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Atmospheric H₂O₂ measurement and modeling campaign during summer 2004 in Zagreb, Croatia

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Abstract

Hydrogen peroxide (H₂O₂) in the gas phase and a number of other atmospheric components and variables (O₃, CO, SO₂, NO, NO₂, benzene, toluene, ethylbenzene and xylene (BTEX)) were simultaneously measured during a field study performed in Zagreb, Croatia, from May until July 2004 (for selected variables until October 2004). Meteorological data from the nearby stations were provided by the Geophysical Institute and by Meteorological and Hydrological Service of Croatia. The collected data adjusted to hourly averages were used for modeling diurnal concentration behavior and development over a couple of days using Master Mechanism model developed by S. Madronich (NCAR, Boulder, CO). The H₂O₂ mixing ratios were found to vary between <0.05 and 6.2 ppb and also exhibited a strong diurnal pattern very similar to that of ozone, with concentration maxima in the afternoon, between 15:00 and 16:00 h, CET. Linear regression analysis showed that, during daytime, H₂O₂ positively correlated with ozone ($r = 0.4$) and solar radiation ($r = 0.52$), but showed only very weak negative correlations with NO₂, CO and BTEX. Our H₂O₂ data are the first such reported data for the region and their modeling, along with ozone data, gives a valuable insight into the interplay of pollutants that affect their concentrations.

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Keywords: Air; Hydrogen peroxide; Master Mechanism model; Oxidants; Ozone

1. Introduction

The role of hydrogen peroxide (H₂O₂) in atmospheric chemistry and its contribution to the formation of free radicals have been studied more intensively over the last few decades. Free radicals

(superoxide O₂^{•-}, hydroperoxy HO₂[•] and hydroxyl OH[•]) formed within the cells can oxidize biomolecules such as lipids, nucleic acids, proteins, amines and carbohydrates. This may lead to cell death and tissue injury. For this reason, free radicals are considered to cause more than 100 diseases including eye disorders, cataract and glaucoma (Izzoti et al., 2006), heart illnesses, stroke, atherosclerosis, diabetes and cancer (deZwart et al., 1999; Oktay et al., 2003). Owing to its good solubility, gaseous

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phase H_2O_2 is efficiently removed in upper respiratory tract during breathing. However, peroxide dissolved in fine particles makes possible the entrance of H_2O_2 deeper into the lung. Toxicological studies have shown that H_2O_2 concentrations measured in aerosols may damage alveoli (Hasson and Paulson, 2003).

In the troposphere, H_2O_2 may originate from recombination of HO_2^\bullet radicals (which are secondary products of photolysis of ozone and aldehydes), from reaction of ozone (O_3) with alkenes (ozonolysis), by the decay of ozone in weakly acidic and alkaline aqueous solutions, photochemically, by electron transfer to O_2 in aqueous phase (photocatalysis) and from biomass burning (Möller et al., 2002).

Several studies have shown other ways of H_2O_2 formation. Sauer et al. (1999) described the formation of H_2O_2 by the reaction of ozone and biogenic hydrocarbons like isoprene and isobutene in water droplets, without HO_2^\bullet radicals. The same mechanism can be expected for terpenes.

Organic peroxides (ROOH) contribute to the oxidizing power of the troposphere (Lee et al., 2000), defined as the total burden of ozone, HO_x^\bullet radicals and H_2O_2 . They also constitute an important radical reservoir. In the presence of solar radiation ($\lambda > 320$), water vapor and O_3 , the short-lived OH^\bullet radical is produced and converted into peroxyradicals (HO_2^\bullet , RO_2^\bullet) through the oxidation of CO, CH_4 and non-methane hydrocarbons. The combination of peroxyradicals is the main photolytic source of ROOH. However, competing reactions with NO can suppress the formation of hydroperoxides, depending on the level of NO present (Frey et al., 2005). Photolysis and attack by the OH^\bullet radical are the main photochemical sinks for hydroperoxides. In the presence of liquid water, H_2O_2 is quickly dissolved. H_2O_2 can also be removed from the air by heterogeneous processes of wet and dry deposition. H_2O_2 formation in aqueous phase, like in gaseous phase, proceeds mainly by reaction of hydroperoxy radicals. Owing to its good solubility, HO_2^\bullet radical enters into aqueous phase usually by capture from gaseous phase or by dissolving gaseous H_2O_2 from air (Lee et al., 2000). Physical and chemical processes in the atmospheric multiphase system significantly influence the transport, distribution and removal of chemical species from the atmosphere. In fact, aqueous-phase reactions potentially act either as the sink or as the source of atmospheric trace

compounds like H_2O_2 , depending on the physical and chemical characteristics of the cloud droplets (Laj et al., 1997).

Hydroperoxide has drawn much attention since its role was recognized in acid generation in the atmosphere. H_2O_2 is the most dominant oxidant of SO_2 in atmospheric aqueous phases, especially when pH is lower than 4.5 (Penkett et al., 1979; Calvert et al., 1985). Heterogeneous formation of sulfuric acid in rain and clouds has been subject of several field experiments and it was found to be much more important than homogeneous gas phase reactions (e.g. Kelly et al., 1985; Laj et al., 1997; Valverde-Canossa et al., 2005). Measurements on Greenland ice cores showed that H_2O_2 concentrations increased over the past 200 years and most of the increase has occurred over the past 20 years (Möller, 1999). Before 1975, levels of H_2O_2 were low because high sulfur dioxide concentrations from fossil fuel combustion consumed H_2O_2 . After 1975, SO_2 emissions from industrial and domestic sources were reduced globally. This in turn led to an increase in tropospheric H_2O_2 . Using a model with existing values of NO, CO, CH_4 emissions and changes in stratospheric ozone, Thompson et al. (1991) calculated H_2O_2 concentrations for the period 1985–2035. By 2035, they predicted an increase in H_2O_2 concentration of 100% in urban areas and a global increase of 22%.

With decreased SO_2 emission a further increase in peroxide is expected. Methods that efficiently removed industrial SO_2 probably caused higher levels of H_2O_2 in Croatia, as well. Concentrations of SO_2 and black smoke have been measured in Zagreb from 1965. In the 1960s and 1970s SO_2 concentrations were occasionally higher than $1000 \mu\text{g m}^{-3}$ in the air of Zagreb. However, over the last 20 years concentrations of SO_2 , black smoke and total suspended matter have decreased, mainly as the result of lower coal consumption and introduction of natural gas for heating (Fugaš, 1997; Vađić and Hršak, 2000). At the same time, NO_2 concentrations increased (Vađić and Hršak, 2000). In 2005, daily NO_2 concentrations in the center of Zagreb ranged between 10 and $120 \mu\text{g m}^{-3}$ (annual average $37 \mu\text{g m}^{-3}$). However, hourly NO_2 concentrations occasionally exceeded $250 \mu\text{g m}^{-3}$, especially in the rush hours (Pehnek et al., 2006). The first measurements of ozone in Zagreb were carried out in the summer of 1975 (Božičević et al., 1976; Cvitaš et al., 1979; Cvitaš et al., 1997) and since 1989 at a remote location Puntijarka (960 a.s.l.) on Mt. Medvednica

(Klasinc et al., 1997; Butković et al., 2002) overlooking the city. Today there are six stations in Zagreb that measure ozone concentrations using automatic devices and manual methods. Ozone concentrations sometimes exceed levels set by Croatian legislation (Pehnc et al., 2005). Average daily ozone concentrations higher than $200 \mu\text{g m}^{-3}$ were recorded during a heat wave in August 2003 (Butković et al., 2004; Alebić-Juretić et al., 2007). Other oxidants, such as H_2O_2 , are not measured in Croatia now. H_2O_2 measurements in the rest of the world are relatively sparse and limited due to the need of expensive and sophisticated equipment. Only a few data exist for a wider region (Kalabokas et al., 1997; Möller et al., 2002; Walker et al., 2006). Our study brings the first results of hydrogen peroxide measurements in Croatia. At one location in Zagreb, German and Croatian researchers continuously monitored atmospheric H_2O_2 , O_3 , CO , SO_2 , NO , NO_2 , benzene, toluene, ethylbenzene, xylene (BTEX) and solar radiation from May to August 2004. The results, in the form of 1-h averages, were used to model diurnal concentration behavior. Our results give some insight into the presence of atmospheric photooxidants, and make it possible to evaluate the role of ozone and H_2O_2 in the photochemical processes within surficial air over Croatia.

2. Experimental

2.1. Site description

The capital of Croatia, Zagreb, is an industrial and traffic hub with population of nearly 1 million people, situated at the foot of the mountain Medvednica (highest peak 1035 m a.s.l.) to the north and by the River Sava to the south. The climate is continental. The measurement site was located at the Ruđer Bošković Institute (RBI) campus in the northern, residential part of Zagreb (180 m a.s.l., $45^\circ 50' \text{N}$, $15^\circ 59' \text{E}$). The site is remote from local pollution sources, at about 500 m distance from a street with modest traffic density, and at least 100 m from any building.

2.2. Meteorology and solar radiation measurements

Meteorological data (average daily temperature, relative humidity, pressure and precipitation) were obtained from the national Meteorological and Hydrological Service (DHMZ). Their measurement

site is placed at park Maksimir, about 2 km south-east of RBI. Data on solar radiation measured at the surface were obtained from the nearby Department of Geophysics (GFZ), University of Zagreb ($45^\circ 50' \text{N}$; $15^\circ 60' \text{E}$, 191.8 m a.s.l.). Pyranometer-type Kipp&Zonen CM 6b, placed at the roof of the GFZ, measured values in the wavelength range from 305 to 2800 nm. Sensitivity of the instrument was 9.45 mV W m^{-2} with sampling frequency 1 Hz.

2.3. Methods for the determination of H_2O_2 , O_3 , NO , NO_2 , SO_2 , CO and BTEX in the air

In this study, we used a commercial H_2O_2 analyzer (AL 1002, Aerolaser GmbH, Germany) based on the fluorimetric method described by Lazrus et al. (1985). The analytical procedure includes the scrubbing of all soluble peroxides (H_2O_2 , organic peroxides) from sampled air (flow rate 2 L min^{-1}) into stripping coils continuously wetted by diluted potassium hydrogenphthalate buffer; then dimerization of *p*-hydroxyphenyl acetic acid in the presence of peroxides catalyzed by peroxidase, excitation of the fluorescent dimer product at 326 nm, and detection of the emitted radiation between 400 and 420 nm. To distinguish between H_2O_2 and organic peroxides, two parallel channels are in operation. In channel (A) the sum of all soluble peroxides is determined, whereas in channel (B) the amount of organic peroxides is measured after selective destruction of H_2O_2 by catalase (efficiency $> 95\%$). The H_2O_2 mixing ratio is calculated from the differences between the two channels. The limit of detection is 50 ppt. The instrument is equipped with an internal zero trap and permeation device to carry out automatic zeroing (every morning) and calibration procedures (weekly, at midnight). A liquid H_2O_2 standard ($1 \mu\text{mol L}^{-1}$) was used for daily manual external calibration. The device was operated in an air-conditioned environment at about 20°C (container) with a very short PTFE inlet outside, altogether $\sim 2.5 \text{ m}$ above ground.

The container also hosted the devices to measure O_3 , NO , NO_2 , SO_2 , CO , CO_2 , H_2O , BTEX; for details see Table 1. All instruments were maintained and serviced regularly. The accuracy of the instruments for NO_x and SO_2 was tested previously at the intercomparison workshop organized by World Health Organization in Langen, Germany, in May 2004. Measurement campaign lasted from 12 May to 20 August. Unfortunately, it was recognized later

Table 1
Measurement techniques used in the campaign

Compound	Instrument	Method	Detection limit	Period of measurement
NO/NO ₂	AC 30 M, Ansyco Environment s.a.	Chemiluminescence	1 ppb	10 June–20 August
SO ₂	AF 21 M, Ansyco Environment	UV fluorescence (320 nm)	1 ppb	18 May–20 August
BTEX	VOC 71 M, Environment s.a.	Automatic gas chromatograph with PID detector	0.1 ppb	18 June–17 August
O ₃	O ₃ 41 M–LCD Environment s.a.	UV absorption (253.7 nm)	0.1 ppb	12 May–20 August
CO	CO 11 M–LCD Environment s.a.	IR absorption (4.67 μm)	0.1 ppm	25 June–20 August
H ₂ O ₂	AL2011CA Aero-laser GbmH	Oxidation of <i>p</i> -hydroxyphenylacetic acid, fluorescence (400–420 nm)	50 ppt	12 May–6 July

that the CO₂/H₂O (humidity) instrument has malfunctioned, and its data had to be discarded. Instead, we used the 24-h data from the nearby DHMZ station Maksimir.

2.4. Model description

The Master Mechanism is a multi-task interactive atmospheric box model program that gives an insight into the time behavior of chosen initial amounts of atmospheric constituents under selected, either fixed or variable, conditions (Madronich and Calvert, 1990; Aumont et al., 2000). It does not include transport, and describes best the reactions and transformations that occur within an air package at rest in a horizontal plane under the influence of sunlight and meteorological parameters. However, the model can also include the effects of some other processes like time-dependent dilution by mixing and/or planetary boundary layer (PBL), temperature and pressure change, emission, or deposition. The location from which we collected our data is not optimal for interpretation by any model; however, the fact that data were collected from one single point made the Master Mechanism approach seem most desirable. It allows one to predict the time evolution of any reactive air composition as dictated by corresponding reaction rate constants and physical parameters. A comparison between modeled and actual composition at later times makes it possible to trace the unaccounted for the effects of changes in box reactant composition caused by transport, dilution by PBL level change, or deposition, etc.

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 ~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 (TUV, 2006; Madronich and Flöcke 1998). For TUV model the following environmental conditions, common for all days were used: latitude: 45°50'; longitude: 15°59'; time zone: 1; surface elevation: 0.180 km; surface albedo: 0.1; aerosol optical depth at 550 nm: 0.235; single-scattering albedo of aerosols: 0.99; air number density: 2.53×10^{19} molecules cm⁻³.

For modeling purposes, we analyzed the campaign period from 25 June to 5 July because over that period all instruments operated correctly. Measurements were carried out mostly under clear-sky conditions, except on days 25 June, 29 June, and 2 July. Cloud correction was done for all days according to the data on solar radiation from GFZ. For each day, data on total ozone column were obtained from NASA/TOMS website while data on average daily air temperature and pressure were obtained from DHMZ.

Average daily values obtained by our measurements were used as initial volume fractions for O₃, H₂O₂, CO, H₂O, benzene, toluene and xylene. For CO₂, we used the average of 330 ppm. Previous analysis showed that modeling with the initial average daily volume fractions of NO and NO₂ did not produce good agreement with measurements.

This is because of the emission of NO_x from local sources, which cannot be ignored. Unfortunately, Master Mechanism is a box model and it does not include the transport of species. The analysis of NO_x data shows that overnight NO volume fractions were low, often lower than the detection limit of the instrument (1 ppb). During daytime there were “peaks” in the morning and in the afternoon as the result of local traffic (employees arriving at and leaving the Institute). For that reason, we included the daily cycle of minimum NO values in the model (assumed zero value overnight) and average daily NO_2 volume fraction as the initial value. According to the data from literature (Kalabokas et al., 1997) and from the first measurements of VOC at RBI, 1 ppb was chosen as an initial volume fraction for C_2H_4 , C_3H_6 , CH_2O , CH_3CHO and CH_3COCH_3 . Deposition was included in all calculations, the changes of PBL over the day were also put in the model according to the values from Jeričević et al. (2004). The mixing height ranged from 250 m over night to 1200 m in the noon.

3. Results and discussion

3.1. The measuring campaign

All measured volume fractions of species were transformed to 1- and 24-h averages. Hourly averages were obtained for solar radiation, for other meteorological parameters (temperature, pressure, relative humidity and precipitation) only 24-h averages were available. During the campaign, daily averages of air temperature ranged from 9.6 to

27.5 °C (average 19.5 °C) while relative humidity ranged between 46% and 92% (average 68%). There were 33 days with precipitation and, in an average, 10.4 sunny hours per day. Table 2 summarizes the results from the measuring campaign. Data were divided into two groups: day values (solar radiation $>0 \text{ W m}^{-2}$, between 5 a.m. and 8 p.m. local time) and night values (from 8 p.m. to 5 a.m. local time). During the measuring period, local time corresponded to Central European Time (CET).

Volume fractions of SO_2 were lower over the whole period. Maximum hourly value was 10 ppb. Most of the days SO_2 volume fractions were below 2 ppb, often below the detection limit of the instrument (1 ppb). Average volume fractions of NO and NO_2 were also low during the whole measuring period. Maximum volume fractions were observed in the morning and in the afternoon, that is when RBI employees were arriving at and leaving the Institute. NO_x ($\text{NO} + \text{NO}_2$) volume fractions were especially low in August (summer vacations); hourly NO volume fractions were around 1 ppb or higher during the day and below detection limit overnight. In our calculations, we assumed zero NO value overnight. Similar distribution was observed for CO and BTEX volume fractions (“peaks” between 8 and 9 a.m. and 18 p.m. local time). BTEX volume fractions were approximately 40% lower in the daytime than overnight. Average daytime volume fractions of CO and NO_2 were 20% higher, and average ozone volume fractions were about 10% higher. For H_2O_2 , average daytime volume fractions were twice higher than average nighttime volume fractions (Table 2).

Table 2

Summary statistics for the concentration of species (hourly averages, ppb) and solar radiation (W m^{-2}) during measuring campaign

Compound	Total			Day			Night		
	N	Mean (SD)	Range	N	Mean (SD)	Range	N	Mean (SD)	Range
NO	1708	1.1 (3.30)	<1–46.3	1066	1.5 (5.07)	<1–46.3	642	0.4 (0.68)	<1–3.7
NO_2	1708	6.7 (8.51)	<1–69.8	1066	7.1 (9.52)	<1–69.8	642	5.9 (6.41)	<1–29.9
H_2O_2	1101	0.3 (0.50)	<0.05–6.2	701	0.4 (0.56)	<0.05–6.2	400	0.2 (0.35)	<0.05–4.2
O_3	2147	44.1 (16.29)	9.5–104.8	1340	45.8 (15.93)	9.6–104.8	807	41.3 (16.49)	9.5–102.1
CO	1339	284.8 (131.6)	16.5–857.4	835	301.3 (147.3)	16.5–857.4	504	257.5 (94.3)	58–739.6
Benzene	2023	1.4 (1.17)	<0.1–11.9	1254	1.5 (1.35)	<0.1–11.9	769	1.2 (0.77)	<0.1–5.6
Toluene	2023	3.0 (3.09)	<0.1–32.1	1254	3.2 (3.49)	<0.1–32.1	769	2.8 (2.27)	<0.1–16.5
<i>o</i> -Xylene	2023	0.3 (0.74)	<0.1–7.5	1254	0.4 (0.84)	<0.1–7.5	769	0.2 (0.51)	<0.1–3.8
(<i>m</i> + <i>p</i>)-Xylene	2023	2.2 (2.64)	<0.1–23.3	1254	2.3 (2.95)	<0.1–23.3	769	2.0 (2.01)	<0.1–20.5
Ethylbenzene	2023	0.5 (1.03)	<0.1–8.9	1254	0.6 (1.20)	<0.1–8.9	769	0.4 (0.64)	<0.1–4.8
Radiation	1704	216.6 (292.3)	0–988.3	1065	346.5 (302.8)	0–988.3	–	–	–

Figs. 1 and 2 show daily variations of H_2O_2 and O_3 volume fractions. Fig. 3 shows the daily variations of all measured species at 26 June 2004.

Ozone and hydrogen peroxide volume fractions showed similar distributions, with greater participation of lower values, especially in the case of H_2O_2 . The most represented fraction was 0.10–0.15 ppb for H_2O_2 and 40–45 ppb for O_3 . Daily H_2O_2 maximum occurred between 15 and 16 h while ozone reached maximum values between 14 and 17 h, CET (Figs. 1 and 2). During many days ozone peaked at midnight (Fig. 2). This is the main reason for similar average ozone volume fractions during daytime and nighttime (Table 2). These nighttime peaks suggested that NO was very low (probably zero, as we assumed in calculations).

It is known from the literature that H_2O_2 volume fractions in the troposphere show characteristic daily variations, with higher values over the day. Sunlight has a key role in the formation of peroxides so it was expected that the H_2O_2 volume fractions would be the highest at noon, at the maximum solar radiation. Similar daily variations were found in other investigations (Jackson and Hewitt, 1996; Möller et al., 2002; Kang et al., 2002; Takami et al., 2003). Moortgart et al. (2002) reported that the major hydroperoxide present throughout the campaign at different places around

Berlin in summer 1998 was H_2O_2 , but the organic peroxides (methyl hydroperoxide and hydroxymethyl hydroperoxide) were also occasionally found (0.06–0.4 ppb). On an average, H_2O_2 /total peroxide ratio was about 2:3 during the daylight hours on sunny days. Peroxides showed pronounced diurnal variations with peak mixing ratios in the early afternoon. At times, a second maximum was observed in the late afternoon (Moortgart et al., 2002). Sauer et al. (1997) measured H_2O_2 in the air and rain above the sea in France and did not find significant daily variations.

A few years ago Lee et al. (2000) reviewed chemistry, properties, measurement methodology and tropospheric distribution of gas-phase hydrogen peroxide and organic hydroperoxide in the troposphere and reported numerous results from airborne, mountaintop, ground and shipboard measurements. Table 3 shows the results of H_2O_2 measurements found in the literature together with the results from this paper.

Linear correlation coefficients were calculated between hourly volume fractions of all measured compounds and hourly solar radiation, separately for daytime and nighttime. The best correlation ($r = 0.73$) was found between NO and NO_2 during the day, and between BTEX (0.90–0.97), which indicates that they all have a common origin,

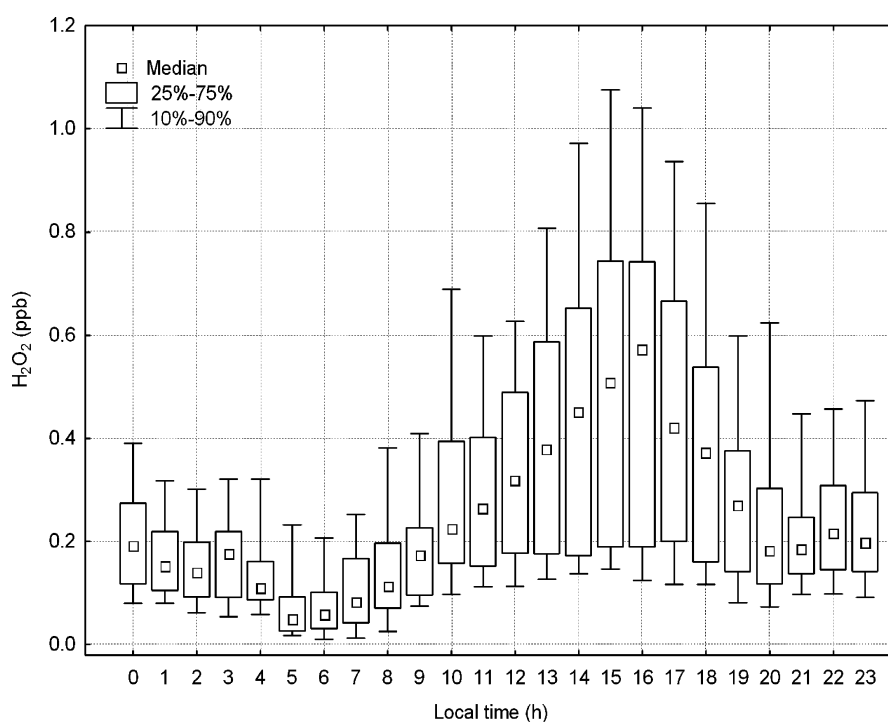


Fig. 1. Daily variations of H_2O_2 volume fractions.

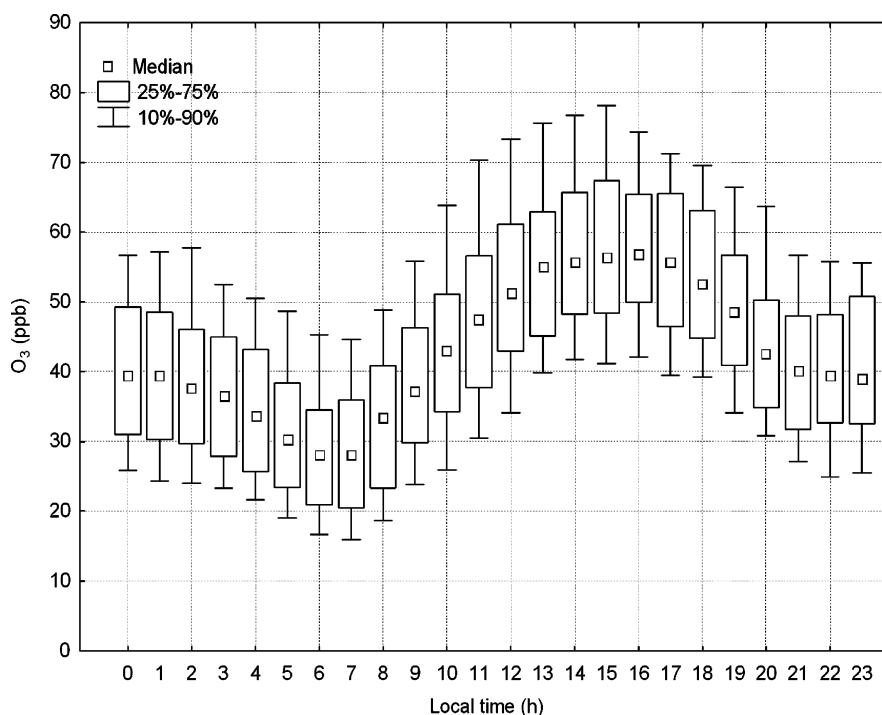


Fig. 2. Daily variations of O₃ volume fractions.

probably traffic. The correlation coefficient for NO/NO₂ is much lower ($r = 0.26$) during the nighttime. For BTEX, lower correlation coefficient was also found during the nighttime, but the difference was not significant (r between 0.71 and 0.91). Correlation coefficients between NO₂ and BTEX, although statistically significant as a consequence of great number of hourly averages, were not high ($r \sim 0.20$), and there was no difference between nighttime and daytime. Hourly CO averages do not correlate with NO_x, but correlate with BTEX (r between 0.53 and 0.65 over the day and between 0.26 and 0.47 over the night).

According to the chemical processes described in the introduction, it is expected that H₂O₂ will show positive correlation with solar radiation intensity and with concentrations of ozone, aldehydes and volatile hydrocarbons and negative correlation with oxides of nitrogen, sulfur dioxide and sulfates (Möller et al., 2002; Lee et al., 2000). In this work, we found positive correlation between hourly values of H₂O₂ and O₃ ($r = 0.40$ over daytime, $r = 0.14$ over nighttime) and between H₂O₂ and solar radiation ($r = 0.33$). H₂O₂ did not correlate at all with NO₂, CO and BTEX over the night, while over the day a very weak, although statistically significant, negative correlation was found (r between 0.11 and 0.15). It was also found that ozone positively correlated with solar radiation ($r = 0.50$). Similar to

H₂O₂, ozone showed weak negative correlation with CO ($r = -0.31$) and BTEX (-0.24 to -0.30) during the day and no significant correlation overnight.

Other authors also found a positive correlation between concentrations of hydrogen peroxide, ozone and solar radiation (Möller et al., 2002; Kang et al., 2002; Takami et al., 2003). Kang et al. (2002) found that H₂O₂ correlated with ozone, temperature and aldehydes and negatively correlated with NO₂, CO and SO₂. Takami et al. (2003) found positive correlation with ozone and temperature and a weak negative correlation with humidity. NO_x correlated positively with H₂O₂ to 1.5 ppb and negatively if NO_x volume fractions were higher than 1.5 ppb. Weak correlation was found between sunlight and hydrocarbons (isoprene and α -pinene). Sauer et al. (1997) found a significant negative correlation between H₂O₂ and NO_x during summer months and between H₂O₂ and NO₃ when there was rain. Möller et al. (2002, 2003) also found correlation between gaseous H₂O₂ and ozone.

Obtained volume fractions and solar radiation data, in the form of 1-h averages, were subjected to the factor analysis in order to define virtual variables which will describe their interdependence. Factors were based on principal component extraction and rotated by normalized varimax method. Three significant factors were extracted for daytime and nighttime (Fig. 4). The total variance explained

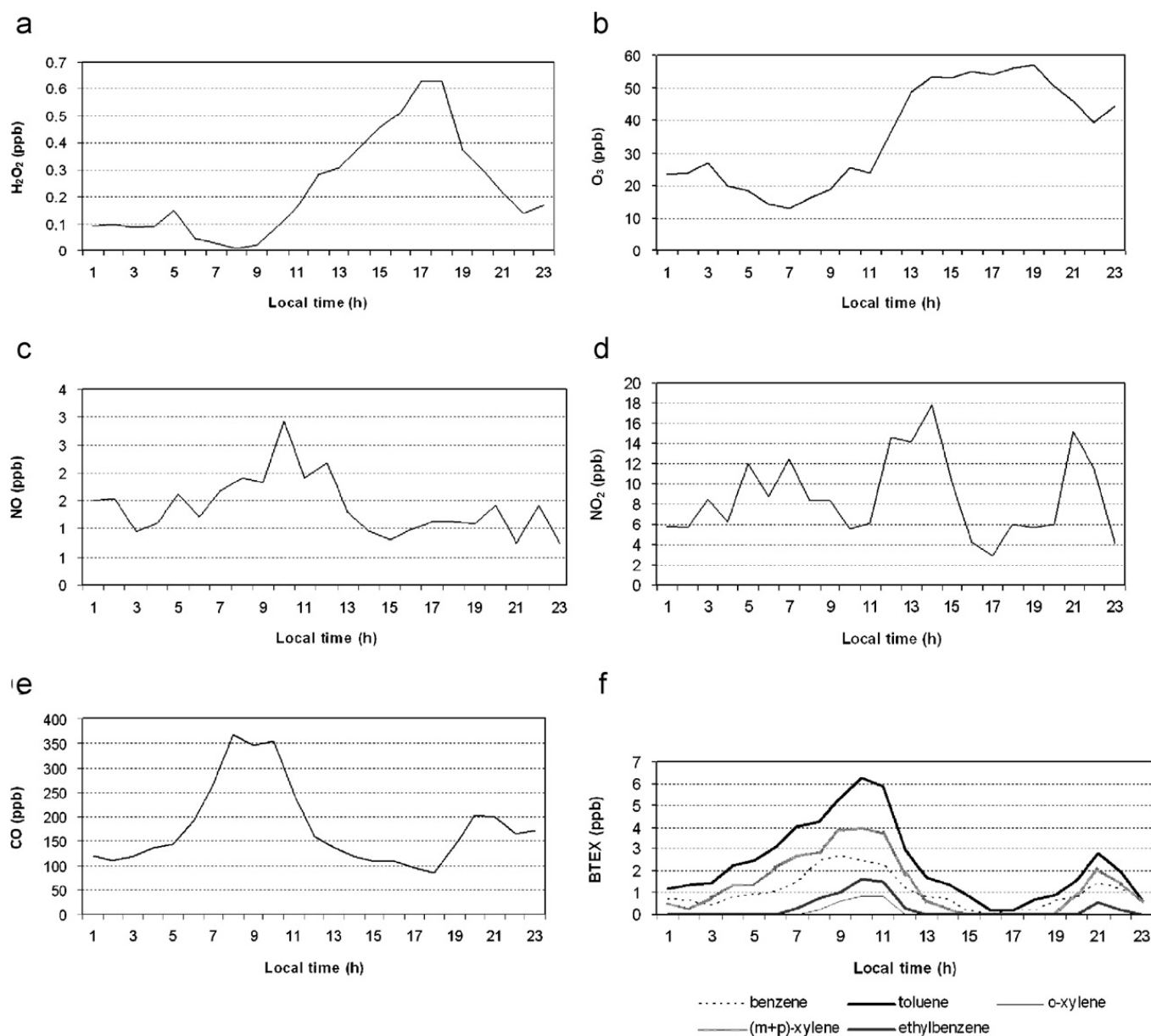


Fig. 3. Daily variations of measured species at 26 June 2004.

by three factors amounted 79.9% and 71.0%, respectively. The first factor describes BTEX and CO relationship and recognizes fuel combustion as its common origin. The connection between BTEX and CO is stronger over the day. The second factor separates NO and NO_2 . The third factor describes the strong influence of solar radiation on ozone and H_2O_2 formation.

3.2. Modeling results

For days 25 June–5 July 2004, volume fractions of different species were calculated using the Master Mechanism model. Fig. 5a and b shows the

comparison of modeled and observed mixing ratios of H_2O_2 and O_3 for 1 July (clear-sky conditions). Fig. 6a and b shows the comparison of modeled and observed mixing ratios of H_2O_2 and O_3 for 3 July (cloudy conditions), with included cloud correction. Fig. 7a and b shows the comparison between modeled and observed mixing ratios of H_2O_2 and O_3 on 25 June when 32 mm of rain fell during the day (cloud correction included in calculations). Average daily values of measured compounds were used as initial conditions because we wanted to see how well the model predicted daily cycles of H_2O_2 and O_3 with data which are usually available from the Croatian monitoring station reports (usually

Table 3
Measurements of gaseous H₂O₂ in the atmosphere (in ppb)

When	Where	Mean	Range	Reference
March 1988	Bahia (BR)	1.0	0.2–3.9	Jacob et al. (1990)
1988/1989	North Carolina (USA)		0–3.3	Claiborn and Aneja (1990)
1987–1990	San Bernardino (USA)		1–3	Sakugawa and Kaplan (1993)
1988–1994	Harwell (GB)	0.38 ^c , 0.1 ^d		Dollard and Davies (1993)
1989–1991	Schauinsland (DE)	0.33	0.09–0.93 ^a	Gilge (1994)
1990	Mt. Wank (DE)	0.3	0.05–0.85 ^a	Junkermann et al. (1992)
1992 ^b	Grand Canyon (USA)	1–1.5	0.7–6	Tanner and Schorran (1995)
1993 ^b	Bretagne (FR)	0.2	<0.1–1.2	Sauer et al. (1997)
1993 ^b	Great Dun Fell (GB)		<0.05–1.2	Preiß et al. (1994)
August 1993	Mt. Norikura (JP)	1.1	0.01–4.5	Watanabe et al. (1995)
June 1994	central Portugal	0.27	<0.025–0.63	Jackson and Hewitt (1996)
1996 ^c	Mt. Szrenica (PL)		0.05–2	Acker et al. (1999)
1997/1998	Antarctic	0.15	0.05–0.4	Riedel et al. (2000)
1998 ^c	vicinity of Berlin (DE)		<0.015–1.5	Moortgart et al. (2002)
1998/1999	Seoul (South Korea)	0.1 ^c , 0.04 ^d	<0.01–0.38	Kang et al. (2002)
May 2000	Beijing (CN)	2.33		Peng et al. (2003)
June 2000		0.34		
2000 ^c	Berlin (DE)	0.16	0.02–1.8	Möller et al. (2002)
2000/01 ^d		0.03	<0.02–0.26	
May–Aug. 2001	Los Angeles (USA)		0.5–3.5	Hasson and Paulson (2003)
Autumn 2001	Mt. Schmücke (DE)		<0.130	Valverde-Canossa et al. (2005)
2000 ^c , 2002 ^c	West Antarctic Ice	0.33	<0.03–0.92	Frey et al. (2005)
2001 ^c	Sheet	0.65	0.14–1.21	
Feb/Mar 2003	Mt. Jungfrauoch (CH)	0.21	<0.02–1.42	Walker et al. (2006)
1998–2005	Mt. Hohenpeißenberg (DE)	0.59 ^{a,c}	0.05–1.82 ^{a,c}	Gilge (2007)
		0.21 ^{a,d}	0.04–1.5 ^{a,d}	
May–July 2004	Zagreb (HR)	0.3	<0.05–6.2	This work

^aFrom monthly means.

^bSpring.

^cSummer.

^dWinter

only daily, monthly and annual averages of NO_x, SO₂, CO, BTEX) and from meteorological stations.

The results show that Master Mechanism model predicts well ozone volume fractions under both, cloudy and clear sky conditions. The relative difference between modeled and observed values is less than 12% for maximum and 25% for average values. In the case of hydrogen peroxide the differences are much greater, especially on cloudy and rainy days. On these days, modeled H₂O₂ results are usually much higher than those measured. However, maximum hourly H₂O₂ values can be predicted on clear-sky days with an uncertainty of less than 20%. The main reason for the error in peroxide calculations is probably the influence of traffic emission. The formation of H₂O₂ is very sensitive to NO_x concentrations, much more than ozone formation. In addition, the differences between the modeled and observed values were more pronounced during the night (modeled values

were higher than measured). Measurements have shown that benzene volume fractions usually increase overnight, probably due to the transport of polluted air masses from the city center. In addition, at night, H₂O₂ is removed from the gas phase by deposition and by capture on the water part of the aerosols.

4. Conclusion

A comprehensive study of air quality in the region of Zagreb was performed from May to October 2004. The H₂O₂ volume fractions shown in this paper are the first such data reported for the region. The results show that hourly H₂O₂ volume fractions varied from <0.05 to 6.2 ppb while ozone volume fractions ranged from 9.5 to 105 ppb. H₂O₂ showed a strong diurnal pattern, very similar to that of ozone with concentration maxima in the afternoon, between 15 and 16 h, local time. Linear regression

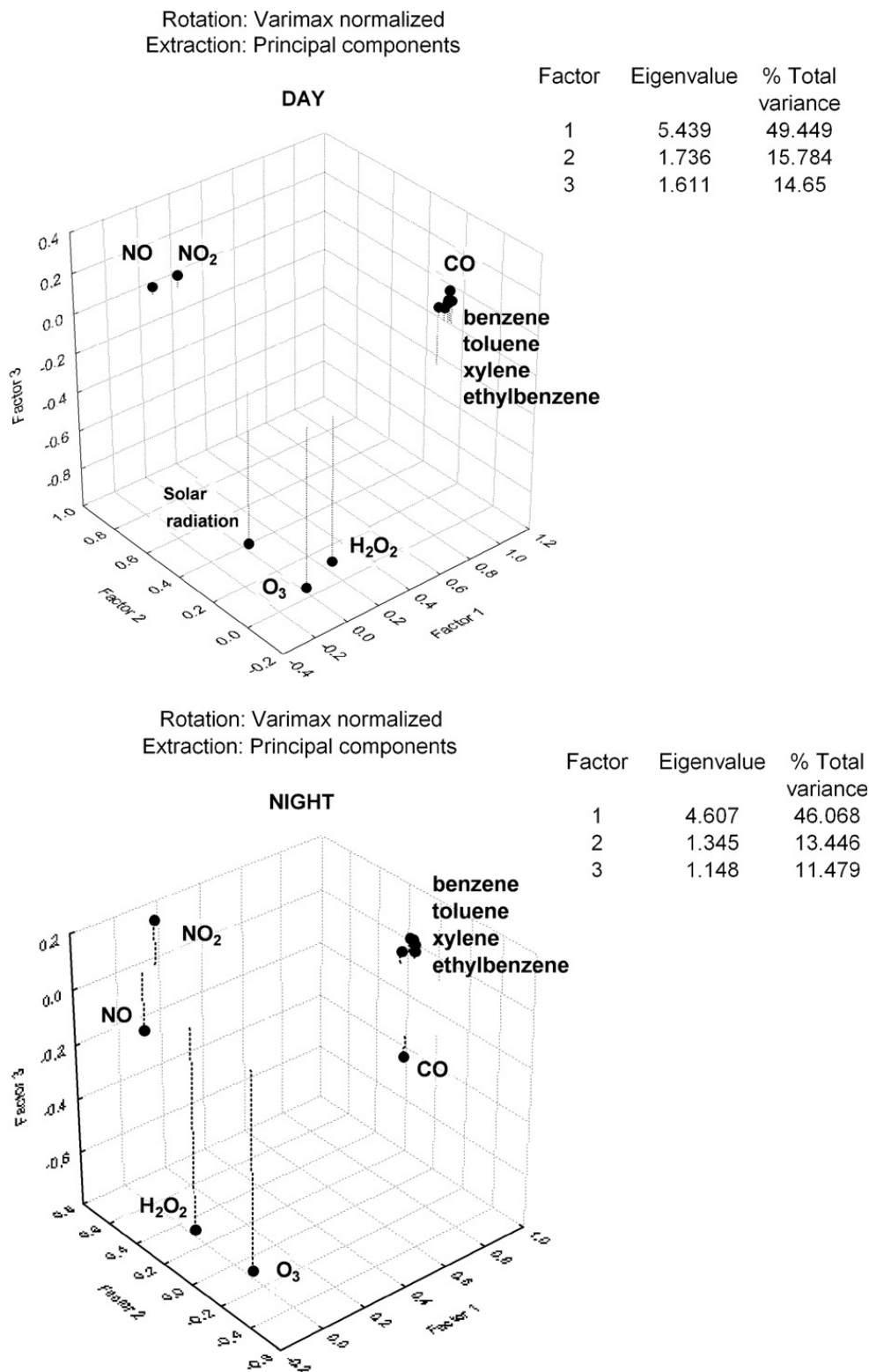


Fig. 4. Three-dimensional plot of factor loadings (hourly volume fractions of measured species and solar radiation data).

analysis showed that, during daytime, H₂O₂ positively correlated with ozone ($r = 0.4$) and solar radiation ($r = 0.52$), but showed only a weak correlation with NO₂, CO and BTEX. Factor

analysis extracted three significant factors. The first factor describes BTEX and CO relationship and recognizes fuel combustion as its common origin. The second factor separates NO and NO₂. The third

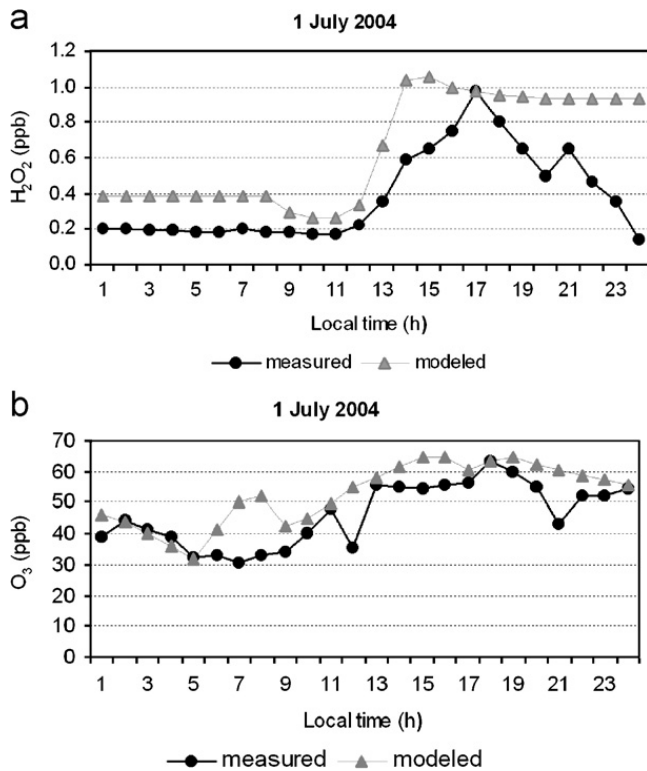


Fig. 5. Comparison of measured and modeled H₂O₂ (a) and O₃ (b) volume fractions (ppb) in clear weather.

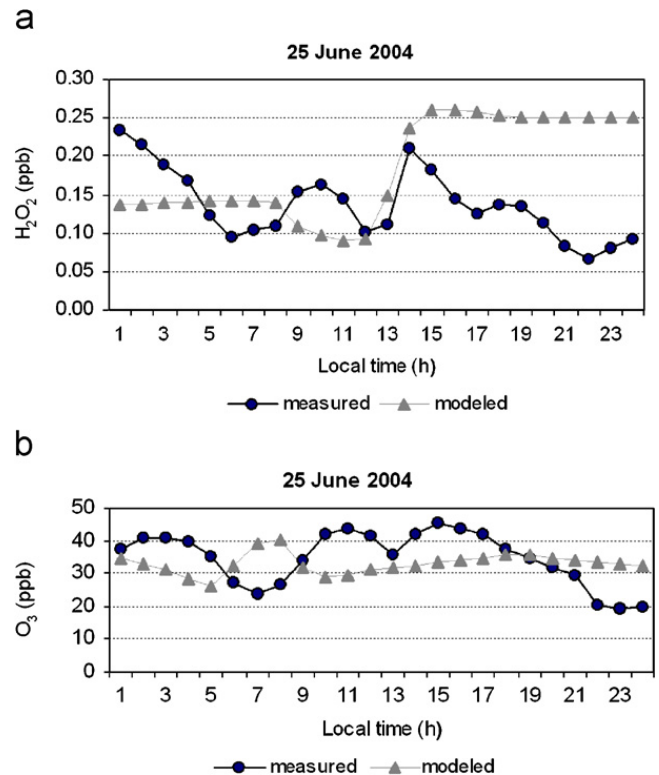


Fig. 7. Comparison of measured and modeled H₂O₂ (a) and O₃ (b) volume fractions (ppb) on rainy day.

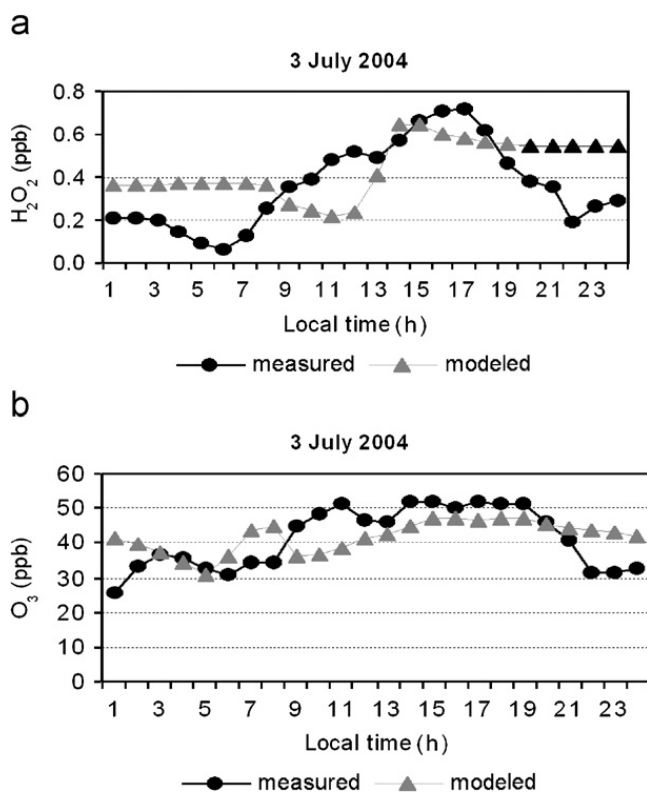


Fig. 6. Comparison of measured and modeled H₂O₂ (a) and O₃ (b) volume fractions (ppb) in cloudy weather.

factor describes the strong influence of solar radiation on ozone and H₂O₂ formation.

The volume fractions of H₂O₂ and O₃ were modeled using the Master Mechanism model. Comparison between the modeled and observed values shows that this model predicts well ozone concentrations in both cloudy and clear weather. The error is less than 12% for maximum and 25% for average values. In the case of hydrogen peroxide the differences are much greater, especially on cloudy and rainy days. On these days, modeled H₂O₂ results are usually much higher than those measured. However, maximum hourly H₂O₂ values can be predicted on clear-sky days with an uncertainty of less than 20%. Our findings showed that Master Mechanism model is appropriate for the estimation of diurnal variations of oxidants in Zagreb.

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