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**ACQUISITION, REVIEW, AND ANALYSIS OF  
AUTO-GC VOC DATA IN THE HOUSTON AREA  
1998-2001**

**FINAL REPORT  
STI-900670-2224-FR**

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# 1. INTRODUCTION

## 1.1 BACKGROUND

Ozone is a secondary pollutant formed by the reaction of nitrogen oxides (NO<sub>x</sub>) and hydrocarbons. Motor vehicle exhaust, industrial emissions, gasoline vapors, biogenic hydrocarbon emissions, and chemical solvents are some of the major sources of NO<sub>x</sub> and hydrocarbons, also known as ozone precursors. These precursors have both anthropogenic and biogenic origins. The formation of ozone begins with the photodissociation of nitrogen dioxide (NO<sub>2</sub>) in the presence of sunlight.



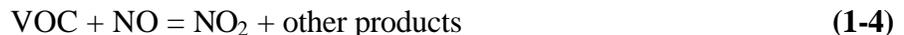
The atomic oxygen (O) quickly combines with molecular oxygen (O<sub>2</sub>) to form ozone (O<sub>3</sub>):



Once formed, ozone reacts with NO to regenerate NO<sub>2</sub>:



Most of the nitrogen oxides emitted into the atmosphere are emitted as NO; if ozone exists near where NO is emitted, then the NO will reduce ozone concentrations by scavenging. However, volatile organic compounds (VOCs) remove the NO as shown (greatly simplified) in Equation 1-4. Thus, NO is not available to re-combine with ozone to form NO<sub>2</sub> and ozone can accumulate.



The formation and accumulation of ozone generally occurs over a period of a few hours. However, transient high ozone events occur in Houston. A transient event is a rapid increase in ozone concentration followed either immediately or after a few hours by a rapid decrease in ozone (Allen and Durrenberger, 2002). These events are of short duration (as little as 15 minutes), have occurred at nearly all monitors, and can be spatially isolated events.

The Houston area has an extensive database of ozone precursor data including hourly, year-round measurements of VOCs measured at several sites. By better understanding the spatial and temporal characteristics of the VOCs through field measurements and data analysis, researchers hope to better understand these ozone events.

## 1.2 PROJECT OBJECTIVES AND TECHNICAL APPROACH

This work order has two primary objectives:

1. To acquire, review, and validate automated gas chromatograph (auto-GC) data in order to prepare the data for subsequent analyses.

2. To integrate Sonoma Technology, Inc. (STI) and Texas Natural Resource Conservation Commission (TNRCC) analyses of auto-GC data.

Analyses ranged from summarizing overall characteristics to performing detailed case studies of the data. The hydrocarbon data were inspected in several different forms and metrics:

- Concentration (ppbC).
- Weight percent or weight fraction (species concentration divided by the total). This is a convenient form because it normalizes the fluctuations in concentration and allows the analyst to investigate the sample composition.
- Median. Because the distribution of concentrations is more log normal than normal, the median was used instead of the average to represent the central tendency of the data sets.
- Reactivity-weighted concentration or weight percent. Hydrocarbons vary in their potential to assist in the formation of ozone. By multiplying hydrocarbon concentrations or weight fractions by some measure of reactivity, some hydrocarbons that comprise a small portion of the total nonmethane organic compound (TNMOC) concentration are found to be much more important to ozone formation than some more abundant hydrocarbons. Reactivity scales are discussed in Section 1.4.

Data summaries consisted of individual, species groups, and TNMOC concentrations by site, year, season, and time of day. Similar summaries were prepared for weight percent and reactivity-weighted data. Time series, scatter, and fingerprint plots (hydrocarbons plotted in the order in which they elute from the chromatograph) were used to investigate diurnal changes, species relationships, and compositional differences. Case study analyses consisted of investigating the differences in hydrocarbon composition on ozone episodes versus non-episodes; differences in composition by wind sector; and the changes from hour to hour and site to site on selected days of interest. We also performed cluster and factor analyses to obtain some understanding of potential emission sources impacting the sites and compared the auto-GC data to other data sets (including to a total hydrocarbon monitor and to collocated canisters).

### 1.3 PREVIOUS WORK

This report builds upon several previous studies using the auto-GC data collected in Houston:

- Analyses made as a part of the Coastal Oxidant Study (COAST) in 1993. Data collected at Clinton Drive and Galleria (a site dominated by motor vehicle emissions) were summarized and compared to the emission inventory (Haney et al., 1995; Anderson and Roberts, 1994).
- Characterization of auto-GC data in Houston (Main et al., 2001). This extended outline integrated TNRCC staff analyses with preliminary analyses of the 1998-2000 data.
- Summary of data validation of 2001 auto-GC data (Main and Brown, 2002a). Most of the information in this interim report is included in this report. Please refer to this report for details on samples that we flagged as suspect.

- Preliminary analyses of Houston auto-GC 1998-2001 data: episode/non-episode differences (Main and Brown, 2002b). Most of the information in this interim report is included in this report.
- Preliminary characterization of 2001 event-triggered VOC and carbonyl samples, Interim Reports #1 and #2 (Brown et al., 2002b, 2002c). Canister and cartridge samples of VOCs and carbonyls were taken during August-November of 2001 at a variety of sites in the Houston area when monitors were “triggered” by ozone events. In previous interim reports (Brown et al., 2002b, 2002c), no single compound appeared on a concentration or weight percent basis or on either reactivity scale during these rapid ozone rises. Through trajectory analysis, it appears that meteorological patterns also play an important role in the location, time scale, and amount of ozone formation. It was also found that there were significant compositional differences between individual half-hour samples, showing the importance of detailed speciation on a small time scale.
- Meteorological and ozone characteristics in the Houston area from August 23 through September 1, 2000 (MacDonald and Roberts, 2002).
- Analysis of year 2000 air quality data collected by the Baylor University aircraft (MacDonald et al., 2001).
- Preliminary results of total hydrocarbon and NO<sub>x</sub> analysis at the San Jacinto Monument site (Houston, Texas), August 15 to October 24, 2001 (Brown et al., 2002a).
- Preliminary VOC, olefin, and conceptual model results for Houston (Roberts et al., 2002). Several studies were presented including aircraft flights over the Houston area (MacDonald et al., 2001), detailed meteorological analyses during a two-week period in 2000 (MacDonald and Roberts, 2002), and analysis of results from a total hydrocarbon (THC) and NO<sub>x</sub> analyzer at the San Jacinto Monument site (Brown et al., 2002a). These studies found that advection patterns can play a significant role in the time and location of ozone formation, that local emissions contribute around 70% to the peak urban ozone concentrations, and that the THC/NO<sub>x</sub> ratio is generally above 13, indicating a NO<sub>x</sub>-limited regime. The conceptual model (Roberts et al., 2002) work focused on establishing links and patterns on high and low ozone days between meteorological (radiation, advection patterns, etc.) and air quality data (ethene, propene, TNMOC, NO<sub>x</sub>). No clear link was established between the air quality parameters and elevated ozone, as meteorological conditions played an important role in ozone formation.

TNRCC and the University of Texas at Austin have established web sites that contain interim and final reports and meeting presentations that represent the state of the science in Houston. We made extensive use of these sites:

- <http://www.utexas.edu/research/ceer/texaqsarchive/>
- [http://www.tnrcc.state.tx.us/cgi-bin/monops/site\\_info?air](http://www.tnrcc.state.tx.us/cgi-bin/monops/site_info?air)
- [http://www.tnrcc.state.tx.us/air/aqp/airquality\\_science.html](http://www.tnrcc.state.tx.us/air/aqp/airquality_science.html)
- <http://www.tnrcc.state.tx.us/air/aqp/airmodeling.html>

The 2001 extended outline on the auto-GC data (Main et al., 2001), noted above, contained some discussions that are not included in this report:

- Sections 2.2 and 2.4, discussion of 24-hr canister data and comparison to auto-GC. Comparisons of the auto-GC with collocated 30-minute canisters (triggers) in 2001 are discussed by Brown et al., 2002b. The 24-hr data presented in Main et al., 2001 were less pertinent to the investigation of ozone episodes and were not included in this report.
- Section 3.7, a discussion of unusually high VOC concentrations. Instead of including this Main et al. (2001) discussion, we focused on compositional and concentration differences between ozone episodes and non-episodes in this report.
- Section 3.10.1, discussion of trends during TexAQS 2000 study period prepared by TNRCC staff. This discussion addressed very specific questions to put the study period in historical context.
- Section 3.10.2, discussion of trends in concentrations at Clinton since 1993 prepared by TNRCC staff. The focus of the current report is on the 1998-2001 data. Additional investigation of the 1993 data would be useful in the context of emission inventory evaluation then (1993) and now (2000 or 2001).
- Section 3.10.3, discussion of trends in toxic species prepared by TNRCC staff. This analysis focused on the 24-hr canister data record. One of the issues identified in the current work is the danger of comparing composition from year to year at the Clinton site because of significant changes in wind direction, and subsequently the sources impacting the site.
- Section 3.12, discussion of case studies. Portions of this section from Main et al. (2001) are incorporated in the current report, particularly the wind direction/species concentration dependence at Clinton Drive.

#### **1.4 HYDROCARBONS IMPORTANT IN OZONE FORMATION**

TNRCC published its current definition of highly-reactive VOCs<sup>1</sup>: acetaldehyde; 1,3-butadiene; all butenes (butylenes); ethene (ethylene); all ethyltoluenes; formaldehyde; isoprene; all pentenes; propene (propylene); toluene; all trimethylbenzenes; and all xylenes. One of the primary hypotheses investigated in this report is whether these (or other hydrocarbons) are a greater fraction of the TNMOC in the mornings of ozone episodes. One of the implications of higher reactive TNMOC fractions is that unique (or industrial upset) conditions may lead to these high concentrations and trigger ozone episodes. To pursue this hypothesis, we focused on the summer months of July-September when there were a large number of days with high ozone concentrations. We defined an ozone episode day (according to TNRCC guidelines) as a day in which the ozone concentration in the Houston area exceeded 125 ppb.

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<sup>1</sup> TNRCC Chapter 115, Control of Air Pollution from Volatile Organic Compounds, Rule Log No. 2002-046b-115-AI, page 44.

## 1.5 OZONE PRODUCTION POTENTIAL: REACTIVITY SCALES

The degradation of VOCs by photochemistry and the resulting conversion of NO to NO<sub>2</sub> and formation of ozone do not occur at the same rate for all VOCs. The ozone formation potential of a specific hydrocarbon depends on its concentration, structure, and removal pathways. If a reactive compound is low in concentration, it will generally not have a high ozone formation potential while a somewhat unreactive compound with a high concentration may have a larger ozone formation potential. One scale on which to gauge VOC ozone formation potential is the hydroxyl reactivity scale (OH) (Atkinson 1989, 1994), which utilizes the reaction coefficient of an individual hydrocarbon with hydroxyl radical. This is strictly the rate at which the hydrocarbon is oxidized by hydroxyl radical only and does not consider competing removal mechanisms for either the VOC or hydroxyl radical or the influence from the overall composition of VOCs in an air mass.

Incremental reactivity (Carter, 1994, 2001) is the change in ozone caused by adding a small amount of test VOC to the emissions in an episode, divided by the amount of test VOC added: g ozone/g C or moles ozone/mole C. Incremental reactivity may be used to assess the effect of changing emissions of a given VOC on ozone formation, to compare the ambient VOC mix among sites or episodes, or to investigate VOCs important to ozone formation. This scale considers NO<sub>x</sub> sinks as well as the generation and loss of hydroxyl radicals, all of which affect the rate of reaction for VOCs. The maximum incremental reactivity (MIR) scale was developed by W.P.L. Carter (1994) and used in "low emission vehicles and clean fuels" regulations in California. The MIR list was recently expanded to include more VOCs and MIR values were updated (Carter, 2001).

In assessing VOC data, analysts have found that the MIR scale is most useful in a relative (i.e., is an ambient sample more reactive than another?) rather than absolute (i.e., how much ozone can be generated with this air parcel?) manner. Furthermore, the uncertainty associated with MIR scale values and the notion that total reactivity equals the sum of incremental reactivities from individual species is unverified. The analyst needs a low unidentified fraction of TNMOC to best assess the potential reactivity of a hydrocarbon mixture. If high unidentified fractions exist, this analysis is less useful. When comparing samples, the weight percent of each hydrocarbon multiplied by its reactivity is often used. Scaling by a sample's TNMOC allows for differences of the entire sample to be assessed on a relative basis (see equation 1-5), instead of on a per species basis (via concentration(reactivity as in Equation 1-6).

$$\text{By concentration: } [\text{ppbCHC}] * \frac{\text{molO}_3}{\text{molair}} = \frac{\text{molC}}{\text{molair}} * \frac{\text{molO}_3}{\text{molC}} = \text{ppbO}_3 \quad (1-5)$$

$$\text{By weight percent: } \frac{[\text{ppbCHC}]}{\text{ppbCTNMOC}} * \frac{\text{molO}_3}{\text{molC}} = \frac{\text{ppbO}_3}{\text{ppbCTNMOC}} \quad (1-6)$$

Where:

HC = a particular hydrocarbon  
TNMOC = total non-methane organic carbon

There are a number of differences between the two reactivity scales. One is that carbonyl compounds are much more reactive on the MIR scale than on the OH scale. Another is that isoprene is much more reactive on the OH scale, so that even small amounts become significantly amplified. Propene is much more reactive than ethene on the OH scale, but less so on the MIR scale. Lastly, styrene is much more reactive on the OH scale than on the MIR scale, so that low amounts appear more significant on the OH scale than on the MIR scale. Values for a number of species on the OH and MIR reactivity scales are given in **Table 1-1**.

It is often useful to find the relative contribution of each hydrocarbon or species family to the total reactivity on both scales. This is done by dividing the individual compound's concentration or weight percent on the reactivity scale by the sum of all species' concentration or weight percent on the reactivity scale. There is no difference whether this reactivity composition is calculated by concentration or weight percent because both the numerator (hydrocarbon weight percent + reactivity) and denominator (sum of all hydrocarbons (their reactivities)) are scaled by the total identified fraction when using weight percent numbers. These values cancel out and yield the same result as if pure concentration values were used. This is shown in Equations 1-7 and 1-8.

$$\text{Contribution of HC by concentration: } \frac{[HC] \times R_{HC}}{\sum_k [HC_k] \times R_{HC_k}} * 100\% = \% \text{ Reactivity from HC} \quad (1-7)$$

$$\text{Contribution of HC by weight percent: } \frac{\frac{HC}{TNMOC} \times R_{HC}}{\sum_k \frac{HC}{TNMOC} \times R_{HC_k}} * 100\% = \% \text{ Reactivity from HC} \quad (1-8)$$

Where:

- HC = a particular hydrocarbon
- R = reactivity coefficient
- TNMOC = total non-methane organic carbon

Table 1-1. Reactivity values (MIR and OH) for selected hydrocarbons.

Compound	MIR Reactivity (mol O <sub>3</sub> /mol C)	OH Reactivity (rate constant with OH (10 <sup>12</sup> ) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
Ethene	2.65	8.5
Propene	3.38	26.3
n-butane	0.4	2.4
Trans-2-butene	4.07	64
Isopentane	0.51	3.7
Cis-2-pentene	2.99	67
m/p-xylene	2.06	23.6
Toluene	1.09	5.95
1,3,5-trimethylbenzene	3.12	57.5
Isoprene	3.03	101

## **1.6 REPORT OUTLINE**

The remainder of this report includes a summary of data availability and validation, general characteristics, the role of advection patterns in ozone formation, and a detailed analysis of differences between ozone episode and non-episode days. Not all statistics and plots are provided in this report; the remainder of the plots and statistics are provided on a compact disk (CD) accompanying this report.

## 2. DATA AVAILABILITY AND COMPLETENESS

The large volume of hourly hydrocarbon data collected from 1998 to 2001 in the Houston area required a significant amount of data processing and validation in order to make the data manageable and useful. This section details the instrumentation used, the data processing and validation techniques, the resultant data availability and quality, and the implications thereof.

### 2.1 INSTRUMENTATION

Hourly hydrocarbon data were collected at a variety of sites in the Houston area using auto-GCs. Collocated with these monitors, hourly ozone, NO<sub>x</sub> and meteorological data were also obtained. This section details the instrument setup and analysis methods.

#### 2.1.1 Auto-GC Instrument Setup

Auto-GC monitors measure speciated hydrocarbons and TNMOC<sup>1</sup> on an hourly basis, seven days a week. These monitors are deployed in the Houston area as part of the Photochemical Assessment Monitoring Station (PAMS) program.

The auto-GC methodology is performed completely at the field monitor. The instrument pumps outside air into an automated thermal desorber for 40 minutes. During the remaining 20 minutes, the air sample is cooled and split into light and heavy compounds. To prevent freezing of the cold trap, a Nafion dryer is used to remove water vapor. This, however, results in the removal of polar organic compounds, so species such as carbonyls or oxygenated compounds are not analyzed with this instrument. The air streams are then heated and pumped to the GC. Two capillary columns, one for the light compounds and one for the heavy compounds, separate the hydrocarbons. The compounds are separated and elute at constant and known rates because of each compound's unique boiling point. Flame ionization detectors (FIDs) are used to ionize the species in an air/hydrogen flame; the strength of the ionization current in the flame is recorded on a chromatograph. The area under each peak corresponds to the concentration of a hydrocarbon. Each compound elutes at a characteristic time based on a given instrument temperature and flow rate, so both of these operating conditions must be kept constant to ensure accurate identification. Species concentrations determined by the auto-GC are reported as hourly averages.

Auto-GCs and FIDs have some limitations in the types of compounds they can speciate. Polar compounds are absorbed and consequently lost by use of the Nafion dryer (Gong and Demerjian, 1995). If not lost in the Nafion dryer, formaldehyde, other oxygenated compounds, and heavily halogenated compounds are difficult to quantify and/or detect with FID. There is also a significant chance for misidentification when using an auto-GC. Sometimes the chromatograph shows two compounds co-eluting (having overlapping peaks), and an operator may have trouble identifying the peaks as one compound or two. This is further discussed in

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<sup>1</sup> Note that TNMOC is the PAMS definition (sum of all mass, identified and unidentified peaks, from C2 through C12 hydrocarbons, AIRS code 43102). This quantity is often referred to as nonmethane hydrocarbon (NMHC).

Section 2.4. A list of the species identified by auto-GC as part of the PAMS program is provided in Appendix A.

The TNMOC measured by auto-GC will differ from other methods reporting total hydrocarbons. For example, TNRCC also operated a 5-minute THC analyzer in the Houston area which does not utilize a Nafion dryer. The THC total, therefore, includes polar and halogenated compounds that the auto-GC's TNMOC does not. Similarly, canister collection of hydrocarbons with subsequent GC-FID analysis does not use a Nafion dryer, which also makes the TNMOC values different.

### 2.1.2 Other Instruments

Other meteorological and air quality parameters measured on an hourly basis at Houston auto-GC sites include wind direction and speed, NO<sub>x</sub>, ozone, and sometimes total reactive odd nitrogen (NO<sub>y</sub>). NO<sub>x</sub> and NO<sub>y</sub> were measured using chemiluminescence. A UV photometric monitor was used for continuous ozone measurements.

## 2.2 DATA PROCESSING

Data were obtained from Environmental Protection Agency's (EPA) Aerometric Information Retrieval System (AIRS) for all years through 2000. TNRCC provided data via e-mail for August through October 2001.

Hourly auto-GC data were collected from 1998-2001 year-round at Clinton and Deer Park, at Bayland from January 1998 to August 2000, at Aldine in September 2000, and at Channelview, Haden Rd., and Baytown from August through October 2001. Locations and specific sampling periods of auto-GCs are listed in **Table 2-1**. A map of sampling sites is shown in **Figure 2-1**. Sites with multiple years of data include Bayland (1998-2000), Clinton (1993, 1998-2001) and Deer Park (1998-2001).

Table 2-1. Locations and operational periods of auto-GCs.

Site	Year	TNRCC Site Code	AIRS Code	Operational
Aldine	2000	C8/C108/C150	482010024	9/1-9/30
Bayland	2000	C53/C146/C181	482010055	1/1-8/6
	1999			1/1-12/31
	1998			3/24-12/31
Channelview	2001	C15/C115		8/4-10/31
Clinton	2001	C403/C113/C304	482011035	8/1-10/31
	2000			1/1-12/31
	1999			1/1-12/31
	1998			1/1-12/31
Deer Park	2001	C35/C139	482011039	8/1-10/31
	2000			1/1-12/31
	1999			1/1-12/31
	1998			1/1-12/31
Haden Rd.	2001	C603/C114		8/21-10/31
Baytown	2001	C148		8/27-10/31



### 2.3.1 Data Validation Tool

VOCDat (Main and Prouty, 2000) was used to perform the VOC data validation. VOCDat allows the analyst to display the VOC data in order to perform QC tasks on the data, and to begin data analysis. VOCDat displays data using scatter, fingerprint, and time series plots. Scatter plots, enable the analyst to investigate the relationship among species at one site or at a number of sites. Fingerprint plots show the concentration of each species in a sample (in chromatographic order) and help identify unique characteristics of the samples. Time series plots show the concentrations of species in every sample over a specified time period and are useful in showing the diurnal behavior of a species.

Other features of VOCDat that facilitate data validation and data analysis follow:

- Computation of concentrations for species groups including unidentified hydrocarbons, sum of PAMS target species, aromatic hydrocarbons, total olefins, total paraffins, and total compounds.
- Customizable screening checks.
- Computation and display of the weight percent of each individual species.
- Computation of reactivity-weighted data—concentration or weight percent data may be multiplied by a reactivity scale, such as the maximum incremental reactivity scale (MIR) developed by Carter (1994, 2001) or hydroxyl reactivity scale (OH) developed by Atkinson (1991, 1994).
- Preparation of exported files suitable for use in other analysis software (e.g., SYSTAT).

### 2.3.2 Validation Steps

To validate a data set, we inspect a time series plot of every species, prepare numerous scatter plots, inspect the fingerprint plot of every sample, and compute and review summary statistics. Visual inspection is useful to identify diurnal patterns, concentration spikes, the periodicity of concentration increases or decreases, the relationship among various species, and sample-to-sample differences in the VOC composition via fingerprint analysis. These investigations assist the analyst in establishing site-specific patterns in concentration, determining specific samples for which there are questions, singling out data collected during ozone episodes, and discovering problems in the data set that need correction.

Specific investigations were performed during data validation:

- Checked the species list for missing abundant species. Sometimes a key hydrocarbon, such as toluene or o-xylene, does not get reported to AIRS. Samples with missing species were further inspected (for overall concentrations or their concentrations in the hours before and after a sample) and possibly flagged as suspect.
- Ran custom screening checks that included checking each sample for the presence of abundant species, failure to meet typical relationships (e.g., benzene > toluene), and gross outliers. Samples that failed screening were reviewed in more detail.

- Prepared summary statistics including minimum, maximum, mean, and median values for each parameter.
- Used time series plots to investigate the concentrations of species in every sample over a specified time period. These plots are useful in showing the diurnal behavior of a species. Time series plots of all species, plotting several species at a time, were inspected to find time periods and samples that warranted additional inspection.
- Prepared scatter plots of hydrocarbons that are likely to be emitted by the same source and that typically correlate well, such as benzene and acetylene, propane and ethane, i-butane and n-butane, i-pentane and n-pentane, 2-methylpentane and 3-methylpentane, ethylbenzene and 1,2,4-trimethylbenzene, and the xylene isomers (o-xylene should be less than the sum of m-&p-xylenes); benzene and toluene (toluene concentrations typically exceed benzene and these species generally correlate well); toluene and 2-methylheptane (sometimes these species are misidentified); and every hydrocarbon and species group with TNMOC (looking for gross outliers).
- Inspected fingerprint plots of every sample with an emphasis on the flagged samples (based on the above investigations) and on the surrounding samples (looking for gaps in data, odd fingerprints, abrupt changes, and missing data).
- Entered a comment in a log file about why a quality control (QC) code was changed when we identified samples or individual species that needed to be flagged. VOCDat retains a list of these comments and the changes to the QC codes.

### 2.3.3 Flagging Data

Our strategy is to flag entire samples when we identify a problem with two or more of the most abundant species (e.g., toluene, i-pentane, i-butane, n-butane, benzene, acetylene, ethane, xylenes, propane). Individual species are flagged as suspect when there are problems noted and the concentration of the hydrocarbon is low compared to other species in the sample. Our approach is not to invalidate data outright, but to flag data as suspect that do not meet our conceptual model of hydrocarbon emissions, formation, and removal. The flags are placed on the data so that the monitoring staff can check the data to rule out possible monitoring or analytical problems. After reporting agencies review the data, some suspect data may be deemed invalid, some data may be reprocessed and re-reported by the agency, and other data may remain suspect (cause unknown). These latter samples remain flagged in the database for the attention of future data analysts.

## 2.4 DATA QUALITY, AVAILABILITY, AND IMPLICATIONS

Data were previously validated by TNRCC staff and reviewed by STI. We summarized our data validation efforts for data in 1998-2000 Main et al. (2001), and for 2001 data in Main and Brown (2002a). Data quality is very good. In the 1998-2000 data, only a few samples failed screening checks (**Table 2-2**). Key missing data in 2000 and 2001, the focus of many analyses, are summarized in **Table 2-3**.

Table 2-2. Summary of data failing screening criteria in 1998-2000.

Site	Dates and Times	Comments
Aldine	5/20/00 0500-0700, 1300-1400 5/27/00 0500-0700, 1300-1400 6/2/00 0500-0700, 1300-1400 6/23/00 0500-0700, 1300-1400	High percent unidentified
	9/28/00 1800	C2-C4 concentrations=0
	Many samples	Ethene>ethane, propene>propane, benzene>toluene
Bayland Park	Many samples	Ethene>ethane, propene>propane, benzene>toluene
Clinton	Many samples	Ethene>ethane, propene>propane, benzene>toluene
	7/27/00 0800	C2-C4 concentrations=0
	8/4/00 1900	Ethane <2 ppbC and benzene >2 ppbC (possible problem with cold trap)
	1/24/98 2000 2/21/98 0400 4/1/98 0100	i-pentane data missing
	10/7/98 0600-0700 6/13/99 1800	C2-C5 concentrations=0
	1/16/99 1000-1400 8/11/99 0400 9/7/99 1700 10/30/99 1000 12/17/00 1200	High percent unidentified
	12/13/99 0900	Low concentrations of abundant species
	Deer Park	3/6/00 1000-1200 3/7/00 1000 to 3/8 0600 11/6/00 0500
4/25/00 1500-1700 11/23/98 1100		C2-C5 concentrations=0
12/5/00 0800		toluene concentration=0
11/13/00-11/14/00 all hours 11/23/00-11/30/00 all hours		Ethane data missing
11/25/98 1000 to 12/4/98 0100		m-&p-xylenes data missing
11/23/98 1100 to 12/4/98 0100		toluene data missing
7/7/99 1700 9/20/99 1800		Missing abundant species

Table 2-3. Key missing data in 2000 and 2001.

Site	Site Code	Operational	% Available	Notes
Data availability for 2000				
Aldine	C8/C108/C150	9/1-9/30	77	
Bayland	C53/C146/C181	7/1-8/6	73	No propylene 7/1-7/14
Clinton	C403/C113/C304	7/1-9/30	62	No ethylene 9/1-9/30
Deer Park	C35/C139	7/1-9/30	21	No TNMOC 7/1-7/22, 9/21-9/30
Data availability for 2001				
Channelview	C15/C115	8/4-10/31	78	No propene 8/16, 8/21, 8/27 No TNMOC 10/1-10/3
Clinton	C403/C113/C304	8/1-10/31	90	No data 9/22!
Deer Park	C35/C139	8/1-10/31	84	No TNMOC 10/1-10/2, 10/14-10/16, 10/22- 10/23
Haden Rd.	C603/C114	8/21-10/31	86	No data 9/22! No benzene, toluene, xylene, 9/24-9/26
Baytown	C148	8/27-10/31	89	No TNMOC 8/27, 8/29, 10/12-10/13

In 2001, due to the quick time frame under which the project progressed, TNRCC supplied data that had not undergone all levels of scrutiny normally applied. Only a few samples failed screening as shown in **Table 2-4**. However, as summarized in **Table 2-5**, significant data were missing.

Table 2-4. Summary of data from the August-October 2001 operational period that failed screening criteria.

Site	Dates and Times	Comments	Action Performed
Channelview	8/16, 8/21, 8/27 All samples	No propene	Entire sample flagged
	10/2/01 1400-1600, 10/13/01 0200-0900	No ethane, propane, n-butane, n-pentane, isopentane, n-hexane, benzene	Entire sample flagged
	Many samples	Ethene>ethane, propene>propane, benzene>toluene	Probably real due to dense industry, no action taken
	Many samples	3-methylpentane=0	Species flagged
	10/2/01 1400	Zero concentration of toluene, xylenes	Entire sample flagged
Clinton	10/29 All samples	Zero concentration of propane, n-pentane	Entire sample flagged
	Many samples	Ethene>ethane, propene>propane, benzene>toluene	Probably real due to dense industry, no action taken
	10/8 1000, 9/18 0900	Ethene=0	Entire sample flagged
	10/8 1000, 10/29 1100	Propene=0	Entire sample flagged
	8/30 0700 All samples	Zero concentration of benzene, toluene, xylenes	Entire sample flagged

Table 2-4. Summary of data from the August-October 2001 operational period that failed screening criteria.

Site	Dates and Times	Comments	Action Performed
Deer Park	Many samples	Ethene>ethane, propene>propane, benzene>toluene	Probably real due to dense industry, no action taken
	10/22 0900	Zero concentration of ethane, ethene, propane, propene	Entire sample flagged
	8/8 1000, 8/12 1200, 8/16 1200, 8/18 1300, 8/20 1200, 9/19 1300	Propene=0	Entire sample flagged
	8/2 1200	Zero concentration of xylenes	Entire sample flagged
Haden Rd.	Many samples	Ethene>ethane, propene>propane, benzene>toluene	Probably real due to dense industry, no action taken
	10/2 1100, 10/3 1000, 10/12 2100	C <sub>2</sub> -C <sub>6</sub> concentrations=0	Entire sample flagged
	9/24 1400-9/26 1800	Zero concentration of benzene, toluene, xylenes	Entire sample flagged
	10/3 1000, 10/23 1400	Ethane<2 ppbC and benzene>2 ppbC (possible problem with cold trap)	Entire sample flagged
Baytown	8/27, 8/29, 9/22 All samples	Zero concentration of benzene, toluene, xylenes	Entire sample flagged
	Many samples	Ethene>ethane, propene>propane, benzene>toluene	Probably real due to dense industry, no action taken

Table 2-5. Times and dates of missing auto-GC data from August through October 2001.

Site	Year	Dates	Comments
Channelview	2001	8/17 0100-8/21 1100 8/22 0000-8/27 0900 9/4 0500-1300 9/12 1500-9/13 1700 9/18 1000-9/19 1500 9/24 1700-9/25 1300 9/26 0000-1100 9/27 0000 -10/1 1000 10/12 0000-2300 10/16 0900-1200	All data missing
		8/16 0000-2300 8/21 0000-2300 8/27 0000-2300	No propene
		10-1 1000-10/3 1200	No TNMOC
Clinton	2001	8/30 1200-9/2 0400 9/5 0800-1200 9/18 0000-0900 9/21 1200-9/24 1200 10/8 0000-1000 10/27 0300-10/29 1300	All data missing

Table 2-5. Times and dates of missing auto-GC data from August through October 2001.

Site	Year	Dates	Comments
Deer Park	2001	8/7 0000-1300 8/15 0900-1200 9/5 0600-0900 9/9 0900-1200 9/25 0000 -10/1 0100 10/4 0000 -10/5 0900 10/13 0000 -10/14 1200 10/14 1300-2300 10/15 0000-0800 10/16 0800 10/18 0000 -10/22 1200	All data missing
		10/1 0000 -10/2 1300 10/14 0000 -10/16 0900 10/22 0900-10/23 1200	No TNMOC
Haden Rd.	2001	8/30 0700 9/2 1200 9/5 1100,1300 9/6 0000-9/11 0200 9/14 1900 9/17 1300 9/20 0800-1500 9/21 1500-9/24 1500 9/25 2000 9/26 1500 9/27 1000 10/2 1100-1700 10/18 1000,1200-1500 10/23 0000-0900	All data missing
		8/21 0000 - 8/28 0600 9/5 0000-2300 9/24 1400-9/26 1900 10/22 0000 - 10/24 1200	No TNMOC No TNMOC No TNMOC, benzene, toluene, xylenes No TNMOC

Table 2-5. Times and dates of missing auto-GC data from August through October 2001.

Site	Year	Dates	Comments
Baytown	2001	8/28 0700, 0900	All data missing
		8/31 1100-1600	
		9/1 0000 - 9/5 0400	
		9/5 1300	
		9/6 0800	
		9/18 1200-1700	
		9/19 0500-0800	
		9/20 1800-2300	
		9/21 0900-1900	
		9/26 0700	
10/6 2000-2300	No TNMOC		
10/11 0000-2300			
8/27 0000-2300			
8/29 0000-2300	No isoprene		
10/12 0000 - 10/13 0900			
9/15 0000 - 9/30 2300	No n-octane		
9/21 0000 - 9/24 2300			
9/5 0000 - 9/19 2300	No 1,2,3-trimethylbenzene		

Suspect data were generally not used in analyses except on a case-by-case basis. Data were missing from key time periods, including September 22, 2001, at Clinton and Haden Rd., which affected some of the case study analyses.

**Table 2-6** summarizes the sites and missing data from 1998 to 2001 at Clinton. Since the focus of the work has been on ozone episodes during the summer, missing data at the sites with only one year of data (Aldine, Channelview, Haden Rd., Baytown) are listed only for the summer. Missing data from other sites (Bayland, Clinton, Deer Park) are detailed for the entire year. The percentage available is equal to the number of hourly samples divided by the number of expected hourly samples during periods in which the sites were operational. We assumed that there were 22 hourly samples in a given day and that the remaining two hours were devoted to calibrations (no data reported).

Generally, more than 75% of the data (a commonly used threshold for completeness) are available during the time periods of interest. Missing data can become a serious problem during ozone episodes when analyses are focused on hour-to-hour details. Only at Bayland in 1998, Clinton in 2000, and Deer Park in 2000 have less than 75% data availability during the July-September period. Data were collected at Aldine and Bayland in 2000 for only one month each; overall completeness for the two sites in summer 2000 is less than 50%, which makes inter-site comparisons in ozone episode analysis difficult. The lack of complete data on an annual basis

also makes annual trends difficult to establish. There are also a large number of missing data during the TexAQS 2000 study (MacDonald and Roberts, 2002) between August 15, 2000, and September 15, 2000, which curtailed many detailed analyses. During August-November 2001, canister samples were also taken in the Houston area (Brown et al., 2002b); there are number of times in which the collocated auto-GC data were missing, making a comparison between analytical methods somewhat difficult.

## **2.5 OTHER DATA AND STUDIES**

Other data were also collected in separate studies during this period. Aircraft data were collected by Baylor University in 2000 (MacDonald et al., 2001) and in 2001 (Buhr, 2001). Detailed meteorological data were collected as part of TexAQS 2000 study for use in a conceptual model (MacDonald and Roberts, 2002). Trigger canisters for both VOCs and carbonyl compound sampling were collected during rapid rises of ozone, and detailed analysis of the data was performed (Brown et al., 2002b, 2002c). Five-minute THC, ozone,  $\text{NO}_x$ , and  $\text{NO}_y$  were also sampled in summer 2001 at the San Jacinto Monument site (Brown et al., 2002a). This wealth of data enables additional analyses in conjunction with the auto-GC data collected and provides a more detailed picture of both the meteorology and air quality in the Houston area.

Table 2-6. Table of expected and available auto-GC data during July-September 1998-2000 and August-October 2001. Counts are based on concentration data.

Site	Year	Site Code	Operational	Number of Hourly Data in Summer (1 day = 22 sample hours, 2 calibration hours)		
				Expected	Available	% Available
Bayland <sup>a</sup> /Aldine	2000	C8/C108/C150	7/1-8/6, 9/1-9/30	1452	935	64
Bayland	1999	C53/C146/C181	7/1-9/30	2024	1567	77
Bayland	1998	C53/C146/C181	7/1-9/30	2024	1084 <sup>b</sup>	53
Channelview	2001	C15/C115	8/4-10/31	1958	1525 <sup>c</sup>	78
Clinton	2001	C403/C113/C304	8/1-10/31	2024	1820	90
Clinton	2000	C403/C113/C304	7/1-9/30	2024	1260 <sup>d</sup>	62
Clinton	1999	C403/C113/C304	7/1-9/30	2024	1696	83
Clinton	1998	C403/C113/C304	7/1-9/30	2024	1758 <sup>e</sup>	86
Deer Park	2001	C35/C139	8/1-10/31	2024	1697 <sup>f</sup>	84
Deer Park	2000	C35/C139	7/1-9/30	2024	425	21
Deer Park	1999	C35/C139	7/1-9/30	2024	1768	86
Deer Park	1998	C35/C139	7/1-9/30	2024	1533 <sup>g</sup>	75
Haden	2001	C603/C114	8/21-10/31	1584	1355 <sup>h</sup>	86
Baytown	2001	C148	8/27-10/31	1452	1295 <sup>i</sup>	89

<sup>a</sup> The site at Bayland was moved to Aldine on August 6, 2000; no data were collected August 7 through 31, overall data recovery is 46%.

<sup>b</sup> 94 of these hours have no TNMOC data with which to calculate weight percent (48% availability).

<sup>c</sup> 97 of these hours have no TNMOC data with which to calculate weight percent (73 % availability).

<sup>d</sup> Ethene concentrations missing during August 2000 due to analytical problems .

<sup>e</sup> 809 of these hours have no TNMOC data with which to calculate weight percent (46% availability).

<sup>f</sup> 60 of these hours have no TNMOC data with which to calculate weight percent (72 % availability).

<sup>g</sup> 1299 of these hours have no TNMOC data with which to calculate weight percent (11% availability).

<sup>h</sup> 266 of these hours have no TNMOC data with which to calculate weight percent (69% availability).

<sup>i</sup> 82 of these hours have no TNMOC data with which to calculate weight percent (84% availability).

### 3. GENERAL CHARACTERISTICS

The small amount of biogenic emissions (such as isoprene) and a high density of industrial activity make Houston a unique urban environment. In order to generally characterize hydrocarbon concentrations in the area, summary statistics for the summer and entire year were generated by site and year. Hydrocarbon concentrations were also characterized by month, day of week, and hour. General trends were assessed, and initial relationships among species were found using correlation and scatter plot matrices.

#### 3.1 SUMMARY STATISTICS

##### 3.1.1 Overview

Summary statistics of selected hydrocarbon concentrations by year for each auto-GC site are shown in **Table 3-1**. Species abbreviations are defined in Appendix A. Annual statistics for all individual hydrocarbons at Clinton Drive are shown in Appendix B. Complete summary statistics for all sites and years are provided in the CD that accompanies this report.

Table 3-1 provides an overall perspective of the data. TNMOC concentrations show VOC source strength near sites. Ethene concentrations are of interest because of its high ozone formation potential and Houston Ship Channel sources. Isoprene is a biogenic emission but also has anthropogenic sources in the Ship Channel. Benzene is of interest because of its carcinogenicity. The unidentified VOC mass demonstrates how well the PAMS target species represent the Houston VOC mix. Finally, the xylenes-to-benzene (X/B) ratio is a common indicator of air mass age with higher ratios indicating fresher emissions than lower ratios. Observations from Table 3-1 include the following:

- At Clinton Drive, maximum and median TNMOC, isoprene, and benzene concentrations were similar from year to year. Ethene concentrations show a downward trend while the median unidentified mass remained constant. X/B data show that high concentration air parcels impacted the site.
- At Bayland, hydrocarbon concentrations were much lower than at Clinton Drive, consistent with the site's proximity to the Ship Channel. The median X/B ratios were similar to Clinton Drive, however, indicating fresh emissions impacted the site.
- At Deer Park, TNMOC concentrations were lower than at Clinton Drive but higher than at Bayland. Maximum ethene concentrations were highest at this site, indicating a nearby source of this hydrocarbon. Isoprene, benzene, and unidentified mass concentrations were generally lower than at Clinton Drive. X/B ratios were lowest at this site which seems surprising given its relative proximity to the Ship Channel.
- Data for Channelview, Haden Rd., and Baytown are available from summer 2001 only. TNMOC concentrations at these sites were comparable to Clinton Drive. Channelview and Haden Rd. exhibited significantly higher median ethene concentrations than at other sites, indicating the sites experienced elevated ethene concentrations more frequently.

Table 3-1. Summary statistics (maximum and median) by site and year for Houston auto-GCs. All concentrations are in ppbC.

		TNMOC		Ethene		Isoprene		Benzene		Unidentified VOC Mass		X/B
Site	Year	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Med.
Clinton Drive	1998	6478	210	597	6.6	33	0.59	682	2.6	522	16	2.7
	1999	5921	170	440	5.2	41	0.63	466	2.4	6626	12	2.6
	2000	5830	174	213	3.8	14	0.42	313	3.1	615	15	1.7
	2001	7346	156	163	4.4	42	0.34	261	2.3	896	14	1.8
Bayland	1998	806	74	67	2.6	10	1.0	22	1.5	81	7.9	2.0
	1999	1335	70	141	2.6	2.0	0.03	30	1.6	142	2.9	1.5
	2000	956	41	30	1.6	12	2.0	12	0.66	775	1.6	1.7
Deer Park	1998	3210	150	1801	3.8	12	0.3	149	0.69	191	14	0.8
	1999	3632	117	536	4.8	20	0.5	193	0.74	245	6.6	1.1
	2000	1827	100	298	4.3	31	0.3	61	0.65	283	12	1.3
	2001	2602	83	634	3.4	61	0.4	50	0.58	234	2.3	1.1
Channelview	2001	3538	158	288	16	22	1.0	266	3.2	257	14	0.87
Haden Rd.	2001	4371	233	181	7.6	21	1.3	82	5.2	383	28	1.3
Baytown	2001	2618	223	240	3.7	63	0.09	27	2.6	2213	19	1.0

### 3.1.2 Overall Data Composition: TNMOC and Species Groups

#### TNMOC

TNMOC is measured as the total area under all peaks on a chromatogram and is measured in conjunction with individual species. TNMOC can be used as an indicator of emission source strength impacting a site. During the night and early morning there is little vehicular traffic; thus, high concentrations are often due to industrial emissions, while vehicles are often the primary source of high concentrations occurring during commute hours in the morning and evening.

Box whisker plots are commonly used to display a large amount of data and are particularly useful in assessing differences among data. Box whisker plots are drawn in different ways by different software programs. However, most box whisker plots show an interquartile range (i.e., 25<sup>th</sup> to 75<sup>th</sup> percentile) and some way to illustrate data outside this range. **Figure 3-1** shows an illustrated box whisker and notched box whisker plot. The box shows the 25<sup>th</sup>, 50<sup>th</sup> (median), and 75<sup>th</sup> percentiles. The whiskers always end on a data point; when the plots show no data beyond the end of a whisker, the whisker shows the value of the highest or lowest data point. The whiskers have a maximum length equal to 1.5 times the length of the box (the interquartile range). If there are data outside this range, the points are shown on the plot and the whisker ends on the highest or lowest data point within the range of the whisker. The “outliers” are also further identified with asterisks representing the points that fall within 3 times the interquartile range from the end of the box and circles representing points beyond this.

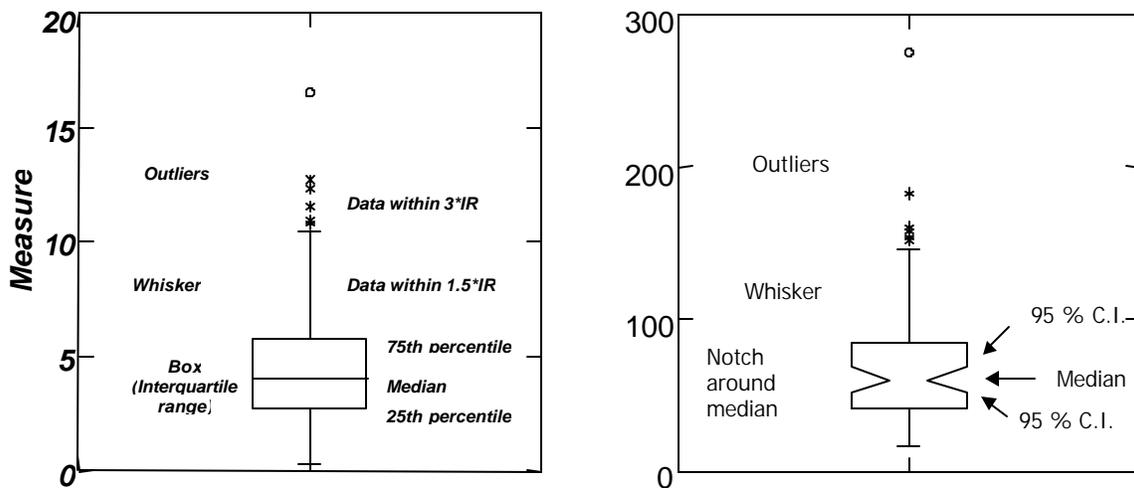


Figure 3-1. Illustration of a box-whisker plot and a notched box whisker plot as defined by SYSTAT statistical software.

Since sample size is also an important consideration when one begins to stratify data, notched box whisker plots (see Figure 3-1) have been used to analyze data in this study. These plots include notches that mark confidence intervals. The boxes are notched (narrowed) at the

median and return to full width at the lower and upper confidence interval values<sup>1</sup>. We selected 95% confidence intervals. If the 95% confidence interval is beyond the 25<sup>th</sup> or 75<sup>th</sup> percentile, then the notches extend beyond the box (hence the "folded" appearance).

Box whisker plots of TNMOC concentrations by hour for each year at Bayland (1998-2000), Clinton (1998-2001), and Deer Park (1999-2001) are shown in **Figures 3-2 through 3-11**. A line at 1000 ppbC is provided for referencing between plots (note that the scales change site to site and year to year). Common among all sites and years is the occurrence of high outlying concentrations during the late night and early morning hours. The high frequency of high concentrations with no distinct diurnal pattern (such as elevated vehicular emissions during commute hours) indicates that routine industrial emissions may be the primary source of these outliers. Also found at all sites in each year was an increase in concentrations throughout the early morning. This is most likely due to industrial emissions trapped during the night in the nocturnal boundary layer, then mixing with increased commute traffic emissions, and released with increasing winds, vertical mixing, and solar radiation later in the morning. Concentrations were generally higher than those found in other urban environments in the Northeast and Mid-Atlantic (Main and O'Brien, 2001).

Spatial variability of TNMOC among sites is also evident. Concentrations were consistently highest at Clinton Drive, followed by Deer Park; Bayland often exhibited the lowest concentrations. This spatial pattern is consistent with each site's proximity to industrial sources; Clinton is located on the Ship Channel, an industry-rich environment, and is therefore frequently impacted by industrial emissions high in VOC content. Deer Park is not immediately within an industrial environment, but as evidenced by high concentrations found there, it is often impacted by industrial emissions. Bayland is the farthest removed from a dense concentration of industry and therefore has the lowest TNMOC concentrations. Each of these sites is impacted by emissions of different composition due to different source strengths and source types impacting each site and chemistry changes as air masses age during transport. The differences between sites show that each site has value in characterizing emissions, atmospheric chemistry, and understanding ozone formation in the Houston area.

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<sup>1</sup> SYSTAT literature uses methodology documented by McGill, Tukey, and Larsen (1978) to show simultaneous confidence intervals on the median of several groups in a box plot. If the intervals around two medians do not overlap, one can be confident at about the 95% level that the two population medians are different.

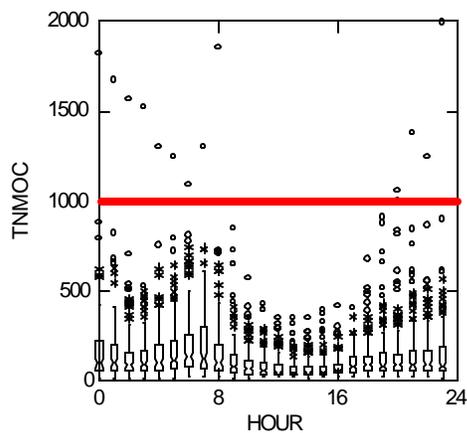


Figure 3-2. TNMOC concentrations (ppbC) at Bayland in 1998 by hour.

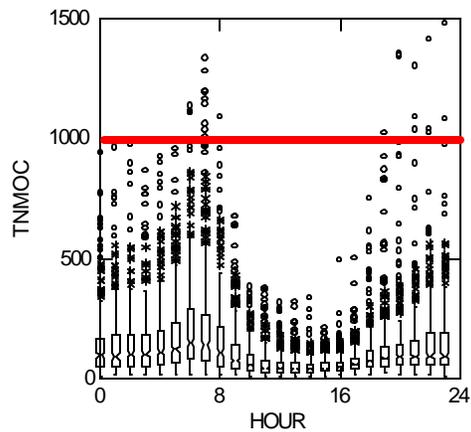


Figure 3-3. TNMOC concentrations (ppbC) at Bayland in 1999 by hour.

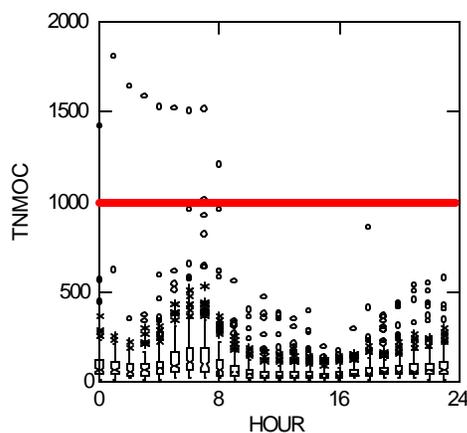


Figure 3-4. TNMOC concentrations (ppbC) at Bayland in 2000 by hour.

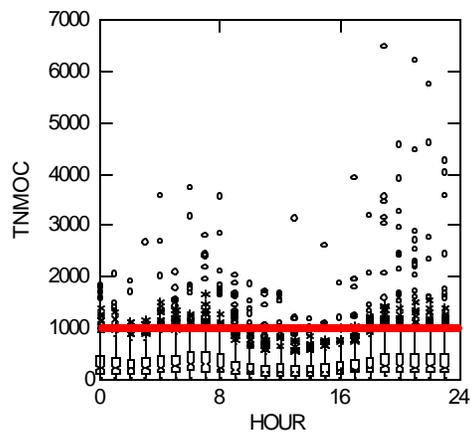


Figure 3-5. TNMOC concentrations (ppbC) at Clinton in 1998 by hour.

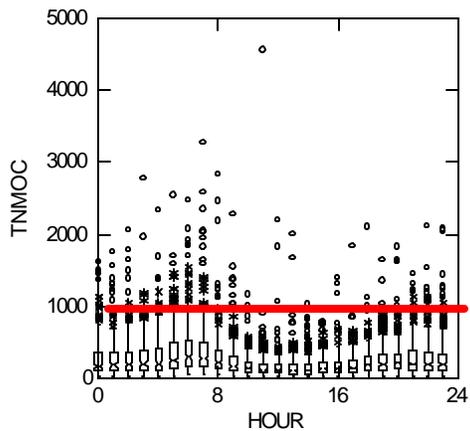


Figure 3-6. TNMOC concentrations (ppbC) at Clinton in 1999 by hour.

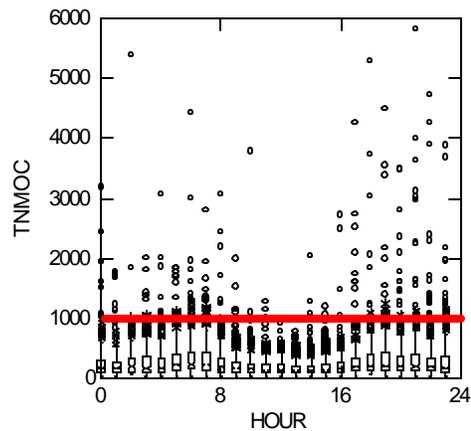


Figure 3-7. TNMOC concentrations (ppbC) at Clinton in 2000 by hour.

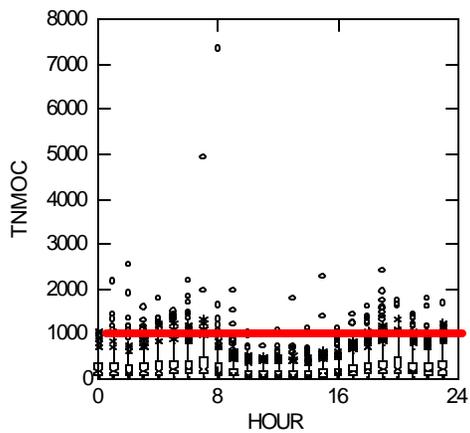


Figure 3-8. TNMOC concentrations (ppbC) at Clinton in 2001 by hour.

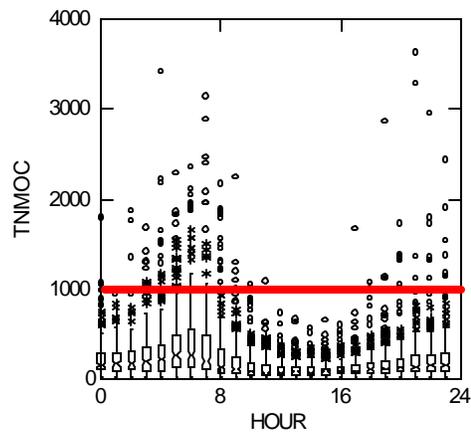


Figure 3-9. TNMOC concentrations (ppbC) at Deer Park in 1999 by hour.

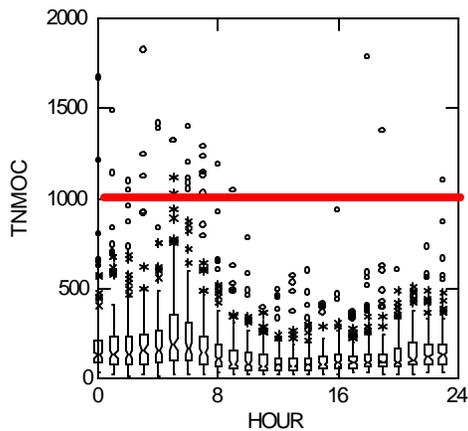


Figure 3-10. TNMOC concentrations (ppbC) at Deer Park in 2000 by hour.

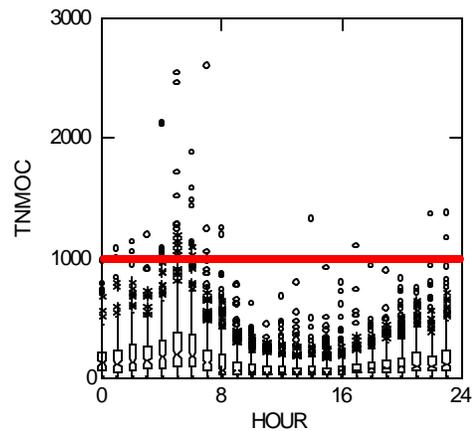


Figure 3-11. TNMOC concentrations (ppbC) at Deer Park in 2001 by hour.

### Species Groups

The types of VOCs collected by auto-GC fall into three groups: paraffins, olefins, and aromatics. For each hourly sample, each of these groups is calculated as the sum of the concentrations of each species in that group. This is useful to determine patterns of emissions, rates of chemical reactions, and whether chemical families are emitted from the same source. Box whisker plots of each species group plus unidentified mass by hour for each year at Bayland, Clinton, and Deer Park are shown in **Figures 3-12 through 3-21**.

Similar to TNMOC, concentrations of paraffins, olefins and unidentified mass are higher in the late night and early morning, probably due to nighttime industrial emissions trapped in the nighttime boundary layer. Concentrations of paraffins are the highest of all species groups for all hours, followed by olefins and aromatics. Aromatics such as toluene and benzene are associated with vehicular emissions, and the low amount of aromatics relative to other species groups may indicate that vehicular emissions are not a primary source of VOCs in the Houston area. Extreme outlying concentrations of all species groups generally occurred during most hours of the day, though at all sites in every year they were most abundant late at night or early in the morning. Concentrations again varied between sites in a similar pattern as found with TNMOC; Clinton concentrations were highest, followed by Deer Park and Bayland.

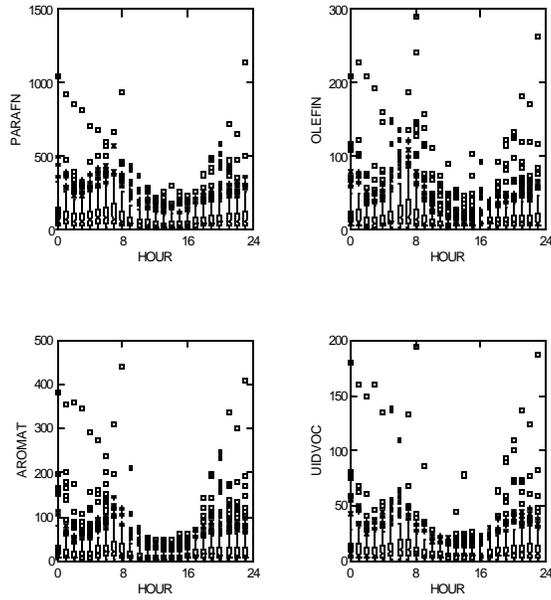


Figure 3-12. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Bayland in 1998.

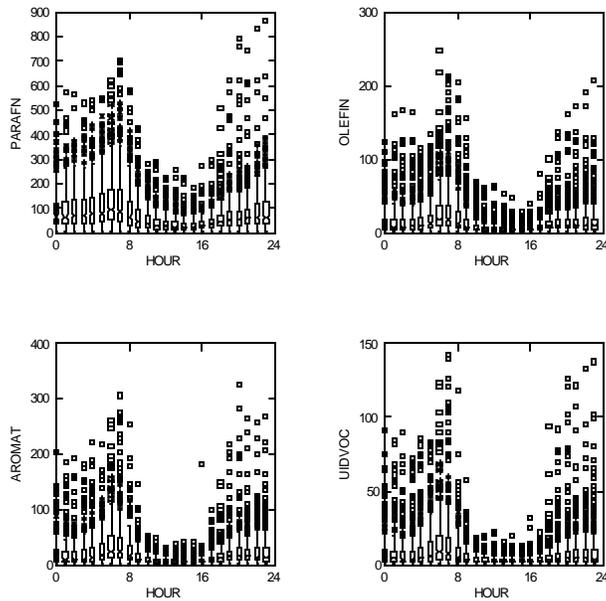


Figure 3-13. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Bayland in 1999.

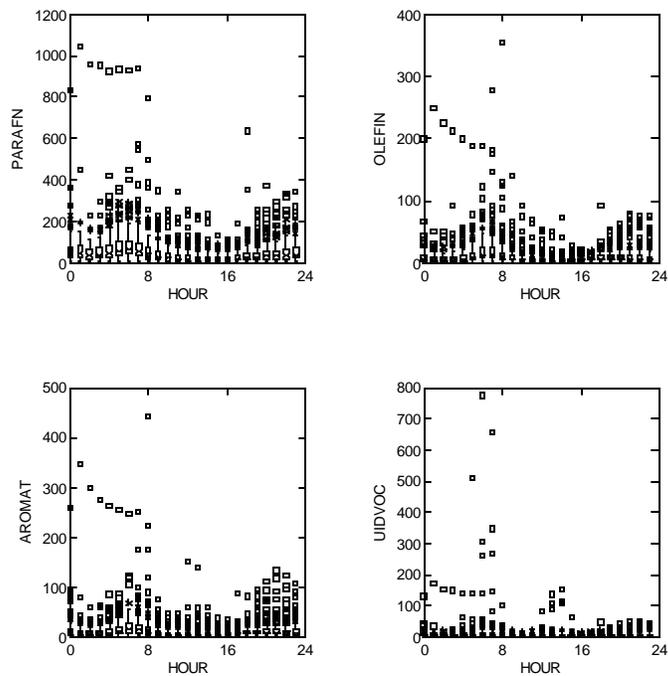


Figure 3-14. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Bayland in 2000.

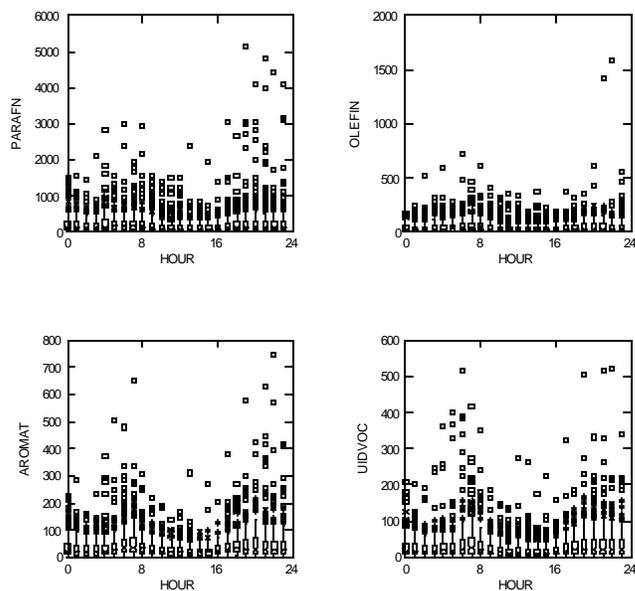


Figure 3-15. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Clinton in 1998.

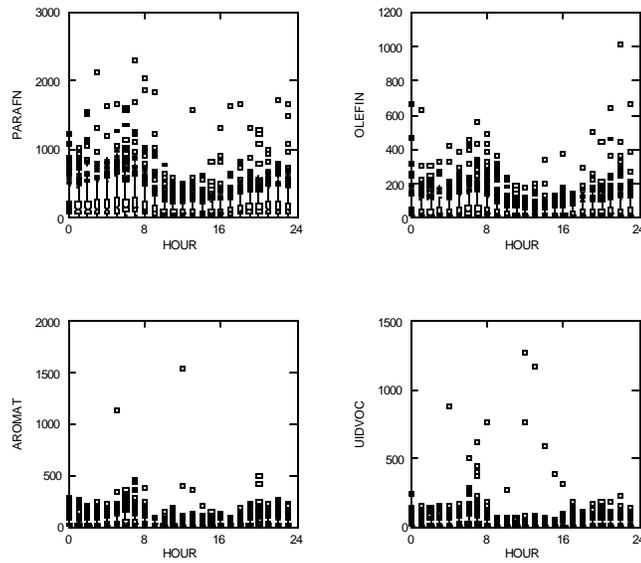


Figure 3-16. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Clinton in 1999.

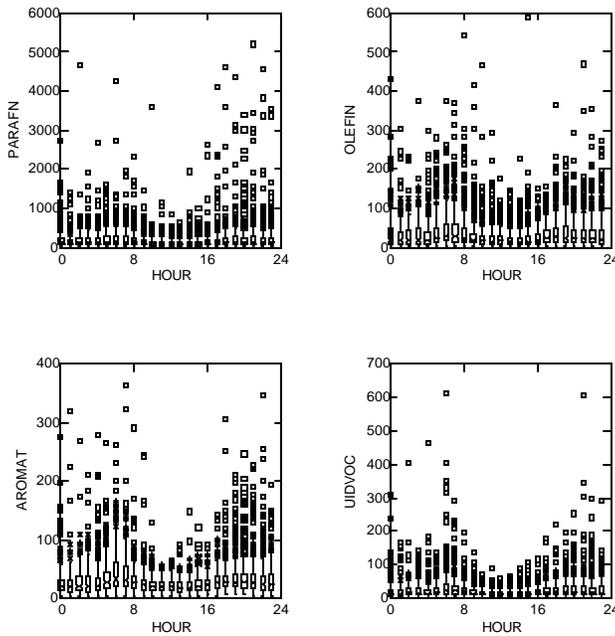


Figure 3-17. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Clinton in 2000

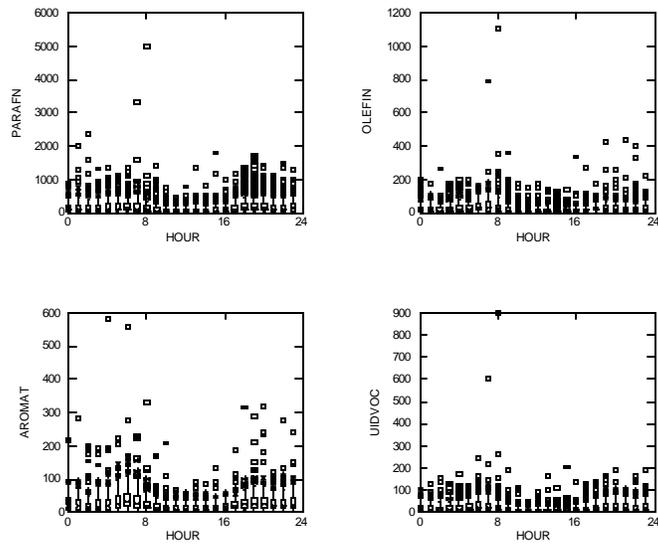


Figure 3-18. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Clinton in 2001.

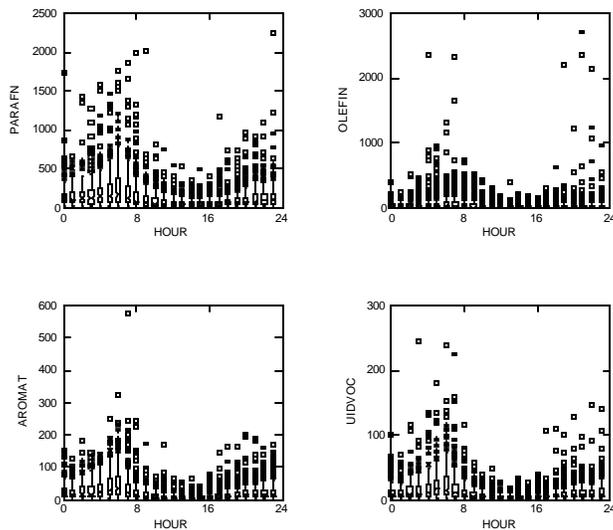


Figure 3-19. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Deer Park in 1999.

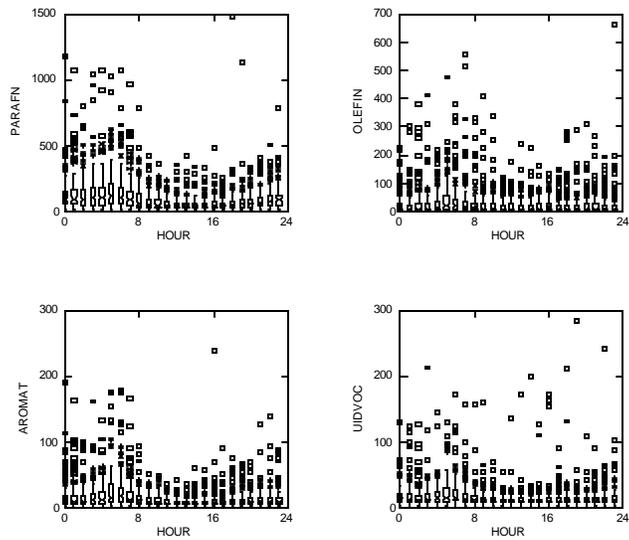


Figure 3-20. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Deer Park in 2000.

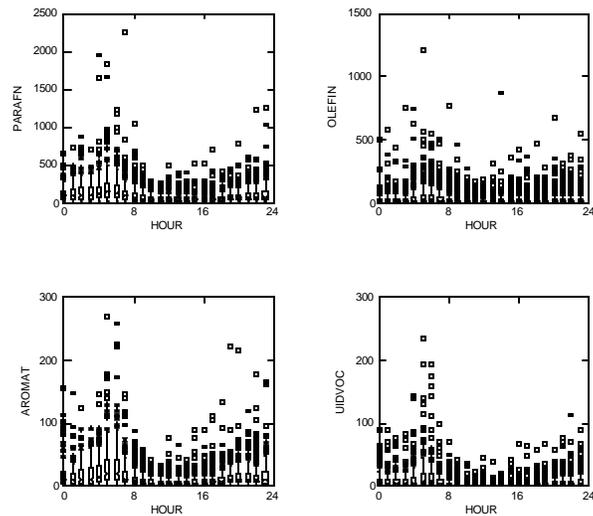


Figure 3-21. Hourly box whisker plots of concentrations (ppbC) of paraffins (PARAFN), olefins, aromatics (AROMAT), and unidentified (UIDVOC) at Deer Park in 2001.

### 3.1.3 Air Mass Age

A number of hydrocarbons are used as indicators of ozone formation potential and tracers of various urban emissions. Assuming that the ratio of these species of interest in the emissions are relatively constant throughout the day, the relative abundance of the more reactive species (olefins and reactive aromatics such as xylenes) should decrease with time during the daylight hours, as they are reacted away via photochemistry. The relative abundance of less reactive species such as paraffins and less reactive aromatics (such as benzene) will, therefore, appear to increase. The ratios of more reactive species concentrations to less reactive species concentrations can, therefore, be used as indicators of the relative changes in air mass composition and age. Analysis of such ratios on an hourly basis shows the diurnal variations in air mass age. This analysis may also be used to investigate the presence of fresh emissions or the presence of unique regional sources of particular hydrocarbons. Commonly used ratios include xylenes/benzene (X/B), toluene/benzene (T/B), and acetylene/ethEne (A/E) (Nelson and Quigley, 1983; Main, 2001; Chan et al., 2002). In an emission-rich area such as Houston, where emissions are most often fresh with small transport times between source and receptor site, it is expected that ratios will generally be higher in the night as industrial emissions are trapped in the nighttime boundary layer and decrease during the day as reactive compounds are depleted by photochemistry.

The median X/B and T/B ratios by hour at all sites during the summer of 2001 are shown in **Figures 3-22 and 3-23**. Overall, the relatively unchanging ratios throughout the day suggest that the composition of the air mass is fresh. The daytime average X/B and T/B ratios in downtown Phoenix during the summer of 2001, a motor vehicle-dominated site, were 2.2 and 4.1, respectively. Compared to Phoenix (Main, 2001), the Houston ratios were typically lower, indicating that perhaps benzene was enhanced relative to xylenes and toluene. Higher benzene concentrations are likely from industrial emissions. X/B ratios were higher during the night and early morning at Deer Park. It is not clear what causes this pattern. In a review of industrial versus motor vehicle-dominated signatures at Clinton Drive presented in Section 4, the data show elevated aromatic hydrocarbons for industrial signatures compared to the motor vehicle signature.

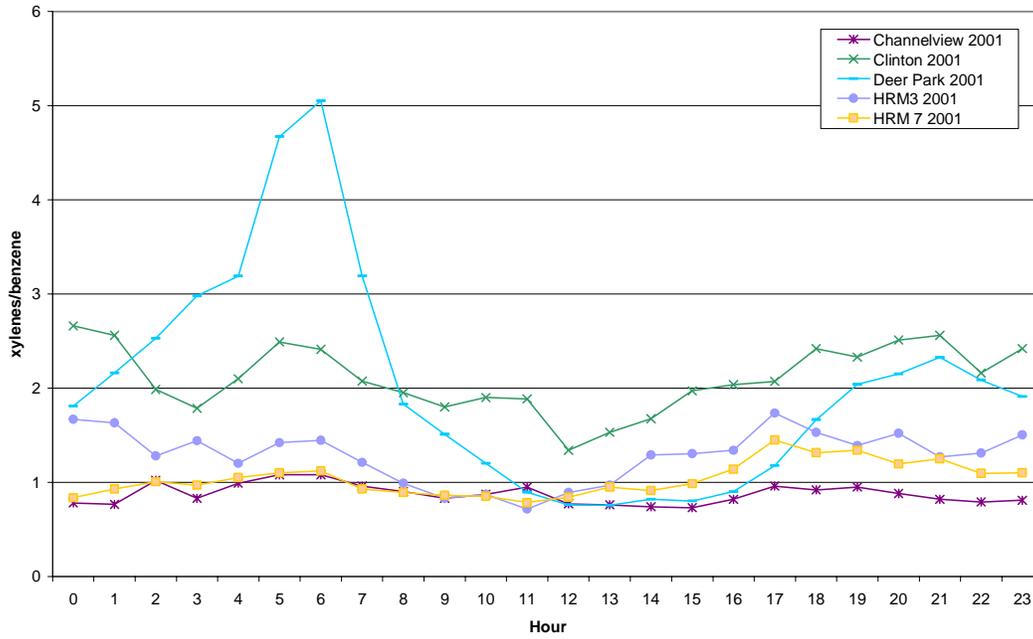


Figure 3-22. Median X/B ratios during summer 2001.

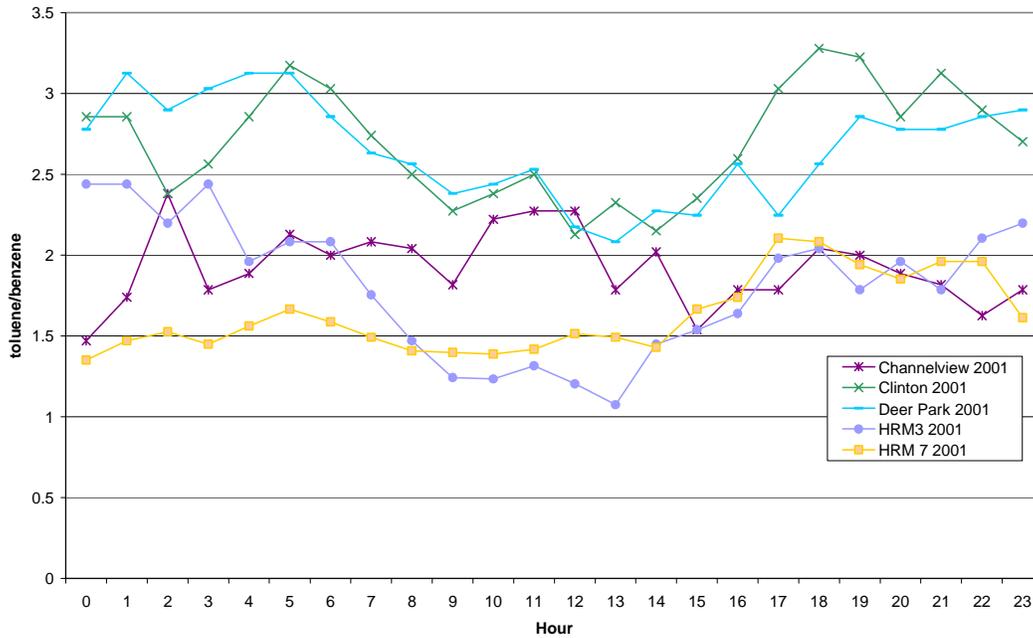


Figure 3-23. Median T/B ratios during summer 2001.

### 3.1.4 Abundant Species

Given the large number of hydrocarbons measured by auto-GC, we focused many analyses on the most abundant species. Two approaches were used to determine abundant species. The first was to rank median concentrations by site (summer only). The ten most abundant hydrocarbons by concentration at each site during each summer (July-September) are given in **Table 3-2**. Ethane, propane, n-butane, isobutane, n-pentane, isopentane, and toluene were all consistently among the ten species highest in concentration. Ethene was among the top ten at all sites and years except at Clinton in 2000. Propene was among the top ten at all sites and years except at Bayland and Clinton in 2000. Xylenes were in the top ten at a number of sites and years. Isoprene, a primary marker of biogenic activity, was in the top ten only at Bayland in 2000, indicating that biogenic emissions were only a small part of the VOCs in Houston. Other compounds in the top ten include n-hexane, benzene, and 2-methylpentane.

The second approach was to rank the reactivity-weighted data (wt% (MIR)). On a reactivity-weighted basis, ethene and propene were both consistently in the top three at each site and year (**Table 3-3**). Toluene, n-butane, xylenes, and isopentane were all in the top ten at each site and in each year. Trimethylbenzenes, isobutane, propane, and isoprene were in the top ten at most sites and in most years. Propane was in the top ten at all sites except in 1998 at Clinton and Bayland; the consistent absence of propane in the top ten at Clinton may be due to the presence of fresher emissions of reactive compounds compared to other sites. Other compounds in the top ten include n-pentane, 1,3-butadiene, trans-2-butene, 3-methyl-1-butene, and ethane. It is remarkable that relatively unreactive species such as ethane and propane were present among the top ten on a reactivity-weighted basis. This demonstrates that even though their relative ozone formation potential is low, their large fraction of TNMOC makes ethane and propane a significant contributor to ozone formation.

Table 3-2. Most abundant species by concentration at each site during each summer (July-September).

Species	Bayland 1998	Bayland 1999	Bayland 2000	Clinton 1998	Clinton 1999	Clinton 2000	Clinton 2001	Channel- view 2001	Deer Park 1999	Deer Park 2000	Deer Park 2001	Haden Rd. 2001	Baytown 2001
Ethane	1	1	1	3	3	4	2	2	1	1	1	2	2
Propane	2	2	2	2	2	3	1	1	2	2	2	1	1
Isopentane	3	3	3	1	1	1	4	5	3	5	6	4	4
n-Butane	4	4	4	4	4	2	3	3	4	3	3	3	3
Toluene	5	5	6	9	8	6	6	7	7	8	7	6	7
i-Butane	6	6	8	5	5	5	5	4	5	4	4	5	5
n-Pentane	7	7	9	7	7	7	7	9	8	10	9	9	6
Xylenes	8	9	10	6	6	8	9			9		10	
Ethene	9	8	7	8	9		8	6	6	7	5	8	9
2-methyl pentane	10	10				9							
propene				10	10		10	8	9	6	8	7	10
isoprene			5										
Benzene								10					
n-hexane						10			10		10		8

Table 3-3. Most abundant species by weight percent (MIR by site during each summer (July-September)).

Species	Bayland 1998	Bayland 1999	Bayland 2000	Clinton 1998	Clinton 1999	Clinton 2000	Clinton 2001	Channel- view 2001	Deer Park 1999	Deer Park 2000	Deer Park 2001	HADE N RD. 2001	BAYT OWN 2001
Ethene	1	1	2	1	3	3	1	2	1	1	1	2	2
Propene	2	2	3	3	2	2	2	1	2	2	2	1	1
Toluene	4	3	5	5	6	5	5	3	4	4	3	4	7
n-butane	9	8	9	6	9	7	6	4	8	8	6	6	5
i-butane		10		10		8	7	5	6	6	5	7	8
Xylenes	3	4	4	2	1	1	3	6	3	3	4	3	6
Propane		9	10					7	7	7	8	8	9
i-pentane	5	5	6	4	5	4	4	8	5	5	7	5	4
Isoprene	7		1	7	8	10		9	10	9		9	
1,2,3- trimethylbenzene	10		7		7			10					
n-pentane				9			9				10	10	10
1,3-butadiene							10						3
1,2,4- trimethylbenzene	6	7	8	8	4	6			9				
t-2-butene	8	6					8						
3-methyl-1- butene					10	9							
ethane										10	9		

## 3.2 ANNUAL, SEASONAL, MONTHLY, AND DAY OF WEEK DIFFERENCES

### 3.2.1 Annual Variations

Fingerprints of median concentrations were generated for 1998-2001 at Clinton and Deer Park and 1998-2000 at Bayland to examine any annual differences (shown in **Figures 3-24 through 3-26**). Concentrations were generally similar from year to year at each site; the only exception was at Bayland, where concentrations in 2000 were much lower than in previous years. This exception, however, is probably due to lack of data during this year when data collection was infrequent and lasted only through August 7 (concentrations tend to be highest in winter). At Clinton and Deer Park, median concentrations of most species were similar from year to year. The Deer Park butanes and pentanes were lower in 2001 compared to other years. This could be due to lower ambient temperatures or to changes in fuel volatility. As noted earlier, incomplete data sets make annual comparisons difficult. Meteorological patterns, and thus source impacts on the sites, also appear to be different during the summer each year, as discussed in Section 4. The changes in wind direction and speed from year to year introduce another factor that may make annual comparisons difficult.

Notched box whisker plots of TNMOC by year at Bayland (1998-2000), Clinton (1998-2001), and Deer Park (1998-2001) are shown in **Figures 3-27 through 3-29**. In general, TNMOC concentrations in 1998 were the highest; 2000 and 2001 concentrations were lower than the previous years. The frequency of high outlying concentrations, however, did not appear to decrease annually; some of the highest concentrations of TNMOC occurred in 2000 and 2001.

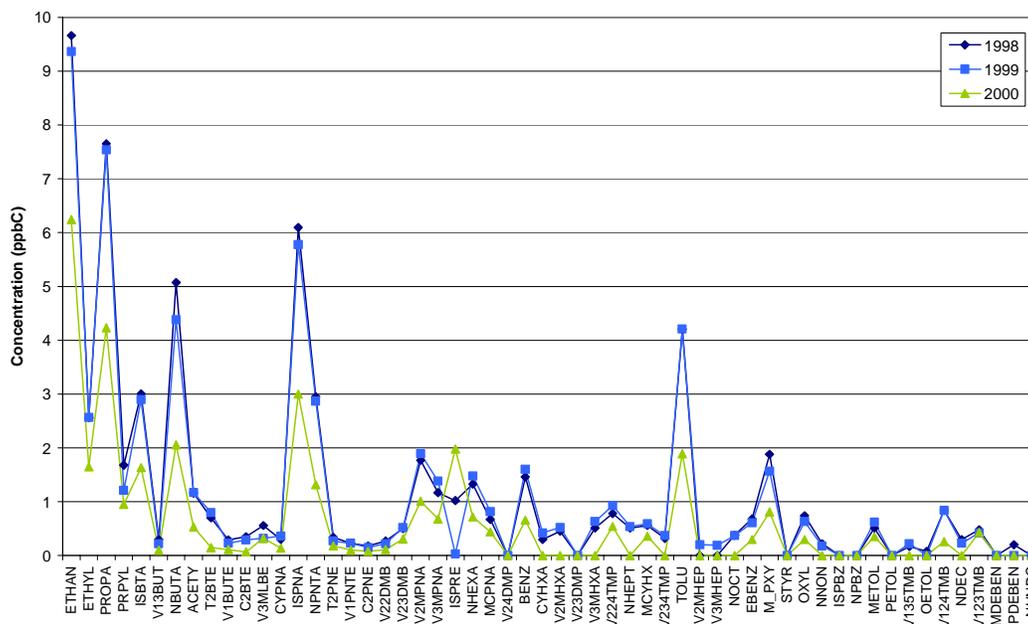


Figure 3-24. Fingerprint of median concentrations at Bayland, 1998-2000 (entire year). In 2000, data were only collected through August 7.

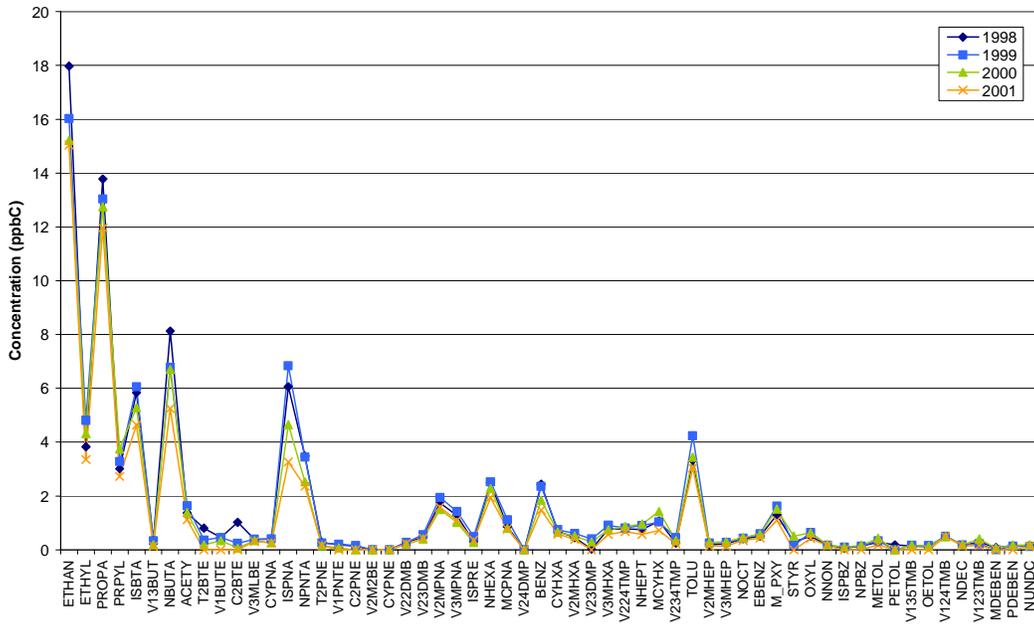


Figure 3-25. Fingerprint of median concentrations at Deer Park, 1998-2001 (entire year).

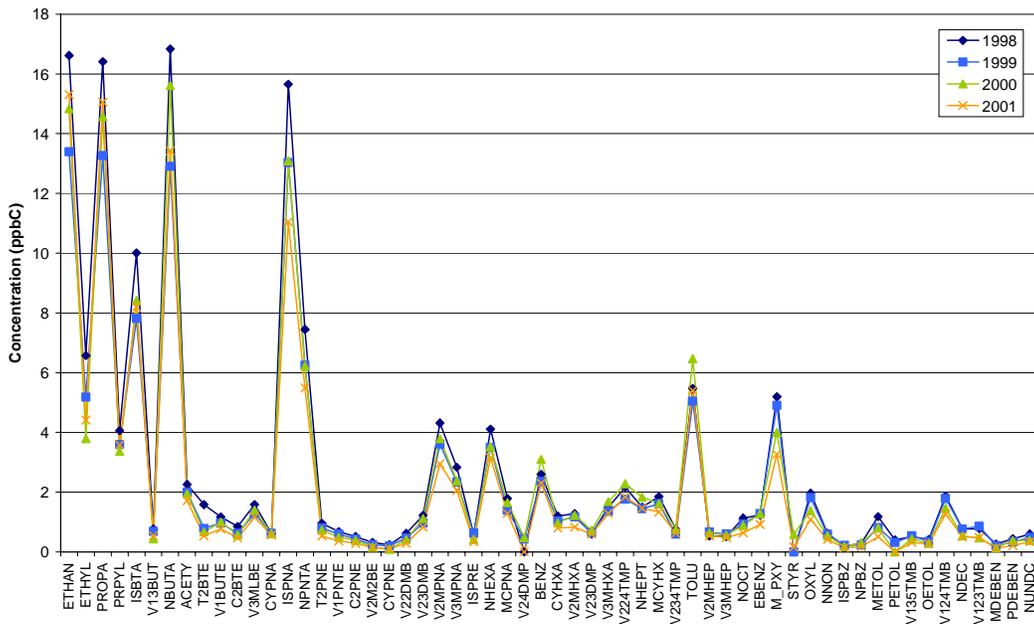


Figure 3-26. Fingerprint of median concentrations at Clinton, 1998-2001 (entire year).

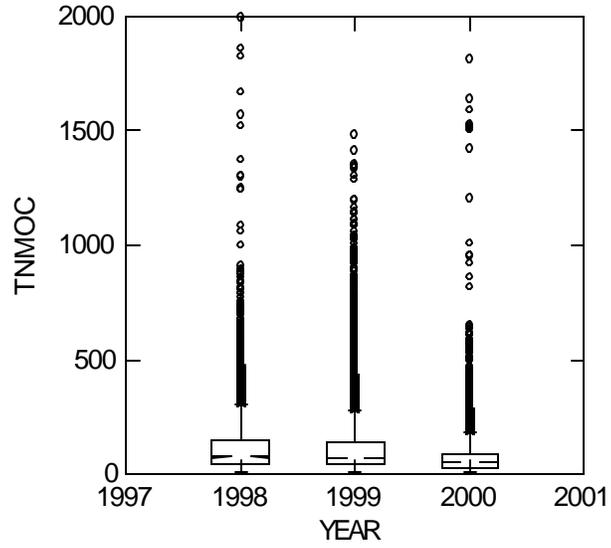


Figure 3-27. Notched box whisker plot of TNMOC concentrations (ppbC) by year at Bayland (2000 data only available through August 7).

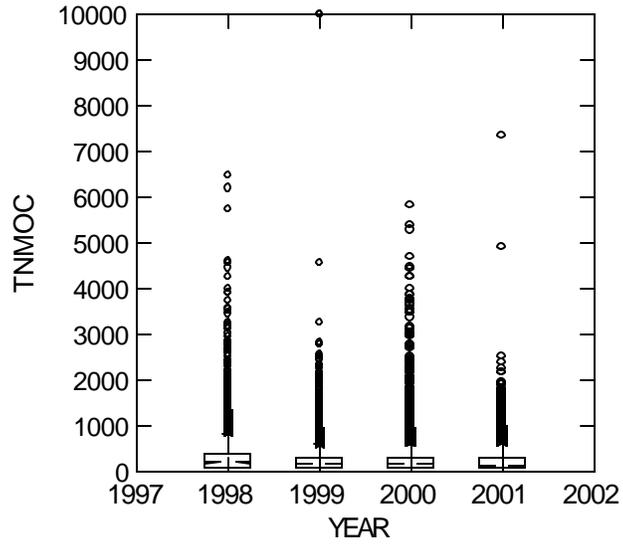


Figure 3-28. Notched box whisker plot of TNMOC concentrations (ppbC) by year at Clinton.

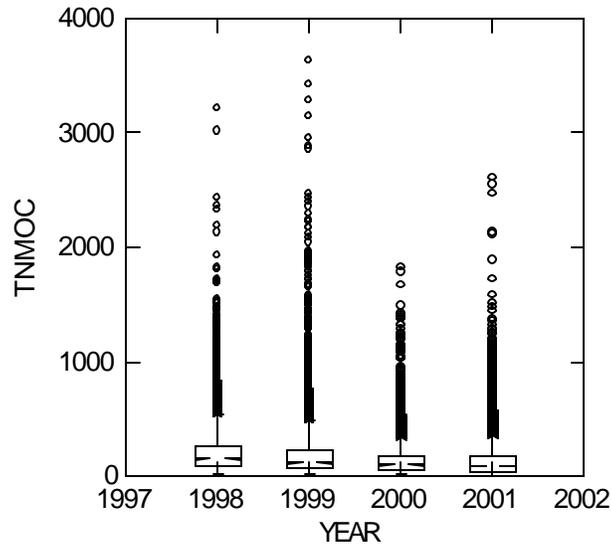


Figure 3-29. Notched box whisker plot of TNMOC concentrations (ppbC) by year at Deer Park.

### 3.2.2 Seasonal Variations

Inspecting data by season allows better understanding of concentration and composition differences due to large scale seasonal, meteorological, and potential emission changes. Box whisker plots were generated for Bayland (1998-2000) and Clinton and Deer Park (1998-2001) during the summer and winter. With less mixing and lower mixing heights, winter-time concentrations are expected to be higher. Box whisker plots of selected species concentrations and ratios by season at Deer Park for 1998-2001 are shown in **Figures 3-30 through 3-32**. Plots include totals (TNMOC, olefins, and aromatic and unidentified hydrocarbons); reactive species of interest (ethene, propene, and 1,3-butadiene), acetylene-to-ethene (A/E) ratio in which the ratio is higher for motor vehicle emission than for industrial emissions; and reactive or carcinogenic aromatic hydrocarbons (toluene, benzene, and xylenes), and a commonly used indicator or air mass age (X/B ratio). Box whisker plots by season for other sites and years are available on the CD that accompanies this report.

While both interquartile ranges of concentration were relatively low, it is significant to note that high extreme outlying concentrations occur in all seasons which indicates little seasonal difference in emissions.

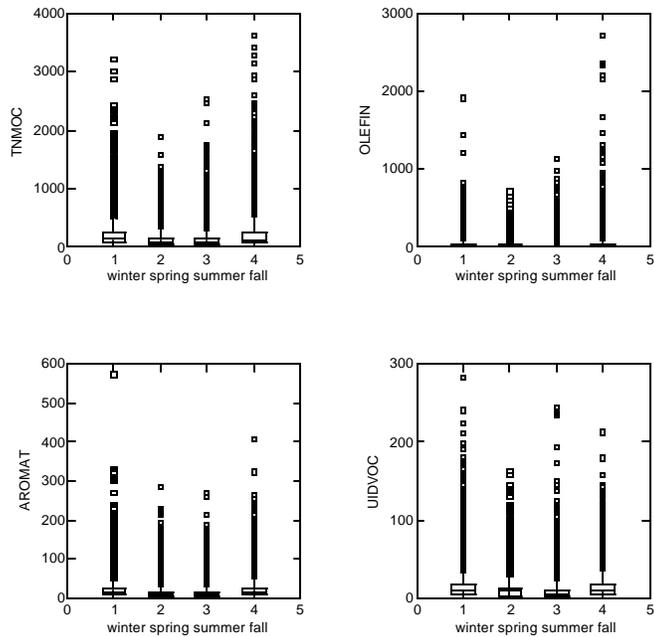


Figure 3-30. Notched box whisker plots by season of TNMOC, olefin, aromatic (AROMAT), and unidentified (UIDVOC) concentrations (ppbC) at Deer Park, 1998-2001.

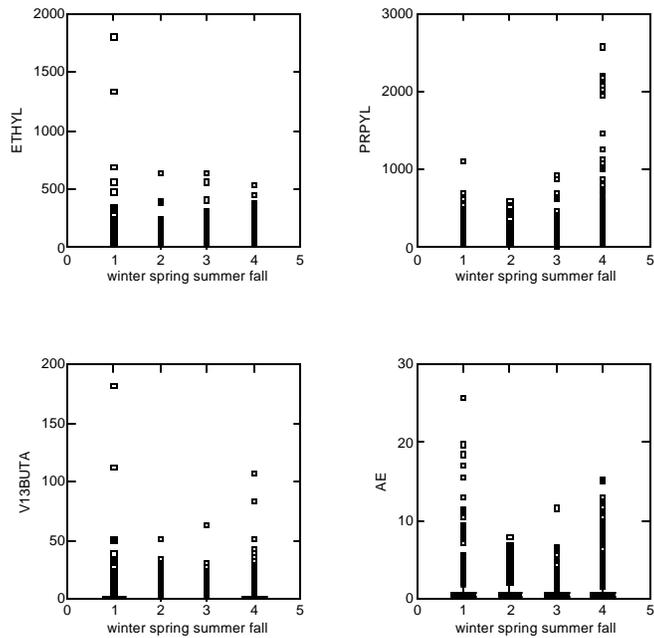


Figure 3-31. Notched box whisker plots by season of ethene (ETHYL), propene (PRPYL), 1,3-butadiene (V13BUTA) concentrations (ppbC) and acetylene/ethene (AE) ratio at Deer Park 1998-2001.

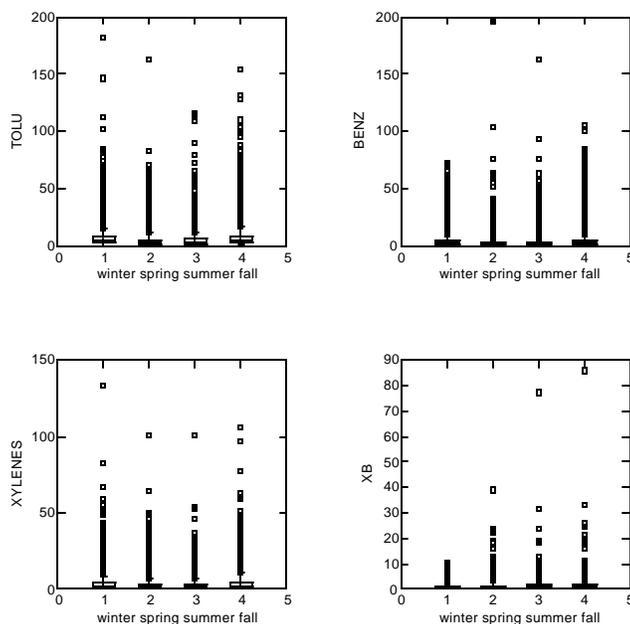


Figure 3-32. Notched box whisker plots by season of toluene (TOLU), benzene (BENZ), xylenes concentrations (ppbC) and xylene/benzene (XB) ratio at Deer Park, 1998-2001.

### 3.2.3 Monthly Variations

Monthly variations were investigated by generating box whisker plots of concentrations by month over a period of three and four years at Bayland and Clinton and Deer Park, respectively. These box whisker plots are shown in **Figures 3-33 through 3-41**. Generally, concentrations were somewhat higher in the winter months when there were more days of stagnant air movement, and inversion layers capped lower levels of the atmosphere holding in emissions. However, the increase in cloud cover and decrease in solar radiation inhibited ozone production during these winter months. Extreme outlying concentrations occurred during all months, indicating that high concentrations were a frequent occurrence and did not follow a monthly or seasonal variation.

TNMOC concentrations were noticeably lower in March and April while a number of high outlying concentrations of propene and xylenes occurred at Deer Park in October and November 1999. Outliers of 1,3-butadiene were found in abundance at Clinton in May and June 1998. Concentrations of aromatics such as toluene, xylenes, and benzene exhibited a decrease in the summer months from the winter at Bayland. This could be due to seasonal changes in emissions, or, more likely, a combination of decreased transport during the summer from sources to the Bayland site and increased photochemistry depleting these aromatics' concentrations in the summer.

An abrupt change in 1,3-butadiene concentrations in the spring at Clinton Drive was observed. **Figure 3-42** shows a plot of 1,3-butadiene concentrations as a function of wind

direction and month. It is clear that the high concentrations of 1,3-butadiene were coming from a south-southwest (180-220 degrees) source.

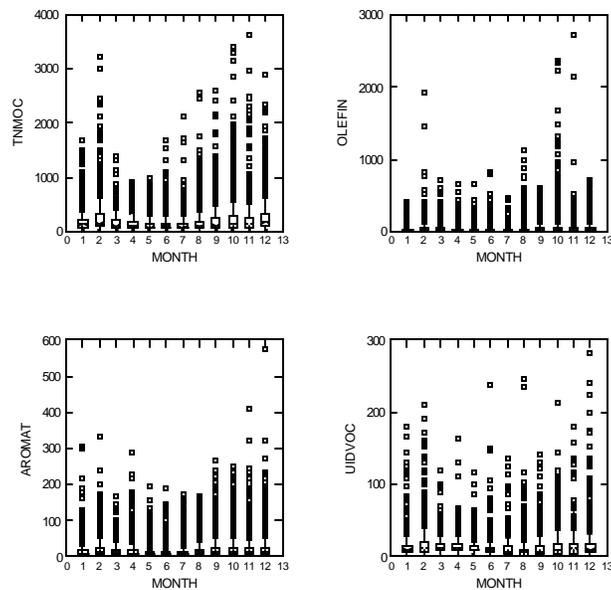


Figure 3-33. Notched box whisker plots by month of TNMOC, olefin, aromatic (AROMAT), and unidentified (UIDVOC) concentrations (ppbC) at Deer Park, 1998-2001.

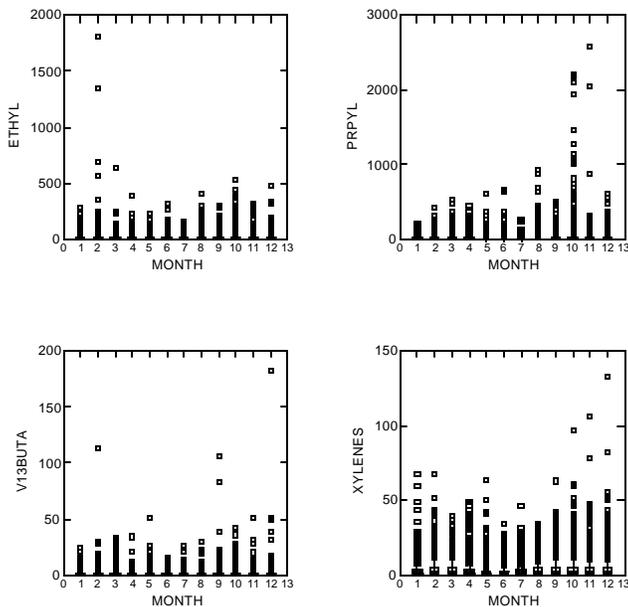


Figure 3-34. Notched box whisker plots by month of ethene (ETHYL), propene (PRPYL), 1,3-butadiene (V13BUTA), and xylenes concentrations (ppbC) at Deer Park, 1998-2001.

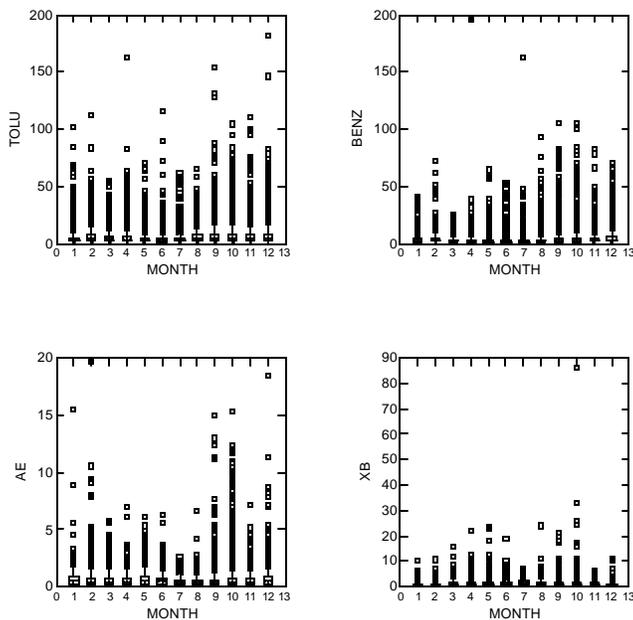


Figure 3-35. Notched box whisker plots by month of toluene (TOLU) and benzene (BENZ) concentrations (ppbC) and acetylene/ethene (AE) and xylenes/benzene (XB) ratios at Deer Park, 1998-2001.

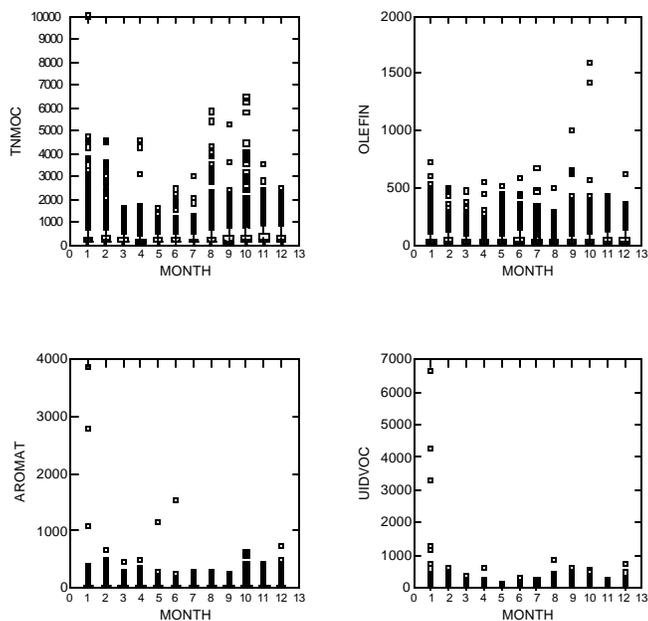


Figure 3-36. Notched box whisker plots by month of TNMOC, olefin, aromatic (AROMAT), and unidentified (UIDVOC) concentrations (ppbC) at Clinton, 1998-2001.

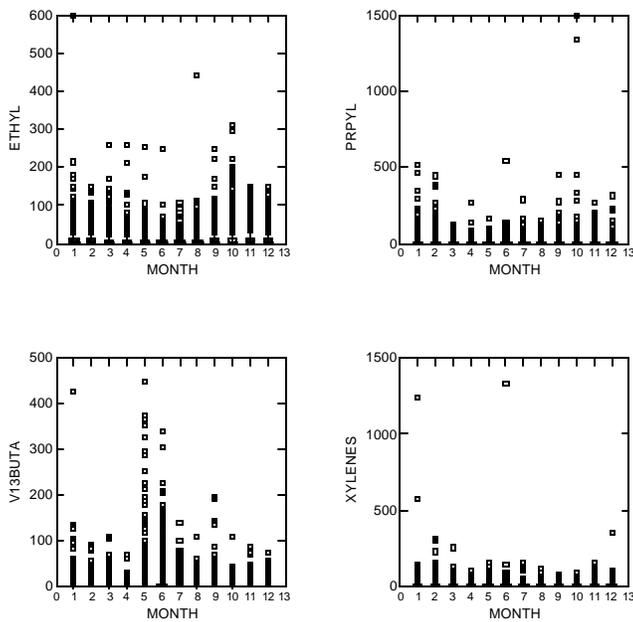


Figure 3-37. Notched box whisker plots by month of ethene (ETHYL), propene (PRPYL), 1,3-butadiene (V13BUTA), and xylenes concentrations (ppbC) at Clinton, 1998-2001.

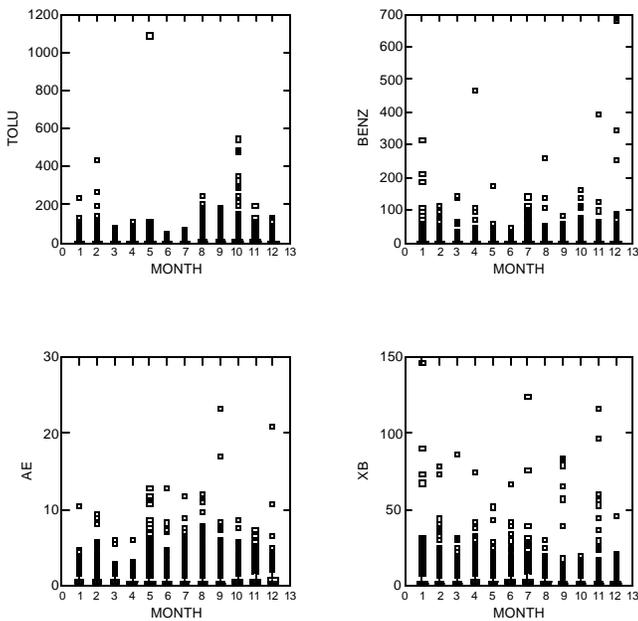


Figure 3-38. Notched box whisker plots by month of toluene (TOLU) and benzene (BENZ) concentrations (ppbC) and acetylene/ethene (AE) and xylenes/benzene (XB) ratios at Clinton, 1998-2001.

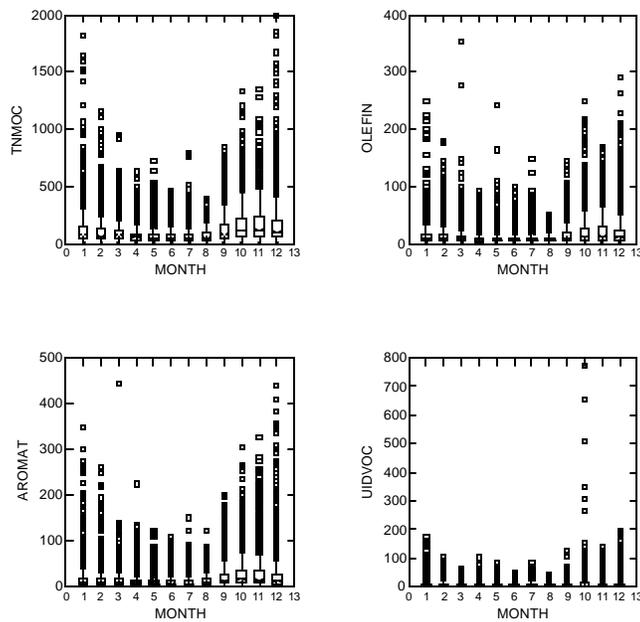


Figure 3-39. Notched box whisker plots by month of TNMOC, olefin, aromatic (AROMAT), and unidentified (UIDVOC) concentrations (ppbC) at Bayland, 1998-2000.

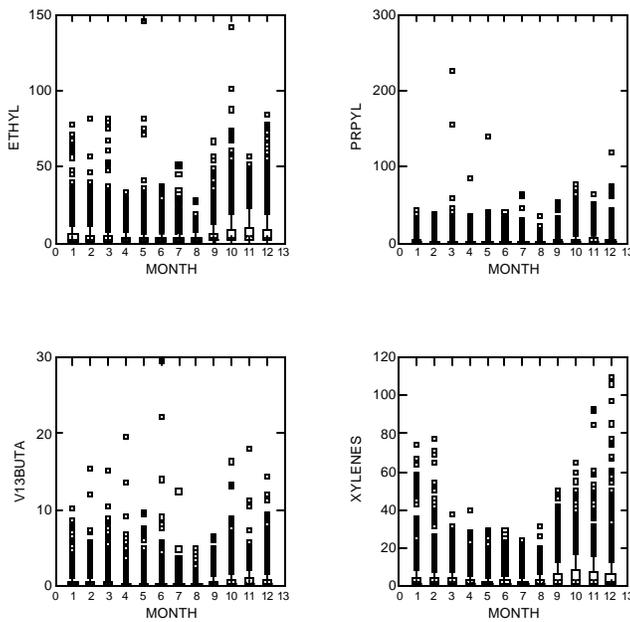


Figure 3-40. Notched box whisker plots by month of ethene (ETHYL), propene (PRPYL), 1,3-butadiene (V13BUTA), and xylenes concentrations (ppbC) at Bayland, 1998-2000.

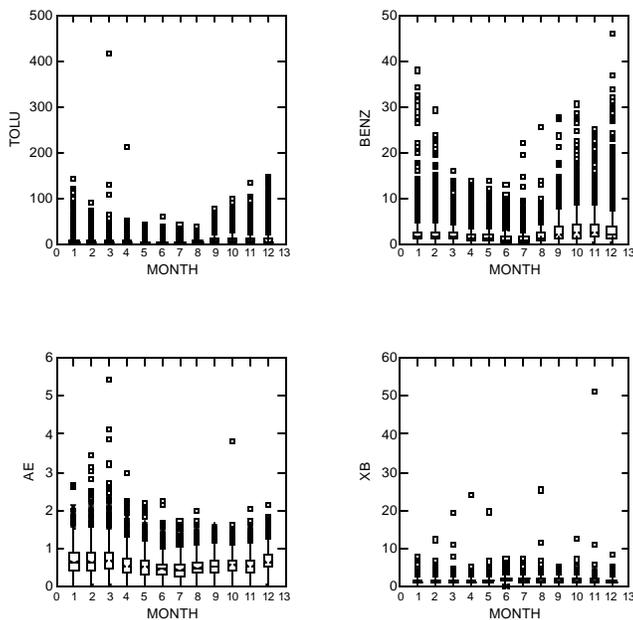


Figure 3-41. Notched box whisker plots by month of toluene (TOLU) and benzene (BENZ) concentrations and acetylene/ethene (AE) and xylenes/benzene (XB) ratios at Bayland, 1998-2000.

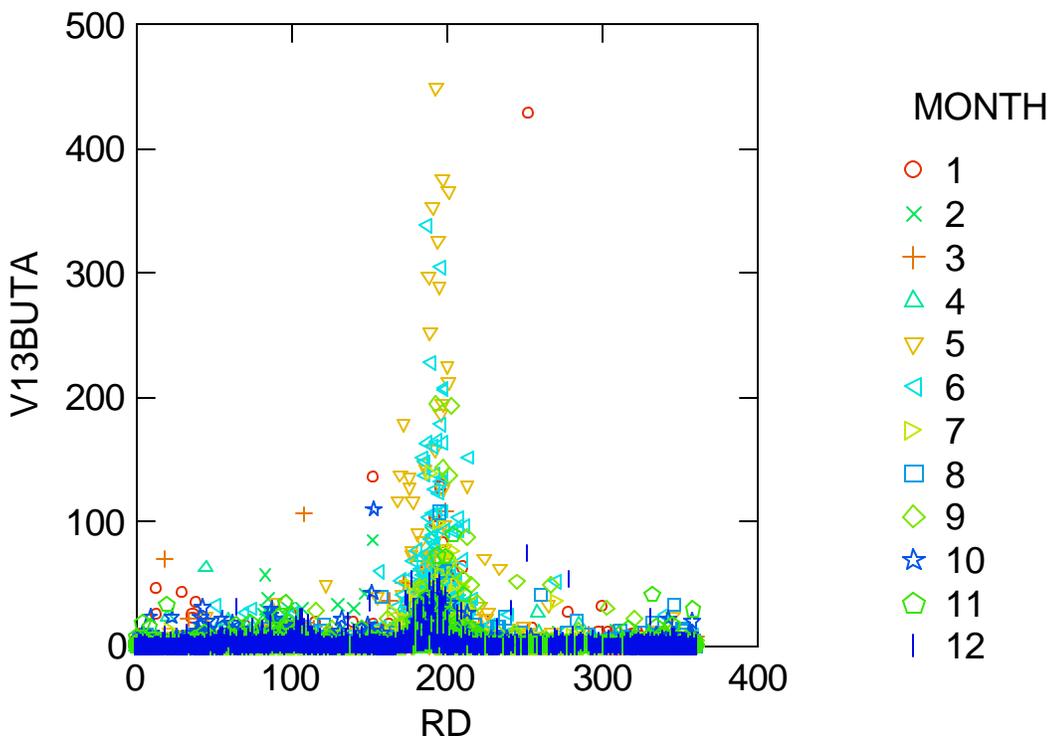


Figure 3-42. 1,3-butadiene (V13BUTA) concentrations (ppbC) as a function of wind direction (RD) and month at Clinton Drive, 1998-2001.

### 3.2.4 Day-of-Week Analysis

Other studies (e.g., Coe et al., 2001) have demonstrated the difference between weekday and weekend anthropogenic activities. For example, since traffic patterns depend largely on the Monday-Friday workweek, one might expect to see notable differences in motor vehicle-related hydrocarbon concentrations as a function of the day of the week. In contrast, industrial emissions may not have a day-of-week dependence because operations occur at all hours of the day every day of the week. Notched box whisker plots during the morning hours (0500 CST-0900 CST) by day of week were created at Clinton for summer 2001 (shown in **Figures 3-43 and 3-44**). Box whisker plots for other sites and years (both for summer only and the entire year) are provided on the CD that accompanies this report.

Following are the results of this analysis:

- Most species and ratios show little difference from day to day, indicating that the majority of emissions near the Clinton Drive site were fairly constant and exhibited no weekend-weekday differences.
- During the summer, TNMOC concentrations were lower on Sunday. This is consistent with less traffic and the significant contribution of vehicle emissions (especially compared to other auto-GC sites in the Ship Channel) to total hydrocarbons at this site.
- Extreme outliers regularly occurred on every day of the week; this high frequency of outlying concentrations indicates that emissions do not follow a daily pattern.

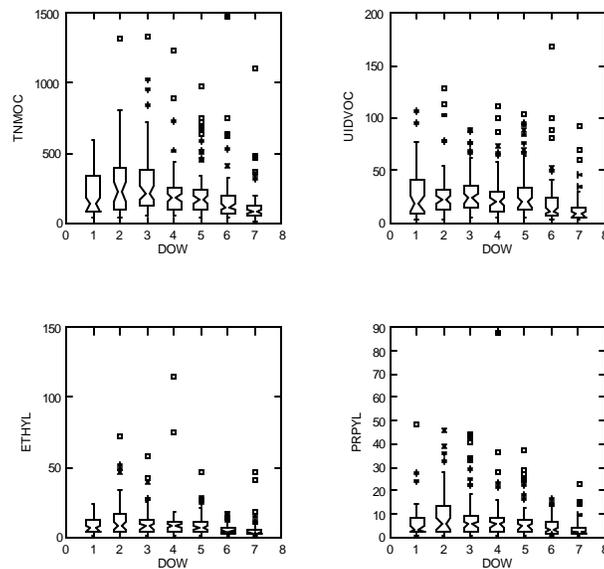


Figure 3-43. Notched box whisker plots of TNMOC, unidentified (UIDVOC), ethene (ETHYL), and propene (PRPYL) concentrations (ppbC) by day of week at Clinton during summer 2001 (Monday=1).

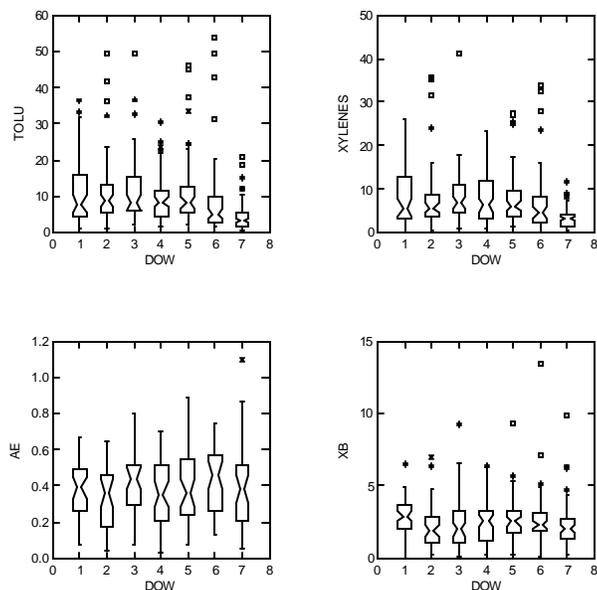


Figure 3-44. Notched box whisker plots of toluene (TOLU) and xylenes concentrations (ppbC) and acetylene/ethene (AE) and xylenes/benzene (XB) ratios by day of week at Clinton during summer 2001 (Monday=1).

### 3.3 TIME-OF-DAY ANALYSIS

Concentrations and composition often change over the course of a day as different air masses, mixing heights, winds, and emissions influence a particular site. Emissions are often highest in the morning when low mixing heights, minimal winds, and lack of solar radiation encourage accumulation of emissions in the lower atmosphere. Morning is also a time of peak vehicle commute traffic. Industrial emissions occur throughout the night and, when coupled with meteorological factors, usually result in high VOC concentrations in the morning. With increased solar radiation, expansion of mixing heights, and an increase in winds, concentrations generally decrease in the afternoon as compounds are reacted or advected away. Notched box whisker plots of the diurnal variation of selected species concentrations and ratios for summer 2001 at Clinton Drive are shown in **Figures 3-45 and 3-46**.

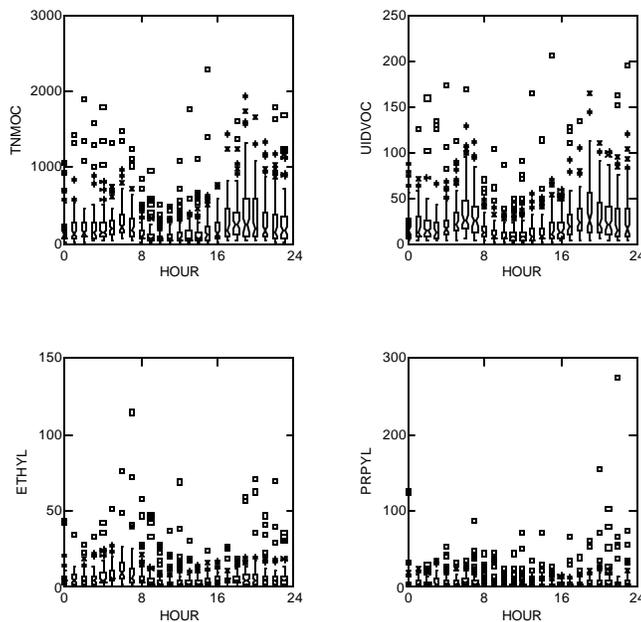


Figure 3-45. Notched box whisker plots of TNMOC, unidentified (UIDVOC), ethene (ETHYL), and propene (PRPYL) concentrations (ppbC) by hour at Clinton in summer 2001.

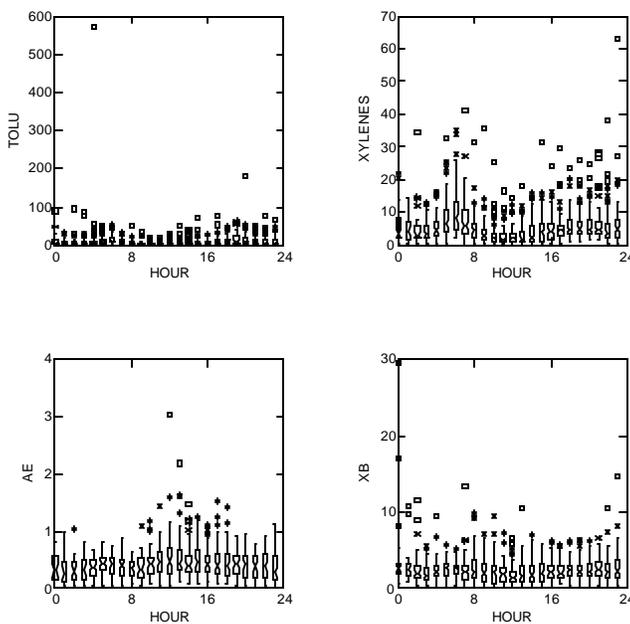


Figure 3-46. Notched box whisker plots of toluene (TOLU) and xylenes concentrations (ppbC) and acetylene/ethene (AE) and xylenes/benzene (XB) by hour at Clinton in summer 2001.

### 3.4 RELATIONSHIPS AMONG SPECIES

In order to investigate whether certain species share a common source and consistently impact a receptor site together, scatter plot matrices and correlation matrices were developed. Scatter plots (and their corresponding correlation coefficients) help in understanding which species potentially originate from the same source, what typical ratios are between hydrocarbons or groups, and which species have similar chemical depletion mechanisms.

Scatter plot matrices of concentrations of abundant and reactive species were prepared for each site using data collected during the summer of each year. Scatter plot matrices of data at Channelview, Clinton, Deer Park, Haden Rd., and Baytown in 2001 are shown in **Figures 3-47 through 3-51**. Corresponding correlation matrices were also prepared; **Tables 3-4 through 3-10** detail linear correlation coefficients at these sites in 2001.

Following are observations from the scatter plots and correlation tables:

- In general, a large amount of scatter and number of outliers affect the correlations.
- Compared to other urban areas in the country, the Houston auto-GC data show much more scatter, indicating a larger mix of sources. The hydrocarbons in most other cities with auto-GCs are dominated by motor vehicle emissions sources.
- At Channelview, the trimethylbenzenes and ethyltoluenes correlate reasonably well indicating a shared source.
- At Clinton Drive, while there is a significant amount of scatter in the relationships, there are many very strong “edges” evident. Edges are the ratios between two hydrocarbons that bound the spread in the data; these edges probably represent sources. Toluene and 2,2,4-trimethylpentane (a gasoline component) correlate well, likely indicating motor vehicle sources. Ethene and propene correlate as well.
- At Deer Park, the aromatic hydrocarbons correlate well with each other in general. There are many outliers indicating nearby sources influencing concentrations at this site occasionally. The “edges” at this site are much less strongly defined as at Clinton Drive. The t-2-pentene relationship with the aromatic hydrocarbons may indicate a common source.
- At Haden Rd., a motor vehicle influence is evident based on the relationship between the aromatic hydrocarbons and 2,2,4-trimethylpentane. There is an interesting bifurcation in the relationship between benzene and 1,3-butadiene concentrations, for example. This could indicate well-defined sources existing in two different directions that impact the site.
- At Baytown, there is a strong (and bifurcated) relationship between t-2-butene and t-2-pentene, again indicating two potential sources from differing wind directions.
- When the data are segregated by wind direction at Clinton Drive (into industrial- and motor vehicle-dominated segments), ethene, propene, 1,3-butadiene, and acetylene correlate reasonably well from the industrial sector. Higher correlations in general are seen for the industrial sector showing the emissions are relatively consistent. The motor vehicle sector shows lower correlations which may be indicative of a more aged air mass when winds are from the west.

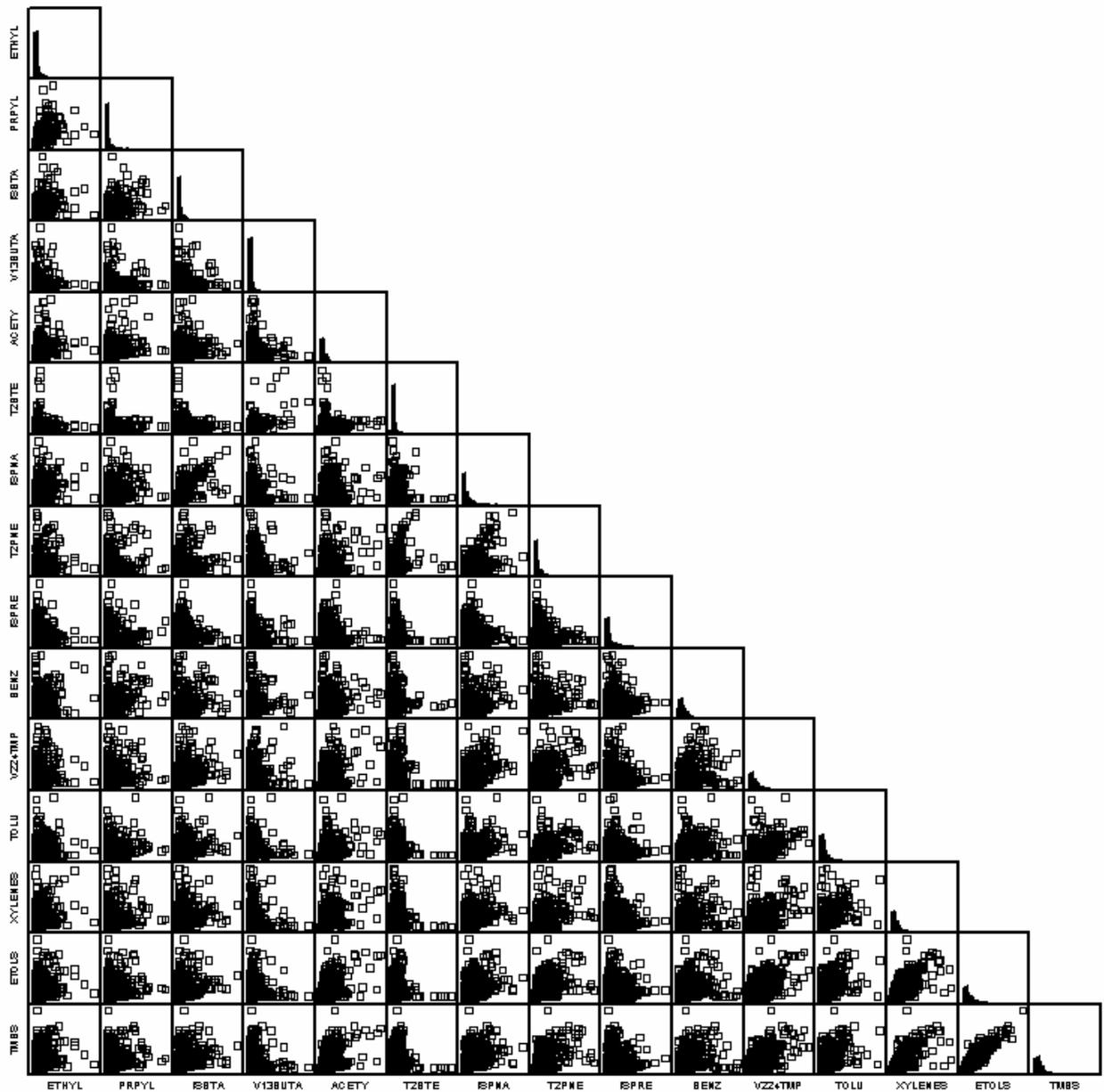


Figure 3-47. Scatter plot matrix of concentrations at Channelview in summer 2001.

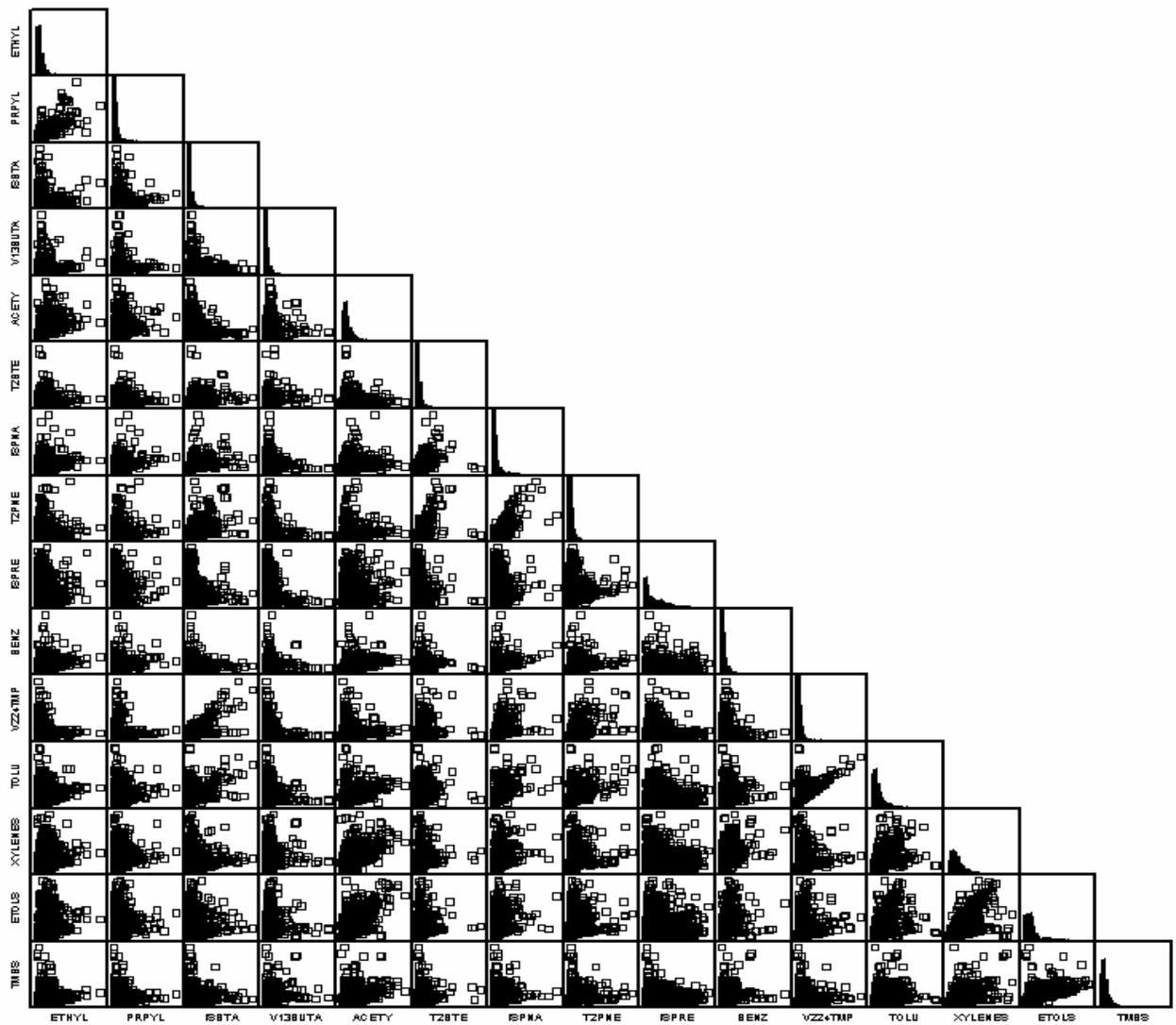


Figure 3-48. Scatter plot matrix of concentrations at Clinton in summer 2001.

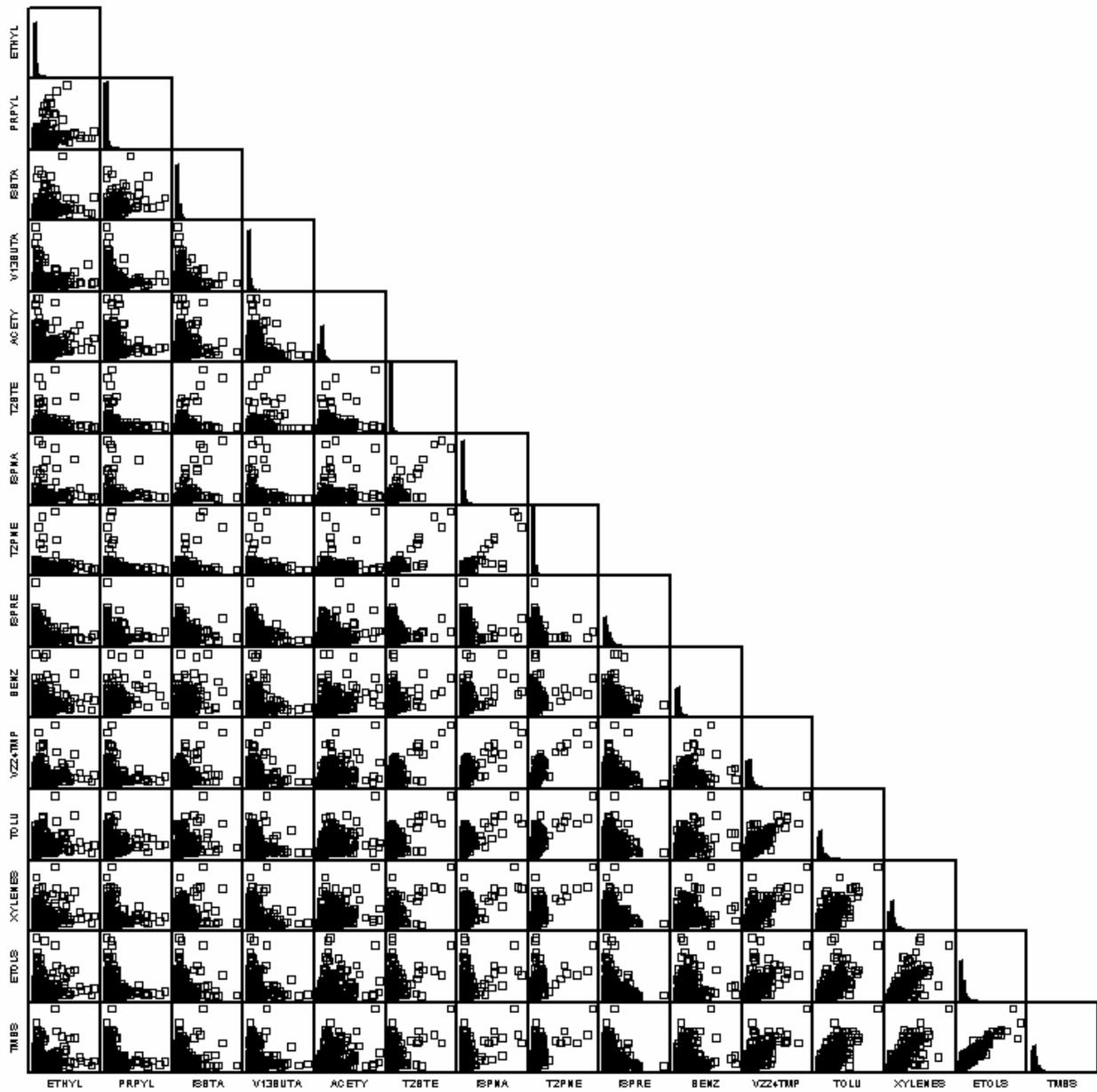


Figure 3-49. Scatter plot matrix of concentrations at Deer Park in summer 2001.

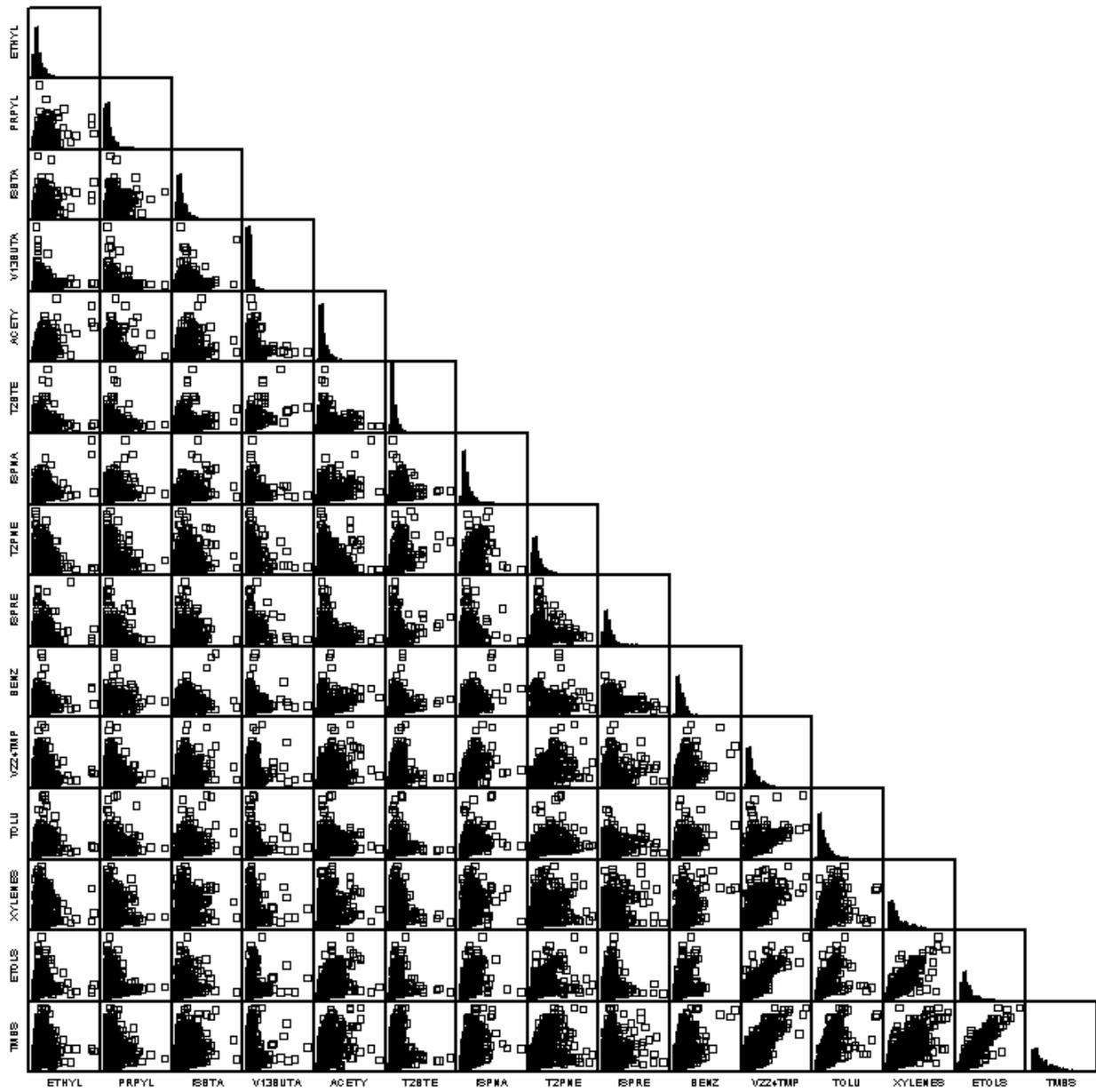


Figure 3-50. Scatter plot matrix of concentrations at Haden Rd. in summer 2001.

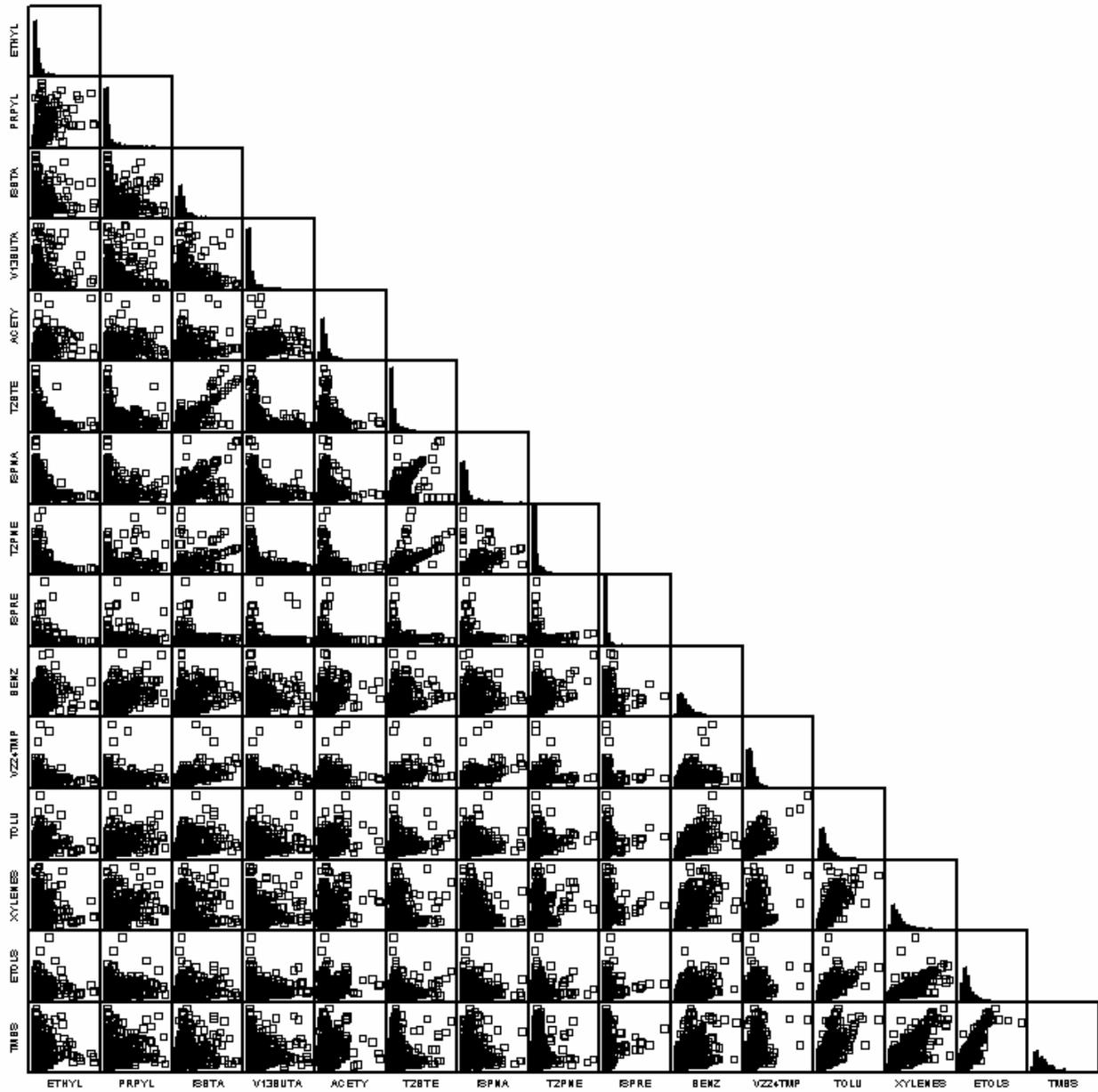


Figure 3-51. Scatter plot matrix of concentrations at Baytown in summer 2001.

Table 3-4. Correlation coefficients of concentrations at Channelview, summer (July-October) 2001.

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1.00													
Propene	0.66	1.00												
i-butane	0.54	0.54	1.00											
1,3-Butadiene	0.17	0.19	0.20	1.00										
Acetylene	0.43	0.47	0.33	0.17	1.00									
t-2-butene	0.14	0.17	0.13	0.58	0.18	1.00								
i-pentane	0.47	0.43	0.69	0.17	0.43	0.22	1.00							
t-2-pentene	0.28	0.28	0.31	0.25	0.46	0.43	0.62	1.00						
Isoprene	0.01	0.09	0.05	0.06	0.11	0.01	0.03	-0.01	1.00					
Benzene	0.39	0.45	0.41	0.26	0.42	0.19	0.45	0.35	0.12	1.00				
2,2,4-trimethylpentane	0.29	0.27	0.41	0.24	0.52	0.19	0.61	0.60	0.06	0.44	1.00			
Toluene	0.26	0.30	0.36	0.13	0.46	0.15	0.50	0.55	0.13	0.41	0.58	1.00		
Xylenes	0.39	0.32	0.36	0.12	0.57	0.16	0.53	0.58	0.09	0.39	0.60	0.61	1.00	
Ethyltoluenes	0.34	0.30	0.36	0.14	0.60	0.18	0.53	0.61	0.10	0.40	0.66	0.59	0.78	1.00
Trimethylbenzenes	0.38	0.34	0.39	0.15	0.61	0.19	0.57	0.64	0.08	0.43	0.67	0.62	0.80	0.93

Table 3-5. Correlation coefficients of concentrations at Clinton, summer (July-October) 2001.

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1.00													
Propene	0.77	1.00												
i-butane	0.15	0.22	1.00											
1,3-Butadiene	0.23	0.22	0.09	1.00										
Acetylene	0.52	0.35	0.00	0.20	1.00									
t-2-butene	0.20	0.27	0.42	0.30	0.09	1.00								
i-pentane	0.44	0.48	0.49	0.15	0.31	0.58	1.00							
t-2-pentene	0.25	0.31	0.58	0.11	0.16	0.67	0.82	1.00						
Isoprene	0.04	0.02	-0.02	-0.07	0.06	-0.03	0.05	0.07	1.00					
Benzene	0.48	0.46	0.15	0.20	0.48	0.26	0.51	0.37	0.08	1.00				
2,2,4-trimethylpentane	0.12	0.17	0.79	0.05	0.16	0.36	0.56	0.63	0.05	0.22	1.00			
Toluene	0.39	0.37	0.57	0.15	0.51	0.36	0.64	0.60	0.07	0.48	0.75	1.00		
Xylenes	0.44	0.35	0.17	0.26	0.66	0.28	0.45	0.34	-0.03	0.58	0.29	0.63	1.00	
Ethyltoluenes	0.43	0.31	0.18	0.23	0.72	0.25	0.43	0.33	0.01	0.46	0.31	0.62	0.75	1.00
Trimethylbenzenes	0.32	0.24	0.12	0.35	0.52	0.25	0.31	0.25	-0.06	0.39	0.21	0.48	0.65	0.67

Table 3-6. Correlation coefficients of concentrations at Deer Park, summer (July-October) 2001.

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1.00													
Propene	0.54	1.00												
i-butane	0.45	0.60	1.00											
1,3-Butadiene	0.25	0.22	0.23	1.00										
Acetylene	0.37	0.31	0.33	0.30	1.00									
t-2-butene	0.29	0.17	0.41	0.40	0.35	1.00								
i-pentane	0.32	0.24	0.54	0.23	0.38	0.81	1.00							
t-2-pentene	0.27	0.13	0.40	0.26	0.39	0.86	0.86	1.00						
Isoprene	0.05	0.09	0.13	0.08	0.18	0.15	0.16	0.09	1.00					
Benzene	0.38	0.53	0.53	0.32	0.56	0.42	0.54	0.39	0.19	1.00				
2,2,4-trimethylpentane	0.28	0.14	0.39	0.28	0.53	0.62	0.73	0.78	0.14	0.49	1.00			
Toluene	0.35	0.29	0.42	0.29	0.56	0.53	0.64	0.66	0.13	0.61	0.85	1.00		
Xylenes	0.33	0.20	0.36	0.27	0.53	0.52	0.61	0.65	0.08	0.52	0.81	0.84	1.00	
Ethyltoluenes	0.28	0.14	0.24	0.24	0.47	0.41	0.45	0.54	0.03	0.42	0.72	0.77	0.82	1.00
Trimethylbenzenes	0.28	0.13	0.26	0.27	0.49	0.47	0.52	0.63	0.05	0.44	0.80	0.81	0.85	0.95

Table 3-7. Correlation coefficients of concentrations at Haden Rd., summer (July-October) 2001.

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1.00													
Propene	0.51	1.00												
i-butane	0.50	0.50	1.00											
1,3-Butadiene	0.08	0.11	0.26	1.00										
Acetylene	0.50	0.28	0.33	0.15	1.00									
t-2-butene	0.18	0.14	0.27	0.56	0.12	1.00								
i-pentane	0.43	0.38	0.54	0.13	0.40	0.34	1.00							
t-2-pentene	0.17	0.12	0.26	0.15	0.17	0.55	0.60	1.00						
Isoprene	0.15	0.11	0.16	0.17	0.01	0.20	0.15	0.12	1.00					
Benzene	0.34	0.40	0.41	0.18	0.42	0.26	0.56	0.36	0.13	1.00				
2,2,4-trimethylpentane	0.18	0.14	0.33	0.20	0.47	0.28	0.63	0.58	0.24	0.50	1.00			
Toluene	0.30	0.24	0.42	0.12	0.31	0.22	0.54	0.52	0.19	0.58	0.66	1.00		
Xylenes	0.25	0.25	0.37	0.13	0.31	0.19	0.53	0.40	0.32	0.51	0.70	0.62	1.00	
Ethyltoluenes	0.19	0.13	0.22	0.17	0.55	0.21	0.52	0.52	0.07	0.48	0.83	0.63	0.83	1.00
Trimethylbenzenes	0.31	0.23	0.39	0.16	0.48	0.23	0.59	0.51	0.22	0.54	0.82	0.74	0.79	0.90

Table 3-8. Correlation coefficients of concentrations at Baytown, summer (July-October) 2001.

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1													
Propene	0.62	1.00												
i-butane	0.24	0.21	1.00											
1,3-Butadiene	0.27	0.21	0.12	1.00										
Acetylene	0.43	0.36	0.22	0.37	1.00									
t-2-butene	-0.02	0.07	0.81	-0.05	-0.03	1.00								
i-pentane	-0.05	0.04	0.65	-0.03	-0.03	0.65	1.00							
t-2-pentene	-0.03	0.26	0.51	-0.07	-0.06	0.74	0.54	1.00						
Isoprene	0.06	0.16	0.11	0.03	-0.08	0.04	0.06	0.10	1.00					
Benzene	0.36	0.54	0.44	0.25	0.46	0.34	0.30	0.47	0.15	1.00				
2,2,4-trimethylpentane	0.05	0.11	0.56	0.16	0.22	0.46	0.57	0.31	0.10	0.42	1.00			
Toluene	0.21	0.40	0.38	0.24	0.43	0.26	0.27	0.30	0.19	0.70	0.71	1.00		
Xylenes	0.14	0.33	0.21	0.12	0.30	0.18	0.13	0.28	0.16	0.61	0.45	0.80	1.00	
Ethyltoluenes	0.13	0.20	0.17	0.12	0.26	0.13	0.09	0.12	0.13	0.52	0.42	0.68	0.79	1.00
Trimethylbenzenes	0.16	0.23	0.21	0.14	0.26	0.13	0.11	0.12	0.24	0.49	0.46	0.73	0.80	0.88

Table 3-9. Correlation coefficients of concentrations at Clinton, summer (July-October) 2001, from 60-150 degrees (industry).

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1													
Propene	0.72	1.00												
i-butane	0.25	0.22	1.00											
1,3-Butadiene	0.78	0.64	0.52	1.00										
Acetylene	0.76	0.59	0.43	0.95	1.00									
t-2-butene	0.54	0.47	0.77	0.80	0.75	1.00								
i-pentane	0.62	0.55	0.79	0.85	0.82	0.88	1.00							
t-2-pentene	0.60	0.48	0.80	0.86	0.81	0.89	0.95	1.00						
Isoprene	-0.25	-0.19	-0.06	-0.24	-0.26	-0.21	-0.17	-0.17	1.00					
Benzene	0.59	0.46	0.32	0.69	0.70	0.53	0.63	0.61	-0.25	1.00				
2,2,4-trimethylpentane	0.51	0.42	0.84	0.76	0.71	0.81	0.93	0.93	-0.07	0.55	1.00			
Toluene	0.61	0.45	0.45	0.76	0.76	0.59	0.71	0.71	-0.12	0.56	0.70	1.00		
Xylenes	0.73	0.62	0.42	0.88	0.91	0.70	0.83	0.82	-0.21	0.68	0.74	0.78	1.00	
Ethyltoluenes	0.65	0.49	0.29	0.63	0.67	0.49	0.64	0.63	-0.22	0.51	0.57	0.62	0.75	1.00
Trimethylbenzenes	0.49	0.41	0.18	0.51	0.50	0.34	0.50	0.42	-0.13	0.40	0.37	0.45	0.62	0.56

Table 3-10. Correlation coefficients of concentrations at Clinton, summer (July-October) 2001, from 225-315 degrees (freeway).

	Ethene	Propene	Isbta	13Buta	Acety	T2bte	Ispna	T2pne	Ispre	Benzene	224TMP	Toluene	Xylenes	Ethyltoluenes
Ethene	1.00													
Propene	0.59	1.00												
i-butane	0.59	0.51	1.00											
1,3-Butadiene	0.63	0.38	0.46	1.00										
Acetylene	0.57	0.39	0.37	0.62	1.00									
t-2-butene	0.43	0.37	0.53	0.50	0.35	1.00								
i-pentane	0.52	0.49	0.61	0.47	0.46	0.83	1.00							
t-2-pentene	0.38	0.34	0.52	0.42	0.32	0.88	0.88	1.00						
Isoprene	0.20	0.14	0.17	0.30	0.13	0.16	0.21	0.17	1.00					
Benzene	0.15	0.15	0.12	0.15	0.15	0.22	0.18	0.21	0.07	1.00				
2,2,4-trimethylpentane	0.30	0.24	0.58	0.42	0.42	0.64	0.75	0.71	0.17	0.15	1.00			
Toluene	0.57	0.44	0.55	0.55	0.63	0.68	0.80	0.74	0.21	0.26	0.75	1.00		
Xylenes	0.29	0.22	0.30	0.39	0.40	0.48	0.43	0.45	-0.03	0.24	0.45	0.65	1.00	
Ethyltoluenes	0.44	0.32	0.45	0.56	0.65	0.66	0.65	0.63	0.09	0.22	0.69	0.79	0.62	1.00
Trimethylbenzenes	0.35	0.25	0.36	0.49	0.46	0.55	0.53	0.53	0.07	0.23	0.54	0.73	0.64	0.70

### 3.5 TOTAL REACTIVITY ANALYSIS

In order to investigate whether one hydrocarbon or a small group of species were dominating the total reactivity at a site, or whether there was simply a mélange of species all contributing a small part to the total, the composition of total reactivity was investigated. The following sections present findings for ethene, propene, C2-C5 alkanes, aromatic hydrocarbons, and other olefins.

#### 3.5.1 Ethene and Propene

Ethene and propene are two very reactive light olefins that are emitted from a wide range of industrial and combustive sources. The unique density of industrial activities in the Houston area suggests that these compounds may be the most important on a reactivity basis. While their weight percents in most samples are generally low, their high reactivities make it possible for these hydrocarbons to dominate the total reactivity of a sample.

Scatter plots of the sum of these two species' weight percents scaled by their MIR reactivities versus the total reactivity (on the wMIR scale) were created for summer mornings for each site and year. **Figure 3-52** shows a scatter plot of ethene and propene reactivity-weighted values versus the sum of all species wMIR at Clinton during the summers of 1998-2001. Ethene and propene can be up to 86% of the total reactivity but can also be as little as 3% and, on average, about 34%. The large amount of scatter strongly influences the averages and linear regressions; median values probably give a better indication of the influence of these compounds on the total reactivity.

**Figures 3-53 and 3-54** show the median contribution of ethene and propene (%) to the total reactivity (wt% (MIR and wt% (OH, respectively) during the summer for each site and year. These values vary widely among sites and years where ethene and propene together contribute 15%-35% to the total reactivity on the MIR scale, and 9% to 26% of the total OH reactivity (propene is more important on this scale relative to ethene). While these light olefins can dominate some samples on a reactivity basis, they do not appear to be the sole contributors to the total reactivity on either scale.

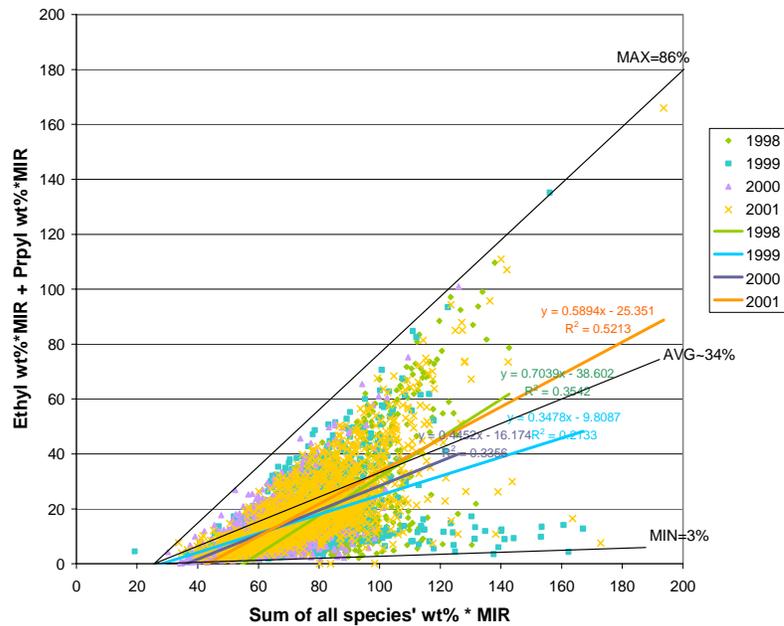


Figure 3-52. Ethyl wt% \*MIR + Prpyl wt% \*MIR versus sum of all species' wt% \*MIR at Clinton during summers 1998-2001.

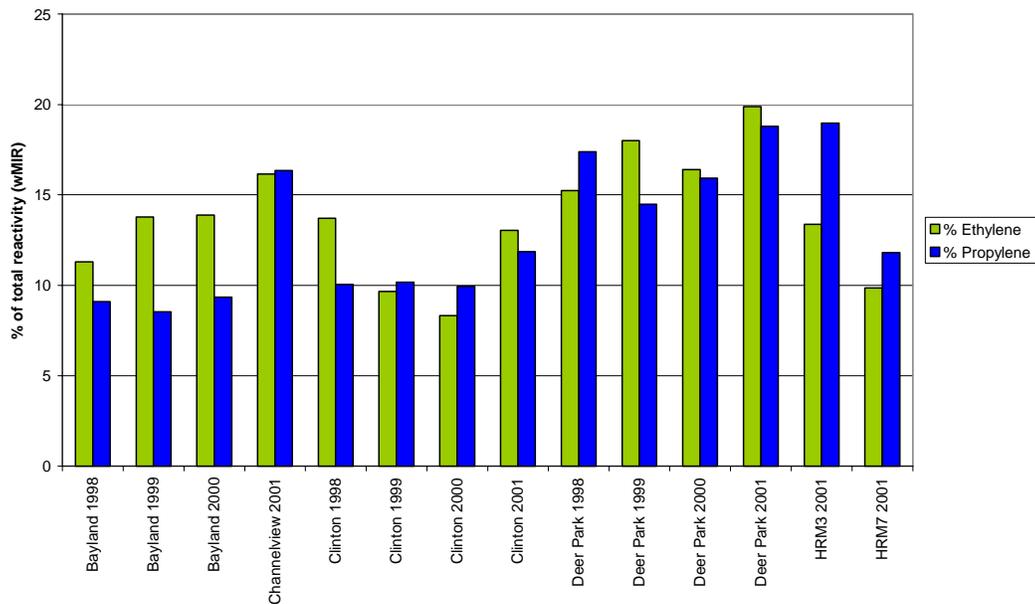


Figure 3-53. Median contribution of ethylene and propylene (%) to the total reactivity (sum of all species' wt% \*MIR) during the summer by site and year.

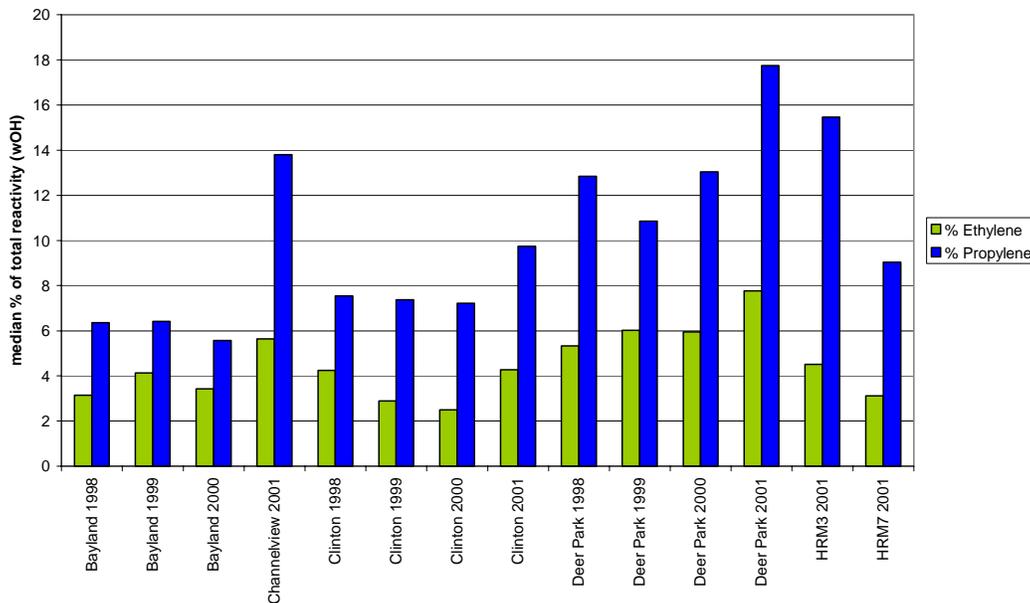


Figure 3-54. Median contribution of ethylene and propylene (%) to the total reactivity (sum of all species' wt% \*OH) during the summer by site and year.

### 3.5.2 Light Alkanes

While light alkanes (C2-C5) are present in abundance, their low reactivity values suggest that these compounds may be inconsequential on a total reactivity basis. However, because their concentrations are generally among the highest of any VOC, their sheer abundance makes light alkanes important on a reactivity scale.

**Figure 3-55 and 3-56** show the median contribution (%) of ethane, propane, and the C4-C5 alkanes to the total reactivity on a wMIR and wOH basis, respectively. While ethane and propane are not a large part of the total reactivity (1%-4%) on either scale, the C4-C5 alkanes contribute 13%-21% on the MIR scale and 7%-14% on the OH scale. This is almost as much as the reactive light olefins ethene and propene and demonstrates that, despite a low reactivity, the high concentrations of these alkanes are enough to affect the total reactivity of an air mass. Results were consistent across all sites and years.

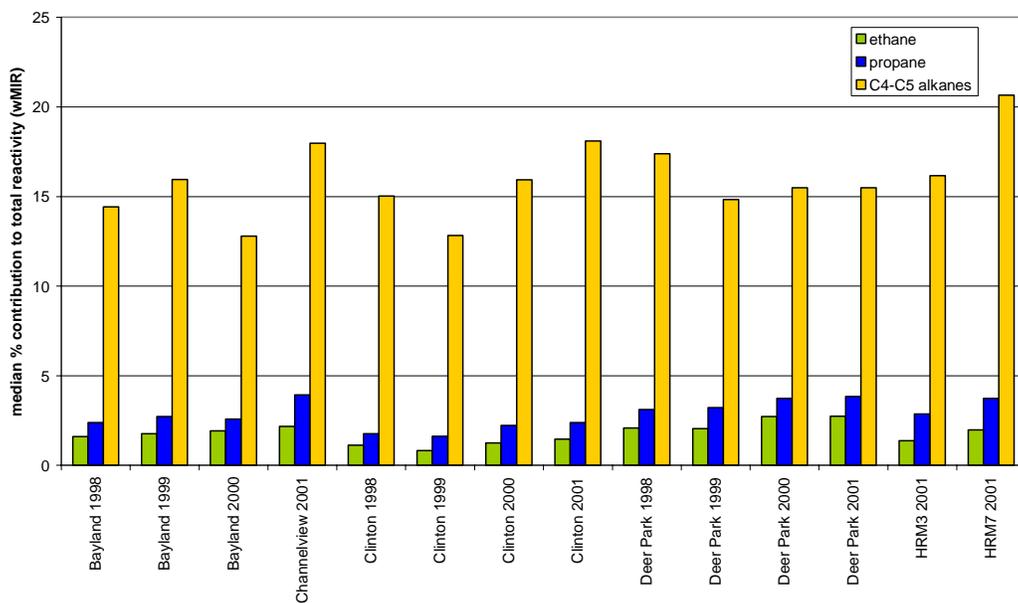


Figure 3-55. Median contributions (%) of ethane, propane and, C4-C5 alkanes to the total reactivity (wt% \*MIR) during the summer by site and year.

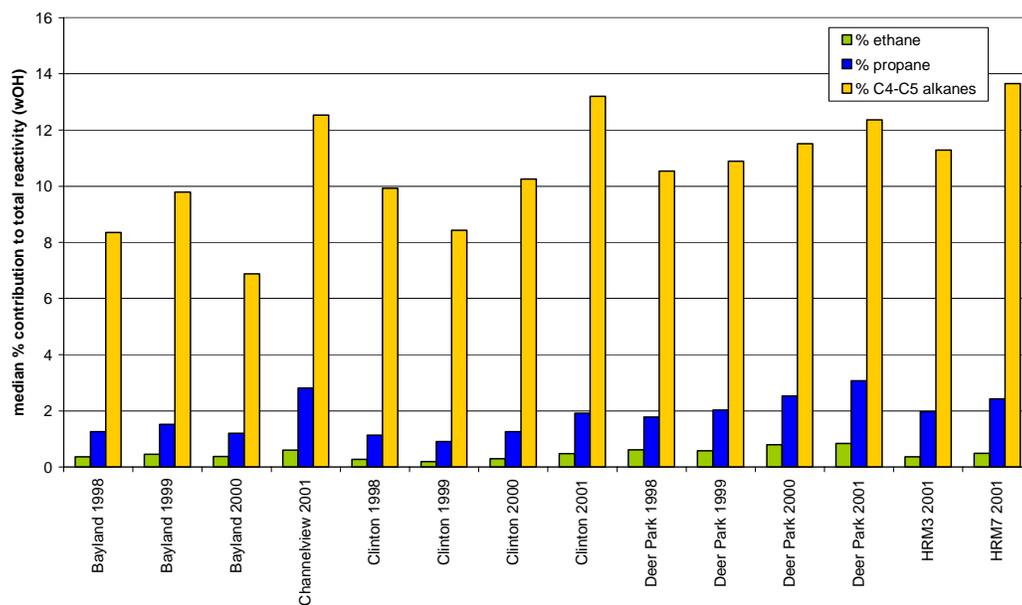


Figure 3-56. Median contributions (%) of ethane, propane, and C4-C5 alkanes to the total reactivity (wt% \*OH) during the summer by site and year.

### 3.5.3 Aromatic Hydrocarbons

With the light olefins and paraffins contributing on average only about 50% of the total reactivity, other compounds may also play a significant role in the total reactivity of an air mass. Aromatics such as toluene and trimethylbenzenes have a fairly high reactivity and can be found in high concentrations in the industry-rich area of Houston.

Figures 3-57 and 3-58 show the median contributions of toluene, xylenes, trimethylbenzenes, and ethyltoluenes to the total reactivity (wMIR and wOH, respectively) during the summer for each site and year. Contributions range from 3% to 14% for each hydrocarbon on both scales. Trimethylbenzenes are more important on the OH scale, while xylenes are generally the highest aromatic when the MIR scale is used. Ethyltoluenes contribute no more than 3% of the total reactivity on either scale at any site; while these aromatics are an important part of the total reactivity, they are not dominant at any site. This is consistent with the overall picture that many species influence the atmospheric chemistry in Houston.

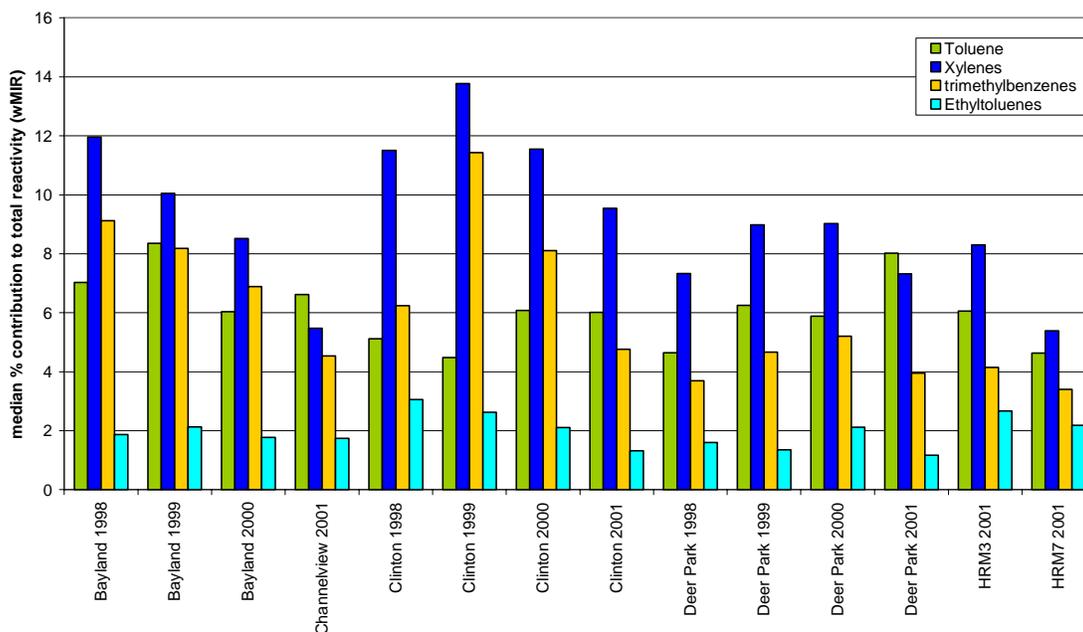


Figure 3-57. Median contributions (%) of toluene, xylenes, trimethylbenzenes, and ethyltoluenes to the total reactivity (wt%\*MIR) during the summer by site and year.

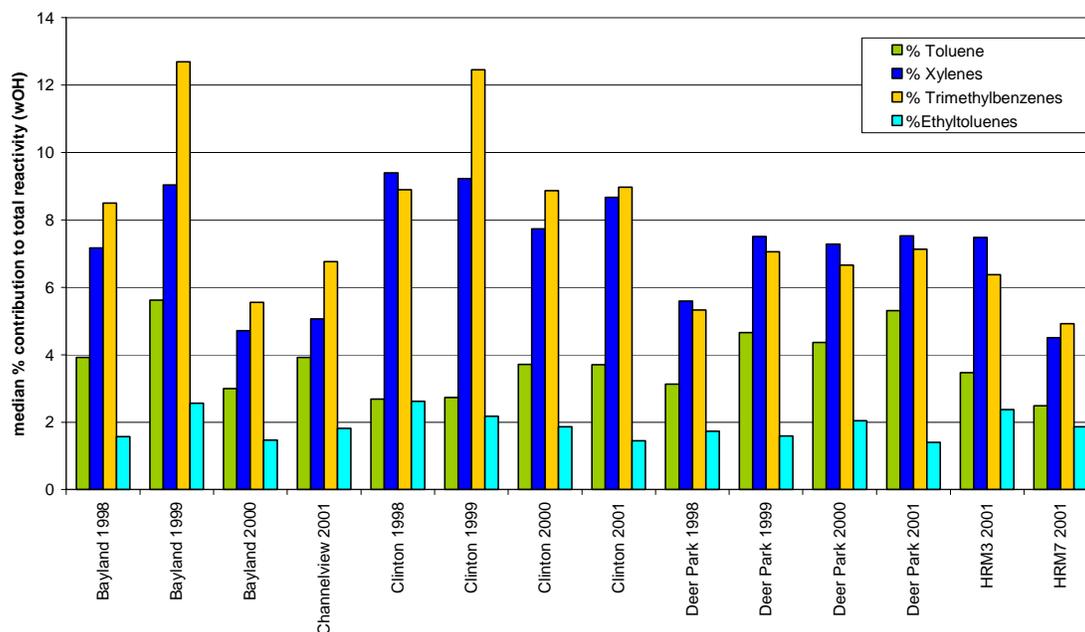


Figure 3-58. Median contributions (%) of toluene, xylenes, trimethylbenzenes and ethyltoluenes to the total reactivity (wt% \*OH) during the summer by site and year.

### 3.5.4 1,3-Butadiene, Butenes, Pentenes, and Other Compounds

While ethene, propene, the light paraffins and aromatics have all been significant (5% to 20%) contributors to the total reactivity, we still have only accounted for 60%-75% of the total reactivity. Other reactive compounds that may be a factor include 1,3-butadiene, the butenes, and the pentenes. 1,3-butadiene is extremely reactive, which is one reason why high concentrations are rarely found, even in the emission rich area of Houston. Butenes and pentenes are also not found in high concentrations (usually lower than ethene or propene) but with a somewhat high reactivity may also be notable contributors to the total reactivity.

**Figures 3-59 and 3-60** show the median contributions (%) of 1,3-butadiene, total butanes, and total pentenes to the total reactivity (wMIR and who, respectively) for each site and year during the summer. Similar to other compounds, none of these dominate, but each can contribute up to 17% of the total reactivity on OH and 9% on MIR. The only exception is at Deer Park in 2001 where contributions of these compounds to total reactivity on either scale were less than 4%. This is most likely due to the elevated ethene and propene levels in summer 2001 at Deer Park.

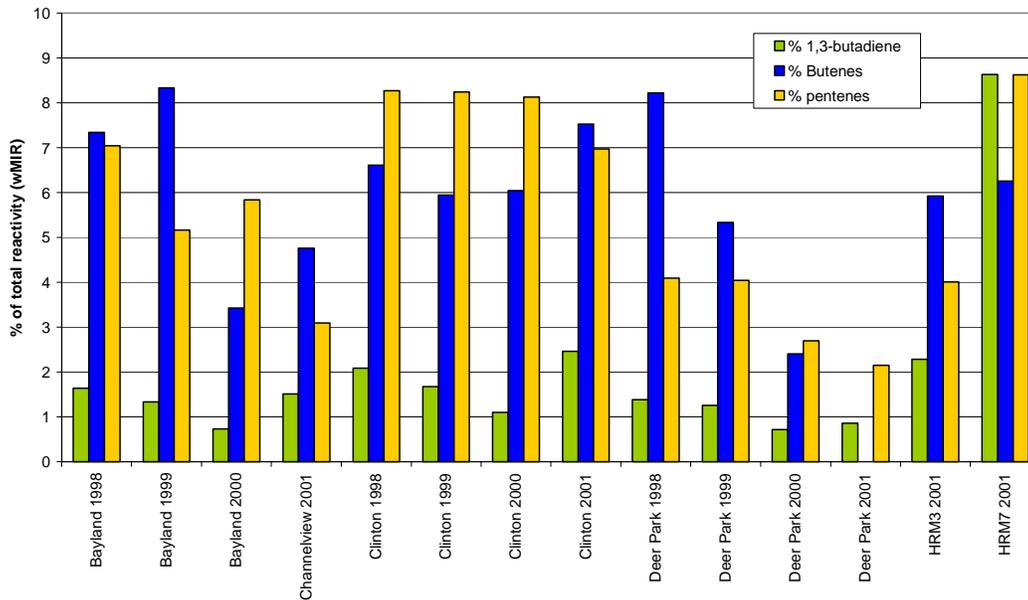


Figure 3-59. Median contributions (%) of 1,3-butadiene, butenes and pentenes to the total reactivity (wt% \*MIR) during the summer by site and year.

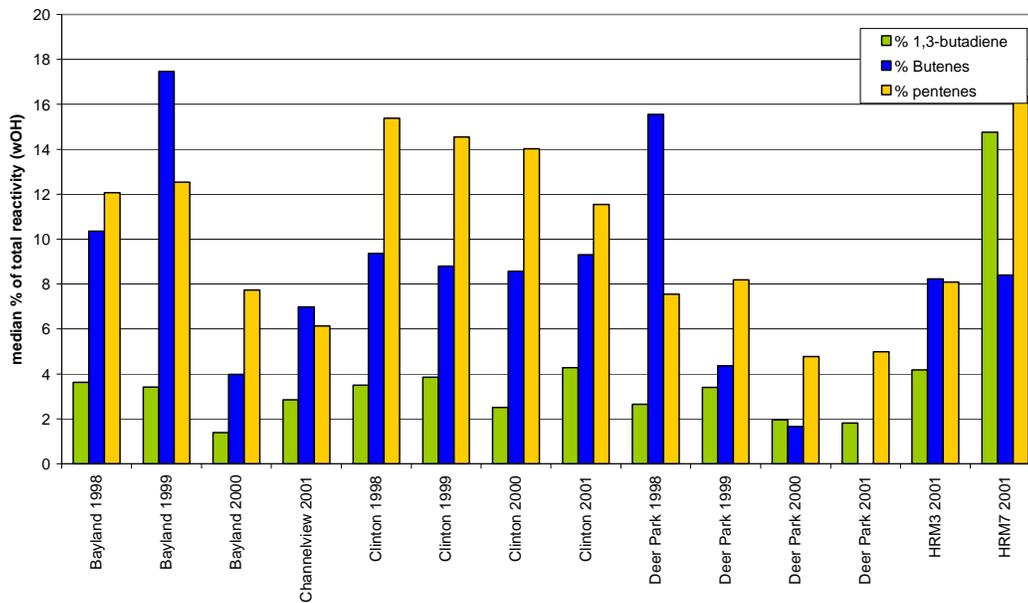


Figure 3-60. Median contributions (%) of 1,3-butadiene, butenes and pentenes to the total reactivity (wt% \*OH) during the summer by site and year.

### 3.5.5 Overall Composition

**Figure 3-61** details the overall composition of reactivity, using the MIR scale, during the summer at each site in each year; the overall composition on the OH scale is shown in **Figure 3-62**. There are a number of differences among sites and in different years. At Clinton, ethene and propene accounted for a lower amount of the total reactivity on both scales in 1999 and 2000 compared to 1998 and 2001 while trimethylbenzenes contributed to a higher fraction of the reactivity during 1999 and 2000. This could be caused by different prevalent meteorological conditions among the years or by changes in emissions.

Propene and ethene were large contributors to the total reactivity in 2001 at Channelview, Clinton, Deer Park, and Haden Rd. 1,3-butadiene was the largest fraction of the reactivity (on both scales) at Baytown among all sites and years while xylenes and toluene were the lowest; this could be due to spatial distributions in sources. Pentenes were a lower fraction of the reactivity (on both scales) at Deer Park and Channelview, suggesting that either the sources influencing these sites were different or the air masses sampled at these sites were different in their chemical age compared to those impacting other sites. Isoprene was a significant fraction of the total MIR reactivity only at Bayland 2000, which may be an artifact from incomplete data. Conversely, isoprene was a significant fraction at all sites and years on the OH scale, excluding Baytown in 2001. Contributions of C4-C5 alkanes, xylenes and toluene to total reactivity (excluding Baytown for the last two) were similar among all sites.

The compounds already discussed are ones that were found in the highest concentration or have high reactivities. While none of the remaining 50 or so compounds contributed more than 1% to the total reactivity, the sum of these species' reactivities was enough to contribute 10%-30% to the total. That these other compounds influenced total reactivity may be due to large amounts of fresh industrial emissions, a unique feature of the Houston area.

Overall, no single hydrocarbon or hydrocarbon group appeared to dominate ozone formation potential.

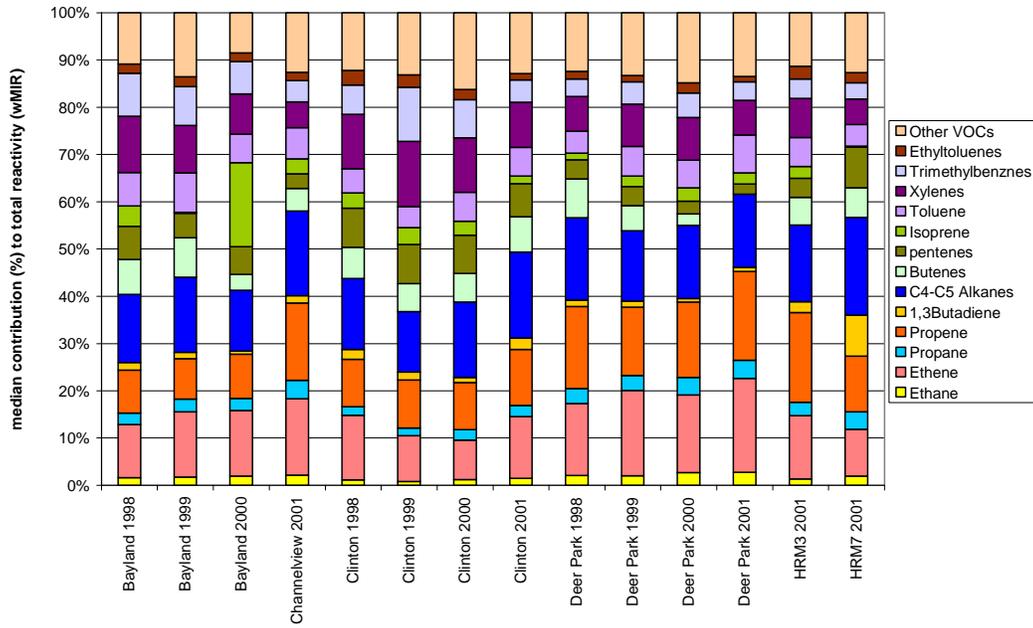


Figure 3-61. Median contributions (%) to total reactivity (wMIR) during the summer at all sites and years.

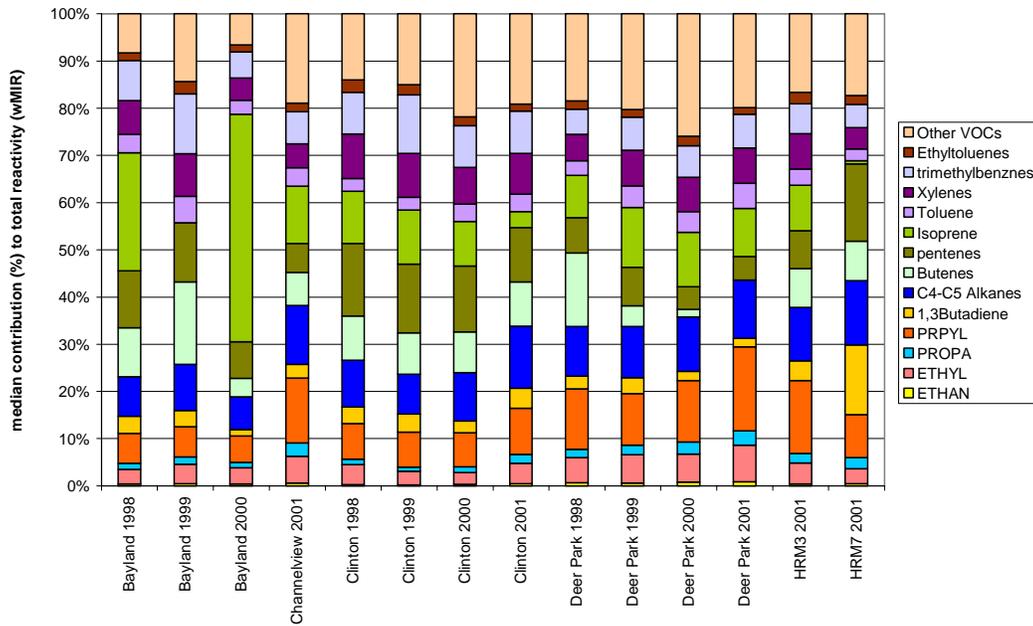


Figure 3-62. Median contributions (%) to total reactivity (wOH) during the summer at all sites and years.

## 4. WIND DIRECTION AND METEOROLOGY

Meteorology can play an important role in ozone formation, by either enhancing formation potential with temperature inversions and limiting cloud production or decreasing formation potential with strong vertical mixing. In addition, the Houston area has so many industrial sources of VOC that wind direction becomes important in understanding the VOC composition at monitoring sites. Summer is the focus of this section because most ozone episodes occur during this time period.

### 4.1 GENERAL METEOROLOGY OF THE HOUSTON AREA

High ozone concentrations occur in the Houston area when a high pressure ridge aloft dominates the flow patterns, causing sinking in the lower levels of the atmosphere (Nielsen-Gammon, 2002; MacDonald and Roberts, 2002; Roberts et al., 2002). This causes an inversion layer to form as the sinking air adiabatically warms and, therefore, limits vertical mixing. An example 500-mb chart showing an upper level high is shown in **Figure 4-1**. Ozone production is inhibited when an upper level low is dominant because this feature facilitates strong vertical motion and the formation of clouds or rain.

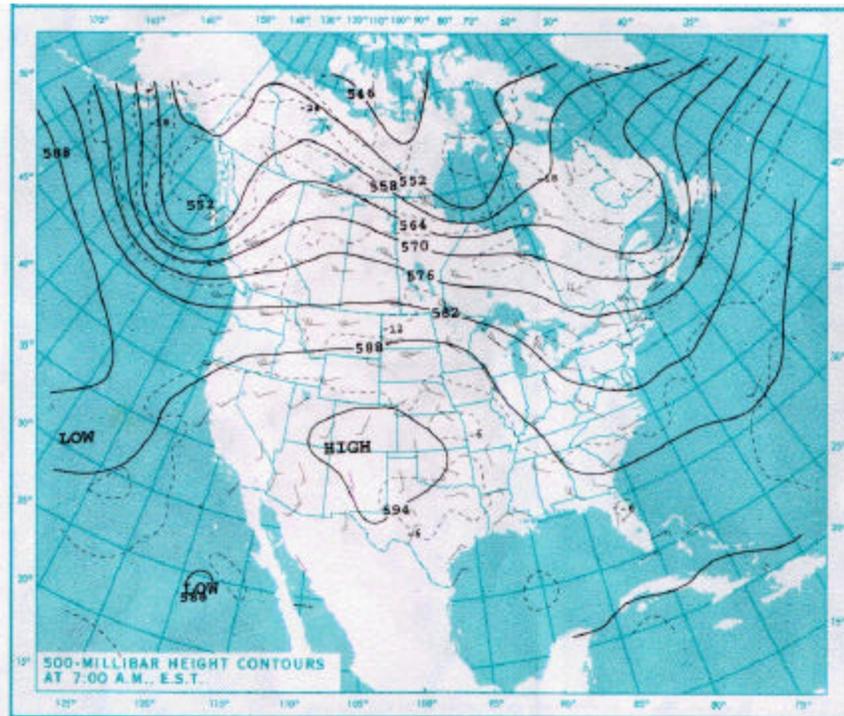


Figure 4-1. Example of an upper-level high pressure influencing the Houston area: contours of the height of the 500-mb surface pressure for August 25, 2000, at 0600 CST.

A circulation driven by the diurnal land-ocean/bay temperature contrasts is often a prevailing meteorological feature, an example of which is shown in **Figure 4-2**. This typically results in a sea breeze from the southeast, driven by the consistent high pressure area (the Bermuda High) in the Gulf of Mexico. This influence can be greatly reduced if a ridge of high pressure is dominant over eastern Texas, a frequent occurrence in the summer. This can result in light northerly winds in the early morning and the creation of a rotation in the wind pattern from morning land breeze to afternoon Bay or Gulf breeze. The morning land breeze can advect night-time emissions out in the morning just offshore where photochemistry and increased mixing can occur. The midday bay breeze then advects these emissions onshore where more mixing with fresh emissions can create a rapid increase in ozone formation. This pattern causes stagnation, minimal advection of pollutants, and a small recirculation and generally leads to the buildup of pollutant levels and a greater potential for high ozone (Roberts et al., 1995; Haney et al., 1995).

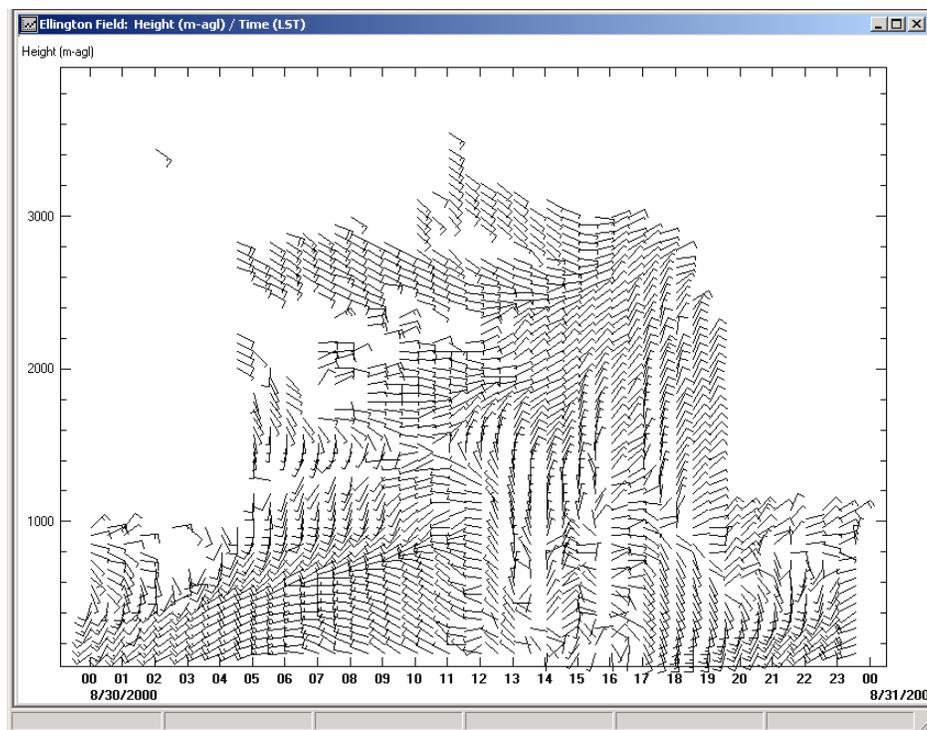


Figure 4-2. Example of land-/bay-breeze recirculation: time-height cross-section of radar profiler winds collected at Ellington Field on August 30, 2000. Moderate southwest winds occurred until about 0500 CST, when they shifted to the west. From 0830 and 1300 CST the winds decreased in speed and were from the northwest. Winds were light and variable and generally northeasterly from 1330 through 1630 CST. At 1730 CST, there was a southeasterly gulf breeze at the surface that slowly swung through the southwest and was west by midnight.

During the night, an inversion layer forms capping all emissions within the nighttime boundary layer, leading to increases in VOC concentrations throughout the night. With the onset of the morning land breeze and increase in solar radiation, the nighttime boundary layer breaks up, and these concentrations diminish via photochemical reactions, advection out with the land

breeze, or vertical mixing. The land/sea breeze interaction allows the elevated nighttime VOCs to advect together over Galveston Bay where reactions driven by photochemistry can produce ozone and alter VOC composition. This air mass can then advect back over land, bringing elevated ozone levels, or bringing an air mass mixture that has secondary compounds (such as carbonyls) with a high potential for ozone formation. The arrival of this new air mass is often associated with rapid changes in VOC concentrations and composition.

An example time series plot of olefin, aromatic, isobutane, NO<sub>x</sub>, and O<sub>3</sub> concentrations, along with wind direction on August 30, 2000, at Clinton is shown in **Figure 4-3**. As noted earlier, the advection of a new air mass as wind shifts from the southwest to the north to the southeast radically alters the concentrations and composition of VOCs at the sampling site. Note that this sampling site is approximately 16 km away from the Ellington Field profiler site, so times and wind direction may not match exactly. No VOC data were available at the closer Deer Park site on August 30, 2000.

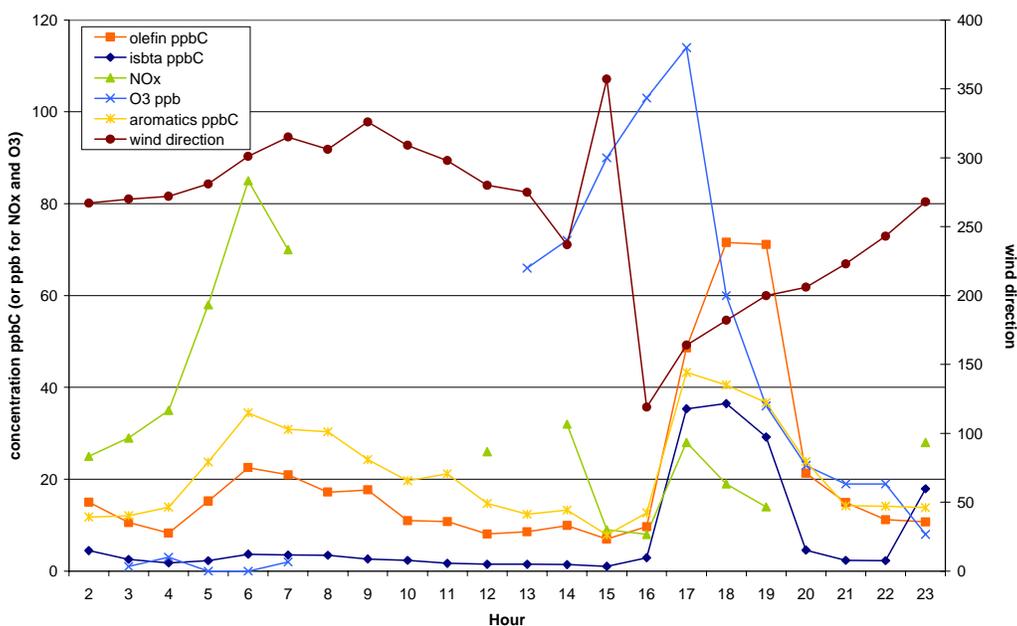


Figure 4-3. Time series plot of concentrations of olefins (ppbC), aromatics (ppbC), isobutane (ppbC), NO<sub>x</sub> (ppb), ozone (ppb), and wind direction (degrees, south=180, north=360=0) at Clinton, on August 30, 2000.

## 4.2 ANNUAL DIFFERENCES IN ADVECTION PATTERNS

A major assumption in analyzing VOC concentration or composition patterns on an episodic or annual basis is that wind patterns are consistent from year to year. In order to pursue this assumption, wind roses at Clinton Drive for the summer mornings of 1998-2001 were compiled using WRPlot (Lakes Environmental Software) (see **Figures 4-4 through 4-7**). There is a distinct difference in wind direction (and speed) among all four years. We know that the VOC composition at Clinton Drive is highly dependent upon wind direction. Thus, annual

comparisons of morning concentrations must be viewed with caution or performed strictly on a wind section by wind sector basis to be most meaningful.

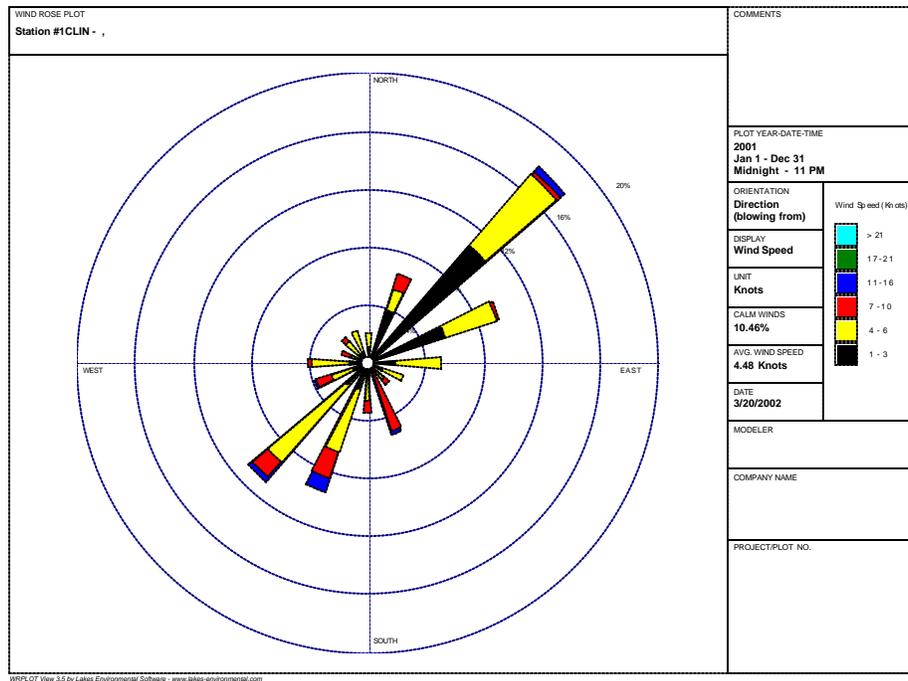


Figure 4-4. Wind rose at Clinton, 0500-0900 CST, August-October 2001.

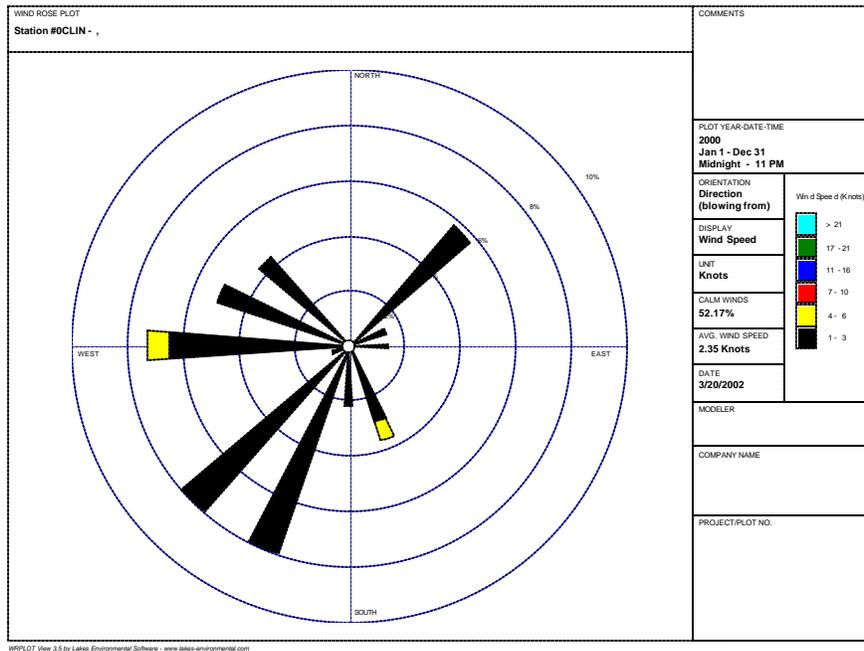


Figure 4-5. Wind rose at Clinton, 0500-0900 CST, July-September 2000.

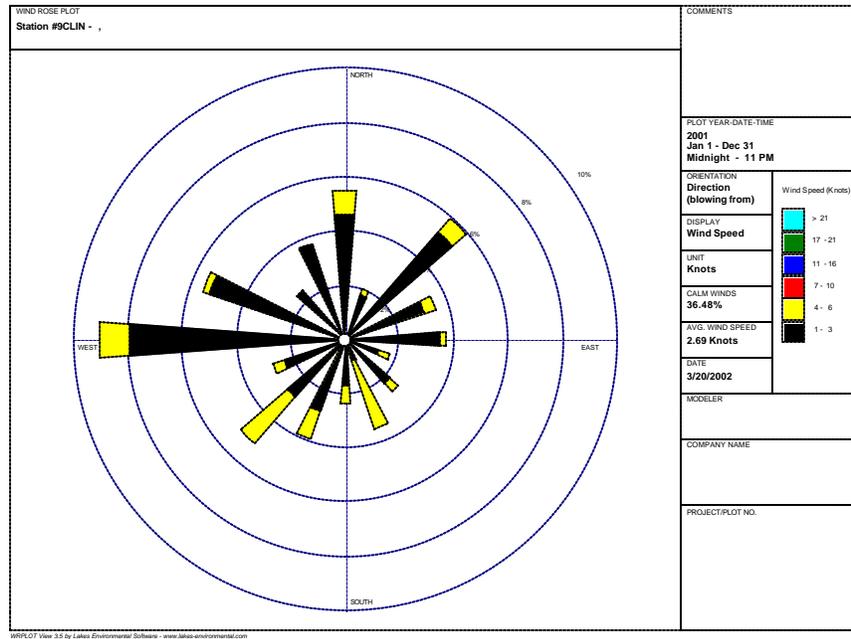


Figure 4-6. Wind rose at Clinton, 0500-0900 CST, July-September 1999.

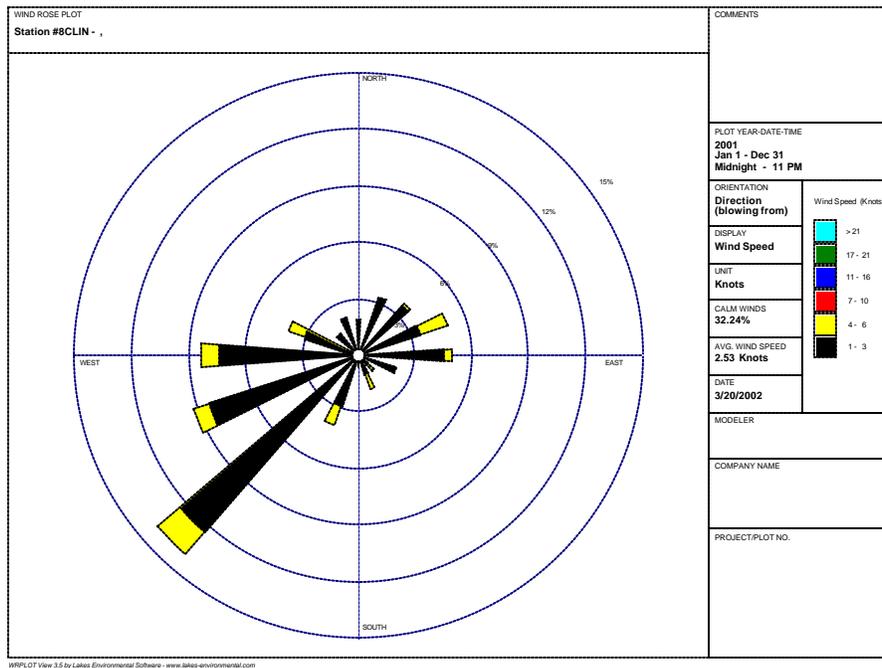


Figure 4-7. Wind rose at Clinton, 0500-0900 CST, July-September 1998.

### 4.3 ABUNDANT SPECIES BY WIND DIRECTION

While the same species were generally abundant at all sites (Section 3.1.2), impacts from specific sources or source areas can be found when species' concentrations are segregated by wind direction. Eight wind octants of 45 degrees were defined by their cardinal directions, as shown in **Figure 4-8**; wind octant one was defined as north (337.5 to 22.5 degrees), wind octant two as northeast (22.5 to 67.5 degrees), and so on. The median concentrations and weight percent (MIR values for each hydrocarbon were then found by these wind octants for each site and year during the summer. The ten most abundant species by median concentration and weight percent (MIR by wind octant for Clinton Drive are provided in **Tables 4-1 through 4-8**. Results for all other sites and years are provided in Appendix C.

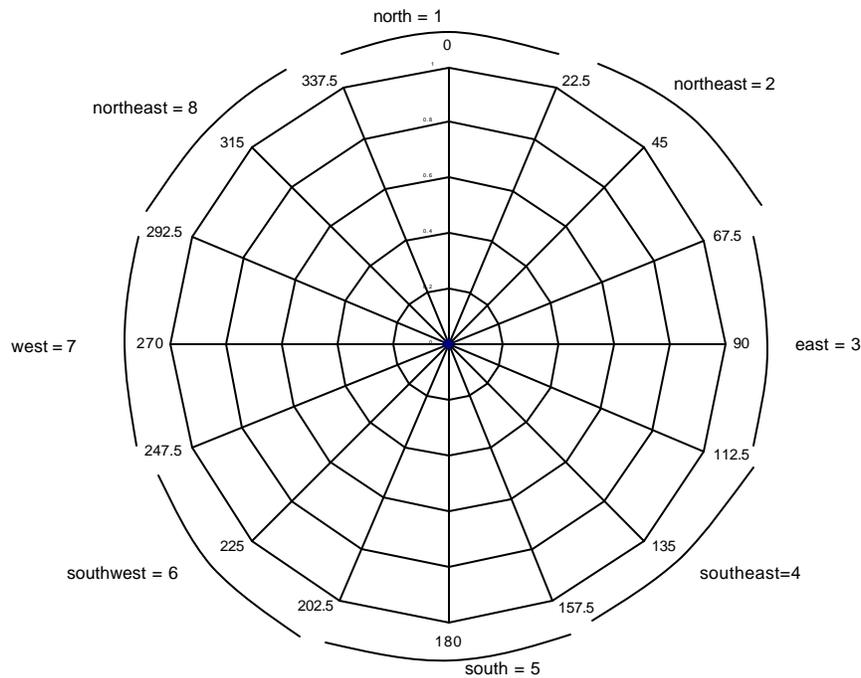


Figure 4-8. Sample radar plot showing assigned wind octants by degree (0-360).

High concentrations of C2-C5 paraffins, xylenes, and toluene were evident at Clinton Drive. On a weight percent (MIR scale, butenes were in the top ten in abundance with wind from the south, suggesting a source area for these reactive olefins that differs from other directions. In contrast to other sites, xylenes were often the highest species on a weight percent (MIR scale, indicating that the Houston Ship Channel area around Clinton may be a prime source of xylenes.

Table 4-1. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by concentration at Clinton in 2001. Species abbreviations are provided in Appendix A.

Wind Q	ethan	propa	isbta	nbuta	ethyl	prpyl	ispna	tolu	npnta	xylenes	nhexa	v2mpna
North	1	2	6	4	9		3	5	8	7		10
Northeast	1	2	5	4	6	10	3	7	8	9		
East	5	3	4	2	8	7	1	9	6		10	
Southeast	3	2	5	1	9	10	4	7	6	8		
South	5	4	1	2		8	3	7	6		9	10
Southwest	2	1	9	4	6	8	3	7	10	5		
West	1	2	9	5	6	10	3	4	8	7		
Northwest	2	1	7	5	8		3	4	9	6	10	

Table 4-2. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by concentration at Clinton in 2000. Species abbreviations are provided in Appendix A.

Wind Q	ethan	propa	nbuta	ispna	npnta	tolu	isbta	ethyl	xylenes	v2mpna	v224tmp	prpyl	benz
North	1	2	4	3	9	5	6	7	8	10			
Northeast	1	2	6	4	8	7	5	3	10			9	
East	3	2	4	1	6	8	5	7		10		9	
Southeast	3	4	1	2	7	6	5		8	9	10		
South	5	4	1	2	7	6	3		9	10	8		
Southwest	1	2	5	3	8	4	7	10	6			9	
West	1	2	5	3	9	4	7	8	6		10		
Northwest	1	2	5	3	7	4	8		6		9		10

Table 4-3. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by concentration at Clinton in 1999. Species abbreviations are provided in Appendix A.

Wind Q	ethan	propa	nbuta	ispna	npnta	tolu	isbta	ethyl	xylenes	v2mpna	prpyl	nhexa	benz
North	2	1	4	3	8	7	5	9	6	10			
Northeast	1	2	4	3	9	7	5	6	8		10		
East	4	3	2	1	6	10	5	7			8	9	
Southeast	4	3	2	1	6	8	7		5	9		10	
South	5	4	3	2	7	8	1		6	9		10	
Southwest	3	4	7	1	5	6	10	9	2		8		
West	2	3	8	1	9	4		7	5		6		10
Northwest	2	3	7	1	6	4	9	8	5	10			

Table 4-4. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by concentration at Clinton in 1998. Species abbreviations are provided in Appendix A.

Wind Q	ethan	propa	nbuta	ispna	npnta	tolu	isbta	ethyl	xylenes	v2mpna	prpyl	mcyhx	nhexa
North	1	2	4	3	7	8	5	6	9	10			
Northeast	2	1	5	3	7	9	4	6			8		10
East	5	3	2	1	6	10	4	7	9		8		
Southeast	6	4	3	2	5	8	1		7	9			10
South	3	2	5	1	8	10	9	7	4			6	
Southwest	2	4	8	1	7	5		6	3	10	9		
West	2	3	8	1	6	5		7	4	10		9	
Northwest	2	3	6	1	7	4	9	8	5	10			

Table 4-5. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by weight percent (MIR at Clinton in 2001). Species abbreviations are provided in Appendix A.

Wind Q	ethyl	prpyl	tolu	nbuta	propa	isbta	ispna	xylenes	1bute	t2bte	npnta	123tmb	ispre	124tmb	13buta	c2bte	3mlbe
North	1	3	4	6	7	9	5	2				10	8				
Northeast	1	2	5	6	9	8	4	3					7		10		
East	2	1	6	5	10	7	4	3	8		9						
Southeast	1	2	6	4		7	5	3		8	10					9	
South	5	1	7	4		2	6	3		8						9	10
Southwest	1	2	3	8			4	5		10				6	7		9
West	2	1	3	7			4	5				10	6	8	9		
Northwest	1	3	2	6	8	9	5	4					10	7			

Table 4-6. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by weight percent (MIR at Clinton in 2000). Species abbreviations are provided in Appendix A.

Wind Q	ethyl	prpyl	tolu	xylenes	124tmb	ispna	123tmb	nbuta	propa	isbta	t2bte	3mlbe	ispre	1bute	t2pne	135tmb	npnta
North	2	3	4	1	6	5	9	7	8	10							2
Northeast	2	1	5	3	9	4		8	10	7			6				2
East	1	2	5	3		4		6		7			8	9			1
Southeast	5	3	6	1	10	2		4		7			8	9			5
South	8	4	6	1		3		2		7	5	10		9			8
Southwest	2	1	5	4	3	6	8					7			9	10	2
West	1	2	3	4	5	6	8	10				9	7				1
Northwest	3	5	4	1	7	6	8	9				10	2				3

Table 4-7. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by weight percent (MIR at Clinton in 1999). Species abbreviations are provided in Appendix A.

Wind Q	Ethyl	Prpyl	Tolu	Xylenes	124tmb	Ispna	123tmb	Nbuta	Propa	Isbta	T2bte	3mlbe	Ispre	1bute	135tmb	C2bte
North	2	3	6	1	5	4	7	8	9	10						
Northeast	1	2	8	3	7	5	6	9		10			4			
East	1	2	8	3	10	4		7		6			5	9		
Southeast	2	3	6	1	5	4		8		10		9	7			
South	3	2		1	6	5		8		4	7			9		10
Southwest	2	1	6	3	4	7	5					9	8		10	
West	2	1	5	3	4	8	7					10	6		9	
Northwest	2	3	4	1	5	6	8					10	7		9	

4-10

Table 4-8. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) by weight percent (MIR at Clinton in 1998). Species abbreviations are provided in Appendix A.

Wind Q	ethyl	prpyl	tolu	xylenes	124tmb	ispna	123tmb	nbuta	isbta	t2bte	3mlbe	ispre	1bute	npnta	c2bte	metol	13buta
North	2	5	4	1	8	6	7	9				3				10	
Northeast	1	2	6	4		5	8	7	10			3					9
East	1	2	8	3		4		5	6				10	7			9
Southeast	2	3	5	1		4		6	8	7	9			10			
South	2	3	9	1		5			8	6	10		7		4		9
Southwest	1	2	5	3	6	4	9				8	7		10			
West	2	1	4	3	7	6	9					5		10		8	
Northwest	2	3	4	1	7	5	8					6		10		9	

At Baytown, elevated butenes and pentenes were found on a weight percent (MIR basis with wind from the southeast and south. Ethene and propene, usually among the top five species by weight percent (MIR, were not even in the top ten with wind from the southeast where the butenes and pentenes were evident. This suggests a very unique VOC source to the southeast. High ethene and propene concentrations were found from the southwest, indicating a strong nearby source of these reactive olefins. 1,3-butadiene concentrations were high from the north, and the highest species on a weight percent (MIR basis from the northwest, north and northeast, suggesting a nearby source of this highly reactive compound.

At Deer Park, xylenes were often not in the top ten species by concentration although they were always evident on a weight percent (MIR basis. High propene concentrations were found from the northeast, suggesting a nearby source. Overall, the C2-C5 paraffins were dominant on a concentration basis and were significant on a weight percent (MIR basis, along with the light olefins, toluene, and xylenes.

Bayland and Haden Rd. VOCs were dominated by the C2-C5 paraffins, toluene and xylenes, and ethene and propene on the weight percent (MIR scale. Pentenes were significant only with wind from the southwest at Haden Rd., which may be from a region to the southwest of Baytown where high pentenes also occurred. Xylenes at Channelview were often not within the top ten species by concentration, and were lower in rank on the weight percent (MIR scale than at other sites. The only exception was with wind from the west and northwest, which may be the same source area influencing Clinton.

#### **4.4 DEPENDENCE OF CONCENTRATIONS ON WIND DIRECTION**

##### **4.4.1 Bayland**

As seen at Clinton Drive in Section 4.2.1, wind direction was not consistent during the summer from year to year. In both 1998 and 1999 at Bayland, high concentrations of ethene, propene and butanes were found with wind direction between 10 and 120 degrees (shown in **Figures 4-9 and 4-10**). In 2000, there were very few samples in which wind was from this direction. These high concentrations are from the direction of central Houston and the Ship Channel. This indicates that the dense amount of emissions from the Ship Channel area can influence sites that are not immediately adjacent to it.

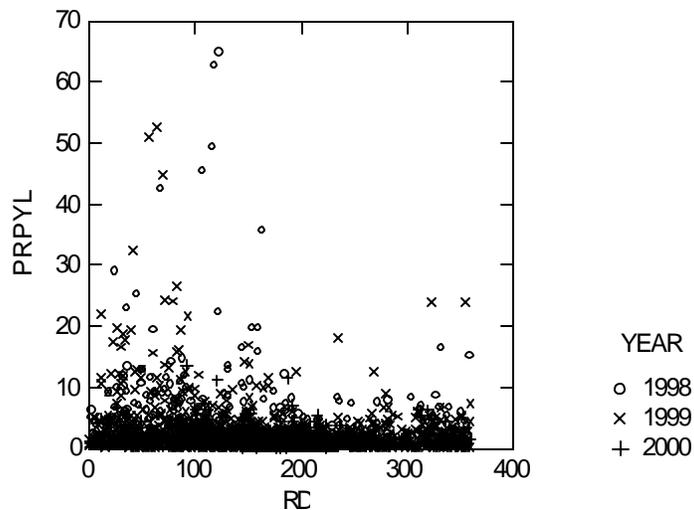


Figure 4-9. Propene (PRPYL) concentrations (ppbC) at Bayland, July-September 1998-2000, by wind direction (RD).

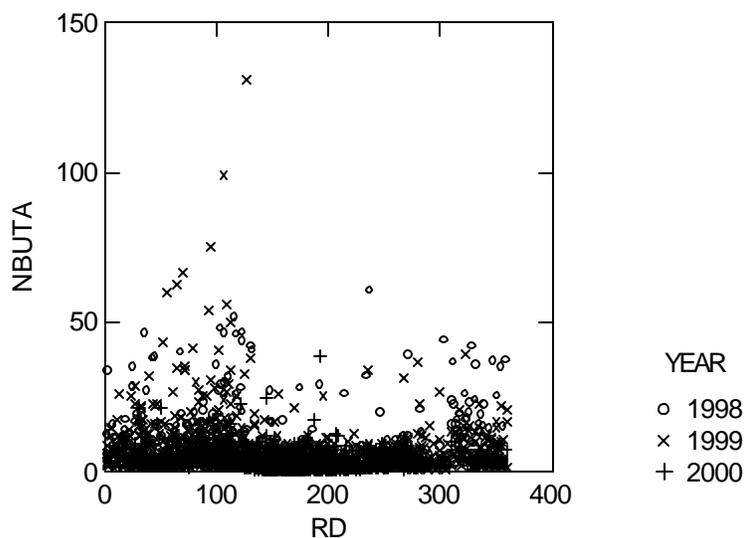


Figure 4-10. N-butane (NBUTA) concentrations (ppbC) at Bayland, July-September 1998-2000, by wind direction (RD).

#### 4.4.2 Deer Park

The source of most concentration outliers at Deer Park originated when the wind direction was between 320 and 60 degrees, the direction of the Ship Channel and major freeways. Ethene, propene, butanes, benzene, and toluene all showed outliers (see **Figures 4-11 through 4-14**). Both acetylene and the acetylene/ethylene ratio showed high values in a narrower angle between 0 and 50 degrees (**Figures 4-15 and 4-16**).

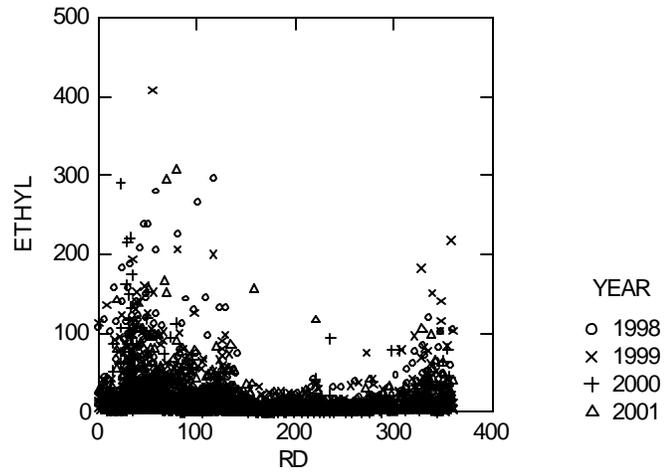


Figure 4-11. Ethene (ETHYL) concentrations (ppbC) by wind direction (RD) at Deer Park, July-September 1998-2001.

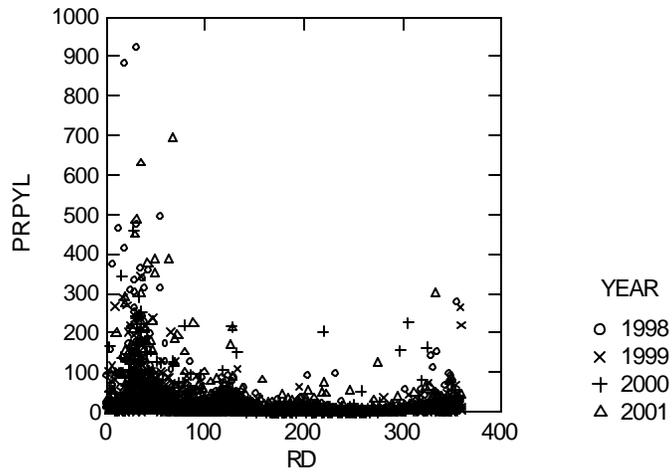


Figure 4-12. Propene (PRPYL) concentrations (ppbC) by wind direction (RD) at Deer Park, July-September 1998-2001.

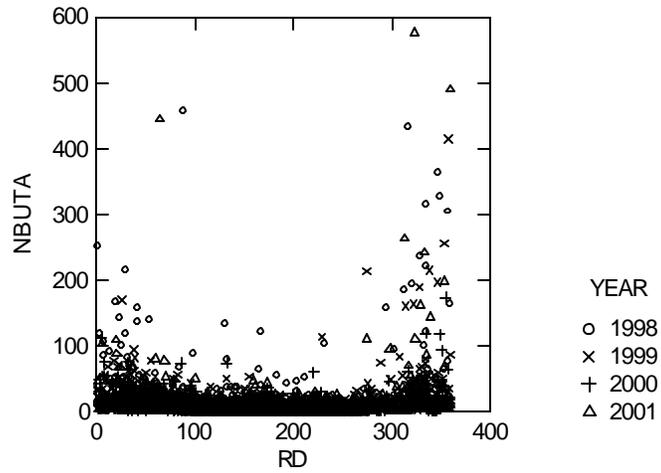


Figure 4-13. N-butane (NBUTA) concentrations (ppbC) by wind direction (RD) at Deer Park, July-September 1998-2001.

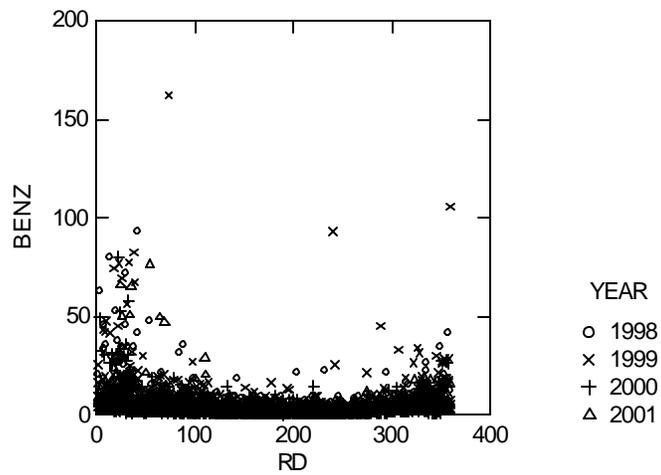


Figure 4-14. Benzene (BENZ) concentrations (ppbC) by wind direction (RD) at Deer Park, July-September 1998-2001.

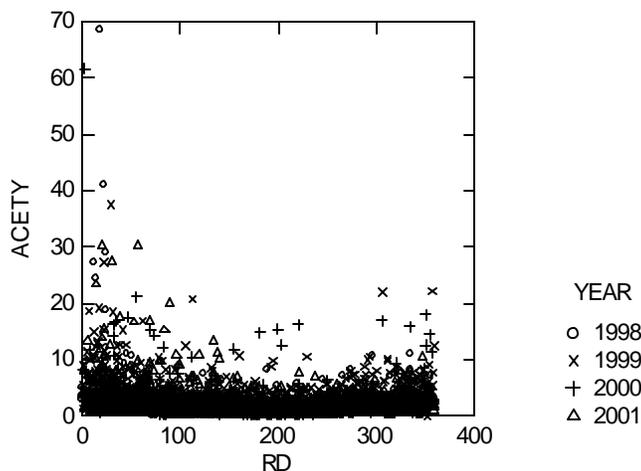


Figure 4-15. Acetylene (ACETY) concentrations (ppbC) by wind direction (RD) at Deer Park, July-September 1998-2001.

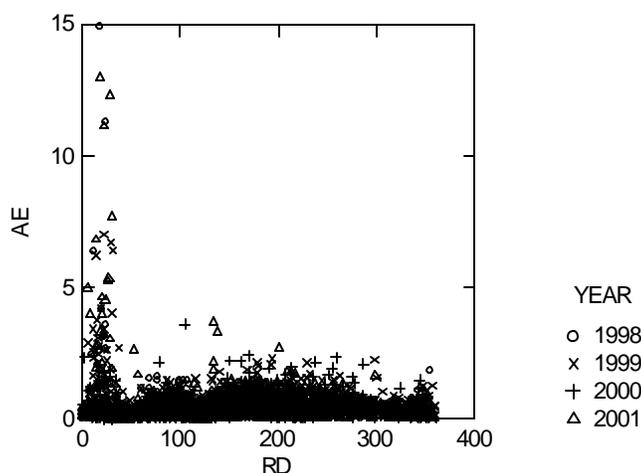


Figure 4-16. Acetylene/ethene (AE) by wind direction (RD) at Deer Park, July-September 1998-2001.

#### 4.4.3 Channelview

Concentrations of ethene, propene, n-butane, and toluene at Channelview in August-October 2001 by wind direction are shown in **Figures 4-17 through 4-20**. There appears to be an olefin source (ethene and propene most notably) to the south of Channelview, which is in the direction of the Ship Channel. This is also the direction of high toluene and n-butane concentrations.

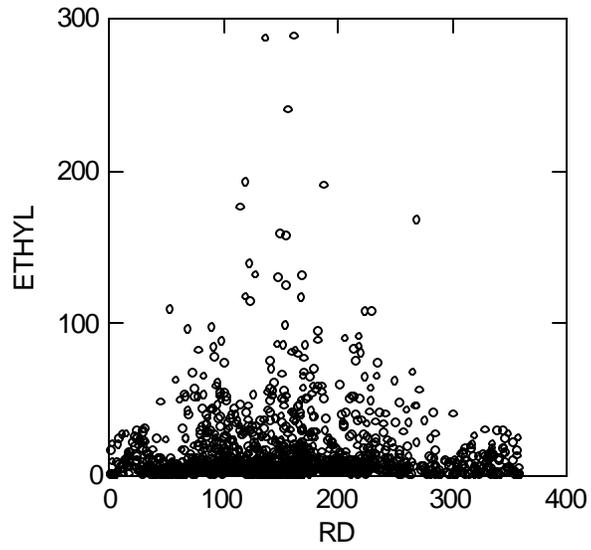


Figure 4-17. Ethene (ETHYL) concentrations (ppbC) by wind direction (RD) at Channelview, August-October 2001.

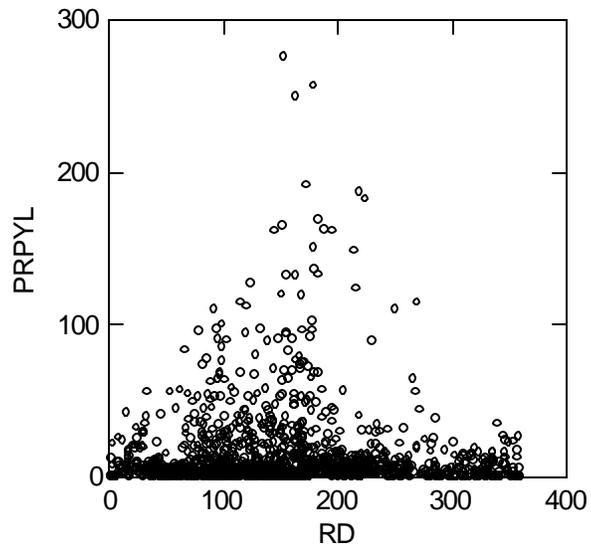


Figure 4-18. Propene (PRPYL) concentrations (ppbC) by wind direction (RD) at Channelview, August-October 2001.

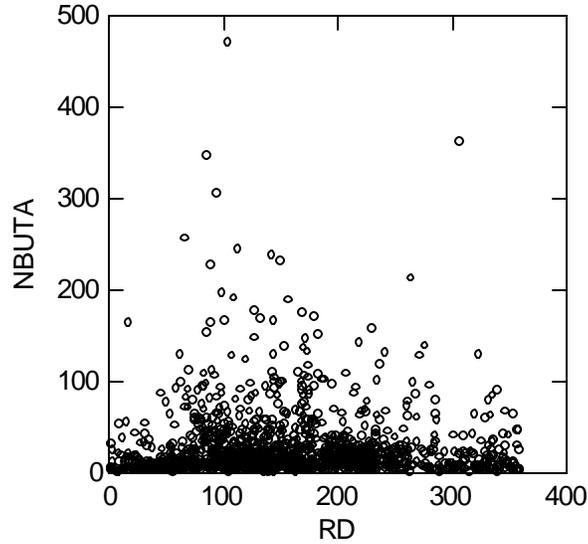


Figure 4-19. N-Butane (NBUTA) concentrations (ppbC) by wind direction (RD) at Channelview, August-October 2001.

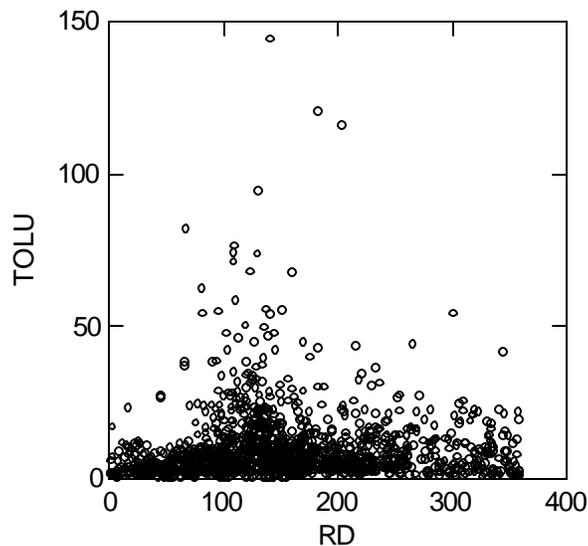


Figure 4-20. Toluene (TOLU) concentrations (ppbC) by wind direction (RD) at Channelview, August-October 2001.

#### 4.4.4 Baytown

Propene and toluene concentrations and acetylene/ethene ratios are shown in **Figures 4-21 through 4-23**. There was a significant source of high propene directly to the south of Baytown that often impacted the monitoring site. To the southeast was a toluene source, which is also associated with a high acetylene/ethene ratio.

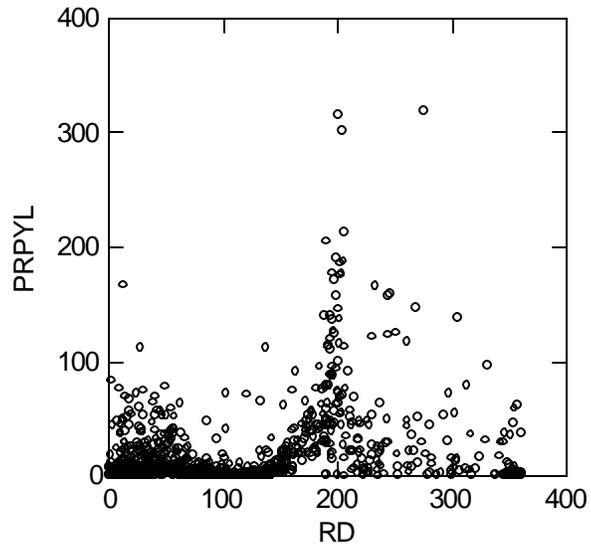


Figure 4-21. Propene (PRPYL) concentrations (ppbC) by wind direction (RD) at Baytown, August-October 2001.

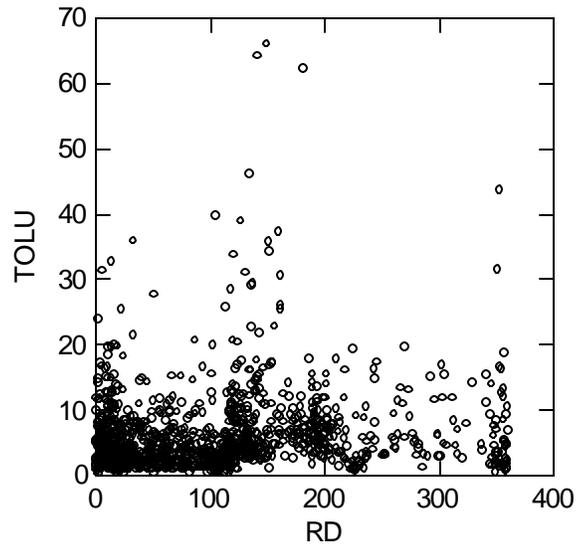


Figure 4-22. Toluene (TOLU) concentrations (ppbC) by wind direction (RD) at Baytown, August-October 2001.

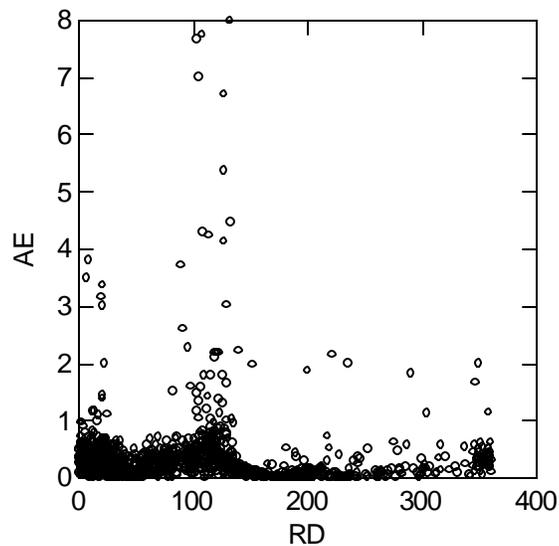


Figure 4-23. Acetylene/ethene (AE) ratios by wind direction (RD) at Baytown, August-October 2001.

#### 4.4.5 Haden Rd.

Concentrations at Haden Rd. by wind direction of ethene, propene, and toluene during August-October 2001 are shown in **Figures 4-24 through 4-26**. To the southeast was an olefin source (ethene and propene), which is in the direction of part of the Ship Channel area. To the south was an aromatic source (toluene), again along the Ship Channel area. These high concentrations of many species from the south demonstrate that different emission sources are found along the Ship Channel, and that a wide variety of compounds are emitted in generous quantities within the Ship Channel area.

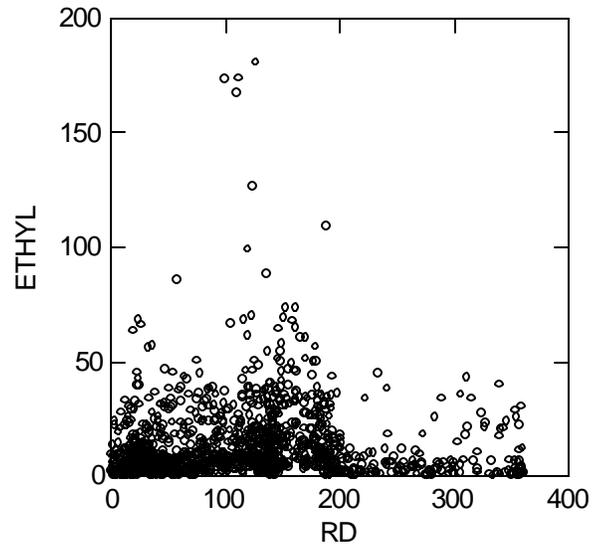


Figure 4-24. Ethene (ETHYL) concentrations (ppbC) by wind direction (RD) at Haden Rd., August-October 2001.

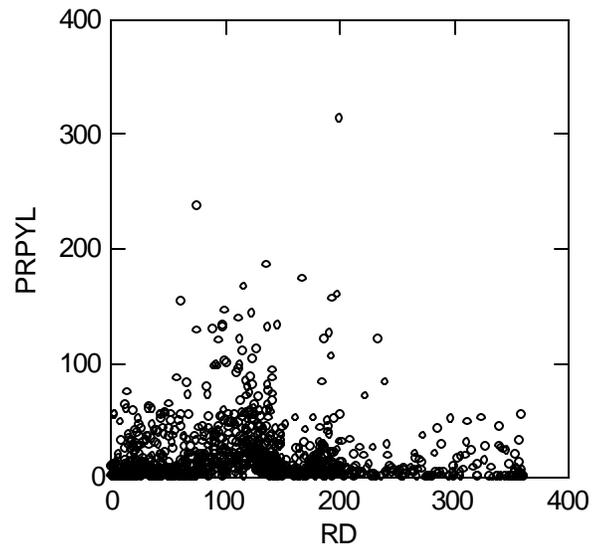


Figure 4-25. Propene (PRPYL) concentrations (ppbC) by wind direction (RD) at Haden Rd., August-October 2001.

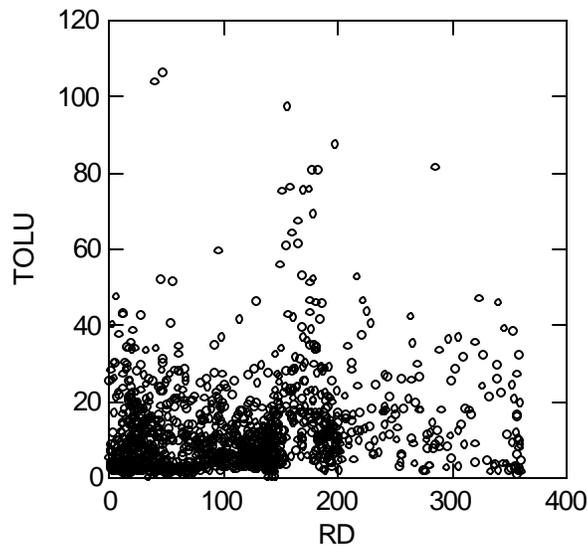


Figure 4-26. Toluene (TOLU) concentrations (ppbC) by wind direction (RD) at Haden Rd., August-October 2001.

## 4.5 CASE STUDIES

### 4.5.1 Clinton Wind Direction Analysis

To further investigate the dependence of species' concentrations on wind direction, we performed a case study at Clinton. Sample concentrations and composition were compared between samples when the wind direction was from the Ship Channel (60-150 degrees, south-southeast) and when it was from the freeway area (225-315 degrees, west). **Figure 4-27** details these angles on an orthoquad photo. These directions were selected because of the contrast of dominant sources in each direction. The Ship Channel is dominated by industrial emissions, while emissions from the west would be primarily from vehicles. Since there are usually fresh emissions being sampled, the fingerprints garnered from this analysis would be representative of signatures of industrial and freeway emissions at this site.

The median values of each hydrocarbon in each of the two designated wind quadrants were calculated for August-October 2001. A comparison of concentrations between morning (0500-0900 CST) and afternoon (1300-1700 CST) from both directions is shown in **Figure 4-28**. The same comparison for all summers at Clinton in 1998-2001 is shown in **Figure 4-29**. Both figures show that concentrations were highest when air arrived from the Ship Channel area in the morning. Morning concentrations were higher when compared to the afternoon due to lower mixing heights, less photochemistry, and accumulation of pollutants. Concentrations were higher from the Ship Channel in both the morning and afternoon than at any time from the freeway, indicating that the Ship Channel area was an extremely rich source of emissions during the day. This was particularly true for the light olefins ethene and propene and light paraffins

(C2-C5). Xylenes, toluene, and benzene also exhibited higher concentrations with air masses arriving from the Ship Channel.

Composition fingerprints are shown in **Figure 4-30**. Compositional differences can be seen between morning and afternoon, most probably due to increased photochemistry. Morning emissions from the Ship Channel showed a higher amount of ethene, propene, and isobutane, while freeway emissions had a larger amount of 2,2,4-trimethyl pentane (an octane booster in gasoline) and toluene.

Further analysis of these fingerprints during episode and non-episode days may indicate whether higher emissions from a particular quadrant are related to high ozone concentrations. **Figure 4-31** shows the weight percent fingerprints during the morning (0500-0900 CST) from both wind quadrants on episode and non-episode days at Clinton in August-October 2001. Only ethane, propane, and isobutane were higher on episode days from the Ship Channel; other compounds showed very little difference between episode and non-episode days from either direction. This indicates that the frequency of these types of emissions was very high and that ozone episodes were not necessarily linked to mornings with a specific VOC composition.

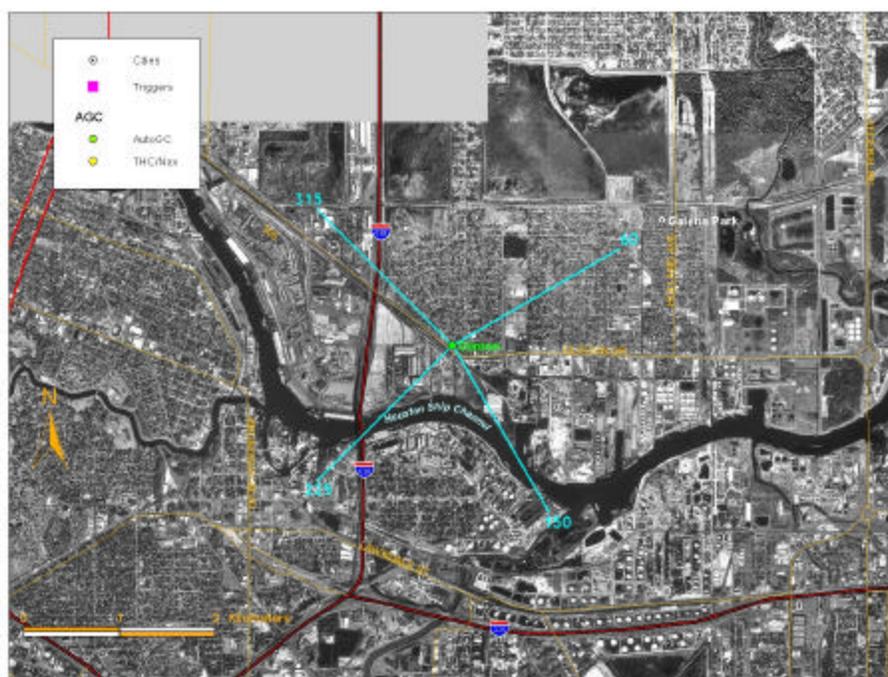


Figure 4-27. Industry (60-150 degrees) and freeway (225-315 degrees) designated on an orthoquad satellite photo of Clinton.

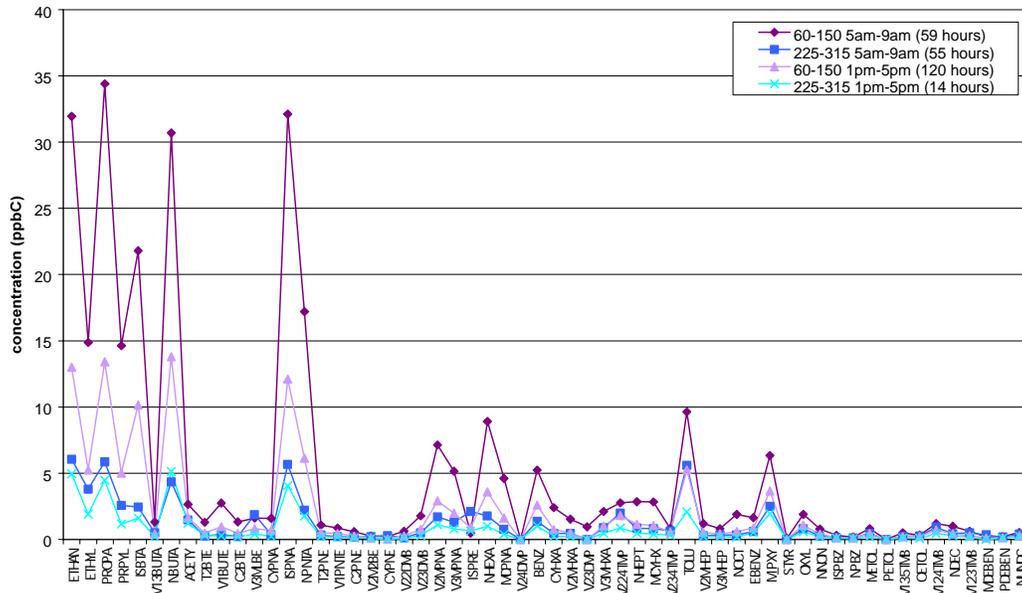


Figure 4-28. Fingerprint of concentrations, 0500-0900 CST and 1300-1800 CST at Clinton, August-October 2001, from 60 to 150 degrees (Ship Channel) and 225 to 315 degrees (freeway).

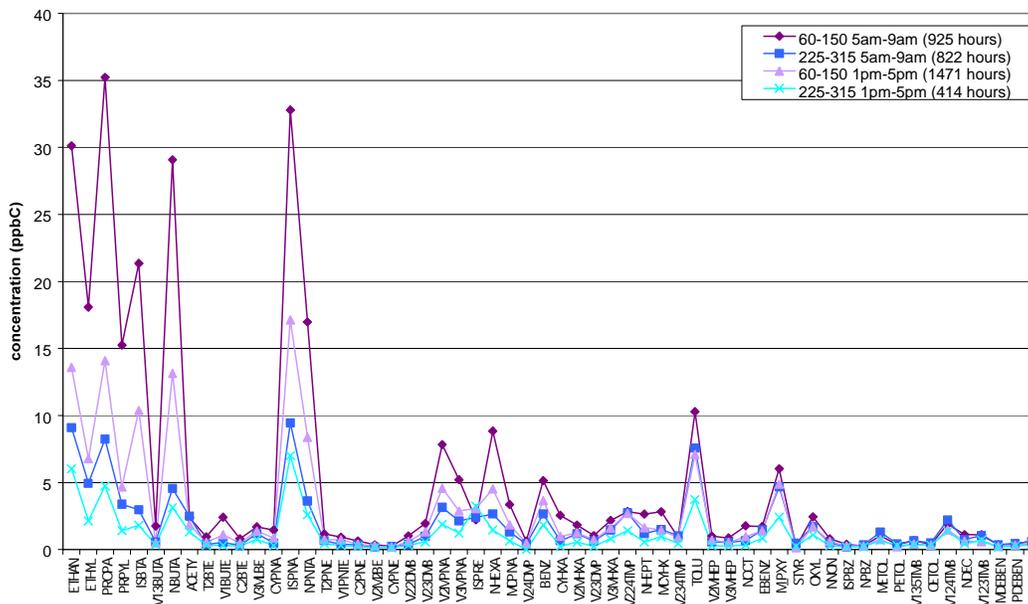


Figure 4-29. Fingerprint of concentrations, 0500-0900 CST and 1300-1800 CST at Clinton, July-October 1998-2001, from 60 to 150 degrees (Ship Channel) and 225 to 315 degrees (freeway).

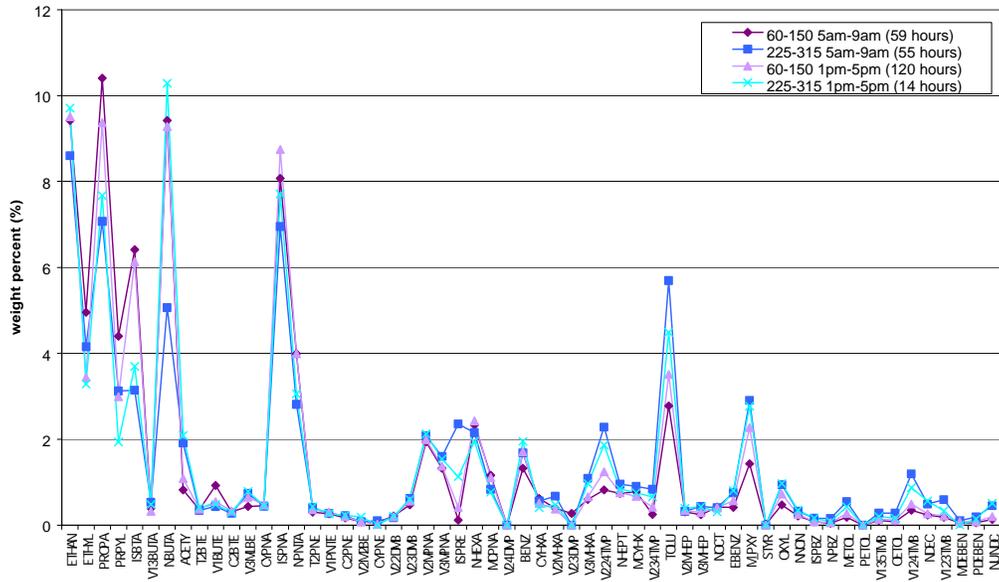


Figure 4-30. Fingerprint of weight percents during 0500-0900 CST and 1300-1700 CST at Clinton, August-October 2001, from 60 to 150 degrees (Ship Channel) and 225 to 315 degrees (freeway).

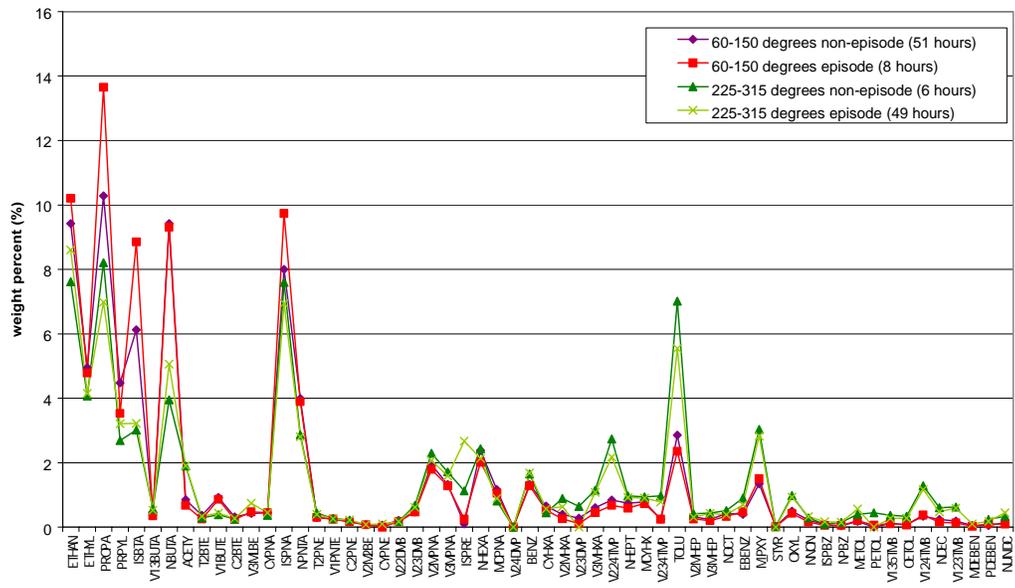


Figure 4-31. Fingerprint of weight percents during 0500-0900 CST at Clinton, August-October 2001, from 60 to 150 degrees (Ship Channel) and 225 to 315 degrees (freeway) on episode and non-episode days.

#### 4.5.2 Is Isoprene an Industrial Emission?

Isoprene is a reactive olefin that is copiously emitted from biogenic sources and is often used as a biogenic tracer (Stoeckenius et al., 1994; Main and Roberts, 2000). However, it can also be used in a number of industrial chemical processes such as petroleum refining and in the polymer and rubber industry. It is a highly reactive olefin with a high ozone formation potential (Atkinson, 1989, 1994; Carter, 1994, 2001). If isoprene is primarily biogenic, there will be a distinct diurnal pattern with low concentrations during the night. If there are concentrations during the night that are near daytime levels, industrial emissions are a likely source<sup>1</sup>.

To investigate whether isoprene was primarily from biogenic sources or industrial emissions, box whisker plots of isoprene concentrations at Clinton and Baytown for summer 2001 hour and by wind octant were generated. **Figures 4-32 and 4-33** show the diurnal profile of isoprene concentrations at Clinton Drive and Baytown, respectively. Isoprene concentrations show a typical diurnal profile (higher concentrations during the daytime), which indicates that there was a general background of biogenic origin. However, the presence of outlying concentrations during the nighttime hours that are similar and sometimes higher than those in the daytime indicate that industrial emissions were also an isoprene source. The three highest concentrations at Clinton occurred at 2100, 2200, and 0600 CST and were likely of anthropogenic origin. The highest concentrations at Baytown occurred at 2200, 2300, 0000, and 0200 CST, and were also probably anthropogenic. A large number of additional outliers at Baytown occurred throughout the night and early morning, further demonstrating that industrial emissions may be significant sources of isoprene.

**Figures 4-34 and 4-35** demonstrate that there can be a significant dependence of isoprene concentrations on wind direction. The two highest outliers at Clinton came from the south-west, suggesting the possible location of industrial isoprene use. These two outliers actually occurred on the same day from 2100 to 2200 CST (see **Figure 4-36**). Baytown shows a higher dependence on wind direction, where emissions from the north and northeast were much higher in isoprene concentration consistent with biogenic sources. Isoprene from the Ship Channel direction (west) was actually 15% lower than from the freeway direction (east), again indicating that the sources to the west were not a primary source of isoprene. Isoprene was present at all hours of the day, but from no specific direction at this site, suggesting that it may have been a common emission from industry in Houston. We note however, that the periodicity of likely industrial isoprene emissions is much lower than that observed for ethene and propene.

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<sup>1</sup> We have observed elevated isoprene concentrations at night in the northeastern United States that were later linked to transported biogenic emissions or forest fire emissions.

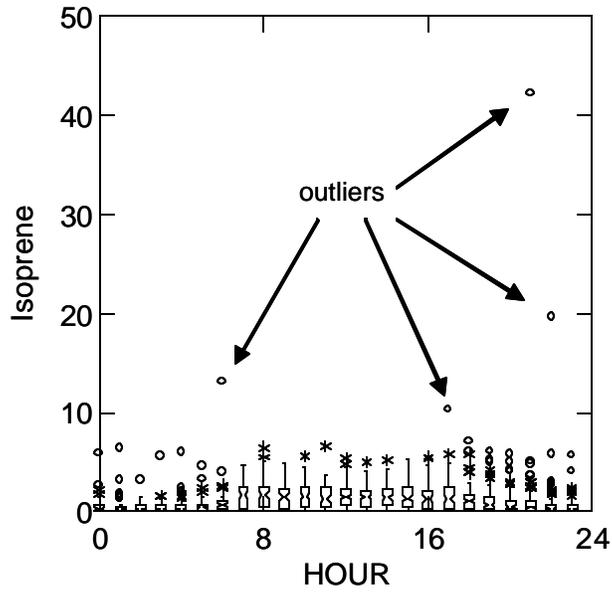


Figure 4-32. Box whisker plot of isoprene concentrations (ppbC) by hour at Clinton, August-October 2001.

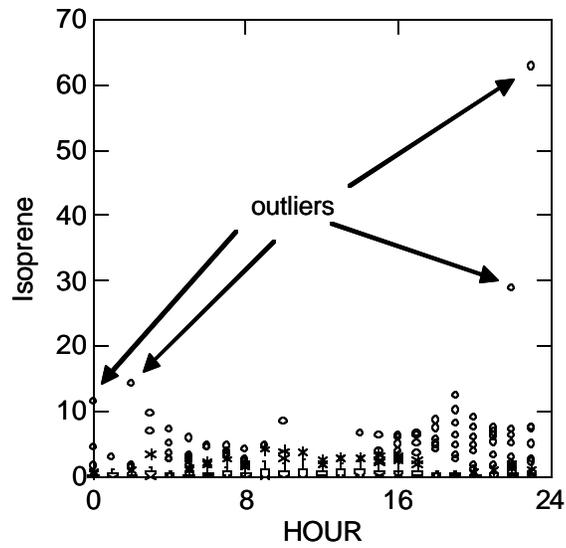


Figure 4-33. Box whisker plot of isoprene concentrations (ppbC) by hour at Baytown, August-October 2001.

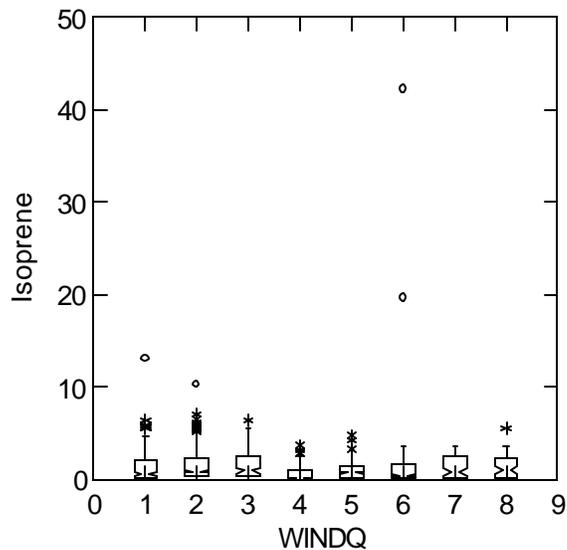


Figure 4-34. Box whisker plot of isoprene concentrations (ppbC) by wind octant at Clinton, August-October 2001.

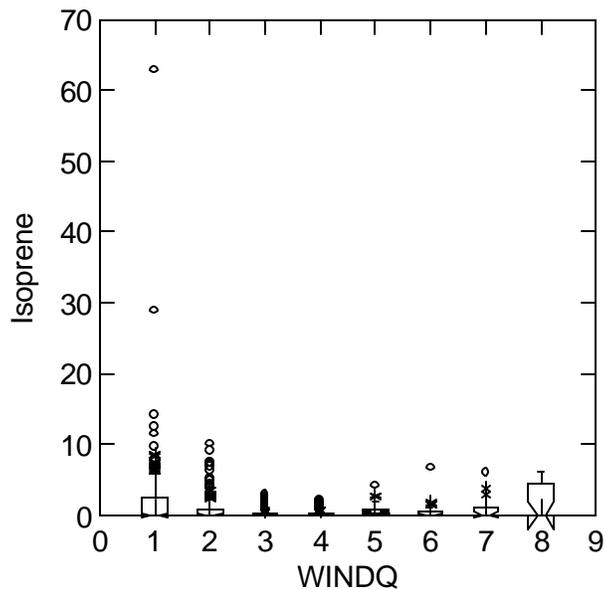


Figure 4-35. Box whisker plot of isoprene concentrations (ppbC) by wind octant at Baytown, August-October 2001.

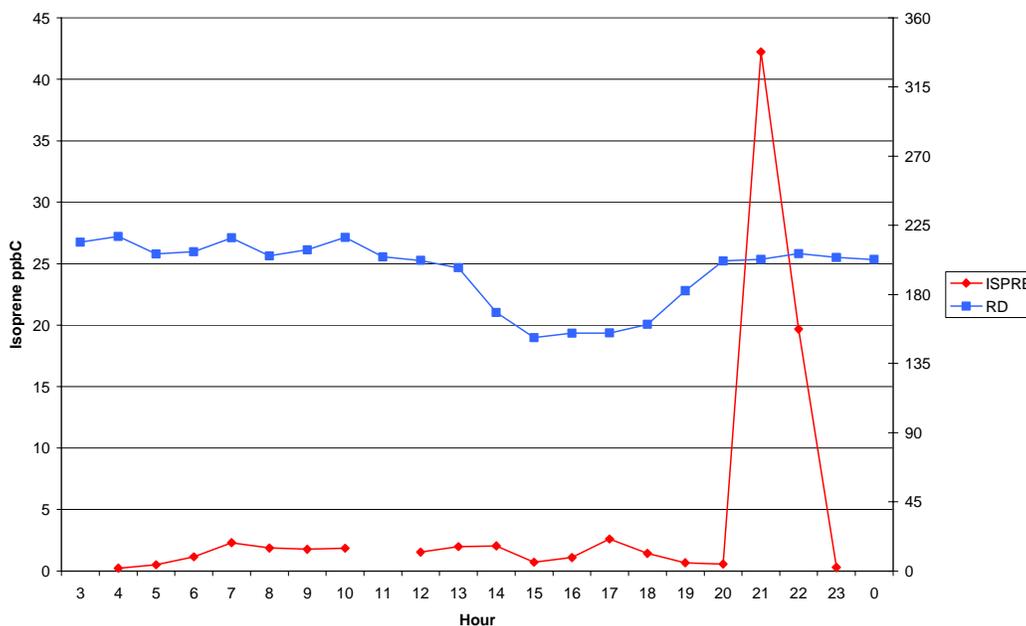


Figure 4-36. Isoprene concentrations (ppbC) and wind direction by hour at Clinton on August 8, 2001.

### 4.5.3 Is Acetylene Associated With Industrial Flares?

Acetylene is a relatively unreactive olefin in terms of ozone potential (Carter, 1994, 2001). It is most often associated with vehicular exhaust (Stoeckenius et al., 1994) and is often used as a tracer of motor vehicle activity. However, it can also be a component of industrial flares; significant industrial influence on acetylene concentrations may compromise use of this compound as a vehicular exhaust tracer.

**Figure 4-37** shows a box plot of acetylene concentrations by hour at Clinton in August-October 2001. There is a diurnal pattern, with concentrations higher in the mornings and evening. This profile is consistent with motor vehicle activity and meteorology. Wind direction analysis, shown in **Figures 4-38 through 4-40**, shows elevated acetylene concentrations when air masses arrived from the Ship Channel area compared to the freeway area. Further analysis shows distinct differences in concentrations by wind direction. When air advects from between the northwest to the east, there are elevated acetylene levels. Even though there is a major freeway in these directions, the absence of higher concentrations from the nearby freeway to the east suggests that a significant fraction of acetylene emissions may have been from industrial emissions.

These findings make the application of the chemical mass balance model a bit problematic in Houston because acetylene and ethene are normally used as key tracers for motor vehicle exhaust.

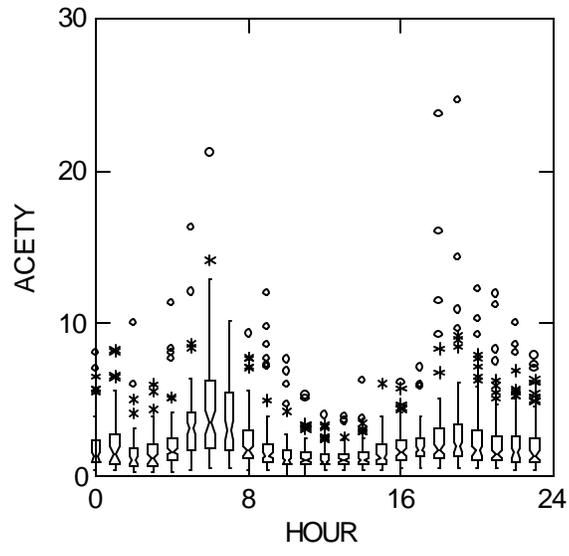


Figure 4-37. Notched box whisker plot of acetylene concentrations (ppbC) by hour at Clinton, August-October 2001.

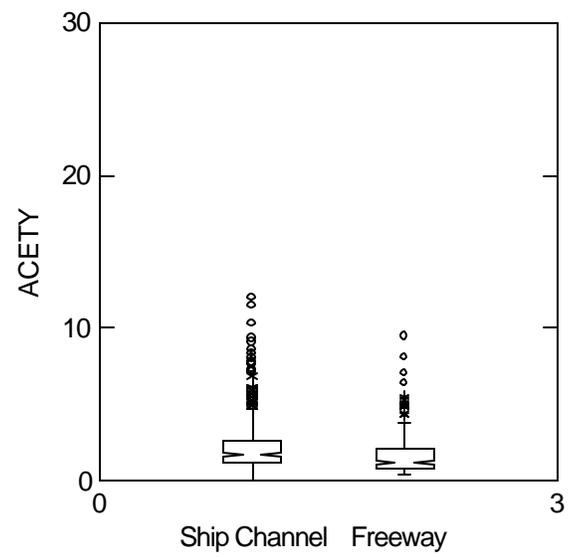


Figure 4-38. Notched box whisker plot of acetylene concentrations (ppbC) from the Ship Channel (60-150 degrees) and from the freeway (225-315 degrees) at Clinton, August-October 2001.

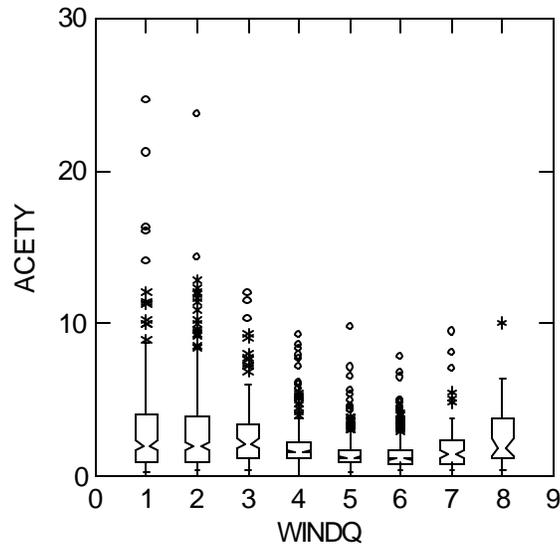


Figure 4-39. Notched box whisker plot of acetylene concentrations (ppbC) by wind octant at Clinton, August-October 2001.

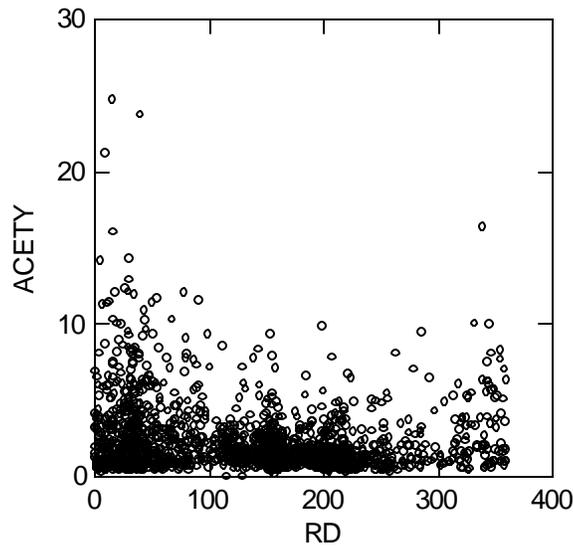


Figure 4-40. Scatter plot of acetylene concentrations (ppbC) versus wind direction at Clinton, August-October 2001.

#### 4.6 SOURCE APPORTIONMENT BY FACTOR ANALYSIS

Factor analysis was performed using SYSTAT software to further investigate the auto-GC data. Factor analysis is a useful first look at data before other, more sophisticated analytical tools are employed, such as UNMIX or positive matrix factorization (PMF). Factor analysis is a statistical procedure for grouping data by similarity among variables (i.e., variables that are

highly correlated are grouped). The analyst then infers possible sources by comparing the resulting “profiles” with measured source profiles, likely sources and their location, and knowledge of the changes species undergo during transport. A comprehensive source apportionment analysis using more sophisticated multivariate tools (e.g., PMF, chemical mass balance model) combined with trajectory analyses, such as analyses discussed by Polissar et al. (2001), was beyond the scope and budget of this project.

We selected a varimax rotation (the results are easier to interpret) and used the data collected during the summer of 2001 at Clinton, Deer Park, and Baytown. Additional analysis was also performed. At Clinton, the results from industry- and freeway-dominated directions (60-150 degrees and 225-315 degrees, respectively) were compared. At Deer Park, the results from the Ship Channel direction (330-60 degrees) were compared to results from the less industrialized southern quadrant (150-240 degrees). At Baytown, four quadrants were used (northeast 0-90 degrees, southeast 90-180 degrees, etc.).

We summarized the factors for each site in tables and made some educated guesses about likely source types. The factors are very difficult to interpret because there are few unique tracers in this data set (e.g., acetylene is present in both motor vehicle exhaust and industrial combustion sources). However, the factors do show surprising similarities among sites.

#### 4.6.1 Clinton

**Table 4-9** details the factor analysis overall at Clinton. About 12% of the variance in VOC concentrations is associated with motor vehicle exhaust, 22% from evaporative emissions, and about 40% from various industrial sources. This is consistent with earlier analyses suggesting motor vehicles are not the dominant source of VOCs in the Houston area. **Figures 4-41 through 4-44** show scatter plots of concentrations of the “odd” factors (isoprene and isopropylbenzene, styrene and 1,3-butadiene). There is a fair amount of scatter between isoprene and isopropylbenzene although high concentrations of both are found between 0600 and 1000 CST, which may be indicative of an industrial source. There is some correlation between styrene and 1,3-butadiene and high concentrations of both are found at all hours of the day; these species may truly be from the same source or source region.

Further analysis by wind direction (shown in **Tables 4-10 and 4-11**) allows for isolation of a stronger motor vehicle signature (37%) from the east (location of a major freeway), along with a mixture of vehicular and industrial emissions (30%), and other industrial emissions (15%). To the south-southwest, in the Ship Channel direction, evaporative industrial emissions account for 25% of the variance, industrial combustion, 12%, and industrial sources of aromatics, 22%. This further demonstrates both the potency of industrial emissions and their predominant source region in the Ship Channel area.

Table 4-9. Factors, percent of variance the factor accounts for, key species in the factor, and likely sources at Clinton, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	12	Trimethylpentanes, dimethylpentanes toluene	Likely motor vehicle although missing combustion components
2	18	Ethyltoluenes, trimethylbenzenes, xylenes, toluene, C10-11 paraffin, ethane	Industrial aromatics and combustion
3	22	C5-C7 paraffins	Paraffin source – evaporative?
4	7	Ethene, propene, propane, ethane	Light olefin/paraffin emissions (industrial?)
5	3	Propylbenzene, 1,2,4-trimethylbenzene	Second aromatic source
6	9	Pentenes and butenes	Second olefin (industrial) source
7	2	Isoprene, i-propylbenzene	Unknown
8	4	Styrene, 1,3-butadiene	Unknown industrial
9	5	C8-C9 paraffins	Unknown

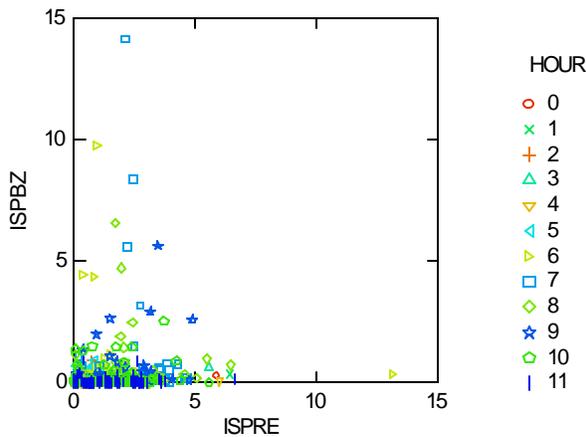


Figure 4-41. Concentrations (ppbC) of isoprene (ispre) versus isopropylbenzene (ispbz) by hour, 0000-1100 CST at Clinton, August-October 2001.

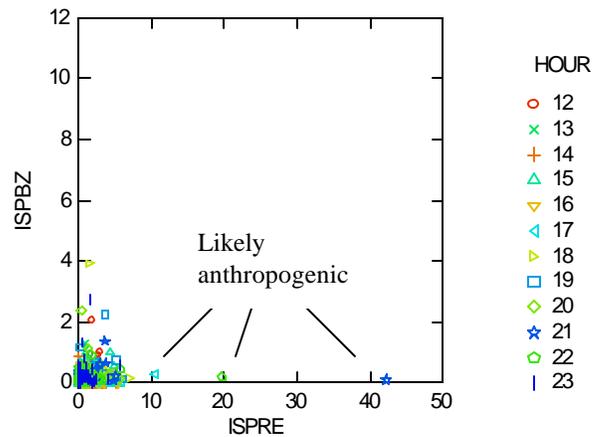


Figure 4-42. Concentrations (ppbC) of isoprene (ispre) versus isopropylbenzene (ispbz) by hour, 1200-2300 CST at Clinton, August-October 2001.

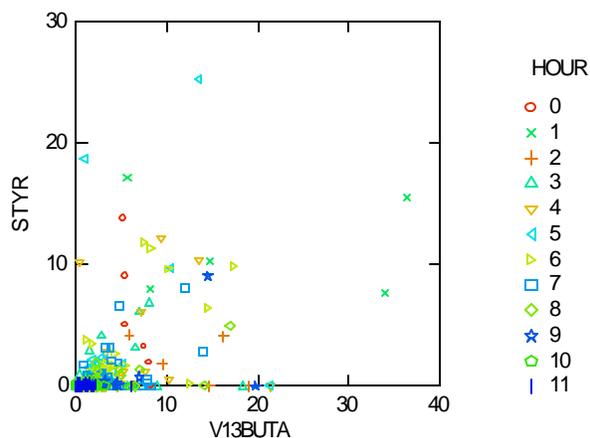


Figure 4-43. Concentrations (ppbC) of 1,3-butadiene (v13buta) versus styrene (styr) by hour, 0000-1100 CST at Clinton, August-October 2001.

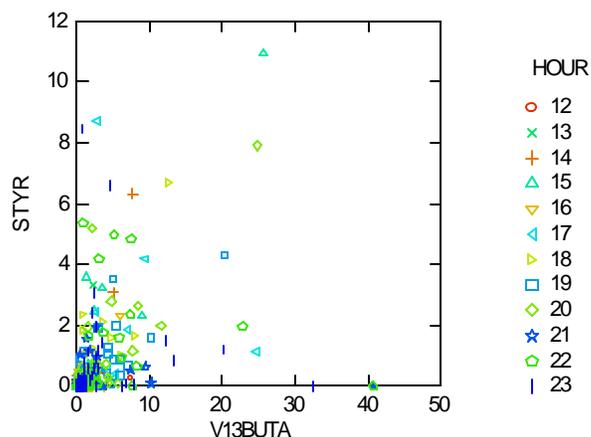


Figure 4-44. Concentrations (ppbC) of 1,3-butadiene (v13buta) versus styrene (styr) by hour, 1200-2300 CST at Clinton, August-October 2001.

Table 4-10. Factors, percent of variance the factor accounts for, key species in the factor, and likely source from 225-315 degrees (freeway) at Clinton, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	37.0	Acetylene, benzene, toluene, C10-11, dimethylbutanes	Motor vehicle
2	29.9	Butenes, pentenes, dimethylbutanes, dimethylpentanes, trimethylpentanes,	Mix of motor vehicles and industry
3	7.5	Propene, i-propylbenzene, butene	Industry
4	7.8	Isoprene, ethane, propane	Background (biogenic and aged)
5	7.0	1,2,4-trimethylbenzene, 3-methylheptane, heptane	Unknown industrial source?

Table 4-11. Factors, percent of variance the factor accounts for, key species in the factor, and likely source from 60-150 degrees (Ship Channel industry) at Clinton, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	17.8	Pentenes, butenes, C5-C6 paraffins	Evaporative?
2	12.1	Ethene, propene, 1,3-butadiene, C8-C11 paraffin, acetylene	Industrial combustion source?
3	11.7	Ethyltoluenes, trimethylbenzenes, ethylbenzene	Aromatics (industry?)
4	4.2	1,2,4-trimethylbenzene, n-propylbenzene	Second aromatic source
5	20.5	C2-C7 paraffins	Paraffin source
6	7.4	Dimethyl and trimethyl pentanes	Evaporative emissions
7	6.0	m,p,o- xylenes	Xylenes source
8	2.7	Isoprene	Background/biogenic

#### 4.6.2 Deer Park

Factor analysis completed at Deer Park is detailed in **Table 4-12**. A source of high carbon number aromatic hydrocarbons and paraffins is dominant at Deer Park, accounting for 24% of the variance. A source of C4-C5 olefins and C6 paraffins, possibly evaporative or industrial emissions, accounts for another 21%. A number of different paraffin sources, partitioned by chain length, account for 25% of the variance. An olefin source of ethene and propene, 7%, also appears and an odd combination of isoprene and benzene account for another 3% of the variance. Scatter plots of concentrations of isoprene and benzene by hour are shown in **Figures 4-45 and 4-46**. There is a fair amount of scatter, and it appears that there are higher concentrations of both species in the morning although, as noted earlier, there are high isoprene concentrations during the night as well. There are also two lines of convergence in the morning hours, suggesting more than one source influencing these concentrations.

Further analysis was done by segregating data by wind direction, between the more residential area to the south (150-240 degrees) and the Ship Channel area to the north (330-60 degrees); these analyses are detailed in **Tables 4-13 and 4-14**. To the south a motor vehicle signature accounted for 29% of the variance, followed by the heavy aromatic and paraffin signature (19%), various olefin sources (23%), aromatic sources (9%), paraffin (4%) and an odd isoprene and 1,3-butadiene factor which may derive from urban background sources or from industrial emissions. Scatter plots of isoprene and 1,3-butadiene concentrations by hour are shown in **Figures 4-47 and 4-48**. Concentrations from the south are generally low, especially during the night, with a few outliers that often do not correlate well.

Table 4-12. Factors, percent of variance the factor accounts for, key species in the factor, and likely source at Deer Park, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	24	Trimethylbenzenes, C9-C11 paraffins, xylenes, ethyltoluenes	Aromatic + heavy compounds
2	21	Butenes, pentenes, methyl pentanes, dimethyl butanes	Possible evaporative
3	12	C6-C8 paraffins	Paraffin source
4	7	Ethene, propene	Olefin source
5	7	C4-C5 paraffins	Paraffin source
6	7	Ethane, propane	Paraffin source or background/aged air
7	3	Isoprene, benzene	Odd background, industry?

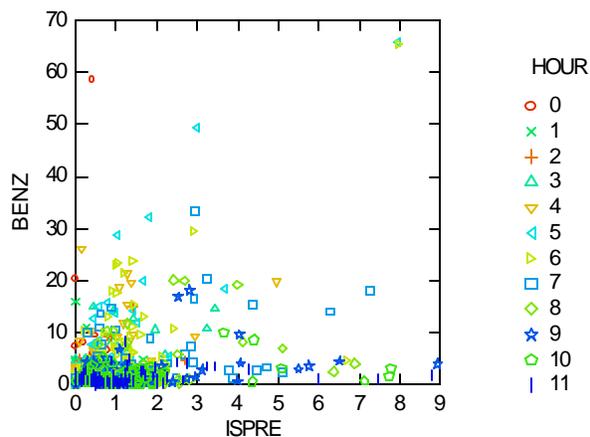


Figure 4-45. Concentrations (ppbC) of isoprene (ispre) versus benzene (benz) by hour, 0000-1100 CST at Deer Park, August-October 2001.

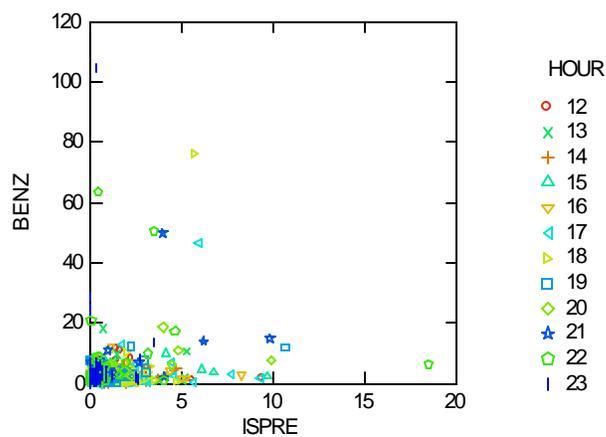


Figure 4-46. Concentrations (ppbC) of isoprene (ispre) versus benzene (benz) by hour, 1200-2300 CST at Deer Park, August-October 2001.

Table 4-13. Factors, percent of variance the factor accounts for, key species in the factor, and likely Source from 150-240 degrees (mostly residential) at Deer Park, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	29	2,2,4-trimethylpentane, benzene, toluene, isopentane, C6-C8 paraffins	Motor vehicle + some industry
2	19	Trimethylbenzenes, C10-C11, ethyltoluenes	Aromatics + heavy compounds
3	12	Pentenes, butenes	Olefin source
4	6	Propene, ethene	Olefin source
5	5	1-butene, ethene	Olefin source
6	4	Styrene, isopropylbenzene	Aromatics source
7	6	Xylenes, ethylbenzene	Aromatics source
8	4	Propane, ethane	Paraffin source or background/ aged air
9	3	1,3-butadiene, isoprene	Background? Industrial?

Table 4-14. Factors, percent of variance the factor accounts for, key species in the factor, and likely source from 330-60 degrees (Ship Channel) at Deer Park, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	26.2	Trimethylbenzenes, C10-C11, ethyltoluenes, xylenes	Aromatics + heavy compounds
2	8.5	Ethene, ethane, propene, propane, C6 paraffins	Industrial source?
3	22.8	Pentenes, butenes, C6-C7 paraffins	Evaporative?
4	14.9	C4-C7 paraffins	Paraffin source
5	4.3	Benzene, isoprene	Odd source or background
6	4.5	Isopropylbenzene, 1,3-butadiene	Industrial source?

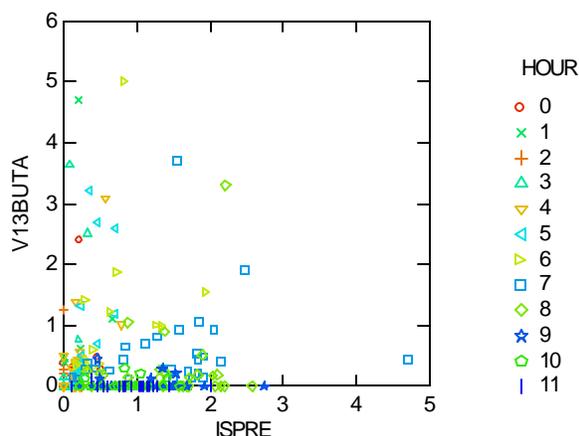


Figure 4-47. Concentrations (ppbC) of isoprene (ispre) versus 1,3-butadiene (v13buta) at Deer Park from the south (150-240 degrees, residential) by hour, 0000-1100 CST, August-October 2001.

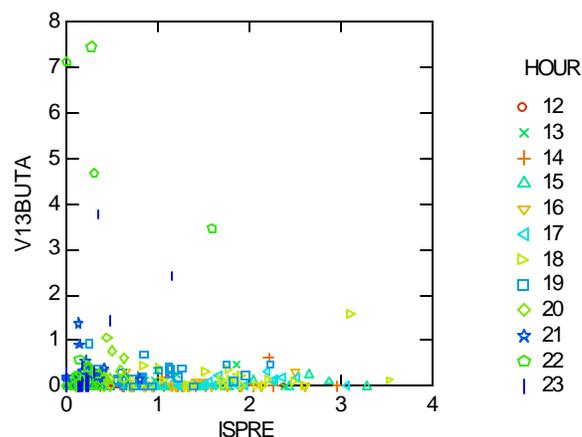


Figure 4-48. Concentrations (ppbC) of isoprene (ispre) versus 1,3-butadiene (v13buta) at Deer Park from the south (150-240 degrees, residential) by hour, 1200-2300 CST, August-October 2001.

With winds from the more industrialized north, the high carbon number aromatic hydrocarbons and paraffin signature was again dominant at 26%, followed by an olefin and paraffin signature that may originate from evaporative emissions (23%), an paraffin source (15%), an odd mix of the light olefins and paraffins with C6 paraffins (9%), and two more odd combinations, benzene and isoprene (4%) and isopropylbenzene and 1,3-butadiene (5%). Scatter plots of concentrations of benzene versus isoprene and 1,3-butadiene versus isopropylbenzene by hour are shown in **Figures 4-49 through 4-52**. There again appear to be two lines of convergence, between benzene and isoprene, consistent with earlier analyses incorporating all wind directions. There is some correlation between isopropylbenzene and 1,3-butadiene, especially in the evening and nighttime hours, suggesting that these species may be emitted together from a nearby industrial source or source region. There are a number of instances in which elevated concentrations of both species are found, indicating they may both be emitted from an industrial source.

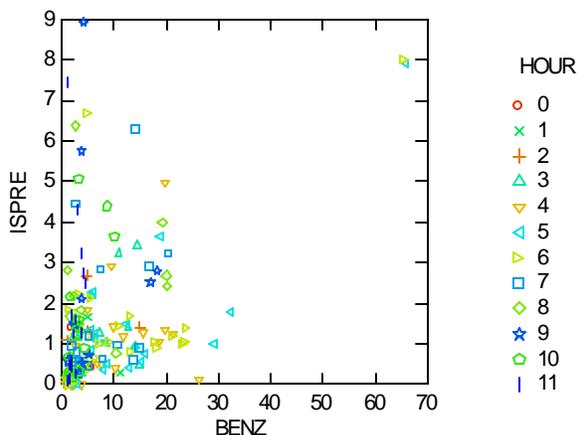


Figure 4-49. Concentrations (ppbC) of isoprene (ispres) versus benzene (benz) at Deer Park from the north (330-60 degrees, Ship Channel) by hour, 0000-1100 CST, August-October 2001.

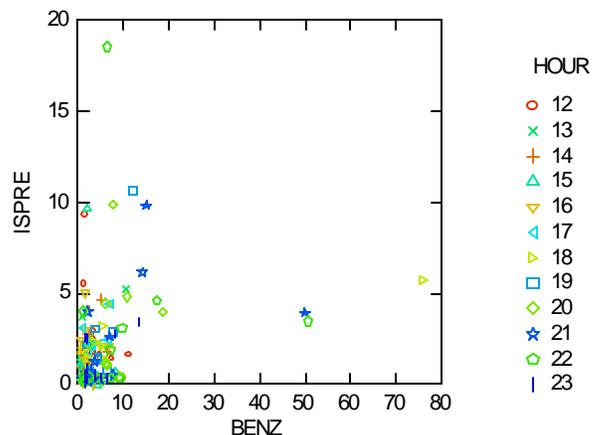


Figure 4-50. Concentrations (ppbC) of isoprene (ispres) versus benzene (benz) at Deer Park from the north (330-60 degrees, Ship Channel) by hour, 1100-2300 CST, August-October 2001.

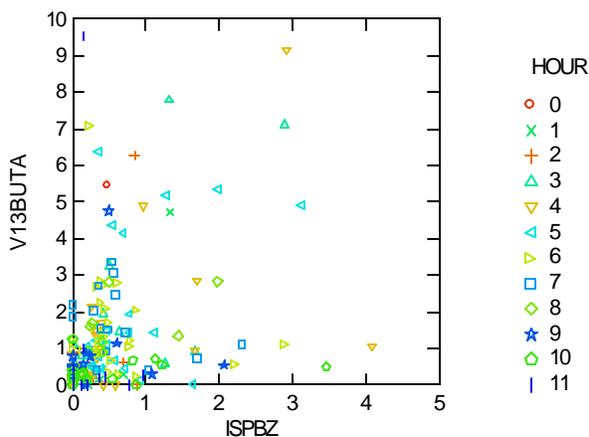


Figure 4-51. Concentrations (ppbC) of isopropylbenzene (ispbz) versus 1,3-butadiene (v13buta) at Deer Park from the north (330-60 degrees, Ship Channel) by hour, 0000-1100 CST, August-October 2001.

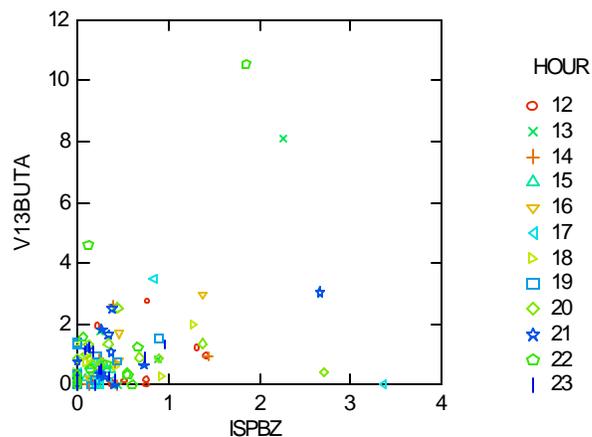


Figure 4-52. Concentrations (ppbC) of isopropylbenzene (ispbz) versus 1,3-butadiene (v13buta) at Deer Park from the north (330-60 degrees, Ship Channel) by hour, 1200-2300 CST, August-October 2001.

### 4.6.3 Baytown

Overall factor analysis results at Baytown are shown in **Table 4-15**. Ten factors were found at this site, mostly from a variety of specific aromatic, olefin, and paraffin sources. Factor three (7.1% of total variance) appears to be a mixture of vehicles (acetylene, benzene) and industry (propene) or may simply be a unique industrial source. The absence of acetylene and benzene from factor 5, a likely motor vehicle signature, makes it difficult to use these compounds as a tracer for vehicular emissions at this site. The high carbon number aromatic and paraffin signature seen at other sites was again found here, accounting for 22% of the variance. Other factors include possible evaporative emissions (14%), paraffin sources (12%), olefin sources (6%), aromatic sources (11%), and an odd combination of isoprene and 1,3-butadiene (3%), which may be background or originate from a specific source. Scatter plots of isoprene and 1,3-butadiene concentrations by hour at Baytown are shown in **Figures 4-53 and 4-54**. There is no correlation between the species, consistent with the negative and positive values for these species in the factor.

Table 4-15. Factors, percent of variance the factor accounts for, key species in the factor, and likely source at Baytown, August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	21.5	Xylenes, trimethylbenzenes, C8-C11 paraffins	Aromatics + heavy compounds
2	13.9	Butenes, C4-C6 paraffins	Evaporative?
3	7.1	Ethene, propene, acetylene, benzene, ethane, propane	Vehicles + industry?
4	7.2	C6-C7 paraffins	Paraffin source
5	7.4	Trimethylpentanes, toluene	Motor vehicle?
6	6.3	Pentenes	Olefin source
7	2.8	Isoprene, 1,3-butadiene	Background? Industry?
8	2.9	o-ethyltoluene, 1,3,5-trimethylbenzene	Aromatic source
9	4.3	Dimethylbutanes	Paraffin source
10	8.2	Isopropylbenzene, m-ethyltoluene, 1,2,3-trimethylbenzene	Aromatic source

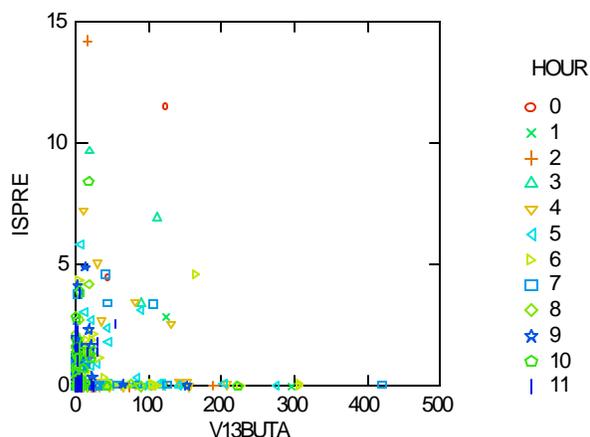


Figure 4-53. Concentrations (ppbC) of isoprene (ispire) versus 1,3-butadiene (v13buta) at Baytown by hour, 0000-1100 CST, August-October 2001.

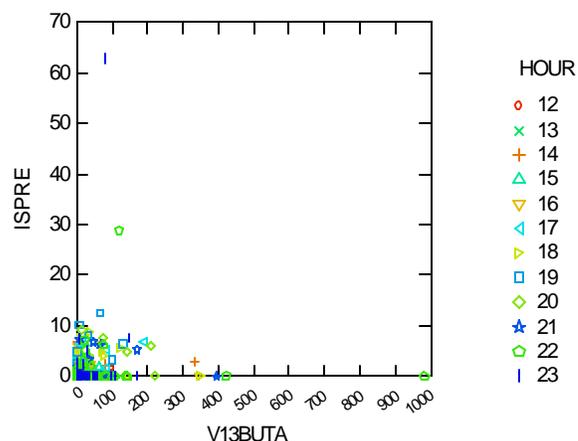


Figure 4-54. Concentrations (ppbC) of isoprene (ispire) versus 1,3-butadiene (v13buta) at Baytown by hour, 1200-2300 CST, August-October 2001.

Factor analysis by wind direction was also carried out; two wind quadrants, the southeast (90-180 degrees) and the southwest (180-270 degrees) had previously been found to have sources of elevated toluene and propene concentrations, respectively (section 4.4.4).

**Tables 4-16 and 4-17** detail the analyses for these two wind quadrants. From the southeast, the heavy aromatic and paraffin signature accounts for 36% of the variance, consistent with earlier findings of elevated aromatic hydrocarbons. A mixture of C4-C5 olefins and C5-C7 paraffins accounts for 27%, possibly from industrial evaporative emissions. The vehicle-industry mix with ethene, propene, acetylene and benzene is once again evident at 8%, similar to results using all wind directions. A motor vehicle source is found (6%), as well as a paraffin source (4%), and an odd isoprene and 1,2,3-trimethylbenzene combination, either a background or unique industrial signature (3%). Scatter plots of the concentrations of these last two species by hour are shown in **Figures 4-55 and 4-56**. There are a number of instances in which elevated concentrations of both species are found, perhaps indicating that they share a similar source or source region.

Table 4-16. Factors, percent of variance the factor accounts for, key species in the factor, and likely source at Baytown from the southeast (90-180 degrees), August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	35.5	Xylenes, toluene, trimethylbenzenes, ethyltoluenes, C8-C11 paraffins	Aromatics + heavy compounds
2	26.9	Pentenes, butenes, C5-C7 paraffins	Olefin/paraffin source – evaporative?
3	8.3	Ethene, propene, 1,3-butadiene, acetylene, benzene	Vehicles + industry?
4	6.2	2,4-dimethylpentane, 2,3,4-trimethylpentane, toluene	Motor vehicles?
5	3.9	Dimethylbutanes	Paraffin source
6	3.1	Isoprene, 1,2,3-trimethylbenzene	Background? Industry?
7	2.5	Cyclopentene	Unknown

Table 4-17. Factors, percent of variance the factor accounts for, key species in the factor, and likely source at Baytown from the southwest (180-270 degrees), August-October 2001.

Factor #	% Variance	Key Species	Source Estimate
1	23.0	Pentenes, C5-C7 paraffins, isoprene, benzene	Olefin + paraffin mix – evaporative? Inclusion of isoprene is odd.
2	16.5	Trimethylbenzenes, ethyltoluenes, C11 paraffin	Aromatics + heavy compounds
3	19.9	C4-C9 paraffins	Paraffin source
4	6.7	Propene, propane, acetylene, pentane	Industry
5	7.9	2,3-dimethylbutane, propane, 2,3,4-trimethylpentane	Paraffin source
6	3.4	Ethene, n-decane	Unknown
7	4.9	Styrene, 1,3-butadiene, acetylene	Reactive and unknown
8	3.4	m/p-xylenes, i-pentane	Unknown

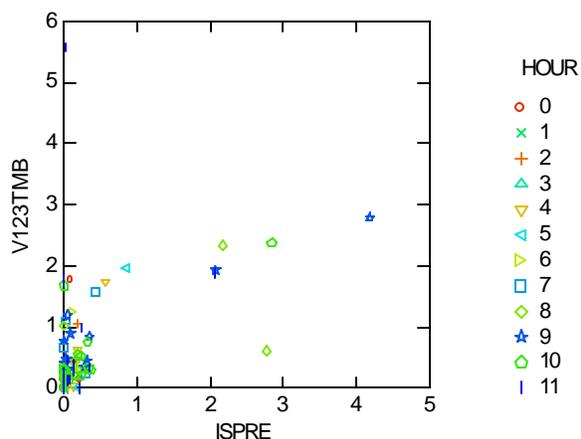


Figure 4-55. Concentrations (ppbC) of isoprene (ispre) versus 1,2,3 trimethylbenzene (v123tmb) at Baytown from the southeast (90-180 degrees) by hour, 0000-1100 CST, August-October 2001.

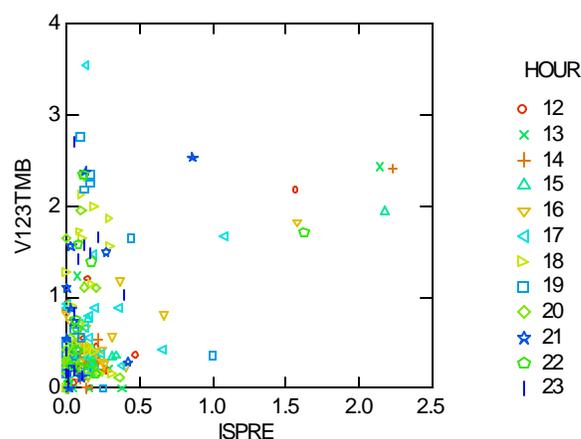


Figure 4-56. Concentrations (ppbC) of isoprene (ispre) versus 1,2,3-trimethylbenzene (v123tmb) at Baytown from the southeast (90-180 degrees) by hour, 1200-2300 CST, August-October 2001.

From the southwest, a region of elevated olefins, the olefin-paraffin mix is the highest (23%) and may be from evaporative emissions. Paraffin sources contribute 28% of the variance, followed by the heavy aromatic mixture at 17%. In addition to these differences, no clear motor vehicle signature was found, probably due to the absence of a major freeway in this direction; industrial complexes and the Ship Channel sources dominate this direction. Other factors include an industrial source of light VOCs (7%), an odd source of styrene, 1,3-butadiene, and acetylene (5%), another odd source of ethene and n-decane (3%), and another unknown source of m-/p-xylenes and isopentane (3%). Scatter plots of concentrations of species in these factors are shown in **Figures 4-57 through 4-62**. There appears to be some correlation between ethene and n-decane during the afternoon and evening hours although none is apparent during the morning. While there appears to be little correlation between styrene and 1,3-butadiene, high concentrations of both these species do appear to occur in the same sample, indicating that they may be from the same source region. Some correlation is evident between m-/p-xylenes and i-pentane; but as these are both abundant species and can be from a number of different sources, it is difficult to determine if they are mostly from a single source region.

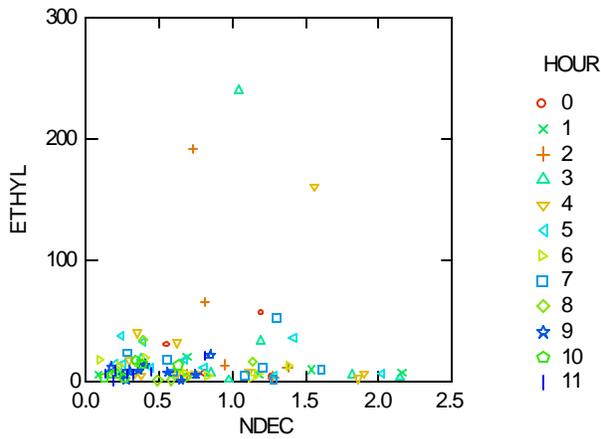


Figure 4-57. Concentrations (ppbC) of n-decane (ndec) versus ethene (ethyl) at Baytown from the southwest (180-270 degrees) by hour, 0000-1100 CST, August-October 2001.

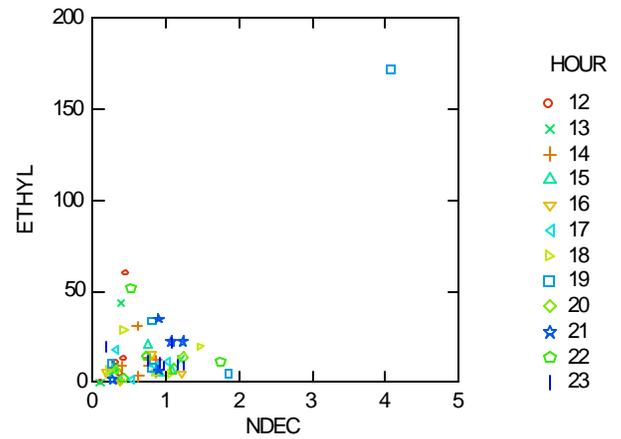


Figure 4-58. Concentrations (ppbC) of n-decane (ndec) versus ethene (ethyl) at Baytown from the southwest (180-270 degrees) by hour, 1200-2300 CST, August-October 2001.

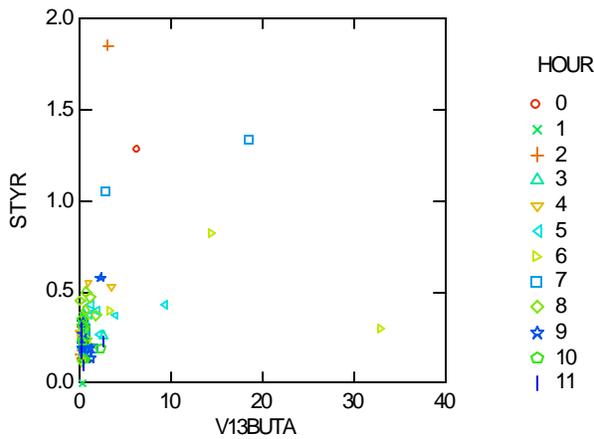


Figure 4-59. Concentrations (ppbC) of 1,3-butadiene (v13buta) versus styrene (styr) at Baytown from the southwest (180-270 degrees) by hour, 0000-1100 CST, August-October 2001.

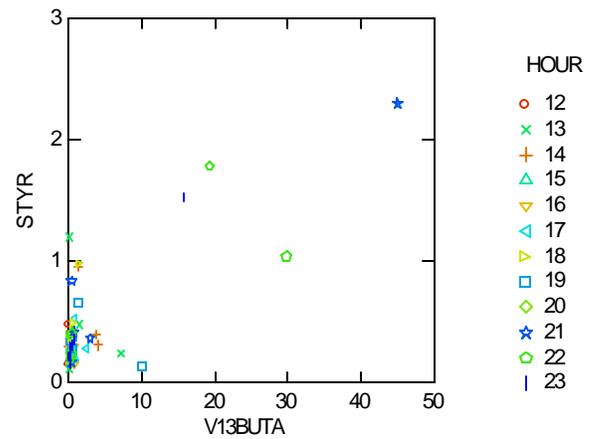


Figure 4-60. Concentrations (ppbC) of 1,3-butadiene (v13buta) versus styrene (styr) at Baytown from the southwest (180-270 degrees) by hour, 1200-2300 CST, August-October 2001.

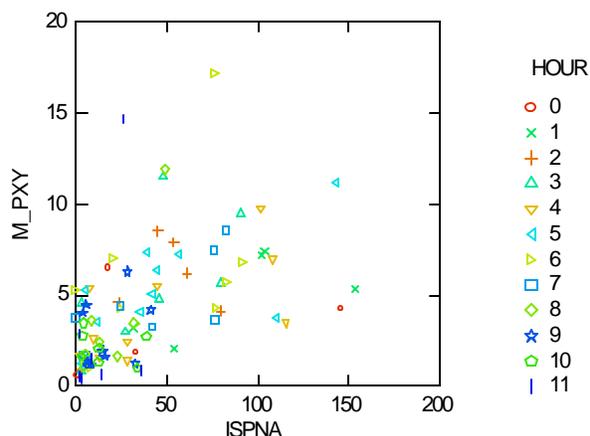


Figure 4-61. Concentrations (ppbC) of isopentane (ispna) versus m/p-xylenes (m\_pxy) at Baytown from the southwest (180-270 degrees) by hour, 0000-1100 CST, August-October 2001.

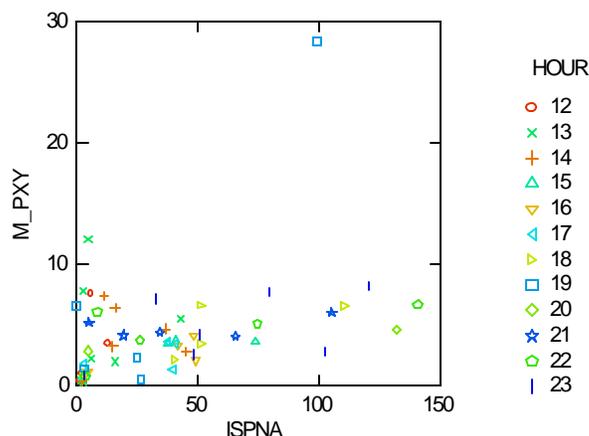


Figure 4-62. Concentrations (ppbC) of isopentane (ispna) versus m/p-xylenes (m\_pxy) at Baytown from the southwest (180-270 degrees) by hour, 1200-2300 CST, August-October 2001.

#### 4.6.4 Trends Among Sites

While it is difficult from this preliminary and exploratory analysis to draw many conclusions or pinpoint sources, there were many similarities among sites.

- Overall, the motor vehicle signature is not dominant, as is usually observed in cities with auto-GCs, and is not even evident from some directions at various sites. Acetylene and benzene are not consistent between sites and wind quadrants, making use of these species as vehicular markers difficult.
- The overall dominance of industrial emissions is consistent with other analyses performed in this report.
- The factor of heavy aromatics and other compounds appears at all sites and often accounts for the most variance of all the factors. While the heavy aromatics may have a similar source region, the inclusion of other compounds, such as n-decane and n-undecane, may be more a result of analytical bias than of the species being from a similar source. These compounds all elute at the end of the chromatogram, and without specific relative response factors for the aromatics versus the paraffins, it is difficult to conclusively associate the two types of compounds.
- Another factor evident at all sites is the mixture of C4-C5 olefins (often excluding 1-butene) and C4-C7 paraffins. This mixture may derive from evaporative emissions, refining processes, or a combination of both.

While the most dominant factors could often be associated with either industrial or evaporative or motor vehicle emissions, a number of lesser factors were unusual and not typical of any specific source known to the authors. A number of these factors included isoprene, usually a tracer of biogenic emissions; but, as illustrated in this report, it is also a likely industrial emission. Some of the unknown factors include isoprene and benzene (Deer Park), isoprene and isopropylbenzene (Clinton), isoprene and 1,3-butadiene (Deer Park, south), and isoprene and 1,2,3-trimethylbenzene (Baytown, southeast). Other factors found that are unknown include isopropylbenzene and 1,3-butadiene (Deer Park, north), styrene and 1,3-butadiene (Clinton), ethene and n-decane (Baytown, southwest), and m-/p-xylenes and isopentane (Baytown, southwest). Further investigation of these unknown factors may reveal unique sources in the Houston area and their influence on the VOC composition.

## 5. OZONE EPISODE ANALYSIS

One of the primary hypotheses being investigated in this study is what compounds, such as olefins (e.g., ethene, propene, 1,3-butadiene) or aromatics (e.g., toluene, 1,2,4-trimethylbenzene, xylenes), are a greater fraction of TNMOC in the mornings of ozone episodes. One of the implications of higher reactive TNMOC fractions is that unique (or industrial upset) conditions may lead to these high concentrations and trigger ozone episodes. To pursue this hypothesis, we focused on the summer months of July-September when there were a large number of days with high ozone concentrations.

### 5.1 EPISODE ANALYSIS SCHEME

We used TNRCC's definition of an ozone "episode" as a day on which a 1-hr average ozone concentration exceeded 125 ppb at an ozone monitor in the Houston area. The list of episodes was provided by TNRCC and confirmed by STI in order to be consistent with other investigations. All samples at all auto-GC sites on these days were then flagged as an episode day.

To explore the role of individual compounds in ozone formation, the median values of PAMS species' concentration, weight percent, reactivity-weighted data, and reactivity-weighted concentrations were examined on ozone episode and non-episode days for a variety of sites from July-September 1998-2001. Some of the investigations were focused on the 0500 to 0900 CST time period because it is the critical period when emissions are high, mixing heights are low, and ozone formation chemistry is set. Selected olefin-to-NO<sub>x</sub> ratios were also explored to determine whether there was a distinct difference in these "reactive" ratios between episode and non-episode days. As discussed earlier in Section 1.5, the MIR scale is the primary reactivity scale used, although we also compared the results using the MIR scale and the OH reactivity scale. Lastly, dependence of composition and reactivity on wind direction was also explored, as well as the effect of changing meteorological conditions from year to year on the frequency and intensity of ozone episodes.

### 5.2 FINGERPRINT ANALYSIS OF EPISODE VERSUS NON-EPISODE DAYS

**Figure 5-1** shows an example fingerprint plot for Clinton in 1999 in which the median concentration of each PAMS hydrocarbon during the morning hours (0500-0900 CST) for episode and non-episode days is shown in elution order. **Figures 5-2 through 5-4** show the episode/non-episode fingerprints at Clinton in 1999 using the median weight percent, reactivity-weighted composition, and reactivity-weighted concentrations, respectively.

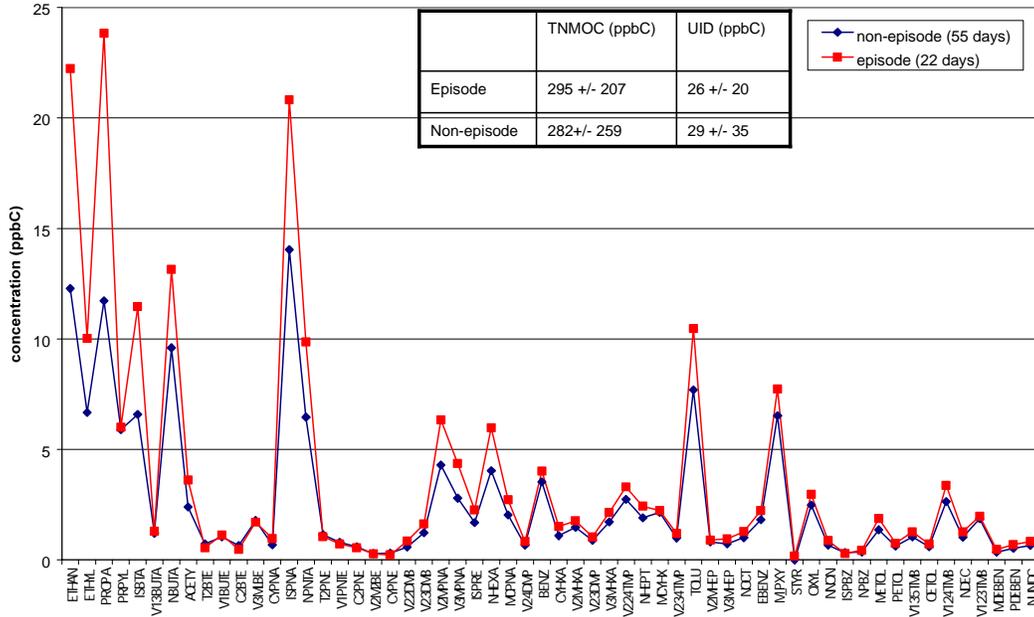


Figure 5-1. Fingerprint of PAMS hydrocarbon median concentrations (ppbC) by episode and non-episode days at Clinton, July-September 1999 (0500-0900 CST). Species abbreviations are listed in Appendix B. UID = unidentified mass.

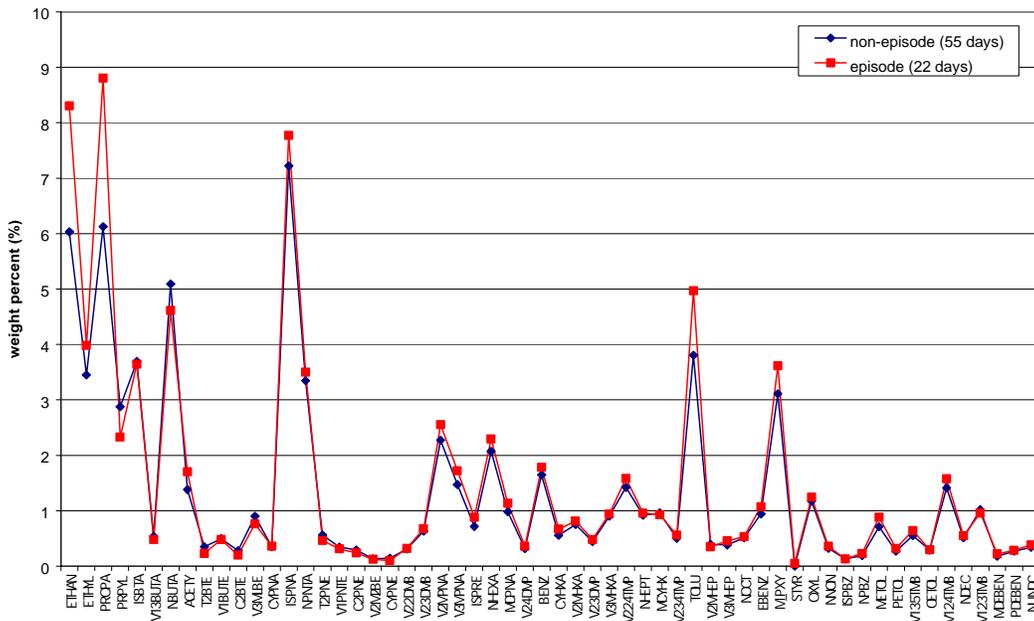


Figure 5-2. Fingerprint of PAMS hydrocarbon median weight percent by episode and non-episode days at Clinton, July-September 1999 (0500-0900 CST). Species abbreviations are listed in Appendix B.

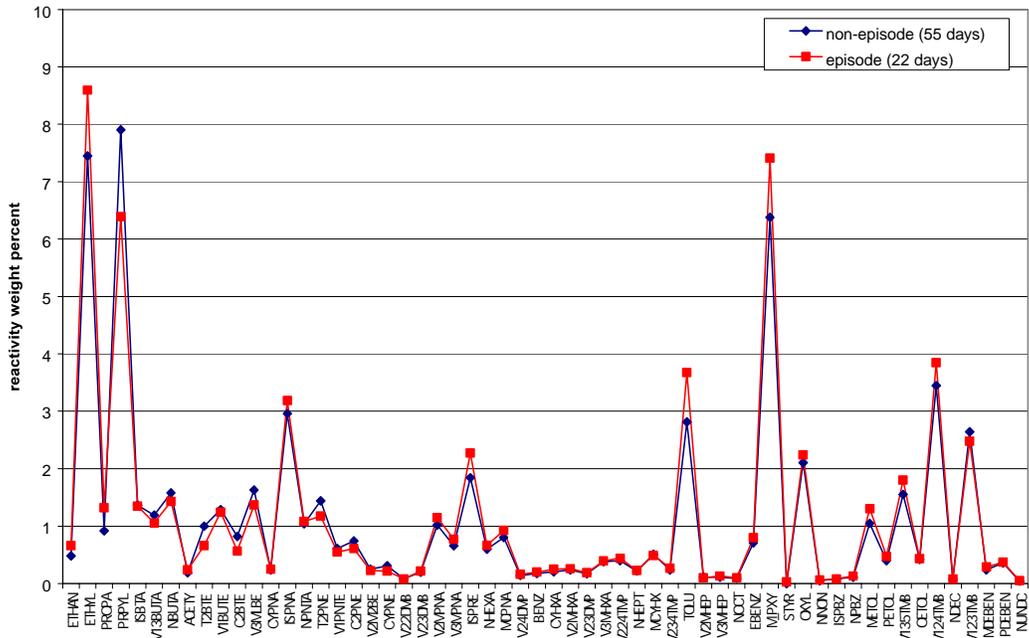


Figure 5-3. Fingerprint of PAMS hydrocarbon median reactivity-weight percent (MIR in mol ozone per mol C) by episode and non-episode days at Clinton, July-September 1999 (0500-0900 CST). Species abbreviations are listed in Appendix B.

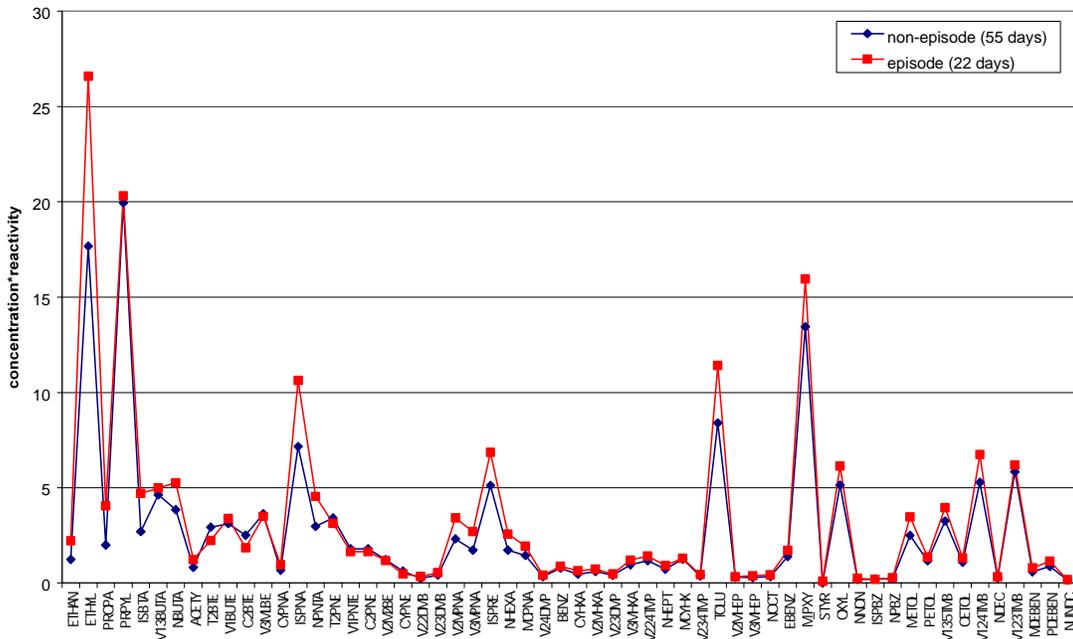


Figure 5-4. Fingerprint of PAMS hydrocarbon median concentration (in ppbC) \*reactivity (MIR in mol ozone per mol C) by episode and non-episode days at Clinton, July-September 1999 (0500-0900 CST). Species abbreviations are listed in Appendix B.

Significant findings from this fingerprint analysis include

- Concentrations of all species were generally higher during the mornings of ozone episode days. This finding is consistent with other investigations of episode/non-episode days (e.g., Main and O'Brien, 2001; Main and Brown, 2002b).
- There was little difference in composition (weight percent) between episode and non-episode mornings when all data are included, regardless of wind direction.
- Weight percents of reactive species (e.g., ethene, propene, xylenes, etc.) were actually higher on non-episode days at a number of sites and during some years, and most sites showed no consistency from year to year as to whether the reactive species were higher during episodes or non-episodes.
- The lack of compositional difference between mornings of ozone episodes and non-episodes suggests that emissions were similar on both ozone episode and non-episode days. If there was no difference in emissions on days of episodes and non-episodes, it would appear that, on any given day with the correct meteorology, an ozone episode could have occurred.
- The reactivity-weighted concentrations were also very similar between episode and non-episode days during the morning for all sites and years.

### 5.3 HYDROCARBONS OF INTEREST

Because of the general interest in the more reactive hydrocarbons, ethene, propene, isoprene, 1,3-butadiene, m- and p-xylenes, toluene, and 1,2,4-trimethylbenzene were investigated further. **Table 5-1** lists, for each site and year (July-September, 0500-0900 CST), whether episode or non-episode median weight percents of these reactive hydrocarbons are higher and whether the values are different at a 95% confidence level in accordance with a t-test. Few consistent patterns were observed. Key findings of this analysis follow.

**Ethene and propene** are reactive olefins that are among the most abundant on a reactivity-weight percent basis and, as such, can play an important role in ozone formation. Previous investigations have suggested that these two compounds may be elevated on ozone episode days. Both compounds generally had higher concentrations on episode days but not always on a relative basis (as shown in Table 5-1). T-tests also confirm that ethene and propene weight percents are generally not statistically different between episode and non-episode days. The only exceptions were that ethene was higher on a weight-percent basis on episode days at Deer Park and Clinton during summer 1999, and propene was statistically higher on non-episode days at Clinton in 1998-2001, Deer Park and Baytown in 2001, and Bayland in 1998. At most sites, there is no consistency among years as to whether non-episode or episode median weight percents are higher. At Deer Park, ethene was higher on episode days in 1999 and 2000, and propene was higher on non-episode days at Clinton in 1998-2000; all other sites showed little consistency from year to year. Ethene and propene do not follow the same pattern as to whether episode or non-episode median weight percents are higher. This is consistent with earlier analyses (Section 3.5) showing that these two compounds are fairly independent of each other.

**Isoprene** is a reactive olefin that is emitted from biogenic sources (Stoeckenius et al., 1994; Main and Roberts, 2000); it can be an important contributor to ozone formation. Anthropogenic sources are possibly important in the Houston Ship Channel because isoprene is also used in the polymer and rubber industry. Fingerprint analysis shows that isoprene is sometimes higher in concentration in Houston on days of ozone episodes, consistent with findings from other parts of the country (Dye et al., 1998). Again, there is no compositional (weight-percent) difference between episode and non-episode mornings. Isoprene fractions were consistently higher on episode days (though statistically different only in 1998) at Clinton in 1998-2000 and were higher on non-episode days at Deer Park in 1999-2000. No other sites exhibited consistent trends.

**1,3-butadiene** is another highly reactive and toxic compound and is used as a tracer for motor vehicle exhaust. This compound was generally higher on non-episode days, consistently so at Clinton in 1998-2000 (and significantly different in 1999-2000). It was statistically higher on non-episode days at Aldine in 2000 and at Channelview in 2001, but statistically higher on episode days at Deer Park in 2000. Sites other than Clinton were not consistent from year to year.

**Butenes and pentenes** are sets of compounds with high reactivity and ozone formation potential. Butenes (C4 olefins) include trans- and cis-2-butene and 1-butene, while pentenes (C5 olefins) are trans- and cis-2-pentene, 1-pentene, 3-methyl-1-butene, 2-methyl-2-butene, and cyclopentene. At most sites, neither of these groups was significantly higher on episode mornings. The only exception is that butenes were significantly higher on episode mornings at Deer Park in 1999-2001. The lack of consistency between Deer Park and other sites indicates that elevated butenes at Deer Park may not necessarily lead to ozone episodes; it could be that advection patterns on episode days simply allow for butene transport from a nearby source.

**Toluene** is a fairly reactive compound that is emitted mainly from solvent use, refining, and mobile source emissions. Due to its high reactivity and potential for ozone formation, as well as its abundance in the urban Houston area, toluene is of interest. Toluene was generally higher on a weight-percent basis on episode days, but only significantly so at Bayland in 1998, Channelview in 2001, and Clinton in 1998 and 1999; weight percents were higher on non-episode days (though not significantly) at Bayland in 2000 and Deer Park in 1999. Note that toluene was consistently higher on episode days at Clinton in 1998-2001, and significantly so in 1998 and 1999. The other sites showed little consistency on an annual basis.

**Other reactive aromatics** include the three xylene isomers, 1,2,4-trimethylbenzene, and ethyltoluenes, which can be emitted from sources such as refining, mobile sources, and solvent use. These compounds showed no consistent difference in weight percent between episode and non-episode days. Xylenes were significantly higher on episode days at Bayland in 1998 and Channelview in 2001, but significantly higher on non-episode days at Deer Park in 1999. 1,2,4-trimethylbenzene was significantly higher on non-episode days at Bayland in 1999, Clinton in 2000, and Deer Park in 1999, and higher on episode days in 2001 at Channelview. Ethyltoluenes were significantly higher on episode days at Bayland in 1998, and Channelview and Baytown in 2001, but significantly higher on non-episode days at Clinton in 2000 and Deer Park in 1999. The only site that was consistent year to year was Deer Park where 1,2,4-trimethylbenzene was higher on non-episode days in 1999-2000. Note that the reactive aromatics were statistically higher on episode days at Channelview in 2001. However, without data during other years, it is difficult to assess whether this is a trend or an aberration.

Table 5-1. Results of two-sample t-tests for ethene, propene, and isoprene by location and year, July-September, 0500-0900 CST: number of days in each episode and non-episode median, whether episode or non-episode median weight percents are higher and whether these differences are different at a 95% confidence level. Significant differences are highlighted in boldface.

Species	Site	Year	Number of days/episode (ep)	Number of days/non-episode (non)	Which median weight percent is higher?	Different at a 95% confidence level?
Ethene	Aldine	2000	5	16	ep>non	No
Ethene	Bayland	2000	8	19	non>ep	No
Ethene	Bayland	1999	22	48	ep>non	No
Ethene	Bayland	1998	7	36	non>ep	No
Ethene	Channelview	2001	56	10	non>ep	<b>Yes</b>
Ethene	Clinton	2001	67	13	non>ep	No
Ethene	Clinton	2000	23	35	non>ep	No
Ethene	Clinton	1999	22	54	ep>non	<b>Yes</b>
Ethene	Clinton	1998	16	26	non>ep	No
Ethene	Deer Park	2001	56	14	non>ep	No
Ethene	Deer Park	2000	8	9	ep>non	No
Ethene	Deer Park	1999	24	54	ep>non	<b>Yes</b>
Ethene	Haden Rd.	2001	44	5	ep>non	No
Ethene	Baytown	2001	49	7	ep>non	No
Propene	Aldine	2000	5	16	ep>non	No
Propene	Bayland	2000	6	15	ep>non	No
Propene	Bayland	1999	22	48	ep>non	No
Propene	Bayland	1998	7	26	non>ep	<b>Yes</b>
Propene	Channelview	2001	53	10	non>ep	<b>Yes</b>
Propene	Clinton	2001	67	13	non>ep	<b>Yes</b>
Propene	Clinton	2000	48	23	non>ep	<b>Yes</b>
Propene	Clinton	1999	22	54	non>ep	<b>Yes</b>
Propene	Clinton	1998	16	26	non>ep	<b>Yes</b>
Propene	Deer Park	2001	56	14	non>ep	<b>Yes</b>
Propene	Deer Park	2000	8	9	non>ep	No
Propene	Deer Park	1999	24	54	ep>non	No
Propene	Haden Rd.	2001	44	5	non>ep	No
Propene	Baytown	2001	49	7	non>ep	<b>Yes</b>
Isoprene	Aldine	2000	5	16	ep>non	No
Isoprene	Bayland	2000	8	19	non>ep	<b>Yes</b>
Isoprene	Bayland	1999	22	48	non>ep	No
Isoprene	Bayland	1998	7	36	ep>non	No
Isoprene	Channelview	2001	53	10	ep>non	No
Isoprene	Clinton	2001	67	13	ep>non	No
Isoprene	Clinton	2000	48	23	ep>non	No
Isoprene	Clinton	1999	22	54	ep>non	No
Isoprene	Clinton	1998	16	26	ep>non	<b>Yes</b>
Isoprene	Deer Park	2001	56	14	non>ep	No
Isoprene	Deer Park	2000	8	9	non>ep	No
Isoprene	Deer Park	1999	24	54	non>ep	No
Isoprene	Haden Rd.	2001	32	5	non>ep	No
Isoprene	Baytown	2001	49	7	non>ep	<b>Yes</b>

Table 5-1. Results of two-sample t-tests for ethene, propene, and isoprene by location and year, July-September, 0500-0900 CST: number of days in each episode and non-episode median, whether episode or non-episode median weight percents are higher and whether these differences are different at a 95% confidence level. Significant differences are highlighted in boldface.

Species	Site	Year	Number of days/episode (ep)	Number of days/non-episode (non)	Which median weight percent is higher?	Different at a 95% confidence level?
1,3-butadiene	Aldine	2000	5	16	non>ep	<b>Yes</b>
1,3-butadiene	Bayland	2000	7	26	non>ep	No
1,3-butadiene	Bayland	1999	22	48	ep>non	No
1,3-butadiene	Bayland	1998	7	36	non>ep	No
1,3-butadiene	Channelview	2001	53	10	non>ep	<b>Yes</b>
1,3-butadiene	Clinton	2001	67	13	non>ep	No
1,3-butadiene	Clinton	2000	24	31	non>ep	<b>Yes</b>
1,3-butadiene	Clinton	1999	22	54	non>ep	<b>Yes</b>
1,3-butadiene	Clinton	1998	16	26	non>ep	No
1,3-butadiene	Deer Park	2001	56	14	non>ep	No
1,3-butadiene	Deer Park	2000	8	9	ep>non	<b>Yes</b>
1,3-butadiene	Deer Park	1999	24	54	non>ep	No
1,3-butadiene	Haden Rd.	2001	44	5	non>ep	No
1,3-butadiene	Baytown	2001	42	5	non>ep	No
Butenes	Aldine	2000	17	5	Non>ep	No
Butenes	Bayland	2000	20	8	Non>ep	No
Butenes	Bayland	1999	48	22	Non>ep	No
Butenes	Bayland	1998	31	6	Non>ep	<b>Yes</b>
Butenes	Channelview	2001	54	10	Non>ep	<b>Yes</b>
Butenes	Clinton	2001	68	14	Non>ep	<b>Yes</b>
Butenes	Clinton	2000	49	33	Non>ep	<b>Yes</b>
Butenes	Clinton	1999	55	22	Non>ep	<b>Yes</b>
Butenes	Clinton	1998	23	16	Non>ep	No
Butenes	Deer Park	2001	57	14	Ep>non	<b>Yes</b>
Butenes	Deer Park	2000	9	9	Ep>non	<b>Yes</b>
Butenes	Deer Park	1999	54	25	Ep>non	<b>Yes</b>
Butenes	Haden Rd.	2001	42	3	Non>ep	No
Butenes	Baytown	2001	49	7	Ep>non	No
Pentenes	Aldine	2000	17	5	Non>ep	No
Pentenes	Bayland	2000	20	8	Non>ep	<b>Yes</b>
Pentenes	Bayland	1999	49	23	Non>ep	<b>Yes</b>
Pentenes	Bayland	1998	21	5	Ep>non	No
Pentenes	Channelview	2001	54	10	Non>ep	<b>Yes</b>
Pentenes	Clinton	2001	68	14	Non>ep	No
Pentenes	Clinton	2000	49	33	Non>ep	<b>Yes</b>
Pentenes	Clinton	1999	55	22	Non>ep	<b>Yes</b>
Pentenes	Clinton	1998	27	18	Non>ep	<b>Yes</b>
Pentenes	Deer Park	2001	57	16	Ep>non	No
Pentenes	Deer Park	2000	6	3	Non>ep	No
Pentenes	Deer Park	1999	54	25	Non>ep	No
Pentenes	Haden Rd.	2001	45	5	Non>ep	No
Pentenes	Baytown	2001	49	7	Non>ep	<b>Yes</b>

Table 5-1. Results of two-sample t-tests for ethene, propene, and isoprene by location and year, July-September, 0500-0900 CST: number of days in each episode and non-episode median, whether episode or non-episode median weight percents are higher and whether these differences are different at a 95% confidence level. Significant differences are highlighted in boldface.

Species	Site	Year	Number of days/episode (ep)	Number of days/non-episode (non)	Which median weight percent is higher?	Different at a 95% confidence level?
Toluene	Aldine	2000	5	16	ep>non	No
Toluene	Bayland	2000	6	15	non>ep	No
Toluene	Bayland	1999	22	48	ep>non	No
Toluene	Bayland	1998	7	26	ep>non	<b>Yes</b>
Toluene	Channelview	2001	53	10	ep>non	<b>Yes</b>
Toluene	Clinton	2001	67	13	ep>non	No
Toluene	Clinton	2000	32	48	ep>non	No
Toluene	Clinton	1999	22	54	ep>non	<b>Yes</b>
Toluene	Clinton	1998	16	26	ep>non	<b>Yes</b>
Toluene	Deer Park	2001	56	14	ep>non	No
Toluene	Deer Park	2000	8	9	ep>non	No
Toluene	Deer Park	1999	24	54	non>ep	No
Toluene	Hayden Rd.	2001	44	5	non>ep	No
Toluene	Baytown	2001	49	7	non>ep	No
m-&p-xylene	Aldine	2000	5	16	non>ep	No
m-&p-xylene	Bayland	2000	6	15	non>ep	No
m-&p-xylene	Bayland	1999	22	48	ep>non	No
m-&p-xylene	Bayland	1998	7	26	ep>non	<b>Yes</b>
m-&p-xylene	Channelview	2001	53	10	ep>non	<b>Yes</b>
m-&p-xylene	Clinton	2001	67	13	ep>non	No
m-&p-xylene	Clinton	2000	32	48	ep>non	No
m-&p-xylene	Clinton	1999	22	54	non>ep	No
m-&p-xylene	Clinton	1998	16	26	non>ep	No
m-&p-xylene	Deer Park	2001	56	14	non>ep	No
m-&p-xylene	Deer Park	2000	8	9	ep>non	No
m-&p-xylene	Deer Park	1999	24	54	Non>ep	<b>Yes</b>
m-&p-xylene	Haden Rd.	2001	44	5	non>ep	No
m-&p-xylene	Baytown	2001	49	7	non>ep	No
1,2,4trimethylbenzene	Aldine	2000	5	16	ep>non	No
1,2,4trimethylbenzene	Bayland	2000	6	15	non>ep	No
1,2,4trimethylbenzene	Bayland	1999	22	48	non>ep	<b>Yes</b>
1,2,4trimethylbenzene	Bayland	1998	7	26	ep>non	No
1,2,4trimethylbenzene	Channelview	2001	53	10	ep>non	<b>Yes</b>
1,2,4trimethylbenzene	Clinton	2001	67	13	non>ep	No
1,2,4trimethylbenzene	Clinton	2000	32	48	non>ep	<b>Yes</b>
1,2,4trimethylbenzene	Clinton	1999	22	54	ep>non	No
1,2,4trimethylbenzene	Clinton	1998	16	26	non>ep	No
1,2,4trimethylbenzene	Deer Park	2001	56	14	non>ep	No
1,2,4trimethylbenzene	Deer Park	2000	8	9	non>ep	No
1,2,4trimethylbenzene	Deer Park	1999	24	54	non>ep	<b>Yes</b>
1,2,4trimethylbenzene	Haden Rd.	2001	44	5	non>ep	No
1,2,4trimethylbenzene	Baytown	2001	49	7	non>ep	No

Table 5-1. Results of two-sample t-tests for ethene, propene, and isoprene by location and year, July-September, 0500-0900 CST: number of days in each episode and non-episode median, whether episode or non-episode median weight percents are higher and whether these differences are different at a 95% confidence level. Significant differences are highlighted in boldface.

Species	Site	Year	Number of days/episode (ep)	Number of days/non-episode (non)	Which median weight percent is higher?	Different at a 95% confidence level?
ethyltoluenes	Aldine	2000	17	5	Ep>non	no
Ethyltoluenes	Bayland	2000	20	8	Non>ep	No
Ethyltoluenes	Bayland	1999	49	23	Ep>non	No
Ethyltoluenes	Bayland	1998	37	8	Ep>non	<b>Yes</b>
Ethyltoluenes	Channelview	2001	54	10	Ep>non	<b>Yes</b>
Ethyltoluenes	Clinton	2001	68	16	Ep>non	No
Ethyltoluenes	Clinton	2000	48	34	Non>ep	<b>Yes</b>
Ethyltoluenes	Clinton	1999	55	22	Ep>non	No
Ethyltoluenes	Clinton	1998	27	18	Ep>non	No
ethyltoluenes	Deer Park	2001	56	16	Non>ep	No
Ethyltoluenes	Deer Park	2000	9	8	non>ep	No
Ethyltoluenes	Deer Park	1999	54	25	Non>ep	<b>Yes</b>
Ethyltoluenes	Haden Rd.	2001	184	25	Non>ep	No
Ethyltoluenes	Baytown	2001	240	33	Ep>non	<b>Yes</b>

#### 5.4 DIURNAL CHARACTERISTICS

Sixteen species, based on their abundance in concentration and reactivity-weight percent, were examined at each site on an hourly basis for days of ozone episodes and non-episodes. Hourly notched box whisker plots of these species were generated to examine any diurnal variations between ozone episode and non-episode days. Example notched box whisker plots of isobutane, ethene, propene, and toluene by weight percent at Clinton in 1999 for episode and non-episode days are shown in **Figures 5-6 and 5-7**.

Significant findings include

- Consistent with earlier findings, concentrations of most species are often higher on episode days.
- While concentration differences were observed for most species between episode and non-episode days, there was generally little difference in weight percent or reactivity-weighted data between ozone episodes and non-episodes.
- The lack of compositional differences indicates that these types of emissions occurred frequently.
- Weight percents of reactive species such as ethene and propene were generally higher in the morning; this is consistent with nighttime emissions into a near stagnant atmosphere, followed by depletion via photochemistry in the morning.

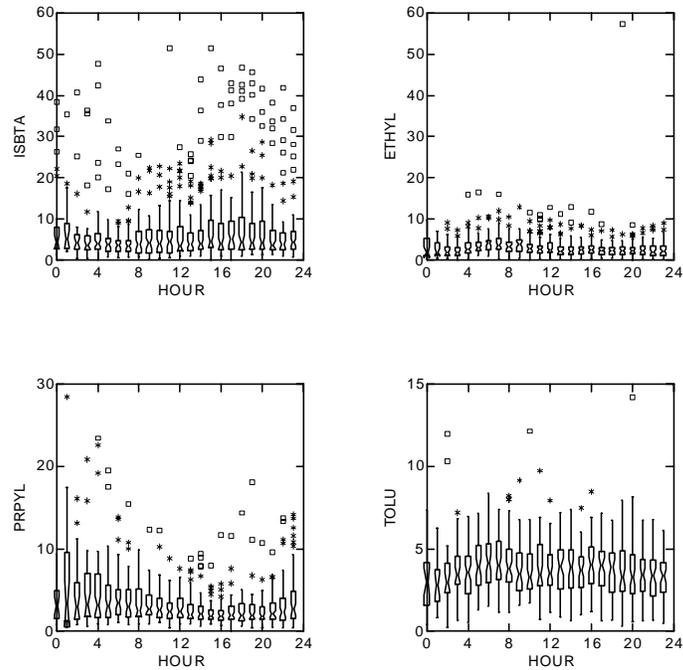


Figure 5-6. Notched box whisker plots of isobutane (ISBTA), ethene (ETHYL), propene (PRPYL), and toluene (TOLU) by weight percent for non-episode days at Clinton, July-September 1999. Scales differ from Figure 5-7.

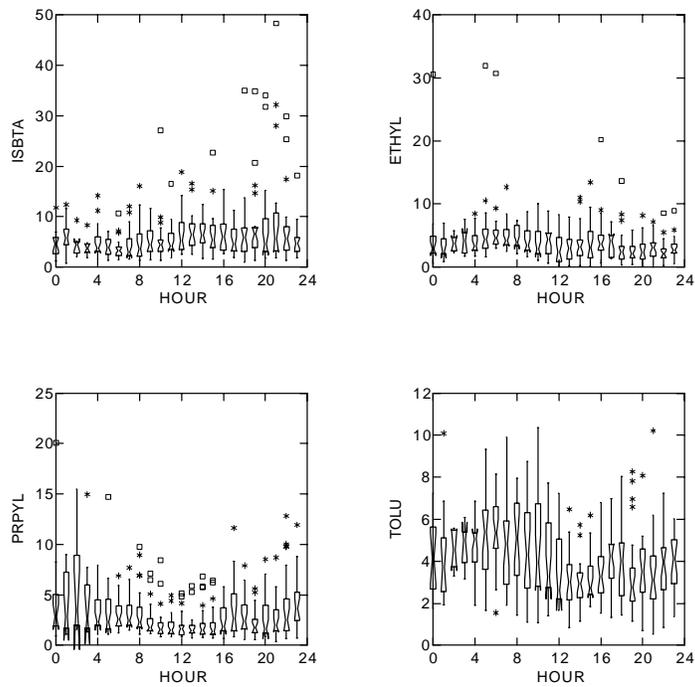


Figure 5-7. Notched box whisker plots of isobutane (ISBTA), ethene (ETHYL), propene (PRPYL), and toluene (TOLU) by weight percent for episode days at Clinton, July-September 1999. Scales differ from Figure 5-6.

## 5.5 ARE HIGH TNMOC DAYS CONTRIBUTING TO HIGH OZONE?

While previous analyses are showing little compositional difference between ozone episode and non-episode days, median hydrocarbon concentrations are often higher on episode days. To investigate whether high concentrations are closely related to ozone production, the 95<sup>th</sup> percentile for TNMOC and individual species was found. **Table 5-2** lists these values at Clinton for all of 1998-2001. The number of samples during the summer that had high concentrations during ozone episode days and non-episode days were then compared.

Table 5-2. Statistics for hydrocarbon concentrations (ppbC) at Clinton, July-September 1998-2001.

	Ethene	Propene	1,3-butadiene	C4-C5 Alkanes	Xylenes	TNMOC
Total number of samples	7522	8032	7475	7943	8099	6670
Median values	4.58	3.73	0.68	41.6	6.41	170.1
95 <sup>th</sup> percentile values	25.21	25.88	13.83	309.47	22.37	768.75
Number of samples in 95 <sup>th</sup> percentile	377	402	374	398	406	334
Percent of samples in 95 <sup>th</sup> percentile on non-episode days	72	81	93	74	60	70
Percent of samples in 95 <sup>th</sup> percentile on episode days	28	19	7	26	40	30

While concentrations of species were generally higher on episode days, the values in the 95<sup>th</sup> percentile for ethene, propene, 1,3-butadiene, the C4-C5 alkanes, and xylenes occurred mostly on non-episode days at Clinton during the summers of 1998-2001. This indicates high concentrations of these reactive species and abundant paraffins do not necessarily lead to high ozone production. The 95<sup>th</sup> percentile values of TNMOC also occurred mostly on non-episode days, showing that high concentrations of total VOCs do not always lead to high ozone concentrations.

## 5.6 OLEFIN-TO-NO<sub>x</sub> RATIOS

One indicator of ozone formation potential is a ratio between reactive olefin concentrations, such as ethene, propene, and 1,3-butadiene, to NO<sub>x</sub>. A higher ratio is thought of as “hot”, or more reactive, and can be indicative of a potential rapid increase in ozone formation. The median ratios on episode and non-episode mornings (0500-0900 CST) were calculated for each site and year. The Clinton site in July-August 2001 was selected to examine the variation

of olefin-to-NO<sub>x</sub> ratios based on wind direction. A detailed map of the area around the Clinton site (**Figure 5-8**) shows a dense area of industry to the east and southeast while to the west is a major freeway. Therefore, the olefin-to-NO<sub>x</sub> ratios were compared between advection from the HSC (60-150 degrees) and from the freeway (225-315 degrees). These ratios were calculated on a strict ppb-to-ppb basis. (Hydrocarbons are generally reported in ppbC; to convert to ppb the concentration needs to be divided by the number of carbons in the hydrocarbon, i.e., 2 ppbC ethene = 1 ppb ethene.)

General findings include

- Olefin-to-NO<sub>x</sub> ratios were generally below 2, with median values ranging from 0.03 to 0.32.
- Olefin-to-NO<sub>x</sub> ratios were two to eight times higher at Clinton with advection from the Ship Channel area (60-150 degrees) during the morning, and three to seven times higher from the east during all hours. This observation indicates that the industrial emissions from the east have a greater ozone formation potential than the lower ratios found in emissions from the west.
- There was generally little difference in olefin-to-NO<sub>x</sub> ratios between episode and non-episode days by wind direction.

Median ethane-to-NO<sub>x</sub> ratios varied between 0.05 and 0.4, and are shown in **Figure 5-9**. Median propene-to-NO<sub>x</sub> ratios were between 0.03 and 0.15 (shown in **Figure 5-10**), while 1,3-butadiene ratios were below 0.015 (not shown). There is generally little difference between the median ratio on episode and non-episode days for most sites and years. One exception is at Deer Park in 1999, where episode days had a ratio nearly twice that of non-episode days. This result is not consistent between years. There was also no corresponding difference of propene or 1,3-butadiene ratios between episode and non-episode days at this site and year, which suggests that ethene is somewhat independent of other light olefin emissions.

Olefin to NO<sub>x</sub> ratios were also investigated based on wind direction at Clinton. Similar to analyses done in Section 4.2, the olefin to NO<sub>x</sub> ratios were computed when wind was coming from the Ship Channel area (60-150 degrees) and from the freeway (225-315 degrees). These box whisker plots are shown in **Figures 5-11 and 5-12**. The Ship Channel ratios were consistently much higher than the ratios when wind was coming from the freeway area. This suggests that the fresh industrial emissions from the Ship Channel area are “hot”, and have higher ozone formation potential than the emissions from the freeway area. These ratios are also higher than the median over all wind directions, again indicating that the Ship Channel region has higher than normal emissions of reactive species.



Figure 5-8. 3.5-minute digital orthophotoquads of the area surrounding the Clinton monitoring site. Photos are circa 1995 from the U.S. Geological Survey.

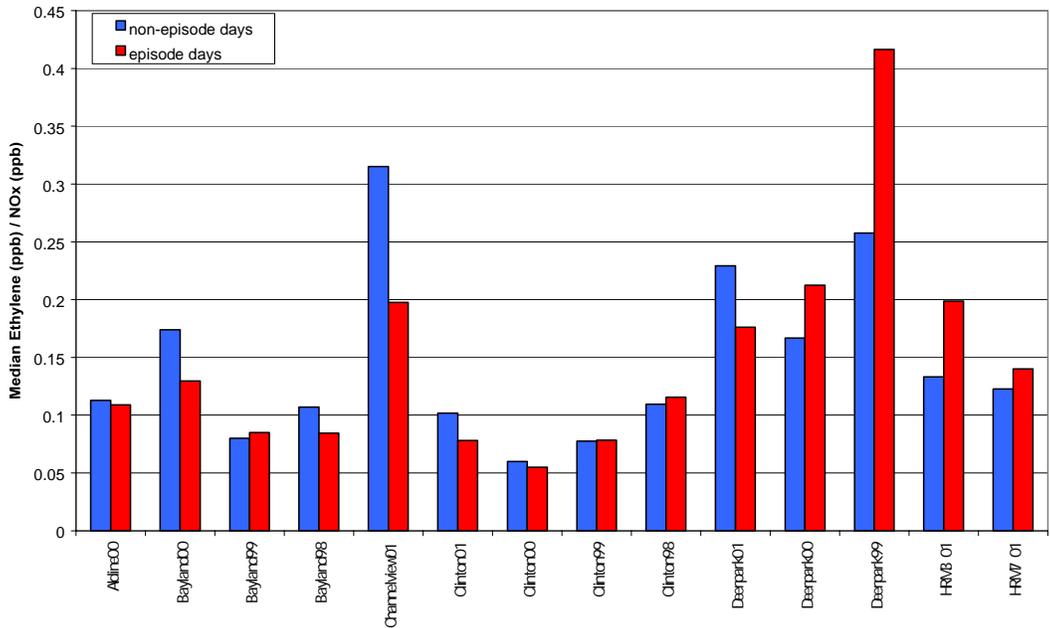


Figure 5-9. Median ethene (ppb)/NO<sub>x</sub> (ppb) ratios for each site and year during episode and non-episode mornings (0500-0900 CST).

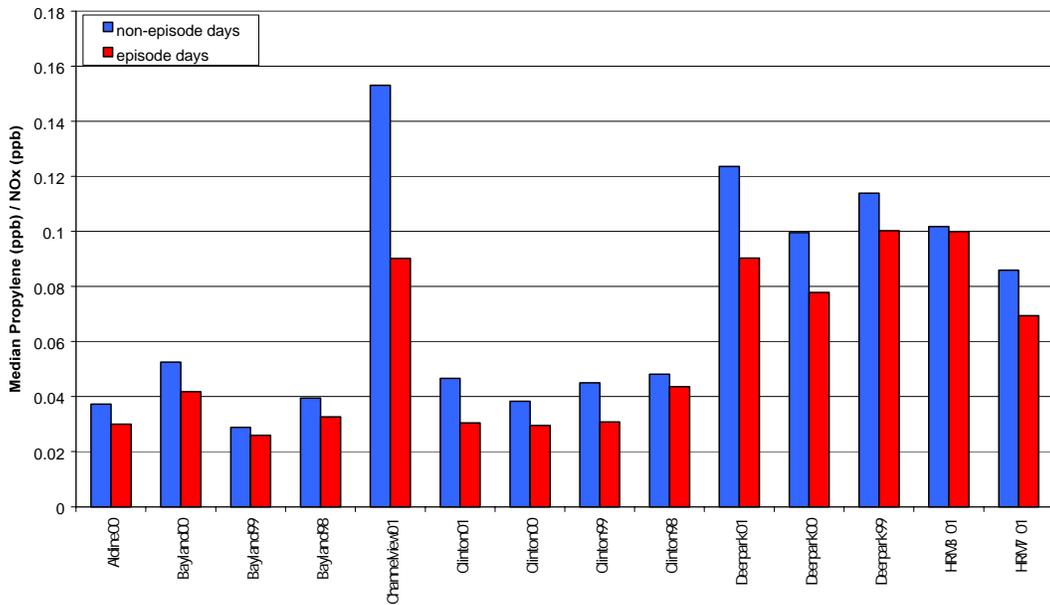


Figure 5-10. Median propene (ppb)/NO<sub>x</sub> (ppb) ratios for each site and year during episode and non-episode mornings (0500-0900 CST).

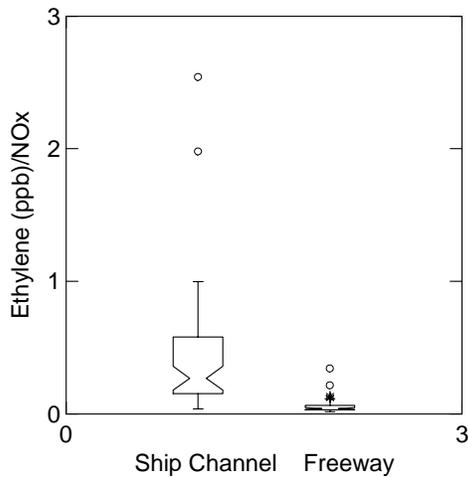


Figure 5-11. Notched box whisker plots of ethene (ppb)/NO<sub>x</sub> at Clinton, August-October 2001 (0500-0900 CST), from the Ship Channel (60-150 degrees) and freeway (225-315 degrees).

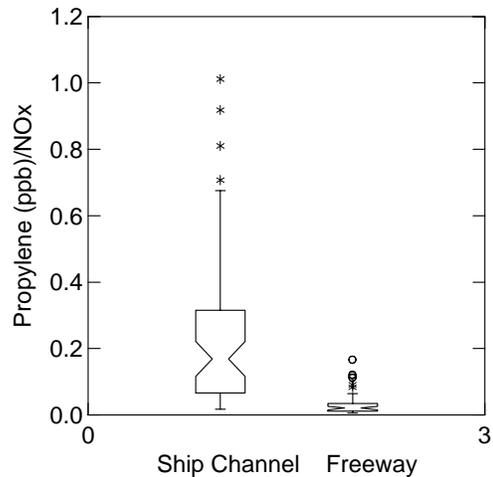


Figure 5-12. Notched box whisker plots of propene (ppb)/NO<sub>x</sub> at Clinton, August-October 2001 (0500-0900 CST) from the Ship Channel (60-150 degrees) and freeway (225-315 degrees).

## 5.7 TOTAL REACTIVITY

While there was no significant difference between episode and non-episode days on a weight percent basis, a measure of the total reactivity provides another scale to gauge the presence of a “hot”, or reactive, mixture on episode versus non-episode days. Even if there is no significant difference on a weight percent basis, on a reactivity weighted scale small differences can become more pronounced, which may then yield a difference in total reactivity between episode and non-episode days. To investigate this, the sum of all species’ weight percents multiplied by their individual MIR reactivity were compared between episode and non-episode days during the morning to see if the presence of hot VOC mixtures led to ozone episodes. This total reactivity would be higher if reactive species such as ethene, propene, or toluene comprised a larger fraction of the total composition of the air mass.

The sum of all species’ weight percents \*MIR for each site during episode and non-episode mornings is shown in **Figure 5-13**. At most sites and years, there is little difference in the sum wMIR between episode and non-episode days. Since the composition of episode and non-episode days by weight percent was generally not significantly different, this lack of difference on the wMIR scale is consistent. One surprise is the high wMIR during episode mornings at Bayland in 1999. Pie charts are shown in **Figures 5-14 and 5-15** detailing which species comprise the total reactivity on episode and non-episode mornings at Bayland in 1999. There does not appear to be a large difference between the composition of episode and non-episode days, so the slight increase of a number of reactive (ethene, toluene) and abundant (C4-C5 alkanes) species was responsible for the higher amount of total reactivity.

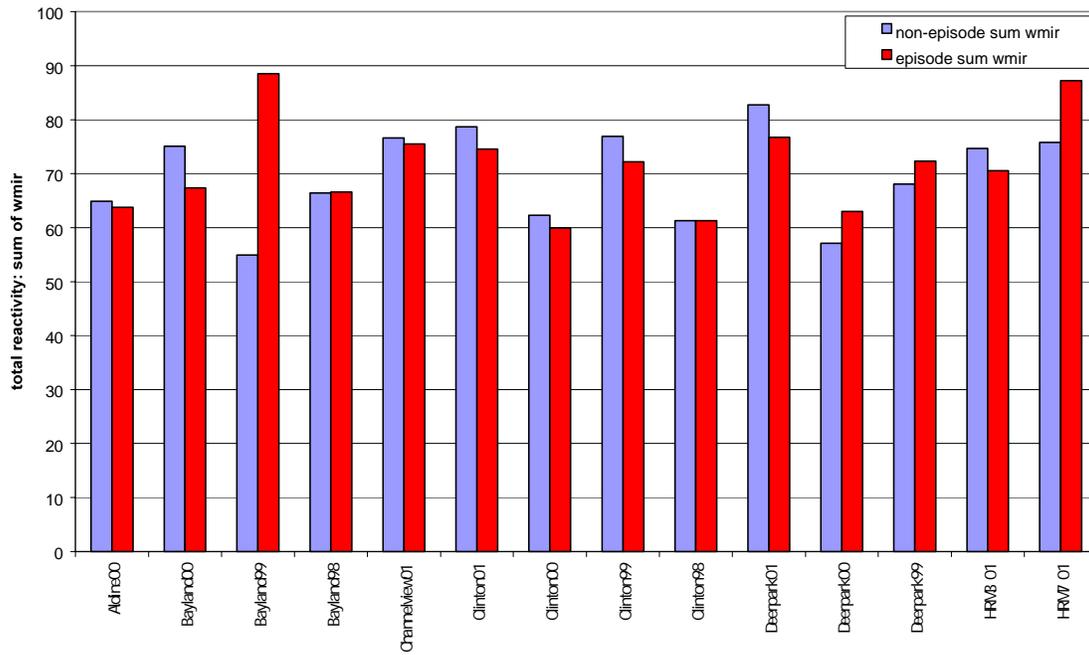


Figure 5-13. Sum of total reactivity (wt% \*MIR) on episode and non-episode mornings 0500-0900 CST at each site and year.

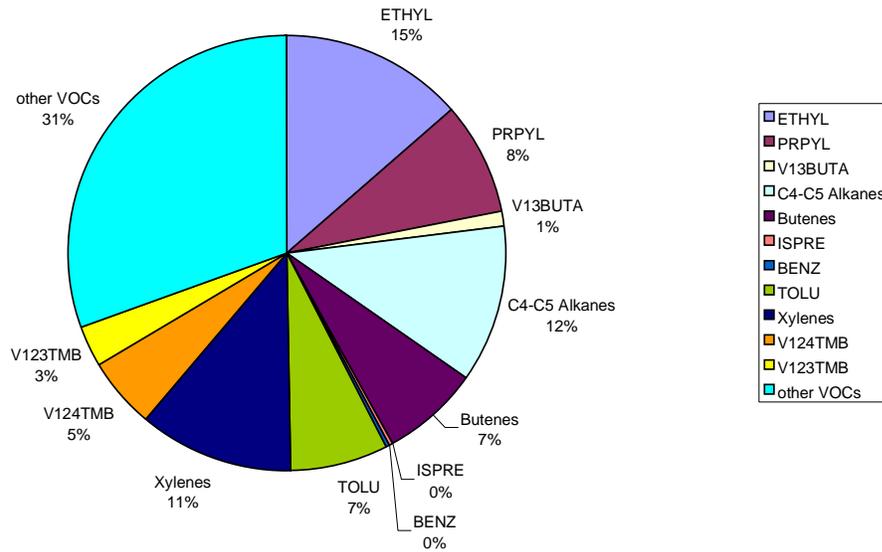


Figure 5-14. Pie chart detailing the composition of total reactivity (wt% \*MIR) at Bayland, 1999 on non-episode mornings (0500-0900 CST).

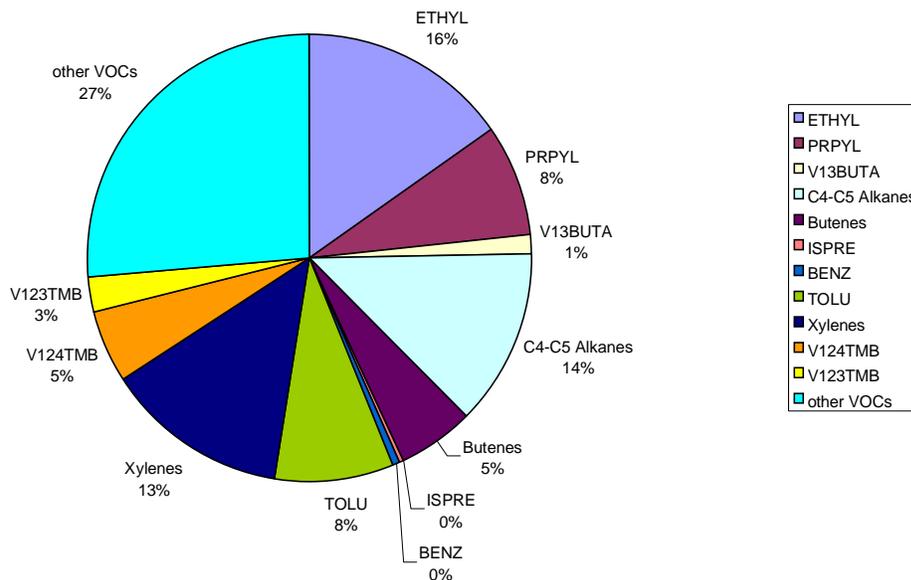


Figure 5-15. Pie chart detailing the composition of total reactivity (wt% \*MIR) at Bayland, 1999 on non-episode mornings (0500-0900 CST).

**Figures 5-16 and 5-17** show notched box whisker plots of total reactivity (on a weight percent \*MIR scale) at Clinton and Deer Park in the summer months (July-October) of 1998-2001 from 0500 to 0900 CST. There is generally no difference in total reactivity between episode and non-episode days evident. This is consistent with other findings in this report where composition, even on a reactivity-weighted scale, is not significantly different between episode and non-episode days.

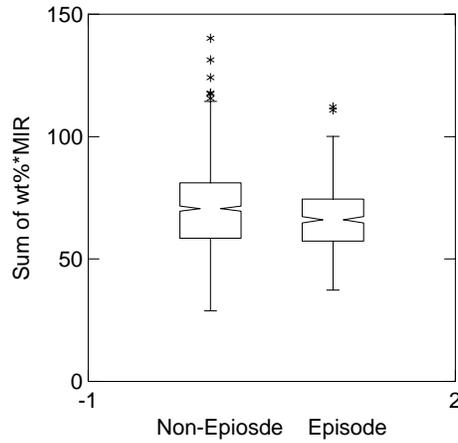


Figure 5-16. Notched box whisker plot of total reactivity (wt% \*MIR) on episode and non-episode mornings (0500-0900 CST), July-October 1998-2001, at Clinton.

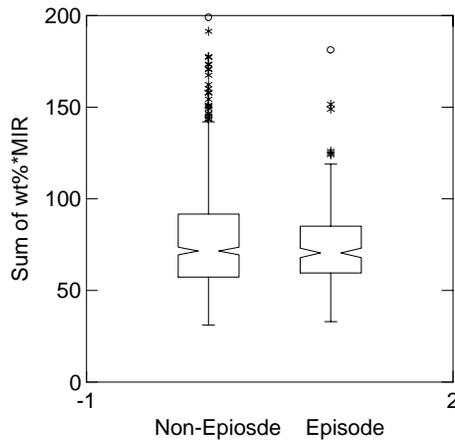


Figure 5-17. Notched box whisker plot of total reactivity (wt% \*MIR) on episode and non-episode mornings (0500-0900 CST), July-October 1998-2001, at Deer Park.

## 5.8 TOTAL REACTIVITY COMPOSITION: WHAT SPECIES ARE IMPORTANT?

As discussed in Section 3.8, no hydrocarbon dominated the total reactivity at any site during the summers of 1998-2001. However, a similar analysis by ozone episode and non-episode days may indicate if particular hydrocarbons are the driving compound behind high ozone days on a reactivity-scale basis. Median values of each species during the summer for each site and year were calculated on episode and non-episode days. Contributions from each compound during the morning (0500-0900 CST) were calculated as the hydrocarbon's median value compared to the sum of all species' median values on a wMIR-scale basis. Results are shown in **Figures 5-18 through 5-22**.

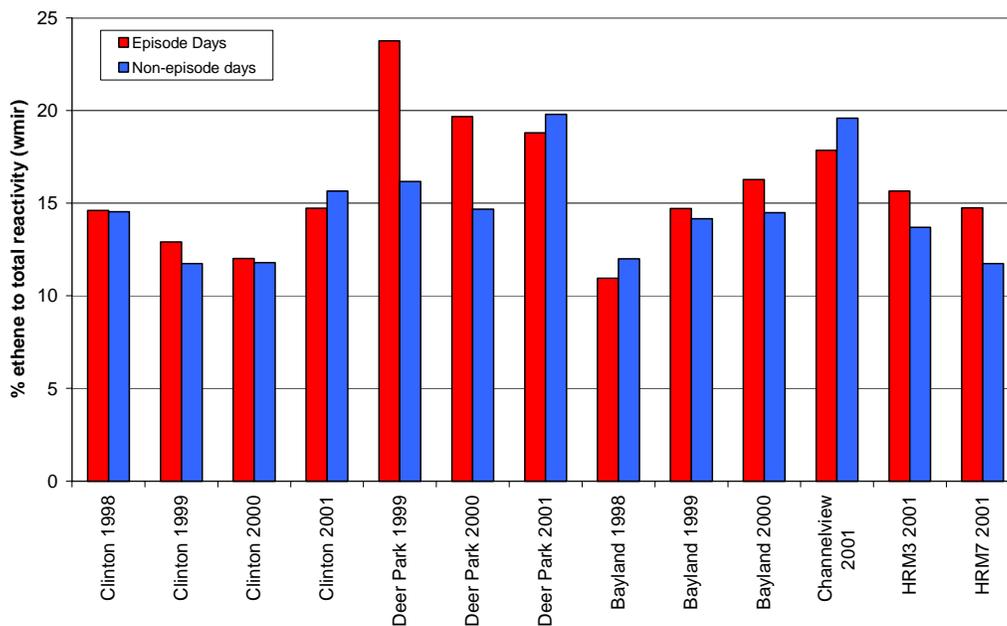


Figure 5-18. Median contribution (%) of ethene to the total reactivity (wMIR) during the summer on episode and non-episode mornings (0500-0900 CST).

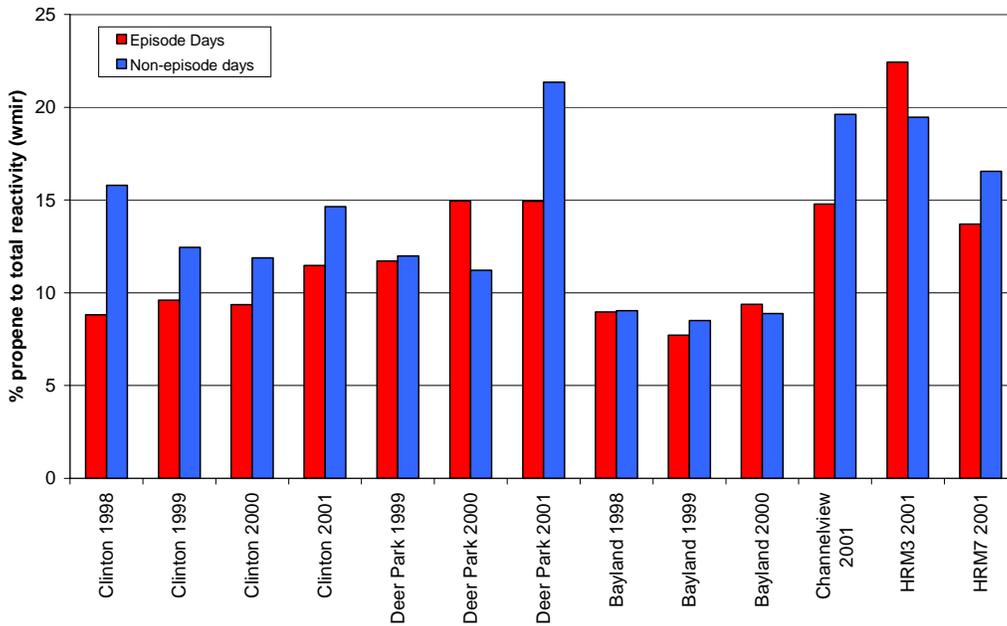


Figure 5-19. Median contribution (%) of propene to the total reactivity (wMIR) during the summer on episode and non-episode mornings (0500-0900 CST).

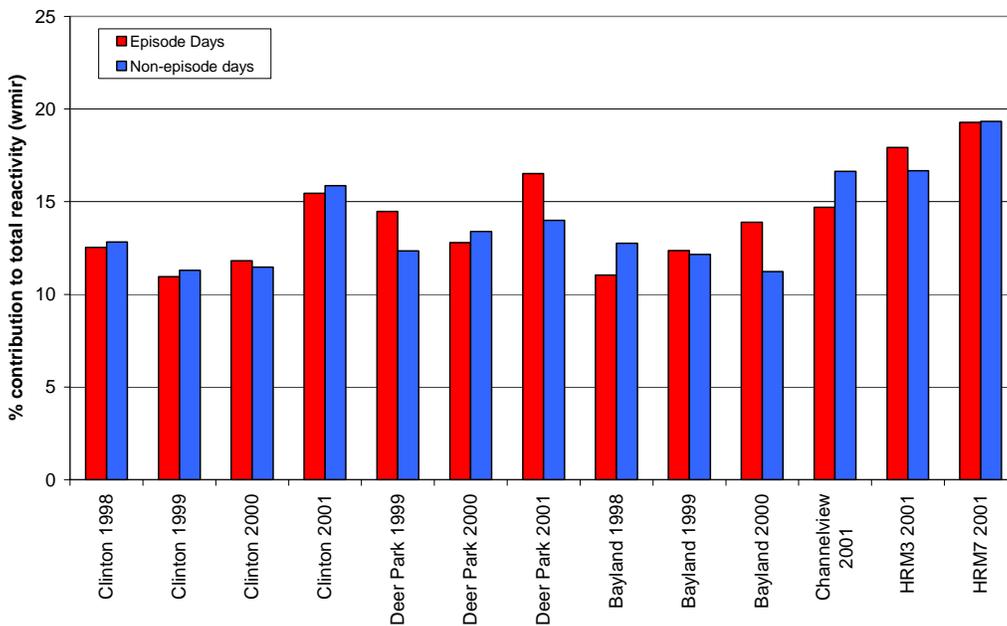


Figure 5-20. Median contribution (%) of C4-C5 alkanes to the total reactivity (wMIR) during the summer on episode and non-episode days.

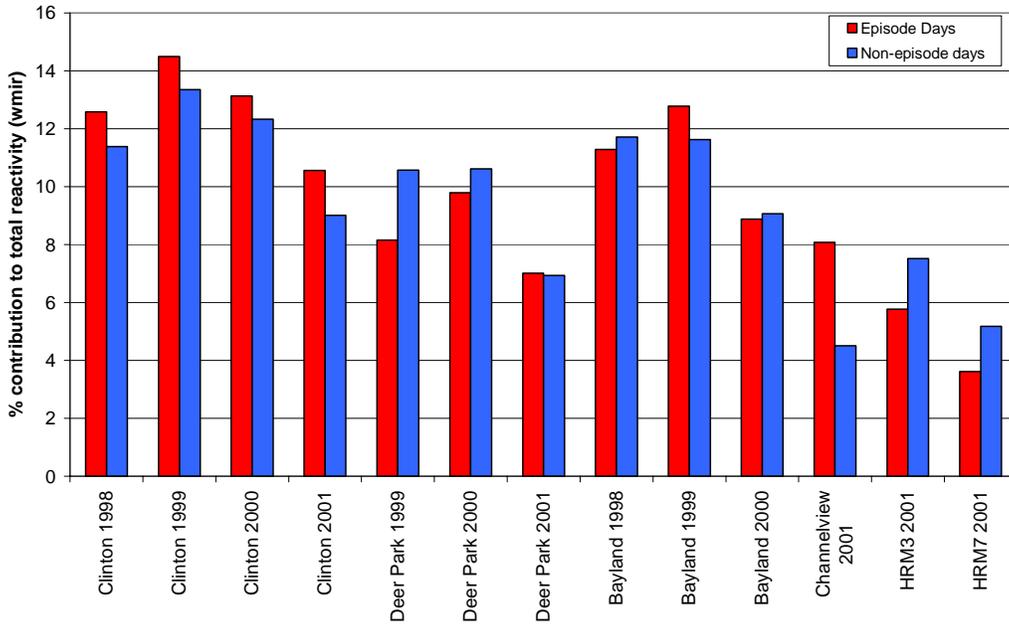


Figure 5-21. Median contribution (%) of xylenes to the total reactivity (wMIR) during the summer on episode and non-episode days.

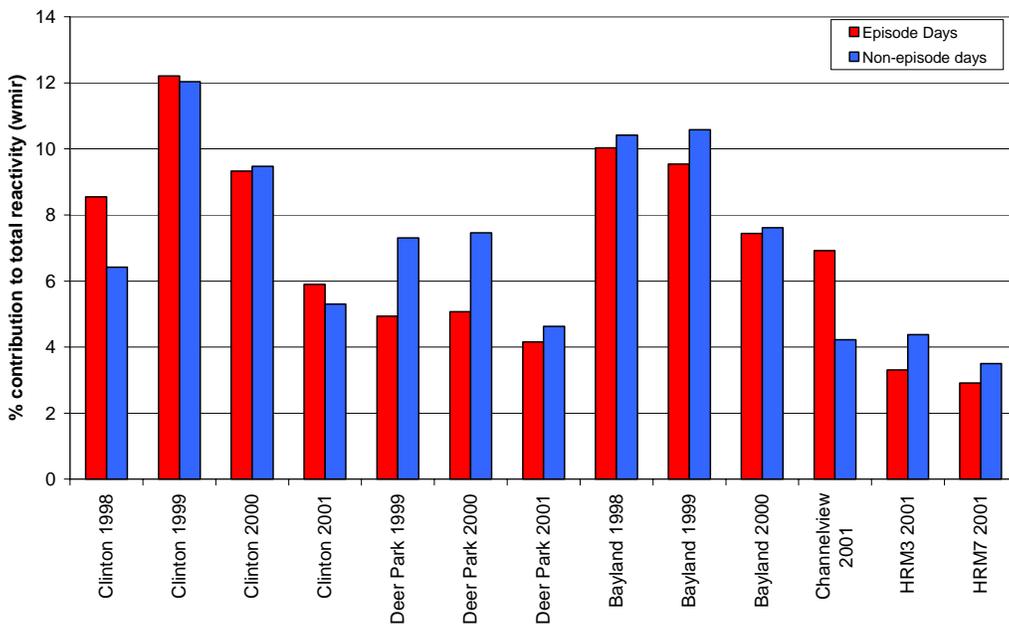


Figure 5-22. Median contribution (%) of trimethylbenzenes to the total reactivity (wMIR) during the summer on episode and non-episode days.

Similar to other analyses, values of reactive (light olefins, aromatics) or abundant (C4-C5 alkanes) species on a weight percent \*MIR scale basis are generally not significantly higher on mornings of ozone episodes. There are two exceptions:

- At Channelview in 2001, the contributions from xylenes and trimethylbenzenes to total reactivity are statistically significantly higher on episode mornings.
- At Deer Park in 1999, contribution of ethene to total reactivity is significantly higher on episode mornings.

As in all the previous analyses, there are no clear patterns observed between episode and non-episode days, indicating that the emissions composition is relatively consistent from day to day.

## 6. CONCLUSIONS AND RECOMMENDATIONS

A wide variety of analyses have been completed using PAMS data collected in the Houston area from 1998 through 2001 in order to characterize the types and concentrations of hydrocarbons present and the conditions leading to elevated ozone levels. Concentrations and relative composition of the hydrocarbons were characterized by site, year, month, day, hour, and wind direction. Comparisons of the hydrocarbons on ozone episode days versus non-episode days were also performed. This section summarizes our conclusions and recommendations.

### 6.1 CONCLUSIONS

#### 6.1.1 Overall Findings

- *Auto-GC data are extremely useful.* Hourly data are essential to capture the temporal-spatial variability in the chemical composition of air masses and meteorological conditions that play a pivotal role in ozone formation in the Houston area.
- *Hydrocarbon speciation is vital to understanding and predicting ozone formation in the Houston area.* For example, a total hydrocarbon (THC) monitor is an insufficient substitute for an auto-GC in a region with large amounts of fresh emissions of widely varying composition.
- *More than one auto-GC site is needed.* Significant spatial differences in the chemical composition of air masses, predominant meteorology, and ozone formation are evident. The availability of data from various sites in the Houston area remains extremely valuable for analysis of ozone events and for determining source impacts on different areas.
- *High hydrocarbon concentrations are a routine occurrence.* Extremely high hydrocarbon concentrations can occur at all sites during any time of the day, week, month and year. This lack of periodicity indicates that sources routinely emit large quantities of various hydrocarbons, including hydrocarbons conducive to ozone formation.
- *The hydrocarbon composition is dominated by industrial emission.* In nearly all other cities with auto-GC data (as a part of the PAMS program), hydrocarbons are dominated by motor vehicle emissions. However, in Houston, the majority of emissions are generally dominated by industrial activity. This signature typically has very high concentrations of all species, including increased olefins and aromatics.
- *No one hydrocarbon dominates ozone formation.* Total reactivity on both OH and MIR scales is not dominated by a single compound or hydrocarbon family. Rather, a wide range of species is important, including the light olefins, C4-C6 paraffins, and several aromatic hydrocarbons. On average, the twelve target species designated by TNRCC were 67% of the total OH reactivity and 65% of the total MIR reactivity. Note that this analysis did not include formaldehyde or acetaldehyde, both of which have been found to be significant in ozone production in the Houston area (Brown et al., 2002c).

- *Hydrocarbon composition is generally the same on all days.* While concentrations of all the hydrocarbons are generally higher on the mornings of ozone episode days, there is little difference in composition between episode and non-episode days. Therefore, given the fairly constant hydrocarbon composition in the Houston area, any day with the correct meteorological conditions (slow air movement, increased solar radiation, etc.) has the potential to be an ozone episode day. The importance of meteorology is consistent with other studies (Brown et al., 2002b, 2002c; MacDonald and Roberts, 2002; Roberts et al., 2002).
- *High hydrocarbon concentrations are necessary but not sufficient for ozone formation.* Days of high TNMOC do not necessarily lead to high ozone concentrations, because meteorology plays the most vital role in ozone formation (Roberts et al., 2002).

### 6.1.2 Site Differences

- *The composition differed significantly from site to site.* Sampling sites at Clinton and Baytown are both heavily influenced by nearby industrial emissions. Distinct source types by wind direction were evident. Motor vehicle and industrial signatures could be separately observed at the Clinton Drive site. Bayland exhibited a more aged urban signature but also showed evidence of influence from the Ship Channel emissions in many samples. Deer Park and Hayden Road also had samples with clear industrial signatures. The composition of the industrial signatures at each site was unique. The number of samples taken at Aldine was insufficient for a meaningful detailed analysis.

### 6.1.3 Composition

- *Significant anthropogenic isoprene emissions occur.* Isoprene shows a typical biogenic diurnal pattern. However, there are a number of high concentrations evident during the night and early morning that are most likely industrial emissions. At some sites, a clear source region of elevated isoprene was found by wind direction analysis, again suggesting industrial emissions contribute to the total isoprene found in the Houston area.
- *Acetylene is associated with both vehicular and industrial emissions.* Acetylene and ethene are typically used as tracers for vehicle exhaust in chemical mass balance analyses. However, both these hydrocarbons have significant industrial sources and, thus, cannot be used as unique tracers for vehicle exhaust.
- *Very high concentrations of 1,3-butadiene were sometimes observed.* 1,3-butadiene is generally not in abundance and appears to have minimal impact on ozone formation potential. However, extreme high concentration outliers were detected at all hours during all times of the week and year. These extremely high concentrations may impact ozone formation in a small time frame and may indicate that 1,3-butadiene is emitted in generous quantities but is reacted away prior to impacting the sampling sites.
- *The auto-GC appears to capture most of the C2-C12 hydrocarbons important to ozone formation.* Other studies that included carbonyl sampling (Brown et al., 2002c) found that the PAMS species sampled by auto-GC often capture most species contributing to

the total reactivity. On either the MIR or OH reactivity scales, only 1% of the total reactivity was from non-carbonyl, non-PAMS (auto-GC) species.

- *Carbonyl compounds are important to ozone formation.* While not a part of this analysis, carbonyl compounds were investigated in a complementary study. On the MIR and OH scales respectively, carbonyls accounted for 43% and 22% of the total reactivity during rapid ozone rises (Brown et al., 2002c).

## **6.2 RECOMMENDATIONS**

### **6.2.1 Monitoring**

- *Include carbonyls such as formaldehyde, acetaldehyde, and higher carbonyls in routine monitoring programs.* Other studies have indicated that these polar species are both abundant and important in ozone formation (e.g., Brown et al., 2002c).
- *Continue using auto-GCs in the Houston area to characterize VOCs.* Augmenting the auto-GCs with a THC monitor, such as the one at San Jacinto, is desirable, but THC monitors should not be used as substitutes for auto-GCs.
- *Continue current level of data validation and quality control.* The quality of auto-GC data from the Houston sites was excellent.
- *Continue auto-GC monitoring at Clinton and Deer Park.* These sites are important to establish long-term trends in emissions and to continue to provide data with which to investigate conditions necessary for ozone formation.
- *Consider continuing monitoring at Baytown.* This site exhibits unique industrial influences. This site appears to be impacted by source types different from those impacting Clinton and can be further utilized to assess compliance regulations and characterize emissions in the eastern Houston area.
- *Consider establishing an auto-GC monitoring site to the north of central Houston.* Such a site would be useful to characterize emissions in this region, establish the locations of significant VOC sources, and investigate transient ozone events in the late afternoon and evening as they advect from the central source area of the Houston Ship Channel to other locations via the Bay breeze.

### **6.2.2 Additional Analyses to Consider**

- Investigate the differences (emission sources, advection patterns) between air masses when ethene and propene and/or aromatic hydrocarbons dominate the overall reactivity.
- Integrate auto-GC hydrocarbon analyses with other analyses including emission inventory evaluation, triggered and special canisters, and the conceptual model.
- Investigate the reported industrial upsets (in which speciation of the VOCs is known) using wind direction and auto-GC data. Particular attention could be paid to ozone episode days.

- Compare long-term trends of selected hydrocarbons with control program implementation.
- Analyze data from a site north of central Houston (such as Aldine) when sufficient data are available.
- Utilize chemical models such as UNMIX, positive matrix factorization (PMF) and/or chemical mass balance (CMB) to determine contributions from specific sources and source areas to VOC concentrations and ozone formation potential.

When we delivered our extended outline in 2001, we prepared a table that contained a list of additional analyses to consider to completely fill in all the gaps in the extended outline. In this report, we have addressed many but not all of the analyses described. The following analyses were not performed as a part of this work order in order to meet schedule and budget commitments, but should be considered for future work:

- Follow-up on the comparison of the TexAQS 2000 study period with previous years of hydrocarbon data (initiated by TNRCC in 2001). Now that the hydrocarbon data are validated and we have a better understanding of the changes in wind direction from year to year at Clinton Drive, for example, this analysis could be expanded. Box whisker plots of the abundant hydrocarbons by wind sector from previous years should be compared to the 2000 study period results by wind sector (or other study periods). Ratios, extreme values, and wind roses should also be examined.
- Extend the comparison of the 1993 Clinton Drive data with 1998-2001 data by addressing the emission inventory changes from then (1993) to now (2000 or 2001). Again, analyses should consider wind direction, use a variety of statistical metrics (including median and extreme values), and use different forms of the data (including weight percent and reactivity-weighted data).
- Compare long-term trends in auto-GC data with trends in toxics data.
- Expand the high i-butane concentration episode (and possibly investigate other high VOC episodes) by including an evaluation of hourly mixing height, wind direction, wind speed, and other supplemental data.

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## **APPENDIX A**

### **HYDROCARBON NAMES, AIRS CODES, ABBREVIATIONS, AND SPECIES GROUPS**

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Table A-1. AIRS code, abbreviation, hydrocarbon name, and species group (O=olefin, P=paraffin, A=aromatic).

AIRS code	Abbreviation	Hydrocarbon	Species Group
43206	acety	Acetylene	O
43203	ethyl	Ethylene	O
43202	ethan	Ethane	P
43205	prpyl	Propylene	O
43204	propa	Propane	P
43214	isbta	Isobutane	P
43280	1bute	1-Butene	O
43212	nbuta	n-Butane	P
43216	t2bte	trans-2-Butene	O
43217	c2bte	cis-2-Butene	O
43282	3mlbe	3-Methyl-1-Butene	O
43221	ispna	Isopentane	P
43224	1pnte	1-Pentene	O
43220	npnta	n-Pentane	P
43243	ispre	Isoprene	O
43226	t2pne	trans-2-Pentene	O
43227	c2pne	cis-2-Pentene	O
43228	2m2be	2-Methyl-2-Butene	O
43244	22dmb	2,2-Dimethylbutane	P
43283	cypne	Cyclopentene	O
43234	4mlpe	4-Methyl-1-Pentene	O
43242	cypna	Cyclopentane	P
43284	23dmb	2,3-Dimethylbutane	P
43285	2mpna	2-Methylpentane	P
43230	3mpna	3-Methylpentane	P
43246	2mlpe	2-Methyl-1-Pentene	O
43231	nhexa	n-Hexane	P
43289	t2hex	trans-2-Hexene	O
43290	c2hex	cis-2-Hexene	O
43262	mcpna	Methylcyclopentane	P
43247	24dmp	2,4-Dimethylpentane	P
45201	benz	Benzene	A
43248	cyhxa	Cyclohexane	P
43263	2mhxa	2-Methylhexane	P
43291	23dmp	2,3-Dimethylpentane	P
43249	3mhxa	3-Methylhexane	P
43250	224tmp	2,2,4-Trimethylpentane	P
43232	nhept	n-Heptane	P
43261	mcyhx	Methylcyclohexane	P
43252	234tmp	2,3,4-Trimethylpentane	P
45202	tolu	Toluene	A

Table A-1. AIRS code, abbreviation, hydrocarbon name, and species group (O=olefin, P=paraffin, A=aromatic).

AIRS code	Abbreviation	Hydrocarbon	Species Group
43960	2mhép	2-Methylheptane	P
43253	3mhép	3-Methylheptane	P
43233	noct	n-Octane	P
45203	ebenz	Ethylbenzene	A
45109	m/pxy	m/p-Xylene	A
45205	mxyíl	m-Xylene	A
45206	pxyl	p-Xylene	A
45220	styr	Styrene	A
45204	oxyl	o-Xylene	A
43235	nnon	n-Nonane	P
45210	ispbz	Isopropylbenzene	A
45209	npbz	n-Propylbenzene	A
43256	apine	alpha-Pinene	O
45207	135tmb	1,3,5-Trimethylbenzene	A
45208	124tmb	1,2,4-Trimethylbenzene	A
43257	bpine	beta-Pinene	O
45211	oetol	o-Ethyltoluene	A
45212	metol	m-Ethyltoluene	A
45213	petol	p-Ethyltoluene	A
45218	mdeben	m-diethylbenzene	A
45219	pdeben	p-diethylbenzene	A
45225	123tmb	1,2,3-trimethylbenzene	A
43238	ndec	n-Decane	P
43954	nundc	n-Undecane	P
43102	tnmoc	Total Non-Methane Organic Compounds	
43502	form	Formaldehyde	C
43503	aceta	Acetaldehyde	C
43551	acet	Acetone	C
43218	13buta	1,3-butadiene	O
43225	2m1bte	2-methyl-1-butene	O
43295	3ethex	3-ethylhexane	P
43955	25mhex	2,5-dimethylhexane	P
43293	hex24m	2,4-dimethylhexane	P
43294	hex23m	2,3-dimethylhexane	P
43222	propa22m	2,2-dimethylpropane	P
43270	ibute	Isobutene	O
43240	mcpne	Methylcyclopentene	O
43395	4mhpte	4-Methylheptane	P
43000	pamshc	Sum PAMS Target Species	

## **APPENDIX B**

### **SUMMARY STATISTICS FOR HYDROCARBON CONCENTRATIONS AT THE CLINTON DRIVE SITE, 1998-2001**

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Table B-1. Summary statistics by concentration at Clinton in 1998.

SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
ETHAN	7132	0	287.7	16.62	23.69	22.09	0.93
ETHYL	7132	0	597.4	6.57	11.50	17.35	1.51
PROPA	7132	0	582.5	16.41	23.80	24.75	1.04
PRPYL	7132	0	1493	4.06	9.51	30.99	3.26
ISBTA	7132	0	3528	10.01	42.47	138.17	3.25
NBUTA	7132	0	1923	16.835	36.31	79.08	2.18
V13BUTA	7132	0	448.9	0.77	4.63	19.41	4.19
ACETY	7132	0	148.3	2.26	3.29	3.89	1.18
T2BTE	6789	0	63.74	1.58	3.37	5.38	1.59
V1BUTE	7132	0	144.3	1.17	3.17	6.62	2.09
C2BTE	7132	0	49.2	0.85	2.57	4.36	1.70
V3MLBE	7132	0	79.03	1.58	3.71	6.20	1.67
CYPNA	6065	0	497	0.61	1.36	8.55	6.27
ISPNA	7129	0	714.5	15.66	27.71	35.64	1.29
NPNTA	7132	0	420.7	7.445	12.59	17.43	1.38
T2PNE	7132	0	51.54	0.955	2.43	4.25	1.75
V1PNTA	7132	0	26.89	0.68	1.48	2.31	1.57
C2PNE	7132	0	27.33	0.51	1.29	2.27	1.77
V2M2BE	7132	0	9.12	0.32	0.65	0.94	1.44
CYPNE	7132	0	84.8	0.24	0.51	1.46	2.86
V22DMB	7132	0	130	0.62	1.05	2.28	2.17
V23DMB	7131	0	107.5	1.22	2.18	3.70	1.70
V2MPNA	7132	0	714.2	4.32	8.40	21.40	2.55
V3MPNA	7132	0	529.5	2.83	5.63	15.89	2.82
ISPRE	7084	0	33.08	0.59	1.72	2.64	1.53
NHEXA	6995	0	847	4.11	8.37	25.92	3.10
MCPNA	7125	0	449.3	1.79	3.72	13.41	3.61
V24DMP	7125	0	65.48	0	0.74	2.27	3.09
BENZ	7125	0	682.1	2.6	4.33	10.97	2.53
CYHXA	6975	0	590.2	1.2	2.53	8.86	3.50
V2MHXA	6815	0	315.8	1.28	2.58	9.44	3.65
V23DMP	6975	0	128.8	0.6	1.20	4.02	3.35
V3MHXA	6653	0	411.1	1.5	3.11	12.27	3.94
V224TMP	7125	0	102.8	2.16	3.70	5.08	1.37

Table B-1. Summary statistics by concentration at Clinton in 1998.

SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
NHEPT	7125	0	320.7	1.5	3.23	9.61	2.98
MCYHX	7125	0	97.59	1.85	3.23	4.37	1.35
V234TMP	7125	0	46.6	0.75	1.32	2.05	1.55
TOLU	7125	0	543	5.47	10.33	20.39	1.97
V2MHEP	7125	0	68.56	0.53	1.02	2.31	2.26
V3MHEP	7125	0	102.9	0.51	1.18	3.29	2.80
NOCT	7125	0	27.69	1.13	1.74	2.08	1.20
EBENZ	7125	0	142.7	1.24	1.87	2.90	1.55
M_PXY	7125	0	286.3	5.19	7.61	9.36	1.23
STYR	7125	0	37.71	0	0.53	1.51	2.86
OXYL	7125	0	283.7	1.97	2.98	6.77	2.27
NNON	7125	0	18.02	0.62	0.88	1.00	1.13
ISPBZ	7125	0	9.3	0.19	0.30	0.51	1.73
NPBZ	7124	0	12.26	0.28	0.42	0.56	1.31
METOL	7125	0	36.94	1.18	1.72	1.86	1.08
PETOL	7125	0	18.31	0.4	0.63	0.89	1.40
V135TMB	7125	0	27	0.51	0.86	1.21	1.42
OETOL	7125	0	12.99	0.41	0.58	0.65	1.13
V124TMB	7125	0	57.57	1.87	2.67	2.97	1.11
NDEC	7125	0	31.47	0.76	1.04	1.27	1.22
V123TMB	7125	0	17.06	0.78	1.19	1.40	1.17
MDEBEN	7125	0	102.8	0.26	0.63	3.43	5.47
PDEBEN	7125	0	13.29	0.44	0.60	0.68	1.13
NUNDC	7125	0	12.82	0.6	0.75	0.75	1.01
TNMOC	5036	22.75	6478	209.6	341.69	423.06	1.24
PAMSHC	7132	0.63	5902.56	185.43	302.28	367.51	1.22
AROMAT	7125	0	745.51	24.89	37.24	44.83	1.20
OLEFIN	7132	0	1587.39	30.685	49.86	60.72	1.22
PARAFN	7132	0.1	5160.75	130.23	224.72	310.69	1.38
UIDVOC	5036	0.53	522.18	16.305	29.44	40.01	1.36

Table B-2. Summary statistics of concentrations at Clinton in 1999.

SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
ETHAN	6094	0	218.6	13.395	20.25	22.05	1.09
ETHYL	6094	0	440.4	5.185	10.28	17.56	1.71
PROPA	6094	0	563.2	13.27	20.95	25.63	1.22
PRPYL	6094	0	443.8	3.6	8.25	17.14	2.08
ISBTA	6094	0	1129	7.81	20.88	47.78	2.29
NBUTA	6094	0	906.5	12.9	24.34	43.00	1.77
V13BUTA	6094	0	143.1	0.69	2.37	6.67	2.81
ACETY	6094	0	84.05	1.99	3.07	4.10	1.33
T2BTE	6094	0	125.4	0.785	1.93	3.81	1.98
V1BUTE	6094	0	752.5	0.97	3.47	20.68	5.96
C2BTE	6094	0	91.22	0.62	1.55	2.99	1.93
V3MLBE	6094	0	68.92	1.29	2.52	3.84	1.52
CYPNA	6094	0	19.03	0.62	1.05	1.39	1.32
ISPNA	6094	0	572.2	13.03	23.36	32.09	1.37
NPNTA	6094	0	288.6	6.245	10.34	13.71	1.33
T2PNE	6094	0	41.5	0.8	1.66	2.58	1.55
V1PNTA	6094	0	23.92	0.6	1.17	1.77	1.51
C2PNE	6094	0	22.28	0.43	0.88	1.35	1.55
V2M2BE	6094	0	155.2	0.24	0.48	2.11	4.36
CYPNE	6094	0	31.57	0.2	0.42	0.96	2.26
V22DMB	6094	0	19.93	0.47	0.80	1.03	1.29
V23DMB	6094	0	31.68	0.96	1.62	2.03	1.25
V2MPNA	6094	0	165.7	3.61	6.18	8.24	1.33
V3MPNA	6094	0	130.3	2.34	4.02	5.58	1.39
ISPRE	6094	0	41.45	0.63	1.15	1.53	1.33
NHEXA	6073	0	154.5	3.5	5.81	7.83	1.35
MCPNA	5485	0	52.88	1.39	2.49	3.45	1.38
V24DMP	5485	0	41.74	0.44	0.82	1.40	1.71
BENZ	6073	0	465.5	2.36	4.50	10.71	2.38
CYHXA	6073	0	119.1	1.04	2.10	4.51	2.14
V2MHXA	6073	0	47.3	1.16	1.70	1.97	1.16
V23DMP	6073	0	22.03	0.65	0.91	1.12	1.23
V3MHXA	6073	0	53.29	1.36	2.02	2.33	1.15
V224TMP	6073	0	48.38	1.77	2.78	3.34	1.20
NHEPT	6073	0	118.8	1.45	2.30	3.00	1.30
MCYHX	6073	0	348.4	1.61	2.35	5.19	2.21
V234TMP	5702	0	17.65	0.59	0.95	1.17	1.23
TOLU	6073	0	1085	5.04	8.31	17.40	2.09
V2MHEP	6073	0	169.4	0.66	0.92	2.41	2.63
V3MHEP	6073	0	43.18	0.6	0.86	1.12	1.30
NOCT	6073	0	645.1	0.93	1.62	8.81	5.42
EBENZ	6073	0	158.9	1.28	1.87	3.46	1.85

Table B-2. Summary statistics of concentrations at Clinton in 1999.

SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
M_PXY	6073	0	1136	4.91	7.90	22.05	2.79
STYR	5343	0	94.73	0	0.35	2.37	6.77
OXYL	6073	0	240.4	1.81	2.70	5.50	2.04
NNON	6073	0	72.26	0.59	0.92	1.76	1.91
ISPBZ	5485	0	181.2	0.22	0.34	2.88	8.51
NPBZ	5595	0	187.3	0.23	0.42	3.12	7.38
METOL	5999	0	297	0.82	1.40	5.33	3.80
PETOL	6073	0	57.69	0.31	0.55	1.28	2.31
V135TMB	6073	0	326.1	0.54	1.09	6.48	5.95
OETOL	6073	0	115.7	0.35	0.57	2.10	3.69
V124TMB	6073	0	567.5	1.79	2.76	10.61	3.85
NDEC	5498	0	114.2	0.76	1.16	2.91	2.51
V123TMB	5914	0	249.1	0.865	1.41	5.14	3.65
MDEBEN	6073	0	206.1	0.21	0.65	5.12	7.84
PDEBEN	6073	0	169.7	0.34	0.57	3.29	5.78
NUNDC	5747	0	16.53	0.48	0.68	0.84	1.23
TNMOC	5921	0.02	5921	170.1	261.14	333.24	1.28
PAMSHC	6246	0	5729.3	146.3	226.44	258.25	1.14
AROMAT	6073	0	3862.87	23.25	35.23	76.14	2.16
OLEFIN	6094	0	1007.27	22.56	39.21	51.37	1.31
PARAFN	6246	0	2305.41	101.02	159.59	185.97	1.17
UIDVOC	5921	0.02	6625.56	12.59	22.98	117.43	5.11

Table B-3. Summary statistics of concentrations at Clinton in 2000.

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SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
ETHAN	7298	0	245.6	14.84	20.61	19.28	0.94
ETHYL	6787	0.06	212.8	3.79	7.33	11.95	1.63
PROPA	7297	0	638.7	14.57	22.43	29.55	1.32
PRPYL	7276	0	539.3	3.37	8.08	16.70	2.07
ISBTA	7298	0	8185	8.42	44.15	332.16	7.52
NBUTA	7298	0.09	3473	15.615	45.76	151.68	3.32
V13BUTA	6719	0	195.2	0.44	2.52	8.30	3.29
ACETY	7298	0	81.72	1.95	2.95	3.74	1.27
T2BTE	7298	0	114.6	0.67	2.35	5.43	2.31
V1BUTE	7276	0	81.91	1	2.34	4.13	1.77
C2BTE	7298	0	74.14	0.57	1.89	3.92	2.07
V3MLBE	6684	0	93.9	1.4	3.32	5.90	1.78
CYPNA	7288	0	47.17	0.61	1.03	1.63	1.58
ISPNA	7298	1.45	1514	13.09	25.99	44.18	1.70
NPNTA	7298	0.19	1511	6.22	11.00	28.13	2.56
T2PNE	7172	0	53.78	0.73	1.81	3.23	1.78
V1PNTE	7276	0	105.9	0.49	1.10	2.20	1.99
C2PNE	7298	0	28.4	0.39	0.95	1.68	1.77
V2M2BE	3869	0	38.45	0.16	0.45	1.07	2.36
CYPNE	3344	0	13.51	0.09	0.27	0.65	2.40
V22DMB	7298	0	53.49	0.41	0.72	1.32	1.83
V23DMB	7298	0	125.8	1.12	2.33	5.02	2.16
V2MPNA	7298	0.35	202	3.79	6.15	7.92	1.29
V3MPNA	7298	0	127.4	2.38	3.75	4.85	1.29
ISPRE	6296	0	14.42	0.42	0.92	1.17	1.28
NHEXA	7295	0.23	223.7	3.52	5.59	7.95	1.42
MCPNA	7295	0	79.27	1.65	2.57	3.41	1.33
V24DMP	7143	0	69.55	0.48	1.03	2.64	2.56
BENZ	7295	0.43	313.1	3.1	4.98	8.56	1.72
CYHXA	7295	0	132.2	0.97	1.57	2.95	1.88
V2MHXA	7295	0	27.06	1.23	1.76	1.91	1.09
V23DMP	7295	0	38.42	0.72	1.09	1.67	1.53

Table B-3. Summary statistics of concentrations at Clinton in 2000.

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SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
V3MHXA	7295	0.12	37.3	1.68	2.34	2.35	1.00
V224TMP	7295	0	522.9	2.28	5.52	17.59	3.19
NHEPT	7295	0.11	80.06	1.83	2.62	2.99	1.14
MCYHX	7295	0	54.31	1.62	2.23	2.25	1.01
V234TMP	7295	0	222.7	0.76	2.05	7.39	3.61
TOLU	7295	0.76	244.6	6.47	9.65	12.20	1.26
V2MHEP	7295	0	24.21	0.64	0.98	1.15	1.18
V3MHEP	7295	0	14.82	0.56	0.78	0.80	1.02
NOCT	7295	0	67.56	0.89	1.34	1.74	1.30
EBENZ	7295	0	23.8	1.28	1.74	1.76	1.01
M_PXY	7295	0.19	97.58	4	5.68	6.76	1.19
STYR	7295	0	78.59	0.59	1.06	1.78	1.68
OXYL	7295	0	31.2	1.38	1.89	2.06	1.09
NNON	7294	0	28.28	0.54	0.76	0.86	1.13
ISPBZ	7222	0	15.63	0.18	0.26	0.38	1.44
NPBZ	7038	0	5.32	0.295	0.38	0.36	0.95
METOL	6524	0	15.39	0.8	1.10	1.27	1.15
PETOL	6524	0	8.3	0	0.30	0.59	1.97
V135TMB	7295	0	10.23	0.43	0.64	0.78	1.21
OETOL	7295	0	6.25	0.29	0.39	0.44	1.12
V124TMB	5553	0	64.03	1.46	2.18	2.77	1.27
NDEC	6182	0	40.37	0.53	0.71	0.90	1.27
V123TMB	7295	0	33.1	0.47	0.76	1.08	1.41
MDEBEN	2381	0	39.63	0.14	0.26	1.17	4.47
PDEBEN	5043	0	5.83	0.38	0.47	0.38	0.82
NUNDC	7295	0	25.61	0.38	0.51	0.74	1.45
TNMOC	6640	23.54	5830	174	277.07	361.81	1.31
PAMSHC	7298	18.75	7298	154.9	276.96	535.68	1.93
AROMAT	7295	2.43	363.08	23.05	30.74	29.77	0.97
OLEFIN	7298	0.68	590.43	19.89	34.75	43.24	1.24
PARAFN	7298	11.79	7298	111.94	217.21	508.92	2.34
UIDVOC	6637	2.06	615.36	15.41	23.51	28.92	1.23

Table B-4. Summary statistics of concentrations at Clinton in 2001.

SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
ETHAN	3736	1.43	285.4	15.315	22.14	23.20	1.05
ETHYL	3736	0	162.98	4.41	7.65	11.23	1.47
PROPA	3736	0	320.1	15.06	22.50	25.19	1.12
PRPYL	3567	0	275.16	3.58	7.51	12.82	1.71
ISBTA	3736	0.17	1516	8.2	34.42	89.54	2.60
NBUTA	3736	0.03	1328	13.425	27.78	48.30	1.74
V13BUTA	3736	0	70.17	0.54	1.35	2.90	2.14
ACETY	3736	0	41.86	1.71	2.63	3.09	1.17
T2BTE	3736	0	267.7	0.54	1.47	6.00	4.07
V1BUTE	3736	0	253.2	0.77	2.05	7.18	3.51
C2BTE	3736	0	200.2	0.47	1.22	4.48	3.67
V3MLBE	1676	0	38.37	1.16	2.10	2.88	1.37
CYPNA	3736	0	30.39	0.565	1.03	1.61	1.57
ISPNA	3736	0.09	1099	11.045	21.36	36.30	1.70
NPNTA	3736	0	368.9	5.49	9.86	14.99	1.52
T2PNE	3736	0	115.5	0.53	1.34	3.26	2.44
V1PNTA	3736	0	73.55	0.37	0.87	1.97	2.28
C2PNE	3736	0	59.05	0.28	0.69	1.66	2.41
V2M2BE	619	0	4.84	0.15	0.27	0.43	1.57
CYPNE	619	0	15.22	0.1	0.32	0.83	2.62
V22DMB	3736	0	17.61	0.29	0.57	0.97	1.72
V23DMB	3736	0	29.53	0.83	1.67	2.45	1.46
V2MPNA	3727	0	115.93	2.95	5.33	7.80	1.46
V3MPNA	3680	0	156	2.06	3.61	5.85	1.62
ISPRE	3370	0	42.23	0.34	0.91	1.42	1.57
NHEXA	3759	0.25	126.06	3.15	5.46	8.07	1.48
MCPNA	3147	0	95.22	1.29	2.57	4.97	1.93
V24DMP	3147	0	30.69	0	0.64	2.06	3.24
BENZ	3759	0.24	261.18	2.3	3.94	7.06	1.80
CYHXA	3759	0	32.82	0.8	1.32	1.95	1.48
V2MHXA	3759	0	30.94	0.83	1.32	1.78	1.35
V23DMP	3759	0	42.48	0.6	1.18	2.53	2.14

Table B-4. Summary statistics of concentrations at Clinton in 2001.

SPECIES	NUMBER	MIN	MAX	MEDIAN	MEAN	SD	CV
V3MHXA	3718	0	78.25	1.29	1.94	2.55	1.32
V224TMP	3759	0	151.6	1.84	4.46	9.19	2.06
NHEPT	3759	0	89.6	1.46	2.13	2.77	1.30
MCYHX	3759	0	28.5	1.34	1.90	1.93	1.01
V234TMP	3758	0	77.03	0.63	1.83	4.61	2.51
TOLU	3759	0.28	570	5.4	9.22	14.66	1.59
V2MHEP	3759	0	15.16	0.54	0.86	1.00	1.16
V3MHEP	3759	0	13.24	0.48	0.68	0.74	1.08
NOCT	3759	0	17.44	0.64	0.99	1.13	1.13
EBENZ	3759	0	37.39	0.92	1.37	1.75	1.28
M_PXY	3715	0	129.9	3.27	4.90	6.69	1.36
STYR	3757	0	25.2	0.16	0.59	1.46	2.48
OXYL	3757	0	39.79	1.09	1.67	2.23	1.33
NNON	3759	0	7.4	0.42	0.60	0.61	1.03
ISPBZ	3759	0	14.13	0.14	0.24	0.57	2.34
NPBZ	3759	0	39.69	0.17	0.28	1.14	4.01
METOL	3737	0	20.76	0.51	0.81	1.08	1.32
PETOL	3759	0	13.45	0	0.25	0.62	2.47
V135TMB	3759	0	19.07	0.32	0.53	0.81	1.52
OETOL	3759	0	7.24	0.27	0.39	0.47	1.21
V124TMB	3759	0	52.79	1.26	2.09	2.94	1.41
NDEC	3648	0	6.76	0.51	0.67	0.64	0.95
V123TMB	3759	0	14.55	0.48	0.76	0.99	1.31
MDEBEN	513	0	12.88	0.13	0.28	0.76	2.74
PDEBEN	2866	0	32.14	0.21	0.33	0.90	2.75
NUNDC	3759	0	5.67	0.34	0.47	0.45	0.96
TNMOC	3731	14.52	7346	156.47	257.51	315.57	1.23
PAMSHC	3760	3.78	6449.84	140.025	231.35	286.88	1.24
AROMAT	3759	0.82	583.49	18.39	27.29	31.89	1.17
OLEFIN	3736	0.95	1110.09	16.89	28.30	40.62	1.44
PARAFN	3760	1.66	5010.01	101.285	177.71	236.44	1.33
UIDVOC	3730	0.63	896.16	14.32	22.98	30.16	1.31

## **APPENDIX C**

### **ABUNDANT HYDROCARBONS BY WIND OCTANT AT ALL SITES, 1998-2000**

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Table C-1. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Bayland in 2000 by concentration.

Wind Q	Ethan	Propn	Nbuta	Ispna	Npnta	Tolu	Isbta	Ethyl	Xyl	Ispre	2mpna	Prpyl	Nhexa
North	1	2	5	3	7	4	6	9	8		10		
Northeast	2	1	4	3	7	6	5	8	9				10
East	1	2	5	3	8	4	7	6			9	10	
Southeast	1	2	6	3	9	4	7	5	10	8			
South	1	2	6	3	9	5	8	7	10	4			
Southwest	1	2	4	3	8	7	6	9		5	10		
West	1	2	5	3	8	7	6		10	4	9		
Northwest	1	2	5	4	10	3	8	7	6		9		

C-3

Table C-2. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Bayland in 1999 by concentration.

Wind Q	Ethan	Propn	Nbuta	Ispna	Npnta	Tolu	Isbta	Ethyl	Xyl	2mpna	Nhexa
North	1	2	5	4	7	3	8	9	6		10
Northeast	1	2	5	4	7	3	8	9	6	10	
East	1	2	4	3	7	5	6	8	9	10	
Southeast	1	2	5	3	7	4	6	8	9	10	
South	1	2	5	3	8	4	7	6	9	10	
Southwest	1	2	5	3	7	4	6	9	8	10	
West	1	2	4	3	7	5	6	9	8	10	
Northwest	1	2	5	3	6	4	8	9	7		10

Table C-3. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Bayland in 1998 by concentration

Wind Q	Ethan	Propn	Nbuta	Ispna	Npnta	Tolu	Isbta	Ethyl	Xyl	Ispre	2mpna	Prpyl
North	1	4	6	2	7	3	10	8	5		9	
Northeast	1	2	5	3	7	4	9	8	6		10	
East	1	2	5	3	8	4	6	7	9		10	
Southeast	1	2	4	3	7	5	6	8	9			10
South	1	2	4	3	6	5	8	9	7		10	
Southwest	1	2	4	3	7	5	8		9	6	10	
West	1	2	4	3	7	6	5	8	9		10	
Northwest	2	4	5	1	7	3	8	10	6		9	

C-4

Table C-4. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Bayland in 2000 by weight percent (MIR.

Wind Q	Ethyl	Prpyl	Tolu	Xylenes	V124tmb	Ispna	Ispre	V123tmb	Nbuta	Propa	Isbta	V3mlbe	Ethan
North	1	3	4	2	6	5		7	9	8	10		
Northeast	2	5	3			4	1		6	7	8	10	9
East	1	2	3	6	7	4	5	9		10	8		
Southeast	2	3	4		8	5	1	6	9	10		7	
South	2	3	4		7	5	1	6	9	10		8	
Southwest	2	3	5		10	4	1	6	7	8	9		
West	2	3	4			5	1	6	8	7	9		10
Northwest	1	2	3	4	6	5	9	7	10				

Table C-5. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Bayland in 1999 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Xylenes	V124tmb	Ispna	V123tmb	Nbuta	Propa	Isbta	T2bte	C2bte	Metol
North	1	4	2	3	5	6	8	10	9		7		
Northeast	1	3	2	4	7	5		8	10	9	6		
East	1	3	2	5	6	4		8	10	9	7		
Southeast	1	2	4	6	5	7	8				3	9	10
South	1	3	4	6	5	8	7				2	9	10
Southwest	1	3	2	7	6	5	8			10	4		9
West	1	3	2	4	6	5		8	9	10	7		
Northwest	1	4	2	3	5	6	8	9	10		7		

C-5

Table C-6. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Bayland in 1998 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Xylenes	V124tmb	Ispna	V123tmb	Nbuta	Propa	Isbta	T2bte	V3mlbe	Ispre
North	1	4	2	3	5	6	8	9				10	7
Northeast	1	2	3	4	6	5		9		7	10		8
East	1	2	3	7	6	5	10	9			8		4
Southeast	1	2	5	9	4	6	7				8	10	3
South	3	2	5		4	6	7	10			8	9	1
Southwest	2	3	4		6	5	7	8	10			9	1
West	1	4	3	7	6	5	8	10				9	2
Northwest	4	6	3	1	7	5	8	9				10	2

Table C-7. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Channelview in 2001 by concentration.

Wind Q	Ethan	Propa	Isbta	Nbuta	Ethyl	Prpyl	Ispna	Tolu	Npnta	Benz	Xylenes	Nhexa
North	1	2	3	4	5	6	7	8	9	10		
Northeast	1	2	4	3	7	5	9	8	10	6		
East	1	2	4	3	6	9	5	7	8	10		
Southeast	1	2	5	3	7	9	6	4	8		10	
South	2	1	4	3	5	6	7	9	8			10
Southwest	2	1	4	3	6	7	5	9	8			10
West	2	3	5	1	7		4	6	8		9	10
Northwest	1	2	6	3	7	9	4	5	10		8	

C-6

Table C-8. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Channelview in 2001 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Nbuta	Propa	Isbta	Ispna	Xylenes	1bute	T2bte	Ethan	Npnta	123tmb	Ispre	124tmb
North	1	2	3	5	7	8	9	10					6	4	
Northeast	2	1	5	6	8	7			9	10			4	3	
East	1	2	4	3	5	6	8	7			9	10			
Southeast	1	2	3	4	9	6	7	5				10		8	
South	2	1	4	3	7	5	8	6				9		10	
Southwest	1	2	5	3	8	4	7	6	10				9		
West	1	2	4	5		7	6	3					9	8	10
Northwest	1	2	4	6	10	9	8	3					7	5	

Table C-9. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Deer Park in 2001 by concentration.

Wind Q	Ethan	Propa	Isbta	Nbuta	Ethyl	Prpyl	Ispna	Tolu	Npnta	Xylenes	Nhexa	V2mpna
North	1	2	3	4	8	6	5	9	7		10	
Northeast	3	1	4	5	6	2	7	9	8		10	
East	1	2	3	4	5	6	7	8	9		10	
Southeast	1	2	4	3	5	8	7	6	9		10	
South	1	2	4	3	7		6	5	8	9	10	
Southwest	1	2	4	3	6	10	5	7	9	8		
West	2	1	6	4	7		5	3	8	9	10	
Northwest	1	2	5	4	8	9	3	6	7			10

C-7

Table C-10. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Deer Park in 2000 by concentration.

Wind Q	Ethan	Propan	Nbuta	Ispna	Npnta	Tolu	Isbta	Ethyl	Xylenes	2mpna	Prpyl	Mcyhx	Nhexa	Benz
North	1	2	5	4	7	10	3	8			6			9
Northeast	4	2	7	6	10	9	5	3			1		8	
East	1	2	6	7		8	4	3	10		5		9	
Southeast	1	2	7	5	10	8	6	3			4		9	
South	1	2	5	3		6	4	10	7		8	9		
Southwest	1	2	4	3	8	6	5	7	9			10		
West	1	2	4	3	9	5	6	7	8		10			
Northwest	2	1	4	3	7	6	5	8	9	10				

Table C-11. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Deer Park in 1999 by concentration.

Wind Q	Ethan	Propan	Nbuta	Ispna	Npnta	Tolu	Isbta	Ethyl	Xylenes	2mpna	Prpyl	Nhexa	Benz
North	2	1	5	3	6	9	4	7			8		10
Northeast	3	2	7	6	8	10	4	5			1	9	
East	1	2	6	4	9	7	3	5			8		10
Southeast	1	2	8	4		7	6	3	10		5	9	
South	1	2	5	3	7	4	6	8	9				10
Southwest	1	2	5	3	8	4	6	7	9	10			
West	1	2	5	3	9	4	6	8	7	10			
Northwest	2	3	4	1	6	7	5	8	9			10	

C-8

Table C-12. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Deer Park in 2001 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Nbuta	Propa	Isbta	Ispna	Xylenes	Npnta	Ispre	V124tmb	Ethan	V2mpna
North	2	1	3	5	9	4	6	7	8	10			
Northeast	2	1	4	5	8	3	7	6	9			10	
East	2	1	3	5	6	4	7	8	10			9	
Southeast	1	2	3	5	7	4	6	9	10			8	
South	1	2	3	7	6	5	8			4	10	9	
Southwest	1	2	3	6	8	9	5	7		4	10		
West	1	2	3	8	6	10	5	4		9	7		
Northwest	1	2	4	6	9	7	5	3	8				10

Table C-13. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Deer Park in 2000 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Xylenes	124tmb	Ispna	123tmb	Nbuta	Isbta	Ispre	1bute	Npnta	Ethan	Propa	2mpna
North	2	1	6	3		5		7	4		9	10		8	
Northeast	1	2	5	3		4		8	6		10		9	7	
East	2	1	3	8		5		9	4	6			10	7	
Southeast	2	1	3	7		4		9	8	6			10	5	
South	1	2	3	5		4	10	8	7				9	6	
Southwest	1	2	3	5		4	8	9	6	10				7	
West	1	2	3	4	9	5		8	6	10				7	
Northwest	1	2	4	5	9	3		7	6					8	10

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Table C-14. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Deer Park in 1999 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Xylenes	124tmb	Ispna	123tmb	Nbuta	Isbta	Ispre	1bute	Npnta	Ethan	Propa	2mpna
North	2	1	6	3		5		7	4	9	10			8	
Northeast	1	2	6	3		5		7	4		10	9		8	
East	2	1	3	7		4		9	6	5	10			8	
Southeast	1	2	3	6	9	4			8	5			10	7	
South	1	2	3	7	5	4		10	8	6				9	
Southwest	1	2	3	5	6	4	8	10		7				9	
West	1	3	4	2	6	5		7	8					9	10
Northwest	1	3	5	2	9	4		6	7			10		8	

Table C-15. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Haden Rd. in 2001 by concentration.

Wind Q	Ethan	Propa	Isbta	Nbuta	Ethyl	Prpyl	Ispna	Tolu	Npnta	Benz	Xylenes	Nhexa	Cypne
North	1	2	8	5	9		3	4	7	10	6		
Northeast	2	1	5	3	7		4	6	8	9	10		
East	2	1	4	3	8	6	5	9	7	10			
Southeast	2	1	3	6	5	4	7	8	9			10	
South	3	7	4	2	6	10	1	5	9		8		
Southwest	7	4	6	2			1	5	3	9	8		10
West	5	2	4	3		9	1	7	8	10	6		
Northwest	3	1	5	2		9	4	6	8		7	10	

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Table C-16. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Haden Rd. in 2001 by percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Nbuta	Propa	Isbta	Ispna	Xyl	Npnta	Ispre	124tmb	23tmb	13buta	3mlbe	1bute	T2bte	T2pne	C2pne	cypne
North	2	1	4	6	9		5	3		8	10		7						
Northeast	2	1	4	5	8	7	6	3		9			10						
East	2	1	6	4	8	7	5	3	9						10				
Southeast	2	1	6	8	9	5	7	3	10						4				
South	1	2	4	7		6	5	3						9	10		8		
Southwest	8	3	5	7			4	1	9								6	10	2
West	5	2	3	6	10	8	4	1	7							9			
Northwest	4	2	3	6		9	5	1	8			7			10				

Table C-17. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Baytown in 2001 by concentration.

Wind Q	Ethan	Propa	Isbta	Nbuta	Ethyl	Prpyl	Ispna	Tolu	Npnta	Benz	Xylenes	Nexa	13buta	cyhxa	3mlbe
North	3	2	6	4			5	9	7			8	1	10	
Northeast	1	2	5	3	7	8	4	10	9				6		
East	1	2	5	3			4	7	6	9	10	8			
Southeast	5	3	6	1			2	9	4			8			10
South	5	3	7	4	8	2	1		6			10			9
Southwest	4	2	6	8	3	1	7	10	5			9			
West	4	2	3	6	7	1	5	10	8		9				
Northwest	3	1	5	4		9	2		8			10	6	7	

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Table C-18. Most abundant hydrocarbons by wind octant (1=north, 337.5-22.5 degrees) at Baytown in 2001 by weight percent (MIR).

Wind Q	Ethyl	Prpyl	Tolu	Nbuta	Propa	Isbta	Ispna	Xyl	1bute	T2bte	Ethan	Npnta	13buta	C2bte	3mlbe	T2pne	C2pne	cyhxa
North	3	2	6	7	8	9	4	5				10	1					
Northeast	2	3	6	5	7	9	4	8			10		1					
East	2	1	5	3	6	7	4	8			9	10						
Southeast				2		10	1	5		7		8	9	6	4	3		
South	3	1		10			2	4		7				8	6	5	9	
Southwest	2	1	3			10	6	4	5	9		8			7			
West	2	1	7	5		8	4	3	10			9	6					
Northwest	4	2	9	6		10	5	3	7				1					8

## **APPENDIX D**

### **SUMMARY STATISTICS BY YEAR AND SITE**

This appendix contains summary statistics by site and year for all hydrocarbons measured by auto-GC in Houston as follows:

- Deer Park (summer only and entire year)
- Bayland (summer only and entire year)
- Clinton Drive (summer only and entire year)

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Table D-1. Summary statistics at Deer Park during the summer (June-September) by year, 1998-2001.

Year	Stat	TNMOG	PAMS	%Aromat	%Paraffin	%Olefin	%Unid'd	Ethyl	Prpyl	13Buta	Benz	Tolu	Xylenes	XB	AE
1998	N of cases	799	2107	799	799	799	799	2107	2107	1880	2098	2098	2098	2098	2105
	Minimum	20.85	13.05	0.03	0.25	0.01	0.03	0.00	0.00	0.00	0.29	0.45	0.15	0.09	0.01
	Maximum	1508.00	2938.94	0.42	0.92	0.59	0.47	296.80	921.30	106.30	92.97	88.17	60.82	7.48	15.37
	Median	125.00	102.26	0.10	0.59	0.13	0.11	3.84	2.72	0.29	2.52	3.63	2.25	0.88	0.34
	Mean	210.71	183.53	0.11	0.59	0.18	0.13	13.87	18.08	1.29	4.66	6.28	4.11	1.04	0.49
	Standard Dev	235.41	239.64	0.05	0.12	0.12	0.07	30.64	52.36	4.22	7.68	7.70	5.48	0.69	0.95
	C.V.	1.12	1.31	0.48	0.20	0.71	0.52	2.21	2.90	3.28	1.65	1.23	1.33	0.67	1.93
1999	N of cases	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2435
	Minimum	15.15	12.27	0.01	0.14	0.00	0.01	0.00	0.00	0.00	0.20	0.64	0.00	0.00	0.01
	Maximum	3418.00	3380.53	0.55	0.97	0.77	0.32	536.00	2195.00	39.14	162.10	104.40	96.54	24.38	10.47
	Median	117.75	110.36	0.12	0.63	0.15	0.06	5.01	3.60	0.34	2.46	4.62	2.54	1.12	0.38
	Mean	214.68	201.02	0.13	0.63	0.19	0.06	16.44	24.80	1.05	4.94	8.22	4.77	1.27	0.52
	Standard Dev	296.72	282.94	0.06	0.11	0.12	0.03	36.52	114.13	2.55	8.77	9.97	6.29	1.05	0.68
	C.V.	1.38	1.41	0.45	0.18	0.64	0.42	2.22	4.60	2.41	1.78	1.21	1.32	0.83	1.31
2000	N of cases	482	1511	482	482	482	482	1486	1390	1486	1439	1439	1439	1439	1486
	Minimum	23.09	6.19	0.03	0.13	0.01	0.03	0.22	0.40	0.00	0.19	0.80	0.51	0.14	0.01
	Maximum	1827.00	1629.24	0.23	0.90	0.81	0.38	298.20	1462.00	21.18	80.22	154.20	37.41	8.96	11.83
	Median	104.15	86.64	0.10	0.61	0.11	0.12	3.82	4.05	0.20	1.47	3.31	2.15	1.58	0.41
	Mean	187.84	156.29	0.11	0.61	0.14	0.14	11.38	18.98	0.59	3.11	6.23	3.65	1.70	0.60
	Standard Dev	239.06	199.67	0.04	0.12	0.10	0.07	23.57	57.62	1.35	5.59	9.45	4.59	0.93	0.88
	C.V.	1.27	1.28	0.35	0.19	0.74	0.52	2.07	3.04	2.28	1.80	1.52	1.26	0.55	1.47
2001	N of cases	1599	1696	1599	1599	1599	1599	1696	1696	1696	1696	1696	1696	1689	1695
	Minimum	11.71	7.08	0.01	0.14	0.01	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00
	Maximum	2601.96	2474.57	0.60	0.96	0.81	0.59	306.12	694.50	12.51	104.63	127.34	45.63	86.00	12.98
	Median	97.42	94.54	0.11	0.68	0.14	0.03	4.07	3.44	0.16	1.64	3.57	1.88	1.26	0.34
	Mean	166.08	165.74	0.12	0.67	0.18	0.03	12.59	18.60	0.46	3.20	6.41	3.28	1.59	0.50
	Standard Dev	217.62	224.66	0.07	0.13	0.13	0.02	25.72	50.92	0.99	6.05	8.10	4.09	2.80	0.86
	C.V.	1.31	1.36	0.53	0.20	0.74	0.80	2.04	2.74	2.15	1.89	1.26	1.25	1.77	1.70

Table D-2. Summary statistics at Deer Park for the entire year by year, 1998-2001.

Year	Stat	TNMOC	PAMS	%Aromat	%Paraffin	%Olefin	%Unid'd	Ethyl	Prpyl	13Buta	Benz	Tolu	Xylenes	XB	AE
1998	N of cases	799	2107	799	799	799	799	2107	2107	1880	2098	2098	2098	2098	2105
	Minimum	20.85	13.05	0.03	0.25	0.01	0.03	0.00	0.00	0.00	0.29	0.45	0.15	0.09	0.01
	Maximum	1508.00	2938.94	0.42	0.92	0.59	0.47	296.80	921.30	106.30	92.97	88.17	60.82	7.48	15.37
	Median	125.00	102.26	0.10	0.59	0.13	0.11	3.84	2.72	0.29	2.52	3.63	2.25	0.88	0.34
	Mean	210.71	183.53	0.11	0.59	0.18	0.13	13.87	18.08	1.29	4.66	6.28	4.11	1.04	0.49
	Standard Dev	235.41	239.64	0.05	0.12	0.12	0.07	30.64	52.36	4.22	7.68	7.70	5.48	0.69	0.95
	C.V.	1.12	1.31	0.48	0.20	0.71	0.52	2.21	2.90	3.28	1.65	1.23	1.33	0.67	1.93
1999	N of cases	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2436	2435
	Minimum	15.15	12.27	0.01	0.14	0.00	0.01	0.00	0.00	0.00	0.20	0.64	0.00	0.00	0.01
	Maximum	3418.00	3380.53	0.55	0.97	0.77	0.32	536.00	2195.00	39.14	162.10	104.40	96.54	24.38	10.47
	Median	117.75	110.36	0.12	0.63	0.15	0.06	5.01	3.60	0.34	2.46	4.62	2.54	1.12	0.38
	Mean	214.68	201.02	0.13	0.63	0.19	0.06	16.44	24.80	1.05	4.94	8.22	4.77	1.27	0.52
	Standard Dev	296.72	282.94	0.06	0.11	0.12	0.03	36.52	114.13	2.55	8.77	9.97	6.29	1.05	0.68
	C.V.	1.38	1.41	0.45	0.18	0.64	0.42	2.22	4.60	2.41	1.78	1.21	1.32	0.83	1.31
2000	N of cases	482	1511	482	482	482	482	1486	1390	1486	1439	1439	1439	1439	1486
	Minimum	23.09	6.19	0.03	0.13	0.01	0.03	0.22	0.40	0.00	0.19	0.80	0.51	0.14	0.01
	Maximum	1827.00	1629.24	0.23	0.90	0.81	0.38	298.20	1462.00	21.18	80.22	154.20	37.41	8.96	11.83
	Median	104.15	86.64	0.10	0.61	0.11	0.12	3.82	4.05	0.20	1.47	3.31	2.15	1.58	0.41
	Mean	187.84	156.29	0.11	0.61	0.14	0.14	11.38	18.98	0.59	3.11	6.23	3.65	1.70	0.60
	Standard Dev	239.06	199.67	0.04	0.12	0.10	0.07	23.57	57.62	1.35	5.59	9.45	4.59	0.93	0.88
	C.V.	1.27	1.28	0.35	0.19	0.74	0.52	2.07	3.04	2.28	1.80	1.52	1.26	0.55	1.47
2001	N of cases	1599	1696	1599	1599	1599	1599	1696	1696	1696	1696	1696	1696	1689	1695
	Minimum	11.71	7.08	0.01	0.14	0.01	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00
	Maximum	2601.96	2474.57	0.60	0.96	0.81	0.59	306.12	694.50	12.51	104.63	127.34	45.63	86.00	12.98
	Median	97.42	94.54	0.11	0.68	0.14	0.03	4.07	3.44	0.16	1.64	3.57	1.88	1.26	0.34
	Mean	166.08	165.74	0.12	0.67	0.18	0.03	12.59	18.60	0.46	3.20	6.41	3.28	1.59	0.50
	Standard Dev	217.62	224.66	0.07	0.13	0.13	0.02	25.72	50.92	0.99	6.05	8.10	4.09	2.80	0.86
	C.V.	1.31	1.36	0.53	0.20	0.74	0.80	2.04	2.74	2.15	1.89	1.26	1.25	1.77	1.70

Table D-3. Summary statistics at Bayland during the summer (June-September) by year, 1998-2000.

Year	Stat	TNMOc	PAMS	%Aromat	%Paraffin	%Olefin	%Unid'd	Ethyl	Prpyl	13Buta	Benz	Tolu	Xylenes	XB	AE
1998	N of cases	1507	1612	1507	1507	1507	1507	1612	1408	1612	1544	1544	1507	1423	1599
	Minimum	11.25	9.43	0.01	0.18	0.03	0.01	0.00	0.00	0.00	0.00	0.39	0.00	0.00	0.00
	Maximum	806.30	730.35	0.44	0.88	0.54	0.62	66.92	64.83	13.14	21.94	76.11	50.55	7.12	1.61
	Median	73.94	66.20	0.16	0.60	0.13	0.07	2.56	1.68	0.30	1.46	4.21	2.61	2.00	0.55
	Mean	124.41	109.47	0.16	0.58	0.14	0.13	4.80	3.36	0.60	2.40	7.68	5.07	2.01	0.55
	Standard Dev	127.37	115.45	0.06	0.12	0.05	0.13	6.73	5.25	0.89	2.71	9.50	6.74	0.77	0.26
	C.V.	1.02	1.05	0.36	0.21	0.33	1.00	1.40	1.56	1.48	1.13	1.24	1.33	0.38	0.47
1999	N of cases	2236	2324	2235	2236	2236	2235	2242	2242	2242	2317	2317	2317	2296	2242
	Minimum	8.90	1.88	0.03	0.38	0.02	0.01	0.18	0.00	0.00	0.00	0.53	0.00	0.00	0.00
	Maximum	1335.00	1167.34	0.35	0.93	0.40	0.34	141.40	76.74	16.33	30.44	98.14	65.00	25.37	1.97
	Median	70.11	63.76	0.17	0.64	0.12	0.05	2.57	1.21	0.22	1.60	4.21	2.21	1.53	0.51
	Mean	115.15	103.15	0.17	0.64	0.13	0.06	5.20	3.20	0.48	2.53	7.12	4.16	1.55	0.53
	Standard Dev	134.41	119.53	0.05	0.08	0.05	0.03	8.98	6.54	0.91	2.94	8.86	5.69	0.89	0.27
	C.V.	1.17	1.16	0.30	0.13	0.35	0.49	1.73	2.04	1.91	1.16	1.24	1.37	0.58	0.50
2000	N of cases	624	692	601	602	624	601	670	471	670	669	669	669	515	670
	Minimum	9.59	0.01	0.00	0.03	0.00	0.01	0.18	0.20	0.00	0.00	0.01	0.00	0.00	0.00
	Maximum	955.90	454.80	0.42	0.89	0.54	0.96	29.86	21.29	12.43	12.29	41.46	23.89	5.25	3.83
	Median	40.59	34.69	0.13	0.64	0.16	0.04	1.65	0.95	0.10	0.66	1.89	1.12	1.65	0.37
	Mean	70.92	50.64	0.13	0.62	0.17	0.07	2.83	1.52	0.21	0.92	3.05	1.69	1.62	0.40
	Standard Dev	91.72	50.20	0.06	0.14	0.09	0.13	3.30	2.01	0.58	1.17	3.83	2.32	0.81	0.28
	C.V.	1.29	0.99	0.43	0.22	0.53	1.86	1.17	1.32	2.76	1.27	1.26	1.37	0.50	0.70

Table D-4. Summary statistics at Bayland for the entire year by year, 1998-2000

Year	Stat	TNMOc	PAMS	%Aromat	%Paraffin	%Olefin	%Unid'd	Ethyl	Prpyl	13Buta	Benz	Tolu	Xylenes	XB	AE
1998	N of cases	1507	1612	1507	1507	1507	1507	1612	1408	1612	1544	1544	1507	1423	1599
	Minimum	11.25	9.43	0.01	0.18	0.03	0.01	0.00	0.00	0.00	0.00	0.39	0.00	0.00	0.00
	Maximum	806.30	730.35	0.44	0.88	0.54	0.62	66.92	64.83	13.14	21.94	76.11	50.55	7.12	1.61
	Median	73.94	66.20	0.16	0.60	0.13	0.07	2.56	1.68	0.30	1.46	4.21	2.61	2.00	0.55
	Mean	124.41	109.47	0.16	0.58	0.14	0.13	4.80	3.36	0.60	2.40	7.68	5.07	2.01	0.55
	Standard Dev	127.37	115.45	0.06	0.12	0.05	0.13	6.73	5.25	0.89	2.71	9.50	6.74	0.77	0.26
	C.V.	1.02	1.05	0.36	0.21	0.33	1.00	1.40	1.56	1.48	1.13	1.24	1.33	0.38	0.47
1999	N of cases	2236	2324	2235	2236	2236	2235	2242	2242	2242	2317	2317	2317	2296	2242
	Minimum	8.90	1.88	0.03	0.38	0.02	0.01	0.18	0.00	0.00	0.00	0.53	0.00	0.00	0.00
	Maximum	1335.00	1167.34	0.35	0.93	0.40	0.34	141.40	76.74	16.33	30.44	98.14	65.00	25.37	1.97
	Median	70.11	63.76	0.17	0.64	0.12	0.05	2.57	1.21	0.22	1.60	4.21	2.21	1.53	0.51
	Mean	115.15	103.15	0.17	0.64	0.13	0.06	5.20	3.20	0.48	2.53	7.12	4.16	1.55	0.53
	Standard Dev	134.41	119.53	0.05	0.08	0.05	0.03	8.98	6.54	0.91	2.94	8.86	5.69	0.89	0.27
	C.V.	1.17	1.16	0.30	0.13	0.35	0.49	1.73	2.04	1.91	1.16	1.24	1.37	0.58	0.50
2000	N of cases	624	692	601	602	624	601	670	471	670	669	669	669	515	670
	Minimum	9.59	0.01	0.00	0.03	0.00	0.01	0.18	0.20	0.00	0.00	0.01	0.00	0.00	0.00
	Maximum	955.90	454.80	0.42	0.89	0.54	0.96	29.86	21.29	12.43	12.29	41.46	23.89	5.25	3.83
	Median	40.59	34.69	0.13	0.64	0.16	0.04	1.65	0.95	0.10	0.66	1.89	1.12	1.65	0.37
	Mean	70.92	50.64	0.13	0.62	0.17	0.07	2.83	1.52	0.21	0.92	3.05	1.69	1.62	0.40
	Standard Dev	91.72	50.20	0.06	0.14	0.09	0.13	3.30	2.01	0.58	1.17	3.83	2.32	0.81	0.28
	C.V.	1.29	0.99	0.43	0.22	0.53	1.86	1.17	1.32	2.76	1.27	1.26	1.37	0.50	0.70

Table D-5. Summary statistics at Clinton during the summer (June-September) by year 1998-2001.

Year	Stat	TNMOG	PAMS	%Aromat	%Paraffin	%Olefin	%Unid'd	Ethyl	Prpyl	13Buta	Benz	Tolu	Xylenes	XB	AE
1998	N of cases	1593	2405	1593	1593	1593	1593	2405	2405	2405	2400	2400	2400	2400	2402
	Minimum	36.04	0.63	0.01	0.22	0.02	0.01	0.00	0.00	0.00	0.14	0.29	0.20	0.15	0.01
	Maximum	6478.00	5902.56	0.53	0.88	0.57	0.55	295.90	1493.00	99.05	68.16	543.00	113.57	39.43	1.88
	Median	224.30	185.00	0.12	0.62	0.14	0.08	7.24	4.75	0.92	2.95	6.80	8.60	3.01	0.38
	Mean	368.46	301.24	0.13	0.62	0.16	0.10	12.72	11.43	2.93	4.48	13.32	10.97	3.50	0.39
	Standard Dev	480.52	387.59	0.06	0.10	0.06	0.06	18.43	45.88	6.42	5.47	28.63	9.33	2.63	0.23
	C.V.	1.30	1.29	0.45	0.17	0.40	0.66	1.45	4.01	2.19	1.22	2.15	0.85	0.75	0.60
1999	N of cases	2255	2407	2255	2255	2255	2255	2406	2406	2406	2256	2256	2256	2256	2406
	Minimum	25.23	18.41	0.03	0.16	0.02	0.02	0.04	0.00	0.00	0.13	0.26	0.12	0.04	0.00
	Maximum	2075.00	1785.11	0.73	0.87	0.66	0.63	440.40	288.30	143.10	134.70	80.61	159.77	123.76	23.20
	Median	170.10	146.01	0.15	0.60	0.14	0.09	4.67	3.89	0.69	2.68	5.63	7.08	2.49	0.47
	Mean	247.53	216.38	0.16	0.59	0.15	0.09	9.93	8.74	1.98	4.51	8.38	9.78	3.37	0.71
	Standard Dev	237.86	213.95	0.07	0.11	0.07	0.04	19.77	15.60	5.84	6.44	8.66	10.92	5.28	1.19
	C.V.	0.96	0.99	0.43	0.18	0.43	0.47	1.99	1.78	2.95	1.43	1.03	1.12	1.57	1.67
2000	N of cases	2420	2420	2419	2420	2420	2419	1910	2420	1863	2419	2419	2419	2419	1910
	Minimum	28.02	24.82	0.02	0.11	0.01	0.02	0.07	0.00	0.00	0.43	0.76	0.36	0.03	0.00
	Maximum	5830.00	5478.52	0.61	0.96	0.59	0.50	140.80	167.10	195.20	159.80	244.60	85.77	17.95	11.72
	Median	184.10	164.64	0.13	0.65	0.11	0.10	3.40	3.49	0.38	3.04	7.24	5.54	1.82	0.59
	Mean	316.41	282.78	0.14	0.64	0.11	0.10	5.73	7.16	2.32	5.12	11.89	7.39	1.96	0.74
	Standard Dev	436.72	404.59	0.06	0.10	0.05	0.04	8.07	11.20	9.85	8.62	16.22	7.19	1.33	0.72
	C.V.	1.38	1.43	0.45	0.16	0.46	0.39	1.41	1.57	4.25	1.68	1.36	0.97	0.68	0.97
2001	N of cases	1808	1813	1807	1808	1808	1807	1813	1813	1813	1812	1812	1810	1810	1810
	Minimum	20.58	17.68	0.02	0.25	0.01	0.02	0.00	0.00	0.00	0.26	0.28	0.00	0.00	0.00
	Maximum	2407.98	2184.08	0.60	0.95	0.53	0.40	162.98	275.16	40.71	261.18	182.55	63.08	29.67	3.03
	Median	162.19	144.28	0.11	0.66	0.12	0.09	4.65	3.76	0.59	2.06	5.80	4.67	2.04	0.40
	Mean	263.44	236.60	0.12	0.65	0.13	0.10	8.20	8.02	1.51	3.83	9.04	6.39	2.35	0.44
	Standard Dev	290.23	266.02	0.06	0.11	0.06	0.04	12.04	14.07	3.17	8.63	10.04	6.11	1.72	0.29
	C.V.	1.10	1.12	0.49	0.16	0.44	0.43	1.47	1.75	2.09	2.25	1.11	0.96	0.73	0.67

Table D-6. Summary statistics at Clinton for the entire year by year, 1998-2001.

Year	Stat	TNMOG	PAMS	%Aromat	%Paraffin	%Olefin	%Unid'd	Ethyl	Prpyl	13Buta	Benz	Tolu	Xylenes	XB	AE
1998	N of cases	5036	7132	5036	5036	5036	5036	7132	7132	7132	7125	7125	7125	7114	7127
	Minimum	22.75	0.63	0.00	0.16	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
	Maximum	6478.00	5902.56	0.77	0.96	0.77	0.65	597.40	1493.00	448.90	682.10	543.00	355.58	86.20	1.88
	Median	209.60	185.43	0.10	0.66	0.13	0.08	6.57	4.06	0.77	2.60	5.47	7.18	2.71	0.40
	Mean	341.69	302.28	0.11	0.65	0.14	0.09	11.50	9.51	4.63	4.33	10.33	10.58	3.30	0.43
	Standard Dev	423.06	367.51	0.06	0.11	0.06	0.06	17.35	30.99	19.41	10.97	20.39	13.87	3.14	0.25
	C.V.	1.24	1.22	0.54	0.16	0.43	0.68	1.51	3.26	4.19	2.53	1.97	1.31	0.95	0.58
1999	N of cases	5921	6246	5921	5921	5921	5921	6094	6094	6094	6073	6073	6073	6071	6093
	Minimum	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Maximum	9999.00	5729.30	0.79	0.95	0.66	1.00	440.40	443.80	143.10	465.50	1085.00	1329.90	146.38	23.20
	Median	170.10	146.30	0.13	0.63	0.14	0.07	5.19	3.60	0.69	2.36	5.04	6.83	2.60	0.46
	Mean	261.14	226.44	0.14	0.63	0.15	0.08	10.28	8.25	2.37	4.50	8.31	10.60	3.67	0.62
	Standard Dev	333.24	258.25	0.08	0.11	0.06	0.05	17.56	17.14	6.67	10.71	17.40	27.03	5.78	0.91
	C.V.	1.28	1.14	0.54	0.18	0.42	0.63	1.71	2.08	2.81	2.38	2.09	2.55	1.57	1.48
2000	N of cases	6640	7298	6637	6640	6640	6637	6787	7276	6719	7295	7295	7295	7295	6787
	Minimum	23.54	18.75	0.00	0.10	0.01	0.01	0.06	0.00	0.00	0.43	0.76	0.32	0.03	0.00
	Maximum	5830.00	11677.23	0.61	0.98	0.77	0.60	212.80	539.30	195.20	313.10	244.60	125.40	29.86	12.75
	Median	174.00	154.90	0.13	0.65	0.11	0.09	3.79	3.37	0.44	3.10	6.47	5.40	1.66	0.59
	Mean	277.07	276.96	0.14	0.64	0.13	0.10	7.33	8.08	2.52	4.98	9.65	7.57	1.91	0.76
	Standard Dev	361.81	535.68	0.06	0.10	0.06	0.04	11.95	16.70	8.30	8.56	12.20	8.69	1.50	0.78
	C.V.	1.31	1.93	0.45	0.16	0.49	0.39	1.63	2.07	3.29	1.72	1.26	1.15	0.79	1.03
2001	N of cases	1808	1813	1807	1808	1808	1807	1813	1813	1813	1812	1812	1810	1810	1810
	Minimum	20.58	17.68	0.02	0.25	0.01	0.02	0.00	0.00	0.00	0.26	0.28	0.00	0.00	0.00
	Maximum	2407.98	2184.08	0.60	0.95	0.53	0.40	162.98	275.16	40.71	261.18	182.55	63.08	29.67	3.03
	Median	162.19	144.28	0.11	0.66	0.12	0.09	4.65	3.76	0.59	2.06	5.80	4.67	2.04	0.40
	Mean	263.44	236.60	0.12	0.65	0.13	0.10	8.20	8.02	1.51	3.83	9.04	6.39	2.35	0.44
	Standard Dev	290.23	266.02	0.06	0.11	0.06	0.04	12.04	14.07	3.17	8.63	10.04	6.11	1.72	0.29
	C.V.	1.10	1.12	0.49	0.16	0.44	0.43	1.47	1.75	2.09	2.25	1.11	0.96	0.73	0.67