

Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies

Jingqiu Mao^{a,*}, Xinrong Ren^{a,1}, Shuang Chen^a, William H. Brune^a, Zhong Chen^{a,2}, Monica Martinez^b, Hartwig Harder^b, Barry Lefer^c, Bernhard Rappenglück^c, James Flynn^c, Michael Leuchner^{c,3}

^a Department of Meteorology, Pennsylvania State University, University Park, PA 16802, USA

^b Department of Atmospheric Chemistry, Max Planck Institute for Chemistry, Mainz, Germany

^c Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204, USA

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ABSTRACT

Both similarities and differences in summertime atmospheric photochemical oxidation appear in the comparison of four field studies: TEXAQ2000 (Houston, 2000), NYC2001 (New York City, 2001), MCMA2003 (Mexico City, 2003), and TRAMP2006 (Houston, 2006). The compared photochemical indicators are OH and HO₂ abundances, OH reactivity (the inverse of the OH lifetime), HO_x budget, OH chain length (ratio of OH cycling to OH loss), calculated ozone production, and ozone sensitivity. In terms of photochemical activity, Houston is much more like Mexico City than New York City. These relationships result from the ratio of volatile organic compounds (VOCs) to nitrogen oxides (NO_x), which are comparable in Houston and Mexico City, but much lower in New York City. Compared to New York City, Houston and Mexico City also have higher levels of OH and HO₂, longer OH chain lengths, a smaller contribution of reactions with NO_x to the OH reactivity, and NO_x-sensitivity for ozone production during the day. In all four studies, the photolysis of nitrous acid (HONO) and formaldehyde (HCHO) are significant, if not dominant, HO_x sources. A problematic result in all four studies is the greater OH production than OH loss during morning rush hour, even though OH production and loss are expected to always be in balance because of the short OH lifetime. The cause of this discrepancy is not understood, but may be related to the under-predicted HO₂ in high NO_x conditions, which could have implications for ozone production. Three photochemical indicators show particularly high photochemical activity in Houston during the TRAMP2006 study: the long portion of the day for which ozone production was NO_x-sensitive, the calculated ozone production rate that was second only to Mexico City's, and the OH chain length that was twice that of any other location. These results on photochemical activity provide additional support for regulatory actions to reduce reactive VOCs in Houston in order to reduce ozone and other pollutants.

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1. Introduction

The hydroxyl radical (OH) and the hydroperoxyl radical (HO₂), collectively called HO_x, are central players in the photochemical oxidation and pollution production in metropolitan areas. OH initiates many oxidation reaction sequences, while its close chemical relative, HO₂, is a major precursor of ozone pollution in the

presence of nitrogen oxides (NO_x). To test the understanding of the complex atmospheric oxidation processes occurring in metropolitan areas requires measurements of the OH and HO₂ abundances and the analysis of the production, loss, and cycling of these radicals.

In a metropolitan area as well as the rest of the atmosphere, OH and HO₂ are produced and lost in just a few ways (Fig. 1). In the daytime, the main sources include the photolysis of ozone (O₃) and the photolysis of formaldehyde (HCHO), which makes HO₂ that reacts to form OH. Nitrous acid, HONO, acts as another very important source (Ren et al., 2003c, 2006). Reactions between O₃ and alkenes can produce OH (Donahue et al., 1998), although these reactions are generally only significant during nighttime when HO_x production by photolytic processes is small. Other sources, such as the photolysis of peroxides, are small compared to these other HO_x sources. The HO_x sinks are those reactions that remove OH or HO₂ and do not cycle one into the other. These sinks typically involve

* Corresponding author. Present address: School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138, USA. Tel.: +1 617 496 5348.

E-mail address: mao@fas.harvard.edu (J. Mao).

¹ Present address: Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, USA.

² Present address: Department of Atmospheric and Planetary Science, Hampton University, Hampton, VA 23668, USA.

³ Present address: Fachgebiet für Ökologiklimatologie, Technische Universität München, Freising, Germany.

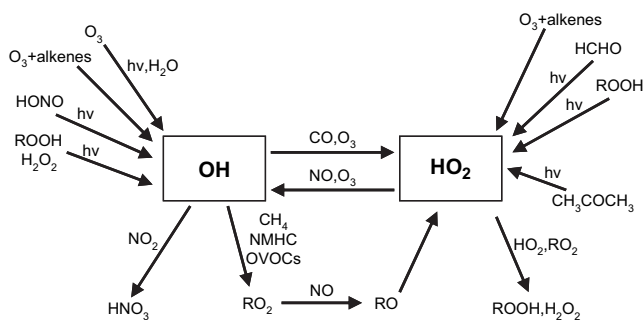


Fig. 1. Schematic diagram of the simplified HO_x mechanism.

either the radical–radical reactions $\text{HO}_2 + \text{HO}_2 \rightarrow \text{HOOH} + \text{O}_2$, $\text{HO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{O}_2$ (where R = an organic radical like CH_3 , C_2H_5), $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$, or the formation of nitric oxide, $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ ($\text{M} = \text{N}_2 + \text{O}_2$). These reactions have been extensively studied, although some uncertainty still exists concerning the reaction between HO_2 and RO_2 .

As the most reactive species in the atmosphere, OH and HO_2 react with other chemical compounds to cycle HO_x between OH and HO_2 . OH reacts with many atmospheric constituents, including CO, methane (CH_4), O_3 , volatile organic compounds (VOCs), in some cases producing HO_2 directly and in other cases initiating a reaction sequence that produces HO_2 . Meanwhile, HO_2 reacts with NO or O_3 and produces OH. Generally the cycling between OH and HO_2 is much faster than HO_x production or loss, although HO_x cycling, production, and loss rates can be comparable in metropolitan areas. The cycling paths and rates are mainly determined by the abundance of other atmospheric constituents and the meteorological conditions. Meanwhile, this cycling is closely related to the atmospheric photochemical activity, especially the production of ozone, particles, and other pollutants.

The sum of the reaction rate coefficients multiplied by the concentrations of reactants with OH is the OH reactivity, which is the inverse of the OH lifetime, and is calculated by the equation:

$$k_{\text{OH}} = \sum k_{\text{OH}+\text{VOC}_i} [\text{VOC}_i] + k_{\text{OH}+\text{CO}} [\text{CO}] + k_{\text{OH}+\text{NO}} [\text{NO}] + k_{\text{OH}+\text{NO}_2} [\text{NO}_2] + k_{\text{OH}+\text{HNO}_3} [\text{HNO}_3] + \dots \quad (1)$$

The OH reactivity includes reactions of atmospheric constituents with OH that both cycle HO_x between OH and HO_2 and terminate HO_x . The calculated OH reactivity, based on measured concentrations of atmospheric constituents, is typically $5\text{--}25 \text{ s}^{-1}$ for midday in US cities (Kleinman et al., 2002). Direct measurements of OH reactivity can now test the calculated OH reactivity (Kovacs and Brune, 2001; Sadanaga et al., 2004; Shirley et al., 2006; Yoshino et al., 2006).

Because the OH reactivity is typically more than $5\text{--}10 \text{ s}^{-1}$, the OH lifetime is much less than 1 s. As a result, OH production, $P(\text{OH})$, and OH loss, $L(\text{OH})$, should be in balance for changes in atmospheric constituents and environmental conditions that occur over seconds or longer. So, $P(\text{OH})$ should be equal to OH reactivity multiplied by the OH concentration. Since both the OH concentration and the OH reactivity are measured, examining this balance should test the understanding of the OH production.

The ratio of OH cycling to OH terminal loss, called the OH chain length, indicates the atmospheric photochemical activity. The OH chain length can be defined by the equation:

$$\text{OH Chain Length} = \frac{k_{\text{OH}} [\text{OH}] - k_{\text{OH}+\text{NO}_2+\text{M}} [\text{OH}] [\text{NO}_2]}{k_{\text{OH}+\text{NO}_2+\text{M}} [\text{OH}] [\text{NO}_2]} \quad (2)$$

where OH reactivity, k_{OH} , and $[\text{OH}]$ are measured and the terminal loss of OH by reaction with NO_2 to form nitric acid is calculated

from measurements. A longer chain length means more ozone, secondary aerosol particles, and other pollutants can be produced for each radical that is produced. For example, since each OH/ HO_2 cycle generates one NO_2 molecule through $\text{HO}_2 + \text{NO}$, this chain length also indicates the role of OH in O_3 production.

VOC– NO_x – O_3 chemistry has been studied for decades. However, the oxidation pathways are complex and most studies have been done in large environmental chambers with high NO_x levels. As a result, even though the basic reaction pathways appear to be understood, much of the detailed chemistry remains to be unresolved (Volz-Thomas et al., 2003). One of the most important consequences of this chemistry is the production of pollutants, particularly ozone. Thus, the ozone production rate is literally the production rate of NO_2 molecules from $\text{HO}_2 + \text{NO}$ and $\text{RO}_2 + \text{NO}$ reactions. The calculated instantaneous ozone production rate $P(\text{O}_3)$ can be written as the equation:

$$P(\text{O}_3) = \left(k_{\text{HO}_2+\text{NO}} [\text{HO}_2] + \sum_i k_{\text{RO}_{2i}+\text{NO}} [\text{RO}_{2i}] \right) [\text{NO}] \quad (3)$$

where $k_{\text{HO}_2+\text{NO}}$ and $k_{\text{RO}_{2i}+\text{NO}}$ are the reaction rate coefficients for reactions of HO_2 and RO_{2i} with NO.

At low NO conditions (NO_x -sensitive), VOCs are more competitive than NO_x for reacting with OH so that radical–radical reactions dominate HO_x chemistry. The produced peroxy radicals can then convert NO to NO_2 . Every NO_2 molecule that is generated from this reaction sequence will make an O_3 molecule. So OH mainly reacts with VOCs, makes more radicals, and potentially increases O_3 in the presence of NO. In the high NO_x condition (VOC-sensitive), the OH reaction with NO_2 should reduce the ozone production because HO_2 reacts with NO to form more OH, which then is terminated by the reaction with NO_2 . Kleinman (2005) introduces a formula to evaluate the O_3 production sensitivity using the ratio of L_N/Q , where L_N is the radical loss via the reactions with NO_x and Q is the total primary radical production. When $L_N/Q < 0.5$, the atmosphere is in the NO_x -sensitive region, and when $L_N/Q > 0.5$, the atmosphere is in the VOC-sensitive region.

This paper presents the results from a multi-investigator field study in Houston in summer 2006 and compares these results with three previous summertime studies in La Porte, TX, which is near Houston, New York City, and Mexico City respectively. The focus of this paper is a comparison of the abundances of OH and HO_2 , the OH reactivity, the balance between OH production and loss, the OH chain length, the HO_x budget, the ozone production rate, and the sensitivity of the ozone production rate to NO_x for these metropolitan areas.

2. Description of measurements

2.1. Site description

The Texas Air Quality Study Radical and Aerosol Measurement Project (TRAMP, thereafter TRAMP2006) was a project aimed to study the air pollution in Houston area. Houston rivals Los Angeles as the US urban area with the highest ozone levels. This study is focused on understanding the impacts of anthropogenic emissions and atmospheric processes on the formation and distribution of ozone and aerosols. All instruments were installed on the top of the north Moody Tower on the University of Houston campus (for site details see Lefer and Rappenglück, 2010). Depending on the wind direction this site could be influenced by the petrochemical emissions from the ship channel to the east and the vehicle emissions from the Houston downtown area to west and to the north. Very low polluted air of maritime origin from the Gulf of Mexico to the south was also sampled. This site provided a good opportunity to

examine the chemistry under different pollution conditions. The measurements reported in this paper were collected from Aug 17th to Sep 28th for about 40 days. For the general meteorological and chemical conditions during TRAMP2006 should be referred to Lefer et al. (this issue).

The Texas Air Quality Study (thereinafter TEXAQS2000) was conducted at La Porte, Texas, which is 40 km southeast of Houston and 20 km from the ship channel (<http://www.utexas.edu/research/ceer/texaqs/>). The main purpose of this study was to understand the factors of controlling the pollution along the southeast Texas Gulf Coast. The comprehensive measurements were conducted from August 15 to September 15 of 2000. Compared to TRAMP2006, this sampling site was farther away from the ship channel, but was situated in the midst of petrochemical plants to the north, east, and south.

The PM_{2.5} Technology Assessment and Characterization Study—New York (PMTACS-NY, thereinafter NYC2001) intensive took place on the campus of Queens College, New York City (<http://www.ascr.cesdm.albany.edu/pmtacsny/local.htm>) in summer 2001. This study was designed to understand the chemical composition of particulate matter and its formation on a regional scale. The field study began on June 30 and ended on August 3 of 2001.

The Mexico City Metropolitan Area 2003 (thereinafter MCMA2003) study was held on the campus of the Autonomous Metropolitan University in Iztapalapa, Mexico from April 1 to May 5 of 2003 (<http://www.mce2.org/fc03/fc03.html>). The major goal of this study was to improve the understanding of the air quality problems in a megacity.

2.2. Measurements

We measured OH and HO₂ with the Ground-based Tropospheric Hydrogen Oxides Sensor (GTHOS) in all four field studies and measured OH reactivity with the Measurement of OH Reactivity (MOHR) instrument in TRAMP2006 and with the Total OH Loss Rate Measurement (TOHLM) instrument in the previous campaigns (MOHR is the new version of TOHLM). Detailed descriptions can be found elsewhere for GTHOS (Ren et al., 2003b; Faloona et al., 2004) and for OH reactivity measurements (Kovacs and Brune, 2001; Shirley et al., 2006; Mao et al., 2009). Here we describe the techniques briefly.

For the measurement of OH and HO₂, the OH signal is detected by Laser Induced Fluorescence (LIF) in a low pressure chamber. OH absorbs laser light at a wavelength near 308 nm and the excited OH emits fluorescence in the wavelength range from 307 nm to 311 nm simultaneously. The fluorescence photons are captured by a gated microchannel plate (MCP) detector, which is set perpendicular to the airflow and the laser beam. HO₂ is converted to OH by pure NO followed by the LIF measurement in the second detection axis of GTHOS system.

OH reactivity is measured by the flow tube technique. OH is produced by photolysis of water vapor with 185 nm UV light in a moveable wand and is then mixed into the sample air. The OH signal is measured by the same LIF technique that is used in GTHOS. The decay of OH signal, which occurs as the moveable wand is pulled back and the reaction time increases, is used to calculate the OH reactivity. Along with our HO_x and OH reactivity measurements, other important measurements were also made simultaneously. Measured atmospheric constituents included NO, NO₂, CO, NO_y, O₃, VOCs, SO₂, and HCHO. Measured meteorological parameters included pressure, temperature, wind direction and speed, and photolysis frequencies.

The absolute calibration for the GTHOS OH and HO₂ measurements is determined primarily by making OH by photolyzing water vapor with 185 nm light in an airflow. The known OH mixing ratios come from calibrating the water vapor concentration, the 185 nm

light flux, and the airflow rate. In the year 2000, a noticeable shift occurred in the absolute calibration, but the cause could not be determined. In early 2007, our primary standard photomultiplier tube (PMT), which is used to calibrate the 185 nm light flux, was recalibrated again against NIST standards and was found to have reduced sensitivity compared to earlier calibrations. By assessing the 185 nm light flux using four different techniques, we determined that the absolute calibration from 2000 to 2006 was a factor of 1.64 too high (Ren et al., 2008). The resulting correction is an increase in the OH and HO₂ mixing ratios by a factor of 1.64. In addition, a small laser-generated interference in conditions of high water vapor and ozone was discovered in 2006 for our ground-based measurements only, resulting in reductions in the reported OH mixing ratios by up to 20% during the day, but more for some occasions at night. These two corrections have been applied to our measurements of OH and HO₂ for TEXAQS2000, NYC2001 and MCMA2003 that are presented in this paper.

3. Results

The comparison among these four field studies provides an excellent opportunity to examine the radical chemistry and oxidation capacity in these metropolitan areas. The comparisons involve the indicators of photochemical activity: OH and HO₂ abundances, OH reactivity, HO_x budget, OH chain length, calculated ozone production, and ozone sensitivity to NO_x and VOCs.

3.1. The abundances of OH, HO₂, and their precursors

The diurnal variations of OH and HO₂ measurements show the expected peak value during midday (Fig. 2). To compare the diurnal variations in different field studies, which have solar noon at different local times, all the measurement times have been shifted so that maximum photolysis frequencies occur at solar noon. The differences in the midday OH abundances are about a factor of 3 for the four studies, which is not surprising considering the differences in photolysis rates and precursor atmospheric constituents (Fig. 3).

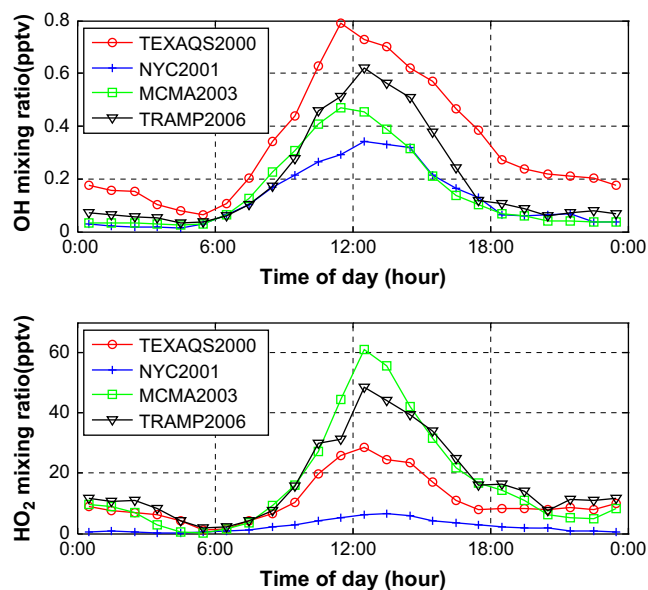


Fig. 2. Diurnal variation of measured OH (upper panel) and HO₂ (lower panel) in four field studies: TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The spread in the maximum HO₂ values is more than a factor of 6, more than twice the spread in the OH values, which shows that the cycling between OH and HO₂ is very different in these four studies. MCMA2003 presents the highest HO₂ level with peak value of 60 pptv, which is due to the highest non-methane volatile organic compounds (NMVOCs), CO, NO_x and photolysis frequencies in this study (Fig. 3). The HO₂ of NYC2001 is much smaller compared to that of the other three locations. This lower HO₂ can be explained in part by the weaker HO_x sources, as indicated by the lower JO (¹D) values, but was primarily due to the greater NO_x/VOC ratio, which shifted the balance of HO_x toward OH, which then reacted with NO₂ to terminate HO_x.

Midday HO₂ during TRAMP2006 is higher than during TEXAS2000 by almost 50% at peak values. Once again, the difference is the greater NO_x/VOC ratio in TEXAS2000 than in TRAMP2006 (Fig. 3), which shifts the balance of HO_x toward OH, as seen in Fig. 2. The shift in the NO_x/VOC ratio is driven by both higher NO_x and lower NMVOCs in TEXAS2000 than in TRAMP2006. This NO_x/VOC difference seems the opposite of what would be expected, since the La Porte site in TEXAS2000 was in the middle of petrochemical plants that should have been dominated by VOCs while TRAMP2006 was in the midst of the Houston urban core that is dominated by a combination of VOC emissions depending on the wind direction (Leuchner and Rappenglück, 2010).

The ambient measurements of temperature, CO, O₃, O₃ photolysis frequency JO (¹D), NO_x and the sum of non-methane VOCs are shown in Fig. 3. Compared to other three studies, MCMA2003 had the highest JO (¹D), CO, NMVOCs and NO_x, and therefore it has the daily highest O₃ concentration with peak value of 120 ppb at noon time. Mexico City is located at a high altitude (~2240 m) and at lower latitude (19°25' N) which explains the relatively high JO (¹D) values in MCMA2003. The midday NO_x in NYC2001 and MCMA2003 was similar, but the much greater NMVOC abundances in MCMA2003 and greater NO_x during morning rush hour led to the

higher ozone levels there. Large NMVOC spikes at night during TRAMP2006 are mainly due to the emission events from plants in the Houston Ship Channel area and coinciding wind flows in the nocturnal boundary layer (Day et al., 2010). These emissions contain high amounts of ethane, propane, and a small amount of other VOCs which are related to natural gas and evaporation, in particular from crude oil and refining compounds and also liquid petroleum gas (Leuchner and Rappenglück, 2010), which are not highly reactive with OH but contribute a big part to carbon emissions. In addition, one week during TRAMP2006 had persistent southerly winds from Gulf of Mexico, resulting in the reduction of all trace gas levels including O₃.

The ranking of the four studies with respect to the level of NMVOC is MCMA2003, TRAMP2006, TEXAS2000, and NYC2001, which is the same ranking of studies with respect to the level of HO₂. This observation is not surprising because more VOCs mean more HO₂ is produced by reaction of OH with the VOCs and because HO_x sources like formaldehyde tend to correlate with VOCs. Note that the ranking according to HO₂ does not anti-correlate with the ranking according to NO_x, which implies that the ranking of HO₂ is not solely determined by the NO_x level. Further, the ranking according to OH does not correlate with either the ranking according to VOCs or to NO_x. Thus HO₂ is a better indicator of photochemical activity than OH.

3.2. OH reactivity and its distribution

OH reactivity has been measured in several urban areas. Kovacs et al. (2003) reported the measured OH reactivity of $11.3 \pm 4.8 \text{ s}^{-1}$ in Nashville, TX in 1999. Ren et al. (2003b) reported the measured OH reactivity of $19 \pm 3 \text{ s}^{-1}$ for the summer in New York City in 2001 and about 25 s^{-1} in winter there in 2004 (Ren et al., 2006). Yoshino et al. (2006) reported that the measured OH reactivity in Tokyo was about 20 s^{-1} . Here we compare the OH reactivity measurements in

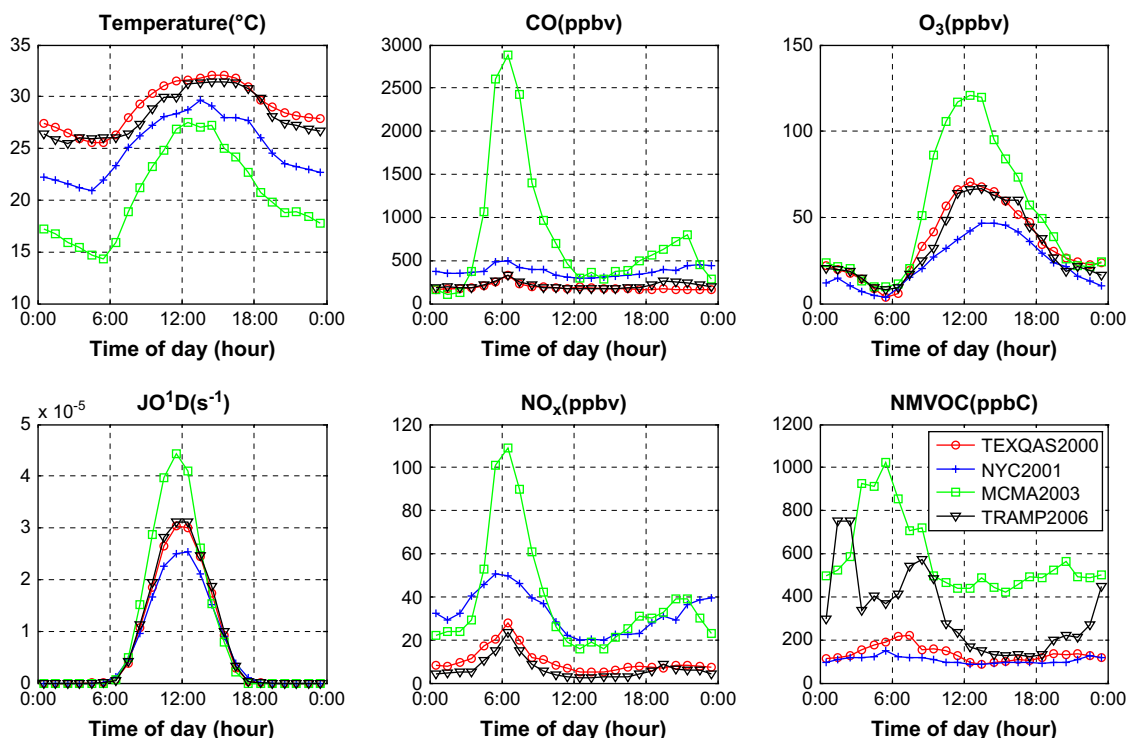


Fig. 3. Median diurnal variation of measured temperature, CO, O₃, JO(¹D), NO_x and Non-methane Volatile Organic Compounds (NMVOCs) in four field studies: TEXAS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006 and the measured and calculated OH reactivity for TRAMP2006.

The measured OH reactivity can be compared to the OH reactivity that is calculated from the measurements of all OH reactants using Eq. (1). The calculated OH reactivity is based on the reaction rate coefficients from Sander et al. (2006), Atkinson and Arey (2003), Atkinson et al. (2006), and Master Chemical Mechanism (<http://mcm.leeds.ac.uk/MCM/>) and the measured concentrations of the OH reactants. The measured OH reactivity has been corrected for $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ using the measured HO_2 decay in the flow tube of the OH reactivity instrument and the *in situ* NO measurement, as described by Shirley et al. (2006).

The median diurnal profiles of measured and calculated OH reactivity for TRAMP2006 are well within measurement and calculated uncertainties (Fig. 4(a)). This good agreement between measured and calculated OH reactivity has also been found in NYC2001 and in TEXAQS2000 (Di Carlo et al., 2004), although measured OH reactivity was greater than calculated OH reactivity by ~30% in Nashville in 1999 (Kovacs et al., 2003) and in Tokyo in 2003 (Yoshino et al., 2006). It was not possible to compare measured and calculated OH reactivity in MCMA2003 because VOCs and OH reactivity were not simultaneously measured (Shirley et al., 2006).

During TRAMP2006, the OH reactivity peak in the morning was due to rush hour traffic; NO_x and alkenes were the two biggest contributors of OH reactivity in this urban environment (Fig. 4b). The CO contribution was relatively constant throughout the day at about 1 s^{-1} , except in the morning when it rose to 1.8 s^{-1} . Meanwhile the contribution from NO_x was largest during the morning

rush hour when NO_x emissions were large and the boundary layer height was still low, and was smallest during the afternoon when the boundary layer height was greatest.

The diurnal variations of the OH reactivity measurement are similar for TRAMP2006, TEXAQS2000, and NYC2001 (Fig. 5). The OH reactivity measurement in TEXAQS2000 could not be corrected for $\text{HO}_2 + \text{NO}$ because the HO_2 decay was not measured in the OH reactivity flow tube during TEXAQS2000. Thus, OH reactivity measurements were reported only when NO is less than 1 ppbv and the correction is less than 10% (Kovacs et al., 2003). In particular, it is interesting that Houston had very high petrochemical emissions and much more VOCs than NYC, but NYC still had a higher OH reactivity due to its higher level of NO_x . On the other hand, the OH reactivity in MCMA2003 is significantly greater than that in any of the US metropolitan areas.

The contributions from the different atmospheric constituents to the OH reactivity, which are based on the measurement of all available OH reactants, are quite different for these four field studies (Fig. 6).

The contribution from CO is very much alike in the four studies (11–14%). The contribution from alkenes is also very similar (20–30%) in three cities except in NYC2001. Compared to other cities, TRAMP2006 has higher contribution of aromatics (15%), which could be possibly due to higher industrial solvent emissions (Leuchner and Rappenglück, 2010). On the other hand, contribution from OVOCs in TEXAQS2000 appears to be relatively large (24%), which may be a result of the location of TEXAQS2000 downwind of the Houston urban pollution plumes compared to TRAMP2006. The contribution to the OH reactivity that stands out for New York City is that of NO_x , which accounts for about 50% of OH reactivity there.

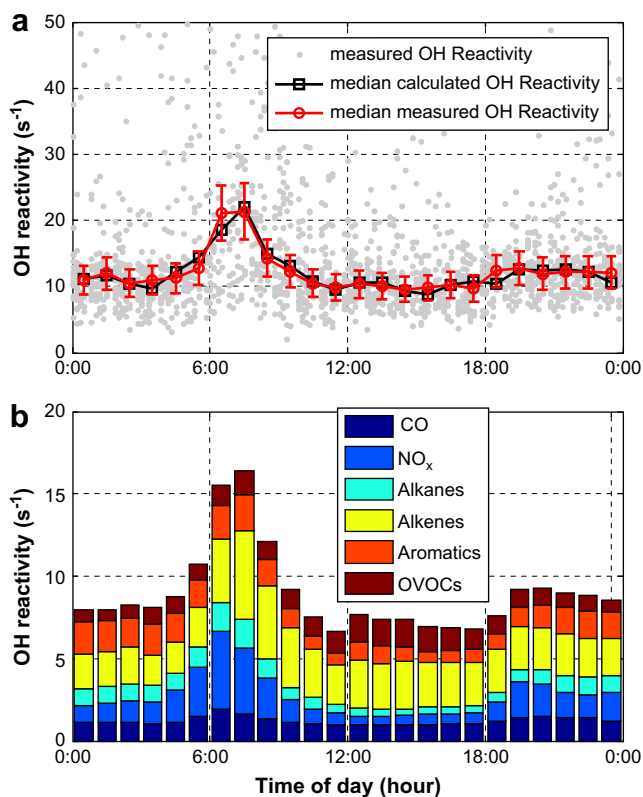


Fig. 4. (a) Median diurnal variation of measured and calculated OH reactivity during TRAMP2006. Vertical bars represent the uncertainty of measurement at 2-sigma level. Individual OH reactivity measurements are presented by blue dots. (b) Median diurnal profile of contributions from all measured species for OH reactivity in Houston, 2006. The bars are colored based on different atmospheric constituents. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. The balance of OH production and loss and the OH chain length

Both the balance of OH production ($P(\text{OH})$) and loss ($L(\text{OH})$) and the OH chain length test the understanding of the HO_x cycling between OH and HO_2 . As seen in Fig. 7, the OH production is greatest in MCMA2003 with a peak value of $3.9 \times 10^8 \text{ molecules cm}^{-3} \text{ s}^{-1}$ and OH loss with peak value of $3.4 \times 10^8 \text{ molecules cm}^{-3} \text{ s}^{-1}$. Thus, the highest photochemical activity among four studies occurs in Mexico City. TEXAQS2000, NYC2001 and

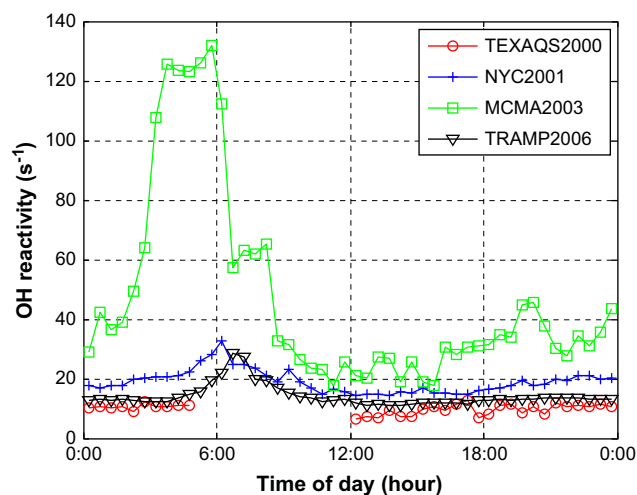


Fig. 5. Comparison of the median diurnal variations for measured OH reactivity in different urban conditions, including TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

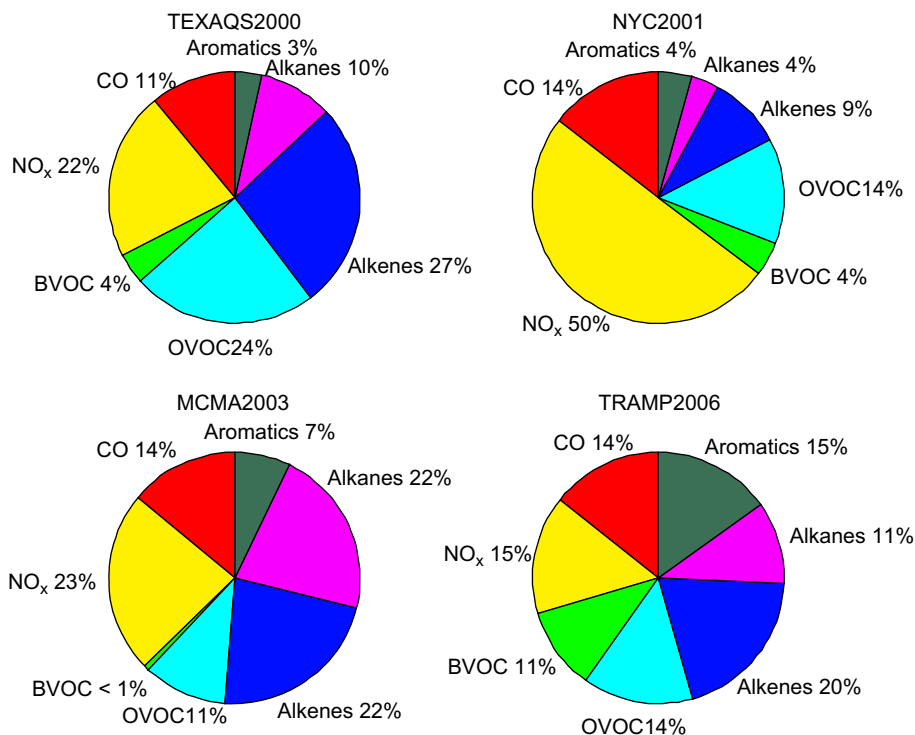


Fig. 6. Contributions of different atmospheric constituents to OH reactivity in TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

TRAMP2006 have similar peak values of $P(\text{OH})$, which is about $1.5 \times 10^{-8} \text{ molecules cm}^{-3} \text{ s}^{-1}$. The calculation shows that the $\text{HO}_2 + \text{NO}$ reaction dominates OH production for all four studies. However, HONO photolysis accounts for more than 10% of the OH

production in NYC2001, which is much higher than other three studies and acts as a significant HO_x source even during daytime.

The net OH production equals $P(\text{OH}) - L(\text{OH})$ and should equal zero if all OH sources and losses are known. However, the net OH

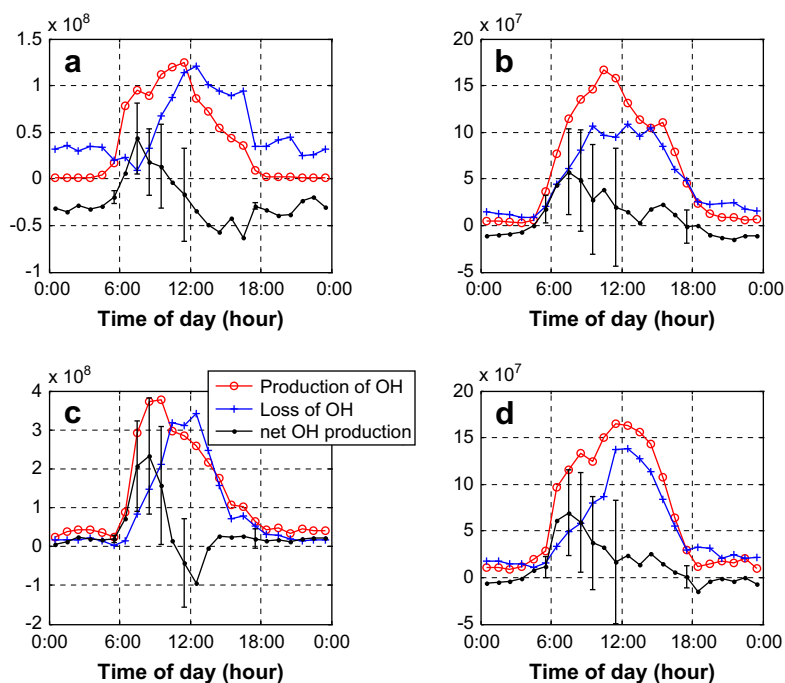


Fig. 7. Median diurnal profiles of OH production, loss and net production ($\text{molecules cm}^{-3} \text{ s}^{-1}$) in (a) TEXAQS2000, (b) NYC2001, (c) MCMA2003 and (d) TRAMP2006. Vertical bar represents the uncertainty of the net OH production (2σ confidence limit). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

production appears to be positive in the morning rush hours for all the four studies. This discrepancy is least obvious in TEXAQS2000. The measured [OH] has the uncertainty of 32% (all 2σ confidence limits) and the measured OH reactivity has the uncertainty of 30%, giving a total uncertainty of calculated OH loss is about 40–50%. However, calculations indicate that the $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ reaction dominates the OH production in the morning rush hour. Thus, some of the absolute uncertainty in the OH production correlates with the absolute uncertainty in the OH loss and the uncertainties cancel, leaving a total uncertainty of approximately 40% (2σ confidence limit) for the net OH production.

In all four studies, the OH production and loss balance to within uncertainties for all times of the day except morning rush hour, when OH production is statistically greater than OH loss. Because the OH loss is the product of measured OH and measured OH reactivity, we would expect that OH production would be less than or equal to OH loss because it is more likely that OH sources would be missed rather than over-estimated. This result is particularly puzzling because the well-studied reaction $\text{HO}_2 + \text{NO}$ dominates OH production.

Model calculations also show the under-predicted HO_2 at high NO levels (more than a few ppb) in most ground-based campaigns, including Nashville, TN (Martinez et al., 2003), New York City (Ren et al., 2003c, 2006), and Mexico City (Shirley et al., 2006). Interestingly this under-predicted HO_2 was also observed by another independent technique, NCAR chemical ionization mass spectrometer (CIMS) (Ren et al., 2003a). It is tempting to think that the same missing chemistry at high NO_x that is responsible for the

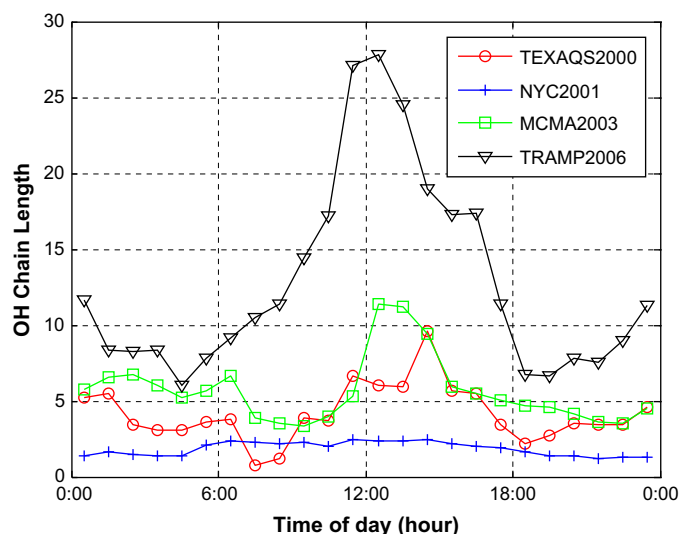


Fig. 8. Median diurnal variation of OH chain length in TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

under-predicted HO_2 is also responsible for the statistically significant net OH production during morning rush hour.

A second indicator of HO_x cycling is the OH chain length. As shown in Fig. 8, MCMA2003 and TEXAQS2000 have chain lengths between 3 and 8, which are similar to the results observed in

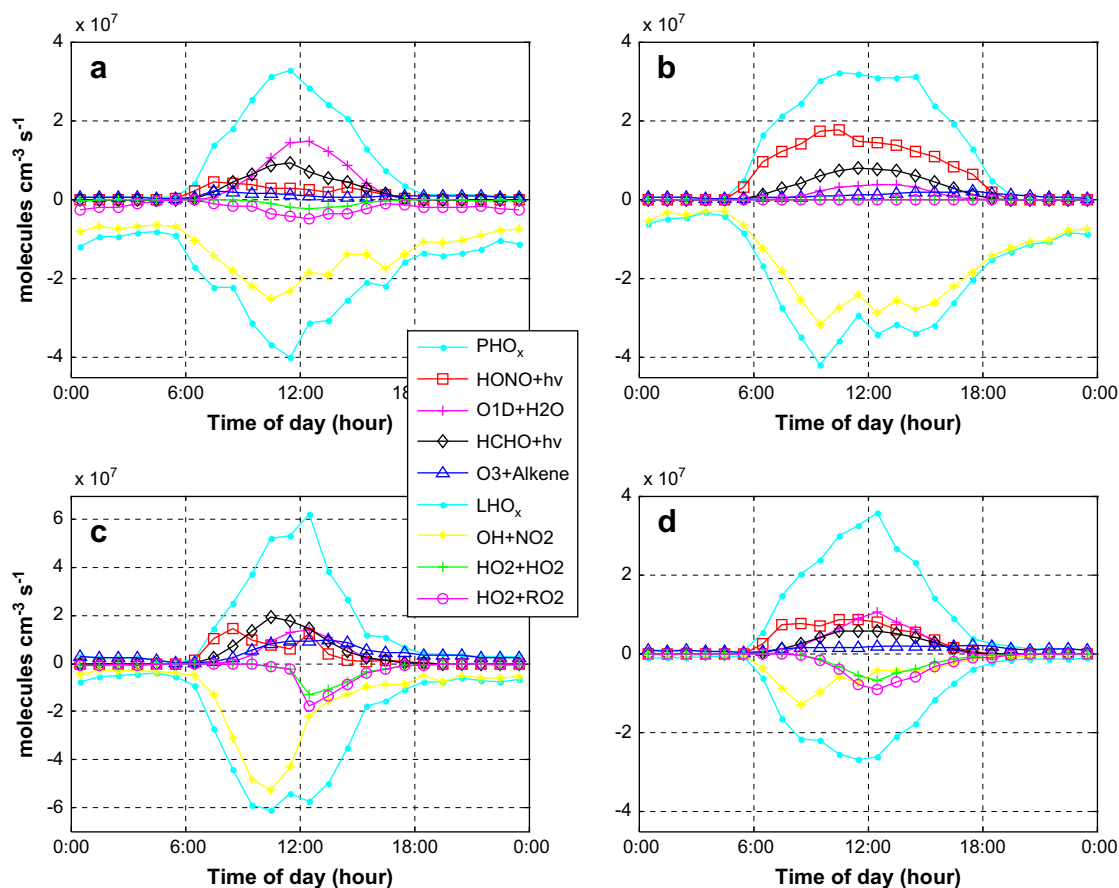


Fig. 9. Median diurnal profiles of HO_x sources and sinks in (a) TEXAQS2000, (b) NYC2001, (c) MCMA2003 and (d) TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

southeast England (Emmerson et al., 2007) and in Nashville, Tennessee (Martinez et al., 2003). Interestingly TRAMP2006 has a much longer chain length than other three studies, especially at noon when the peak value is 28. This large value implies that the ozone production during TRAMP2006 is 2–3 times more efficient than was measured in other US cities and could explain the high ozone events observed in Houston. This long chain length could be due to the relatively low levels of NO_x during TRAMP2006 (Fig. 3) and thus a relatively small sink of $\text{OH} + \text{NO}_2$. Compared to TRAMP2006, NO_2 in TEXAQS2000 is generally a factor of 2 higher and, in particular is about a factor of 3 higher through the whole afternoon. On the other hand, NYC2001 exhibits a much lower value of chain length all day along, which indicates that the OH sink is comparable to its cycling and thus the ozone formation in NYC2001 is the least efficient of four studies.

3.4. HO_x budget

Since $\text{HO}_2 + \text{NO}$ reaction dominates OH production and this reaction is just the cycling between OH and HO_2 , a further evaluation of the radical budget should include the sources and sinks of total HO_x . Here we present the HO_x sources for the four studies, including the photolysis of HONO, HCHO, $\text{O}(^1\text{D}) + \text{H}_2\text{O}$, and peroxides, the ozonolysis of alkenes, and all the other smaller contributing terms that do not include any HO_x cycling. Meanwhile, we also calculated the HO_x sinks, which include the reactions $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$, $\text{HO}_2 + \text{HO}_2 \rightarrow \text{HOOH} + \text{O}_2$, $\text{HO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{O}_2$ and all other smaller contributing reactions that do not include any cycling reactions.

As seen from Fig. 9, HO_x production is dominated by different reactions in different studies. The photolysis of HONO dominates HO_x production for the entire day in NYC2001 (Ren et al., 2003c) and plays a big role in TRAMP2006 and MCMA2003, especially in the morning. However, this contribution is not significant as in TEXAQS2000 mainly due to its much lower level of HONO. Further investigation of HONO formation between TRAMP2006 and TEXAQS2000 will contribute to the understanding of radical activity at two sites. Interestingly the photolysis of HCHO plays a big part in all four studies and HCHO acts as another big HO_x reservoir under urban conditions. Calculations show that the contributions from the photolysis of H_2O_2 and CH_3OOH are much less significant. On the other hand, $\text{O}(^1\text{D}) + \text{H}_2\text{O}$, which is considered the dominating HO_x source in remote regions (Ren et al., 2008), is still the biggest source in the afternoon of TEXAQS2000 and TRAMP2006 but not others. It should also be pointed out that $\text{O}_3 + \text{alkenes}$ contribute mostly at night. Its daytime contribution is insignificant except in the afternoon of MCMA2003, where the high O_3 levels make it a competitive HO_x source. All above indicates that the photolysis of HONO and HCHO acts as two major HO_x sources under urban conditions besides the known $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction. On the HO_x sinks side, $\text{OH} + \text{NO}_2$ dominates HO_x sinks all day in all studies except TRAMP2006. The $\text{HO}_2 + \text{HO}_2$ reaction and $\text{HO}_2 + \text{RO}_2$ reactions start to play a role for HO_x sinks in the afternoon of MCMA2003 and TRAMP2006, which is consistent with their ozone production sensitivity shown in the lower panel of Fig. 10.

3.5. Calculated ozone production and its sensitivity

The calculated instantaneous ozone production rate requires measurements of HO_2 , RO_2 , and NO. Because RO_2 was not measured in these four studies, RO_2 is estimated by multiplying the ratio of the modeled RO_2 to modeled HO_2 by the measured HO_2 . The Regional Atmospheric Chemistry Modeling (RACM) mechanism (Stockwell et al., 1997) is adopted for the model calculation in this purpose and model detail is described by Chen et al. (2010). L_N/Q is

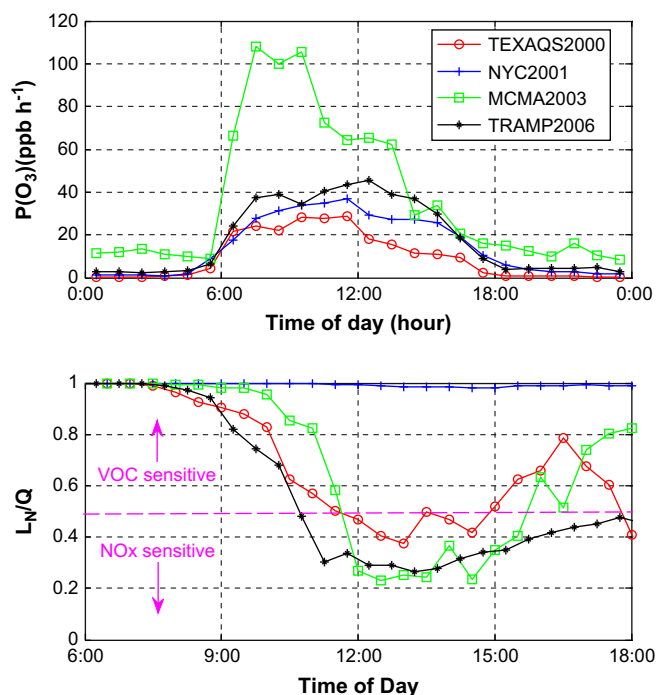


Fig. 10. Median diurnal profiles instantaneous ozone production rate (upper panel) and L_N/Q (lower panel) in TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

also calculated by the RACM mechanism, where L_N represents all the radical loss through nitrogen compounds to form nitric acid and organic nitrates, and Q represents all the primary radical production.

MCMA has the highest calculated instantaneous ozone production rate by more than a factor of 2, whereas NYC2001, TEXAQS2000, and TRAMP2006 have similar calculated instantaneous ozone production rates. It should be pointed out that the $P(\text{O}_3)$ drop in the afternoon of TEXAQS2000 was due to the low level of NO (tens of pptv), although NO_2 was about 5–10 ppbv (Rosen et al., 2004). Because these instantaneous ozone production rates use the measured HO_2 , which is typically larger than the modeled HO_2 at high NO_x conditions, they will be typically larger than the instantaneous ozone production rates calculated with the modeled HO_2 (Chen et al., 2010). For NYC2001, $P(\text{O}_3)$ using measured HO_2 is typically twice $P(\text{O}_3)$ using modeled HO_2 , which can partly explain its surprisingly high $P(\text{O}_3)$ in the upper panel of Fig. 10. Thus, the chemical mechanisms used in air quality models are under-estimating ozone production if the calculated instantaneous ozone production rate (Eq. (3)) represents accurately the real atmospheric ozone production mechanism.

The ozone production sensitivity to NO_x or VOCs has a similar behavior for MCMA2003, TEXAQS2000, and TRAMP2006; it is VOC-sensitive in the early morning and late afternoon but NO_x -sensitive throughout the afternoon. This behavior is typical of US urban areas. In contrast, NYC2001 is extremely VOC-sensitive the entire day. These results are independent of the differences between the measured and modeled OH and HO_2 . Note that the ozone sensitivity in TRAMP2006 and MCMA2003 fall into the NO_x -sensitive regime for most of the daytime. More interestingly MCMA2003 presents a much higher NO_x level than TRAMP2006 in the afternoon. Since ozone production in both studies is in the NO_x -sensitive region, MCMA in 2003 has higher ozone than Houston in 2006 due primarily to the higher levels of NO_x .

4. Conclusions

This study shows differences in the photochemical activity for three metropolitan areas in different climate regions and in quite different stages of air quality regulation. The photochemical activity in New York City is defined by regulatory actions that have greatly reduced VOC emissions while not significantly addressing NO_x emissions. The other end of the spectrum is the photochemical activity of Mexico City, for which regulatory actions are just beginning to have an impact. The photochemical activity in Houston for 2000 and 2006 represents a more typical US city in which regulatory actions have not yet driven VOCs to the low levels seen in New York City. These differences are particularly evident in calculation of NO_x-sensitivity versus VOC-sensitivity that is plotted in Fig. 10.

The comparison of the photochemical activity in the TRAMP study with that of the others indicates where Houston is in terms of the cause of its levels of ozone and other pollutants. Three photochemical indicators are of greatest concern. The first is the seven hours during the day that Houston is in the NO_x-sensitive regime, which is longest among all studied cities. The second is the calculated ozone production, which is second only to MCMA2003 and slightly more than NYC2001. The third and most convincing indicator is the OH chain length, which is much greater in TRAMP2006 than even in MCMA2003. Some of this photochemical activity in Houston is due to the greater photolysis than in New York City, but the dominant cause is the VOC abundances that approach those of MCMA2003 during morning rush hour, even if they become much lower during midday. All of these indicators suggest that substantial effort is still needed to reduce the VOC levels, and thus the photochemical activity, in the Houston metropolitan area.

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References

- Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. *Chemical Reviews* 103, 4605–4638.
- Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., Troe, J., 2006. Evaluated kinetic and photochemical data for atmospheric chemistry: volume II – gas phase reactions of organic species. *Atmospheric Chemistry and Physics* 6, 3625–4055.
- Chen, S., Ren, X., Mao, J., Chen, Z., Brune, W.H., Lefler, B., Rappenglück, B., Flynn, J., Olson, J., Crawford, J., 2010. A comparison of chemical mechanisms based on TRAMP-2006 field data. *Atmospheric Environment* 44, 4116–4125.
- Day, B.M., Rappenglück, B., Clements, C.B., Tucker, S.C., Brewer, W.A., 2010. Nocturnal boundary layer characteristics and land breeze development in Houston, Texas during TexAQ5 II. *Atmospheric Environment* 44, 4014–4023.
- Di Carlo, P., Brune, W.H., Martinez, M., Harder, H., Leshner, R., Ren, X.R., Thornberry, T., Carroll, M.A., Young, V., Shepson, P.B., Riemer, D., Apel, E., Campbell, C., 2004. Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOCs. *Science* 304, 722–725.
- Donahue, N.M., Kroll, J.H., Anderson, J.G., Demerjian, K.L., 1998. Direct observation of OH production from the ozonolysis of olefins. *Geophysical Research Letters* 25, 59–62.
- Emmerson, K.M., Carslaw, N., Carslaw, D.C., Lee, J.D., McFiggans, G., Bloss, W.J., Gravesstock, T., Heard, D.E., Hopkins, J., Ingham, T., Pilling, M.J., Smith, S.C., Jacob, M., Monks, P.S., 2007. Free radical modelling studies during the UK TORCH Campaign in Summer 2003. *Atmospheric Chemistry and Physics* 7, 167–181.
- Faloona, I.C., Tan, D., Leshner, R.L., Hazen, N.L., Frame, C.L., Simpas, J.B., Harder, H., Martinez, M., Di Carlo, P., Ren, X.R., Brune, W.H., 2004. A laser-induced fluorescence instrument for detecting tropospheric OH and HO₂: characteristics and calibration. *Journal of Atmospheric Chemistry* 47, 139–167.
- Kleinman, L.L., Daum, P.H., Imre, D., Lee, Y.N., Nunnermacker, L.J., Springston, S.R., Weinstein-Lloyd, J., Rudolph, J., 2002. Ozone production rate and hydrocarbon reactivity in 5 urban areas: a cause of high ozone concentration in Houston. *Geophysical Research Letters* 29, 4.
- Kleinman, L.L., 2005. The dependence of tropospheric ozone production rate on ozone precursors. *Atmospheric Environment* 39, 575–586.
- Kovacs, T.A., Brune, W.H., 2001. Total OH loss rate measurement. *Journal of Atmospheric Chemistry* 39, 105–122.
- Kovacs, T.A., Brune, W.H., Harder, H., Martinez, M., Simpas, J.B., Frost, G.J., Williams, E., Jobson, T., Stroud, C., Young, V., Fried, A., Wert, B., 2003. Direct measurements of urban OH reactivity during Nashville SOS in summer 1999. *Journal of Environmental Monitoring* 5, 68–74.
- Lefler, B., Rappenglück, B. TRAMP overview. *Atmospheric Environment*, this issue.
- Lefler, B., Rappenglück, B., Flynn, J., Haman, C., 2010. Photochemical and meteorological climate during the Texas-II Radical and Aerosol Measurement Project (TRAMP). *Atmospheric Environment* 44, 4005–4013.
- Leuchner, M., Rappenglück, B., 2010. VOC source–receptor relationships in Houston during TexAQ5-II. *Atmospheric Environment* 44, 4056–4067.
- Mao, J., Ren, X., Brune, W.H., Olson, J.R., Crawford, J.H., Fried, A., Huey, L.G., Cohen, R.C., Heikes, B., Singh, H.B., Blake, D.R., Sachse, G.W., Diskin, G.S., Hall, S.R., Shetter, R.E., 2009. Airborne measurement of OH reactivity during INTEX-B. *Atmospheric Chemistry Physics* 9, 163–173.
- Martinez, M., Harder, H., Kovacs, T.A., Simpas, J.B., Bassis, J., Leshner, R., Brune, W.H., Frost, G.J., Williams, E.J., Stroud, C.A., Jobson, B.T., Roberts, J.M., Hall, S.R., Shetter, R.E., Wert, B., Fried, A., Alicke, B., Stutz, J., Young, V.L., White, A.B., Zamora, R.J., 2003. OH and HO₂ concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999. *Journal of Geophysical Research – Atmospheres* 108, 17.
- Ren, X.R., Edwards, G.D., Cantrell, C.A., Leshner, R.L., Metcalf, A.R., Shirley, T., Brune, W.H., 2003a. Intercomparison of peroxy radical measurements at a rural site using laser-induced fluorescence and Peroxy Radical Chemical Ionization Mass Spectrometer (PerCIMS) techniques. *Journal of Geophysical Research – Atmospheres* 108, 9.
- Ren, X.R., Harder, H., Martinez, M., Leshner, R.L., Oligier, A., Shirley, T., Adams, J., Simpas, J.B., Brune, W.H., 2003b. HO_x concentrations and OH reactivity observations in New York City during PMTACS-NY2001. *Atmospheric Environment* 37, 3627–3637.
- Ren, X.R., Harder, H., Martinez, M., Leshner, R.L., Oligier, A., Simpas, J.B., Brune, W.H., Schwab, J.J., Demerjian, K.L., He, Y., Zhou, X.L., Gao, H.G., 2003c. OH and HO₂ chemistry in the urban atmosphere of New York City. *Atmospheric Environment* 37, 3639–3651.
- Ren, X.R., Brune, W.H., Mao, J.Q., Mitchell, M.J., Leshner, R.L., Simpas, J.B., Metcalf, A.R., Schwab, J.J., Cai, C.X., Li, Y.Q., Demerjian, K.L., Felton, H.D., Boynton, G., Adams, A., Perry, J., He, Y., Zhou, X.L., Hou, J., 2006. Behavior of OH and HO₂ in the winter atmosphere in New York City. *Atmospheric Environment* 40, S252–S263.
- Ren, X.R., Olson, J.R., Crawford, J.H., Brune, W.H., Mao, J.Q., Long, R.B., Chen, Z., Chen, G., Avery, M.A., Sachse, G.W., Barrick, J.D., Diskin, G.S., Huey, L.G., Fried, A., Cohen, R.C., Heikes, B., Wennberg, P.O., Singh, H.B., Blake, D.R., Shetter, R.E., 2008. HO_x chemistry during INTEX-A 2004: observation, model calculation, and comparison with previous studies. *Journal of Geophysical Research – Atmospheres* 113, 13.
- Rosen, R.S., Wood, E.C., Wooldridge, P.J., Thornton, J.A., Day, D.A., Kuster, W., Williams, E.J., Jobson, B.T., Cohen, R.C., 2004. Observations of total alkyl nitrates during Texas Air Quality Study 2000: implications for O-3 and alkyl nitrate photochemistry. *Journal of Geophysical Research – Atmospheres* 109, 15.
- Sadanaga, Y., Yoshino, A., Kato, S., Yoshioka, A., Watanabe, K., Miyakawa, Y., Hayashi, I., Ichikawa, M., Matsumoto, J., Nishiyama, A., Akiyama, N., Kanaya, Y., Kajii, Y., 2004. The importance of NO₂ and volatile organic compounds in the urban air from the viewpoint of the OH reactivity. *Geophysical Research Letters* 31, 4.
- Sander, S.P., Friedl, R.R., Ravishankara, A.R., Golden, D.M., Kurylo, M.J., Molina, M.J., Moortgat, G.K., Keller-Rudek, H., Finlayson-Pitts, B.J., Wine, P.H., Huie, R.E., Orkin, V.L., 2006. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation Number 15.
- Shirley, T.R., Brune, W.H., Ren, X., Mao, J., Leshner, R., Cardenas, B., Volkamer, R., Molina, L.T., Molina, M.J., Lamb, B., Velasco, E., Jobson, T., Alexander, M., 2006. Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003. *Atmospheric Chemistry and Physics* 6, 2753–2765.
- Stockwell, W.R., Kirchner, F., Kuhn, M., Seefeld, S., 1997. A new mechanism for regional atmospheric chemistry modeling. *Journal of Geophysical Research – Atmospheres* 102, 25847–25879.
- Volz-Thomas, A., Pätz, H.W., Houben, N., Konrad, S., Mihelcic, D., Klüpfel, T., Perner, D., 2003. Inorganic trace gases and peroxy radicals during BERLIOZ at Pabstthum: an investigation of the photostationary state of NO_x and O-3. *Journal of Geophysical Research – Atmospheres* 108, 15.
- Yoshino, A., Sadanaga, Y., Watanabe, K., Kato, S., Miyakawa, Y., Matsumoto, J., Kajii, Y., 2006. Measurement of total OH reactivity by laser-induced pump and probe technique – comprehensive observations in the urban atmosphere of Tokyo. *Atmospheric Environment* 40, 7869–7881.