



## Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas

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### Abstract

Urban air pollution is characterized by high ozone levels, formed when volatile organic compounds (VOCs) are oxidized in the presence of nitrogen oxides (NO<sub>x</sub>). VOC and NO<sub>x</sub> emissions controls have traditionally been implemented to reduce urban ozone formation, however, a separate chemical species implicated in ozone formation in Houston, TX and possibly other urban areas is the chlorine radical (Cl·). Cl· enhances tropospheric VOC oxidation, but is not included in models used to develop air quality attainment plans. We present results of a three-fold approach to elucidate the importance of Cl· in urban ozone formation: (1) the first direct evidence of chlorine chemistry in the urban troposphere, (2) enhanced ozone formation (> 75 parts per 10<sup>9</sup> (ppb/h) observed when small amounts of chlorine (Cl<sub>2</sub>) are injected into captive ambient air, and (3) enhanced ozone formation (~16 ppb) predicted by regional photochemical models employing Cl· chemistry. These results suggest that reducing chlorine emissions should be considered in urban ozone management strategies.

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### 1. Introduction

Ozone typically forms when hydroxyl radical (OH·) ubiquitous to the daytime troposphere, oxidizes VOCs in the presence of NO<sub>x</sub>. Chlorine radical (Cl·) can

similarly initiate ozone formation (Tanaka et al., 2000; Hov, 1985; Finlayson-Pitts, 1993), but reacts up to 2 orders of magnitude faster with VOCs than does OH· (Atkinson et al., 1999). This rate enhancement implies that Cl· can promote urban ozone formation by enhancing VOC oxidation. To confirm and quantify the impact of Cl· chemistry in the urban troposphere, a three-fold approach was undertaken as part of the Texas Air Quality Study (TEXAQS, 2000) during the summer

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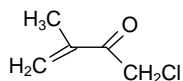
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of 2000 at La Porte, TX (a mixed residential–industrial area east of Houston): (1) Ambient air was analyzed for the unique reaction products of  $\text{Cl}\cdot$  with isoprene and for secondary chloride in aerosol (2)  $\text{Cl}_2$  was injected into captive ambient air to determine the ozone enhancement potential of chlorine, and (3)  $\text{Cl}\cdot$  chemistry was incorporated into a regional photochemical model used to estimate the impact of  $\text{Cl}\cdot$  chemistry on air quality in Southeast Texas. La Porte was chosen because of its proximity to the heavily industrialized Houston Ship Channel, which is located approximately 8 km to the north and northwest. An inventory of chlorine emissions developed by the University of Texas, suggests that several metric tons/day of  $\text{Cl}_2$  are emitted from the Ship Channel region (Chang et al., 2001, 2002).

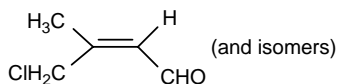
## 2. Detecting products of chlorine chemistry in ambient air: CMBO/CMBA

### 2.1. Introduction

One method to confirm the role of  $\text{Cl}\cdot$  chemistry in the urban troposphere is through detection of reaction products, or marker species, unique to the reaction of  $\text{Cl}\cdot$  with VOCs 1-Chloro-3-methyl-3-butene-2-one (CMBO) (Nordmeyer et al., 1997; Ragains and Finlayson-Pitts, 1997; Riemer and Apel, 2001)



and chloromethylbutenal (CMBA)



a CMBO isomer, are two such products of a series of reactions between  $\text{Cl}\cdot$  and isoprene. Isoprene is emitted in large quantities from biogenic sources around Houston and the eastern United States. Detecting CMBO and CMBA in ambient air would therefore confirm that  $\text{Cl}\cdot$  chemistry plays a role in the Houston area.

### 2.2. Methods

Ambient air was continuously sampled from 20–26 August 2000 and 29 August–12 September 2000. The target analytes (including isoprene, CMBO, and CMBA) were preconcentrated, separated by gas chromatography and detected with a mass selective detector. Detection limits varied from less than 1 part per  $10^{12}$  (ppt) for isoprene and CMBA, to 5–9 ppt for CMBO. Additional experimental details are provided elsewhere (Riemer and Apel, 2001).

### 2.3. Results and discussion

CMBO and/or CMBA were detected in 110 and 121 of 837 samples (13% and 14%), respectively, collected and on 16 of the 22 days (73%) during the TEXAQs study when ambient measurements of CMBO and CMBA were made. The ranges of daily peak mixing ratios were 12–126 ppt and 11–145 ppt, respectively. The highest mixing ratios of both species were detected on the morning of 22 August 2000.

Fig. 1 displays the ozone, CMBO, and CMBA mixing ratios detected on the 3 days with highest ozone mixing ratios detected during the La Porte field campaign: 30, 31, August and 5 September 2000. The coincidental detection of marker species and increased ozone confirms the occurrence of  $\text{Cl}\cdot$  chemistry in the air masses that contributed to the early afternoon ozone peaks on 30, 31, August and 5 September. Similar to the 3 days shown here, the daily maxima in CMBO/CMBA mixing ratios on other days were mostly observed in the morning.

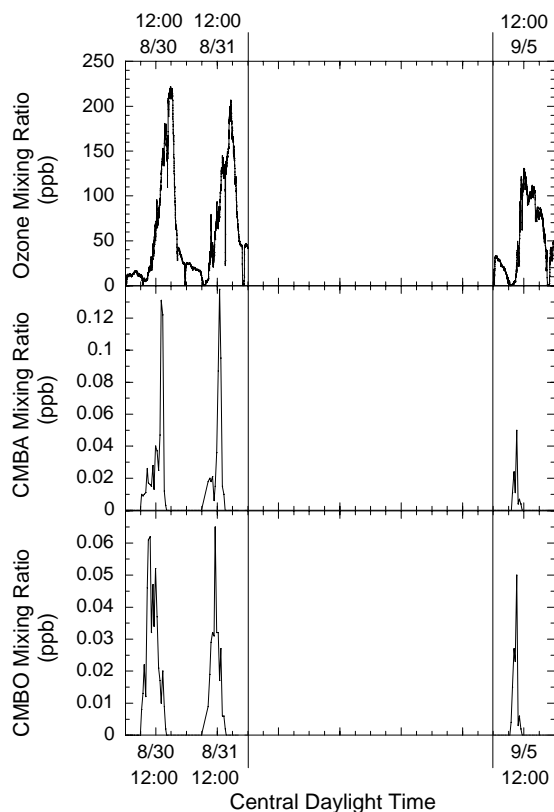


Fig. 1. Ozone, CMBO, and CMBA mixing ratios for 30, 31, August and 5 September 2000 at the La Porte, TX site. Data from 1–4 September are not included to improve clarity. As shown, the unique products of  $\text{Cl}\cdot$  with isoprene (CMBO and CMBA) were detected in the morning hours after sunrise, coincident with increases in the ozone mixing ratio.

### 3. Detecting products of chlorine chemistry in ambient air: secondary aerosol chloride

#### 3.1. Introduction

Another product of  $\text{Cl}\cdot$ -hydrocarbon chemistry is hydrochloric acid (HCl) (Atkinson et al., 1999). Aerosol can scavenge HCl to form secondary chloride. By measuring the amount of secondary chloride present in an aerosol, it is possible to infer the exposure of the aerosol to HCl in the air. Because HCl is directly produced by the abstraction of hydrogen from hydrocarbons by  $\text{Cl}\cdot$ , measurements of secondary chloride may provide insight into the availability of chlorine in air encountered by the collected aerosol.

#### 3.2. Methods

To measure secondary chloride during the **TEXAQS 2000** field study, the Aerodyne Aerosol Mass Spectrometer (AMS) was employed to provide real-time quantitative chemical analysis of volatile and semi-volatile aerosol components with simultaneous measurement of particle aerodynamic diameter. Described elsewhere are the operation of (Jayne et al., 2000) and initial field data (Jimenez et al., 2003) from the AMS. A brief summary is provided here.

The AMS was operated by focusing a sample of submicron particles onto a resistively heated surface under high vacuum (approximately  $10^{-7}$  Torr). Upon impact, the volatile and semi-volatile aerosol components vaporize and are detected by a quadrupole mass spectrometer. The time-resolved detection of particles across a known flight distance to the heated surface allows the determination of particle aerodynamic diameter. During the **TEXAQS 2000** study, the particles were vaporized at a temperature of approximately  $600^\circ\text{C}$ . This temperature was high enough to allow detection of secondary chloride (i.e., ammonium chloride), but not high enough to allow for detection of sea salt chloride.

#### 3.3. Results and discussion

Fig. 2 displays the concentration of secondary chloride detected by the AMS during the **TEXAQS 2000** study period. These data indicate that the highest levels of secondary chloride were detected predominantly in the morning. This trend is similar to that observed in the CMBO and CMBA data. A direct correlation cannot be made between the CMBO/CMBA data and the AMS data because the formation of secondary chloride is dependent on the availability of aerosol, aerosol pH, availability of species such as ammonia, and other properties of the aerosol. However, the similar trend towards morning peaks observed in the AMS and

CMBO/CMBA data support the importance of chlorine chemistry to the oxidative chemistry above Houston.

Despite the quantitative measurements of the marker species and secondary chloride concentrations, it is not possible to determine from these measurements the extent to which  $\text{Cl}\cdot$  chemistry affected ozone mixing ratios. Therefore, captured air experiments were performed to help determine the impact of  $\text{Cl}\cdot$  on ozone formation in Houston area air.

### 4. Captive air experiments

#### 4.1. Introduction

Environmental chambers enable precise quantities of gases to be injected into an air mass that can then be irradiated with sunlight. By performing outdoor experiments in identical outdoor environmental chambers, the response of captured ambient air to injections of various gases can be studied under conditions encountered in the urban environment. During the captive air experiments reported here, molecular chlorine ( $\text{Cl}_2$ ), a photolytic precursor of  $\text{Cl}\cdot$ , was injected into captive ambient air. In this manner, the potential for  $\text{Cl}\cdot$  to enhance ozone formation in ambient air was evaluated under conditions encountered in the Houston area.

#### 4.2. Methods

Simultaneous captive air experiments were performed in three,  $2\text{ m}^3$  outdoor, mobile fluorinated ethylene-propylene (FEP) Teflon environmental chambers at the La Porte site. Ozone and  $\text{NO}_x$  were measured with one set of instruments connected to a 4-way, Teflon valve. Chamber grab samples were collected and then analyzed using GC/MS and a GC equipped with a flame ionization detector. Isoprene, alkanes, alkenes, and various aromatics were typically detected in captive ambient air during the field study. Temperature, relative humidity, and light intensity were also measured. Additional details about typical experimental procedures are provided elsewhere (Tanaka et al., 2002a).

#### 4.3. Results and discussion

Fig. 3 displays the mixing ratios of ozone, isoprene, and CMBO from the 6 September 2000 set of environmental chamber experiments performed under sunny conditions. All three chambers started with captive ambient air and were enclosed in a dark, opaque cover. Approximately 190 ppb propane was injected into Chambers B and C at approximately 08:15 (Central Daylight Time) to determine the efficacy of  $\text{Cl}\cdot$  to enhance ozone formation in alkane-enriched ambient air. Although propane does not directly affect CMBO

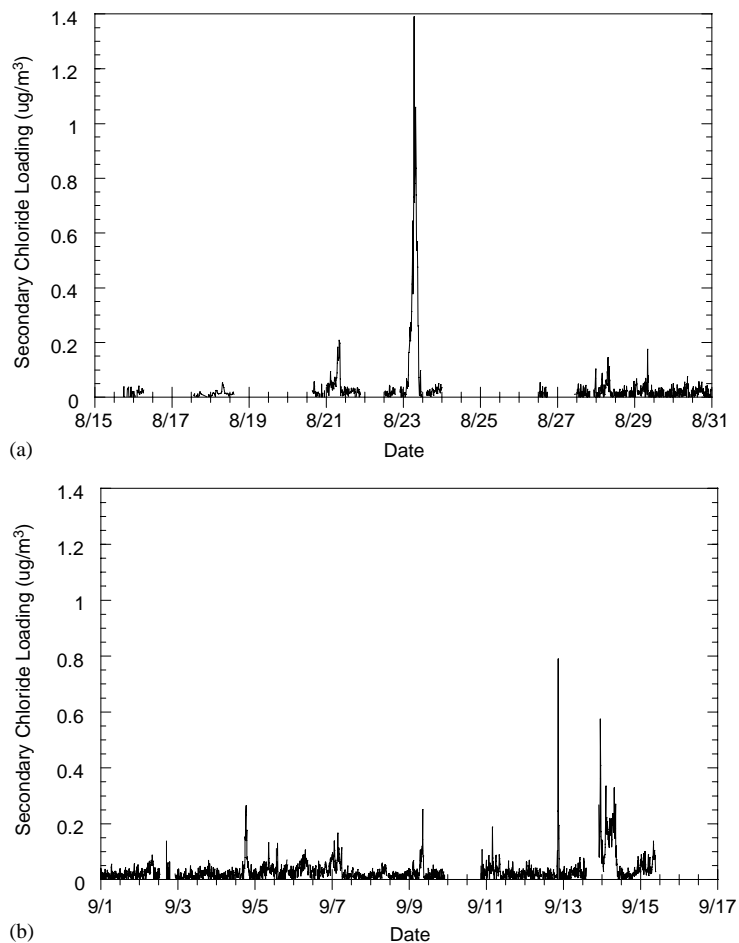


Fig. 2. Secondary chloride detected in ambient air by AMS at the La Porte site during the following periods: (a) 15–31 August 2000 and (b) 1–15 September 2000.

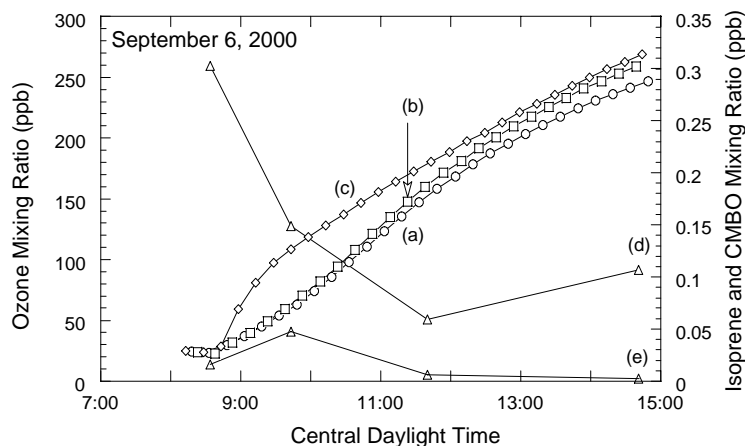


Fig. 3. Ozone, isoprene, and CMBO during a captive ambient air experiment—6 September 2000. Ozone mixing ratios are plotted for each of three chambers (a)–(c) run simultaneously. Isoprene (d) and CMBO (e) mixing ratios are plotted for Chamber C only. The chamber starting mixtures were as follows: (a) Chamber A—Ambient air only, (b) Chamber B—Ambient air enriched with 190 ppb propane, and (c) Chamber C—Ambient air enriched with 190 ppb propane and 6 ppb  $\text{Cl}_2$ .

production, propane may be important to ozone formation when  $\text{Cl}\cdot$  are present.  $\text{Cl}_2$  was subsequently injected (6 ppb equivalent) into Chamber C at 08:38, followed by the immediate removal of the opaque cover from the chambers. During the first hour, Chamber C exhibits enhanced ozone formation (approximately 78 ppb/h) compared to the chambers (A, B) without  $\text{Cl}_2$  injected (approximately 36 ppb/h). The CMBO mixing ratio also increased from 16 to 49 ppt in the first hour of the experiment. The mixing ratio of CMBO detected here (49 ppt) was within the range of peak levels detected in ambient air throughout the study. This suggests a similarity between the magnitude of chlorine available in ambient air during the study and the amount of chlorine injected during the captive air experiments. The early peak in CMBO level during the captive air experiment on 6 September 2000 (Fig. 3) occurs because  $\text{Cl}_2$  has a short lifetime against photolysis (calculated to be less than 15 min at 09:00).  $\text{Cl}\cdot$  are formed rapidly at the start of experiment and react with isoprene in the captured ambient air to form CMBO. However, as  $\text{Cl}_2$  and isoprene are depleted, CMBO formation slows and the CMBO mixing ratio decreases due to continued reaction with  $\text{OH}\cdot$ .

Based on observed enhancement of ozone formation in the captive air experiment and detection of CMBO in ambient air and the captive air experiment, we conclude that  $\text{Cl}\cdot$  chemistry occurs and enhances ozone formation in the Houston area. However, the regional ozone enhancement due to  $\text{Cl}\cdot$  in the Houston area is also dependent on emissions and meteorology. These factors can be simultaneously accounted for only by employing a regional photochemical model such as the Comprehensive Air Quality Model with extensions (CAMx) [Environ, 2000].

## 5. Regional photochemical modeling with CAMx

### 5.1. Introduction

To estimate the regional impact of  $\text{Cl}\cdot$  chemistry, simulations were performed using CAMx with the Carbon Bond IV mechanism (Gery et al., 1989) modified to include chlorine chemistry. We examine the impact of chlorine chemistry on ozone mixing ratios for the period 6–11 September 1993. This period is currently being modeled by the Texas Natural Resource Conservation Commission (TNRCC), the Texas state environmental regulatory body, to evaluate the effectiveness of air quality improvement plans in the Houston/Galveston area (TNRCC, 2000). These dates were chosen by the TNRCC for evaluating air quality regulation because the meteorological conditions observed during this period are representative of conditions encountered with elevated ozone mixing ratios. Although selection of a

2000 episode during the TEXAQS field campaign would have been preferable, development and performance evaluation of modeling episodes for this period will not be completed until late 2002. The 1993 episode has undergone rigorous performance evaluation and scrutiny by the TNRCC and the US Environmental Protection Agency (TNRCC, 2000). Therefore, the 1993 episode was selected to provide a preliminary assessment of temporal and regional-scale spatial trends in ozone formation due to chlorine chemistry.

### 5.2. Methods

As mentioned previously, the chemical mechanism employed by the CAMx regional photochemical model was modified to include chlorine radical chemistry. The original chemical mechanism used by CAMx is based on the Carbon Bond IV mechanism (Gery et al., 1989). Because of the parameterized representation of complex organics in the Carbon Bond IV mechanism, only 13 reactions were incorporated in the chemical mechanism employed by CAMx to describe chlorine chemistry relevant to an urban atmosphere such as in Houston. Among the 13 reactions included were the reactions of isoprene with  $\text{Cl}\cdot$  to form CMBO, and the subsequent reaction of CMBO by  $\text{OH}\cdot$ . These reactions were included to provide estimates of CMBO concentrations across the modeled domain. Further details of the development of the mechanism are provided elsewhere (Tanaka et al., 2002b).

Chlorine emissions from cooling towers, swimming pools, marine sources, and point sources were used with the modified chemical mechanism in CAMx to simulate the effect of chlorine emissions on ozone formation in the Houston area. The emission inventory is described in detail elsewhere (Chang et al., 2001, 2002).

### 5.3. Results and discussion

One-hour averaged mixing ratios of ozone and CMBO for the case without chlorine emissions were compared to the simulation with chlorine emissions. Figs. 4 and 5 display the maximum enhancement of ozone and CMBO predicted for 11 September 1993, the day when greatest enhancement above the base case is predicted for both species during the modeled period. Maximum predicted ozone enhancement and CMBO mixing ratios were 16 ppb and 59 ppt, respectively, on 11 September 1993. Fig. 5 also shows a time series of predicted CMBO mixing ratios for 11 September 1993 at the location of the predicted maximum.

Although we cannot quantitatively compare the CMBO mixing ratios predicted by the model for 11 September 1993 with the summer 2000 ambient monitoring data, we expect the mixing ratios to be qualitatively similar since the meteorology and isoprene

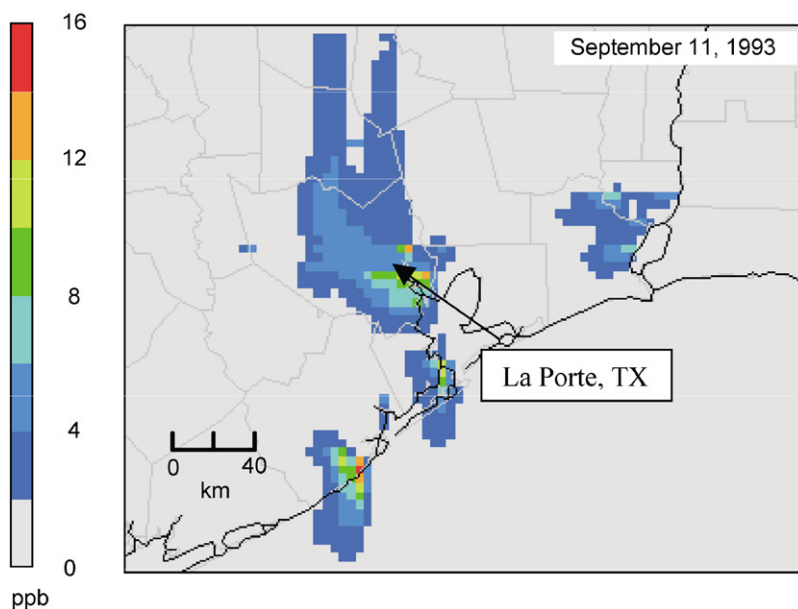


Fig. 4. Maximum ozone enhancement predicted for 11 September 1993 when chlorine emissions are included in the photochemical model. Plotted is the difference between ozone mixing ratio predicted with chlorine emissions included and not included. This day exhibited the location with maximum ozone enhancement during the modeled period.

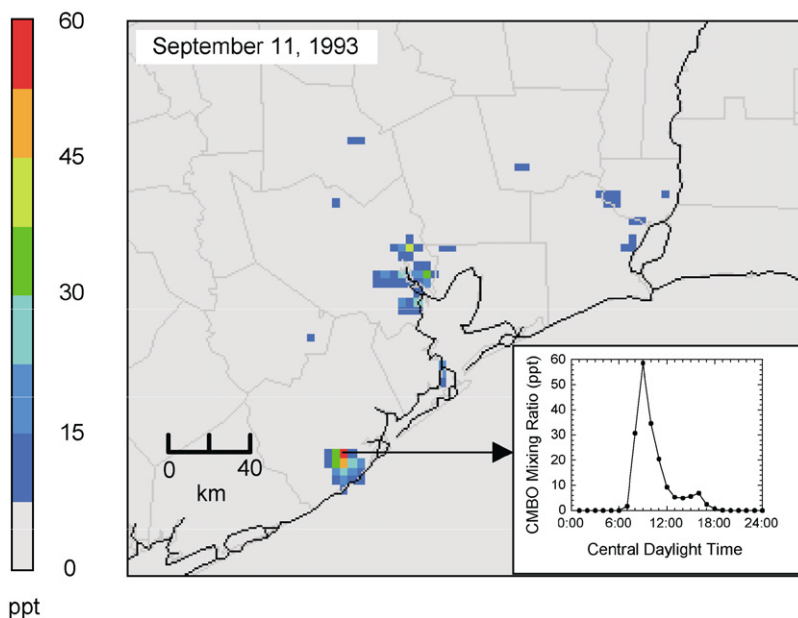


Fig. 5. CMBO mixing ratios at the time of model-predicted CMBO maximum (09:00, 11 September 1993). A time series of the CMBO mixing ratio is provided for the location where the maximum CMBO mixing ratio was predicted.

and chlorine emissions are similar for the two periods. The morning increase in CMBO mixing ratio observed during the field campaign (Fig. 1) is replicated by the model results presented in Fig. 5. The maximum

predicted CMBO mixing ratio is also similar to that detected in the captive air experiments and within a factor of two of the highest mixing ratios detected during ambient measurements.

## 6. Summary

We report the first direct evidence of Cl $\cdot$  chemistry in an urban area through quantification of CMBO and CMBA, species unique to the Cl $\cdot$  + isoprene reaction in ambient air. Measurements of secondary chloride in aerosol provide supporting evidence for the importance of Cl $\cdot$  chemistry. When chlorine was made available in captive air experiments, CMBO was produced, and ozone formation was enhanced. Regional photochemical model predictions that include anthropogenic chlorine emissions are consistent with ambient observations and suggest that chlorine chemistry enhances ozone formation primarily in the late morning hours in Houston, TX. The early temporal enhancement may affect the 8-h average ozone levels in the Houston area and warrants further study. Given that reported industrial chlorine emissions from Houston area point sources represent less than 1% of the US total, as reported through the Toxics Release Inventory (TRI, 2001), Cl $\cdot$  chemistry could be important to ozone formation in other urban areas.

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