Conceptual Model for Ozone Formation
in the Houston-Galveston Area

Appendix A
to
Phase I of the Mid Course Review Modeling Protocol and
Technical Support Document

Technical Support Section
Technical Analysis Division
TCEQ

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EXECUTIVE OVERVIEW

Local ozone production in the Houston-Galveston area (HGA) peaks at the same time of year and for many of the same reasons as in other areas of Texas and the United States. However, the ozone season in Houston lasts longer than in many other areas. The HGA also has a relatively high frequency of ozone compared to the national averages, reflecting the persistent hot, sunny and relatively stagnant conditions associated with high pressure in the Gulf of Mexico during the summer as well as the large population and the number of mobile, area and industrial sources in the area.

Ozone is generally associated with relatively clear skies, light winds, abundant sunshine, and temperatures above 80 to 85 degrees Fahrenheit. Typically, these meteorological conditions are associated with the high pressure areas which migrate across the US during the summer season. However, the persistent summertime high pressure area in the Gulf of Mexico and the flow reversals associated with the land/sea breeze phenomenon make the Houston situation unique.

High pressure areas have two characteristics that encourage ozone formation: light winds and subsidence inversions. Typically the winds circulating around a High are too weak to ventilate the urban area well, so local emissions tend to accumulate. The subsidence reduces vertical mixing, further aggravating the situation by concentrating the local pollutants near the surface.

Ozone formation in the HGA has also been associated with the daytime/nighttime flow reversal of the land/sea breeze since the Gulf of Mexico Air Quality Study (GMAQS) in 1993. Land/sea breezes are quite common in many coastal areas and have been associated with ozone formation in Athens, Greece and Barcelona, Spain as well as in the Houston area.

Land/sea breeze flow reversal occurs when high pressure dominates the area, resulting in light synoptic scale forcing. The light winds and subsidence allow high concentrations of pollutants to accumulate during the night and morning hours, and the land breeze carries the pollutants out over Galveston Bay and into the Gulf of Mexico. During the afternoon, the sea breeze flow reversal carries the ozone back into the city. In contrast, on low ozone days, precursor emissions are diluted and carried away by persistent winds.

A number of other specific factors add considerably to the complexity of the HGA situation. For example, the large cluster of petrochemical industries and point sources in the Ship Channel emit a variety of NOx and VOC precursors not typically found in other urban areas. Oak forests near the city also emit large amounts of isoprene which reacts strongly with the numerous NOx sources in the area. Background concentrations and transport issues appear to play a minor role in the HGA when compared to local sources, but will probably play a larger role in the future as local emissions reductions are implemented.
Conceptual Model for Ozone Formation in the Houston-Galveston Area

The HGA is extremely complex in terms of both emissions and meteorology. Ozone formation in the area is consequently quite complicated and multi-faceted, and occurs under a wide variety of conditions. This document explores the major factors thought to affect ozone concentrations in the HGA and provides a broad overview of the conditions under which unhealthy concentrations of ozone form. However, these factors may interact differently in each ozone episode. So individual ozone episodes must be evaluated on a case-by-case and day-specific basis to understand the factors involved in each episode.

Temporal Analysis

Seasonal Patterns

Figure 1 shows that the Houston area has more ozone exceedances than any other city in Texas. As a result of the meteorological and climatic conditions along the Texas Gulf Coast, the ozone season in the HGA is also quite long compared to other areas in Texas. Ozone exceedances occur primarily from March through October in the HGA, and may even occur during the winter months. However, ozone exceedances in the HGA occur more frequently in late summer with a significant peak in late August and early September. The number of exceedances drops dramatically in late September, though exceedances still occur as late as the third week of October. Ozone is generally associated with relatively clear skies, light winds, abundant sunshine, and temperatures above 80 to 85 degrees Fahrenheit. These meteorological conditions are associated
with the high pressure areas which migrate across the US during the summer season. However, there appear to be three specific climatological factors that account for the summertime maximum ozone in the Houston area: high temperature, light winds and onshore wind flow. High temperatures occur in the summer because the sun moves into the northern hemisphere in the summer, resulting in higher temperatures and more sunlight than in other seasons. But analysis of other climatological data, particularly winds, adds considerably to the picture.

Table 1 shows that the lightest wind speeds of the year occur during August and September. This pattern occurs because during the summer, the jet stream moves to the north, pushing the frontal boundary and activity out of the Houston area. In place of the fronts, a relatively stable high pressure area forms in the Gulf of Mexico. This Gulf of Mexico High has several effects in addition to reducing the wind speed in the Houston area.

The stable high pressure region develops a persistent on-shore pressure gradient, which results in on-shore wind perpendicular to the coastline in March and April as well as in August, September and October. The winds tend to be stronger during the spring, preventing the degree of accumulation of pollutants that occurs during the summer. The highest average daily maximum temperatures occur in July and August.

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Table 1  Houston Meteorological Factors Affecting Ozone formation

When all three of these factors (wind speed, wind direction, and average maximum temperature) are combined, a trend remarkably similar to that shown in the Monthly Ozone Frequency graph (Figure 1) is produced. Figure 2 shows the results of multiplying weighted factors for monthly wind speed,
cosine of the wind direction with respect to the Texas coastline, and average maximum temperature. Data for the Table 1 and Figure 2 came from the Local Climatological Data (LCD) for Houston, Texas (IAH). Wind speed and direction data were based upon 28 years of data. The average daily maximum temperature data was based upon 31 years of data.

This analysis suggests that wind speed, wind direction and daily maximum temperature are important factors in Houston ozone analysis.
El Nino/Southern Oscillation

El Nino events typically last from 14-24 months but they peak during the December-January “Christmas” season, leading to the name “El Nino” (for the Christ child). Although El Nino events affect wintertime temperatures in the central US and rainfall along the Gulf Coast, El Nino has remarkably little effect on Houston ozone. Figure 3 below shows that over the last 27 years, the correlation between the number of Houston ozone exceedances in August and September and the El Nino Multivariate ENSO Index (MEI) for the period is very weak and has been essentially random. The correlation coefficients ($R^2$) for both the leading period (July-Aug) and coincident period (Aug-Sept) are less than 0.01.

![Houston Ozone Exceedances vs El Nino Multivariate ENSO Index (MEI)](image)

**Figure 3** Houston Ozone Vs El Nino [1974-2001] (TNRCC)

Hurricanes and Tropical Storms

The summer ozone frequency maximum in the HGA (Figure 1) appears to coincide with the hurricane season, and high ozone events have occurred occasionally when hurricanes and tropical storms are active in the Gulf of Mexico. It is clear that ozone episodes do not occur when hurricanes and storms are actively affecting the Houston area. However, from a mass balance perspective, substantial subsidence must occur some distance away from the hurricane to counter the strong upward vertical motions generated in the core of the hurricane. Subsidence, clear skies and light winds always support the accumulation of pollutants, and the summer high temperatures and
sunlight activate the photochemical mechanism that forms ozone.

**Day-of-Week Pattern**

For most cities, the frequency of high ozone events varies between weekdays and weekends. Typically, changes in the weekend emissions from the mobile source component of the inventory are reflected in the day of the week analysis. For Houston, the day-of-the-week graph (Fig 4) indicates that ozone occurs with roughly the same frequency on each day of the week and that weekends are neither more nor less likely to have an ozone occurrence. Statistical analysis of the data using a Chi-Square test confirms that the day-to-day variations in the graph are probably due to normal variation and the small sample size. Also, there appears to be no significant difference in ozone frequency when urban and suburban areas are compared. This pattern suggests that the emissions that do not systematically vary with day-of-week (e.g., industrial emissions) contribute significantly to the ozone problem.

![HG Ozone Frequency by Day of Week 1997-1999](image)

**Figure 4**  Houston Ozone Frequency by Day of the Week (TCEQ) ozone problem.
Diurnal Pattern

Ozone seen at the Houston area monitoring stations frequently appears on time series graphs as distinct peaks at individual stations that last only an hour or two (Fig 5). If the ozone concentrations peaked at nearly the same time all over the domain, one could attribute the ozone to photochemical reaction of generalized, somewhat homogeneous emissions from mobile and area sources. However, peaks are frequently observed an hour or two later at downstream monitors, apparently as the parcel is carried by the wind. These pulses of ozone appear to form near eastern Harris County and then traverse across the HGA domain, where they are observed briefly as they pass each monitoring site.

Figure 5  Hourly Ozone in the Houston Galveston Area [July 7, 2000] (TCEQ)
Geographical Analysis

Ozone exceedances in the HGA occur throughout the domain; however, the highest monitored values occur most frequently near the Ship Channel, suggesting a relationship between the ozone spike phenomenon and the numerous industrial sources in the area. Depending upon changes in the wind speed and direction, ozone exceedances appear to move across the domain and may be seen at least briefly over the entire area. Ozone peaks on individual days may occur anywhere in the city core and as far away from the city as Clute, Galveston Island and Baytown.

Exceedance Analysis

Analysis of the frequency of ozone daily and hourly exceedances indicates that the city has three high frequency ozone areas, at Deer Park in the east, Croquet/Bayland Park in the west and Aldine in the north (Fig 6). Each of these areas experiences more than 30 exceedance days per year.

Design Value Analysis

However, analysis of the four highest ozone exceedances occurring during the 1998-2000 period also shows that the highest ozone concentrations are measured in the area east of the city core. Design values above 180 ppb stretch from Aldine to Deer Park, and the maximum design value for the period (199 ppb) occurred at the Clinton Drive monitor (Fig 7).

Both figures indicate an area in the city center running southeast-northwest through the city core that has lower values for both ozone frequency and the design value. It is assumed that this area of low ozone is the result of NOx scavenging in the area, probably associated with mobile source emissions along Interstate 45 and Highway 290 since the Crawford monitor sees relatively high measured NOx concentrations.

Analysis for the previous three year period (1997-1999) indicated that the highest design value for that period occurred at the Deer Park monitor. This factor suggests that even though the location of the design value may migrate from year to year, the general location of the highest measured ozone stays in the eastern portion of the city. It is also important to recognize that while the highest ozone levels appear to occur in eastern Harris county, ozone precursors are generated by numerous mobile, area and point sources throughout the nonattainment area.
Figure 6 Houston/Galveston/Brazoria Area Expected Ozone Exceedance Days [1998-2000] (TCEQ)

Figure 7 Houston/Galveston/Brazoria Area Ozone Design Values 1998-2000

Figure 7 Houston/Galveston/Brazoria Ozone Design Values [1998-2000] (TCEQ)
Analysis

Emissions Comparison

A comparison between Houston and Dallas emissions is instructive. Dallas and Houston have roughly similar populations, but significant differences in emissions. Figure 8 shows that VOC and NOx emissions from area and mobile sources in both cities are very similar. However, the VOC and NOx emissions from point sources are very different. Houston point source emissions are much larger, reflecting the numerous industrial sources in the Houston area.

Many of these point sources are located along the Ship Channel, reflecting the high concentration of industry in this area. Figures 9 and 10 show the relative concentration of industrial point sources in the area. Since many of these petrochemical industries emit both NOx and VOC, the co-location of sources and the mix of precursors appears to be partly responsible for the relatively high concentrations of ozone measured near the Ship Channel area as shown in Figure 7.

Figure 8  Emissions Comparison for Dallas and Houston (TCEQ)
Figure 9 1998 NOx Point Sources (TCEQ)

Figure 10 1998 VOC Point Sources (TCEQ)
Airborne measurements of NOx, VOC, and ozone concentrations during the TExAQS 2000 study support the importance of the industrial sources to the formation of ozone in the area.

Figure 11 shows the data measured during an aircraft mission flown on August 28, 2000. The winds on that day were from the south so the aircraft flew east-west transects north and south of the city. The aircraft measurements made on that day at 2000 feet clearly show an ozone plume stretching downwind from the ship channel.
Aircraft Measurements of Ozone and Formaldehyde

Figure 13 shows the ozone and formaldehyde measured at approximately 2000 feet above the ground on August 28, 2000, the same day as in the previous figure. This track was flown from west to east approximately 40 kilometers north of the city center. The data show the ozone and formaldehyde measured downwind of the Parish power plant, the urban core and the Ship Channel. The ozone concentrations downwind of the industrial area are much larger than the ozone measured downwind of the power plant and the urban core.

Ratios of VOC to NOx from these aircraft measurements indicate that the VOC concentrations measured in the atmosphere downwind of the Ship Channel are much higher than suggested by the emissions inventory data. Also, aircraft measurements taken during the study indicate that the concentrations of olefins (especially ethylene and propylene) are also considerably higher than in the inventory. Figure 13 also shows that the concentrations of formaldehyde rises with the ozone peak downwind of the ship channel.

![Figure 13](image)

**Figure 13** Aircraft Measurements of Ozone and Formaldehyde [Aug 28, 2000] (Trainer)

The high ozone concentrations correlate very closely with the formaldehyde measurements, suggesting that either the ethylene emissions and chemistry are responsible for the formaldehyde, or that formaldehyde emissions are also significantly understated in the reported inventory. Since olefins are highly reactive, and aldehydes are formed as the first step in the photochemical reaction that forms ozone, olefin emissions probably account for the high ozone measured downwind of the industrial areas.
LIDAR Measurements During TxAQS

Aircraft measurements of ozone taken with a LIDAR on September 6\textsuperscript{th} also suggest that Ship Channel sources are a significant factor in ozone formation in the Houston area. The winds on this day blew steadily from the northeast, so the aircraft flew transects perpendicular to the wind flow, starting in the Ship Channel and moving downwind to the southwest. Figure 14 shows two long, narrow ozone plumes extending from the Ship Channel and Texas City southwest roughly parallel to the coast line. Ozone concentrations measured by the LIDAR on this day in these plumes range from 160 ppb near the Ship Channel sources to approximately 100 ppb measured 90 miles downstream.

![Figure 14 Ozone Plumes Measured Downwind of Industrial Sources on Sept 6\textsuperscript{th}, 2000 (Senff)](image)

LIDAR Ozone Profiles
Figure 15 shows a vertical profile of the ozone measured by the NOAA DC-3 LIDAR on September 6, flown between the A and B locations on Figure 14. Figure 15 shows the two plumes observed during the transect. The weaker, southern plume comes from the Texas City area. The larger, denser plume comes from the Houston ship channel.

The LIDAR data also shows that the ozone in the stronger plume is mixed from the surface to approximately 1300 meters on that day. Ozone measured in the plume is approximately 155 ppb, confirming the 156 ppb measured at the Croquet monitor at 1300 CST that day, and indicating that the ozone is not just an elevated plume measured by the aircraft, but relatively well mixed through the layer.

It is possible to have ozone plumes aloft that are not mixed down to the surface, especially during the nighttime and early morning hours. However, Lidar measurements made from the NOAA DC-3 in the afternoon generally show the atmosphere is well mixed, and the ozone plumes have higher concentrations near the surface and are mixed from the surface well up into the atmosphere.
Wind Pattern Analysis

During the summer, the persistent high pressure area in the Gulf of Mexico leads to generally stagnant meteorological conditions and relatively weak (but onshore) pressure gradients. This relatively weak synoptic scale forcing allows smaller scale factors to affect the local weather patterns. In the Houston area this results in relatively persistent sea breezes along the coastline, land/sea breeze flow reversals and a shoreline convergence zone which can be observed as a cloud band in satellite photos as it moves inland a short distance from the coast.

EPA Analysis Method

EPA guidance for episode selection recommends analyzing the wind patterns between 7 AM and 10 AM to determine the relative frequency of wind patterns and calms associated with ozone formation. (Guideline for Regulatory Application of the Urban Airshed Model, EPA-450/4-91-013, July 1991). The guidance further recommends selecting one of the top three events in each category for modeling. During the COAST study, the TCEQ recognized the importance of the morning/afternoon land/sea breeze flow reversal and therefore enhanced the EPA morning method by including 4 hours of afternoon winds in the analysis. Review of wind patterns during high ozone events using the improved TCEQ morning/afternoon method indicated that the wind directions change dramatically during the day as a result of the sea breeze flow reversal (Fig 16).

24-Hour Analysis Method

However, more recent analysis of daily wind patterns suggest that even the TCEQ-enhanced method of morning/afternoon analysis of wind directions may still not fully describe the HGA situation. For example, the easterly winds observed between 11:00 and 1:00 are described as a Galveston Bay breeze but cannot be attributed to land/bay temperature differences.

Recent analysis suggests a similar picture but proposes a more dynamic explanation. Analysis of the most recent three peak ozone seasons (August through September of 1998, 1999, and 2000) shows that the surface winds typically change direction continuously during the 24-hour day, with wind vectors veering clockwise through all the compass directions (Fig 17). This continuously changing wind pattern occurs over the entire HGA domain, not just near the coastline. Although it is still true that on high ozone days, the early morning winds tend to come from the northwest and the afternoon winds tend to come from the southeast, the new picture is much more complex than the previous explanation.

On average, the winds associated with ozone formation appear to come from the west at midnight, shifting to the northwest at 6 AM. The winds are generally light during the night and early morning hours. By noontime, the winds have rotated to the east, and then strengthen from the southeast as the sea breeze comes in during the afternoon. However, as will be explained in more detail later, this is the average pattern, and it varies considerably from day to day.
Figure 16 Traditional View of Land/Sea Breeze (TCEQ)

Figure 17 Recent Analysis of Land/Sea Breeze in Houston Area (TCEQ)
Patterns

On high ozone days (68 ozone events with ozone $\geq$125 ppb) winds typically come from the west between midnight and 6 AM, and shift to the northwest and the northeast in the morning hours throughout the HGA domain. By noontime, the winds become easterly and then veer to the southeast in the afternoon, again at all stations in the domain. After sunset, the wind direction shifts again, returning to the west. Since there is northerly flow in the morning hours, replaced by southerly flow in the afternoon, the land/sea breeze flow reversal identified by earlier analyses is still apparent, but the simple diurnal pattern is replaced by a 24-hour rotational pattern.

Figure 18 shows the average diurnal change in wind direction by connecting the tails of each of the hourly wind vectors. Effectively, the wind veers clockwise through all four quadrants during the 24-hour period. As a result, when averaged over 24 hours the wind vectors from opposing directions tend to cancel each other out; therefore the net transport vector (magenta) is relatively small and pollutants are not transported far from their source regions. However, on average, the veering flow pattern moves the HGA morning emissions from the urban and industrial areas gently to the southeast, and then back toward the city at noontime before carrying the parcels back over the city in the afternoon and evening.

Figure 18 Wind Vector pattern on High Ozone Days (TCEQ)

This rotating wind pattern can only occur when the synoptic scale pressure gradient is relatively weak, which allows local geography and land/sea temperature differences to drive the local wind patterns.
Low Ozone Wind Patterns

In contrast, on low ozone days (ozone < 125 ppb, 115 low ozone events) the westerly component is not evident in the average wind pattern over the domain (Fig 19). The predominant wind direction is from the east and southeast, suggesting persistent rather than reversing flow. The northwesterly component is missing in the early morning hours, and generally the northeasterly component is missing during the late morning hours. Since the westerly and northerly winds are missing or light, effectively there is no flow reversal on these days. Further, the net wind vectors over the 24-hour period during low ozone days are stronger than on high ozone days, with a relatively persistent sea breeze flowing from the southeast, indicating increased ventilation and transport rather than recirculation.

The low ozone wind pattern seems to occur when the synoptic scale pressure gradient is strong enough to result in persistent easterly and southeasterly winds. These relatively strong winds ventilate the HGA and keep the ozone relatively low. If the synoptic scale pressure gradient is strong enough, the persistent winds bring in clean maritime air and relatively low ozone. However, a persistent wind pattern strong enough to ventilate the Houston area is also likely to carry Houston emissions downstream to other areas in Texas, as will be seen later.

Figure 19 Wind Vector Pattern on Low Ozone Days (TCEQ)
Trajectory Analysis

Trajectories Based upon Surface Winds

Trajectories depict the movement of a parcel of air over time by integrating wind speed and direction into one composite image. Surface wind trajectories calculated from the domain wide hourly average wind vectors suggest that the wind patterns for high and low ozone days are substantially different. On high ozone days, the trajectory diagram shows limited transport during the night and early morning, coming back into the city in the afternoon (Fig 20). In contrast, during the low ozone events, the trajectory diagram shows that the winds blow continuously from the southeast, ventilating the area, and transporting the pollutants and ozone out of the urban area (Fig 21).

Back Trajectories Based upon Upper Air Winds in the Transport Layer

Back trajectories developed from meteorological models and transport level winds for high ozone days illustrate the net southeasterly flow pattern in Figure 20. Analysis of 32 hour back trajectories in the 500 meter transport layer for Houston high ozone days occurring in 1995 and 1996 suggest that on a day to day basis, HGA ozone is associated with transport level winds coming from several different directions - from the north, through the east and southeast to the southwest (Fig 22). Transport level winds from the west and northwest are only rarely associated with ozone events in the Houston area. Statistical analysis (Fig 23) of this data shows that the winds in the transport layer come most frequently from the southeast, confirming the net southeast orientation of the surface trajectory patterns discussed in Figures 20 and 21.

Limitations of Trajectory Analysis

It is important to point out that transport layer back trajectories for ozone episodes are based upon archived upper air data from meteorological models, and interpolated from a coarse grid which smooths out the local perturbations and geographical details. Trajectories developed from transport layer winds do not necessarily represent the wind fields at the surface, especially on a day to day basis. Individual trajectories have error bars which increase with time and distance, and so must be interpreted with caution. However, when a large number of trajectories for ozone episodes are analyzed statistically, they provide a reliable picture of the most likely flow patterns and source regions affecting an area.

Surface winds and surface trajectories have the opposite limitations. Winds measured at surface sites reflect only the surface conditions and the geographic features near the measurement site. Surface winds measured at CAMs and other surface stations may be affected by local obstructions and may not represent areas outside the immediate vicinity of the measurement site. Surface winds also do not necessarily represent the wind speed and direction in the transport layer. Therefore individual trajectories based on winds at surface monitors must be interpreted carefully. However, conclusions drawn from time and space averages of surface winds are reliable if used in a general rather than site or day specific sense.
Figure 20 Average Surface Wind Trajectory on Ozone Exceedance Days (TCEQ)

Figure 21 Average Surface Wind Trajectory on Low Ozone Days (TCEQ)
Figure 22 Back Trajectory Pattern for Ozone Exceedance Days (TCEQ)

Figure 23 Statistical Analysis of Back Trajectory Wind Directions (TCEQ)
Mechanism for Houston Ozone Formation

The veering wind vector analysis described in Figures 17, 18, and 20 suggests a mechanism for ozone formation in the HGA. It appears that on high ozone days, emissions from mobile and industrial sources accumulate overnight as a result of the light northwesterly winds and the limited night time mixing. These relatively high concentrations of ozone precursors are trapped in the shallow mixing layer and drift southeast toward Galveston Bay.

After sunrise the photochemical reactions begin and the precursors are converted into ozone by sunlight. The concentrations remain high as a result of the limited mixing over water during the morning hours. After noon, the wind flow rotates to the southeast as a result of the sea breeze which carries these parcels with their high ozone back across the HGA domain.

This moving pool mechanism for ozone formation accounts for some of the previously unexplained results coming from analyses of time series data. Time series data from ozone monitoring stations on high ozone days (Fig 24) show a series of transient ozone peaks which briefly impact different stations at different times during the day. Typically, high ozone is first measured southeast of the Ship Channel in the Deer Park/ La Porte area at approximately noontime and then appears briefly at other stations later in the day. This analysis suggests that a relatively compact parcel of ozone forms in the vicinity of the Ship Channel, and moves over the city, triggering ozone peaks at different times and monitors in a moving geographic sequence.

![Hourly Ozone in the Houston–Galveston Area](image)

Figure 24 Ozone Time Series for August 25, 2000 (TCEQ)
Time of peak analysis also supports the moving parcel hypothesis. If HGA ozone were attributed primarily to air stagnation with a uniform pool of emissions, we would expect to see ozone rise at roughly the same rate at all stations, and all stations would hit their individual peaks at roughly the same time during the afternoon. However, the map (Fig 25) shows the average time of the ozone peak at stations across the HGA domain. The data shows that on average the earliest ozone peaks tend to occur in the Deer Park/La Porte area at approximately noon, and that the peaks at all the other stations occur later in the day. For example, Conroe peaks tend to occur much later in the afternoon, at about 5 PM. This again suggests that the ozone-rich parcels start near the Ship Channel and move across the domain.

Figure 25 Time of Ozone Peak (TCEQ)
Plotting the average trajectory patterns on a map suggests the most frequent path for the ozone peaks as they move across the Houston area. (Figure 26) Depending upon the direction of the wind, the high ozone parcel may move across the city hitting several different monitors in succession. Based on the average flow vectors, the most frequent transport direction appears to be from the southeast to the northwest, although there is considerable variation on a day to day basis. If synoptic scale forces dominate the winds, the daily flow patterns may carry ozone to the southwest, the northeast and even to the east.

Houston Classic Flow Pattern on High Ozone Days
Based on the evidence above, it appears that on many high ozone days, ozone precursors accumulate during the early morning hours, developing relatively high concentrations as a result of the light winds and low mixing height during the nighttime hours. These high levels of precursors are supplemented by mobile source emissions in the morning rush hour. This pool of emissions is carried southeast toward Galveston Bay. During the morning hours, these parcels begin forming ozone. When the wind direction shifts as a result of the sea breeze, the parcels are carried over the Deer Park and La Porte monitors, which typically experience their highest ozone before the other stations (Fig 26).

The ozone laden parcels are then transported over other parts of the city. Depending upon the day to day variations in synoptic forces, the winds can carry the ozone parcel over different parts of the city, so that the daily maximum may occur at different locations. On some days, the winds match the average pattern, and the ozone pool is carried to the northwest. On other days, the variations in wind carry the parcel to other areas of the city. And on other days, if the winds are very light, the pool of high ozone remains in the local area as result of the stagnant conditions.
Ozone Days

In contrast, on low ozone days, the synoptic scale pressure gradient is strong enough to override the flow reversal phenomena. Typically, the winds on low ozone days vary in strength during the day but are relatively stable in direction. These persistent wind flow patterns transport the pollutants out of the HGA where, although diluted, they affect downwind regions and cities. When the persistent winds come from the south and southeast, the ozone is carried into central and northern Texas. When the persistent winds are from the north and northwest the pollutants are carried out into the Gulf of Mexico.

![Houston Ozone Mechanism](image)

In summary, there appears to be two distinctly different sets of meteorological conditions affecting ozone concentrations in the Houston area. When the surface winds are relatively light, urban and industrial emissions accumulate, move to the southeast and then move back over the city in the afternoon with the sea breeze. When the winds are stronger and persistent in direction, they dilute the emissions somewhat and carry them out of Houston to other areas, raising the background concentrations in rural areas and adding to the ozone concentrations in other cities in Texas.

Other Factors that Influence Ozone in the Houston Area
Mixing Height

During the TexAQS 2000 summer ozone study mixing height was measured at five different locations in the Houston area by several different methods: wind profilers, rawinsondes, and aircraft measurements. Wind profiler data was post-processed to assess the evolution of the mixing height during the day, and the profiler measurements were in general confirmed by the rawinsonde data.

Figure 28 shows the evolution of the mixing height on August 26, 2000. The mixing height starts at a minimum during the early morning hours, rising to a maximum during the morning and mid day, and then decreasing sharply in the afternoon as the sea breeze pushes inland and brings cooler air to the region. However, in areas further from the coastline, the mixing heights continued to rise until much later in the afternoon.

Aircraft Measurements of Mixing Height

![Wind profiler and radio sonde BL depths 26 AUG](image)

**Figure 28** Mixing Heights on August 26, 2000 (Senff)
Aircraft measurements of mixing height using the downward looking Lidar provide additional perspective on the evolution and development of mixing height because aircraft can provide information on the mixing heights over a large geographical area as well as taking measurements over water areas that would not be available from ground based systems. Because of the complex interaction between the Houston industrial emissions and the sea breeze flow reversal it is particularly important to get mixing height data over Galveston Bay and the Gulf of Mexico to validate the results of the meteorological modeling.

Figure 29 shows the mixing heights measured by Lidar on August 26, 2000, the same day displayed in Figure 28. Aircraft measurements show that mixing heights vary from 500-600 meters over the Gulf of Mexico, to 1000-1200 meters over Galveston Bay, to more than 2000 meters further inland away from the coast.
Mixing Height Analysis

Mixing height appears to play a significant role in the concentrations of ozone developed in the Houston area. On August 30 and 31, the wind flow patterns at the surface and in the mixed layer are remarkably similar, and the peak concentrations on both days were measured in approximately the same area. However, the ozone concentrations on these two days are significantly different, evidently because of differences in the mixing height.

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<tr>
<td>August 31, 2000</td>
<td>Deer Park</td>
<td>15:00</td>
<td>168 ppb</td>
<td>2800 meters</td>
</tr>
</tbody>
</table>

The mixing height rises steadily during the day as the air mass over the profiler is heated by the sun. The peak mixing height on both days was measured at 15:00 Central Standard Time, and then decreased rapidly as the sea breeze carried cooler air into the area.

Figure 30  Ellington Mixing Heights on August 30, and August 31, 2000 (Senff)
Rapid Ozone Formation and Spike Phenomena

The Houston area is characterized by very rapid increases in ozone concentrations measured at individual monitors. This phenomena is observed much more frequently in the Houston area than in the Dallas area, and was observed frequently during the TexAQS study.

Figure 31 shows the distribution of maximum hourly rises in Houston. The histogram includes every event at every monitor that exceeded 125 ppb between 1990 and 2000. The graph is skewed to the right, indicating many events with large hourly rises occur in Houston. The median hourly rise in ozone is 40 ppb, and hourly rises as large as 80 ppb occur 5% of the time.

Since rapid rises in hourly ozone greater than 40 ppb occur relatively frequently in the Houston area, they are “normal” for the area, and too important to ignore. The Houston ozone assessment must not exclude the cases with relatively large hourly rises simply because they are unusual in other regions of the U.S.

Moving Parcel Analysis
The moving parcel theory proposed in previous sections provides an explanation for the rapid rise of ozone measured in the Houston area. (Fig 32) If we assume that a parcel with high ozone moves across the domain, then the same parcel is measured at different times and places during the day.

When the parcel with high ozone arrives, the concentration measured at the monitor increases rapidly. If the same parcel is measured by different monitors, then the steep rise in ozone measured at a single monitor (the green line) is composed of two components. The first component is simply due to movement of the parcel. The second component (the red line) is the actual change in ozone within the parcel caused by photochemical activity over time, and the blue line represents the increase in ozone within the last hour.

Focusing on the large hourly rises measured at a monitor is misleading, because it assumes that Houston ozone occurs under stagnant conditions like other cities in the US. Houston analysis should acknowledge that in Houston the parcels move across the domain.

**Figure 32** Rapid Ozone Rise (TCEQ)
There is evidence that Houston experiences higher ozone when high regional levels of pollutants are carried in as background from other areas in the US. Analysis of ozone and precursor data from upwind monitors suggests that although the HGA contributes greatly to its own ozone, HGA ozone is frequently aggravated by upstream contributions.

Long range back trajectories for two episodes in 1999 (Figs 33, 34) suggest that air sometimes comes from the Ohio valley carrying emissions from Midwestern sources. This situation occurs when a high pressure dome sets up in the central US, and brings air south over Kentucky, Tennessee and Louisiana out into the Gulf of Mexico. As the high pressure area drifts to the east, the winds become easterly, southeasterly and even southerly, bringing the regional background levels of ozone and precursors into Houston and central Texas.

**Figure 33** Potential for Regional Contributions

**Figure 34** Potential for Regional Contributions
Ozone Yield

Data from the Houston area indicate that the sharpest rises in ozone concentration are measured near the industrial sources in the Ship Channel area. It appears that the parcels arriving at stations near the shoreline of Galveston Bay have high concentration gradients which are manifested at the monitor as rapid rises in ozone. Aircraft measurements taken during the TexAQS study also indicate that the mix of precursors in the Houston Ship Channel area produces roughly three times as much ozone per NOx molecule as is observed in other cities. (Figure 35) It appears that the transport and photochemical mechanisms combine to form the rapid rises and spikes measured in the Houston area.

![Figure 35 Enhanced Ozone Yield in the Houston Ship channel Area](image)

The emissions inventory data summarized in Figure 8 suggest that the differences in ozone between Houston and Dallas are due in large part to the industrial contributions of VOC and NOx. Figures 5 and 24 suggest that the that the highest measured ozone concentrations occur when the ozone from industrial sources is added to the generalized urban ozone concentrations that affect the rest of the city. On a given day, some areas experience the high ozone resulting from adding the industrial contributions to the urban ozone and other areas experience only the urban ozone concentrations.
NOx Emissions

Point Source NOx emissions are relatively well known since they generally come from continuous combustion sources and are based on relatively reliable emissions factors and stable activity factors. Further, point source NOx emissions are reliable because they are based upon a large body of CEM (continuous emissions monitor) data. Most of the larger NOx emissions sources in Houston report their emissions based upon actual CEM monitored data or stack tests.

Figure 36 shows the distribution of aircraft measurements of NOx taken during the TexAQS 2000 study, and the NOx measurements made in other cities by the TexAQS scientists, plotted on a log-probability scale. The Houston NOx measurements are greater than measured in other cities for all concentrations above the 40th percentile. Since the x-axis is a log scale, the difference at the high end of the scale actually represents a factor of about two.

The NOx data plots as a straight line on this graph, indicating that NOx concentrations are a log-normal distribution. A log-normal distribution is expected because NOx emissions come primarily from continuous combustion sources and are affected by normal atmospheric diffusion and dispersion processes.
Ethylene Emissions

Figure 37 shows the cumulative frequency distribution of ethylene concentrations measured by aircraft during the TexAQS study, compared to the same cities and again plotted on a log-probability scale. It is clear that starting at the 15 percentile ethylene concentrations are much larger than in the other cities. At the upper end of the scale, Houston ethylene concentrations are 10 to 20 times the concentrations measured in Dallas, Nashville, and Atlanta.

The ethylene data also plots as a straight line on this log-probability scale indicating that ethylene concentrations are a log-normal distribution and there is no breakpoint between normal and high concentrations. The distribution does not have two peaks, and there is no indication of two separable populations. This suggests that distribution of ethylene emissions is not driven by occasional large upsets.
VOC Reactivity

Figure 38 shows the total reactivity of the VOC concentrations measured in the air over five different cities. This data is taken from the top 10% of the reactivity measurements. It is clear that the total reactivity of the VOCs in Houston is much larger than in other cities. The largest component is due to the anthropogenic portion of hydrocarbons coming from the industrial sources in Houston.

It is interesting that the reactivity of the first four VOC categories in Houston is approximately equal to the total reactivity from all the VOCs measured in Nashville, New York, and Phoenix.

Figure 38  Top 10% of VOC Reactivities in 5 Cities (Kleinman)
Olefin Reactivity

Within the total VOC category low molecular weight alkenes (olefins) contribute a disproportionally large part of the ozone generation because they are so much more reactive than paraffins and many other VOCs. Figure 39 shows the average VOC reactivity of 26 most reactive VOC samples taken by the Baylor Twin Otter during TexAQS 2000. Ethene, propene and butenes (a.k.a. ethylene, propylene and butylenes) contribute about 50% of the total VOC reactivity measured in the air above Houston. The alkanes (paraffins) and aromatics contribute about 25% of the total reactivity, and isoprene and terpenes contribute a relatively small amount to the total reactivity.

Chemistry is dependent upon both NOx and VOCs. In Houston, both NOx and VOC concentrations are higher than in other cities, but NOx is only slightly higher. The high total VOC reactivity (frequently driven by the highly reactive olefins component) is the primary cause of the rapid ozone formation and the high ozone yields seen in the Houston area industrial plumes.
Chlorine Chemistry

The role of chlorine in Houston ozone is also being examined. Some industries use chlorine directly in their processes, but cooling towers and swimming pools appear to be the primary sources.

Modeling sensitivity studies have shown that chlorine chemistry accelerates the speed of formation of ozone and increase the ozone concentrations within a few kilometers of the chlorine sources by as much as 10 ppb.

Chlorine appears to affect ozone chemistry by activating the alkane (paraffin) compounds, which normally make a small contribution to total reactivity. However, in general, the sensitivity studies have shown that chlorine chemistry has a relatively small impact (1 - 3 ppb) on the peak ozone generated in the non-attainment area.

Figure 40 Effect of Chlorine on Speed of Reaction (Kimura)
Other Factors

In addition to the conceptual picture above, there are other factors that may play a role in Houston ozone exceedances. These factors may be added to the conceptual model later once their roles have been identified and their impact upon Houston has been defined and quantified. Some of these other factors are discussed in the “Accelerated Science Evaluation of Ozone Formation in the Houston-Galveston Area”, which is available on the TCEQ web site.