Atmospheric H$_2$O$_2$ measurement and modeling campaign during summer 2004 in Zagreb, Croatia

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Received 17 August 2007; received in revised form 4 December 2007; accepted 4 December 2007

Abstract

Hydrogen peroxide (H$_2$O$_2$) in the gas phase and a number of other atmospheric components and variables (O$_3$, CO, SO$_2$, NO, NO$_2$, 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 H$_2$O$_2$ 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, H$_2$O$_2$ positively correlated with ozone ($r = 0.4$) and solar radiation ($r = 0.52$), but showed only very weak negative correlations with NO$_2$, CO and BTEX. Our H$_2$O$_2$ 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.

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

1. Introduction

The role of hydrogen peroxide (H$_2$O$_2$) 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 O$_2$$^-$$^,$ hydroperoxy HO$_2$ 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
phase H₂O₂ is efficiently removed in upper respiratory tract during breathing. However, peroxide dissolved in fine particles makes possible the entrance of H₂O₂ deeper into the lung. Toxicological studies have shown that H₂O₂ concentrations measured in aerosols may damage alveoli (Hasson and Paulson, 2003).

In the troposphere, H₂O₂ may originate from recombination of HO₂ radicals (which are secondary products of photolysis of ozone and aldehydes), from reaction of ozone (O₃) with alkenes (ozonolysis), by the decay of ozone in weakly acidic and alkaline aqueous solutions, photochemically, by electron transfer to O₂ in aqueous phase (photocatalysis) and from biomass burning (Möller et al., 2002).

Several studies have shown other ways of H₂O₂ formation. Sauer et al. (1999) described the formation of H₂O₂ by the reaction of ozone and biogenic hydrocarbons like isoprene and isobutene in water droplets, without HO₂ 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, HO₂ radicals and H₂O₂. They also constitute an important radical reservoir. In the presence of solar radiation (λ > 320), water vapor and O₃, the short-lived OH radical is produced and converted into peroxyradicals (HO₂, RO₂) through the oxidation of CO, CH₄ 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 radical are the main photochemical sinks for hydroperoxides. In the presence of liquid water, H₂O₂ is quickly dissolved. H₂O₂ can also be removed from the air by heterogeneous processes of wet and dry deposition. H₂O₂ formation in aqueous phase, like in gaseous phase, proceeds mainly by reaction of hydroperoxy radicals. Owing to its good solubility, HO₂ radical enters into aqueous phase usually by capture from gaseous phase or by dissolving gaseous H₂O₂ 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 H₂O₂, 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. H₂O₂ is the most dominant oxidant of SO₂ 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 H₂O₂ 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 H₂O₂ were low because high sulfur dioxide concentrations from fossil fuel combustion consumed H₂O₂. After 1975, SO₂ emissions from industrial and domestic sources were reduced globally. This in turn led to an increase in tropospheric H₂O₂. Using a model with existing values of NO, CO, CH₄ emissions and changes in stratospheric ozone, Thompson et al. (1991) calculated H₂O₂ concentrations for the period 1985–2035. By 2035, they predicted an increase in H₂O₂ concentration of 100% in urban areas and a global increase of 22%.

With decreased SO₂ emission a further increase in peroxyde is expected. Methods that efficiently removed industrial SO₂ probably caused higher levels of H₂O₂ in Croatia, as well. Concentrations of SO₂ and black smoke have been measured in Zagreb from 1965. In the 1960s and 1970s SO₂ concentrations were occasionally higher than 2500 µg m⁻³ in the air of Zagreb. However, over the last 20 years concentrations of SO₂, 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; Vadić and Hršak, 2000). At the same time, NO₂ concentrations increased (Vadić and Hršak, 2000). In 2005, daily NO₂ concentrations in the center of Zagreb ranged between 10 and 120 µg m⁻³ (annual average 37 µg m⁻³). However, hourly NO₂ concentrations occasionally exceeded 250 µg m⁻³, especially in the rush hours (Pehnec 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.
(Klasine 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 (Pehnec et al., 2005). Average daily ozone concentrations higher than 200 µg m⁻³ were recorded during a heat wave in August 2003 (Butković et al., 2004; Alebić-Juretić et al., 2007). Other oxidants, such as H₂O₂, are not measured in Croatia now. H₂O₂ 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 H₂O₂, O₃, CO, SO₂, NO, NO₂, 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 H₂O₂ in the photochemical processes within surfacial 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 Rudjer Bošković Institute (RBI) campus in the northern, residential part of Zagreb (180 m a.s.l., 45°50′N, 15°59′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°50′N; 15°60′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 H₂O₂, O₃, NO, NO₂, SO₂, CO and BTEX in the air

In this study, we used a commercial H₂O₂ analyzer (AL 1002, Aerolaser GmbH, Germany) based on the fluorimetric method described by Lazzrus et al. (1985). The analytical procedure includes the scrubbing of all soluble peroxides (H₂O₂, 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 H₂O₂ 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 H₂O₂ by catalase (efficiency > 95%). The H₂O₂ 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 H₂O₂ standard (1 µmol 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 ~2.5 m above ground.

The container also hosted the devices to measure O₃, NO, NO₂, SO₂, CO, CO₂, H₂O, BTEX; for details see Table 1. All instruments were maintained and serviced regularly. The accuracy of the instruments for NO, and SO₂ 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
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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: $2.53 \times 10^{19}$ 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 O$_3$, H$_2$O, CO, H$_2$O, benzene, toluene and xylene. For CO$_2$, we used the average of 330 ppm. Previous analysis showed that modeling with the initial average daily volume fractions of NO and NO$_2$ did not produce good agreement with measurements.
This is because of the emission of NO\textsubscript{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\textsubscript{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 (employers 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\textsubscript{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\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, CH\textsubscript{2}O, CH\textsubscript{3}CHO and CH\textsubscript{3}COCH\textsubscript{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: daytime values (solar radiation > 0 W m\textsuperscript{-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\textsubscript{2} were lower over the whole period. Maximum hourly value was 10 ppb. Most of the days SO\textsubscript{2} volume fractions were below 2 ppb, often below the detection limit of the instrument (1 ppb). Average volume fractions of NO and NO\textsubscript{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\textsubscript{x} (NO + NO\textsubscript{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\textsubscript{2} were 20% higher, and average ozone volume fractions were about 10% higher. For H\textsubscript{2}O\textsubscript{2}, average daytime volume fractions were twice higher than average nighttime volume fractions (Table 2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Total</th>
<th>Mean (SD)</th>
<th>Range</th>
<th>Day</th>
<th>Mean (SD)</th>
<th>Range</th>
<th>Night</th>
<th>Mean (SD)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td></td>
<td></td>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>1708</td>
<td>1.1 (3.30)</td>
<td>&lt; 1–46.3</td>
<td>1066</td>
<td>1.5 (5.07)</td>
<td>&lt; 1–46.3</td>
<td>642</td>
<td>0.4 (0.68)</td>
<td>&lt; 1–3.7</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>1708</td>
<td>6.7 (8.51)</td>
<td>&lt; 1–69.8</td>
<td>1066</td>
<td>7.1 (9.52)</td>
<td>&lt; 1–69.8</td>
<td>642</td>
<td>5.9 (6.41)</td>
<td>&lt; 1–29.9</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>1101</td>
<td>0.3 (0.50)</td>
<td>&lt; 0.05–6.2</td>
<td>701</td>
<td>0.4 (0.56)</td>
<td>&lt; 0.05–6.2</td>
<td>400</td>
<td>0.2 (0.35)</td>
<td>&lt; 0.05–4.2</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>2147</td>
<td>44.1 (16.29)</td>
<td>9.5–104.8</td>
<td>1340</td>
<td>45.8 (15.93)</td>
<td>9.6–104.8</td>
<td>807</td>
<td>41.3 (16.49)</td>
<td>9.5–102.1</td>
</tr>
<tr>
<td>CO</td>
<td>1339</td>
<td>284.8 (131.6)</td>
<td>16.5–857.4</td>
<td>835</td>
<td>301.3 (147.3)</td>
<td>16.5–857.4</td>
<td>504</td>
<td>257.5 (94.3)</td>
<td>58–739.6</td>
</tr>
<tr>
<td>Benzene</td>
<td>2023</td>
<td>1.4 (1.17)</td>
<td>&lt; 0.1–1.19</td>
<td>1254</td>
<td>1.5 (1.35)</td>
<td>&lt; 0.1–1.19</td>
<td>769</td>
<td>1.2 (0.77)</td>
<td>&lt; 0.1–5.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>2023</td>
<td>3.0 (3.09)</td>
<td>&lt; 0.1–32.1</td>
<td>1254</td>
<td>3.2 (3.49)</td>
<td>&lt; 0.1–32.1</td>
<td>769</td>
<td>2.8 (2.27)</td>
<td>&lt; 0.1–16.5</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>2023</td>
<td>0.3 (0.74)</td>
<td>&lt; 0.1–7.5</td>
<td>1254</td>
<td>0.4 (0.84)</td>
<td>&lt; 0.1–7.5</td>
<td>769</td>
<td>0.2 (0.51)</td>
<td>&lt; 0.1–3.8</td>
</tr>
<tr>
<td>t(m+p)-Xylene</td>
<td>2023</td>
<td>2.2 (2.64)</td>
<td>&lt; 0.1–23.3</td>
<td>1254</td>
<td>2.3 (2.95)</td>
<td>&lt; 0.1–23.3</td>
<td>769</td>
<td>2.0 (2.01)</td>
<td>&lt; 0.1–20.5</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>2023</td>
<td>0.5 (1.03)</td>
<td>&lt; 0.1–8.9</td>
<td>1254</td>
<td>0.6 (1.20)</td>
<td>&lt; 0.1–8.9</td>
<td>769</td>
<td>0.4 (0.64)</td>
<td>&lt; 0.1–4.8</td>
</tr>
<tr>
<td>Radiation</td>
<td>1704</td>
<td>216.6 (292.3)</td>
<td>0–988.3</td>
<td>1065</td>
<td>346.5 (302.8)</td>
<td>0–988.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Figs. 1 and 2 show daily variations of H$_2$O$_2$ 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$_2$O$_2$. The most represented fraction was 0.10–0.15 ppb for H$_2$O$_2$ and 40–45 ppb for O$_3$. Daily H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$, but the organic peroxides (methyl hydroperoxide and hydroxymethyl hydroperoxide) were also occasionally found (0.06–0.4 ppb). On an average, H$_2$O$_2$/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$_2$O$_2$ 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$_2$O$_2$ 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,
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 \( r \approx 0.20 \), and there was no difference between nighttime and daytime. Hourly CO averages do not correlate with NOₓ, 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 NOₓ, 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. NOₓ correlated positively with H₂O₂ to 1.5 ppb and negatively if NOₓ volume fractions were higher than 1.5 ppb. Weak correlation was found between sunlight and hydrocarbons (isoprene and \( \beta \)-pinene). Sauer et al. (1997) found a significant negative correlation between H₂O₂ and NOₓ 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
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 NO₂. The third factor describes the strong influence of solar radiation on ozone and H₂O₂ 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 H₂O₂ and O₃ for 1 July (clear-sky conditions). Fig. 6a and b shows the comparison of modeled and observed mixing ratios of H₂O₂ and O₃ for 3 July (cloudy conditions), with included cloud correction. Fig. 7a and b shows the comparison between modeled and observed mixing ratios of H₂O₂ and O₃ 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 H₂O₂ and O₃ with data which are usually available from the Croatian monitoring station reports (usually

Fig. 3. Daily variations of measured species at 26 June 2004.
only daily, monthly and annual averages of NO$_x$, SO$_2$, 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 H$_2$O$_2$ results are usually much higher than those measured. However, maximum hourly H$_2$O$_2$ 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 the influence of traffic emission. The formation of H$_2$O$_2$ 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, H$_2$O$_2$ 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 H$_2$O$_2$ volume fractions shown in this paper are the first such data reported for the region. The results show that hourly H$_2$O$_2$ volume fractions varied from <0.05 to 6.2 ppb while ozone volume fractions ranged from 9.5 to 105 ppb. H$_2$O$_2$ 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
analysis showed that, during daytime, $\text{H}_2\text{O}_2$ positively correlated with ozone ($r = 0.4$) and solar radiation ($r = 0.52$), but showed only a weak correlation with NO$_2$, 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 NO$_2$. The third
factor describes the strong influence of solar radiation on ozone and H$_2$O$_2$ formation.

The volume fractions of H$_2$O$_2$ and O$_3$ 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 H$_2$O$_2$ results are usually much higher than those measured. However, maximum hourly H$_2$O$_2$ 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.

Acknowledgments

We wish to thank Dr. Sasha Madronich from The National Centre for Atmospheric Research, Boulder, Colorado, for helpful discussion and suggestions. We are also grateful to Dr. Mirko Orlić and Dr. Antun Marki from the Department of...
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