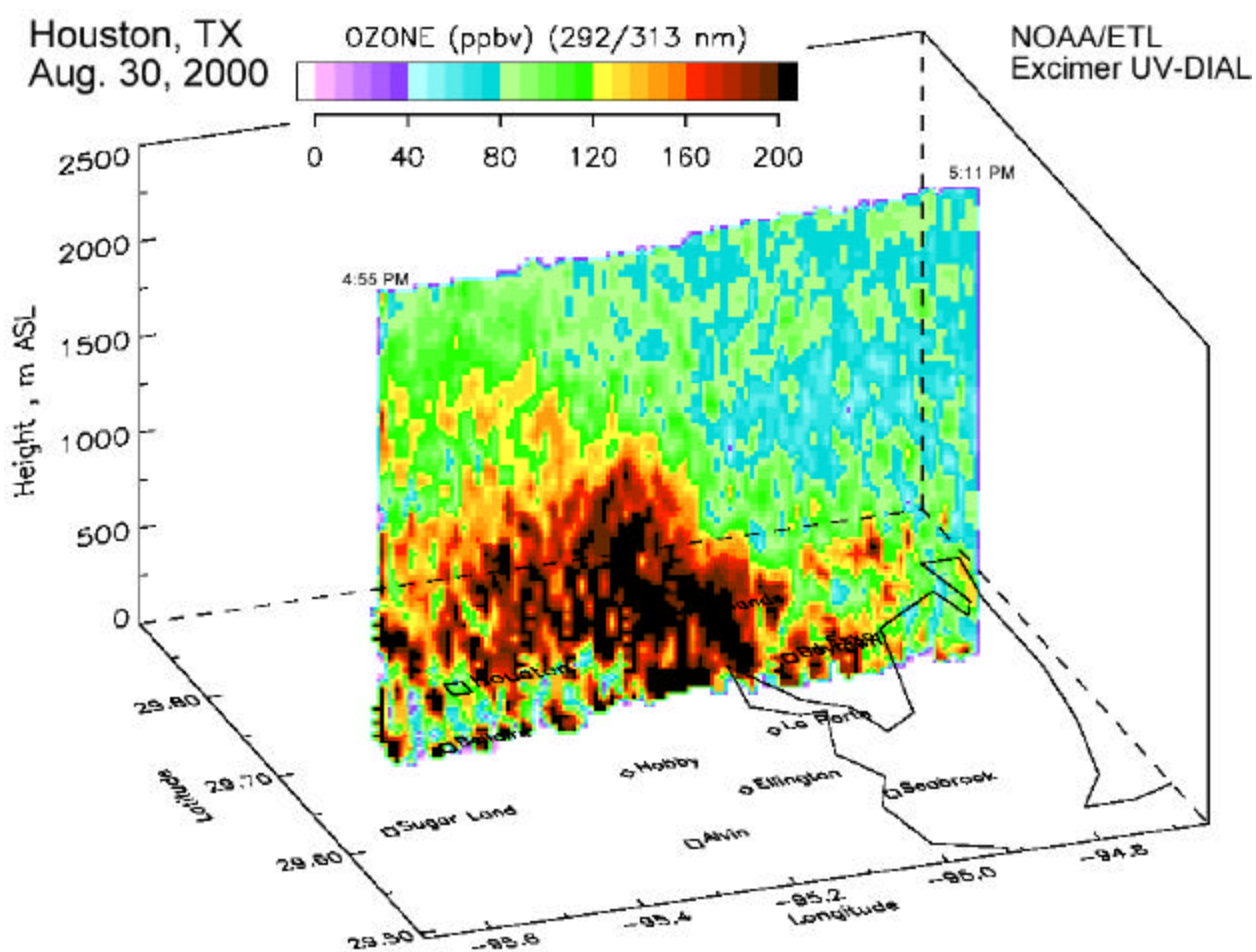# ACCELERATED SCIENCE EVALUATION of OZONE FORMATION IN THE HOUSTON-GALVESTON AREA:

Atmospheric Chemistry

Working Group

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Summary

This document summarizes the status of key issues in atmospheric chemistry associated with the Accelerated Science Evaluation of ozone formation in the Houston-Galveston area. Understanding the issues in atmospheric chemistry is critical because ozone, the focus of the evaluation, is not emitted to the atmosphere directly; rather, it is formed by chemical reactions that occur in the atmosphere. Understanding which reactions lead to ozone formation is essential if effective ozone reduction strategies are to be developed.

A major goal of the Accelerated Science Evaluation is providing policy relevant findings that can inform the Texas Natural Resource Conservation Commission's decisions on air quality management in the Houston-Galveston area. Photochemical air quality models are generally used to quantitatively evaluate the potential effectiveness of policies. Therefore, the accelerated science evaluation focusses on both a qualitative understanding of the key issues in atmospheric chemistry and the ability of current quantitative models to describe the chemistry.

The key issues to be addressed are:

1. *Can simplified chemical mechanisms currently used in photochemical air quality modeling qualitatively predict the rapid and efficient ozone formation observed in southeast Texas?*

2. *Are there chemical mechanisms contributing to ozone formation in southeast Texas that are not adequately represented in the current models?*

3. *Which hydrocarbon species are the most significant contributors to ozone formation?*

4. *What magnitudes of reactive hydrocarbon and NO_x emissions are necessary to produce the ozone formation rates and ozone concentrations observed in southeast Texas?*

5. *Are the chemistries of dominant hydrocarbon species adequately represented in current models of ozone formation chemistry?*

Findings in each of these areas are summarized below.

1. Can simplified chemical mechanisms currently used in regional air quality modeling qualitatively predict the rapid and efficient ozone formation observed in southeast Texas?

Finding: The Carbon Bond Version IV (CB-IV) mechanism, and other simplified chemical mechanisms commonly used in regional photochemical modeling, are capable of qualitatively replicating rapid ozone formation caused by high concentrations of reactive hydrocarbons.

2. Are there chemical mechanisms contributing to ozone formation in southeast Texas that are not adequately represented in the current models?

Findings: Chemistries that may be contributing to ozone formation in southeast Texas, but that have not historically or are not currently represented in models, include the reactions of atomic chlorine, night-time production of free radicals, and heterogeneous reactions on particle surfaces. Ongoing studies suggest that chlorine chemistry enhances ozone formation in Houston, and that local peak enhancements are likely in the range of 5-15 ppbv ozone. Regional enhancements are likely in the range of 2-4 ppbv. Emission inventories and chemical reaction mechanisms that account for this chemistry have been incorporated into a version of the photochemical models used by the State. No work is currently underway to assess the roles of heterogeneous chemistry or night-time production of free radicals and it is unclear how important these processes are.

3. Which hydrocarbon species are the most significant contributors to ozone formation?

Findings: High concentrations of light alkanes, alkenes, and aromatics are all observed during episodes of rapid and efficient ozone formation. The alkenes and aromatics (especially ethene, propylene, toluene and xylenes) have the potential to react rapidly, enhancing ozone formation.

Concentrations of hydrocarbons tend to be slightly higher on ozone episode days, compared to non-episode days, however, the composition of the hydrocarbons on episode and non-episode days is virtually identical. Further, while the median magnitude of hydrocarbon concentrations has decreased in the last decade, with a few minor exceptions (isopentane, in particular), the concentration ratios of atmospheric hydrocarbons observed in Houston have remained consistent for a decade or more.

4. What magnitudes of reactive hydrocarbon and NO_x emissions are necessary to produce the ozone formation rates and ozone concentrations observed in southeast Texas?

Findings: Sensitivity analyses performed using a simple photochemical "box" model, designed to replicate Houston conditions, indicate that episodic emissions of approximately 100 pounds of highly reactive hydrocarbons can cause localized (1 km^2 area) increases in ozone concentration of approximately 50 ppb. Dilution of these emissions over a larger area does not necessarily reduce the mass of ozone formed, although it does reduce peak concentrations.

5. *Are the chemistries of dominant hydrocarbon species adequately represented in current models of ozone formation chemistry?*

Findings: Sensitivity analyses performed using a simple photochemical "box" model, designed to replicate Houston conditions, indicate that the ozone formation potentials of episodic releases of hydrocarbons exhibit complex behaviors that differ from compound to compound. It is not yet clear whether these differences are captured by current simplified chemical mechanisms. Ongoing work will clarify this issue.

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Background

Photochemical smog is a complex mixture of constituents that are emitted directly to the atmosphere (primary pollutants) and constituents that are formed by chemical and physical transformations that occur in the atmosphere (secondary pollutants). Ozone, along with many other constituents of photochemical smog (such as hydrogen peroxide, peroxyacetyl nitrate or PAN, aldehydes and nitric acid) are secondary pollutants, and as a consequence, understanding the chemical and physical transformations that occur in the atmosphere is crucial to understanding ozone formation.

The chemical and physical processes that lead to ozone formation in the lower atmosphere have been studied extensively. The chemistry that leads to ozone formation is generally initiated by the photolysis of nitrogen dioxide. In the presence of sunlight, hv, NO_2 photolyzes, producing NO and atomic oxygen. The atomic oxygen reacts with O_2 to produce O_3

$$NO_2 + hv \rightarrow NO + O \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3}$$

where M is any third body molecule (most likely N_2 or O_2 in the atmosphere) that remains unchanged in the reaction. This process produces a steady-state concentration of O_3 that is a function of the concentrations of NO and NO_2, the solar intensity, and the temperature.
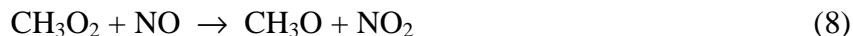
$$[O_3] = k\ [NO_2]/[NO]$$

where $[O_3]$, $[NO_2]$, and $[NO]$ are the atmospheric concentrations of ozone, nitrogen dioxide and nitric oxide and k is a constant dependent on temperature and solar intensity. Although these reactions are extremely important in the atmosphere, the steady-state O_3 produced by the reactions of nitrogen oxides alone is much lower than the observed concentrations, even in clean air. In order for ozone to accumulate, there must be a mechanism that converts NO to NO_2 without consuming a molecule of O_3, as does reaction 3. Reactions involving hydroxyl radicals and hydrocarbons constitute such a mechanism. In clean air OH may be generated by

$$O_3 + hv \rightarrow O_2 + O(^1D) \tag{4}$$

$$O(^1D) + H_2O \rightarrow 2\ OH \tag{5}$$

where $O(^1D)$ is an excited form of an O atom that is produced from a photon at a wavelength between 280 and 310 nm. The $O(^1D)$ most often collides with O_2 or N_2, and the collision dissipates the excess energy of the excited state, producing aground state atomic oxygen (O), which can then produce ozone through reaction 2. The $O(^1D)$ can

also react with water vapor, as shown in reaction 5, producing hydroxyl radical (OH). This seed OH can then participate in a chain reaction with hydrocarbons. The reactions with methane are shown below. (Note that methane is used in this example because of the simplicity of the reactions – methane is much less reactive than many other hydrocarbons and is normally not a significant contributor to smog formation chemistry)

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{6}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{7}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{8}$$

One of the outcomes of reactions 6-8 is the conversion of NO into NO_2. NO_2 can then photolyze producing O_3 (eqs.1 and 2) and less NO is available to scavenge the ozone (eq. 3), resulting in a higher steady state ozone concentration. In addition, the CH_3O radical continues to react:

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{9}$$

$$HO_2 + NO \rightarrow NO_2 + OH \tag{10}$$

Reactions 9 and 10 result in an additional NO to NO_2 conversion and the regeneration of the hydroxyl radical.

Further, the formaldehyde photodissociates:

$$HCHO + h\nu \rightarrow H_2 + CO \tag{11}$$

$$\rightarrow HCO + H \tag{12}$$

$$HCO + O_2 \rightarrow HO_2 + CO \tag{13}$$

$$H + O_2 \rightarrow HO_2 \tag{14}$$

and the HO_2 from both equations 13 and 14 can form additional NO_2. Moreover, CO can be oxidized:

$$CO + OH \rightarrow CO_2 + H \tag{15}$$

and the H radical can form another NO_2 (eqs. 14 and 10). Thus, the oxidation of one CH_4 molecule is capable of producing three O_3 molecules and two OH radicals. The routes involve both the direct reactions of methane and the reactions of its oxidation products.

Finally, the chain reactions can be terminated by radical-radical recombination, or by radical reactions with more stable species. Two examples are given below.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{16}$$

$$OH + NO_2 \rightarrow HNO_3 \tag{17}$$

Examination of reactions 6-17 reveals that the chemical sequence initiated by the reaction of hydroxyl radical with a hydrocarbon can lead to the enhancement of ozone concentration, by converting NO to NO_2, and the generation of additional free radicals. The chemistry is complex and depends on the reactions of both the original hydrocarbon species and its reaction products. Because of the complexity of the reactions it is common to characterize the ozone formation potential of hydrocarbons using parameters such as those shown in Table 1. These parameters are the rate of reaction of a hydrocarbon with hydroxyl radical, and the incremental reactivity of the hydrocarbon.

The rate of reaction of the hydrocarbon with hydroxyl radical characterizes the rate at which the initial reaction (analogous to reaction 6) occurs, and is expressed in Table 1 as the rate constant for the bimolecular reaction with hydroxyl radical, in units of cm^3 $molecule^{-1} s^{-1}$. In general, internally bonded olefins are the most reactive, followed in decreasing order by terminally bonded olefins, multialkyl aromatics, monoalkyl aromatics, C_5 and higher paraffins, C_2-C_4 paraffins, benzene, acetylene, and ethane (Atkinson, 1989, 1994, 1997).

The incremental reactivity (Carter, 1994, 2001) characterizes the ozone formation potential of the hydrocarbon and all of its reaction products. It is expressed as grams of ozone formed per gram of hydrocarbon added to a mixture and is determined by adding an incremental amount of hydrocarbon to a base mixture of hydrocarbons typically found in urban areas, and determining the incremental amount of ozone formed. This incremental reactivity depends on the composition of the base mixture. The values shown in Table 1 are the maximum values of the incremental reactivities for each of the hydrocarbons and are based on average base hydrocarbon compositions of urban atmospheres. Values tend to be highest for species that produce reaction products that are also highly reactive. (The material in pages 5 through this point has been drawn from Allen, 2002)

Table 1. Reactivities of VOCs (Atkinson, 1989, 1994, 1997; Carter, 1994, 2001)

Compound	Rate constant for reaction with $OH*10^{12}$ ($cm^3 molecule^{-1} s^{-1}$)	Incremental Reactivity (grams ozone formed per gram VOC added to a base mixture)
Methane	0.01	0.0139
Isopentane [78-78-4]	3.7	1.67
n-butane [106-97-8]	2.44	1.33
Toluene [108-88-3]	3.8	3.97
Propane [74-98-6]	1.12	0.56
Ethane [74-84-0]	0.254	0.31
n-pentane [109-66-0]	4.0	1.54
Ethene [74-85-1]	8.5	9.08
m-xylene [108-38-3]	20	10.61
p-xylene [106-42-3]	10	4.25
2-methylpentane [107-83-5]	5.3	1.80
Isobutane [75-28-5]	2.4	1.35
Propylene	26.3	11.58
Isoprene [78-79-5]	101	10.69

Ozone formation chemistry in southeast Texas

Data collected during the Texas Air Quality Study suggest that the processes that generate ozone in Houston are more rapid and efficient than in other urban areas. The rate of ozone formation is illustrated in Figure 1, which shows estimates of instantaneous rates of ozone formation (expressed in units of ppb/hr) based on measurements collected by an aircraft operated by Brookhaven National Laboratory. Figure 2 and Table 2 show that these rates of ozone production are 2 to 5 times higher than observed rates of ozone formation in Nashville, TN; New York, NY; Phoenix, AZ, and Philadelphia, PA (Kleinman, et al., 2002).

Figure 1a. Very rapid ozone formation (>50 ppb/hr) is observed in the Houston area, particularly in the industrial corridor north and northwest of Galveston Bay (Daum, 2001)
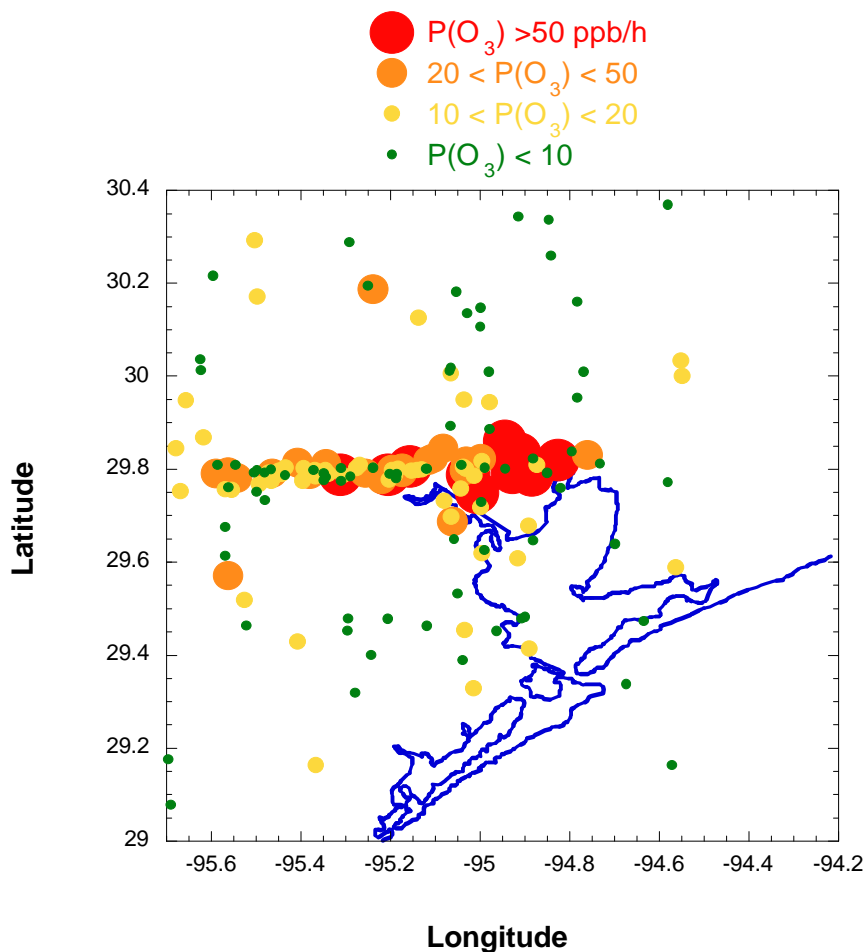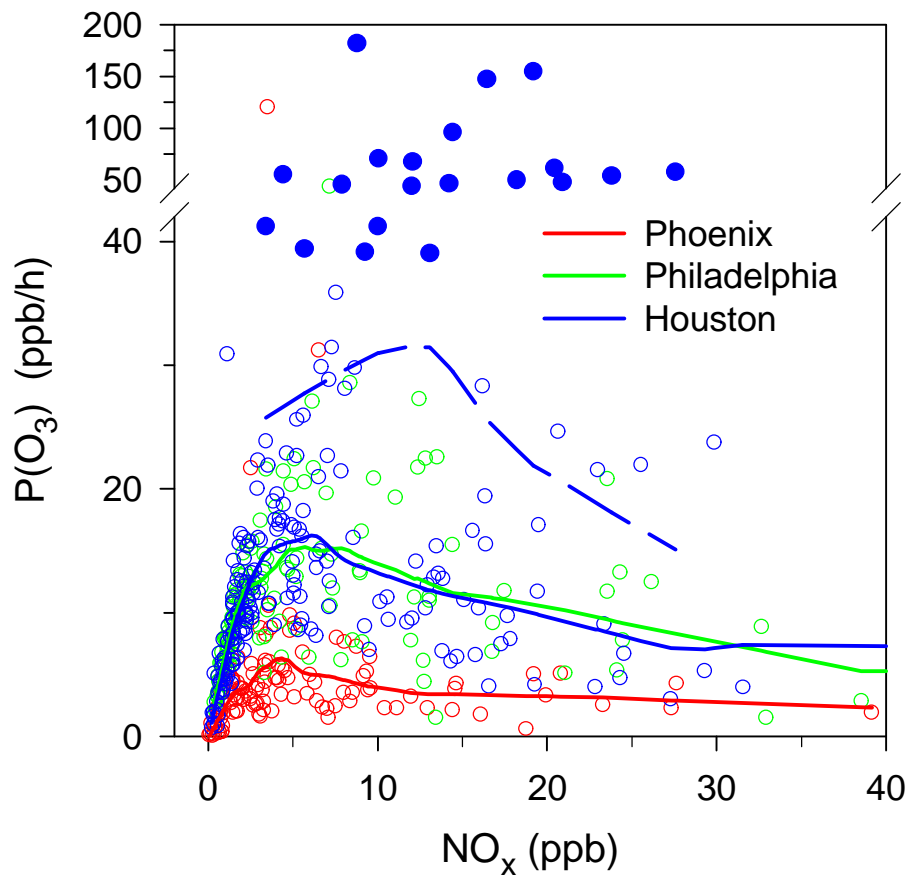
Figure 1b. Ozone productivities in U.S. cities as a function of NOx concentrations; ozone production rates observed in Houston are higher than those observed in other U.S. cities especially at high NO_x concentrations; note that virtually all of the reported ozone production rates above 40 ppb/hr are from Houston.
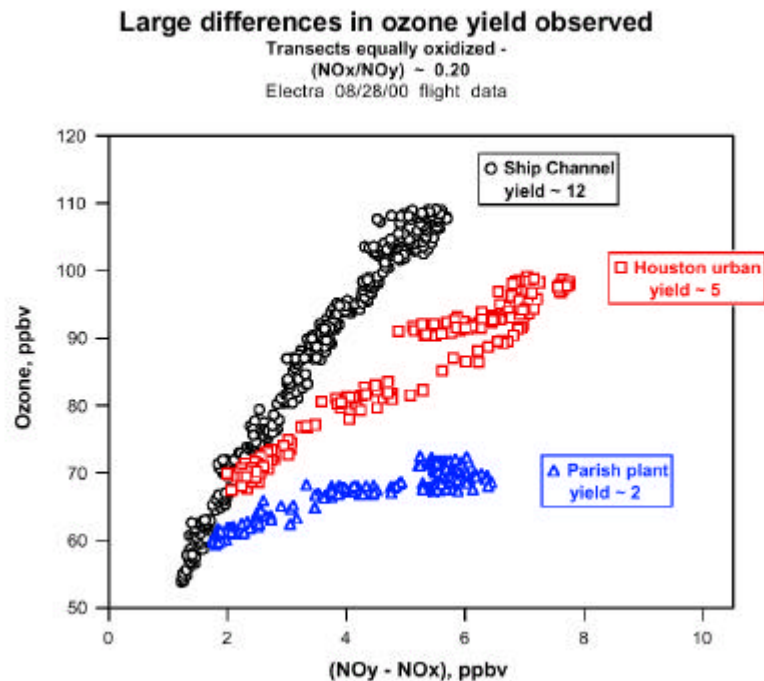
Table 2. Summary of O_3 monitoring data, aircraft O_3 observations, and calculated O_3 production rates for 5 cities, collected by the Brookhaven aircraft (Kleinman, et al., 2002)

City	Monitoring Data[1]		Aircraft Observations				CSS* Calculations		
	# Days O_3>120 ppb	Max. O_3 (ppb)	Dates (m/yy)	# flights	# flights O_3>120 ppb	Max. O_3 (ppb)	# Calc.	Median $P(O_3)$ (ppb h^{-1})	90th % $P(O_3)$ (ppb h^{-1})
Nashville	1	124	6/95 – 7/95	17	3	146	81	6.2	15.2
NYC	5	138	7/96	13	0	119	67	4.3	14.7
Phoenix	1	123	5/98 – 6/98	24	0	101	117	3.5	7.6
Philadelphia	2	154	7/99 – 8/99	20	1	147	131	11.3	22.3
Houston	38	225	8/00 – 9/00	18	9	211	206	11.3	39.1

[1] Monitoring data is for the entire year in which each field campaign was conducted and for regions that are approximately coincident with the aircraft sampling
*Constrained Steady State calculations of ozone production rate

Figure 2 (data collected by the National Oceanic and Atmospheric Administration during the summer of 2000) shows the ratio of ozone to reacted nitrogen oxides (NO_y-NO_x = NO_z) observed in plumes downwind of a power plant (the Parish facility in Fort Bend county), urban Houston, and the ship channel region.

Figure 2. Comparison of ozone productivities from data taken in power plant, urban and petrochemical plumes. The co-location of anthropogenic reactive VOC with NO_X leads to rapid ozone formation in very high yield [from Ryerson and Trainer, 2001].

Large differences in ozone yield observed
Transects equally oxidized -
(NOx/NOy) ~ 0.20
Electra 08/28/00 flight data

○ Ship Channel yield ~ 12
□ Houston urban yield ~ 5
△ Parish plant yield ~ 2

Ozone, ppbv

(NOy - NOx), ppbv

While the ozone productivities measured in the plume of the power plant and downwind of urban Houston are comparable to values measured in other North American cities, the high ozone productivity measured downwind of the ship channel is unprecedented (Ryerson, et al, 2000; Ryerson and Trainer, 2001). The highly efficient ozone production in the plumes originating from the Ship Channel has been attributed to high concentrations of hydrocarbons in the plumes.

The plumes exhibiting rapid and efficient ozone formation also tend to exhibit a complex spatial structure. Figure 3 shows the spatial structure of ozone concentrations as mapped by airborne LIDAR during the Texas Air Quality Study (TexAQS). The LIDAR measurements indicate that, over length scales as small as a few kilometers, ozone concentrations may vary by 50 ppb or more.

Figure 3. Downlooking LIDAR (Excimer UV-DIAL) ozone concentrations taken by the NOAA Environmental Technology Laboratory Aircraft flying west-to east and east-to-west transects over Houston on August 30, 2000. (Data have a 10 second time resolution and a 90 meter vertical resolution, flying at 60-70 m/s) (Senff, et al., 2001)
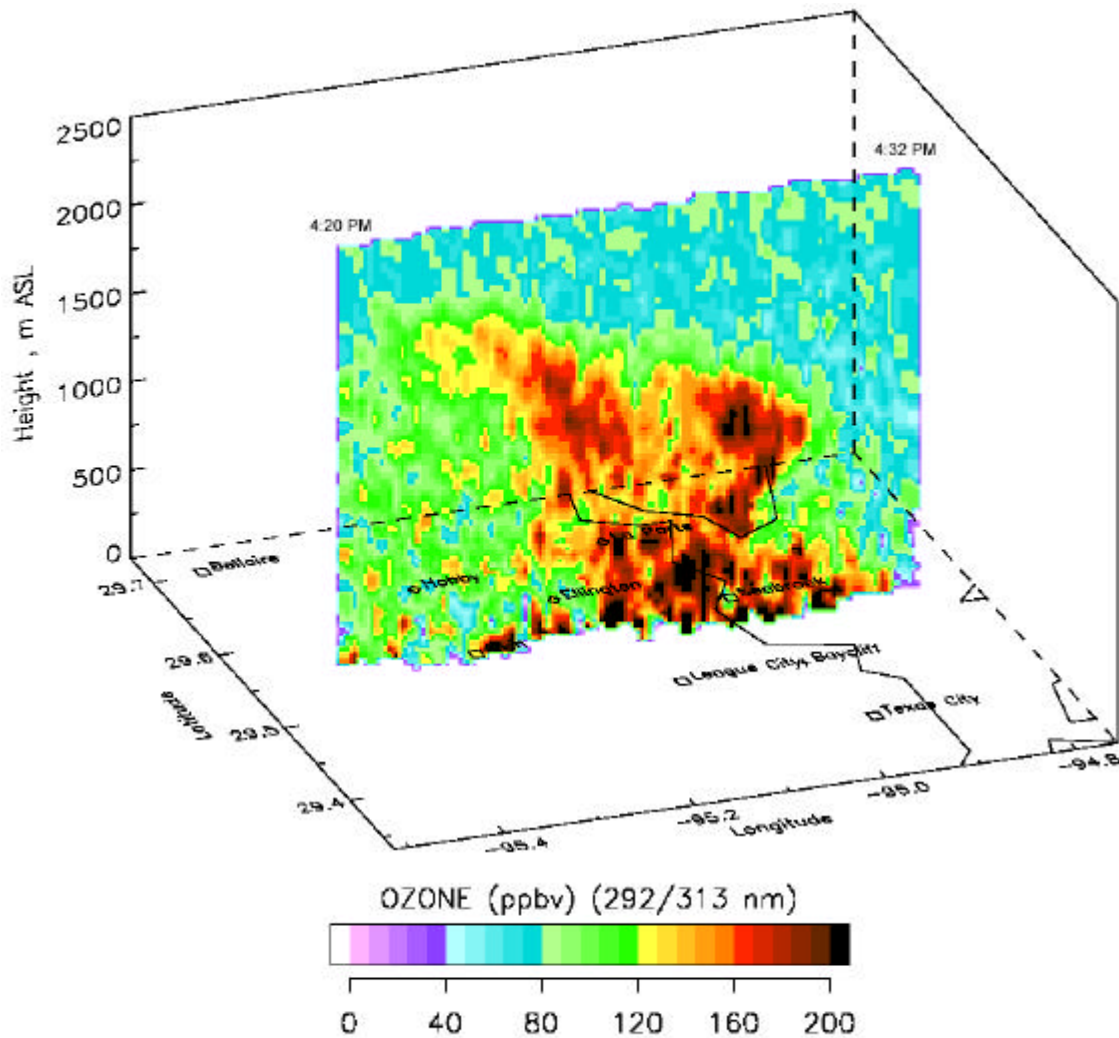
Taken collectively, the data shown in Figures 1-3 suggest that many transient high ozone events observed at ground monitors in the Houston-Galveston Area may be due to rapid and efficient ozone formation in industrial plumes. These plumes maintain a complex spatial structure, and contain high concentrations of hydrocarbons. These observations and findings suggest that a number of complex chemical processes are occurring in these plumes. A number of hypotheses have emerged to explain the location, duration and intensity of the rapid and efficient ozone formation observed in southeast Texas. These include (but are not limited to) the following:

- High concentrations of reactive hydrocarbons (especially ethene, propylene, butadiene, and aromatics) are co-emitted with NO_x from industrial point sources. The resulting plumes containing both hydrocarbons and NO_x have very high ozone productivities and very rapid rates of ozone formation due to the high concentrations of reactive hydrocarbons.
- Possible alternative chemical pathways that have been shown to produce rapid ozone formation, and which have not historically been accounted for in current models, may contribute to rapid ozone formation. Reaction products of atomic chlorine, detected during TexAQS, suggest the reactions of methane and alkanes may be more important in ozone formation in Houston than they are in other urban areas.
- High concentrations of radicals observed at night indicate that ozone-alkene chemistry or other pathways lead to enhanced radical production at night, which may be important in accounting for rapid ozone formation.

These hypotheses can be examined qualitatively and semi-quantitatively using the data generated during the Texas Air Quality Study. It is also desirable, however, to incorporate these phenomena into evaluations of potential air quality policies. In order to perform quantitative evaluations of air quality on a regional scale (to model policy alternatives), the most accurate representation of the chemical processes occurring in the atmosphere must be included in photochemical models.

The section below briefly describes the models for atmospheric chemistry currently employed by the State of Texas in photochemical grid modeling.

Modeling Atmospheric Chemistry at Urban and Regional Scales

Given the complexity of the chemistry that drives ozone formation and the multitude of hydrocarbon species and other ozone precursors that are emitted into the atmosphere, it is not yet possible to quantitatively describe all possible chemical reactions that lead to ozone formation. Further, because chemical mechanisms must be combined with meteorological models and other inputs to predict ozone concentrations at regional scales, it is necessary to simplify the chemistry used to describe ozone formation.

Two of the most commonly employed simplified mechanisms used to describe ozone formation are the Carbon Bond (CB) mechanism and the mechanism developed by Dr.

William Carter of the Statewide Air Pollution Research Center in California (SAPRC). These two chemical mechanisms have been the primary tools for describing the chemistry of regional ozone formation in Texas, and so it is useful to briefly describe these mechanisms.

The Carbon Bond mechanism was developed in the 1980's by Atmospheric Research Associates and System Applications International. It simplifies the hydrocarbon chemistry associated with ozone formation by grouping or "lumping" molecules or parts of molecules into reactivity classes. For example, all alkanes are modeled as paraffinic carbons that react at identical rates. Alkenes are handled differently. Recognizing that one part of the molecule (the double bond) reacts with hydroxyl radical more rapidly than other parts of the molecule (the saturated carbons), the CB mechanism breaks a single alkene molecule into an olefin group and paraffin groups. Other hydrocarbons, that are present at high concentrations or that have unusual reaction mechanisms (such as ethene and isoprene), are handled as individual, rather than lumped species, in the CB mechanism. Details of the mechanism and a history of its evolution are reported by Adelman (1999).

Version IV of the CB mechanism (CB-IV) has been used in most of the photochemical modeling performed in Texas. Therefore, an important issue to be examined in the Accelerated Science Evaluation is whether the CB-IV mechanism provides enough detail in the hydrocarbon chemistry, and other mechanisms that lead to ozone formation, to accurately predict ozone formation in Southeast Texas. If the level of detail in CB-IV is not sufficient, the most viable alternative mechanism is SAPRC.

The chemical mechanism developed by Bill Carter of the Statewide Air Pollution Research Center (SAPRC) in California contains a much more detailed representation of hydrocarbons than is available in CB-IV. The most recent version contains explicit reaction mechanisms for several hundred hydrocarbon species, as well as more computationally efficient, lumped mechanisms. Although SAPRC has not yet been used to model regional ozone formation in Texas, it is currently being incorporated as an optional mechanism in the photochemical grid model used in Texas.

Key scientific questions

The critical issues in atmospheric chemistry that need to be addressed through the Accelerated Science Evaluation are:

1. *Can simplified chemical mechanisms currently used in photochemical air quality modeling qualitatively predict the rapid and efficient ozone formation observed in southeast Texas?*

2. *Are there chemical mechanisms contributing to ozone formation in southeast Texas that are not adequately represented in the current models?*

3. *Which hydrocarbon species are the most significant contributors to ozone formation?*

4. *What magnitudes of reactive hydrocarbon and NO_x emissions are necessary to produce the ozone formation rates and ozone concentrations observed in southeast Texas?*

5. *Are the chemistries of dominant hydrocarbon species adequately represented in current models of ozone formation chemistry?*

Each of these issues is discussed below.

1.   Can simplified chemical mechanisms, such as CB-IV and SAPRC, qualitatively predict the rapid and efficient ozone formation observed in southeast Texas?

Ozone formation in Houston is rapid and efficient and often results in hourly changes in ozone concentrations observed at ground monitors that are in excess of 40 ppb/hr, and may be greater than 100 ppb/hr. Analyses performed by Jeffries (available in the report and data archive at www.utexas.edu/research/ceer/texaqsarchive) and co-workers have shown that photochemical grid modeling done for Houston as part of the December, 2000 State Implementation Plan, using the CB-IV mechanism, rarely predicted changes in ozone concentrations that exceeded 40 ppb/hr.

If the photochemical grid model does not reproduce the rate of change of ozone concentrations at ground sites, it is important to determine whether that failure is due to the chemical mechanism or some other feature of the model. To investigate this question, Jeffries and co-workers performed a series of environmental chamber experiments designed to produce rapid ozone formation and then modeled these experiments using the CB-IV mechanism.

Shown in Figure 4a are the results of an experiment in which 0.6 ppm of ethene was injected into one of 2 side by side environmental chambers in which NO_x and a synthetic mixture of hydrocarbons representative of urban areas were reacting. The injection of ethene causes rapid ozone formation, at a rate of several hundred ppb/hr. Similar results are shown in Figure 4b, with 2.4 ppm of ethene injected. While ppm level concentrations are not often detected at monitoring sites in the Houston area, they are not unknown, and a 2 ppm concentration could be obtained in a photochemical grid model if a 2000 pound release occurred over the course of an hour in a single surface grid cell.
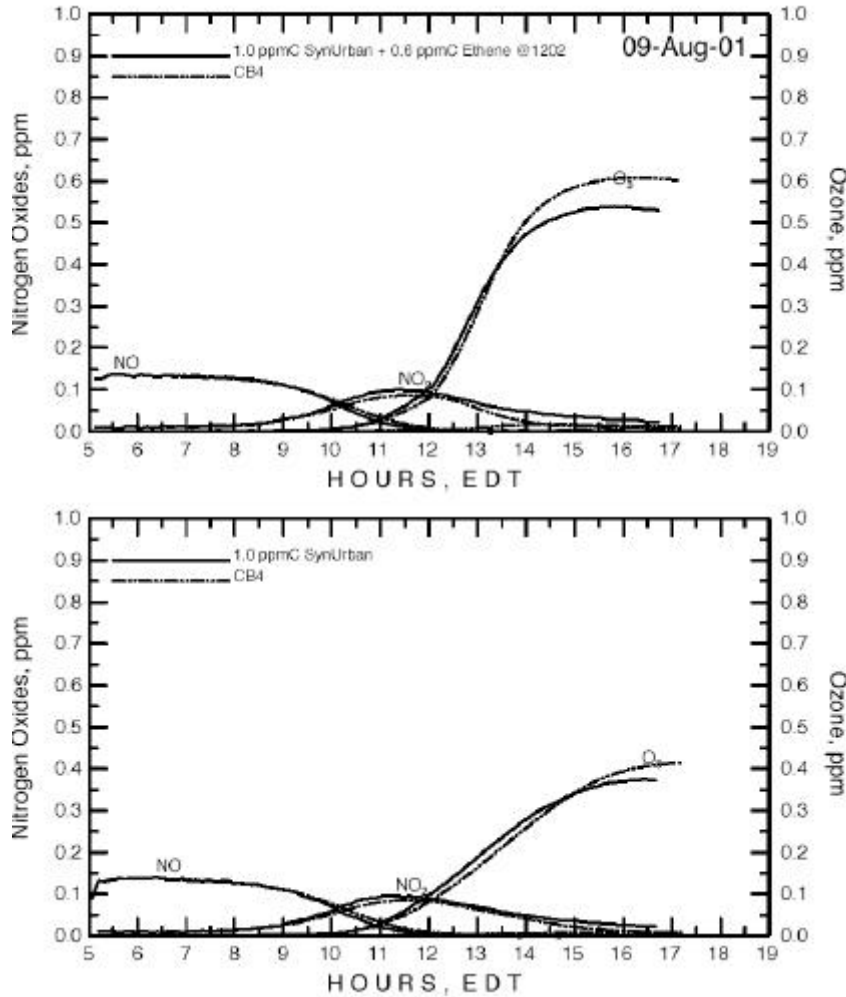
Figure 4a: Concentrations of ozone, and nitrogen oxides obtained in two parallel outdoor environmental chambers at the University of North Carolina. Both of the chambers contained NO_x and 1.0 ppmC of a mixture of hydrocarbons representative of urban emissions. In one of the chambers, an amount of ethene sufficient to produce 0.6 ppmC initial concentration was injected. This ethene injection accelerated ozone formation and increased the peak ozone concentration. The CB-IV mechanism accurately modeled this experiment.

Figure 4b. Concentrations of ozone, and nitrogen oxides obtained in two parallel outdoor environmental chambers at the University of North Carolina. Both of the chambers contained NO_x and 1.2 ppmC of a mixture of hydrocarbons representative of urban emissions. In one of the chambers, an amount of ethene sufficient to produce 2.4 ppmC initial concentration was injected. This ethene injection accelerated ozone formation and increased the peak ozone concentration. Although not shown on this figure, the CB-IV mechanism accurately modeled this experiment.
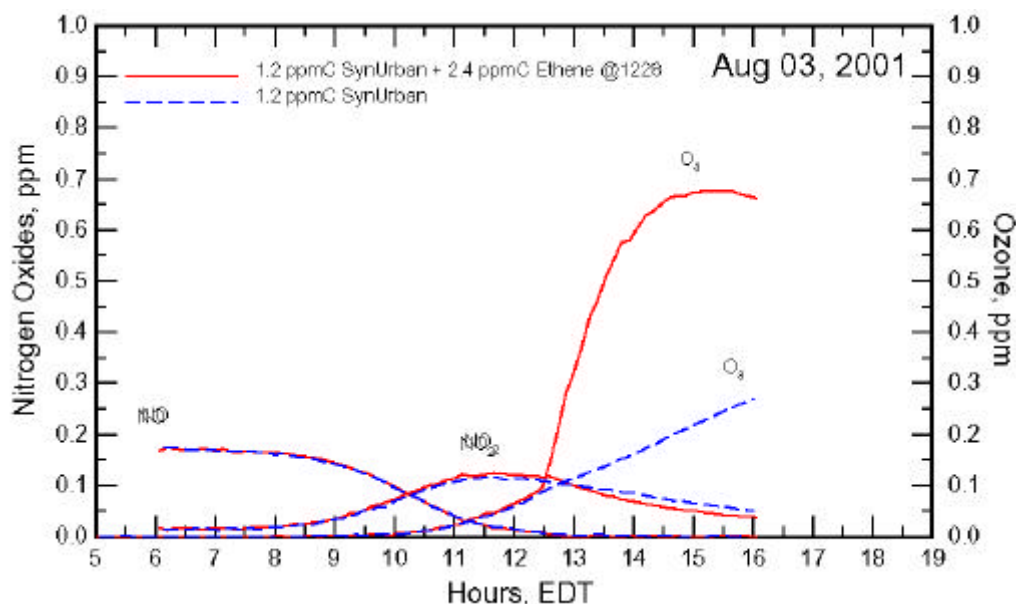
The results in Figure 4a clearly indicate that the CB-IV mechanism is capable of predicting high rates of ozone formation, similar to those observed in Houston. This does not necessarily mean that model is complete enough to accurately account for all of the chemical processes that may be important for ozone formation in Houston (see the issues outlined below). However, it does mean that it may be possible to describe the basic features of ozone formation in Houston without employing new chemical mechanisms in the photochemical modeling.

2.   *Are there chemical mechanisms contributing to ozone formation in southeast Texas that are not adequately represented in the current models?*
Existing, simplified chemical mechanisms for ozone formation have the potential to predict rapid and efficient ozone formation. While this is a significant finding, it does not immediately lead to the conclusion that these models account for all of the chemical processes that are important in ozone formation in Houston. Data from the Texas Air Quality Study and the scientific literature suggest that there are at least three chemistries that may be contributing to ozone formation in southeast Texas, that are have not historically been represented in models, such as CB-IV and SAPRC. These are the

reactions of atomic chlorine, night-time production of free radicals, and heterogeneous reactions on particle surfaces.

Atomic chlorine Tanaka, et al. (2000) have proposed that anthropogenic emissions of chlorine may lead to enhanced ozone formation in southeast Texas. Atomic chlorine alters ozone formation in two ways. First, molecular chlorine can be an important source of free radicals, particularly just after sunrise when emissions of atomic chlorine precursors that have accumulated overnight may rapidly photolyze. Second, because atomic chlorine reacts rapidly with methane and alkanes (which react slowly with hydroxyl radical), the presence of atomic chlorine can alter the relative importance of methane, alkanes, alkenes, and aromatics in ozone formation.

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) during the summer 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 Cl· with isoprene, 2) Cl_2 was injected into captive ambient air to determine the ozone enhancement potential of chlorine, and 3) Cl· chemistry was incorporated into a photochemical grid model used to estimate the impact of Cl· chemistry on air quality in Southeast Texas.

One method to confirm Cl· chemistry in the urban troposphere is through detection of reaction products, or marker species, unique to the reaction of Cl· with VOCs. 1-Chloro-3-methyl-3-butene-2-one (CMBO) (Nordmeyer, et al., 1997; Ragains and Finlayson-Pitts, 1997; Reimer, 2001) and chloromethylbutenal (CMBA), a CMBO isomer, are two such products of a series of reactions between Cl· and isoprene. Isoprene is emitted in large quantities from biogenic sources around Houston. Detecting CMBO and CMBA in ambient air would therefore confirm Cl· chemistry above the Houston area. To accomplish this, ambient air was continuously sampled from August 20-August 26, 2000 and August 29-September 12, 2000.   CMBO and/or CMBA were detected on 16 days during this period, with quantified ranges of daily peak mixing ratios of 12 - 126 ppt and 11 - 145 ppt, respectively. The highest mixing ratios of both species were detected on the morning of August 22, 2000.

Figure 5 displays the ozone, CMBO, and CMBA mixing ratios detected on the three days with highest ozone mixing ratios detected during the La Porte field campaign: August 30, 31, and September 5, 2000.   The coincidental detection of marker species and increased ozone confirms the occurrence of Cl· chemistry in the air masses that contributed to the early afternoon ozone peaks on August 30, 31, and September 5. Similar to the three days shown here, the daily maxima in CMBO and CMBA mixing ratios on other days were observed predominantly in the morning. Another product of Cl·-hydrocarbon chemistry is hydrochloric acid (HCl). 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 historical loading of HCl in the air to which the aerosol had been exposed. Because HCl is directly produced by the abstraction of hydrogen from hydrocarbons by Cl·, measurements of

secondary chloride may provide insight into the availability of chlorine in air sampled by the collected aerosol.

Figure 5. Ozone, CMBO, and CMBA mixing ratios for August 30, 31, and September 5, 2000 at the La Porte, TX site. As shown, the unique products of Cl· with isoprene (CMBO and CMBA) were detected in the morning hours after sunrise, coincident with increases in the ozone mixing ratio (Riemer, 2001; Riemer, et al., 2002).
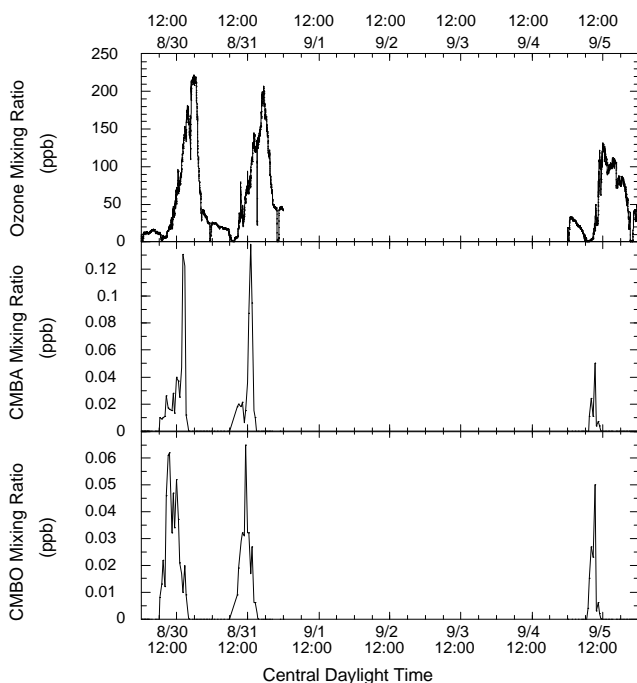
The Aerodyne Aerosol Mass Spectrometer (AMS) was employed during the TEXAQS 2000 study to provide real-time quantification of secondary chloride and other volatile and semi-volatile aerosol components with simultaneous measurement of chemically-speciated particle aerodynamic diameter. The operation of and initial field data from the AMS are described elsewhere (Jayne, et al., 2000; Jimenez, et al., 2001).

Figure 6 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 yet 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.

Figure 6. Secondary chloride detected in ambient air by AMS at the La Porte site during the following periods a) August 15-31, 2000 and b) September 1-15, 2000.
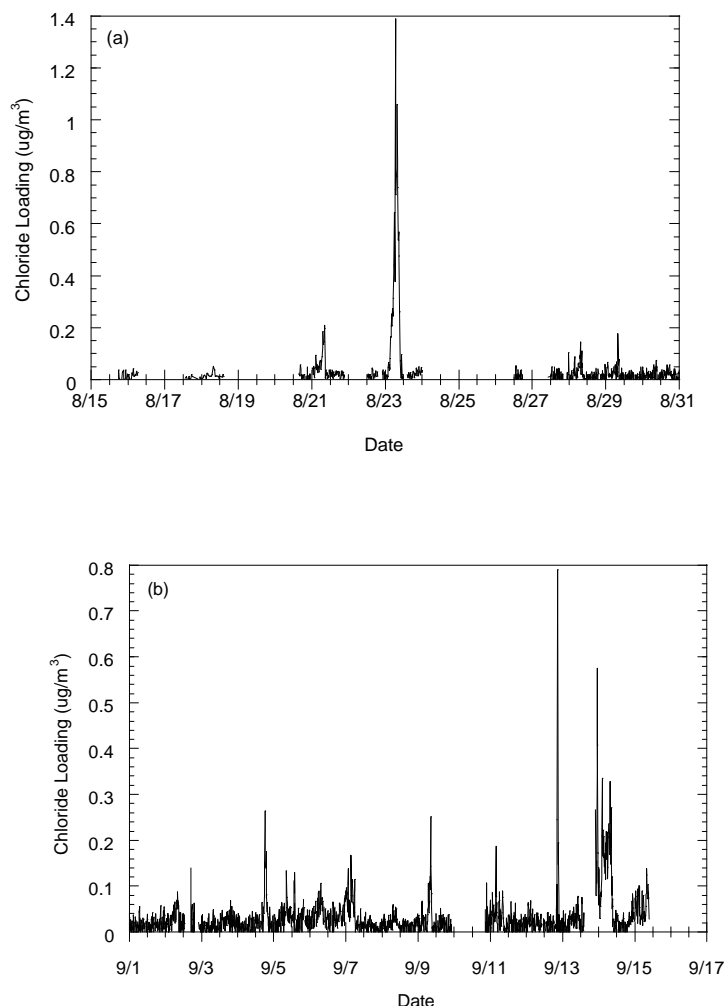
Despite the quantitative measurements of the marker species and secondary chloride concentrations, it is not possible to determine the extent to which Cl· chemistry affected ozone mixing ratios from these data alone. Therefore, captured air experiments were performed to help determine the impact of Cl· on ozone formation in Houston area air. Simultaneous captive air experiments were performed in three, 2 m^3 outdoor, mobile fluorinated ethene-propylene (FEP) Teflon environmental chambers at the La Porte site. Figure 7 displays the mixing ratios of ozone, isoprene, and CMBO for a set of environmental chamber experiments performed under sunny conditions on September 6, 2000. All three chambers started with captive ambient air. Cl$_2$ was injected (6 ppb equivalent) into Chamber C. Chambers B and C were also enriched with approximately 190 ppb propane to determine the efficacy of Cl· to

enhance ozone formation in alkane-enriched ambient air. Although propane does not directly affect CMBO production, propane may be important to ozone formation when Cl· are present. During the first hour, Chamber C exhibits enhanced ozone formation (approximately 78 ppb/hr) compared to the chambers (A, B) without Cl_2 injected (approximately 36 ppb/hr). The CMBO mixing ratio also increased from 16 ppt to 49 ppt in the first hour of the experiment. Because Cl_2 has a short photolysis half-life (typically less than 15 minutes), Cl· are formed rapidly at the start of experiment and react with isoprene to form CMBO. However, as Cl_2 and isoprene are depleted, CMBO formation slows and the CMBO mixing ratio decreases due to continued reaction with OH·.

Figure 7. Ozone, isoprene, and CMBO during a captive ambient air experiment – September 6, 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 Cl_2.
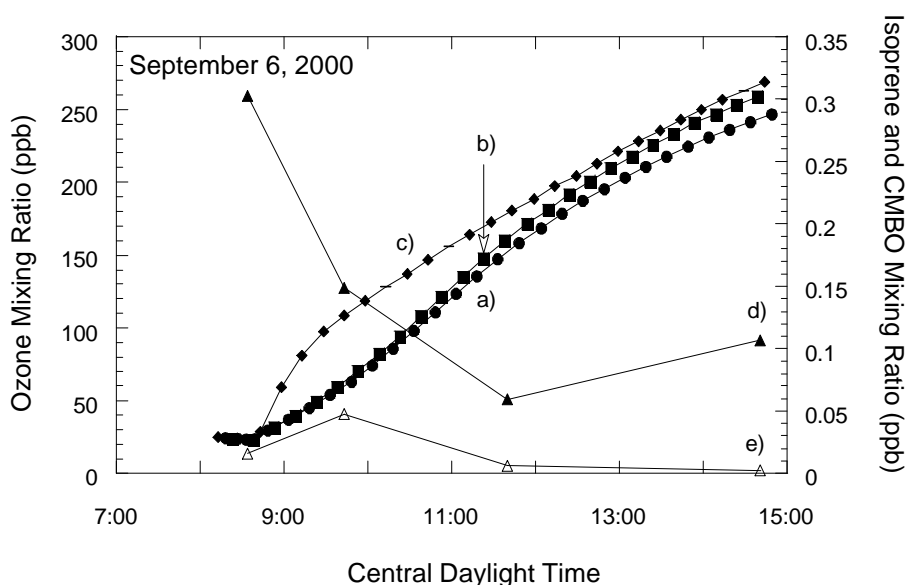
Based on observed enhancement of ozone formation in the captive air experiment reported here and ozone enhancements in other captive air experiments (Tanaka, et al. 2002a), and based on detection of CMBO in ambient air and in the captive air experiments, it can be concluded that Cl· chemistry occurs and enhances ozone formation in the Houston area. However, the regional ozone enhancement due to Cl· in the Houston area is also dependent on emissions and meteorology. These factors can be simultaneously accounted for only by employing a photochemical grid model such as the Comprehensive Air Quality Model with extensions (CAMx)(ENVIRON, 2000).

To estimate the impact of Cl· chemistry, simulations were performed using CAMx with the Carbon Bond IV mechanism (Gery, et al., 1989) modified to include chlorine chemistry. Thirteen reactions have been added to the chemical mechanism used by CAMx to describe chlorine chemistry in the urban atmosphere. The reactions include photolysis of chlorine radical (Cl·) precursors, Cl· + hydrocarbon reactions, and Cl· + ozone reactions. The hydrocarbon reactions include the reaction of Cl· with isoprene and 1,3-butadiene that yield unique reaction products, or marker species (Tanaka and Allen, 2001; Tanaka, et al., 2002b).

The impact of chlorine chemistry on ozone mixing ratios for the period September 6-11, 1993 was examined. This period has been modeled by the Texas Natural Resource Conservation Commission (TNRCC), to evaluate the effectiveness of air quality improvement plans in the Houston/Galveston area. 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 mid-2002. The 1993 episode has undergone rigorous performance evaluation and scrutiny by the TNRCC and the U.S. Environmental Protection Agency (TNRCC, 2000). Therefore, the 1993 episode was selected to provide a preliminary assessment of temporal and urban-scale spatial trends in ozone formation due to chlorine chemistry.

One-hour averaged mixing ratios of ozone and CMBO for the case without chlorine emissions were compared to the simulation with chlorine emissions. Chlorine emissions from cooling towers, swimming pools, marine sources, and point sources were included, as described in the Accelerated Science Evaluation Document on Emission Inventories and by Chang, et al. (2001, 2002). Anthropogenic emissions, particularly from cooling towers and swimming pools, dominated the emissions. Figures 8 and 9 display the maximum enhancement of ozone and CMBO predicted for September 11, 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 September 11, 1993. Figure 9 also shows a time series of predicted CMBO mixing ratios for September 11, 1993 at the location of the predicted maximum.

Although we cannot quantitatively compare the CMBO mixing ratios predicted by the model for September 11, 1993 with the summer 2000 ambient monitoring data, we expect the mixing ratios to be qualitatively similar since the meteorology and isoprene and chlorine emissions are similar for the two periods. The morning increase in CMBO mixing ratio observed during the field campaign (Figure 5) is replicated by the model results presented in Figure 9. The maximum predicted CMBO mixing ratio is also similar to that detected in the captive air experiments and is a factor of two lower than the highest mixing ratios detected during ambient measurements (suggesting that the modeling is a conservative estimate of the extent of chlorine chemistry).

The relative importance of various chemical reactions associated with the ozone enhancements was also examined using CAMx (Tanaka, et al. 2002b). Similar enhancements of ozone concentrations were found in scenarios when all chlorine reactions were included and when the only chlorine-hydrocarbon reaction was the chlorine-methane reaction. These results would seem to suggest that the contribution to ozone enhancement by chlorine is dominated on regional scales by the reaction of chlorine with methane.

Figure 8. Maximum ozone enhancement predicted for September 11, 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 maximum ozone enhancement during the modeled period.
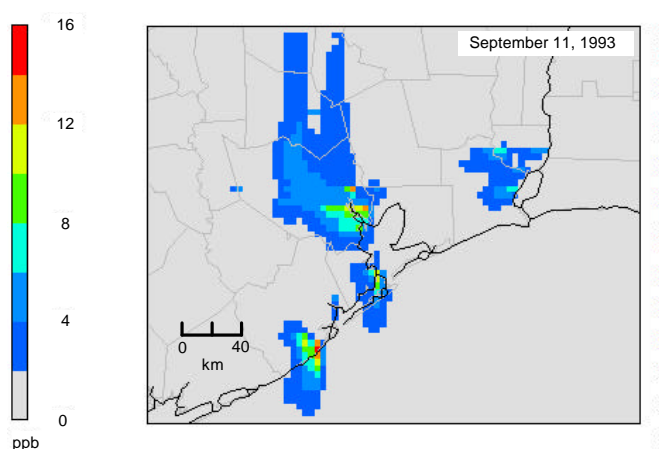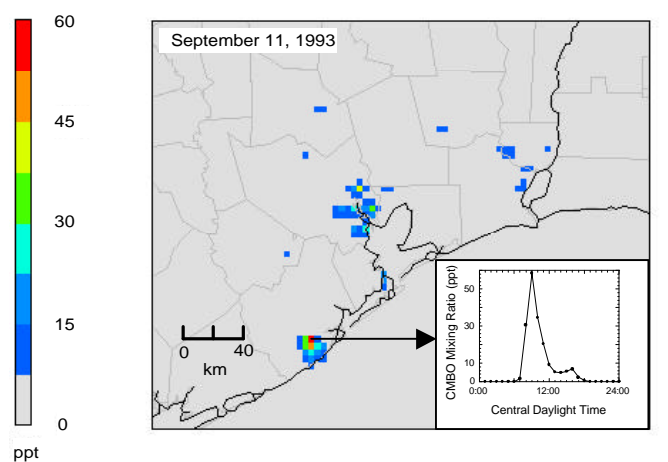

Figure 9   CMBO mixing ratios at the time of model-predicted CMBO maximum (09:00, September 11, 1993). A time series of the CMBO mixing ratio is provided for the location where the maximum CMBO mixing ratio was predicted.

In summary, data collected during TexAQS provide the first direct evidence of Cl·
chemistry in an urban area through quantification of CMBO and CMBA, species
unique to the Cl· + isoprene reaction in ambient air. Additional evidence for Cl·
chemistry was obtained by quantifying secondary chloride in ambient aerosols.
When chlorine was made available in captive air experiments, CMBO formed, and
ozone formation was enhanced. Photochemical model predictions that include
anthropogenic chlorine emissions are consistent with ambient observations and
suggest that chlorine chemistry enhances ozone formation in Houston.

Additional work that needs to be performed includes:
- Improving the accuracy of the emission inventory for atomic chlorine precursors;
  while this is addressed in the Accelerated Science Evaluation document
  involving emission inventories, improving the inventory also requires a better
  understanding of the chemistry of the processes that generate atomic chlorine in
  the atmosphere (such as the reactions of chlorinated organics, the reactions of sea
  salt, and the partitioning of water treatment chemicals into the atmosphere)
- Testing of the chemical mechanism in laboratory experiments and further
  evaluating the sensitivity of regional ozone formation to estimated values of
  chemical rate parameters
- Additional measurements of molecular markers for chlorine chemistry; the most
  compelling evidence for the significance of chlorine chemistry in southeast
  Texas is the detection of unique molecular markers of this chemistry by Riemer
  (2001). Modeling suggests that these measurements are consistent with increases
  in ozone concentration of 5-15 ppb, but these measurements have been made in
  only one location (LaPorte). Additional measurements would allow for more
  rigorous evaluation of emission inventories and chemical mechanisms.


Nighttime production of free radicals Measurements made at LaPorte during the
Texas Air Quality Study indicate that mixing ratios of free radicals observed at night
were on occasion as high as daytime levels (see Figure 10). It has been suggested
that this nighttime production of free radicals (particularly HO_2) may be due to
ozone-alkene reactions (see Figure 11). This suggests that free radical yields from
ozone-alkene reactions may be a particularly important parameter in chemical
mechanisms describing ozone formation in southeast Texas and recent data on the
values of these yields may not be incorporated into current photochemical models.

Therefore, additional work that needs to be performed includes:
- Incorporate updated estimates of radical yields from ozone-alkene reactions into
  chemical mechanisms and investigate whether nighttime olefin releases lead to
  predictions of free radical concentrations consistent with observations made at
  LaPorte

Figure 10. Free radical concentrations measured at the
Quality Study; a number of days exhibit high HO$_2$ et
al., 2001)

TEXAQS HOx data, Aug 14 to Sep 15, 2000
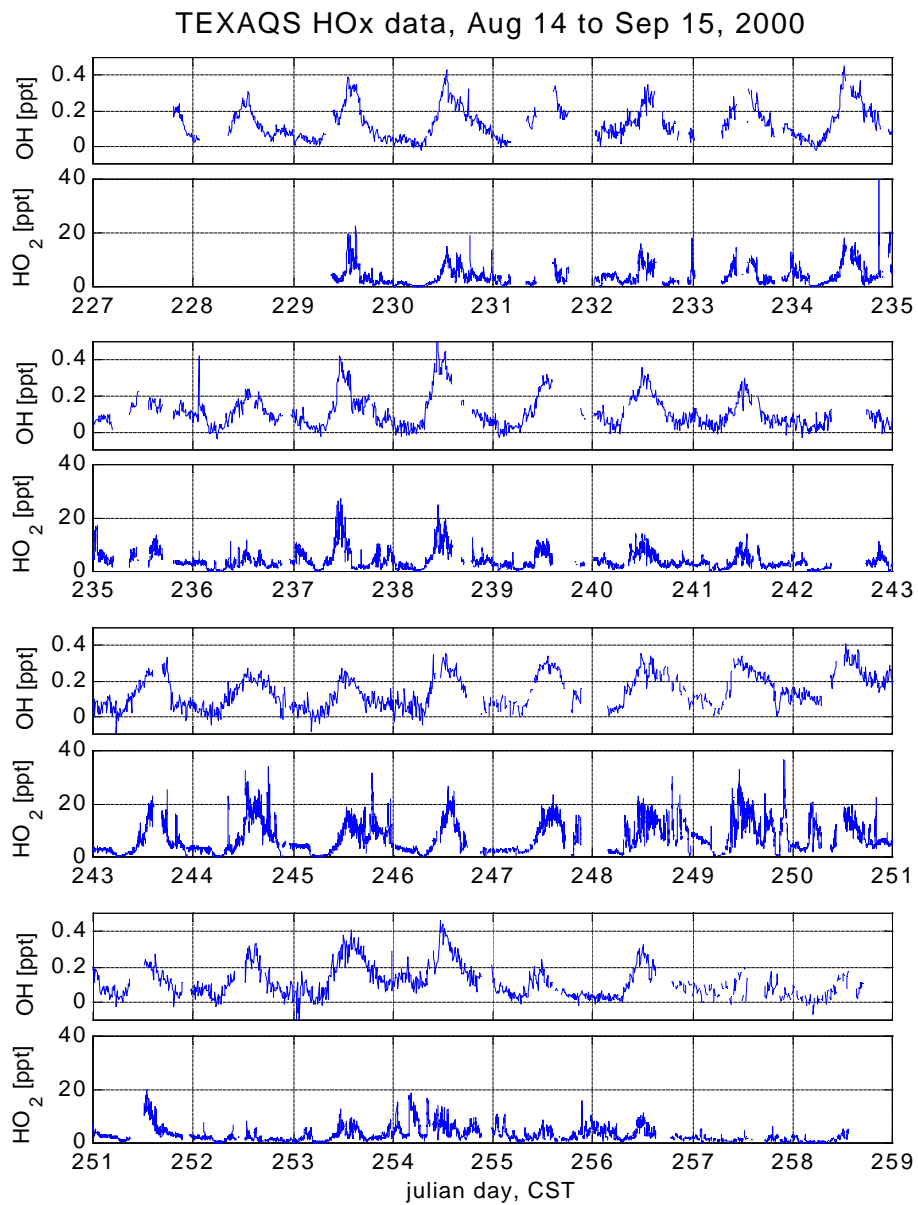
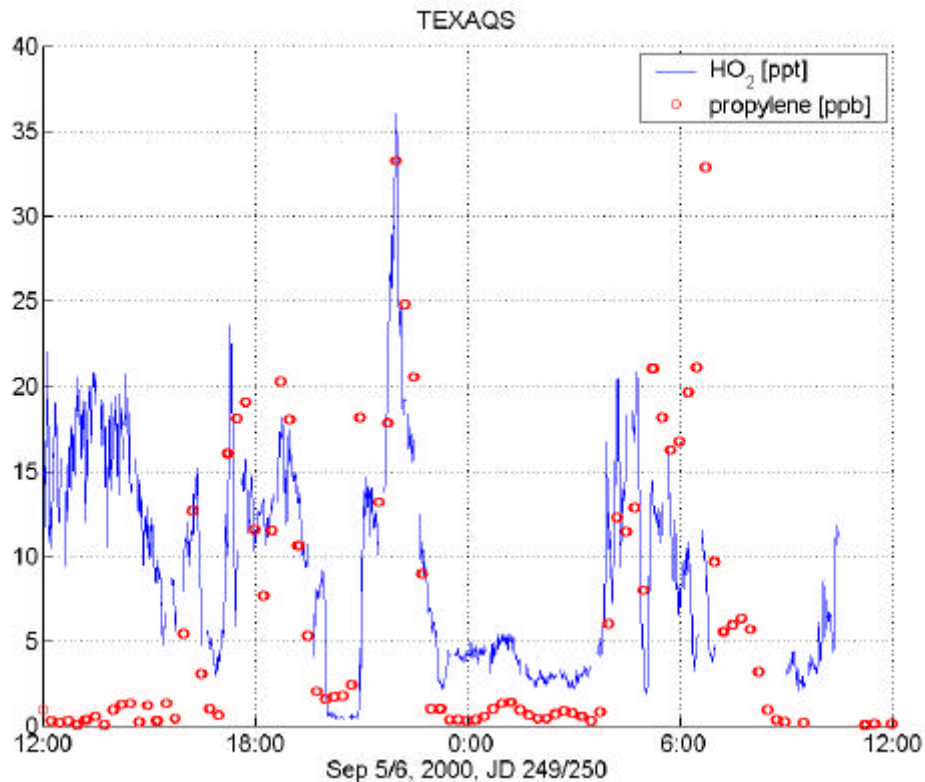Figure 11. Comparison of time series for propylene and HO mixing ratios observed
at   alkene reactions may be a
significant source of free radicals at night. (Martinez,

Heterogenous reactions on particle surfaces
atmospheric particles may be either a source or a sink for ozone. Ozone may react
directly with particle surfaces, lowering ozone concentrations. Heterogeneous
HO_x peroxy
radicals and HO) and oxides of nitrogen (NO leading to HONO; N O$_5$
nitric acid). The rates and extent of many of these reactions are unknown and it
would be difficult to include these reactions in simplified chemical mechanisms.

reactions may influence ozone concentrations in southeast Texas, especially if these
reactions (such as $_x$ leading to HONO) might be a source of free radicals during

One approach, suggested by Jacob (2000) in a critical review of heterogeneous
chemistry commissioned by NARSTO, is to calculate uptake and reaction of gas

formulation, the overall rate of uptake is computed by multiplying the rate of

collision of gas molecules with a particle surface by the probability that a collision results in uptake and reaction. Jacob (2000) suggests probabilities for a number of potentially important heterogeneous reactions. Li, et al. (2001) have estimated collision frequencies of gas phase species with particles, based on a typical urban aerosol number and size distribution. The results suggest that if the probability of uptake on collision is of order 10^{-4}, then reactions with particles may be important sinks for gas phase species, potentially influencing gas phase chemistry. Jacob reports uptake probabilities that are orders of magnitude higher than 10^{-4} for several reactions, including uptake of NO_2 and N_2O_5. These very preliminary results suggest that heterogeneous processes may be important as sinks for reactive species in southeast Texas, and should be evaluated.   Since aerosol size distributions are available for multiple sites in Houston, it would be possible to provide preliminary estimates of the potential significance of these reactions.

Therefore, additional work that needs to be performed includes:
- Incorporate preliminary estimates of the rates of heterogeneous chemistry into current chemical mechanisms; identify potentially significant reaction pathways and their impact on ozone formation

3. Which hydrocarbon species are the most significant contributors to ozone formation?

Although chlorine chemistry, heterogeneous chemistry and the radical productivity of ozone-alkene reactions may all need to be included in chemical mechanisms for ozone formation, current evidence suggests that the dominant phenomena in describing rapid and efficient ozone formation in Houston involve gas phase hydrocarbon reactions initiated by hydroxyl radicals. These chemistries are complex, as shown by reactions 1-17, and, as shown in Table 1, differences between hydrocarbons can be significant. It is therefore important that simplified chemical mechanisms used in photochemical grid modeling are detailed enough to accurately represent the chemistry of the most significant hydrocarbons. But, which hydrocarbons are most significant?

Historical data on the relative abundance of hydrocarbons in the Houston atmosphere are shown in Tables 3 and 4. These data were collected during the Coastal Oxidant Assessment for Southeast Texas (COAST Study). The data in the Tables are concentrations of gas phase hydrocarbons, averaged over all samples collected during the study at the Clinton site (in the Ship Channel region) and the Galleria site (in west Houston near major freeways). The data indicate that the most prevalent hydrocarbons in the Ship Channel in 1993 were alkanes with less than 10% alkenes. Lower concentrations, but similar distributions of species are seen at the Galleria site.

Similar analyses have been performed for the period 1998-2001 (Main and Brown, 2002) and the results for the summer of 2000 are also shown in Table 3 and 4. As shown in Figure 12, the magnitudes of the concentrations observed in 2000 are lower than those observed in 1993, but, Tables 3 and 4 indicate that the composition profiles are virtually

identical. (Note that there are slight differences between the total hydrocarbon concentrations reported by Fujita, et al. (1995) and Main, et al. (2001), but the main features are consistent) The dominant hydrocarbons are light alkanes, with some light alkenes and aromatics.

Table 5 provides a more detailed analysis, showing the most abundant hydrocarbons detected during the summers of 1998-2001 at multiple ground stations (Main and Brown, 2002). Again, the profiles are consistent, indicating that while concentration magnitudes have changed over time, the composition profiles, as measured at ground sites, have remained constant.

Figure 12 Average and median total non-methane hydrocarbon concentrations observed at the Clinton site, 1993-1998. (Main, et al., 2001)
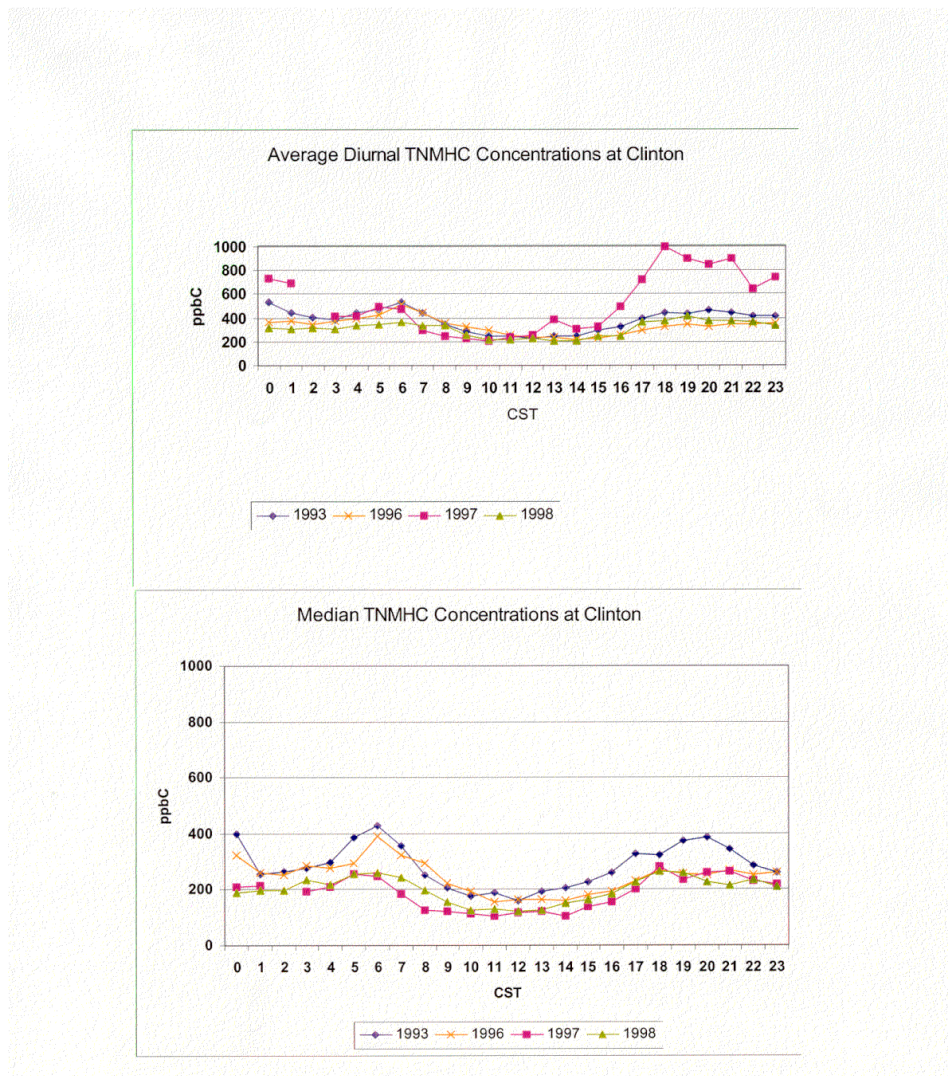
Table 3. Fifteen most abundant hydrocarbon species detected at the Clinton site during the 1993 COAST Study (Fujita, 2001)

Summer 1993

Compound	Average (ppbC)	Non-methane Hydrocarbons	Concentration (
Isopentane/cyclopentane	43.7	8.2	13
Ethane	29.5	7.4	15
n-butane	27.5	5.1	15.5
n-propane	24.0	5.6	14.5
Toluene	22.9	4.2	6.5
n-pentane	22.3	4.3	6
n-hexane	21.0	3.7	3.5
Isobutane	16.5	2.8	8.5
2-methylpentane	13.8	2.4	4
Propene	12.5	2.2	3.5
Ethene	12.1	2.4	4
Meta- and para-xylene	11.8	2.3	4
3-methylpentane	11.6	2.0	2.5
Benzene	8.7	1.6	3.0
n-heptane	5.8	1.1	2.0

Table 4. Fifteen most abundant hydrocarbon species detected at the Galleria site during the 1993 COAST Study (Fujita, et al., 1995) and at Aldine (also a residential site) during the summer of 2000 (Main, et al., 2001)

Compound	Galleria Summer 1993		Aldine Summer 2000
	Average Concentration (ppbC)	Percentage of Non-methane Hydrocarbons	Average Concentration (ppbC)
Isopentane/cyclopentane	20.7	7.1	6.5
Ethane	21.3	7.7	14
n-butane	16.6	5.5	8.5
n-propane	18.5	6.6	13
Toluene	12.5	3.9	3.5
n-pentane	8.8	3.1	3.5
n-hexane	3.9	1.3	2
Isobutane	8.3	2.6	5
2-methylpentane	5.6	2.0	2
Propene	7.5	2.6	2
Ethene	8.4	2.6	4
Meta- and para-xylene	8.5	2.9	1.5
3-methylpentane	3.6	1.3	1
Benzene	5.0	1.5	2
Species in top 15 at Galleria but not at Clinton in 1993			
2,2,4 trimethylpentane	4.2	1.2	1
acetylene	4.2	1.3	2

Table 5.
Ten most abundant hydrocarbons, ranked by concentration in ppbC, during July-September, by site and year (Main and Brown, 2002)

	ethane	propane	Iso-pentane	n-butane	Iso-butane	ethene	toluene	n-pentane	Trans-2-butene	n-hexane	propene	xylene	2-methyl pentane	acetylene	isoprene	benzene
Deer Park 1998	1	2	3	4	5	6	7	8	9	10						
Deer Park 1999	1	2	3	5	4	6	7	8			9	10				
Deer Park 2000	1	2	3	4	5	7	6	10			8	9				
Deer Park 2001	1	2	5	4	3	6	7	9		10	8					
Clinton 1998	3	2	1	4	6	8	9	7			10	5				
Clinton 1999	3	2	1	4	6	9	8	7			10	5				
Clinton 2000	3	2	1	4	5	>10	6	8				9	10	7		
Clinton 2001	2	1	4	3	5	9	6	7			10	8				
Bayland 1998	1	2	3	4	7	8	5	6				9				
Bayland 1999	1	2	3	5	7	8	4	6				9				
Bayland 2000	1	2	3	4	8	7	6	9				10				
Aldine 2000	1	2	3	4	5	6	7	>10		10		8	9			
Channelview 2001	2	1	5	3	4	6	7	9			8					10
HRM-3 '01	2	1	4	3	5	8	6	9			7	10				
HRM-7 2001	2	1	4	3	5	9	7	6			8	10				

Table 6.
Ten most abundant hydrocarbons measured in NOAA/NCAR aircraft samples, that would also be detected by auto-GC, ranked by concentration in ppbC
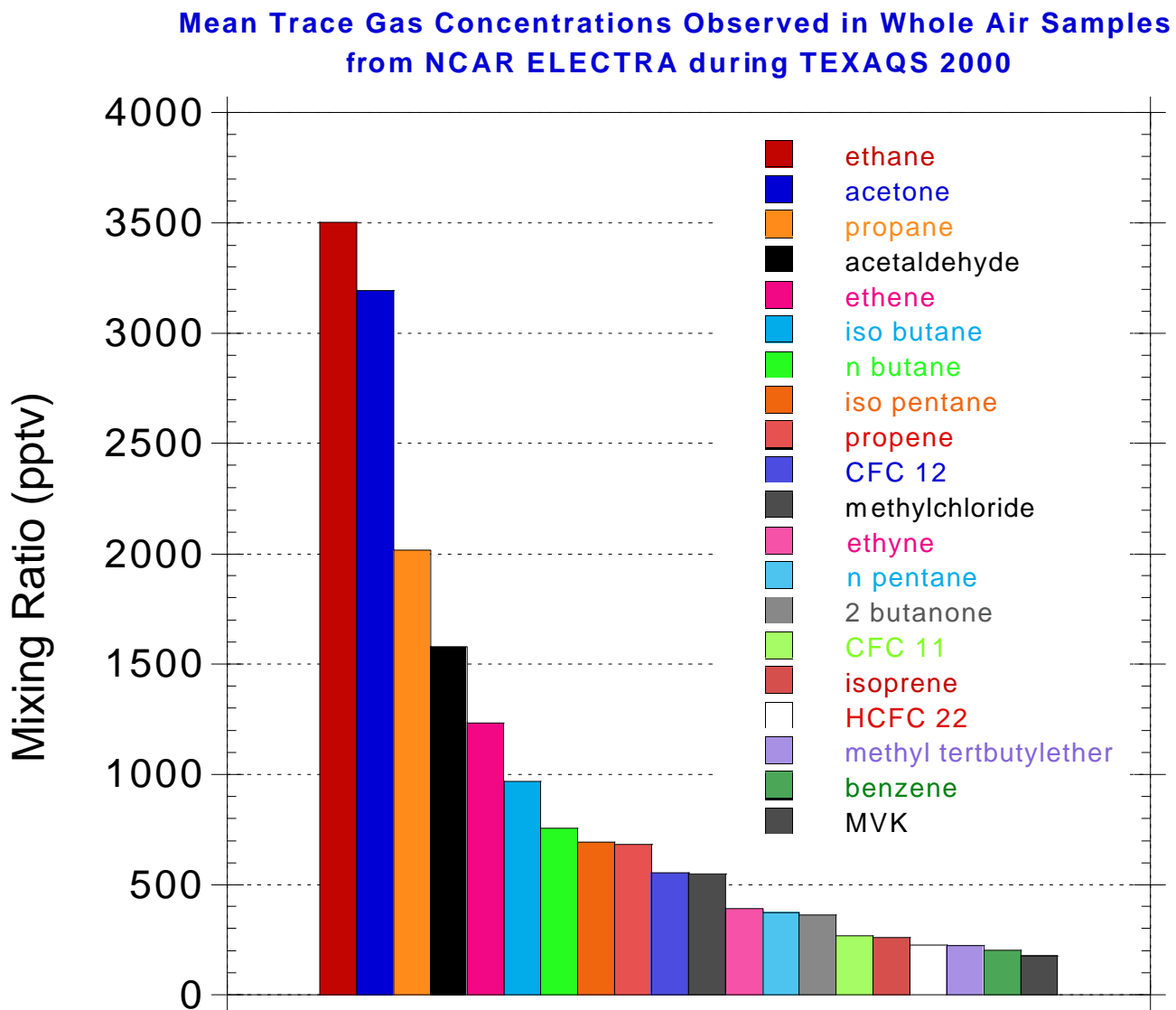
	ethane	propane	Iso-pentane	n-butane	Iso-butane	ethene	toluene	n-pentane	Trans-2-butene	n-hexane	propene	xylene	2-methyl pentane	acetylene	isoprene	benzene
Aircraft	1	2	4	5	3	6		7			8				9	10

Aircraft data collected during the Texas Air Quality Study can also be used to examine the mix of hydrocarbon concentrations. As shown in Figure 13 and Table 6, the most abundant hydrocarbon species detected by the NOAA/NCAR Electra, are generally consistent with the ground measurements (note that Figure 13 is reported as ppbv, while the convention for reporting the ground concentrations is ppbC). The same alkenes and alkanes dominate the measurements. Some differences are apparent, but most are readily reconciled. The presence of chlorinated compounds and oxygenated compounds in the NCAR/NOAA data and their absence in the 1993 COAST data are due to differences in analytical methods. The presence of isoprene in the NOAA/NCAR data and its absence among the commonly detected species at the ground sites is likely due to differences in sampling locations. Along with these differences due to methodologies, however, there also appear to be some real differences in the hydrocarbon composition. In particular, aromatic species appear to be detected at higher concentrations at the ground sites than in the NOAA/NCAR aircraft samples.

One method that can be used to quantitatively assess the differences in concentrations of aromatic species in the ground and aircraft samples is to examine the ratios of the concentrations to a relatively inert species, detected at high concentration, such as ethane. For example, the ratios of average ethene to average ethane concentrations are similar for the aircraft samples and the ground samples. For the aircraft, the ratio of the average concentrations is approximately 0.35 (Figure 13), while for the ground samples, the ratio of the average concentrations for the summer of 2000 is approximately 0.3 (see Figure 14). This suggests that the ethene concentrations detected by the aircraft and at the ground sites were consistent. In contrast, the ratio of average concentration of toluene (ppbC) to average concentration of ethane (ppbC) for the summer of 2000 at the ground sites was 0.25-0.4 (Figure 14). A similar ratio for the NOAA/NCAR aircraft would give a concentration comparable to that observed for n-pentane (see Figure 13).

The differences in average aromatic concentrations observed at ground sites and by the NOAA/NCAR aircraft may be explained by data collected by the DoE G-1 aircraft (Daum, et al., 2002). In most samples collected by the G-1 aircraft that were associated with high ozone productivities, the primary contributors to instantaneous hydrocarbon reactivity were alkenes, as observed in the NOAA/NCAR data. However, on some flights, very high concentrations of aromatics, particularly toluene, were observed. In fact, the maximum concentration of toluene observed by the G-1 aircraft (>200 ppbv) was higher than any of the alkene concentrations observed in the high reactivity plumes. This suggests that the average aromatic concentrations observed at the ground sites are consistent with aircraft data, but that extreme values of aromatic concentrations may be strongly influencing average concentrations.

Figure 13.

**Mean Trace Gas Concentrations Observed in Whole Air Samples
from NCAR ELECTRA during TEXAQS 2000**

Figure 14. Average hydrocarbon concentrations observed at Clinton during the summer of 2000 (Main, et al., 2001).

This general phenomenon, of very high concentrations of hydrocarbons in isolated regions, was observed by aircraft at multiple times during the Texas Air Quality Study. Assuming that these isolated regions of elevated concentrations represent plumes, the plumes can be described as very narrow and are generally confined to industrial source regions. This is shown in Figures 15 and 16. Figure 15 shows the concentration of ethene observed by the NOAA/NCAR Electra on a single flight (9/01/00). Ethene concentrations were generally below 10 ppb, except for one sample, which was in excess of 30 ppb. Concentration measured a few minutes before the high concentration were only about 1 ppb. Since the aircraft flies at 100 m/s, this suggests that this ethene plume was narrow. Recognizing that the hydrocarbon concentration data set collected by the aircraft may have data from a number of such isolated plumes, it is useful to examine maximum concentrations of hydrocarbons observed by the aircraft. These are shown in Figure 16.

Figure 15. Ethene concentrations (dots) observed during the NOAA/NCAR Electra flight of 9/01/00 indicate the presence of a narrow plume of ethene. The aircraft flies at a velocity of approximately 100 m/s, so 100 seconds represents a distance of 10 km.
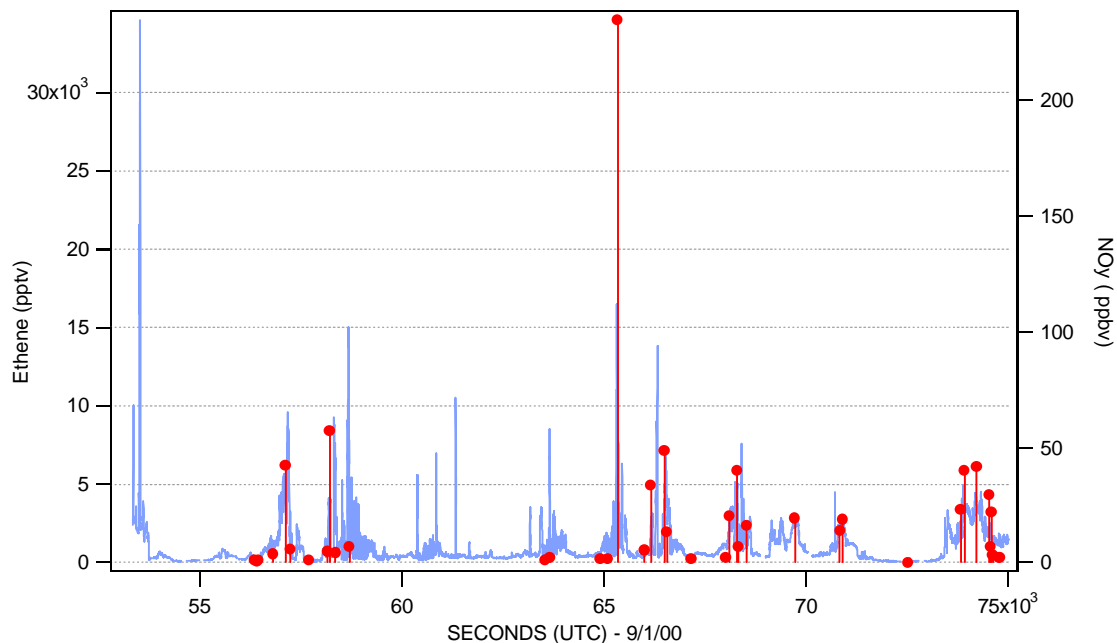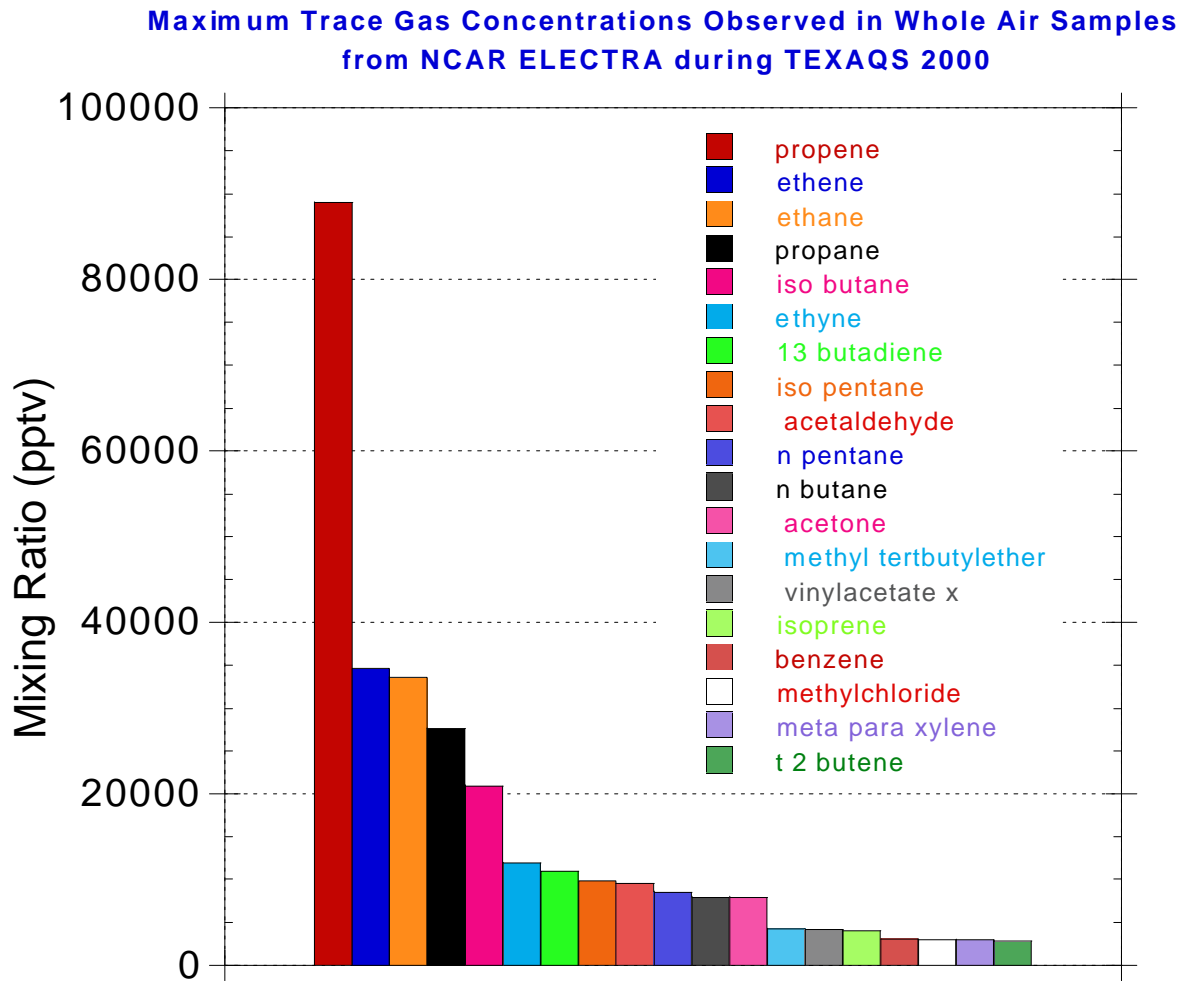
Figure 16.

Maximum Trace Gas Concentrations Observed in Whole Air Samples from NCAR ELECTRA during TEXAQS 2000

Legend:
- propene
- ethene
- ethane
- propane
- iso butane
- ethyne
- 13 butadiene
- iso pentane
- acetaldehyde
- n pentane
- n butane
- acetone
- methyl tertbutylether
- vinylacetate x
- isoprene
- benzene
- methylchloride
- meta para xylene
- t 2 butene

The hydrocarbons that exhibit the highest concentrations were ethane, ethene, propane and propylene in the NOAA flights; toluene and isopentane were also observed at high concentrations in the Brookhaven flights. This distribution of hydrocarbons with high concentrations can be contrasted with the observations made in 1993, shown in Table 6. During 1993, ethene was rarely among the top 10, when compounds were ranked by maximum observed concentration.

Table 6. Maximum hydrocarbon concentrations observed at three sites during the COAST Study in 1993 (Fujita, et al., 1995)

Compound	Clinton site maximum concentration (ppbC)	Galleria site maximum concentration (ppbC)	Baytown site maximum concentration (ppbC)
Isopentane	266.8	185.4 (1)	437.5
Toluene	269.8	176.7	362.6
Isobutane	136.5	63.2	505.3
n-propane	62	114.3	264.6
Ethane	127.5	175.3	282.5
Meta/para xylene	453.4 (1)	29.9	69.8
n-butane	50.1	127.0	352.7
n-pentane	101.9	53.2	118.3
2-methyl pentane	56.5	36.4	57.4
acetylene	95.4	38.9	69.4
ethene	21.5	19.2	146.2

The data can also be contrasted with ground samples collected during the summer of 2000 at the Clinton, Aldine and Deer Park sites (Main, et al., 2001). These data suggest that the highest concentrations of some aromatics (such as toluene and xylenes) are comparable to the highest concentrations of any other species, including propylene, ethene and the light alkanes.

The aircraft data collected during the Texas Air Quality Study allow a much better understanding of the spatial distribution of atmospheric hydrocarbons than was available in 1993 or from the ground site data available for 1998-2001. Figure 17 shows the measurements (over multiple flights) of ethene. The spatial distributions of high concentrations of these species can be contrasted with the spatial distribution of high concentrations of methyl tert-butyl ether, shown in Figure 18. High MTBE concentrations can be found over major freeways, while high concentrations of ethane, ethene, and propylene are largely confined to industrial source regions.

Figure 17. Concentrations of ethene measured by the NOAA/NCAR Electra during multiple flights conducted during the Texas Air Quality Study (Atlas, et al., 2001)
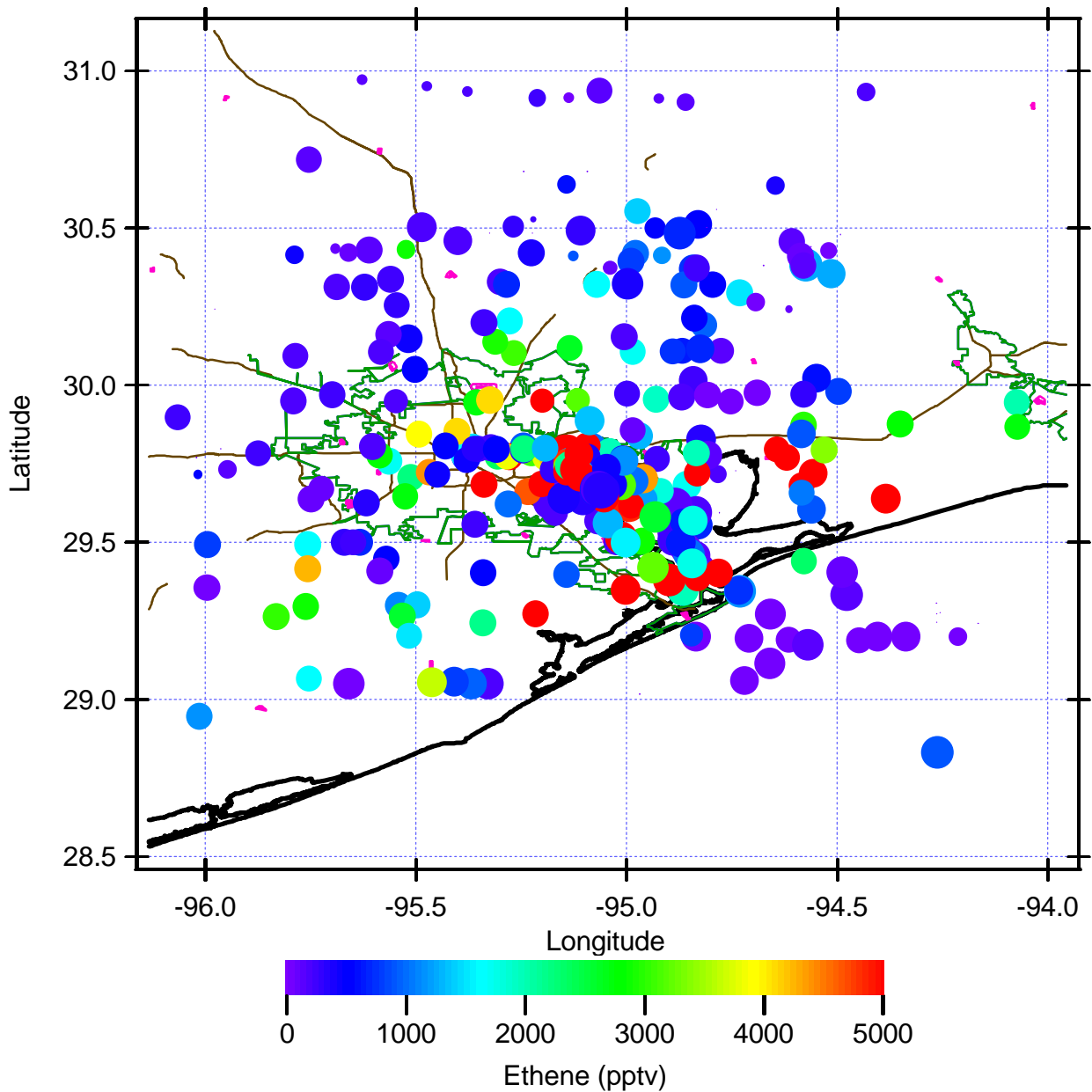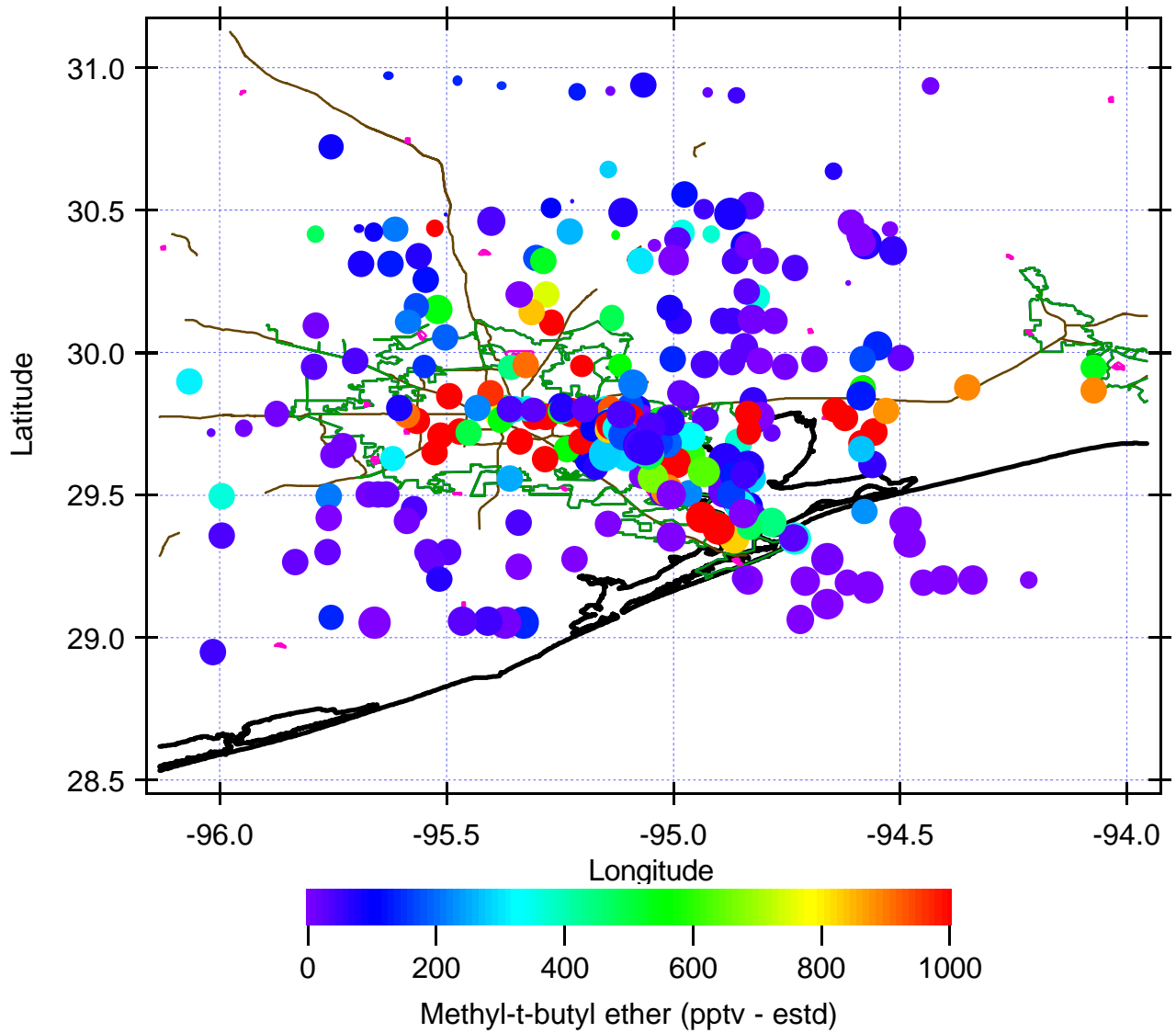
Figure 18. Concentrations of MTBE measured by the NOAA/NCAR Electra during multiple flights conducted during the Texas Air Quality Study (Atlas, et al., 2001)

Finally, it is important to recognize that while the presence of high concentrations of reactive hydrocarbons, such as alkenes and aromatics, often lead to rapid and efficient ozone formation, the presence of high hydrocarbon concentrations alone may not be sufficient to cause rapid and efficient ozone formation. Analysis of hydrocarbon concentrations measured at ground sites on summer days, when no ground monitors detected exceedances of the national ambient air quality standard for ozone, show concentrations that can be among the highest measured. On average, however, total concentrations of hydrocarbons measured at ground sites are higher on episode days, as opposed to non-episode days. There are, however, no appreciable differences in the average composition of hydrocarbons observed on episode days and non-episode days.

In summary, an examination of aircraft and ground based sampling of hydrocarbons, both historically and during the Texas Air Quality Study leads to the following findings:

- High concentrations of light alkanes, alkenes, and aromatics are all observed during episodes of rapid and efficient ozone formation. The alkenes and aromatics (especially ethene, propylene, toluene and xylenes) have the potential to react rapidly, enhancing ozone formation.
- Concentrations of hydrocarbons tend to be slightly higher on ozone episode days, compared to non-episode days, however, the composition of the hydrocarbons on episode and non-episode days is virtually identical. Further, while the magnitude of hydrocarbon concentrations has decreased in the last decade, with a few minor exceptions (isopentane, in particular), the concentration ratios of atmospheric hydrocarbons observed in Houston have remained consistent for a decade or more.

Additional work that needs to be performed includes

- Detailed analysis of events during the Texas Air Quality Study when high hydrocarbon concentrations were detected should be performed; events that led to high ozone concentrations should be contrasted with events that did not lead to high ozone concentrations.

4.   *What magnitudes of reactive hydrocarbon and NO$_x$ emissions are necessary to produce the ozone formation rates and ozone concentrations observed in southeast Texas?*

Elevated concentrations of alkanes, alkenes, and aromatics are all associated with ozone exceedances, and/or rapid ozone formation in Houston. To assess the role that each of these species might play in ozone formation, a series of box model simulations was performed employing a detailed chemical mechanism (Kimura, et al., 2002). The horizontal dimensions used for the box model simulation were 1 km by 1 km and the height of the box ranged from 250 m to 1250 m over the course of a day, based on estimates of the mixing depth. The box was given initial hydrocarbon and NO$_x$ concentrations typical of those observed in the morning near industrial sites in the HG area (details available in Kimura, et al., 2002). Additional emissions were added to the box model over the course of a day to simulate routine emissions. The SAPRC-99 gas phase reaction mechanism, developed at the University of California, Riverside (Carter, 2002) was used in the box model calculations.

The base case inputs to the SAPRC mechanism led to the temporal evolution of ozone and ozone precursor concentrations shown in Figure 19.
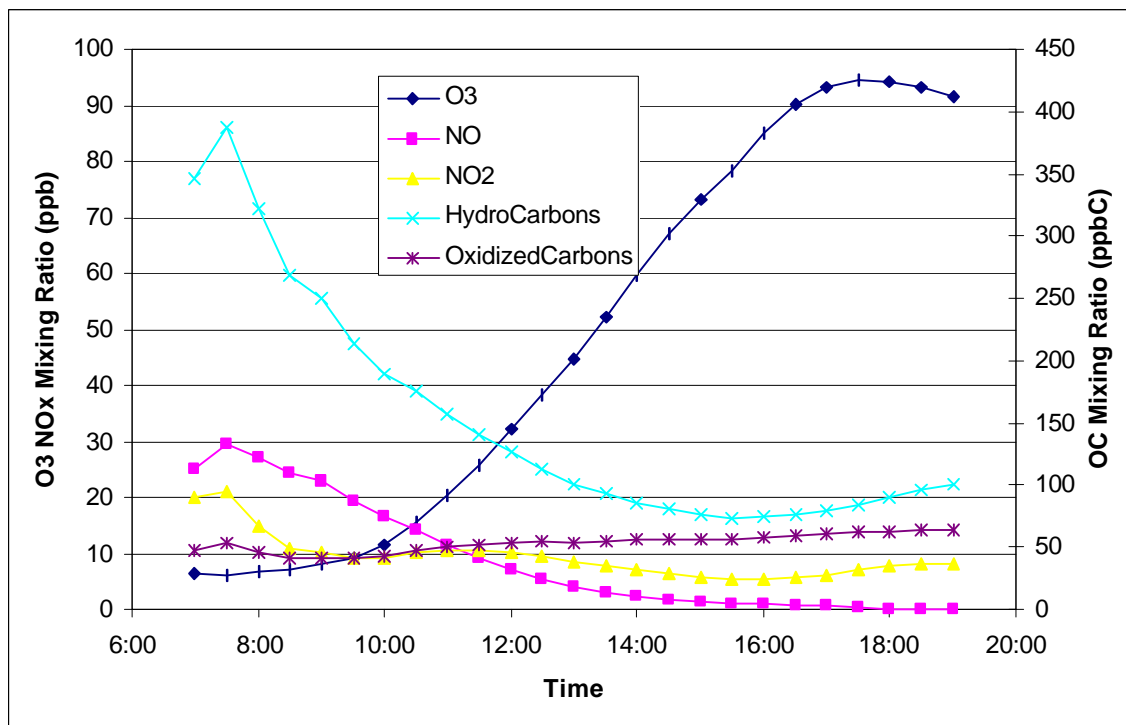

Figure 19. Box model basecase simulation (Kimura, et al., 2002)

Using this as the basecase, emissions were added to the box to represent a variety of events that could lead to high hydrocarbon concentrations. The calculations addressed the following questions:

- How does ozone productivity associated with hydrocarbon releases vary with the chemical composition of the emissions?
- Does the time of day of the release event affect ozone production?
- Does the VOC to NO_x ratio in the release affect ozone production?
- How does ozone productivity vary with the magnitude of the release?
- How does the duration of the release event affect ozone productivity?
- How does the rate of dilution of the upset affect ozone productivity?

These box calculations are, in principle, quite similar to the incremental ozone reactivity calculations performed by Carter (Carter 1994, Carter et al. 1995, Carter 1995). The difference is that in Carter's calculations, the addition of reactive hydrocarbons represented an incremental addition of reactivity to the reacting mixture. When reactive VOCs (olefins and aromatics) were added to the base mixture in Carter's work, the mass added was typically a few percent to 10 percent of the VOC mass of the base mixture. For less reactive hydrocarbons (alkanes) the mass added was 100 to 200% of the base mixture. In contrast, the releases considered in the calculations reported here are dramatic perturbations of the base conditions. Typically, a release might change total hydrocarbon concentrations from a few hundred ppbC to thousands of ppbC.

To develop a set of hydrocarbon and/or NO_x release events that would be typical for the Houston area, upset records for August and September of 2000 were obtained from the TNRCC. A total of 268 upset events were reported for the period August 15 – September 15, 2000, for an average of 9 events per day. The upset records were sorted by chemical species, and based on these records, a set of representative upset events, involving highly reactive compounds (ethene, propylene, 1,3-butadiene, and xylene) and less reactive (ethane, propane) species, were selected for analysis with the box model. The scenarios examined in the box model are listed in Table 8. Note that these modeled scenarios were not designed to precisely describe the actual upset events. Rather, the scenarios were selected to be representative of the types of events reported in the Houston-Galveston area.

Table 8 lists the hydrocarbon species that were added to the base case emissions in the scenario, the time of the release (all releases were initially assumed to be one hour in duration) and the extent of dilution. In the case of no dilution, the releases were added to the base case box model simulation, which grew in vertical dimension, but did not grow in horizontal dimensions. Recognizing that upset releases would cause concentration gradients and possible horizontal diffusion, a series of scenarios were performed to assess the effect of diluting the release. The dilution air in these cases was added beginning immediately after the release ended. The dilution air was assumed to have the same composition as the base case simulation (with no additional release emissions) at the same hour of the day as the dilution was occurring. Table 7 shows the rate by which the

horizontal dimension was expanded (horizontal area added per hour). The range of dilutions considered was based on a qualitative analysis of plumes observed by a NOAA team employing downward looking LIDAR during the Texas Air Quality Study. A broad range of growth rate (1.1 to 71 km^2/ of horizontal area added per hour) was considered.

In addition, for each simulated upset scenario (upset time, chemical species and dilution), a matrix of hydrocarbon and NO_x releases were considered. For each release scenario, upset hydrocarbon emissions of 0, 100, 250, 500, 1000, 1320, 2640, 3960 and 5280 pounds were considered (based on one of the larger emission scenarios during the August and September 2000 period). For each of the 9 levels of VOC emissions, NO_x upset emissions were considered selecting from following 9 levels; 0, 14, 36, 72, 143, 189, 377, 566 and 754 lb. The upper bound on the NO_x emissions was established by calculating the amount of NO_x that would be released by a flare burning 500,000 lb/hr of a typical hydrocarbon at 99% efficiency. AP-42 emission factors were used to calculate the NO_x emissions (U.S. EPA, 2002).

Table 8. Summary of Simulations

Scenario	VOC	Time of Release	Chlorine	Horizontal growth rate of plume
1	Ethene	07:00 to 08:00	0 lb/hr	0 km^2/hr
2	Propylene	07:00 to 08:00	0 lb/hr	0 km^2/hr
3	1,3-Butadiene	07:00 to 08:00	0 lb/hr	0 km^2/hr
4	Xylene	07:00 to 08:00	0 lb/hr	0 km^2/hr
5	Ethane	07:00 to 08:00	0 lb/hr	0 km^2/hr
6	Propane	07:00 to 08:00	0 lb/hr	0 km^2/hr
7	Ethene	12:00 to 13:00	0 lb/hr	0 km^2/hr
8	Propylene	12:00 to 13:00	0 lb/hr	0 km^2/hr
9	1,3-Butadiene	12:00 to 13:00	0 lb/hr	0 km^2/hr
10	Xylene	12:00 to 13:00	0 lb/hr	0 km^2/hr
11	Ethane	12:00 to 13:00	0 lb/hr	0 km^2/hr
12	Propane	12:00 to 13:00	0 lb/hr	0 km^2/hr
13	Ethene	07:00 to 08:00	100 lb/hr	0 km^2/hr
14	Ethane	07:00 to 08:00	100 lb/hr	0 km^2/hr
15	Ethene	12:00 to 13:00	100 lb/hr	0 km^2/hr
16	Ethane	12:00 to 13:00	100 lb/hr	0 km^2/hr
17	Ethene	07:00 to 08:00	0 lb/hr	71 km^2/hr
18	Ethene	07:00 to 08:00	0 lb/hr	36 km^2/hr
19	Ethene	07:00 to 08:00	0 lb/hr	18 km^2/hr
20	Ethene	07:00 to 08:00	0 lb/hr	9 km^2/hr
21	Ethene	07:00 to 08:00	0 lb/hr	4.4 km^2/hr
22	Ethene	07:00 to 08:00	0 lb/hr	2.2 km^2/hr
23	Ethene	07:00 to 08:00	0 lb/hr	1.1 km^2/hr

Tanaka et al. (2000, 2001) have recently suggested that anthropogenic emissions of chlorine may play a role in the reactivity of hydrocarbon emissions in the HG area. Therefore, for some of the upset scenarios, emissions and reactions of chlorine were incorporated into the simulations. The mechanism for chlorine chemistry was based on Carter et al. (1997) and Tanaka et al. (2001). Carter (1997) included reactions of chlorine with inorganic and selected organic species based on information from a variety of sources (Atkinson 1997, Atkinson et al. 1997, 1999, 2000, Coquet 2000, Demoore 1997).

Tanaka (2001) developed a mechanism for lumped CBIV species and the rates used by Tanaka were modified as appropriate and used for the lumped species in the SAPRC mechanism. The emission rate of chlorine (as Cl_2) was set to be 40 lb/hr for entire simulation period. This value corresponded to 40 % of the largest point source of chlorine reported in an emission inventory assembled by the University of Texas (Chang et al., 2001, 2002). The level of chlorine emission was selected such that daily maximum level of chlorine molecule mixing ratio became 5-10 ppb, which is consistent with the concentrations of molecular tracer species of chlorine reactions measured in Houston (Reimer, et al., 2001). Releases of VOC and NO_x were simulated in the same way as the scenarios without the chlorine emissions and chemistry, however, only upsets of ethene and ethane were considered. The reactions of these two VOCs with atomic chlorine are represented explicitly in the chemical mechanism.

Typical simulation results for upset scenarios are shown in Figures 20 and 21. Figure 20 shows the evolution of mixing ratios for ethene, non-ethene hydrocarbons, oxidized hydrocarbons, O_3, NO and NO_2 for an ethene release of 5280 pounds that occurred between 0700 and 0800 hours; no NO_x was included in the upset. This scenario is representative of a very large process upset (Kimura, et al., 2002). Most of the ethene reacts within a few hours; the peak ozone concentration is reached a few hours after the release ends and much of the ozone production occurs during the upset or in the first hour after the upset. Figure 21 shows the evolution of mixing ratios if NO_x is added to the ethene upset of Figure 20 (at a 7:1 VOC to NO_x mass ratio). The peak ozone concentration is slightly delayed, but the ozone concentrations reach much higher values if the reacting mixture has more NO_x available. Figure 22 shows a simulation analogous to the simulation shown in Figure 20, except that ethane is the hydrocarbon released in the upset rather than ethene. The lower reactivity of ethane leads to a lower peak ozone concentration and lower ozone formation rate than shown in Figure 20.
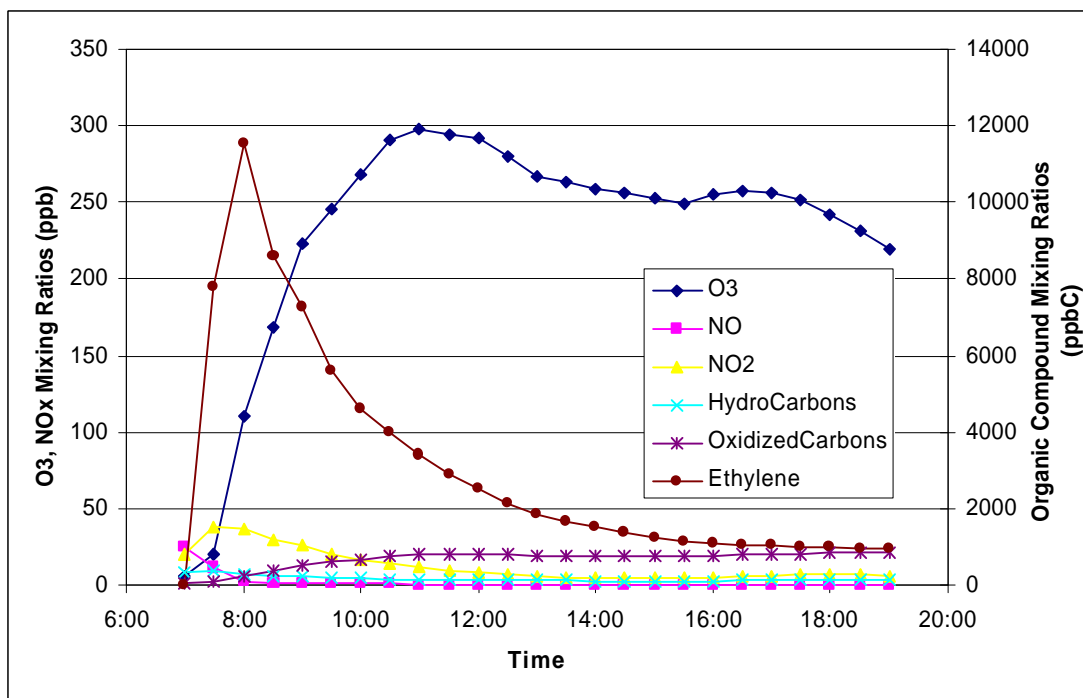
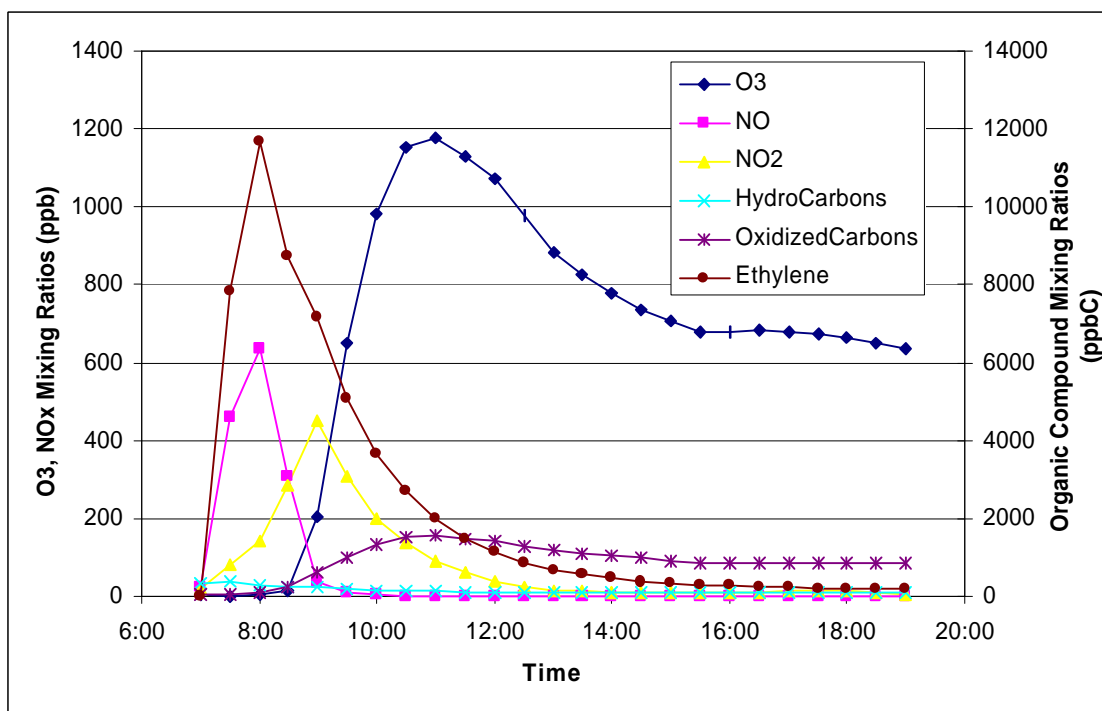**Figure 20. Ethene Release (without NO$_x$) during 7:00 to 8:00**

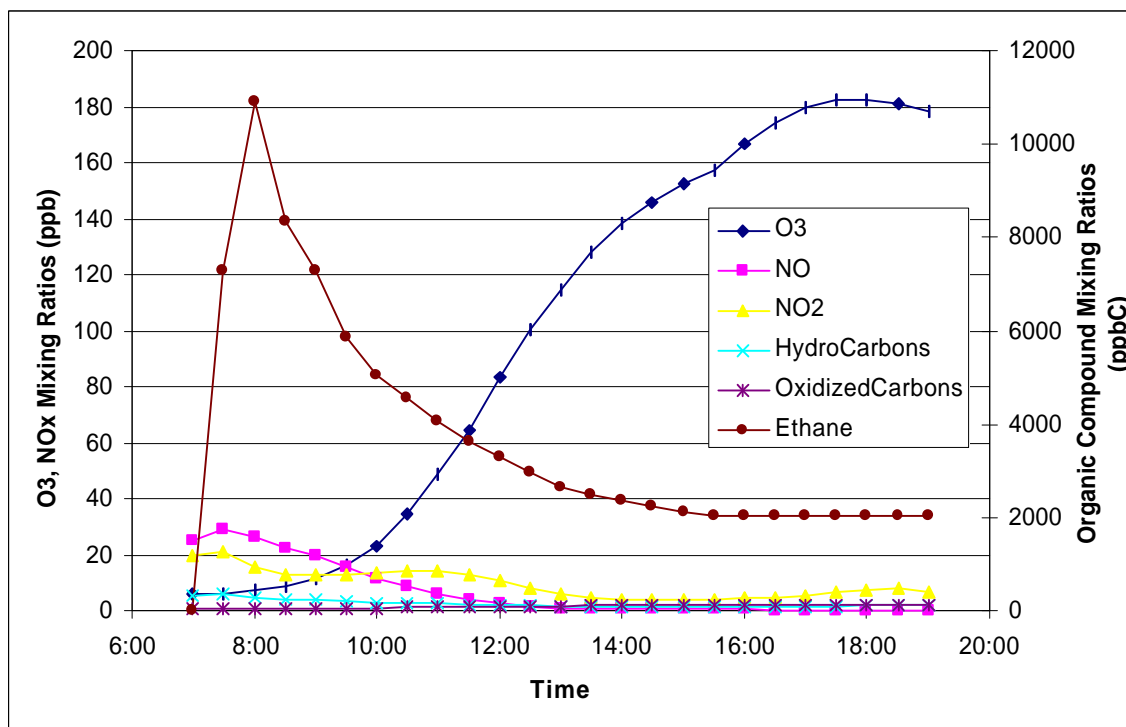**Figure 21. Ethene/NO$_x$ Release (VOC/NO$_x$ = 7) during 7:00 to 8:00**

Figure 22. Ethane Release (without NO$_x$) during 7:00 to 8:00

Analysis of hundreds of box model simulations led to the following conclusions:

- Releases of alkenes, diolefins and aromatics contributed substantially to maximum ozone formation. Depending on precise conditions, an upset of 1000 pounds or more into a box with a ground area of 1 km^2 could lead to increases of ozone concentrations much larger than 100 ppb (Figures 23 and 24).
- Release of alkenes, diolefins and aromatics of as little as 100 pounds into the box used in the simulations may lead to more than 50 ppb of increase in maximum ozone (Figures 23 and 24).
- If NO$_x$ was emitted together with alkanes, the titration effect of ozone by NO masks any effect of alkane emissions. If alkanes were emitted without NO$_x$ in the upset, the alkanes enhance ozone formation, however the magnitude of the effect was smaller than for other species (Figures 23 and 24).
- Among four reactive VOC species examined (ethene, propylene, 1,3-butadiene and xylene), ethene contributed the most per pound released to the daily maximum ozone concentration, followed by propylene and 1,3-butadiene, and xylene (Figures 23 and 24).
- When VOC and NO$_x$ were released together, the daily maximum ozone concentration increased almost linearly with the amount of the release (Figure 23).
- When VOC species were released without NO$_x$, the response of the daily maximum ozone concentration was more complex. Maximum ozone formation due to emissions of alkanes (ethane and propane) increased linearly with the amount released. Ethene and xylene releases increased daily maximum ozone,

but the increases plateau above 2000 lb and 50 lb of release, respectively. Further release of these VOCs did not lead to further rise in the daily maximum ozone. Propylene and 1,3-butadiene had yet another pattern in terms of contribution to daily maximum ozone. The maximum ozone concentration peaks with a release of 500 lb, and further releases decrease the daily maximum ozone concentration (Figure 24).

- All of above observations were largely independent of the time of day of release (07:00 to 08:00 versus 12:00 to 13:00), although the contribution of releases to ozone formation was slightly larger when release occurs in the morning than in the afternoon.
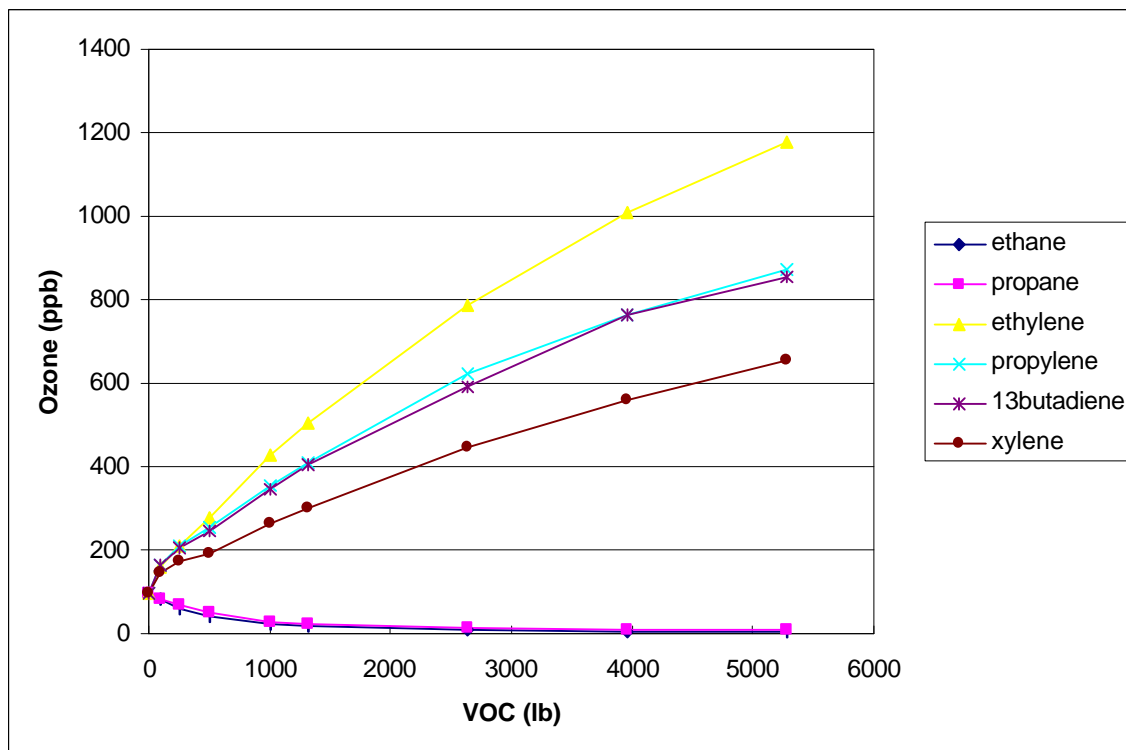

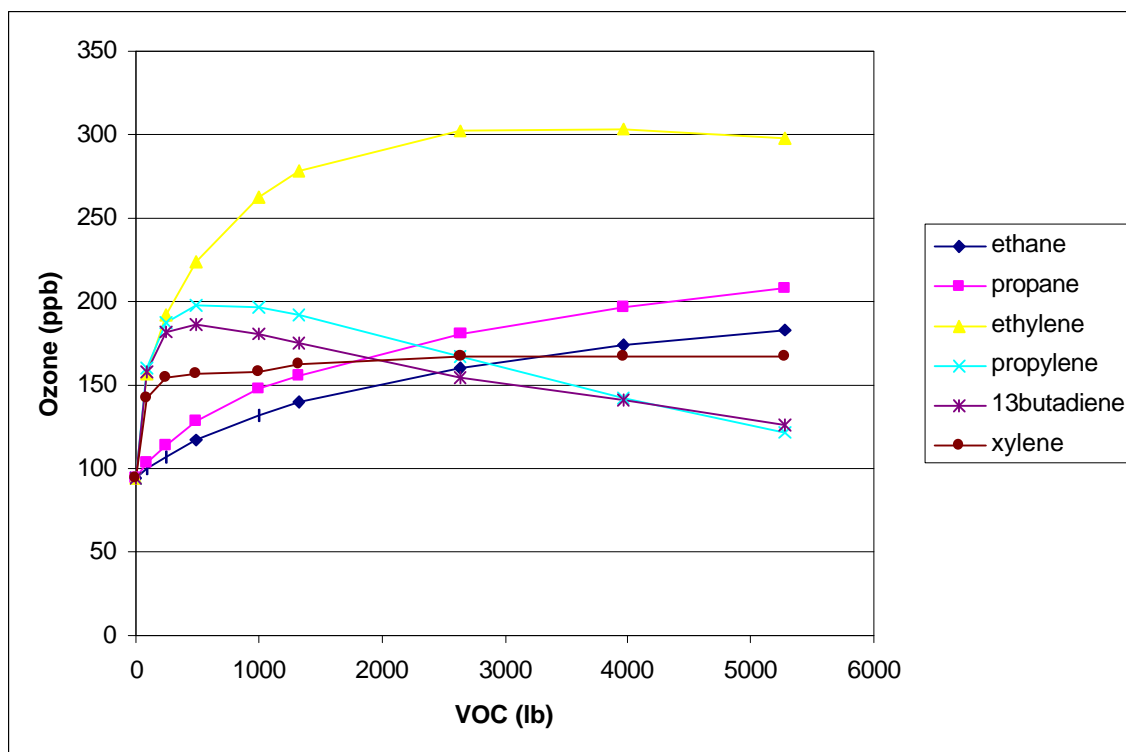**Figure 23. Daily maximum ozone with release of VOC/NO$_x$ = 7 at 07:00 to 08:00**

Figure 24. Daily maximum ozone with release of VOC only at 07:00 to 08:00

- Initial rapid formation of ozone was also a function of species emitted. Prompt enhancements of ozone concentration are similar to enhancements of maximum ozone concentration with one exception. When ethene and NO_x were emitted simultaneously in the morning, they led to higher daily maximum ozone than any other species. However initial ozone formation was far slower than any other reactive species. This behavior was not observed when release occurs in the afternoon. A mid-day release of ethene leads to both high daily maximum ozone and a fast initial rate of ozone formation (Figures 25 and 26).
- Of the reactive VOC species studied, propylene and 1,3-butadiene contributed the most to the rapid increase in ozone immediately following the release. Xylene and ethene reactions were slower (Figures 25 and 26).
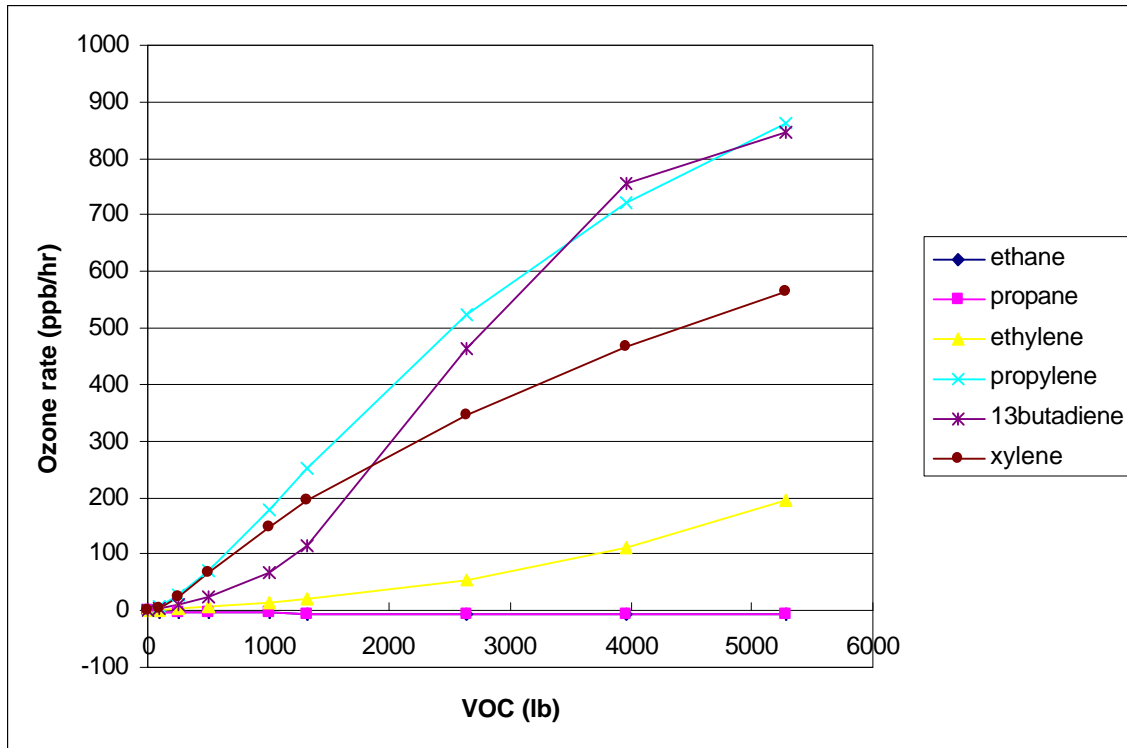
Figure 25. Extra ozone (simulation with additional release-base case) formed within one hour of release of VOC/NO$_x$=7, 7:00 to 8:00
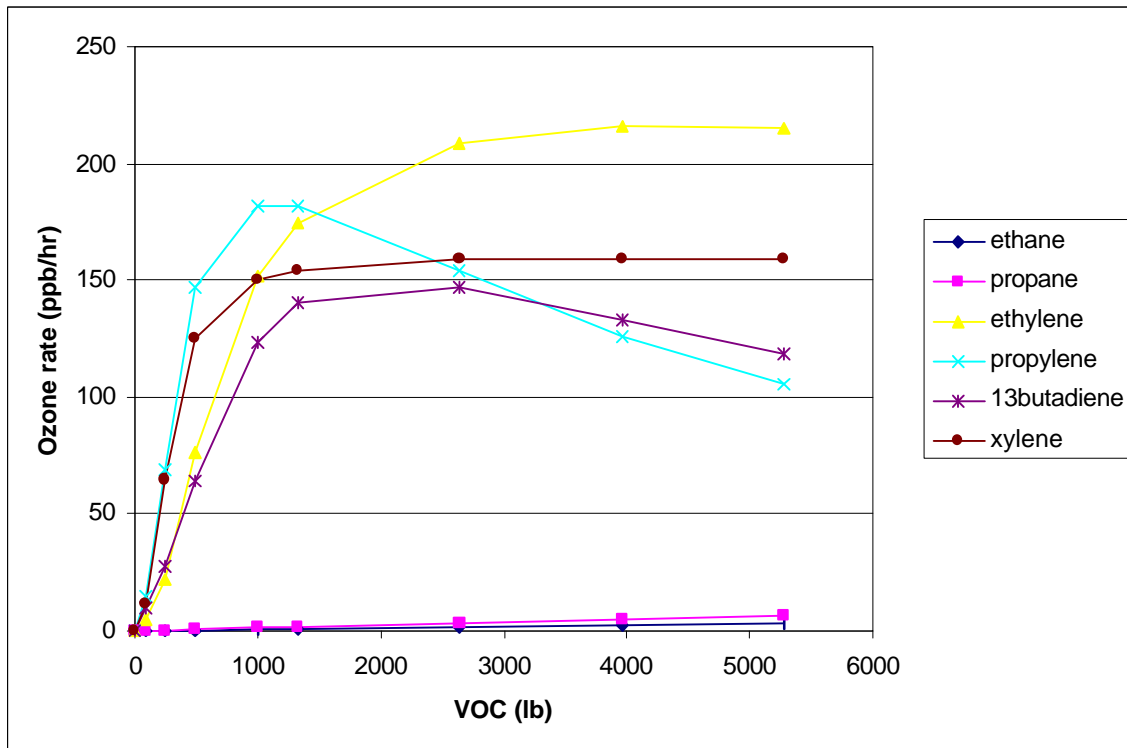

Figure 26. Extra ozone (simulation with additional release-base case) formed within one hour of release of VOC only, 7:00 to 8:00

- Chlorine emissions and chemistry had minor effects on releases involving ethene. The same observation would likely hold for other reactive hydrocarbons.
- Chlorine emissions and chemistry had dramatic effects on upsets involving ethane (and presumably other alkanes). With chlorine present, the ozone formation potential of alkane upsets is similar to the ozone formation potential of alkene and diolefin releases.
- Chlorine emissions and chemistry had a dramatic effect on the ozone formation potential of releases involving only NO_x or low VOC/NO_x ratios. By enhancing NO to NO_2 conversion, the chlorine emissions and chemistry reduced the amounts of ozone titration by NO.
- Dilution of upset plumes reduces peak ozone concentrations but can significantly increase total ozone formation if the upset emissions are low in NO_x or if the upset occurs late in the day (see Figures 27 and 28).
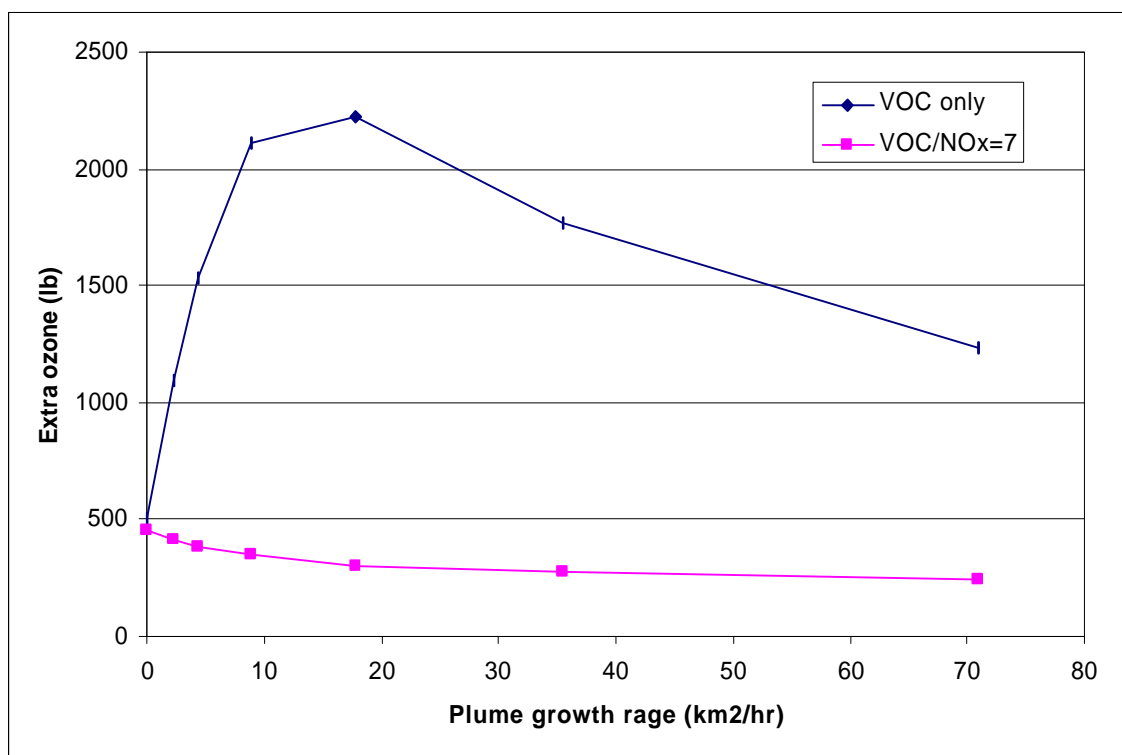

Figure 27. Extra ozone mass generated in box model calculations at 09:00, for a 5280lb ethyelene release 07:00 to 08:00; the box model's ground area was increased by the amount shown on the horizontal axis in the hour immediately after the upset; the dilution air composition was that of the base case at the hour simulated

Figure 28. Extra ozone mass generated in box model calculations at 14:00, for a 5280lb ethyelene release 12:00 to 13:00; the box model's ground area was increased by the amount shown on the horizontal axis in the hour immediately after the upset; the dilution air composition was that of the base case at the hour simulated
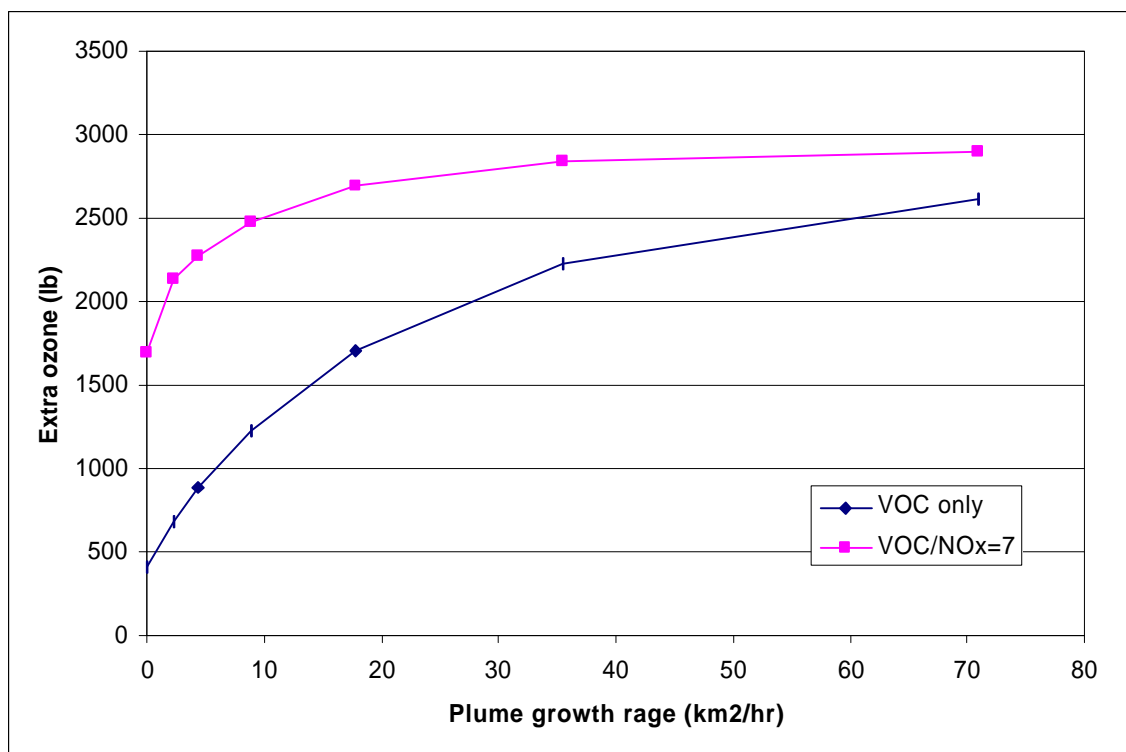
5.   *Are the chemistries of dominant hydrocarbon species adequately represented in current models of ozone formation chemistry?*

The box model analyses have shown that the ozone formation potentials for different hydrocarbons have the potential to be significantly different.   At the moment, there is insufficient information to determine whether CB-IV chemistry, with its lumped species provides sufficient chemical resolution to distinguish the type of compound specific behavior shown in Figures 24-26. A short term research priority should be to compare the response of compound specific box models calculations to lumped CB-IV mechanisms.

Summary of findings and data analysis needs

The key issues to be addressed are:

1. *Can simplified chemical mechanisms currently used in regional air quality modeling qualitatively predict the rapid and efficient ozone formation observed in southeast Texas?*

2. *Are there chemical mechanisms contributing to ozone formation in southeast Texas that are not adequately represented in the current models?*

3. *Which hydrocarbon species are the most significant contributors to ozone formation?*

4. *What magnitudes of reactive hydrocarbon and NO_x emissions are necessary to produce the ozone formation rates and ozone concentrations observed in southeast Texas?*

5. *Are the chemistries of dominant hydrocarbon species adequately represented in current models of ozone formation chemistry?*

Findings and near term analyses to be performed in each of these areas are summarized below.

1. *Can simplified chemical mechanisms currently used in regional air quality modeling qualitatively predict the rapid and efficient ozone formation observed in southeast Texas?*

Finding: The Carbon Bond Version IV (CB-IV) mechanism, and other simplified chemical mechanisms commonly used in regional photochemical modeling, are capable of qualitatively replicating rapid ozone formation caused by high concentrations of reactive hydrocarbons.

2. *Are there chemical mechanisms contributing to ozone formation in southeast Texas that are not adequately represented in the current models?*

Findings: Chemistries that may be contributing to ozone formation in southeast Texas, but that have not historically or are not currently represented in models, include the reactions of atomic chlorine, night-time production of free radicals, and heterogeneous reactions on particle surfaces. Ongoing studies suggest that chlorine chemistry enhances ozone formation in Houston, and that local peak enhancements are likely in the range of 5-15 ppbv ozone. Regional enhancements are likely in the range of 2-4 ppbv. Emission inventories and chemical reaction mechanisms that account for this chemistry have been incorporated into the photochemical models used by the State. No work is currently underway to assess the roles of

heterogeneous chemistry or night-time production of free radicals and it is unclear how important these processes are.

The following tasks need to be performed to improve the characterization of the reactions of atomic chlorine, night-time production of free radicals, and heterogeneous reactions on particle surfaces.

Atomic chlorine chemistry:
- Improve the accuracy of the emission inventory for atomic chlorine precursors; while this is addressed in the chapter involving emission inventories, improving the inventory also requires a better understanding of the chemistry of the processes that generate atomic chlorine in the atmosphere (such as the reactions of chlorinated organics, the reactions of sea salt, and the partitioning of water treatment chemicals into the atmosphere)
- Test the chemical mechanism in laboratory experiments and evaluating the sensitivity of regional ozone formation to estimated values of chemical rate parameters
- Perform additional measurements of molecular markers for chlorine chemistry; the most compelling evidence for the significance of chlorine chemistry in southeast Texas is the detection of unique molecular markers of this chemistry by Riemer (2001). Modeling suggests that these measurements are consistent with increases in ozone concentration of 5-15 ppb, but these measurements have been made in only one location (LaPorte). Additional measurements would allow for more rigorous evaluation of emission inventories and chemical mechanisms.

Night-time production of free radicals
- Incorporate updated estimates of radical yields from ozone-alkene reactions into chemical mechanisms and investigate whether nighttime olefin releases lead to predictions of free radical concentrations consistent with observations made at LaPorte

Heterogeneous reactions on particle surfaces
- Incorporate preliminary estimates of the rates of heterogeneous chemistry into current chemical mechanisms; identify potentially significant reaction pathways and their impact on ozone formation

3. Which hydrocarbon species are the most significant contributors to ozone formation?

Findings: High concentrations of light alkanes, alkenes, and aromatics are all observed during episodes of rapid and efficient ozone formation. The alkenes and aromatics (especially ethene, propylene, toluene and xylenes) have the potential to react rapidly, enhancing ozone formation.

Concentrations of hydrocarbons tend to be slightly higher on ozone episode days, compared to non-episode days, however, the composition of the hydrocarbons on episode and non-episode days is virtually identical. Further, while the median magnitude of hydrocarbon concentrations has decreased in the last decade, with a

few minor exceptions (isopentane, in particular), the concentration ratios of atmospheric hydrocarbons observed in Houston have remained consistent for a decade or more.

Additional work that needs to be performed includes

- Detailed analysis of events during the Texas Air Quality Study when high hydrocarbon concentrations were detected; episodes that led to high ozone concentrations should be contrasted with episodes that did not lead to high ozone concentrations.

4. *What magnitudes of reactive hydrocarbon and NO_x emissions are necessary to produce the ozone formation rates and ozone concentrations observed in southeast Texas?*

Findings: Sensitivity analyses performed using a simple photochemical "box" model, designed to replicate Houston conditions, indicate that episodic emissions of approximately 100 pounds of highly reactive hydrocarbons can cause localized (1 km^2 area) increases in ozone concentration of approximately 50 ppb. Dilution of these emissions over a larger area does not necessarily reduce the mass of ozone formed, although it does reduce peak concentrations.

Additional work that needs to be performed includes

- Detailed analysis of events during the Texas Air Quality Study when high hydrocarbon concentrations were detected should be performed; events that led to high ozone concentrations should be contrasted with events that did not lead to high ozone concentrations.

5. *Are the chemistries of dominant hydrocarbon species adequately represented in current models of ozone formation chemistry?*

Findings: Sensitivity analyses performed using a simple photochemical "box" model, designed to replicate Houston conditions, indicate that the ozone formation potentials of episodic releases of hydrocarbons exhibit complex behaviors that differ from compound to compound. It is not yet clear whether these differences are captured by current simplified chemical mechanisms. Ongoing work will clarify this issue.

Additional work that needs to be performed includes:

- Critically evaluate the mechanisms used in CB-IV and SAPRC to assess their ability to model ozone formation for the most significant hydrocarbon species.

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