

CHARACTERIZATION OF AUTO-GC DATA IN HOUSTON

**Extended Outline
STI-900610-2112-EO**

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This extended outline is intended to provide the basis for a data analysis report. Several pieces of this outline have been provided by TNRCC staff who previously investigated the hydrocarbon data collected in Houston.

1. INTRODUCTION

This document will ultimately blend analyses previously performed by TNRCC (and their documentation) with analyses performed as a part of this project. The current version of this document is an extended outline with recommendations for additional analyses (generally in *italics*) and examples of new analyses. Integration and interpretation of the analyses will be performed as part of the next phase.

1.1 OVERVIEW

Transient high ozone events are occurring 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, 2001). 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 volatile organic compounds (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 ANALYSIS OBJECTIVES

TNRCC has sponsored large-scale field projects (e.g., COAST, TexAQS 2000), data analyses, and other research. TNRCC staff have also performed many investigations into the characteristics of VOCs in Houston. Objectives of this data analysis project include

- Summarize pertinent analyses made previously (and include in a final report)
- Identify and fill in gaps in the analyses
- Use these analyses to investigate high ozone events
- Provide recommendations to modeling efforts

1.3 GUIDE TO THE REPORT

2. DATA AVAILABILITY

2.1 AGC DATA

2.1.1 Instrumentation

Automated gas chromatograph (AGC) monitors measure speciated hydrocarbons and total nonmethane organic compounds (TNMOC)¹ on an hourly basis, seven days a week. These monitors have been deployed in Houston as a part of the Photochemical Assessment Monitoring Station (PAMS) program.

The AGC methodology is performed completely at the field monitor. The instrument pumps outside air into an automated thermal desorber for forty minutes. During the remaining twenty minutes of the hour, 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 and consequently, other polar compounds. The air streams are then heated and pumped to the gas chromatograph (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 their unique boiling points. 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 the peak corresponds to the concentration of the species. Each compound elutes at a characteristic time based on the given temperature and flow rate of the air sample, so both of these operating conditions must be kept constant to ensure accurate identification (Cramers and McNair, 1993). Species concentrations determined by the AGC are reported as hourly averages.

Add paragraph describing calibration procedures and audit results. Discuss potential problems with contamination and high concentrations.

The AGC and FID detector have some limitations in the types of compounds they can speciate. Polar compounds are absorbed and consequently lost by 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 the FID. There is also a significant chance for misidentification when using the AGC. The chromatograph sometimes shows two compounds having overlapping curves (co-elution) and an operator may have trouble identifying the peaks as one compound or two. Two species that have been commonly misidentified in the past in Texas are 2-methyl-2-pentene and 2-methyl-1-pentene. Throughout the PAMS program, commonly misidentified species also include 2- and 3-methylpentanes and toluene and 2-methylheptane.

Table 2-1 provides the list of species identified with auto-GCs as a part of PAMS.

¹ TNMOC is used in the PAMS program nomenclature. The measurements by AGC should more realistically be termed total nonmethane hydrocarbon (TNMHC) as the AGC's operated using a Nafion dryer do not quantify oxygenated compounds.

Table 2-1. AIRS code, abbreviation, hydrocarbon name, and species group (O=olefin, P=paraffin, A=aromatic) for PAMS target species.

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	I-butane	P
43280	1bute	1-Butene	O
43270	ibute	Isobutene	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	2m1pe	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

Table 2-1. AIRS code, abbreviation, hydrocarbon name, and species group (O=olefin, P=paraffin, A=aromatic) for PAMS target species.

AIRS code	Abbreviation	Hydrocarbon	Species Group
45202	tolu	Toluene	A
43960	2mhpe	2-Methylheptane	P
43253	3mhpe	3-Methylheptane	P
43233	noct	n-Octane	P
45203	ebenz	Ethylbenzene	A
45109	m/pxy	m/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
45207	135tmb	1,3,5-Trimethylbenzene	A
45208	124tmb	1,2,4-Trimethylbenzene	A
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
43000	pamshc	Sum PAMS Target Species	

2.1.2 AGC Sites

AGCs are currently operated at three sites in Houston as summarized in **Table 2-2**. The AGC at Aldine was previously at Bayland Park (see map).

The Clinton AGC is located 0.5 miles north of the Houston Ship Channel in Harris County, Texas. Large VOC-emitting industries (including petroleum refineries and petrochemical plants) are located south, southeast, and east of the monitor. Residential and urban areas are to the west and northwest. Ambient concentrations when the winds are from the south and east are predominately influenced by industrial emissions. Automobile emissions predominately influence the VOC composition when winds are westerly and northerly.

- *Other items to consider adding here:* Provide a map of auto-GC and canister sites. Include illustrative photos (such as Clinton Drive view to the south showing the industrial presence). Describe each site.

Table 2-2. Houston Auto-GC site information (to be completed)

Site	AIRS Number	Data Record	NO _x	Ozone	CO	Surface Met.	Carbonyls
Clinton Drive	482011035	1993 ^a , 1996 ^b - 2000 ^c	✓	✓	✓	✓	✓
Deer Park	482011039	1997-2000 ^d	✓	✓	✓	✓	✓
Bayland Park	482010055	1998-2000 ^e	✓	✓	✓	✓	✓
Aldine	482010024	2000 ^f	✓	✓	✓	✓	✓

^a 6/18/93 through 11/30/93 (COAST study)

^b 8/20/96 through 12/31/96

^c Other years have data from 1/1 through 12/31 except 1998 with data beginning on 4/1/98 and 1999 with data ending on 12/17/99.

^d Data are available from 1/1 through 12/31 except 1997 data began on 1/16; in 1998 data began on 4/1.

^e Data are available from 1/1 through 12/31 except in 1998 data began on 5/4 and in 2000 data ended on 8/7.

^f Data are available from 8/31 through 12/31.

2.2 CANISTER DATA

In addition to the AGCs operated in Houston, a network of sampling sites with canisters exists. The canisters are collected at sites covering a broader geographic area than the AGCs but provide less temporal coverage. The canisters are collected on every sixth day and intake air into the canister for twenty-four hours.

The VOC canister method requires that an ambient air sample be first collected at the field monitor. The sample is stored in a stainless steel canister and then taken to a laboratory for analysis. The detection method consists of a gas chromatograph-mass spectrometer (GC-MS) to identify and quantify the collected compounds. In the mass spectrometer, electrons are pulsed into a cavity and interact with the air sample causing the molecules to ionize. The ions are then separated within an electrical field by mass and charge. The currents are recorded and are graphed as straight lines, called the mass spectrum. Each line represents a species and there is little chance of misidentification. The laboratory mass spectrometer has been shown to exhibit greater sensitivity in speciation than the field-operated AGC.

The canister collection with GC-MS analysis can provide a much longer list of identified compounds than the AGC as evidenced by **Table 2-3**. **Table 2-4** lists the sites at which these measurements are currently made.

Table 2-3. Identified compounds using canister collection with GC-MS analysis.

1,1,1-Trichloroethane	Isobutane
1,1,2-Trichloroethane	Isopentane
1,1-Dichloroethane	Isoprene
1,1-Dichloroethylene	Isopropylbenzene
1,2,3-Trimethylbenzene	Methyl t-Butyl ether
1,2,4-Trimethylbenzene	Methylcyclohexane
1,2-Dichloroethane	Methylcyclopentane
1,2-Dichloropropane	Methylene Chloride
1,3,5-Trimethylbenzene	Propane
1,3-Butadiene	Propylene
1-Butene	Styrene
1-Heptene	TNMOC (ppbC)
1-Pentene	Tetrachloroethylene - Perchloro
2,2,4-Trimethylpentane	Toluene
2,2-Dimethylbutane - Neoheptane	Trichloroethylene
2,3,4-Trimethylpentane	Trichlorofluoromethane
2,3-Dimethylbutane	Vinyl Chloride
2,3-Dimethylpentane	Xylenes - Total
2,4-Dimethylpentane	a-Pinene
2-Chloropentane	b-Pinene
2-Methyl-1-Pentene	c-2-Butene
2-Methyl-2-Butene	c-2-Hexene
2-Methylheptane	c-2-Pentene
2-Methylhexane	m-Diethylbenzene
2-Methylpentane - Isohexane	m-Ethyltoluene
3-Methyl-1-Butene	n-Butane
3-Methylheptane	n-Decane
3-Methylhexane	n-Heptane
3-Methylpentane	n-Hexane
4-Methyl-1-Pentene	n-Nonane
Acetylene	n-Octane
Benzene	n-Pentane
Bromomethane	n-Propylbenzene
Carbon Tetrachloride	n-Undecane
Chlorobenzene	o-Ethyltoluene
Chloroform	o-Xylene
Chloroprene	p-Diethylbenzene
Cyclohexane	p-Ethyltoluene
Cyclopentane	p-Xylene + m-Xylene
Cyclopentene	t-2-Butene
Ethane	t-2-Hexene
Ethyl Benzene	t-2-Pentene
Ethylene	

Table 2-4. Canister sites in Houston.

AIRS	Sitename	County	Latitude	Longitude	Address
480391003	Clute C11	Brazoria	29.0111	95.3983	426 Commerce Street
481670005	Texas City C147	Galveston	29.3852	94.9317	2516 1/2 Texas Ave.
481670014	Galveston C34	Galveston	29.2631	94.8563	8715 Cessna Street
481670053	Nessler Pool C100	Galveston	29.3900	94.9194	17th and 5th Avenue
482010024	Aldine	Harris	29.9008	95.3269	4510 1/2 Aldine Mail Rd
482010026	Channelview	Harris	29.8025	95.1252	1405 Sheldon Rd.
482010029	Northwest Harris	Harris	30.0394	95.6750	16822 Kitzman Street
482010055	Bayland Park	Harris	29.6947	95.4942	6400 Bissonnet St.
482010057	Galena Park	Harris	29.7341	95.2383	304 Stewart St.
482010058	Baytown C148	Harris	29.7716	95.0311	7210 1/2 Bayway Dr.
482010061	Shore Acres	Harris	29.6147	95.0181	3903 1/2 Old Hwy 146
482010064	Allendale	Harris	29.6991	95.2667	3100 Old Galveston Road
482010069	Milby Park	Harris	29.7000	95.2667	2001 1/2 Central Street
482010803	HRM Site 3	Harris	29.7652	95.1811	1504 1/2 Haden Drive
482011035	Clinton	Harris	29.7330	95.2567	9525 1/2 Clinton Drive
482011039	Deer Park C35	Harris	29.6692	95.1277	5414 1/2 Durant St.
482011041	San Jacinto Monument	Harris	29.7472	95.0897	3824 1/2 Battleground Rd.

2.3 OTHER DATA

- *Other items to add to this section:* Describe the meteorological data available at the VOC measurement sites (and listed in Table 2-1). Describe additional air quality data available at the VOC sites (also listed in Table 2-1).

2.4 COMPARING AGC AND COLLOCATED CANISTER DATA

There are more sites with 24-hr canister data available in Houston than there are AGC sites (see Tables 2-2 and 2-4). Thus, it may be of interest to expand some spatial or trends analyses to include the canister data. In analyses that use both data sets, it is important to understand the differences between the two measurements in order to properly interpret the results. Objectives of such comparisons include:

- Identifying compounds in the canisters that are abundant and/or important to ozone formation not reported by the AGC.
- Investigating potential biases between the two methods for individual species.
- Investigating potential biases between the two methods for TNMOC (including unidentified mass).

TNRCC staff performed a comparison of auto-GC and 24-hr canisters collected at sites in Houston. Three air monitors in Houston have both AGC and canister data at concurrent times: Bayland Park, Clinton, and Deer Park. Because the two methods differ in their abilities to speciate, this analysis only includes those compounds measurable by both instruments (this excluded polar compounds, chlorinated compounds, and a few others from the analysis- see **Table 2-5**). To compare concentrations on a species by species basis, two changes to the data had to be made. First, a twenty-four hour average concentration was computed for each of the hydrocarbons from the AGC data. And second, the canister data had to be converted from ppbv to ppbC. The data used in this analysis came from the TNRCC MOTHER database.

Table 2-5. Species not included in the comparison of AGC and canister measurements.

Site	Species
Clinton	Ethane, ethylene, propane, propylene, 2-methyl-2-butene, o-ethyltoluene, c-2-hexene, 1,3-butadiene, cyclopentene; oxygenated and halogenated compounds
Deer Park	ethane, o-ethyltoluene, c-2-hexene, 1,3-butadiene, cyclopentene; oxygenated and halogenated compounds
Bayland Park	2-methyl-2-butene, o-ethyltoluene, c-2-hexene, 1,3-butadiene, cyclopentene; oxygenated and halogenated compounds

Add discussion of why the list in Table 2-5 varies among sites.

The daily hydrocarbon concentrations from each collection method were compared in the following ways:

- A trend analysis of daily total identified concentrations by collection method. The species measurable by both methods were summed.
- The compounds were categorized into chemical groups of alkanes, alkenes, and aromatics and compared by collection method on a day-by-day basis. Daily percent differences were also calculated between collection methods (equation 1).
- The percent difference of average total concentrations was calculated between the canister and the AGC data (equation 2). The percent differences were graphed as a time series.
- The percent difference of average species concentrations was calculated between the canister and AGC data (equation 3). The percent differences were graphed in a species fingerprint plot.

$$\text{Daily chemical group percent difference} = \frac{(\sum \text{AGC alkanes} - \sum \text{canister alkanes}) / ((\sum \text{AGC alkanes} + \sum \text{canister alkanes}) / 2) * 100, \text{ for day}_x}{(1)}$$

$$\text{Daily total percent difference} = \frac{(\text{AGC total} - \text{canister total}) / ((\text{AGC total} + \text{canister total}) / 2) * 100, \text{ for day}_x}{(2)}$$

$$\text{Average species percent difference} = \frac{(\text{average AGC species X} - \text{average canister species X})}{((\text{average AGC species X} + \text{average canister species X}) / 2)} * 100 \quad (3)$$

The trend plots of the sum of identified species (not shown here) showed daily variations in concentrations at each site. Overall, the daily concentrations of AGC and canister data follow a similar trend over the analyzed time period. There are many days when the concentrations of the two methods closely agreed, but there are also a number of days that had large differences. For example, on Oct. 30, 1996 at Clinton Drive, the AGC and canister sum of identified species (TNMHC on other plots) concentrations were 235 ppbC and 47 ppbC, respectively (**Figure 2.4-1**). A species by species comparison showed that the canister data had lower concentrations for almost every compound. The largest percent differences in concentrations occurred for cyclohexane, cyclopentane, c-2-butene, n-octane, hexane, isoprene, and the methyl group compounds.

Days with higher canister measurements than the AGC occurred at all the monitors as well. **Table 2-6** shows the number of days at each site when the daily total percent difference was within 25%, and when it was greater than 50%, 75%, and 100%. A positive percent difference shows that the average AGC TNMHC concentration was higher, a negative percent difference shows the average canister concentration was higher.

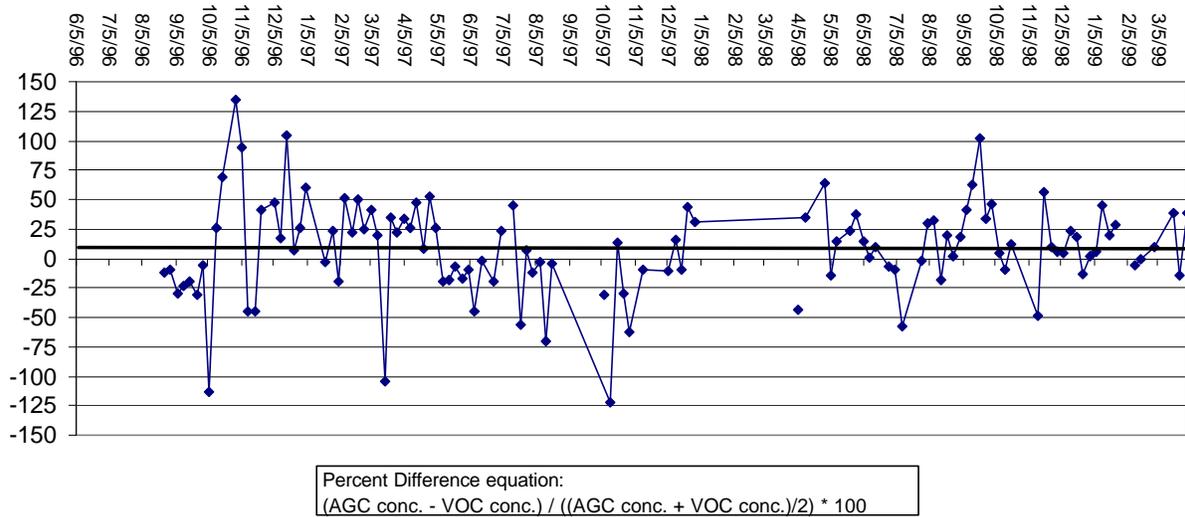


Figure 2.4-1. Percent difference between the sum of identified species, measured by AGC and canister (designated “VOC” in the plot), at Clinton from 1996 to 1999.

Table 2-6. Percent difference between AGC and canister total concentrations of measurable compounds.

	Deer Park	Clinton	Bayland Park
Percent difference within $\pm 25\%$	36 days	61 days	26 days
$\pm 25\% <$ Percent difference $\leq \pm 50\%$	21 days	34 days	8 days
$\pm 50\% <$ Percent difference $\leq \pm 75\%$	11 days	12 days	2 days
$\pm 75\% <$ Percent difference $\leq 100\%$	5 days	1 day	0 days
Percent Difference $> \pm 100\%$	2 days	6 days	0 days
Total number of sampling days	75 days	114 days	36 days

Species that had the greatest average percent differences between the AGC species concentration and the VOC species concentration are listed in **Table 2-7**. Several species had consistently large percent differences during this time period including 1-butene (canister values higher than the AGC), 2-methyl-2-butene (canister higher), and 3-methyl-1-butene (AGC higher).

Table 2-7. Average percent differences between concentrations reported by the AGC and canister methods for individual species.

Species	Average % Difference ¹	Range of % Differences ¹	Monitors
2-methyl-2-butene ²	141%, canister higher	138%	Deer Park
1-butene	110%, canister higher	97%-132%	Deer Park, Clinton, Bayland Park
3-methyl-1-butene	180%, AGC higher	171%-186%	Deer Park, Clinton, Bayland Park
3-methylheptane	89%, AGC higher	82%-96%	Deer Park, Clinton, Bayland Park
acetylene	95%, canister higher		Deer Park

¹ Absolute value reported.

² 2-methyl-2-butene did not have complete data at Clinton or Bayland Park and percent differences were not calculated for those monitors.

There were a number of species in addition to the ones listed in Table 2-7 that had lower percent differences but were measured at consistently higher concentrations at either the AGC or canister monitor at each location (see the percent difference of species concentrations plots in **Figures 2.4-2 through 2.4-8**).

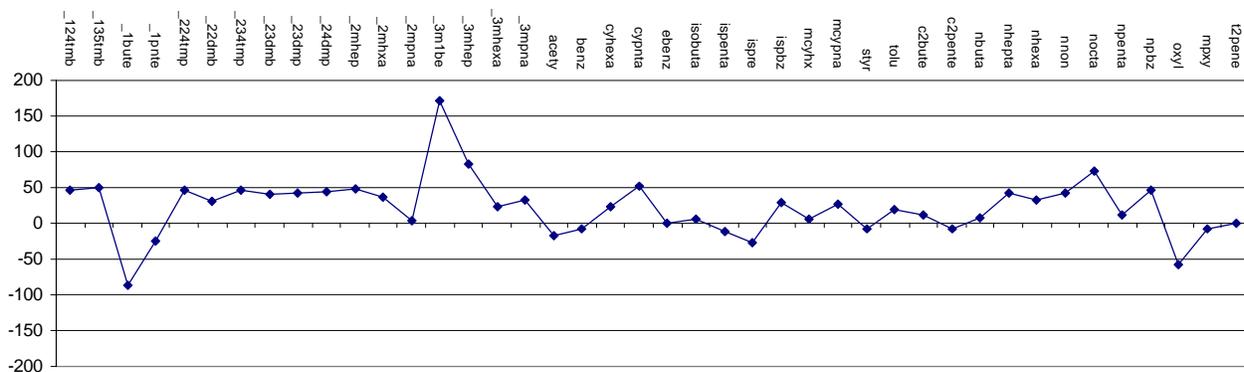


Figure 2.4-2. Average percent differences of species concentrations measured by AGC and canister at Clinton from 1996 to 1999.

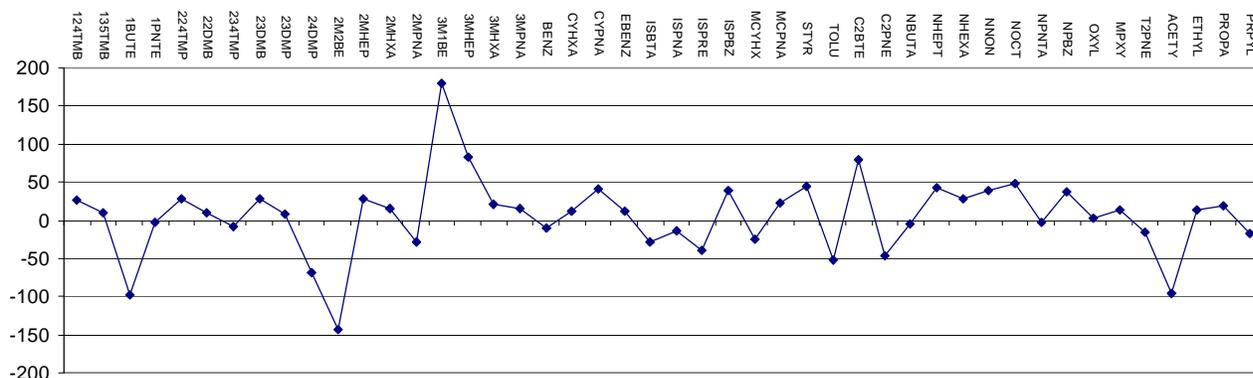


Figure 2.4-3. Average percent differences of species concentrations measured by AGC and canister at Deer Park from 1996 to 1999.

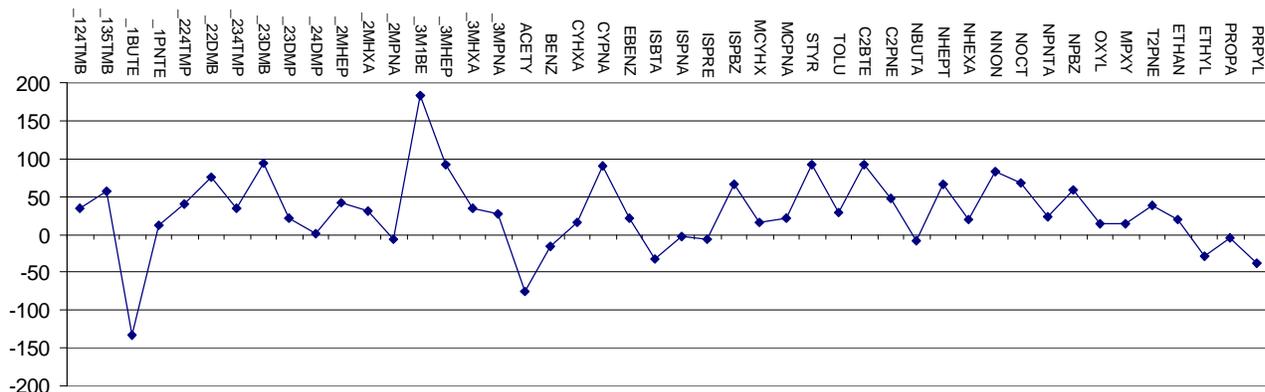


Figure 2.4-4. Average percent differences of species concentrations measured by AGC and canister at Bayland Park from 1996 to 1999.

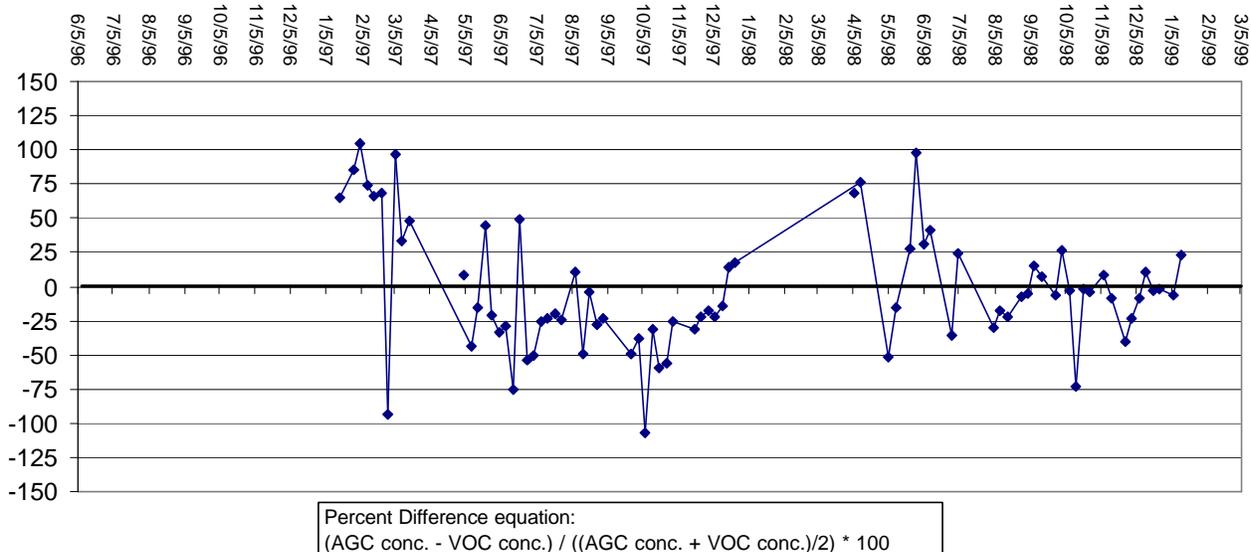


Figure 2.4-5. Percent difference between the sum of identified species measured by AGC and canister (VOC on the plot) at Deer Park from 1996 to 1999.

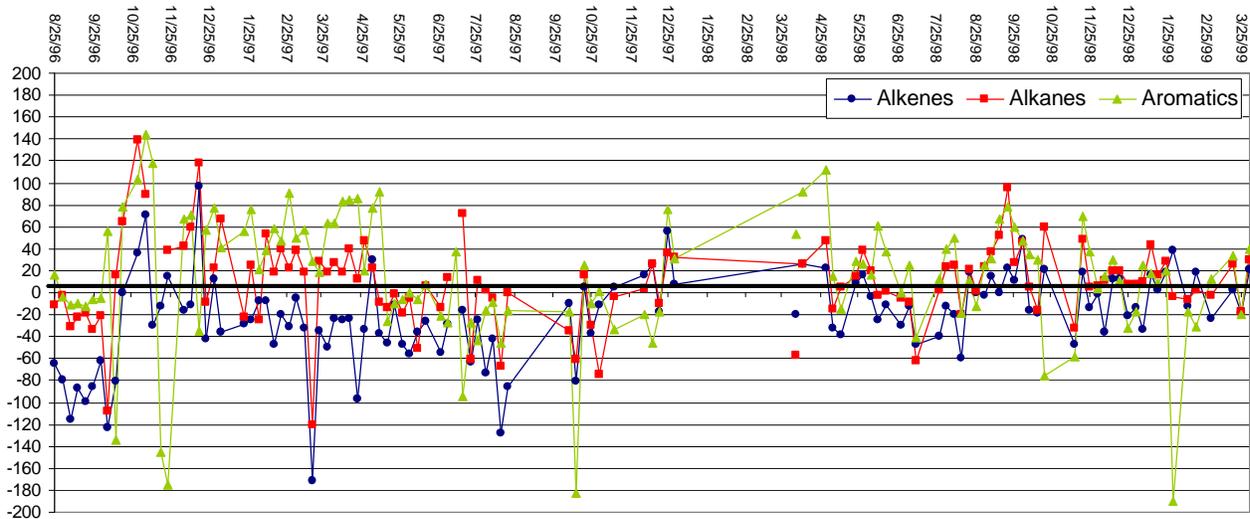


Figure 2.4-6. Percent difference between the sum of species by functional groups measured by AGC and canister at Clinton from 1996 to 1999.

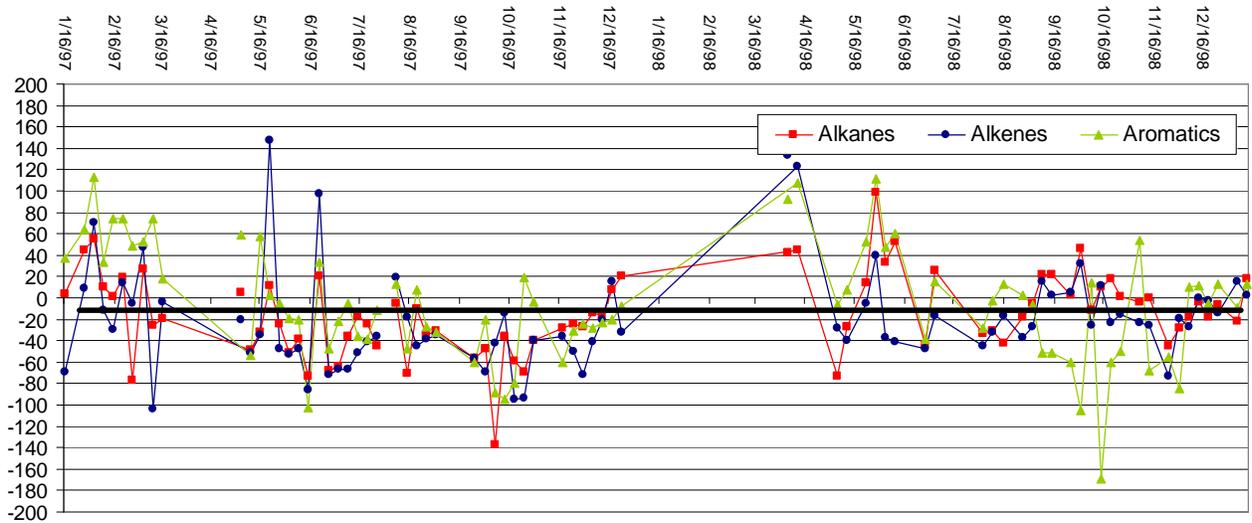


Figure 2.4-7. Percent difference between the sum of species by functional groups measured by AGC and canister at Deer Park from 1996 to 1999.

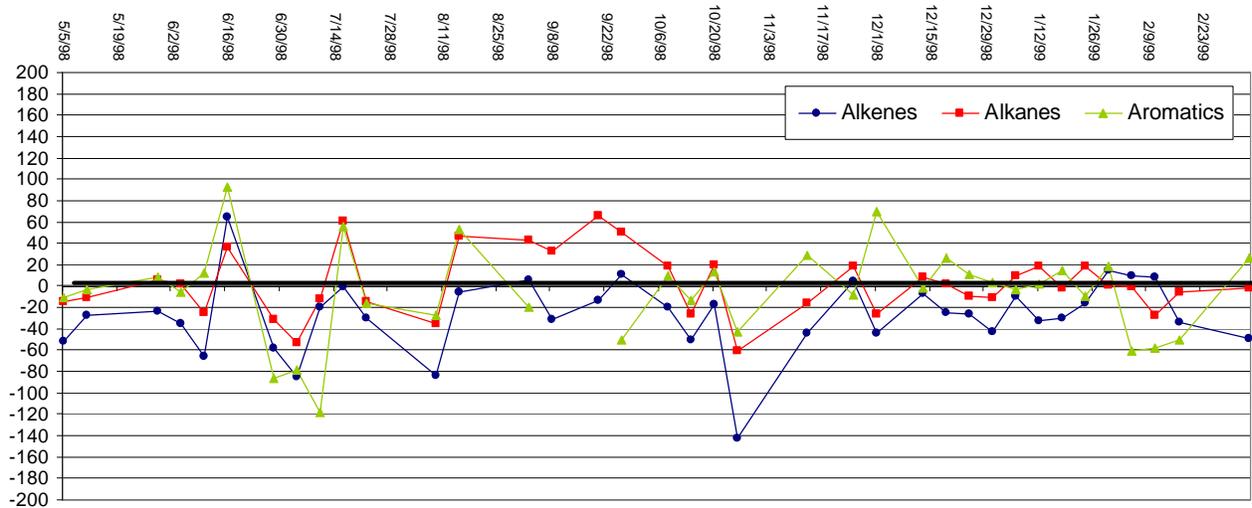


Figure 2.4-8. Percent difference between the sum of species by functional groups measured by AGC and canister at Bayland Park from 1996 to 1999.

When the data are plotted as the total by time and as the percent difference by time, fluctuations in daily concentrations. At all monitors it is common for AGC total concentrations to be higher than the canisters on one day but lower than the canister concentrations on the next. These fluctuations show that neither the AGC nor the canister is measuring higher total concentrations on a consistent, day-by-day basis. A pattern is visible, though, on the total percent difference plots for Deer Park (Figure 2.4-5) and Clinton (Figure 2.4-6). From February to December 1997, the daily fluctuations of percent differences are very similar at both sites, meaning that the AGC concentrations are higher than the canister concentrations on many of the same days, and vice versa, around the Houston Ship Channel in 1997.

The tendency for canister alkene concentrations to be higher than AGC alkene concentrations can be seen from the percent difference graphs of alkanes, alkenes, and aromatics (Figures 2.4-6 through 2.4-8). For the aromatic species the AGC concentrations were higher at Clinton 62% of the time. No such trend is seen for aromatics at Deer Park and Bayland Park or for the alkane species at the three monitors.

There are three primary differences between the two methods that contribute to differences in concentration reported:

- The AGC does not sample the air during the entire 24-hr period of a day. During each hour, there is a twenty-minute period of analysis when the ambient air is not being collected and the sample is being analyzed in the GC (see **Figures 2.4-9 through 2.4-11**). Also, for two hours each day the GC is calibrated (done using 14 species daily and 56 species every two weeks) and a blank is run. Calibrations and blanks are usually run during the hours of midnight to 4 AM. In urban areas, early morning hydrocarbon concentrations are usually high due to routine industrial emissions, upset emissions, and pollutant accumulation in the stable nighttime lower atmosphere. A fast moving plume of pollutants could move over the monitor at this time and not be detected. The canisters collect an ambient air sample for the entire twenty-four hours so such an upset would be detected.
- The canisters are not analyzed immediately after the air is sampled. Transport time for the canisters from the site to a laboratory varies from four days to up to three weeks. Precautions are made to ensure that the canister air sample has the same species composition as it did when it was collected (e.g., canisters are not subject to photo-induced chemical effects – Oliver et al., 1985) but changes can occur. The heavier carbon compounds (C9+) tend to adhere to the stainless steel and may have lower recoveries. Isopentane has been known to contaminate the canister due to exhaust fumes getting in during transport. For example, prior to 1997, C2 and C3 compounds (ethane, propane, ethylene, propylene, and acetylene) were not measured with as much accuracy because mass spectrometry is not as sensitive to these lighter species. Since 1997 an FID has been used to measure these lighter compounds in the canisters.
- There are differences between FID and mass spectrometry.

While this analysis points out many large differences between the two measurements, the analysis also showed that for most species the concentrations were within 25% of each other.

- *Additional analyses to consider include:* Add more discussion and further investigation into “why” there may be differences between the two measurements. Recent Battelle work for EPA (Bortnick et al., 2000) sheds some light on this; compare results of this analysis with the Battelle analysis. Consider reordering plots by functional group or order of elution. Are there species in the canisters not measured in the AGC that are important to ozone formation? Are there species not currently measured by the auto-GC (but measurable by canister) that are abundant and important to ozone formation or source identification? If collocated canisters collected over a shorter sampling time period (i.e., less than 24-hr) are available, compare these to the AGC).

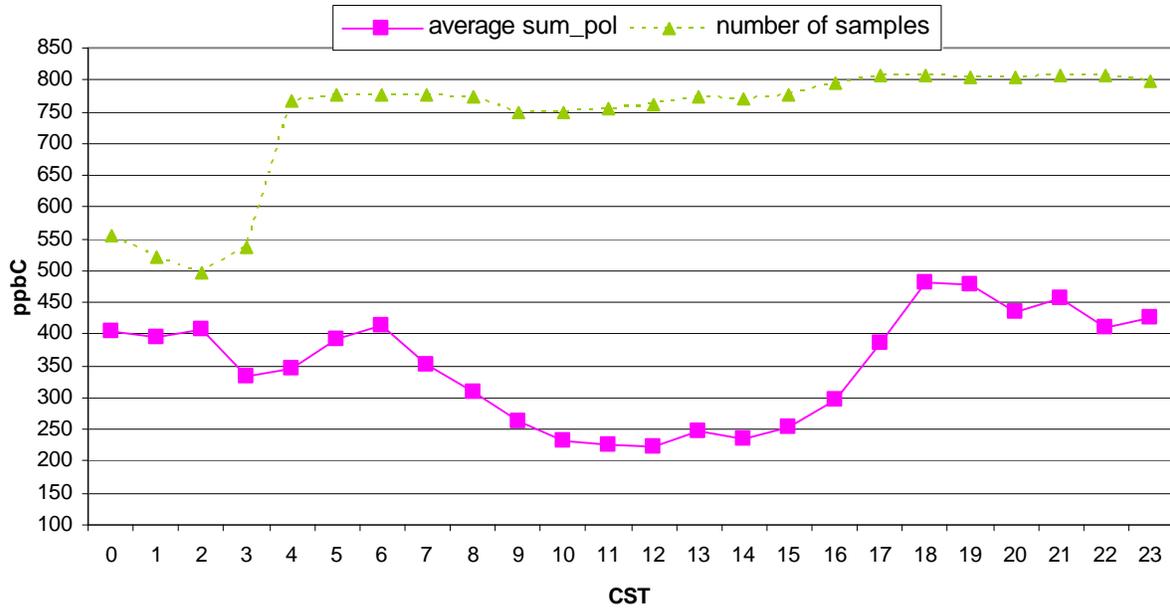


Figure 2.4-9. Average total identified concentrations and number of samples per hour measured by auto-GC at Clinton from 1996 to 1999.

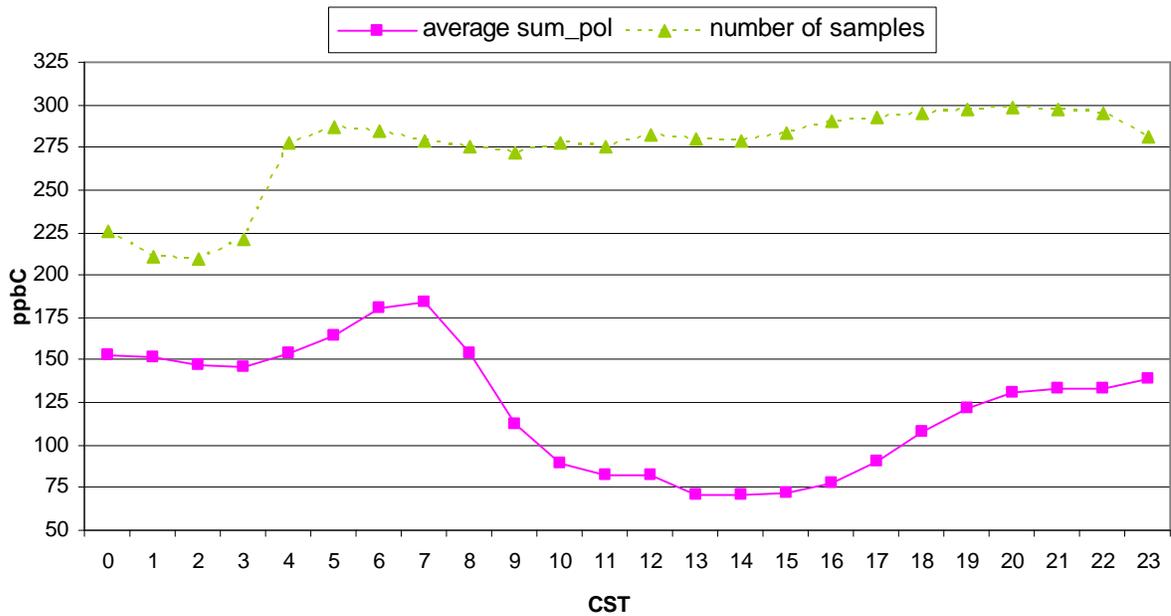


Figure 2.4-10. Average total identified concentrations and number of samples per hour measured by auto-GC at Bayland Park from 1998 to 1999.

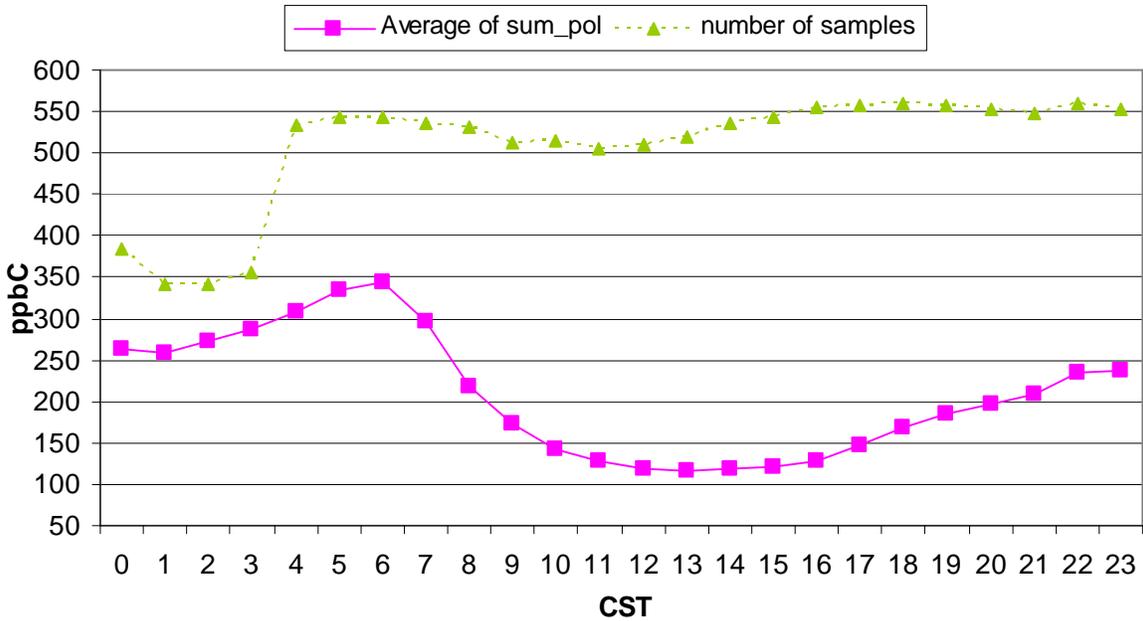


Figure 2.4-11. Average total identified concentrations and number of samples per hour measured by auto-GC at Deer Park from 1997 to 1999.

2.5 DATA QUALITY AND COMPLETENESS

Table 2-8 shows data available for 1998-2000 at the AGC sites. TNRCC staff had previously validated the data. To perform a quick check of the data quality, screening criteria were applied to the data using VOCdat software. Only a few samples failed the screening criteria; these data are summarized in Table 2-9.

Table 2-8. Available AGC data for 1998–2000.

Page 1 of 2

Site	Site Code	Year	Quarter	# of Samples
Aldine	0024	1998	1	0
			2	0
			3	15
			4	0
		1999	1	0
			2	0
			3	62
			4	19
		2000	1	0
			2	25

Table 2-8. Available AGC data for 1998–2000.

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			3	478 ¹		
			4	1121		
Bayland Park	0055	1998	1	0		
			2	794 ²		
			3	978 ³		
			4	1638		
		1999	1	1714		
			2	1614		
			3	1358 ⁴		
			4	1818		
		2000	1	1226		
			2	1641		
			3	457 ^{3,5}		
			4	14		
Clinton Drive	1035	1998	1	1893		
			2	1616		
			3	949 ³		
			4	1860		
		1999	1	1597		
			2	1472		
			3	1696		
			4	1177		
		2000	1	1932		
			2	1672		
			3	1260 ⁶		
			4	1264 ³		
		Deer Park	1039	1998	1	1505
					2	1375 ³
					3	1533
					4	1500 ³
1999	1			252		
	2					
	3			1768		
	4			1808		
2000	1			710 ⁷		
	2			1508		
	3			425 ³		
	4			287 ⁴		

¹ POC code 3 used for determining sample number. POC code 6 had 35 samples.

² Missing TNMOC in many samples

³ Missing propylene in many samples

⁴ Value represents complete samples; many samples were missing either the A or B column results.

⁵ POC code 1 used for determining sample number. POC code 4 had 22 samples.

⁶ Missing ethylene in many samples.

⁷ For many samples, TNMOC is reported but no individual species data are shown.

Table 2-9. Summary of data failing screening criteria.

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

3. CHARACTERIZING HYDROCARBONS IN HOUSTON

This section contains descriptions and interpretation of the hydrocarbon data in Houston. The current version of this section includes analyses performed by TNRCC, brief descriptions of analyses performed by STI, and suggestions for additional analyses. Additional analyses, interpretation and summary of results will be prepared later.

3.1 OVERALL CHARACTERISTICS

It is helpful to have an overall understanding of the database before proceeding to a more detailed analysis. **Table 3.1-1** summarizes the summary statistics (minimum, maximum, mean, median, 75th, and 95th percentile) for TNMOC and unidentified concentrations, isoprene percentages, and ethene-to-ethane and toluene-to-benzene ratios at each site.

Prepare and Insert Table 3.1-1. Add observations from the table to the bullets below:

- TNMOC concentrations are an indicator of emission source strength impacting the site.
- The unidentified hydrocarbon concentrations are computed by taking the difference between the reported TNMOC and the sum of the identified hydrocarbons.
- Isoprene is typically the only tracer for biogenic emissions that is reported in the PAMS program. Isoprene also has industrial sources as well.
- The toluene/benzene ratio is also an indicator of source strength and the proximity of fresh emissions. Toluene reacts away faster in the atmosphere than benzene and, thus, a lower ratio can be an indication of a more aged air mass.
- Typically, ethane concentrations exceed ethene because of the much higher reactivity of ethene. However, in the Houston area, there are many ethene sources and the ratio often exceeds 1.

Another way to compare sites and obtain an overall understanding of the data is to inspect various stratifications of selected hydrocarbons and species groups. The data may be stratified in different ways: by site, year, month, day of week, and time of day. Box whisker plots are commonly used to display a large amount of data and are particularly useful in assessing differences between data. Box whisker plots are drawn in different ways by different software programs. However, most box whisker plots show an interquartile range (i.e., 25th to 75th percentile) and some way to illustrate data outside this range. **Figure 3.1-1** shows an illustrated box whisker plot. The box shows the 25th, 50th (median), and 75th percentiles. The whiskers always end on a data point, so 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 three times the interquartile range from the end of the box and circles representing points beyond this.

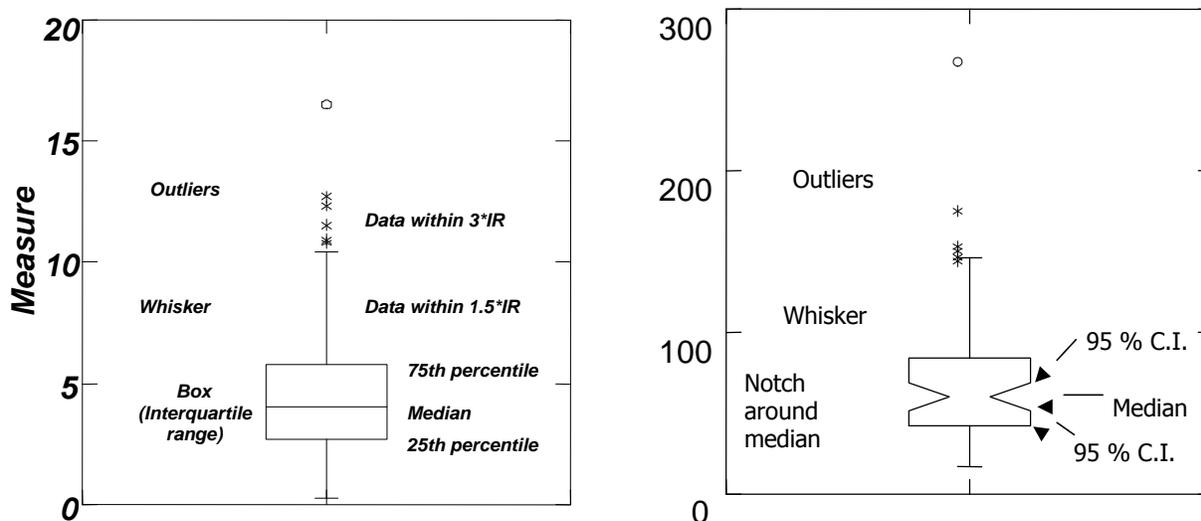


Figure 3.1-1. Illustration of box-whisker plots and notched box whisker plots as defined by SYSTAT statistical software.

Since sample size is also an important consideration when one begins to stratify data, notched box whisker plots have been used to analyze data in this study (see Figure 3.1-1). 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 values¹. We selected 95% confidence intervals. If the 95% confidence interval is beyond the 25th or 75th percentile, then the notches extend beyond the box (hence the "folded" appearance).

Figures 3.1-2 through 3.1-4 show the diurnal variation of the TNMOC and species group concentrations at Aldine, Clinton, and Deer Park in 2000 using notched box plots.

3.2 ABUNDANT SPECIES

There are more than 55 PAMS target species in the AGC database. To help focus the analyses, it is important to identify the most abundant species. Abundance is assessed based on both concentration and on reactivity-weighted composition because some hydrocarbons, while very abundant (e.g., ethane), are less important to the ozone formation process, while others are less abundant but more reactive and thus important for ozone formation. There are various methods to weight data based on reactivity, including reaction rates with OH, propylene equivalents, and maximum incremental reactivity (MIR). The MIR scale (Carter 1994, 2000) was used to characterize the reactivity of the samples. The MIR scale provides an estimate of moles ozone formed per mole carbon of each hydrocarbon measured, where the ozone formation estimates are intended to be used in a relative rather than absolute manner. The reactivity of each species is estimated by multiplication of its weight percent or

¹ 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.

concentration by its MIR factor. Note that the unidentified mass can be a significant contributor to the total carbon and its potential reactivity is unknown.

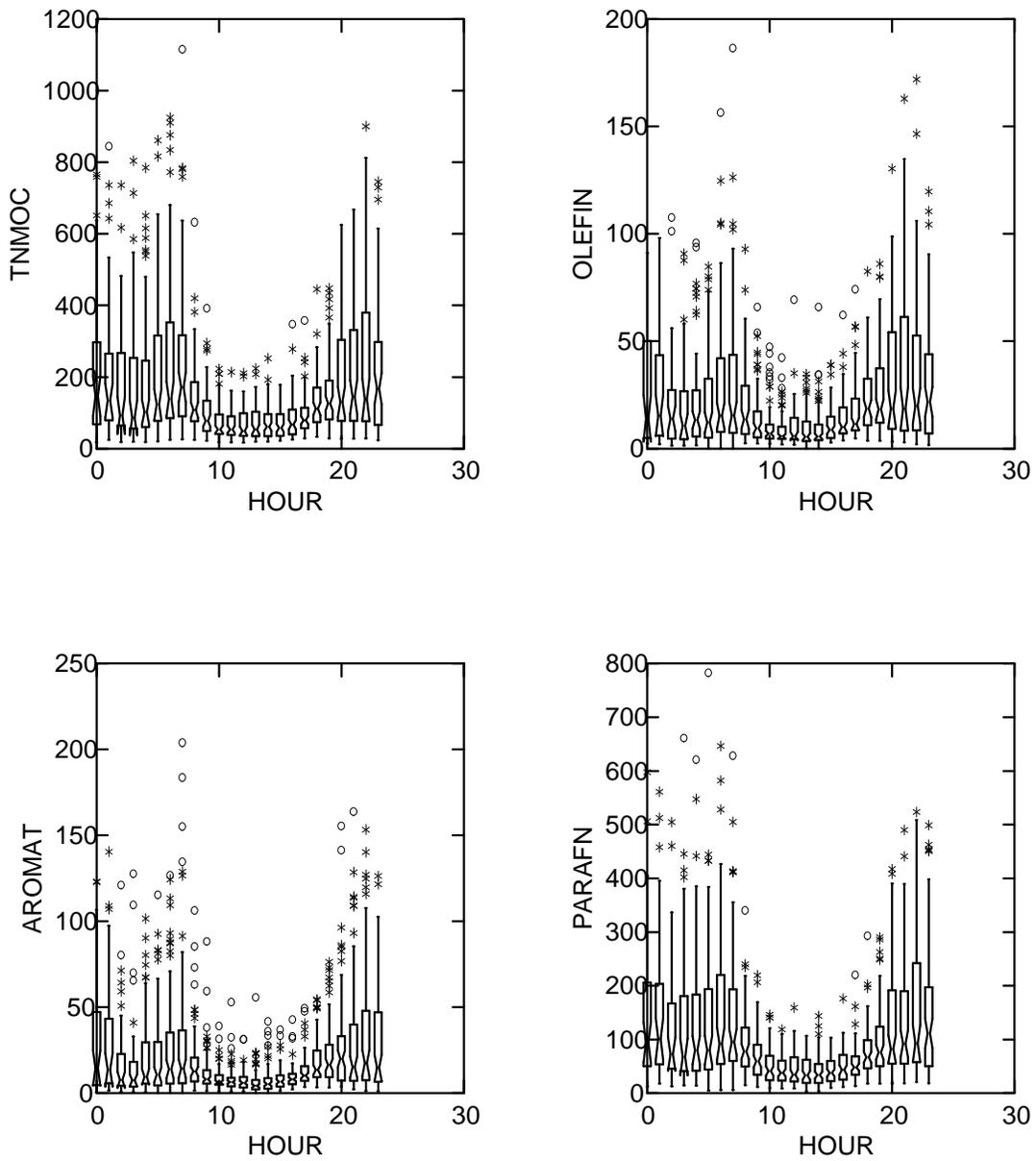


Figure 3.1-2. Notched box plot of TNMOC, olefin, aromatic hydrocarbon, and paraffin concentrations (ppbC) by time of day at Aldine in 2000.

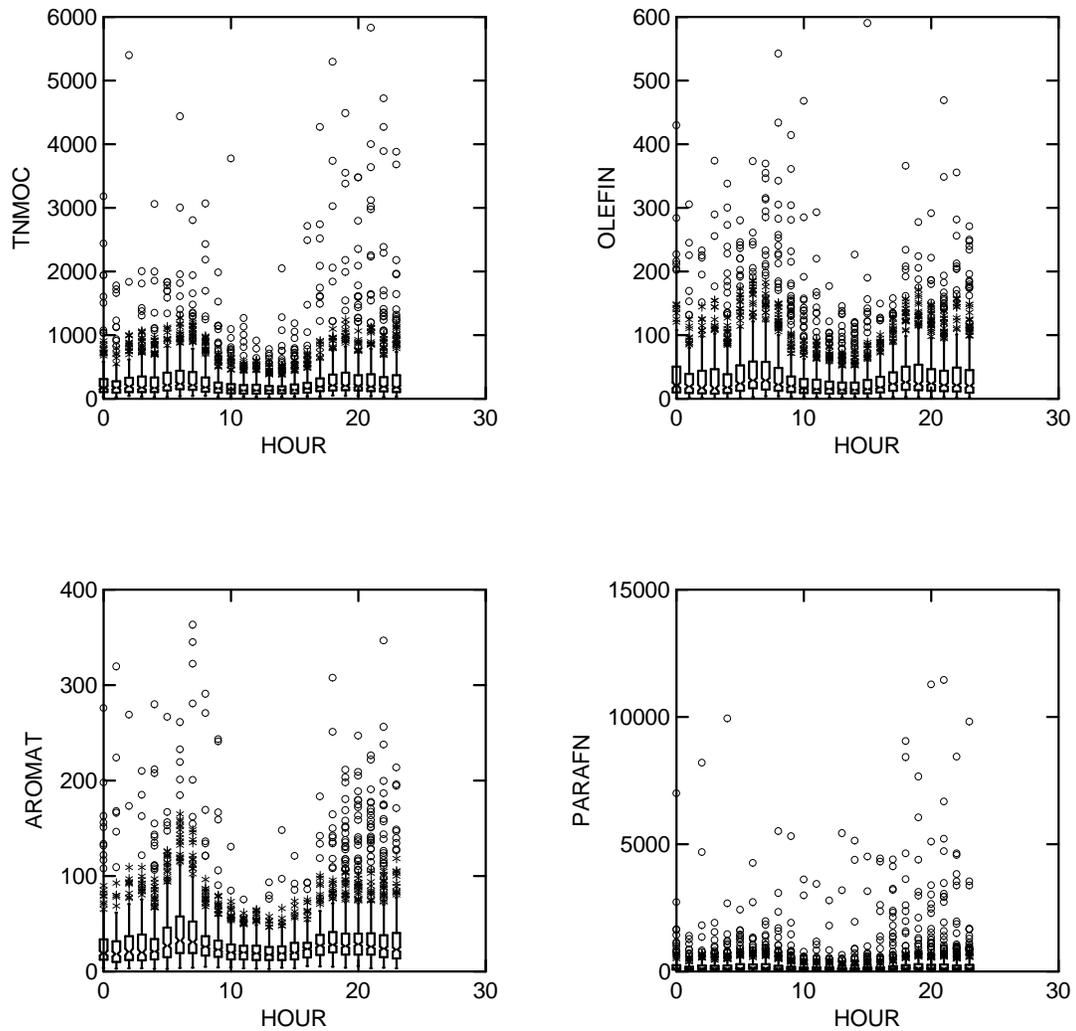


Figure 3.1-3. Notched box plot of TNMOC, olefin, aromatic hydrocarbon, and paraffin concentrations (ppbC) by time of day at Clinton in 2000. Note that several samples with high paraffin concentrations were missing TNMOC data.

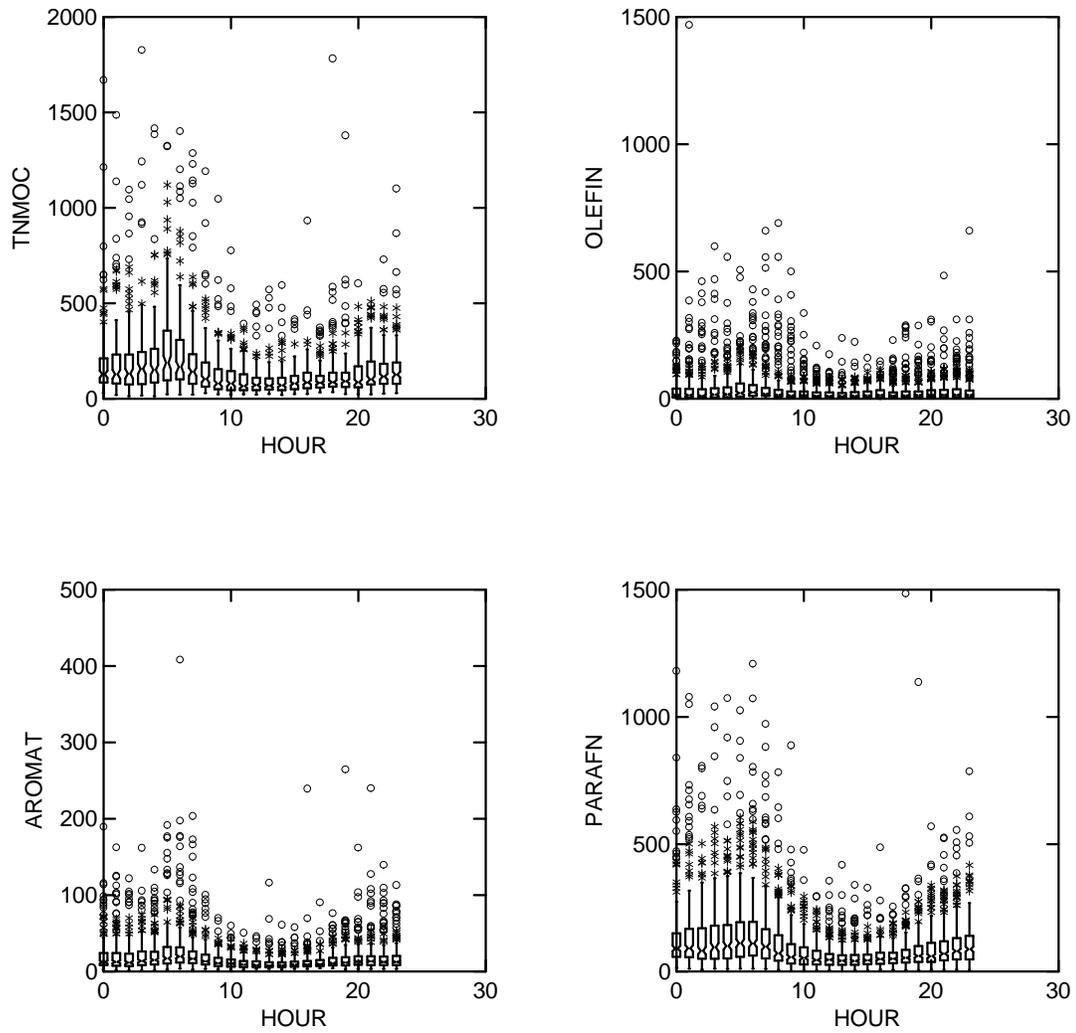


Figure 3.1-4. Notched box plot of TNMOC, olefin, aromatic hydrocarbon, and paraffin concentrations (ppbC) by time of day at Deer Park in 2000.

Tables 3.2-1 and 3.2-2 list the ten most abundant hydrocarbons on a concentration basis and on a reactivity-weighted basis, respectively at Aldine, Clinton, and Deer Park in 2000.

Table 3.2-1 Ten most abundant hydrocarbons at Aldine, Clinton, and Deer Park in 2000.

Species	Aldine	Clinton	Deer Park
ethane	1	2	1
propane	2	3	2
n-butane	3	1	3
i-pentane	4	4	5
i-butane	5	5	4
ethene	6	9	6
n-pentane	7	7	9
toluene	8	6	8
propene	9		7
xylenes	10	8	
2-methylpentane		10	
n-hexane			10

Table 3.2-2 Ten most abundant hydrocarbons on a reactivity-weighted basis (using Carter's MIR) at Aldine, Clinton, and Deer Park in 2000

Species	Aldine	Clinton	Deer Park
ethene	1	2	2
propene	2	1	1
xylenes	3	3	3
i-pentane	4	4	5
toluene	5	6	4
n-butane	6	5	
1,2,4-trimethylbenzene	7	7	9
propane	8		7
i-butane	9	8	6
1,2,3-trimethylbenzene	10		
3-methyl-1-butene		9	
1-butene		10	
ethane			8
n-pentane			10

Given the high density of emission sources in Houston, the abundance of hydrocarbons as a function of wind direction was also investigated. **Tables 3.2-3 through 3.2-8** summarize the ten most abundant hydrocarbons at the three sites by wind quadrant.

- *Additional analyses to consider:* Investigate whether this list has changed over time (e.g., compare to 1993 Clinton data); investigate the variability of abundant species by episode.

Table 3.2-3 Ten most abundant hydrocarbons by wind quadrant at Aldine in 2000.

Species	Wind Quadrant							
	0-45°	45-90°	90-135°	135-180°	180-225°	225-270°	270-315°	315-360°
ethane	1	1	1	1	1	1	1	1
propane	2	2	2	4	2	2	2	2
n-butane	3	3	3	2	3	3	3	3
isopentane	4	4	6	3	4	4	4	4
isobutane	5	5	4	5	7	5	6	5
n-pentane	6	7	9	8	9	8	5	6
ethene	7	6	5	6	6	7	8	7
toluene	8	8	8	7	5	6	7	8
acetylene	9							9
benzene	10							
n-hexane		9					10	
2-methylpentane		10					9	
propene			7	9		10		
xylenes			10	10	8	9		10
isoprene					10			

Table 3.2-4 Ten most abundant hydrocarbons by wind quadrant on a reactivity-weighted basis (using Carter's MIR) at Aldine in 2000.

Species	Wind Quadrant							
	0-45°	45-90°	90-135°	135-180°	180-225°	225-270°	270-315°	315-360°
ethene	1	1	1	1	1	1	1	1
propene	2	2	2	2	2	2	3	2
xylenes	3	5	3	3	3	3	4	3
isopentane	4	3	6	5	6	5	5	5
toluene	5	6	4	4	4	4	6	6
n-butane	6	4	5	6	9	7	2	4
1,2,4-trimethylbenzene	7	9	10	7	5	6	8	7
propane	8	7	8			8	7	8
isobutane	9	8	7	8		9	9	9
ethane	10	10					10	10
isoprene					7			
1-butene			9	10				
1,2,3-trimethylbenzene				9	8	10		
3-methyl-1-butene					10			

Table 3.2-5 Ten most abundant hydrocarbons by wind at Clinton in 2000.

Species	Wind Quadrant							
	0-45°	45-90°	90-135°	135-180°	180-225°	225-270°	270-315°	315-360°
ethane	1	1	1	5	2	1	1	1
propane	2	2	2	3	1	2	2	2
n-butane	3	3	3	1	4	4	4	3
isopentane	4	4	4	2	3	3	3	4
isobutane	5	5	5	4	5	8	7	5
toluene	6	9	8	7	7	5	5	6
n-pentane	7	7	6	6	8	10	8	7
xylenes	8			8	6	6	6	8
2-methylpentane	9			9				9
ethene	10	6	9		9	7	9	
acetylene								
benzene			10				10	
n-hexane		10		10				10
propene		8	7		10	9		

Table 3.2-6 Ten most abundant hydrocarbons by wind quadrant on a reactivity-weighted basis (using Carter's MIR) at Clinton in 2000.

Species	Wind Quadrant							
	0-45°	45-90°	90-135°	135-180°	180-225°	225-270°	270-315°	315-360°
ethene	1	2	2	5	3	2	1	2
xylenes	2	5	3	1	2	3	2	1
propene	3	1	1	3	1	1	3	3
toluene	4	7	6	7	7	4	4	5
n-butane	5	4	5	4	8	7	8	4
isopentane	6	3	4	2	6	6	5	6
propane	7	9				10	10	8
1,2,4-trimethylbenzene	8				4	5	6	7
isobutane	9	8	7		10			9
ethane	10							
n-pentane			9					
isoprene							7	
1-butene		10	8	10				
1,2,3-trimethylbenzene						9		
3-methyl-1-butene			10	9	9	8	9	10
1,3-butadiene		6			5			
trans-2-butene				6				
cis-2-butene				8				

Table 3.2-7 Ten most abundant hydrocarbons by wind at Deer Park in 2000.

Species	Wind Quadrant							
	0-45°	45-90°	90-135°	135-180°	180-225°	225-270°	270-315°	315-360°
propene	1	6	3	9	8	10	10	7
propane	2	2	2	2	2	2	1	2
ethane	3	1	1	1	1	1	2	1
isobutane	4	4	6	5	5	5	5	5
n-butane	5	3	5	3	3	3	3	3
isopentane	6	7	8	4	4	4	4	4
ethene	7	5	4	8	7	7	8	6
n-pentane	8	8		7	9	8	7	8
toluene	9	9	7	6	6	6	6	9
benzene	10							
xylenes			10	10	10	9	9	
2-methylpentane								
acetylene								
n-hexane		10	9					10

Table 3.2-8 Ten most abundant hydrocarbons by wind quadrant on a reactivity-weighted basis (using Carter's MIR) at Deer Park in 2000.

Species	Wind Quadrant							
	0-45°	45-90°	90-135°	135-180°	180-225°	225-270°	270-315°	315-360°
propene	1	1	1	1	1	2	2	
ethene	2	2	2	2	2	1	1	
isobutane	3	3	4	8	8	8	7	
xylenes	4	7	5	3	3	3	3	
1,3-butadiene	5	10						
toluene	6	8	3	4	4	4	4	
isopentane	7	5	8	5	5	5	5	
n-butane	8	4	7	7	6	7	6	
propane	9	6	6	6	7	6	8	
1-butene	10		10					
1,2,4-trimethylbenzene				10	9	9	9	
ethane		9	9	9	10	10		
n-pentane							10	

3.3 DISTRIBUTION OF VOCs AT EACH SITE

It is important to understand the distribution of concentrations of abundant hydrocarbons in order to better understand which statistics are applicable.

Prepare and insert histograms and discussion.

Figure 3.3-1 compares median fingerprints at Aldine, Clinton, and Deer Park in 2000. The fingerprint plots are designed to show the hydrocarbon species in the order of elution from the chromatograph.

- *Additional analyses to consider:* Histograms of key species (based on the lists developed in section 3.2) and the totals (TNMOC, species groups). Fingerprints of median, 75th, 95th, and maximum concentrations by site. Discuss implications to preparation of averages, medians, and other statistical analyses.

3.4 DIURNAL CHARACTERISTICS

Understanding the variation of concentrations of abundant hydrocarbons helps us understand potential sources, implications to ozone formation, and possible control measures.

Figures 3.4-1 through 3.4-6 show box plots of abundant species by site and time of day in 2000.

- *Additional analyses to consider:* Median fingerprints by time of day. Additional box plots of abundant species.

3.5 DAY OF WEEK

Investigating the day of week patterns in hydrocarbon concentrations can provide insight into likely sources of the hydrocarbons. For example, since traffic patterns largely depend on the Monday-Friday workweek, one might expect to see large differences in motor vehicle-related hydrocarbon concentrations as a function of day of the week. Some industrial emissions, in contrast, may not have a day of week dependence because operations occur on a 24-7 schedule.

TNRCC staff investigated the day of week differences of AGC data in Houston. AGC data were obtained from the MOTHER database for the months of peak ozone, April through October. At the time of the analysis, data were available at Bayland Park (a residential area far from industry) from 1998, at Deer Park (an area that is residential and surrounded by heavy industry) from 1997, and at Clinton (a site located in heavy industry) from 1996. A day of the week average was calculated for selected species and the total identified concentrations. The species examined included acetylene, propylene, ethylene, benzene, toluene, o-xylene, m-&p-xylenes, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, n-butane, i-butane, c-2-butene, and styrene, as well as the sum of the identified (sum_pol). Plots of the average concentrations by day of week at the three sites are shown in **Figure 3.5-1**.

Add observations.

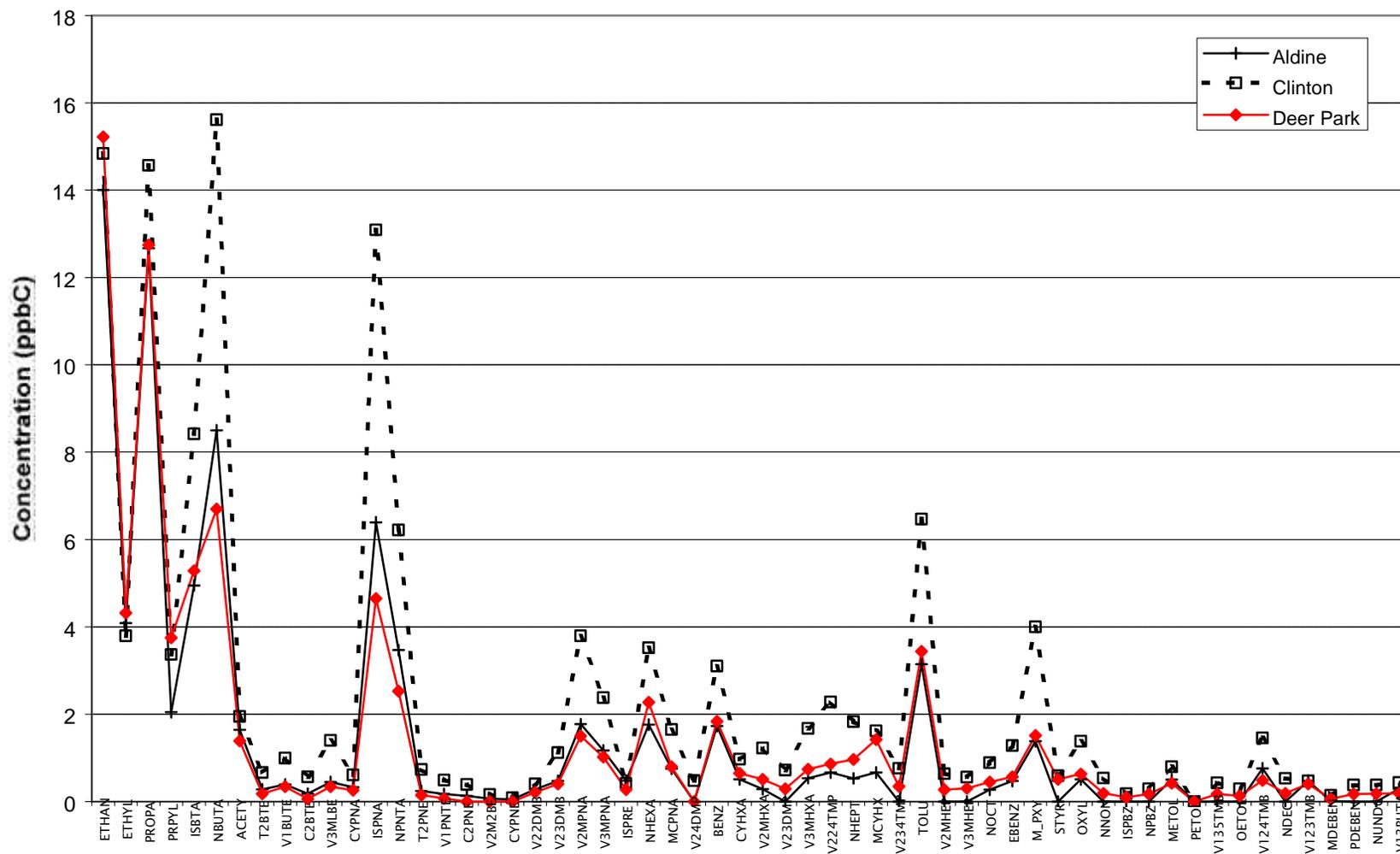


Figure 3.3-1 Comparison of median PAMS target species concentrations in 2000 at Aldine, Clinton, and Deer Park. Species abbreviations are provided in Appendix A.

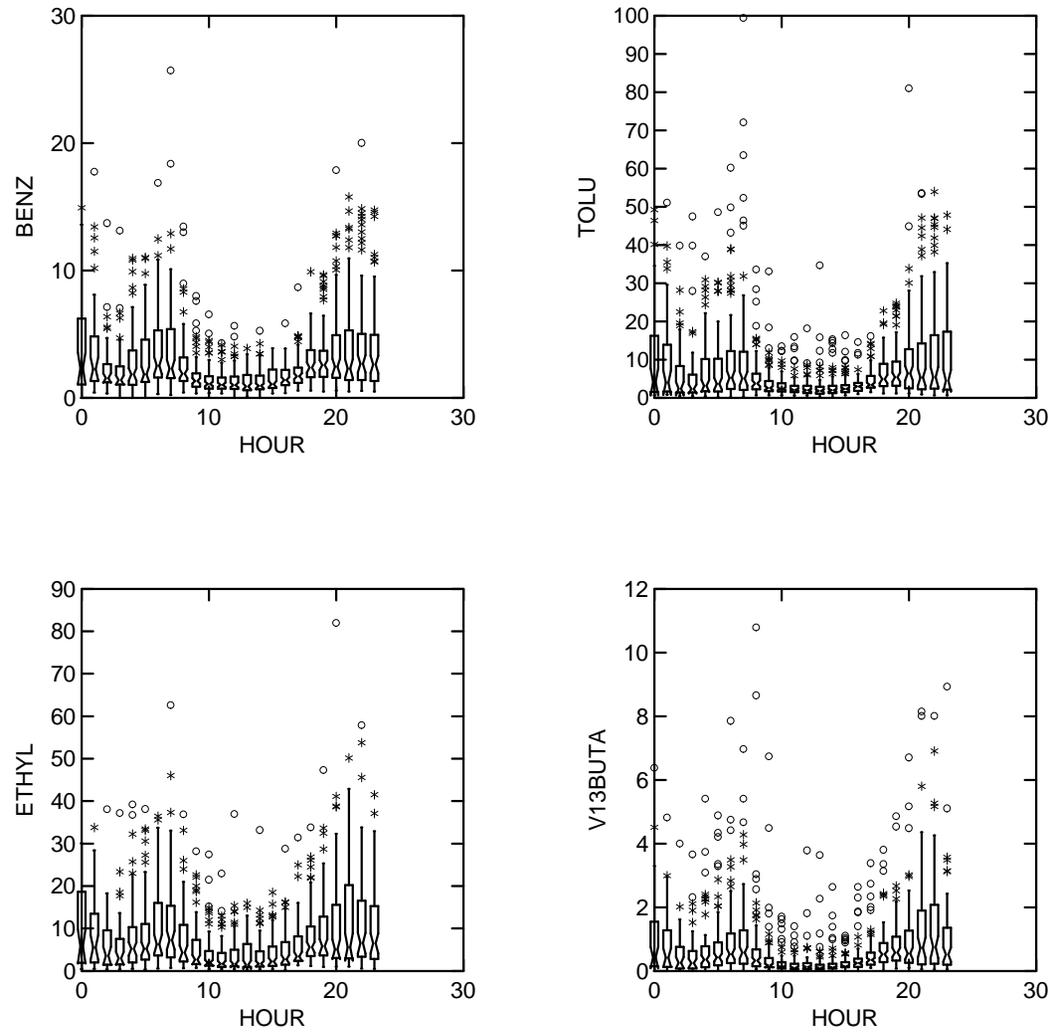


Figure 3.4-1. Notched box plots of benzene (BENZ), toluene (TOLU), ethene (ETHYL), and 1,3-butadiene (V13BUTA) concentrations (ppbC) by time of day in 2000 at Aldine.

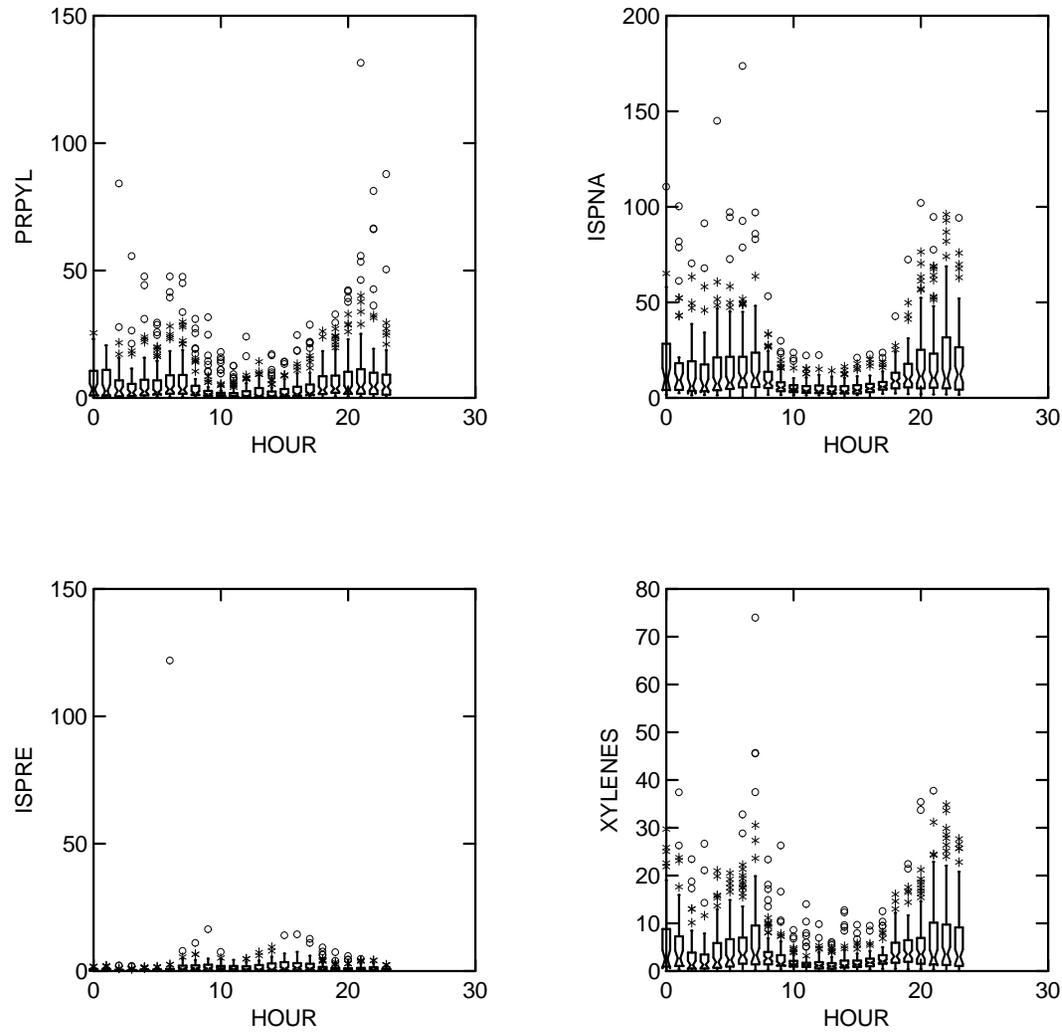


Figure 3.4-2. Notched box plots of propane (PRPYL), i-pentane (ISPNA), isoprene (ISPRE), and total xylenes concentrations (ppbC) by time of day in 2000 at Aldine.

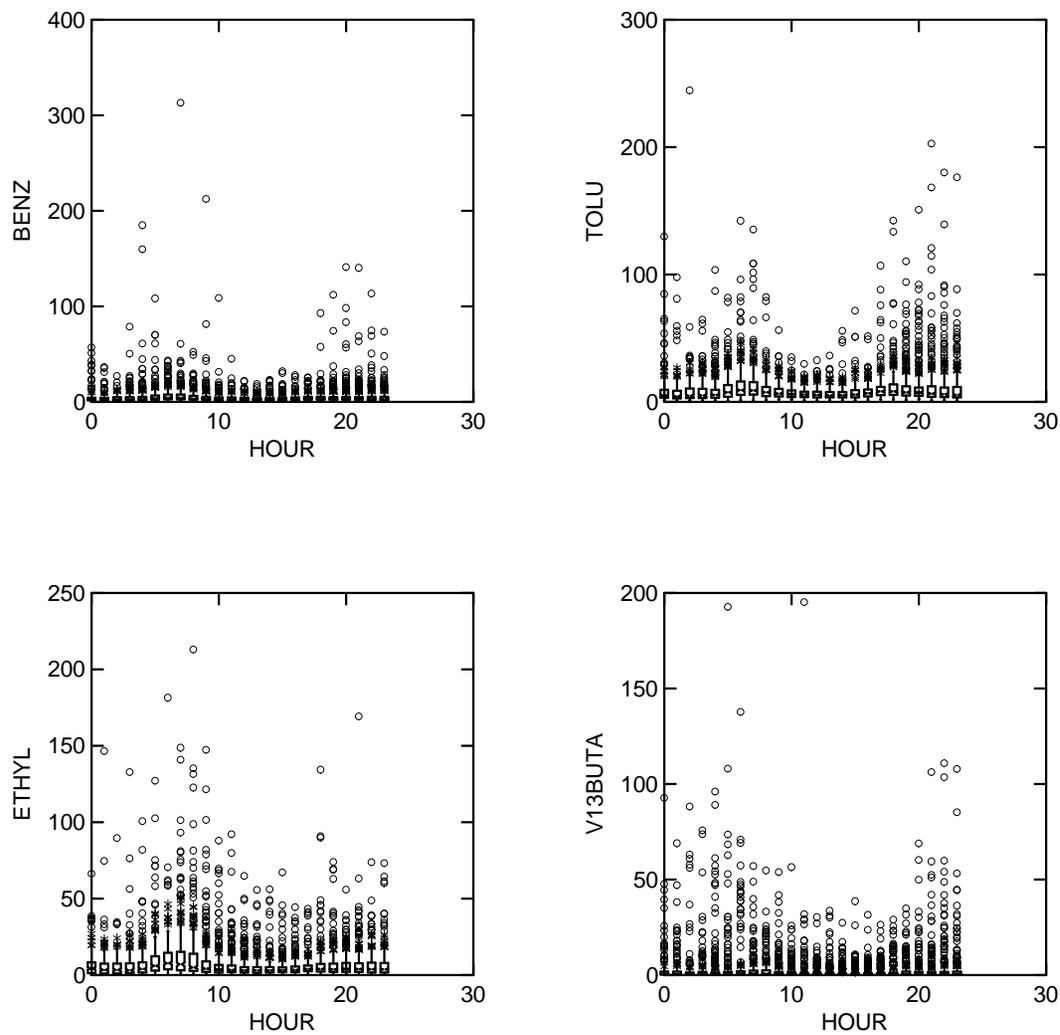


Figure 3.4-3. Notched box plots of benzene (BENZ), toluene (TOLU), ethene (ETHYL), and 1,3-butadiene (V13BUTA) concentrations (ppbC) by time of day in 2000 at Clinton.

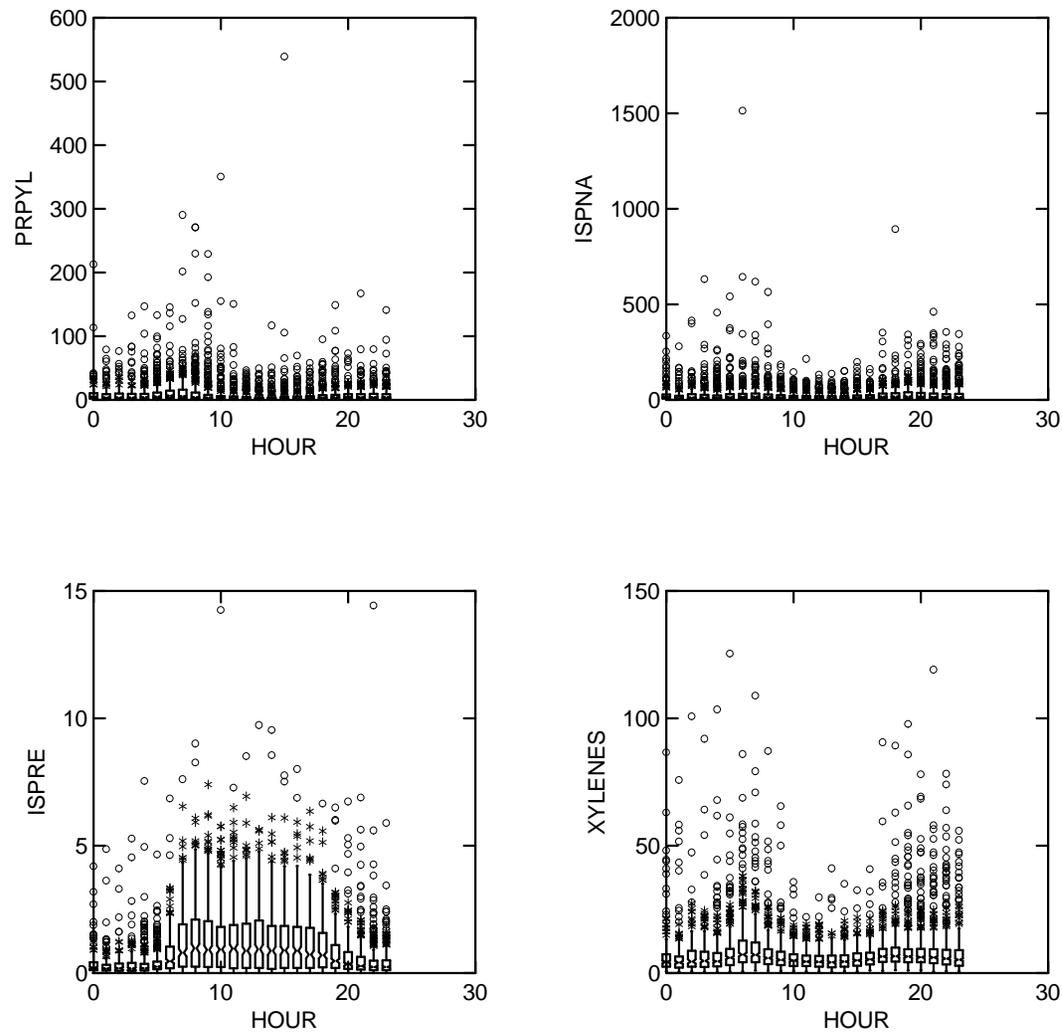


Figure 3.4-4. Notched box plots of propane (PRPYL), i-pentane (ISPNA), isoprene (ISPRE), and total xylenes concentrations (ppbC) by time of day in 2000 at Clinton.

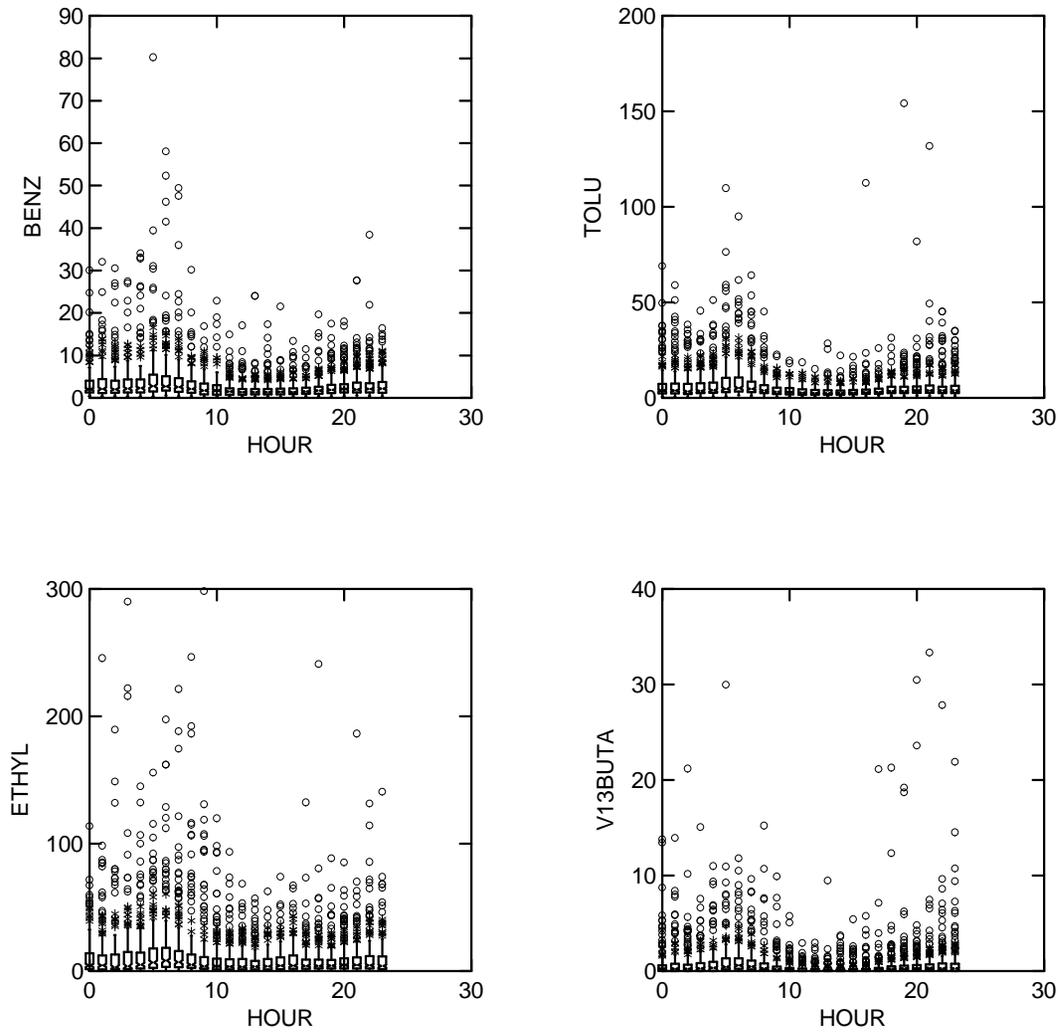


Figure 3.4-5. Notched box plots of benzene (BENZ), toluene (TOLU), ethene (ETHYL), and 1,3-butadiene (V13BUTA) concentrations (ppbC) by time of day in 2000 at Deer Park.

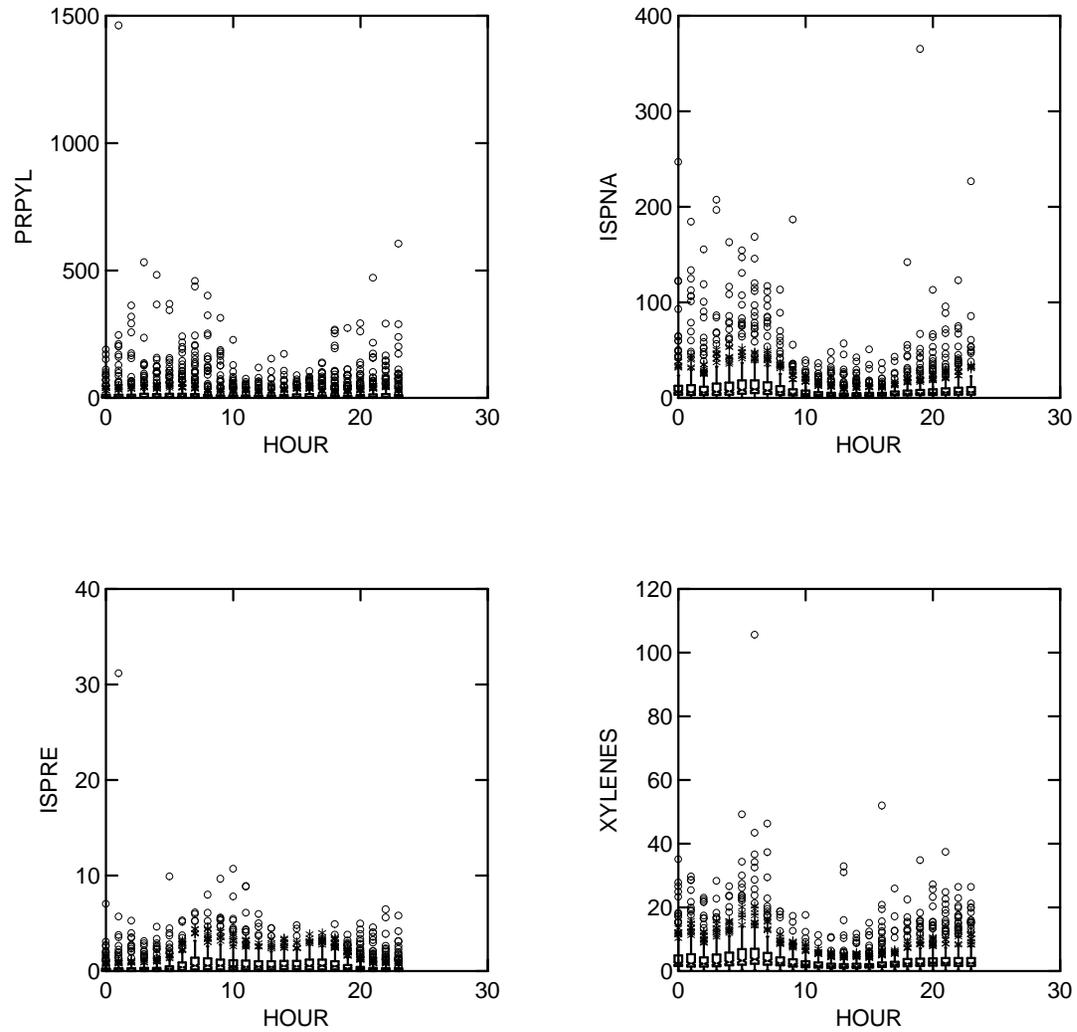


Figure 3.4-6. Notched box plots of propane (PRPYL), i-pentane (ISPNA), isoprene (ISPRE), and total xylenes concentrations (ppbC) by time of day in 2000 at Deer Park.

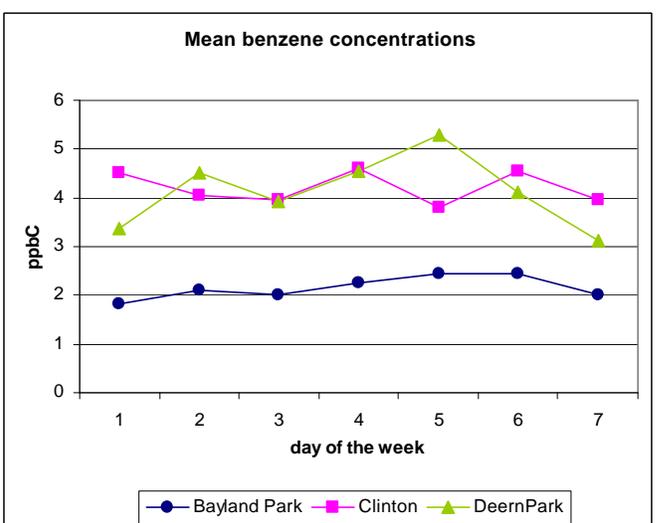
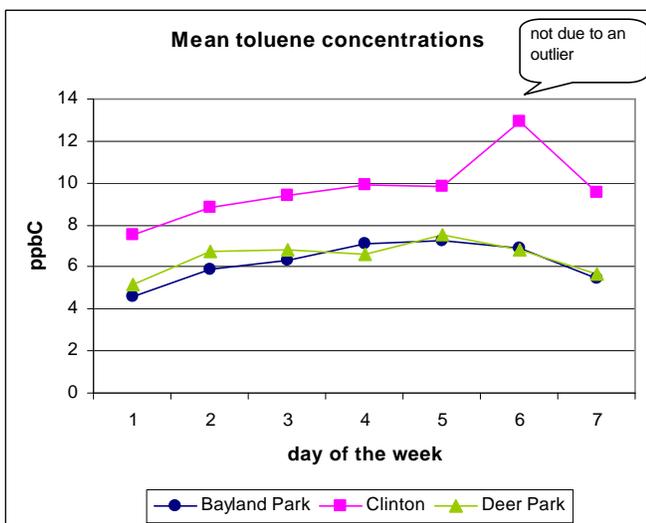
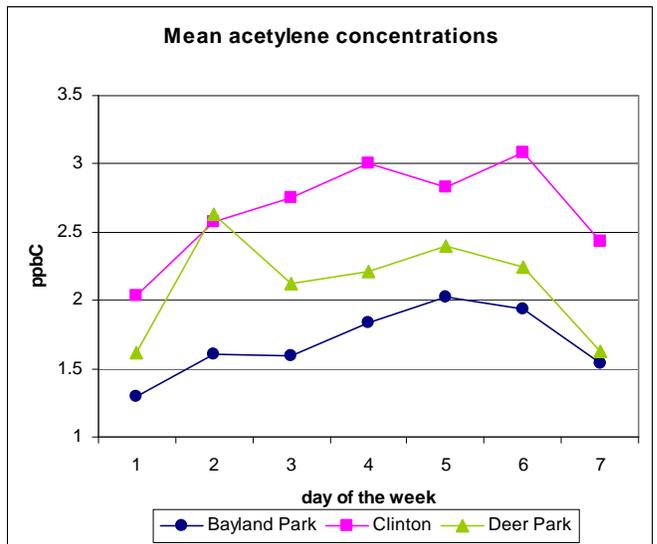
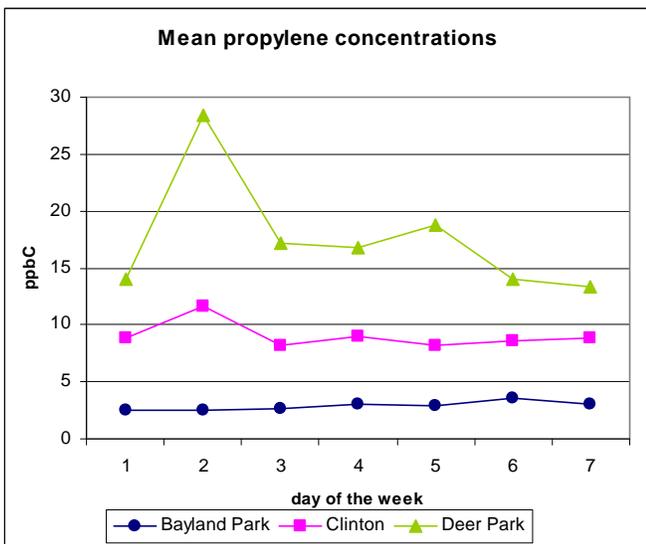
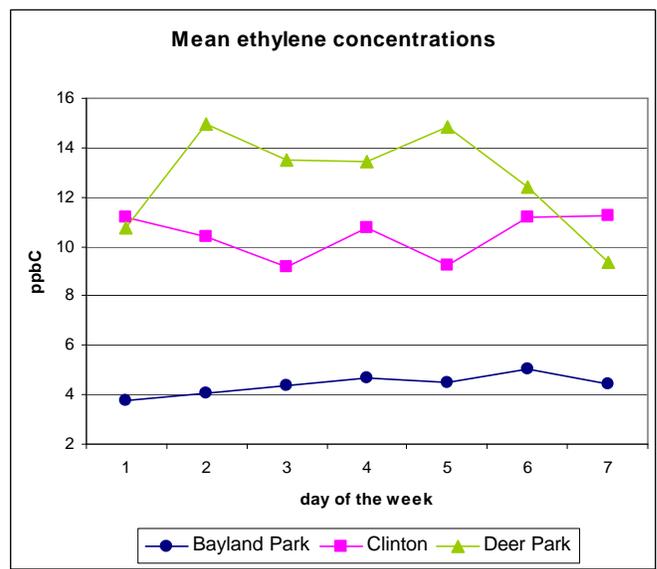
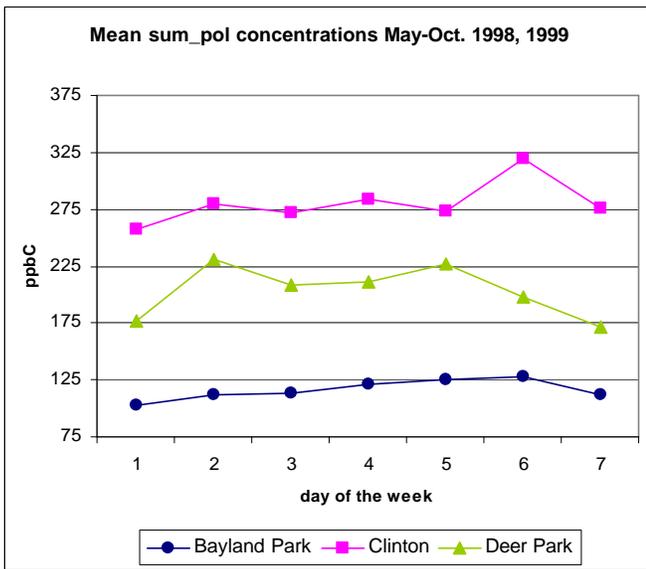


Figure 3.5-1a. Average May-October 1998/1999 concentrations by day of week (Sunday=1) at Bayland Park, Clinton, and Deer Park (continued next page).

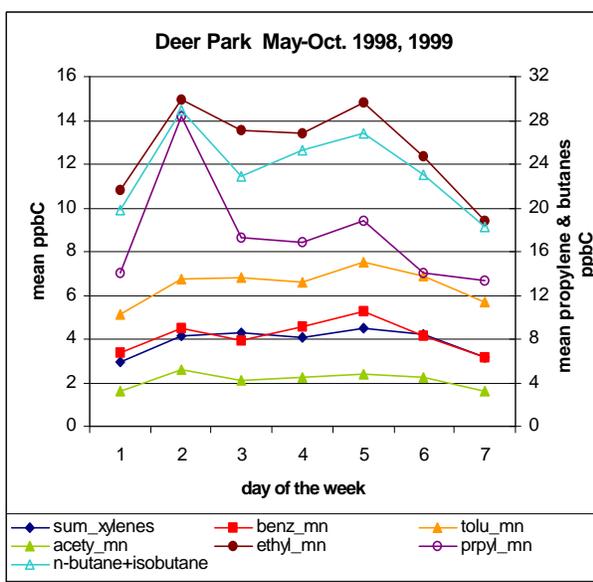
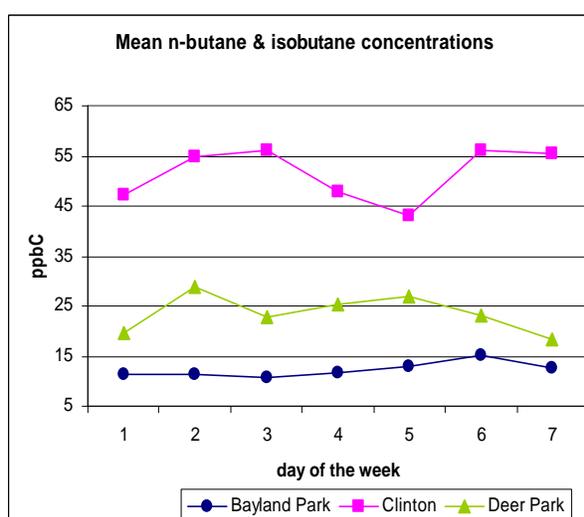
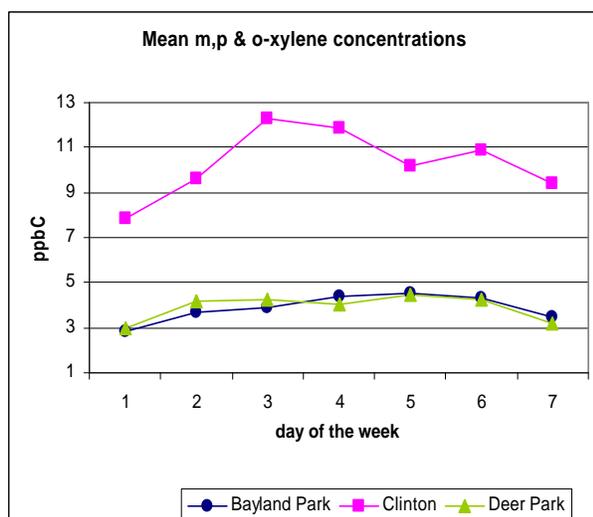
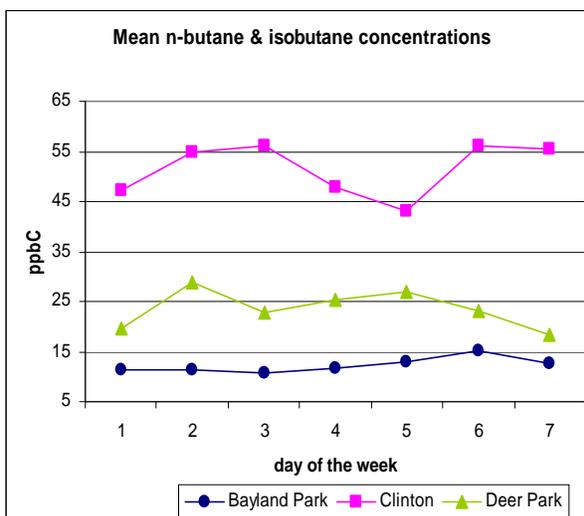
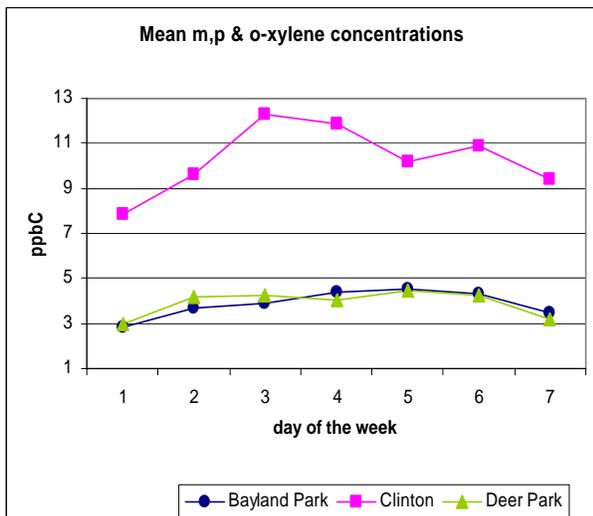


Figure 3.5-1b. Average May-October 1998/1999 concentrations by day of week (Sunday=1) at Bayland Park, Clinton, and Deer Park.

- Bayland Park showed a day of the week pattern that was predominantly influenced by mobile emissions. The lowest species concentrations almost always occurred on the weekends with Sunday being the day with the lowest average concentrations. This pattern was seen with all species except for i-butane, n-butane, and c-2-butene indicating alternative sources of these species. Also, average species concentrations appeared to increase from Monday until Friday before decreasing sharply on Saturday.
- At Deer Park, a similar day of the week trend was observed. Species concentrations were consistently lowest on the weekends, particularly on Sundays. One interesting observation for this site was that many species concentrations tended to be highest on Mondays and Thursdays. Propylene and acetylene appeared to be highest on Monday.
- At Clinton, an overall day of the week trend was much less apparent. For some species, including acetylene, toluene, xylenes, and benzene, average concentrations were lower on the weekends. For other species, including the sum of the identified, ethene, i-butane, and n-butane, a weekly trend in the average was not apparent. Toluene appeared to be highest on Friday.
 - *Additional analyses to consider:* Use the abundant species list to select additional species to investigate. Prepare box plots (to show more of the distribution including outliers) by day of week overall and for morning only (or by time of day) – box plots will help analysts assess statistically significant day of week differences as averages may not be as appropriate for this data set; look at all species, particularly the ones with outliers. Look at day of week patterns in high concentrations (e.g., 95th percentile). Discuss implications to source types, ozone formation.

3.6 EPISODE ANALYSIS

One of the objectives of these analyses is to better understand the conditions (including precursor composition and concentrations) that lead to high ozone episodes in Houston. What do the composition, concentrations, and reactivity-weighted data look like during these days with high ozone concentrations vs. other days?

Figures 3.6-1 through 3.6-3 show the median concentration, weight percent, and reactivity-weighted composition at 0500 CST on episode versus non-episode days.

Clinton 2000
at 0500

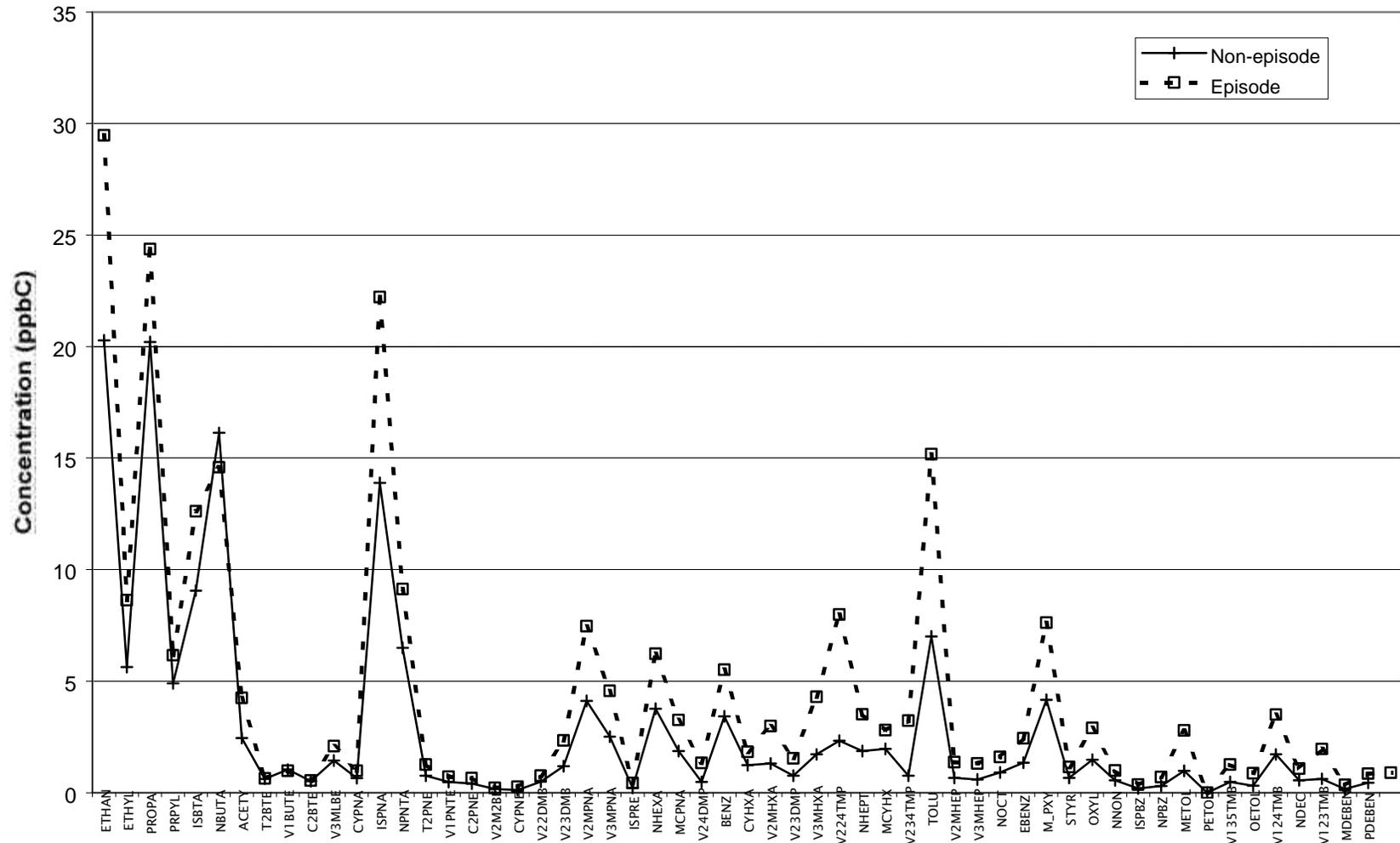


Figure 3.6-1. Median concentrations (ppbC) of PAMS target hydrocarbons at 0500 CST at Clinton During 2000 on ozone episode and non-episode days

Clinton 2000
at 0500

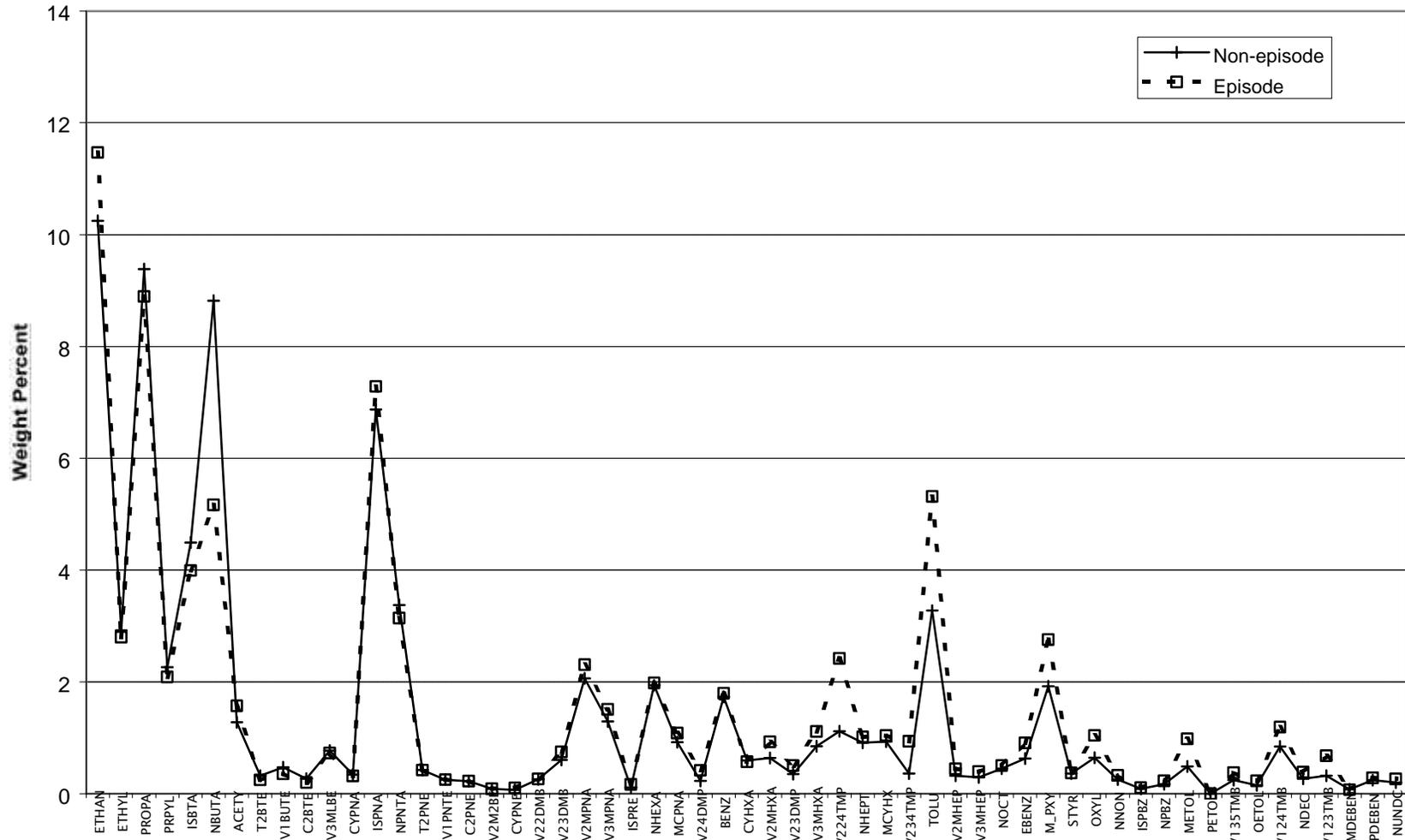


Figure 3.6-2. Median weight percent of PAMS target hydrocarbons at 0500 CST at Clinton During 2000 on ozone episode and non-episode days

Clinton 2000
at 0500

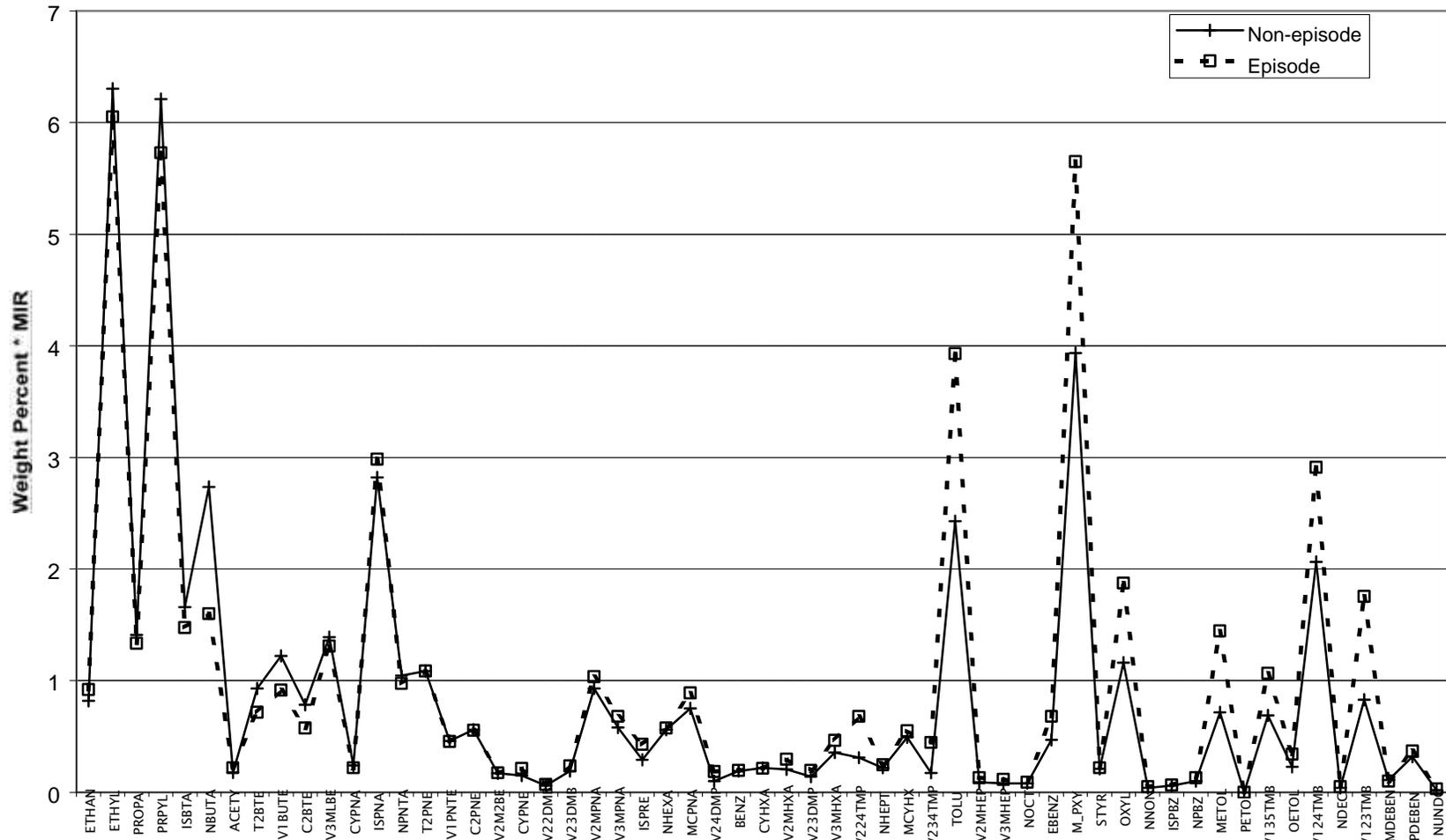


Figure 3.6-3. Median weight percent * MIR (reactivity-weighted composition) of PAMS target hydrocarbons at 0500 CST at Clinton During 2000 on ozone episode and non-episode days.

Figures 3.6-4 and 3.6-5 show the diurnal distribution of propene, i-pentane, isoprene, and xylenes concentrations (ppbC) at Clinton during 2000 on episode vs. non-episode days.

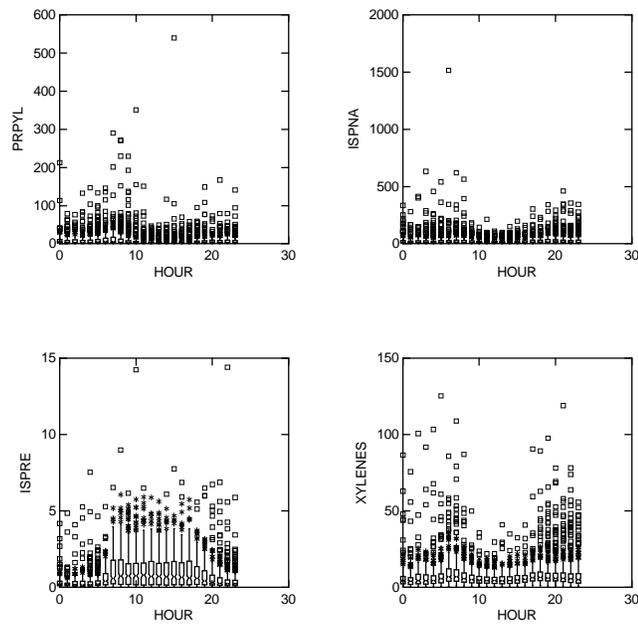


Figure 3.6-4. Diurnal distribution of propene (PRPYL), i-pentane (ISPNA), isoprene (ISPRE), and xylenes concentrations (ppbC) at Clinton during 2000 on non-episode days.

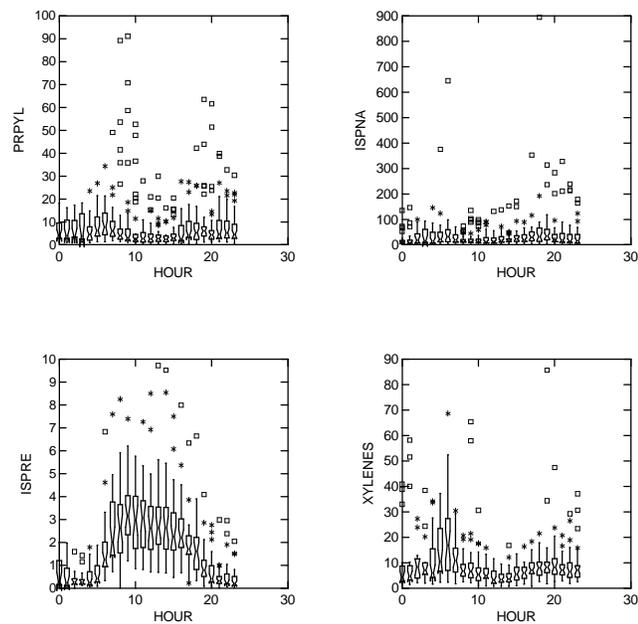


Figure 3.6-5. Diurnal distribution of propene (PRPYL), i-pentane (ISPNA), isoprene (ISPRE), and xylenes concentrations (ppbC) at Clinton during 2000 on episode days.

Insert observations about the figures, discussion of how episodes were selected and a list of episodes.

- *Additional analyses to consider:* Prepare fingerprints of concentration and box plots or summary statistics contrasting the two day types. Investigate how the concentrations vary with time of day between the two day types. This analysis could also include investigation of the meteorology of episodes vs. non-episode days.

3.7 UNUSUALLY HIGH CONCENTRATIONS

What sources are contributing to high VOC concentrations in Houston? Are these high concentrations important in the ozone formation process?

Figures 3.7-1 through 3.7-3 show the median concentration, weight percent, and reactivity-weighted composition in samples above and below 1000 ppbC at Clinton in 2000.

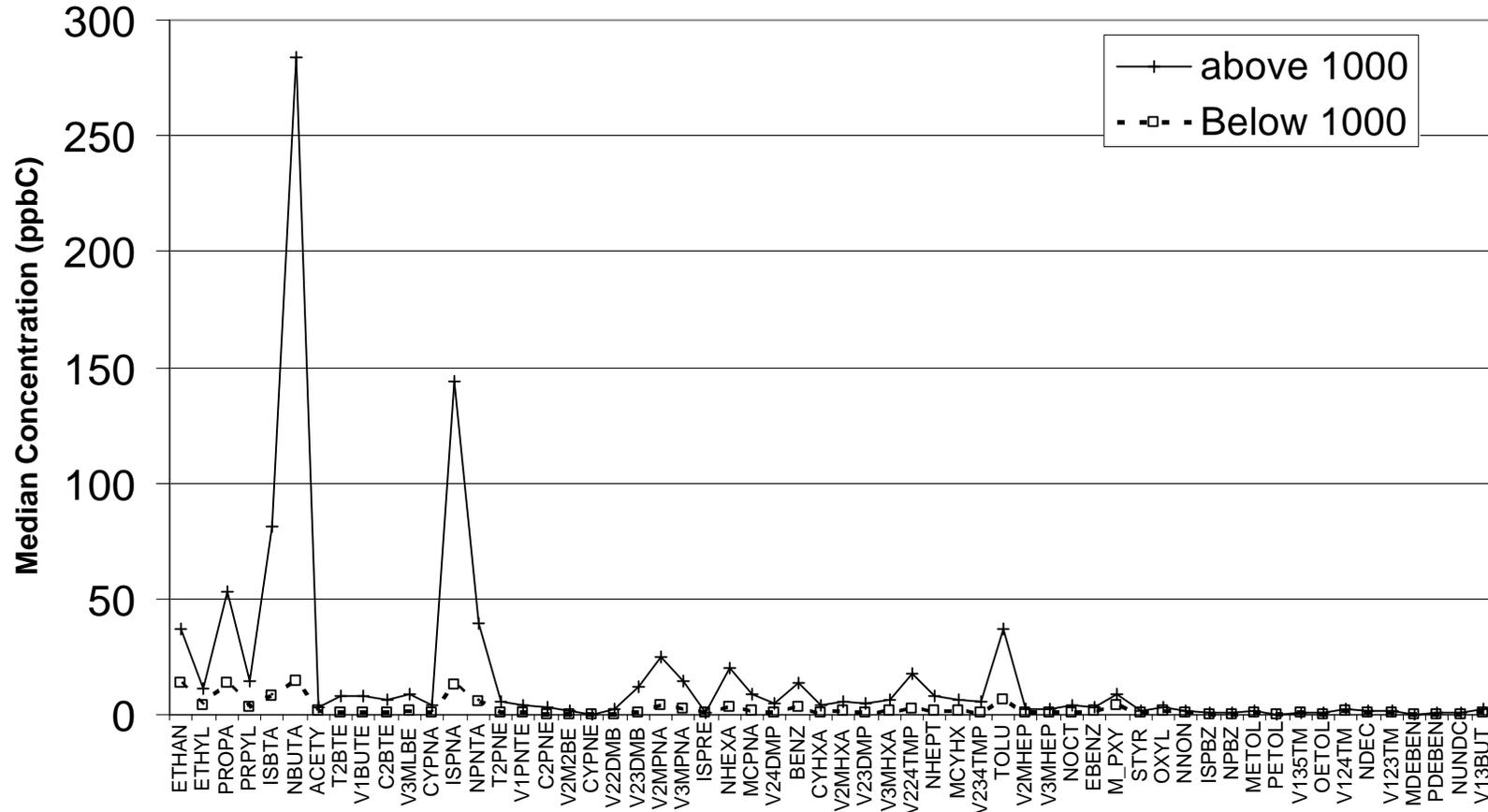


Figure 3.7-1. Median concentrations (ppbC) of PAMS target species at Clinton in 2000 for samples with TNMOC concentrations above and below 1000 ppbC.

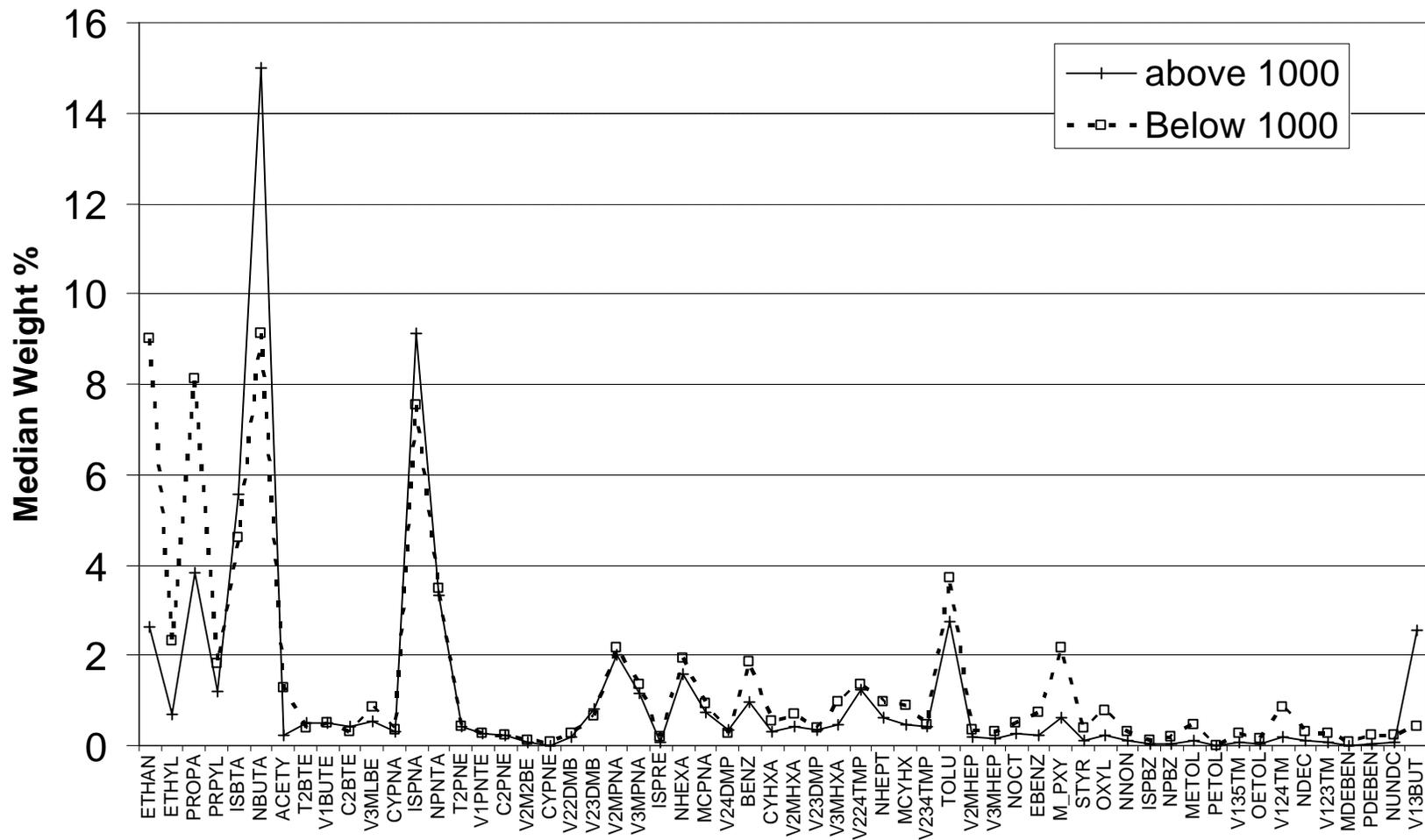


Figure 3.7-2. Median weight percent of PAMS target species at Clinton in 2000 for samples with TNMOC concentrations above and below 1000 ppbC.

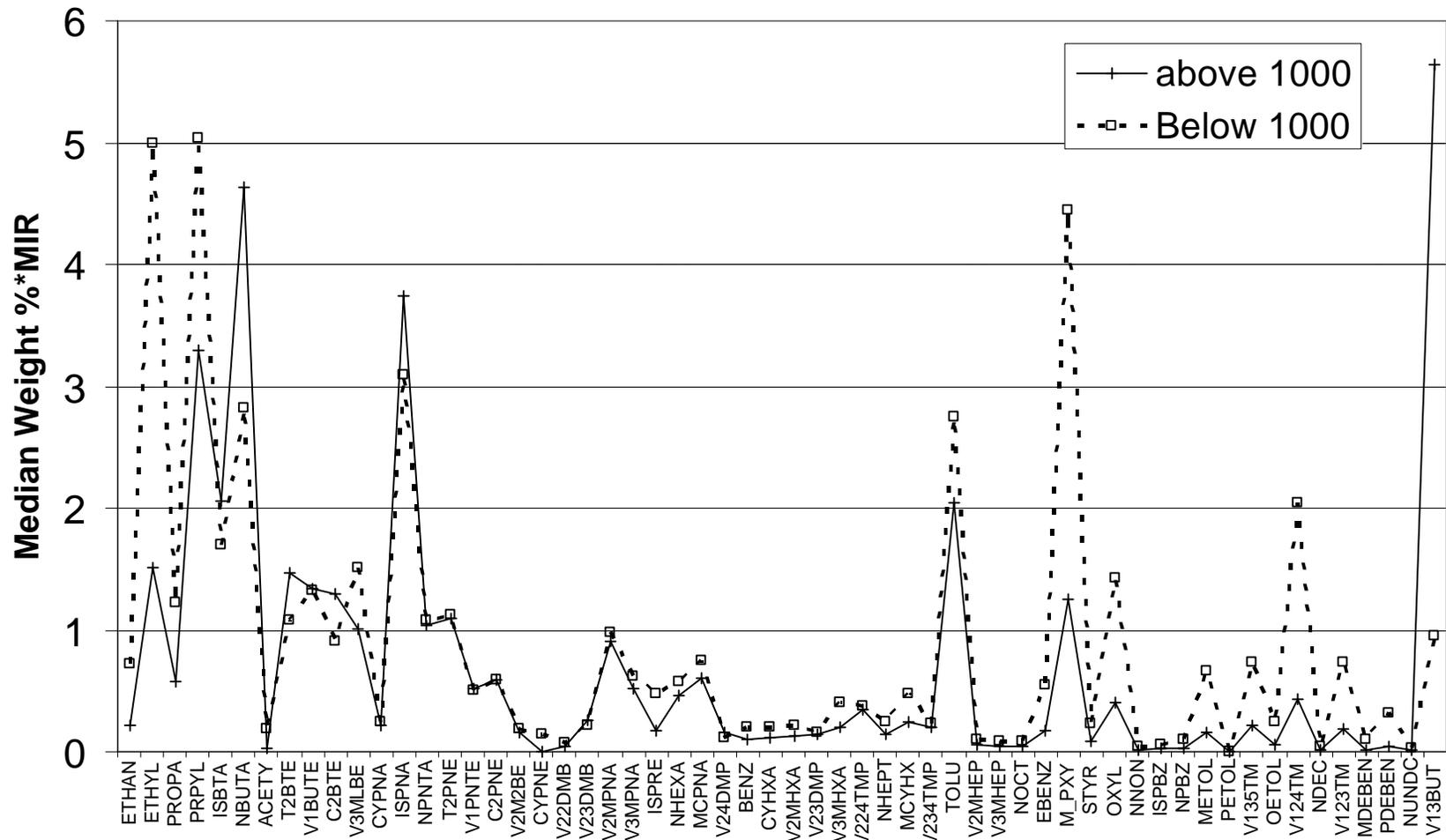


Figure 3.7-3. Median reactivity-weighted values of PAMS target species at Clinton in 2000 for samples with TNMOC concentrations above and below 1000 ppbC.

Figures 3.7-4 and 3.7-5 contrast the diurnal distribution of TNMOC, olefins, aromatics, and paraffins at Clinton in 2000 from two different wind quadrants.

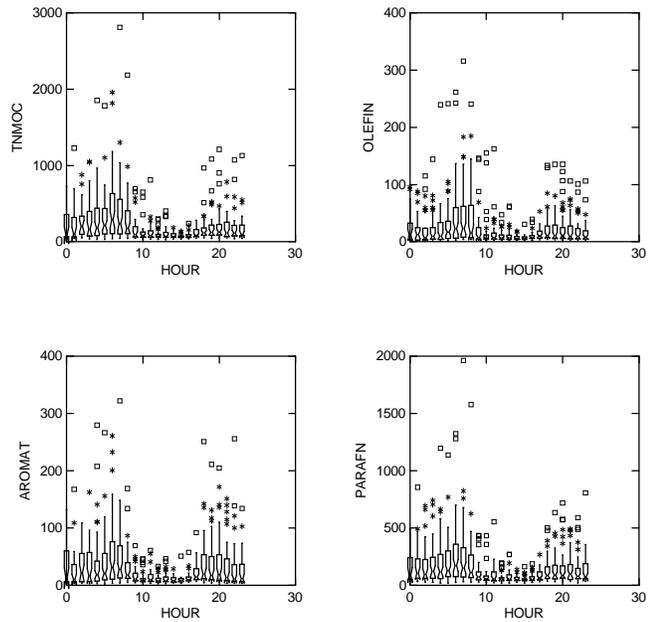


Figure 3.7-4. TNMOC, olefin, aromatic hydrocarbon, and paraffin concentrations (ppbC) by hour at Clinton in 2000 when winds were from 0 to 45 degrees.

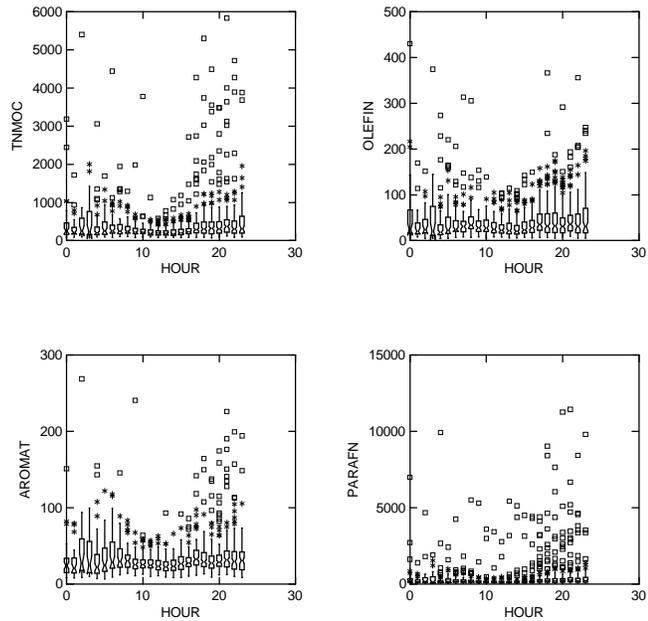


Figure 3.7-5. TNMOC, olefin, aromatic hydrocarbon, and paraffin concentrations (ppbC) by hour at Clinton in 2000 when winds were from 135 to 180 degrees.

- *Additional analyses to consider:* Provide additional interpretation. Investigate the wind direction dependence of high concentrations. What is the composition of high concentration samples compared to others? Investigate possible sources (trajectory analysis, source profile analysis).

3.8 AGE OF AIR MASS

Many of the hydrocarbon species are used as indicators of ozone formation potential and tracers of 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 more reactive aromatic hydrocarbons such as xylenes) should decrease with time during the daylight hours, and the relative abundance of less reactive species (paraffins and the less reactive aromatic hydrocarbons) will appear to increase. The ratios of more reactive species concentrations to less reactive species concentrations are also useful as indicators of the relative changes in species composition and age. Comparisons of the ratios among sites can be made to estimate the relative age of air parcels and help provide evidence of transport. In addition, this analysis may present evidence of the presence of fresh emissions or the presence of unique regional sources for a species. Commonly used ratios include xylenes/benzene, toluene/benzene, and ethane/acetylene. In this type of analysis, it is important to assess several different species ratios and look for consensus among the results. Analytical problems, nearby emissions of selected species, and other factors make it risky to rely upon the results of a single ratio.

Figures 3.8-1 through 3.8-3 show the diurnal variation of four ratios at Aldine, Clinton, and Deer Park in 2000. The ratios plotted in the figures include propene/propane, ethene/ethane, xylenes/benzene, and benzene/toluene.

- *Additional analyses to consider:* Investigate the diurnal variation of additional ratios including toluene to ethylbenzene, and others. Prepare a ratio analysis by wind direction and by episode.

3.9 RELATIONSHIPS AMONG VOCS, OZONE, NO_x, AND METEOROLOGY

- *Additional analyses to consider:* Investigate relationships among selected hydrocarbons, ozone, NO_x, wind speed, wind direction, and temperature using scatter plot matrices, time series, and box plots. Prepare plots of TNMOC/NO_x ratios by time of day and month at the sites.

3.10 ANNUAL AND SEASONAL TRENDS

3.10.1 Trends During TexAQS 2000 Study Period

In 2000, an intensive air pollution study called the Texas Air Quality Study 2000 (TexAQS 2000) was performed from August 14 to September 15, 2000 in Houston and surrounding areas to study the air chemistry and meteorology of southeast Texas. During the study the Bayland AGC was moved to Aldine. To put the study period in historical perspective,

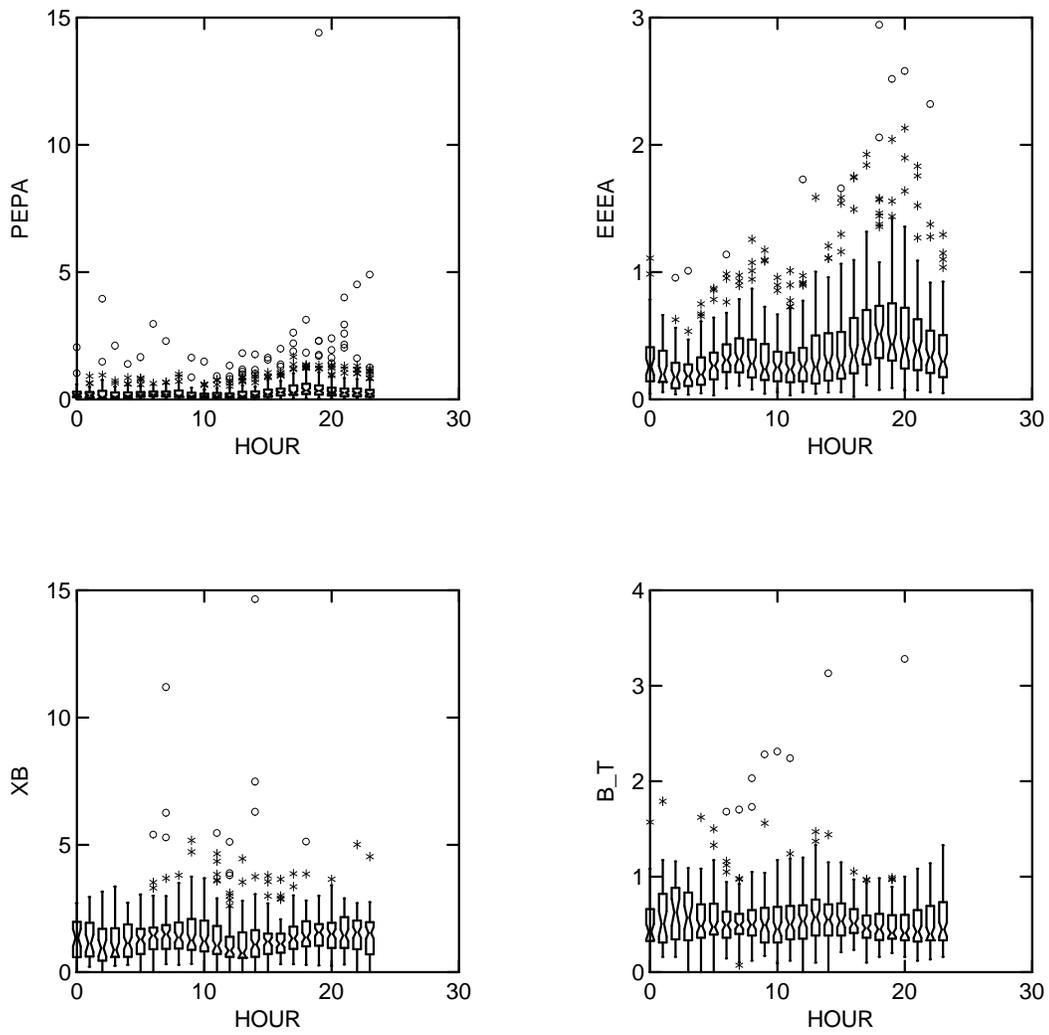


Figure 3.8-1. Diurnal variation of propene/propane (PEPA), ethene/ethane (EEEE), xylenes/benzene (XB), and benzene/toluene (B_T) at Aldine in 2000.

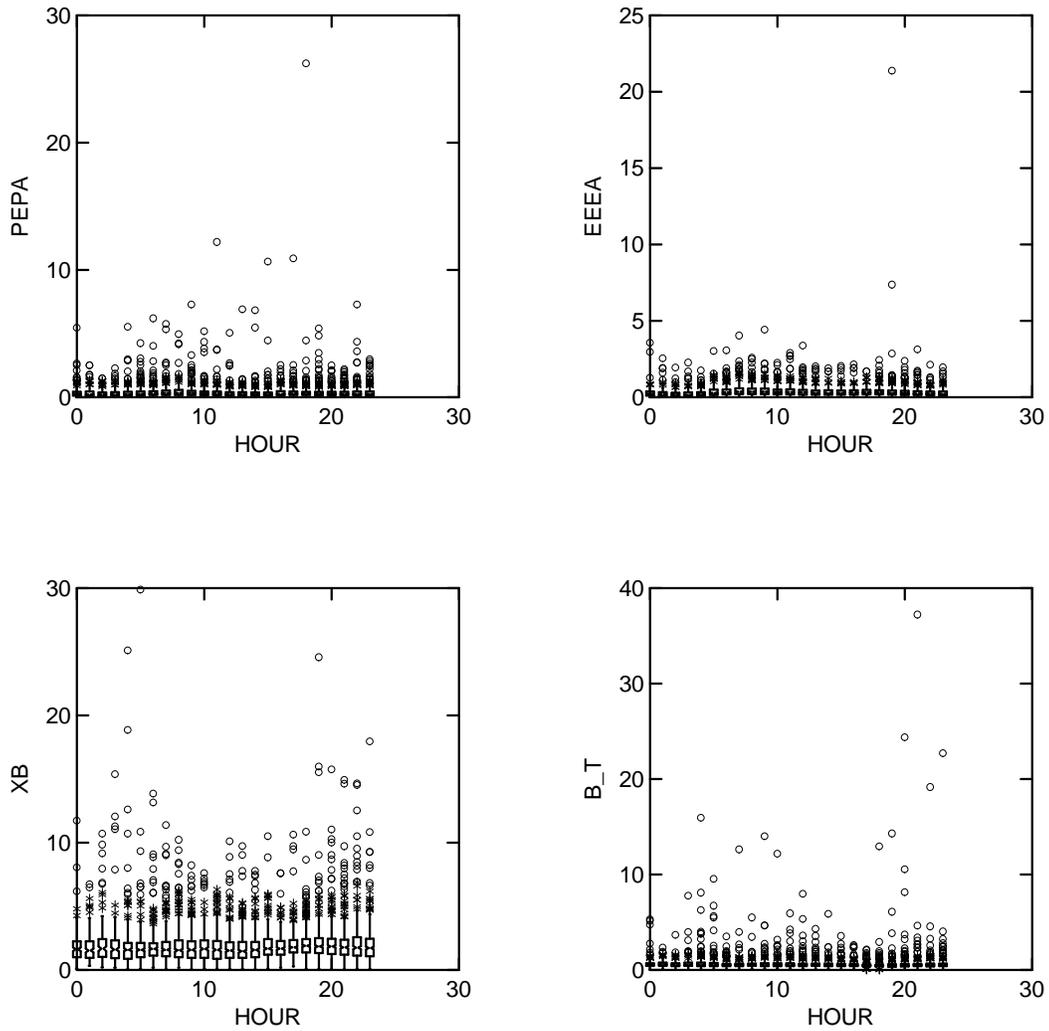


Figure 3.8-2. Diurnal variation of propene/propane (PEPA), ethene/ethane (EEEE), xylenes/benzene (XB), and benzene/toluene (B_T) at Clinton in 2000.

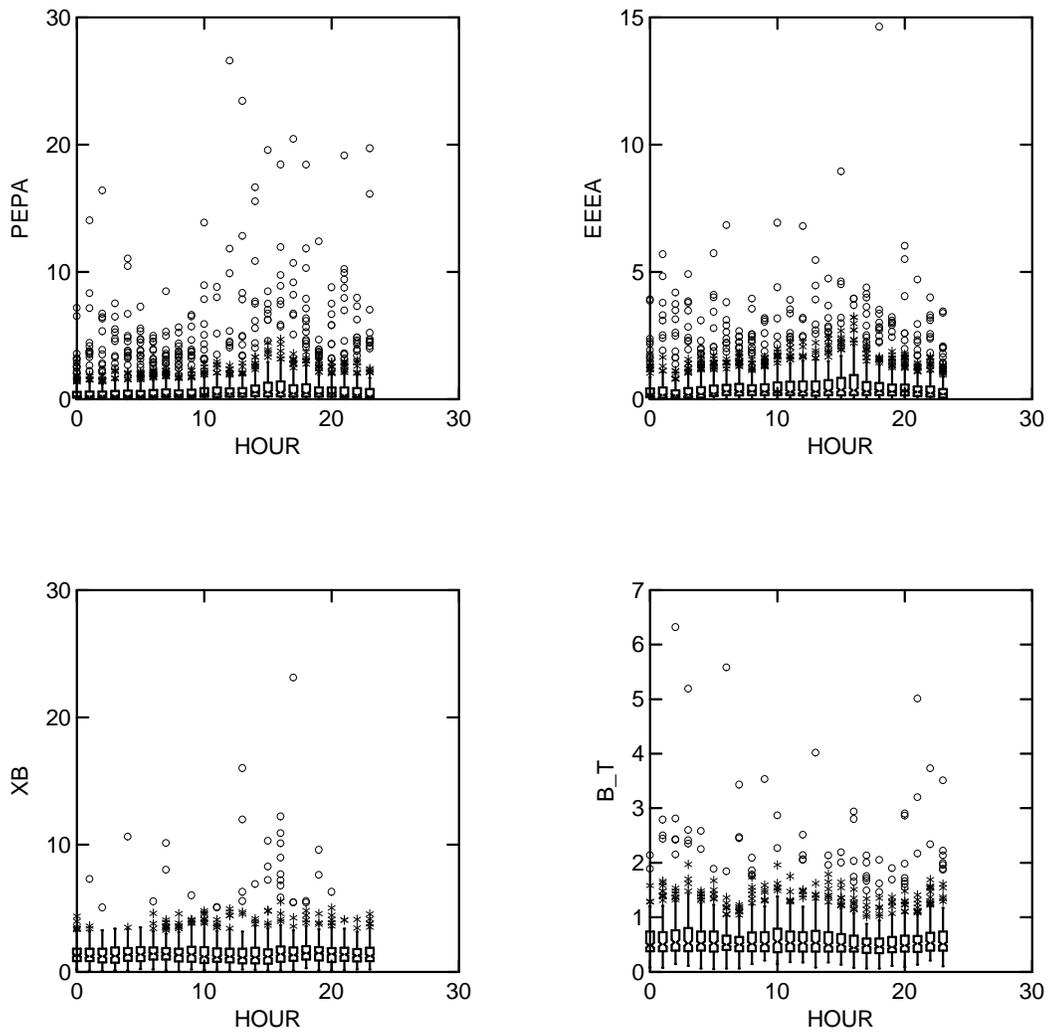


Figure 3.8-3. Diurnal variation of propene/propane (PEPA), ethene/ethane (EEEE), xylenes/benzene (XB), and benzene/toluene (B_T) at Deer Park in 2000.

TNRCC performed an analysis of trends over the years in concentrations during this month period.

TNMOC concentrations measured during the TexAQS 2000 study were compared to TNMOC concentrations measured during previous years at Clinton and Deer Park. Data were obtained from MOTHER for the period Aug.14-Sept.15, 1996-1999; not-yet-validated 2000 data were obtained from the Monitoring Division. The 5th, 25th, 75th, and 95th percentiles, mean, and median were computed by site and year for the sum_pol (summation of approximately 55 hydrocarbons) and for acetylene, benzene, propylene, toluene, i-butane, and ethylene. These species represent various emission sources, both mobile and industrial. The concentrations were also investigated by year and wind direction to look for possible changes in area source emissions. Radar plots were prepared for the total concentration to investigate variations in year and wind direction for both sites. Fingerprint plots were also prepared for each year.

At Clinton, the median sum_pol concentrations have decreased since 1996, except that 2000 concentrations were higher than those in 1999. Median benzene and toluene concentrations during this four-week period have decreased by around 50% since 1996. The 2000 data are most similar to those concentrations in 1999.

Prepare and insert supporting figures.

At Deer Park, median sum_pol concentrations have remained relatively constant since 1997. Benzene and toluene concentrations were particularly low in 2000 while n-butane and propane concentrations were higher than usual. The radar plot also shows that sum_pol concentrations were unusually high in the northeast direction and lesser so in the east and southeast while lower than usual in the westerly directions.

Prepare and insert supporting figures.

- *Additional analyses to consider:* Include validated 2000 data in this analysis. Prepare box plots by year to see more of the distribution. Inspect changes in ratios to help normalize the data. Look at trends in the extremes. How did the meteorology compare from year to year? What conclusions can be drawn? What are the implications to an analysis of high ozone events?

3.10.2 Trends in Concentrations at Clinton since 1993

TNRCC investigated trends in concentrations of selected hydrocarbons at the Clinton site in Houston since 1993. For each year the hourly TNMOC concentrations were sorted by corresponding wind direction (1996 is not included because of incomplete data).

Figure 3.10.2-1 shows that the median concentrations for each year are the highest when the winds are from the east and south. Winds from the westerly direction had the lowest concentrations. Yearly median TNMOC concentrations without regard to wind direction have dropped 27% from 1993-1998. The largest reductions in TNMOC were observed over this time period when the winds were from the northeast (44%), the southeast (29%) and the south (27%).

Consider box plots by wind quadrant to show more of the distribution. Were the changes statistically significant?

Wind direction radar plots were made for benzene, toluene, m-&p-xylenes, and o-xylene concentrations (**Figures 3.10.2-2 and 3.10.2-3**). For most wind directions, the lowest species concentrations were measured in 1998. The greatest reductions were observed when the winds were from the northeast, east, and south. There is less variation by year when the winds were from the southwest and northwest.

Consider box plots by wind quadrant. Were changes statistically significant? How did meteorological differences affect the concentration changes? Did ratios change?

Hydrocarbons typically have a diurnal pattern of maximum concentrations during the morning and evening hours and lower concentrations during the afternoon as illustrated in **Figure 3.10.2-4**. The higher concentrations during these hours are usually from increased automobile traffic, lower levels of atmospheric mixing, and accumulation of nighttime industrial emissions. The evening averages in 1997 are significantly higher than the other years. The biggest difference between average concentrations in 1993 and 1998 were observed during the early morning hours, midnight until 0800.

Consider box plots by time of day to inspect trends in outliers and other statistical metrics.

Diurnal concentrations were plotted for benzene, toluene, m-&p-xylenes, and o-xylene (**Figures 3.10.2-5 and 3.10.2-6**). The 1993 and 1996 species concentrations appear to be higher than 1997 and 1998 concentrations during most hours, and most significantly during the early morning and evening.

Consider box plots by time of day to inspect trends in outliers, median concentrations, interquartile ranges.

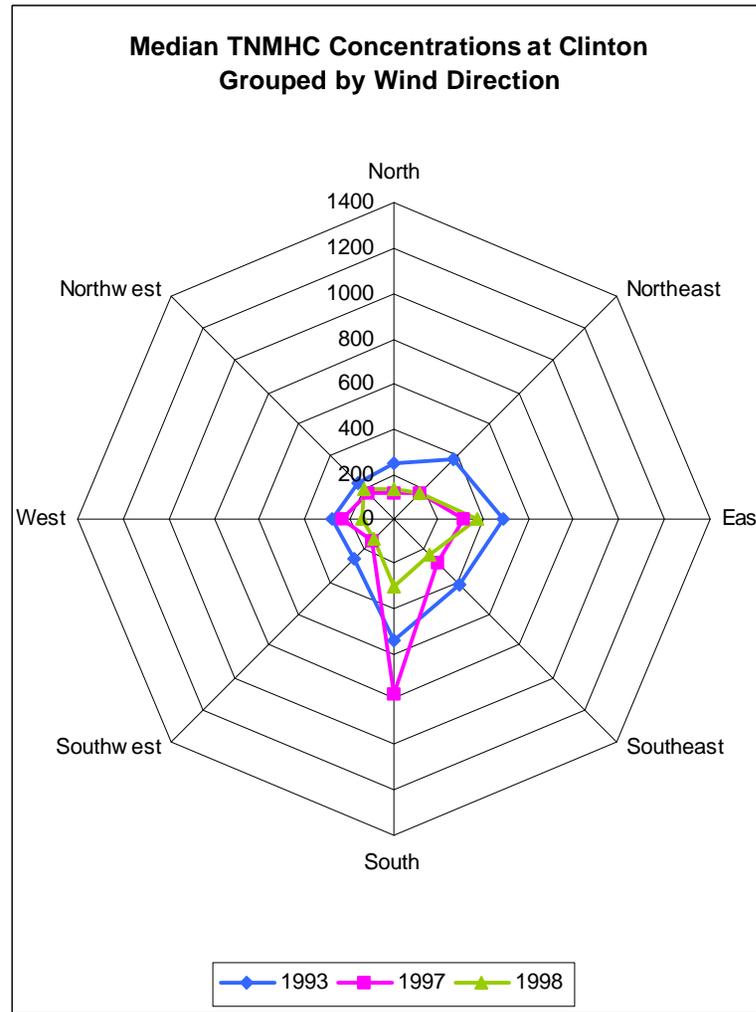
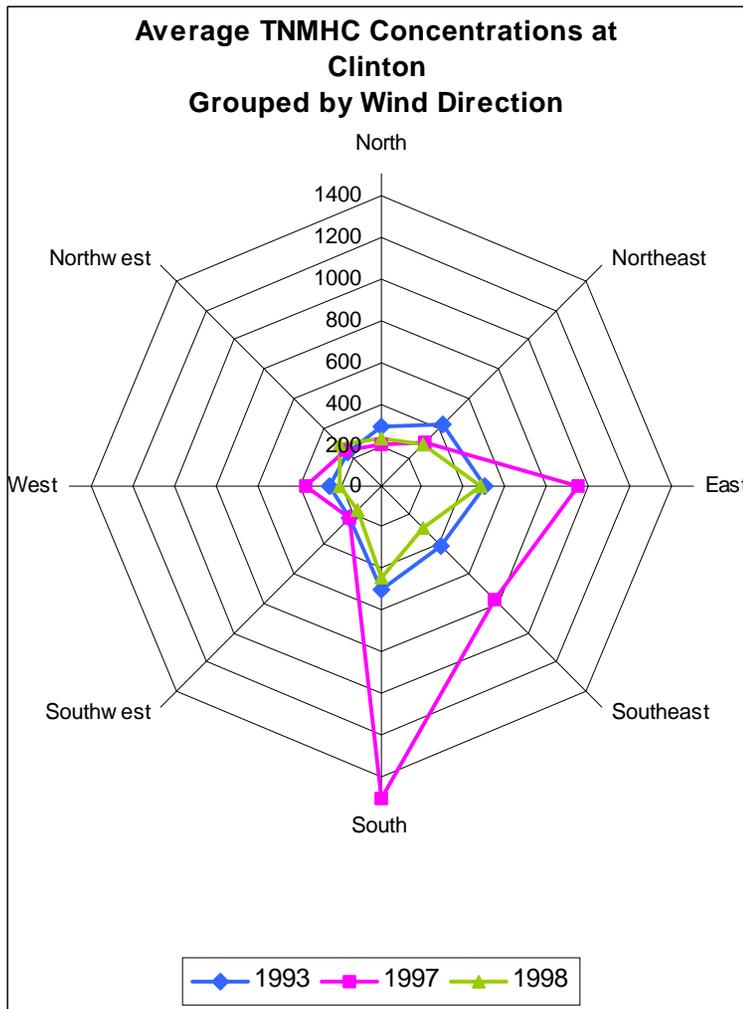


Figure 3.10.2-1. Yearly average and median TNJHC concentrations at each wind direction.

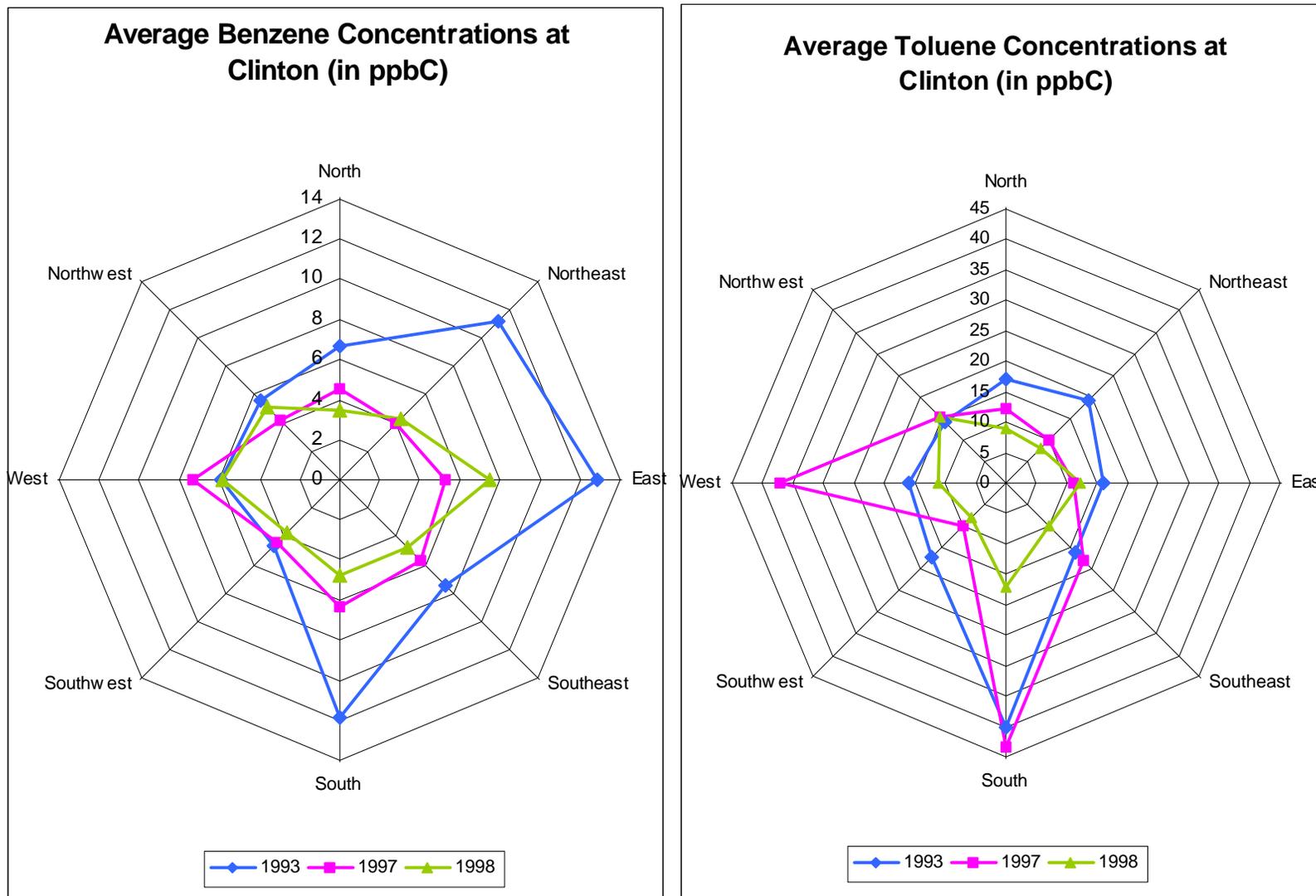


Figure 3.10.2-2. Average benzene and toluene concentrations at each wind direction.

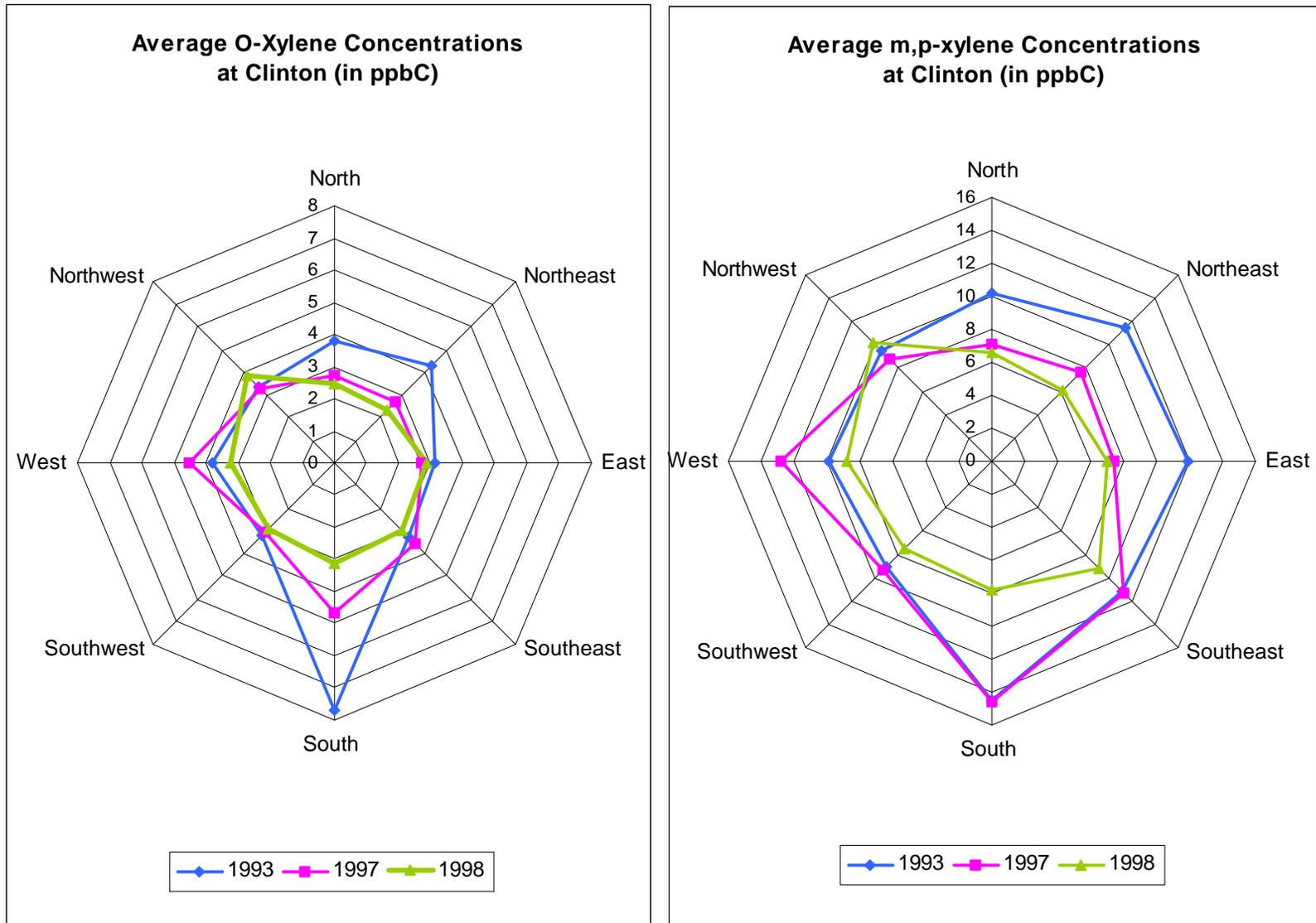


Figure 3.10.2-3. O-xylene and m,p-xylene concentrations at each wind direction.

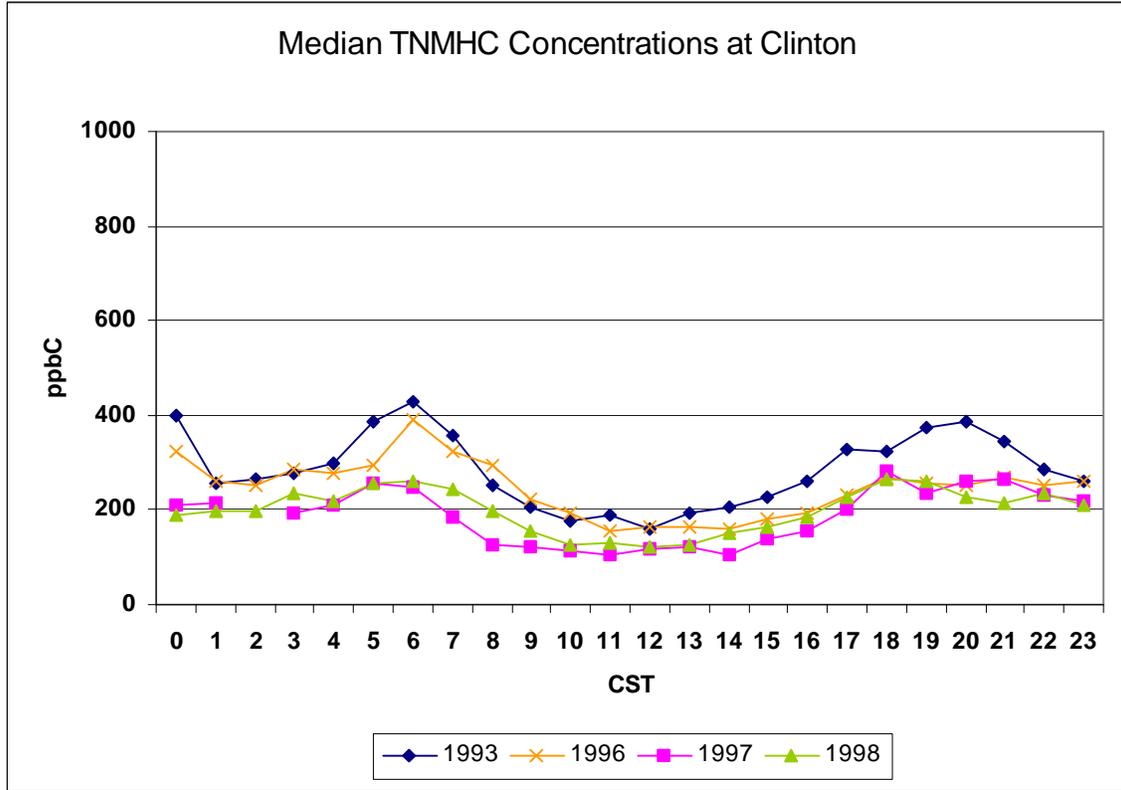
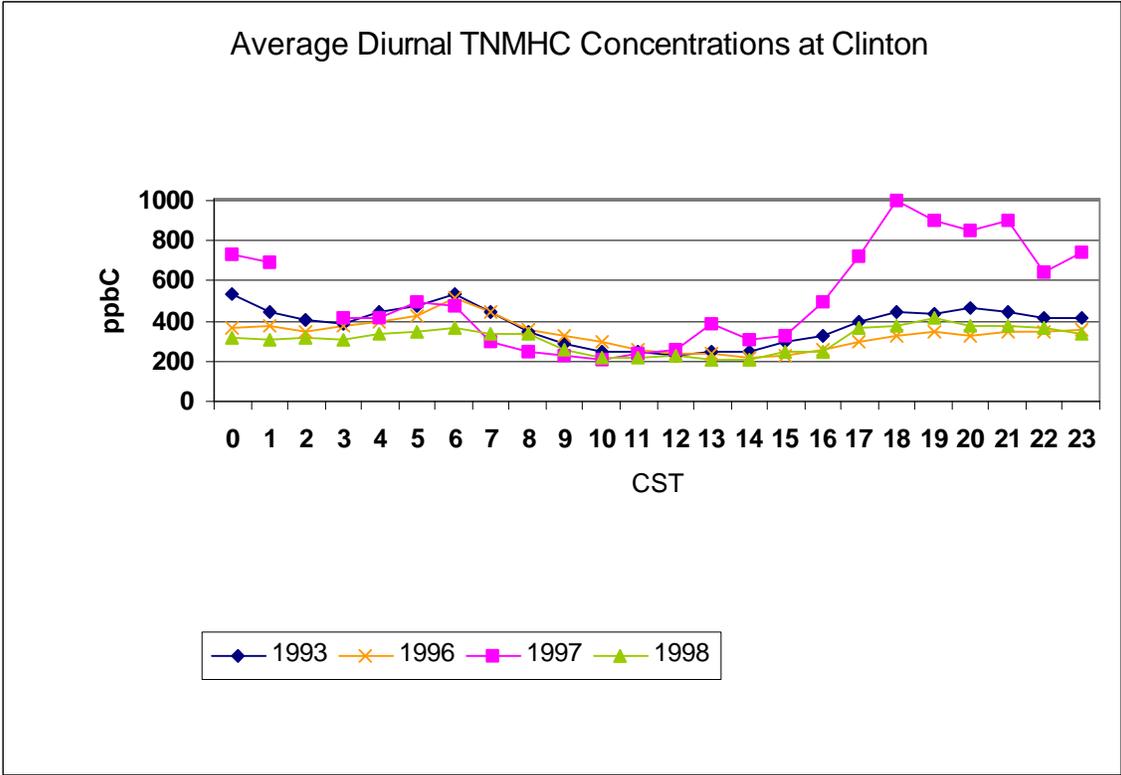


Figure 3.10.2-4. Hourly average and median TNMHC concentrations.

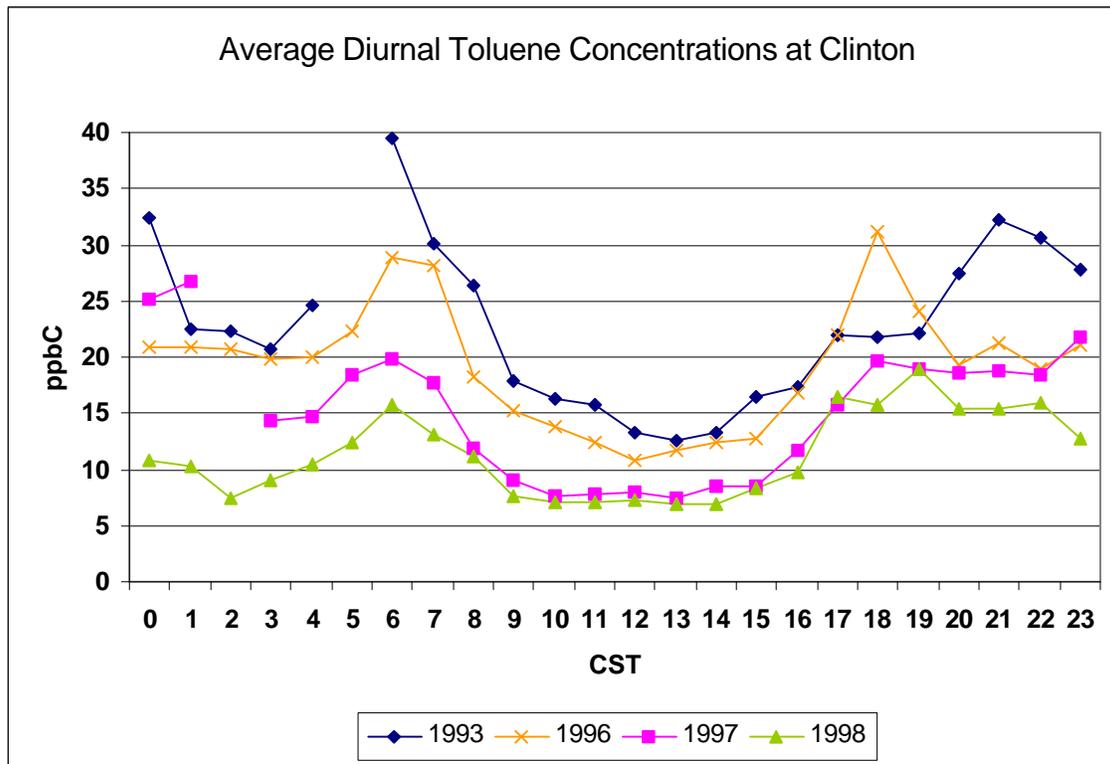
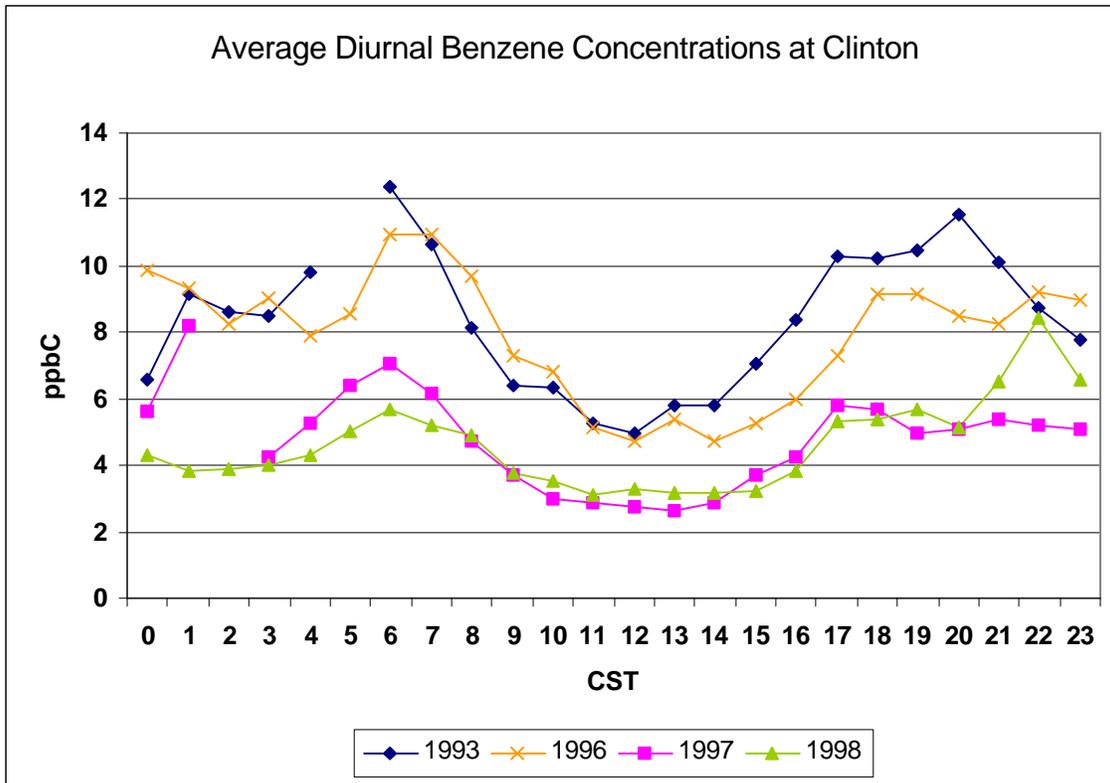


Figure 3.10.2-5. Hourly average benzene and toluene concentrations.

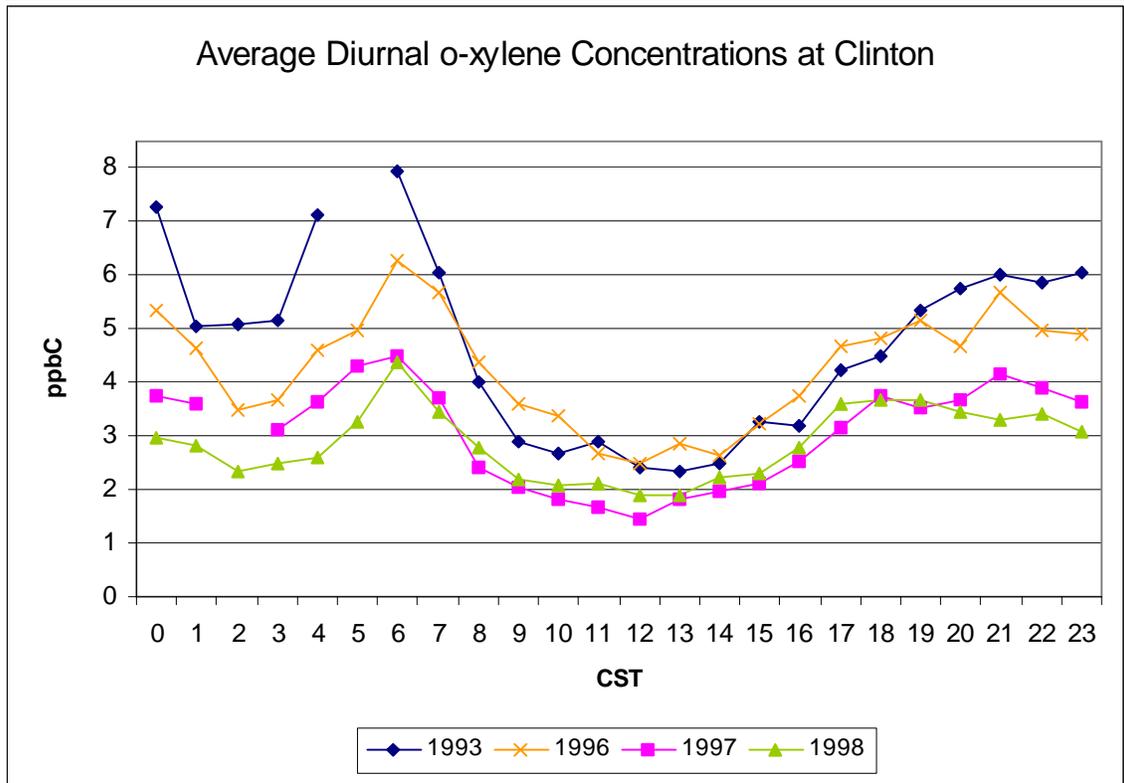
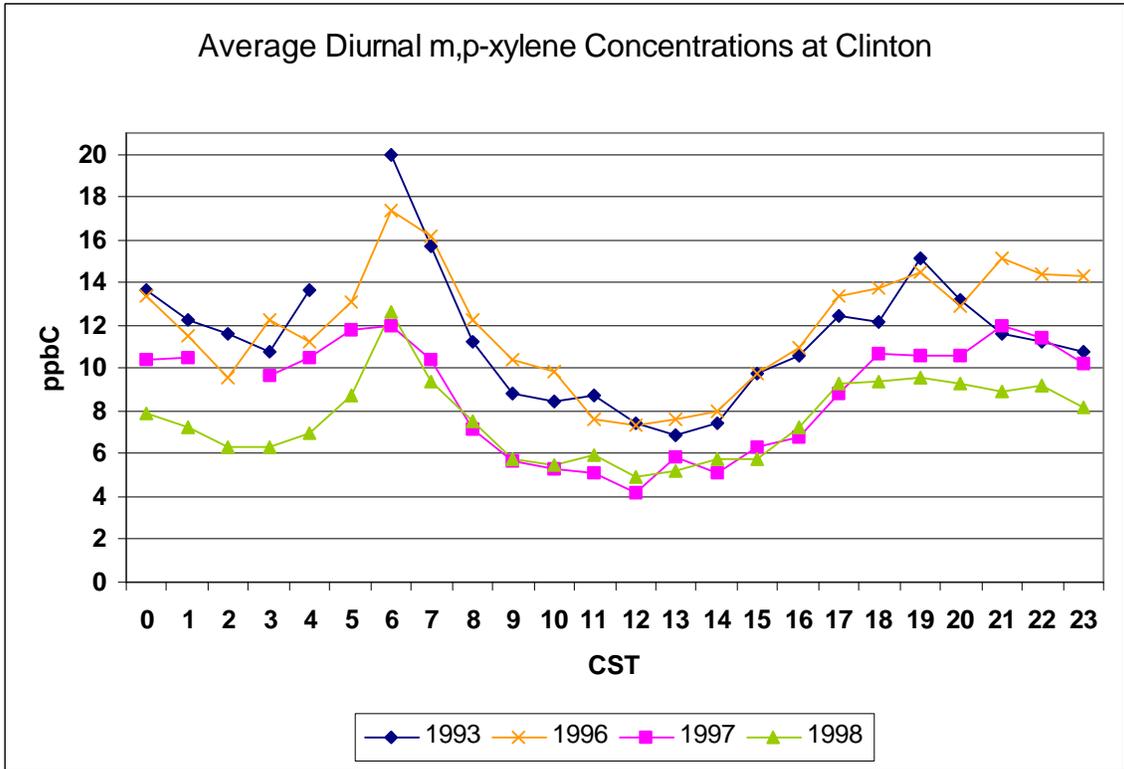


Figure 3.10.2-6. Hourly average m,p-xylene and o-xylene concentrations.

Since the hydrocarbon data include extreme maximums, the average concentrations of the species may be biased high. Thus, another way to analyze the data is to investigate the trends in other metrics including the geometric mean, median, and maximum concentrations (**Table 3.10.2-1**). The largest reduction in geometric means occurred between 1993 and 1998 for the TNMOC and aromatic hydrocarbon concentrations. But there is also a significant reduction in concentrations between 1996 and 1997.

Figure 3.10.2-7 shows the yearly average concentrations of the PAMS target species. Observed reductions in concentrations from 1993-1998 include those for benzene, ethane, propylene, toluene, n-hexane, n-pentane, m-&p-xylenes, and o-xylene. The remaining hydrocarbons show little difference between years. **Figure 3.10.2-8** also illustrates that median benzene concentrations are lower in 1997-1999 than 1993-1996.

Consider replacing Figure 3.10.2-7 with median concentrations and place species in elution order.

- *Additional analyses to consider include:* Expand the analyses to include data collected over a broader time period to provide more data; investigate additional species with respect to diurnal and wind direction changes over time; analyses were performed on concentration data – how did composition (weight percent) change when concentrations are normalized (or ratios, another way to normalize)?; tie the changes observed with actual emissions changes (e.g., RFG, industrial changes; control measures); establish some sort of meteorological adjustment to take into account changes from year to year in meteorology; investigate trends over the years for each month separately. Provide additional speculation on possible causes of the annual changes in concentration – are they consistent with sources, control measures?

3.10.3 Trends in Toxics Species

TNRCC assessed trends in toxic species formaldehyde, 1,3-butadiene, benzene, chloroform, and carbon tetrachloride measured in the canister data. Because of the abundance and high reactivity of ethylene and propylene (AGC data) in the Houston Area, these compounds were also included in this analysis.

Yearly averages for each compound were calculated for sites that had quarters with 50% (at least 7 valid sampling days per quarter) and 75% completeness (at least 12 valid sampling days per quarter). For sites that had at least 3 years of valid data, slopes were calculated to examine the yearly trends.

Table 3.10.2-1. Comparison of geometric means and other statistical calculations.

TNMHC	1993	1996	1997	1998	%change of geomeans		
	June18-Nov30	Aug20-Dec31	July1-Dec31	June18-Dec31	1993-1996	1996-1997	1997-1998
Mean	375	329	528	309	-6.7	-14.3	1.4
Median	274	235	184	199			
Geometric Mean	270	252	216	219	1993-1997	1996-1998	1993-1998
Maximum	5390	3330	16670	5972	-20.0	-13.1	-18.9
Observations	3285	2421	3499	3987			
Benzene							
	1993	1996	1997	1998	%change of geomeans		
	June18-Nov30	Aug20-Dec31	July1-Dec31	June18-Dec31	1993-1996	1996-1997	1997-1998
Mean	8.6	7.8	4.8	5.0	-9.6	-37.8	0.0
Median	5.8	5.3	2.8	2.7			
Geometric Mean	7.3	6.6	4.1	4.1	1993-1997	1996-1998	1993-1998
Maximum	111.0	113.3	292.5	682.1	-43.8	-37.8	-43.8
%benzene/TNMHC	2.7	2.6	1.9	1.9			
Observations	3402	2138	3468	3942			
Toluene							
	1993	1996	1997	1998	%change of geomeans		
	June18-Nov30	Aug20-Dec31	July1-Dec31	June18-Dec31	1993-1996	1996-1997	1997-1998
Mean	22.9	19.3	14.6	11.3	-16.0	-30.3	-21.7
Median	14.1	11.5	7.6	5.8			
Geometric Mean	15.7	13.2	9.2	7.2	1993-1997	1996-1998	1993-1998
Maximum	1075	1120	535.4	543.0	-41.4	-45.5	-54.1
%toluene/TNMHC	5.8	5.2	4.3	3.3			
Observations	3401	2130	3468	3942			
m,p-xylene							
	1993	1996	1997	1998	%change of geomeans		
	June18-Nov30	Aug20-Dec31	July1-Dec31	June18-Dec31	1993-1996	1996-1997	1997-1998
Mean	11.8	12.1	8.8	8.4	-3.2	-24.2	-5.8
Median	8.5	7.8	5.8	5.5			
Geometric Mean	9.4	9.1	6.9	6.5	1993-1997	1996-1998	1993-1998
Maximum	225	122.9	165.4	286.4	-26.6	-28.5	-30.9
%m,pxylene/TNMHC	3.5	3.6	3.2	3			
Observations	3401	2183	3465	3942			
o-xylene							
	1993	1996	1997	1998	%change of geomeans		
	June18-Nov30	Aug20-Dec31	July1-Dec31	June18-Dec31	1993-1996	1996-1997	1997-1998
Mean	4.8	4.3	3.2	2.7	-4.8	-17.5	-9.1
Median	2.8	2.8	2.1	2.0			
Geometric Mean	4.2	4.0	3.3	3.0	1993-1997	1996-1998	1993-1998
Maximum	145	77.2	230	69	-21.4	-25.0	-28.6
%o-xylene/TNMHC	1.6	1.6	1.5	1.4			
Observations	3402	2138	3468	3942			

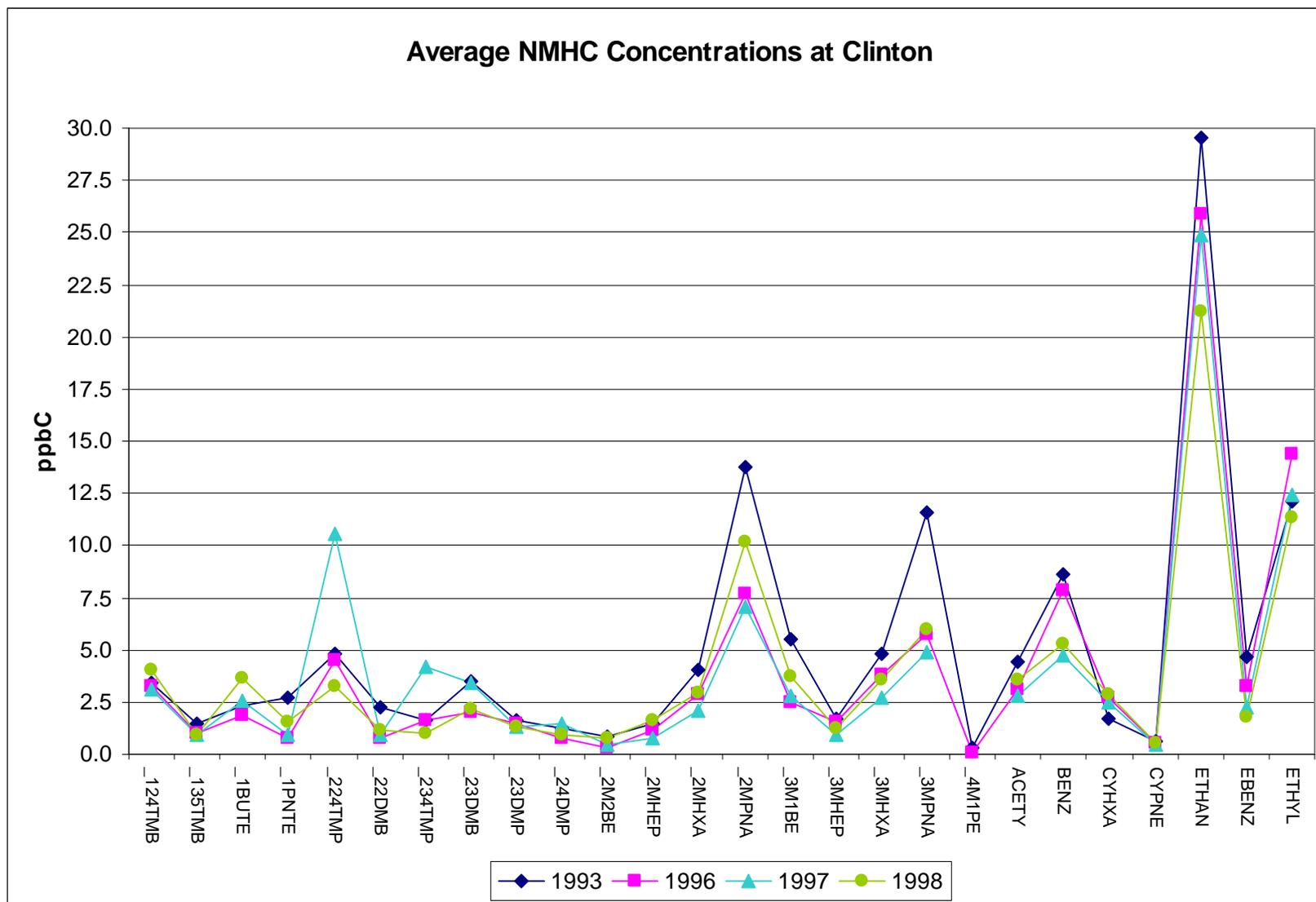


Figure 3.10.2-7a. Yearly average concentration of each measured nonmethane hydrocarbon.

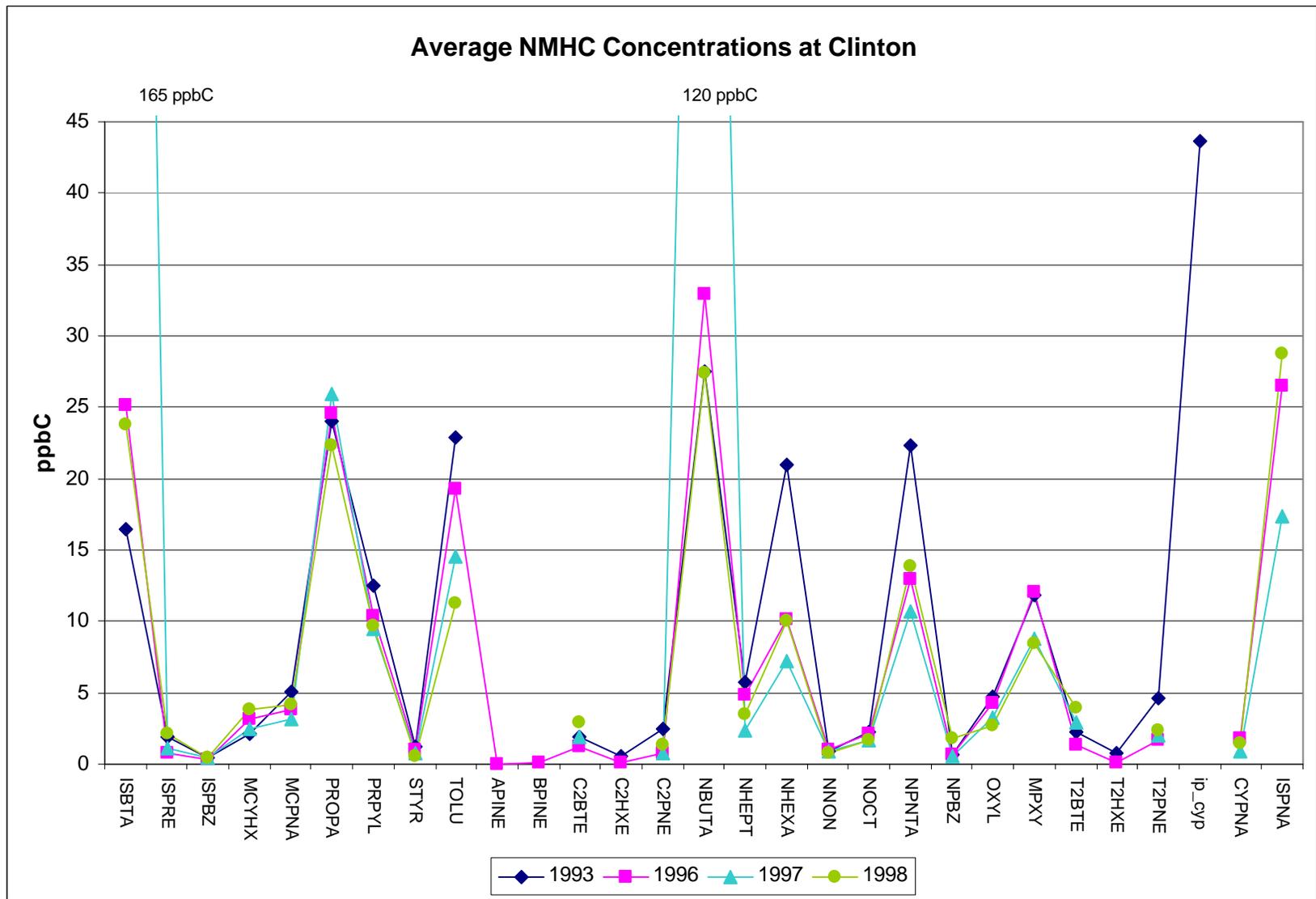


Figure 3.10.2-7b. Yearly average concentration of each measured nonmethane hydrocarbon.

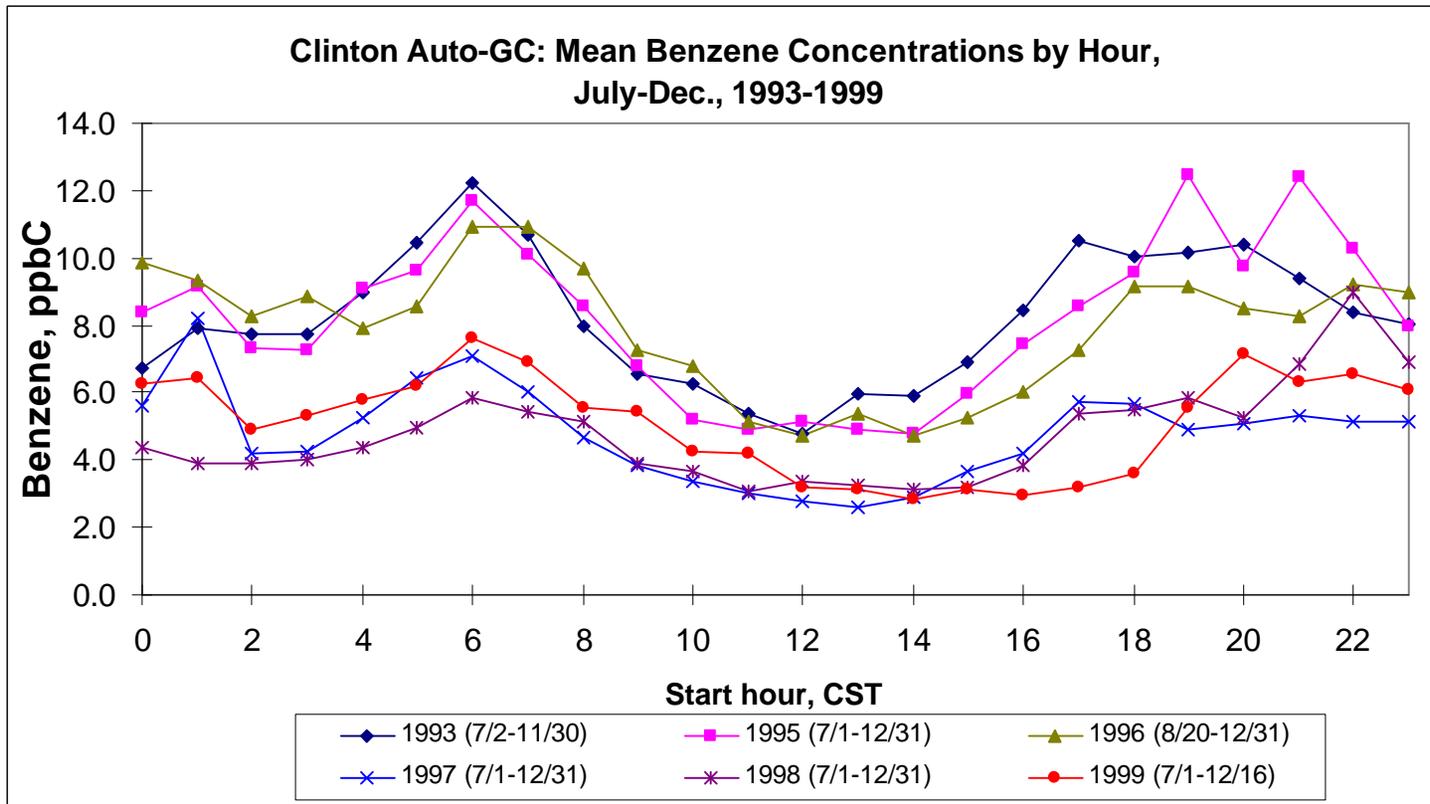


Figure 3.10.2-8. Yearly average concentration of each measured nonmethane hydrocarbon.

Benzene concentrations appear to have decreased since 1993 in Houston/Galveston (Figures 3.10.3-1 and 3.10.3-2).

- *Additional analyses to consider:* Assess trends in other indicator ratios; trends in sample reactivity; tie results to emissions reductions; how have extreme values or trends in different levels of the data behaved (maximum, median, 95th percentile)?. Compare to trends in AGC data.

3.11 SOURCE APPORTIONMENT

Obtain and review the results from the following analyses:

- STAR Program (Ron Henry): Use multivariate techniques to investigate the PAMS VOCs to tease out emission inventory information.
- STAR Program (Eric Fujita): Critical review of CMB application to PAMS data.
- DRI-COAST: Spatial and temporal analyses of VOCs in Houston during the COAST study including radar plots, time series by source type, and sensitivity tests.
- *Additional analyses to consider:* Prepare scatter plot matrices of abundant species based on reactivity – could segregate by wind sector. Perform cluster or factor analysis also using wind sector. Perform these analyses on the extreme concentration data? Assess the implications of the above studies to our understanding of the high ozone events.

3.12 CASE STUDIES

3.12.1 High i-Butane Concentrations on September 5, 1998 at Clinton

On September 5, 1998 an ambient i-butane concentration of 1863 ppbC was detected from 0200-0300 CST at the Clinton monitor in Houston, Texas. TNRCC investigated this incidence of high concentration because of its severity and because it occurred during a week of ozone exceedances in Houston. Chemical and meteorological data used in this study include ambient i-butane concentrations, resultant wind directions, and resultant wind speeds for the months of January- September, 1998. The 1998 data shows that abnormally high i-butane concentrations do not follow a seasonal pattern, but do follow a diurnal one. Extreme i-butane concentrations were measured only during the evening hours. **Table 3.12.1-1** lists the ten highest i-butane concentrations measured at Clinton in 1998. High concentrations correlate with both hour and wind direction (from the south southeast).

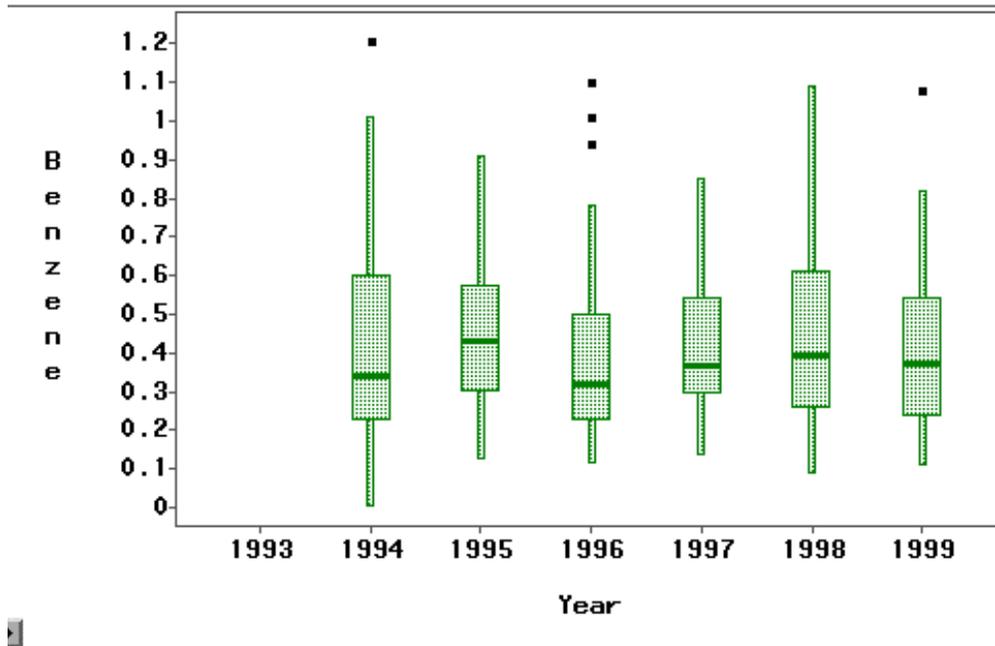


Figure 3.10.3-1 Distribution of benzene concentrations (ppbC) by year in North Houston as measured by 24-hr canister samples.

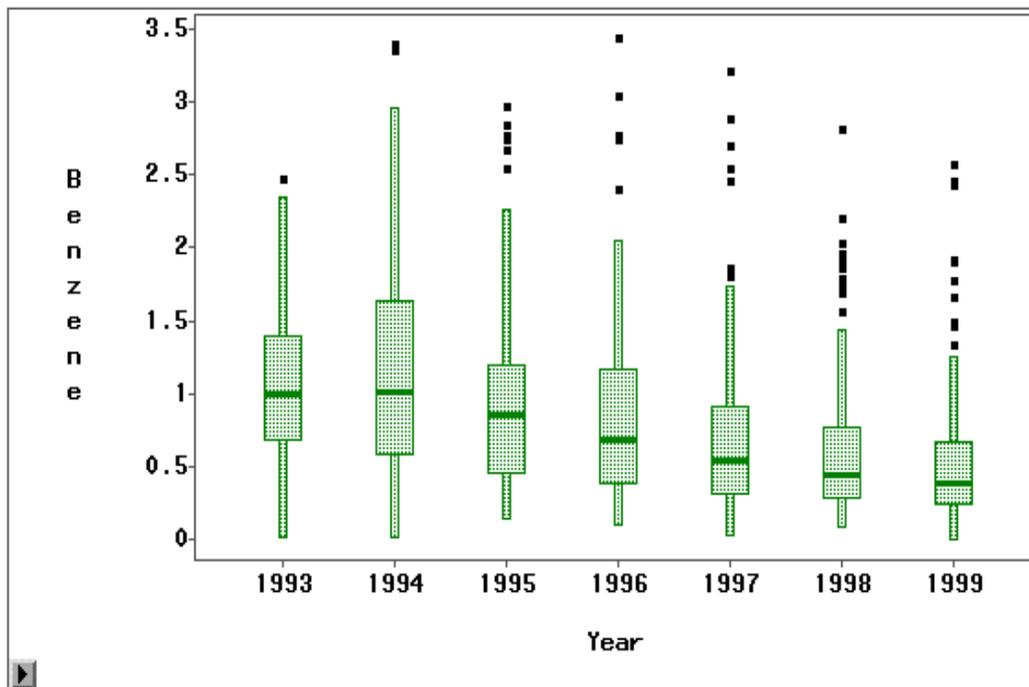


Figure 3.10.3-2 Distribution of benzene concentrations (ppbC) by year in Houston/Galveston as measured by 24-hr canister samples.

Table 3.12.1-1. Summary of high i-butane concentrations at Clinton in 1998.

Date	Hour	I-butane ^a	Wind Speed ^b	Wind Dir ^c	Date	Hour	I-butane ^a	Wind Speed ^b	Wind Dir ^c
9/4/98	0	11.9694	3.78	232.35	9/5/98	2	1863.086	6.29	167.21
9/4/98	1	10.0964	4.1	237.35	9/5/98	3	27.7713	0.56	92.82
9/4/98	4	25.1872	2.56	256.94	9/5/98	4	62.8523	3.6	8.57
9/4/98	5	42.689	1.14	266.39	9/5/98	5	49.625	3.25	20.99
9/4/98	6	22.3161	1.03	278.02	9/8/98	6	33.7687	3.31	26.58
9/4/98	7	9.7856	2.22	244.03	9/5/98	7	19.5693	3.75	35.67
9/4/98	8	9.1806	3.27	205.47	9/5/98	8	9.1782	4.26	44.9
9/4/98	9	90.0597	4.49	200.13	9/5/98	9	15.0562	4.9	81.67
9/4/98	0	134.4505	6.77	166.92	9/5/98	10	13.0884	4.38	83.88
9/4/98	11	99.5694	6.53	160.43	9/5/98	11	22.8698	5.19	97.98
9/4/98	12	55.2727	6.13	167.49	9/5/98	12	31.5669	5.1	105.68
9/4/98	3	24.3337	6.15	132.22	9/5/98	13	24.8931	4.34	86.15
9/4/98	14	149.1515	8.38	150.51	9/5/98	14	19.3651	5.58	92.93
9/4/98	15	99.3929	9.09	154.82	9/5/98	15	4.5605	8.29	126.34
9/4/98	16	58.4444	9.73	154.79	9/5/98	16	2.8515	10.15	128.3
9/4/98	17	827.244	9.18	158.4	9/5/98	17	7.5094	7.58	126.29
9/4/98	18	625.7906	8.81	161.44	9/5/98	18	74.1605	7.92	135.71
9/4/98	19	699.9121	7.06	161.66	9/5/98	19	519.9021	9.57	157.72
9/4/98	20	642.0016	6.28	161.98	9/5/98	20	27.7484	6.32	183.23
9/4/98	21	907.45	5.75	166.06	9/5/98	21	17.8843	4.64	205.65
9/4/98	22	155.02	4.8	166.9	9/5/98	22	3.5336	4	231.67
					9/5/98	23	2.7089	4.08	236.4

^a Concentration of i-butane in ppbC.

^b Wind speed in miles/hour.

^c Wind direction in degrees.

The i-butane concentrations preceding and following the extremes listed in Table 3.12.1-1 show that in most cases they are abrupt measurements and appear as outliers. This means that they were not detected after the build up from a gradual increase but instead are short-term pollution episodes. This suggests that these extreme i-butane concentrations were not caused by temperature inversions but may be due to the site's proximity to hydrocarbon sources. The monitor is just north of the Houston Ship Channel and north of a large industrial complex. Many of these industries are large VOC emitters, including nearby Lyondell-Citgo Refinery, Phibro Energy USA, Inc., and Texas Petrochemicals Corp. (see emissions tables). These industries are important because they are located south or southeast of the monitor. The extreme concentrations were measured when the winds were from the same direction (150-170 degrees), making these industries likely upwind sources.

The VOC Point Source map (**Figure 3.12.1-1**) shows the locations and VOC emissions of Lyondell-Citgo and Texas Petrochemicals. Phibro Energy USA, Inc. is shown on the map as Valero Refinery. (The VOC map was made from the Emissions Inventory database that has

been updated more recently than the AIRS and LANDVIEW data.) All three emission inventory sources list the point source as a petroleum refinery and as a significant VOC emitter.

The AGC data reveal that the unusually high i-butane concentrations at Clinton did not correlate with most other hydrocarbon concentrations except for 1-pentene, c-2-butene, c-2-pentene, and n-butane. But these correlations were detected during some and not all of the i-butane episodes and not during the hours of the highest 1998 i-butane concentrations. The high levels of i-butane at Clinton seem to be unique in that they are isolated and independent events.

Isobutane, a component of gasoline and natural gas, is used by industry in aerosol propellants, stove fuels, organic synthesis, motor fuels, and the synthesis of rubber. This hydrocarbon is also a by-product of methyl tert butyl ether (MTBE) synthesis and is produced in the process from n-butane isomerization. Refineries along the Texas Coast produce 84% of the total U.S. MTBE production. Three of these producers are Phibro Energy USA, Inc. (plant capacity–160 million pounds/year), Texas Petrochemical Corporation (2,090 million pounds), and Lyondell Citgo Refinery (285 million pounds). Texas Petrochemicals is located 2.44 miles, 197 degrees southwest of Clinton Monitor. Phibro Energy USA is 1.06 miles and 168 degrees south of Clinton. Lyondell Citgo is 1.80 miles, 152 degrees SSE (see **Figure 3.12.1-2**). In 1998, the ten highest i-butane concentrations were measured when the winds were from the SSE at an average of 163 degrees and at an average speed of 8.60 mph. Though Texas Petrochemicals is a major MTBE producer and emits 66 tons/year of i-butane (1996), it is ruled out as a point source for the i-butane pollutant episodes at Clinton because of its SSW location. Lyondell Citgo and Phibro Energy USA are possible point sources. They both produce MTBE and are located within two miles of the monitor. Phibro and Lyondell are not listed as i-butane point sources in the Emissions Inventory but they do have large VOC emissions (3137 tons/ year and 7666 tons/year respectively).

As listed in Table 3.12.1-1, high concentrations of i-butane from Sept. 4 1700 (CST) until Sept. 5- 0200 (CST) correspond directly with steady winds from the SSE (158-167 degrees). Besides the five-hour period of high concentrations, i-butane was detected in low amounts for the rest of the two days. There is one significant increase to 519 ppbC at 1900 (CST) on Sept. 5 when the wind was from the SSE (157 degrees). During hours of low concentrations, the winds were predominantly from the north and east.

Though i-butane has many sources and uses, the characteristics of the 1998 i-butane episodes suggest that their point source was possibly an MTBE producer. Part of the evidence is that no other hydrocarbons correlated directly with the high i-butane concentrations. For example, if the high i-butane was from a fuel or gas release, concentrations of propane and pentanes should also be high. N-butane was measured in significantly higher concentrations during hours of high i-butane, though their concentrations didn't correlate directly. N-butane is also used in MTBE production.

- *Additional analyses to consider:* Prepare time series of concentrations, wind speed, and wind direction for this example. Add mixing height if available for case studies. Are MTBE data available during this time period from the canisters? Are other dates important to investigate – other species with high concentrations - using this approach?

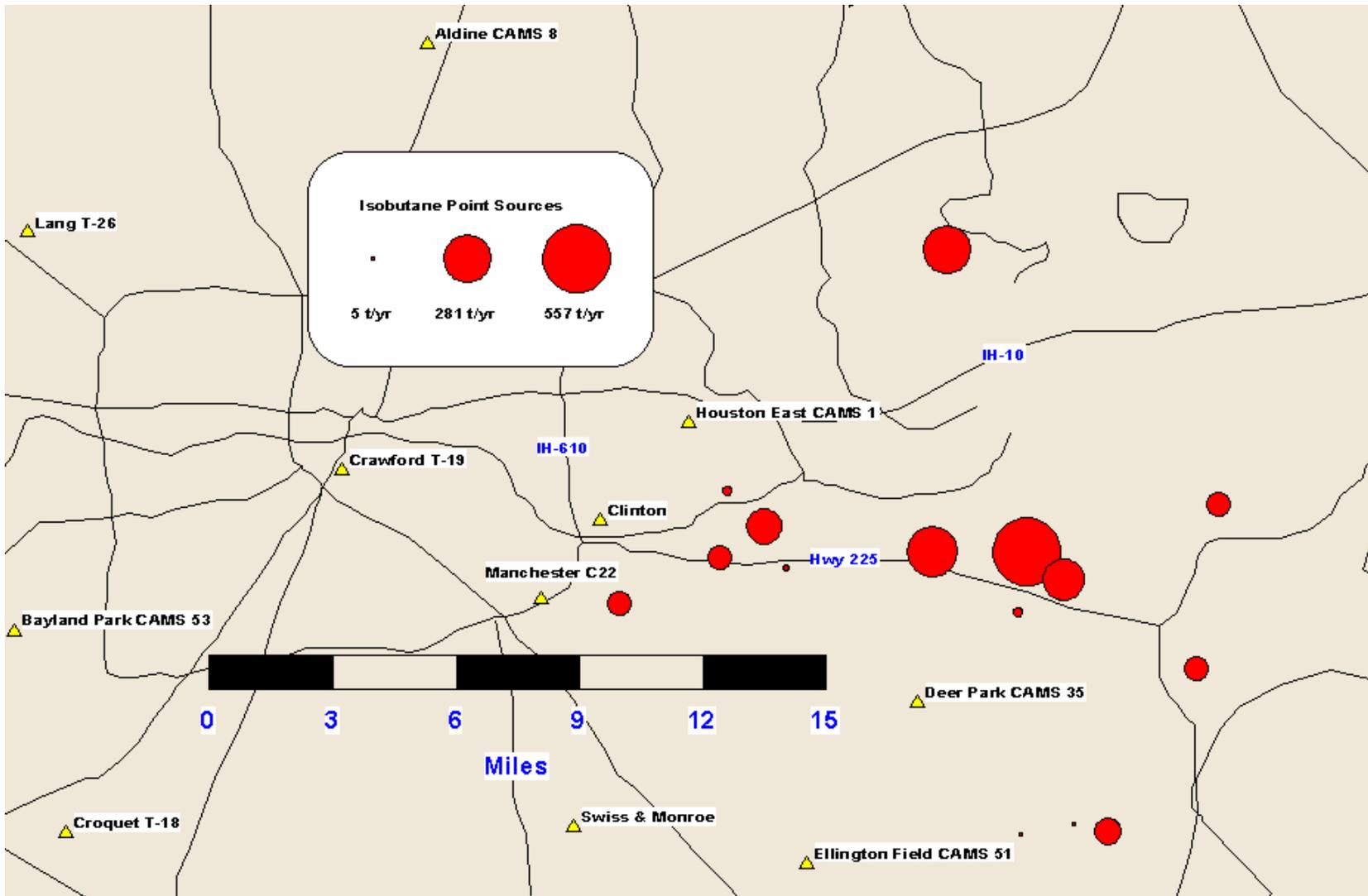


Figure 3.12.1-1. Point sources of i-butane n Houston.

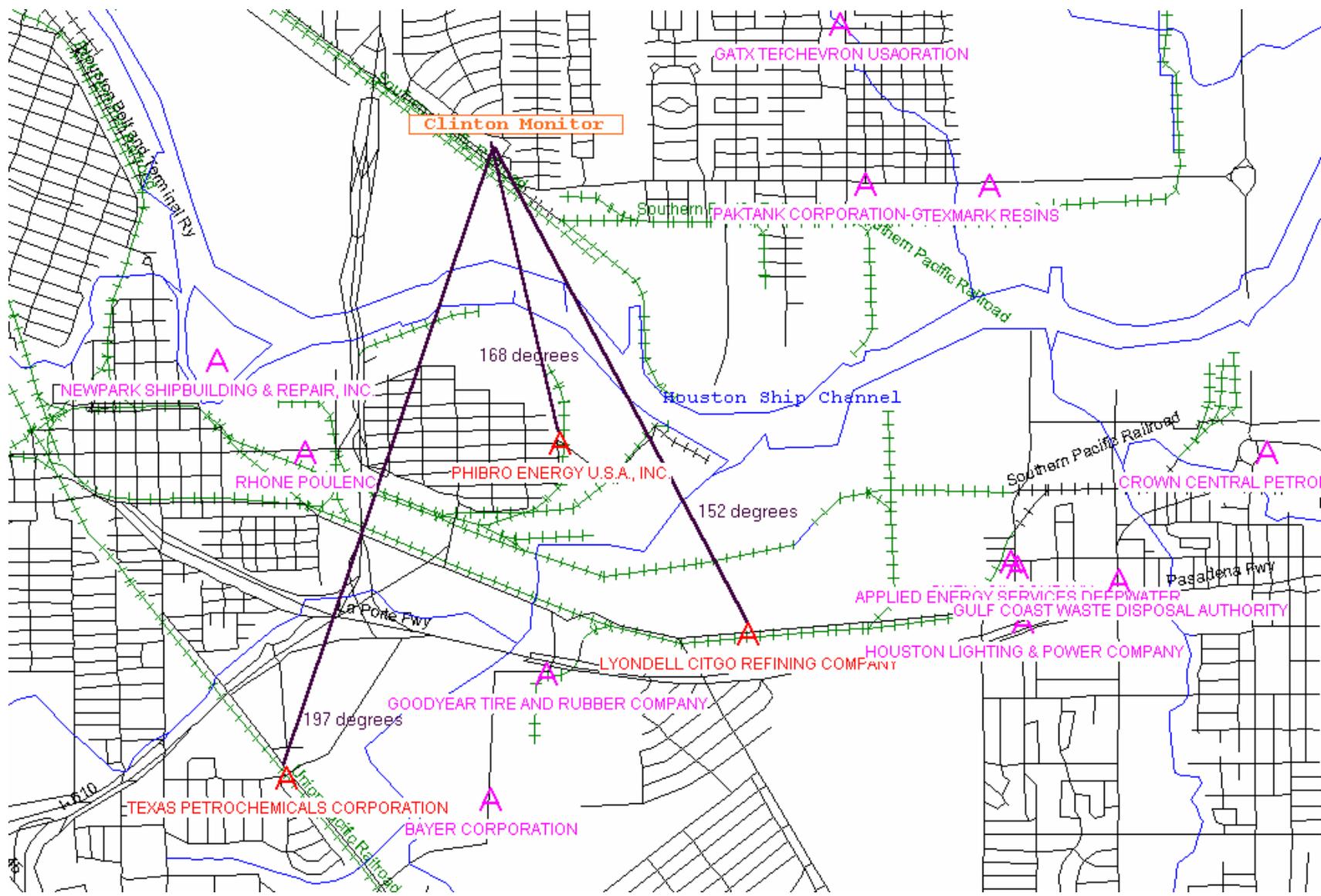


Figure 3.12.1-2. Map of potential i-butane sources with respect to the Clinton monitoring site.

3.12.2 Exploring the Link Between Meteorology and Pollutant Concentrations at Clinton on August 21, 2000

Hydrocarbon data collected at the Clinton Drive PAMS site in Houston TX during 2000 were used as a case study to illustrate the relationship between meteorology, proximity of sources, and pollutant concentrations (Bortnick et al., 2001). **Figures 3.12.2-1 and 3.12.2-2** show the hourly concentrations of benzene, toluene, and m-&p-xylenes (in ppbC) and hourly wind speed and wind direction data for the Clinton site on August 21, 2000. High concentrations were observed during the morning rush period because of increased motor vehicle emissions, low mixing heights, and relatively low wind speeds. The mixing height began to increase at about 0900 and concentrations briefly dropped in response. At 1100 and 1200, the toluene concentrations were high. Typically, with the increasing mixing height, we might expect concentrations to drop midday. However, at the Clinton Drive site, the combination of relatively low wind speeds at these hours and the shift of wind direction (and toluene sources) resulted in higher concentrations. At 1400, the wind direction shifted slightly and wind speeds increased resulting in further pollutant concentration changes. At 1700, the nocturnal boundary layer began to form and wind speeds were relatively high. After 1700, toluene and benzene concentrations rose. In this example, most of the concentration changes were explained by mixing height, wind direction, and wind speed data.

The relationship of wind direction and pollutant concentration is further illustrated in **Figure 3.12.2-3**. This scatter plot of 1,3-butadiene and wind direction at the Clinton Drive site in Houston shows that the high concentrations occurred when winds were from the south (across the ship channel). Other plots of wind direction and concentration are provided in **Figures 3.12.2-4 through 2.12.2-7** for Clinton Drive and Deer Park in 2000.

- *Additional analyses to consider:* Perform similar analysis for other high concentration days of other selected species. Investigate wind direction and concentrations by time of day (such as before 0900 and between 0900 and 1400).

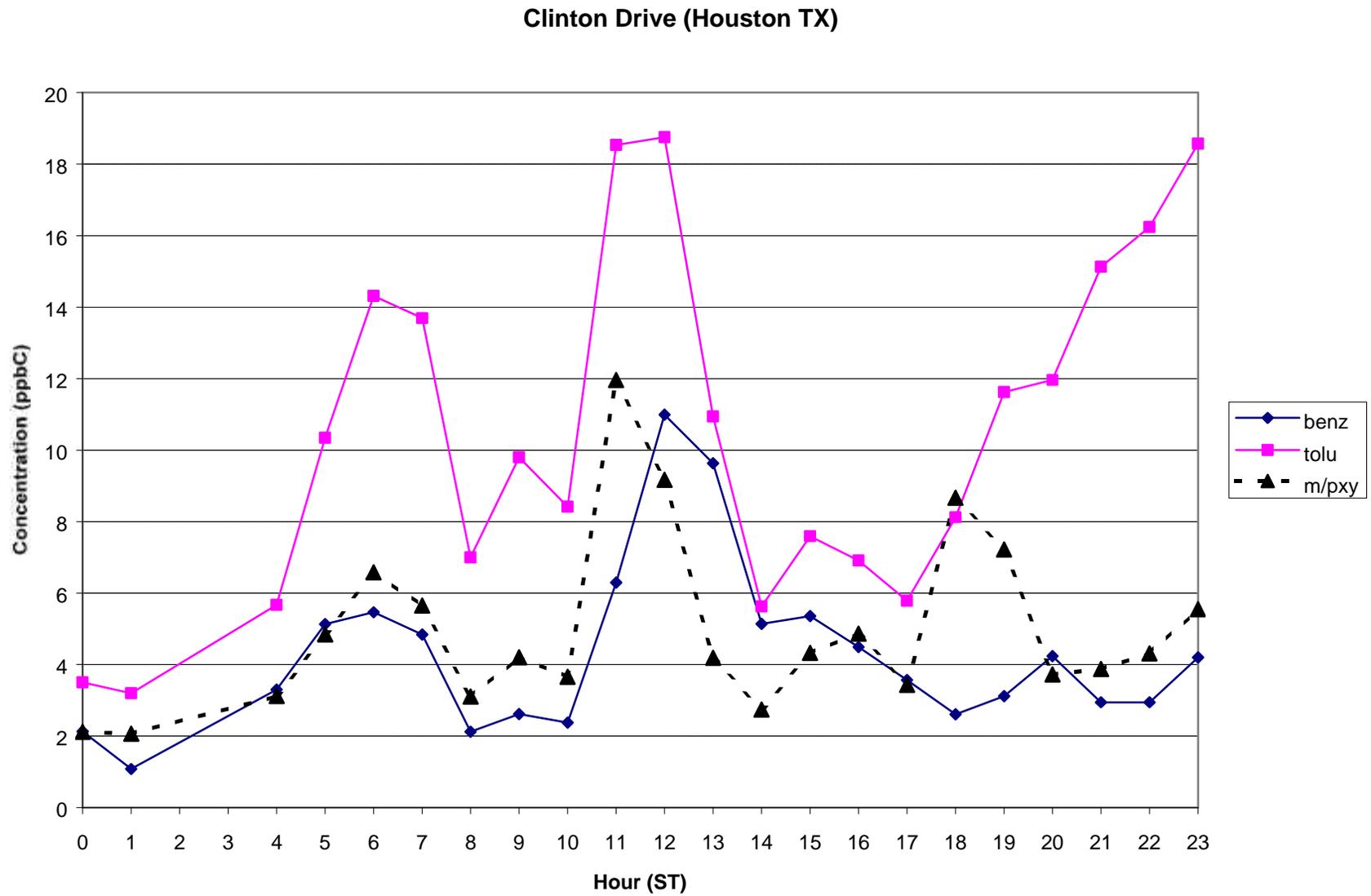


Figure 3.12.2-1. Benzene, toluene, and m-&p-xylenes concentrations (ppbC) at Clinton Drive (Houston TX) on August 21, 2000.

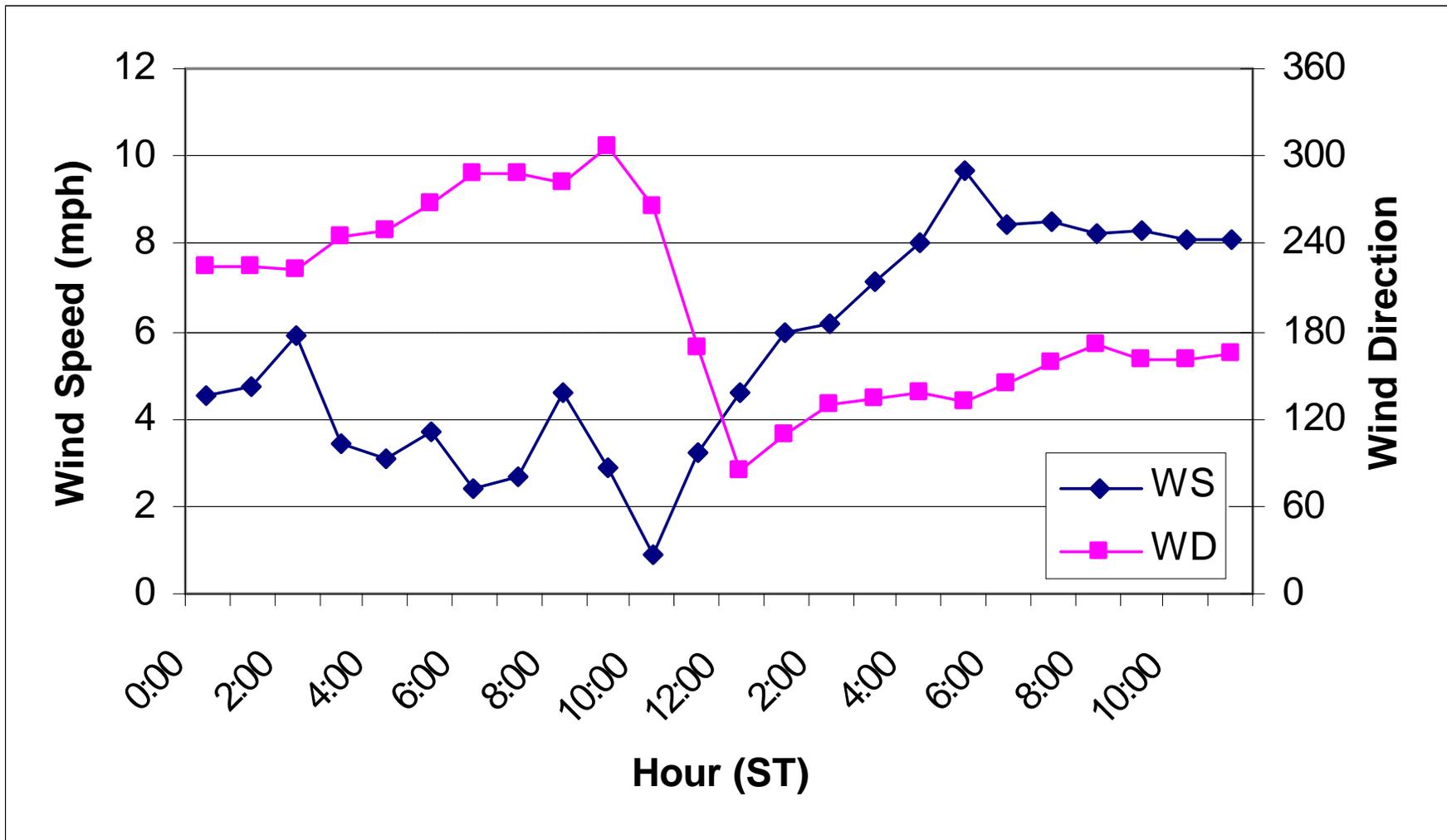


Figure 3.12.2-2. Wind speed and wind direction at Clinton Drive in Houston TX on August 21, 2000.

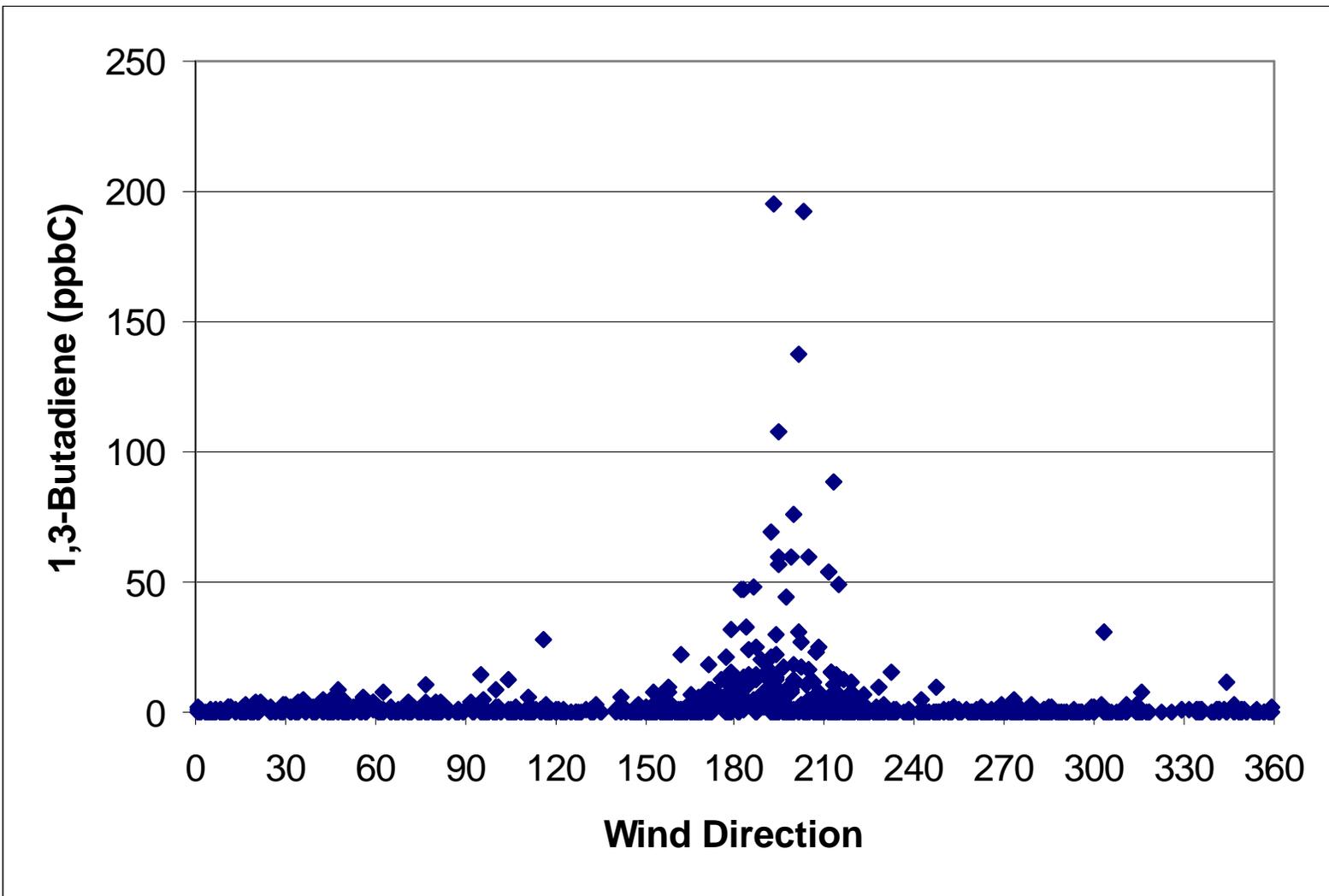


Figure 3.12.2-3. Concentrations of 1,3-butadiene (ppbC) as a function of wind direction at the Clinton Drive, Houston TX, PAMS site in 2000.

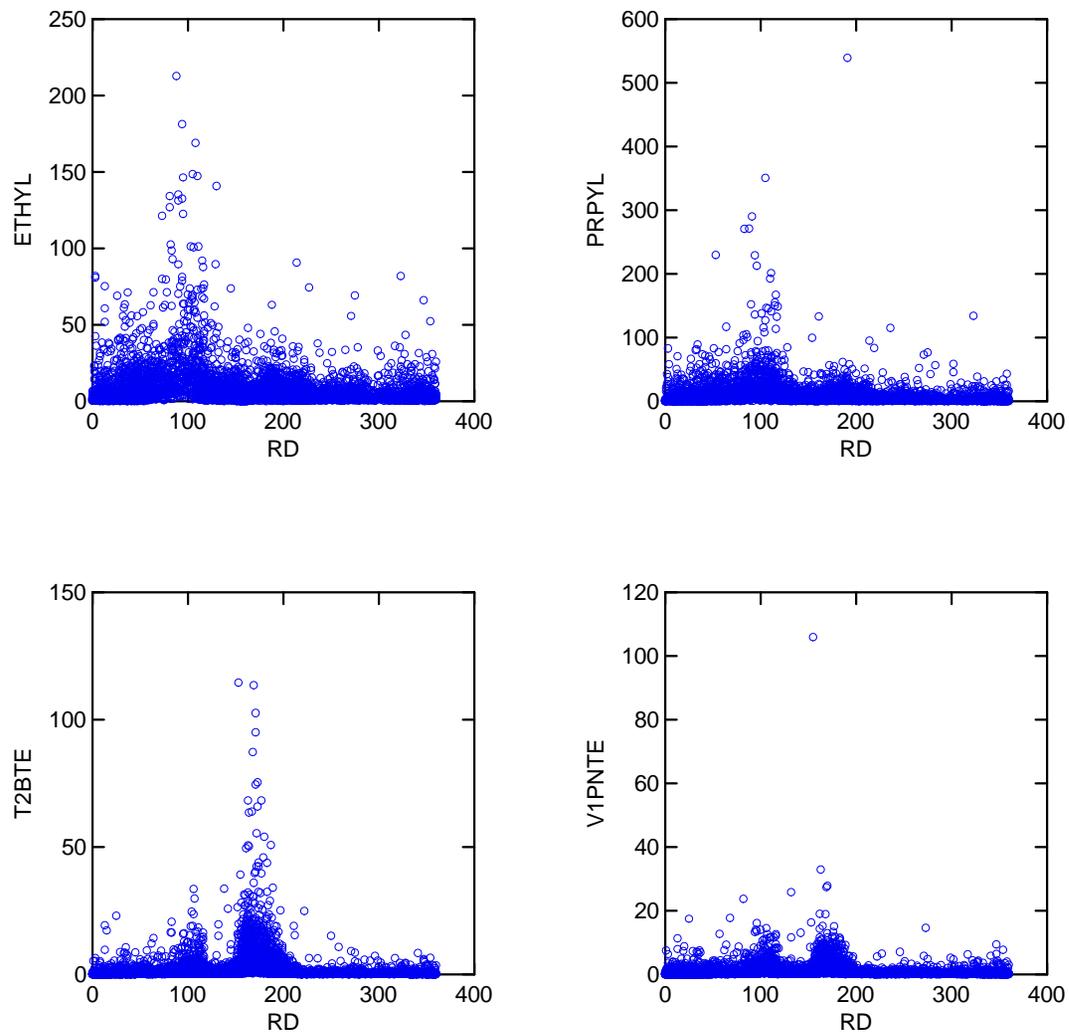


Figure 3.12.4-4. Concentrations (ppbC) as a function of wind direction for ethene (ETHYL), propene (PRPYL), t-2-butene (T2BTE), and 1-pentene (V1PNTE) at Clinton Drive in 2000.

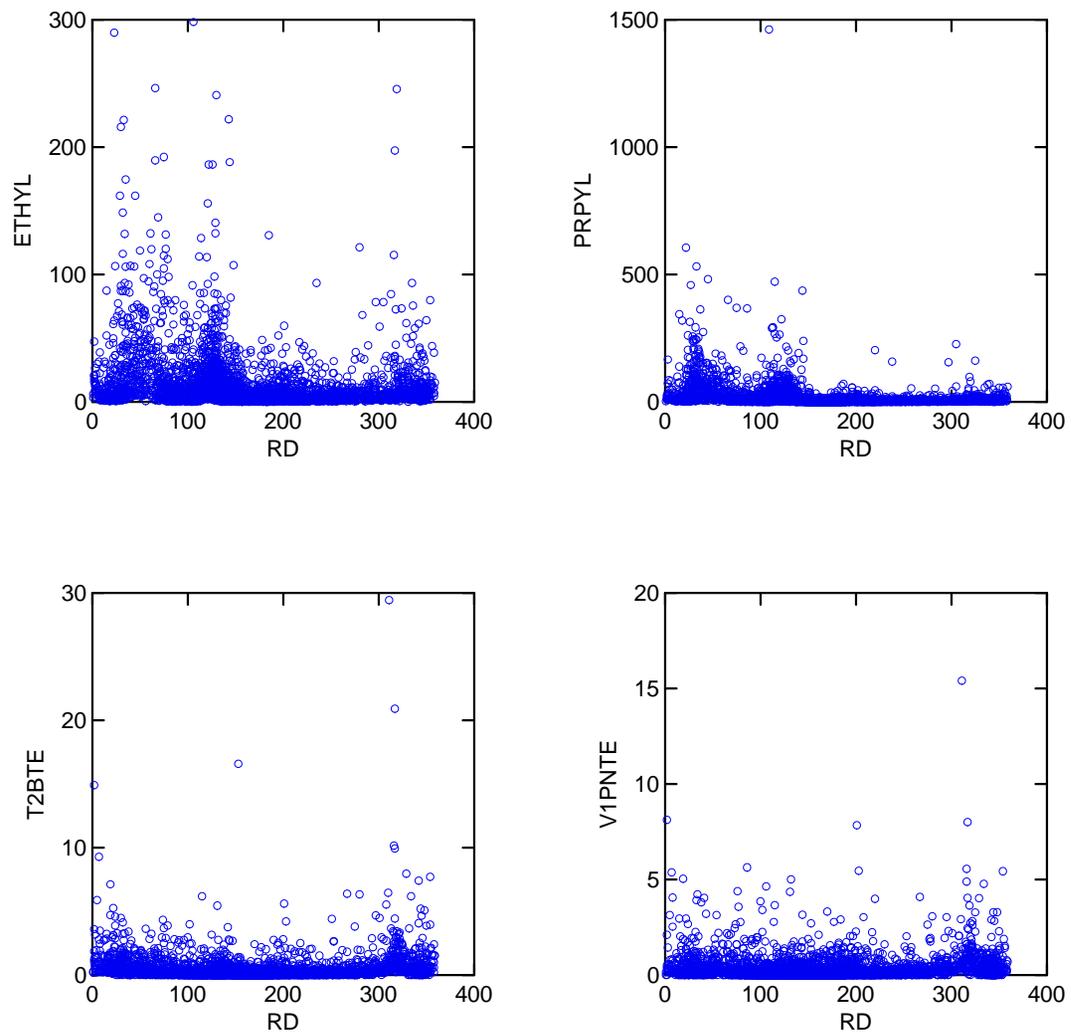


Figure 3.12.4-5. Concentrations (ppbC) as a function of wind direction for ethene (ETHYL), propene (PRPYL), t-2-butene (T2BTE), and 1-pentene (V1PNTE) at Deer Park in 2000.

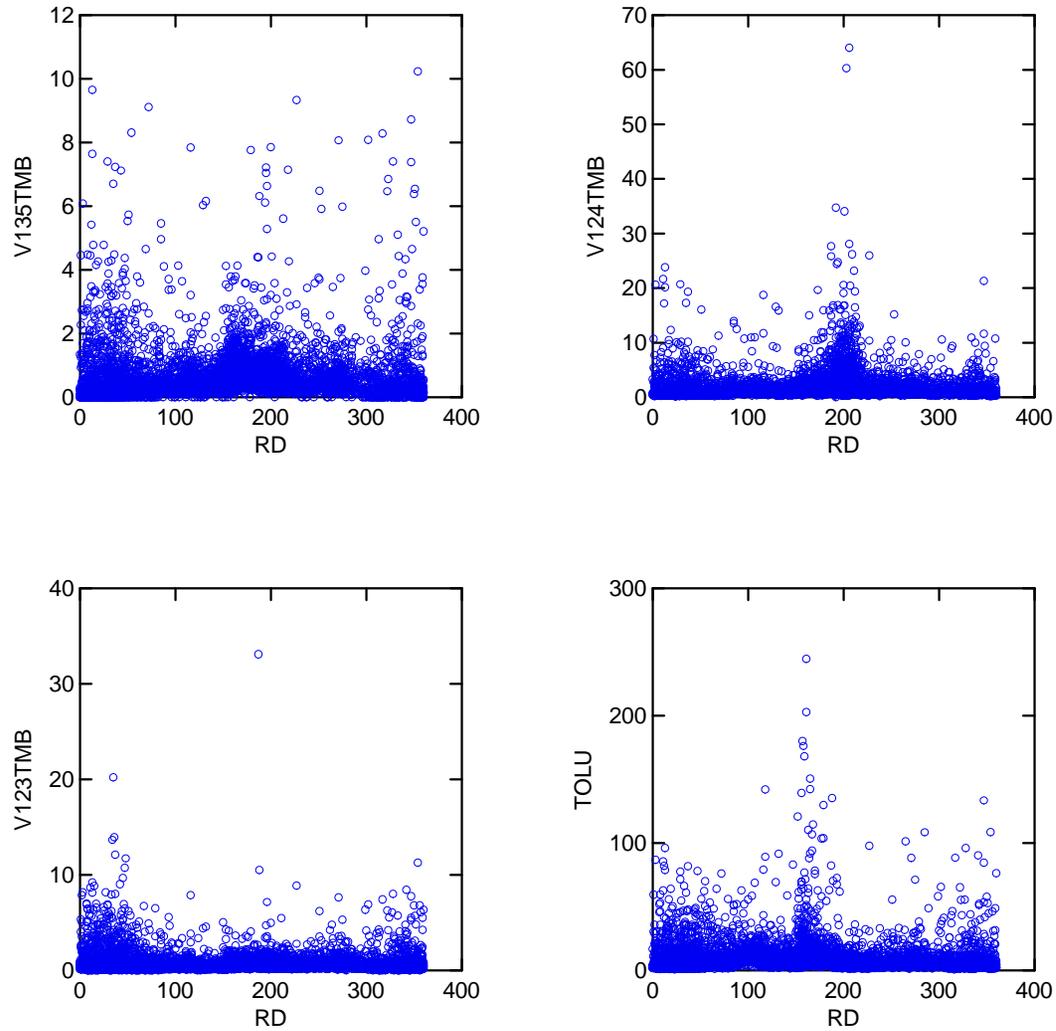


Figure 3.12.4-6. Concentrations (ppbC) as a function of wind direction for 1,3-5-trimethylbenzene (V135TMB), 1,2,4-trimethylbenzene (V124TMB), 1,2,3-trimethylbenzene (V123TMB), and toluene (TOLU) at Clinton Drive in 2000.

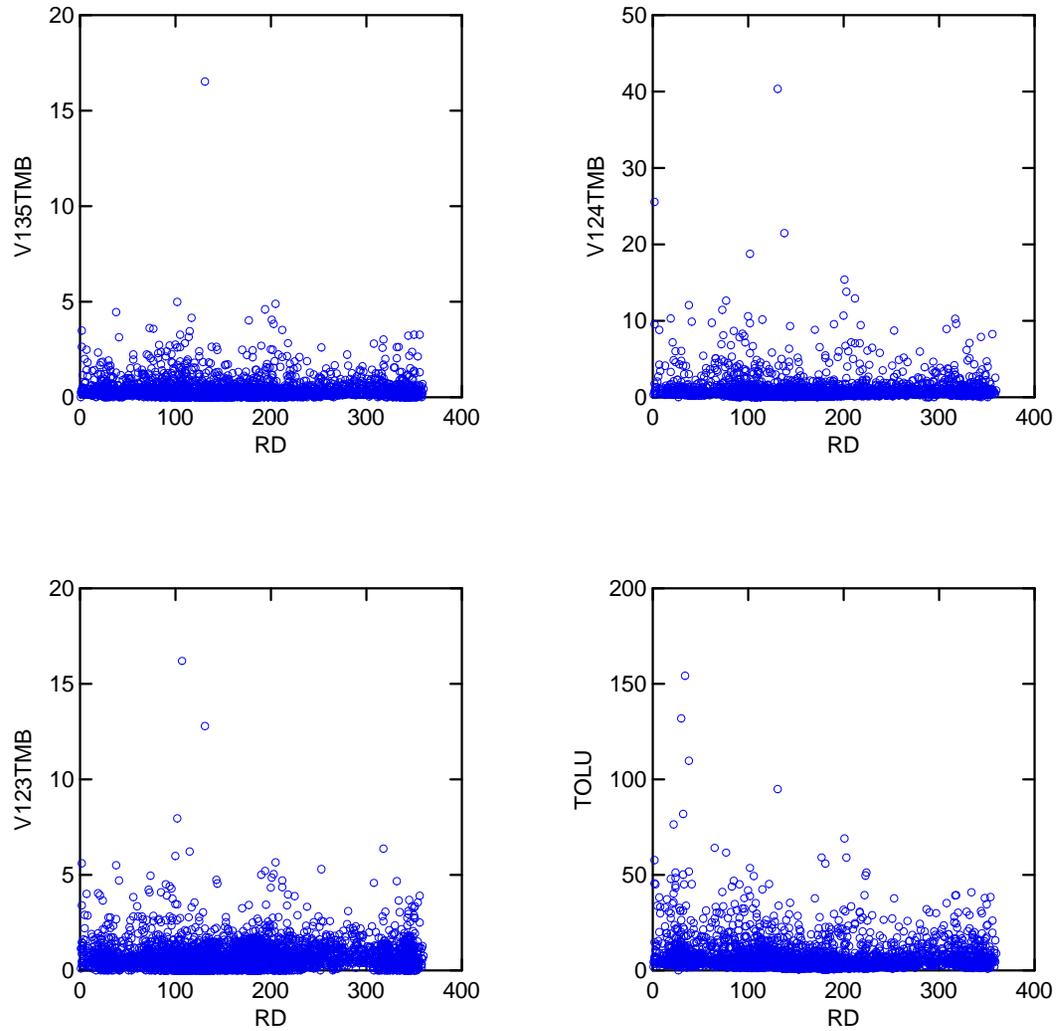


Figure 3.12.4-7. Concentrations (ppbC) as a function of wind direction for 1,3-5-trimethylbenzene (V135TMB), 1,2,4-trimethylbenzene (V124TMB), 1,2,3-trimethylbenzene (V123TMB), and toluene (TOLU) at Deer Park in 2000.

4. CONCLUSIONS AND RECOMMENDATIONS

5. REFERENCES

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