



**ANALYSIS OF  
BATON ROUGE OZONE AND  
OZONE PRECURSOR DATA  
FOR 1997-2004**

**Prepared for:**

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## Executive Summary

This report presents an analysis of ozone and ozone precursor data collected in the Baton Rouge area during 1997-2004. The report presents four separate data analysis efforts, actually, that are tied together inasmuch as they all relate to sudden ozone concentration increases and the factors that may cause them. Sudden ozone concentration increases, which are sometimes referred to as ozone spikes, are rapid increases in ozone levels observed at monitoring sites that are sometimes, but not always, followed by rapid decreases in the monitored ozone levels. Sudden ozone concentration increases are not new phenomena but their perceived importance in the study of ozone formation and control in places like Baton Rouge and Houston has increased recently due to concerns that they may be caused by sudden sharp increases in the ambient levels of highly reactive volatile organic compounds that have not been completely accounted for, traditionally, in ozone control strategy planning.

The four separate but related components of this study were designed to answer the following questions:

- What are the spatial and temporal patterns in sudden ozone concentration increases and how do they relate to ozone precursor levels and meteorological variables?
- What specific volatile organic compounds account most for the ozone formation potential in Baton Rouge and how do VOC levels and reactivity vary spatially and temporally in the Baton Rouge area?
- Can ambient measurements of highly reactivity VOC in Baton Rouge be reconciled with estimates of stationary source emissions? and
- What are the chemical composition profiles of sources that account most for the VOC mass measured in Baton Rouge ambient air?

Key findings and recommendations of this study are summarized below.

### ES.1 Sudden Ozone Concentration Increases

#### **What are the spatial and temporal patterns in sudden ozone concentration increases and how do they relate to ozone precursor levels and meteorological variables?**

From 1997 to 2004, sudden ozone concentration increases, defined as hour to hour ozone concentration increases of greater than 40 ppb, were measured at one or more monitoring sites in the Baton Rouge area on an average of about 11 days per year. The frequency of occurrence has

decreased over this span, from an average of 13.5 per year during 1997-2000 to an average of 8.25 per year during 2001-2004. The Port Allen monitor recorded twice as many sudden ozone concentration increases over this entire 8-year span than any other Baton Rouge monitor. The smallest numbers of these events were monitored at the outlying sites of Grosse Tete, Pride, French Settlement, and Dutchtown.

Sudden ozone concentration increases of greater than 40 ppb/hr occurred on about 50% of the ozone 1-hour exceedance days during 1997-2004 (although, not always at the same site where the exceedance was measured). Sudden ozone concentration increases of greater than 40 ppb/hr occurred on about 25% of the days during 1997-2004 when 8-hour ozone levels exceeded the level of the 8-hour standard (although, not always at the same site where the highest 8-hour average concentration was measured). These observations suggest that sudden ozone concentration increases, in addition to traditional urban and regional ozone formation processes, are important to consider as LDEQ transitions toward implementation of the 8-hour ozone standard.

Sudden ozone concentration increases occurred most often between about 8:00 a.m. and 10:00 a.m., the same daily period when ozone levels normally increased fastest as result of normal photochemical and meteorological processes. These events tended to occur on mornings having very low wind speeds, a condition that is conducive for accumulating relatively high levels of locally emitted ozone precursors before and shortly after sunrise. Indeed, higher than average levels of NO<sub>x</sub> and VOC were usually measured on days when a sudden ozone concentration increase was measured.

At the Capitol site, the VOC species having the greatest concentration increases on mornings when ozone levels increased by greater than 30 ppb/hr were n-pentane, isopentane, C6-C11 alkanes, ethylene, and propylene. The average levels of these compounds were more than 3 times greater on mornings when ozone levels increased by greater than 30 ppb/hr compared with all mornings. At Bayou Plaquemine, the VOC species having the greatest concentration increase on mornings when ozone level increased by greater than 30 ppb/hr was ethylene. The average ethylene level was more than 3 times greater for samples collected on mornings when ozone levels increased by greater than 30 ppb/hr compared with all mornings, while the levels of propylene and other VOC ranged up to 2.3 times greater. NO<sub>x</sub> levels were increased by factor of 1.6 at both the Capitol and Bayou Plaquemine sites during the morning hours when ozone levels increased by greater than 30 ppb/hr.

Future work should consider various indicators of NO<sub>x</sub> and VOC limitation during the hours when the rates of ozone concentration increases were high to determine more precisely the relative effectiveness of controlling NO<sub>x</sub> or VOC emissions as a means for reducing sudden ozone concentration increases.

## ES.2 VOC Levels and Reactivity

### **What specific volatile organic compounds account most for the ozone formation potential in Baton Rouge, how do VOC levels and reactivity vary spatially and temporally in the Baton Rouge area, and how do they relate to sudden ozone concentration increases?**

Averaged over all Baton Rouge monitoring sites, ethylene, propylene, and isoprene accounted for greater percentages of the total VOC reactivity than any other compound that was routinely measured by LDEQ<sup>1</sup>. Together, these compounds accounted for 40% of the average total reactivity. Highly reactive VOC (defined by LDEQ as ethylene; propylene; toluene; 1,3-butadiene; all isomers of butene; and all isomers of xylene), accounted for various percentages of the total VOC reactivity, ranging from site to site between 35% and 53%. Isoprene varied the most from site to site, accounting for an average of 3% of the total reactivity at South Scotlandville and 30% of the total reactivity at Pride.

The highest VOC levels and reactivities were found, on average, in samples collected near the Mississippi River near north and central Baton Rouge. This spatial pattern closely mirrored the spatial pattern in the frequency of sudden ozone concentration occurrence. Day to day variations in VOC reactivity at each monitoring site were greater than any diurnal, weekly, annual, or long-term trends. This suggests that fluctuations in emissions or the random variations in the weather conditions that transport and disperse emissions are mostly responsible for the variability in the measured VOC levels that was observed.

VOC samples collected at the same time and place where ozone levels increased by greater than 40 ppb/hr usually had higher than average reactivity. The same was true for samples collected near back trajectory paths from where sudden ozone concentration increases were measured. No single compound or group of compounds accounted for the increased reactivity found in these samples. For the 35 samples collected at the time and place where a sudden ozone concentration increase was measured or near the back trajectory path, HRVOC accounted for 19% to 67% of the total reactivity.

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<sup>1</sup> VOC reactivity is defined here in terms of the Maximum Incremental Reactivity (MIR) as estimated by Carter (2003).

Future work should attempt to address whether high reactivity typically found in VOC samples associated with sudden ozone concentration increases results from accumulation of routine emissions on mornings having very low wind speeds or from non-routine emissions.

### **ES.3 Emissions Inventory Assessment**

#### **Can ambient measurements of highly reactivity VOC in Baton Rouge be reconciled with estimates of stationary source emissions?**

The average ratios of ethylene/NO<sub>x</sub> measured during 9:00 p.m. to 5:00 a.m. ranged from four to 10 times greater at sites where 3-hour VOC samples were routinely collected, compared with ethylene/NO<sub>x</sub> ratio derived from estimated emissions for stationary sources located within 15 miles of the respective sites. Comparisons of VOC/NO<sub>x</sub> levels measured in ambient air with similar ratios derived from emissions estimates are sometimes used to gauge inaccuracies in VOC emissions inventories, assuming that the NO<sub>x</sub> emissions are accurately estimated, no significant measurement errors exist, and that NO<sub>x</sub> and VOC emitted from the same source or group of sources are transported and dispersed uniformly in the atmosphere with no significant losses due to deposition or chemical reactions.

Disagreements between monitored propylene/NO<sub>x</sub>; butene/NO<sub>x</sub>; and 1,3-butadiene/NO<sub>x</sub> ratios and the corresponding ratios derived from stationary source emission estimates were generally greater than the discrepancies found for the ethylene/NO<sub>x</sub> ratios. In the cases of butene/NO<sub>x</sub> and 1,3-butadiene/NO<sub>x</sub>, measurement uncertainties may have been a significant factor in the magnitude of disagreement between the monitored ratios and those derived from emissions estimates. The average levels of these compounds were near or below the method detection limits, at levels at which the signal to noise ratio of the measured values may be large.

The results of this analysis suggest that HRVOC may be under-represented in the emissions inventory but uncertainties in the analysis, itself, limit any quantitative assessments. Future work should examine the emissions inventory process from the bottom up, with particular attention to VOC speciation, to identify potential weaknesses in the traditional VOC emissions estimation approaches.

## ES.4 VOC Source Apportionment

### **What are the chemical composition profiles of sources that account for most of the VOC mass measured in Baton Rouge ambient air?**

Source apportionment using a beta test version of the EPA PMF was used to identify the chemical composition profiles of sources that accounted most for the VOC mass measured at Baton Rouge monitoring sites. The source apportionment analysis focused on 3-hour VOC samples collected at the Capitol site and short-term samples collected at the Capitol, Port Allen, South Scotlandville, and Southern sites that were triggered by high levels of total nonmethane organic compounds. In this way, the source apportionment analysis focused on the monitoring sites where the highest VOC levels were typically measured.

Thirteen source profiles were identified for 3-hour VOC samples collected at the Capitol site having start times ranging from 9:00 p.m. to 6:00 a.m. Six source profiles containing different combinations of mostly C3-C6 alkanes accounted for 52% of the total speciated VOC mass, on average. The greatest concentrations associated with these source profiles were usually associated with northerly, northwesterly or west-northwesterly winds. Other source profiles that accounted for comparatively high percentages of the total VOC mass included a background accumulation source profile containing mostly ethane, propane, and n-butane; a motor vehicle source profile containing toluene; benzene; xylene; acetylene; and 1,2,4-trimethylbenzene; and an ethylene source profile. These source profiles accounted for 16%, 11%, and 8%, respectively of the total VOC mass. Similar source profiles were identified for the triggered samples collected at each monitoring site, with source profiles containing C3-C6 alkanes accounting for greater than 50% of the total speciated VOC mass at each site.

A cursory examination of sample to sample variability in the source profile contributions to total VOC mass in the triggered samples showed that at times individual source profile contributions varied independently with respect to one another while at other times the contributions from all source profiles seemed to vary uniformly. This suggests that episodic emissions from individual sources, in addition to routine emissions, account at times for the levels of VOC measured in the triggered VOC samples.

Future work should investigate the sensitivity of the source apportionment results to different model inputs. Performing source apportionment on a reactivity basis would also be helpful toward identifying the source types that have the greatest potential to impact ozone formation. A more comprehensive analysis of source contribution variability is also needed to better address the relative importance of routine and episodic emissions.

## 1.0 Introduction

This report presents an analysis of ozone and ozone precursor data collected in Baton Rouge during 1997-2004, with emphasis on sudden ozone concentration increases and the factors that cause them. This work was sponsored by the Louisiana Department of Environmental Quality (LDEQ) in response to recommendations made by the Baton Rouge HRVOC Work Group, Data Analysis Subgroup, which LDEQ formed in 2003 to evaluate ozone formation and control in the area.

### 1.1 Background

In 1991 the United States Environmental Protection Agency (EPA) classified Baton Rouge a *serious* ozone nonattainment area (56 FR 56694). Since that time, significant air quality improvements have been measured in Baton Rouge. In fact, by 2001 the area had nearly attained the 1-hour ozone standard and LDEQ was developing a plan for new controls on oxides of nitrogen (NO<sub>x</sub>) sources in the area that, according to computer model projections, would provide the additional air quality improvement needed for attainment (LDEQ, 2001). However, exceedances of the 1-hour ozone standard in 2002 and 2003, and new findings pertaining to ozone formation in Houston, prompted LDEQ to reexamine the Baton Rouge ozone problem beginning in 2003 (LDEQ, 2003).

In 2000 the Texas Commission on Environmental Quality (TCEQ), the United States Department of Energy (DOE), the National Oceanic and Atmospheric Administration (NOAA), and other organizations conducted the 2000 Texas Air Quality Study (TexAQS 2000). Two of the major findings of TexAQS 2000 were that ozone forms much more rapidly in the plumes of industrial sources in the Houston area than in most other environments and that a relative abundance of a few highly reactive volatile organic compounds (HRVOC), in the presence of NO<sub>x</sub>, was most responsible for the especially high rates of ozone formation that were observed (Kleinman, et al., 2002). Additionally, TexAQS 2000 researchers measured greater amounts of HRVOC in the ambient air downwind from industrial sources than could be accounted for using conventional emissions estimates (Ryerson, et al., 2003). These findings led to major changes in Texas' strategy for attaining the ozone standards Houston, shifting some of the focus away from NO<sub>x</sub> controls and towards controlling HRVOC (TCEQ, 2002).

Noting similarities in the evolution of recent high ozone events in Baton Rouge to those in Houston as well as similarities in the types of industry, LDEQ formed the Baton Rouge HRVOC Work Group to study the Baton Rouge ozone problem and recommend solutions to help the area attain the EPA standards. Subgroup 1 of the HRVOC Work Group; which focused on

data analysis and included representatives from LDEQ, EPA, public interest groups, and industry; met approximately six times from October 2003 to January 2004. Subgroup 1 found that HRVOC levels, NO<sub>x</sub> levels, and meteorological conditions all appeared to affect ozone formation to some extent and recommended that a comprehensive statistical analysis of historical monitoring data be conducted to determine which variables are most significant (Hazlett, 2004a).

## 1.2 Objectives

In general terms, the purpose of this study was to help identify the causes of 1-hour and 8-hour ozone exceedances in the Baton Rouge area, with emphasis on exceedances resulting from short-term or transient spikes. No minimum rate of ozone increase universally defines an ozone spike; however, researchers studying the Houston ozone problem have commonly used 40 ppb/hr as a threshold for deciding whether a spike has occurred. This is because some of the earlier modeling conducted to support the Texas State Implementation Plan (SIP) did not reproduce any of the hour to hour increases in ozone levels greater than 40 ppb/hr that were monitored during the modeling episode. In a later SIP revision, TCEQ formally defined a *sudden ozone concentration increase* (SOCI) as an hour to hour increase of at least 40 ppb and noted that SOCI is believed to be caused by sudden increases in HRVOC emissions (TCEQ, 2004).

To achieve the overall goal of this study, LDEQ outlined a series of tasks to address:

- The frequency of sudden ozone concentration increases; their trends over time; and their relationships to other monitoring parameters including VOC, NO<sub>x</sub>, and meteorological conditions.
- The spatial and temporal patterns in VOC levels and photochemical reactivity, including an assessment of the relative importance of the speciated VOC to sudden ozone concentration increases;
- An assessment of the emissions inventory by comparing monitored VOC and NO<sub>x</sub> levels to the reported emissions; and
- VOC source apportionment.

## 1.3 Organization of this Report

This report is organized into eight sections: This introduction (Section 1); a discussion of the data used in the study (Section 2); a statistical analysis of sudden ozone concentration increases (Section 3); an analysis of speciated VOC reactivity (Section 4); an emissions inventory assessment (Section 5); VOC source apportionment (Section 6); and a summary, conclusions, and recommendations (Section 7). References are provided in Section 8.

## 2.0 Data Base

LDEQ monitors ambient ozone levels and an assortment of other air quality and meteorological parameters at the ten stations in the Baton Rouge area shown in Figure 2-1 and listed in Table 2-1. Hourly measurement results from all ten sites and for all measurement parameters were provided by LDEQ for the period of January 1997 through September 2004 in a series of spreadsheet files, with each file containing the hourly data for a single parameter for a single year. The data were subsequently loaded into and merged in a relational database for validation and analysis. Data validation for meteorological parameters consisted of checks for consistency of data with measurement results from nearby sites and with the normal ranges of variation for a given parameter. Data judged to be invalid were deleted from the database. Air quality data received from LDEQ had already been validated (Hazlett, 2004b) and a cursory review of the ozone and NO<sub>x</sub> data confirmed that to be the case.

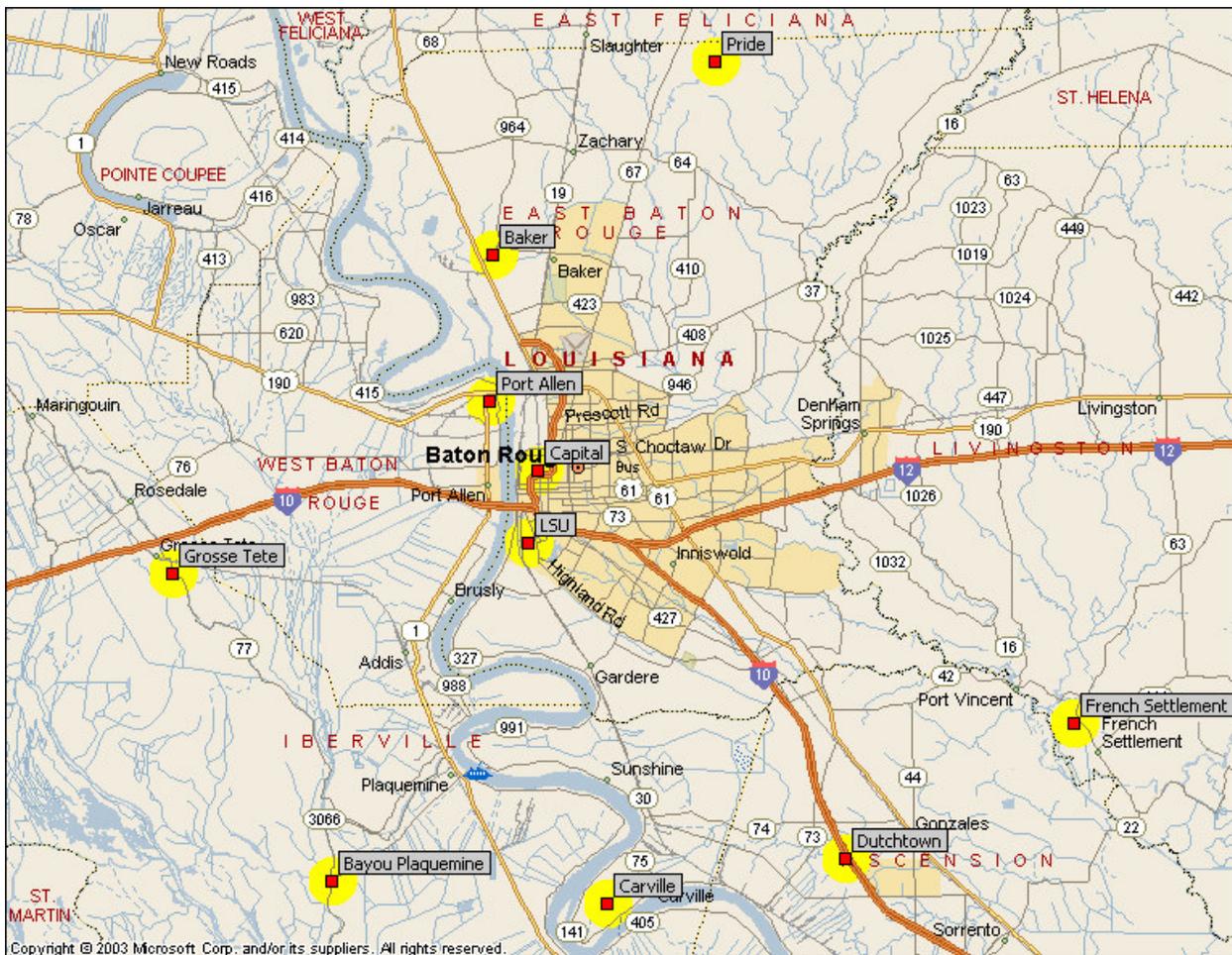
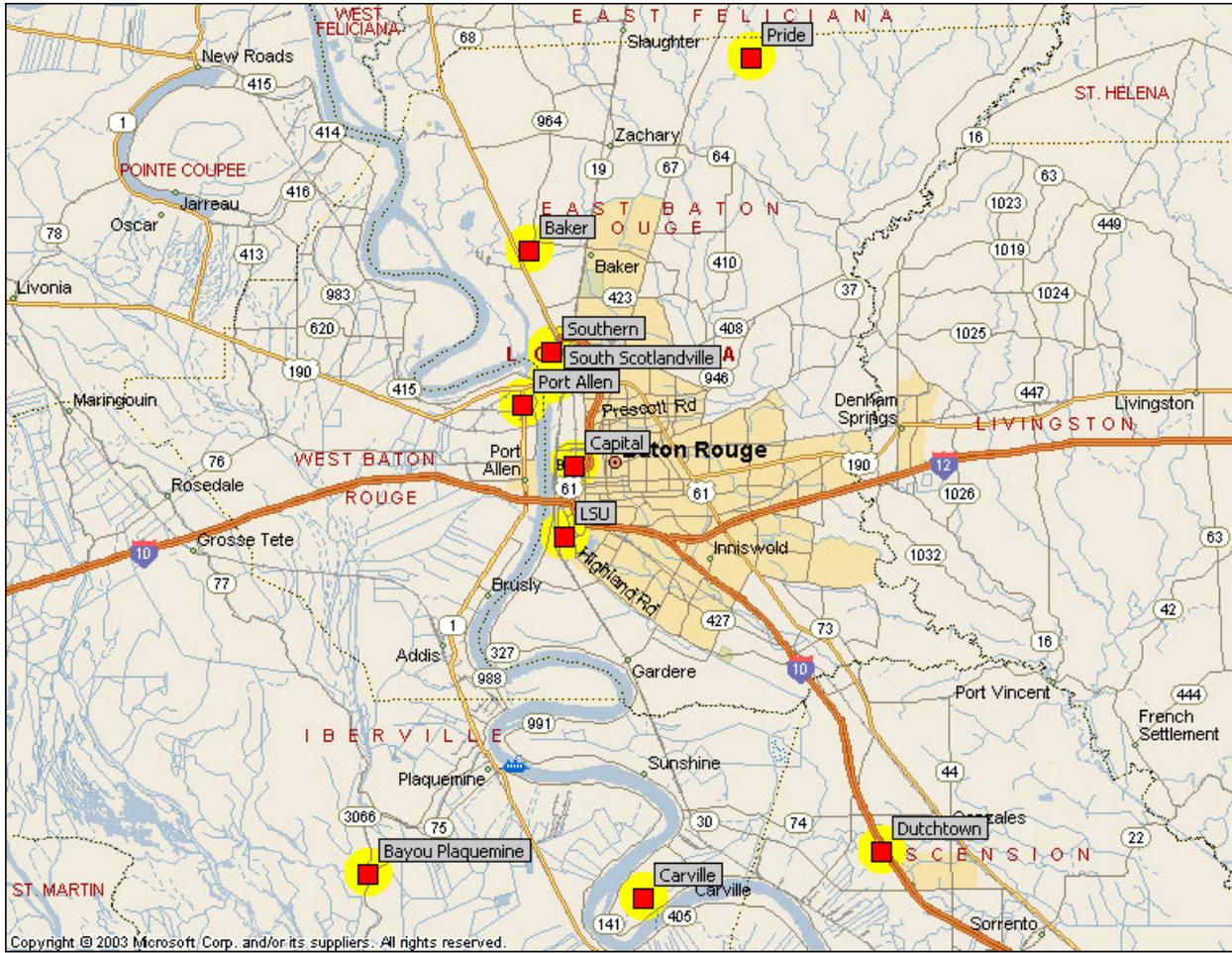


Figure 2-1. LDEQ Baton Rouge Ozone Monitoring Network

**Table 2-1. LDEQ Baton Rouge Area Monitoring Sites and Parameters**

Site	NO <sub>x</sub>	O <sub>3</sub>	Met	VOC			
				3-Hr (Daily)	3-Hr (Every 3rd Day)	24-Hr (Every 6 <sup>th</sup> Day)	25-Minute (Triggered by 2 ppm THMHC)
Capitol	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
LSU	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
Bayou Plaquemine	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	
Port Allen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>			<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
Pride	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	
Dutchtown	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>			<input checked="" type="checkbox"/>	
Baker	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>			<input checked="" type="checkbox"/>	
Carville	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>
Grosse Tete	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>				
French Settlement	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>				
Southern						<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
South Scotlandville						<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>

LDEQ monitors the levels of 56 ozone precursor VOC at the 10 Baton Rouge area monitoring stations listed in Table 2-1 and shown in Figure 2-2. Samples for VOC were collected in specially prepared stainless steel canisters and subsequently analyzed using gas chromatography with flame ionization detection according to the EPA method TO-15. LDEQ samples the ambient air for VOC in 3-hour and 24-hour sampling intervals according to the schedule listed in Table 2-1. Additionally, short-term (25-minute) samples are collected at six sites when triggered by 2 ppm or greater total nonmethane hydrocarbon (THMHC) levels, which are monitored continuously at the six triggered canister sites. VOC monitoring results for January 1997 through September 2004 were also provided in a series of spreadsheet files and subsequently loaded into a relational database. Data from 1997 were omitted from the analyses described in this report because of data formatting problems that were encountered. All the VOC data provided by LDEQ were assumed to be valid.



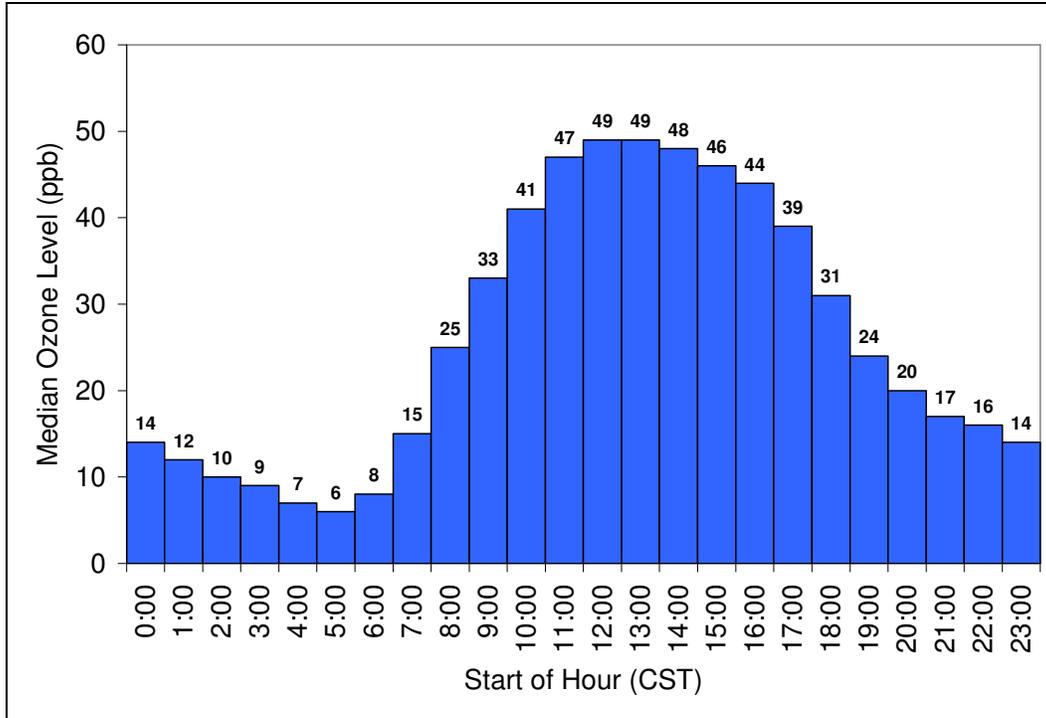
**Figure 2-2. LDEQ Baton Rouge VOC Sampling Network**

### 3.0 Sudden Ozone Concentration Increases

An ozone spike, loosely defined, is a sudden increase in ozone level observed at a monitoring site that is sometimes, but not always, followed by sudden decrease. No specific threshold rate of ozone increase defines a *spike*; however, TCEQ defines a *sudden ozone concentration increase* (SOCI) as an hour to hour increase of at least 40 ppb (TCEQ, 2004). Sudden ozone concentration increases may result from rapid ozone formation at a monitoring site or from steep ozone concentration gradients in air that is advected to a monitoring site by wind currents. Though the terms *ozone spike* and *sudden ozone concentration increase* are sometimes used interchangeably, the latter term is more accurate since some of the high ozone events that follow a rapid increase in ozone level at a monitoring site persist for several hours.

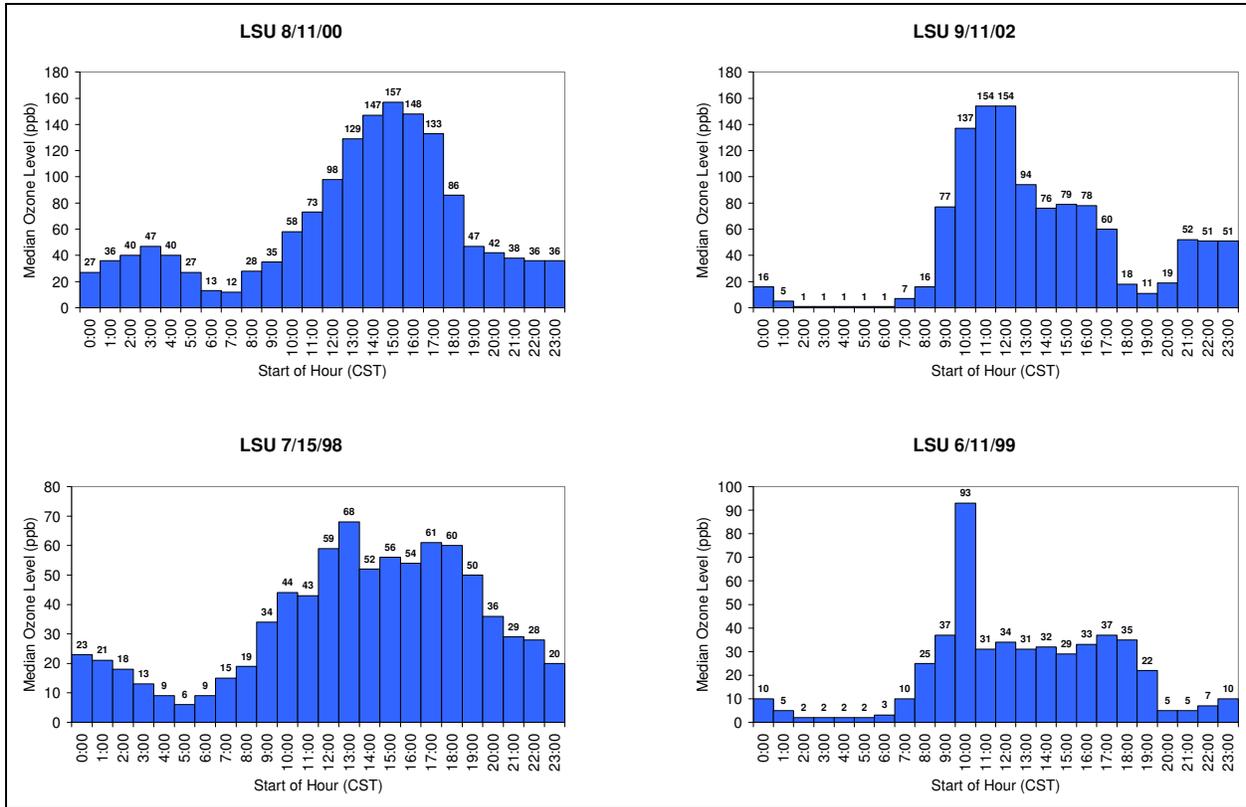
#### 3.1 Ozone Diurnal Variations

Figure 3-1 shows the average diurnal variation in ozone observed by the Baton Rouge LSU monitor for ozone season days (May – September) during 1997 – 2004. Note that ozone levels were typically lowest during the hour beginning at 5:00 a.m. Central Standard Time (CST) and rose most rapidly, on average, between the hours beginning at 8:00 a.m. to 10:00 a.m. The average rate of ozone increase during this period was about 8 ppb/hr to 10 ppb/hr.



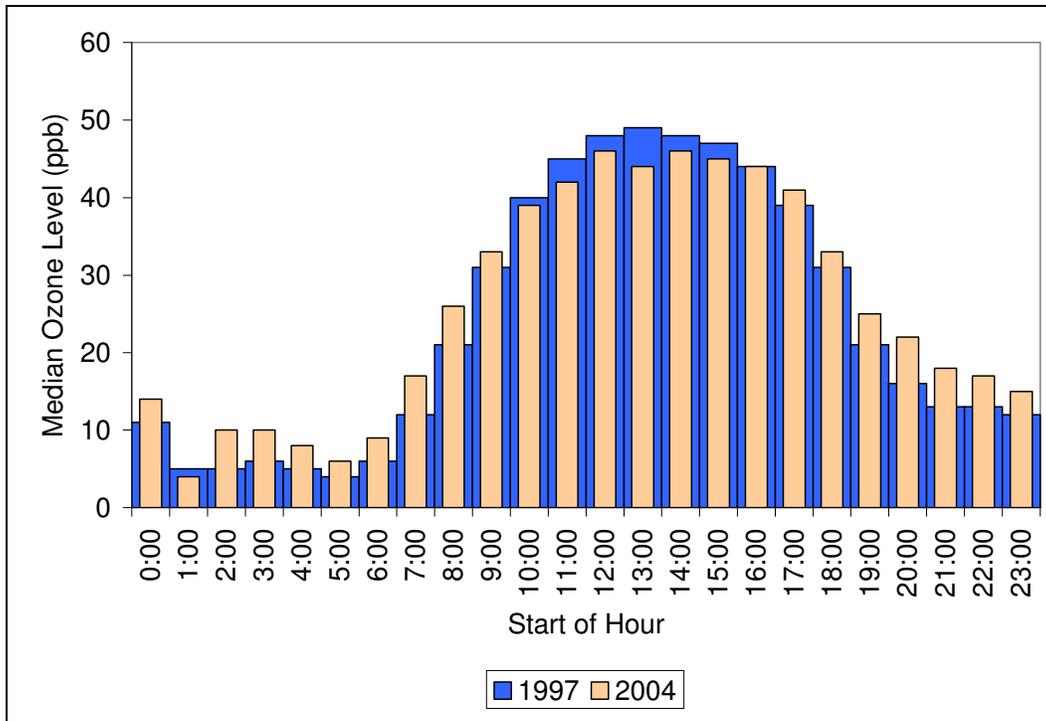
**Figure 3-1. Ozone Average Diurnal Variation Observed at the LSU Monitor During the 1997 – 2004 Ozone Seasons**

On any day during the ozone season the diurnal ozone variation may differ markedly from the composite shown in Figure 3-1 due to day to day variability in the processes that lead to ozone formation, transport, and decay. Note in Figure 3-2, which is based on ozone levels monitored on four separate days at the LSU site, that ozone levels can rise gradually or rapidly on ozone exceedance days (top left and top right of Figure 3-2, respectively) as well as gradually or rapidly on ozone non-exceedance days (bottom left and bottom right of Figure 3-2, respectively).

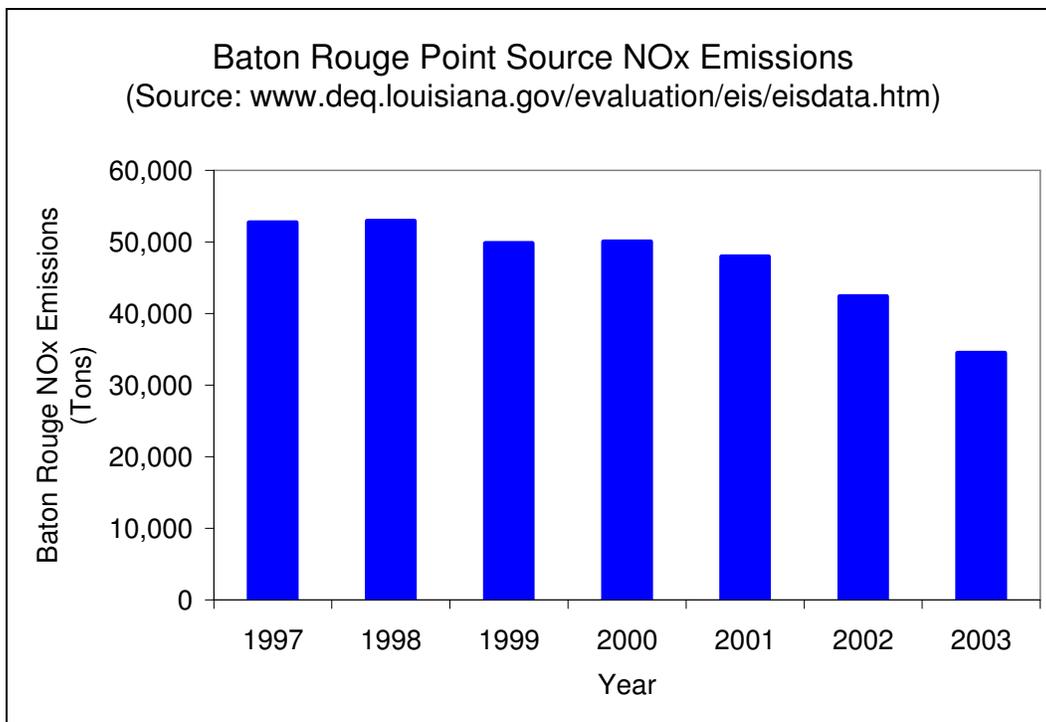


**Figure 3-2. Examples of Ozone Diurnal Variations Measured at the LSU Monitoring Site**

Interestingly, the average shape of the ozone diurnal variation at the LSU monitor flattened slightly between the 1997 and 2004 ozone seasons. Relative to the 1997 ozone season, the average ozone levels were lower at midday in 2004 but higher during the morning, late afternoon, and nighttime periods (Figure 3-3). This could be a sign that NO<sub>x</sub> emission reductions that were made between 1997 and 2004 (Figure 3-4) were effective at reducing midday peak ozone levels but had the opposite effect during the photochemically inactive times of day when fresh NO<sub>x</sub> emissions can destroy ozone.

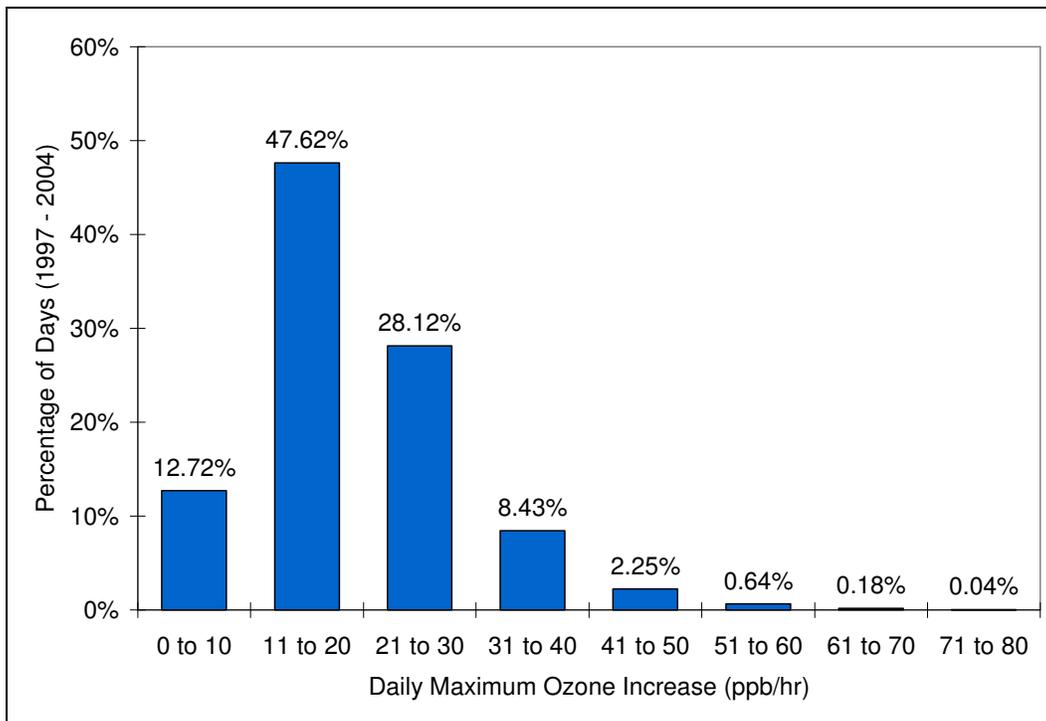


**Figure 3-3. Ozone Average Diurnal Variations Observed at LSU During the 1997 and 2004 Ozone Seasons**

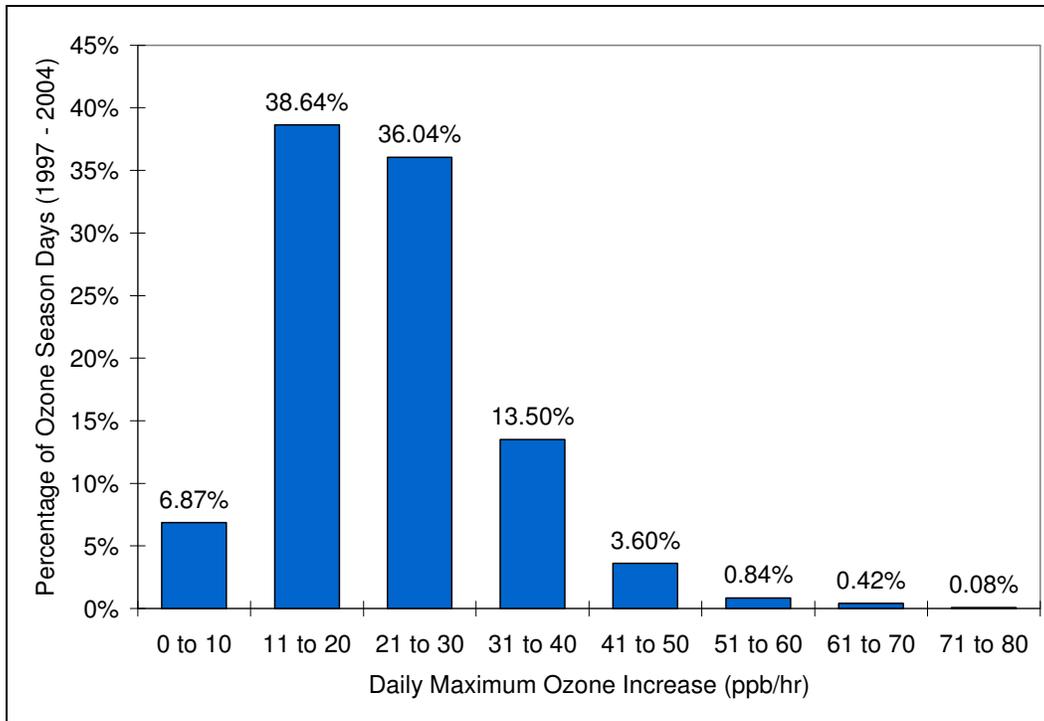


**Figure 3-4. Trend in Baton Rouge Point Source NO<sub>x</sub> Emissions from 1997 to 2003**

The greatest hourly ozone concentration increase in the Baton Rouge area on any given day during 1997-2004 was usually between 11 ppb and 30 ppb. About 75% of *all days* having valid ozone monitoring data had maximum ozone concentration increases in that range (Figure 3-5). About 75% of the *ozone season days* also had maximum ozone concentration increases between 11 ppb and 30 ppb (Figure 3-6); however, a relatively greater percentage of days during the ozone season had ozone concentration increases greater than 30 ppb/hr, compared with all days. Note that the percentage of ozone season days having maximum ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr was about 18% and 5%, respectively.



**Figure 3-5. Histogram Chart Showing the Percentage of all Days Having Maximum Ozone Concentration Increases in Various Ranges**

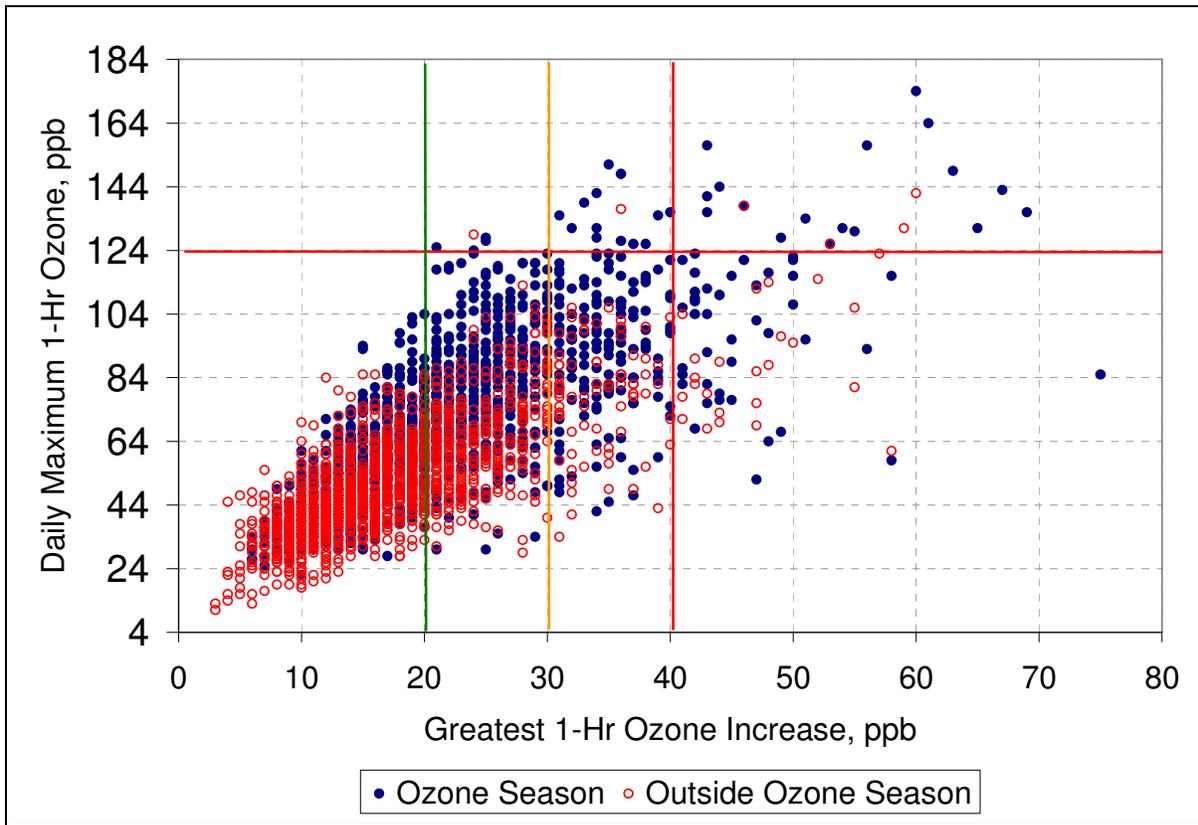


**Figure 3-6. Histogram Chart Showing the Percentage of Ozone Season Days Having Maximum Ozone Concentration Increases in Various Ranges**

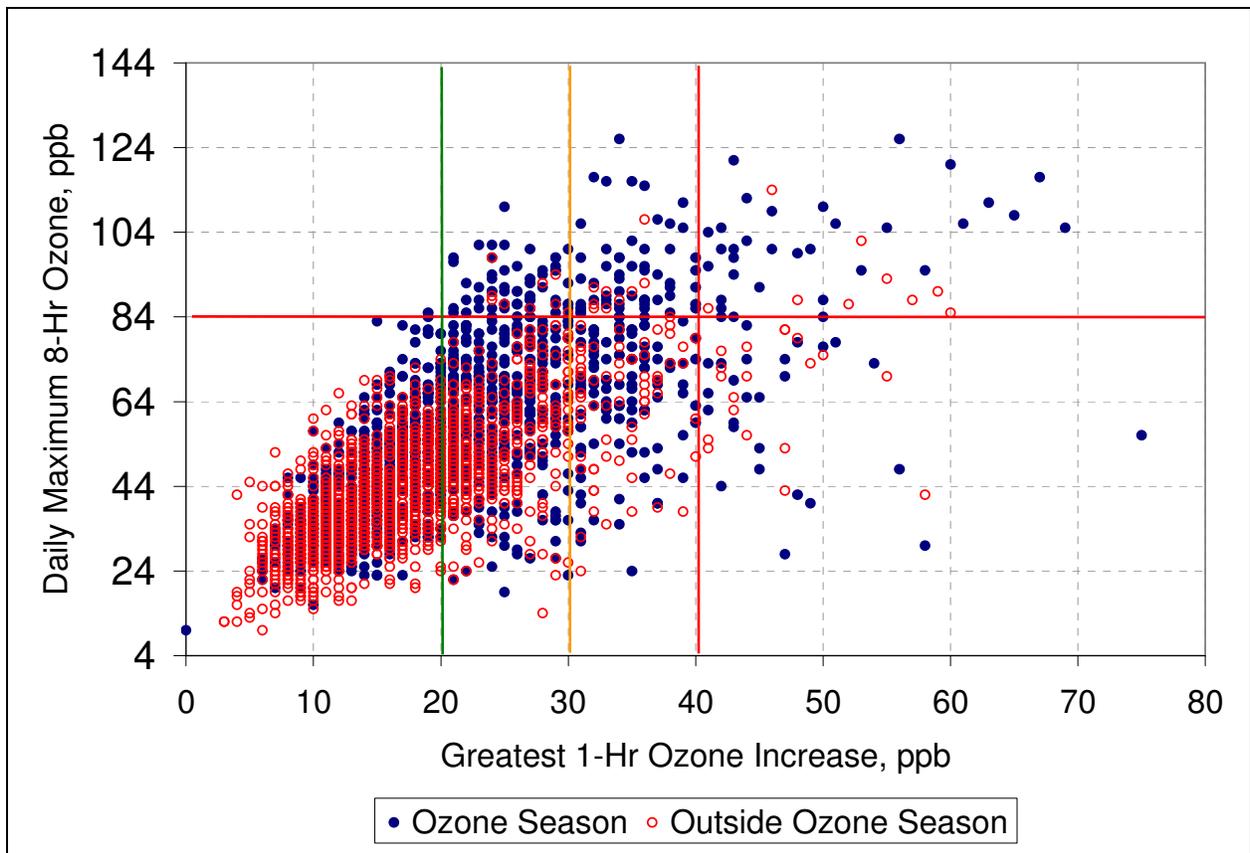
### **3.2 Relationship of Sudden Ozone Concentration Increases to 1-Hour and 8-Hour Exceedances**

The daily maximum 1-hour and 8-hour ozone levels tended to be higher in the Baton Rouge area on days when ozone levels increased relatively fast; however, the relationship is complex. See, for example Figure 3-7, which compares the daily maximum ozone increase, in ppb/hr, observed by the LDEQ network of Baton Rouge ozone monitors (x-axis) with the maximum 1-hour ozone level observed on the same day (y-axis), for all days during January 1997 to September 2004 having valid measurement data. The shaded circles represent ozone season days while the open circles represent days outside the ozone season. Ozone concentration increases of at least 40 ppb/hr were observed on about 50% of the days when the 1-hour ozone standard was exceeded (i.e., days with daily maximum ozone concentration greater than 124 ppb); however, most days having ozone concentration increases greater than 40 ppb/hr were not 1-hour exceedance days. Note that ozone concentration increases of at least 30 ppb/hr were monitored on nearly all the 1-hour exceedance days.

Figure 3-8 is similar to Figure 3-7, except the y-axis represents the daily maximum 8-hour ozone level. Note that ozone concentration increases of greater than 40 ppb/hr were observed on only about 25% of the 8-hour exceedance days (i.e., days with daily maximum 8-hour ozone level greater than 84 ppb). Ozone concentration increases greater than 30 ppb/hr were observed on about 60% of the 8-hour exceedance days but most days having ozone concentration increases of greater than 30 ppb/hr did not exceed the 8-hour standard.



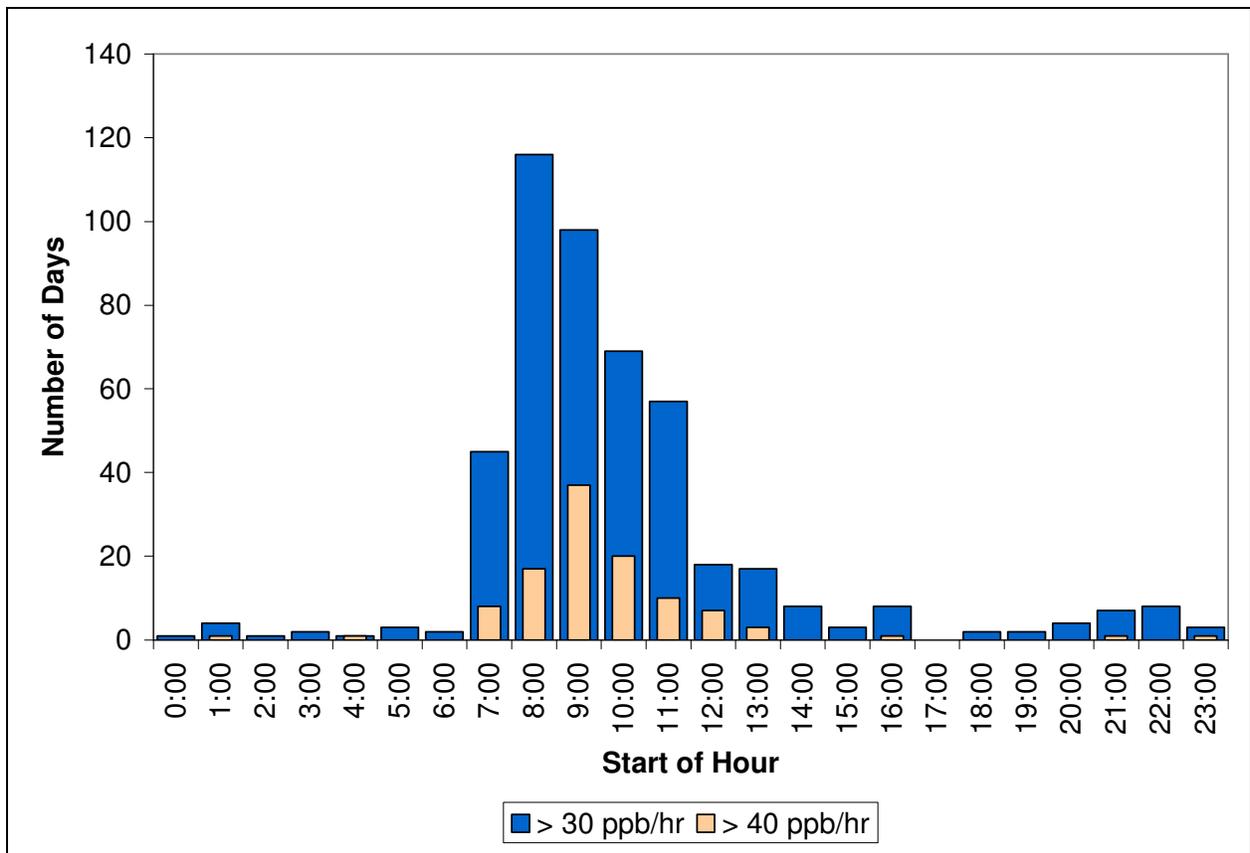
**Figure 3-7. Scatter Plot Showing the Relationship Between the Daily Maximum 1-Hour Ozone Level in Baton Rouge and the Greatest 1-Hour Ozone Concentration Increase**



**Figure 3-8. Scatter Plot Showing the Relationship Between the Daily Maximum 1-Hour Ozone Level in Baton Rouge and the Greatest 8-Hour Ozone Concentration Increase**

### 3.3 Temporal and Spatial Trends of Sudden Ozone Concentration Increases

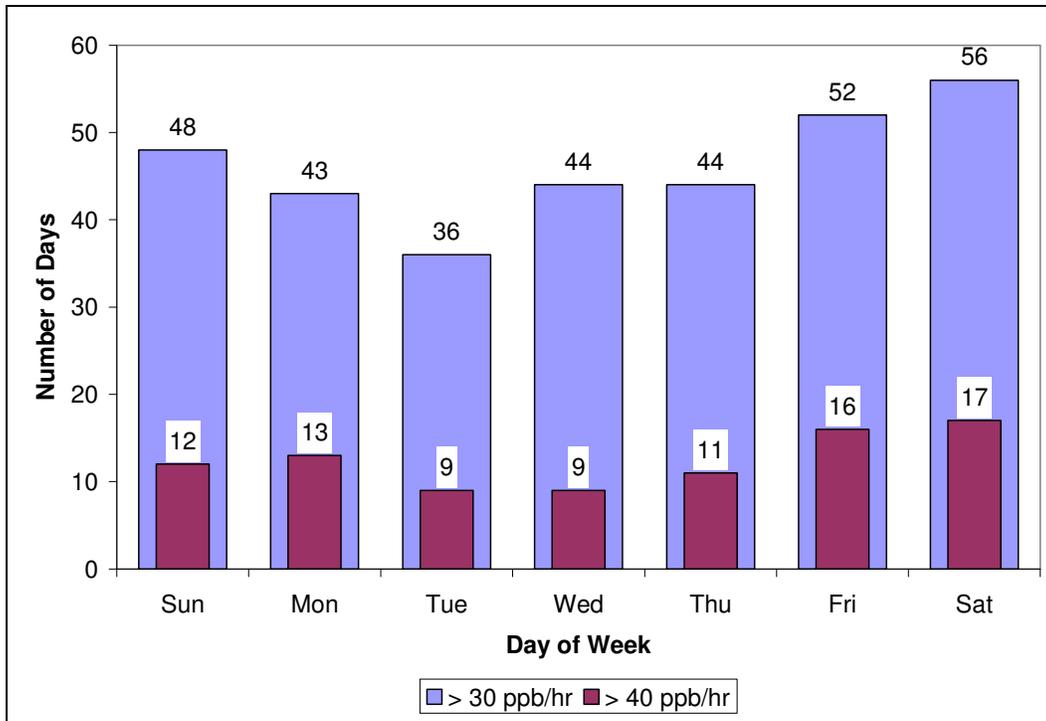
Most hour to hour ozone concentration increases greater than 40 ppb occurred between 8:00 a.m. and 10:00 a.m. CST (Figure 3-9), the time of day when ozone levels typically rose the fastest (see, for example, Figure 3-1); however, a few sudden ozone concentration increases occurred outside that window. Ozone concentration increases greater than 30 ppb/hr but less than 40 ppb/hr also occurred most often between 8:00 a.m. and 10:00 a.m. CST, with the greatest frequency of occurrence one hour earlier than the ozone concentration increases above 40 ppb/hr. Sudden ozone concentration increases that occurred outside the photochemically active period of day were probably caused by horizontal or vertical transport of air having steep concentration gradients.



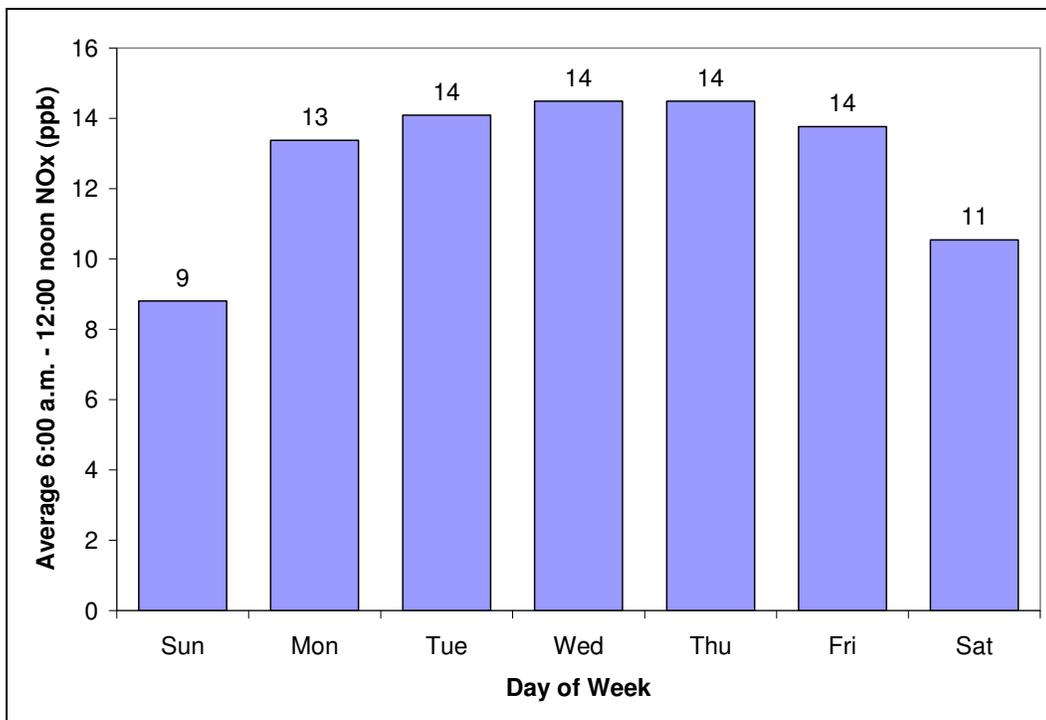
**Figure 3-9. Histogram Chart Showing the Number of Days When Ozone Levels Increased by Greater than 30 ppb/hr and 40 ppb/hr at Various Times of Day**

Ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr occurred more often on Fridays and Saturdays than on any other day of the week (Figure 3-10). This pattern does not appear to be related to a weekly pattern in 6:00 a.m. to 12:00 noon NO<sub>x</sub> levels, which peaks during midweek but is lowest on Sunday (Figure 3-11).

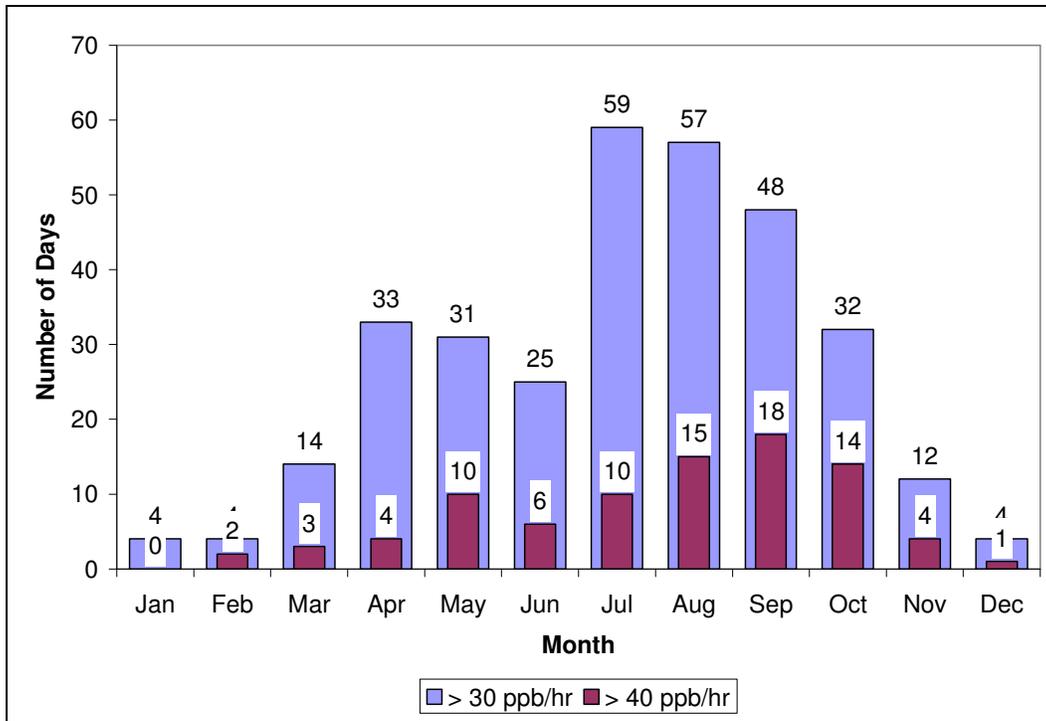
Ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr occurred most often during July through October, with a secondary peak during April through June (Figure 3-12). This pattern roughly mimics the monthly frequency pattern for 1-hour and 8-hour exceedance days (Figure 3-13). Note that the late summer to early fall peak extends beyond the traditional May to September ozone season for Baton Rouge.



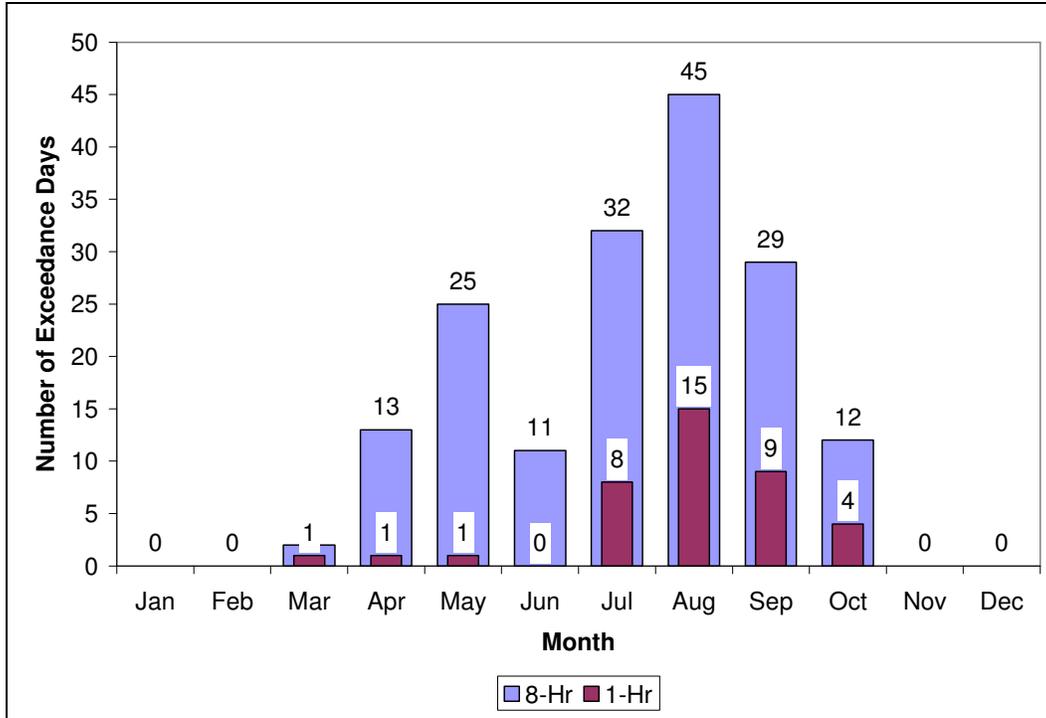
**Figure 3-10. Number of Days Having Ozone Concentration Increases Greater Than 30 ppb/hr and 40 ppb/hr for Different Days of the Week**



**Figure 3-11. Average Ozone Season 6:00 a.m. to 12:00 Noon NO<sub>x</sub> Levels Measured in Baton Rouge for Different Days of the Week During 1997 to 2004**

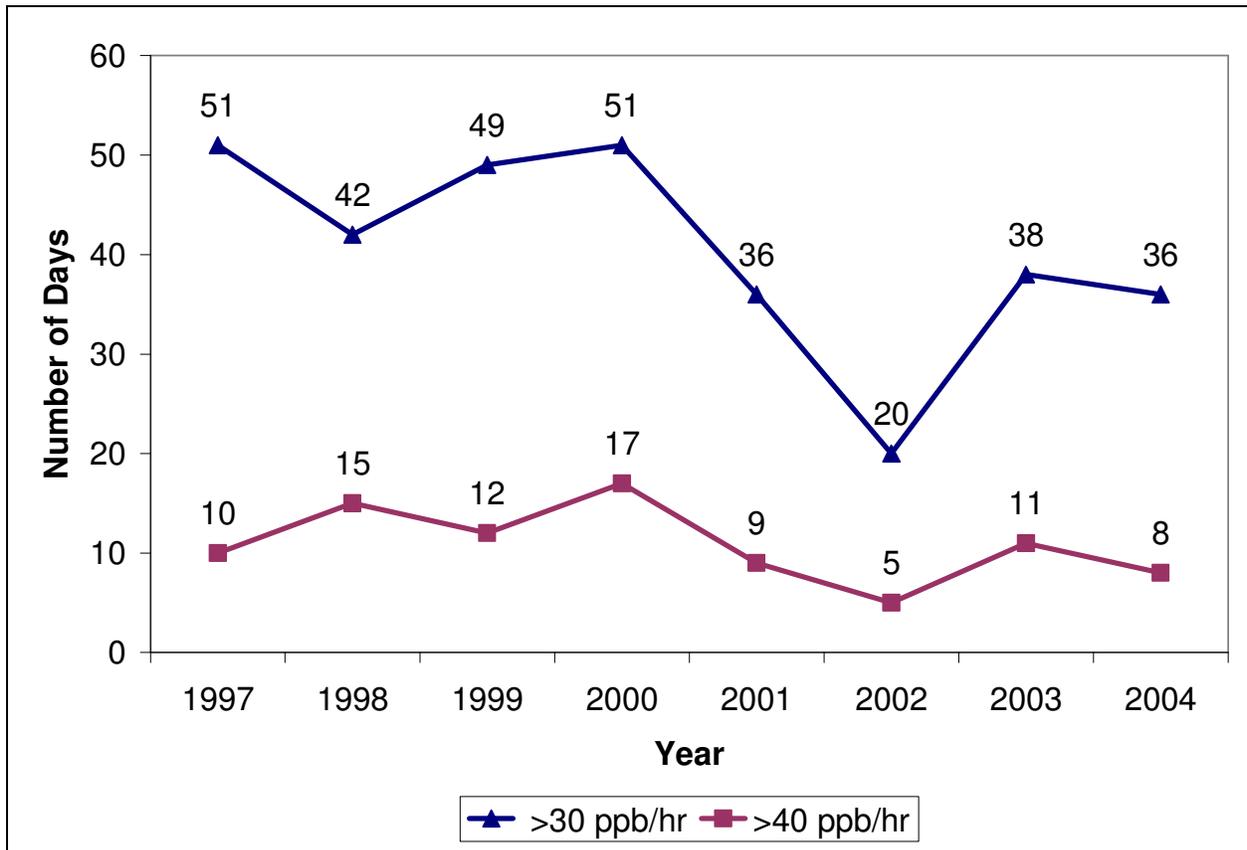


**Figure 3-12. Monthly Occurrences of Ozone Concentration Increases Greater Than 30 ppb/hr and 40 ppb/hr During 1997 to 2004**



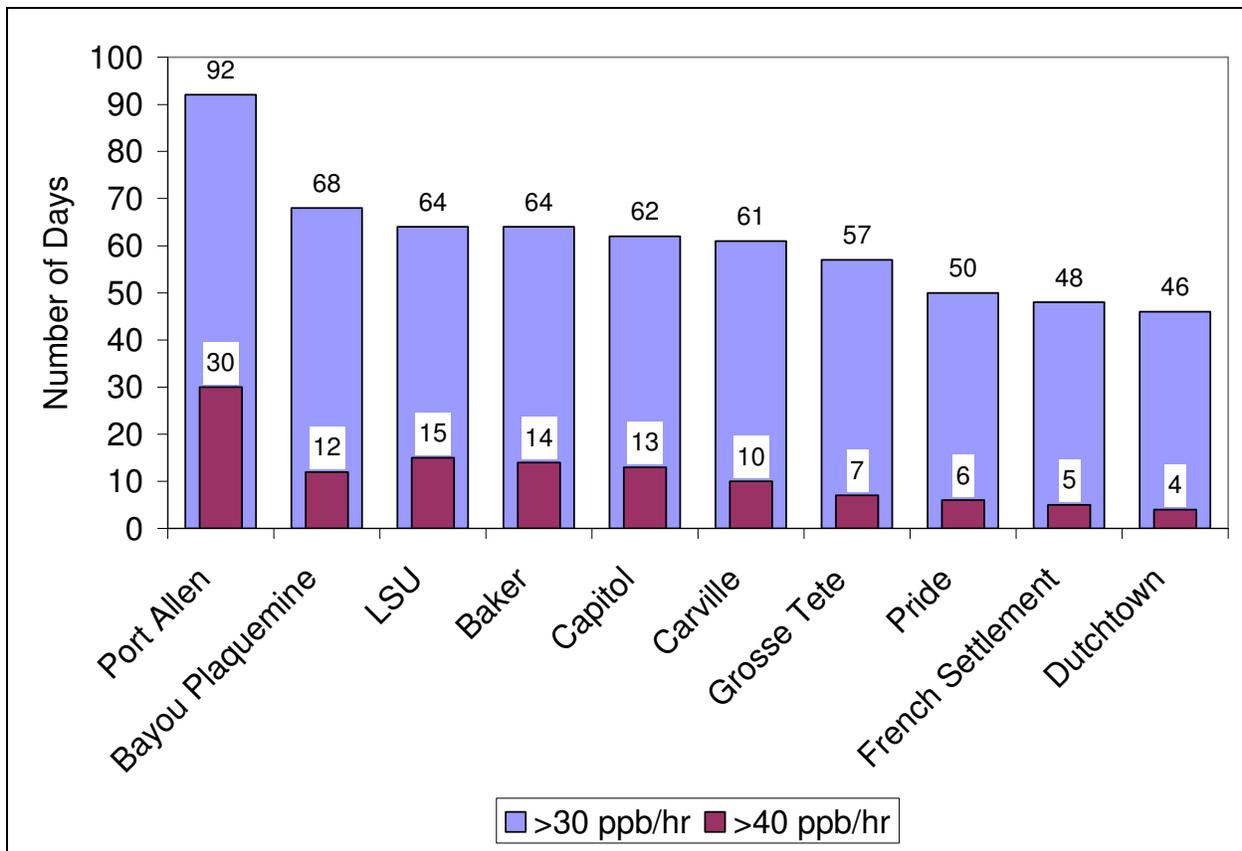
**Figure 3-13. Monthly Occurrences of 1-Hour and 8-Hour Ozone Standard Exceedances During 1997 to 2004**

The number of days per year having ozone concentration increases greater than 30 ppb/hr or 40 ppb/hr in Baton Rouge decreased from 1997 to 2004 (Figure 3-14). This trend is most apparent when considering the averages for the two separate four year periods beginning 1997 and 2001. During 1997-2000, the numbers of days having ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr were 48 and 14, respectively, while during 2001-2004 the numbers of days dropped to 33 and 8, respectively.



**Figure 3-14. Long-Term Trend in the Number of Days Having Ozone Concentration Increases Greater than 30 ppb/hr and 40 ppb/hr**

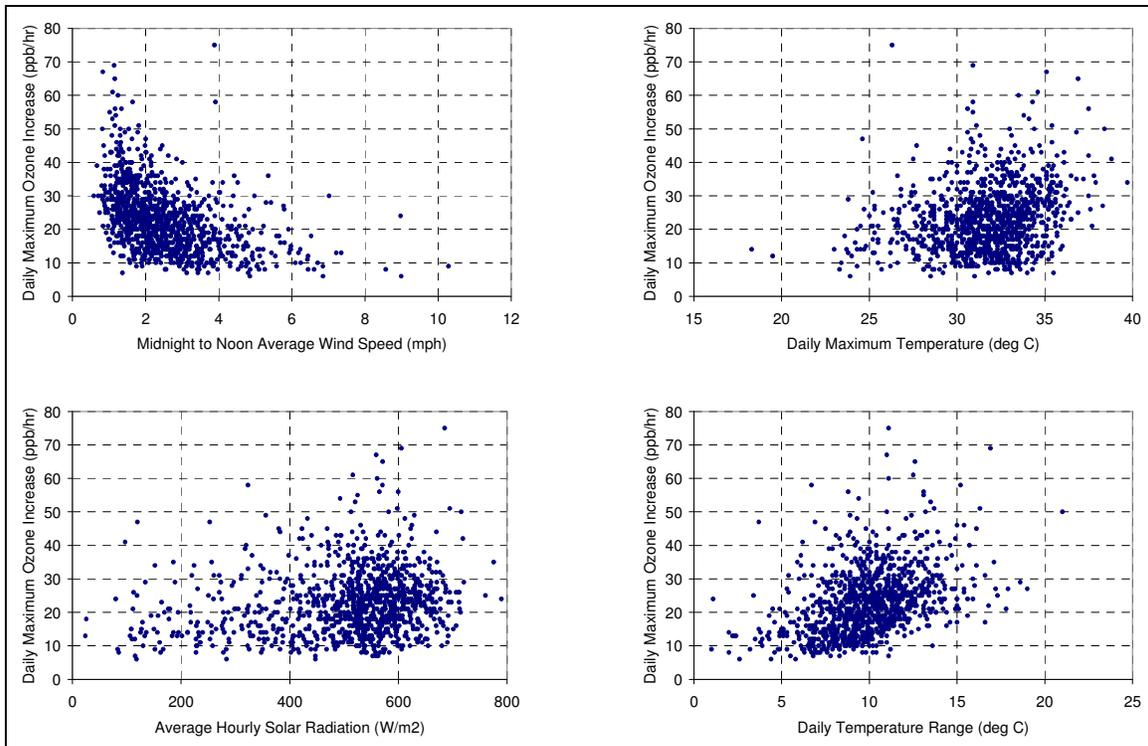
The Port Allen site had the greatest number of days with daily maximum ozone concentration increases greater than 40 ppb/hr. The same was true for days having ozone concentration increases greater than 30 ppb/hr (Figure 3-15). French Settlement, Dutchtown, Grosse Tete, and Pride had the fewest numbers of days having ozone concentration increases greater than 30 ppb/hr or 40 ppb/hr. The Baker, Capitol, LSU, Bayou Plaquemine, and Carville sites had relatively uniform and midrange numbers of days with sudden ozone concentration increases compared with Port Allen and the outlying sites at French Settlement, Grosse Tete, and Pride.



**Figure 3-15. Number of Days Having Ozone Concentration Increases Greater than 30 ppb/hr and 40 ppb/hr at Individual Monitoring Sites**

### 3.4 Relationship of Sudden Ozone Concentration Increases to NO<sub>x</sub>, VOC, and Meteorological Variables

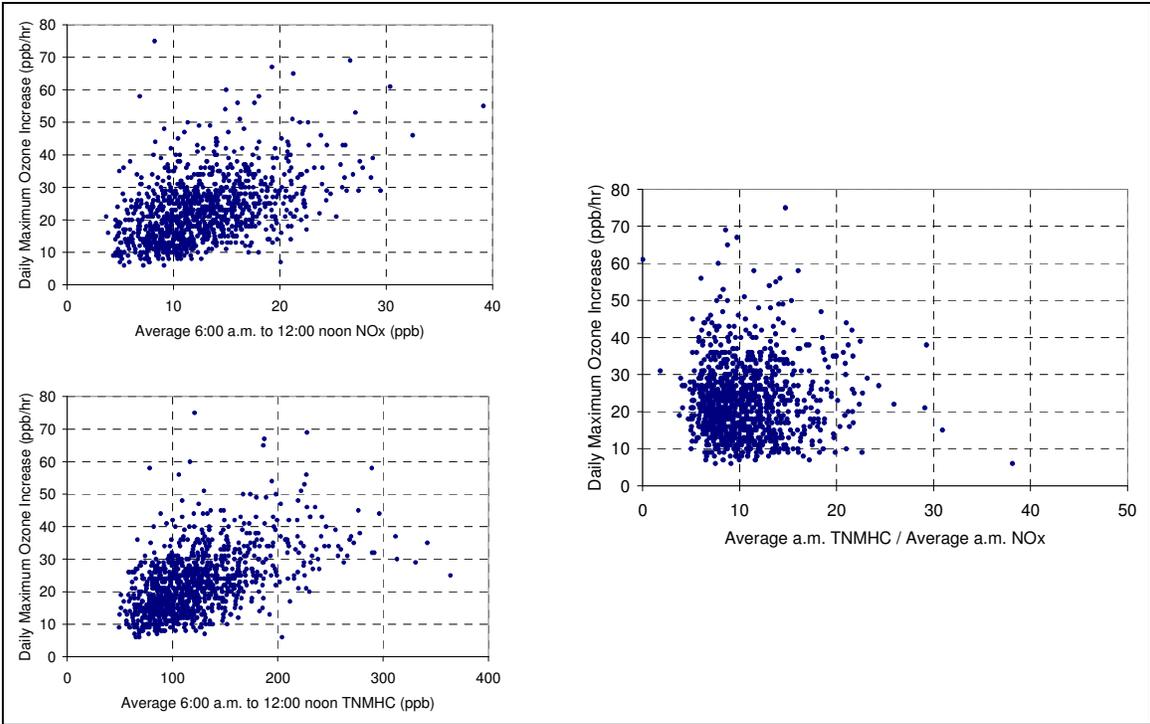
The maximum ozone concentration increase on any given day appears to be more strongly related to the average wind speed in the morning than to any other meteorological variable. See, for example, the upper left hand graph in Figure 3-16, which relates the daily maximum ozone concentration increase observed in Baton Rouge on ozone season days during 1997-2004 to the corresponding 12:00 a.m.-12:00 pm. average wind speed observed on the same day. The 12:00 a.m.-12:00 pm. average wind speed for each morning was calculated by first estimating the average wind speed for each LDEQ Baton Rouge monitoring site and then taking the median of all the sites. Note that nearly all days having morning average wind speeds less than 2 mph had daily maximum ozone concentration increases greater than 40 ppb/hr.



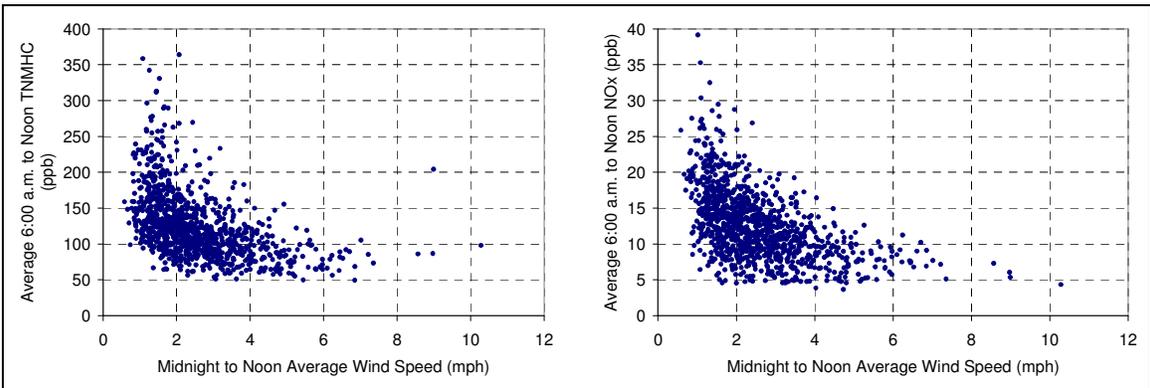
**Figure 3-16. Scatter Plots Showing the Apparent Relationships Between the Daily Maximum Ozone Concentration Increase in Baton Rouge to Meteorological Variables for Ozone Season Days During 1997 to 2004**

The daily maximum ozone concentration increase also appears to be related somewhat to the daily maximum temperature, daily temperature range, and the 6:00 a.m.-12:00 p.m. average solar radiation observed on the same day; however, the relationships to these variables do not appear to be strong.

The daily maximum ozone concentration increase appears to be related to both 6:00 a.m.-12:00 p.m. average  $\text{NO}_x$  levels and TNMHC levels but not the average TNMHC to average  $\text{NO}_x$  ratio. These patterns are shown in Figure 3-17. Note, in particular, that ozone concentration increases greater than 30 ppb/hr occurred on almost all days when the morning average TNMHC level exceeded 200 ppb. The morning TNMHC and  $\text{NO}_x$  levels tend to be highest on days with low wind speeds, similar to the apparent relationship between the daily maximum ozone concentration and wind speed (Figure 3-18).



**Figure 3-17. Scatter Plots Showing the Apparent Relationships Between the Daily Maximum Ozone Concentration Increase in Baton Rouge to the Average Morning NO<sub>x</sub> (Upper Left) and TNMHC Levels (Lower Left), and TNMHC/NO<sub>x</sub> Ratio (Right), for Ozone Season Days During 1997 to 2004**



**Figure 3-18. Scatter Plots Showing the Apparent Relationship Between the Morning Wind Speed and the Average Morning TNMHC (Left) and NO<sub>x</sub> Levels (Right) for Ozone Season Days During 1997 to 2004**

A classification and regression tree (CART) analysis was performed to further define the relationships and relative importance of meteorological and chemical variables to the rate of ozone increase at a monitoring site. CART is a multivariate statistical technique that partitions data into similar groups of numerical or categorical variables based on the answers to simple yes/no questions (e.g., was the wind speed less than 2 miles per hour). The CART output is a decision tree that terminates in a series of nodes, each having certain distinguishing characteristics in terms of the independent variables (e.g., average wind speed, daily maximum temperature, etc.).

The CART analysis was performed with the 1997 – 2004 ozone season data using the region wide daily maximum ozone concentration increase as the dependent variable and the following parameters as the independent variables (upper air data were from the National Weather Service radiosonde station in Lake Charles):

- 12:00 a.m.-12:00 p.m. average wind speed (median of all sites);
- Daily maximum temperature (median of all sites);
- Daily temperature range (median of all sites);
- Maximum 6:00 a.m.-12:00 p.m. 1-hour NO<sub>x</sub> level (highest of all sites);
- Maximum 6:00 a.m.-12:00 p.m. 1-hour TNMHC level (highest of all sites);
- 6:00 a.m.-12:00 p.m. total solar radiation (median of all sites);
- 850 millibar wind direction (6:00 a.m.);
- 850 millibar wind speed (6:00 a.m.);
- Surface – 850 millibar temperature difference (6:00 a.m.);
- 700 millibar height (6:00 a.m.); and
- 500 millibar height (6:00 a.m.).

The terminal node having the greatest ozone concentration increases, on average, was characterized by having 12:00 a.m.-12:00 p.m. average wind speeds less than 2.05 miles per hour, daily temperature ranges of greater than 11.85 °C, and an hourly maximum TNMHC level during 6:00 a.m.-12:00 p.m. of at least 506 ppb. CART ranked the top four independent variables in the following order of importance:

1. 6:00 a.m.-12:00 p.m. maximum hourly TNMHC level;
2. 12:00 a.m.-12:00 p.m. average wind speed;
3. 6:00 a.m.-12:00 p.m. maximum hourly NO<sub>x</sub> level; and
4. Daily temperature range.

### 3.5 Summary of Sudden Ozone Concentration Increases

Ozone concentration increases of greater than 30 ppb/hr and 40 ppb/hr were observed at one or more of the LDEQ Baton Rouge monitoring sites on about 18% and 5% of the ozone season days during 1997 to 2004, respectively. In some cases these rapid ozone concentration increases were followed by sudden decreases; however, in most cases they were followed by a continued rise, leveling off, or gradual decrease in ozone concentrations. The TCEQ has defined these events as *sudden ozone concentration increases* when the hour to hour ozone increase exceeds 40 ppb/hr.

Ozone concentration increases of greater than 40 ppb/hr were observed on about 50% of the days when ozone exceeded the level of the 1-hour standard during 1997 – 2004; although, not always at the same site where the exceedance was measured. Ozone concentration increases of greater than 30 ppb/hr were observed on almost every 1-hour exceedance day; although, not always at the same site where the exceedance was measured. The 1-hour ozone standard was not exceeded on most of the days that ozone levels increased by greater than 40 ppb/hr or greater than 30 ppb/hr.

Ozone concentration increases of greater than 40 ppb/hr were observed on about 25% of the days when ozone exceeded the level of the 8-hour standard during 1997 – 2004; although, not always at the same site where the exceedance was measured. Ozone concentration increases of greater than 30 ppb/hr were observed on 60% of the 8-hour exceedance days; although, not always at the same site where the exceedance was measured. The 8-hour ozone standard was not exceeded on most of the days that ozone levels increased by greater than 40 ppb/hr or greater than 30 ppb/hr.

Ozone concentration increases of greater than 40 ppb/hr almost always occurred between 7:00 a.m. and 1:00 p.m., and most often between 8:00 a.m. and 10:00 a.m. These are approximately the times of day when ozone levels rose most rapidly on average due to typical photochemistry and atmospheric dynamics. Ozone concentration increases of greater than 30 ppb/hr occurred at least once during nearly every hour of the day in Baton Rouge during 1997 to 2004 but they occurred most often between 7:00 a.m. and 11:00 a.m.

A weekly pattern appears to exist in the frequency of ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr. These events were observed most often on Fridays and Saturdays, and least often on Tuesdays. This pattern does not appear to be related to the weekly pattern in average NO<sub>x</sub> levels, which were lowest on Saturdays and Sundays.

The greatest frequency of ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr were observed during July through October, with a secondary maximum during April through June. This pattern mirrors the annual pattern in exceedances of the 1-hour and 8-hour ozone standards. The late summer to early fall peak in the frequency of sudden ozone concentration increases extends beyond the tradition Baton Rouge ozone season.

Ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr were observed on at least 20 days and 5 days per year, respectively, since 1997. On average the numbers of these events per year were less in 2001-2004 than during 1997-2000, suggesting a downward trend.

Ozone concentration increases greater than 30 ppb/hr and 40 ppb/hr were observed more often at Port Allen than at any other LDEQ Baton Rouge monitoring site. The fewest numbers of these events were observed at the outlying sites at Grosse Tete, Pride, French Settlement, and Dutchtown. The frequency of occurrence at the Bayou Plaquemine, LSU, Baker, Capitol, and Carville monitoring sites was relatively uniform and mid range compared with the other sites.

Daily maximum ozone concentration increases were greatest on days having low wind speeds; although, not all low wind speed days, even during the ozone season, had comparatively large hour to hour ozone concentration increases. Daily maximum ozone concentration increases did not appear to be as strongly correlated with daily maximum temperatures; however, nearly all days when ozone concentration increases exceeded 40 ppb/hr had daily maximum temperatures above 30 degrees C (86 degrees F).

Daily maximum ozone concentration increases were usually greater on days having comparatively higher 6:00 a.m.-12:00 p.m. average TNMHC and NO<sub>x</sub> levels but they did not appear to be correlated with the ratio of the average TNMHC to average NO<sub>x</sub>.

## 4.0 VOC Levels and Reactivity

LDEQ measures the levels of 56 common ozone precursor VOC in air samples that are periodically collected at 10 Baton Rouge area sampling sites. This section presents the spatial and temporal patterns in VOC levels and reactivity and their apparent relationships to sudden ozone concentration increases.

Throughout this section, VOC reactivity is expressed in terms of the *maximum incremental reactivity* (MIR). The MIR is a relative measure of the maximum incremental ozone formation potential resulting from VOC added to an ambient air mixture (Carter, 1994). Site to site comparisons of VOC reactivity are made by multiplying the measured VOC concentrations from each site by compound-specific MIR constants, creating, in effect, a reactivity-weighted concentration.

### 4.1 Geographic Distribution of VOC Levels and Reactivity

The average levels of total nonmethane organic carbon (TNMOC) measured in 24-hour samples were greatest for sampling sites near the Mississippi River in north and central Baton Rouge, and least for the outlying sampling sites (Table 4-1). This was also true for the total MIR (Table 4-1 and Figure 4-1). The MIR values in Table 4-1 and Figure 4-1 were calculated first for each individual VOC species that was monitored by LDEQ, using the compound-specific MIR constants derived by Carter (2003)<sup>2</sup>, summed for all the compounds detected in each sample, and averaged across all the 24-hour samples collected at a given sampling site.

Table 4-2 gives the median levels of the speciated VOC at each sampling site in parts per billion-carbon (ppb-c). These estimates were derived from all the 24-hour samples collected at each site. The compounds are sorted in descending order of average concentration. The geographic variations for most of the individual VOC mirror the patterns presented in Table 4-1 and Figure 4-1. For example, the median ethylene levels were highest at Port Allen and South Scotlandville, and lowest at Pride and Bayou Plaquemine. The same was true for propylene, another HRVOC. Other compounds, such as propane, n-butane, and isopentane (which are not generally considered to be HRVOC) had similar geographic patterns. Geographic variations in VOC levels are discussed in greater detail below, in terms of VOC reactivity.

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<sup>2</sup> [VOC Reactivity Data \(Excel format\) as of February 5, 2003 \(r02tab.xls\).](http://pah.cert.ucr.edu/~carter/reactdat.htm#update02)  
<http://pah.cert.ucr.edu/~carter/reactdat.htm#update02>

**Table 4-1. Average Levels of TNMOC and MIR for 24-Hour Canister Samples**

Site	TNMOC (ppb-C)		MIR		Period of Record
	Mean	Median	Mean	Median	
Port Allen	517	339	228	171	September '03 - October '04
South Scotlandville	264	220	205	164	May '99 - October '04
Southern	273	175	195	131	May '99 - October '04
LSU	218	195	119	116	August '03 - October '04
Capitol	224	193	145	120	January '98 - October '04
Baker	171	150	117	82	July '02 - October '04
Carville	125	116	74	68	May '04 - October '04
Dutchtown	117	103	80	73	January '99 - October '04
Bayou Plaquemine	114	101	72	63	January '98 - October '04
Pride	91	70	74	68	January '98 - October '04

Averaged across all the LDEQ Baton Rouge VOC sampling sites, ethylene, propylene, and isoprene contributed more to the total MIR than any other measured compounds (Figure 4-2). Together, these chemicals, on average, comprised nearly 40% of the total MIR (Figure 4-3). In general, the relative contributions to the total MIR for each compound or groups of compounds did not change much from site to site (Figure 4-4); however, a few differences are noteworthy.

In particular, isoprene had the largest geographical differences in terms of relative contribution to the average total MIR. It contributed 3% to the average total MIR at South Scotlandville and 30% at Pride (surprisingly, isoprene contributed 15% to the average total MIR at the Port Allen monitoring site). Additionally, butanes and pentanes combined for 23% of the total MIR, on average, at the Southern site but only 9% at Pride. Note that the butanes and pentanes average contribution to the total MIR at the Southern site was as great as the combined average contributions of ethylene and propylene. The average total contribution of all HRVOC (i.e., ethylene; propylene; toluene; xylenes; butanes; and 1,3-butadiene) ranged from 35% to 53% of the total MIR (Figure 4-5).

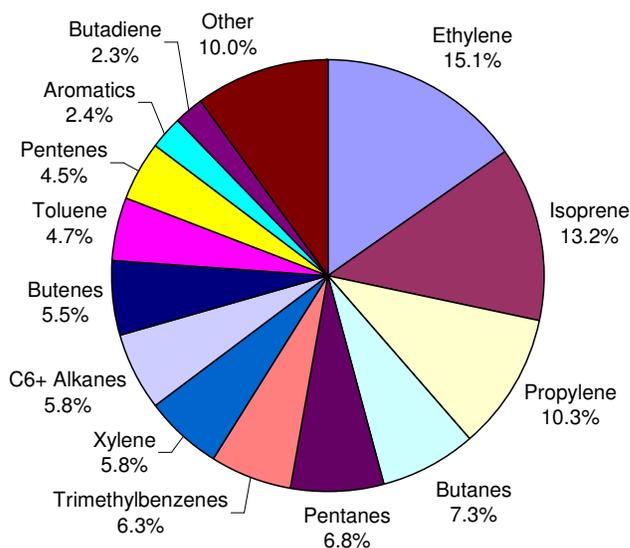


**Table 4-2. Median Levels of Speciated VOC at LDEQ Baton Rouge Area Monitoring Sites**

Compound Name	Median Concentration (ppb-c)								
	Baker	Bayou Plaquemine	Capitol	Carville	Dutchtown	LSU	Port Allen	Pride	South Scotlandville
Ethane	10.86	11.78	13.93	13.26	10.26	11.89	13.11	6.79	15.14
Propane	11.22	10.30	11.94	8.26	8.94	10.31	17.38	5.55	15.41
n-Butane	6.85	5.31	10.96	4.80	5.22	8.35	19.44	3.24	16.84
Isopentane	5.93	4.31	10.89	4.88	4.93	9.05	16.61	2.66	15.86
Isobutane	5.69	4.56	7.10	4.08	3.37	5.42	9.71	2.08	9.20
Ethylene	3.95	3.30	5.69	4.22	3.84	5.73	7.47	2.20	8.89
n-Pentane	3.97	2.53	5.45	2.88	2.71	4.74	11.34	1.51	7.47
Toluene	2.93	2.05	5.80	3.15	3.24	5.13	5.58	1.55	6.83
Isoprene	2.96	3.81	2.68	2.65	2.00	3.40	4.78	5.30	1.97
Propylene	1.51	1.07	3.29	1.93	1.99	2.98	5.27	0.81	4.81
Benzene	1.88	1.89	3.12	2.43	2.36	2.83	4.03	1.53	3.60
2-Methylpentane	1.57	1.18	2.94	1.37	1.40	2.41	4.17	0.74	4.24
n-Hexane	1.30	1.30	3.33	1.40	1.35	1.83	3.27	0.67	3.47
Acetylene	1.90	1.39	2.60	1.03	1.66	2.44	2.18	1.21	2.92
3-Methylpentane	1.35	0.97	2.50	1.32	1.13	1.93	3.82	0.60	3.20
m/p Xylene	1.32	0.99	2.84	0.90	1.43	2.54	2.15	0.68	2.99
2,2,4-Trimethylpentane	0.97	0.70	2.25	0.60	0.80	1.71	2.20	0.50	3.00
Methylcyclopentane	0.71	0.64	1.70	0.82	0.78	1.30	1.71	0.33	2.38
1,2,4-Trimethylbenzene	0.68	0.46	1.37	0.49	0.64	1.08	0.98	0.47	1.77
o Xylene	0.64	0.45	1.24	0.40	0.62	1.01	0.99	0.36	1.48
3-Methylhexane	0.52	0.40	1.00	0.34	0.50	0.86	1.03	0.30	1.19
2,3-Dimethylbutane	0.44	0.38	0.93	0.37	0.42	0.78	1.20	0.22	1.30
1-Butene	0.62	0.43	1.00	0.21	0.57	0.73	0.95	0.40	1.10
Ethylbenzene	0.51	0.39	0.93	0.48	0.53	0.91	0.74	0.28	1.02
n-Heptane	0.47	0.40	0.98	0.43	0.44	0.84	1.06	0.24	0.93
2-Methylhexane	0.41	0.33	0.87	0.38	0.40	0.72	0.95	0.20	1.10
trans-2-Pentene	0.63	0.00	0.82	0.28	0.20	0.61	1.07	0.00	1.36
m-Ethyltoluene	0.45	0.27	0.90	0.27	0.40	0.81	0.58	0.28	0.99
Methylcyclohexane	0.38	0.43	0.73	0.45	0.39	0.66	0.92	0.18	0.74
1-Pentene	0.43	0.25	0.74	0.18	0.32	0.51	0.94	0.23	0.87
2,3,4-Trimethylpentane	0.32	0.21	0.80	0.20	0.29	0.64	0.73	0.04	1.09
1-Hexene	0.71	0.19	0.63	0.28	0.41	0.60	0.75	0.18	0.66
Styrene	0.33	0.30	0.51	0.30	0.42	0.44	0.82	0.36	0.77
Cyclohexane	0.35	0.40	0.70	0.37	0.30	0.51	0.74	0.15	0.64
n-Octane	0.27	0.24	0.61	0.23	0.26	0.47	0.60	0.20	0.57
2,2-Dimethylbutane	0.31	0.23	0.44	0.22	0.27	0.36	0.63	0.00	0.75
1,3-butadiene	0.29	0.12	0.48	0.16	0.30	0.39	0.65	0.00	0.90
Cyclopentane	0.29	0.19	0.40	0.21	0.21	0.39	0.65	0.00	0.70
2,3-Dimethylpentane	0.24	0.20	0.51	0.23	0.22	0.42	0.57	0.00	0.63
cis-2-Pentene	0.22	0.00	0.43	0.16	0.15	0.33	0.63	0.00	0.79
2,4-Dimethylpentane	0.19	0.00	0.49	0.15	0.20	0.36	0.56	0.00	0.70
o-Ethyltoluene	0.17	0.26	0.40	0.14	0.20	0.39	0.34	0.22	0.40
1,2,3-Trimethylbenzene	0.00	0.18	0.58	0.14	0.22	0.33	0.31	0.29	0.41

**Table 4-2. (Continued)**

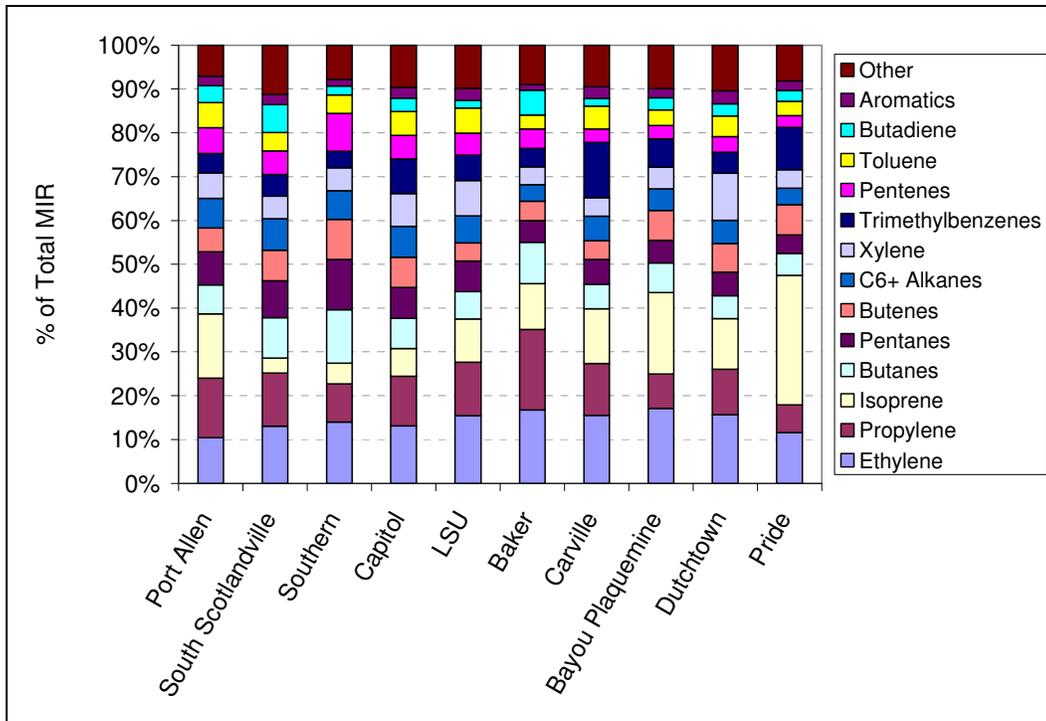
Compound Name	Median Concentration (ppb-c)								
	Baker	Bayou Plaquemine	Capitol	Carville	Dutchtown	LSU	Port Allen	Pride	South Scotlandville
n-Nonane	0.21	0.00	0.46	0.16	0.18	0.40	0.45	0.00	0.45
trans-2-Butene	0.16	0.00	0.35	0.09	0.10	0.18	0.59	0.00	0.67
n-Undecane	0.13	0.13	0.47	0.21	0.20	0.42	0.30	0.00	0.38
n-Decane	0.08	0.00	0.50	0.13	0.16	0.48	0.36	0.00	0.45
cis-2-Butene	0.17	0.00	0.38	0.04	0.00	0.19	0.52	0.00	0.64
2-Methylheptane	0.15	0.00	0.39	0.14	0.12	0.29	0.41	0.00	0.40
p-Ethyltoluene	0.17	0.00	0.40	0.11	0.10	0.34	0.34	0.00	0.42
3-Methylheptane	0.12	0.00	0.39	0.13	0.10	0.30	0.38	0.00	0.40
1,3,5-Trimethylbenzene	0.04	0.00	0.40	0.10	0.16	0.37	0.28	0.00	0.44
p-Diethylbenzene	0.00	0.00	0.30	0.10	0.00	0.27	0.17	0.00	0.28
n-Propylbenzene	0.00	0.00	0.27	0.00	0.00	0.26	0.22	0.00	0.30
m-Diethylbenzene	0.00	0.00	0.22	0.12	0.00	0.22	0.26	0.00	0.20
Cumene	0.00	0.00	0.20	0.00	0.00	0.15	0.24	0.00	0.00



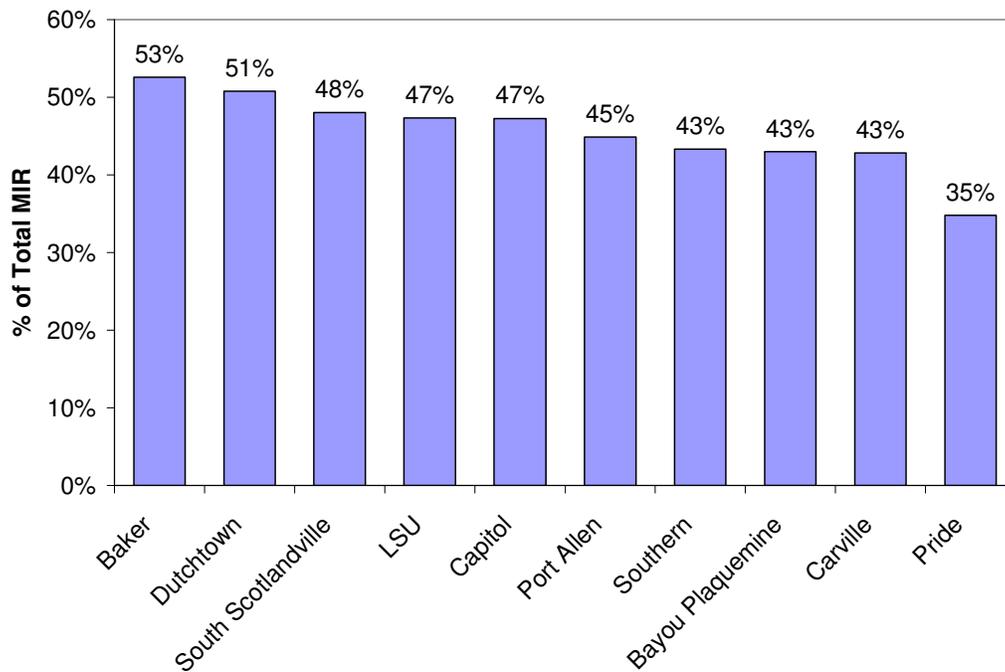
**Figure 4-3. Average Percentage Contributions to the Total MIR by Chemical Group (See Table 4-3 for Explanation of Chemical Groups)**

**Table 4-3. Definition of Chemical Groups for Reactivity Assessment**

<b>Chemical Group</b>	<b>Compound Name</b>
Alkanes (C6+)	2,2-Dimethylbutane; 2,3,4-Trimethylpentane; 2,3-Dimethylbutane; 2,3-Dimethylpentane; 2,4-Dimethylpentane; 2-Methylheptane; 2-Methylhexane; 2-Methylpentane; 3-Methylheptane; 3-Methylhexane; 3-Methylpentane; n-Decane; n-Heptane; n-Hexane; n-Nonane; n-Octane; n-Undecane
Aromatics	Benzene; Cumene; Ethylbenzene; m-Diethylbenzene; n-Propylbenzene; p-diethylbenzene; Styrene
Butadiene	1,3-butadiene
Butanes	Isobutane; n-Butane
Butenes	1-Butene; cis-2-Butene; trans-2-Butene
Ethylene	Ethylene
Isoprene	Isoprene
Pentanes	Isopentane; n-Pentane
Pentenes	1-Pentene; cis-2-Pentene; trans-2-Pentene
Propylene	Propylene
Toluene	Toluene
Trimethylbenzenes	1,2,3-Trimethylbenzene; 1,2,4-Trimethylbenzene; 1,3,5-Trimethylbenzene
Xylenes	m/p-Xylene; o-Xylene
Other	1-Hexene; Acetylene; Cyclohexane; Cyclopentane; Ethane; Methylcyclohexane; Methylcyclopentane; m-Ethyltoluene; o-Ethyltoluene; p-Ethyltoluene; Propane



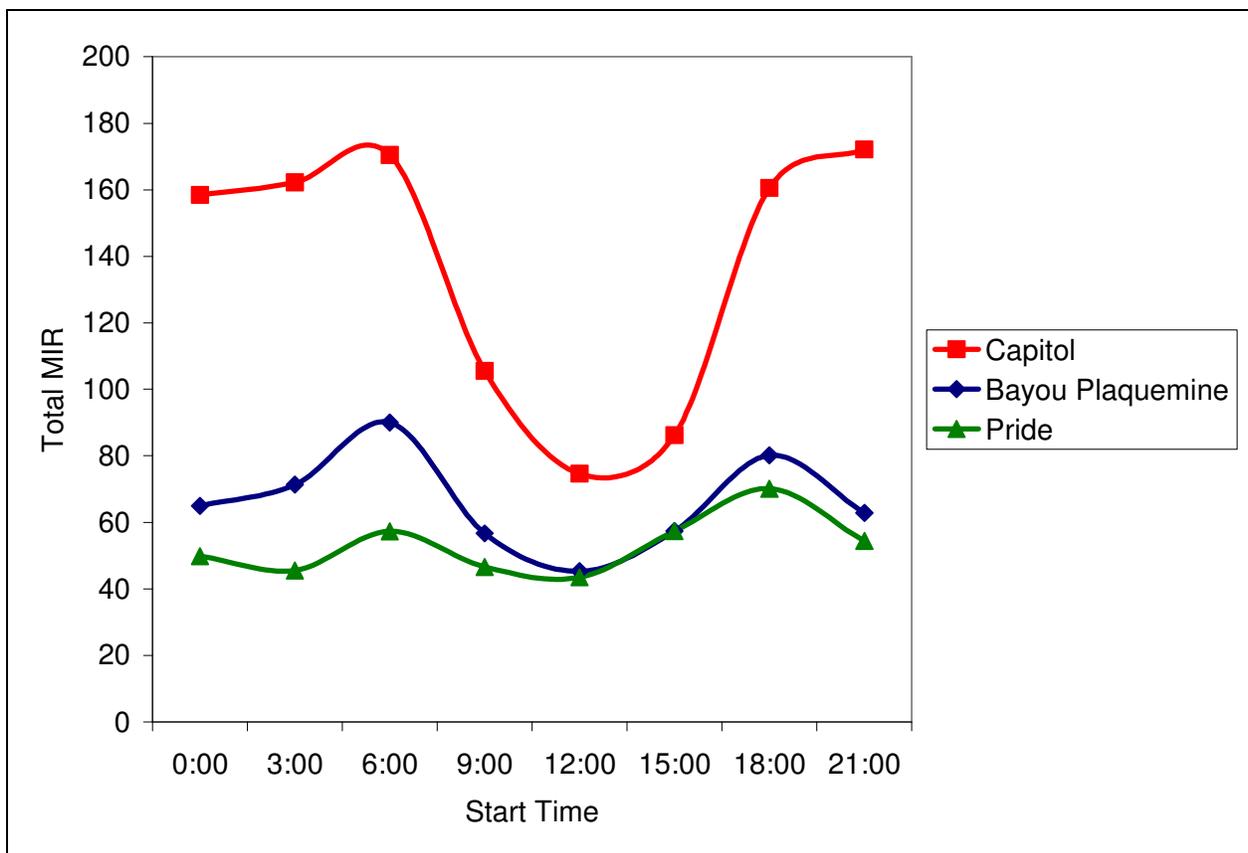
**Figure 4-4. Average Percentage Contributions to the Total MIR by Chemical Group**



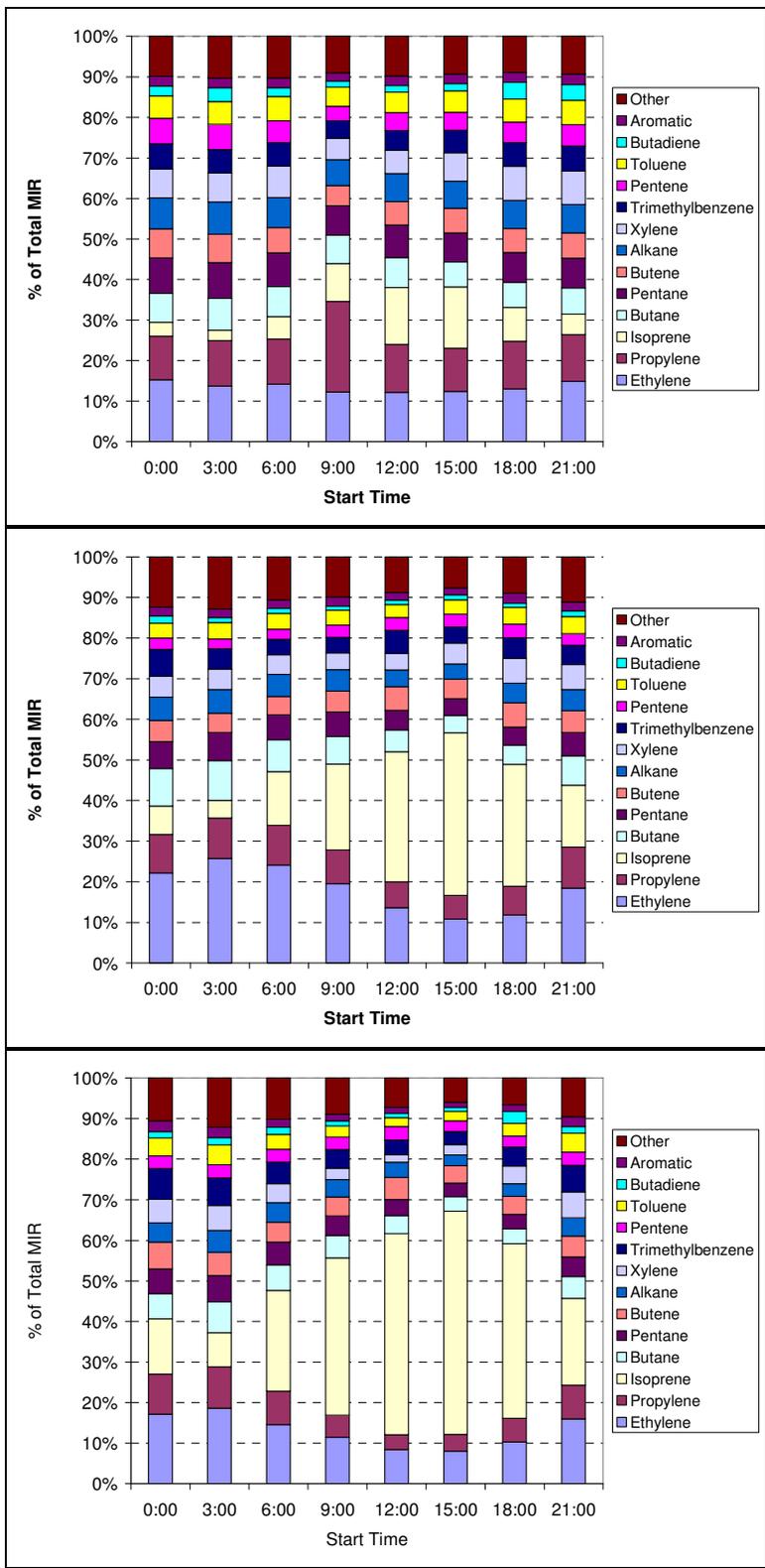
**Figure 4-5. Average Percentage Contributions to the Total MIR by all HRVOC (i.e., Ethylene; Propylene; Toluene; Xylenes; Butenes; and 1,3-Butadiene)**

#### 4.6 Temporal Trends in VOC Reactivity

Diurnal patterns in VOC reactivity were evident for all the sampling sites having long-term 3-hour data (i.e., Bayou Plaquemine, Capitol, and Pride). At all the sites, VOC reactivity tended to be lower during midday and higher during the early evening, nighttime, and early morning (Figure 4-6). This pattern was most pronounced at the Capitol site and least pronounced at Pride, where VOC levels were generally lower and biogenic isoprene made up a greater percentage of the total MIR. See Figure 4-7, for example, which shows that isoprene accounted for about 50% of the afternoon MIR at the Pride monitor but less than 20% of the afternoon MIR at the Capitol site.

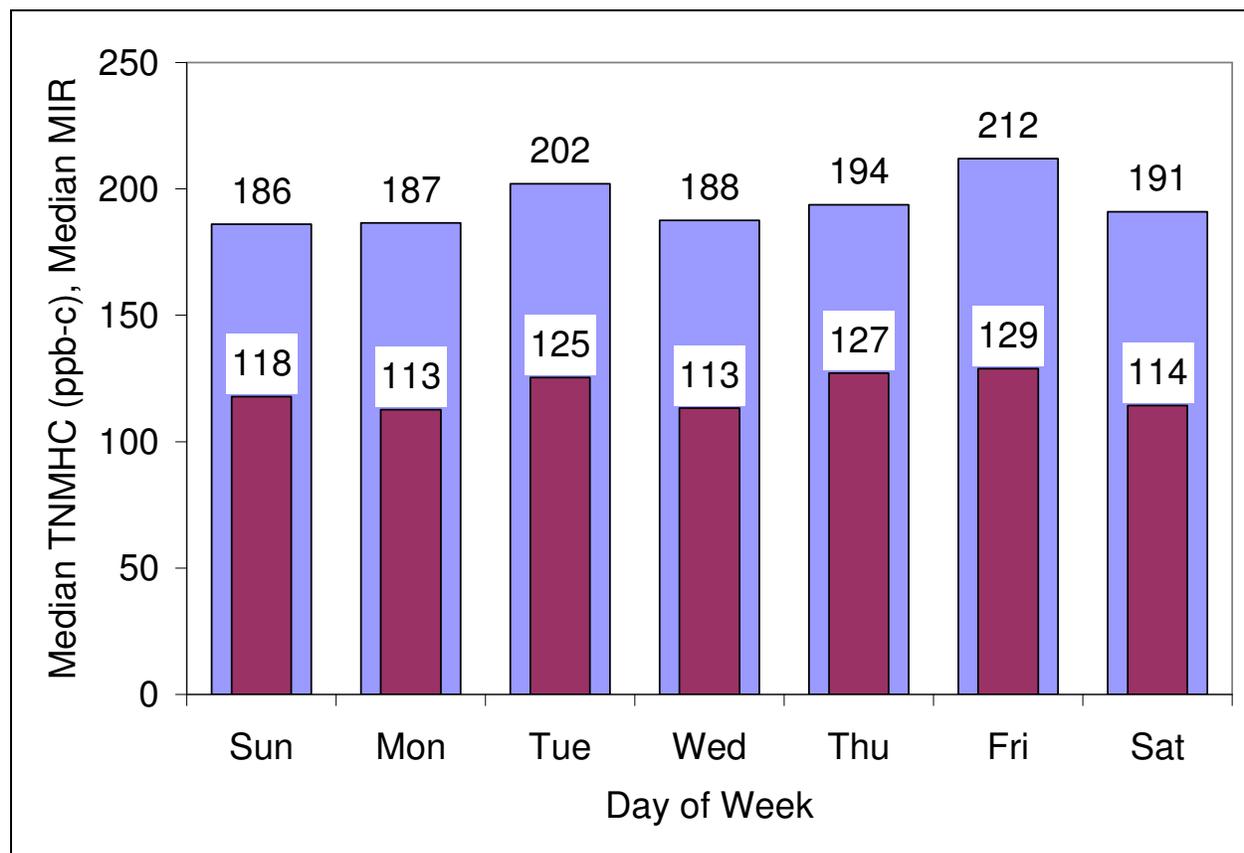


**Figure 4-6. Average Diurnal Variation of Total MIR at the Capitol, Bayou Plaquemine, and Pride Monitoring Sites**



**Figure 4-7. Average Diurnal Variation in MIR for Various Chemical Groups at the Capitol (Top), Bayou Plaquemine (Center), and Pride (Bottom) Sampling Sites, as a Percentage of the Total**

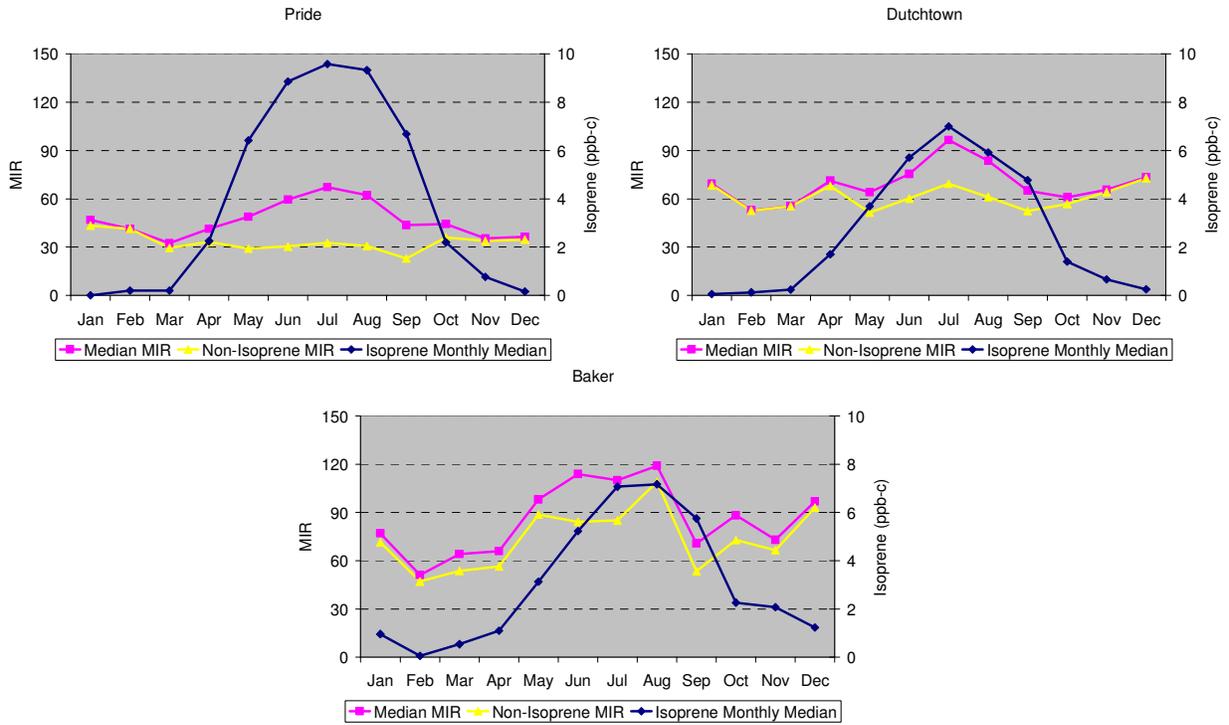
No significant or systematic weekly pattern appears to exist in either the median TNMHC levels or median total MIR at the Capitol monitoring site (Figure 4-8). The Capitol monitoring site, located in central Baton Rouge, is more likely to be influenced by mobile sources of VOC and therefore more likely to exhibit a weekly pattern in VOC levels or reactivity, if one existed.



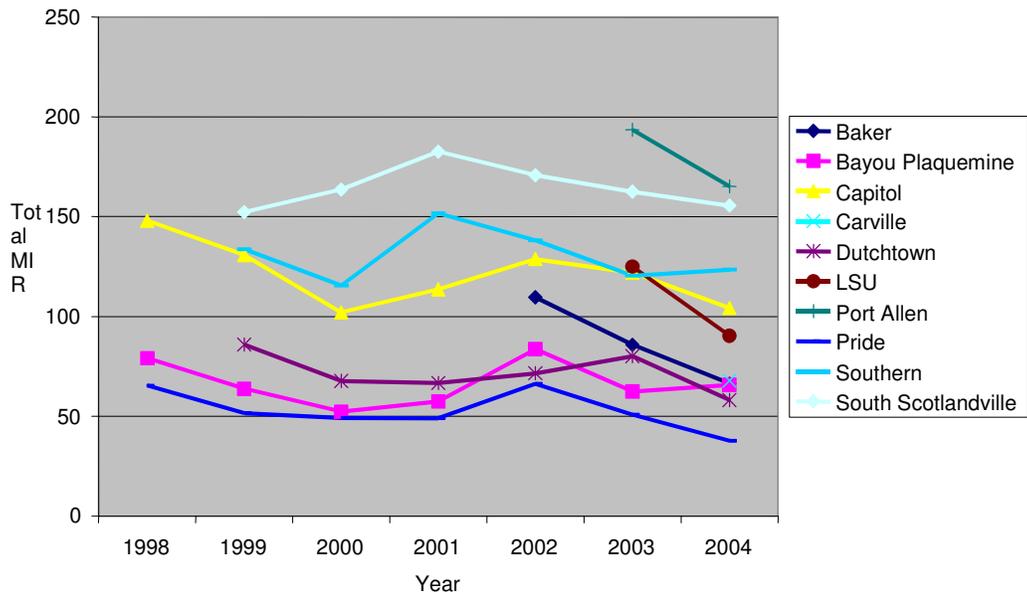
**Figure 4-8. Median TNMHC and MIR Values by Day of the Week at the Capitol Monitoring Site**

The Baker, Dutchtown, and Pride monitoring sites were the only locations where an annual pattern in VOC reactivity appeared to exist. The median MIR values at those sites tended to be higher during summer (June –August) and lower the rest of the year. This pattern appears to be caused by a summertime peak in biogenic isoprene levels at the Pride and Dutchtown monitoring sites but not at Baker (Figure 4-9).

The annual median MIR decreased from 2002 to 2004 at most Baton Rouge sampling sites; although, no significant long-term trends are apparent (Figure 4-10).

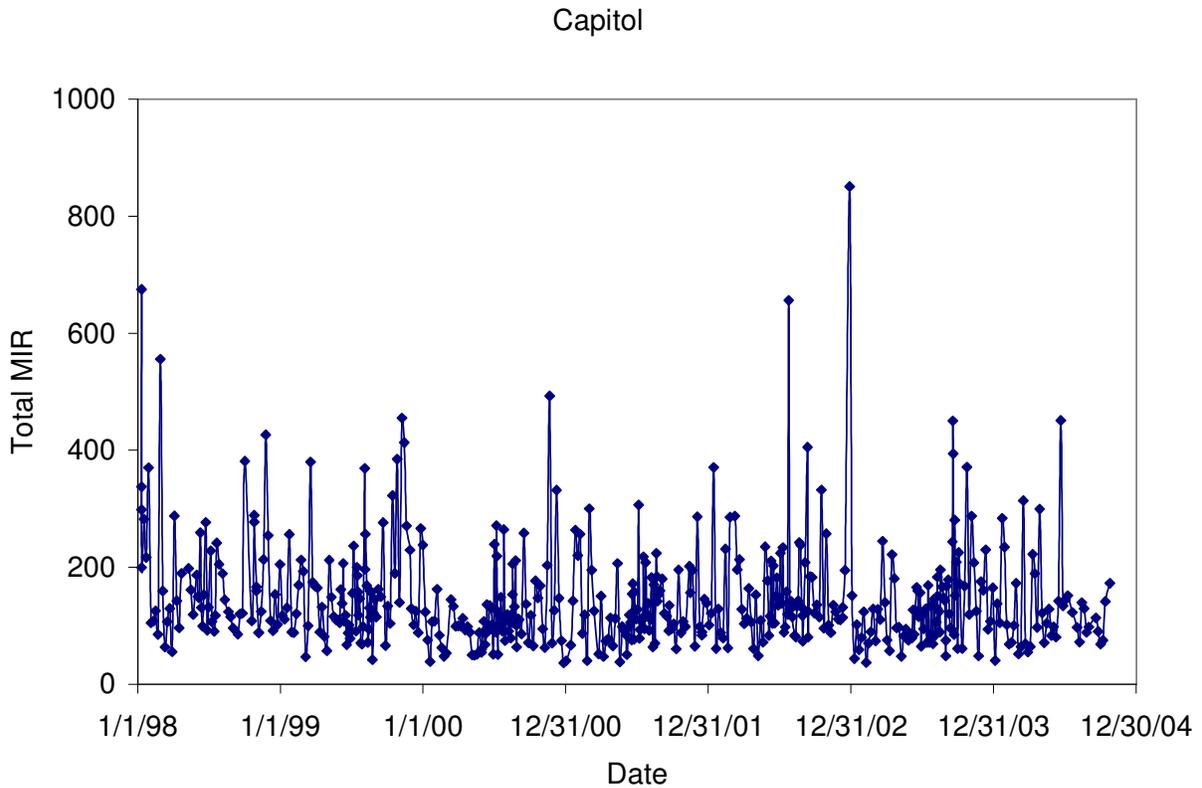


**Figure 4-9. Median Monthly MIR, Isoprene Levels, and Non-Isoprene MIR at the Pride, Dutchtown, and Baker Monitoring Sites**



**Figure 4-10. Median Annual MIR at Baton Rouge Monitoring Sites During 1998 – 2004**

Day to day variations in MIR appear to be greater than any diurnal, weekly or annual cycle, or long-term trend. See Figure 4-11, for example, which shows the time series of 24-hour MIR values derived from 24-hour canister samples collected at the Capitol site from January 1998 through October 2004. Day to day variations are most likely due to random variations in emissions or the weather conditions that transport and disperse emissions rather than any predictable or repetitive pattern.



**Figure 4-11. Day-to-Day Variations in MIR Estimated from 24-Hour Canister Samples Collected at the Baton Rouge Capitol Site January 1998 through October 2004**

### 4.3 Relationships of Speciated VOC Levels and Reactivity to Sudden Ozone Concentration Increases

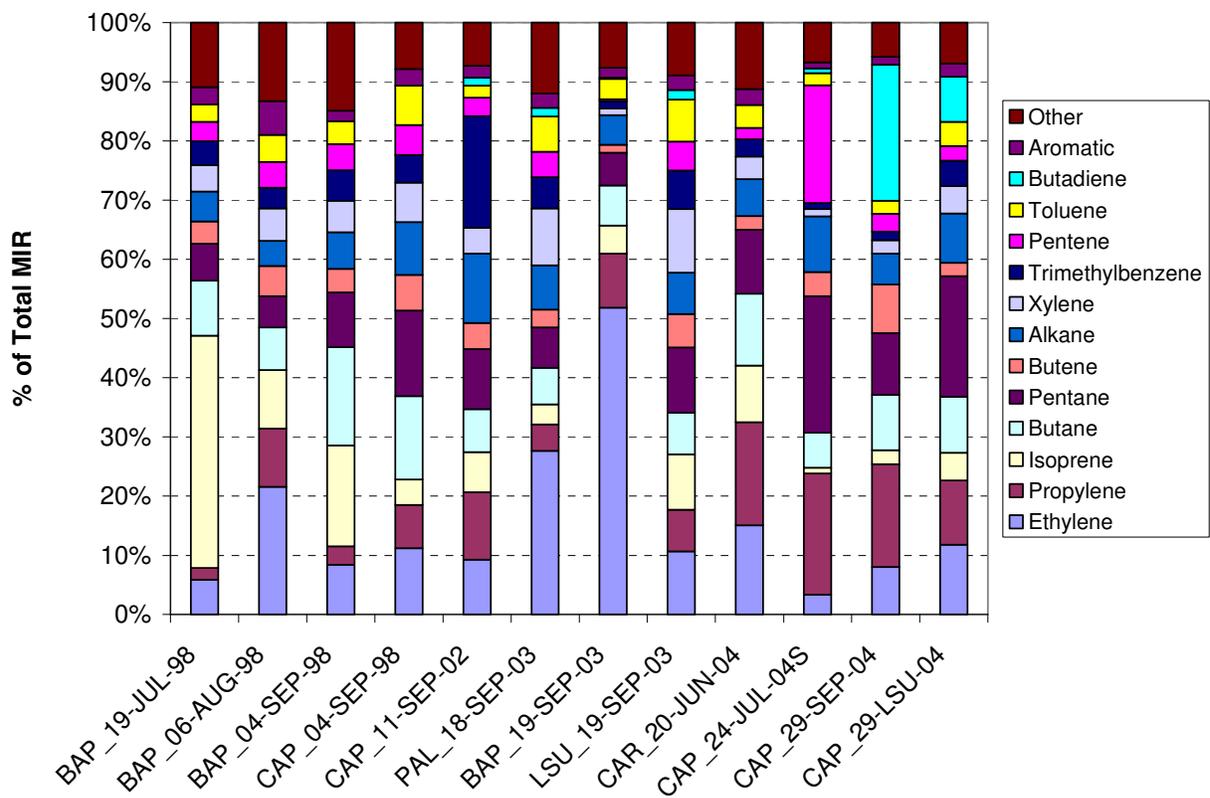
Thirteen times when ozone levels increased by greater than 40 ppb/hr at an LDEQ Baton Rouge monitoring site during 1998-2004 a canister sample for VOC analysis was also collected at the same site and time. Nine of these times the canister was a 3-hour sample that overlapped the time of the sudden ozone concentration increase; three times the canister was a 24-hour sample; and once the canister was a 25-minute sample that was triggered by high levels of TNMHC. Table 4-4 gives the locations, dates, sample start times, TNMOC level, and total MIR for each of these 13 samples. The median MIR, based on all the 24-hour and 3-hour samples collected at the same site and start time as each sample listed in Table 4-4 is also provided. Note that for ten of the samples listed in Table 4-4, the MIR was substantially greater (by factors ranging from 1.5 to 13) than the corresponding median. In three cases, specifically the Bayou Plaquemine samples collected in 1998, the MIR of the samples that overlapped the sudden ozone concentration increase was not significantly different from median.

**Table 4-4. TNMOC and MIR for VOC Samples Collected During Sudden Ozone Concentration Increases (greater than 40 ppb/hr)**

Date	Site	Sample Start Time	Duration (Hours)	Total NMOC (ppb-c)	Total MIR for Sample	Median MIR for Site and Time of Day
7/19/98	Bayou Plaquemine	6:00 a.m.	3	157	104	90
8/6/98	Bayou Plaquemine	9:00 a.m.	3	108	66	56
9/4/1998	Bayou Plaquemine	6:00 a.m.	3	185	98	90
9/4/1998	Capitol	9:00 a.m.	3	922	577	106
9/11/02	Bayou Plaquemine	Midnight	24	954	405	120
9/18/03	Port Allen	Midnight	24	577	349	171
9/19/03	Bayou Plaquemine	9:00 a.m.	3	291	234	106
9/19/03	LSU	Midnight	24	480	267	116
6/20/04	Carville	9:00 a.m.	3	218	122	68
7/24/04	Capitol	7:00 a.m.	0.42	3212	2248	170
7/24/04	Capitol	6:00 a.m.	3	1574	864	170
9/29/04	Capitol	9:00 a.m.	3	842	644	106
9/29/04	LSU	9:00 a.m.	3	338	203	116

For the samples listed in Table 4-4 that had greater than average MIR, no single chemical or chemical group accounted for the increased reactivity in every case (Figure 4-12). For example, samples collected at Port Allen and Bayou Plaquemine in September 2003 (PA\_18-SEP-03 and BAP\_18-SEP-03, respectively) had relatively high percentages of the total MIR due to ethylene while the Capitol sample from 24-July-2004 (CAP\_24-JUL-04S) had relatively high percentages of total reactivity from pentanes and pentenes. The Capitol sample from 29-September-2004 (CAP\_29-JUL-04) had a comparatively high percentage of the total reactivity due to 1,3-butadiene.

HRVOC (i.e., ethylene, propylene, butane, butadiene, toluene, and xylene) accounted for 19% to 67% of the total MIR of samples collected during sudden ozone concentration increases, varying from sample to sample. On average, about 40% of the MIR of these samples was from HRVOC. This is a slightly smaller percentage than the average based on all the 24-hour samples collected during January 1998 through October 2004 (Figure 4-5).



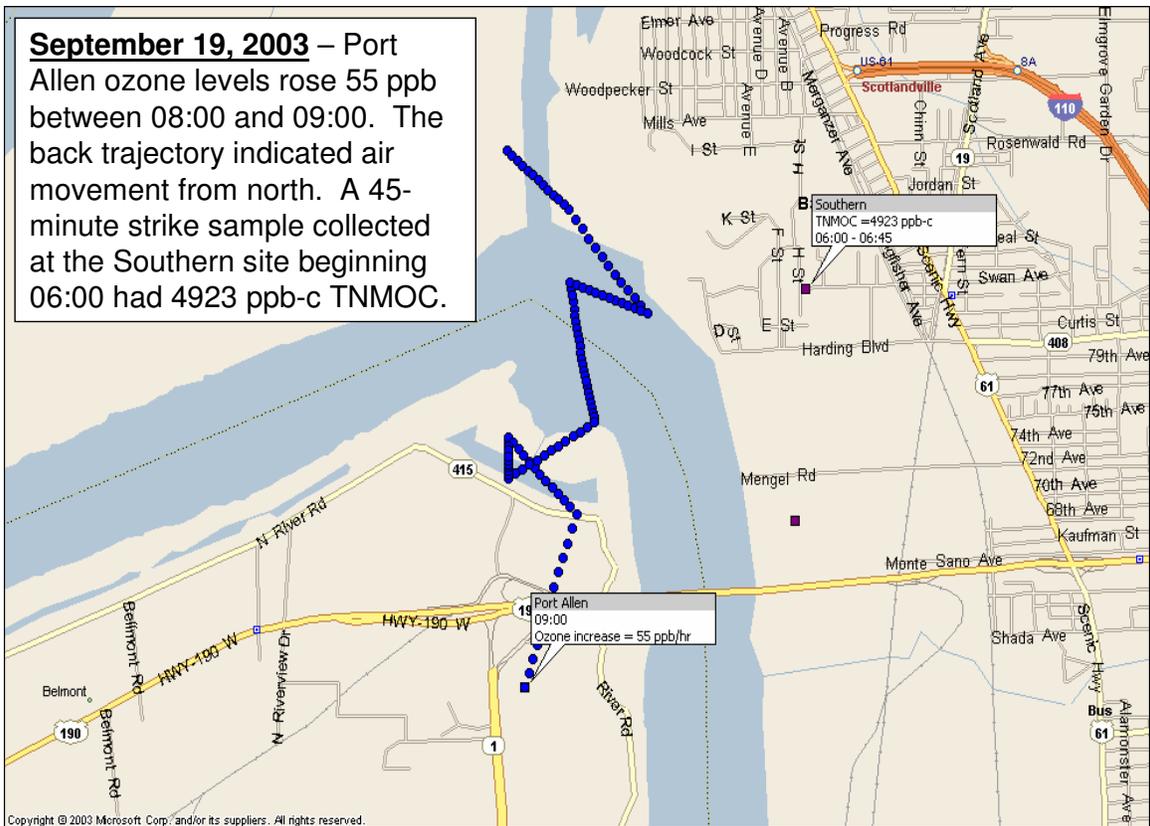
**Figure 4-12. Reactivity Apportionment by Chemical Group for VOC Samples Collected at the Same Place and Time Where Ozone Levels Increased by Greater than 40 ppb/hr**

Trajectories were estimated back from the place and time when ozone levels increased by greater than 40 ppb/hr to determine whether additional VOC samples, which might have been collected upwind of a sudden ozone concentration increase, could be added to this analysis. The back trajectories were estimated using the surface wind speed and wind direction data collected by LDEQ and a software program that interpolates the wind field in between monitors based on a weighted average of all the valid wind data. The trajectories were calculated back 12 hours from the time of the sudden ozone concentration increase.

No VOC samples were identified that were collected precisely on a back trajectory; however, assuming a large margin of uncertainty in the trajectory paths 26 samples were in the approximate upstream direction of where a sudden ozone concentration increase (greater than 40 ppb/hr) was measured. Figure 4-13 gives an example of a trajectory path and its rough proximity to an “upwind” VOC sampling site. A list of the VOC sampling dates, locations, start times, sampling durations, and TNMOC levels for all the samples collected near a trajectory leading to the site of a sudden ozone concentration increase is given in Table 4-5. Like the samples listed in Table 4-4, some of the samples listed in Table 4-5 were 24-hour samples, some were 3-hour samples, and some were shorter duration triggered samples.

In general the TNMOC and total MIR levels for the routine 3-hour and 24-hour samples listed in Table 4-5 are greater than the median levels estimated from all samples collected at the same time of day and location. Eleven of the samples listed in Table 4-5 were triggered by high levels of TNMHC and therefore, by design, had greater than average VOC levels. These data support findings presented elsewhere in this report that sudden ozone concentration increases tend to occur on mornings having greater than average levels of VOC reactivity; however, any inferences of a cause and effect relationship must be weighed against the large uncertainties in the trajectory paths needed to relate a specific VOC sample with a downwind sudden ozone concentration increase.

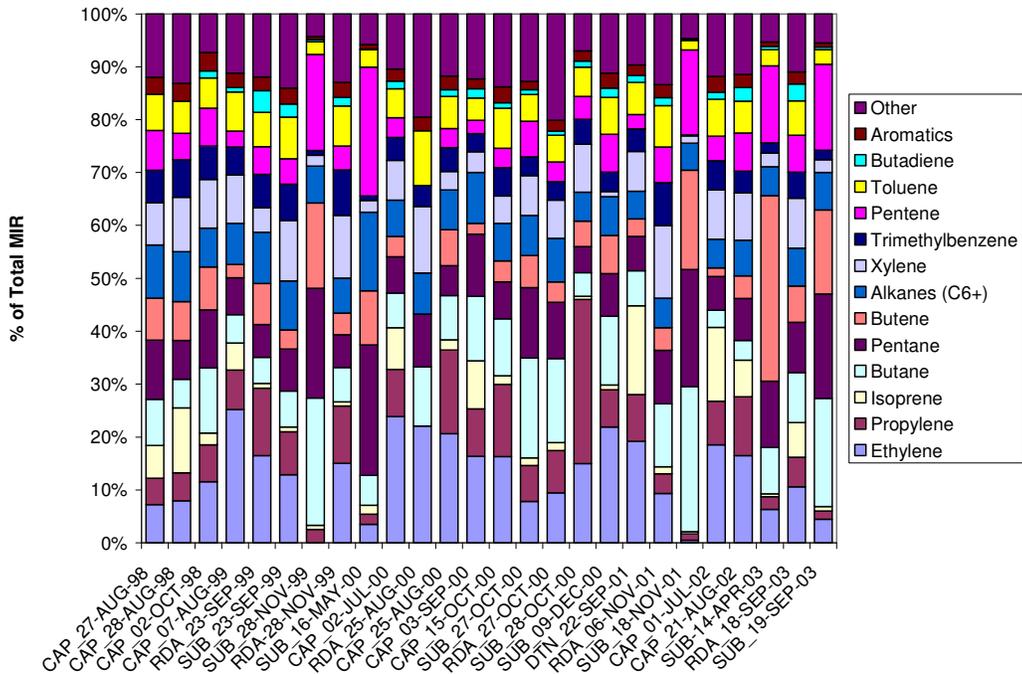
Figure 4-14 gives the reactivity apportionment by compound and compound group, in terms of the percentage of total MIR, for each sample listed in Table 4-5. No single compound or group of compounds dominates the reactivity for all the samples; however, five samples had disproportionately high reactivity from butanes, pentanes, butenes, and pentenes. These samples, labeled SUB\_28-NOV-99, SUB\_16-MAY-00, SUB\_18-NOV-01, SUB\_14-APR-03, and SUB\_19-SEP-03, were triggered by high TNMHC levels at the Southern sampling site. HRVOC accounted for 21% to 67% of the total MIR of samples collected “upwind” of sudden ozone concentration increases, varying from sample to sample. On average, about 42% of the MIR of these samples was from HRVOC.



**Figure 4-13. Example Back Trajectory from the Site of a Sudden Ozone Concentration Increase and the Location of an “Upwind” VOC Sampling Site**

**Table 4-5. TNMOC and MIR for VOC Samples Collected Near Trajectory Paths Leading to Sites of Sudden Ozone Concentration Increases (Greater than 40 ppb/hr)**

Date	Site	Start Time	Duration (Hours)	TNMOC (ppb-c)	Total MIR	Median MIR for Site and Time of Day
8/27/98	Capitol	6:00 a.m.	3	325	204	170
8/29/98	Capitol	Midnight	3	355	257	158
10/2/98	Capitol	6:00 a.m.	3	1,149	839	170
8/7/99	Capitol	6:00 a.m.	3	333	269	170
9/23/99	South Scotlandville	10:00 p.m.	0.75	1,203	877	--
9/23/99	Southern	10:00 p.m.	0.75	1,146	747	--
11/28/99	Southern	3:00 a.m.	0.75	11,673	7,244	--
11/28/99	South Scotlandville	1:00 a.m.	0.75	1,352	983	--
5/16/00	Southern	Midnight	0.75	7,995	5,154	--
7/2/00	Capitol	6:00 a.m.	3	303	235	170
8/25/00	South Scotlandville	6:00 a.m.	0.75	229	131	--
8/25/00	Capitol	6:00 a.m.	3	625	440	170
9/3/00	Capitol	9:00 a.m.	3	280	173	106
10/15/00	Capitol	6:00 a.m.	3	275	187	170
10/27/00	Southern	Midnight	24	612	335	131
10/27/00	South Scotlandville	Midnight	24	663	297	164
10/28/00	Southern	Midnight	24	1,056	1,166	131
12/9/00	Southern	1:00 a.m.	0.75	1,561	1,002	--
9/22/01	Dutchtown	Midnight	24	100	86	73
11/6/01	South Scotlandville	11:00 p.m.	0.75	1,121	717	--
11/18/01	Southern	6:00 a.m.	0.75	8,264	5,065	--
7/1/02	Capitol	6:00 a.m.	3	150	121	170
8/21/02	Capitol	6:00 a.m.	3	545	388	170
4/14/03	Southern	5:00 a.m.	0.75	2,392	2,086	--
9/18/03	South Scotlandville	Midnight	24	333	244	164
9/19/03	Southern	6:00 a.m.	0.75	4,923	3,187	--

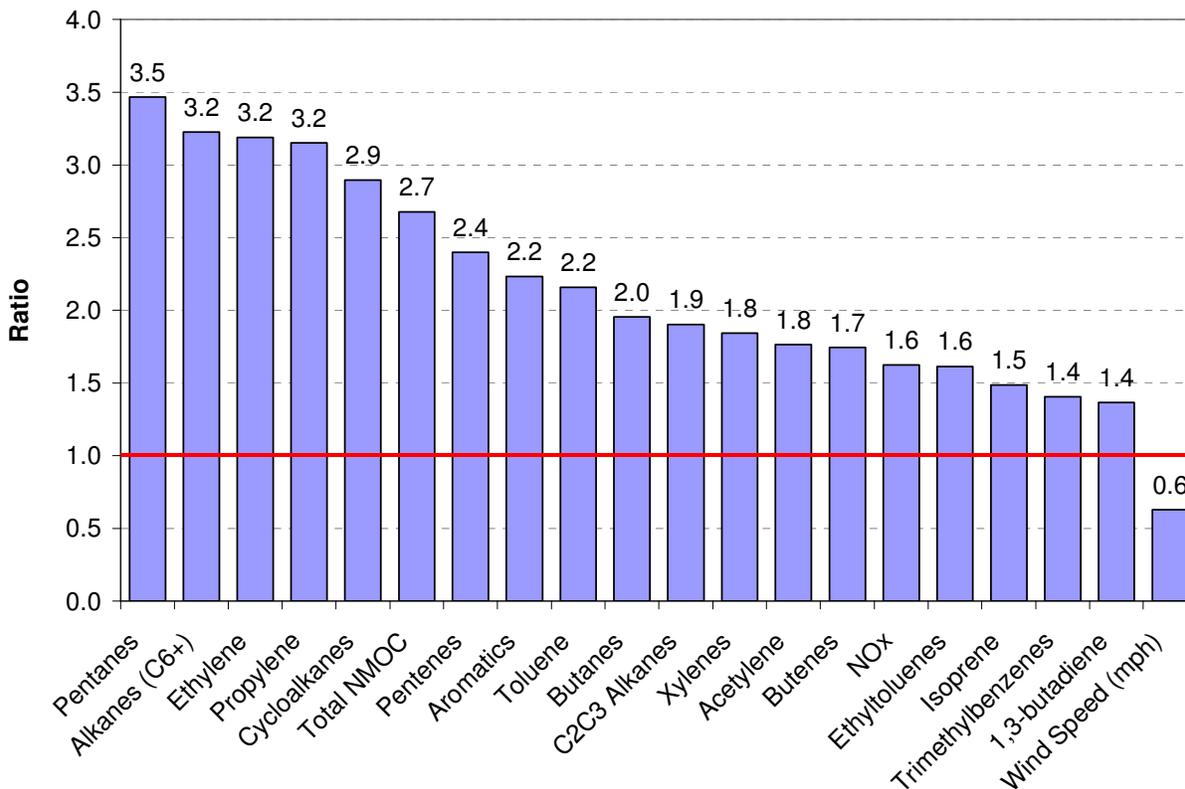


**Figure 4-14. Reactivity Apportionment by Chemical Group for VOC Samples Collected Near a Trajectory Leading to a Site Where Ozone Levels Increased by Greater Than 40 ppb/hr**

This analysis was next expanded to consider 3-hour VOC samples that were collected at times when ozone levels increased at a rate greater than *30 ppb/hr*. Only samples collected at the Capitol or Bayou Plaquemine sites and having start times of 6:00 a.m. or 9:00 a.m. were considered in this part of the analysis as these were the only sites where more than four 3-hour samples were collected at times when ozone levels were increasing by greater than 30 ppb/hr. Ozone concentration increases that were greater than 30 ppb/hr usually occurred between 7:00 a.m. and 11:00 a.m., a period which is spanned by the 6:00 a.m. and 9:00 a.m. canister samples.

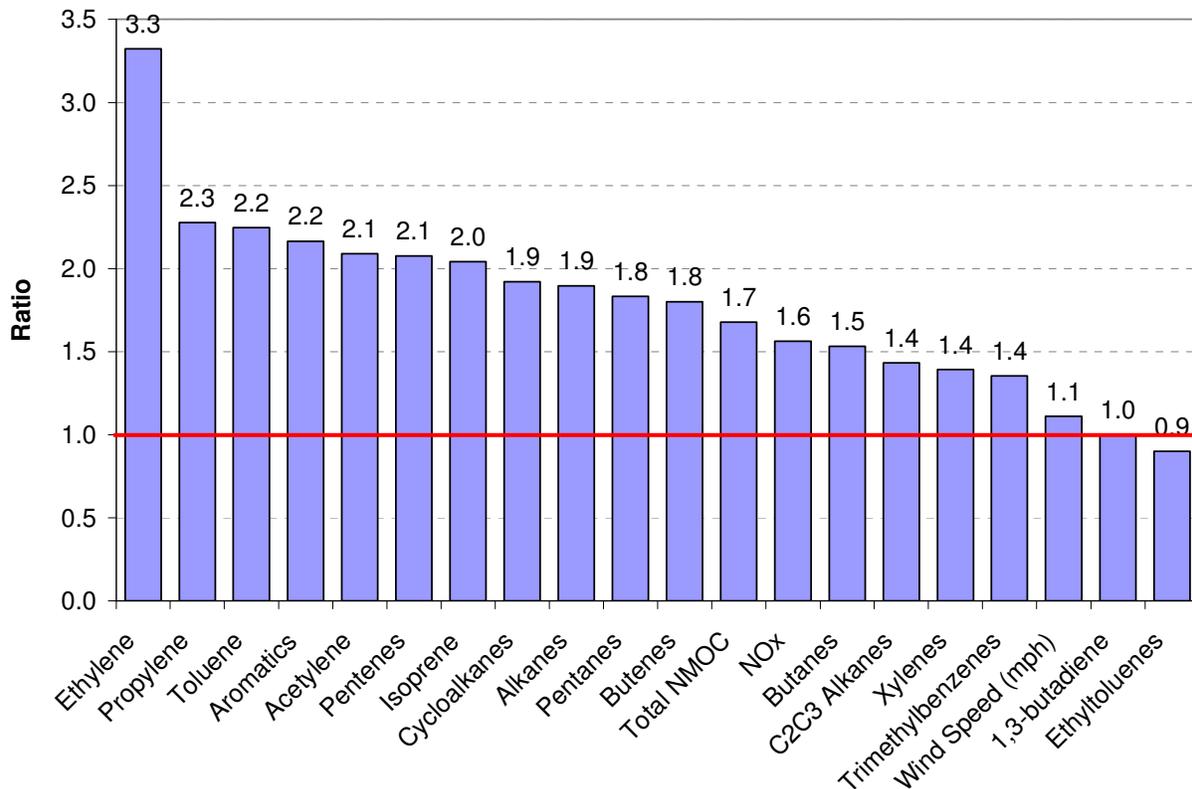
At the Capitol site, ozone levels increased by greater than 30 ppb/hr a total of 17 times between 6:00 a.m. and 11:00 a.m., during 1998-2003, when a 3-hour canister sample happened to be collected. At the Bayou Plaquemine site, this occurred 15 times. At the Capitol site, the VOC species having the greatest concentration increases on mornings when ozone levels increased by greater than 30 ppb/hr were n-pentane, isopentane, C6-C11 alkanes, ethylene, and propylene. The average levels of these compounds were more than 3 times greater on mornings when ozone levels increased by more than 30 ppb/hr compared with all mornings (Figure 4-15). NO<sub>x</sub> levels were 1.6 times greater and wind speeds were only 0.6 times as great (i.e., 40% lower) at times when ozone levels increased by more than 30 ppb/hr. At Bayou Plaquemine, the VOC species having the greatest concentration increase on mornings when ozone level increased by

greater than 30 ppb/hr was ethylene (Figure 4-16). The average ethylene level was more than 3 times greater for samples collected on mornings when ozone levels increased by greater than 30 ppb/hr compared with all mornings, while the levels of propylene and other VOC ranged up to 2.3 times greater. NO<sub>x</sub> levels were increased by factor of 1.6 at the Bayou Plaquemine site.



**Figure 4-15. Ratio of VOC Median Levels - 6:00 AM and 9:00 AM Samples Collected at the Capitol Site at Times when Ozone Levels Increased by Greater Than 30 ppb/hr Relative to all 6:00 AM and 9:00 AM Samples**

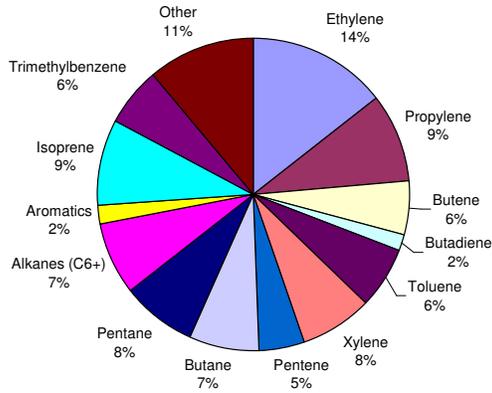
Note that isoprene levels were 2 times the average at Bayou Plaquemine and 1.5 times the average at the Capitol site on mornings when ozone levels increased by greater than 30 ppb/hr. This suggests that stagnation of routine emissions was at least partly responsible for the relative abundance of VOC on these mornings, assuming the isoprene emissions were biogenic and did not vary episodically.



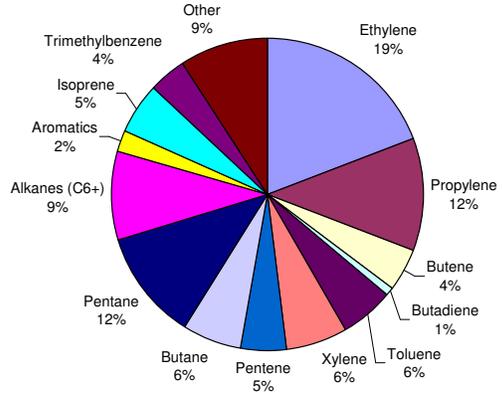
**Figure 4-16. Ratio of VOC Median Levels - 6:00 AM and 9:00 PM Samples Collected at the Bayou Plaquemine Site at Times when Ozone Levels Increased by Greater Than 30 ppb/hr Relative to all 6:00 a.m. and 9:00 a.m. Samples**

Note that the median total MIR for 6:00 a.m. and 9:00 a.m. samples collected during ozone concentration increases greater than 30 ppb/hr was more than twice as great as the median MIR based on all 6:00 a.m. and 9:00 a.m. samples at the Capitol and Bayou Plaquemine sites (Figures 17 and 18, respectively). Note also that ethylene, propylene, pentanes, and C6+ Alkanes contributed a greater percentage to the total MIR reactivity during periods when ozone was increasing rapidly at the Capitol Site. At the Bayou Plaquemine site, ethylene was the only compound that contributed a greater percentage of the total reactivity for samples collected during rapid ozone increases.

All 6:00 a.m. and 9:00 a.m. Samples  
Total MIR = 83

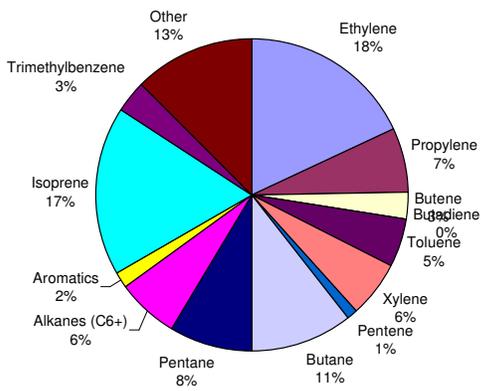


6:00 a.m. and 9:00 a.m. Samples With > 30 ppb/hr Ozone Increase  
Total MIR = 202

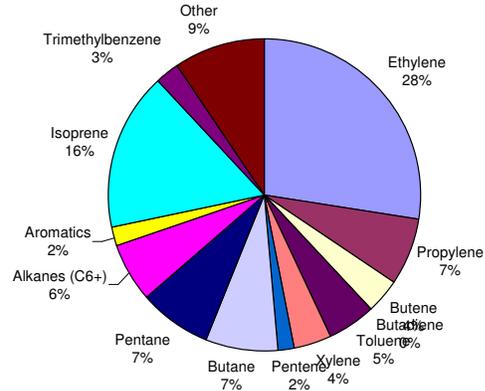


**Figure 4-17. Total MIR and Average Percent Contributions to the Total MIR for 6:00 AM and 9:00 AM Samples at the Capitol Site**

All 6:00 a.m. and 9:00 a.m. Samples  
Total MIR = 42



6:00 a.m. and 9:00 a.m. Samples With > 30 ppb/hr Ozone Increase  
Total MIR = 92



**Figure 4-18. Total MIR and Average Percent Contributions to the Total MIR for 6:00 AM and 9:00 AM Samples at the Bayou Plaquemine Site**

#### 4.4 Summary of VOC Levels and Reactivity

The average levels of TNMOC and reactivity-weighted VOC concentrations, expressed in terms of MIR, were greatest at sampling sites near the Mississippi River in north and central Baton Rouge and least at outlying sampling sites. This geographic pattern is similar to the pattern that was found for sudden ozone concentration increase frequency of occurrence.

Averaged across all sampling sites, ethylene, propylene, and isoprene were the greatest individual contributors to the total reactivity, accounting for 40% of the total MIR. The relative importance of isoprene with respect to the total MIR varied considerably from site to site, ranging from 3% of the total MIR at South Scotlandville to 30% of the total MIR at Pride. Surprisingly, isoprene accounted for 15% of the total MIR, on average, at the Port Allen site. Butanes and pentanes were important contributors to the total MIR at the Southern site, accounting for as much of the total MIR as ethylene and propylene. Compounds classified as HRVOC in Baton Rouge accounted for 43% to 53% of the total MIR, on average, at all the sampling sites except Pride. The average HRVOC contribution to the total MIR at Pride was 35%.

A diurnal pattern in MIR was found for all monitoring sites where 3-hour VOC samples were routinely collected, with the highest MIR levels tending to be found in samples with start times of 6:00 a.m. and 6:00 p.m. Total MIR levels were typically lowest during midday, when atmospheric mixing and photochemical reactivity are typically greatest. This diurnal pattern was most pronounced at the Capitol site and least pronounced at Pride, where biogenic isoprene levels accounted for about 50% of the midday reactivity.

No discernable weekly pattern in MIR levels was detected, nor was any seasonal or annual pattern in MIR levels detected, except at the Pride, Dutchtown, and Baker sampling sites. Summertime peaks in total MIR at the Pride and Dutchtown sampling sites appear to be attributed entirely to increases in biogenic isoprene. This does not appear to be the case at Baker.

Day to day variations in 24-hour VOC levels and reactivity-weighted concentrations appear to be greater than any systematic diurnal, weekly, or annual cycle. Day to day variations are caused by random fluctuations in emissions or the weather factors that disperse and transport emissions.

No significant long-term trend in MIR is apparent at any of the Baton Rouge sampling sites; however, average MIR levels decreased nearly uniformly at all sites between 2002 and 2004.

VOC samples collected during times when ozone levels increased by greater than 30 ppb/hr or 40 ppb/hr tended to have greater than average VOC and MIR levels, as well as greater than average NO<sub>x</sub> levels and lower than average wind speeds. At the Capitol site, the median levels of pentanes, C6-C10 alkanes, ethylene, and propylene, were each more than three times greater than average for 6:00 a.m. and 9:00 a.m. samples that spanned a period when ozone levels increased by greater than 30 ppb/hr. At the Bayou Plaquemine site, the median ethylene level was more than three times greater than average for 6:00 a.m. and 9:00 a.m. samples that spanned a period when ozone increased by greater than 30 ppb/hr, while propylene, toluene, aromatics, acetylene, and isoprene were about twice as great. The relative abundance of isoprene, in particular, suggests that stagnation of routine emissions accounts at least for some the relatively high VOC levels measured in these samples.

VOC samples collected near trajectory paths leading to monitors that measured sudden ozone concentration increases usually had greater than average VOC and MIR levels. Because of uncertainties in the trajectory analysis, this analysis perhaps is more of an indication that sudden ozone concentration increases tend to occur on days having high VOC levels than it is a demonstration of a causal relationship.

## 5.0 Comparing Ambient Monitoring Data with Emissions Estimates

One of the key findings of the TexAQS 2000 field study, as well as follow up studies conducted by TCEQ, was that measurements of HRVOC levels in ambient air downwind of industrial facilities in Houston generally could not be reconciled with emissions inventories without inferring substantial uncertainties in the emissions estimates. In this section, ambient monitoring results for HRVOC in Baton Rouge are compared with emissions estimates to determine whether similar uncertainties exist in the Baton Rouge data.

### 5.1 Approach and Assumptions

The approach used for evaluating the HRVOC emissions estimates was similar to the approach used by TCEQ (Estes, 2002). Basically, this approach compares the average HRVOC/NO<sub>x</sub> ratio derived from ambient monitoring data with the HRVOC/NO<sub>x</sub> ratios derived from the emissions estimates. The basic assumption of this approach is that HRVOC and NO<sub>x</sub> emitted by the same source or group of sources are transported and dispersed identically in the atmosphere and, therefore, should appear at downwind monitoring sites in the same proportions as what was emitted. Discrepancies between the monitored HRVOC/NO<sub>x</sub> ratios and those derived from upwind emissions estimates suggest possible errors in either the HRVOC or NO<sub>x</sub> emissions estimates, notwithstanding uncertainties in the underlying assumptions of analysis. Generally, emissions estimate uncertainties inferred from this type of analysis are attributed to HRVOC emissions rather than NO<sub>x</sub> emissions because the variety of HRVOC source types and uncertainties inherent in the conventional VOC emissions estimating techniques present greater potential for error. Some of the key assumptions of this analysis and their implications are given in Table 5-1.

HRVOC emissions estimates for 2003 were used as the basis for this analysis. The emissions data were estimated and reported to LDEQ by industrial facilities in Baton Rouge 5-parish area and seven surrounding parishes as part of a special emissions inventory process. Table 5-2 summarizes the number of facilities reporting HRVOC or NO<sub>x</sub> emissions greater than 0 tons per year and the total emissions reported for the 12 parishes. Ethylene; propylene; butenes (all isomers); and 1,3-butadiene were the only HRVOC addressed in this analysis.

**Table 5-1. Key Assumptions of the Emission Inventory Evaluation and Their Implications**

Assumption	Implication
HRVOC and NO <sub>x</sub> emissions from the same source or group of sources are homogenously mixed by the time the emissions reach the monitoring site.	This assumption might not always be true, especially when NO <sub>x</sub> is emitted from elevated hot stacks and HRVOC are emitted from ground level fugitive sources. Uncertainties associated with this assumption could be minimized by limiting the analysis to midday when atmospheric mixing is greatest.
Emissions from stationary sources can be isolated from mobile and area source emissions.	This assumption may not always be true, especially when stationary sources are located in the same direction from the monitoring site as densely populated areas or major roadways. Uncertainties introduced by this assumption can be minimized by using only ambient monitoring data collected during nighttime, when traffic volume and area source activity are comparatively low.
The ambient HRVOC and NO <sub>x</sub> levels are influenced mostly by fresh emissions with negligible losses from chemical reactions or deposition.	Chemical losses of photochemically reactive HRVOC could be minimized using only ambient monitoring data collected during periods of little or no sunlight.
Measurement errors are insignificant.	Uncertainties in the analysis caused by measurement errors can be minimized through careful validation of the monitoring data and by using data from times of day when the measurement signal to noise ratio is relatively high. Based on the observed HRVOC and NO <sub>x</sub> diurnal variations, this includes late afternoon, nighttime, and the morning.

**Table 5-2. 2003 Emissions Summary for NO<sub>x</sub> and HRVOC**

	NO <sub>x</sub>	1,3-Butadiene	Ethylene	Propylene	Butenes
Number of Facilities Reporting > 0	173	12	26	24	17
Total Emissions (Tons Per Year)	96,167	52.45	1,039.05	654.5	186.4

The HRVOC ambient monitoring data used in this analysis consisted of the 3-hour canister data collected at the Capitol, Bayou Plaquemine, Pride, and Carville sampling sites during 2002-2004 (no other Baton Rouge sampling sites routinely collected 3-hour canister data). The 2002-2004 period ensured that the monitoring data were close to the same vintage as the 2003 emissions data that were used, while also providing a more robust dataset than would have been utilized in the analysis had only the 2003 monitoring results been considered. Hourly measurements of NO<sub>x</sub> that were collected at these sites were also used in the analysis.

## 5.2 HRVOC and NO<sub>x</sub> Level Variations with Respect to Wind Direction

Before comparing the monitored and emitted HRVOC/NO<sub>x</sub> ratios, the ambient monitoring data were analyzed to determine whether the wind directions at the times when comparatively high HRVOC and NO<sub>x</sub> levels were measured were consistent with the geographic distribution of known emissions sources. This was done by sorting the monitored HRVOC and NO<sub>x</sub> levels from each site according to the wind directions at the times the measurements were made and then calculating the median concentration levels for each of 36 discrete 10-degree wind direction sectors. The results are presented in Figures 5-1 through 5-20. Figure 5-1, for example, shows a polar coordinate graph illustrating how the NO<sub>x</sub> median level varied with wind direction at the Capitol site. The polar graph is superimposed on a map of the Baton Rouge area, which shows the locations and relative magnitudes of NO<sub>x</sub> stationary sources. The wind directional dependence of the monitored NO<sub>x</sub> levels relative to the Capitol site was generally consistent with the locations of NO<sub>x</sub> stationary sources and the Baton Rouge urban core. Similar graphs, depicting how NO<sub>x</sub> levels varied with wind direction at the Bayou Plaquemine, Carville, and Pride sites are shown in Figures 5-2, 5-3 and 5-4, respectively.

Figures 5-5 through 5-20 contain similar graphs depicting the variations with wind direction for ethylene; propylene; 1-butene; and 1,3-butadiene median levels at the Capitol, Bayou Plaquemine, Carville, and Pride monitoring sites. Note that the monitored HRVOC levels generally varied with wind direction in patterns that are consistent with the emissions source locations with only a few exceptions, suggesting that most, if not all, emissions sources are accounted for in the emissions inventory. A couple of notable exceptions are ethylene and butene levels measured at the Capitol site, which were elevated above the background when the winds were west-northwesterly with no apparent sources in that direction.



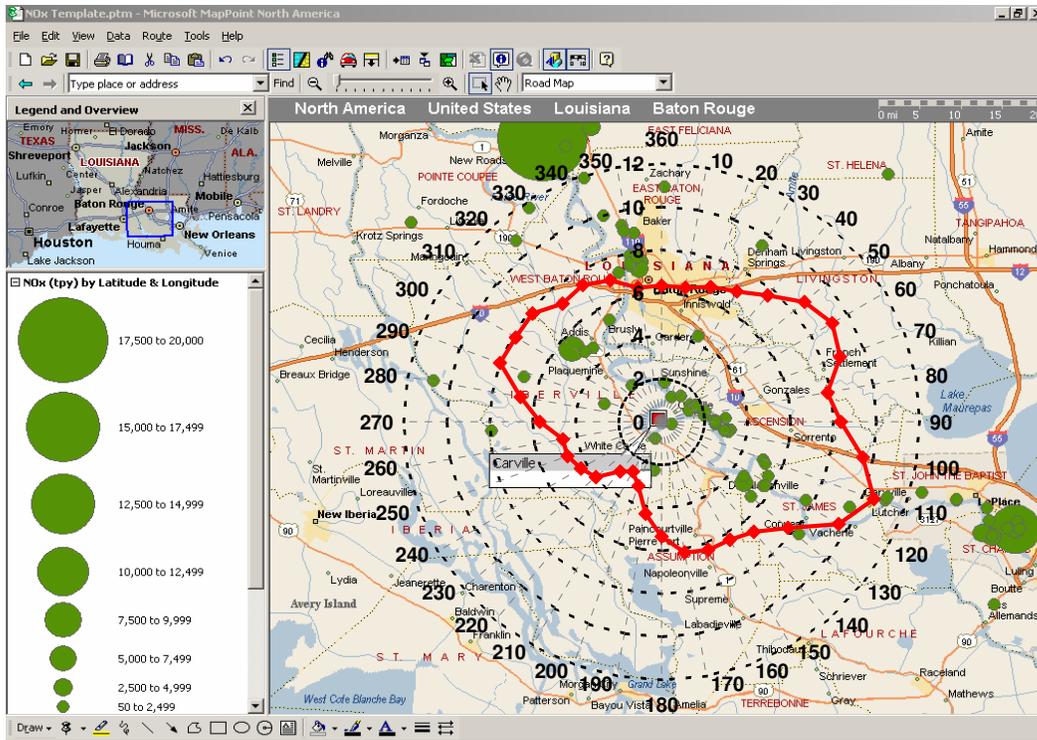


Figure 5-3. Variation of Median NOx Levels with Wind Direction at Carville

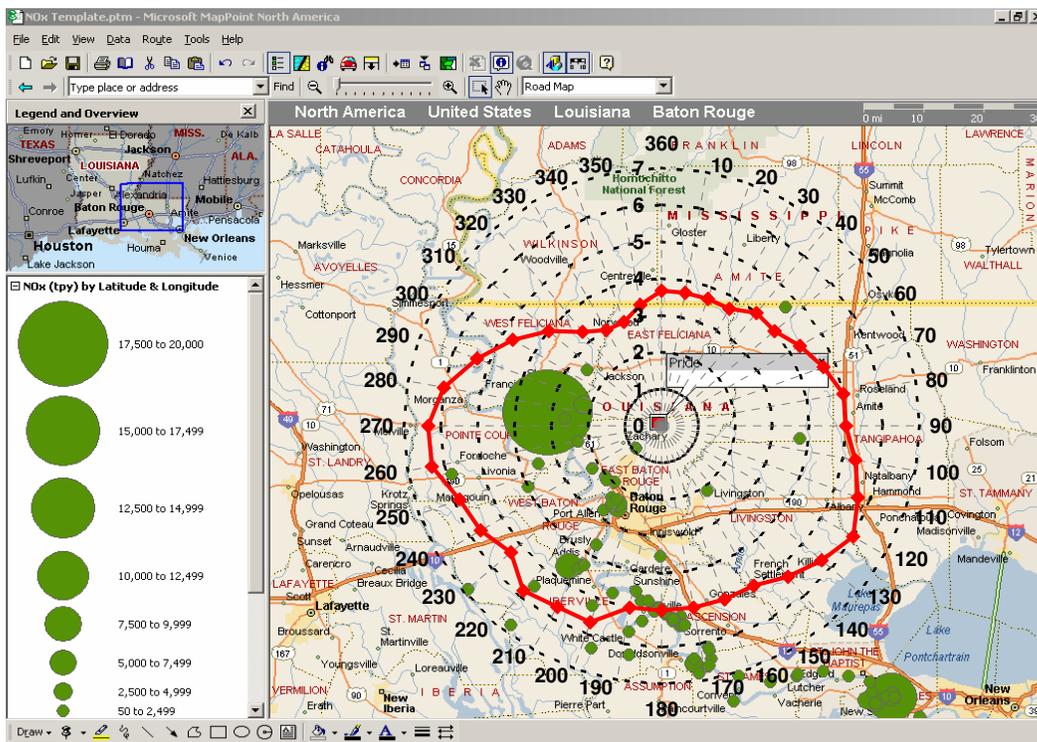
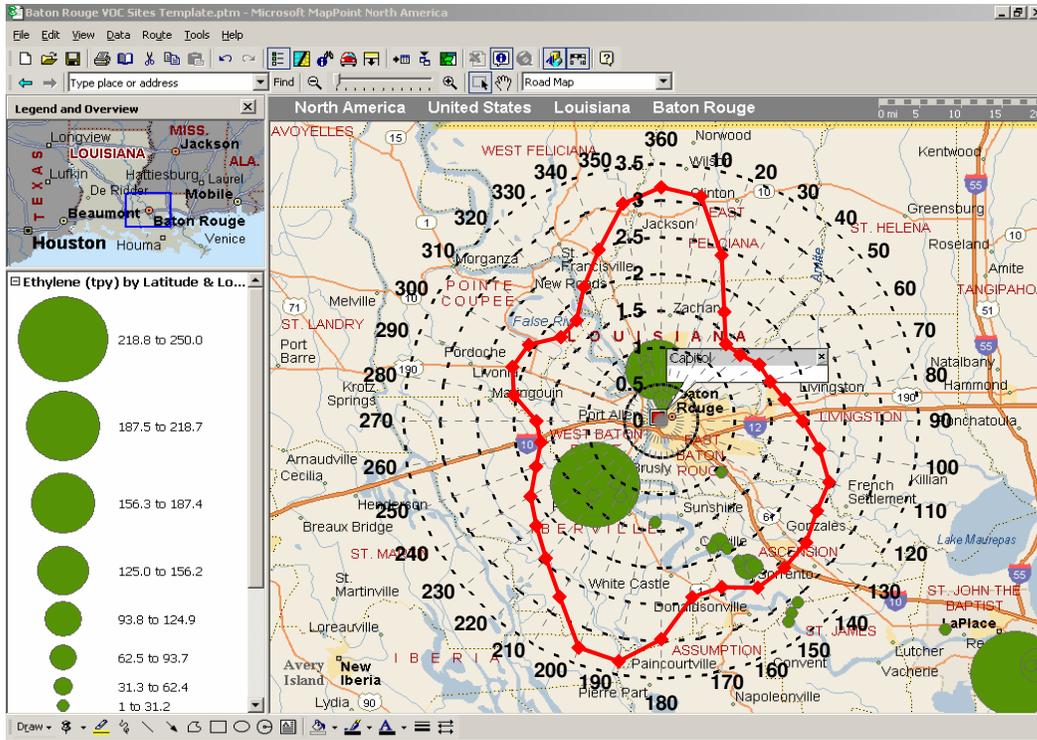
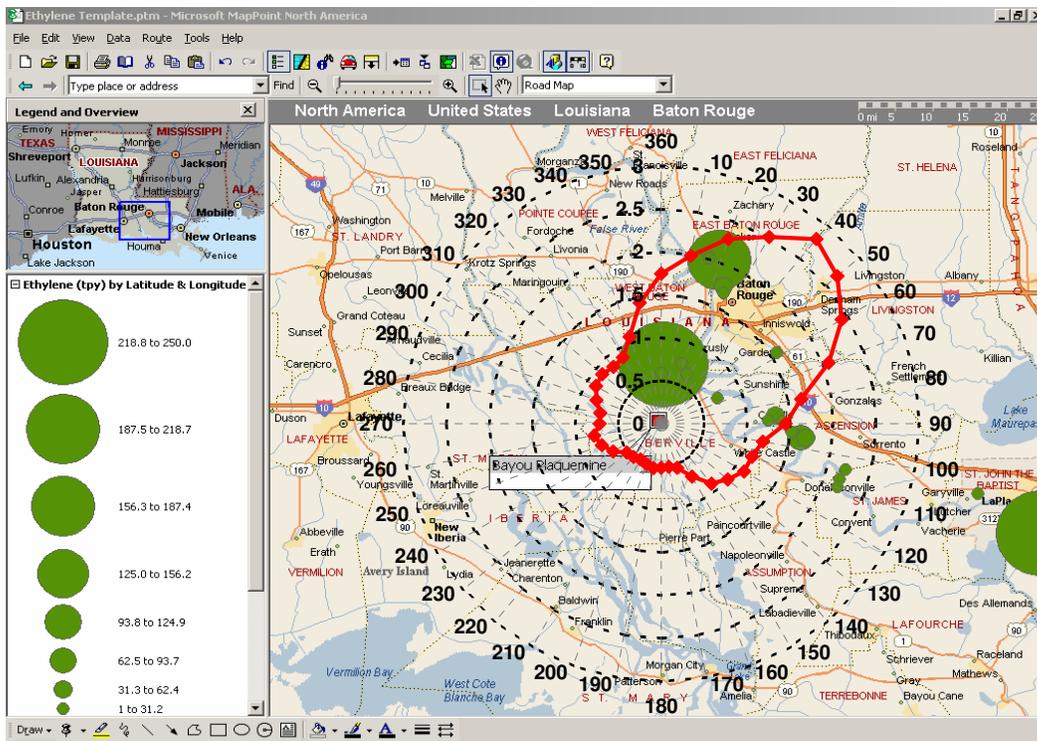


Figure 5-4. Variation of Median NOx Levels with Wind Direction at Pride



**Figure 5-5. Variation of Median Ethylene Levels with Wind Direction at the Baton Rouge Capitol**



**Figure 5-6. Variation of Median Ethylene Levels with Wind Direction at Bayou Plaquemine**

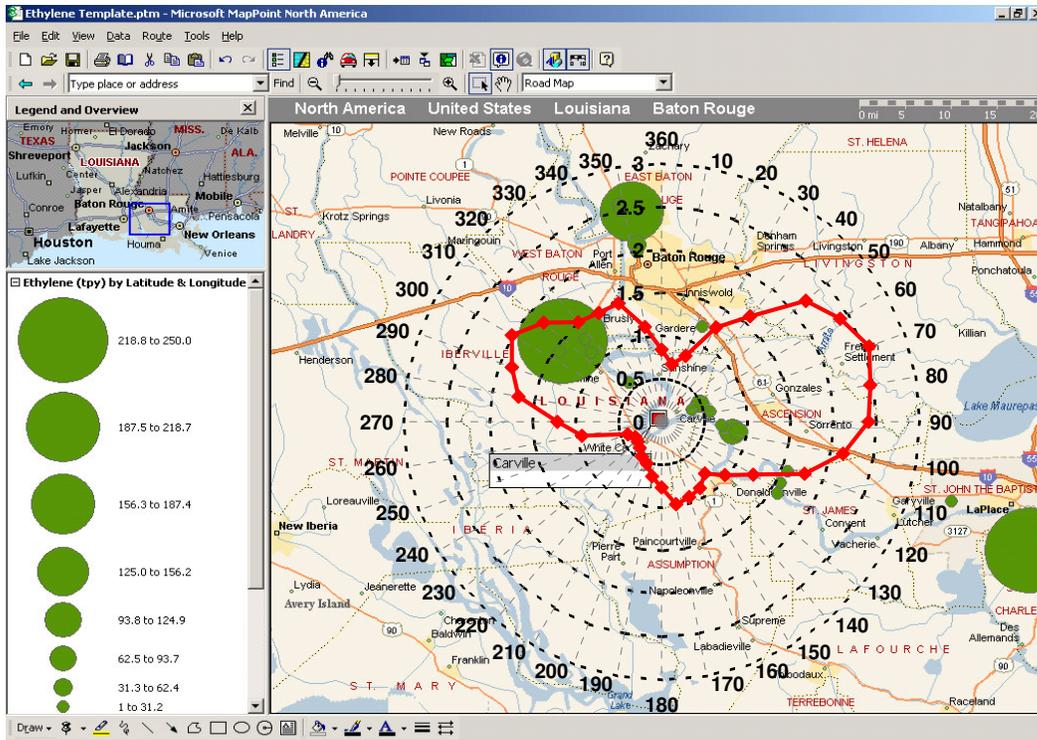


Figure 5-7. Variation of Median Ethylene Levels with Wind Direction at Carville

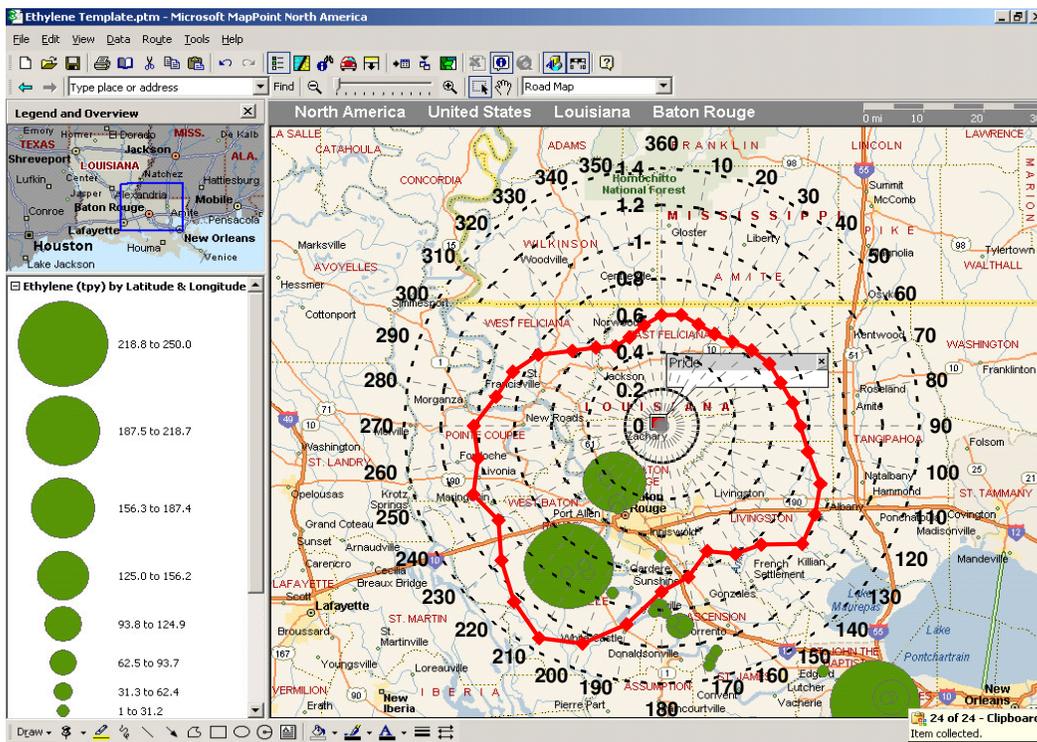
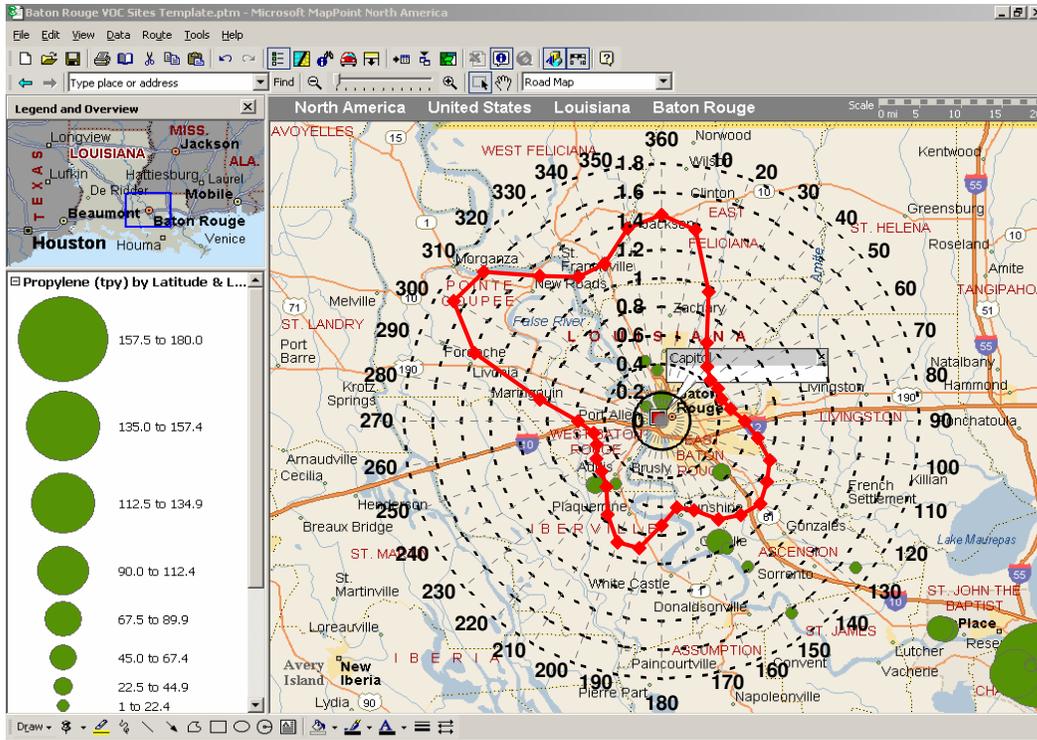
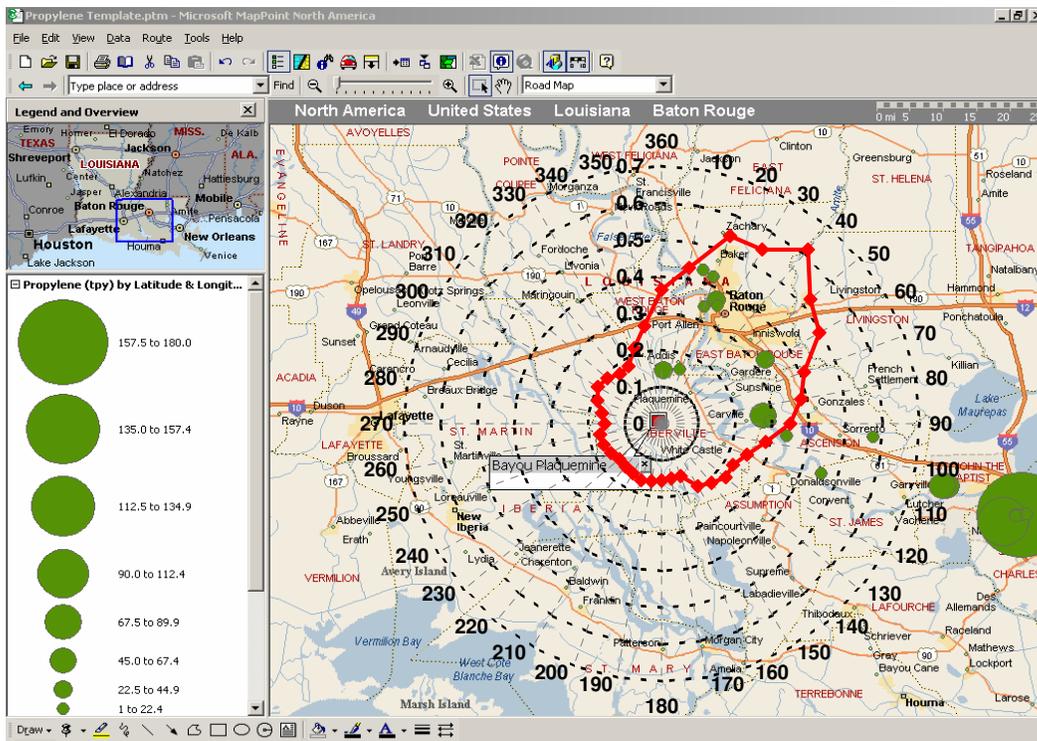


Figure 5-8. Variation of Median Ethylene Levels with Wind Direction at Pride



**Figure 5-9. Variation of Median Propylene Levels with Wind Direction at the Baton Rouge Capitol**



**Figure 5-10. Variation of Median Propylene Levels with Wind Direction at Bayou Plaquemine**





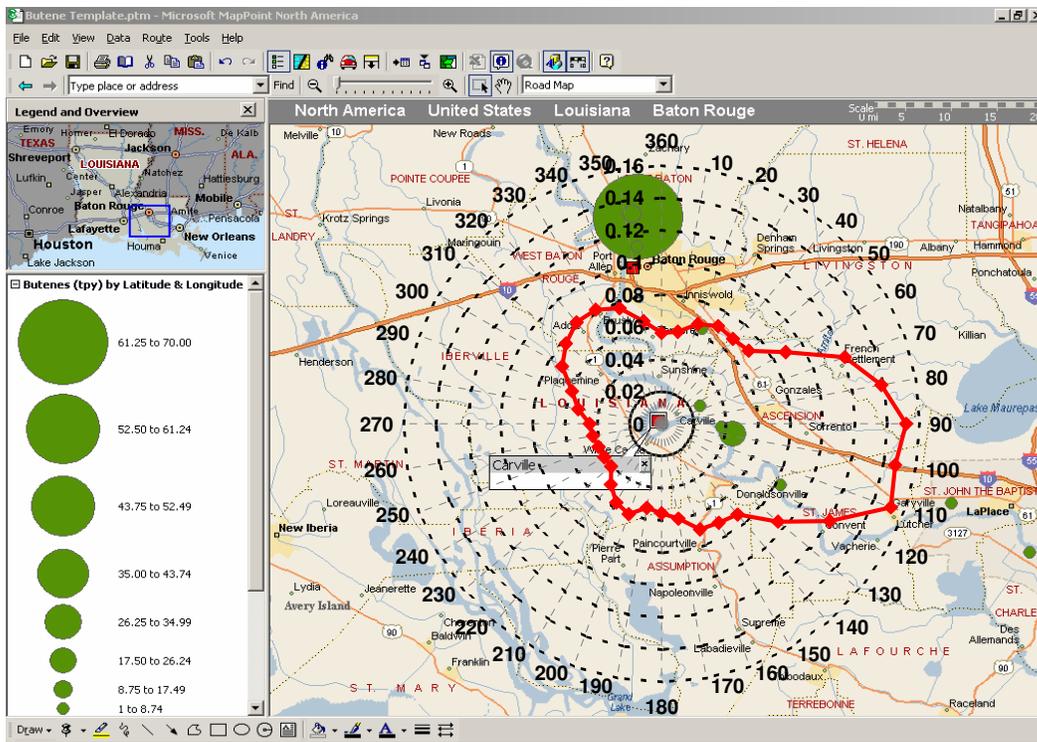


Figure 5-15. Variation of Median 1-Butene Levels with Wind Direction at Carville

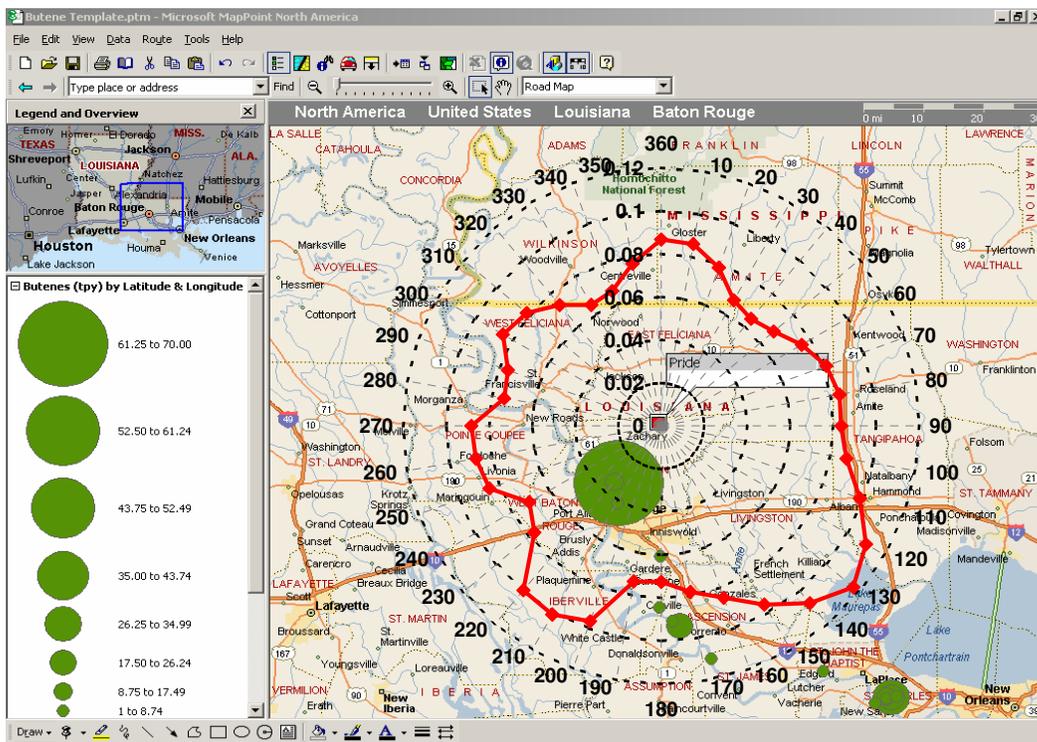
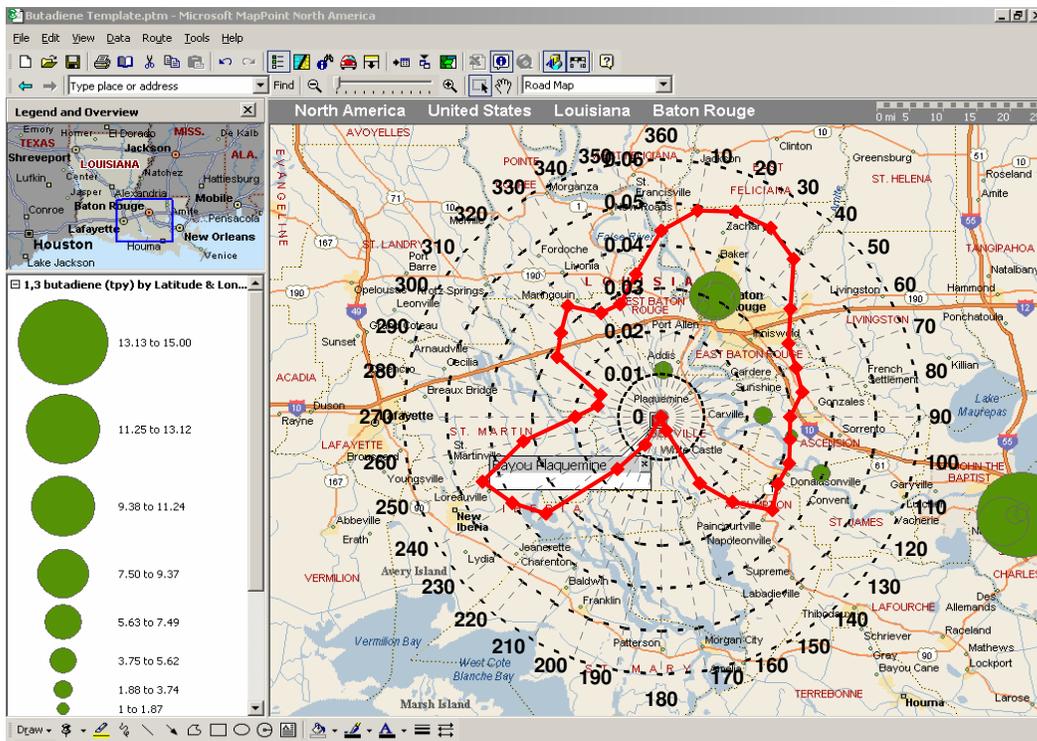
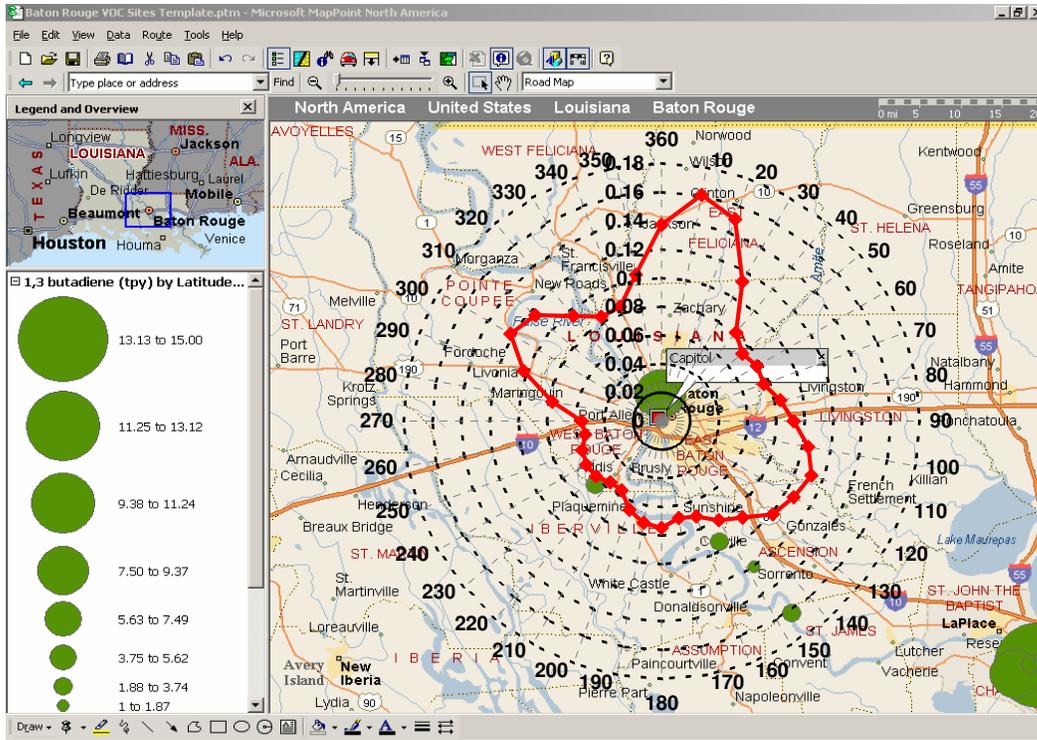


Figure 5-16. Variation of Median 1-Butene Levels with Wind Direction at Pride



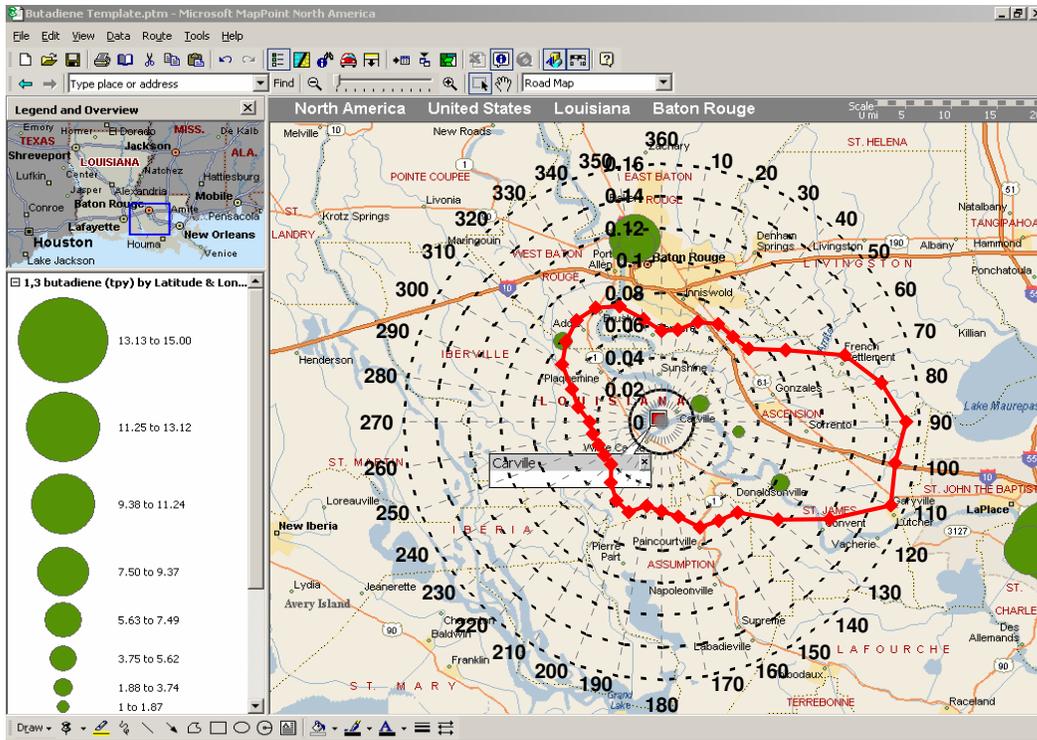


Figure 5-19. Variation of Median 1,3-Butadiene Levels with Wind Direction at Carville

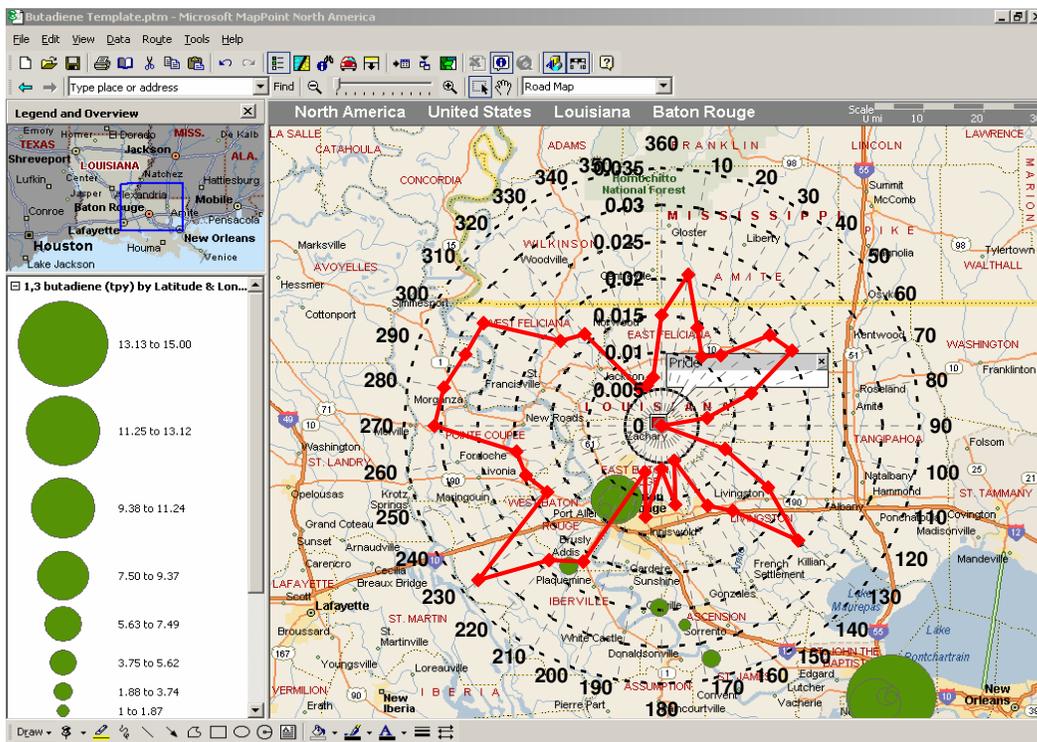


Figure 5-20. Variation of Median 1,3-Butadiene Levels with Wind Direction at Pride

### 5.3 Comparison of Monitored HRVOC/NO<sub>x</sub> Ratios with Emissions Estimates

The next step was to compare the monitored HRVOC/NO<sub>x</sub> ratios from each site with similar ratios derived from the 2003 emissions estimates. The ambient monitoring data used for this comparison was limited to measurement results obtained between 9:00 p.m. and 6:00 a.m. This included the 3-hour canister samples having start times of 9:00 p.m., 12:00 a.m., and 3:00 a.m.; and NO<sub>x</sub> averages for the hours beginning 9:00 p.m. through 5:00 a.m. The main reason for limiting the data to these time periods was to minimize the influence of fresh mobile and area source emissions on the ambient monitoring data, assuming that traffic volume and area source emissions are comparatively low at those times of day. Additionally, losses of the photochemically reactive HRVOC are expected to be minimal during that time period. Moreover, measurement uncertainties might be comparatively low, in general, during 9:00 p.m. to 6:00 a.m. and other times of day when the levels of NO<sub>x</sub> and HRVOC are generally higher relative to the detection limits. Tables 5-3 and 5-4 give the average HRVOC and NO<sub>x</sub> levels and monitored HRVOC/NO<sub>x</sub> ratios, respectively for data collected between 9:00 p.m. and 6:00 a.m.

**Table 5-3. Monitored Average HRVOC and NO<sub>x</sub> Levels for 9:00 P.M. to 6:00 A.M.**

Monitoring Site	Ethylene (ppb-v)	Propylene (ppb-v)	Butenes (ppb-v)	1,3-Butadiene (ppb-v)	NO <sub>x</sub> (ppb-v)
Bayou Plaquemine	3.17	0.70	0.34	0.12	8.11
Capitol	4.31	1.71	0.68	0.45	28.00
Carville	2.34	0.84	0.40	0.09	10.70
Pride	1.38	0.43	0.26	0.08	5.72

**Table 5-4. Monitored HRVOC/NO<sub>x</sub> Average Ratios**

Monitoring Site	Ethylene/NO <sub>x</sub>	Propylene/NO <sub>x</sub>	Butenes/NO <sub>x</sub>	1,3-Butadiene/NO <sub>x</sub>
Bayou Plaquemine	0.391	0.086	0.042	0.014
Capitol	0.154	0.061	0.024	0.016
Carville	0.218	0.078	0.038	0.008
Pride	0.241	0.075	0.045	0.013

Based on the average wind speeds during 9:00 p.m. to 6:00 a.m., which were generally low (about 3 mph), one can argue that a source's influence extends no further than about 15 miles downwind. An alternative assumption is that all sources in the 12-parish region reporting HRVOC emissions impact all the monitoring sites but the impact of any given source on a specific monitor decreases with distance from the monitor.

HRVOC/NO<sub>x</sub> ratios from emissions estimates were calculated using each of these assumptions. For example, see Table 5-5, which presents two estimates of the emitted

ethylene/NO<sub>x</sub> molar ratio: (1) based on all emission sources located within 15 miles of the Bayou Plaquemine, Capitol, Carville, and Pride monitoring sites and (2) based on all emission sources in the 12-parish region, weighted by one over the distance from each monitor. The average ethylene/NO<sub>x</sub> ratio derived from measurements at each monitoring site is also presented. Note that the monitored ethylene/NO<sub>x</sub> ratio at any given site was 4 to 10 times greater than the corresponding ratio of ethylene/NO<sub>x</sub> emissions derived from estimates of stationary source emissions within 15 miles of the respective site. The best agreement between the average monitored ethylene/NO<sub>x</sub> ratio and the ethylene/NO<sub>x</sub> ratio derived from emissions estimates was found at the Capitol site.

Tables 5-6 through 5-8 are similar to Table 5-5, except the monitored and emitted ratios with respect to NO<sub>x</sub> are given for the other HRVOC. Generally, the agreements between the monitored and emitted propylene/NO<sub>x</sub>, butene/NO<sub>x</sub> and 1,3-butadiene/NO<sub>x</sub> were not as good as was found for ethylene/NO<sub>x</sub>. Note, however, that the average monitored levels of butene, and 1,3-butadiene, in particular, were very low. Because of the large uncertainties in the ambient measurements generally found at these low levels, the discrepancies between the monitored and emitted ratios with respect to NO<sub>x</sub> might not be good indications of the relative uncertainties in the emissions estimates.

**Table 5-5. Average Ethylene/NO<sub>x</sub> Ratios from Monitoring Results and Emissions Estimates**

Monitoring Site	Monitored Average Ethylene/NO <sub>x</sub> Ratio	Ethylene/NO <sub>x</sub> Molar Ratio from Emissions Estimates	
		Sources Less Than 15 Miles from Monitor	All Sources in 12-Parish Region – Weighted 1/D
Bayou Plaquemine	0.391	0.038	0.025
Capitol	0.154	0.035	0.017
Carville	0.218	0.036	0.022
Pride	0.241	0.037	0.016

**Table 5-6. Average Propylene/NO<sub>x</sub> Ratios from Monitoring Results and Emissions Estimates**

Monitoring Site	Monitored Average Propylene/NO <sub>x</sub> Ratio	Propylene/NO <sub>x</sub> Molar Ratio from Emissions Estimates	
		Sources Less Than 15 Miles from Monitor	All Sources in 12-Parish Region – Weighted 1/D
Bayou Plaquemine	0.086	0.004	0.007
Capitol	0.061	0.007	0.006
Carville	0.078	0.007	0.007
Pride	0.075	0.003	0.005

**Table 5-7. Average Butene/NO<sub>x</sub> Ratios from Monitoring Results and Emissions Estimates**

Monitoring Site	Monitored Average Butene/NO <sub>x</sub> Ratio	Butene/NO <sub>x</sub> Molar Ratio from Emissions Estimates	
		Sources Less Than 15 Miles from Monitor	All Sources in 12-Parish Region – Weighted 1/D
Bayou Plaquemine	0.042	0.000	0.001
Capitol	0.024	0.003	0.002
Carville	0.038	0.001	0.001
Pride	0.045	0.009	0.002

**Table 5-8. Average 1,3-Butadiene/NO<sub>x</sub> Ratios from Monitoring Results and Emissions Estimates**

Monitoring Site	Monitored Average 1,3-Butadiene/NO <sub>x</sub> Ratio	1,3-Butadiene/NO <sub>x</sub> Molar Ratio from Emissions Estimates	
		Sources Less Than 15 Miles from Monitor	All Sources in 12-Parish Region – Weighted 1/D
Bayou Plaquemine	0.014	0.0002	0.0004
Capitol	0.016	0.0007	0.0007
Carville	0.008	0.0003	0.0004
Pride	0.013	0.0000	0.0004

#### 5.4 Summary of Emissions Inventory Assessment

The levels of HRVOC and NO<sub>x</sub> monitored at the Capitol, Bayou Plaquemine, Carville, and Pride monitoring sites during 2002-2004 were compared with 2003 HRVOC and NO<sub>x</sub> emissions estimates for 2003. In general, the variations of HRVOC and NO<sub>x</sub> levels with respect to wind direction from each site were consistent with locations of stationary source emissions and the Baton Rouge urban core relative to each monitor.

HRVOC/NO<sub>x</sub> ratios based on the average measurements at each site were generally several times greater than the corresponding ratios based on emissions estimates. The best agreement between monitored and emitted ratios relative to NO<sub>x</sub> was found for ethylene at the Capitol site, where the ethylene/NO<sub>x</sub> ratio was about 4 times the ethylene/NO<sub>x</sub> ratio based on estimated point source emissions within 15 miles of the site. At Bayou Plaquemine, Carville, and Pride the average ethylene/NO<sub>x</sub> ratios ranged from 6 to 10 times the ethylene NO<sub>x</sub> ratio derived from estimated point source emissions within 15 miles of the respective site. For propylene/NO<sub>x</sub>; butene/NO<sub>x</sub>; and 1,3-butadiene/NO<sub>x</sub>; the agreements between the monitored and emitted ratios were generally not as good.

Disagreements between a monitored ratio and a corresponding ratio based on nearby emissions estimates may, in some cases, be a relative indicator of the uncertainty in the

emissions estimates; however, one should be mindful that the assumptions used when comparing monitored ratios with ratios derived from emission estimates might not always be valid. For example, HRVOC and NO<sub>x</sub> emissions from the same source or group of sources are assumed to be homogeneously mixed in the atmosphere; however, vertical stratification of the lower atmosphere can prevent NO<sub>x</sub> emitted from elevated stacks to completely mix with ground level fugitive emissions of HRVOC. When this is the case, the monitored HRVOC/NO<sub>x</sub> ratios will be biased high relative to the HRVOC/NO<sub>x</sub> ratio of the emissions.

Measurement uncertainties can also bias a comparison between monitored HRVOC/NO<sub>x</sub> ratios and the corresponding ratios derived from emissions estimates, especially at the low levels of butene and 1,3-butadiene that were typically monitored in Baton Rouge. Note that average levels of butene and 1,3-butadiene at Bayou Plaquemine, Carville, and Pride were below the analytical detection limits<sup>3</sup> so the signal to noise ratio of the measurement results may be very large.

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<sup>3</sup> Based on laboratory detection limits provided by Jim Hazlett, LDEQ.

## 6.0 Source Apportionment

Source apportionment of VOC measured at Baton Rouge sampling sites was performed using Positive Matrix Factorization (PMF). PMF is a multivariate factor analysis tool that estimates the number and chemical composition profiles of sources that best account for the measured VOC at a sampling site, as well as the amount of VOC mass that each source profile contributes to the measured levels. The mathematical framework of PMF is described elsewhere (Paatero, 1997; Hopke, 2001). Unlike the Chemical Mass Balance (CMB) model, which has had widespread use in the past, PMF does not require any initial input of source profile information to determine the combination of source profiles that best account for the measured concentrations. The implementation of PMF for this study was performed using a beta test version of EPA PMF 1.0 (Eberly, 2004). EPA PMF is a software tool developed by EPA that includes the PMF model and a graphical user interface.

### 6.1 Objective and Approach

The objective of the source apportionment was to determine the source profiles that contributed most to VOC levels measured in 3-hour canister samples collected at the Baton Rouge Capitol as well as short-term triggered canister samples collected at the Capitol, Port Allen, South Scotlandville, and Southern sampling sites. In this way, the analysis focused on the area of Baton Rouge where the greatest VOC levels and reactivity were usually measured. The Baton Rouge Capitol was the only monitoring site among those mentioned where 3-hour samples were routinely collected. Only the 3-hour samples having start times between 9:00 p.m. and 6:00 a.m. were used in the analysis. This was to minimize any uncertainties caused by photochemistry.

### 6.2 Results

EPA PMF can resolve from three to 17 different source profiles from an ambient air monitoring data set; it is up to the data analyst to decide how many. Normally, this is done as an iterative process by examining statistical indicators of the fit. For the Capitol 3-hour samples, a 17-source profile solution achieved the best fit; however, some source profiles were found to account for very little of the total VOC mass while others seemed to correlate very well with one another. Therefore, a 13-source profile solution was run for the final analysis.

Figures 6-1 through 6-13 give the source profiles that were computed based on the 3-hour samples collected at the Capitol monitoring site. Each source profile is accompanied by a polar coordinate graph showing how the relative source contribution varied with respect to wind direction. For example, the top half of Figure 6-1 shows that Source Profile 1 contains 2,2,4-trimethylpentane; 2,3,4-trimethylpentane; toluene; and 2-methylpentane in greatest abundance;

with smaller amounts of other aromatic and aliphatic hydrocarbons. Many of these chemicals are found in gasoline evaporative emissions and auto exhaust. The bottom half of Figure 6-1 shows that the greatest concentrations associated with this source profile were usually found when the winds were northerly or east-southeasterly. On average, this source profile accounted for 6% of the total speciated VOC mass.

Source Profile 2 (Figure 6-2) contains mostly 1,3-butadiene. On average, this source profile accounted for 1% of the total speciated VOC mass. The greatest concentrations associated with Source Profile 2 were usually associated with northwesterly, northerly, or southeasterly winds.

Source Profile 3 (Figure 6-3) contains mostly n-hexane, methycyclopentane, and 3-methylpentane. On average, this source profile accounted for 6% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with northwesterly and northerly winds.

Source Profile 4 (Figure 6-4) contains mostly n-butane, n-pentane, and isopentane; with smaller contributions from benzene, toluene, methylpentanes, and other C6-C7 hydrocarbons. On average, this source profile accounted for 12% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with northwesterly or north-northwesterly winds.

Source Profile 5 (Figure 6-5) contains acetylene; ethane; toluene; benzene; ethylbenzene; xylene; and 1,2,4-trimethylbenzene. On average, this source profile accounted for 11% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with east-southeasterly winds. This is probably a motor vehicle source.

Source Profile 6 (Figure 6-6) contains mostly propane and n-pentane. On average, this source profile accounted for 6% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with northwesterly and northerly winds.

Source Profile 7 (Figure 6-7) contains mostly propylene, with smaller amounts of ethane, propane, and n-hexane. On average, this source profile accounted for 4% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with northwesterly or northerly winds.

Source Profile 8 (Figure 6-8) contains mostly ethane, propane, and n-butane. On average, this source profile accounted for 16% of the total speciated VOC mass (the greatest contribution of all the identified source profiles). The concentrations associated with this source

profile were almost uniform for all wind directions. This is probably a background source resulting from accumulation of these low-reactivity VOC.

Source Profile 9 (Figure 6-9) contains mostly isopentane, propane, and n-butane. Lower levels of ethane, pentenes, and methylpentanes were also found in this source profile. On average, Source Profile 9 accounted for 13% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with west-northwesterly, or northerly winds.

Source Profile 10 (Figure 6-10) contains mostly isobutane, with a smaller amount of propane. On average, this source profile accounted for 6% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with west-northwesterly or northerly winds.

Source Profile 11 (Figure 6-11) contains mostly ethylene, with smaller amounts of ethane, propylene, propane, isopentane, benzene. On average, this source profile accounted for 8% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with southerly winds.

Source Profile 12 (Figure 6-12) contains mostly isobutane, n-butane, isopentane, and n-pentane. On average, this source profile accounted for 9% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with northwesterly, northerly, or northeasterly winds.

Source Profile 13 (Figure 6-13) contains mostly isoprene. On average this source profile accounted for 3% of the total speciated VOC mass. The greatest concentrations associated with this source profile were usually associated with east-northeasterly or westerly winds. This is probably a biogenic source.

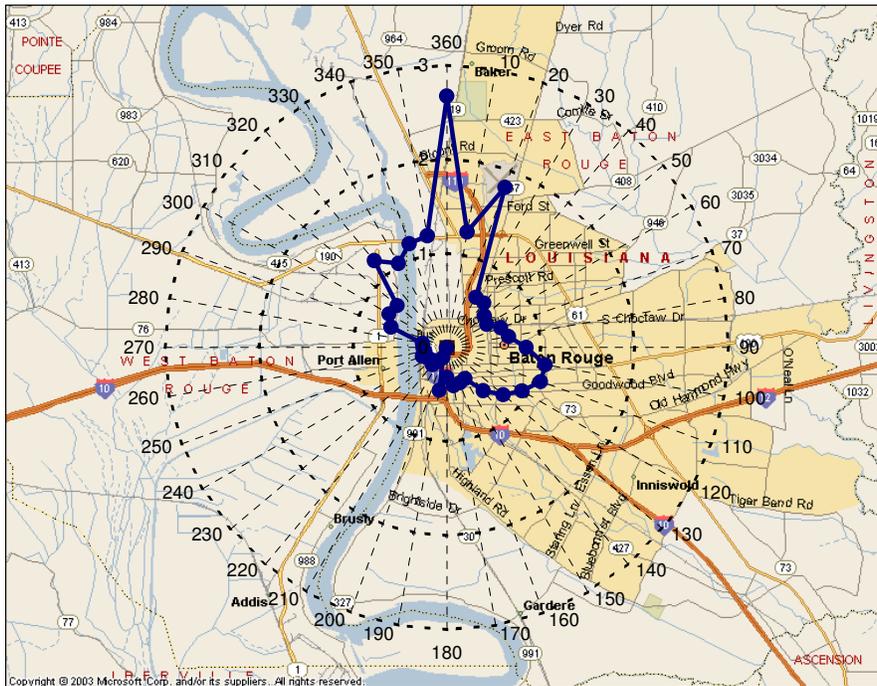
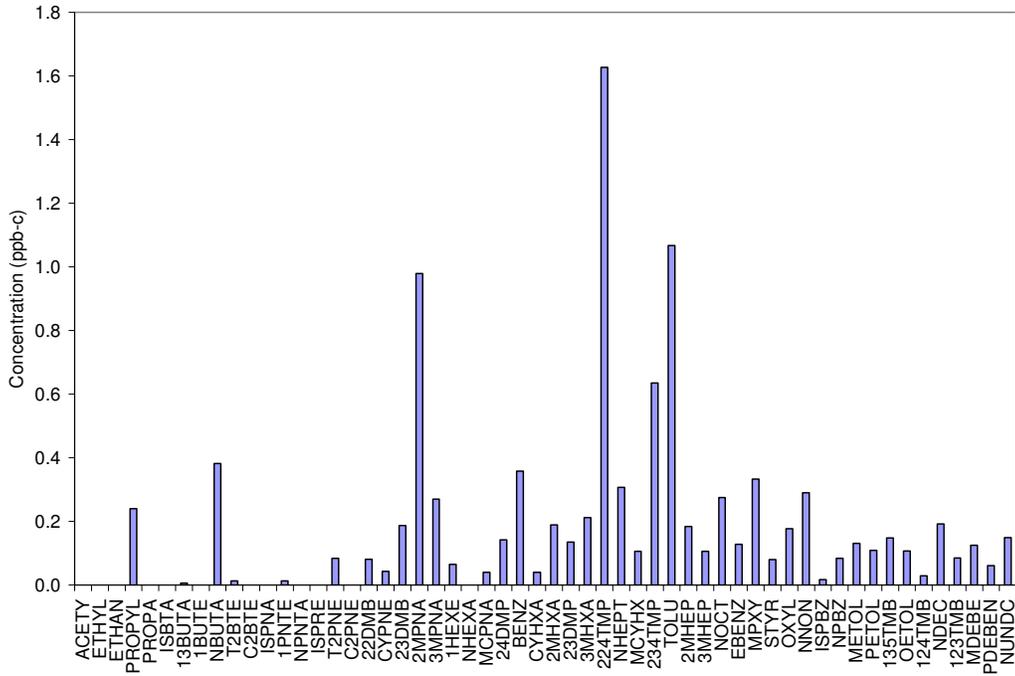


Figure 6-1. Concentration of Each Species in Source Profile 1 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

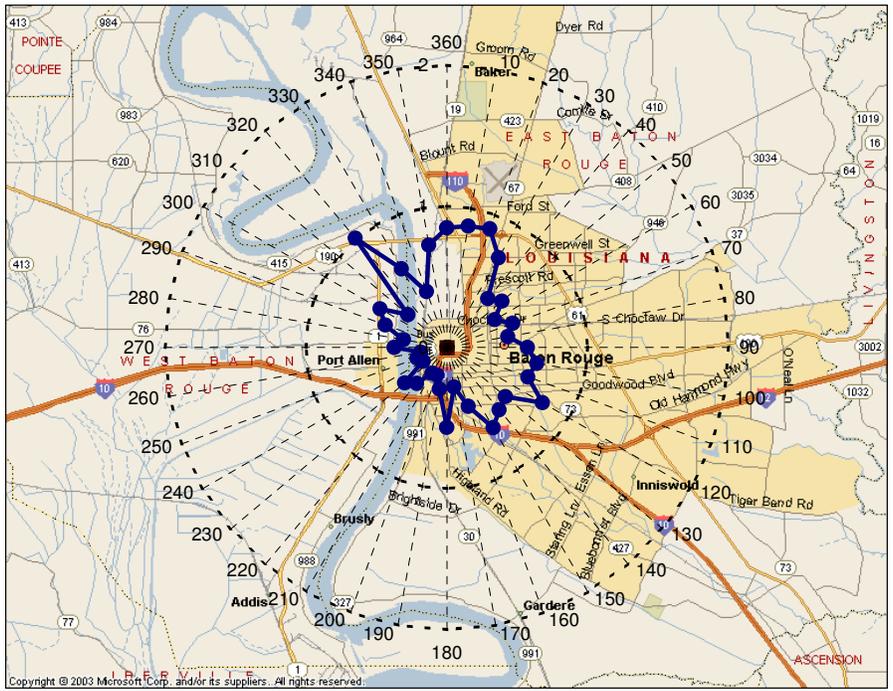
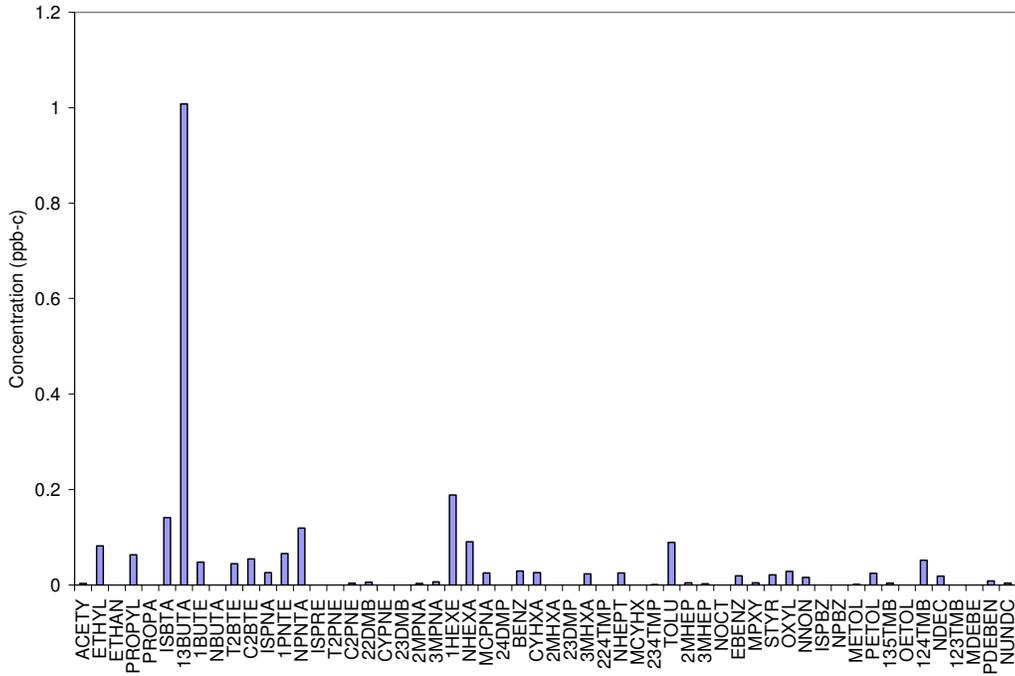
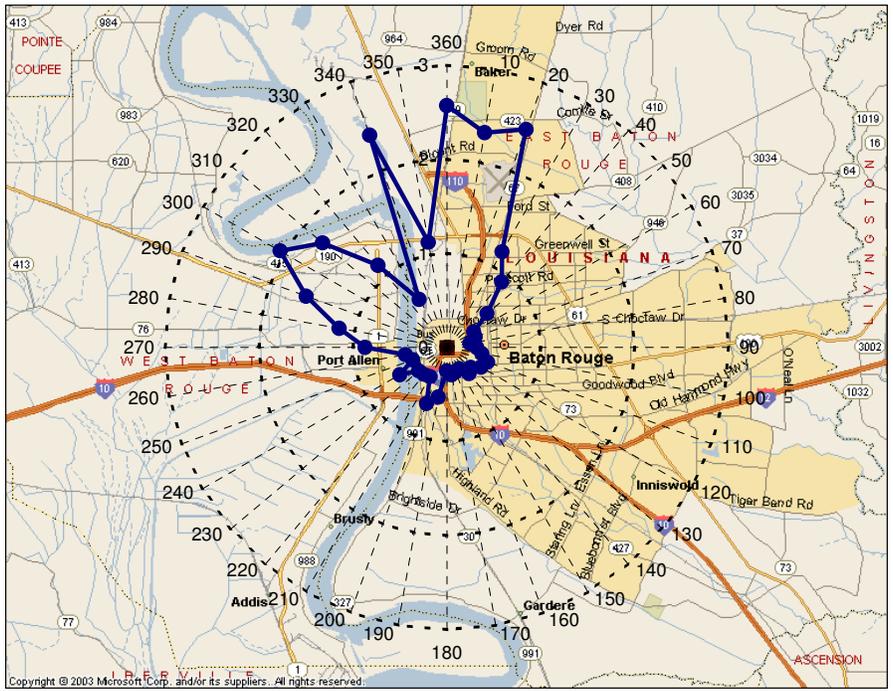
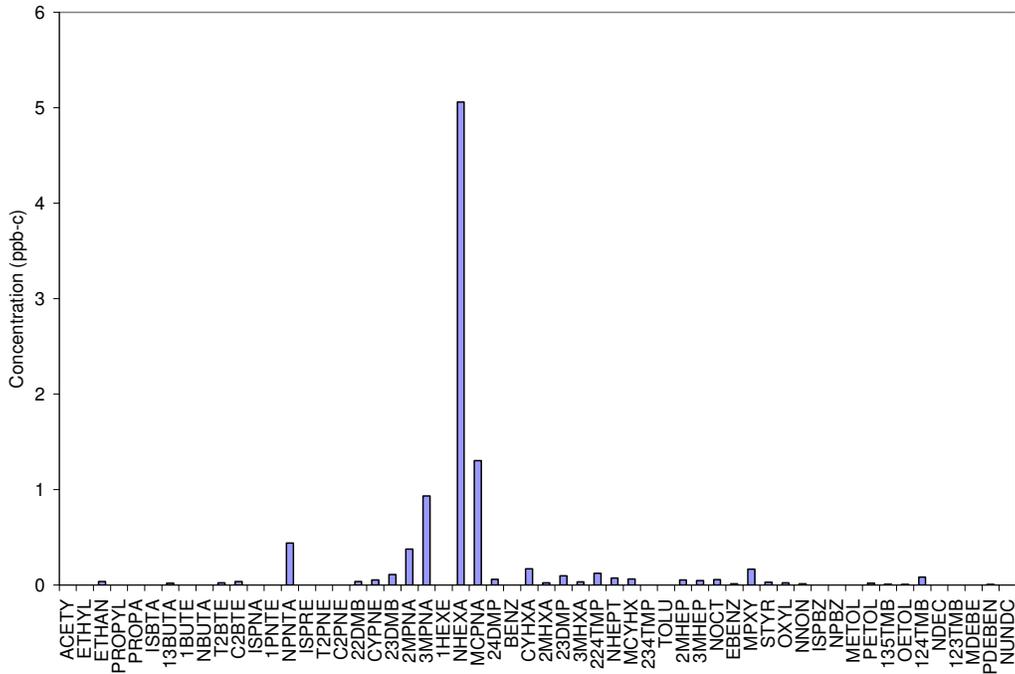


Figure 6-2. Concentration of Each Species in Source Profile 2 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)



**Figure 6-3. Concentration of Each Species in Source Profile 3 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)**

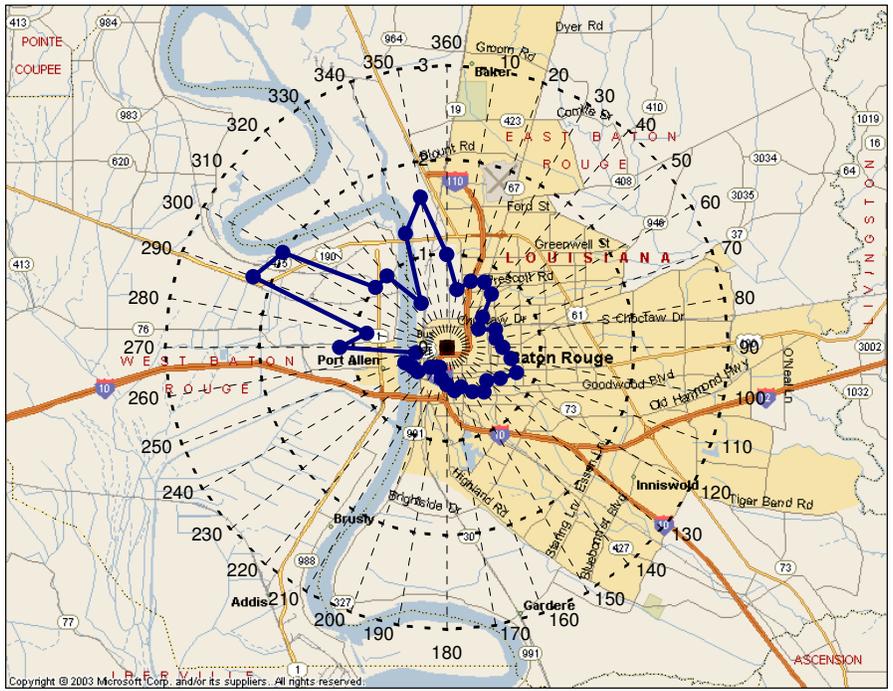
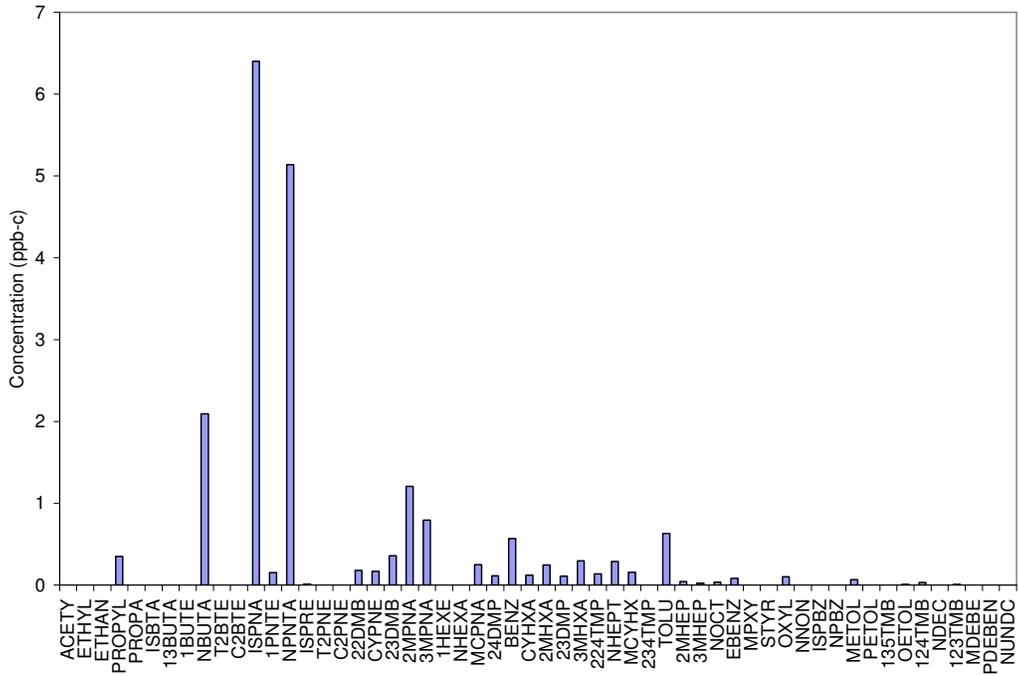


Figure 6-4. Concentration of Each Species in Source Profile 4 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

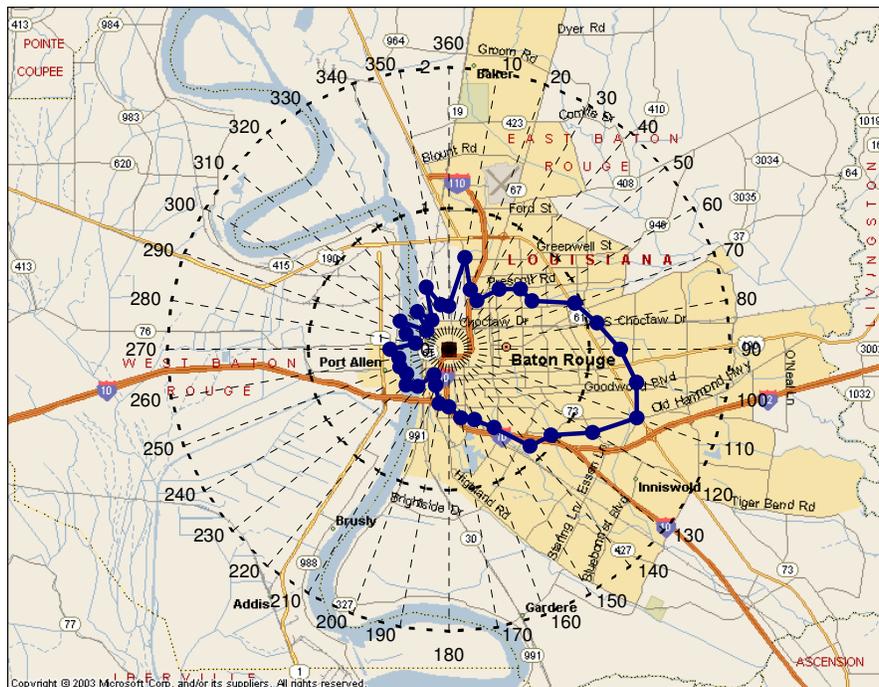
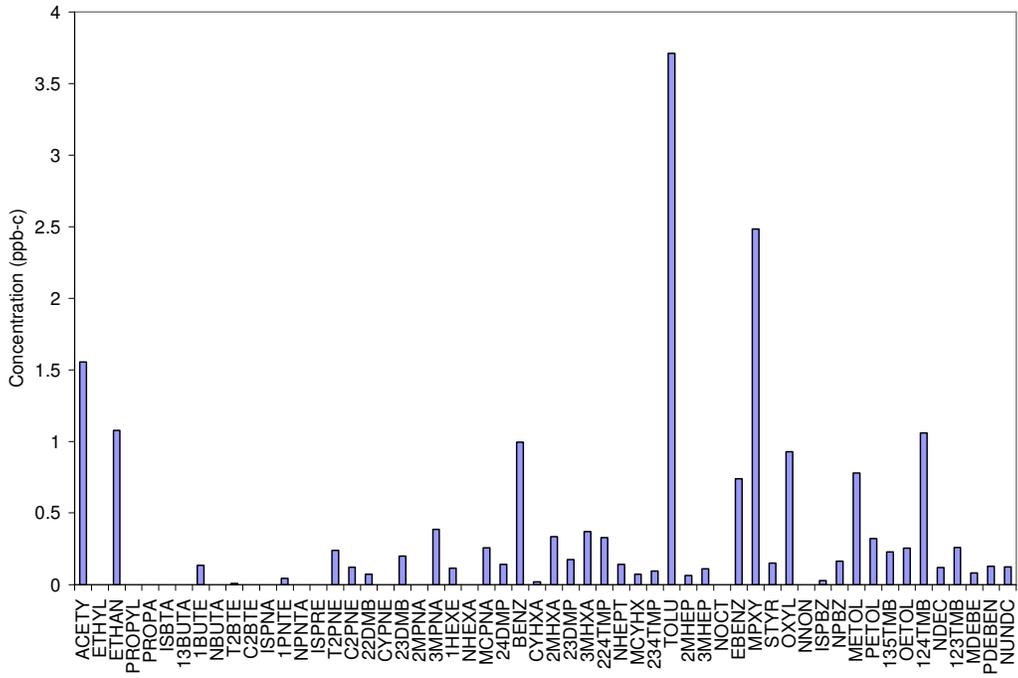


Figure 6-5. Concentration of Each Species in Source Profile 5 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

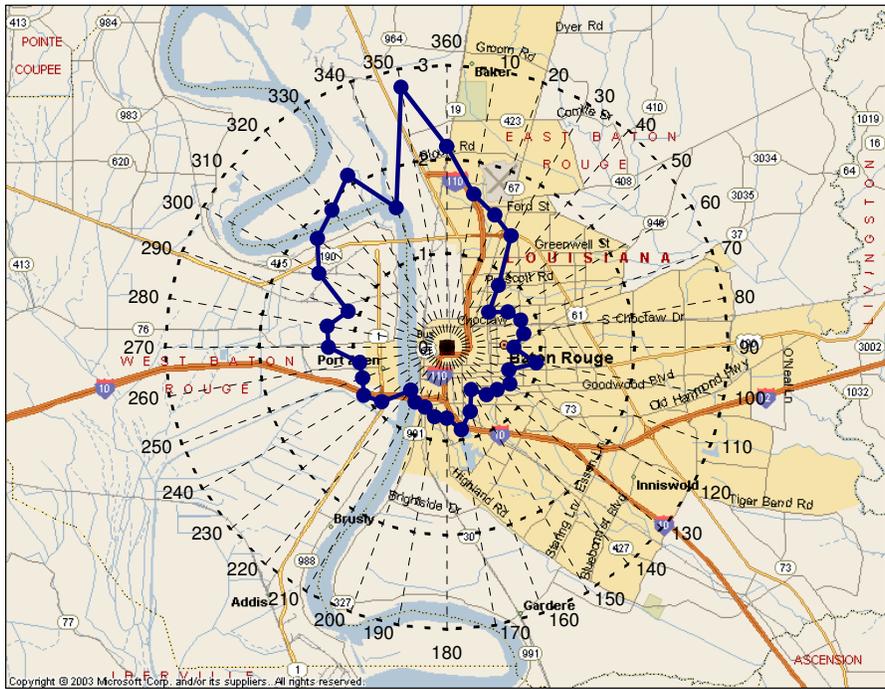
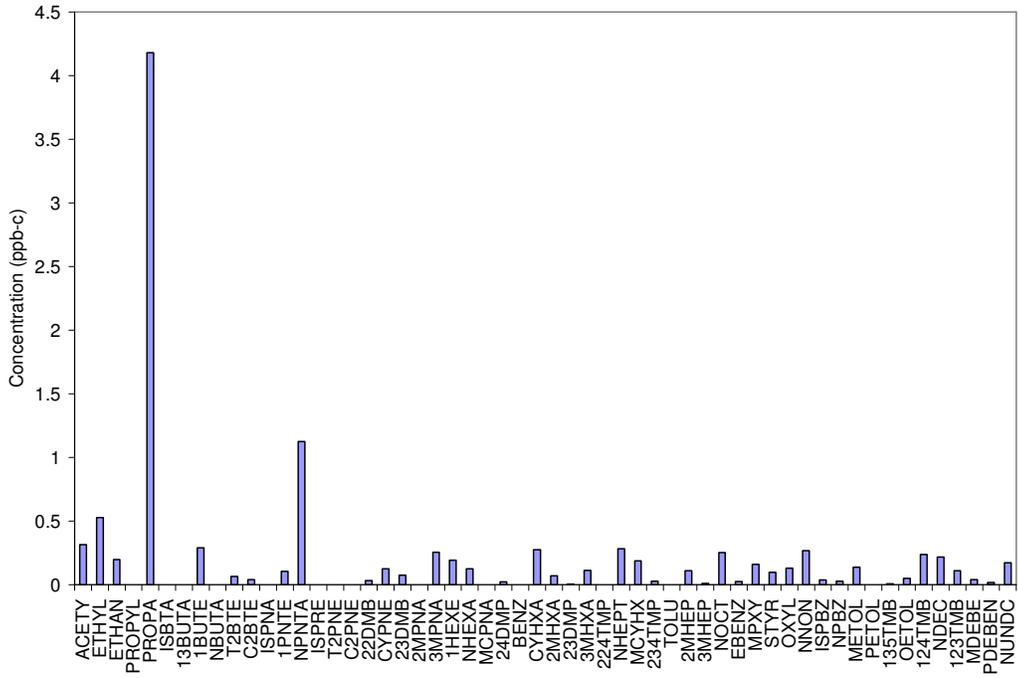


Figure 6-6. Concentration of Each Species in Source Profile 6 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

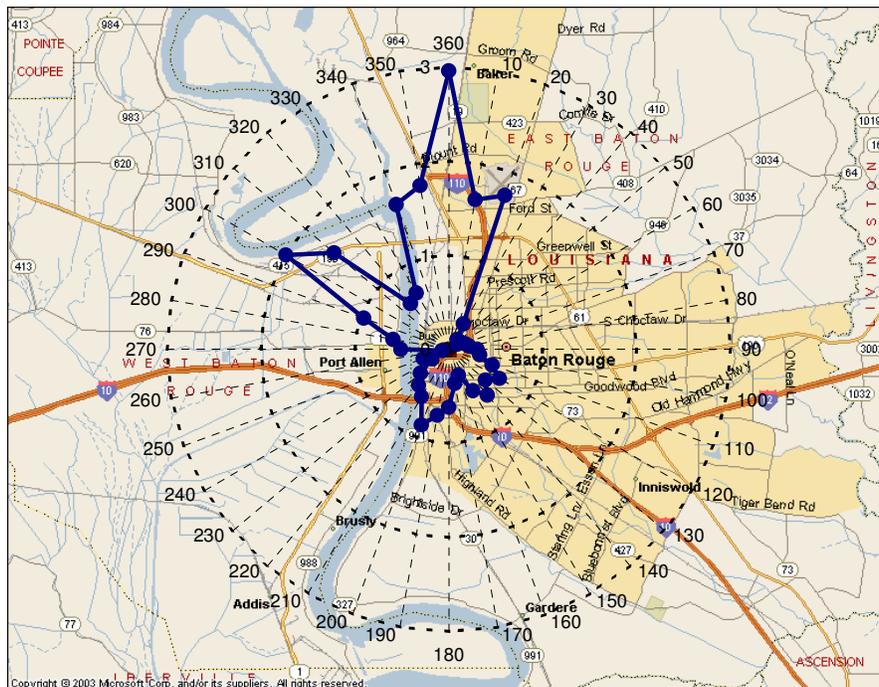
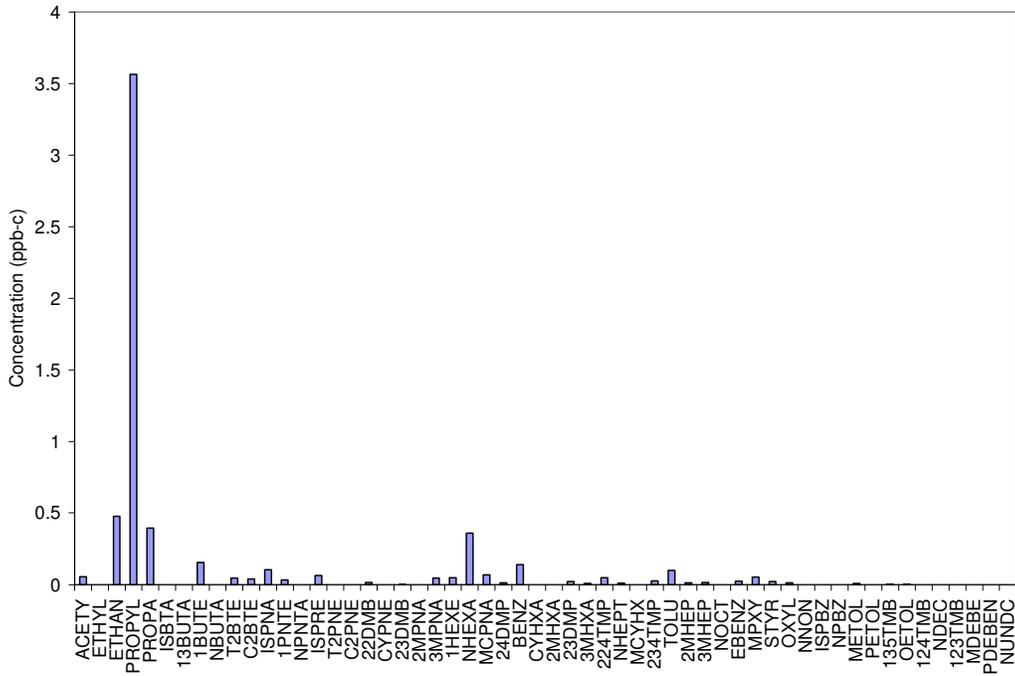
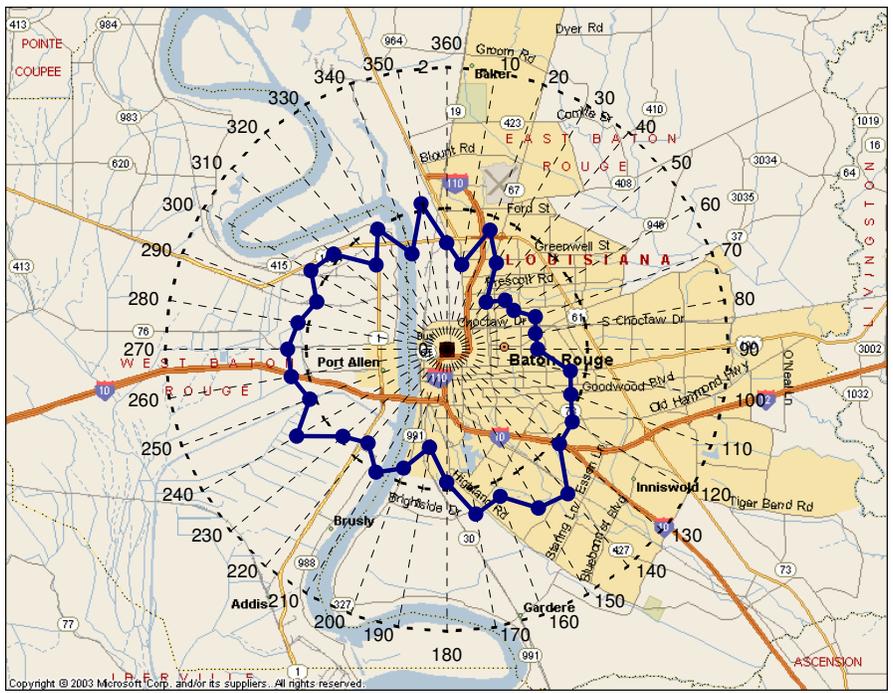
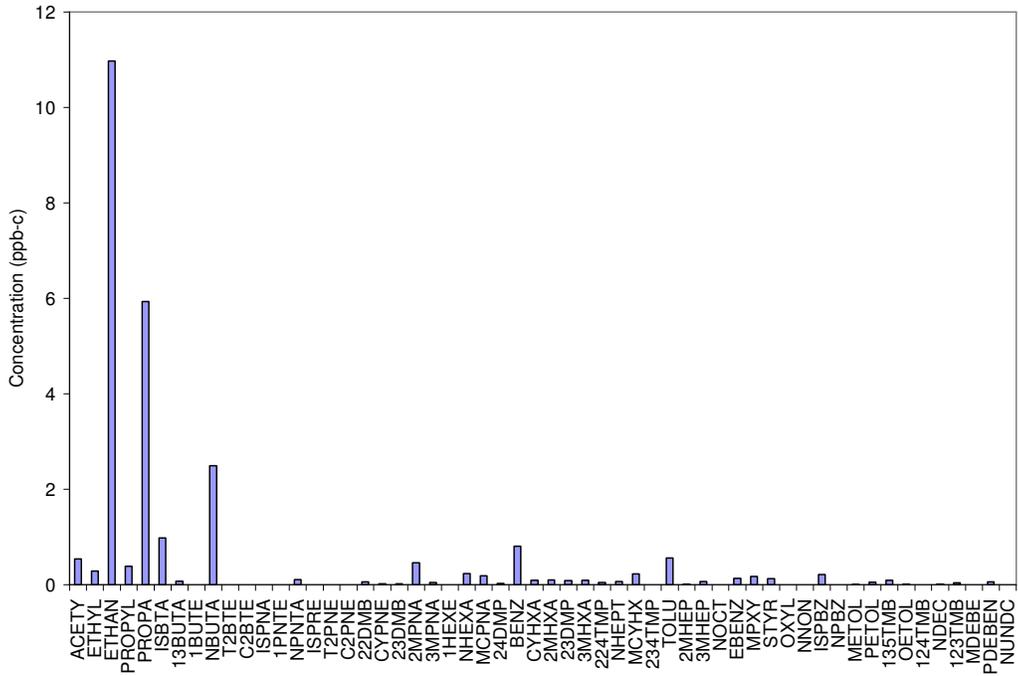


Figure 6-7. Concentration of Each Species in Source Profile 7 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)



**Figure 6-8. Concentration of Each Species in Source Profile 8 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)**

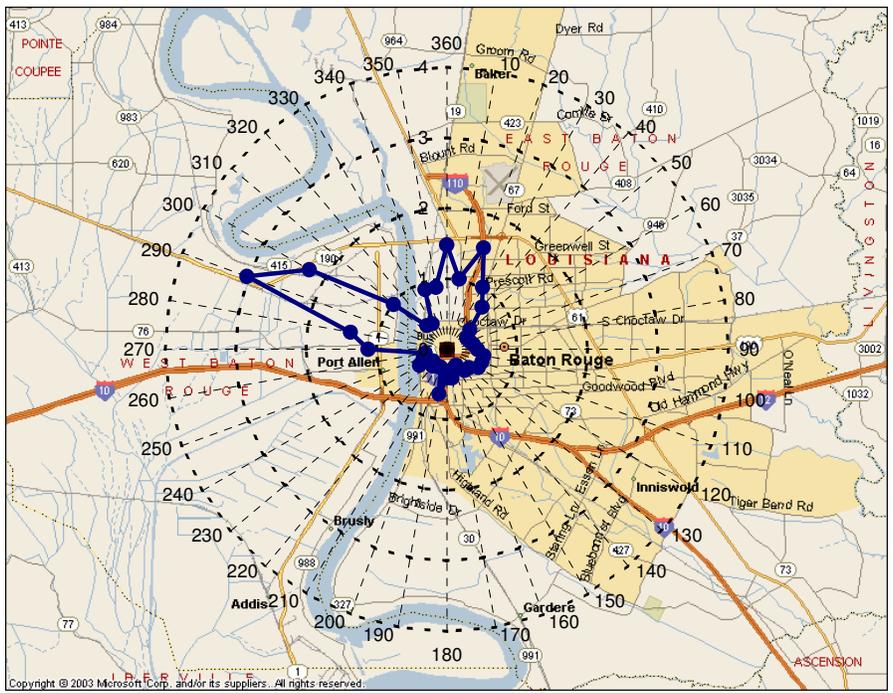
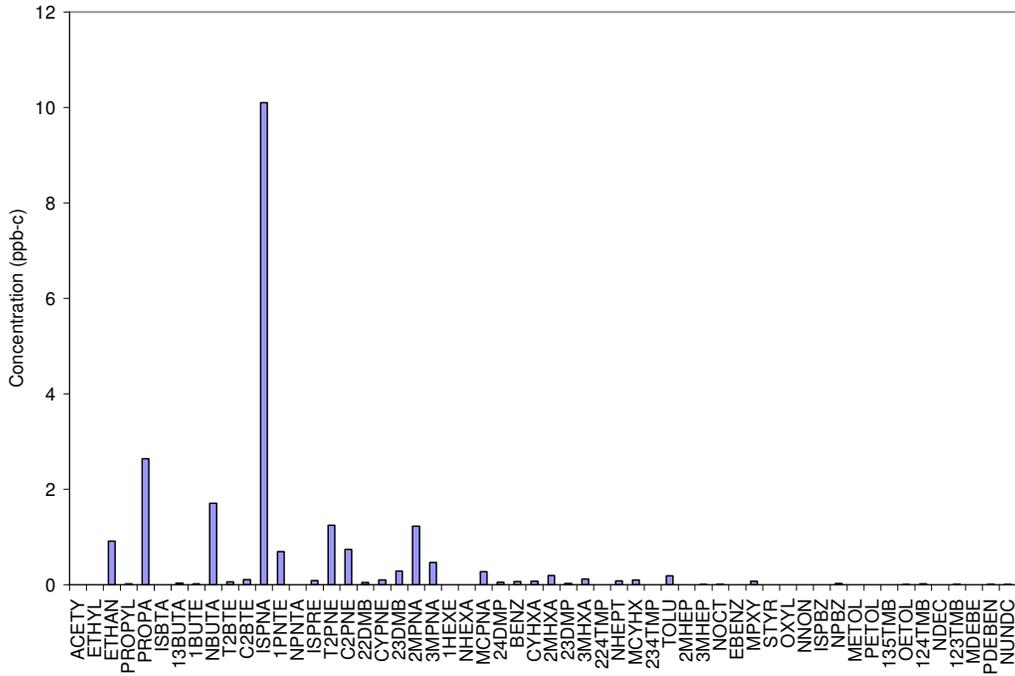


Figure 6-9. Concentration of Each Species in Source Profile 9 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

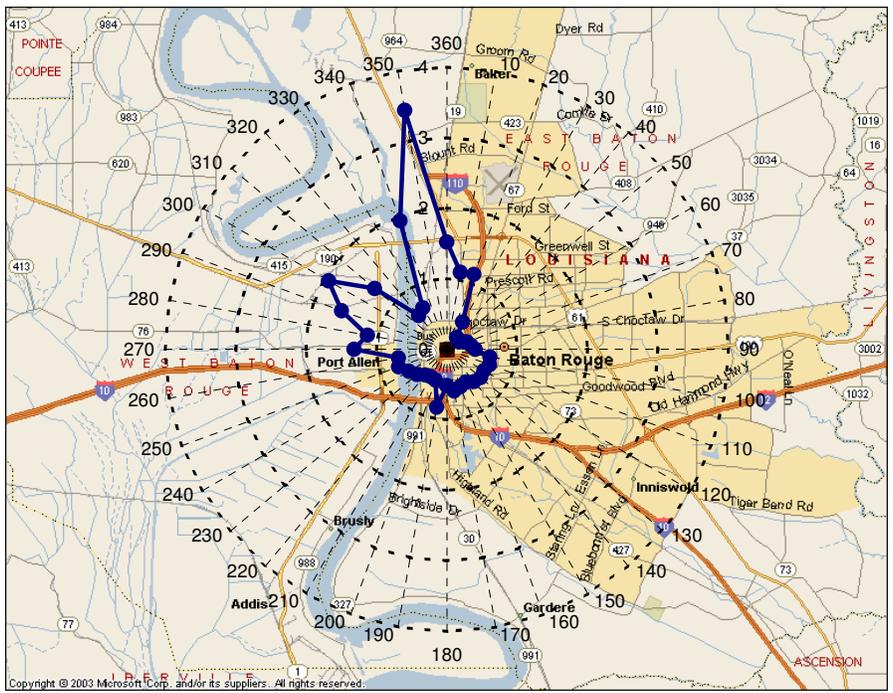
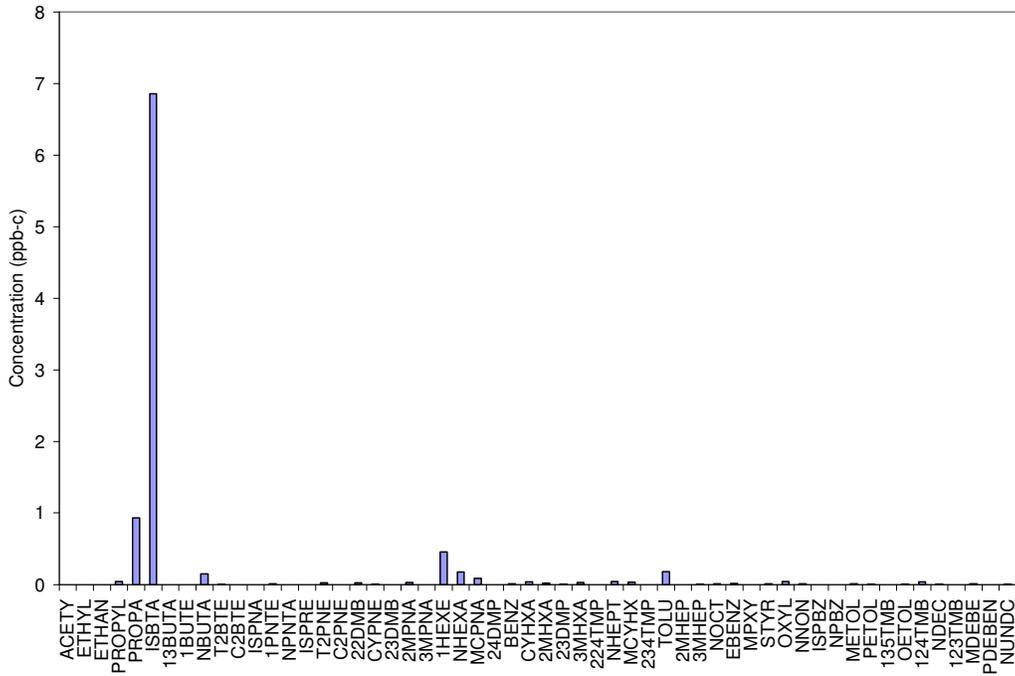


Figure 6-10. Concentration of Each Species in Source Profile 10 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

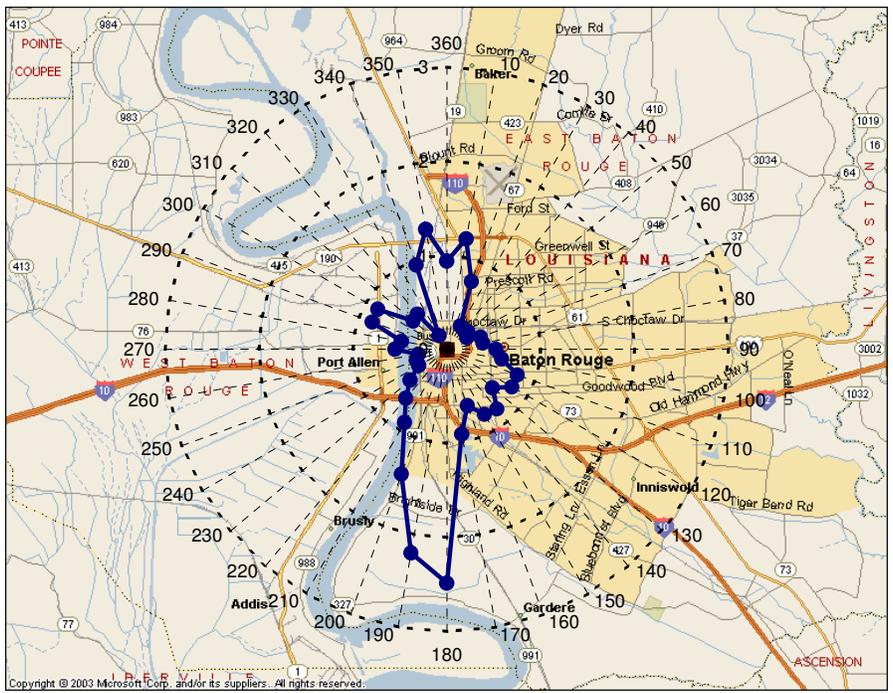
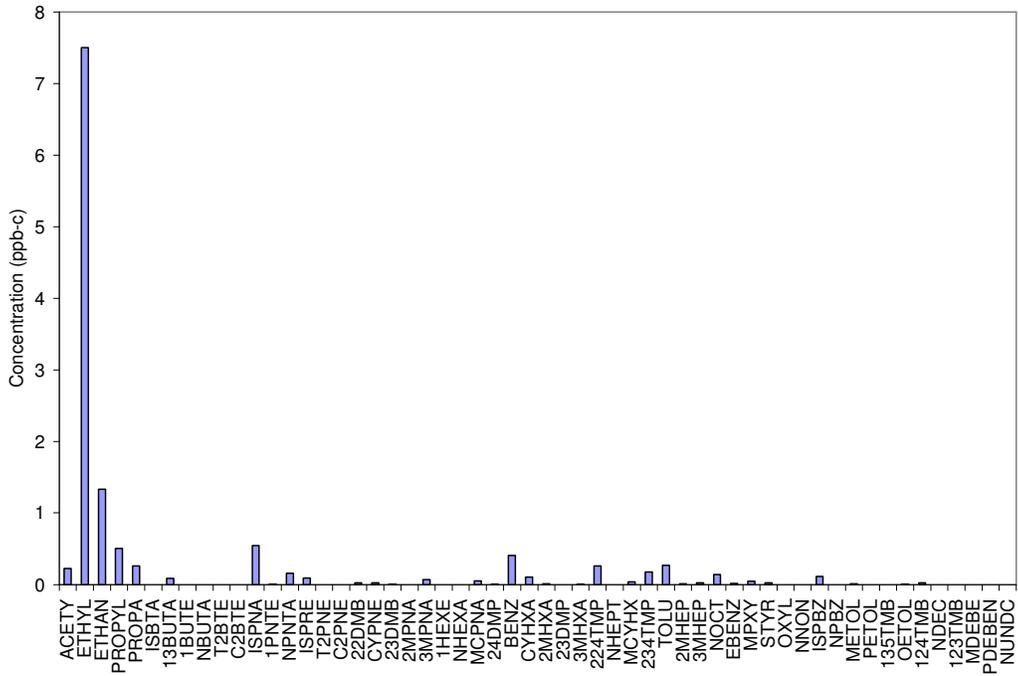


Figure 6-11. Concentration of Each Species in Source Profile 11 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)



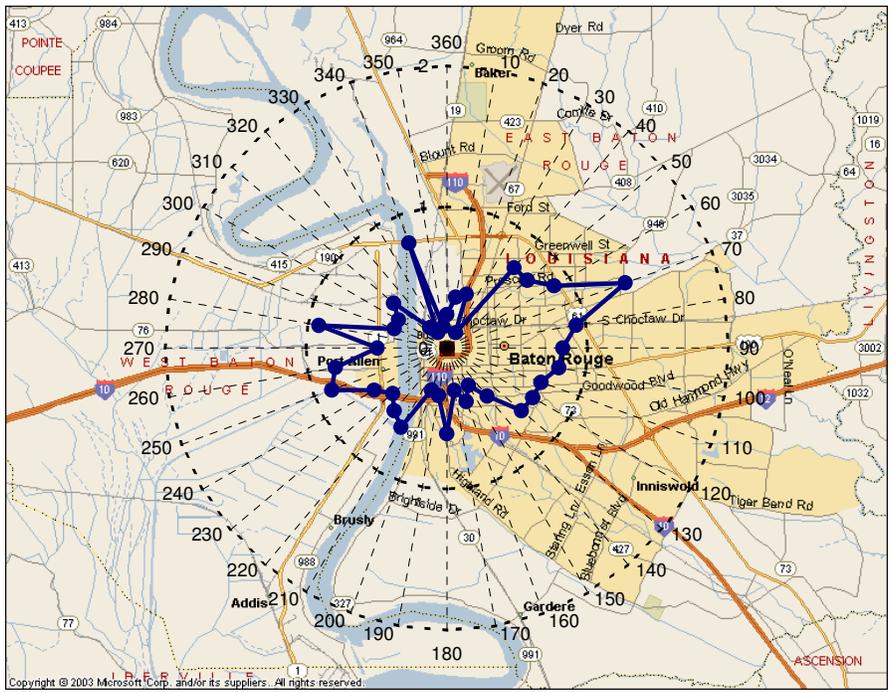
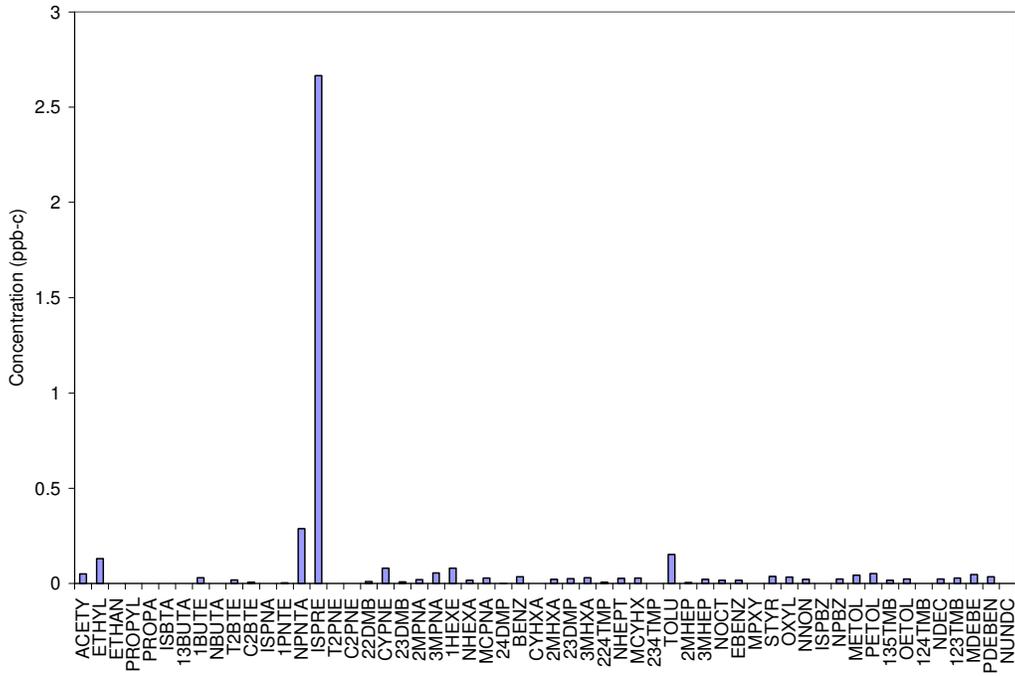


Figure 6-13. Concentration of Each Species in Source Profile 13 (Top Chart) and Relative Variation with Wind Direction (Bottom Chart)

Table 6-1 summarizes the source apportionment results for the 3-hour canister samples collected at the Capitol monitoring site, while Tables 6-2 through 6-5 summarize the results for short-term triggered samples collected at the Capitol, Port Allen, Southern, and South Scotlandville sites. Note that 17 source profiles are reported for the Southern and South Scotlandville as the maximum number of source profiles allowed by EPA PMF was needed to obtain a good fit. At all four monitoring sites, the source profiles that account for the greatest percentages of the total speciated VOC mass found in triggered canister samples are the ones that contain mostly different combinations of C2-C6 alkanes.

C4-C6 alkanes, in particular, correlated more strongly with TNMOC than did other compounds. For example, see Figure 6-14, which is a scatter plot matrix showing the relationships among ethylene, propylene, selected light alkanes, and TNMOC. Note that n-butane, n-pentane, and isopentane correlated much more strongly with TNMOC than did ethylene or propylene (the two most abundant HRVOC).

Figures 6-15 through 6-18 are time series graphs showing how the relative contributions to the total speciated VOC mass varied from sample to sample at each site (the x-axis is the LDEQ Sample ID, ordered chronologically from left to right). One might expect the relative source contributions for all source profiles to vary almost uniformly with respect to one another if the relatively high VOC levels found in the triggered samples were caused just by the meteorological stagnation and accumulation of routine emissions. Outliers, in contrast, may be the result of episodic or non-routine emissions. In Figures 6-15 through 6-18 there appears to be indications of both.

**Table 6-1. Capitol 3-Hour Source Apportionment Results**

Factor	Important Species	Total Mass Average (%)s	Most Important Wind Directions
1	Trimethylpentane, toluene, 2-methylpentane	6	N,NW,ESE
2	1,3-Butadiene	1	N,NW,ESE
3	C-6 Alkanes	6	N,NW
4	Isopentane, n-pentane, n-butane	12	N, NE, ESE, WNW
5	Toluene, xylenes, benzene, acetylene, ethane	11	ESE
6	Propane, n-pentane	6	NW, N
7	Propylene	4	WNW, N
8	Ethane, propane, n-butane	16	All (except NE)
9	Isopentane, n-butane, propane, ethane	13	WNW, NNE
10	Isobutane	6	WNW, N
11	Ethylene	8	S,N
12	n-Butane, isopentane, n-pentane, isobutane	9	NNE, WNW, N
13	Isoprene	3	E,W

**Table 6-2. Capitol Triggered Sample Source Apportionment Results**

Factor	Important Species	Total Mass Average (%)	Most Important Wind Directions
1	Toluene, xylene, trimethylpentene, acetylene	9	SE, W
2	C2-C9 alkanes, xylene,	3	WNW, NW, ESE
3	C6 Alkanes, propane, ethane, propylene	4	SE, WNW
4	C5 – C6 alkanes, benzene, toluene	17	SE, WNW
5	Isobutane	6	NE, SE, WNW
6	C2-C5 Olefins	3	NNW, N, NE
7	Ethylene, Isobutane	6	SE, W, N
8	Propylene, propane, n-butane	5	SE, WNW, N
9	N-Butane, isopentane	15	NE, SE, NW
10	1,3-Butadiene	3	WNW, N
11	Isopentane, n-butane, n-pentane	15	NE, WNW
12	Ethane, Propane, n-Butane	6	N
13	Acetylene, ethylene, n-butane, isopentane	7	All

**Table 6-3. Port Allen Triggered Sample Source Apportionment Results**

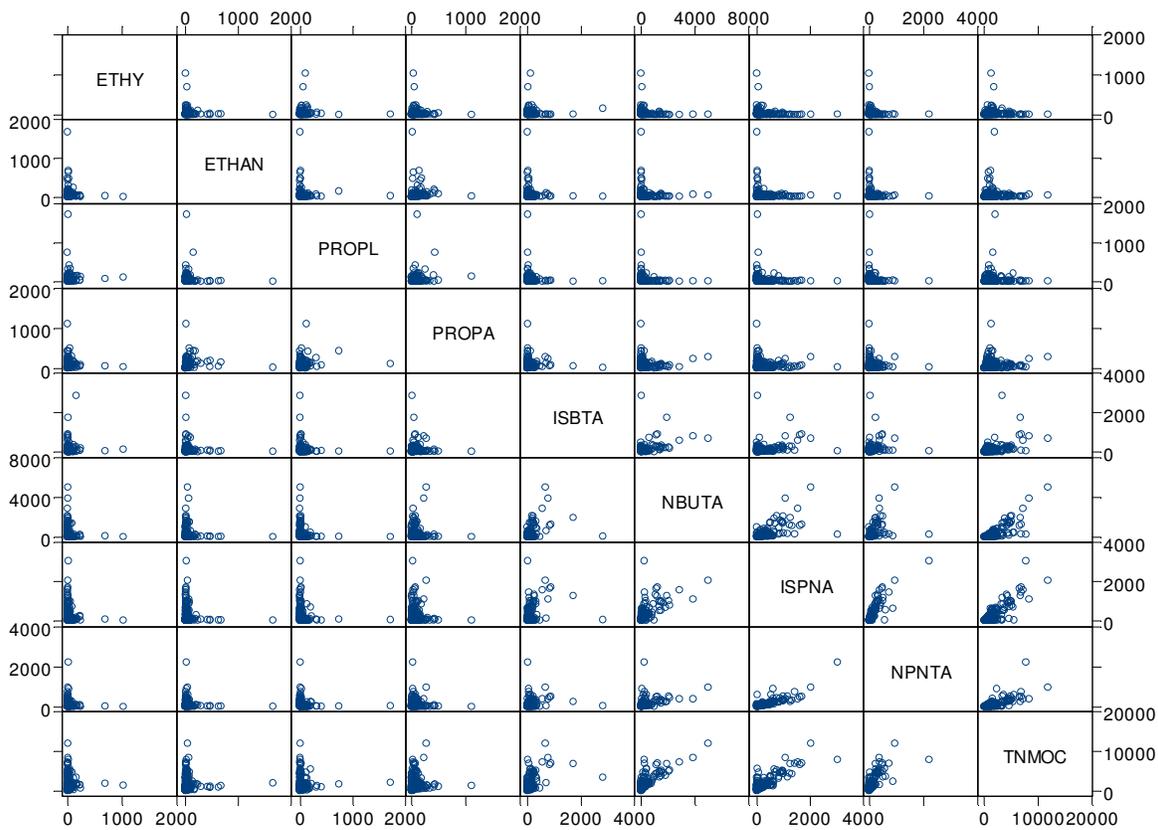
Factor	Important Species	Total Mass Average (%)	Most Important Wind Directions
1	Isopentane, n-pentane, 2-methylpentane	19	SE
2	Ethane, Propane, isobutane, n-butane	10	All
3	Isobutane, propane	5	S
4	Isopentane, n-pentane	7	SE, S
5	Toluene, xylene n-butane, acetylene, ethylene	7	N, S
6	Benzene, ethane, propane, toluene, n-pentane	4	SE, N
7	Ethane, propylene, isobutane, n-butane, trimethylbenzenes	6	S
8	C4 alkanes and olefins	6	S
9	N-Butane, isopentane	15	S, SE, NE
10	N-hexane, methylpentanes, n-butane	8	S, SE, NE
11	C2-C6 olefins, propane	8	SE, NE
12	Isopentane, n-pentane, methylcyclohexane	3	S, SE
13	Ethane, propylene, propane, 1,3-butadiene, styrene	3	SE, SW

**Table 6-4. Southern Triggered Sample Source Apportionment Results**

Factor	Important Species	Total Mass Average (%)	Most Important Wind Directions
1	Propylene, 1,3-butadiene	2	N, NE
2	Isopentane, n-pentane	10	SE
3	N-butane, benzene	2	All
4	C3-C9 alkanes, aromatics	3	All
5	Butanes, isopentane	9	NE, SE
6	C4-C6 alkanes, pentenes	9	SE, WNW
7	Butenes, i-butane, propane	3	S, NW
8	i-pentane, n-pentane, i-butane	13	S
9	Trimethylpentanes, toluene	3	NE, SE, W
10	Pentanes, n-butane, toluene	8	NE, SE, W
11	Pentanes, pentenes	9	NE, S
12	C6 Alkanes, n-butane	3	S, SE
13	Acetylene toluene, trimethylbenzenes	2	NE, S, WNW
14	Ethane, Propane	6	NE
15	Ethylene	3	All
16	Propane	6	SE, NE, WNW
17	Toluene, xylene, 2-methylpentane	4	All

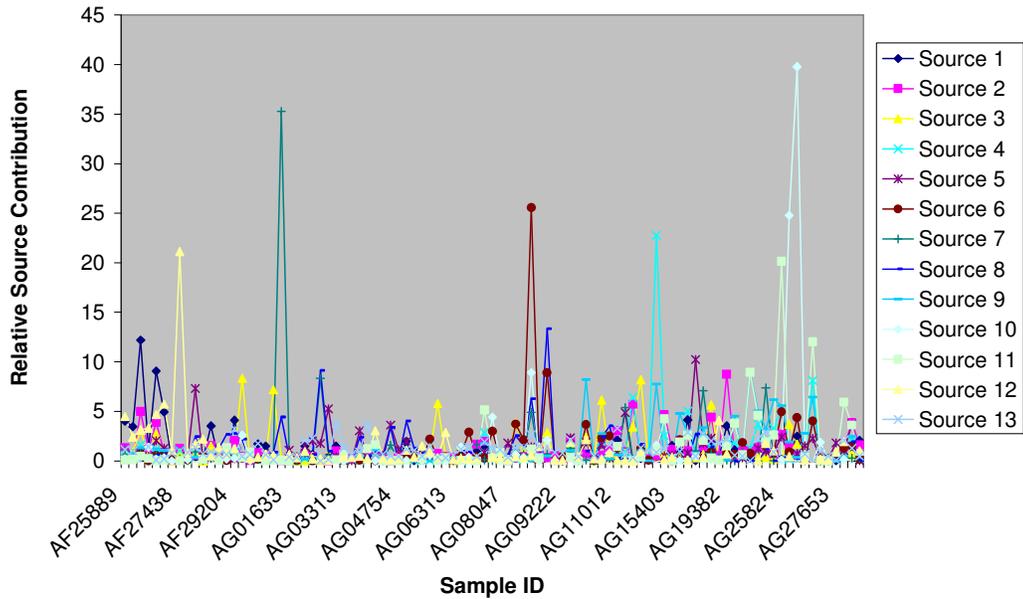
**Table 6-5. South Scotlandville Triggered Sample Results**

<b>Factor</b>	<b>Important Species</b>	<b>Total Mass Average (%)</b>	<b>Most Important Wind Directions</b>
1	N-butane, isopentane	4	S
2	Propylene, propane	7	NE, SE
3	Propane, n-pentane, trimethylbenzenes	2	NE, SE, S
4	Ethylene, isobutane, isopentane	3	S
5	1,3-butadiene	6	S
6	Trimethylpentenes, toluene, xylene	3	S
7	Toluene, xylenes, trimethylbenzenes	2	SE, S
8	i-pentane, n-pentane	16	S
9	Isopentane n-pentane, pentenes	12	S
10	Ethane, Propane	5	NE, SE
11	C2-C11 alkanes, benzene	3	S
12	Benzene, toluene, isopentane	4	SSE
13	Acetylene, toluene, xylene, n-butane	5	S
14	C6Alkanes	6	SE
15	C3-C5 Alkanes	12	S
16	C2-C8 Alkanes, benzene, toluene	3	S
17	C6 Alkanes, propane, ethane	4	S



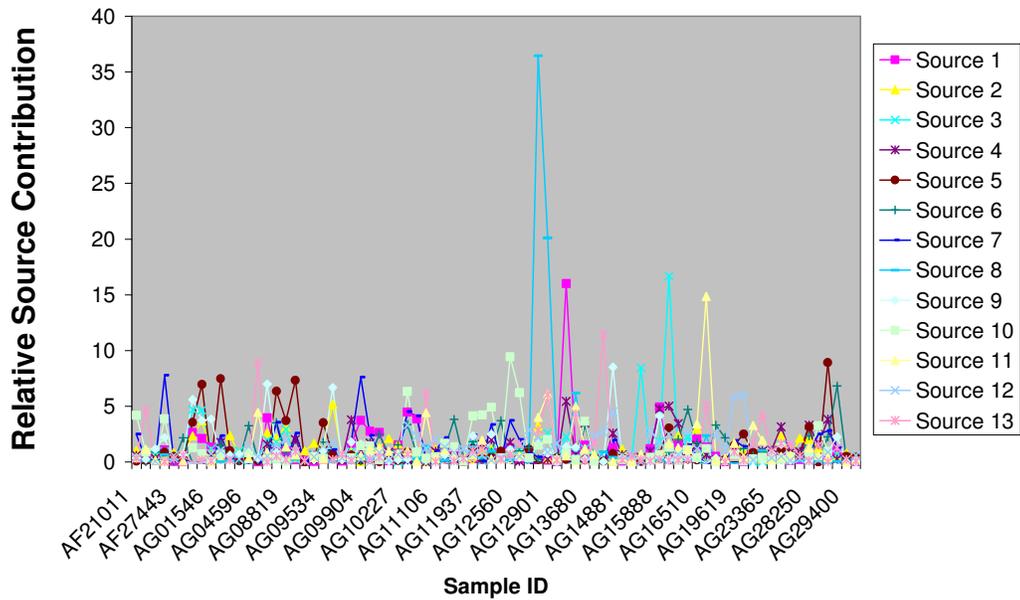
**Figure 6-14. Scatter Plot Matrix Showing the Relationships Between Ethylene, Propylene, Selected Light Alkanes, and TNMOC in Short-Term Triggered Samples Collected at the Capitol, Port Allen, Southern, and South Scotlandville Monitoring Sites.**

### Capitol Strike Samples



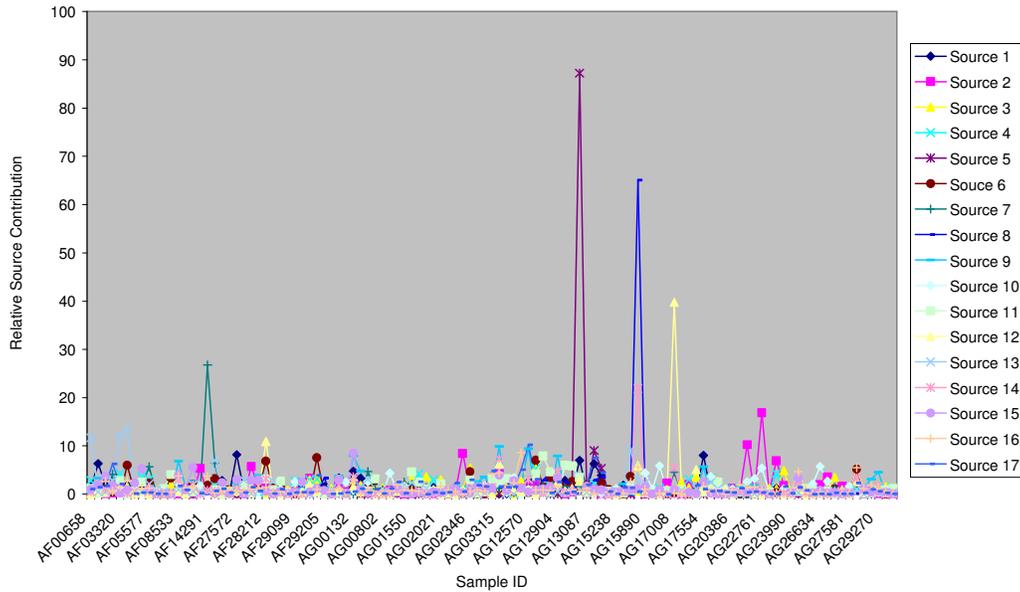
**Figure 6-15. Time Series Graph Showing Sample to Sample Variability in Source Profile Relative Contributions for Capitol Site Triggered Canister Samples**

### Port Allen Strike Samples



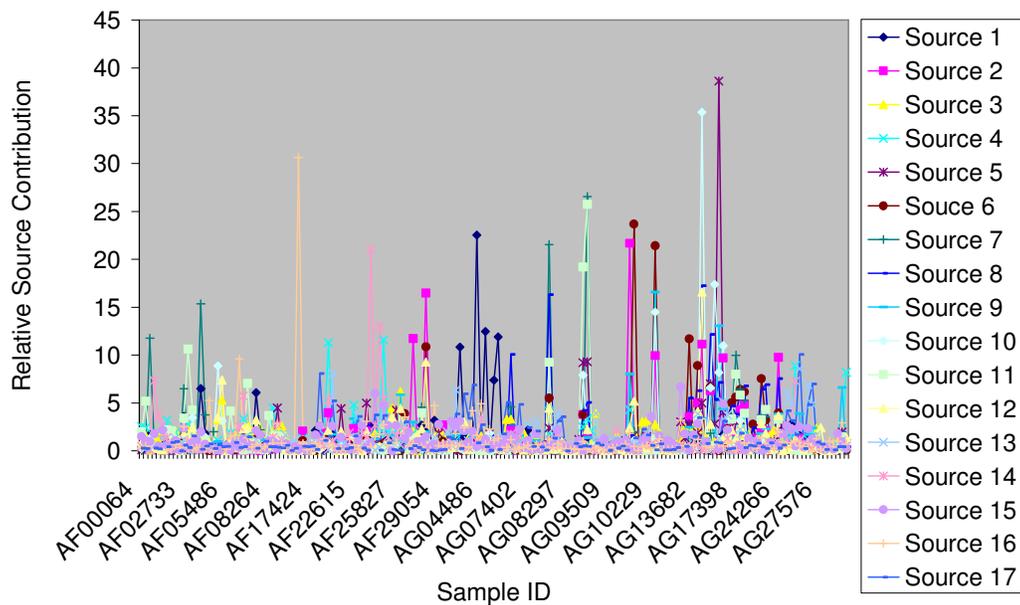
**Figure 6-16. Time Series Graph Showing Sample to Sample Variability in Source Profile Relative Contributions for Port Allen Triggered Canister Samples**

### South Scotlandville Strike Samples



**Figure 6-17. Time Series Graph Showing Sample to Sample Variability in Source Profile Relative Contributions for South Scotlandville Triggered Canister Samples**

### Southern Strike Samples



**Figure 6-18. Time Series Graph Showing Sample to Sample Variability in Source Profile Relative Contributions for Southern Triggered Canister Samples**

### 6.3 Summary of Source Apportionment Analysis

A test version of EPA PMF was used to perform exploratory source apportionment of VOC measured at the Capitol, Port Allen, Southern, and South Scotlandville monitoring sites. Thirteen unique source profiles were identified for 3-hour canister samples collected at the Capitol site between 9:00 p.m. and 9:00 a.m., with each source profile accounting, on average, for 1% to 16% of the total speciated VOC mass.

A source profile containing mostly ethane, propane, and n-butane accounted for the greatest percentage of the speciated VOC mass on average. This profile might be a natural gas source or a background source resulting from accumulation of low reactivity VOC. The relative contribution of this source to the VOC levels at the Capitol site was almost uniform with respect to wind direction.

A source profile resembling motor vehicle exhaust accounted for 11% of the total speciated VOC mass in 3-hour samples collected at the Capitol site between 9:00 p.m. and 9:00 a.m. The greatest contributions from this source were usually found when the winds were from the southeast or east-southeast, consistent with the direction of the Baton Rouge urban core with respect to the monitoring site.

Six source profiles containing different combinations of mostly C2-C6 alkanes were identified in 3-hour samples collected at the Capitol site between 9:00 p.m. and 9:00 a.m. (labeled Source Profiles 3, 4, 6, 9, 10, and 12). Together, these source profiles accounted for 52% of the total speciated VOC mass, on average. The greatest concentrations associated with these source profiles were usually associated with northerly, northwesterly or west-northwesterly winds.

Source profiles containing mostly different combinations of C2-C6 alkanes accounted for the greatest fractions of the speciated VOC in short-term triggered samples collected at the Capitol, Port Allen, Southern, and South Scotlandville monitoring sites. The levels of C4-C6 alkanes, in particular, correlated more strongly with TNMOC than did ethylene or propylene, the two most abundant HRVOC.

Sample to sample variability of the relative source profile contributions suggests both routine and non-routine emissions contribute to the VOC collected in triggered canister samples.

## 7.0 Summary of Findings and Recommendations

This report presents an analysis of ozone and ozone precursor data collected in the Baton Rouge area during 1997-2004. The report presents four separate data analysis efforts, actually, that are tied together inasmuch as they all relate to sudden ozone concentration increases and the factors that may cause them. Sudden ozone concentration increases, which are sometimes referred to as ozone spikes, are rapid increases in ozone levels observed at monitoring sites that are sometimes, but not always, followed by rapid decreases in the monitored ozone levels. Sudden ozone concentration increases are not new phenomena but their perceived importance in the study of ozone formation and control in places like Baton Rouge and Houston has increased recently due to concerns that they may be caused by sudden sharp increases in the ambient levels of highly reactive volatile organic compounds that have not been completely accounted for, traditionally, in ozone control strategy planning.

The four separate but related components of this study were designed to answer the following questions:

- What are the spatial and temporal patterns in sudden ozone concentration increases and how do they relate to ozone precursor levels and meteorological variables?
- What specific volatile organic compounds account most for the ozone formation potential in Baton Rouge and how do VOC levels and reactivity vary spatially and temporally in the Baton Rouge area?
- Can ambient measurements of highly reactivity VOC in Baton Rouge be reconciled with estimates of stationary source emissions? and
- What are the chemical composition profiles of sources that account most for the VOC mass measured in Baton Rouge ambient air?

Key findings and recommendations of this study are summarized below.

### 7.1 Sudden Ozone Concentration Increases

#### **What are the spatial and temporal patterns in sudden ozone concentration increases and how do they relate to ozone precursor levels and meteorological variables?**

From 1997 to 2004, sudden ozone concentration increases, defined as hour to hour ozone concentration increases of greater than 40 ppb, were measured at one or more monitoring sites in the Baton Rouge area on an average of about 11 days per year. The frequency of occurrence has decreased over this span, from an average of 13.5 per year during 1997-2000 to an average of 8.25 per year during 2001-2004. The Port Allen monitor recorded twice as many sudden ozone concentration increases over this entire 8-year span than any other Baton Rouge monitor. The

smallest numbers of these events were monitored at the outlying sites of Grosse Tete, Pride, French Settlement, and Dutchtown.

Sudden ozone concentration increases of greater than 40 ppb/hr occurred on about 50% of the ozone 1-hour exceedance days during 1997-2004 (although, not always at the same site where the exceedance was measured). These events occurred on about 25% of the days during 1997-2004 when 8-hour ozone levels exceeded the level of the 8-hour standard (although, not always at the same site where the highest 8-hour average concentration was measured). These findings suggest that sudden ozone concentration increases in addition to traditional urban and regional ozone formation processes are important to consider as LDEQ transitions toward implementation of the 8-hour ozone standard.

Sudden ozone concentration increases occurred most often between about 8:00 a.m. and 10:00 a.m., the same daily period when ozone levels normally increased fastest as result of normal photochemical and meteorological processes. These events tended to occur on mornings having very low wind speeds, a condition that is conducive for accumulating relatively high levels of locally emitted ozone precursors before and shortly after sunrise. Indeed, higher than average levels of NO<sub>x</sub> and VOC were usually measured on days when a sudden ozone concentration increase was measured.

At the Capitol site, the VOC species having the greatest concentration increases on mornings when ozone levels increased by greater than 30 ppb/hr were n-pentane, isopentane, C6-C11 alkanes, ethylene, and propylene. The average levels of these compounds were more than 3 times greater on mornings when ozone levels increased by greater than 30 ppb/hr compared with all mornings. At Bayou Plaquemine, the VOC species having the greatest concentration increase on mornings when ozone level increased by greater than 30 ppb/hr was ethylene. The average ethylene level was more than 3 times greater for samples collected on mornings when ozone levels increased by greater than 30 ppb/hr compared with all mornings, while the levels of propylene and other VOC ranged up to 2.3 times greater. NO<sub>x</sub> levels were increased by factor of 1.6 at both the Capitol and Bayou Plaquemine sites during the morning hours when ozone levels increased by greater than 30 ppb/hr.

Future work should consider various indicators of NO<sub>x</sub> and VOC limitation during the hours when the rates of ozone concentration increases were high to determine more precisely the relative effectiveness of controlling NO<sub>x</sub> or VOC emissions as a means for reducing sudden ozone concentration increases.

## 7.2 VOC Levels and Reactivity

### **What specific volatile organic compounds account most for the ozone formation potential in Baton Rouge, how do VOC levels and reactivity vary spatially and temporally in the Baton Rouge area, and how do they relate to sudden ozone concentration increases?**

Averaged over all Baton Rouge monitoring sites, ethylene, propylene, and isoprene accounted for greater percentages of the total VOC reactivity than any other compound that was routinely measured by LDEQ<sup>4</sup>. Together, these compounds accounted for 40% of the average total reactivity. Highly reactive VOC (defined by LDEQ as ethylene; propylene; toluene; 1,3-butadiene; all isomers of butene; and all isomers of xylene), accounted for various percentages of the total VOC reactivity that ranged from site to site between 35% and 53%. Isoprene varied the most from site to site, accounting for an average of 3% of the total reactivity at South Scotlandville and 30% of the total reactivity at Pride.

The highest VOC levels and reactivities were found, on average, in samples collected near the Mississippi River near north and central Baton Rouge. This spatial pattern closely mirrored the spatial pattern in the frequency of sudden ozone concentration occurrence. Day to day variations in VOC reactivity at each monitoring site were greater than any diurnal, weekly, annual, or long-term trends. This suggests that fluctuations in emissions or the random variations in the weather conditions that transport and disperse emissions are mostly responsible for the variability in the measured VOC levels.

VOC samples collected at the same time and place where ozone levels increased by greater than 40 ppb/hr usually had higher than average reactivity. The same was true for samples collected near back trajectory paths from where sudden ozone concentration increases were measured. No single compound or group of compounds accounted for the increased reactivity found in these samples. For the 35 samples collected at the time and place where a sudden ozone concentration increase was measured or near the back trajectory path, HRVOC accounted for 19% to 67% of the total reactivity.

Future work should attempt to address whether high reactivity typically found in VOC samples associated with sudden ozone concentration increases is just the result of accumulation of routine emissions on mornings having very low wind speeds or the result of non-routine emissions.

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<sup>4</sup> VOC reactivity is defined here in terms of the Maximum Incremental Reactivity (MIR) as estimated by Carter (2003).

### 7.3 Emissions Inventory Assessment

#### **Can ambient measurements of highly reactivity VOC in Baton Rouge be reconciled with estimates of stationary source emissions?**

The average ratios of ethylene/NO<sub>x</sub> measured during 9:00 p.m. to 5:00 a.m. ranged from four to 10 times greater at sites where 3-hour VOC samples were routinely collected than the ethylene/NO<sub>x</sub> ratio derived from estimated emissions for stationary sources located within 15 miles of the respective sites. Comparisons of VOC/NO<sub>x</sub> levels measured in ambient air with similar ratios derived from emissions estimates are sometimes used to gauge inaccuracies in VOC emissions inventories, assuming that the NO<sub>x</sub> emissions are accurately estimated, no significant measurement errors exist, and that NO<sub>x</sub> and VOC emitted from the same source or group of sources are transported and dispersed uniformly in the atmosphere with no significant losses due to deposition or chemical reactions.

Disagreements between monitored propylene/NO<sub>x</sub>; butene/NO<sub>x</sub>; and 1,3-butadiene/NO<sub>x</sub> ratios with the corresponding ratios derived from stationary source emission estimates were generally greater than the discrepancies found for the ethylene/NO<sub>x</sub> ratios. In the cases of butene/NO<sub>x</sub> and 1,3-butadiene/NO<sub>x</sub>, measurement uncertainties may have been a significant factor in the magnitude of disagreement between the monitored ratios and those derived from emissions estimates. The average levels of these compounds were near or below the method detection limits, at levels at which the signal to noise ratio of the measured values may be large.

The results of this analysis suggest that HRVOC may be under-represented in the emissions inventory but uncertainties in the analysis, itself, limit any quantitative assessments. Future work should examine the emissions inventory process from the bottom up, with particular attention to VOC speciation, to identify potential weaknesses in the traditional VOC emissions estimation approaches.

### 7.4 VOC Source Apportionment

#### **What are the chemical composition profiles of sources that account for most of the VOC mass measured in Baton Rouge ambient air?**

Source apportionment using a beta test version of the EPA PMF was used to identify the chemical composition profiles of sources that accounted most for the VOC mass measured at Baton Rouge monitoring sites. The source apportionment analysis focused on 3-hour VOC samples collected at the Capitol site and short-term samples collected at the Capitol, Port Allen, South Scotlandville, and Southern sites that were triggered by high levels of total nonmethane organic compounds. In this way, the source apportionment analysis focused on the monitoring sites where the highest VOC levels were typically measured.

Thirteen source profiles were identified for 3-hour VOC samples collected at the Capitol site having start times ranging from 9:00 p.m. to 6:00 a.m. Six source profiles containing different combinations of mostly C3-C6 alkanes accounted for 52% of the total speciated VOC mass, on average. The greatest concentrations associated with these source profiles were usually associated with northerly, northwesterly or west-northwesterly winds. Other source profiles that accounted for comparatively high percentages of the total VOC mass included a background accumulation source profile containing mostly ethane, propane, and n-butane; a motor vehicle source profile containing toluene; benzene; xylene; acetylene; and 1,2,4-trimethylbenzene; and an ethylene source profile. These source profiles accounted for 16%, 11%, and 8%, respectively of the total VOC mass. Similar source profiles were identified for the triggered samples collected at each monitoring site, with source profiles containing C3-C6 alkanes accounting for greater than 50 of the total speciated VOC mass at each site.

A cursory examination of sample to sample variability in the source profile contributions to total VOC mass in the triggered samples showed that at times individual source profile contributions varied independently with respect to one another while at other times the contributions from all source profiles seemed to vary uniformly. This suggests that episodic emissions from individual sources, in addition to routine emissions, account at times for the levels of VOC measured in the triggered VOC samples.

Future work should investigate the sensitivity of the source apportionment results to different model inputs. Performing source apportionment on a reactivity basis would also be helpful toward identifying the source types that have the greatest potential to impact ozone formation. A more comprehensive analysis of source contribution variability is also needed to better address the relative importance of routine and episodic emissions.

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