

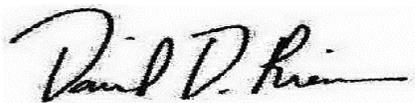
Final Report to:

Texas Natural Resource Conservation Commission
Contract 582034743

Title:

**CONFIRMING THE PRESENCE AND EXTENT OF OXIDATION BY CI IN THE HOUSTON, TEXAS
URBAN AREA USING SPECIFIC ISOPRENE OXIDATION PRODUCTS AS TRACERS**

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I. Introduction

Atomic chlorine (Cl) has been identified as an important component of the atmospheric oxidation cycle in the marine boundary layer [Finlayson-Pitts, 1993] and has been implicated in tropospheric ozone formation in certain urban areas such as Houston, Texas [D. Allen, personal communication; Tanaka *et al.*, 2000]. In Harris County, Texas yearly emissions of Cl₂ have ranged from a high of 329,000 kg in 1988 to a low of 67,000 kg in 1996. The last year for which there are data shows emissions of 132,000 kg in 1999 [http://www.epa.gov/tri] (Figure 1).

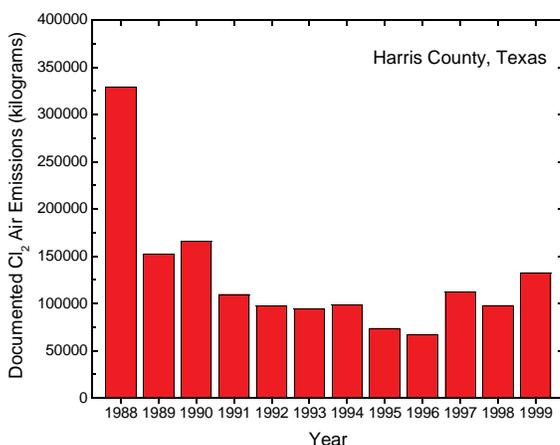


Figure 1. Documented Cl₂ air emissions for Harris County, Texas for years 1988 through 1999.

To determine the presence and extent of Cl chemistry in the Houston area, we measured specific tracers from isoprene oxidation by Cl. Isoprene is a highly reactive nonmethane hydrocarbon (NMHC) that is emitted by vegetation, and to a lesser degree, by anthropogenic activities. Laboratory studies have shown that the reaction of isoprene with Cl forms several unique tracers which could be used as evidence for Cl chemistry [Nordmeyer *et al.*, 1997]. We investigated the isoprene oxidation process under ambient conditions at the LaPorte airport experimental site, and were able to characterize the different oxidation processes that were occurring. Our results confirm that Cl is indeed an oxidant in the Houston urban area. Unfortunately, the extent to which Cl serves as the major contributor to the persistent ozone problems in Houston is yet to be determined.

Isoprene oxidation chemistry is driven primarily by OH and O₃ with additional oxidation by NO₃ during the nighttime. In Houston oxidation by Cl also occurs. Figure 2 depicts the primary pathways of isoprene oxidation. Isoprene oxidation by OH and O₃ results in the formation of methacrolein (MACR), methyl vinyl ketone (MVK) and formaldehyde (CH₂O). Isoprene oxidation by Cl addition forms the unique reaction products 1-chloro-3-methyl-3-butene-2-one (CMBO) and several isomers of chloromethylbutenal (CMBA). 2-methylene-3-butenal (MBA) is formed as a result of H-abstraction by Cl. CMBO and CMBA serve as robust tracers of Cl chemistry. Rate coefficients for the isoprene oxidation reactions are shown in Table 1. Isoprene lifetimes with respect to the different oxidation processes are presented for ranges or medians of oxidation potential observed or estimated for Houston.

As part of TexAQS 2000, we completed two separate investigations to determine the presence and extent of Cl chemistry in the Houston urban area. The first set of investigations included a series of laboratory experiments to characterize the products and yields for the isoprene + Cl reaction. The second set of investigations consisted of field studies at the LaPorte municipal airport, where we made ambient

measurements of isoprene, methacrolein, methyl vinyl ketone and two products specific to the reaction of isoprene + Cl, CMBO and CMBA.

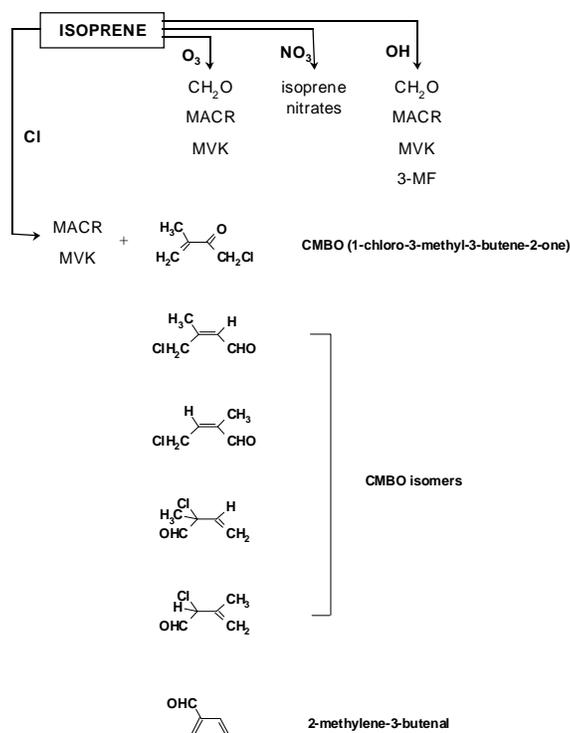


Figure 2. Isoprene oxidation pathways. CMBO and its isomers, products formed from isoprene-Cl chemistry, are good tracers of Cl chemistry in the Houston, Texas area.

Table 1. Lifetime of isoprene relative to the oxidation processes found in the Houston, Texas area.

Oxidant Concentration	k_{oxidant} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Isoprene Lifetime (τ_{ox}) (min.)*
OH (molecules cm^{-3}) ^a 2.46×10^6	^b 101×10^{-12}	67
O_3 (ppb) ^c below detection limit-212	^d 12.8×10^{-18}	>280
Cl (molecules cm^{-3}) ^e below detection limit- 10^5	^f 460×10^{-12}	35-360

^aMedian OH concentration for LaPorte Airport (data source - W. Brune, Penn. State University); ^bAtkinson, 1994. ^cRange O_3 concentration for LaPorte Airport (data source - E. Williams, NOAA-AL); ^dAtkinson, 1994; ^eThis work; ^fSee text; *Lifetimes calculated as $1/([\text{oxidant}] \times k_{\text{oxidant}})$

II. Research Investigations

a. Laboratory Studies

i. Background

To concisely interpret data collected during the field study portion of TexAQS 2000, we needed reliable values for both the rate coefficient and the specific product yields for reaction of Cl + isoprene. Rate coefficients for the reaction of isoprene + Cl have been studied extensively using a variety of

absolute and relative rate techniques [Bedjanian *et al.*, 1998; Canosa-Mas *et al.*, 1999; Fantechi *et al.*, 1998; Orlando *et al.*, in preparation (this work included therein); Notario *et al.*, 1997; Ragains and Finlayson-Pitts, 1997; Suh and Zhang, 2000]. The mean of all data obtained near 1 atmosphere total pressure and 298 K give a value of $(4.6 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The major reaction pathways resulting from addition of Cl to isoprene in NO_x free air are shown in Figure 3 and are based on the results of several research groups [Fantechi *et al.*, 1998; Nordmeyer *et al.*, 1997; Orlando *et al.*, in preparation (this work included therein); Ragains and Finlayson-Pitts, 1997; Suh and Zhang, 2000]. The main expected products from the chemistry are: 1-chloro-3-methyl-3-buten-2-one (CMBO); four isomers of chloromethylbutenal: 4-chloro-3-methyl-2-butenal, 2-chloro-2-methyl-3-butenal, 4-chloro-2-methyl-2-butenal, 2-chloro-3-methyl-3-butenal; methyl vinyl ketone; methacrolein; HCOCl ; and formaldehyde. 2-methylene-3-butenal results from the abstraction of H from the methyl group on isoprene. Earlier studies have determined that the abstraction channel accounts for approximately 15 percent of the total reaction [Fantechi *et al.*, 1998; Ragains and Finlayson-Pitts, 1997; Suh and Zhang, 2000].

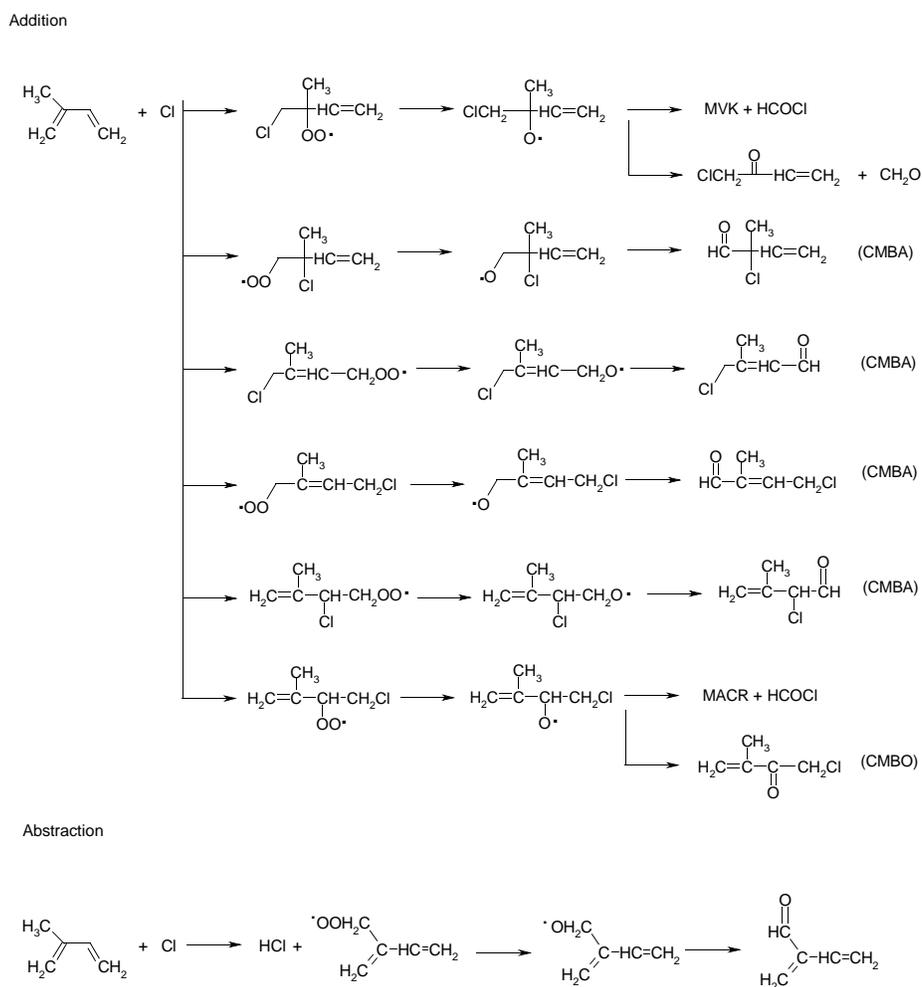


Figure 3. Mechanism for the Cl initiated oxidation isoprene showing both the addition and abstraction channels. Only the addition channels yield CMBO and the CMBA isomers.

ii. Experimental Methods

All the experiments were conducted in a stainless steel environmental chamber that has been described previously [Shetter *et al.*, 1987]. The chamber is constructed of stainless steel and is 2 meters in length with an internal volume of 47 liters. The chamber is interfaced to a Bomem Fourier transform infrared spectrometer via a set of Hanst-type multi-pass optics which provided an optical pathlength of 37.6 m. Contents of the chamber were determined from infrared spectra recorded over the range 800-3900 cm^{-1} , with a spectral resolution of 1 cm^{-1} . Photolysis of gas mixtures in the chamber was carried out using the filtered (235-400 nm) output of a Xe-arc lamp.

The product yield experiments involved the photolysis of mixtures of Cl_2 and isoprene in 700-740 Torr of O_2/N_2 diluent. Typically four-eight irradiations of the chamber contents were conducted each being from 15-60 seconds. An IR spectrum was recorded following each irradiation. Products were quantified via spectral stripping routines or infrared absorption cross section data.

Chamber gases were also analyzed with GC/MS/FID techniques. Samples were withdrawn from the chamber via a 1/8" PFA Teflon tube and collected on a 1/16" Silcosteel trap held at $-145\text{ }^\circ\text{C}$. Typically, 10-25 mL at STP are trapped. The trap was then warmed and the contents injected onto a chromatographic column (Agilent Technologies, HP-624, 20 meter x 0.20 mm i.d., 1.1 μm film) installed in a custom oven enclosure. The compounds eluted into a mass spectrometer (Agilent Technologies, 5973). The mass spectrometer was run in full scan mode for all laboratory studies. The chromatographic column was held at $35\text{ }^\circ\text{C}$ for 1 minute then heated at $20\text{ }^\circ\text{C min}^{-1}$ to $120\text{ }^\circ\text{C}$ and was held there for a total run time of 8 minutes.

Chemicals were obtained from the following sources: isoprene (Aldrich Chemicals); Cl_2 (Matheson Gases); nitrogen (US Welding), and oxygen (US Welding). Isoprene was degassed by several freeze-pump-thaw cycles before use. Isoprene and Cl_2 were added to the reaction chamber via expansion from smaller calibrated volumes, while nitrogen and oxygen were added directly to the chamber.

The GC/MS/FID system was calibrated with gravimetrically prepared high pressure standards for isoprene, methacrolein, and methyl vinyl ketone. The standards were diluted to ranges applicable to the laboratory studies. Chloromethylbutenone and the isomers of chloromethylbutenal are not available commercially and the synthesis of these compounds does not result in a sufficiently pure form of the compounds. We therefore chose to use the technique of effective carbon number with a flame ionization detector (FID) to quantify CMBO and the CMBA isomers for the laboratory studies [see for example: *Apel et al.*; 1998; *Jorgensen et al.*, 1990; *Riemer et al.*, 1998; *Scanlon and Willis*, 1985].

iii. Results and Discussion

Our studies involved the photolysis of mixtures of Cl_2 ($1.0\text{-}3.7 \times 10^{15}$ molecule cm^{-3}), isoprene in 700-740 Torr of synthetic air. The only products observable via IR spectroscopy were formaldehyde ($9.5 \pm 1.0\%$) and HCOCl ($5.1 \pm 0.7\%$). Simultaneous GC/MS/FID measurements showed the presence of the following compounds: methacrolein (MACR), methyl vinyl ketone (MVK), 2-methylenebutenal (MBA), 1-chloro-3-methyl-3-buten-2-one (CMBO) and three of the four possible isomers of chloromethylbutenal (CMBA1, CMBA2, and CMBA3) (see Figure 4). The mass spectra of the compounds we chose to focus on as tracers of Cl chemistry in Houston CMBO and one isomer of the 3 CMBA isomers, CMBA1 are shown in Figure 5.

The product formation as a function of isoprene loss is shown in Figure 6. Based upon these data we calculated product yields which are presented in Table 2. Total product yield from these experiments is very low, approaching only 20% for the products measurable by GC/MS. In fact, the yields of the two products we quantified in Houston during TexAQS 2000 were only 5.2% for CMBO and 5.1% for CMBA1. We have no other data to compare with in this instance. Although the results of *Nordmeyer et al.* [1998] show the same products being formed, absolute product yields for each product are not given; they only state "the sum of the products gives 77% of the total chromatographic peak areas of the products" and that "CMBO comprises 28% of the peak areas for CMBO and the CMBA isomers". Hence,

there is some uncertainty in the yields of CMBO and CMBA1. Considering the uncertainties in this yield and the effects these uncertainties have on interpretation of the field investigation data, we will be reinvestigating this reaction in the laboratory during July 26-August 1, 2001. The results from this study will be incorporated into an amended final report to be submitted to TNRCC. However, the currently available yield data shown in Table 2 will be used in interpretation of the TexAQs 2000 field data from the LaPorte airport for this document.

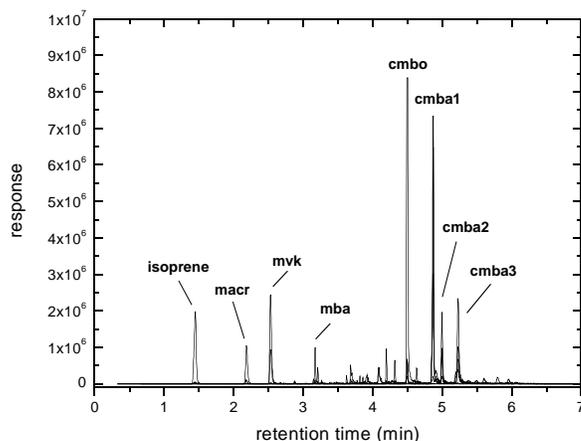


Figure 4. Total ion chromatogram of a chamber study sample of isoprene + Cl. showing the reaction products methacrolein (MACR), methyl vinyl ketone (MVK), 2-methylenebutenal (MBA), chloromethylbutenone (CMBO), and 3 isomers of chloromethylbutenal (CMBA1, CMBA2, CMBA3). Of the compounds unique to the isoprene + Cl reaction only CMBO and CMBA1 were quantified during the field portion of the study.

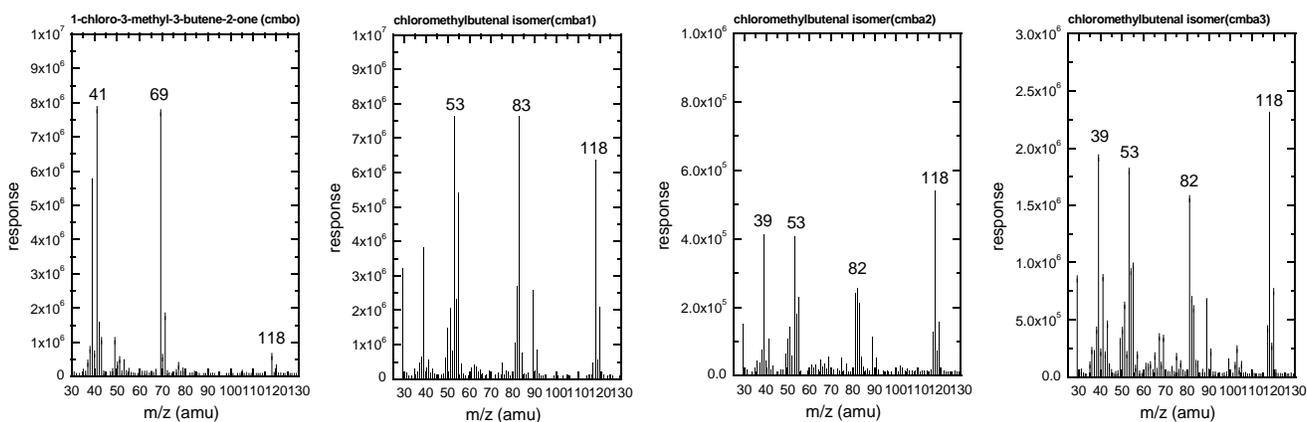


Figure 5. Mass spectra of the most abundant unique reaction products from isoprene + Cl: chloromethylbutenone (CMBO), and 3 isomers of chloromethylbutenal (CMBA1, CMBA2, CMBA3). Note the similarities in the mass spectra for the 3 isomers of CMBA. These similarities and the lack of these compounds in the pure form makes the exact structural identification extremely difficult.

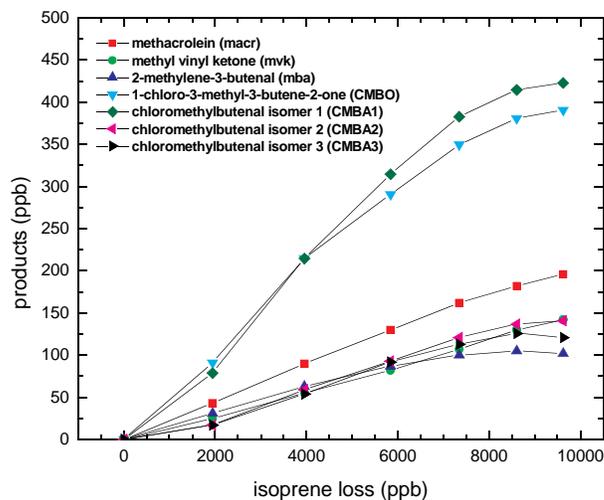


Figure 6. Product data for the isoprene + Cl reaction showing the formation of select products as a function of isoprene loss.

Table 2. Product yields from the isoprene + Cl reaction.*

Compound	Yield \pm s.d. (%)
methacrolein (MACR)	2.2 \pm 0.1
methyl vinyl ketone (MVK)	1.4 \pm 0.1
2-methylene-3-butenal (MBA)	1.4 \pm 0.2
1-chloro-3-methyl-3-butene-2-one (CMBO)	4.7 \pm 0.5
chloromethylbutenone isomer 1 (CMBA1)	4.9 \pm 0.6
chloromethylbutenone isomer 2 (CMBA2)	1.4 \pm 0.3
chloromethylbutenone isomer 3 (CMBA3)	1.3 \pm 0.2

*Only products measured by GC/MS/FID techniques are shown.

b. Field Studies - LaPorte Municipal Airport

i. Background

We conducted our field component of the experiment at the LaPorte Municipal Airport (29.699 °N, 95.064 °W) which is located southeast of the Houston Ship Channel area. The site is located in an ideal location to investigate Cl chemistry due to its proximity to the ship channel and the prevailing wind patterns. While the bulk of Cl₂ emissions occur in the Ship Channel, there are additional emission sources to the southeast of the LaPorte site (Figure 7). Biogenic isoprene emissions that are in close proximity to the field site are located predominantly to the north-northwest and adjacent to the Ship Channel (Figure 8). Under wind regimes from the northwest, freshly emitted isoprene will pass through the Ship Channel. We observed anthropogenic sources of isoprene under certain circumstances. Chlorine atom chemistry is likely to occur when molecular chlorine is emitted from anthropogenic sources and is photolyzed forming atomic chlorine, which then reacts with hydrocarbons.

The principal goal of our field studies was to determine if Cl chemistry is occurring in the Houston area and to what degree it serves as a precursor to the numerous ozone exceedences in that region. We made measurements over the period August 12, 2000 to September 12, 2000. During this period, we made measurements almost continuously, except for instances of instrument failure. At several times during the measurement campaign we observed the compounds CMBO and CMBA giving evidence for the presence of chlorine atom chemistry in Houston, Texas.

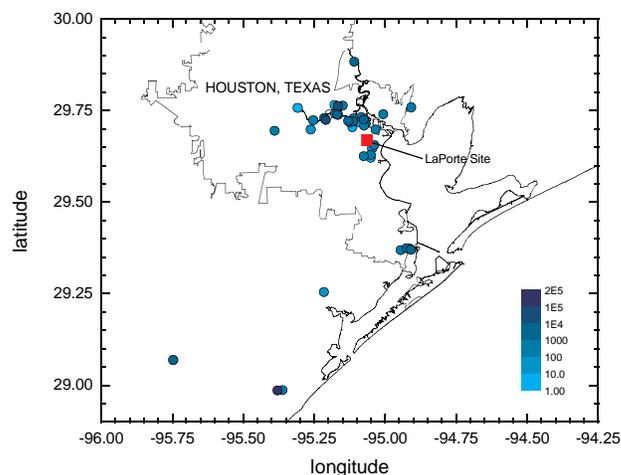


Figure 6. Cl₂ emission map for the Houston, Texas region showing the locations and magnitude of the emissions. Scale is in pounds of Cl₂ emitted. (Data source - <http://www.epa.gov/tri>)

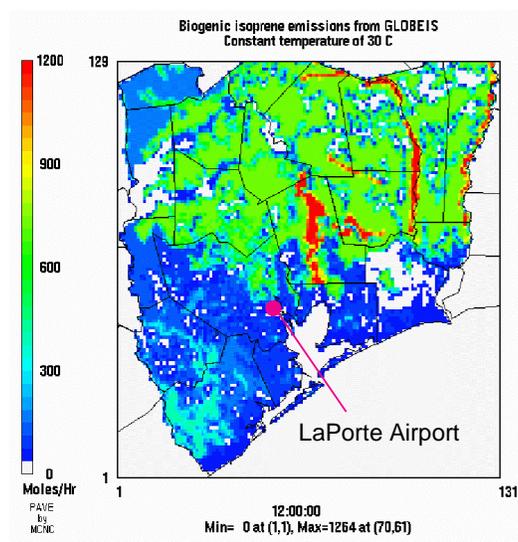


Figure 7. Biogenic isoprene emission map for the areas surrounding Houston, Texas showing the magnitude of the emissions. The scale is in moles isoprene emitted per hour. (Data source - <http://www.utexas.edu/research/ceer/texaqs/images/bioisoprene.gif>)

ii. Experimental Methods

As part of the TexAQS 2000 program, we developed a concentration technique, which allowed for the enrichment of approximately 0.5 liters of ambient air and consequently, the analysis of a series of compounds specific to isoprene chemistry. We focused on the following compounds: isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), chloromethylbutenone (CMBO) and chloromethylbutenal (CMBA). The last two compounds are produced exclusively from the reaction of isoprene + Cl. We quantified all the compounds with mass spectrometry.

The analytical system was contained within a small trailer adjacent to a walk-up platform with a glass manifold. The analytical system was a two-trap design and was custom fabricated. The trapping system used glass beads and carbon sorbents in consecutive traps, and an open tubular cryofocusing trap. All traps and sample lines internal to the concentration system were constructed of fused-silica lined stainless steel (Restek Corporation or Entech Instruments). A schema of the system is shown in Figure 8.

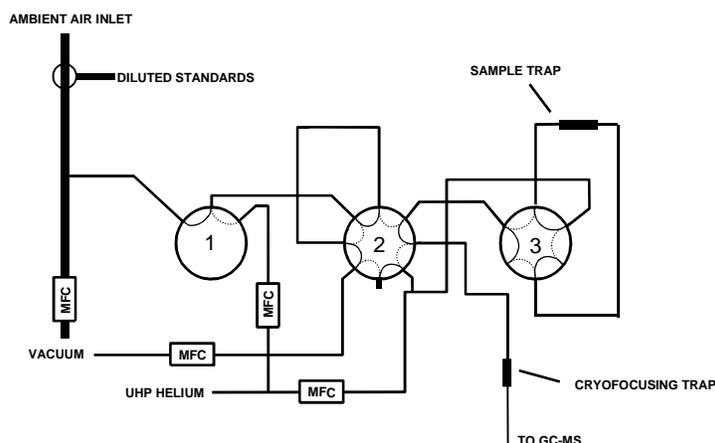


Figure 8. Schema of the analytical system used during the field component of the study.

Ambient air samples were initially drawn from a continuously flushed glass manifold into the concentration system through the sample trap which was held at 20 °C. Sample flow rate through the sample trap was 100 mL min⁻¹ and was measured by a mass flow controller. Sampling time was approximately 5 minutes. The trap was then warmed to 250 °C and backflushed with helium onto a cryofocusing trap where the compounds were trapped at -165 °C. Injection onto the chromatographic column was done by rapidly heating the cryofocuser to 100 °C.

The sample trap consisted of a 25 cm x 0.3175 cm o.d. silcosteel tube packed with 70/80 glass beads, Carbopack C, Carbopack B, and Carboxen 1000 (Supelco, Inc.). The cryofocusing trap was constructed of an open section of 0.74 mm o.d. fused silica lined stainless steel capillary tubing. Transfer lines between the traps and the packed column were 0.159 cm o.d. fused silica lined stainless steel.

Chromatography was performed on a Hewlett-Packard 5890 Series II gas chromatograph. A 60 meter HP-624 column, 0.25 mm i.d. and 1.4 mm phase thickness (Agilent Technologies) was used for compound separation. The temperature program consisted of 35 °C for 5 minutes followed by a temperature ramp of 10 °C min⁻¹ to 200 °C and held at that temperature for 3.5 minutes. Carrier gas was ultra high purity helium passed through a conditioning trap to remove residual moisture, oxygen, hydrocarbons and carbon dioxide impurities. Carrier flow was 2.7 mL min⁻¹ controlled by a Tylan 280 mass flow controller.

Detection was by mass spectrometry used in single ion monitoring mode which allowed very low detection limits. The following ions were detected and used for quantification: 67, isoprene; 70, methacrolein; 55, methyl vinyl ketone; 69, CMBO; and 118, CMBA (Figure 9).

Known mixtures were prepared to calibrate the analytical system. Due to the reactivity of several of the compounds, it was imperative that standardization takes place through the entire system. The standards consisted of a high pressure gravimetrically prepared mixes for isoprene, methacrolein and methyl vinyl ketone. Calibration gases for CMBO and CMBA were originally to be prepared gravimetrically from the synthesized compounds. Unfortunately, the compounds were not pure enough to

warrant gravimetric preparation. Thus, the calibration mixes for CMBO and CMBA were prepared in the laboratory chamber as described earlier. The contents of the chamber were drawn into an evacuated, cleaned and passivated aluminum cylinder with a stainless steel valve. The cylinder was then filled with high purity nitrogen to a pressure of 1800 psi. The resulting mix was then calibrated through effective carbon number techniques (see above). Estimated accuracy of the calibration gases is $\pm 2-3\%$ for isoprene and $\pm <5\%$ for methacrolein and methyl vinyl ketone. The estimated accuracy for CMBO and CMBA is higher at $\pm 20-25\%$ based on comparisons of other halogenated compounds and the effective carbon number technique. Calibration gases were diluted into humidified zero air that was produced by passing ambient air over a platinum on alumina catalyst bed at $350\text{ }^{\circ}\text{C}$. The diluted standard was passed through the entire sampling and analytical system with except for the glass manifold. The standards were diluted to the concentration ranges present in the atmosphere. Detection limits for isoprene was less than 1 ppt; methacrolein and methyl vinyl ketone, 5-9 ppt; CMBO, approximately 1-3 ppt; and CMBA, approximately 1 ppt. Slight variations did occur because of changing noise levels of the system.

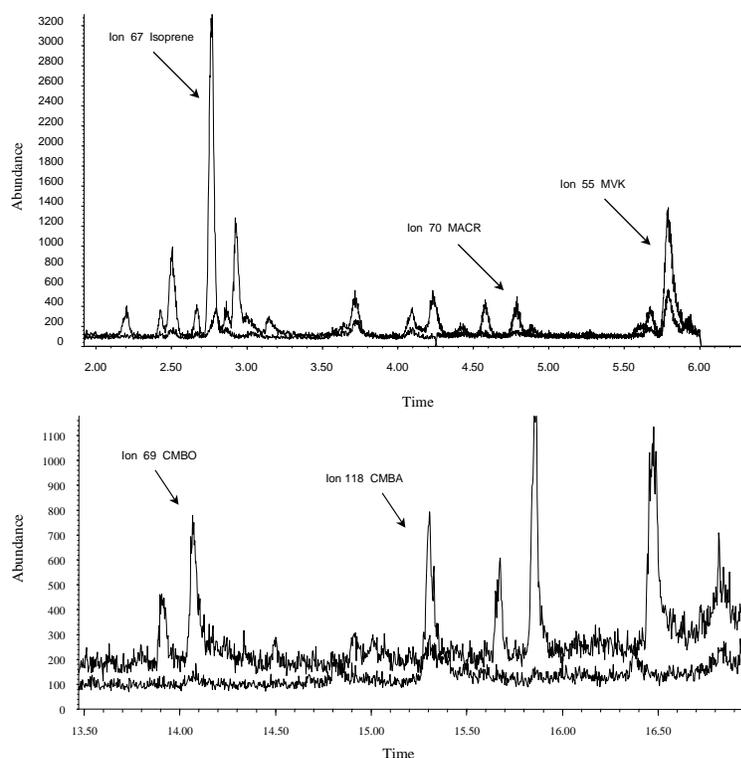


Figure 9. Representative ion chromatograms showing the compounds of interest during the current study.

iii. Results and Discussion

Time series for the complete dataset are shown in Figures 10-15. Additionally, meteorological factors and ozone are included on the plots. A total of sixteen chlorine chemistry episodes occurred during the field experiment. Generally, we observed evidence of active chlorine oxidation on days when the winds were from the north and north-northwest or directly from the Houston Ship Channel. During these episodes, winds were usually less than $2-3\text{ meters sec}^{-1}$. Episodes also occurred under other circumstances with winds from the east and south. During elevated wind velocities, the Cl chemistry tracers were usually not observed. This is likely due to more rapid mixing and dilution of the oxidant plumes compared to more stagnant conditions.

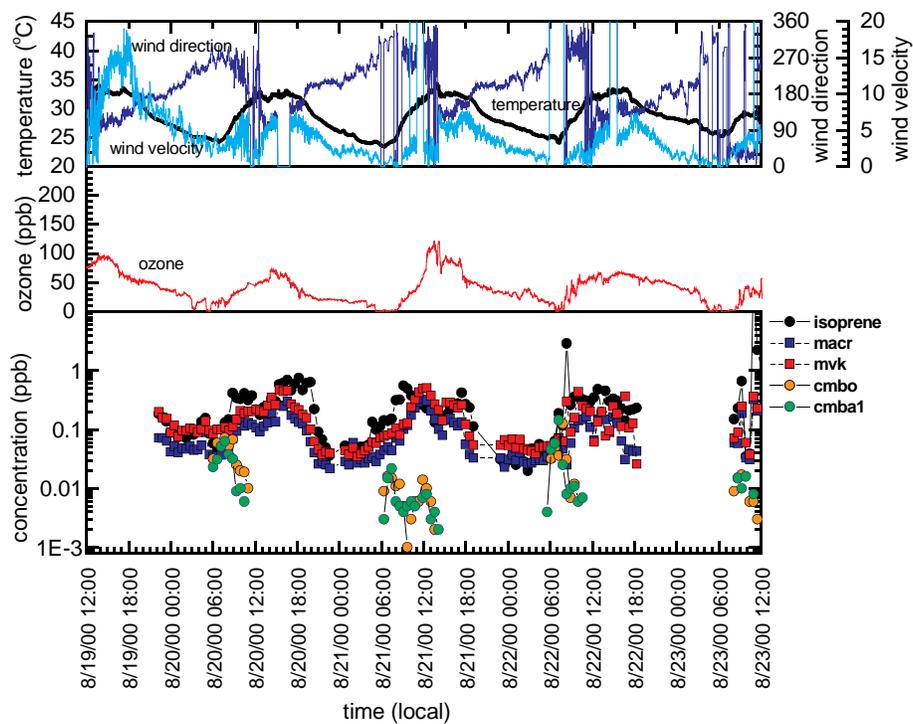


Figure 10. Time series data for August 19, 2000 12:00 - August 23, 2000 12:00 for meteorological parameters, ozone, isoprene and isoprene reaction products. Four episodes showing active Cl chemistry are apparent.

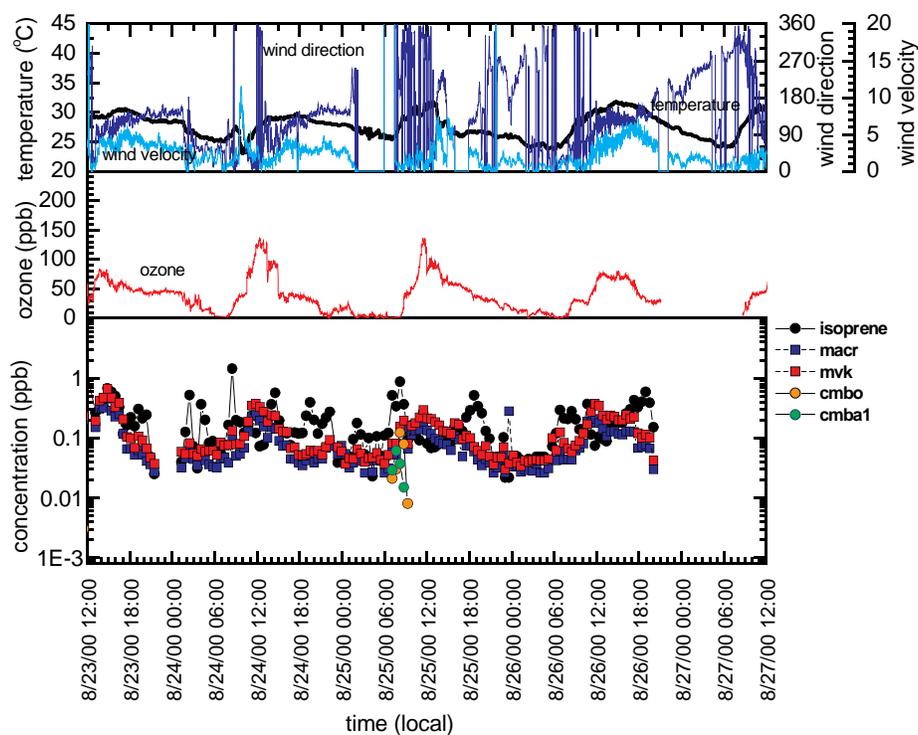


Figure 11. Time series data for August 23, 2000 12:00 - August 27, 2000 12:00 for meteorological parameters, ozone, isoprene and isoprene reaction products. One episode of active Cl chemistry is apparent. Meteorological and ozone data are provided courtesy of Eric Williams (NOAA).

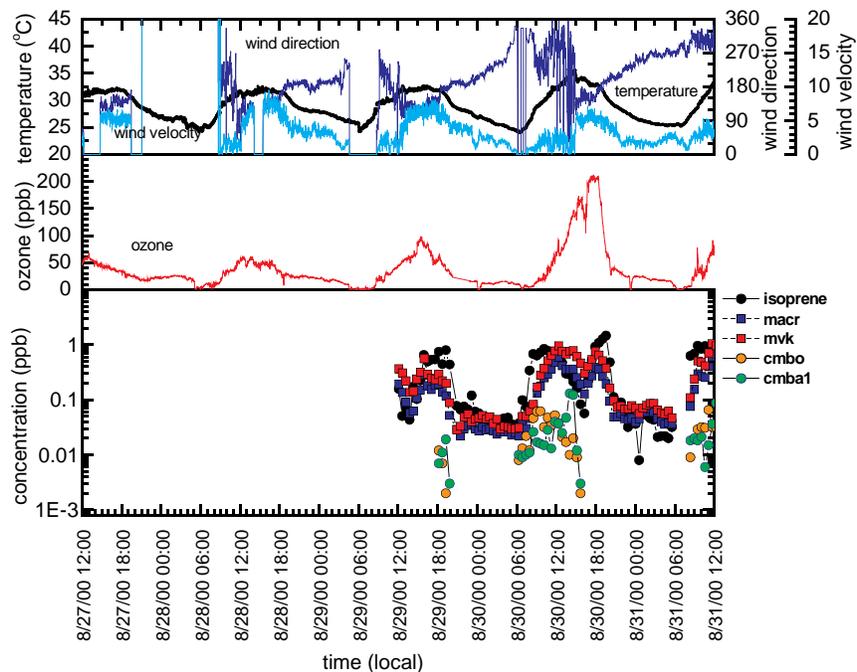


Figure 12. Time series data for August 27, 2000 12:00 - August 31, 2000 12:00 for meteorological parameters, ozone, isoprene and isoprene reaction products. Data from the 27th and 28th of August for isoprene and related compounds are missing due to equipment failure. Three episodes of active Cl chemistry are apparent.

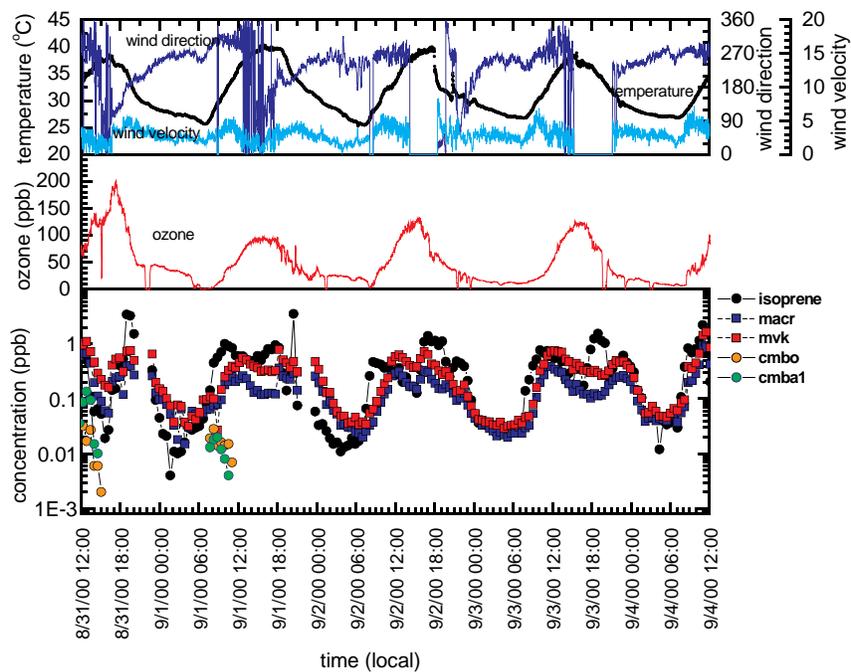


Figure 13. Time series data for August 31, 2000 12:00 - September 4, 2000 12:00 for meteorological parameters, ozone, isoprene and isoprene reaction products. Two episodes of active Cl chemistry are apparent.

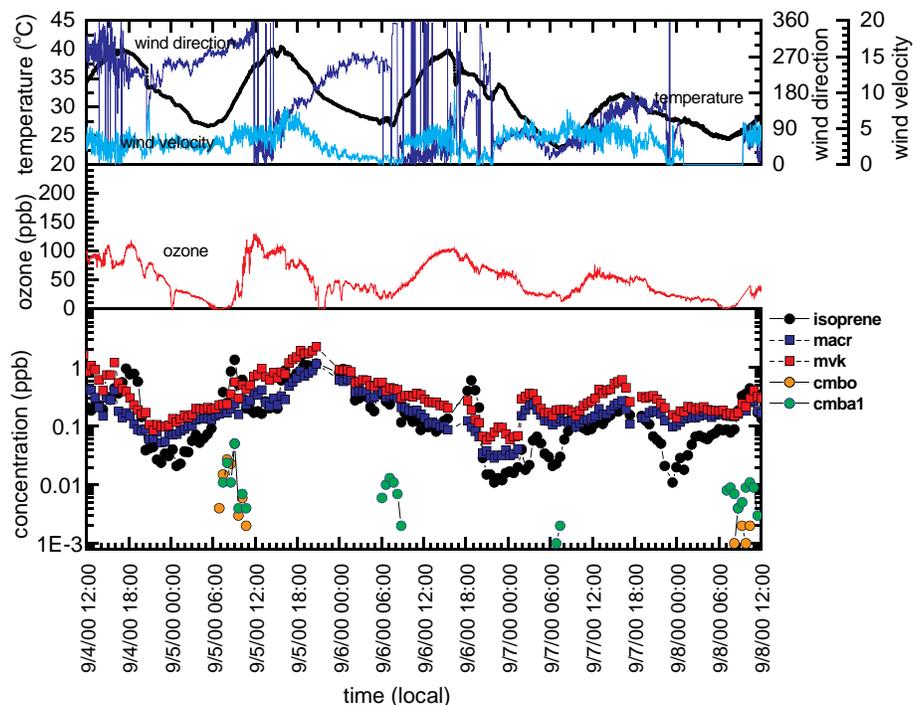


Figure 14. Time series data for September 4, 2000 12:00 - September 8, 2000 12:00 for meteorological parameters, ozone, isoprene and isoprene reaction products. Four episodes of active Cl chemistry are apparent.

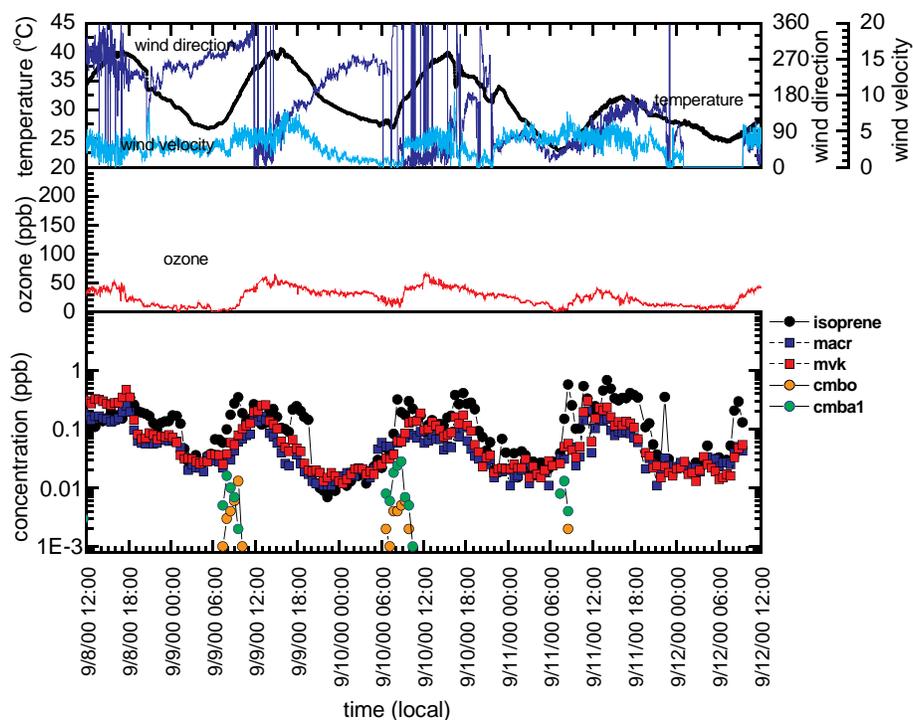


Figure 15. Time series data for September 8, 2000 12:00 - September 11, 2000 12:00 for meteorological parameters, ozone, isoprene and isoprene reaction products. Three episodes of active Cl chemistry are apparent.

Each of the episodes was characterized in terms of its Cl concentration using steady state calculations. The relationships we used to calculate the concentrations of Cl are found in Figure 16. We used the concentrations of isoprene, CMBO, CMBA, and OH to determine the Cl concentrations for each of the Cl chemistry episodes. The results are shown in Table 3. The range of Cl concentrations calculated from our observed CMBO and CMBA concentrations varied from below our detection limit, which is approximately $1\text{-}5 \times 10^3$ Cl atoms cm^{-3} , to 3.3×10^5 Cl atoms cm^{-3} . While several ozone exceedences were preceded by Cl chemistry events, there were also chlorine events that occurred during periods without elevated ozone levels.

We found that our 0-dimensional box model was not adequate to characterize the Cl oxidation process in Houston and we are currently implementing a 2-dimensional chemical model to further characterize our field data.

$$[\text{CMBO}]_{\text{ss}} = \frac{[\text{isoprene}][\text{Cl}]k_{\text{Cl}} \times 0.047}{[\text{Cl}]k_{\text{Cl}} + [\text{OH}]k_{\text{OH}}}$$

$$[\text{CMBA}]_{\text{ss}} = \frac{[\text{isoprene}][\text{Cl}]k_{\text{Cl}} \times 0.049}{[\text{Cl}]k_{\text{Cl}} + [\text{OH}]k_{\text{OH}}}$$

$$[\text{Cl}] = \frac{[\text{CMBO}][\text{OH}]k_{\text{OH}}}{([\text{isoprene}]k_{\text{Cl}} \times 0.047) - [\text{CMBO}]k_{\text{Cl}}}$$

$$[\text{Cl}] = \frac{[\text{CMBA}][\text{OH}]k_{\text{OH}}}{([\text{isoprene}]k_{\text{Cl}} \times 0.047) - [\text{CMBA}]k_{\text{Cl}}}$$

Figure 16. Relationships used to describe the steady state concentration of Cl in relation to CMBO and CMBA at the LaPorte airport site.

Table 3. Periods of observable Cl chemistry and the calculated Cl concentrations during those periods

Date/Time local	[Isoprene] ppb median	[CMBO] ppb median	[CMBA] ppb median	[OH] 10^6 molecules cm^{-3} median	[Cl] 10^5 atoms cm^{-3} median*
8/20 06:02-11:00	0.224	0.041	0.026	3.98	2.2 3.3
8/21 06:21-14:05	0.279	0.008	0.006	4.25	0.82 1.2
8/22 05:34-10:34	0.464	0.029	0.032	2.90	0.96 1.9
8/23 08:10-11:29	5.32	0.008	0.007	2.78	0.04 0.06
8/25 07:06-09:18	0.437	0.052	0.028	2.47	1.1 1.5
8/29 18:09-19:48	0.607	0.005	0.010	2.87	0.19 0.65
8/30 06:19-15:42	0.430	0.028	0.032	3.83	1.3 2.6
8/31 08:24-15:03	0.569	0.024	0.037	4.34	1.2 2.7
9/1 07:43-11:03	0.664	0.016	0.012	2.52	0.42 0.62
9/5 06:52-10:43	0.546	0.017	0.014	2.90	0.60 0.94
9/6 06:04-08:49	0.267	bdl	0.008	2.53	bdl 0.93
9/7 06:54-07:27	0.026	bdl	0.0015	1.45	bdl 0.80
9/8 07:09-11:33	0.237	0.001	0.007	2.87	0.10 1.0
9/9 07:24-10:09	0.191	0.005	0.007	2.83	0.51 1.2
9/10 06:35-10:26	0.172	0.003	0.012	3.38	0.44 0.37
9/11 07:27-08:33	0.254	0.0006	0.008	1.51	0.03 0.60

bdl - below detection limit; *first column is calculated from the median CMBO concentration and the second is calculated from the CMBA concentration. [Cl] is calculated using the relationships shown in Figure 16. Rate coefficients are from *Atkinson* [1994] and *Orlando et al.*, [in preparation, and references therein]; OH data is from B. Brune et al. Pennsylvania State University.

III. Data Status and Availability

The final dataset, in proper NARSTO format, was submitted to both the NOAA Aeronomy Lab FTP site and the TNRCC data archive. The data set consisted of ambient measurements from the LaPorte airport site discussed above and canister samples that were analyzed in support of ambient air chamber studies performed by P. Tanaka and D. Allen (U. Texas).

IV. References

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