

## MODELING/DATA ANALYSIS

### 0. Introduction

In the June 4, 2002 proposed SIP revision, the commission used three separate analyses to answer the question: “Can VOC industrial controls be substituted for the last 10% (or some lesser portion) of industrial NO<sub>x</sub> controls?” Commission modeling staff utilized two different modeling episodes, an observation-based model incorporating the state of the science chemical solver and various data analysis projects to answer this complex question. All of the tools directionally pointed to the same answer: VOC reductions potentially can be utilized to achieve the same level of air quality benefit for the HGA as the reductions in the December 6, 2000 SIP. Since that time, the commission received a number of comments from the many stakeholder groups in the area concerning this three-pronged approach. In response, the TCEQ has significantly revised the approach and expanded the scope of the technical analyses described in this document. The major revisions are as follows:

- This document places increased emphasis on modeling for the August 25 - September 1, 2000 episode. As of June, acceptable model performance had only been achieved for two days of this episode, with rather marginal performance on a third. In the intervening months, the modeling staff have made a number of improvements to the model formulation which have resulted in very good model performance for the majority of the episode. Because this episode occurred during the 2000 Texas Air Quality Study (TexAQS-2000, or simply TexAQS), a vast amount of ambient data is available to help ensure the model is performing well because of correct formulation instead of as a result of compensating errors.
- This Technical Support Document has been restructured along the lines of modeling demonstrations in previous SIP revisions. Because the 2000 TexAQS episode has gained much credibility since June, this TSD now focuses on the modeling conducted for this episode. Other relevant information is now included as Weight-of-Evidence.
- The observation-based modeling conducted by NOAA has been relegated to serve as WoE, since the model by nature cannot represent the full range of physical processes involved in ozone formation. Photochemical grid modeling like that used for the 2000 TexAQS episode includes a much more complete simulation of the complex atmospheric dynamics leading to ozone formation.
- The discussion of modeling for the September 8-11, 1993 episode has been removed. While this modeling was the best available methodology for SIP planning in the HGA prior to the TexAQS, it is impossible to develop the level of confidence in this episode that is available with the TexAQS episode. The September 8-11, 1993 episode occurred after the completion of the Coastal Oxidant for Southeast Texas (COAST) study, hence does not offer the vast array of ambient measurements available for the TexAQS episode. Especially important is the lack of upper-air meteorological data which has proven critical to achieving good model performance in the TexAQS episode. The

comprehensive set of meteorological data used to develop the meteorological characterization for the 2000 TexAQS episode helps ensure that this episode is characterized accurately, hence that the results are credible.

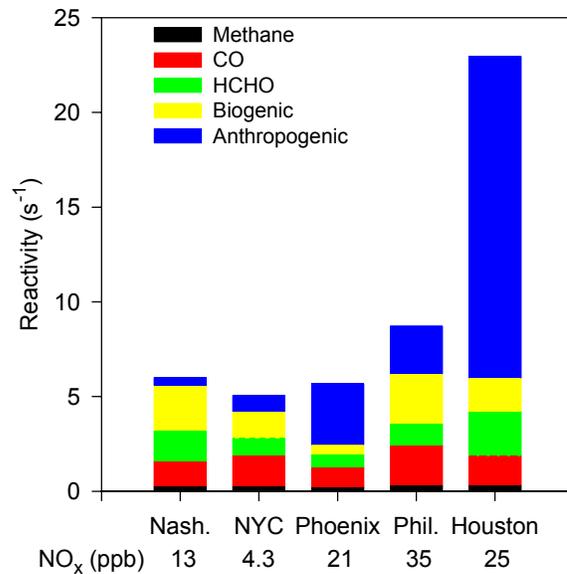
- Modeling results are presented with the unadjusted (reported) emissions inventory as well as with an inventory adjusted to increase industrial olefin emissions. In the June proposal, only modeling conducted with the adjusted emissions was presented. This revision includes both base and future case modeling using the inventory as reported to EPA.
- The future case modeling now includes the so-called “gap” measures adopted in the December, 2000 SIP revision.
- Modeling to determine the levels of VOC and NO<sub>x</sub> reductions necessary to demonstrate attainment of the ozone NAAQS was conducted and is documented in this revision.

The scientific basis for the successful model formulation for the August 25 - September 1, 2000 episode is the Texas Air Quality Study, one of the most extensive field studies ever conducted. The next section describes the study and summarizes many of the findings most relevant to the current modeling implementation.

### **1. The 2000 Texas Air Quality Study**

In August and September 2000, over two hundred scientists from around the world gathered in the HGA and conducted an intensive field study, the Texas Air Quality Study (TexAQS). In 2001 preliminary results were released by many of the scientists based on the early analysis of the samples and data collected. Analysis is likely to continue over the next two to three years. Much of the early analysis focused on why is the HGA different from other areas in the nation. A survey of the area indicates the most striking difference in HGA and other areas in the nation is the extensive refining and petrochemical industry located around the Houston Ship Channel. The HGA produces over half of the chemical and refining needs of the nation. Not surprisingly, the early results have pointed to high levels of VOC emissions from industrial sources in the area; which are much higher than those reported in the annual and special emissions inventories.

Figure 1-1 illustrates the difference in ozone productivity (reactivity) in the Houston area compared to four other cities in the U. S. that have been examined in a major air quality study. Anthropogenic sources are man-made emission sources and in the HGA they are primarily industrial. Figure 1-2 illustrates the difference in olefins (a class of highly reactive VOCs) and paraffins (a class of less reactive VOCs) measured at the LaPorte area of HGA, compared with an average of samples taken in 39 U. S. cities and used as a standard by EPA. Aromatics (another class of reactive VOC's commonly found in gasoline) differ relatively less between the La Porte monitoring site and the 39-cities than do other VOCs. Since the 39-cities data is relatively old (c. 1984 to 1987) it is expected that the aromatic component of the 39-cities is over-represented in the chart because modern cars emit much less VOC than their 1980's era predecessors.



**Figure 1-1** Ozone production (reactivity) in the Houston area compared to four other cities in the U.S. (Kleinman, 2002)

Initial analysis efforts of TexAQS researchers were concentrated on a select number of highly reactive VOCs - ethylene, propylene, and 1, 3 butadiene, because these VOCs contributed to very large portion of reactivity observed on several airborne samples. As more data became available, it became apparent that several additional highly reactive VOC's should be considered in analyzing the causes of high ozone in the HGA. Figure 1-2 indicates paraffins, generally considered to be less reactive, contribute to the ozone problems in HGA. Other scientists have indicated that other VOCs, even though not highly reactive, may have contributed to high ozone levels in HGA because of their extremely high mass.

The effect of having all of these highly reactive VOC emissions is that ozone yield in the HGA is higher than any observed in any other U.S. city. This consequence is primarily due to industrial

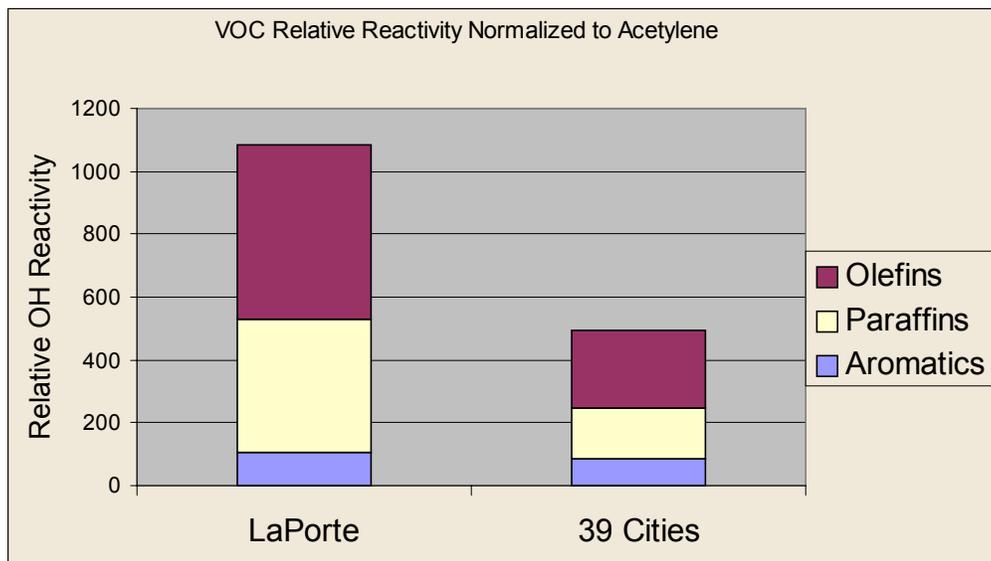


Figure 1-2: VOC Reactivity by Category (Kuster, 2002)

emissions in the Ship Channel area as shown in Figure 1-3. This chart shows that the industrial emissions are extremely effective in producing ozone when compared to the urban area or a large power plant in an area isolated from other industrial sources.

## Large differences in ozone yield observed

Transects equally oxidized -

(NO<sub>x</sub>/NO<sub>y</sub>) ~ 0.20

Electra 08/28/00 flight data

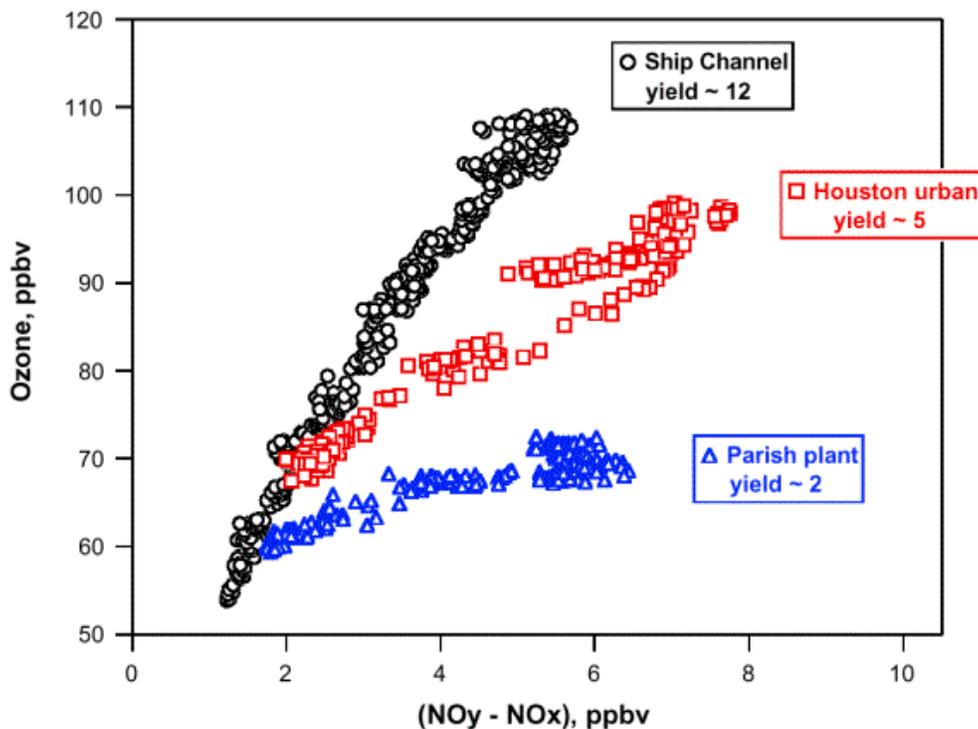


Figure 1-3: Ozone yields by source region (Trainer, 2002)

Preliminary results from the 2000 study, as observed by Dr. Peter Daum, Brookhaven National Lab, DOE are listed below:

- C Measurements strongly suggest alkene emissions are not accurately included in the inventories:  
absence of upset reports suggests ship channel emissions are routine rather than upset driven; and models will not accurately simulate observations until the alkene inventories are realistic.
- C Primary cause of ozone exceedances greater than 200 ppbv in the Houston area appears to be: anthropogenic emissions of very reactive alkenes (ethylene, propylene, 1-3 butadiene); and collated (co-emitted) with large amounts of NO<sub>x</sub>.
- C Measurements and models further suggest that, in general, routine emissions of alkenes, appropriate meteorology and OH chemistry alone are sufficient to explain the observed ozone:

Upsets may play a part, but business-as-usual emissions appear to be sufficient to account for the observed ozone; and

Exceedances are possible on a daily basis; actual occurrence [of a monitored ozone exceedance] is dependant upon daily meteorology and location of monitors.

Dr. David Allen, University of Texas, Austin, participated in the TexAQS and has coordinated the activities of the Interim Science Coordinating Committee Synthesis sub committee's review of the documents and science that has become available since the summer of 2000. Dr. Allen noted nine key findings in the February 28, 2002 Accelerated Science Evaluation (Executive Summary).

- C Almost without exception, air parcels with very high ozone concentrations, observed by aircraft during the TexAQS, had back trajectories that indicated a substantial contribution of emissions from industrial source regions. These air parcels also had chemical compositions that were representative of industrial sources, rather than typical sources.
- C The rate of ozone production in and around the industrial source dominated areas in Houston can be very high, commonly exceeding 50 ppb/hr, and at times approaching instantaneous rates of 200 ppb/hr.
- C The efficiency of ozone production in and around the industrial source dominated areas in Houston can be very high, ranging from 10 - 20 molecules of ozone per molecule of reacted NO<sub>x</sub>.
- C Ozone production in the Houston urban plume was found to be slower and less efficient than in the composite industrial plume from the Ship Channel region and in plumes from isolated petrochemical facilities.
- C The high rates and high efficiencies of ozone production in the industrial plumes are driven by high concentrations of reactive hydrocarbons in the presence of NO<sub>x</sub>.
- C Industrial hydrocarbon emissions are significantly underestimated. Measurements of the ratios of hydrocarbons to NO<sub>x</sub> in the industrial plumes were consistently factors of 3-10 higher, and in some isolated instances even a factor of 100 or more higher, than the ratios reported in the inventories.
- C Observations of wind fields aloft, and other meteorological phenomena during TexAQS, support and refine the evolving conceptual model of meteorological conditions that lead to ozone formation in the HGA.
- C The chemical mechanisms for ozone formation currently employed in models of air quality in the HGA are adequate to explain the main features of rapid and efficient ozone formation observed in industrial plumes.
- C The methods and data that current regulatory models use to calculate ozone formation in industrial plumes may not be adequate to explain the rapid and efficient ozone formation observed in industrial plumes.

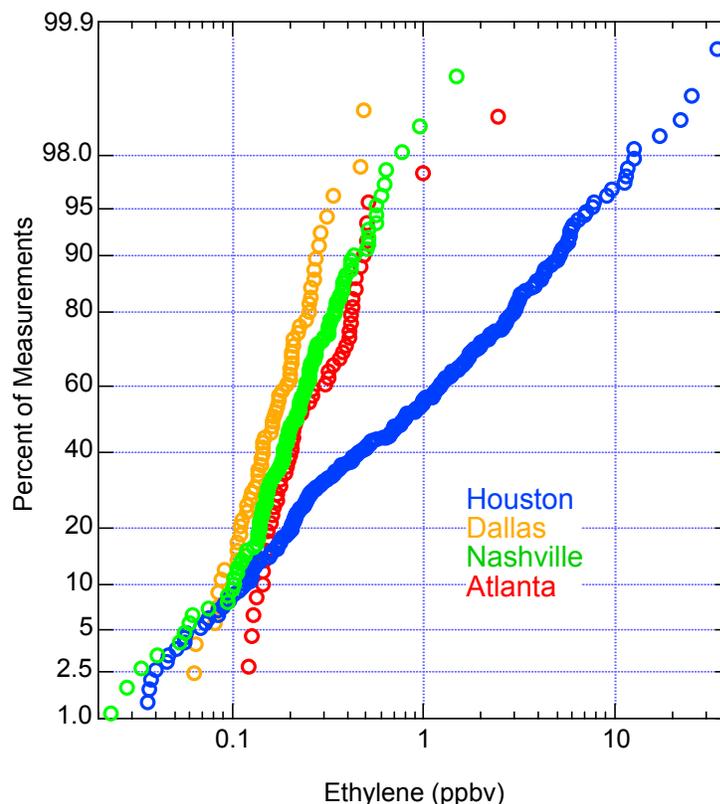
As more information becomes available, Dr. Allen will continue to update the state-of-the-science documents for the HGA. The reader is encouraged to review the materials leading to these conclusions on TCEQ's web site at [www.TCEQ.state.tx.us/air/aqp/airquality\\_science.html](http://www.TCEQ.state.tx.us/air/aqp/airquality_science.html).

Based on the findings of Drs. Daum and Allen, along with dozens of other scientists who have analyzed the TexAQS data, TCEQ has developed the following conclusions regarding the reported versus measured emissions of light olefins.

**A. Ethylene and Other Light Olefins Are Emitted in Much Greater Quantities in Houston than Other Cities.**

Figure 1-4 shows the ethylene concentrations measured in four different cities in recent years by NOAA and NCAR scientists (Parrish et al., 2002). Ethylene concentrations in Houston are drastically higher than those measured in other cities. This discovery is one of the major findings of TexAQS 2000 (Daum et al., 2002): light alkene concentrations are significantly higher in

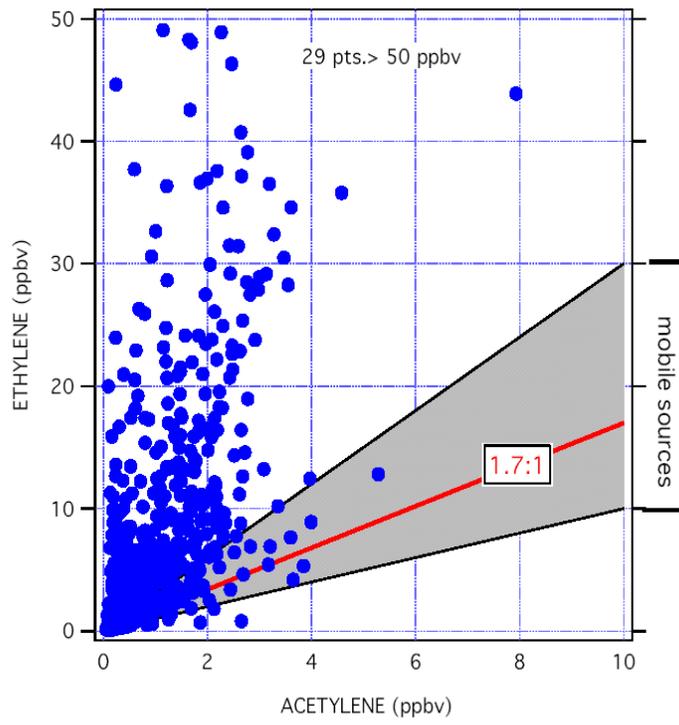
Houston compared to other cities, and their presence contributes greatly to the rapid ozone formation and transient high ozone seen in Houston.



**Figure 1-4:** Ethylene concentrations observed during NOAA/NCAR aircraft flights during the TexAQS 2000 (Parrish, 2002)

**B. The High Concentrations of Ethylene and Other Light Olefins Are Probably Not Due to**

## **Mobile Source Emissions.**

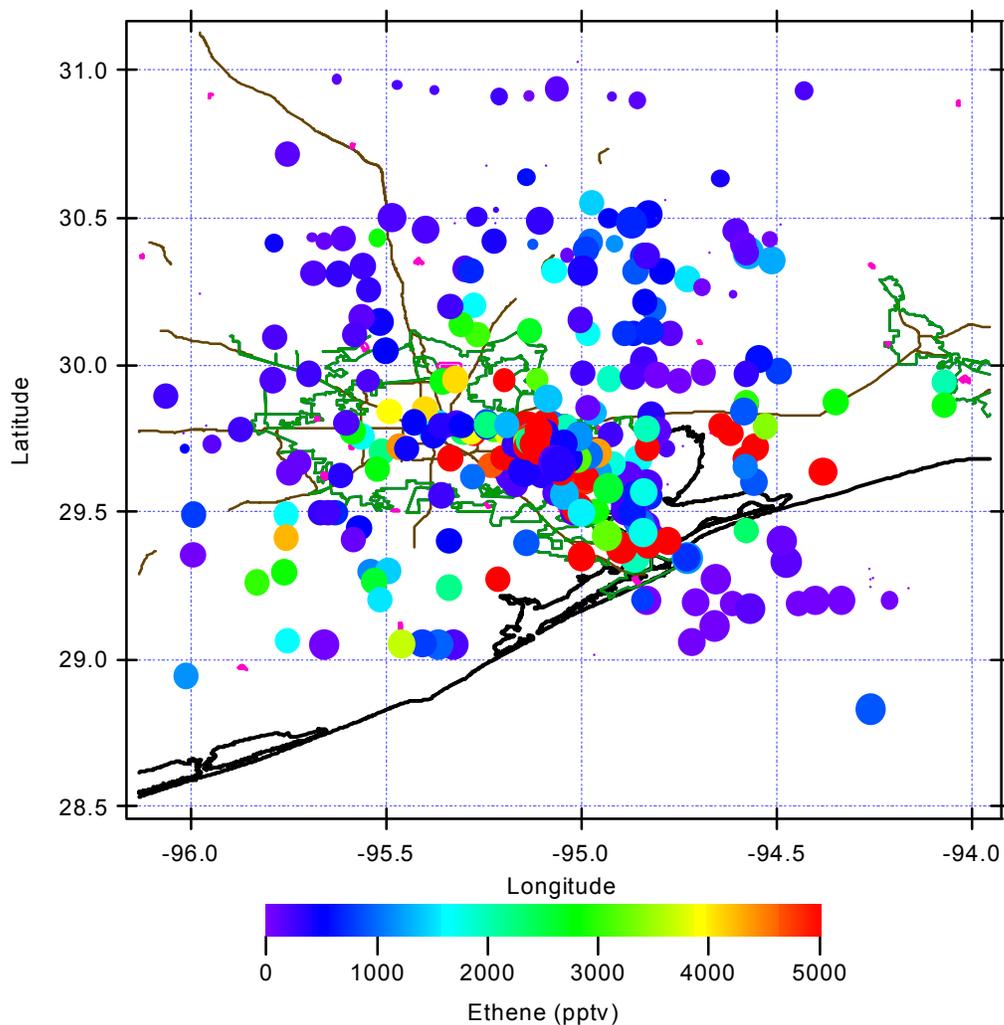


**Figure 1-5:** Ethylene vs. acetylene concentrations, measured at La Porte during TexAQS 2000 (Kuster, et. al, 2002)

Figure 1-5 shows that the ethylene/acetylene ratios measured at La Porte during August-September 2000 are not consistent with the mobile source signature (Kuster et al., 2002). Studies conducted in highway tunnels throughout the U.S. indicate that ethylene and acetylene are released by mobile sources in a characteristic ratio, approximately 1.7 to 1. In Houston, TexAQS 2000 researchers found that emissions from vehicles passing through the Washburn Tunnel yielded an ethylene to acetylene ratio of  $1.85 \pm 0.26$ , as measured by canisters within the tunnel (Harley et al., 2002). However, Figure 1-5 shows that most samples taken at La Porte have an ethylene to acetylene ratio that is much larger than the characteristic mobile source ratio, indicating that there are additional sources of ethylene beyond mobile sources. Additional evidence to support this assertion is in Figure 1-4, which shows that cities dominated by mobile sources generally have much smaller ethylene concentrations than Houston.

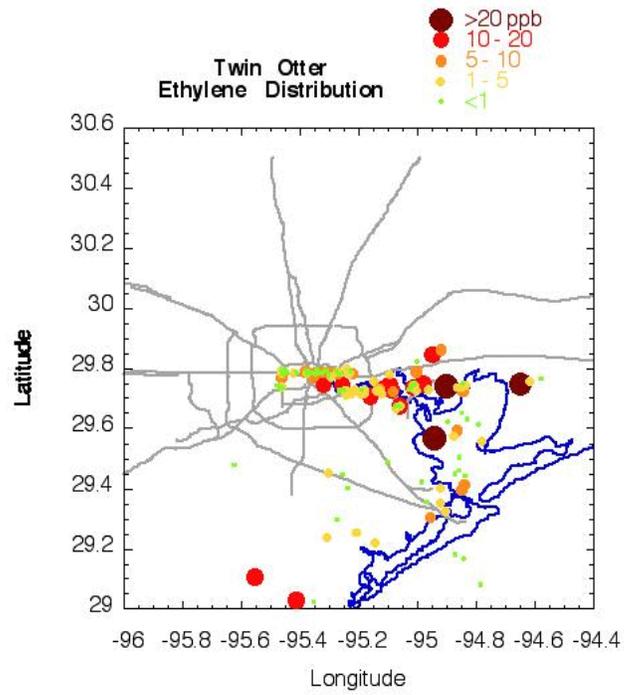
### C. High Concentrations of Ethylene and Other Light Olefins Are Found in and Downwind of Industrial Source Regions

Figure 1-6 shows the geographic distribution of ethylene measurements taken during TexAQS 2000 by the NOAA/NCAR Electra aircraft (Atlas et al., 2002). The highest ethylene concentrations are found in or downwind of the industrial areas of Houston. Figure 1-7 shows that the Baylor aircraft canister samples independently corroborate the geographic distribution found by NOAA/NCAR (Lonneman et al., 2002). Both independent data sets confirm that the highest ethylene and propylene concentrations are likely to be measured in or near the industrial areas of Harris, Chambers, Brazoria, and Galveston counties, and are not likely to be measured in the urban core or rural areas of the domain.

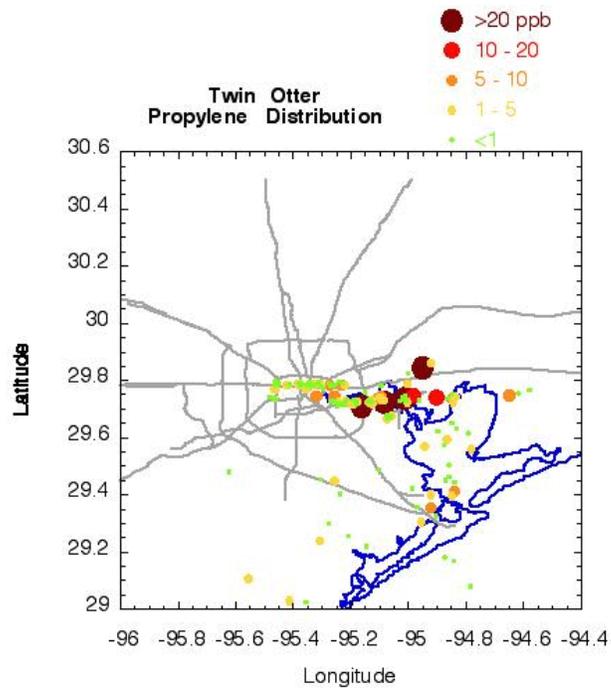


**Figure 1-6:** Geographic distribution of ethene concentrations, from airborne canister samples taken by NCAR/NOAA during the TexAQS 2000 study (Atlas et al., 2002.)

(a)



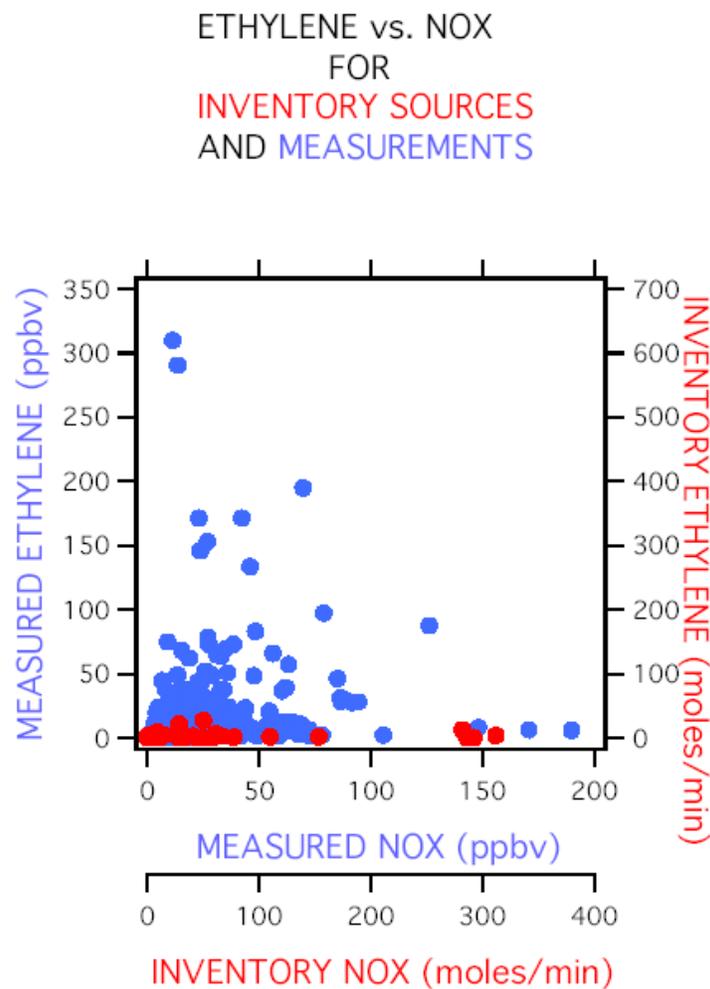
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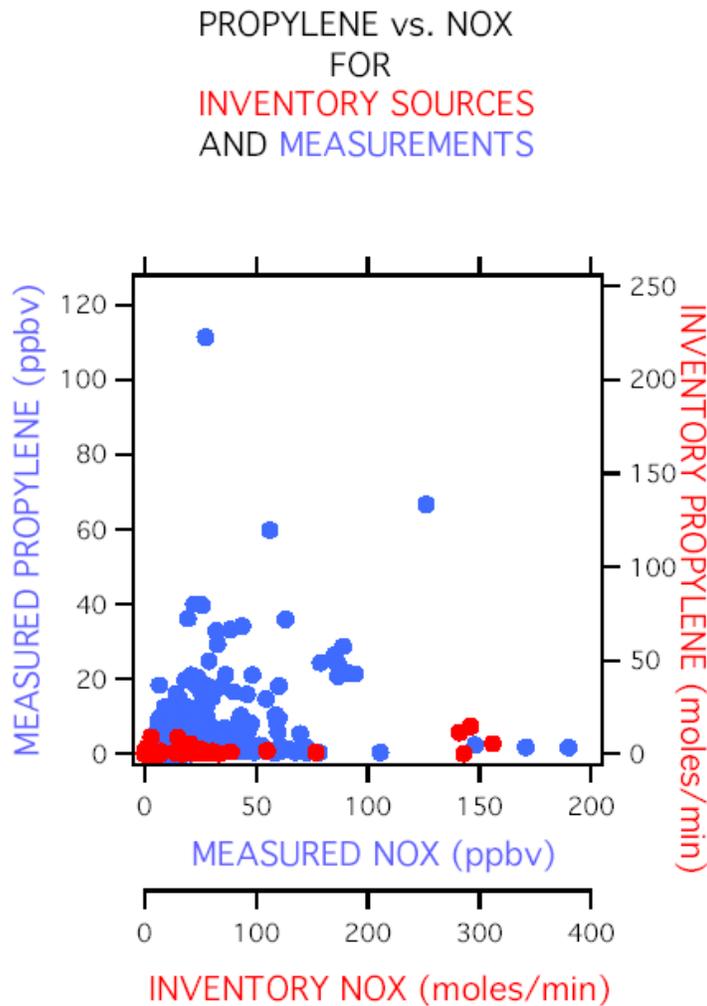
**Figure 1-7:** Geographic distribution of ethylene and propylene concentrations, from canisters samples taken during TexAQS 2000 aboard the Baylor Twin Otter.

### D. Measured Ratios of Olefins to Nitrogen Oxides Are Much Larger than Those Reported in the Emissions Inventories

Figures 1-8 and 1-9 show the ethylene to  $\text{NO}_y$  and propylene to  $\text{NO}_y$  ratios, respectively, measured by NOAA/NCAR at La Porte during TexAQS 2000. Also plotted are the same ratios of emissions from different facilities in Houston, as reported in TCEQ 1999 point source emissions inventory. The ratios in the measurements are extremely different from the reported ratios in the inventory. While this comparison is not conclusive, it certainly suggests that there may be serious underestimates of the light olefins in the emissions inventory. It could also mean that  $\text{NO}_x$  emissions are greatly overestimated, but since  $\text{NO}_x$  emissions are often measured by continuous emissions monitors, there is greater confidence in the  $\text{NO}_x$  inventory than in the VOC inventory.

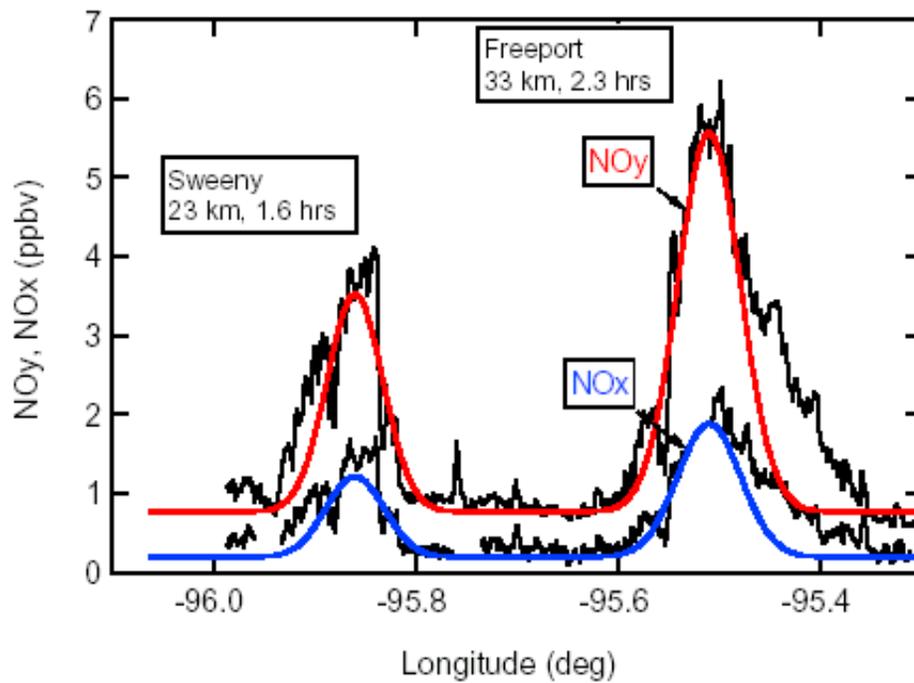


**Figure 1-8:** Measured ethylene and  $\text{NO}_x$  concentrations compared with ethylene/ $\text{NO}_x$  ratios reported for industrial facilities in the TCEQ 1999 emissions inventory (Kuster et al., 2002).

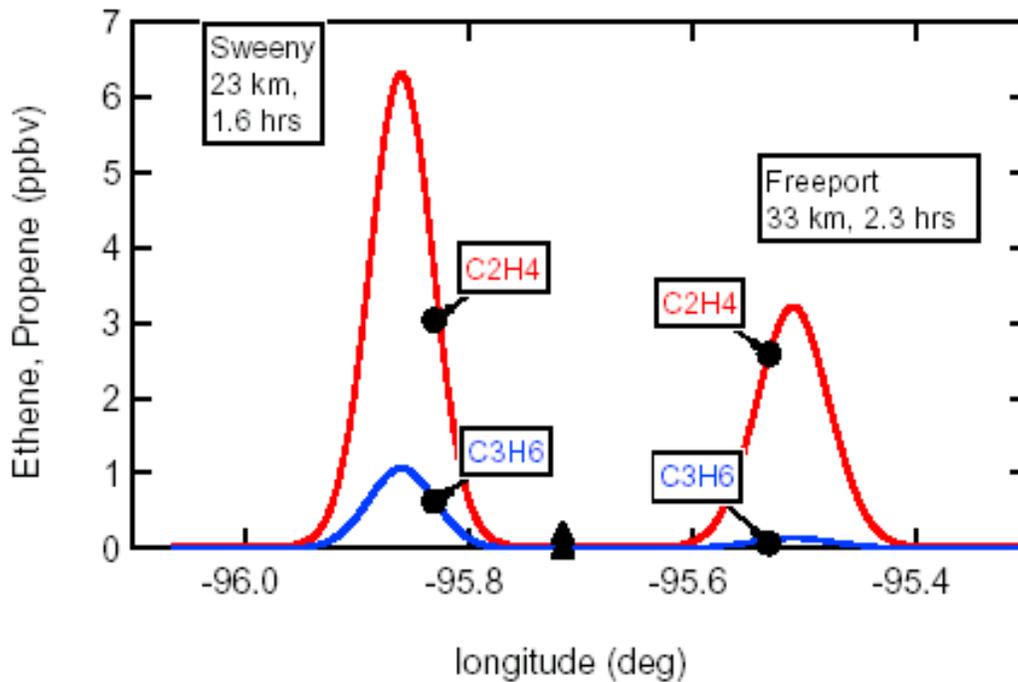


**Figure 1-9:** Measured propylene and NO<sub>x</sub> concentrations compared with propylene/NO<sub>x</sub> ratios reported for industrial facilities in the TCEQ 1999 emissions inventory (Kuster et al., 2002).

Figures 1-10 and 1-11 show the results of Lagrangian plume modeling from two isolated petrochemical facilities located in Sweeny and Freeport (Trainer et al., 2001). Facilities in these areas emit both olefins and NO<sub>x</sub>. The results from Lagrangian modeling seem to indicate that the NO<sub>x</sub> emissions are essentially correct, but that ethylene and propylene emissions are severely underestimated. After the ethylene and propylene emissions have been adjusted to the level indicated by the data, the ozone, formaldehyde, acetaldehyde, PAN, and HNO<sub>3</sub> modeling agree well with the observations; without the appropriate emissions adjustments to ethylene and propylene, model performance for these parameters is poor.

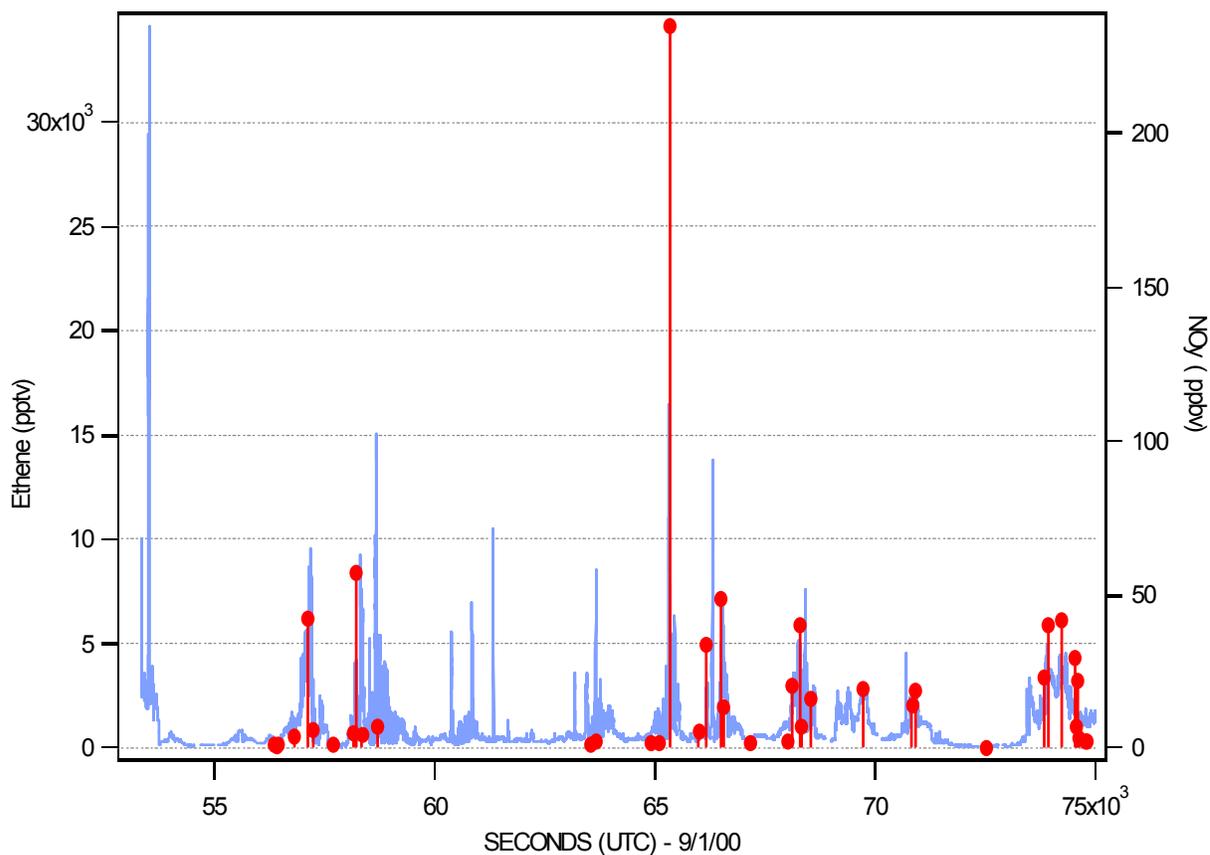


**Figure 1-10** NO<sub>x</sub> and NO<sub>y</sub> observations in the plumes emanating from Sweeny and Freeport source regions on 28 August 2000, and Lagrangian plume modeling results (Trainer et al., 2001).



**Figure 1-11:** Measurements of ethylene (C<sub>2</sub>H<sub>4</sub>) and propylene (C<sub>3</sub>H<sub>6</sub>) compared to Lagrangian plume modeling results (Trainer et al., 2001).

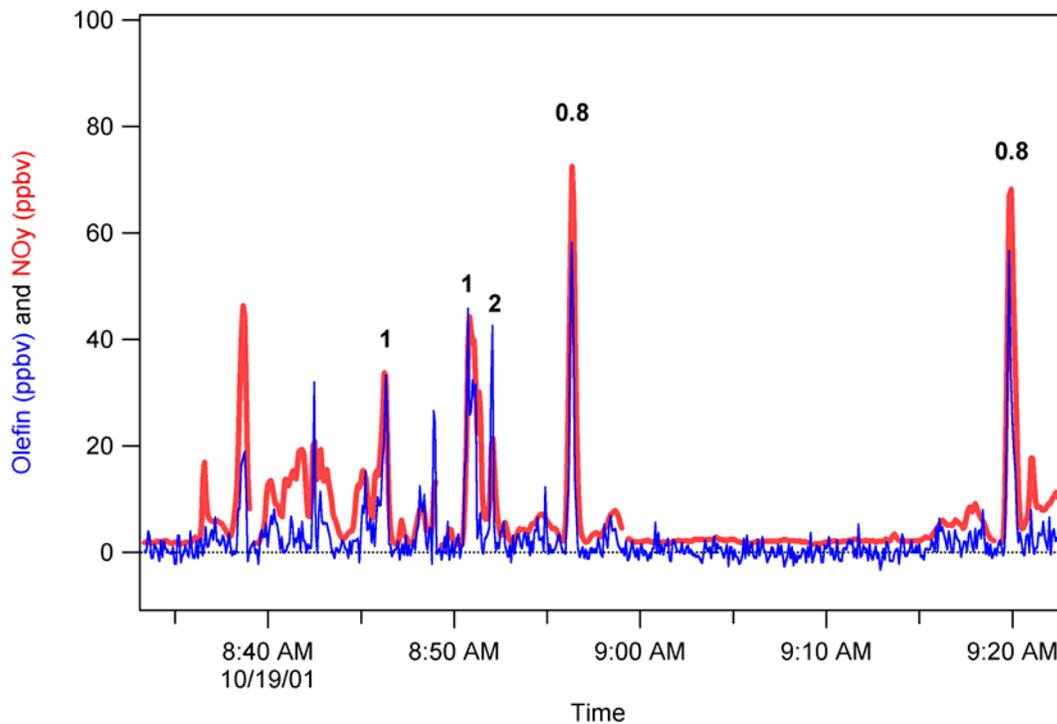
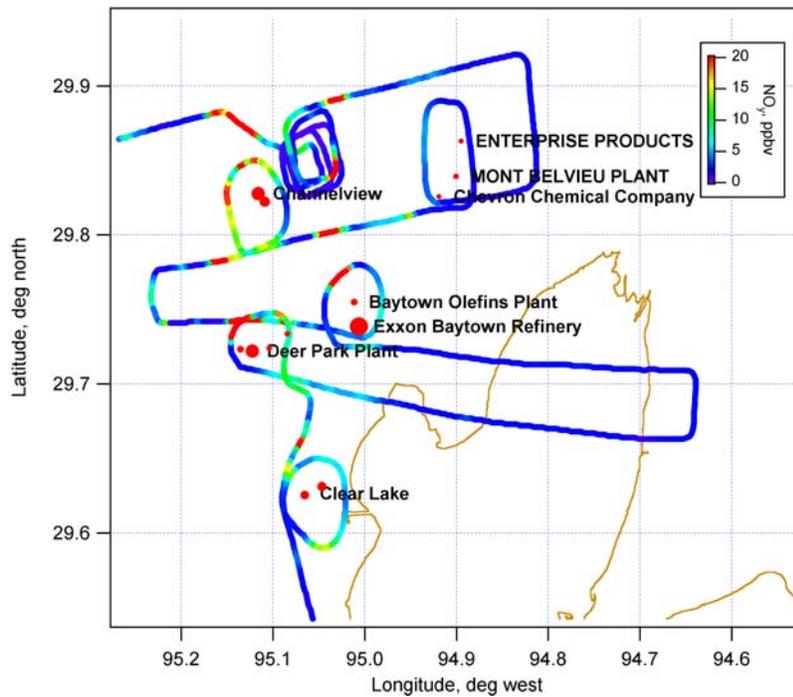
Further evidence supporting the hypothesis that the light olefin emissions are greatly underestimated is presented in Figures 1-12 and 1-13. Figure 1-12 shows ethylene and  $\text{NO}_y$  data collected by NOAA/NCAR in plumes from the industrial areas. These data from September 1, 2000 indicate that ethylene plumes are often coincident with  $\text{NO}_x$  plumes, and that the ethylene concentrations are often similar in magnitude to the  $\text{NO}_x$  concentrations. By contrast, most facilities in the emissions inventory have ethylene to  $\text{NO}_x$  ratios much smaller than 1 to 1.



**Figure 1-12:** Ethene and  $\text{NO}_y$  data collected on 1 September 2000 by the NOAA/NCAR Electra (Atlas et al., 2002).

Figure 1-13 shows that the discrepancies between olefin to  $\text{NO}_y$  ratios are likely to be persistent, not episodic. It presents  $\text{NO}_y$  and olefin data collected by the Baylor aircraft on October 19, 2001, or thirteen months after the completion of TexAQS 2000. Figure 1-13a shows the flight path, with  $\text{NO}_y$  concentrations indicated by the color of the track at each point. Figure 1-13b shows the  $\text{NO}_y$  and continuous olefin concentrations for a portion of the flight path, presented as a time series. The continuous olefin monitor is described in detail in Guenther and Hills, 1998, and can be used to monitor propylene, isoprene and other light olefins, except for ethylene, for which it has less sensitivity. Figure 1-13b shows that olefin and  $\text{NO}_y$  plumes are often coincident, and that the olefin to  $\text{NO}_y$  ratio is between 0.5-2.0 at facilities that emit significant quantities of both. It also indicates that whatever was causing the ratios of olefin/ $\text{NO}_y$  to be drastically larger than the inventory was occurring in Oct 2001 as well as during the TexAQS 2000 study.

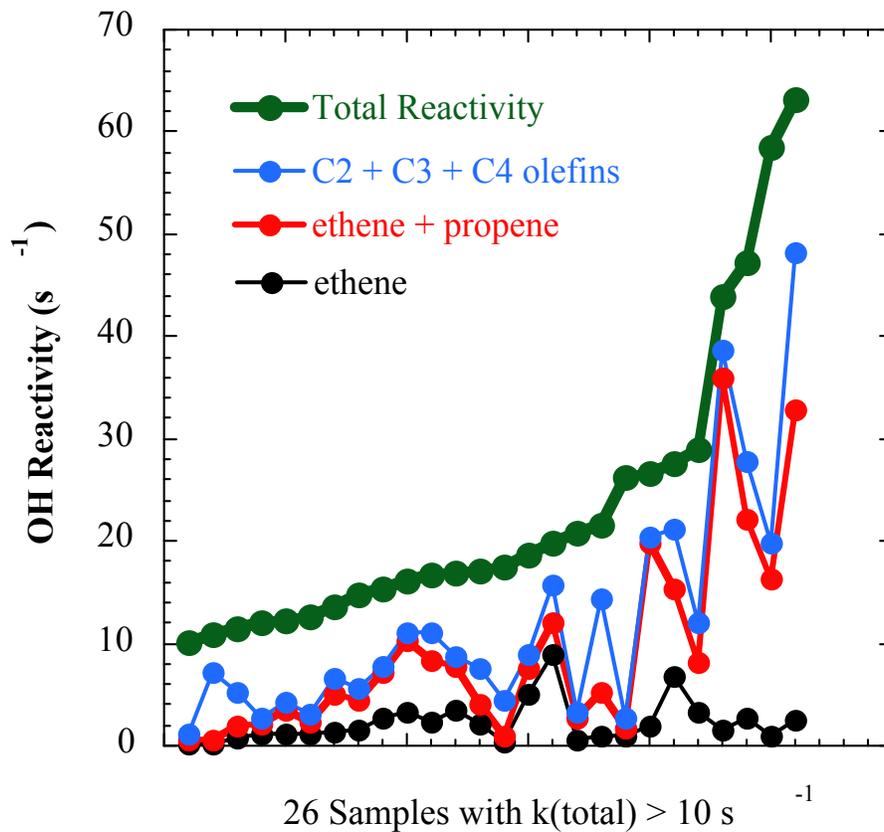
(a)



**Figure 1-13:** (a) Flight path of Baylor Twin Otter aircraft, 19 October 2001 (Guenther and Hills, 1998), (b) Time series of olefins and NO<sub>y</sub> measured during the flight.

These findings indicate that industrial emissions of ethylene, propylene, and other VOCs are probably greatly underestimated by the methods currently used to inventory industrial emissions. One result of this underestimation is that the photochemical models used to simulate ozone episodes do not perform well, in part because the industrial olefin emissions are too low. Thus TCEQ had to develop a more reasonable estimate of the true olefin emissions, so that photochemical modeling and control strategy development could proceed.

Figure 1-14 clearly shows that of 26 VOC samples from the Twin Otter aircraft in some



**Figure 1-14:** Reactivity of samples taken by Twin Otter aircraft Daum, P, 2002)

instances more than half of the reactivity is from non-olefin VOCs. This indicates isoprene, butenes, formaldehyde, acetaldehyde, toluene, pentenes, trimethylbenzenes, xylenes, and ethyltoluenes can contribute to high levels of ozone in the HGA, along with light olefins such as ethylene, propylene and 1,3 butadiene. TCEQ will continue to work to identify the role of various VOCs in the formation of ozone formation in the HGA.

The meteorological measurements that were taken during the study have helped to provide a better understanding of the complex interaction of wind direction and wind speed when combined with emissions. TCEQ has now developed a new conceptual model for ozone formation in the HGA. It is now known that winds in Houston typically progress from a northerly direction early in the morning and then clockwise through a 24 hour period until it

returns to a northerly direction the following morning. Depending on the synoptic wind flow, this local pattern leads to instances of pollution being recirculated into the HGA urban area or transported to other areas. This wind pattern explains instances of some monitors recording high levels of ozone while others may not record elevated levels of ozone. The conceptual model is included as Appendix A.

Readers interested in more information on the study and results are encouraged to review the Bibliography contained in Appendix D and to visit the web site previously referenced.

Based on the results of the TexAQS, TCEQ modeling staff began a series of analyses designed to explore the question of substituting VOC reductions for NO<sub>x</sub> reductions. The following sections describe these analyses.