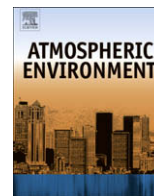




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## Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies

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## ABSTRACT

Both similarities and differences in summertime atmospheric photochemical oxidation appear in the comparison of four field studies: TEXAQS2000 (Houston, 2000), NYC2001 (New York City, 2001), MCMA2003 (Mexico City, 2003), and TRAMP2006 (Houston, 2006). The compared photochemical indicators are OH and HO<sub>2</sub> abundances, OH reactivity (the inverse of the OH lifetime), HO<sub>x</sub> 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<sub>x</sub>), 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 HO<sub>2</sub>, longer OH chain lengths, a smaller contribution of reactions with NO<sub>x</sub> to the OH reactivity, and NO<sub>x</sub>-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<sub>x</sub> 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 HO<sub>2</sub> in high NO<sub>x</sub> 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<sub>x</sub>-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 (HO<sub>2</sub>), collectively called HO<sub>x</sub>, are central players in the photochemical oxidation and pollution production in metropolitan areas. OH initiates many oxidation reaction sequences, while its close chemical relative, HO<sub>2</sub>, is a major precursor of ozone pollution in the

presence of nitrogen oxides (NO<sub>x</sub>). To test the understanding of the complex atmospheric oxidation processes occurring in metropolitan areas requires measurements of the OH and HO<sub>2</sub> 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 HO<sub>2</sub> are produced and lost in just a few ways (Fig. 1). In the daytime, the main sources include the photolysis of ozone (O<sub>3</sub>) and the photolysis of formaldehyde (HCHO), which makes HO<sub>2</sub> that reacts to form OH. Nitrous acid, HONO, acts as another very important source (Ren et al., 2003c, 2006). Reactions between O<sub>3</sub> and alkenes can produce OH (Donahue et al., 1998), although these reactions are generally only significant during nighttime when HO<sub>x</sub> production by photolytic processes is small. Other sources, such as the photolysis of peroxides, are small compared to these other HO<sub>x</sub> sources. The HO<sub>x</sub> sinks are those reactions that remove OH or HO<sub>2</sub> and do not cycle one into the other. These sinks typically involve

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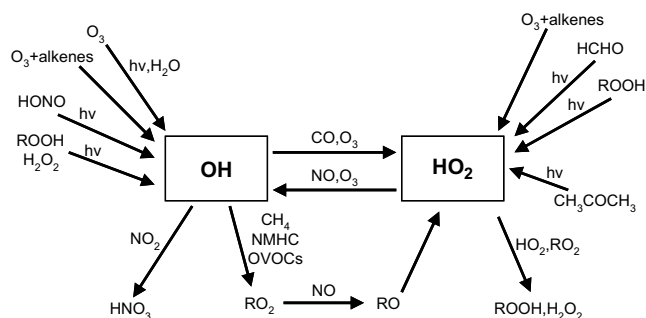


Fig. 1. Schematic diagram of the simplified HO<sub>x</sub> mechanism.

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  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ),  $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$ , 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  $\text{HO}_2$  and  $\text{RO}_2$ .

As the most reactive species in the atmosphere, OH and  $\text{HO}_2$  react with other chemical compounds to cycle  $\text{HO}_x$  between OH and  $\text{HO}_2$ . OH reacts with many atmospheric constituents, including CO, methane ( $\text{CH}_4$ ),  $\text{O}_3$ , volatile organic compounds (VOCs), in some cases producing  $\text{HO}_2$  directly and in other cases initiating a reaction sequence that produces  $\text{HO}_2$ . Meanwhile,  $\text{HO}_2$  reacts with NO or  $\text{O}_3$  and produces OH. Generally the cycling between OH and  $\text{HO}_2$  is much faster than  $\text{HO}_x$  production or loss, although  $\text{HO}_x$  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  $\text{HO}_x$  between OH and  $\text{HO}_2$  and terminate  $\text{HO}_x$ . 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,  $k_{\text{OH}}$ , and  $[\text{OH}]$  are measured and the terminal loss of OH by reaction with  $\text{NO}_2$  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/ $\text{HO}_2$  cycle generates one  $\text{NO}_2$  molecule through  $\text{HO}_2 + \text{NO}$ , this chain length also indicates the role of OH in  $\text{O}_3$  production.

VOC– $\text{NO}_x$ – $\text{O}_3$  chemistry has been studied for decades. However, the oxidation pathways are complex and most studies have been done in large environmental chambers with high  $\text{NO}_x$  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  $\text{NO}_2$  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  $\text{HO}_2$  and  $\text{RO}_{2i}$  with NO.

At low  $\text{NO}_x$  conditions ( $\text{NO}_x$ -sensitive), VOCs are more competitive than  $\text{NO}_x$  for reacting with OH so that radical–radical reactions dominate  $\text{HO}_x$  chemistry. The produced peroxy radicals can then convert NO to  $\text{NO}_2$ . Every  $\text{NO}_2$  molecule that is generated from this reaction sequence will make an  $\text{O}_3$  molecule. So OH mainly reacts with VOCs, makes more radicals, and potentially increases  $\text{O}_3$  in the presence of NO. In the high  $\text{NO}_x$  condition ( $\text{VOC}$ -sensitive), the OH reaction with  $\text{NO}_2$  should reduce the ozone production because  $\text{HO}_2$  reacts with NO to form more OH, which then is terminated by the reaction with  $\text{NO}_2$ . Kleinman (2005) introduces a formula to evaluate the  $\text{O}_3$  production sensitivity using the ratio of  $L_N/Q$ , where  $L_N$  is the radical loss via the reactions with  $\text{NO}_x$  and  $Q$  is the total primary radical production. When  $L_N/Q < 0.5$ , the atmosphere is in the  $\text{NO}_x$ -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  $\text{HO}_2$ , the OH reactivity, the balance between OH production and loss, the OH chain length, the  $\text{HO}_x$  budget, the ozone production rate, and the sensitivity of the ozone production rate to  $\text{NO}_x$  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, this issue). 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<sub>2.5</sub> 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.asc.cestm.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 HO<sub>2</sub> 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 HO<sub>2</sub>, 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. HO<sub>2</sub> 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<sub>x</sub> and OH reactivity measurements, other important measurements were also made simultaneously. Measured atmospheric constituents included NO, NO<sub>2</sub>, CO, NO<sub>y</sub>, O<sub>3</sub>, VOCs, SO<sub>2</sub>, and HCHO. Measured meteorological parameters included pressure, temperature, wind direction and speed, and photolysis frequencies.

The absolute calibration for the GTHOS OH and HO<sub>2</sub> 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 HO<sub>2</sub> 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 HO<sub>2</sub> 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 HO<sub>2</sub> abundances, OH reactivity, HO<sub>x</sub> budget, OH chain length, calculated ozone production, and ozone sensitivity to NO<sub>x</sub> and VOCs.

### 3.1. The abundances of OH, HO<sub>2</sub>, and their precursors

The diurnal variations of OH and HO<sub>2</sub> 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).

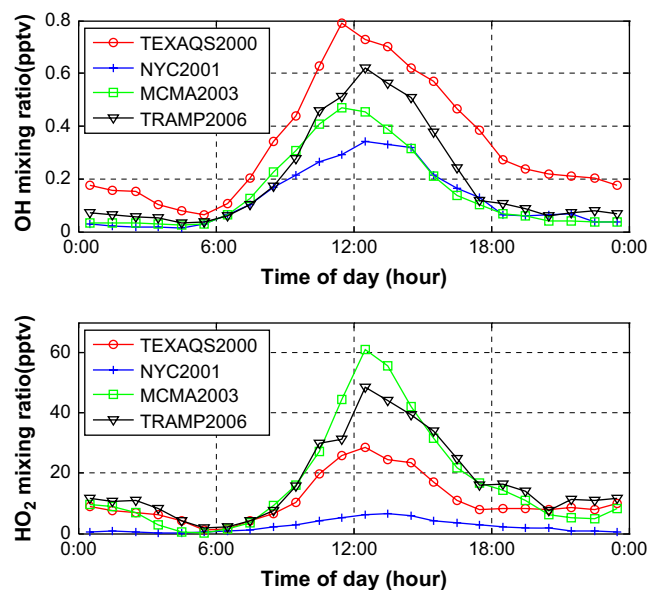


Fig. 2. Diurnal variation of measured OH (upper panel) and HO<sub>2</sub> (lower panel) in four field studies: TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The spread in the maximum HO<sub>2</sub> 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 HO<sub>2</sub> is very different in these four studies. MCMA2003 presents the highest HO<sub>2</sub> level with peak value of 60 pptv, which is due to the highest non-methane volatile organic compounds (NMVOCs), CO, NO<sub>x</sub> and photolysis frequencies in this study (Fig. 3). The HO<sub>2</sub> of NYC2001 is much smaller compared to that of the other three locations. This lower HO<sub>2</sub> can be explained in part by the weaker HO<sub>x</sub> sources, as indicated by the lower JO (<sup>1</sup>D) values, but was primarily due to the greater NO<sub>x</sub>/VOC ratio, which shifted the balance of HO<sub>x</sub> toward OH, which then reacted with NO<sub>2</sub> to terminate HO<sub>x</sub>.

Midday HO<sub>2</sub> during TRAMP2006 is higher than during TEXAS2000 by almost 50% at peak values. Once again, the difference is the greater NO<sub>x</sub>/VOC ratio in TEXAS2000 than in TRAMP2006 (Fig. 3), which shifts the balance of HO<sub>x</sub> toward OH, as seen in Fig. 2. The shift in the NO<sub>x</sub>/VOC ratio is driven by both higher NO<sub>x</sub> and lower NMVOCs in TEXAS2000 than in TRAMP2006. This NO<sub>x</sub>/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, this issue).

The ambient measurements of temperature, CO, O<sub>3</sub>, O<sub>3</sub> photolysis frequency JO (<sup>1</sup>D), NO<sub>x</sub> and the sum of non-methane VOCs are shown in Fig. 3. Compared to other three studies, MCMA2003 had the highest JO (<sup>1</sup>D), CO, NMVOCs and NO<sub>x</sub>, and therefore it has the daily highest O<sub>3</sub> 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 (<sup>1</sup>D) values in MCMA2003. The midday NO<sub>x</sub> in NYC2001 and MCMA2003 was similar, but the much greater NMVOC abundances in MCMA2003 and greater NO<sub>x</sub> 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., this issue). 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, this issue), 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 O<sub>3</sub>.

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 HO<sub>2</sub>. This observation is not surprising because more VOCs mean more HO<sub>2</sub> is produced by reaction of OH with the VOCs and because HO<sub>x</sub> sources like formaldehyde tend to correlate with VOCs. Note that the ranking according to HO<sub>2</sub> does not anti-correlate with the ranking according to NO<sub>x</sub>, which implies that the ranking of HO<sub>2</sub> is not solely determined by the NO<sub>x</sub> level. Further, the ranking according to OH does not correlate with either the ranking according to VOCs or to NO<sub>x</sub>. Thus HO<sub>2</sub> 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  $25 \text{ s}^{-1}$  in winter there in 2004 (Ren et al., 2006). Yoshino et al. (2006) reported that the measured OH reactivity in Tokyo was about  $20 \text{ s}^{-1}$ . Here we compare the OH reactivity measurements in

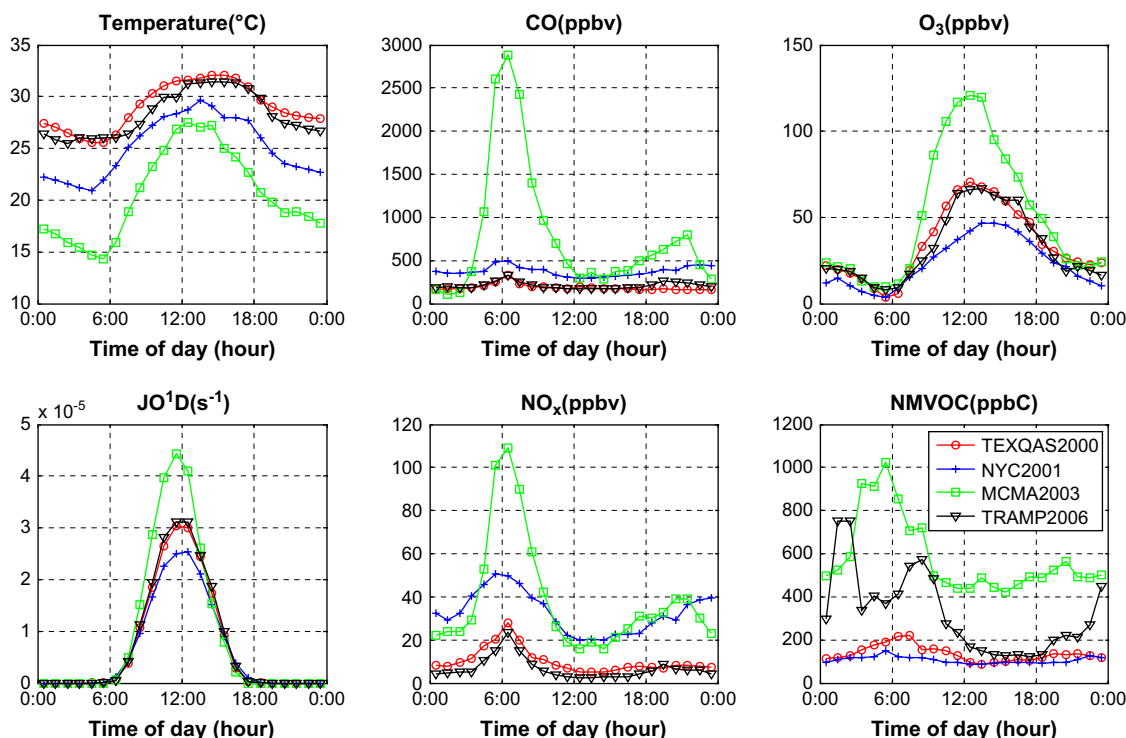


Fig. 3. Median diurnal variation of measured temperature, CO, O<sub>3</sub>, JO (<sup>1</sup>D), NO<sub>x</sub> and Non-methane Volatile Organic Compounds (NMVOCs) in four field studies: TEXAS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, 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  $\text{HO}_2$  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;  $\text{NO}_x$  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  $1 \text{ s}^{-1}$ , except in the morning when it rose to  $1.8 \text{ s}^{-1}$ . Meanwhile the contribution from  $\text{NO}_x$  was largest during the morning

rush hour when  $\text{NO}_x$  emissions were large and the boundary layer height was still low, and was smallest during the afternoon when the boundary layer height was greatest.

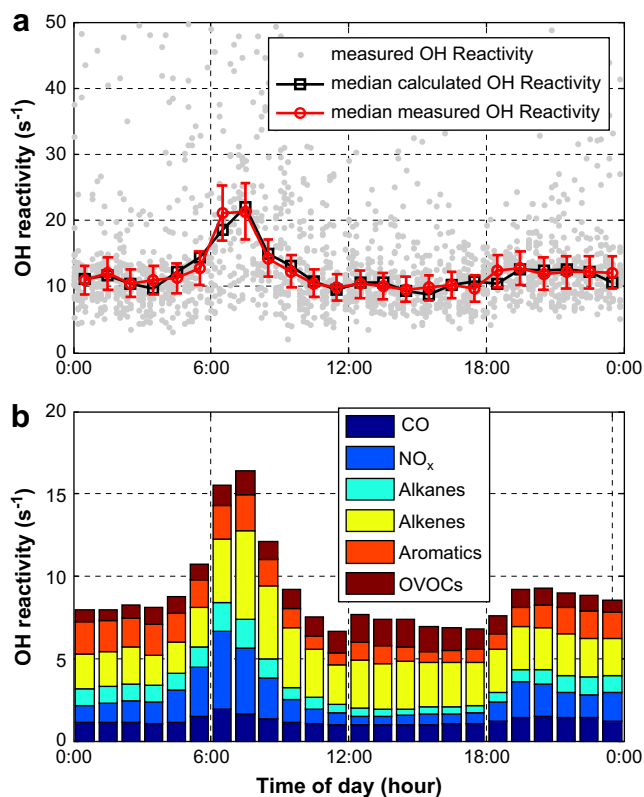
The diurnal variations of the OH reactivity measurement are similar for TRAMP2006, TEXAQS2000, and NYC2001 (Fig. 5). The OH reactivity measurement in TEXAQS2000 could not be corrected for  $\text{HO}_2 + \text{NO}$  because the  $\text{HO}_2$  decay was not measured in the OH reactivity flow tube during 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  $\text{NO}_x$ . 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).

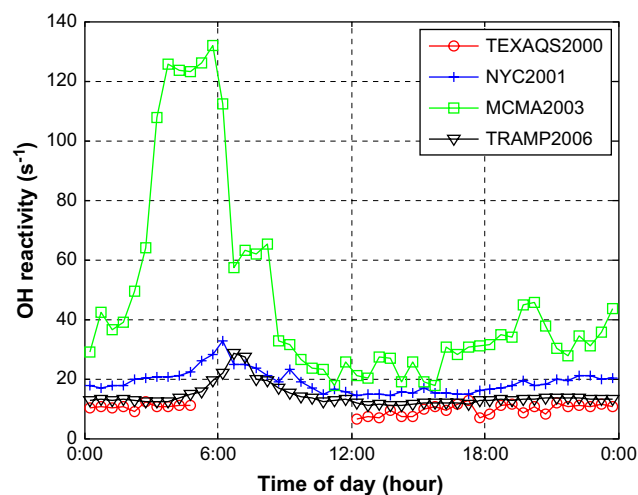
The contribution from CO is very much alike in the four studies (11–14%). The contribution from alkenes is also very similar (20–30%) in three cities except in NYC2001. Compared to other cities, TRAMP2006 has higher contribution of aromatics (15%), which could be possibly due to higher industrial solvent emissions (Leuchner and Rappenglück, this issue). 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  $\text{NO}_x$ , which accounts for about 50% of OH reactivity there.

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

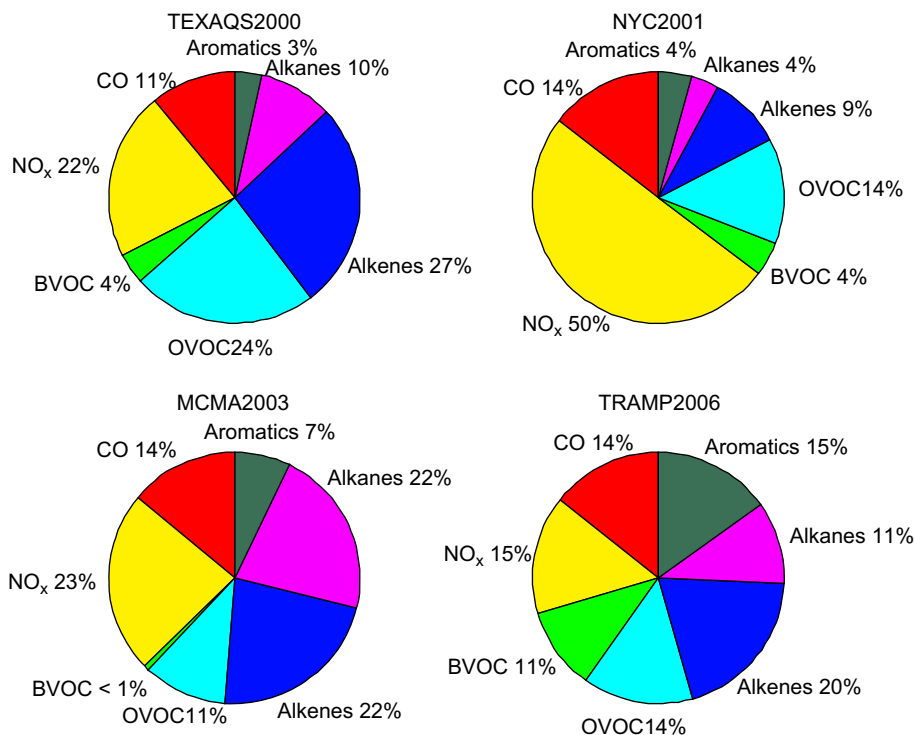
Both the balance of OH production ( $P(\text{OH})$ ) and loss ( $L(\text{OH})$ ) and the OH chain length test the understanding of the  $\text{HO}_x$  cycling between OH and  $\text{HO}_2$ . As seen in Fig. 7, the OH production is greatest in MCMA2003 with a peak value of  $3.9 \times 10^8 \text{ molecules cm}^{-3} \text{ s}^{-1}$  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. 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.)



**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.)

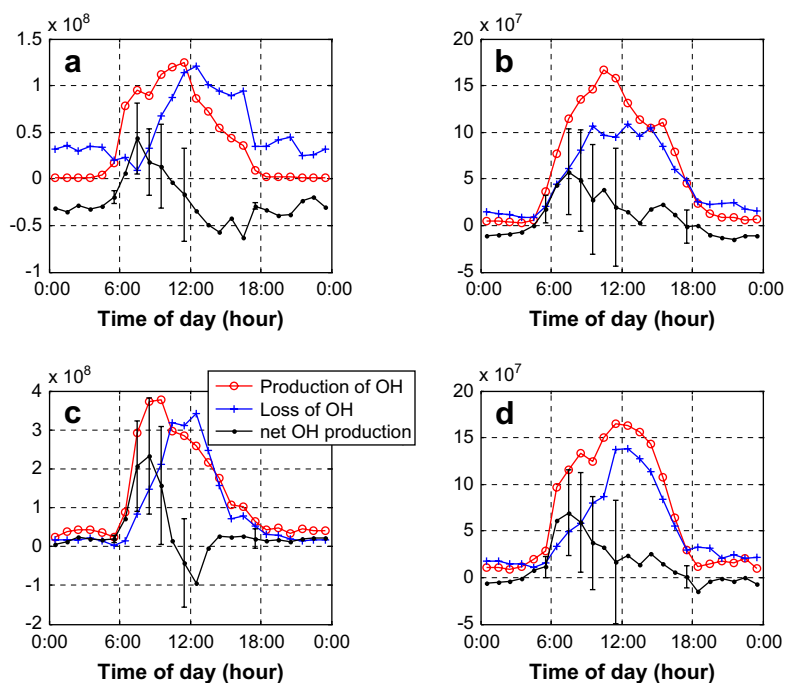


**Fig. 6.** Contributions of different atmospheric constituents to OH reactivity in TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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  $\text{HO}_x$  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 ( $2\sigma$  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  $2\sigma$  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% ( $2\sigma$  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  $\text{HO}_2$  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  $\text{HO}_2$  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  $\text{NO}_x$  that is responsible for the

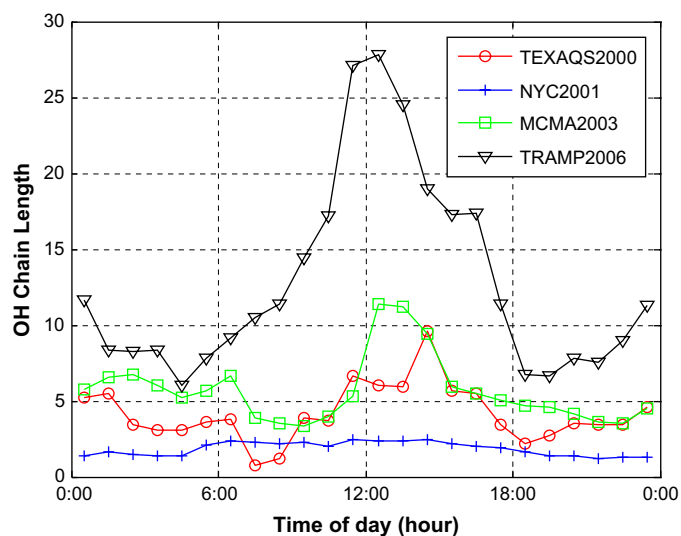


Fig. 8. Median diurnal variation of OH chain length in TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

under-predicted  $\text{HO}_2$  is also responsible for the statistically significant net OH production during morning rush hour.

A second indicator of  $\text{HO}_x$  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

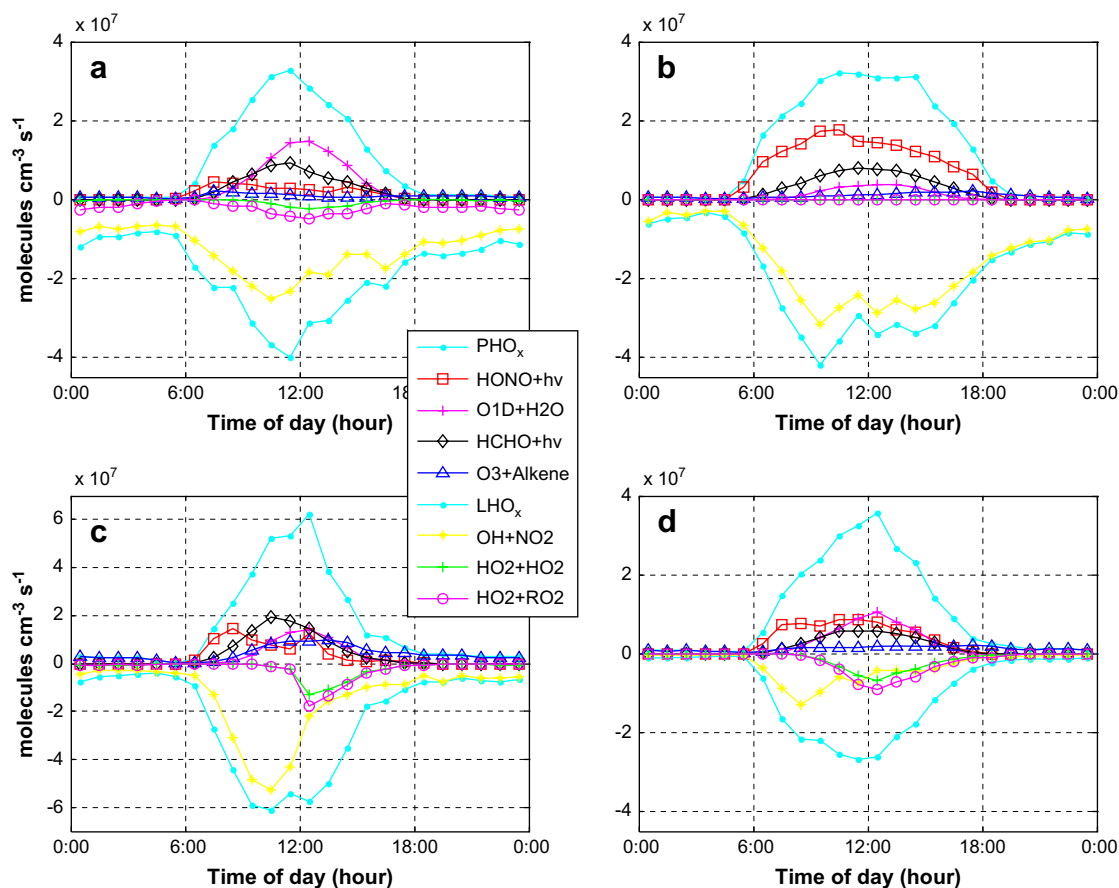


Fig. 9. Median diurnal profiles of  $\text{HO}_x$  sources and sinks in (a) TEXAQS2000, (b) NYC2001, (c) MCMA2003 and (d) TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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  $\text{NO}_x$  during TRAMP2006 (Fig. 3) and thus a relatively small sink of  $\text{OH} + \text{NO}_2$ . Compared to TRAMP2006,  $\text{NO}_2$  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. $\text{HO}_x$ budget

Since  $\text{HO}_2 + \text{NO}$  reaction dominates OH production and this reaction is just the cycling between OH and  $\text{HO}_2$ , a further evaluation of the radical budget should include the sources and sinks of total  $\text{HO}_x$ . Here we present the  $\text{HO}_x$  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  $\text{HO}_x$  cycling. Meanwhile, we also calculated the  $\text{HO}_x$  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,  $\text{HO}_x$  production is dominated by different reactions in different studies. The photolysis of HONO dominates  $\text{HO}_x$  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  $\text{HO}_x$  reservoir under urban conditions. Calculations show that the contributions from the photolysis of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OOH}$  are much less significant. On the other hand,  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ , which is considered the dominating  $\text{HO}_x$  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  $\text{O}_3$  levels make it a competitive  $\text{HO}_x$  source. All above indicates that the photolysis of HONO and HCHO acts as two major  $\text{HO}_x$  sources under urban conditions besides the known  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  reaction. On the  $\text{HO}_x$  sinks side,  $\text{OH} + \text{NO}_2$  dominates  $\text{HO}_x$  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  $\text{HO}_x$  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  $\text{HO}_2$ ,  $\text{RO}_2$ , and NO. Because  $\text{RO}_2$  was not measured in these four studies,  $\text{RO}_2$  is estimated by multiplying the ratio of the modeled  $\text{RO}_2$  to modeled  $\text{HO}_2$  by the measured  $\text{HO}_2$ . 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. (this issue).  $L_N/Q$

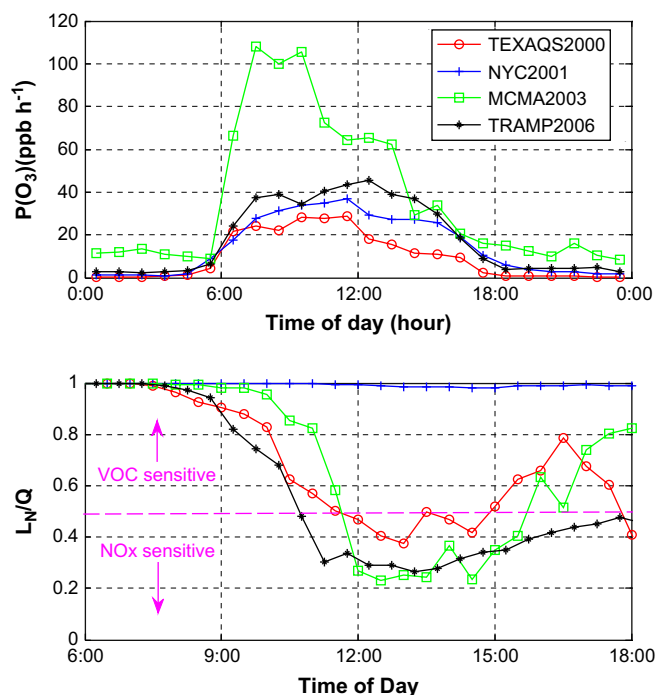


Fig. 10. Median diurnal profiles instantaneous ozone production rate (upper panel) and  $L_N/Q$  (lower panel) in TEXAQS2000, NYC2001, MCMA2003 and TRAMP2006. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$Q$  is 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  $\text{NO}_2$  was about 5–10 ppbv (Rosen et al., 2004). Because these instantaneous ozone production rates use the measured  $\text{HO}_2$ , which is typically larger than the modeled  $\text{HO}_2$  at high  $\text{NO}_x$  conditions, they will be typically larger than the instantaneous ozone production rates calculated with the modeled  $\text{HO}_2$  (Chen et al., this issue). For NYC2001,  $P(\text{O}_3)$  using measured  $\text{HO}_2$  is typically twice  $P(\text{O}_3)$  using modeled  $\text{HO}_2$ , 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  $\text{NO}_x$  or VOCs has a similar behavior for MCMA2003, TEXAQS2000, and TRAMP2006; it is VOC-sensitive in the early morning and late afternoon but  $\text{NO}_x$ -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  $\text{HO}_2$ . Note that the ozone sensitivity in TRAMP2006 and MCMA2003 fall into the  $\text{NO}_x$ -sensitive regime for most of the daytime. More interestingly MCMA2003 presents a much higher  $\text{NO}_x$  level than TRAMP2006 in the afternoon. Since ozone production in both studies is in the  $\text{NO}_x$ -sensitive region, MCMA in 2003 has higher ozone than Houston in 2006 due primarily to the higher levels of  $\text{NO}_x$ .



#### 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<sub>x</sub> 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<sub>x</sub>-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<sub>x</sub>-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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