century measurements performed in 1975 in the city centre at 110 m a.s.l. indicated that within that time gap ozone concentration in Zagreb at least have doubled.[2] Statistical analysis of the latter data showed pronounced daily variations and a connection between particularly high ozone values with slow SE wind *i.e.* with transport from the city's industrial and airport site.[3] Later ozone measurements performed in a northern, residential part of Zagreb at 180 m a.s.l. at the Ruđer Bošković Institute (RBI) revealed a far weaker influence of high ozone levels produced in the south. Measurements at stations Medvedgrad (580 m a.s.l.) and Puntijarka (PUNT, at 980 m a.s.l.) to the north above Zagreb on the Mt Medvednica also revealed that the inversion layer rarely reached their altitude.[4] For this reason, PUNT was included in the EUROTRACTOR[5] network to represent the regional free atmosphere from 1989 to 2002. Ongoing measurements show that elevated AOT40 values ("Accumulated dose over a threshold of 40 ppb") are responsible for the forest damage at Medvednica.[6] In 2004, an extensive measurement campaign took place in Zagreb to determine and model the levels and reactions of photochemical oxidants.[7]

This article reports summer 2006 ozone concentrations and behaviour, at three sites located along the 15 km S-N stretch from Velika Gorica (VG) near the Zagreb Airport in the south over Dugave (DUG) to the Institute for Medical Research and Occupational Health (IMI) about 2.5 km to the north from the city centre (see Figure 1).

EXPERIMENTAL

Ozone concentrations were measured from 7 April to 14 July 2006. The first site, IMI (45.833° N, 15.983° E, 160 m a.s.l.) is located in a northern, residential part of the city with low traffic density. The second site, DUG (45.80° N, 15.933° E, 115 m a.s.l.) is located further south in a densely populated residential area. The third

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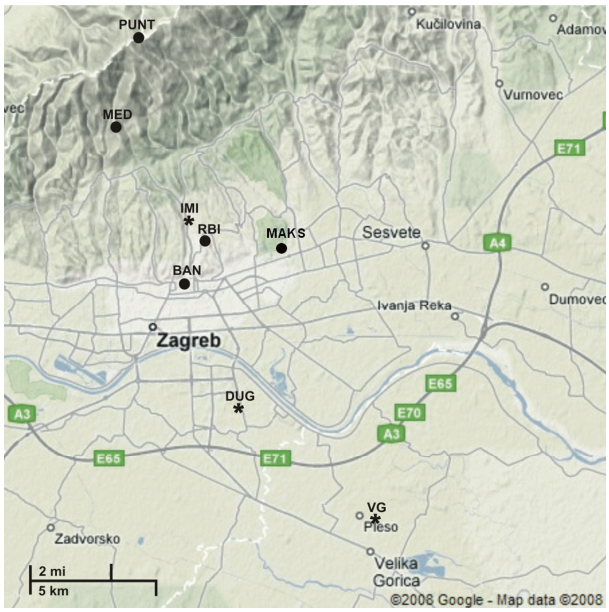

Figure 1. Locations of the monitoring stations (marked by asterisks).

site, VG, is located in a residential area near the Zagreb Airport (45° 45' N 16° 04' E, 105 m a.s.l.) about 10 km to the south from the city centre. Zagreb Airport is the biggest airport in Croatia with 20 442 airplane landings in 2006, passenger traffic of ≈ 1 700 000 passengers, and cargo and mail traffic of 9 061 t and 1 332 t, respectively.[8]

At all the three measuring sites, ozone concentrations were measured using commercial automatic devices based on UV absorption. At IMI, ozone has been measured with an automatic device since 1996 and at DUG since 2006. The measuring site DUG is a part of a national network for continuous air quality monitoring set up by the Croatian Ministry of Environmental Protection, Physical Planning and Construction (MZOPUG).[9]

Daily averages of temperature, relative humidity, pressure and amounts of precipitation were obtained for the station Maksimir (45.817° N, 16.033° E, 130 m a.s.l.) of the national Meteorological and Hydrological Service (see Figure 1, MAKS). Data on wind velocity and wind direction were obtained for 7 h, 14 h and 21 h and as daily averages. Daily averages of wind velocities were calculated as vector averages of these values.

RESULTS AND DISCUSSION

Ozone volume fractions at measuring stations were recorded as a three-minute and one-minute values. Data were transformed into one-hour and 24-hour averages. Summarized data for hourly ozone averages are presented in Table 1. Time series of daily average ozone volume fractions for all three sites are shown in Figure 2. Box-and-whiskers plots for the three sites, based on hourly averages, are shown in Figures 3 a–c.

During measurements, daily temperature ranged from 5.4 °C to 27.7 °C (average 19.5 °C), relative

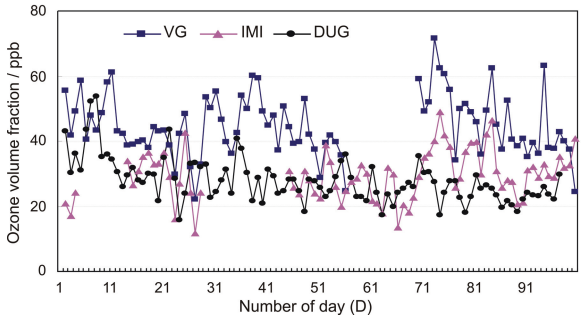

Figure 2. Time series of average daily ozone volume fractions (7 April - 14 July 2006).

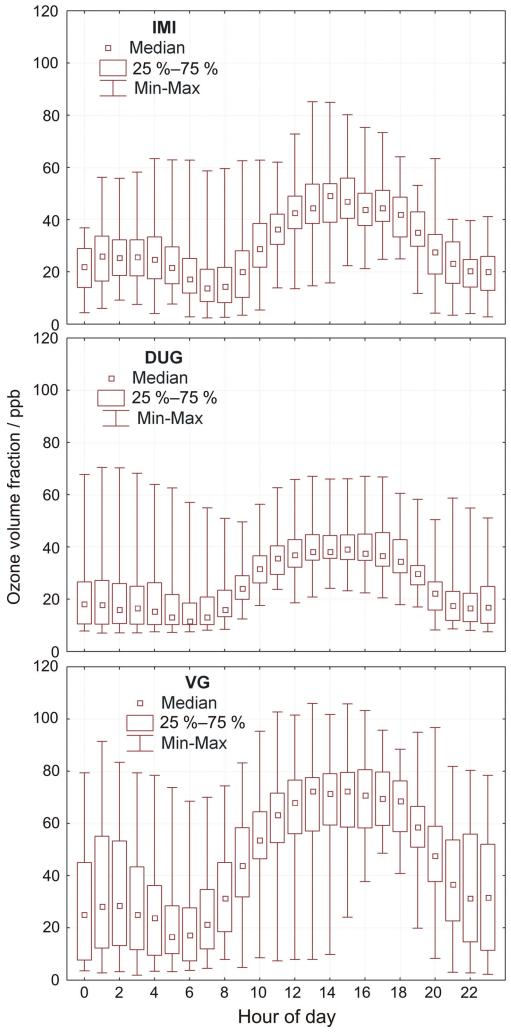

Figure 3. Box-and-whiskers plots for the three sites based on hourly averages.

Table 1. Hourly ozone volume fractions at three sites in Zagreb (7 April − 14 July 2006, totalling 2 352 hours, N_T)

Measuring site	N	(N/N_T) / %	Mean / ppb	Median / ppb	Minimum / ppb	Maximum / ppb	SD / ppb
IMI	1722	73.1	29.5	27.9	2.3	86.0	14.7
DUG	2276	96.8	27.6	26.9	7.0	70.5	12.9
VG	2007	85.3	44.8	46.5	1.9	106.0	23.8

humidity between 47 % and 92 % (average 67.1 %), and air pressure from 990.6 hPa to 1011.6 hPa (average 1001.7 hPa). It rained on 34 days and the highest daily amounts of precipitation by month were recorded for 28 April (Day 21, 26 mm), 29 May (Day 52, 18 mm), 30 May (Day 53, 20 mm), 2 June (Day 56, 18.3 mm), and 7 July (Day 91, 18.5 mm).

Figure 4 shows the wind roses for the measuring period. Except for the NNW direction, all average wind velocities were below 2 m/s.

Daily variations were analysed at all three sites. Average ozone volume fractions were calculated for each hour of a day (Figure 3). At all three sites, ozone volume fractions showed pronounced diurnal variations reaching their maximum between 15 h and 18 h (VG) and between 13 h and 16 h (DUG, IMI) local time (CEST). Average ozone volume fractions at IMI and DUG were similar and showed a similar pattern. At VG, daily variations were more pronounced, with the highest diurnal amplitude. Figure 5 shows differential daily variations of ozone volume fractions for days without precipitation, represented as differences between average hourly ozone values. For IMI and DUG the difference between hourly ozone values was less than 5 ppb for the whole day. Differences VG-DUG were always higher than 5 ppb. Differences VG-DUG and VG-IMI were the smallest in the morning (between 5 h and 6 h CEST) and the greatest (more than 20 ppb) in the afternoon (between 14 h and 20 h CEST) because of the later daily peak at VG.

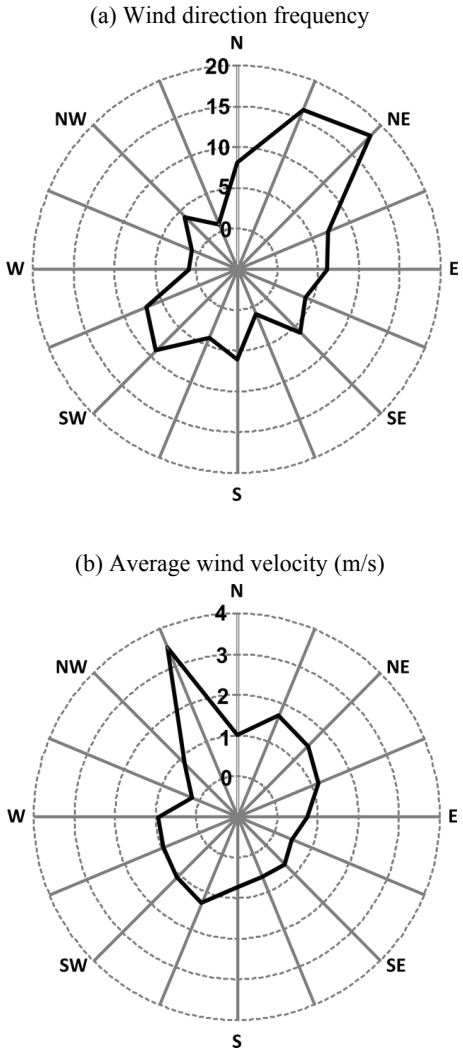

Figure 4. Wind rose from 7 April to 14 July 2006.

Linear correlation coefficients (r) between 24-hour averages of ozone volume fractions and meteorological parameters were calculated for all days and for the days without precipitation. Statistically significant correlations between ozone concentrations were found for all three sites (r between 0.51 and 0.57) because of similar daily variations associated with the intensity of sunlight (Table 2). Statistically significant negative correlations were found between ozone and relative humidity at all three sites. Correlation coefficients between O_3

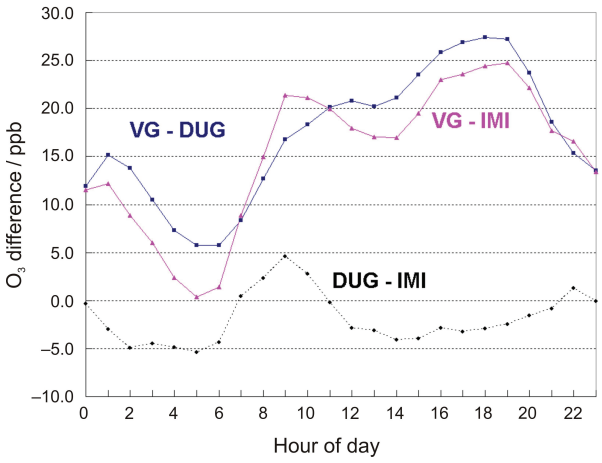

Figure 5. Daily variations in ozone volume fractions, represented as a difference in average hourly values between sites (from 7 April to 14 July 2006, for days without precipitation only).

Table 2. Linear correlation coefficients (r) between 24-hour ozone volume fractions at IMI (O_3-IMI), DUG (O_3-DUG) and VG (O_3-VG) and some meteorological parameters (only for days without rainfall). Marked correlations are significant at $p < 0.05$

	O_3-IMI	O_3-DUG	Temperature	Pressure	Relative humidity
O_3-VG	**0.51**	**0.52**	0.21	−0.09	**−0.45**
O_3-IMI		**0.57**	**0.67**	−0.24	**−0.60**
O_3-DUG			**−0.29**	**−0.27**	**−0.39**
Temperature				0.02	**−0.28**
Pressure					0.00

concentrations and relative humidity were more pronounced over the days without rainfall and they were the highest at IMI (r = −0.60) and the lowest at DUG (r = −0.39). Due to the connection between temperature, insolation and ozone formation, statistically significant positive correlation between ozone and temperature was expected. However, it was found only at IMI (r = 0.67).

Multivariate statistical methods including Principal Component Analysis, Multiple Linear Regression, Partial Least Squares and Principal Component Regression are often used to evaluate the state of ambient air and for modelling purposes. For example, Lengyel *et al.*[10] modelled ozone concentrations in Hungary on the basis of NO_x and CO concentrations and meteorological parameters. Several other studies used Principal Component Analysis to classify variations of ozone concentrations and to identify the main factors influencing ozone concentrations.[11,12,13] Unfortunately, in this study we were not able to measure consecutively hourly values of ozone precursors (NO_x, CO, VOC) and our meteorological data were only on 24-hour bases. However, the frequency distribution of hourly ozone values was founded to be uneven due to different phases in ozone production. They were calculated separately for the periods 10 h to 21 h and 22 h to 9 h CEST (Figure 6). The distribution of ozone values at IMI and DUG between 22 h and 9 h, when there is not enough sunlight to initialize photochemical reactions, was similar to lognormal distribution. Between 10 h and 22 h, when photochemical ozone production is intense, the distribution tends to normal. Distribution at VG was quite different (Figure 6).

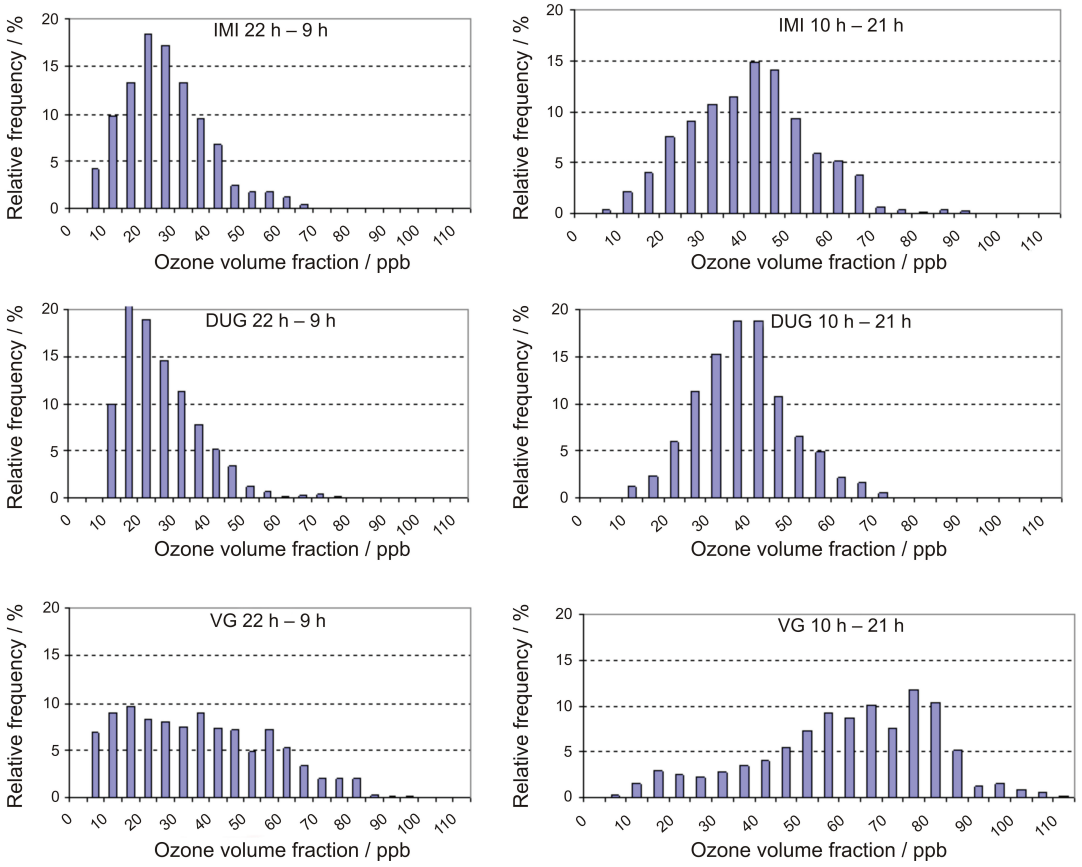

Figure 6. Frequency distribution of hourly ozone volume fractions (7 April−14 July 2006).

Ozone volume fractions at IMI and DUG were similar in value, distribution, and variation over the day. IMI and DUG are located in the city and are both exposed to traffic pollution and NO_x emission. VG stands downwind from the city and is exposed to the influence of the nearby Zagreb Airport. However, neither DUG or VG are far away from the A3 highway (Figure 1). There are several studies concerning to the role of the airports in air pollution. Kim *et al.*[14] analysed measured NO_2 and O_3 concentrations from 1990 to 2000 in Seoul, South Korea. They founded that high NO_2 concentrations were more frequent at the measuring site near the airport, while ozone concentrations exceeded national standards more frequently at the site placed downwind from the airport. O_3 and NO_2 concentrations were also measured in Athens over the summer of 2000, shortly before the operation of the new international airport.[15] Unal *et al.*[16] have used an emission model to estimate aircraft emission near Atlanta, USA. In their study a maximum impact of aircraft emission on ozone levels was estimated to be 56 ppb. Pison and Menut[17] modelled ozone concentrations near airports in Paris area. They founded that NO_x air traffic emissions have a more important impact than VOC (volatile organic compounds) emissions, particularly during the night and near the sources. Emissions from the Turkish airport were also modelled in a study of Kesgin.[18] Unfortunately, there are no continuous data on air pollution in Velika Gorica and there are only a few papers analysing the influence of the Zagreb Airport on the environment, focused mainly on land pollution.[19,20] In order to find the reason for high ozone values at the VG site (*i.e.* to find whether they are the result of local pollution sources or they are caused by transport of air masses from the centre of Zagreb) days with hourly ozone volume fractions higher than 90 ppb and 60 ppb were analysed with respect to wind direction. Hourly ozone values exceeded 90 ppb at VG for more than three hours on 6 May and 16, 17, 27, and 28 June. Figure 7 shows variations in ozone volume fractions for 16−18 and 26−28 June 2006. On 27 and 28 June, daily ozone peak at VG occurred at 10 h and 14 h, about five hours earlier than usual and earlier than at DUG and IMI (Figure 3). This has happened when the N and NNW wind blew in the evening before (21 h) and could be an indication of long range ozone transport (Table 3).

Figure 8 shows hourly ozone volume fractions at all three sites from 23 to 25 April 2006 when the predominant wind was S and SSE (Table 4). It is obvious that this wind did not raise ozone concentrations or a daily peak at DUG and IMI. Daily peaks coincided at all three stations at noon and early afternoon. The wind blowing from the NNW direction at about 21 h probably transported air polluted with NO from the city to VG and caused the low ozone values at VG overnight.

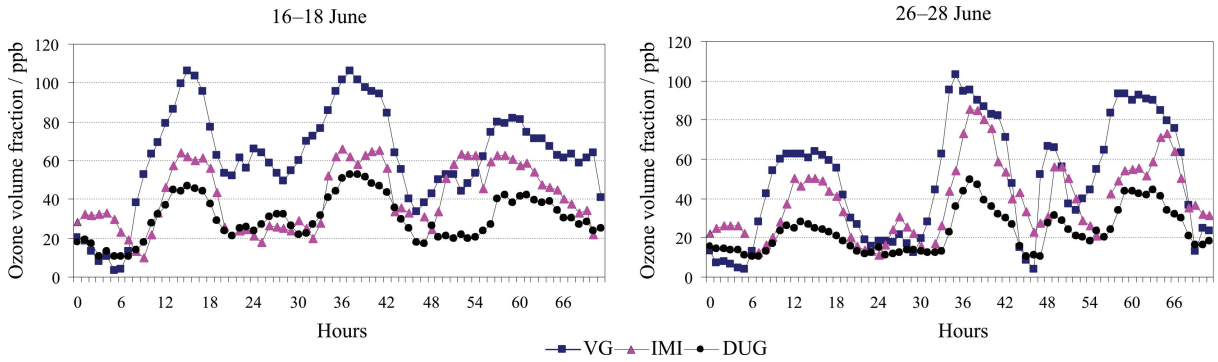

Figure 7. Ozone volume fractions on 16−18 June and 26−28 June 2006 when ozone values exceeded 90 ppb at VG and 60 ppb at IMI.

Table 3. Wind conditions (direction and speed at 7 h, 14 h and 21 h and their daily vector average) on 16−18 June and 26−28 June 2006 when ozone values exceeded 90 ppb at VG and 60 ppb at IMI

Date	Wind direction	Wind strength Beaufort number	Wind direction	Wind strength Beaufort number	Wind direction	Wind strength Beaufort number	Wind direction	Wind speed m s^{-1}
	7 h		14 h		21 h		Daily average	
16 June	Calm	0	S	1	Calm	0	S	0
17 June	S	1	WNW	2	S	1	WSW	1
18 June	N	2	SSW	2	SSW	2	SW	1
26 June	ESE	1	S	2	N	2	ESE	0
27 June	Calm	0	E	2	NNW	1	ENE	1
28 June	W	1	SE	1	NNW	1	WNW	0

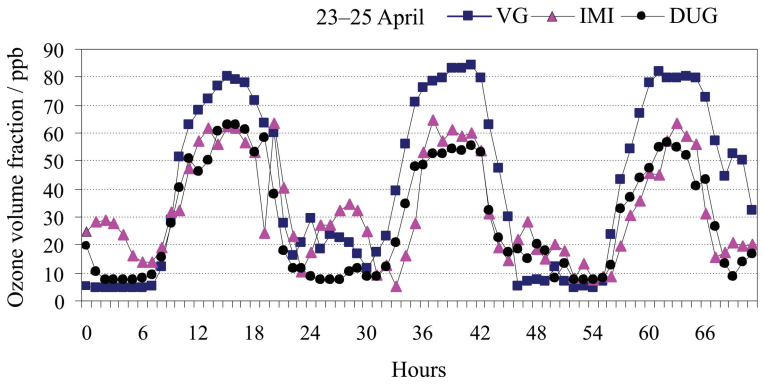

Figure 8. Ozone volume fractions on 23−25 April 2006, with predominant wind from S and SE direction over the day and NW wind in the evening.

Table 4. Wind conditions (direction and speed at 7 h, 14 h and 21 h and their daily vector average) on 23−25 April 2006, with predominant wind from S and SE direction over the day and NW wind in the evening

Date	Wind direction	Wind strength Beaufort number	Wind direction	Wind strength Beaufort number	Wind direction	Wind strength Beaufort number	Wind direction	Wind speed / m s^{-1}
	7 h		14 h		21 h		Daily average	
23 April	Calm	0	SSE	2	WSW	1	S	0.9
24 April	Calm	0	SSE	2	N	1	SE	0.6
25 April	SSE	1	NW	1	NNW	1	NW	0.3

Numerous exposure ozone indices based on maximum (or near maximal values) of hourly ozone data are developed to evaluate damaging ozone effects. While modern instruments record ozone fractions sensitively and selectively, the products of ozone destruction, which are not monitored, are likely to be as much a hazard as ozone itself. Thus, standards based solely on ozone cannot be expected to provide a faithful representation of the air quality: neither at high altitudes where there are few primary pollutants nor at urban sites where many ozone reaction products are not monitored. Cvitaš and Klasinc[21] try to circumvent the problem of monitoring those products by taking into account the local ozone destruction and by including the daily minima into the calculation of a pollution index.[21-23] These simple photochemical indices were calculated as the mean of daily ratios of hourly average maximum to minimum (set at 0.4 if zero). For urban sites with strong photochemical pollution, this index has a value of over 10; in the upper boundary layer and above, where there are no sources of precursor molecules which act also as sinks during night-time, it is less than 2. In less polluted urban and suburban sites as well as in some rural locations, where some photochemistry takes place, it will be of the order of 2 to 5 reflecting formation around noon and destruction during the night. Values obtained over a given period for VG (11.4), DUG (4.0) and IMI (6.7) may be compared with those[24] from summer 1991 for RBI (16), PUN (1.6), Rovinj (4.8), island Iž (1.9) and Hvar (2.7). In our study the highest indices were obtained at VG site suggesting that at this site the highest damaging ozone effects may be expected.

CONCLUSION

The analysis of the summer 2006 ozone data shows considerably higher ozone concentrations in the south of Zagreb (VG) than further north (IMI and DUG). Differential average concentration curves show that IMI and DUG have nearly the same ozone diurnal variation. The distribution of ozone values at IMI and DUG between 22 h and 9 h, when there is not enough sunlight to initialize photochemical reactions, was similar to log-normal distribution. Between 10 h and 22 h, when photochemical ozone production is intense, the distribution tends to normal. The distribution at VG was quite different from other two sites. Photochemical indices calculated in this study showed that VG site is characterized by strong photochemical pollution. The high ozone levels are either formed from local or transported precursors at VG station or further in the south and arrive there by transport. However, the wind rose suggests that there is a low probability that this ozone from VG reaches the city.

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SAŽETAK

Analiza onečišćenja ozonom tijekom ljeta 2006. godine u Zagrebu

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Tijekom ljeta 2006. godine koncentracije ozona mjerene su na tri mjesta na području Zagreba. Mjerne postaje Velika Gorica (VG), Dugave (DUG) i Institut za medicinska istraživanja i medicinu rada (IMI) bile su smještene na istoj nadmorskoj visini duž 15 km duge linije protežući se od zagrebačke zračne luke na jugu (VG) do oko 2,5 km sjeverno od središta grada (IMI). Na sva tri mjesta volumni udjeli ozona pokazali su naglašene dnevne varijacije s najvišim vrijednostima između 15 h i 18 h (VG) te između 13 h i 16 h (DUG, IMI) po lokalnom vremenu (CEST). U sjevernom i južnom stambenom dijelu grada (IMI i DUG) izmjereni prosječni volumni udjeli ozona bili su slični te su također pokazali sličan dnevni hod. U Velikoj Gorici dnevne varijacije bile su više izražene. Analiza podataka o ozonu tijekom ljeta 2006. godine jasno je pokazala povišene koncentracije ozona na najjužnijoj točki (postaja VG). Budući da usporedba dnevnih varijacija na tri mjerne postaje nije potvrdila niti opovrgnula transport prekursora ozona do VG, moguće je da je izvor tih visokih razina ozona kod postaje VG ili južnije. Ruža vjetrova pokazuje da je mala vjerojatnost transporta iz VG prema gradu.