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Original Scientific Paper

Estimation of Ozone and Peroxide Levels in the Air of Croatia*

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Abstract. Volume fractions of different atmospheric gas constituents were modelled using Master Mechanism (MM) model developed by S. Madronich (NCAR, Boulder, CO, USA). Ozone (O_3) and hydrogen peroxide (H_2O_2) seasonal variations were estimated at three different locations in Zagreb. Modelled ozone values showed good agreement with measured values at all three sites. The estimation of H_2O_2 annual variations with the MM model showed typical H_2O_2 seasonal variation at a remote location and at an urban location not exposed to traffic, with the highest values over the summer months, due to higher solar radiation. The summer/winter differences were more pronounced at the remote location. At the site exposed to traffic, H_2O_2 volume fractions did not show seasonal variations and H_2O_2 levels were determined by the levels of nitrogen oxides. The model was also used to estimate oxidant levels during the heat wave in August 2003. It yielded high hydrogen peroxide (2.5 ppb–3.5 ppb) and ozone (> 100 ppb) levels, followed by increased concentrations of OH radicals. The model confirmed that in extreme conditions (high temperature and solar radiation, elevated CO and NO_2 levels) over the summer, the atmospheric oxidizing capacity in Croatia exceedingly rises and may exert harmful effects on the environment.

Keywords: air pollution, Master Mechanism model, oxidants, seasonal variation

INTRODUCTION

Atmosphere contains many oxidants, above all oxygen and ozone (O_3). Tropospheric OH radical is also a strong oxidant formed mostly from tropospheric ozone, and both, O_3 and OH, are sensitive to UV radiation.[1,2] Many compounds emitted in the atmosphere are oxidized by the reaction with OH radical (methane, hydrocarbons, carbon monoxide...), so, in certain conditions, the decrease in OH levels may lead to an increase in the concentrations of some compounds in the atmosphere.[1] The oxidizing capacity of the atmosphere can be defined as the capability of "self-cleaning" by oxidation of traced gases emitted in the environment. However, increased levels of oxidants in the atmosphere have harmful effects on living beings as well. Hydrogen peroxide (H_2O_2) in the gaseous phase of the troposphere is formed mostly by the recombination of two HO_2 radicals. It is removed from the atmosphere through the processes of deposition and wet scavenging (with subsequent liquid-phase reactions). From gaseous phase it can also be removed by photolysis or by reaction with OH radical. H_2O_2 levels indirectly depend on OH levels, so due to its role in atmospheric chemistry, hydrogen peroxide seems to be a better indicator of atmospheric oxidizing capacity than ozone.[3] The reactivity of ozone (as a strong oxidant) and its role in photochemical air pollution have been well described in literature. There are many papers[4–7] with results of ozone measurements in the troposphere. Many models successfully predict its concentrations, and some of them have already been used in some neighbouring countries.[8] Ozone is also the only atmospheric oxidant measured continuously in Croatia by now.[9–11] The measuring results show that over the summer months ozone concentrations exceed air quality standards set by Croatian and European legislation.

By now, measurements of atmospheric H_2O_2 were limited to a few places in the world, mostly due to difficulties during measurements and sophisticated and expensive equipment. The most used analytical procedure is based on fluorimetric detection[12] with previous dimerisation of *p*-hydroxyphenyl acetic acid in the presence of peroxide, catalysed by enzyme horseradish peroxidase.[12,13]

Hydrogen peroxide in the troposphere shows characteristic daily and seasonal variations and depen-

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* Dedicated to Professor Emeritus Drago Grdenić, Fellow of the Croatian Academy of Sciences and Arts, on the occasion of his 90th birthday.

** Author to whom correspondence should be addressed. (E-mail: gpehnec@imi.hr) dence on meteorological conditions. Similar to ozone, it reaches maximum values in the early afternoon, when the sunlight is the most intense. It also shows seasonal variation with the highest concentrations observed in the summer months.[13]

H_2O_2 is considered a major oxidant of SO_2 in aqueous phase. However, successful removal of industrial SO_2 over the last two decades has led to an increase in H_2O_2 concentrations worldwide.[14,15] Similar processes have probably occurred in Croatia as well. The first H_2O_2 measurements in Croatia were carried out in the summer 2004. H_2O_2 volume fractions ranged from < 0.05 ppb to 6.2 ppb (average hourly value 0.3 ppb), and showed diurnal variation with a peak between 15 h and 16 h, local (CEST) time.[16] Average H_2O_2 corresponds to the levels observed in other European countries with similar climate. However, maximum hourly value of 6.2 ppb obtained in July 2004 shows excessive air pollution by oxidants. Due to limited H_2O_2 measurements in Croatia, the purpose of this paper was to investigate seasonal variations of H_2O_2 using an appropriate computation model. We have also used the same model to estimate peroxide and ozone levels in extreme, summer heat wave conditions.

EXPERIMENTAL

Model Description

Levels of ozone, hydrogen peroxide, and other oxidants in the air of Croatia were calculated using the Master Mechanism (MM) model. This model is a multi-task, interactive, atmospheric box model program that gives an insight into the time behaviour of chosen input amounts of atmospheric constituents under selected, either fixed or variable, condition.[17,18] It does not include transport, and describes best reactions and transformations that occur within an air package at rest in a horizontal plane under the influence of sunlight and under given meteorological parameters. However, the model can also include the effects of some other processes such as time-dependent dilution (caused by changes in planetary boundary layer (PBL) height), temperature and pressure change, emission, or deposition. It allows one to predict the time evolution of any reactive air composition as dictated by corresponding reaction rate constants and physical parameters.

In this study we used the NCAR Master Mechanism model, version 2.4., developed by S. Madronich, and updated in April 2006 to model the concentrations of atmospheric compounds. The model includes about 5000 reactions between about 2000 species, but in this study it was limited to about 2300 reactions. Photolysis coefficients were calculated using the Tropospheric Ultraviolet-Visible model (TUV), version 4.4 developed by Sasha Madronich; released May 2003).[19–22] TUV is a multistream radiative transfer model able to quantify the transfer of radiation in a scattering and absorbing atmosphere. Atmospheric curvature (important for low sun conditions) is modelled using a pseudo-spherical approximation. It is a one-dimensional FORTRAN 77 model suitable to compute various radiative quantities over a broad range of environmental conditions. It can be used in the wavelength range of 121–750 nm for calculating the spectral irradiance, the spectral actinic flux, photodissociation coefficients and biological effective irradiance. Output parameters are presented as functions of wavelength and altitude.

The accuracy of the MM model was tested previously by comparing modelled and measured H_2O_2 values at one location in Zagreb (Ruđer Bošković Institute, RBI) during summer 2004.[16] The relative differrence *E* between modelled and measured volume fractions was calculated according to the equation:

$$E = \frac{\varphi(\text{modelled}) - \varphi(\text{measured})}{\varphi(\text{measured})} \times 100$$

where φ is volume fraction of the specie.

It was founded that on cloudless days, maximum hourly H_2O_2 volume fractions were calculated with the relative difference of less than 20 %. For O_3, the relative difference was less than 12.5 % for the calculation of maximum hourly values and less than 25.3 % for the calculation of average daily values. Table 1 presents the relative differences between modelled and measured

Table 1. Relative difference, $E^{(a)}$ (in %) between measured$^{(b)}$ and modelled volume fractions, φ, of H_2O_2 and O_3 (in ppb) at RBI between 26 June and 5 July 2004 (for cloudless days only)

	H_2O_2		O_3	
Date	*E* average daily value	*E* maximum hourly value	*E* average daily value	*E* maximum hourly value
26 June	26.4	1.0	11.3	–12.5
27 June	64.7	23.2	23.6	–4.7
1 July	59.1	20.2	12.0	5.8
3 July	22.1	–10.1	1.2	–8.7
4 July	50.9	12.1	10.4	0.7
5 July	48.4	–21.6	25.3	12.1

(a) $E = \frac{\varphi(\text{modelled}) - \varphi(\text{measured})}{\varphi(\text{measured})} \times 100$

(b) detection limit of the measuring technique is 0.05 ppb

H_2O_2 and O_3 volume fractions for the days without clouds and precipitation. The model overestimates the volume fractions of the H_2O_2 systematically.

The Estimation of O_3 and H_2O_2 Levels

For the TUV model the following environmental conditions, common for all calculations were used:

- time zone: 1

- single scattering albedo of aerosols: 0.99

- air number density: 2.53×10^{19} molecules cm^{-3}

- surface albedo: 0.1 at all wavelengths

- aerosol vertical optical depth: $\tau_{\text{aer}} = 0.235$ at 550 nm from surface to space (for aerosols, vertical profile typical for continental regions from Elterman[23] was assumed).

Additional information included data on corresponding latitude, longitude, surface elevation, temperature, relative humidity, pressure and total ozone column. Meteorological data were obtained from the Meteorological and Hydrological Service of Croatia[24] and from literature.[25] Total ozone column data were obtained from NASA/TOMS web site.[26] Due to the lack of accurate data on emission sources, emission data were not included in the model.

Annual H_2O_2 and O_3 variations were estimated for three locations in Zagreb: Puntijarka (PUNT), Ruđer Bošković Institute (RBI), and Institute for Medical Research and Occupational Health (IMI) using the MM model. These locations were chosen because they have continuous air pollution measurements and data on pollutant concentrations from previous years. Puntijarka is a remote mountain location at 980 m a.s.l. to the north of Zagreb; Ruđer Bošković Institute (180 m a.s.l.) is in the city, but at a distance from road traffic while the Institute for Medical Research and Occupational Health (160 m a.s.l.) is situated in a residential part of the town and is exposed to modest road traffic density. Daily variations of volume fractions of different chemical species were calculated for every 15th day in the month. Tables 2–4 show meteorological data and input volume fractions used for modelling.

Average daily values obtained in previous measurements were used as input volume fractions for O_3, H_2O_2, CO, H_2O, benzene, toluene and xylene (BTX). For CO_2, we used the average of 330 ppm. Previous analysis showed that urban area modelling with input average daily volume fractions of NO and NO_2 did not give good agreement with measurements. The reason is the emission of NO_x from local sources, which can not be ignored. Unfortunately, Master Mechanism is a box model and it does not include the transport of species.

Table 2. Input data for the MM model used to estimate annual variations of oxidants for Puntijarka site (45.950° N, 15.983° E, 980 m a.s.l.)

Month		1	2	3	4	5	6	7	8	9	10	11	12
Volume fraction / ppb	H_2O_2	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
	O_3	36.4	42.4	46.0	48.3	51.3	45.7	53.8	52.7	43.0	39.0	32.5	33.1
	NO	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	NO_2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CO_2	330	330	330	330	330	330	330	330	330	330	330	330
	Benzene	-	-	-	-	-	-	-	-	-	-	-	-
	Toluene	-	-	-	-	-	-	-	-	-	-	-	-
	Xylene	-	-	-	-	-	-	-	-	-	-	-	-
	C_2H_4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	C_3H_6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_2O	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_3CHO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_3COCH_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Temperature / °C		0	2	7	12	16	20	23	21	18	12	6	2
Relative humidity / %		50	50	50	50	50	50	50	50	50	50	50	50
Pressure / hPa		1002	1002	1002	1002	1002	1002	1002	1002	1002	1002	1002	1002
Total ozone column / DU		344	364	372	368	357	340	319	308	288	278	284	306

Table 3. Input data for the MM model used to estimate annual variations of oxidants for Ruđer Bošković Institute site (45.833° N, 15.983° E, 180 m a.s.l.)

Month		1	2	3	4	5	6	7	8	9	10	11	12
Volume fraction / ppb	H_2O_2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	O_3	5.0	5.0	15.0	25.0	35.0	41.0	40.0	40.0	29.0	15.0	10.0	10.0
	NO_2	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7
	CO	285	285	285	285	285	285	285	285	285	285	285	285
	CO_2	330	330	330	330	330	330	330	330	330	330	330	330
	Benzene	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
	Toluene	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9
	Xylene	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	C_2H_4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	C_3H_6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_2O	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_3CHO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_3COCH_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Temperature / °C		0	2	7	12	16	20	23	21	18	12	6	2
Relative humidity / %		50	50	50	50	50	50	50	50	50	50	50	50
Pressure / hPa		1002	1002	1002	1002	1002	1002	1002	1002	1002	1002	1002	1002
Total ozone column / DU		344	364	372	368	357	340	319	308	288	278	284	306

The whole daily cycle of NO was included in the model in order to compensate the influence of transport and emission (not just an average initial value), with an assumed zero value overnight.[16] Average daily volume fraction was used as input value for NO_2. Based on literature data[27] and on the first VOC measurements at Ruđer Bošković Institute, 1 ppb was taken as the input volume fraction for C_2H_4, C_3H_6, CH_2O, CH_3CHO, and CH_3COCH_3. Dry deposition was included in all calculations (MM model calculate deposition as a reaction Compound X → "no products" with corresponding deposition rates from its own database). Changes in PBL during the day were also put in the model, based on the values from Jeričević *et al.*[28]

To estimate annual variations at Puntijarka station, we used the average monthly ozone fractions for the period 1989–1999[29] as input ozone values. Temperature values which were put in the model represent averages for the period 1862–1990.[25] Input of H_2O_2 volume fraction was 0.3 ppb.[16] Volume fractions of NO and NO_2 were obtained from measurements with the CRANOX system on Puntijarka during 1995.[30] BTX values were not put in the model due to lack of BTX measurements at this site. It was supposed that BTX levels were too low (approximately zero) to signifycantly affect the model.

To estimate annual variations at RBI, we used data from literature and from previous measurements at the same location.[31] Average monthly volume fractions for the period 1988–1994 were used as input values for ozone.[9,29] Temperatures used in the model represent averages for the period 1862–1990.[25] For NO, we took minimum daily cycle measured over the summer of 2004, as described by Acker *et al.*,[16] together with average H_2O, CO, BTEX, and NO_2 volume fractions measured during the same campaign.

To estimate annual variations at IMI, we used data on NO, NO_2, and O_3 volume fractions obtained by automatic analyzers for 2005.[32] Other conditions were the same as for the RBI site (for pollutants which have not been measured at IMI we took values obtained at RBI for the summer 2004[16]).

All estimations were made for maximum solar radiation, *i.e.* for cloudless conditions.

We also used the Master Mechanism model to estimate the August 2003 heat wave peroxide and ozone levels. Volume fractions of chemical species were calculated for five days, from 9 to 13 August 2003. Input data included average ozone volume fractions measured at RBI on days before the heat wave[33] and average mass concentrations of CO and NO_2 measured at the station of the National air pollution monitoring network in the city centre on 6 and 7 August.[34] For NO, we put in the model a daily cycle with a peak at 8 a.m. Meteorological data for August 2003 were obtained from the

Table 4. Input data for the MM model used to estimate annual variations of oxidants for the Institute for Medical Research and Occupational Health site (45.833° N, 15.983° E, 160 m a.s.l.)

Month		1	2	3	4	5	6	7	8	9	10	11	12
Volume fraction / ppb	H_2O_2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	O_3	11.5	17.0	22.0	28.5	23.5	42.5	44.0	30.0	8.0	7.5	7.0	9.0
	NO_2	24.6	22.5	23.5	24.0	26.7	29.3	25.1	21.4	21.4	23.5	20.9	22.5
	CO	285	285	285	285	285	285	285	285	285	285	285	285
	CO_2	330	330	330	330	330	330	330	330	330	330	330	330
	Benzene	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
	Toluene	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9
	Xylene	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	C_2H_4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	C_3H_6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_2O	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_3CHO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	CH_3COCH_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Temperature / °C		0	2	7	12	16	20	23	21	18	12	6	2
Relative humidity / %		50	50	50	50	50	50	50	50	50	50	50	50
Pressure / hPa		1002	1002	1002	1002	1002	1002	1002	1002	1002	1002	1002	1002
Total ozone column / DU		344	364	372	368	357	340	319	308	288	278	284	306

national Meteorological and Hydrological Service. For BTEX and H_2O_2 we took average monthly values measured at RBI in August 2004. Table 5 shows all input data.

Table 5. Input data for the MM model used to estimate oxidant levels during the heath wave in August 2003

Temperature / °C	26
Relative humidity / %	50
Pressure / hPa	1002
Total ozone column / DU	310

	Volume fraction / ppb
H_2O_2	0.3
O_3	100
NO_2	31.3
CO	859
CO_2	330
Benzene	1.3
Toluene	2.4
Xylene	2.0
C_2H_4	1.0
C_3H_6	1.0
CH_2O	1.0
CH_3CHO	1.0
CH_3COCH_3	1.0

RESULTS AND DISCUSSION

Estimation of Annual H_2O_2 and O_3 Variations

Ozone and peroxide annual variations were estimated at three different locations (PUNT, RBI, IMI) using the Master Mechanism model. The estimation was done on the basis of calculated average daily values. The modelling results are shown in Figures 1–3 and Table 6. Figures 1–3 show that measured and modelled ozone fractions do not differ significantly. This confirms that we used appropriate input parameters which best described the real conditions.

According to the MM model, average monthly ozone volume fractions at PUNT ranged from 33.8 ppb in December to 53.8 ppb in July, with maximum hourly average of 55.5 ppb in July. Average monthly H_2O_2 volume fractions were between 0.32 ppb in January/December and 0.63 ppb in June/August. Maximum hourly average of 0.90 ppb was obtained for July and August (Table 6). At RBI monthly ozone volume fractions were calculated between 4.0 ppb in January and 33.2 ppb in June, with the maximum hourly value of 45.9 ppb in June and July. Average monthly H_2O_2 volume fractions were estimated to between 0.215 ppb in

Table 6. Maximum hourly and average monthly O_3 and H_2O_2 volume fractions, φ, calculated using the MM model

Month			1	2	3	4	5	6	7	8	9	10	11	12
PUNT	O_3	$\bar{\varphi}$ / ppb	37.3	43.1	47.1	48.9	51.6	51.8	53.8	52.8	44.2	40.3	33.8	33.8
		φ_{max} / ppb	38.4	44.4	48.3	50.1	53.2	53.2	55.5	54.0	45.4	41.6	35.2	34.9
	H_2O_2	$\bar{\varphi}$ / ppb	0.32	0.37	0.46	0.56	0.60	0.62	0.63	0.63	0.57	0.45	0.34	0.32
		φ_{max} / ppb	0.33	0.45	0.63	0.80	0.86	0.89	0.90	0.90	0.81	0.60	0.37	0.33
RBI	O_3	$\bar{\varphi}$ / ppb	4.0	5.9	12.1	19.3	27.5	33.2	32.5	26.9	15.4	10.4	6.2	5.3
		φ_{max} / ppb	12.5	19.7	28.2	35.6	41.4	45.9	45.8	43.8	33.8	25.2	15.9	12.0
	H_2O_2	$\bar{\varphi}$ / ppb	0.220	0.241	0.246	0.2	0.245	0.249	0.249	0.247	0.243	0.236	0.222	0.215
		φ_{max} / ppb	0.300	0.300	0.302	0.31	0.330	0.342	0.334	0.317	0.308	0.304	0.301	0.300
IMI	O_3	$\bar{\varphi}$ / ppb	12.8	19.2	27.8	39.6	33.2	48.2	62.4	43.1	23.1	15.7	14.2	9.7
		φ_{max} / ppb	32.3	42.2	55.6	57.9	51.6	75.6	89.4	75.3	55.7	41.9	30.7	27.1
	H_2O_2	$\bar{\varphi}$ / ppb	0.283	0.267	0.244	0.191	0.198	0.222	0.194	0.203	0.218	0.248	0.181	0.286
		φ_{max} / ppb	0.292	0.284	0.273	0.244	0.248	0.261	0.246	0.251	0.258	0.274	0.238	0.293

$\bar{\varphi}$ - average daily value for 15th day in the month
φ_{max} - maximum hourly value

December and 0.250 ppb in June and July. The maximum hourly H_2O_2 was estimated to 0.342 ppb in June (Table 6). Hydrogen peroxide levels at PUNT show characteristic seasonal variation with peaks in the summer months due to higher solar radiation. At RBI seasonal variations were less pronounced. For monthly H_2O_2 averages they can be even neglected.

In rural areas in England, H_2O_2 showed significant seasonal variation with maximum values in the

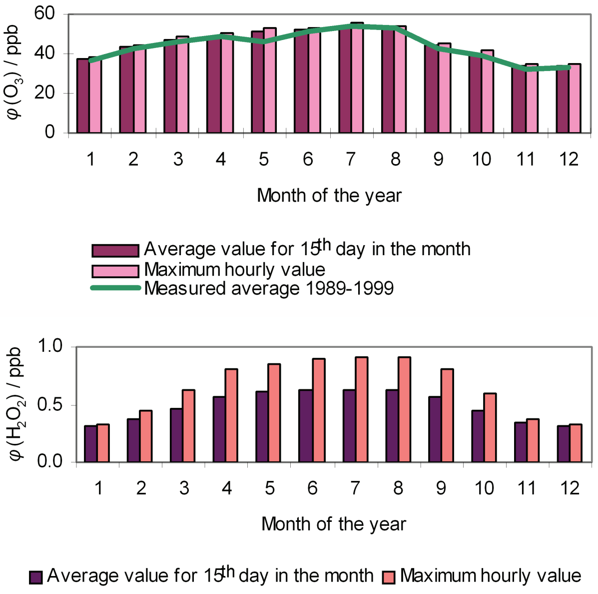

Figure 1. Annual variations of O_3 and H_2O_2 at PUNT estimated using the MM model (modelled average daily values for 15th day in the month and modelled maximum hourly values compared with measured ozone for the period 1989–1999).

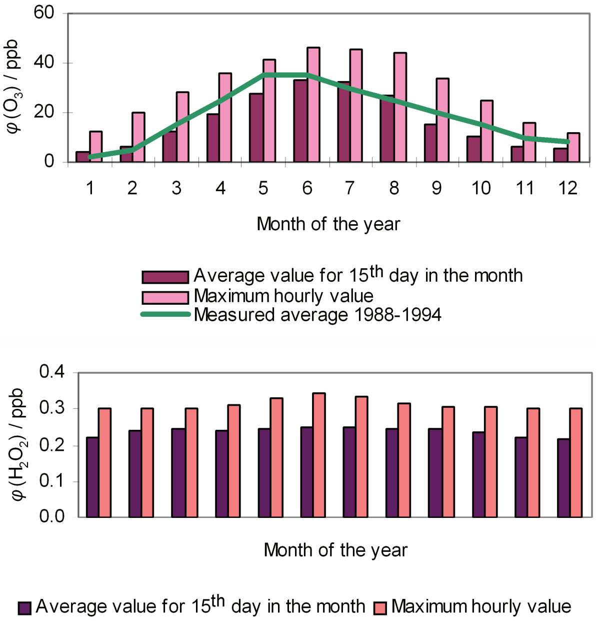

Figure 2. Annual variations of O_3 and H_2O_2 at RBI estimated using the MM model (modelled average daily values for 15th day in the month and modelled maximum hourly values compared with measured ozone for the period 1988–1994).

spring and early summer.[35] H_2O_2 in the air, rain, and suspended matter also showed such variations in Germany. In Berlin, average H_2O_2 volume fractions in the air were 0.04 ppb in the winter and 0.12 ppb in the summer.[13,15] In Great Britain, summer H_2O_2 average was 0.38 ppb while winter average was 0.1 ppb.[35] H_2O_2 measurements in South Korea showed H_2O_2 levels between 0.01 and 0.38 ppb, with pronounced daily and seasonal variations.[36] In Florida, H_2O_2 levels in the rain ranged between 0.3 and 38.6 µmol L^{-1} (average 6.9 µmol L^{-1}). Characteristic seasonal variations were associated with higher solar radiation and higher evaporation of volatile organic compounds.[37] In our study, seasonal variations of H_2O_2 (low concentrations in winter, high concentrations over the summer) calculated with the MM model correspond to the variations measured at similar locations in the world.[13,15,35–37]

At the IMI site, the MM model predicted average monthly ozone volume fractions between 9.7 ppb in December and 62.4 ppb in July, with the maximum hourly value of 89.4 ppb in July. For the summer months, the model produced higher ozone values than were actually measured (Figure 3). Modelled monthly H_2O_2 averages ranged from 0.181 ppb in November to 0.286 ppb in December, with the maximum hourly volume fraction of 0.293 ppb in December. However, no seasonal variations were found at IMI. It seems that H_2O_2 levels depend on the levels of nitrogen oxides from car exhausts (Figure 3). NO reacts directly with HO_2 radical, forming NO_2 and OH radical. During months with higher NO_2 levels, H_2O_2 levels were lower.

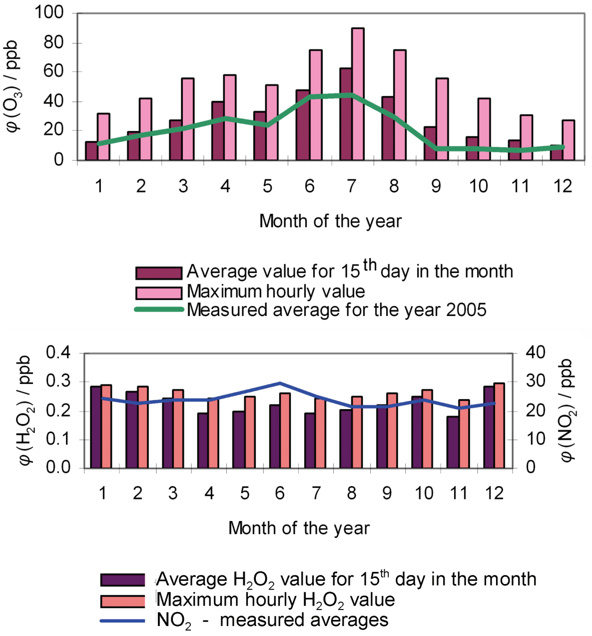

Figure 3. Annual variations of O_3 and H_2O_2 at IMI estimated using the MM model (modelled average daily values for 15th day in the month and modelled maximum hourly values compared with measured ozone for the year 2005).

H_2O_2 and O_3 Levels during the Heat Wave in August 2003

Figure 4 compares modelled and measured ozone volume fractions during the heat wave in Zagreb between 9 and 13 August 2003. Figure 5 shows peroxide levels estimated with the MM model for the same period.

Figure 4 shows that the MM model predicted well the variations of ozone volume fractions at RBI from 9 to 13 August 2003. According to the model, H_2O_2 volume fractions increased on the first day to approximately 3 ppb, and over the following four days ranged between 2.5 ppb and 3.5 ppb with a slow decrease starting after the third day (Figure 5). Volume fractions of OH radicals were between 0 ppb overnight and

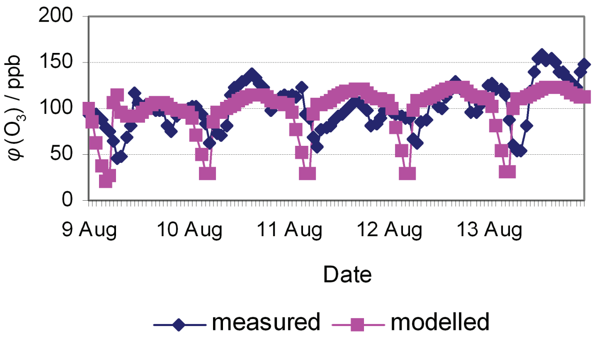

Figure 4. The comparison between measured and modelled O_3 volume fractions during the heat wave in August 2003.

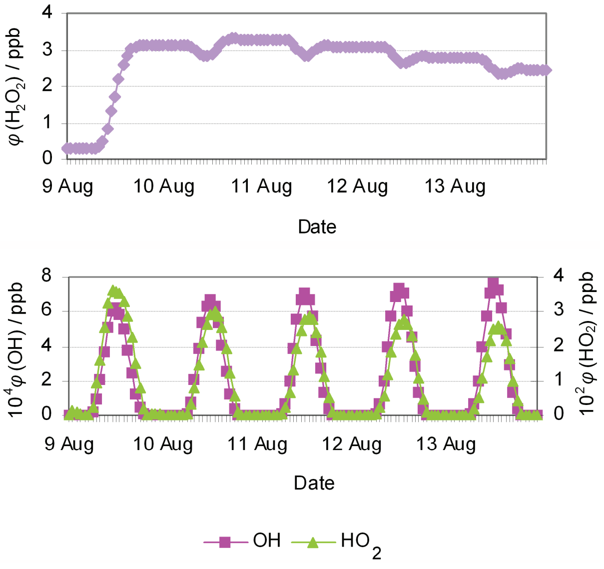

Figure 5. Peroxide levels modelled for the period 9–13 August 2003.

6×10^{-4} ppb during the day. Daily OH maxima slowly increased over the next five days to 8×10^{-4} ppb HO_2 radical levels had the same daily variations as the OH radical, but the noon maxima slowly decreased from 4×10^{-2} ppb to 2.5×10^{-2} ppb. Figure 4 shows estimated O_3 and H_2O_2 levels.

CONCLUSION

The MM model showed a typical seasonal variation of H_2O_2 at the remote Puntijarka location, with the highest values over the summer months. At the urban location not exposed to traffic (IRB) the summer/winter differences were less pronounced and H_2O_2 levels were almost constant over the year. At the site moderately exposed to traffic (IMI), H_2O_2 volume fractions did not show seasonal variations and H_2O_2 levels depended on the levels of nitrogen oxides.

For the August 2003 heat wave, the MM model correctly predicted high ozone levels (> 100 ppb). It also estimated high hydrogen peroxide levels (2.5 ppb–3.5 ppb), followed by increased concentrations of OH radicals. The shape of calculated ozone volume fraction curve is sharper than the measured one. The model is smoother and the measured values can produce sharp notexplainable peaks. The model confirmed that in extreme conditions (high temperature and solar radiation, elevated CO and NO_2 levels) over the summer, the atmospheric oxidizing capacity in Croatia exceedingly rises and may exert harmful effects on the environment.

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REFERENCES

1. S. Madronich, *Tropospheric photochemistry and its response to UV changes*, in: M-L. Chanin (Ed.), *The role of the stratosphere in global change*, Vol. 18, NATO-ASI Series, Springer-Verlag, Amsterdam, 1993.
2. D. J. Jacob, *The oxidizing power of the troposphere*, in: T. Potter and B. Colman (Eds.), *Handbook of Weather, Climate and Water: Atmospheric Chemistry*, *Hydrology, and Societal Impacts*, Wiley, San Francisco, 2003.
3. L. L. deZwart, J. H. Meerman, J. N. M. Commandeur, and N. P. E. Vermeulen, *Free Radical Biol. Med.* **26** (1999) 202–226.
4. J. M. Cape, *Sci. Total Environ.* **400** (2008) 257–269.
5. D. Helmig, S. J. Oltmans, D. Carlson, J-F. Lamarque, A. J. Jones, C. Labuschagne, K. Anlauf, and K. Hayden, *Atmos. Environ.* **41** (2007) 5138–5161.
6. M. Ferretti, M. Fagnano, T. Amoriello, M. Badiani, A. Ballarin-Denti, A. Buffoni, F. Bussotti, A. Castagna, S. Cieslik, A. Costantini, A. De Marco, G. Gerosa, G. Lorenzini, F. Manes, G. Merola, C. Nali, E. Paoletti, B. Petriccione, S. Racalbuto, G. Rana, A. Ranieri, A. Tagliaferri, G. Vialetto, and M. Vitale, *Environ. Pollut.* **146** (2007) 648–658.
7. R. Vingarzan, *Atmos. Environ.* **38** (2004) 3431–3442.
8. A. Lengyel, K. Héberger, L. Paksy, O. Bánhidi, and R. Rajkó, *Chemosphere* **57** (2004) 889–896.
9. L. Klasinc, V. Butković, T. Cvitaš, N. Kezele, I. Lisac, and J. Lovrić, *Ozone measurements in Zagreb and on Mount Medvednica in Croatia*, in: Ø. Høv (Ed.), *Tropospheric ozone research*, Springer-Verlag, Berlin, 1997, 222–229.
10. N. Kezele, T. Cvitaš, and L. Klasinc, *Analysis of measurements with the CRANOX System in Zagreb*, in: P. M. Borrell, P. Borell, T. Cvitaš, and W. Seiler (Eds.), *Proceedings of EUROTRAC Symposium ′94*, SPB Academic Publishing, Hague, 1994, 275–278.
11. V. Butković, T. Cvitaš, K. Džepina, N. Kezele, and L. Klasinc, *Croat. Chem. Acta* **75** (2002) 927–933.
12. A. L. Lazrus, G. L. Kok, S. T. Gitlin, and J. A. Lind, *Anal.Chem.* **57** (1985) 917–922.
13. D. Möller, U. M. Biermann, W. Wieprecht, K. Acker, D. Kalaß, J. Hofmeister, and X. Tian-Kunze, *Anstieg der atmosphärischen Konzentration von Wasserstoffperoxid als Konsequenz der Rauchgasentschwefelung?*, Brandenburgische Technische Universität Cottbus, Berlin, 2002.
14. D. Möller, *Atmos. Environ.* **33** (1999) 2435–2437.
15. D. Möller, M. Bierman, W. Wieprecht, K. Acker, D. Kalass, W Hofmeister, and X. Tian-Kunze, *New insights into atmospheric hydrogen peroxide under polluted and remote influence*, in: K. Šega (Ed.), *Proceedings of the 14th International Conference Air Quality – Assessment and Policy at Local, Regional and Global Scales*, 6–10 Oct 2003, Dubrovnik, Croatia, Croatian Air Pollution Prevention Association, Zagreb, 2003, pp. 489–497.
16. K. Acker, N. Kezele, L. Klasinc, D. Möller, G. Pehnec, G. Šorgo, W. Wieprecht, and S. Žužul, *Atmos. Environ.* **42** (2008) 2530–2542.
17. S. Madronich and J. G. Calvert, *J. Geophys. Res.* **95** (1990) 5697–5715.
18. B. Aumont, S. Madronich, I. Bey, and G. S. Tyndall, *J. Atmos. Chem.* **35** (2000) 59–75.
19. Tropospheric Ultraviolet Visible Model, available at http://cprm.acd.ucar.edu/Models/TUV/index.shtml, displayed 30 June 2008.
20. S. Madronich and S. J. Flocke, *The role of solar radiation in atmospheric chemistry*, in: P. Boule (Ed.), *Handbook of Environmental Chemistry*, Springer-Verlag, Heidelberg, 1998, pp. 1–26.
21. E. C. Weatherhead, *Report on geographic and seasonal variability of UV affecting human and ecological health*, Task report, Contract 4D-5888-WTSA Report to the US EPA.
22. S. Madronich, *UV radiation in the natural and perturbed atmosphere*, in: M. Tevini (Ed.), *Environmental effects of Ultraviolet radiation*, Lewis Publisher, Boca Raton, 1993, pp. 17–69.
23. L. Elterman, *Environ. Res. Papers* **285** (1968) 49.
24. Meteorological and Hydrological Service of Croatia, available at http://meteo.hr/index_en.php, displayed 30 June 2008.
25. I. Lisac and V. Vujnović, *Prorjeđivanje ozonosfere općenito i iznad Hrvatske – sadašnje stanje*, Lošinjska škola, Veli Lošinj, 2005.
26. NASA/TOMS web site, available at http://toms.gsfc.nasa.gov/ozone/ozone_v8.html, displayed 30 June 2008.
27. P. Kalabokas, J. G. Bartiz, T. Bomboi, P. Ciccioli, S. Cieslik, R. Dlugi, P. Foster, D. Kotzias, and R. Steinbrecher, *Atmos. Environ.* **31** (1997) 67–77.
28. A. Jeričević, K. Špoler Čanić, and S. Vidič, *Croat. Meteor. J.* **39**

(2004) 3–14.

29. N. Kezele, *Fotooksidansi u graničnom sloju atmosfere na području Hrvatske*, Doctoral thesis, 2001., Zagreb.
30. V. Butković, T. Cvitaš, J. Injuk, N. Kezele, L. Klasinc, and S. Lulić, *Ozone measurements in Zagreb*, in: M. Borell and P. Borell (Eds.), *Proceedings of EUROTRAC Symposium '98, Transport and Chemical Transformation in the Troposphere*, Vol. 1, WIT Press, Southampton, 1999, pp. 275–280.
31. T. Cvitaš, N. Kezele, L. Klasinc, and S. Lulić, *Croat. Meteor. J.* **31** (1996) 79–87.
32. IMI, *Izvještaj o praćenju onečišćenja zraka na području grada Zagreba* (izvještaj za 2005. godinu) IMI-SG-48, IMI, Zagreb, 2006.
33. A. Alebić-Juretić, T. Cvitaš, N. Kezele, L. Klasinc, G. Pehnec, and G. Šorgo, *Bull. Environ. Contam. Toxicol.* **79** (2007) 468–471.
34. MZOPUG RH, available at http://zrak.mzopu.hr/glavni.asp, displayed 30 June 2008.
35. G. J. Dollard, B. M. R. Jones, and T. J. Davies, *Atmos. Environ.* **25A** (1989) 2039–53.
36. C. M. Kang , J. S. Han, and Y. Sunwoo, *Atmos. Environ.* **36** (2002) 5509–5516.
37. Y. Deng and Y. Zuo, *Atmos. Environ.* **33** (1999) 1469–1478.

SAŽETAK

Procjena razina ozona i peroksida u zraku Hrvatske

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Volumni udjeli različitih plinovitih atmosferskih sastojaka modelirani su korištenjem Master Mechanism (MM) modela, autora S. Madronicha (NCAR, Boulder, CO, USA). Sezonske varijacije ozona (O_3) i vodikova peroksida (H_2O_2) procijenjene su na tri različite lokacije u Zagrebu. Modelirane vrijednosti ozona pokazale su dobro slaganje s izmjerenim vrijednostima na sve tri lokacije. Procjena godišnjega hoda H_2O_2 pomoću MM modela pokazala je tipične sezonske varijacije na udaljenoj lokaciji i na urbanoj lokaciji neizloženoj prometu, s najvišim vrijednostima tijekom ljetnih mjeseci, kada je najjače sunčevo zračenje. Razlike ljeto/zima bile su više izražene na udaljenoj lokaciji. Na lokaciji izloženoj prometu, volumni udjeli H_2O_2 nisu pokazali sezonske varijacije, a razine H_2O_2 bile su određene razinama dušikovih oksida. Model je također korišten za procjenu razina oksidansa tijekom vala vrućine u kolovozu 2003. godine. Dobivene su visoke razine vodikova peroksida (2,5 ppb–3,5 ppb) i ozona (> 100 ppb), popraćene porastom razina radikala OH. Model je potvrdio da usljed ekstremnih uvjeta (visoka temperatura i sunčevo zračenje, povišene razine CO i NO_2) oksidacijski kapacitet atmosfere u Hrvatskoj tijekom ljeta prekomjerno naraste te može imati štetne učinke na okoliš.