

CHAPTER 4: DATA ANALYSIS

Ozone data analysis entails examining, describing, and analyzing ambient air quality data and other information to develop an understanding of ozone formation, transport, and deposition. The results of these analyses supplement the photochemical and meteorological modeling and enhance the decision making process for clean air strategy selection. The following sections summarize the results and conclusions of several analyses that support photochemical modeling efforts. Detailed information on these topics is provided in the appendices, as noted in the text.

Annually, the HGB area has more ozone exceedances than any other area in Texas. Ozone formation in this area is complicated due to the variety and magnitude of industrial emissions, the large population, and the complexity of meteorological conditions. Ozone data analysis for the HGB area has focused on the underlying components of ozone formation, and the relationships among these components. Areas of investigation include:

- Levels and trends in ozone concentrations;
- Effects of wind patterns, such as wind speed and the land/sea breeze flow reversal, on ozone levels;
- Speciated VOC contribution to total reactivity and relationship to ozone; and
- Sources of emissions that contribute significantly to ozone formation.

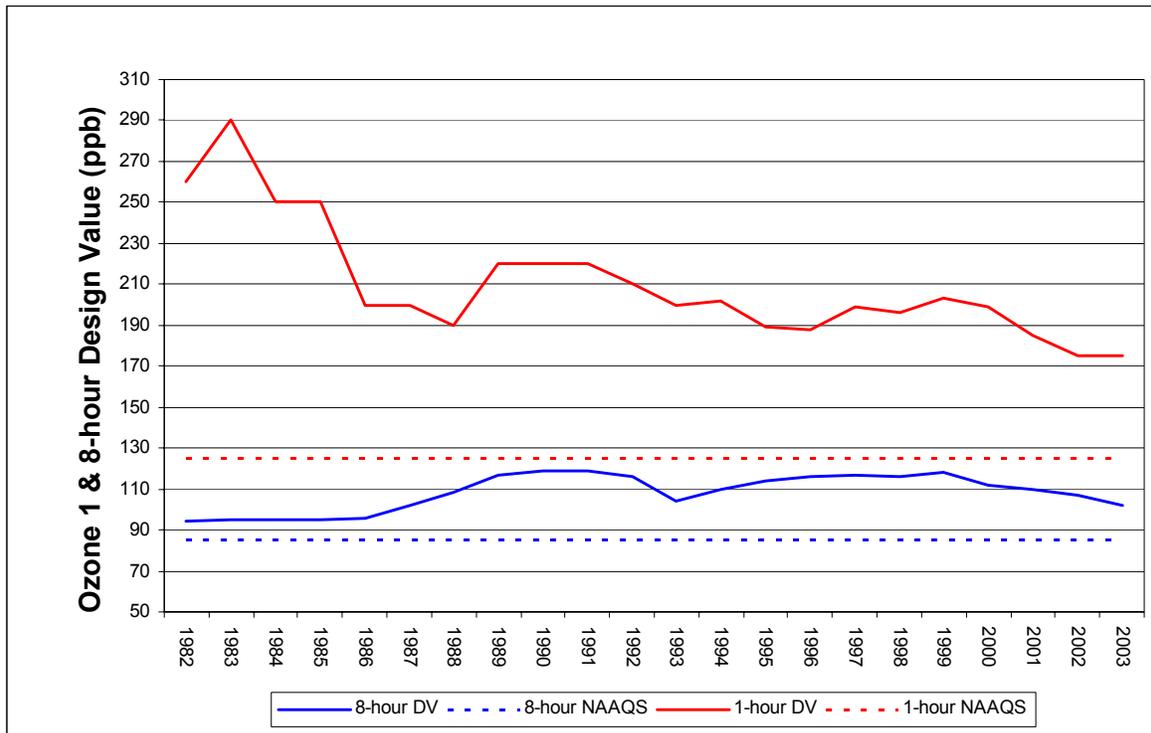
4.1 CHARACTERIZATION OF OZONE EXCEEDANCES IN THE HGB AREA

4.1.1 Ozone Design Value Trends

Trends in the HGB area 1-hour design value for ozone have been studied closely for years. Figure 4.1 shows that 1-hour ozone design values for the HGB area have decreased significantly from 260 ppb in 1982 to 175 ppb in 2003. While the area's design value dropped significantly during the 1980s, it flattened out during the 1990s, hovering around 200 ppb. Starting in the late 1990s, however, design values have again resumed their downward trend and are at the lowest values seen in at least the last twenty years. As mentioned in the previous chapter, the design values are projected to continue this downward trend as additional emission reductions occur.

While there have been improvements in the 1-hour ozone design value, the 8-hour ozone design value trend has remained fairly constant in the HGB area for roughly the last 20 years. However, from 1999 to 2003, the 8-hour ozone design value also experienced a downward trend. With the shift to the 8-hour standards, ozone data analysis projects have shifted to focus on the underlying components of ozone formation over the longer time period.

Figure 4.1-1: Ozone 1-Hour and 8-Hour Design Values for HGB (1982-2003)



4.1.2 Alternative Design Value Calculation

Traditional photochemical modeling can adequately replicate the routine emissions of a large industrial base located in an urban core with mobile source emissions typical of a large city. Traditional modeling cannot, however, replicate ozone produced by the sudden sharp increases in HRVOC emissions that occur in the HGB area. This technical deficiency provides an explanation for why the model's peak simulated ozone concentrations were all below the HGB area's design value in 2000. The actual design value calculated for the years 1999-2001 was 182 ppb, while Base 5b simulated peak ozone concentrations below 160 ppb on every day but August 31. The influence from short-term releases must be removed from the area's design value to determine whether the model is adequately simulating the routine urban ozone formation in the base case. The model would perform adequately if the simulated ozone peak concentrations were consistent with this "alternate" design value.

The TCEQ approximated removing the influence of short-term releases using a method developed by Blanchard (2001). The Blanchard method calculates a design value that excludes the effects of sudden large increases in observed ozone concentrations. Blanchard used a threshold of a 40 ppb rise in ozone concentration in one hour to distinguish sudden rises from the more typical case where ozone increases more gradually.

To apply Blanchard's technique to the year 2000, TCEQ used 1-hour average ozone data for the Houston region from EPA's, Aerometric Information Retrieval System (AIRS) from years of 1999 through 2001. The hour-to-hour difference was calculated for each of the 16 ozone monitors in Houston. If the

difference for any monitor for a given day was greater than 40 ppb, the day was determined to be characterized by a sudden ozone concentration increase (SOCI)¹.

Once a day has been identified to contain a SOCI, that day was removed from the calculation of the design value. The "alternate" (non-SOCI) design value was determined by removing all days with identified SOCIs and recalculating the design value. The alternate design value so calculated is 144 ppb. Base 5b includes seven days with modeled peak ozone > 144 ppb, so the modeled peaks in fact represent very well the (non-SOCI) design value. If SOCIs result primarily from emission events², then it follows that the model is over-predicting the "routine" part of the ozone on these days, so the future concentrations would actually be lower than reported for CS-08.

4.1.3 Characterization of Ozone Exceedances

The TCEQ analyzed ozone levels for temporal and spatial patterns. For example, efforts have been made to determine if high ozone levels vary predictably by day of the week or time of day. Other efforts have sought to determine the pattern of movement of high ozone levels through the area.

Analysis shows that ozone exceedances occur primarily from March through October in the HGB area and typically peak in late August and early September. Exceedances may even occur during the winter months. An analysis of days of the week characterized by high ozone concentrations shows that there is no clear difference between week days and weekend days, indicating that the predominant sources of ozone precursors do not vary appreciably by day of the week. This observation leads to the conclusion that industrial sources are the primary anthropogenic contributors to ozone exceedances in the region. A control strategy targeting industrial emissions is therefore indicated.

Appendix AA presents the results of a study that looked at the time of day that maximum ozone concentrations were measured from 1998 to 2002. The study concluded that daily maximum ozone occurred earlier for non-ozone exceedance days than for ozone exceedance days (ozone peaked between 11:30 and 13:00 Local Standard Time (LST) vs. 13:00 to 14:30 LST, respectively) and might have been due to differences in daily total amount and reactivity of emissions. The location where the earliest daily peak ozone occurred differed by the proximity to the city core. The closer to the southeast of the city core, the earlier the daily peak ozone occurred. Because major industrial centers are located in these districts, the occurrence of these early peaks suggests that they are related to industrial emissions.

Data analysis also indicates that ozone appears to traverse across the HGB domain, and higher ozone levels are observed briefly as plumes pass each monitoring site. The movement of ozone through the HGB area can be explained further by wind patterns in the area.

4.2 EFFECTS OF WIND PATTERNS ON OZONE LEVELS

Numerous studies have examined the effects of wind patterns on ozone levels. During the summer, high pressure typically persists over the southern U.S., often leading to stagnant conditions and weak pressure gradients in southeast Texas. The HGB area has persistent sea breezes along the coastline, bay breezes

¹Blanchard called these sudden ozone increases Transient High Ozone Events (THOEs), but this label is somewhat misleading since some of the events persist for several hours, hence are not "transient."

²Sudden ozone increases have been observed in many cases to result from identified emission events, although there may be cases where rapid ozone rise is triggered by meteorological phenomena.

near Galveston Bay, land-sea breeze flow reversals, and a shoreline convergence zone that may move inland.

Previous data analysis studies, documented as part of the December 13, 2002, HGB SIP Conceptual Model, indicated that for high ozone days, typically the wind direction rotates continuously during a 24-hour period. Winds blow from the southwest around midnight, then gradually shift to northwest and northeast during the morning hours. By noon, winds are from the east, followed by southeasterly flow in the early afternoon. After sunset the winds shift to the south and west, and the pattern may repeat the next day.

On nonexceedance days, the 24-hour winds show a much different pattern. The prevailing wind direction is, on average, from the east to southeast. A persistent sea breeze normally blows from the southeast that results in ventilation and transport of pollutants downwind, rather than concentration and recirculation of pollutants in the Houston area as often occurs on high ozone days.

A more recent data analysis study (Appendix BB) of the effects of wind patterns and degree of flow reversal on ozone levels looked at multiple factors and their importance as predictor variables of peak ozone concentration in the HGB area. This study found that average morning wind speed alone explains about 35 percent of the variance in peak hourly ozone. Hourly peak ozone was higher when wind speeds were lower because the limited ventilation allows ozone precursors to accumulate through the morning.

This study also found that average morning wind speed, coupled with maximum hourly nitrogen dioxide concentrations and solar radiation, explains over 65 percent of the variance in peak 1-hour ozone on all days, but only 17 percent of the variance on exceedance days. Thus, these three factors were not good predictors of ozone exceedance days, and further work would have to be done to identify factors that are good predictors.

Researchers developed new techniques to explore the effects of flow reversal on ozone. Hourly wind data were analyzed using the new methods, defined as the extent of wind rotation and the wind distance ratio (the extent of ventilation). Neither of these factors were significant in predicting ozone in this study. (See Appendix BB for more detail.) In this same study, another method was developed to examine the hours when winds were most disorganized across the domain (blowing from the most different directions). Data for exceedance versus nonexceedance days were grouped by the first hour of the most disorganized winds. The hour of the most disorganized winds, overall, was a good predictor of ozone, but not on exceedance days. Thus, these factors were not good predictors of ozone exceedance days, and further work would have to be done to identify factors that are good predictors.

The analyses described in this section highlight the challenges that have historically faced TCEQ and other researchers when trying to characterize the HGB area's ozone problems. Meteorological factors which are clearly important in the overall makeup of the region's air quality often do not correlate well with observed ozone concentrations or the occurrence of ozone exceedances. Two primary reasons for this difficulty are: first, the atmospheric dynamics and chemistry are highly non-linear, and second, the inter-relationships among a multitude of factors can obscure individual factors' contributions to ozone. The addition of large emission events, possibly un- or under-reported, can further obfuscate relationships between meteorological variables and ozone concentrations.

Thus, standard linear statistical inference techniques are not adequate when trying to characterize ozone formation in a system as complex as Southeast Texas. Photochemical grid models are much better suited to this task, since they internally characterize the physics and chemistry which occurs in the atmosphere.

Field studies such as the Coastal Oxidant Assessment for Southeast Texas (COAST), Texas 2000 Air Quality Study (TexAQS 2000), and the upcoming TexAQS II, are critically important to improving the understanding of ozone formation in Texas and in translating this understanding into accurate model characterizations.

4.3 CONTRIBUTION OF SPECIATED VOCs

The most recent data analysis work has focused on VOCs and their contribution to total reactivity and ozone formation. Projects completed have examined the following: speciated VOC reactivity using multiple data sources; contributions of VOCs and carbonyls to reactivity; contribution of less reactive VOCs to reactivity; and relationship of speciated VOCs to ozone exceedances.

4.3.1 Background Information

TexAQS was a comprehensive research project conducted in August and September 2000 involving more than 40 research organizations and over 200 scientists, studied ozone air pollution in the HGB area and east Texas region. Using TexAQS data, both the TCEQ and outside entities have documented the importance of HRVOCs in the rapid and robust ozone formation that occurs in HGB (TCEQ, 2002 and, for example, Daum et al., 2003, Kleinman et al., 2002, Ryerson et al., 2003). Much of this work has clarified the role that reactive olefins, especially ethylene and propylene, play in this phenomenon. Work has also focused on characterizing the underestimation of olefin emissions in the emissions inventories.

(TexAQS) indicated that ambient concentrations of NO_x and VOC were not consistent with the industrial emission estimates. Specifically, the ratios of VOC to NO_x reported in emission inventories were inconsistent with the ambient ratios of VOC to NO_x measured by TexAQS. Because of the greater certainty associated with NO_x emissions estimates, it was concluded that industrial VOCs, specifically light olefins, were likely underestimated in emissions inventories (Ryerson et al., 2003). This study also found that the high formation rates and efficiencies in industrial plumes are directly attributable to these reactive species.

Aircraft data collected during TexAQS 2000 were also used to determine that ozone is formed more rapidly and more efficiently in plumes from industrial facilities in the Houston area than in other cities studied in the U.S. (Kleinman et al., 2002).

A study conducted by Sonoma Technology (Brown and Main, 2002) of ambient monitoring data found that high hydrocarbon concentrations are a routine occurrence in Houston, and that generally, hydrocarbon composition in Houston is dominated by industrial emissions³.

The TCEQ conducted subsequent analyses (Estes et al., 2002) on 1-hour ambient VOC measurements. Using the maximum incremental reactivity (MIR) and hydroxyl (OH) reactivity scales, several classes of VOCs were identified as important contributors to total reactivity in the region. Four of these, ethylene, propylene, 1,3-butadiene, and butenes, were included in the HRVOC controls in the December 2002 SIP revision. Throughout the remainder of this section, the term "HRVOC" is used to refer to this specific set of compounds.

More in-depth analyses have been conducted on speciated VOCs, and the results from these recent studies are outlined below.

³A notable exception is August 31, 2000, when biogenically-generated hydrocarbons appear to play a dominant role.

4.3.2 Analysis of VOC Reactivity Using Multiple Data Sources

Multiple corroborating VOC data sources were used for the analyses outlined in this section and sources for each project are noted. Surface level VOC data, collected at the TCEQ monitoring stations, includes automated gas chromatograph (Auto-GC) data (40-minute samples collected hourly), and canister data (collected in one-, three-, or 24-hour samples.) Several aircraft also collected speciated VOC data, primarily using canisters, during the TexAQS. In June 2003, seven new industry-sponsored Auto-GCs were brought on line. These monitors measure speciated VOCs and are located close to clusters of point sources, such as the Ship Channel area.

VOC reactivity was determined using a metric called the MIR scale. The MIR scale is based on research by Carter and others at University of California at Riverside, who sought a method of quantifying the reactivity differences among VOCs (Carter, 1995; Carter et al., 1995). The MIR is a measure of the number of grams of ozone that can be formed from one gram of the subject VOC, under ideal conditions. To determine the relative importance of different VOCs from a reactivity perspective, reactivity-weighted concentrations of specific compounds or groups of compounds were calculated. Reactivity-weighted concentrations take into consideration the substances' capability to form ozone as well as their measured ambient concentrations.

The 55 VOCs that the Auto-GCs measure were grouped by chemical structure to facilitate analysis. The reactivity-weighted concentration of each VOC group was calculated by summing the reactivity-weighted concentrations of each compound in the group. Twelve highly reactive compounds were identified as significant contributors to total air mass reactivity. The bulk of the reactivity among these compounds is accounted for by the HRVOCs.

In addition to analyzing the 1-hour Auto-GC data, 24-hour composite canister data were also analyzed (Appendix CC). The analysis of the 24-hour canister data produced results similar to the 1-hour analysis. For 13 of the 17 sites, either ethylene or propylene accounted for the highest percentage of total reactivity for high reactivity days. For the other four sites, butenes accounted for the highest percentage of total reactivity. Wind direction analysis indicated that emissions from the Ship Channel contributed to high ethylene and propylene concentrations.

Another study (summarized in Appendix DD) analyzed data from seven new industry-sponsored Auto-GCs, HRM #3 (C603), Wallisville (C617), Danciger - Sweeney (C618), Mustang Bayou (C619), Texas City (C620), Lynchburg Ferry (C1015) and Lake Jackson (C1016). Data from three nearby TCEQ monitors, Channelview (C15), Deer Park (C35), and Clinton (C403), were also included in this study. (See Figure 4.3-1, *Ambient Air Monitoring Sites Used in Selected Data Analysis Studies*, for location of these monitors.) Data from these monitors becomes available for analysis before it is validated; validation typically takes at least two more months after data become available. Thus, a disclaimer is always included when preliminary results of data analyses are presented that results may change once additional data is validated.

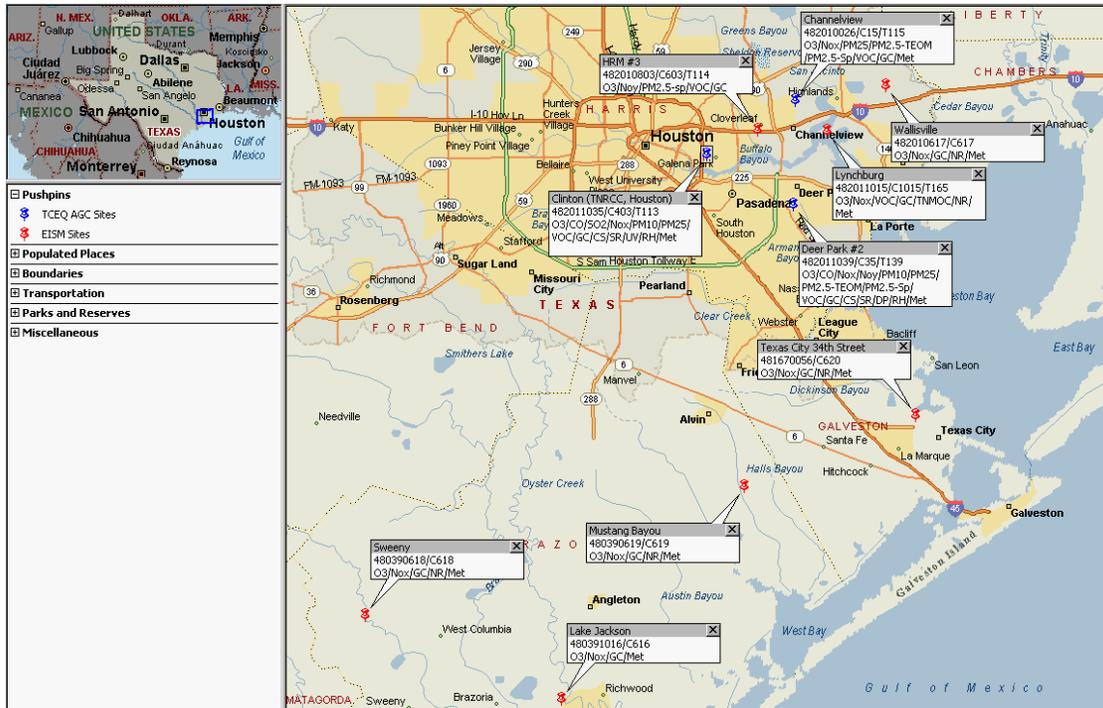


Figure 4.3-1: Ambient Air Monitoring Sites Used in Selected Data Analysis Studies

Results of this study indicate that, in general, ethylene and/or propylene were the biggest contributors to MIR reactivity. At four of the monitors, Lynchburg, Wallisville, Lake Jackson, and Danciger, ethylene and propylene contributed much more to total reactivity during high-reactivity hours than when all hours were examined. At three other monitors, HRM #3, Clinton, and Channelview, the VOC distribution during high-reactivity hours was very similar to the distribution when all hours were examined. The Mustang Bayou monitor showed greater contribution by alkanes during high reactivity hours than when all hours were examined. These new monitors confirm earlier analyses suggesting that VOC reactivity in the Ship Channel is very high. There was also a substantial difference between airmass reactivity in the Ship Channel versus the three Brazoria County monitors⁴.

The monitoring data also suggest that the Lynchburg monitor may be unique in that it measures VOC concentrations that well exceed those of all other monitors. Additional analyses for this site found that high propylene concentrations occur regularly at this monitor.

Additional VOC reactivity analyses on this new industry sponsored monitoring data will be conducted as new data are validated. The new data will provide opportunities for a greater understanding of VOC reactivity in the HGB area.

4.3.3 VOC and Carbonyl Reactivity

⁴No conclusions about the data from the Texas City site are included because at the time the study was conducted, there were some concerns about the validity of the data.

Additional analyses of reactivity, including analyses of carbonyls (particularly formaldehyde and acetaldehyde) which are beyond the scope of this document are provided in Appendices EE and FF.

4.3.4 Less Reactive VOC Contributions to Airmass Reactivity

The TCEQ conducted a limited data analysis study (Appendix GG) that examined the contributions of speciated VOCs to airmass reactivity. The analysis quantified reactivity-weighted species composition of airmasses at the two long-term Auto-GCs in the area, Deer Park and Clinton, using data from 1998-2002. Data from five other Auto-GCs in the area that operated to a lesser extent during this time frame were also analyzed.

Species composition analyses were performed on the following data sets:

- all hours in the entire five-year period;
- morning hours of the entire period, when emissions may have been less likely to have traveled long distances and are less likely to have undergone photochemical reactions;
- hours when the airmass was deemed highly reactive;
- morning hours on days in which one or more monitors in the 8-county area exceeded the 8-hour ozone standard (85 ppb); and,
- hours during which ozone concentrations exceeded the 1-hour ozone standard (125 ppb).

Fifty five VOCs species were divided into sixteen compound groups. Table 4.3-1, *VOC Groups*, provides a complete listing of the individual VOCs and their designated VOC compound groups. For each hour, reactivity-weighted concentrations for each species were summed by VOC group, resulting in reactivity-weighted concentrations for the hour for each of the sixteen groups. The contribution of each VOC group to overall total reactivity was determined by taking the median of all subject hours.

Initial results of this study suggest that ethylene and propylene are generally the most important contributors to total concentration in Houston, but that the butenes, butadiene, butanes, pentanes, and alkanes are contributors as well. For example, when all morning hours from 1998 to 2002 at the seven monitors were analyzed, propylene made up 11 percent to 20 percent of the reactivity-weighted concentration for all VOC compounds, and ethylene made up 13 percent to 17 percent. During these hours, butenes made up 5 percent to 8 percent and 1,3-butadiene between 2 and 9 percent of the reactivity-weighted concentrations. This study also suggests that pentanes, butanes, and alkanes each contributed between 6 and 10 percent of the reactivity-weighted concentration.

These three groups of compounds (pentanes, butanes, and alkanes) have significantly lower reactivities than currently defined HRVOCs, but they have higher ambient concentrations (14 percent, 16 percent, and 18 percent, respectively, of VOC concentration) relative to the ambient concentration of HRVOCs (2 percent to 3 percent for each of each of four compounds). Airmass reactivity is based on both concentration and ozone formation capability, so even though these compounds are much less reactive than HRVOCs, their presence causes them to contribute to total reactivity. The contribution of these three groups of less reactive VOCs was observed in all phases of this analysis. The presence of these compounds may indicate that they come from a variety of sources, both industrial and non-industrial.

The results from this preliminary MIR study on less reactive VOCs need to be corroborated by different reactivity metrics, such as the OH reactivity scale (Kwok and Atkinson, 1995). The OH reactivity scale is a measure of how rapidly a compound begins participating in ozone formation. Although other chemical pathways exist, the speed at which a compound reacts with OH is one of the major factors in determining

how aggressively the compound enters the ozone formation process. Since different VOCs have different reactivities, relative to one another, on the OH and MIR scales, additional analyses may yield different results.

Reactivity does not translate directly into peak ozone concentrations. The MIR scale describes the amount of ozone a compound can produce under specified conditions, not how rapidly it forms. Localized releases of HRVOC emissions in the HGB area have been directly linked to very high ozone concentrations that built very quickly, but the ever-present levels of VOCs are not typically linked to similar events. However, large amounts of VOCs may contribute to regional ozone levels. The TCEQ will continue to investigate the role of these compounds as it develops 8-hour ozone attainment demonstrations.

Table 4-1: VOC Groups		
VOC Group Name	Compounds in the Group	Average MIR Values for Species in Group
Propylene	Propylene	11.58
Ethylene	Ethylene	9.08
Butadiene	1,3-Butadiene	13.58
Butenes	1-Butene, c-2-Butene, t-2-Butene	12.48
Pentenes	1-Pentene, c-2-Pentene, t-2-Pentene	9.42
Isoprene	Isoprene	10.69
C2C3	Ethane, Propane, Acetylene	0.71
Butanes	n-Butane, Isobutane	1.34
Pentanes	n-Pentane, Isopentane	1.60
Alkanes	n-Hexane, 2-Methylpentane, 3-Methylpentane, 2,2,4-Trimethylpentane, 2,3,4-Trimethylpentane, n-Heptane, -Octane, n-Nonane, n-Decane, 2-Methylheptane, 2-Methylhexane, 3-Methylheptane, 3-Methylhexane, 2,2-Dimethylbutane, 2,3-Dimethylbutane, 2,3-Dimethylpentane, 2,4-Dimethylpentane	1.39
Toluene	Toluene	3.97
Xylenes	o-Xylene, — + p-Xylene	5.87
Trimethylbenzenes	1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene	9.89
Aromatics	Benzene, Styrene, Isopropyl Benzene (Cumene), Ethylbenzene, m-Diethylbenzene, p-Diethylbenzene, n-Propylbenzene	3.13
Cyclos	Cyclopentane, Cyclohexane, Methylcyclopentane, Methylcyclohexane	2.14
Ethyltoluenes	o-Ethyltoluene, m-Ethyltoluene, p-Ethyltoluene	6.61

This table provides a complete listing of the individual VOCs and their designated VOC compound groups.

4.3.5 Relationship of Speciated VOCs to Ozone Exceedances

A number of studies examining the relationship between observed concentrations of various VOCs and peak ozone have been conducted, but the results are so far preliminary, so are not reported in this chapter. Reports describing the results of these studies are provided in Appendices BB, DD, and GG, and in Brown and Main, 2002.

4.4 VOC EMISSION SOURCES

As mentioned in Section 4.3.1, aircraft data collected during the TexAQS study indicated that ambient concentrations of NO_x and certain VOC were not consistent with the industrial emission inventories. Specifically, the ratio of these VOC to NO_x emission estimates did not correlate with the ambient ratio of these VOCs to NO_x. Because of the greater certainty associated with NO_x emissions estimates, it has been generally concluded that industrial VOC emissions were underestimated in earlier emissions inventories. Consequently, current data analysis studies have focused on source identification and emission reporting verification using ambient VOC data. Most of the studies relied on local wind patterns and surface level wind measurements around each monitor to discern these sources.

4.4.1 Wind Bin Analysis of Twelve VOC Classes

One data analysis study (Jolly et al., Appendix B.5) compared VOC to NO_x ratios using ambient data with those from emissions data. Each monitor's hourly ambient data was grouped into 36 ten-degree wind direction bins. The median of all ambient ratios for each wind bin was computed. Gridded emissions from point, area, mobile, nonroad, and ship sources were also assigned to wind bins. The emissions were then weighted by the inverse of the distances from the source to the monitor. The distance-weighted emissions within each bin were summed, and emission ratios were then computed. Ambient data from two Auto-GCs were compared for the twelve different VOC classes listed in Table 12-1 above.

Maps of point sources in the area reveal that point sources often cluster in groups that span two or more wind direction bins. For directions dominated by point sources, emission ratios for an entire cluster – spanning from one to eleven wind bins – were compared with ratios from ambient data spanning the same set of wind bins.

For most point source clusters and most VOC groups, the VOC to NO_x emission ratios were less than the ambient ratios by factors ranging from 1 to 6, meaning that reported VOC emissions would have to be multiplied by a factor somewhere in that range to achieve unity with the ambient data. In addition, there were five instances from the two monitors involving different VOC groups where the adjustment factors ranged from 10 to 13.

Directions dominated by non-point sources generally had better agreement between emissions and ambient ratios than did those dominated by point sources, suggesting that the non-point source inventory is more accurate than the point source inventory. Results for less-reactive VOCs were not appreciably different from those of highly-reactive VOCs. The butanes class (consisting of isobutane and n-butane) was unique among the twelve classes studied, in that its emission ratios were often considerably less than ambient ratios, both in point and non-point dominated source regions. This suggests that one or both of these compounds are under reported, not only in the point source inventory, but in one or more of the non-point source inventories as well.

This study supports adjusting HRVOC emissions, and also suggests that some adjustment may be appropriate for other VOCs as well. Work very similar to this, summarized in Appendix B.5, formed the basis for the adjustment used in the ORVOC sensitivity analysis described in Section 3.9.6 of Chapter 3.

4.4.2 Wind Bin Analysis of Propylene

Another source attribution data analysis study (Appendix DD) conducted using propylene VOC data from six Ship Channel monitors included some of the new industry sponsored Auto-GCs brought on line in June 2003. This analysis used a combination of validated and unvalidated data. In this analysis, geometric means of propylene concentrations by wind bin at five monitors were combined with maps of propylene point sources to determine the sources upwind of the highest concentrations. For the three monitors with the highest peak concentrations, maps revealed that each monitor's peak pointed to the Battleground Road area, where a cluster of two large sources is located. This cluster ranges from 3.9 to 14 km distance from the monitors. Propylene emissions from the Battleground Road area appear to be elevated on a regular basis. Furthermore, the median ambient propylene to NO_x ratio was calculated to be 5.8 to 1, whereas the same ratio for emissions sources located in the bin was 1.8 to 1, suggesting that the emission inventory for sources in the bin may be underestimated by over three-fold.

This analysis points to the potential utility of the Enhanced Industry-sponsored Monitoring Network (EISM) in identifying potential sources of underreported emissions. This rich data set promises to be extremely valuable in work on the 8-hour SIPS.

4.4.3 Additional studies related to Emission/Ambient relationships

Several additional studies were conducted, but the results of these analyses are not directly relevant to this attainment demonstration. These include a wind bin analysis for canister data (Appendix CC), factor analysis (Appendix GG), and Positive Matrix Factorization (Brown and Hafner, 2003).

4.5 FUTURE WORK

The results from these projects build upon themselves, thus shaping and directing future work. Strategic planning for future data analysis studies is continually reevaluated as new information becomes available. Future activities may include, but are not limited to, the following projects. As projects are completed, the direction of future work may change based on the new information generated.

4.5.1 Development of Ozone Predictors for Exceedance Days

Variables such as temperature, wind speed, emission events, etc. which are related to ambient ozone concentrations are used as ozone predictors. While these predictors have obvious utility in forecasting ozone action days, they also have considerable value in developing conceptual models of ozone formation and in selecting representative episodes to model. Previous data analysis studies identified several factors that were good predictors of ozone levels when all days are considered, but did not predict ozone well when only considering exceedance days. Better characterizations of these ozone predictors and their relationships to ozone concentrations is an important area for future research. Some possible avenues of exploration include time and duration of wind stagnation, temperatures, and the variability and composition of VOC emissions from industrial emission events. Investigating emission events may be facilitated by a new method currently under development - a technique to measure ozone trends after filtering out the effects of meteorology.

4.5.2 Determination of Speciated VOCs Contribution to Airmass Reactivity

Different VOCs have been shown to contribute differently to airmass reactivity. Given the high hydrocarbon concentrations found on a routine basis in the HGB area, further work is warranted on the significance of these speciated VOCs to airmass reactivity. The less reactive VOCs will be studied to further delineate their contribution using different metrics. In addition, the new VOC data from the industry sponsored monitors will be used to study speciated VOC contribution to airmass reactivity in these different locations. Different data sources, such as canister data, Auto-GC data, and aircraft flight

data, will continue to be used to provide multiple perspectives for analyses corroboration purposes. The relationship between total air mass reactivity and exceedance versus nonexceedance days are also important topics for further study.

4.5.3 Identification of Emission Sources and Verification of Emission Reporting

Industrial VOC emissions are significantly understated in current emission inventories. Work to identify sources and verify emission reporting will continue, including the use of back trajectories to identify sources and studies by wind bins of VOC to NO_x ratios to verify emission reporting. Emission inventory verification of point, mobile, area, and biogenic sources is important to the development of control strategies.

4.5.4 Support for Modeling Work

Numerous data analysis projects can be conducted to support future modeling studies. Improved selection of monitoring sites that more accurately represent the ozone design value, quantification of boundary conditions, and interpolated humidity and temperature fields are potential topics to study.

4.5.5 TexAQS II Data Analysis

The 2005-6 TexAQS II will provide unprecedented amounts of data for the entire eastern half of Texas. As in the first TexAQS, much data collection will be focused on better quantifying emissions in the HGB area, characterizing air mass reactivity, and characterizing the complex coastal meteorology in Southeast Texas. The TCEQ plans to use this wealth of data to further investigate the issues already discussed in this chapter and to participate in the development of a new, better understanding of ozone formation in the region.

In addition, the TexAQS II will provide a rich data set of new meteorological and air quality data for HGB, DFW, BPA, and the EAC areas of Texas, and will provide a unique opportunity to study ozone transport and background levels, factors which are expected to play increasingly important roles in 8-hour ozone formation. The TCEQ will use these data to better quantify the role that transport plays in 8-hour nonattainment in Texas, and to develop model inputs and validation data. Many additional opportunities for relevant data analysis work will arise as the study progresses.

4.6 SUMMARY AND CONCLUSIONS

Data analysis in the Houston area has focused on the underlying factors of ozone formation. Ambient data has been used to track trends in ozone levels, determine the effects of wind patterns on ozone levels, and evaluate and characterize the contribution of speciated VOCs to total reactivity. The sources of air emissions were studied in relation to ambient concentrations to assess the accuracy of reported inventories.

The 1-hour ozone design value was shown to be decreasing with time, while the 8-hour design value has remained relatively constant. However, recent data may indicate that the 8-hour design value is beginning to decrease. An alternative method for calculating the 1-hour design value was introduced, and was used to calculate a design value which filters out the sudden ozone concentration increases which are often characteristic of emission events.

Several studies point out the importance of HRVOC emissions in air mass reactivity and support the TCEQ's control strategy for this 1-hour attainment demonstration. Other VOCs were also seen to contribute to total air mass reactivity. Source-oriented analysis of ambient data corroborates the decision to adjust HRVOC emission inventories in modeling, and also highlights the utility of the recently

deployed network of industry-sponsored Auto-GCs in the area in locating sources of un- or under-reported emissions.

Finally, some of the future data analysis work that the TCEQ expects to perform in the next few years was discussed. The data from the TexAQS II is expected to allow the TCEQ to better characterize emission/ambient relationships, ozone transport, and to better support future attainment demonstrations.

The body of knowledge on ozone formation in Houston continually increases through the collection of additional data and the completion of new data analysis studies. Strategic planning for future data analysis studies is also being developed and the data analysis process is being streamlined to increase efficiency. These data analysis improvements will help to support future SIP revisions.

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