CHAPTER 3: CORROBORATIVE ANALYSIS

3.1 INTRODUCTION

This chapter describes data analyses that corroborate the conclusions of Chapter 2 regarding photochemical modeling. These analyses examine patterns and trends in population, ozone, and ozone precursors.

3.2 OZONE TRENDS

The one-hour and eight-hour ozone design values for the Houston-Galveston-Brazoria (HGB) area from 1991 to 2005 are illustrated in Figure 3-1: *One-Hour and Eight-Hour Ozone Design Values in the HGB Area (1991-2005) and HGB Area Population*. Both values decrease over the past 15 years. The 2005 one-hour design value was 169 parts per billion (ppb), representing a 23 percent decrease from the value for 1991 (220 ppb). The 2005 eight-hour design value was 103 ppb, a 13 percent decrease from the 1991 value of 119 ppb. These decreases occur in spite of a 36 percent increase in area population, as shown in the figure.

This figure also shows linear fit (trend) lines for both design values; these appear as black lines through each data series. Each line has an associated linear regression equation displayed. The eight-hour trend line suggests a decrease of about 0.9 ppb of ozone per year across the 15-year period. The one-hour trend line shows a decrease of nearly three ppb per year during the same time. Both decreases are statistically significant at the 95 percent confidence level.

Despite its repeal, the one-hour ozone standard is still an important metric for analysis. The HGB area has historically seen frequent, very high one-hour ozone concentrations. These have been strongly influenced by rapid, sharp ozone increases driven in part by high concentrations of highly-reactive volatile organic compounds (HRVOC) released by the numerous petrochemical plants in the area (Trainer; Ryerson et al). Regarding HGB air quality, the Texas Commission on Environmental Quality's (TCEQ) greatest priority in recent years has been to reduce the magnitude and frequency of these sharp ozone increases by regulating emissions of four species of HRVOC from area industrial facilities in combination with regulations that bring about substantial nitrogen oxides (NO_X) reductions. The decreases in NO_X and ambient HRVOC (see Section 3.4.1 of this document), suggest that the state has accomplished much in its efforts to control this important aspect of HGB ozone formation.

Another measure used to assess ozone trends is the number of exceedance days per ozone season. Figure 3-2: *HGB Ozone Exceedance Days per Monitor, 1990-2005 (monitors with 4 or more years)* shows a downward trend in the number of eight-hour ozone exceedance days per monitor across this fifteen-year period. See Figure 3-3: *Map of Ozone Monitors in the HGB Area* for HGB ozone monitor locations.

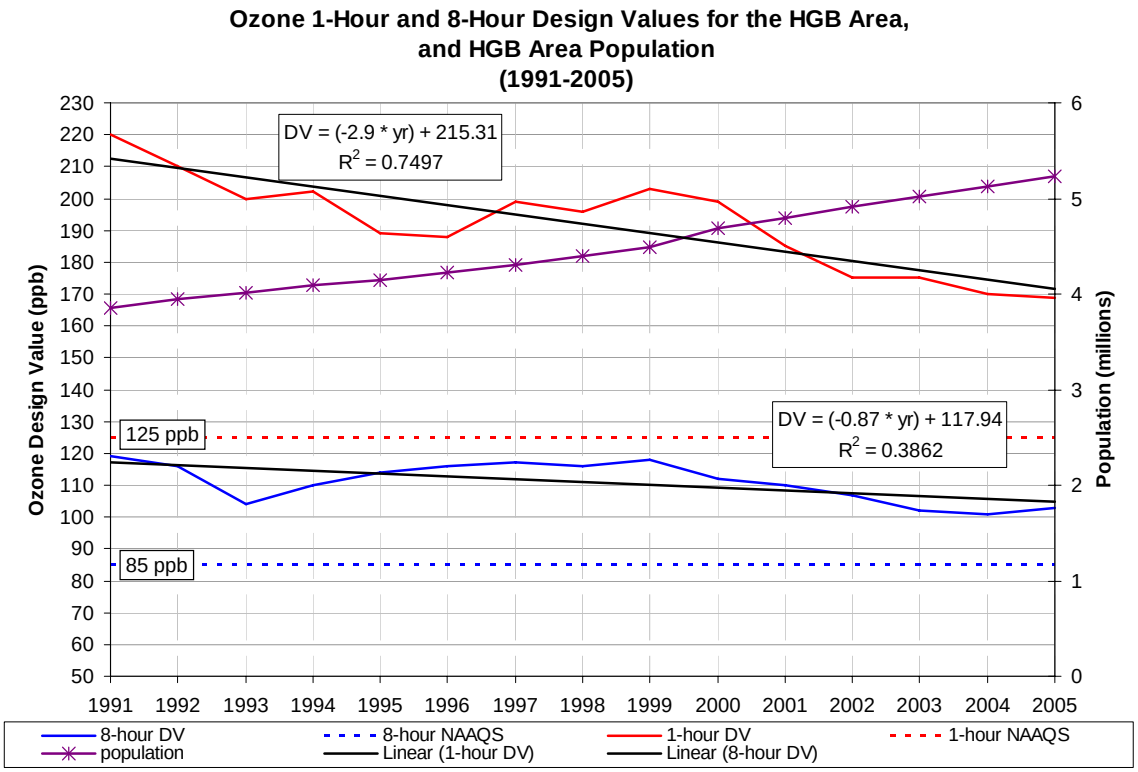

Figure 3-1: One-Hour and Eight-Hour Ozone Design Values in the HGB Area (1991-2005) and HGB Area Population

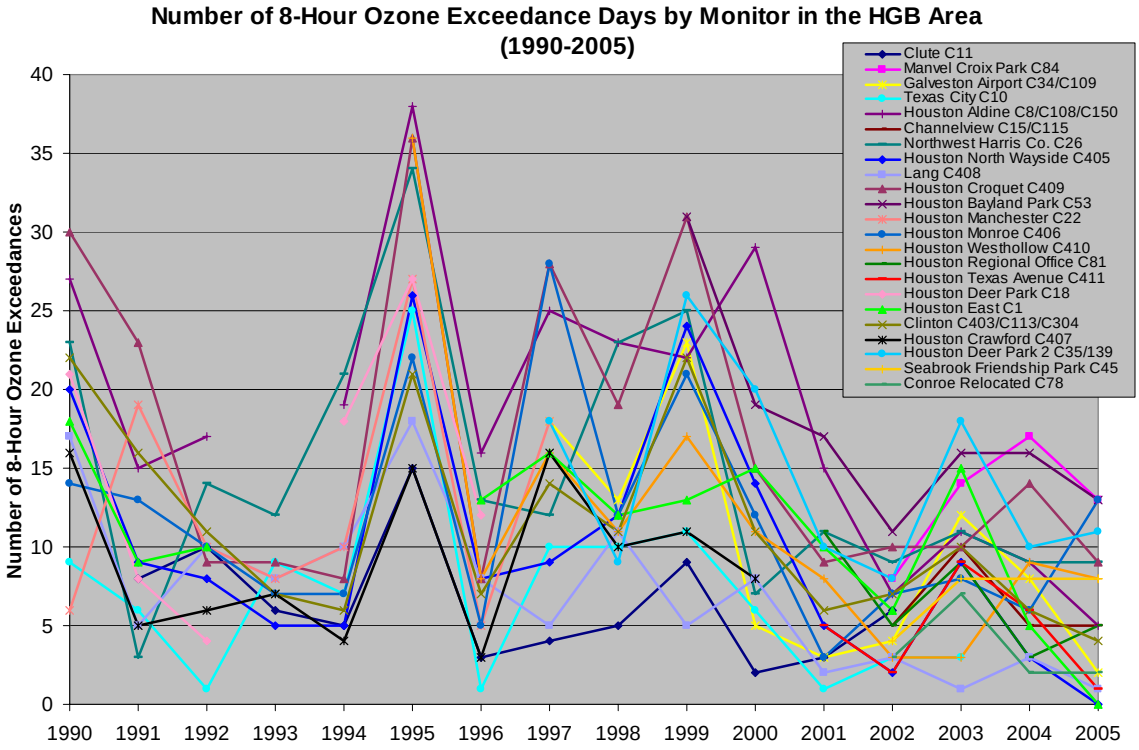

Figure 3-2: HGB Ozone Exceedance Days per Monitor, 1990-2005 (monitors with 4 or more years)

Figure 3-3: Map of Ozone Monitors in the HGB Area

3.3 POPULATION AND GEOGRAPHIC AREA ANALYSIS

Attainment or nonattainment of the eight-hour ozone standard for an area is determined by the eight-hour ozone design value, which is based on ambient measurements at monitor locations. A single monitor whose design value exceeds the National Ambient Air Quality Standard (NAAQS) can cause the entire area to be designated nonattainment. However, within the area designated nonattainment, there may be large areas (and large segments of the population) whose air quality

meets the standard. Put another way, if everyone in the area had an ozone monitor in their backyard, which of these hypothetical monitors would have design values that do not exceed the ozone NAAQS? This section describes the geographical areas in exceedance and the population exposed to concentrations exceeding the NAAQS for 2000 and 2009.

Radius of Representation

In many rural areas, a properly sited monitor should be representative of the air quality for many miles in all directions. However, in an urban area like HGB, with its complex patterns of land use, emission sources, and coastal meteorology, many of the monitors are only representative of the immediate area. In some cases, this immediate area is as small as a few blocks. Despite the very comprehensive monitoring network in the Houston area, many areas (and people) are not directly represented by a monitor. Estimating a design value at each location in the area is possible using spatial interpolation, but such interpolation will not account for the small-scale variations and nonlinear processes that affect ozone formation in an environment as complex as the HGB area.

Modeling vs. Monitoring

Unlike the monitoring network, grid modeling provides air quality information across the entire HGB area. Because the model incorporates emissions, meteorology, atmospheric chemistry, and physics, it can capture much of the smaller-scale variation in the ozone patterns in its predictions. One approach to estimating geographic and population exposed to an exceedance would be to use model output directly, but since the model will not exactly reproduce the design values at the monitors this approach may over- or under-represent the areas and population exposed to exceedances of the standard[1]. The United States Environmental Protection Agency (EPA) has accounted for this expected deviation on page 20 of its guidance document *Guidance on the Use of Models and Other Analyses in Attainment Demonstrations for the Eight-Hour Ozone NAAQS*.

A Combined Approach

Limitations of both the modeling and monitoring approaches discussed above make clear that neither approach is entirely adequate to estimate future attainment status in unmonitored areas. There are a number of ways that the two approaches can be combined into a composite approach that avoids the major objections to each. The EPA has proposed use of a modified version of its BenMAP software as part of an "unmonitored area attainment test." BenMAP has the capability of combining modeled and monitored information. Because the EPA's software is not yet available, the TCEQ modeling staff devised an alternate approach that is conceptually similar to BenMAP. The approach was used to develop maps of predicted areas of nonattainment in both the base (2000) and future (2009) years.

Figure 3-4 through Figure 3-9 used a geostatistical interpolation method known as "kriging." Kriging is a commonly-used method that produces a smooth surface across a region containing irregularly-spaced data, such as observations from a monitoring network. Unlike some other interpolation techniques, kriging does not force the resulting surface to pass exactly through the observations. In the current application, this means that the maps produced will show ozone values at the monitor locations slightly different from those used to create the map.

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[1] Differences between model predictions and monitored design values are not necessarily an indication of any problems with the model. Modeling is conducted over many days, which necessarily exhibit a variety of ozone concentrations, while the design values are based on fourth-highest days at each monitor. Because of the structure of the eight-hour ozone standard, a modeled concentration exceeding 85 parts per billion (ppb) does not indicate that a violation of the standard is expected since it a fourth highest monitored value that is examined for compliance with the standard. So while the model should be representative of elevated ozone levels at the monitor sites, it does not represent the specific days used in the design value calculation.

Directly kriging the design values can produce reasonable-looking surfaces that provide design values across the region of interest. However, as noted earlier, this simplistic method does not account for the complex spatial characteristics of ozone concentrations in the HGB region. Instead, the TCEQ replaced the design values at the monitors with the ratios of the design values to the modeled baseline average concentrations. If the modeled baseline average is close to the design value, the ratio is about 1.0. In the actual HGB modeling, the modeled averages were smaller than the design values at most monitoring locations, and in these cases the ratios were greater than 1.0, but for a couple of monitors the ratios were slightly less than 1.0. Table 3-1: *Monitor Locations Used in Population and Geographic Area Analysis* lists the monitors used in the analysis, along with the baseline design values (DV), modeled baseline average concentrations, and ratios at each.

Table 3-1: Monitor Locations Used in Population and Geographic Area Analysis

Site	Baseline DV (DVc)*	Modeled Average**	Ratio
Bayland Park	107	86.0	1.24
Clinton Drive	93	89.1	1.04
Clute	90	92.3	0.97
Conroe	91	84.4	1.08
Deer Park	107	89.9	1.19
Galveston	98	97.2	1.01
Aldine	108	85.7	1.26
Croquet	102	88.6	1.15
Lang	83	83.3	1.00
NW Harris Co.	104	79.3	1.31
Houston East	102	88.7	1.15
Regional Office	95	88.5	1.07
Monroe	90	88.7	1.02
Wayside	89	85.7	1.04
Shell Westhollow	95	85.7	1.11
La Marque	90	96.2	0.94

*The 2000 Baseline (current) DV, or DVc is actually the average of three years' DV (2000, 2001, & 2002), as per EPA Guidance. This is the value used in calculating future DV for the attainment test.

**The Modeled Average is the average of the highest modeled eight-hour concentrations "near" the monitoring site. It excludes values < 70 ppb, again as per EPA attainment test guidance.

The design value-to-modeled average ratios were then kriged to produce values across the modeling domain. These values represent an adjustment factor by which the modeled averages are multiplied to give model-adjusted design values. At the actual monitor locations, the model-adjusted design values are usually close to the original baseline design values.

For the future case, the kriged adjustment factors are multiplied by the modeled average future-case concentrations to provide future design values across the modeling domain. The future design values at the monitor locations are also usually close to the future design values calculated in the attainment test.

Interpreting the results of analyses using this kriging methodology requires that a few important points be considered. First, spatial interpolation techniques are not reliable outside the geographic range of the observations. Thus, design values estimated in areas beyond the range of the monitoring network (e.g., Waller County) should be viewed with caution. Second, the method's inability to exactly reproduce the original baseline and future-case design values introduces some additional uncertainty in the results. For most monitors, the values derived through the kriging analysis are very close to those calculated using the modeled attainment test, but in a few locations the technique does cause some larger differences; e.g., the kriging-based future design value at Bayland Park is several ppb lower than the modeled attainment test value. Finally, note that the maps shown in Figure 3-4: *Baseline Ozone Design Value 2000 Compared with Future Ozone Design Value 2009* are intended only to provide useful visual representations of design values across the area. Similarly, the summary graphs presented at the end of this section were developed to indicate the relative magnitude of expected improvements in air quality, but are not intended to provide precise estimates of either geographic area or population exposed to ozone concentrations of 85 ppb and greater.

Design Value Maps

Figure 3-4: *Baseline Ozone Design Value 2000 Compared with Future Ozone Design Value 2009* is a map of ozone design values across the HGB area that was produced using the TCEQ approach to combining measured and modeled information. Areas shown in yellow, orange, and red are predicted to be nonattainment (i.e., have design values over the eight-hour NAAQS), while all other areas are predicted to be in attainment[2]. These maps graphically illustrate the expected improvements in air quality in 2009 resulting from existing control strategies.

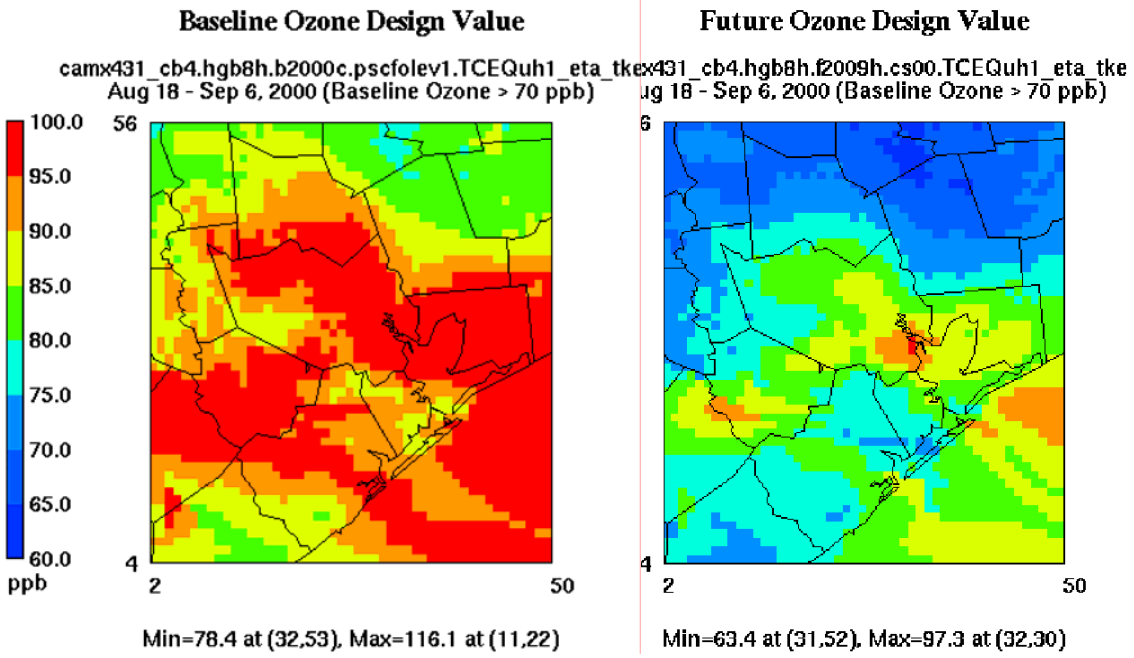

Figure 3-4: Baseline Ozone Design Value 2000 Compared with Future Ozone Design Value 2009

[2] Strictly speaking, an entire group of counties (usually a consolidated metropolitan statistical area) is either attainment or nonattainment under EPA's policy. In this paper, these terms are used also to describe sub-areas within the larger area.

Once the maps for baseline and future years are created, the grid cells where ozone exceeds 85 ppb can be counted and the population within these cells is determined. Population for each cell was calculated from census tracks using GIS software and projected for 2009 using growth projections. The following two graphs provide summary views of the expected improvement in HGB air quality in terms of area and population exposure to ozone nonattainment.

Figure 3-5: *Area in Exceedance of the Eight-Hour Ozone Standard* and Figure 3-6: *Population Exposed to Ozone Concentrations of 85 ppb and Greater* show improvements in area and population in nonattainment, but do not account for how high ozone levels are once the standard is exceeded.

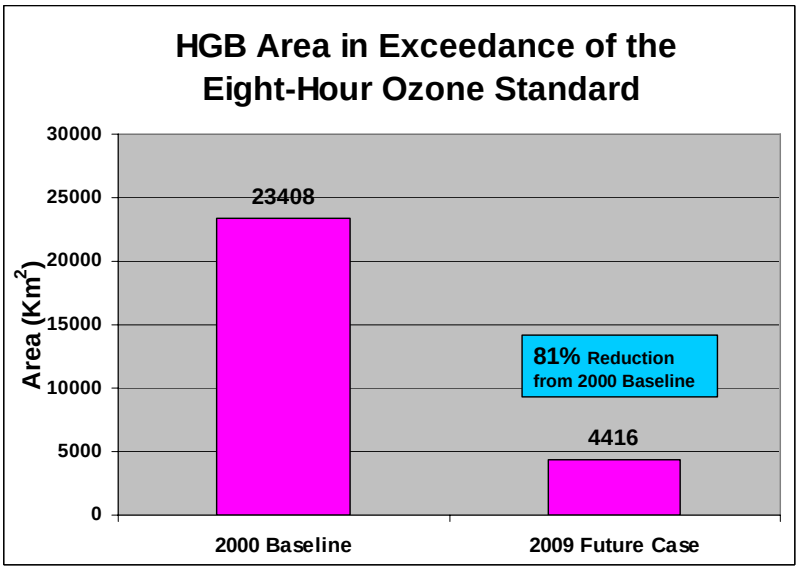

Figure 3-5: Area in Exceedance of the Eight-Hour Ozone Standard

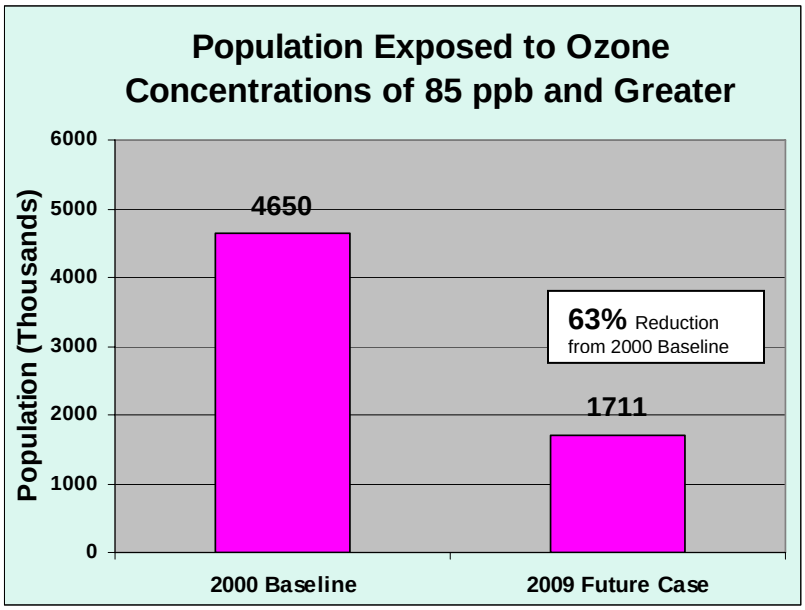

Figure 3-6: Population Exposed to Ozone Concentrations of 85 ppb and Greater

Figure 3-7: *Concentration-Weighted Area in Exceedance of the Eight-Hour Ozone Standard* and Figure 3-8: *Concentration-Weighted Population Exposed to Ozone Concentrations of 85 ppb and Greater* factor in the amount the predicted design value in each grid cell exceeds the standard.

For instance, a value of 89 ppb in a grid cell is weighted twice as heavily as a value of 87 ppb (89-85 = 4; 87-85 = 2). These measures will be referred to as concentration-weighted area in exceedance of the eight-hour ozone standard and concentration-weighted population exposed to ozone concentrations of 85 ppb and greater. Figure 3-7 and Figure 3-8, provide a compact, yet comprehensive, representation of the dramatic improvement expected in HGB air quality from 2000 to 2009.

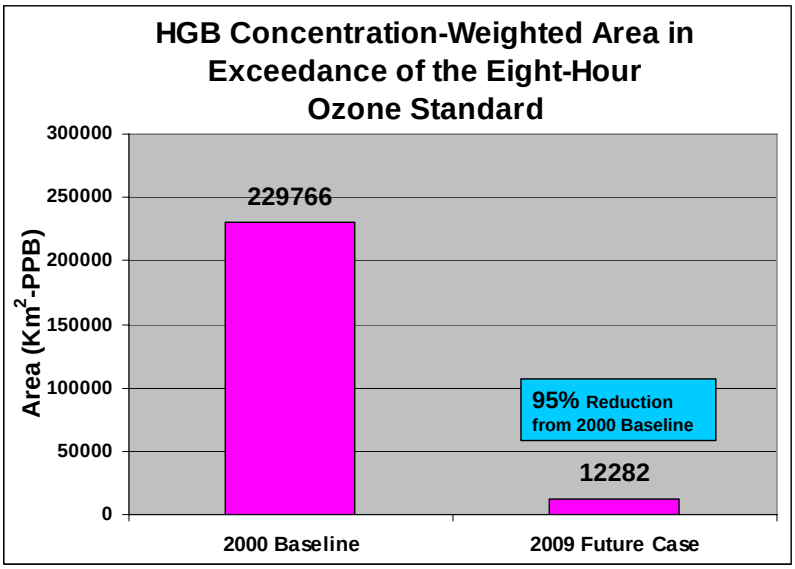

Figure 3-7: Concentration-Weighted Area in Exceedance of the Eight-Hour Ozone Standard

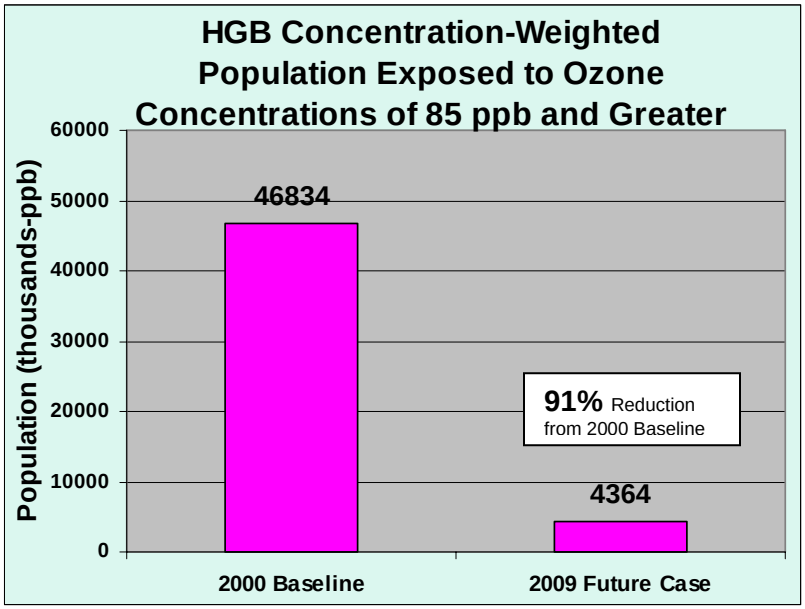

Figure 3-8: Concentration-Weighted Population Exposed to Ozone Concentrations of 85 ppb and Greater

3.4 HRVOC AND NO_X TRENDS

3.4.1 Ambient HRVOC Trends

Starting in the mid-1990s, continuous measurements of ambient volatile organic compounds (VOC) have been taken at two monitors in the HGB area – at Clinton C403, located near the west end of the Houston Ship Channel, and at Deer Park C35, located in the city of Deer Park, a few

miles south of the ship channel. These monitors use automated gas chromatographs (auto-GC) to measure some 55 compounds on an hourly basis. By virtue of this sampling frequency and the range of compounds measured, hundreds of thousands of VOC measurements have been taken in the decade since sampling began. The resulting datasets are valuable for numerous types of analyses, including VOC trends assessment.

In order to assess overall ambient VOC trends in the HGB area, total non-methane hydrocarbon (TNMHC) measurements were used. TNMHC is a commonly used surrogate for total VOC. Figure 3-9: *Geometric Mean Total Nonmethane Hydrocarbon (TNMHC) at Clinton, 1997-2005* and Figure 3-10: *Geometric Mean TNMHC at Deer Park, 1997-2005* show geometric mean values, by year, of TNMHC measurements taken at these two monitors. (Figure 3-11: *Auto-GC Monitors (red icons) and Point Source EI HRVOC Emissions (brown circles) in the Houston Ship Channel Area* shows the locations of these two auto-GCs along with the six others in Harris County.) Both monitors show strong decreases in the study period (1997-2005). At Clinton, mean concentration decreased almost 30 percent in this period, and at Deer Park, the decrease was nearly 35 percent. Both of these decreases are statistically significant at the 95 percent confidence level.

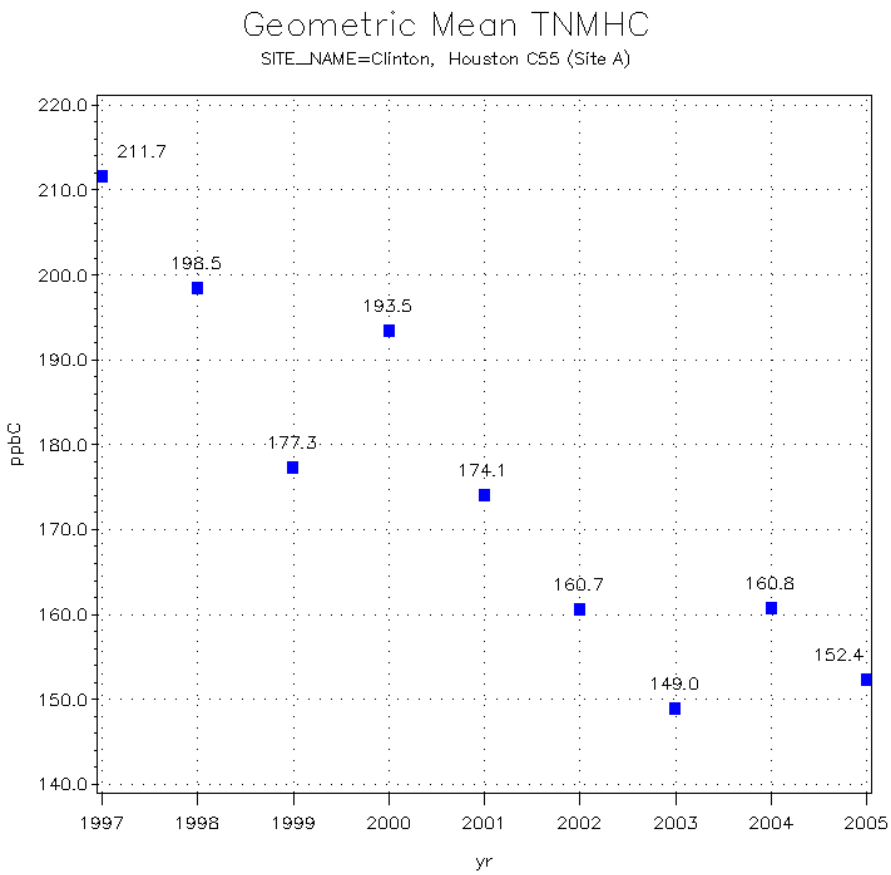

Figure 3-9: Geometric Mean Total Nonmethane Hydrocarbon (TNMHC) at Clinton, 1997-2005

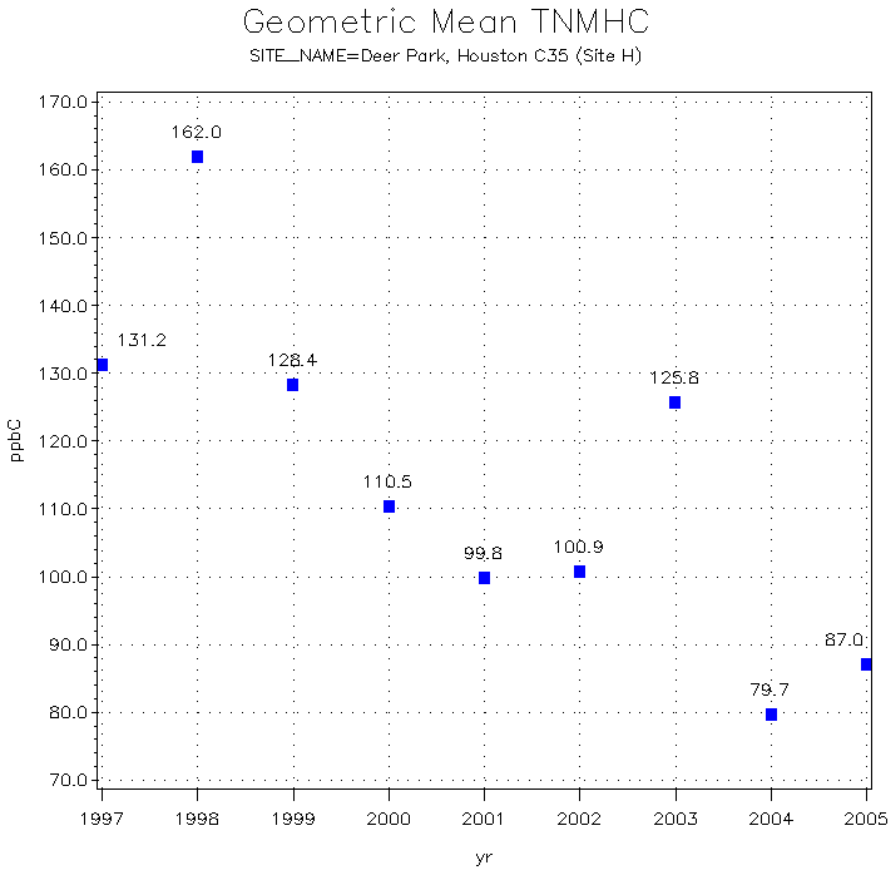

Figure 3-10: Geometric Mean TNMHC at Deer Park, 1997-2005

Houston Ship Channel Auto-GC Monitors and HRVOC Point Source Emission Locations

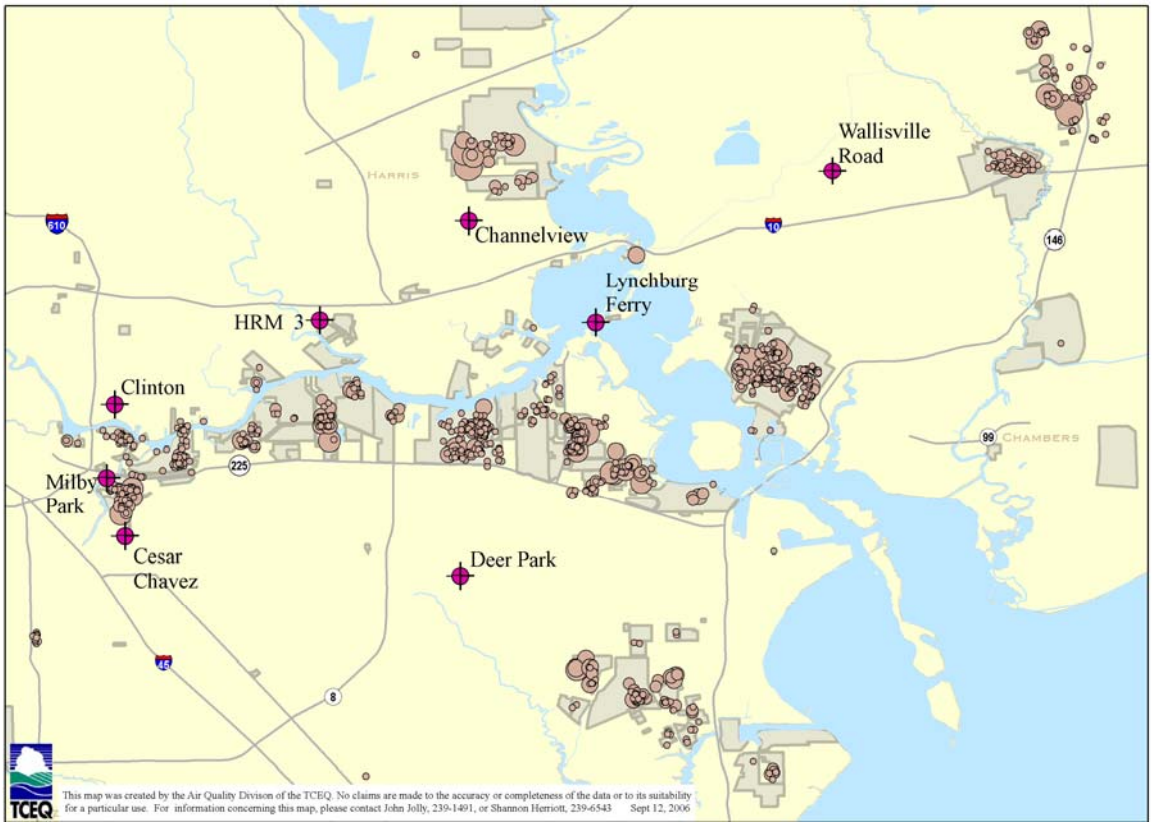

Figure 3-11: Auto-GC Monitors (red icons) and Point Source EI HRVOC Emissions (brown circles) in the Houston Ship Channel Area

Table 3-2: *Ambient HRVOC Trends Results* summarizes results of trends analyses during the same time for the four species of HRVOC: ethylene, propylene, 1,3-butadiene, and butenes (the sum of 1-butene, c-2-butene, and t-2-butene). This table shows that all four species of HRVOC have been decreasing at both monitors, and a majority of these decreases are statistically significant at the 95 percent confidence level. Ethylene and propylene at both monitors showed relatively robust downward trends (R^2 = 0.60-0.71) that were statistically significant at the 95 percent confidence level. This is important because results from the 2000 Texas Air Quality Study showed that these two compounds were the most important VOC in the area, in terms of their contribution to total VOC reactivity.

In addition to looking at overall TNMHC and HRVOC trends, the TCEQ has also looked at trends in certain HRVOC by wind direction. Figure 3-12: *Geometric Mean Propylene by Wind Direction, Eastern Houston Ship Channel, 2003-2005 (Chanelview is 2002-2004)* shows geometric mean propylene concentration for June through August of 2003-2005 at five auto-GCs (2002-2004 at Channelview) in the eastern part of the Houston ship channel, with 2003 propylene point source emissions shown as colored circles. The propylene concentrations are presented as radar plots; the data series for each year and each monitor surrounds the respective monitor. Each series, followed around its full rotation, shows lobes or peaks. These lobes correspond to the wind direction associated with enhanced mean concentration, with the distance from the origin (the monitor) to the tip of the lobe or peak corresponding to the magnitude of concentration at that direction. The largest peak around each monitor has a label showing its mean concentration, enabling one to see the approximate magnitude of some of the other peaks at that monitor. Because the data series surrounding some monitors have been "stretched" so that all monitors' directional and annual trends can be best viewed together, the data series for each monitor are not to scale with those of the other monitors.

Table 3-2: Ambient HRVOC Trends Results

Monitor	HRVOC	Geometric Mean (ppbC)[3]		Linear Trend (ppbC/year)	R^2	Trend Significant? ($\alpha = 0.05$)
		1997	2005			
Clinton	Ethylene	6.96	2.84	-0.43	0.71	Yes
	Propylene	4.07	2.94	-0.13	0.69	Yes
	Butenes	3.34	2.12	-0.21	0.59	Yes
	1,3-Butadiene	1.06	0.53	-0.06	0.65	No
Deer Park	Ethylene	4.29	3.00	-0.18	0.60	Yes
	Propylene	4.28	2.59	-0.20	0.71	Yes
	Butenes	2.19	1.43	-0.07	0.08	No
	1,3-Butadiene	0.57	0.42	-0.02	0.42	No

Figure 3-12 shows at least two notable things. First, the largest peaks for most of the monitors point to a common source region adjacent to Battleground Road, near to and including the large propylene source at the center of the map. While the reported propylene emissions in this area are large, they are similar to those reported in some other areas on this map, such as the sources just north of the Channelview C15 monitor. The fact that the largest peaks for all five monitors point so strongly to Battleground Road indicates that the sources there were emitting disproportionately large amounts of propylene, at least during some of the years presented here. This shows most clearly with the 2003 data series (pink). The other notable finding here is that each monitor shows a sharp decrease in mean concentration from the Battleground Road area in 2005 compared to 2003. The data series around Channelview C15 is 2002 through 2004, and shows this decrease in the last two years. The data from the other four monitors suggests a steep decline in propylene emissions in summer 2005 compared to 2004 and especially 2003. The data from Channelview suggest reductions in both 2003 and 2004, compared to 2002.

Figure 3-13: *Geometric Mean Ethylene by Wind Direction, Eastern and Western Houston Ship Channel, 2003-2005 (Channelview is 2002-2004)* is similar to the previous figure, however ethylene rather than propylene concentrations are plotted, with ethylene point sources displayed as colored circles. Peaks can be seen in several source directions; there is no apparent single source region that has each monitor's strongest peaks pointing at it, unlike with propylene. The plots around Deer Park C35, Wallisville C617, and Lynchburg C1015 suggest that ethylene emissions from the Battleground Road area, or just to the east of it, were lower in 2005 than in the two previous years, but data from Channelview C15 and HRM 3 do not show this pattern.

[3] "ppbC" signifies parts per billion carbon, which is equal to parts per billion by volume (ppbv) times the number of carbon atoms in the molecule. PpbC is a very common unit of measurement for VOC in regards to ozone formation, and is the default unit of measurement for TCEQ's auto-GC data.

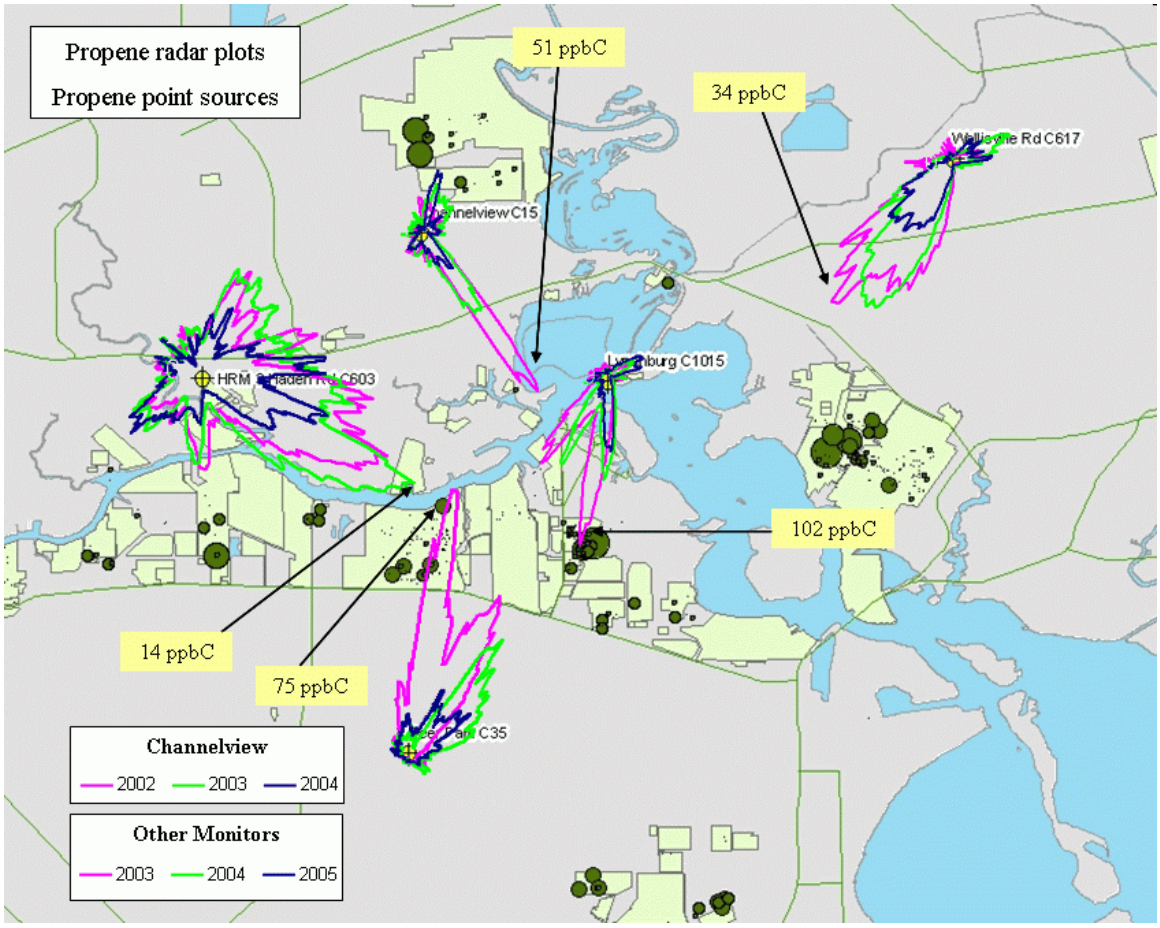

Figure 3-12: Geometric Mean Propylene by Wind Direction, Eastern Houston Ship Channel, 2003-2005 (Chanelview is 2002-2004)

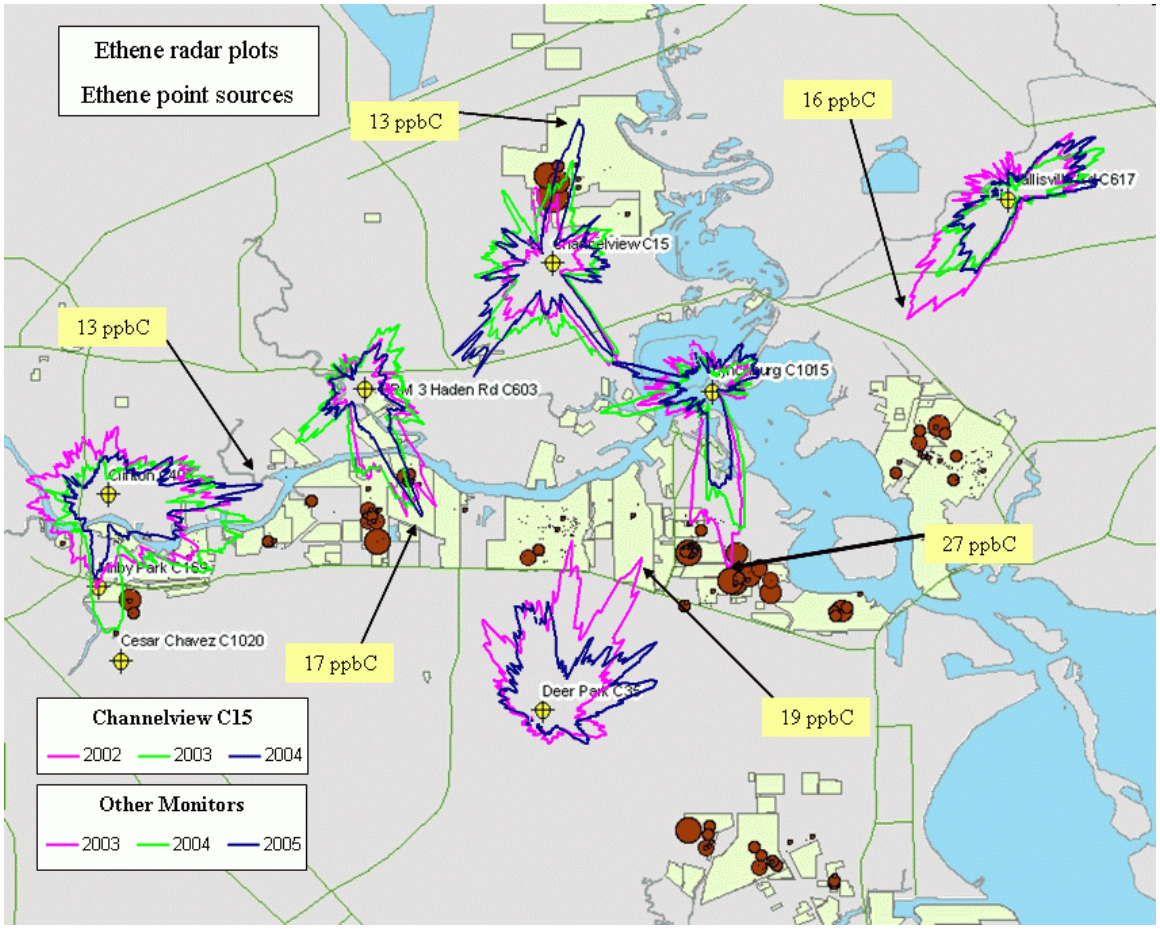

Figure 3-13: Geometric Mean Ethylene by Wind Direction, Eastern and Western Houston Ship Channel, 2003-2005 (Channelview is 2002-2004)

3.4.2 Ambient NO_X Trends

Ambient NO_X trends in HGB were calculated using two methods. In the first method, data were retrieved from nine monitors that started measuring NO_X in 1998 or earlier (see Figure 3-14: *Map of HGB NO_X Monitors Operating Since 1998 or Earlier* for a map showing locations of these monitors). The data are from the months of typical peak ozone, August and September. The distributions of these data are very skewed, therefore statistical trends assessments were performed on the log-transformed measurements. The log-transformed data more closely approximated a normal distribution and was therefore more suitable for standard statistical tests.

Long Term NOx Monitors in the HGB Area

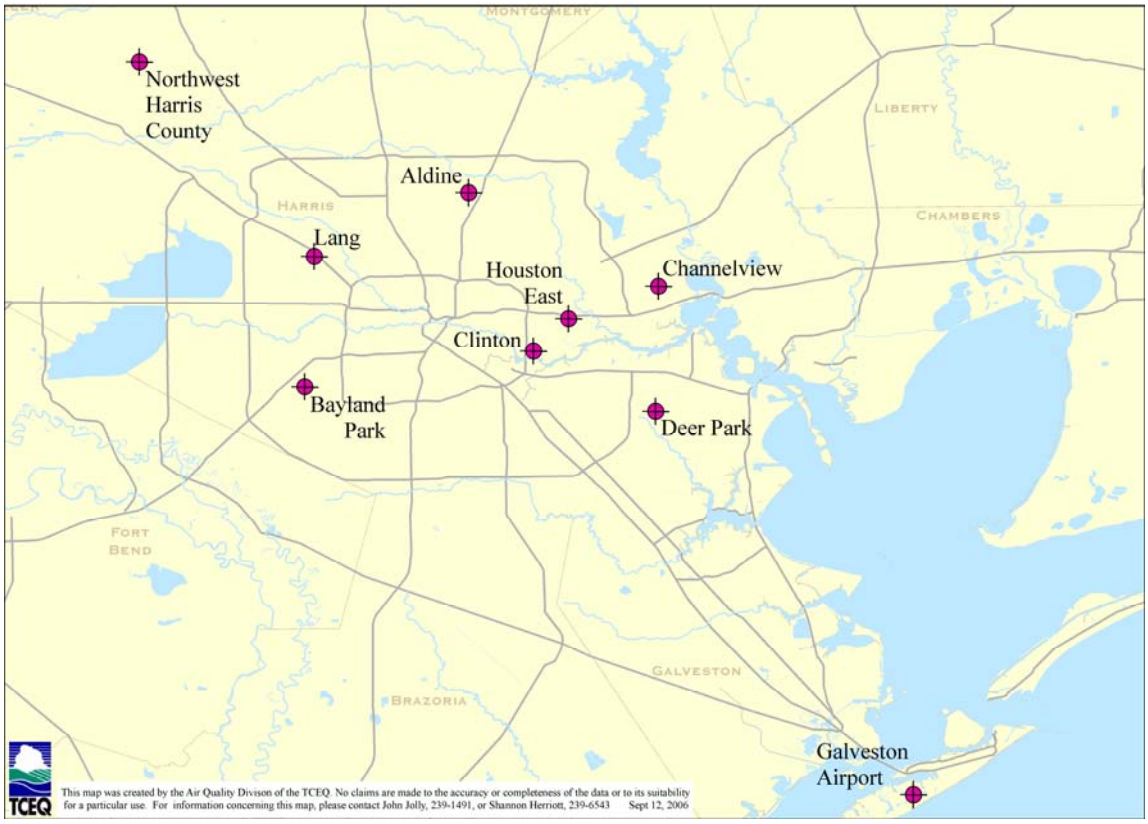

Figure 3-14: Map of HGB NO_X Monitors Operating Since 1998 or Earlier

Table 3-3: *Ambient NO_X Trends Results Using Log-Transformed Data* shows the results of the trends assessment. This table shows that all nine monitors exhibit decreasing trends, with wide-ranging correlations (R^2 = 0.28 to 0.81). At five of the nine monitors, the decreasing trends were statistically significant at the 95 percent confidence level. While not all decreases were statistically significant, the fact that decreases occurred at every monitor, covering a broad geographic area, suggests that ambient NO_X concentrations in the HGB area are decreasing.

Table 3-3: Ambient NO_X Trends Results Using Log-Transformed Data

Results of NO_X Regression Analysis						
Monitor	**Years Analyzed**	**Geometric Mean (ppb)**		**Linear Trend (ppb/year)**	**R^2**	**Trend Significant?** (α = 0.05)
		Start Year	**End Year**			
Aldine	1985-2005	17.8	14.5	-0.45	0.34	No
Bayland Park	1998-2005	13.5	7.32	-0.52	0.41	No
Channelview	1985, 1986, 2001-2005	14.7	11.4	-0.25	0.81	Yes
Clinton	1985-2005	44.2	16.4	-1.0	0.76	Yes
Deer Park	1997-2005	9.87	6.25	-0.22	0.28	No
Galveston Airport	1997-2005	5.67	2.93	-0.30	0.57	Yes

Houston East	1985-2005	22.4	17.8	-0.29	0.32	Yes
Lang	1985-2005	30.3	17.9	-0.64	0.56	Yes
Northwest Harris	1997-2005	7.13	6.53	-0.38	0.35	No

Additionally, ambient NO_X trends were calculated, and statistical assessments performed, using the actual measurements rather than the log-transformed measurements described in the previous paragraph. Using year-round data for the years 1985-2005, quarterly averages were calculated for each monitor, with the highest quarterly average used for trends assessment. Figure 3-15: *HGB Peak Average NO_X by Year and Quarter, 1985-2005* shows these results. One can see both the strong seasonal variation and the steady downward trend across the years. Though the correlation coefficient is rather weak ($R^2 = 0.26$), owing to the seasonal variation, the downward trend – 1.1 ppb per year – is significant at the 95 percent confidence level. The results of the two analyses suggest that NO_X concentrations are decreasing in the HGB area.

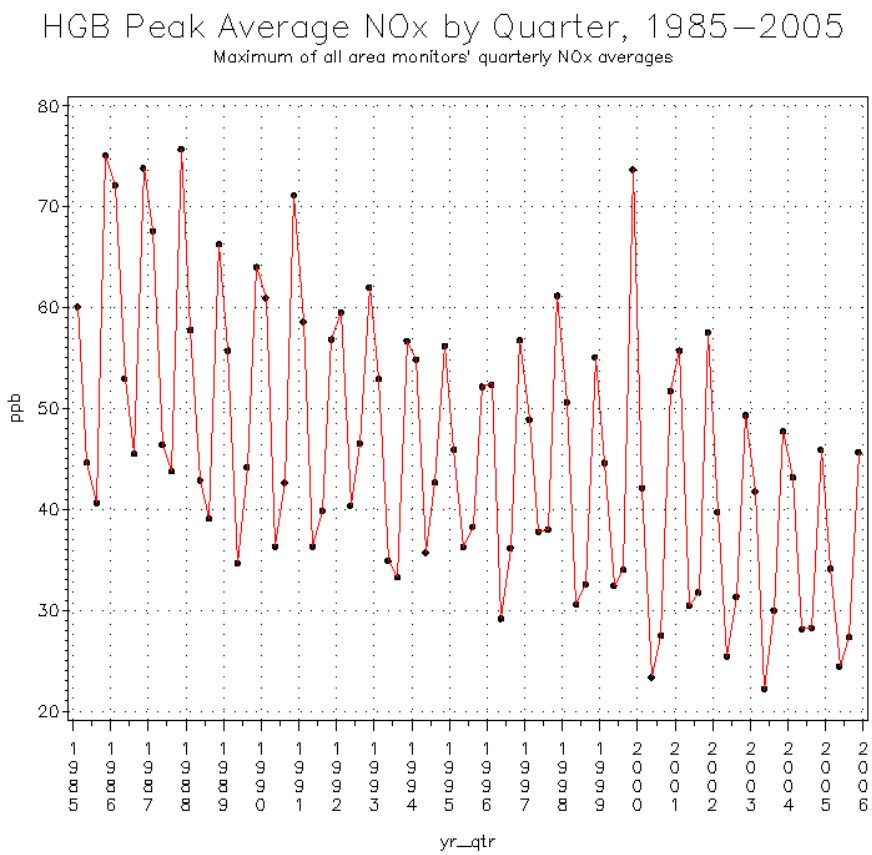

Figure 3-15: HGB Peak Average NO_X by Year and Quarter, 1985-2005

3.4.3 Emissions Inventory NO_X and VOC Trends

Both the NO_X and VOC emission inventories (EI) in the HGB area show trends that agree with the ambient trends described above. Figure 3-16: *HGB VOC EI by Inventory Category, 1990-2003* shows the anthropogenic VOC EI by source category for the area from 1990 to 2003, with an overall emissions decrease of 43 percent from 1990 to 2003. The categories contributing the most to the strong overall decrease are point sources and on-road mobile sources. From 1990 to 2003, point source VOC emissions have decreased about 71,000 tons per year (tpy), or 62

percent, and on-road mobile source VOC Emissions have decreased about 72,000 tpy, or 57 percent. The linear trend line shows that total VOC emissions are decreasing very steadily (R^2 = 0.94), at an estimated rate of nearly 11,000 tpy.

The point source emissions shown in Figure 3-16 are those reported by facilities to the TCEQ for its annual emission inventory and do not reflect the uncertainty found in this category by researchers in recent years (TCEQ).

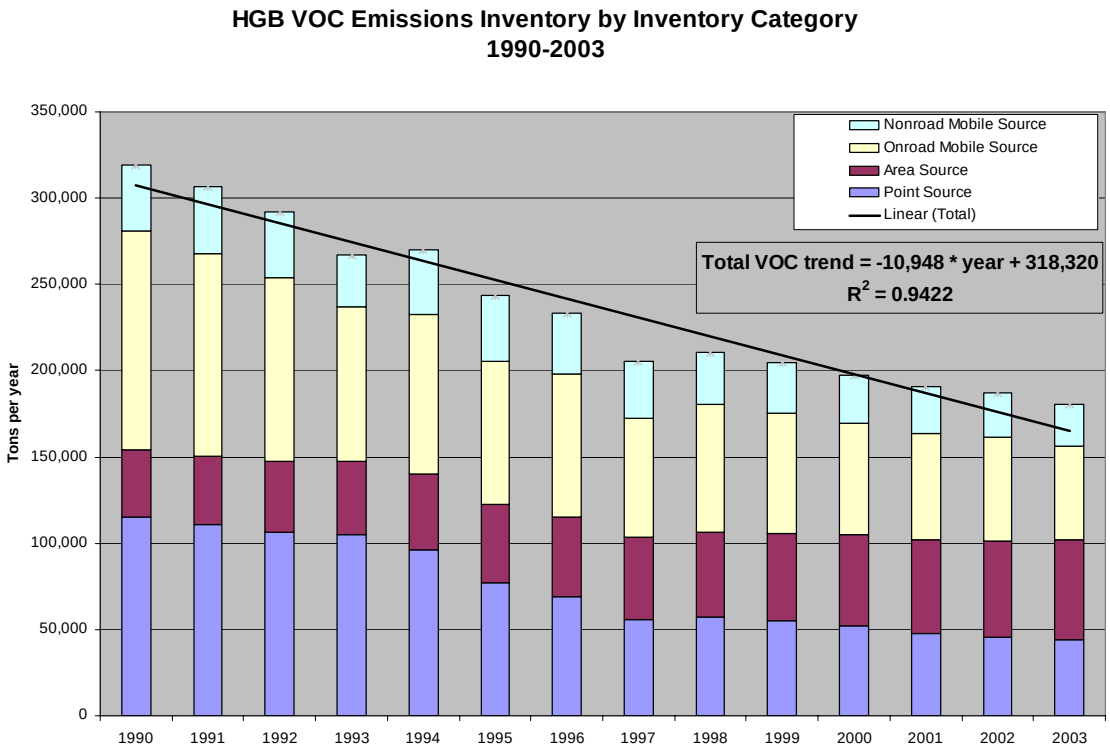

Figure 3-16: HGB VOC EI by Inventory Category, 1990-2003

Similarly, Figure 3-17: *HGB NO_X EI by Inventory Category, 1990-2003* shows the anthropogenic NO_X EI for the area for the same years. While the decrease is not quite as steady as with VOC (R^2 = 0.86), the reductions are nonetheless strong, estimated by the trend line to be about 13,800 tpy. In fact, overall NO_X emissions have decreased even more than VOC – 48 percent from 1990 to 2003. The dominant contributor to this trend is the point source category, which has decreased by 66 percent from 1990 to 2003, from about 277,000 tpy to about 94,000 tpy. This significant trend is expected to continue as the final mass emissions cap and trade program NO_X emission specifications for attainment demonstration become fully effective in April 2007.

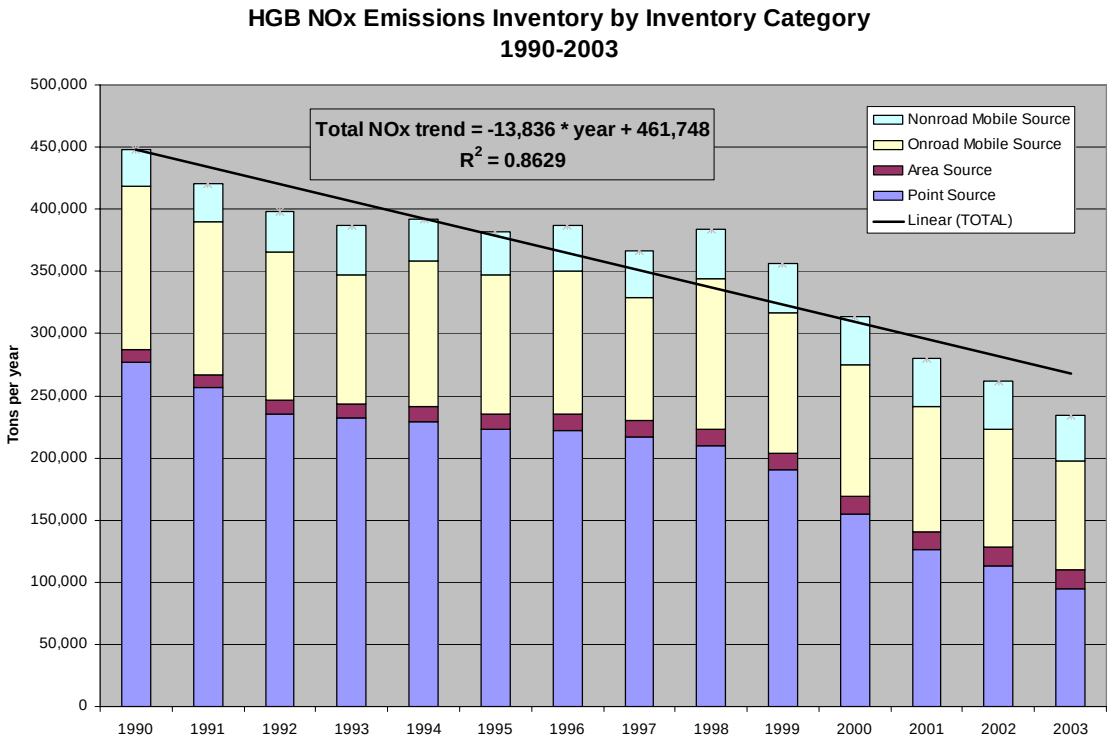

Figure 3-17: HGB NO_X EI by Inventory Category, 1990-2003

In addition to the decreases seen in the VOC and NO_X EI, in recent years the total emissions reported to TCEQ due to "events" – the combination of upset, maintenance, startup, and shutdown emissions – has similarly shown a decrease. Figure 3-18: *Reported Emissions from Upset/Maintenance/Startup/Shutdown Events in HGB Area, FY 2003-2005* shows that from fiscal year 2003 (beginning September 1, 2002) through fiscal year 2005 (ending August 31, 2003) reported event emissions decreased 76 percent, from 18,864 tpy to 4,428 tpy.

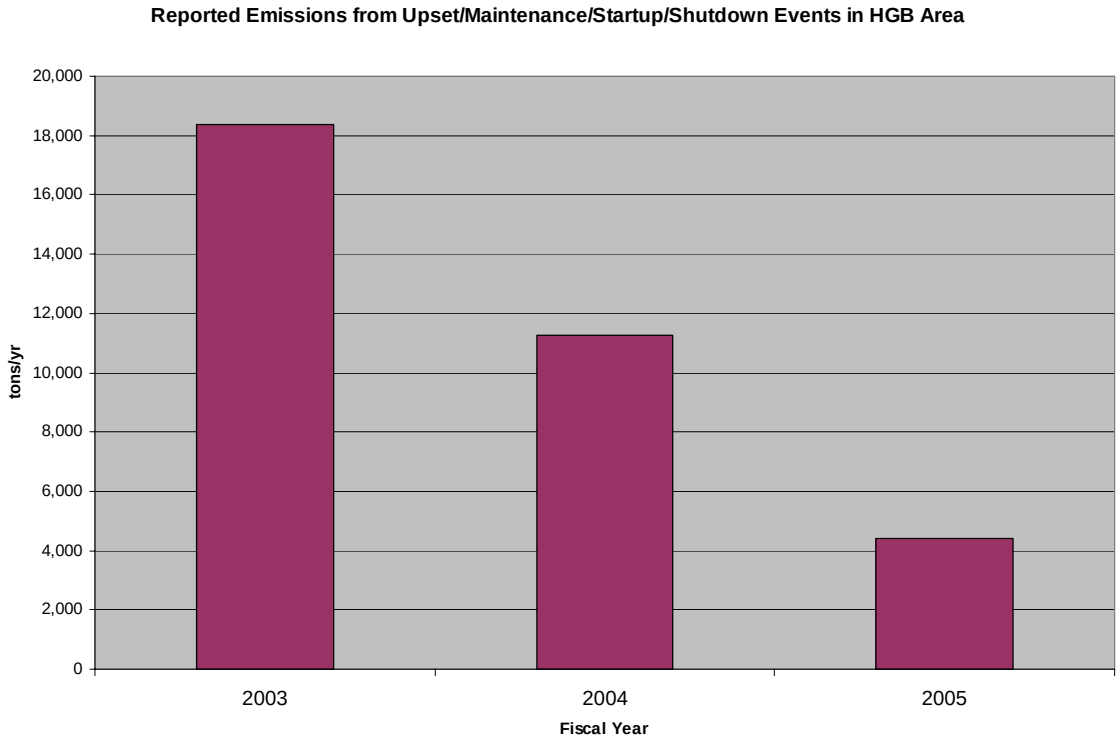

Figure 3-18: Reported Emissions from Upset/Maintenance/Startup/Shutdown Events in HGB Area, FY 2003-2005

The ambient and EI VOC and NO_X trends, and reported event emissions trends, described above are occurring despite a consistent increase in the HGB area population. Figure 3-19: *HGB Population by County, 1990-2005* shows the population by county from 1990 to 2005. As seen in this figure, total area population increased by 39 percent total, or 2.2 percent annually, in the period covered in this chart.

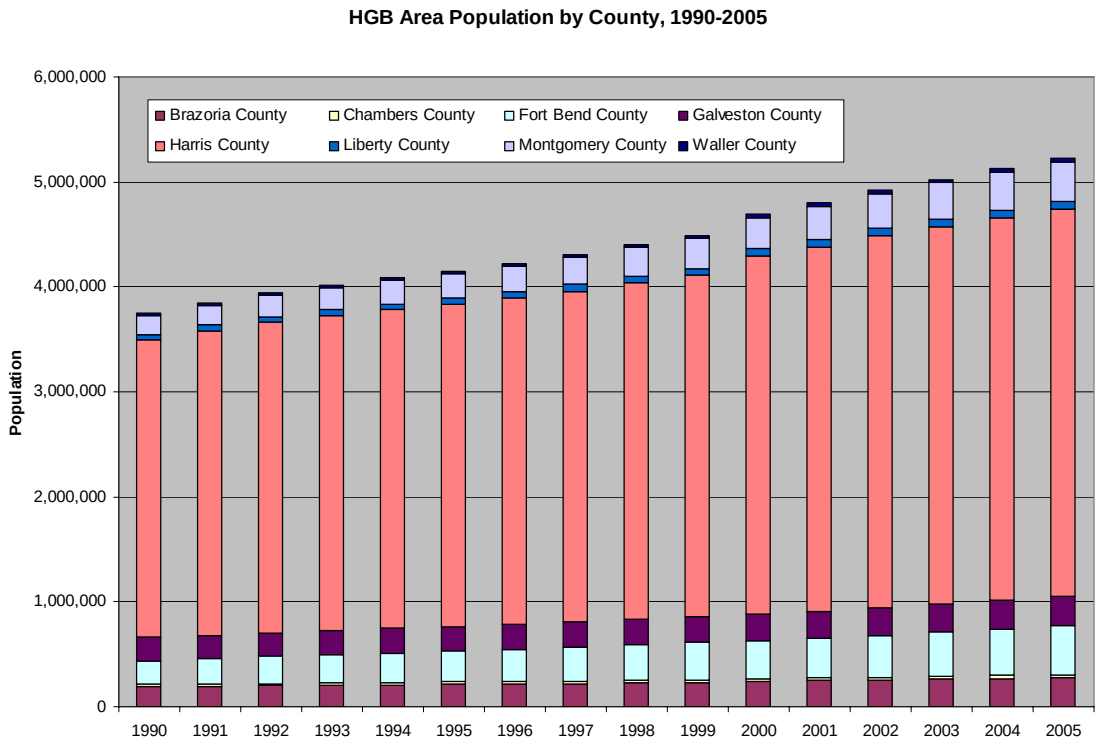

Figure 3-19: HGB Population by County, 1990-2005

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