Combining Climate Change and Air Quality Research
August 2007
Comprehensive Chemical Analysis of TexAQS II Data

I. Introduction

In March 2007, TECQ requested that, in addition to the original twelve SIP-relevant questions addressed in the Rapid Science Synthesis Report, NOAA undertake to provide additional guidance to TCEQ regarding fourteen specific issues and areas of concern that are related to chemical sources and processes that could contribute to air quality issues in East Texas. These fourteen specific issues and areas of concern provide both additional TCEQ guidance concerning emphasis and focus to the original twelve SIP-relevant questions addressed in the Rapid Science Synthesis Report as well as new areas of TCEQ concern that require future analysis and interpretations. The fourteen additional areas of concern are:

- Examine NO/NO$_2$ ratios in point source plumes, in an effort to determine whether the NO/NO$_2$ ratios in the emissions inventories are correct. Is NO$_2$ underestimated in emission inventories?
- Examine role of ethene, propene, 1,3-butadiene, and butenes, other highly volatile volatile organic compounds (HRVOCs), and less reactive volatile organic compounds (VOCs) in ozone formation in Houston, in an effort to identify whether there are additional compounds for which emission reductions could yield substantial (and disproportionally large) ozone reductions.
- Attempt to determine whether ozone formation in various locations throughout greater Houston is limited by availability of NO$_X$ or of radicals.
- Calculate ozone production efficiency in urban, power plant, and industrial plumes.
- Calculate OH radical reaction rates, i.e., OH reactivity.
- Perform sequential reactivity model analysis of PAN and VOC data.
- Radical budget analysis—rates of radical initiation, propagation, destruction.
- Aldehyde emission, production, and photolysis rates.
- Top-down emissions estimates for isolated petrochemical facilities, and Houston Ship Channel (HSC).
- NO$_X$ ship emission estimates.
- Free tropospheric ozone distributions
- Comparisons of emissions of isoprene estimated from aircraft observations to biogenic emissions of isoprene from inventories.
- Hg source investigation (in collaboration with ANL site at Moody Tower).
- Investigate NH$_3$ source.

The initial findings pertaining to this request for additional information were contained in the oral and poster presentations that were given at the TEXAQS II / GoMACCS Data Analysis Workshop that was held in Austin on May 29 – June 1, 2007 or have been gleamed from subsequent analysis of the finalized data. This report is a synopsis of the initial findings and the additional analysis. The findings for the fourteen areas are presented in the form of fourteen brief (two to four pages) summaries of findings from
the analysis that we have carried out to date. However, additional analysis and interpretation of the data can be used to provide much better quantification of the existing findings. To this end, we have included a section that indicates additional analysis that can be undertaken by NOAA that will considerably improve the findings contained in this preliminary report, as well as, the prior analysis for the original twelve SIP-relevant questions documented in the Rapid Science Synthesis Report.
II. NO/NO\textsubscript{2} ratios in point source plumes.

Background
A representative NO/NO\textsubscript{2} emissions ratio from large combustion point sources is generally believed to be roughly 20 moles/mole, but peer-reviewed literature values of this ratio are difficult to find. Changes in this ratio will directly affect the amount of atmospheric ozone formed from these emissions, as each molecule of directly emitted NO\textsubscript{2} represents an additional molecule of O\textsubscript{3} expected downwind, over and above the O\textsubscript{3} formed over time from VOC-mediated photochemistry in the atmosphere. With some caveats, we can begin to quantify NO to NO\textsubscript{2} emissions ratios from large combustion point sources using the data from the TexAQS field studies.

Results
In this preliminary analysis, we use data from the NOAA WP-3D research aircraft during the TexAQS 2006 field study taken in the Oklaunion power plant plume after local sunset on October 10, 2006. All data were reported as 1-second averages, giving roughly 100-meter spatial resolution at typical aircraft flight speeds.

<table>
<thead>
<tr>
<th>Species</th>
<th>Technique</th>
<th>1-sigma uncertainty</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>NO</td>
<td>O\textsubscript{3}-induced chemiluminescence (CL)</td>
<td>±(0.02 ppbv + 5%)</td>
<td>1</td>
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<tr>
<td>NO\textsubscript{2}</td>
<td>narrow-band UV photolysis; CL (P-CL)</td>
<td>±(0.04 ppbv + 9%)</td>
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<tr>
<td>NO\textsubscript{2}</td>
<td>pulsed cavity ring-down spectroscopy (CRDS)</td>
<td>±(0.20 ppbv + 5%)</td>
<td>2</td>
</tr>
<tr>
<td>NO\textsubscript{y}</td>
<td>Au-catalysis with added CO; CL</td>
<td>±(0.20 ppbv + 12%)</td>
<td>3</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>NO-induced CL</td>
<td>±(0.05 ppbv + 3%)</td>
<td>1</td>
</tr>
</tbody>
</table>

Note that two different techniques – photolysis followed by CL, and CRDS - were used to separately measure NO\textsubscript{2} (c.f., Fig. 1). This is especially useful in the present analysis, as retrieving accurate NO\textsubscript{2} data concurrently during high ambient variability of NO mixing ratios in plumes is a difficult test of the P-CL technique. A comparisons is shown in Fig. 1, demonstrating quantitative agreement within the combined uncertainties of the
two NO\textsubscript{2} measurement techniques, even at significant levels of NO in the downwind Oklaunion plume.

**Interpretation and Conclusions**

Near-field plume data taken after local sunset are considered here, to minimize the effects of NO\textsubscript{X} (= NO + NO\textsubscript{2}) oxidation to PANs, HNO\textsubscript{3}, and other species that occur during the daytime. Negligible conversion of NO\textsubscript{X} by nitrate radical chemistry for these transects was confirmed by examining concurrent measurements (not shown) of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} from the aircraft.

The nighttime plume data are still affected by rapid conversion of NO to NO\textsubscript{2} by ambient ozone. This chemistry substantially alters the signature of the original NO\textsubscript{2} to NO ratio between the time of emission and the time of measurement by the aircraft. The plot below (c.f. Figure 2) shows nearly complete depletion of ozone in the plume, accounting for roughly 42 ppbv of the 54 ppbv of NO\textsubscript{2} observed at this transect. In the absence of directly emitted NO\textsubscript{2}, a plot of O\textsubscript{3} versus NO\textsubscript{2} for this transect should have a negative slope of 1.0. A linear fit to the measured data for this example transect gives a tight correlation (r\textsuperscript{2} = 0.994) and a significantly shallower slope of -0.80±0.02. This difference may be interpretable as a measure of the amount of directly emitted NO\textsubscript{2}, and relative to the observed NO. This provides a snapshot of the emissions ratio for this source.

Figure 2. (left) Simultaneous measurement of O\textsubscript{3}, NO, and NO\textsubscript{2} (by two techniques) made during a nighttime crossing of the Oklaunion Power Plant (Northeast Texas) plume. (right) Correlation plot showing the comparison O\textsubscript{3} a versus NO\textsubscript{2} indicating the depletion of ozone in the plume relative to the formation of NO\textsubscript{2}.
III. Examine role of ethene, propene, 1,3-butadiene, and butenes, other HRVOCs, and less reactive VOCs in ozone formation in Houston.

Background
In order to evaluate and predict air quality in the Houston area, it is important to understand the magnitude and variability of sources of Highly Reactive Volatile Organic Compounds in the area, and how these sources are evolving over time. HRVOCs were measured from the NOAA WP-3D aircraft using (1) a whole air sampler (WAS) and subsequent analysis by gas chromatography, (2) a proton-transfer-reaction mass spectrometer (PTR-MS), and (3) a laser photo-acoustic spectroscopy (LPAS) instrument for fast-response measurements of ethene. The data allow to identify the location of the main sources and to determine the emission fluxes. Average mixing ratios of ethene and other HRVOC? species were lower in 2006 than in 2000. The chemical removal of HRVOCs and the formation of secondary species were studied on several flights that made transects at several distances downwind from the ship channel.

Results
The aircraft flights of TexAQS 2000 and 2006 reveal a persistent feature over Houston: on all days conducive to photochemical ozone production, narrow intense plumes of ozone formed and were transported downwind from HSC. Figure 1 shows as an example measurements from a flight on a day when the wind was from the east-northeast. The top two graphs show the measurements of the ozone precursors. NOy represents the NO\textsubscript{X} emissions plus their oxidation products, primarily PAN and nitric acid. Ethylene is an important HRVOC ozone precursor. The concentrations of these two primary emissions are highest over HSC, and define a narrow downwind plume with decreasing concentrations. It is apparent that the NO\textsubscript{X} and ethylene emission sources are not precisely collocated, but the primary sources of both are in the HSC region. The downwind decrease in the concentration of NO\textsubscript{Y} is primarily due to dilution. It is clear that ethylene decreases more rapidly than NO\textsubscript{Y}, due to its much faster removal through photochemical oxidation. The bottom two graphs of Figure 1 show the formation of two secondary photochemical products, ozone and formaldehyde, coincident with the plume of primary emissions. Formaldehyde, which is produced from the photochemical oxidation of ethylene and other HRVOCs, forms during the downwind transport as the HRVOCs are oxidized; formaldehyde itself is an important ozone precursor. Ozone is produced during transport as the precursors emitted from HSC area react, resulting in a concentrated (up to 147 ppbv), narrow plume within the much less concentrated (≤ 100 ppbv), but wider ozone plume from the larger Houston urban area.
Figure 1. Measurements of four species plotted along the flight track of the NOAA WP-3D aircraft on 6 October 2006. The symbols are sized and colored according to the indicated concentrations. Only measurements below 1.5 km altitude are shown. (A close approach to the Parish power plant has been removed from the NOy plot to better show the HSC plume evolution.)

The high temporal resolution of the ethylene measurements by the laser photo-acoustic spectrometer (LPAS) and the wide species coverage of VOC measurements conducted on the canisters from the whole air sampler (WAS) provide detailed characterization of the HRVOC sources in HSC. The map in Figure 2 shows the ethylene measurements from these two systems downwind from six petrochemical facilities; the plumes of ethylene emissions from the facilities are clearly delineated. The four pie charts in Figure 2 indicate the total OH reactivity of the VOCs in 4 of the WAS samples, and show how that reactivity is divided among 4 of the lightest HRVOC species, and the total other VOCs including alkanes, aromatics and biogenics. These 4 examples illustrate the general finding that the HRVOCs dominate the VOC reactivity immediately downwind of the petrochemical facilities, and are responsible for a large fraction of the high ozone production in the Houston area. The total reactivity and the fraction of the reactivity contributed by the HRVOCs decrease downwind in the plumes as expected from their very short lifetimes.
The pie charts in Figure 2 do not include the aldehydes. These oxygenated VOCs, which also account for a significant fraction of the OH reactivity, are primarily secondary products of the oxidation of the HRVOCs. Thus, the contribution of the aldehydes to ozone production increases the fraction of the VOC reactivity in the HSC area that is due to the HRVOCs.
Interpretation and Conclusions

The highest (i.e. > 125 ppbv) ozone concentrations in the Houston Galveston Brazoria (HGB) area result from rapid and efficient ozone formation in relatively narrow, intense plumes, which transport HRVOCs and NO\textsubscript{X} co-emitted from petrochemical facilities. The Houston Ship Channel (HSC) is the source of the most concentrated plumes. The total reactivity and the fraction of the reactivity contributed by the HRVOCs decrease downwind in the plumes as expected from their very short lifetimes. Formaldehyde, which is produced from the photochemical oxidation of ethylene and other HRVOCs, forms during the downwind transport as the HRVOCs are oxidized; formaldehyde itself is an important ozone precursor. The high temporal resolution of the ethylene measurements by the laser photo-acoustic spectrometer (LPAS) and the wide species coverage of VOC measurements conducted on the canisters from the whole air sampler (WAS) provide a detailed characterization of the HRVOC sources in HSC.
IV-a. Is ozone formation in various locations throughout greater Houston limited by availability of NO\textsubscript{X} or of radicals? (Daytime chemistry)

Preface: As originally posed, we presume that this question was aimed at understanding the influence of NO\textsubscript{X} relative to VOCs in ozone formation associated with daytime photochemistry. Part IV-a (below) indicated some important new findings in this regard. However, our research discovered some very surprising nighttime radical chemistry associated with NO\textsubscript{X} that could important consequences subsequent daytime chemistry. Part IV-b (the succeeding section) indicates some of our findings in this regard.

Background
The accurate prediction of the relative response of ozone concentrations to future reductions in NO\textsubscript{X} and VOC emissions is a much sought, but very elusive goal. The prediction is central to the very important SIP-relevant question of “direction of control”—that is, should ozone control efforts in an ozone non-attainment area be focused on: a) decreasing emissions of NO\textsubscript{X} alone, b) decreasing emissions of VOC alone, or c) decreasing emissions of both NO\textsubscript{X} and VOC. The air quality community is still in the early stages of the evaluation process; a process that is limited both by resources for model development, and by the availability of observations with which to compare the models.

The East Texas region provides particular advantages, as well as particular challenges, for achieving the required model development and application. The TexAQS 2000 and TexAQS II field studies have collected data sets that provide unprecedented opportunities for model testing. However, experience has shown that development of needed emission inventories is a challenge that has not been met in all respects. The concentrated plumes that determine the highest ozone values in the Houston area present a further challenge.

Results
Although it is not possible to provide a rigorous answer to the “direction of control” question, we have been able to apply observation and modeling based approaches to approximately establish how the sensitivity of ozone production can be considered. We feel this heuristic approach can provide some useful guidance to air quality managers.

Wert et al. (2003) present a Lagrangian plume model designed to closely reproduce emissions, ozone formation, other secondary photochemical product formation and plume dispersion observed during the TexAQS 2000

![Figure 1. Relationship between ozone and formaldehyde concentrations observed from the Electra aircraft on 1 September 2000 and modeled by the Lagrangian plume model.](image-url)
study. Figure 1 shows that the model accurately reproduced the rapid production of ozone and formaldehyde that was measured in a concentrated plume originating from the Houston Ship Channel region. The model required only two HRVOC - ethene and propene. Two factors were both critical in successfully estimating the highest ozone levels: a large value for the ozone production efficiency as shown by observations, and a rapid rate of ozone production. High ozone production efficiency assures that high ozone can be produced from the emitted precursors, and the rapid rate of ozone production assures that high ozone is produced before the plumes of emissions dilute and disperse.

Figure 2 shows the modeled sensitivity of the ozone production to both NOx and VOC emission reductions for the plume illustrated in Figure 1. The upper panel indicates that NOx emission reductions lead to a more rapid ozone production, but a lower peak ozone concentration, while HRVOC reductions lead to both slower ozone production and a lower peak ozone concentration. The lower panel indicates HRVOC and NOx emission reductions are almost equally effective in reducing the total ozone flux in this plume. It is noteworthy that the ozone response is highly non-linear; reduction of either precursor by one-half, reduces the ozone flux by only about one-quarter.

The ozone flux produced and transported in this plume from the HSC accounts for a substantial fraction of the total ozone produced in the entire Houston area. Combined with other of our results, the calculated plume flux in Figure 2 represents 45 to 80% of the total Houston flux determined on six days during TexAQS 2000 and 2006. These calculations led Wert et al. (2003) to conclude that targeted reductions in either or both emission categories would effectively reduce the highest observed ozone levels.

**Conclusions and Interpretation**

We have attempted to provide a sample of a heuristic approach can provide some useful guidance to air quality managers concerning the relative response of O₃ concentrations to future reductions in NOₓ and VOC emissions. A simple Lagrangian plume model designed to closely reproduce emissions, ozone formation, other secondary...
photochemical product formation and plume dispersion accurately reproduced the rapid production of ozone and formaldehyde that was measured in a concentrated plume originating from the Houston Ship Channel region. These calculations suggest that targeted reductions in either or both VOC and NO\textsubscript{x} emission could reduce the highest observed ozone levels. Hence, these initial modeling results indicate that the high ozone in the Houston/Galveston Bay area is sensitive to both VOC and NO\textsubscript{x} emission reductions.
IV-b. Is ozone formation in various locations throughout greater Houston limited by availability of NOX or of radicals? (Nighttime chemistry)

Preface: As originally posed, we presume that this question was aimed at understanding the influence of NOX relative to VOCs in ozone formation associated with daytime photochemistry. Part IV-a (the preceding section) indicated some important new findings in this regard. However, our research discovered some very surprising nighttime radical chemistry associated with NOx that could important consequences subsequent daytime chemistry. Part IV-b (below) indicates some of our findings in this regard.

Background
The diurnal variation in the atmospheric chemistry of nitrogen oxides depends on the reactions that are important in the presence or absence of sunlight. Daytime convective boundary layers over land generally mix surface emitted pollutants such as NOX (= NO + NO2) to altitudes of 1-2 km during summer. The daytime NOX emissions undergo photochemical cycling in the presence of VOCs and sunlight to generate regional-scale ozone pollution. At night, the mixing height over the surface is typically an order of magnitude shallower, leading to accumulation of nighttime emissions; mixing at all levels of the residual daytime boundary layer is also generally less efficient. Nocturnal nitrogen oxide chemistry occurring within this more stratified environment involves the formation of NO3 and N2O5 from the oxidation of NOX in the presence of O3.

During TexAQS II/GoMACCS, the nighttime P-3 flights were aimed at characterizing the nocturnal reactions, transport and loss of NOX, VOCs and O3, with an emphasis on the role of the nighttime nitrogen oxides, NO3 and N2O5. Because of the large emissions of NOX in this area, it can be possible to convert a large fraction of O3 to NO3 and N2O5. The NO3 that is formed is a radical and is a strong oxidant of reactive VOCs (e.g. alkenes). However, the association of NO3 with NO2 to form N2O5 can be followed by the reaction of N2O5 on wetted aerosol to form HNO3. This effectively removes the NOX and O3 used to form the N2O5 from the atmospheric photochemistry.

In addition, during TexAQS II/GoMACCS, NOAA scientists using chemical ionization mass spectrometry (CIMS) onboard NOAA R/V Ronald H. Brown (RHB) made the first measurements of ClNO2 in the ambient atmosphere. Nitryl chloride, ClNO2, is a known product of nighttime reaction of N2O5 on sea salt that is rapidly photo-dissociated by sunlight releasing atomic chlorine. These new findings have important consequences for our understanding of the relation between ozone formation and the availability of NOX and radicals In the Houston area, 50 - 90% of NOX converted to NO3 + N2O5 overnight.

Results

NOx Radical Chemistry Measured from NOAA WP-3D
Preliminary analysis of the data shows that mixing ratios of NO3 and N2O5 were highly variable and occasionally very large, consistent with previous aircraft measurements of these compounds. Mixing ratios of NO3 reached 400 pptv in plumes from the Houston Ship Channel. At these levels, NO3 is capable of efficiently oxidizing highly reactive
VOCs that might otherwise participate in ozone production on the following day. The nocturnal P-3 flights included multiple, low-level vertical profiles to address the issue of stratification, reduced mixing and their influence on chemical transformation of pollutants at night.

One of the important finding from TexAQS II/GoMACCS was that during the nighttime P-3 flights, the N$_2$O$_5$ hydrolysis to form HNO$_3$ was *surprisingly* slow. A sample of some of the data that was used to support this conclusion is shown in Figure 1. These data were taken on October 10, 2006 during a flight that investigated the plume downwind of the Oklaunion Power Plant Plume that is located in north Texas). Plotted are the time series of measurements made aboard the P3 of O$_3$, NO$_2$, N$_2$O$_5$, and HNO$_3$, during one plume crossing. These measurements illustrate the loss of ozone that occurs when NO is converted to NO$_2$, and NO$_2$ is converted to NO$_3$ and N$_2$O$_5$ followed by the subsequent production of HNO$_3$ through the hydrolysis of N$_2$O$_5$ on aerosols. The data show the production of NO$_2$ and N$_2$O$_5$ but show no evidence for the formation of HNO$_3$ from N$_2$O$_5$ hydrolysis. Also, plotted is O$_X$ the sum of the mixing ratios of O$_3$, NO$_2$, N$_2$O$_5$ and HNO$_3$. Finally, the sum of the species, O$_X$, balances, thus, accounting for the loss of O$_3$. Similar results were obtained from flights made downwind of the Parrish Power Plant located in the Houston metropolitan area.

These results imply that during the nighttime hours the NO$_X$ is conserved in these power plant plumes that are NO$_X$-rich and VOC-lean. Hence at sunrise with daytime heating the NO$_X$ that has been converted to NO$_3$ and N$_2$O$_5$ will be converted back to NO$_X$ and be available to be involved in daytime ozone formation if larger missing ratios of VOCs are present.

**NO$_X$ Radical Chemistry Measured from NOAA RV Ronald H. Brown**

Simultaneous measurements of ClNO$_2$, N$_2$O$_5$, and aerosol size and composition, show that ClNO$_2$ is a general product formed when N$_2$O$_5$ reacts on chloride-containing aerosol. N$_2$O$_5$ is produced from nighttime reactions of NO$_2$ with O$_3$. ClNO$_2$ is relatively stable at night, but photolyzes at sunrise to yield Cl atoms and NO$_2$. These reactions link the nitrogen oxides to halogen activation.
An episode of high ClNO₂ was observed on September 2, 2006 when the R.H. Brown was in the Barbour’s Cut inlet located off Galveston Bay near HSC. Figure 2a (top panel) shows the measured N₂O₅ and ClNO₂ along with the Cl atom production rate calculated from the measured ClNO₂ and solar flux, and known ClNO₂ UV absorption cross section. This Cl atom production rate reached almost 10⁶ sec⁻¹. This is significant since Cl atoms react with VOC up to 100 times more rapidly than OH radicals. Figure 2b (bottom panel) compares O₃ measured on September 2 with the average (±1 std deviation) of the O₃ levels observed during all other times that the RH Brown was in was in the Houston Galveston area during the 2006 study. The September 2 O₃ showed a more rapid rise, and a higher peak concentration than the average. This observation, while not definitive, is consistent with a significant role for Cl atoms in O₃ production in polluted marine air.

A preliminary box model study was conducted to investigate the ClNO₂ formation chemistry and to examine the effect of this Cl source on VOC-NOx photochemistry. The model employed the Master Chemical Mechanism to which the N₂O₅ aerosol chemistry and ClNO₂ photochemistry were added. The model results show that a reaction efficiency of 25% for N₂O₅ on chloride-containing aerosol can account for the measurements in Figure 2b. The Cl atoms produced upon sunrise led to a 2 to 3 fold increase in total peroxy radicals during the morning hours, which resulted in about a 15% higher O₃ level at the end of the afternoon production period. These results amplify the need to add this Cl atom source to current regional photochemical models.

Conclusions and Interpretation

**NOₓ Radical Chemistry Measured from NOAA WP-3D**

Our measurements suggest that at night, in power plant plumes with low mixing ratios of VOCs, NOₓ and Oₓ could be effectively transported in the form of N₂O₅. By contrast in the plumes of petrochemical plants, NOₓ could serve as an effective oxidant. In several cases, VOC loss rates of 0.5 - 4 ppbv hr⁻¹ were observed in Ship Channel plumes. During nighttime, the chemistry of NO₃/N₂O₅ could be strongly influenced by vertical stratification. This could produce shallow, concentrated NOₓ plumes and lead to large difference between surface and aloft.

**NOₓ Radical Chemistry Measured from NOAA RV Ronald H. Brown**
Observations show that nitryl chloride, ClNO₂, is formed within the nocturnal boundary layer when pollution and marine influences are both present. Following sunrise this species photolyzes to yield chlorine atoms, which may lead to more intense O₃ production in the HGB region. The measurements show ClNO₂ mixing ratios up to 1 ppbv during periods of active N₂O₅ aerosol chemistry, and that submicron chloride-containing non-sea salt aerosol is involved in ClNO₂ formation. Preliminary laboratory results confirm that ClNO₂ is produced from N₂O₅ uptake on the aerosol substrates {(NH₄)₂SO₄, (NH₄)HSO₄} that contain chloride ion concentrations that were observed in the TexAQS II/GoMACCS measurements. ClNO₂ photolyzes upon sunrise, producing chlorine atoms (Cl) and NO₂. The impacts of this Cl atom source are far-reaching and include: more intense VOC-NOx photochemistry early in the day, enhanced oxidation in NOₓ plumes from ship emissions, and the preservation of NOₓ that would normally be lost through nighttime chemistry.
V. Estimate the ozone production efficiency in urban, power plant, and industrial plumes.

Background
Ozone is formed over time in the troposphere by photochemical reactions involving the oxides of nitrogen, NO and NO$_2$ (summed as NO$_X$), and reactive volatile organic compounds (VOCs). However, ozone formation rates and yields are dependent on both the absolute concentrations of NO$_X$ and VOCs and the ratios of these species. Results from field studies have confirmed that substantial differences in the timing and magnitude of ozone production consistently occur in plumes downwind of different anthropogenic source types, characterized by different NO$_X$ and VOC emissions rates and the VOC/NO$_X$ ratios that result. Three anthropogenic source types with contrasting emissions rates and VOC/NO$_X$ ratios are fossil-fueled electric power plants, the transportation sources typical of urban areas, and the petrochemical industry.

Results
Measurements obtained from the NCAR Electra in 2000 and the NOAA WP-3 in 2006 on daytime flights in the boundary layer under a variety of meteorological conditions have been used to determine the ozone production efficiency in plumes downwind from an urban power plant and petrochemical industry plants in Houston. During TexAQS 2000, four Electra flights encountered ozone concentrations above 150 ppbv. Figure 1 shows the flight track segments where the highest ozone was observed. In each case, these plumes were traced back to industrial emission sources in the HSC area by trajectory analysis. Measured chemical characteristics of the plumes (simultaneous high NO$_X$, SO$_2$, CO$_2$, and oxidation products of HRVOCs) confirm this source attribution. The

![Figure 1. Highest ozone (red points) observed by the Electra aircraft during four flights in TexAQS 2000. In the left panel flight track segments are color-coded by observed ozone, and in the right panel the dependence of ozone on the products of NO$_X$ oxidation are shown with approximate ozone production efficiencies estimated from fitted slopes.](image-url)
relationship between the transport times derived from the trajectory analysis and the observed enhancements in ozone provided a measure of the net average ozone production rates in the plumes. Figure 1 shows the observed relationship between ozone and the products of NO$_x$ oxidation for those four flights; the slopes of these relationships provide an estimate of the net ozone production efficiencies in these plumes.

By contrast, Figure 2 presents a similar analysis for three NOAA WP-3D daytime flights and the RHB cruise segment during TexAQS 2006 that encountered ozone concentrations near or above 120 ppbv. A simple wind direction analysis, coupled with the chemical plume signatures, indicate that in each case these plumes also trace back to industrial emission sources in the Houston Ship Channel area. Figure 2 also shows the relationship between ozone and the products of NO$_x$ oxidation in these plumes.

![Figure 2. Highest ozone observed by the WP-3D aircraft and RHB research vessel during TexAQS 2006. The figure is in the same format as Figure 1. The dotted rectangle indicates area covered in Figure 1.](image)

**Interpretation and Conclusions**

A comparison of Figures 1 and 2 indicates that the ozone production environment in the Houston area was similar in 2000 and 2006. Similar ozone vs. (NO$_y$-NO$_x$) slopes are seen in each year; the maximum observed ozone in both years were associated with slopes near 7. Lower maximum ozone concentrations were observed in 2006, but this difference may be partially due to meteorological factors; the background ozone, as indicated by the y-intercepts in the two right-hand plots in Figures 1 and 2, is lower in 2006 and the lower background leads to lower maximum concentrations. The lower 2006 background may indicate lesser effects of stagnation that year. Finally, the maximum ozone concentrations are seen at greater distances from the ship channel in 2006 than in 2000 (note difference in area covered in the two maps). This difference may be attributable to slower ozone production or greater transport speeds in 2006.
VI. Calculate OH radical reaction rates, and OH reactivity for ozone precursors.

Background
Volatile Organic Compounds and NO\(_x\) (= \(\text{NO} + \text{NO}_2\)) are vital components in the photochemical production of ozone (O\(_3\)). The first step in initiating the radical cycle responsible for O\(_3\) production is the reaction between •OH (produced in situ during the daytime) and VOCs. Along the Gulf coast of Texas there exists an immense variety of industrial, urban, and natural sources of VOCs. A wide spectrum of VOCs were measured aboard the NOAA R/V Ronald H. Brown during TexAQS/GoMACCS 2006 in an effort to fully characterize their sources and determine the key species responsible for the photochemical ozone production in the Houston/ Galveston area.

Results
The reactivity of the ozone precursors were investigated during TexAQS 2006 from measurement made aboard the NOAA research vessel Ronald H. Brown. The VOC measurements were made with a custom dual channel gas chromatograph (GC) incorporating both a Flame Ionization Detector (FID) associated with an 18m Aluminum oxide column (Al\(_2\)O\(_3\)) for the light hydrocarbons and a quadrupole mass spectrometer (MS) associated with a 20m DB-624 column for the heavier VOCs. Additional measurements of VOCs were made using a modified commercial proton transfer reaction mass spectrometer (PTR-MS). Formaldehyde was measured using a quantum cascade tunable diode laser absorption spectrometer (QC-TDALS). The NO and NO\(_x\) measurements were made with a chemiluminescence NO detector equipped with a UV photolytic converter to convert NO\(_2\) to NO. The accuracy for all compounds is ± 20%.

During the study over two hundred VOCs were measured using the GC-FID/MS. Of these the eighty most abundant have been quantified and the measured mixing ratios that were observed in the Galveston Bay/Houston Ship Channel are summarized in the table on the right and compared with the measured mixing rations of these species that were measured at La Porte during the 2000 study. Also indicated in the table is the OH...
reactivity for these VOCs. These compounds account for approximately 90% of the VOC-OH reactivity.

**Interpretation and Conclusions**

Over all, it was found that the VOCs dominated the OH chemistry at all inland locations. This is illustrated in the Figure 1 that is shown on the right. However, the magnitude and variability of the VOC OH Loss rate depended strongly on: meteorology (wind speed and direction), time of day (day/night), location (sources and emission sources/rates), and VOC chemical processing (fresh vs. aged).

VOC mixing ratios were typically highest during the nighttime. This is related to many factors including meteorology principally limiting vertical mixing and reduced chemical destruction. The nighttime VOC plumes also showed strong indications of industrial sources (e.g., monomers—used in plastics production). There were large quantities of highly reactive VOCs present (alkenes, terpenes, monomers) through early morning that quickly reacted away as ozone production began. Late afternoon VOC composition were characterized by high mixing ratios of aldehydes associated with secondary photochemical formation.

In summary, these results indicated that in Galveston Bay and the Houston Ship Channel ethylene, propylene, isoprene (mostly from industrial as opposed to biogenic sources), formaldehyde, and acetaldehyde were the largest contributors (based on median values) to possible ozone production in the Galveston Bay/Houston area during TexAQS 2006. The magnitude and variability of the VOC/OH reactivity was dependent upon:

- **Location** – Houston Ship Channel and Barbour’s Cut were strongly affected by industrial emissions;
- **Chemistry** – Highly reactive VOCs can accumulate during night (slower loss rates) and react away during day (shorter chemical lifetimes);
- **Time of day** – Meteorology and emission source rates (biogenic, urban, industrial) may vary over 24-hours.

*Fig. 1. OH reactivity for all Galveston Bay and Houston Ship Channel measurements made aboard the NOAA RV RH Brown.*
VII. Sequential reactivity model analysis of PAN and VOC data.

Background
The relationship between primary VOCs and their product compounds is intimately connected to the same photochemistry that produces O₃ and to some extent particles. Complex Lagrangian and Eulerian numerical models are often used to examine these relationships, but their results are dependent on accurate knowledge of sources, transport, and reaction pathways: details that are often unknown or incomplete. A conceptually simple sequential reaction model has been successfully used to examine small pieces of the complex VOC photochemistry in instances where the parent and product VOC measurements are available, and the reaction pathways (rates, branching ratios) are known. The information that has resulted from this type of analyses includes: the time scales on which these processes are occurring, the strong correlation of conversion of parent to product with O₃ formation, and indications of additional chemical pathways not captured by the simple model. This last feature has been used to show the importance of isoprene chemistry to the production of PAN (and therefore O₃) in data from several surfaces sites. An analysis of the TexAQS 2000 measurements at the La Porte site showed that isoprene chemistry was comparatively unimportant at this site.

Results
The preliminary aldehyde-PANs sequential reaction analysis carried out for the TexAQS 2006 data acquired aboard the NOAA R/V Ronald H Brown is substantially different from the 2000 results. These differences seem to be due to differences in the acetaldehyde and to a lesser extent PPN measurements between the two years. At present, we are not sure what the causes are.

Interpretation and Conclusions
Further analysis is required to determine if the differences in data sets are due to different precursor or loss chemistry, time and location of the measurements, or analysis problems.
VIII. Perform radical budget analysis including rates of radical initiation, propagation, destruction.

Background
An extensive set of chemical and physical measurements was made at the La Porte Airport in Houston during the 2000 Texas Air Quality Study. OH and HO\textsubscript{2} mixing ratios were measured using the Penn State Ground-based Tropospheric Hydrogen Oxides Sensor (GTHOS). Total OH reactivity was measured by the Penn State Total OH Loss rate Measurements (TOHLM) method. Extensive measurements of other chemical species and physical parameters were made at the La Porte Airport site during TexAQS 2000.

By way of independent comparison, steady state [OH] and [HO\textsubscript{2}] were calculated simultaneously along with the concentrations of speciated \textit{RO\textsubscript{2}}, \textit{NO\textsubscript{3}}, \textit{N\textsubscript{2}O\textsubscript{5}}, HNO\textsubscript{2}, and HNO\textsubscript{4} by a box model with most other input variables constrained by measurements. A key assumption in the analysis was that OH, HO\textsubscript{2}, and the other calculated species were in steady state with each other and with the constrained measured compounds, which in turn assumes vertical and horizontal homogeneity in the vicinity of the La Porte ground site.

Results
The observed hydroxyl and hydroperoxyl radical concentrations ([OH] and [HO\textsubscript{2}]) at La Porte were compared to those predicted by a steady state box model. The model is constrained by ambient measurements of ozone, reactive nitrogen compounds, carbon monoxide, volatile organic compounds, photolysis rate coefficients, and meteorological variables that were measured at the site. The photochemical production rate of ozone, P(O\textsubscript{3}), due to HO\textsubscript{2} reactions were derived from the observed [HO\textsubscript{2}] and nitric oxide concentration ([NO]) and compared to the model. Budgets of OH and HO\textsubscript{x} were quantified using the model. Model-measurement comparisons of [OH], [HO\textsubscript{2}], [HO\textsubscript{2}]/[OH], and P(O\textsubscript{3}) were further evaluated by considering their dependence on variables such as [NO] and actinic flux.

Interpretation and Conclusions
The radical budgets indicate that chemistry at La Porte was dominated by light alkenes and their photochemical products (oxygenates). The results indicated the impact of nearby industrial and mobile sources, particularly refineries and polymer production plants. The model and measurements are in rough quantitative agreement throughout most of the daytime. However, in general, the model [OH] tends to be lower than the observations in the afternoon, while the model [HO\textsubscript{2}] tends to be higher than the measurements from mid-morning on. These tendencies lead to model overestimates of the [HO\textsubscript{2}]/[OH] ratio during the day. The observed radical sources, sinks, and cycling were in reasonable agreement with the model during periods when the highest concentration of reactive compounds were observed. From these results is appears that photochemistry can easily account for rapid O\textsubscript{3} production seen at La Porte. It should be
noted that some discrepancies were found between model simulations and measurements when the measured concentrations of ozone precursors were low.

Resolution of the differences noted above in the in \( \text{HO}_X \) measurements at La Porte in 2000 and those inferred from the initial model simulations requires further analysis and additional data. Extensive analysis of the 2006 data and reanalysis of the 2000 data using improved modeling approaches are now being undertaken.
IX. Estimate aldehyde emission, production, and photolysis rates.

Background
Formaldehyde and higher aldehydes including acetaldehyde are products of the atmospheric oxidation of hydrocarbons, a potential source of HOx, and a contributing species to determining how HOx is partitioned between OH and HO₂.

Results
Formaldehyde Measurements from NOAA WP-3D
Airborne, 1s measurements of formaldehyde (CH₂O) were performed using a tunable mid-IR difference frequency generation (DFG) laser spectrometer. The average detection limit (S/N=1) for all flights was 117 pptv (1-s average) and 21 pptv (60-s average), respectively. For most flights, the instrument was operated semi-autonomously with a duty cycle of 70% (60 s sample / 30 s background, incl. flushing) affording good spatial coverage and precision. The instrument operated with the quoted performance for over 94% of research flight time. Using an advanced DFG laser source, the present instrument performed with 2x better sensitivity, longer sampling times (60 s), and 70% higher duty cycle, compared to the liquid nitrogen cooled tunable lead-salt diode laser absorption spectrometer (TDLAS) employed during the TexAQS 2000 study.

Results from these measurements are summarized in Figure 1. Compared to the study in 2000 (TexAQS 2000), the median concentrations in the vertical distributions are significantly lower (50%) and this may be due to different ambient sampling/photochemistry conditions (Sep./Oct. 2006 vs. Aug./Sep. 2000) during TexAQS 2006.

<table>
<thead>
<tr>
<th>Flight Altitude Range (m)</th>
<th>TexAQS 2000 Median CH₂O (ppbv)</th>
<th>TexAQS 2006 Median CH₂O (ppbv)</th>
<th>Difference (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 1000</td>
<td>3.3</td>
<td>1.84</td>
<td>1.46</td>
</tr>
<tr>
<td>1000 - 2000</td>
<td>2.7</td>
<td>0.93</td>
<td>1.77</td>
</tr>
<tr>
<td>2000 - 3000</td>
<td>1.0</td>
<td>0.58</td>
<td>0.42</td>
</tr>
<tr>
<td>3000 - 4000</td>
<td>0.26</td>
<td>0.45</td>
<td>-0.19</td>
</tr>
<tr>
<td>4000 - 5000</td>
<td>0.21</td>
<td>0.17</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Figure 1. Measurements of CH₂O made aboard the NOAA WP-3D. The plot on the left shows the altitude profile for all the 1-sec. measurements that were made during the study. The table on the right compares measurement made in 2006 with those obtained in 2000 binned according to altitude.
Downwind plumes from power plants, the Houston shipping channel and selected refineries have been intercepted and CH$_2$O shows a clear signature and correlation with O$_3$ and NO$_Y$. Persistent progression of plume indicates in-situ photochemical production of CH$_2$O during the day.

An important issue that was addressed during the 2006 study pertained to the evidence for primary sources of CH$_2$O. However, because of the rapid formation of CH$_2$O during the daytime the fingerprints of such primary sources of CH$_2$O can only be retrieved from the data with more extensive analysis. During the nighttime however the signatures of primary source should be more apparent. An example of this type of data was afforded by data taken during the NOAA WP-3D flight on October 12$^{th}$. The results shown in Figure 2 shows a missed approach at Montgomery County Airport. In the figure, each symbol represents a 1-s. measurement of CH$_2$O color coded by the altitude of the aircraft. The strong correlation of CH$_2$O with CO in measurements made below 200 m indicates the contribution of primary sources of CH$_2$O. The line drawn through this portion of the correlation between CO and CH$_2$O indicates an upper limit of 1.8 pptv of CH$_2$O emitted for each ppbv of CO. Clearly there are other possible non-primary sources of CH$_2$O that could be contributing to the observed CH$_2$O. These would include CH$_2$O remaining from the daytime photochemical formation and secondary CH$_2$O produced in the reactions of oxidized and/or unsaturated VOC with ozone.

**Formaldehyde Measurements from R/V Brown**

Formaldehyde was measured aboard the NOAA RV Ronald H. Brown using pulsed quantum cascade tunable infrared differential absorption spectroscopy (pQC-TILDAS, Aerodyne Corp.) in the 5.6 μm (1765 cm$^{-1}$) wavelength region. The in-the-field determination of the detection sensitivity resulted in 1-s rms levels of 250 pptv. The wavelength region used for determining CH$_2$O also allowed an opportunistic measurement of formic acid. As was the case with the aircraft measurements, the daytime measurements of CH$_2$O were strongly influenced by photochemical CH$_2$O formation. This largely masked primary sources of CH$_2$O.
In the Houston Ship Channel, the diurnally averaged peak concentration of CH$_2$O was observed to precede the peak concentrations of O$_3$ by 2.5 hours.

Figure 3. This figure shows the simultaneous measurements of CO$_2$ and CH$_2$O that were made in the plume of a large ship (Callsign: WDA8059). The ratio of CH$_2$O relative to CO$_2$ from this plot implies an emission of 0.05 g of CH$_2$O for each kg of fuel burned.

However, even during the daytime it was possible to observe the primary emission of CH$_2$O from the exhaust of large ships. This is illustrated in Figure 3 that shows the intercept of the plume from a large ship that was loitering in the Houston Ship Channel. The figure shows the simultaneous measurements of CO$_2$ and CH$_2$O that were made in plume of this ship. The ratio of CH$_2$O relative to CO$_2$ from this plot implies an emission of 0.05 g of CH$_2$O for each kg of fuel burned. Several such plume intercepts were made during the study and will afford the opportunity to better quantify

Figure 4. Measurements of CH$_2$O made in the turning basin during the night and early morning of August 2nd. The measurements are color coded according to the intensity of sunlight (presented here as the measured photolysis rate for CH$_2$O). The correlation indicates an upper limit for CH$_2$O primary emission of 3 pptv per ppbv of primary CO emissions.
the emission of CH$_2$O from these large diesel powered marine vessels.

In addition to the determination of the emission of CH$_2$O from single isolated sources, nighttime measurements of CH$_2$O also afforded the opportunity to place an upper limit on the primary emissions of CH$_2$O during the nighttime from sources. Figure 4 shows measurements of CH$_2$O that were made in the turning basin during the night and early morning of August 2007. During this period the wind was steady from the west transporting emission from central Houston to the west of the ship channel to the location of the NOAA RV. In the figure, the measurements are color coded according to the intensity of sunlight (presented here as the measured photolysis rate for CH$_2$O). The correlation indicates an upper limit for CH$_2$O primary emission of 3 pptv per ppbv of primary CO emissions, which are predominately due to on-road vehicles.

**Interpretation and Conclusions**

During the TexAQS in 2006, CH$_2$O was measured aboard two of the NOAA mobile research platforms, the WP-3D aircraft and the research vessel Ronald H. Brown. This data set will provide excellent opportunities to better understand the sources and processes involving CH$_2$O in Houston and the surrounding area. In the Houston metropolitan area copious quantities of CH$_2$O are produced photochemically during the day. Elevated mixing ratios of CH$_2$O that are encountered in plumes can be attributed to the rapid photochemical formation of CH$_2$O from the fast photochemistry between odd-hydrogen free radicals, HRVOCs and NO$_X$ in the plumes. In general, this photochemical production masks the smaller primary emissions of CH$_2$O. However, simultaneous measurements of CH$_2$O and CO$_2$ during plume intercepts of the emissions from large diesel marine vessel indicated that under certain conditions a few hundreds of a gram of CH$_2$O might be emitted for each kilogram of fuel consumed.

In addition, limited nighttime measurements of CH$_2$O from both the aircraft and the research vessel indicated that the direct emission of CH$_2$O is a few tenths of a percent or less of the direct emission of CO from the on-road vehicle fleet. However, this small amount of CH$_2$O is an upper limit to the primary emissions, since it could possibly be attributed to residual CH$_2$O remaining from the CH$_2$O formed photochemically during the proceeding day or produced photochemically during the night by ozone or nitrate radical initiated oxidation of HRVOCs.
X. Provide top-down emissions estimates for isolated petrochemical facilities, in and around the Houston Ship Channel.

Background
Improving the quantitative understanding of the location, timing, and speciation of gaseous and aerosol emissions into the atmosphere is critical to the development and improvement of air quality management strategies and approaches. Known or suspected inaccuracies in current emissions inventories account for a substantial uncertainty in model simulations of air quality processes. While some inventories are reasonably accurate others may have substantial errors. In order to evaluate and improve emission inventories that are used for air quality modeling, several new strategies for top-down emission estimates have been developed by NOAA scientists and applied to the evaluation of inventories for emissions from specific industrial point sources. Because of the importance in the formation of ozone in and around the Houston metropolitan area, considerable attention during TEXAQS II was directed to providing top-down emissions estimates for isolated petrochemical facilities, and the Houston Ship Channel.

Results
Volatile Organic Compounds (VOCs) are a vital ingredient in the photochemical production of ozone. Along the gulf coast of Texas there is a variety of industrial, urban, and natural sources of VOCs. Volatile organic compounds (VOCs) were measured on the NOAA WP-3 aircraft using various techniques. These data provide the information necessary for estimating the flux of VOC emissions from individual industrial sources located in the Houston Ship Channel area.

Figure 1. Data from the WP-3D flight on Sept. 25, 2006. The map indicates the aircraft interception of the plume from the Mt. Belvieu petrochemical plant. The arrow shows wind direction and the flight track is color-coded according to the concentration of ethene. The trace (right) indicates the mixing ratio of ethene measured during plume interception.
Ethene is one of the most important of the VOCs in the photochemical formation of ozone. During the study we were able to directly measurement ethene with a newly developed technique, laser photo-acoustic absorption spectroscopy (LPAS). An example of the result is shown in Figure 1. The data were taken during the W-P3 flight on September 25, 2006. The map on the left indicates a portion of the flight track of the aircraft on this day where the aircraft intercepted the plume that analysis indicated was associated with emissions from the Mt. Belvieu petrochemical plant. During this day the wind was from the north and the flight track is color-coded according to the measured concentration of ethene to indicate where the aircraft encountered the plume. The trace on the left shows the measurement of the mixing ratio of ethene during the plume interception. The analysis of the mixing ratio of ethene measured during this encounter yielded the emission flux: 280 kg h$^{-1}$. The estimated flux of ethene measured during the course of this study agreed within a factor of two with flux estimates made independently by ground based solar occultation flux (SOF) measurements made on this same day.

During TexAQS II, volatile organic compounds (VOCs) were also measured on the NOAA research vessel Ronald H. Brown using various techniques. A GC-MS (Gas Chromatograph-Mass Spectrometer) and a (GC)-PIT-MS (Gas Chromatograph-Proton Ion Trap-Mass Spectrometer) were used to collect data on a wide variety of VOCs aboard the Ronald H. Brown during TexAQS/GoMACCS 2006 in an effort to identify and characterize their sources. The two examples below indicate the additional approaches that were used in the Houston Ship Channel area to infer if VOCs were primary or secondary and to place limits on these sources.

The diurnal variations of ethene and formaldehyde at several locations in the Houston Ship Channel were studied. Figure 2 shows the data from Barbour’s Cut as an example. The primary hydrocarbons ethene and propene are high at night, when emissions accumulate in a shallow boundary layer and when photochemistry is absent. Mixing ratios are lower during the day, when the boundary layer expands and reactions with OH remove the alkenes. In contrast, HCHO is highest during the day, indicating that the source of this oxygenated VOC was predominantly photochemistry.

Nighttime measurements onboard the Ronald H. Brown and the NOAA WP-3D provide a means to estimate the direct emissions of formaldehyde during the night. The left panel of Figure 3 shows the relationship of formaldehyde to CO measured on the Ronald H. Brown in the turning basin at the western end of the Ship Channel with winds coming from Houston. The data are color-coded by the measured photolysis rate of
formaldehyde; the nighttime points, in black, show a clear correlation between formaldehyde and CO with a slope of about 3 pptv ppbv$^{-1}$. After sunrise, the formaldehyde to CO ratio increased strongly due to photochemical formation of formaldehyde (daytime points in yellow).

From these observations we estimate the primary emissions of formaldehyde during the night from sources in the area to be 0.18-0.3 % of the CO emissions; this estimate is an upper limit, since it is not possible to exclude the possibility that the sampled air had been photochemically processed earlier to at least a limited extent.

**Interpretation and Conclusions**

NOAA scientists have developed a variety of approaches to provide top-down emissions estimates of NO$_x$, SO$_2$, and a wide variety of VOC sources for isolated petrochemical facilities, in and around the Houston Ship Channel. In addition, the data can be used qualitatively to establish if compounds are primary emission from these sources or are secondary photochemical products. A great deal is yet to be learned from further analysis of the extensive data set taken during TexAQS I and TexAQS II.
XI. Estimates of NO\textsubscript{X} Emissions from Commercial Marine Shipping.

**Background**
Commercial marine vessels range in size from small fishing boats (20-30 meters in length) to extremely large container ships (>300 meters in length). These ships almost without exception use diesel engines for propulsion and auxiliary power generation. The larger ships, comprising bulk carriers, tankers, and container carriers, utilize diesel engines that produce power in the 10 MW to 100 MW range. Such engines typically consume heavy fuel oils, which are high in sulfur content (1%-4.5% by weight). These engines are also extremely efficient, converting essentially all of the carbon in the fuel to CO\textsubscript{2}, but also emitting NO\textsubscript{X}, CO, SO\textsubscript{2}, VOCs, and PM.

**Results**
During TexAQS 2006 our measurements on board the Ronald H. Brown characterized the emissions from a large number of commercial marine vessels. From this data, we have calculated mass-based emission factors for many of the compounds noted above. Table 1 presents the average derived NO\textsubscript{X} emission factors for slow speed diesel (SSD) engines, which are those with maximum power greater than ~10 MW, and medium speed diesel (MSD) engines, which are of lower power. The NO\textsubscript{X} values are within 20% of the average values reported in the Lloyd's (1995) study for both MSD and SSD engines although the measured variability is large for each of the two engine types. These data are sufficient to provide emission factors classified by ship type (e.g., freighters, container ships, tankers, tugs, etc.). It is concluded that Lloyd's (1995) provides an accurate characterization of NO\textsubscript{X} emissions from underway vessels in the HGB region.

The emission factors for CO are within 20% of the value reported in by Lloyd's (1995). There is no trend of increasing CO at lower vessel speeds (used as a surrogate for engine load) which was seen in the earlier Lloyd's data. Measurements of CH\textsubscript{2}O emissions from ships show little distinction between MSD and SSD engines; emission of CH\textsubscript{2}O is less than 5% the emission of CO. Emission factors for SO\textsubscript{2} vary with fuel sulfur content. In the HGB region the mean fuel sulfur derived from the measurements is 0.46% for MSD engines and 1.4% for SSD engines. Measurements of light absorbing carbon (LAC; also known as black carbon) were also made.

<table>
<thead>
<tr>
<th>Engine type</th>
<th>NO\textsubscript{X}</th>
<th>CO</th>
<th>SO\textsubscript{2}</th>
<th>CH\textsubscript{2}O</th>
<th>LAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium speed diesel (MSD)</td>
<td>60</td>
<td>8.7</td>
<td>9.1</td>
<td>0.17</td>
<td>0.41</td>
</tr>
<tr>
<td>Slow speed diesel (SSD)</td>
<td>74</td>
<td>6.6</td>
<td>28</td>
<td>0.20</td>
<td>1.16</td>
</tr>
</tbody>
</table>

All units are grams of species per kilogram fuel consumed. Emission factors for CO are median data.

Given detailed activity data (i.e., marine fuel consumption) for ships in the HGB region an emissions inventory for this source could be constructed. The 2007 report from Eastern Research Group (ERG) to TCEQ (Eastern Research Group, 2007) has such data,
but there appears to be a significant underestimate (factor of 2-8) of fuel consumption, when compared to an estimate from a more comprehensive model (Wang et al., 2007). The NO$_2$ emission factors used in the ERG report agree with our data to within 10%. Thus, for current ship emissions inventory modeling, there is less uncertainty contributed by emission factors than by activity data.

**Interpretation and Conclusions**

Table 2 gives ship emissions of NO$_X$, CO and SO$_2$, relative to the emission of CO$_2$, and compares it to emission ratios for electric power generating units (EGUs) from the 2004 point source emission inventory, that was updated to 2006 with CEMS data. This comparison shows that ships emit 10 to 100 times more NO$_X$ (and only somewhat more CO, and SO$_2$) per unit fuel burned (i.e. CO$_2$ emitted) than large stationary sources. Though the emissions from an individual vessel might be 10-100 times lower than from an EGU, the volume of ship traffic in the HGB region is sufficient that emissions from commercial shipping, in aggregate, cannot be neglected. Accurate fuel consumption or other ship activity data are needed to accurately quantify these emissions. Importantly, while emissions from stationary sources are a focus of ongoing control measures, emission controls on commercial shipping are not likely to be implemented due to technical reasons and complications arising from international law.

<table>
<thead>
<tr>
<th>Emission source</th>
<th>NO$_X$/CO$_2$</th>
<th>CO/CO$_2$</th>
<th>SO$_2$/CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial vessel, SSD</td>
<td>22</td>
<td>6.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Commercial vessel, MSD</td>
<td>18</td>
<td>8.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Electric power generating unit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W. A. Parish</td>
<td>0.23</td>
<td>0.51</td>
<td>1.9</td>
</tr>
<tr>
<td>Welsh</td>
<td>0.88</td>
<td>1.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>

All units are molecules of species per 1000 molecules of CO$_2$.

In addition, during the TexAQS/GoMACCS 2006 field campaign, the NOAA R/V Ronald H. Brown often encountered small marine recreational craft while sailing close to the Texas coast, especially in Galveston Bay. Measurement of a suite of trace gases at high time resolution (1 Hz) allowed us to calculate emission factors (EFs), relative to carbon dioxide, for nitrogen oxides (NO$_X$), sulfur dioxide (SO$_2$) and carbon monoxide (CO) for distinct exhaust plumes from these vessels. As previously observed along the New England coast, gasoline-powered craft showed significantly higher NO$_X$/CO$_2$ and lower CO/CO$_2$ EFs than current emissions inventories predict, although in agreement with the most recent published literature. These findings imply lower volatile organic compound emissions from these vessels, although this was not directly measured.
XII. Investigate free tropospheric ozone distributions.

Background
Tropospheric ozone is a central trace gas that determines the oxidizing capacity of the troposphere. Most of the tropospheric ozone burden is produced from anthropogenic emissions resulting in widespread ozone increases since the late 1800s. A recent development in our understanding of tropospheric ozone is the discovery of an O$_3$ maximum during summertime within the upper tropospheric anticyclone above the southern United States. The ozone enhancement is believed to be the result of convective lofting of surface ozone, and in situ production involving anthropogenic NO$_X$, lightning NO$_X$, and in part HO$_X$ radicals produced from convectively lifted formaldehyde. The ozone could be produced over many days due to the trapping of the ozone precursors in the semi-permanent upper tropospheric anticyclone located above eastern North America during summer.

Results
Daily ozonesondes were launched from 14 North American sites during August 2006 (c.f., Figure 1A). These measurements provide the best set of free tropospheric ozone measurements ever gathered across the continent in a single season. The data reveal a distinct upper tropospheric ozone maximum above eastern North America, and centered over the southeastern USA (c.f., Figure 1A). Recurring each year, the location and strength of the ozone maximum is influenced by the summertime upper tropospheric anticyclone that traps convectively lofted ozone, ozone precursors and lightning NO$_X$ above the southeastern USA. Figure 1B shows the residual ozone that is left after the estimated ozone from the stratosphere has been subtracted. In addition, this result is supported by calculations from a general circulation model that indicates that lightning NO$_X$ emissions led to the production of 25-30 ppbv of ozone at 250 hPa above the southern United States during the study period.

Interpretation and Conclusions
The measurements made during the summer of 2006 provided 410 ozone profiles across North America. The study confirmed the hypothesis that the upper free tropospheric O$_3$ maximum above eastern North
America is a recurring summertime feature and that the exact location and strength varies inter-annually with the mean location and strength of the upper tropospheric anticyclone. Independently, modeling work indicates that lightning NOX led to the production of 25-30 ppbv ozone in layers approximately 10-11 km altitude above the southern United States during August 2006.
XIII. Compare emission estimates of isoprene derived from aircraft measurements to inventory-estimated biogenic emissions of isoprene.

Background
In order to understand the photochemical formation of ozone on local to regional scales, it is necessary to have reliable estimates of the contribution of the natural emissions of VOCs, such as isoprene, to the total VOCs that are available in those areas. During TexAQS in 2006, volatile organic compounds (VOCs) were measured on the NOAA WP-3D aircraft using a PTR-MS instrument and from whole air samples (WAS) using various gas chromatographic techniques. Using the online measurements on the aircraft, isoprene emission fluxes were estimated and directly compared to the BEIS-3 inventory (EPA Biogenic Emissions Inventory System). The BEIS-3 data were also incorporated in a Lagrangian particle dispersion model (FLEXPART) and results were compared with measurements.

Results
An example of the results obtained by PTR-MS is given in Figure 1, which shows the measurements from a flight over an area with high isoprene emissions in northeast Texas. Isoprene mixing ratios are high and highly variable in the boundary layer, and quickly drop off to zero above the boundary layer. The monoterpene levels are relatively low at 60 pptv or less, whereas in other regions of the US, levels over 200 pptv have been observed from the NOAA WP-3D.

The correlation between measured isoprene mixing ratios from all flights and the BEIS-3 emissions inventory (for nominal, standard meteorology) is shown in Figure 2. It can be seen that measured isoprene was generally higher above areas with higher emissions. An exception is an area to the southeast of Dallas-Fort Worth, where the highest emissions are expected according to the inventory, but where the NOAA WP-3D only measured moderately enhanced mixing ratios.

Figure 1. Flight track of the NOAA WP-3D on September 16, 2006, color-coded by the measured mixing ratio of isoprene. The lower panel shows the time series of isoprene along with that of the monoterpenes and the flight altitude.
Figure 2. Correlation between the BEIS-3 isoprene emission inventory and the isoprene mixing ratios measured from the NOAA WP-3D in 2006 and the NCAR Electra in 2000.

Measurements from the NCAR Electra during TexAQS 2000 are shown for comparison. They show higher isoprene in this area southeast of Dallas/Ft. Worth.
Interpretation and Conclusions

In general, the comparison between measurements and inventory showed an agreement within ±50%, somewhat dependent on the day and the location. The OH reactivity of the biogenic VOCs, which is important for the ozone production efficiency, was also compared to the OH reactivity from anthropogenic VOCs separated into urban and industrial VOCs. Before final conclusions are reached, several important issues must be investigated including the different drought stress on the vegetation within these two study years, and the influence of recalculating the BEIS-3 isoprene emissions with the actual meteorology specific to the time of the isoprene measurements.
XIV. Hg Source Investigation.

Background
Gas-phase elemental mercury (Hg(0)), while long-lived in the atmosphere, is thought to be the primary source of mercury (II) and particulate mercury species, which are far more toxic, soluble, and bioavailable. Anthropogenic sources of Hg(0) to the atmosphere include emissions from coal-fired power plants, waste incineration, cement and steel manufacturing, smelting, petroleum refining, and industrial processes such as used in chlor-alkali plants. Gas-phase Hg(0) was measured aboard the NOAA research vessel Ronald H. Brown during the TexAQS II project in order to evaluate potential emissions sources of this compound along the Texas coastline and in industrialized harbor areas.

Results
Mercury data were reported at 1-second intervals for the TexAQS II RHB cruise, which sampled extensively in the Gulf, Galveston Bay, the Houston Ship Channel (HSC), for a full day in the Beaumont-Port Arthur area (BPA), and for several hours in Matagorda Bay. A modified Ohio Lumex instrument was used to detect atmospheric Hg(0) using absorption of the 253.7 nm emission line of a mercury lamp in a 10-m multipath sample cell. Specificity was afforded by high-frequency modulation of the emission lamp into three polarized Zeeman components, with the $s^-$ line uniquely absorbed by atomic mercury. Instrument zeroes were regularly checked by sampling ambient air through an iodinated charcoal trap, and instrument calibration was routinely evaluated by adding a known standard of Hg(0) to the ambient sample. 1-sigma uncertainties of the 1-second data averaged ±(2 ng/m$^3$ + 16%) of the reported value.

The RHB ship track in the TexAQS II study region is shown in Figure 1, scaled by 1-minute averages of Hg(0) concentration measured aboard the ship.

Outside of the industrialized source areas, the data show an average Hg(0) concentration of 1.5 ± 1.4 ng/m$^3$, broadly consistent with the expected background value of 1.7 ng/m$^3$ for this season and latitude. No strong signature of Hg emissions is seen outside of the industrial areas, despite extensive sampling very close to oil and natural gas drilling and
production platforms in the Gulf, and in the very concentrated plumes of large commercial vessels burning a variety of bunker fuels.

Within the industrialized Houston Ship Channel and Beaumont-Port Arthur areas, the data show very concentrated, spatially narrow plumes, as shown in detail below.

![Graphs of Hg(0) data from industrial source regions during TexAQS II](image)

**Figure 2.** Hg(0) data from industrial source regions during TexAQS II. Note changes in scales between the two graphs; missing data are due to automated instrument calibration or zeroing.

The Hg(0) plume in the Houston Ship Channel, shown in Figure 2, was encountered on each of four transits in approximately the same location when local winds were southerly, suggesting a single source. No enhancement was seen when winds were northerly. Peak enhancements for this plume ranged from 250 to 15 ng/m³, with the variability potentially affected by differences in dilution, transport, and variability in the source strength, during each transit. A second plume (not shown) was encountered at a different geographic location in HSC, indicative of a separate source. The BPA plume was observed during the single RHB visit to Beaumont. Winds were steadily onshore during the visit to Matagorda Bay, precluding sampling the decommissioned chlor-alkali plant emissions by the instrument aboard the *R/V Ronald H. Brown*.

**Interpretation and Conclusions**

Most interesting is that all observed Hg(0) enhancements were completely uncorrelated with any of the very wide range of other measurements made on RHB; a list of these measurements is available [here](link). This complete lack of correlation rules out most known source types, which can be expected to co-emit one or more of the suite of species measured concurrently aboard the *Ronald H. Brown*. Further, the RHB mercury observations are not consistent with the latest TCEQ, AIRS, EGRID, and TRI inventory source locations for known Hg emitters in this region.
XV. Investigate NH$_3$ source emissions.

Background
The presence of fine aerosol in the troposphere affects air quality by threatening human health and lowering visibility. In some regions of the United States, secondary formation of ammonium nitrate aerosol can account for a significant fraction of particle mass and reduce visibility. Ammonium nitrate aerosol is formed from the reaction of gas phase ammonia (NH$_3$) and nitric acid (HNO$_3$). Anthropogenic emissions of NH$_3$ and NO$_X$ (= NO + NO$_2$), which in sunlight can be oxidized to form HNO$_3$, can result in observations of elevated ammonium nitrate levels. In the present study, the sources and processes associated with ammonium nitrate formation were observed from the NOAA WP-3D aircraft over Houston. To accomplish this the TexAQS 2006 study combined fast-response measurements of NH$_3$, HNO$_3$, particle composition, and particle size distribution.

Results
Sources of NH$_3$ in the Houston area include automobiles, industrial facilities, and outlying agricultural activity. Figure 1 shows the altitude profile of all the 1-second measurements of NH$_3$ mixing ratios that were made aboard the NOAA WP-3D during the 2006 study. Typically, NH$_3$ mixing ratios over the urban area ranged from 0.2 to 3 ppbv. In general, NH$_3$ mixing ratios decreased with increasing altitude. In addition, several plumes with high NH$_3$ levels were sampled on different flights and plumes with NH$_3$ mixing ratios greater than 5 ppbv, though infrequent, were observed in the boundary layer below 1 km. The NH$_3$ mixing ratios in these plumes ranged from 5 to over 50 ppbv.

Figures 2 and 3 illustrate the observation of these plumes. Figure 2 shows the flight track of NOAA WP-3D on October 6, 2006. The color-coding on the flight track (c.f., color bar on the right) indicates the NH$_3$ mixing ratio, while the barbs indicate two-minute averaged wind speed and direction. As indicated the wind was reasonably steady from the east-southeast during the flight. As the color-coding on the flight track indicates, during this flight plumes containing ammonia were intercepted during transects labeled 1 and 2 on the flight track. Also, identified on the
map is Cedar Bayou, which is the location of the only significant NH$_3$ point source upwind of the observed NH$_3$ plume that is listed in the National Emission Inventory of 1999 (NEI99v3). Figure 3 shows the times series of NH$_3$, NOx, and CO$_2$ measurements that were made during the transect labeled 1 in Figure 2. Though these high NH$_3$ plumes were downwind of NEI99v3 point source at Cedar Bayou, other simultaneously measured gas-phase species, suggest the influence from other sources too (or only other?).

However, in all these plumes, the observed NH$_3$ enhancement was found to be accompanied by a corresponding decrease in HNO$_3$ mixing ratios and a corresponding increase in the particulate NO$_3^-$ concentration that indicated ammonium nitrate formation. In these plumes the magnitude of the observed HNO$_3$ loss and NO$_3^-$ formed is consistent with ammonium nitrate formation within a factor of 2.

**Interpretation and Conclusions**

During TexAQS 2006 the observed NH$_3$ mixing ratios typically ranged from 0.1 to 3 ppbv, though a few plumes with NH$_3$ mixing ratios greater than 5 ppbv were also sampled. The sources were located in the Houston metropolitan area, around Beaumont and in St. James Parrish in Louisiana. In addition to industrial plumes, NH$_3$ plumes that were associated with biomass burning were also encountered. Many of the NH$_3$ plumes that we encountered could not be traced to point sources in the NEI99v3 inventory. This highlights the need to revise and update the NH$_3$ inventories. Additional analysis will be directed toward the correlation of the NH$_3$ plumes with other compounds that were measured aboard the WP-3D (e.g., VOCs). This will allow a better identification of the sources and estimation of the amount of NH$_3$ that is emitted.
With regard to processes that involve NH$_3$, we observed coincident decreases in HNO$_3$ mixing ratio and increases in aerosol NO$_3^-$ and fine particle volume indicating ammonium nitrate formation in these plumes. The magnitude of the observed HNO$_3$ lost and NO$_3^-$ formed is within a factor of 2 consistent with ammonium nitrate formation. Further analysis of the particle size distribution and aerosol composition data is needed to fully assess the quantitative agreement between the gas-phase and aerosol observations.