

ACCELERATED SCIENCE EVALUATION of OZONE FORMATION IN THE HOUSTON- GALVESTON AREA: EMISSION INVENTORIES



Working Committee

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Summary

This document summarizes findings concerning emission inventories emerging from the Accelerated Science Evaluation of ozone formation in the Houston-Galveston area. As noted by a multi-national commission (NARSTO – created as the North American Research Strategy for Tropospheric Ozone), “after 20 years of effort, emission estimates continue to be one of the weakest links in the air-quality management process and a major source of uncertainty in the development of O₃ control strategies.”

For the Houston-Galveston area, the key issues that must be assessed are:

1. Are the magnitudes of the emissions correct?
2. Are the emissions adequately and correctly speciated?
3. Are the emissions correctly distributed spatially and is the spatial resolution sufficient for accurately predicting ozone formation?
4. Are the emissions correctly distributed temporally and is the temporal resolution sufficient for accurately predicting ozone formation?

Observational data collected during the Texas Air Quality Study of 2000 suggest that some components of current emission inventories are incorrect or incomplete. Specifically, measurements of the ratios of non-methane organic compound concentrations to the concentrations of oxides of nitrogen (NMOC/NO_x), especially in industrial plumes, is much higher than documented by inventoried emissions. High values of NMOC/NO_x have also been observed in previous field studies, although the composition of NMOC observed in the Texas Air Quality Study of 2000 appears somewhat different than the compositions reported in previous studies. In addition, the current body of evidence suggests that the major uncertainties are associated with the point source inventory.

These, and other observational data and data analyses, summarized in this document, lead to the following findings:

1. Are the magnitudes of the emissions correct?

Finding 1: Emission factors for vehicular emissions, calculated based on data collected in the Washburn Tunnel, indicate that vehicular emission factors in Houston are comparable to those observed in other urban areas.

Finding 2: Observational data collected during the Texas Air Quality Study suggest that biogenic emissions are primarily located north of the Houston urban area, and contributed relatively little to urban ozone formation during the Texas Air Quality Study of 2000.

Finding 3: NMOC/NO_x ratios observed by aircraft in industrial plumes, and at ground monitoring stations, are higher than values observed in other urban areas.

NMOC concentrations observed in industrial plumes in Houston are substantially higher than concentrations observed in other urban areas, while observed NO_x concentrations are more typical of other urban areas with significant NO_x point sources.

Finding 4: Observations made by aircraft suggest that plumes from petrochemical facilities are heterogeneous, with NO_x rich regions, NMOC rich regions, and regions rich in both NMOC and NO_x. In addition, data on NMOC/NO_x ratios, taken over multiple years at ground monitoring stations in industrial source dominated areas, show substantial temporal variability. Because of this spatial and temporal heterogeneity, isolated measurements of NMOC/NO_x ratios must be viewed with caution. Nevertheless, the ensemble of measurements available clearly indicate that average NMOC/NO_x ratios observed in industrial plumes are higher than documented in current inventories.

Finding 5: Underestimates of fugitive emissions, emissions from flares and emissions from cooling towers are expected to be the most likely causes of differences between observed NMOC/NO_x ratios and NMOC/NO_x ratios in the inventories.

2. Are the emissions adequately and correctly speciated?

Finding 6: Data on NMOC compositions are available at only a few locations, however, at these locations, the average composition of NMOC in Houston has remained relatively constant for a decade or more. While the average composition of NMOC is well established, the composition of NMOC downwind of petrochemical facilities shows wide variability.

3. Are the emissions correctly distributed spatially and is the spatial resolution sufficient for accurately predicting ozone formation?

Finding 7: Since the main uncertainties are in the point source inventory, rather than the area, non-road, on-road or biogenic inventories, spatial resolution of the inventory is not a major area of uncertainty. Audits performed during the winter of 2001-2002 showed that point source geographic locations are reasonably accurate.

4. Are the emissions correctly distributed temporally and is the temporal resolution sufficient for accurately predicting ozone formation?

Finding 8: Ground observations, taken over a period of several years, and other data, suggest that emissions exhibit significant temporal variability. The implication of this finding is that NMOC/NO_x ratios will be variable, and individual plumes may have very different ozone formation potentials at different times. The extent the observed variability is caused changes in emissions or changes in meteorological conditions such as wind direction, vertical mixing and atmospheric stability, has not been determined.

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Background

Photochemical smog is a complex mixture of pollutants that are directly emitted into the atmosphere (primary pollutants) and pollutants that are formed by chemical and physical transformations that occur in the atmosphere (secondary pollutants). Ozone is the secondary pollutant found at highest concentrations in photochemical smog, and because it is a secondary pollutant, understanding the formation of ozone in urban atmospheres requires estimates of the emissions of the primary pollutants that lead to its formation. The principal precursor emissions that lead to ozone formation in urban atmospheres are reactive organic compounds and oxides of nitrogen.

Reactive organic compounds include hydrocarbons and partially oxygenated hydrocarbons and are referred to by a variety of similar, but not identical terms, including volatile organic compounds (VOCs), non-methane hydrocarbons (NMHC), and non-methane organic compounds (NMOC). In this report reactive organic compounds will be referred to as NMOC. Determining both the magnitude and composition of NMOC emissions is critical because a large number of different NMOCs are emitted in urban areas and because these compounds can have dramatically different reactivities. In addition, many industrial sources in the Houston-Galveston area emit NMOC species, which are rarely significant in other urban areas, but are significant in this region.

The oxides of nitrogen that are emitted directly to the atmosphere are mixtures of NO and NO₂, referred to as NO_x. Other oxides of nitrogen (for example, N₂O₅ and NO₃) are important in describing atmospheric chemistry, but are not, in general, emitted directly.

Emissions other than NMOC and NO_x can also lead to ozone formation. Emissions that lead to the formation of free radicals and emissions of particles that may influence heterogeneous reactions in the atmosphere may be of some concern in the Houston Galveston area (Allen, et al., 2001), and these emissions are described later in this report.

In addition to determining the magnitude and composition of NMOC and NO_x emissions, it is necessary to characterize the spatial and temporal distribution of the emissions. Photochemical grid models, used to describe ozone formation and to evaluate emission reduction strategies, generally use day specific inventories of emissions with a temporal resolution of one hour and a spatial resolution of approximately 2-4 km. It is not yet clear if finer temporal and spatial resolution of emissions will be required to accurately model ozone formation in the Houston-Galveston (HG) area, and this issue will be discussed in other reports associated with the Accelerated Science Evaluation.

Inventories of NMOC and NO_x emissions that contribute to ozone formation have generally been categorized into biogenic and anthropogenic emissions, and within the anthropogenic category, emissions are further classified as on-road mobile, non-road mobile, point, and area. Each of these terms is defined below. The definitions are drawn from Texas Commission on Environmental Quality (TCEQ, formerly the Texas Natural Resource Conservation Commission, TNRCC) documentation for the HG State Implementation Plan (SIP) (TNRCC, 2000)

Biogenic emissions:

Biogenic emissions include NMOC emissions from crops, lawn grass, and forests as well as a small amount of NO_x emissions from soils, which may increase with the application of nitrogen based fertilizers. Plants are sources of NMOCs such as isoprene, monoterpenes, and sesquiterpenes. Tools for estimating emissions include satellite imaging for mapping of vegetative types, field biomass surveys, and modeling of emissions based on emission factors by plant species. Biogenic emissions can be highly dependent on temperature and sunlight intensity, so data on these parameters are also necessary for emission estimates.

Anthropogenic emissions:

Point source emissions:

Major point sources are defined for inventory reporting purposes as industrial, commercial, or institutional sources which emit or have the potential to emit criteria pollutants at or above threshold levels. The levels vary depending on the air quality status of the area. For non-attainment areas, typical reporting thresholds are: 10 tons/year (t/y) VOC, 25 t/y NO_x or 100 t/y of any other criteria pollutants that include CO, SO₂, PM₁₀ or lead. Any source that generates or has the potential to generate at least 10 t/y of any single hazardous air pollutant (HAP) or 25 t/y aggregate of HAP is also required to report emissions (more detailed definitions of categories of point sources and emission thresholds that trigger reporting can be found in Title 30, Section 101.10 of the Texas Administrative Code) .

The TCEQ uses an emission inventory questionnaire (EIQ) to collect emissions and industrial process operating data from plants that have emissions that are above the threshold levels described above. The EIQ is used to report the emissions from each point or area of fugitive emissions. Information on the amount of each species of NMOC is requested. Included are the type of emission (stack, fugitive, flare, etc.), process equipment diagrams, operation schedules, emissions control devices, and abatement device control efficiency. Also included are source location, height, stack diameter, gas exhaust temperature and exhaust gas velocity.

On-road Mobile Source emissions

On-road mobile sources consist of automobiles, trucks, motorcycles, and other motor vehicles traveling on public roadways. Combustion related emissions are estimated for vehicle engine exhaust. Evaporative NMOC emissions are estimated for the fuel tank and other evaporative leak sources. Emission factors have been developed using EPA's MOBILE models. (U.S. EPA, 2002; Perkinson, 2000) Inputs for the mobile model are vehicle speed by roadway type, vehicle registration by vehicle type and age, percentage of vehicles in cold start mode, percentage of miles traveled by vehicle type, type of inspection and maintenance program, and gasoline vapor pressure. Travel activity, represented as vehicle miles traveled (VMT), is developed from travel demand models run by the Texas Department of Transportation or the local council of governments. The

travel demand models have been validated with a large number of traffic counters. Estimates of area-wide VMT are calibrated with the federal Highway Performance Monitoring System (HPMS). Roadway speeds used in the MOBILE model are calculated by a post-processor to the travel demand model. On-road mobile emissions are determined for each roadway link and are based on the emission factor from the MOBILE model and the VMT from the travel demand model. Speciation of emissions in the Houston-Galveston area is based on locally collected data.

Non-road Mobile emissions

Non-road mobile emission sources are aircraft operations, marine vessels, recreational boats, railroad locomotives and off-highway equipment. Emission calculations are based on emission factors and activity. Activity data is based on equipment population, engine horsepower, load factor, and annual usage. For southeast Texas, diesel powered construction equipment emissions were based on activity data developed by an extensive survey (TNRCC, 2000), except for equipment less than 50 HP and cranes. An extensive study of commercial marine activity in the HG area was conducted to estimate marine vessel emissions. Aircraft emissions were estimated from landing and takeoff data from airports using the EDMS aircraft emissions model (TNRCC, 2000). Airport ground support equipment emissions were estimated with new methods using local survey data. Locomotive emissions were developed from fuel use and track mileage data obtained from the railroads. Emissions from all other non-road mobile source categories were calculated with EPA's NONROAD (U.S. EPA, 2001b; TNRCC, 2000) model.

Area emissions

Area sources include those point sources that fall below the threshold reporting level for point sources, along with sources that are widely dispersed (e.g., personal care products). These are sources that are too numerous or too small to identify individually and emissions are calculated on the basis of a source category or group. Typically area sources are commercial, small scale industrial and residential sources that use materials or operate processes that generate emissions. Area sources can be divided into two groups; those that have hydrocarbon evaporative emissions and those that have fuel combustion emissions. Examples of evaporative losses include: painting (surface coating), industrial coatings, degreasing solvents, leaking underground storage tanks, gasoline service station tank filling and vehicle refueling. Fuel combustion sources include stationary fuel combustion at residences and businesses (small industrial boilers, water heaters), outdoor burning, structural fires and wildfires.

Summary of Current Inventory Data

A number of spatially and temporally resolved emission inventories of ozone precursors have been developed for the Houston-Galveston (HG) area. These inventories include gridded and temporally resolved inventories developed for photochemical modeling applications and county level emission inventories developed for the Environmental Protection Agency's 1999 National Emissions Inventory (NEI) data set (U.S. EPA, 2001c).

Inventories developed for photochemical modeling applications

The TNRCC developed a gridded and temporally resolved emission inventory for an episode in September 1993 that was used in photochemical modeling performed for revisions to the HG area air quality State Implementation Plan (SIP). TNRCC also developed an extensive, hourly, speciated emissions inventory for an August 1993 episode, but the August 1993 episode was not used extensively in SIP development.

In March 2002 the TNRCC completed a comprehensive, hourly, speciated emissions inventory for an August-September 2000 episode. The magnitude and speciation for the point source emissions in this inventory were based on special reports covering the period being modeled. These reports detailed on an hourly basis the magnitude and species of all point source emissions. Also included was a quantification and speciation of emissions from non-routine emissions, upsets and maintenance activities. For the 11 county area around the HG nonattainment area, the special reports were estimated to have covered 82 percent of the total non power plant point source emissions of NO_x and 71 percent of the total VOC emissions. These emissions have been assembled into a gridded, temporally resolved inventory for photochemical modeling.

Other gridded, temporally resolved inventories, that include the Houston-Galveston area, have been developed for 1995, 1996 and 1999 episodes. However, these inventories were designed for photochemical modeling in other cities and do not have fine scale spatial and temporal resolution in the HG area.

To provide an overview of emissions in the HG area, the data for the 2000 photochemical modeling episode will be presented.

Data from the 2000 emission inventories used for the modeling in the HG SIP are presented in Table 1. These data summarize the NO_x and VOC emissions from point, area, on-road mobile, non-road mobile, and biogenic sources. Summary results for the 2000 EI are shown in Figures 1-3.

Table 1. 2000 Summary of emissions in the 8-county Houston/Galveston nonattainment area for August 30, 2000 (TNRCC, 2002)

	VOC tons/day	NOx tons/day
Point source	174	501
Area/Non-road mobile source	248	182
On-road mobile	149	246
Biogenic	1713	21

For photochemical modeling the emissions must be processed into model ready files. These emissions files must be developed for each hour of the model episode and for each hour they must specify the emissions located in each grid cell covered by the modeling domain. For the HG area, the typical model grid cell is 4 km x 4 km. However, the 2000 EI was processed for grid cells that are 2 km x 2 km. For any hour being modeled, output from the photochemical model can be used to display the emissions in each grid cell over the modeling domain. These plots are commonly called “tile plots”. The tile plots can be developed to show the sum of all emissions in each grid cell over each day being modeled. They can also sum the emissions over all grid cells over each hour and present a diurnal profile. Tile plots can be analyzed to evaluate the spatial and temporal distribution of emissions by major source category. Some representative tile plots for the summer of 2000 are shown in Appendix A (TNRCC, 2002).

County-level National Emission Inventory Data

Beginning with 1990, TNRCC has developed a periodic emissions inventory (EI) for ozone nonattainment areas every three years. Unfortunately the same level of analysis is not available for each year. As indicated above, the EI data for 1993 and 2000 have been used extensively for photochemical modeling and therefore contain data that have fine spatial and temporal resolution. The 1996 and 1999 emission inventory data have not been as extensively used in modeling applications, therefore the spatial and temporal resolution for these inventories tends to be more coarse.

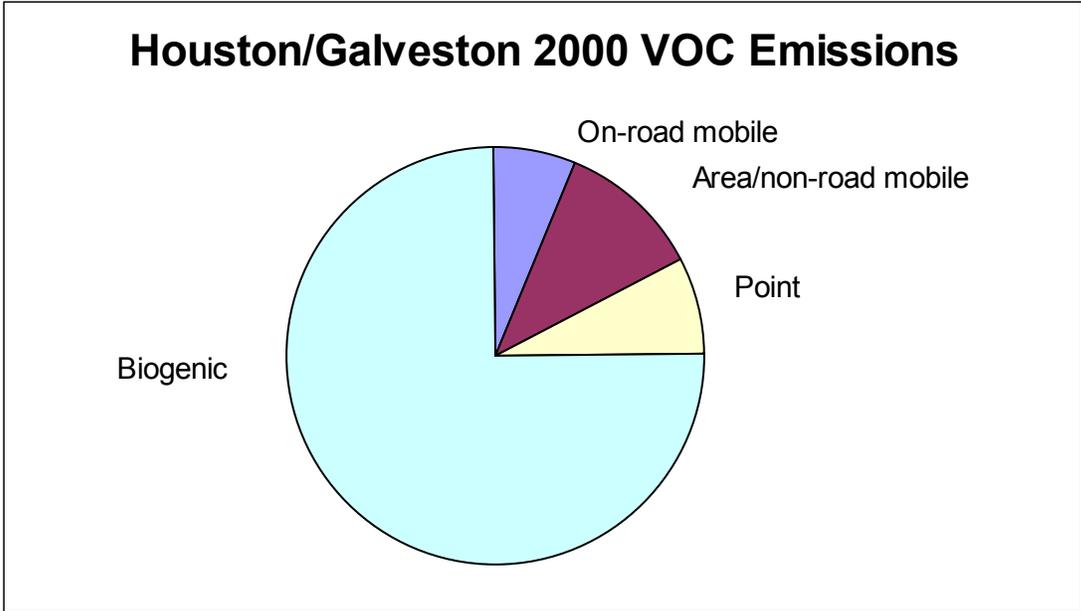


Figure 1. Total VOC Emissions, Houston/Galveston nonattainment area, 2000 Emissions Inventory (TNRCC, 2002).

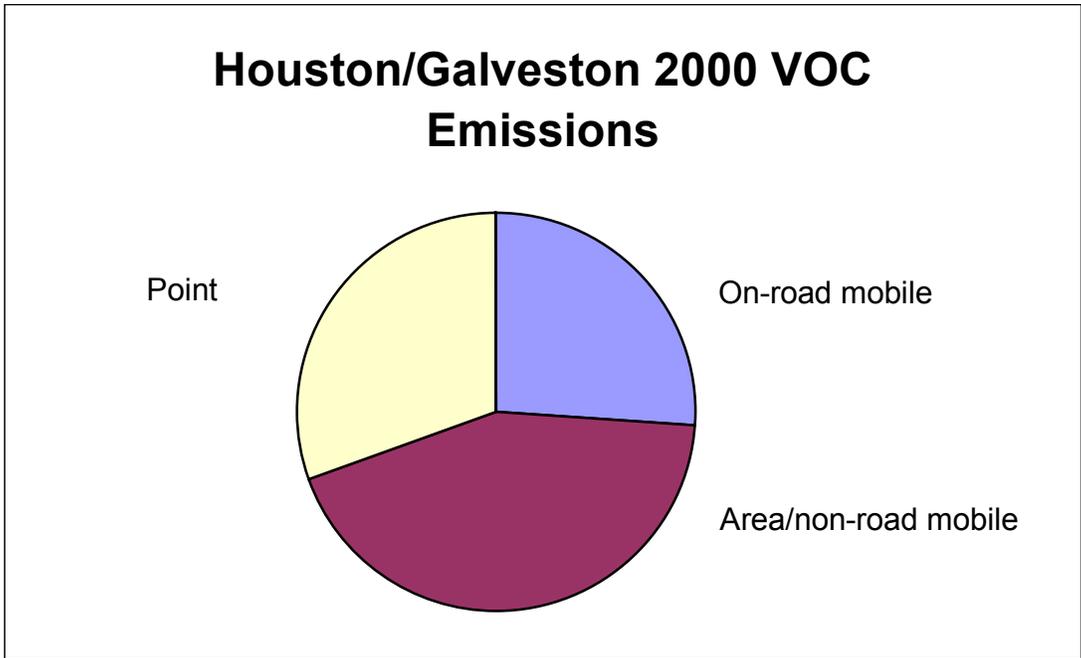


Figure 2. Total VOC Emissions without biogenics, Houston/Galveston nonattainment area, 2000 Emissions Inventory.

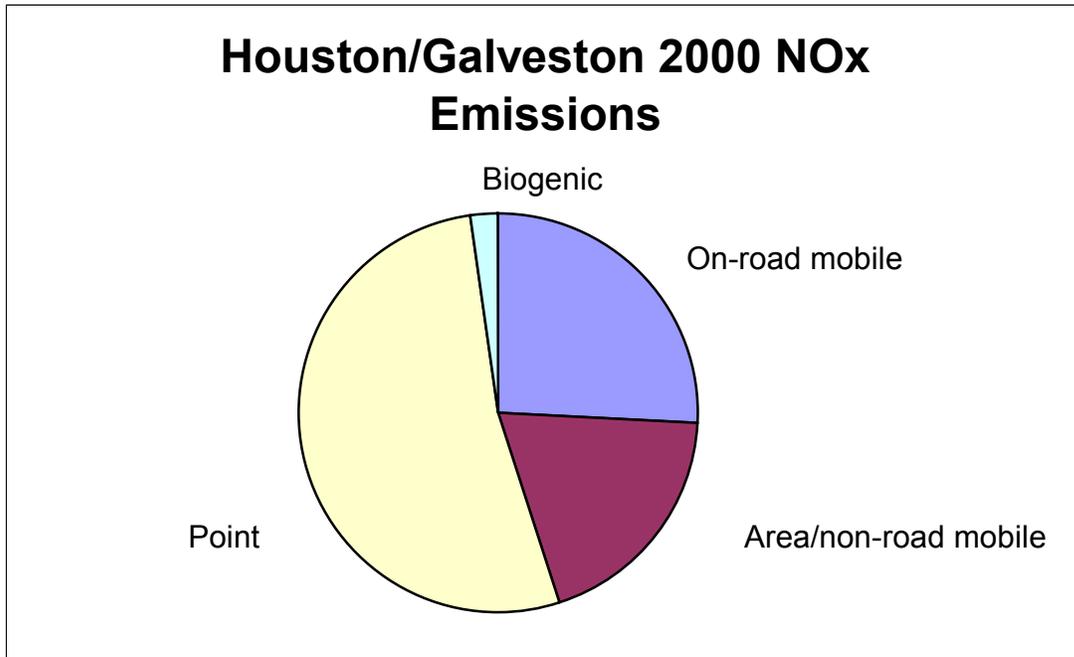


Figure 3. Total NO_x Emissions, Houston/Galveston nonattainment area, 2000 Emissions Inventory (TNRCC, 2002).

Shown in Figures 4 and 5 are an analysis of the major sub-categories of sources that contribute to non-point source emissions in the 2000 inventory

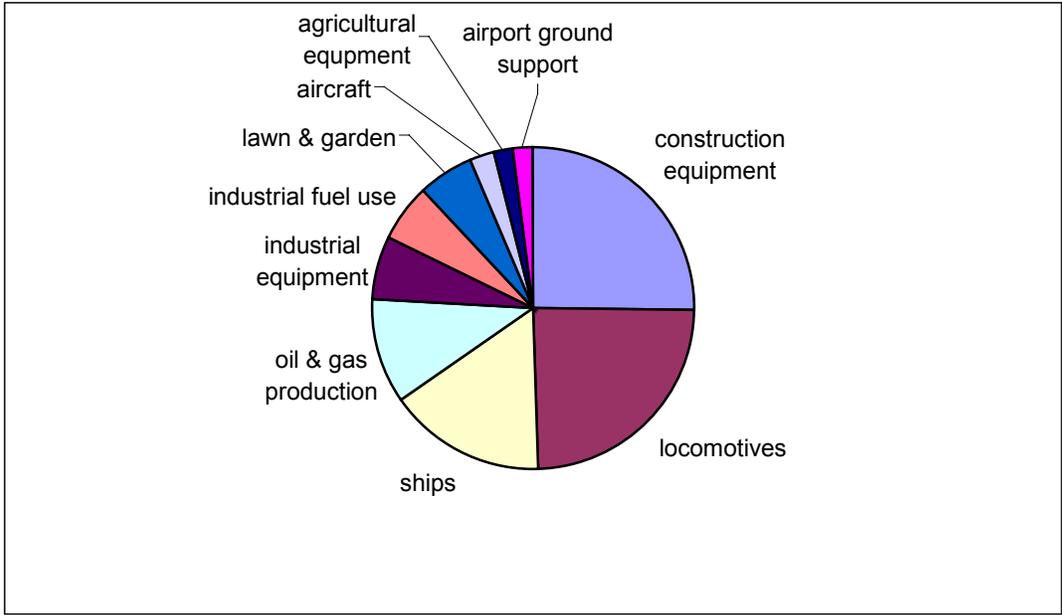


Figure 4. Top Ten area/non-road source categories for NO_x, tons/day, Houston/Galveston nonattainment area, 1999 Emissions Inventory.

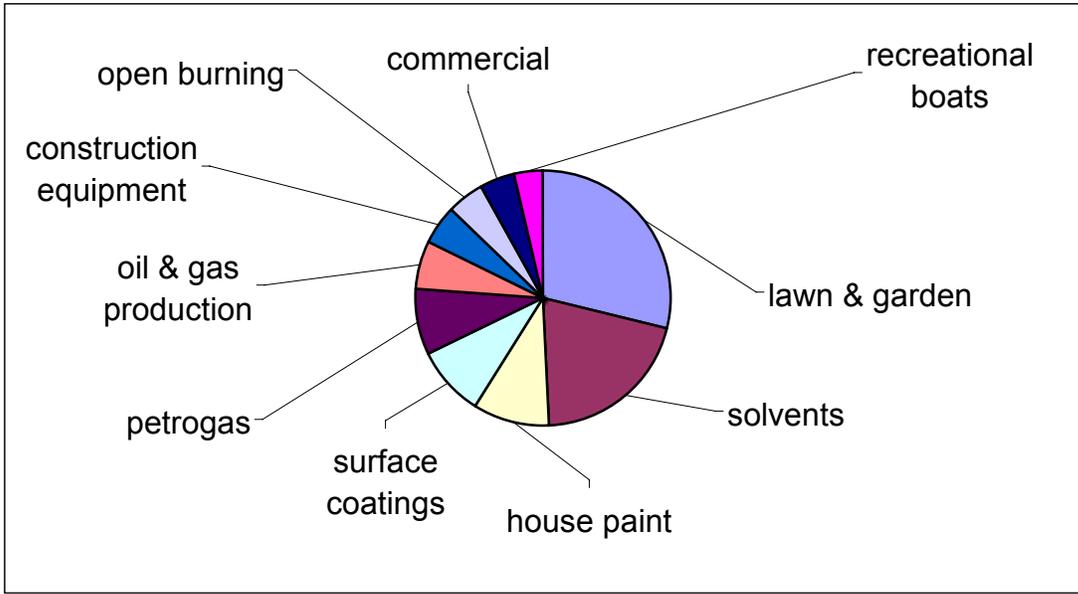


Figure 5. Top Ten area/non-road source categories for VOC, tons/day, Houston/Galveston nonattainment area, 1999 Emissions Inventory.

Performance Evaluation of Emissions Inventories

In July 2000, a multi-national commission (NARSTO – created as the North American Research Strategy for Tropospheric Ozone) released *An Assessment of Tropospheric Ozone Pollution* (Chameides, et al., 2000), which included an assessment of the importance of emission inventories. The synthesis team concluded that:

“After 20 years of effort, emission estimates continue to be one of the weakest links in the air-quality management process and a major source of uncertainty in the development of O₃ control strategies.”

“For the most part, studies using source apportionment methods have suggested that mobile sources are responsible for a larger portion of total VOC emissions than that predicted by emission inventories.”

“Despite the improvements that have been made, there remains a great deal of uncertainty in [point source] estimates.”

“NO_x and VOC emissions from stationary area sources are even more difficult to accurately characterize.”

The accuracy of emission inventories can be assessed in a variety of ways. Since the mid 1980's ratios of monitored concentrations of NMOC to NO_x have been compared to ratios of emissions of NMOC to NO_x. These comparisons are typically performed with monitoring data collected 6:00 am to 9:00 am to reduce confounding effects of reactions. In 1987 the Texas Air Control Board (TACB) found that ratios of NMOC to NO_x in the HG area had a mean of 19.2:1 and 25.2:1 for 1985 and 1986 respectively (Hemphill, 1987). EPA compared measured NMOC to NO_x ratios with the corresponding ratios from emissions. They concluded, “In Houston, the predicted NMOC levels area are always lower than the observed NMOC levels. On average predicted NMOC concentrations in Houston are 5.9 times lower than observed values” (Baugues, 1992).

With the 1993 Coastal Oxidant Assessment for Southeast Texas (COAST Study; Lawson, et al., 1995) data, a number of comparisons were made between ratios of monitored concentrations of NMOC to NO_x and ratios of emissions of NMOC to NO_x (Korc, 1995; PAMS Data Analysis Workshop, 1996). For the emissions inventory data, only the chemical species that were capable of being detected by the gas chromatographs at the monitoring stations were considered. These compounds represent approximately 75 percent of the total emissions in the inventory. Emissions were converted from a mass basis to a molar basis to place the monitored data and the emissions data on the same basis. Results are shown in Figures 6 and 7 (PAMS Data Analysis Workshop, 1996). The Galleria site referred to in the figures was located in the western part of the HG area far away from the industrial area (very close to the Williams Tower site used in the 2000 Texas Air Quality Study, www.utexas.edu/research/ceer/texaqs). The Clinton site is a permanent TNRCC monitoring location that is located in the HG industrial area, very

close to Houston Regional Monitoring Network Site 3, which was used in the 2000 Texas Air Quality Study. The measured ratios of NMOC to NO_x ranged from 4-12, and the measured ratios were consistently larger than those from the emissions inventory (Korc, 1995; PAMS Data Analysis Workshop, 1996).

Figure 6.

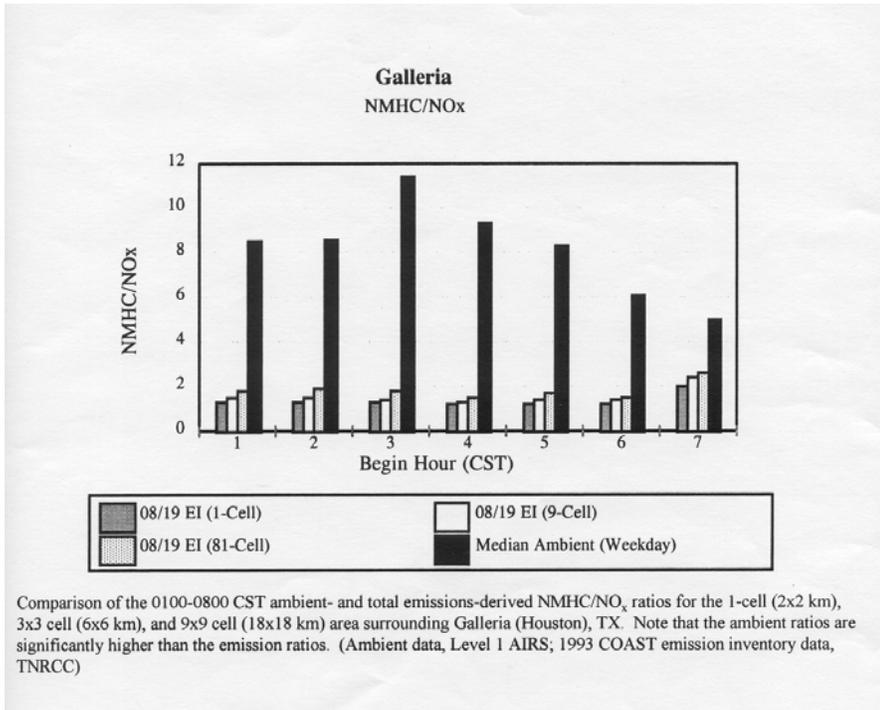
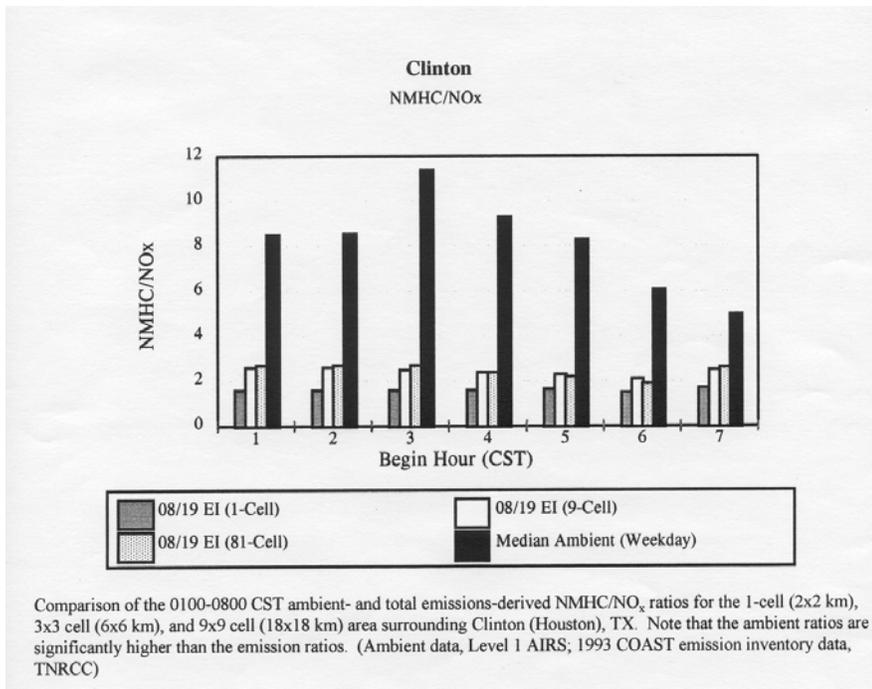


Figure 7.



Comparisons of measured total NMOC/ NO_x ratios to the ratios predicted using the emissions inventory can provide an overall indication of the performance of the emission inventory. More detailed assessments can be performed by comparing ratios of individual compounds. Using the 1993 COAST data, composites of measurements and emissions of paraffins, olefins, aromatics, and other NMOC compounds were developed, and compared (Korc, 1995; PAMS Data Analysis Workshop, 1996). Emissions were converted from a mass basis to a molar basis to place the monitored data and the emissions data on the same basis. Monitored concentrations at 6:00 am were used for this analysis. The results are shown in Figures 8 and 9. At both sites the composition of aromatic species in the EI was slightly higher than the corresponding measured values. For olefins the EI values are slightly higher than the measured values. For paraffins the EI values are similar at Clinton, and slightly lower than the measured values at Galleria. These differences between predicted and observed values for the relative abundance of specific NMOC compound classes are minor, however, relative to the differences in the overall magnitude of NMOC/NO_x ratios, shown in Figures 6 and 7. This suggests that for the 1993 inventory, the average composition of emissions in the inventory was much more accurate than the overall magnitude of the emissions.

Figure 8.

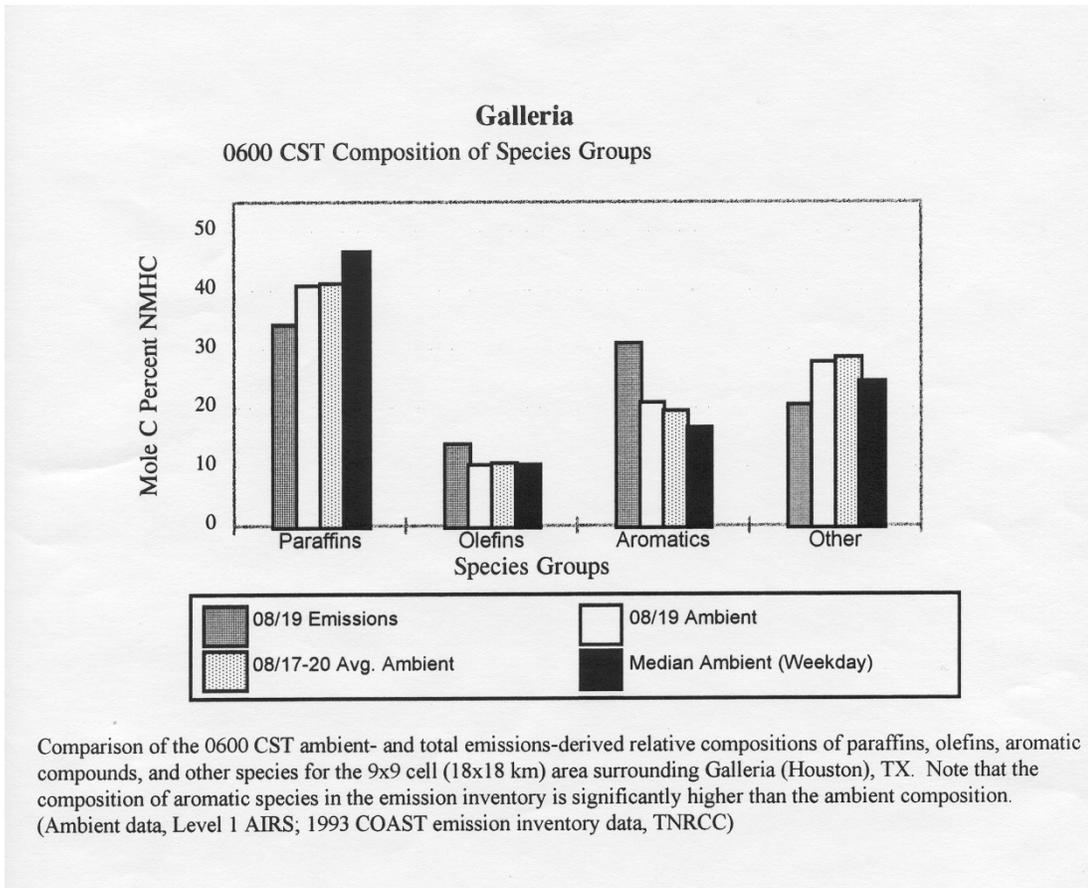
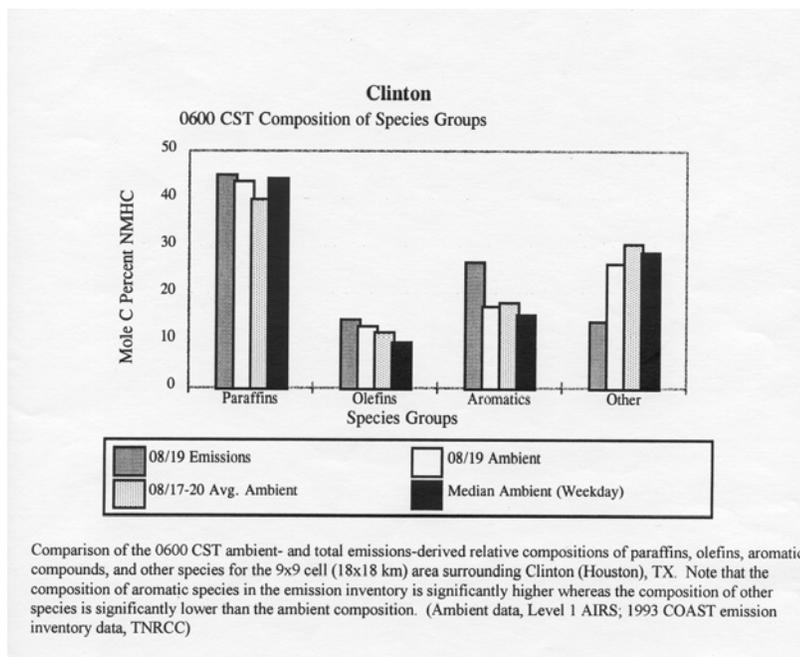


Figure 9.

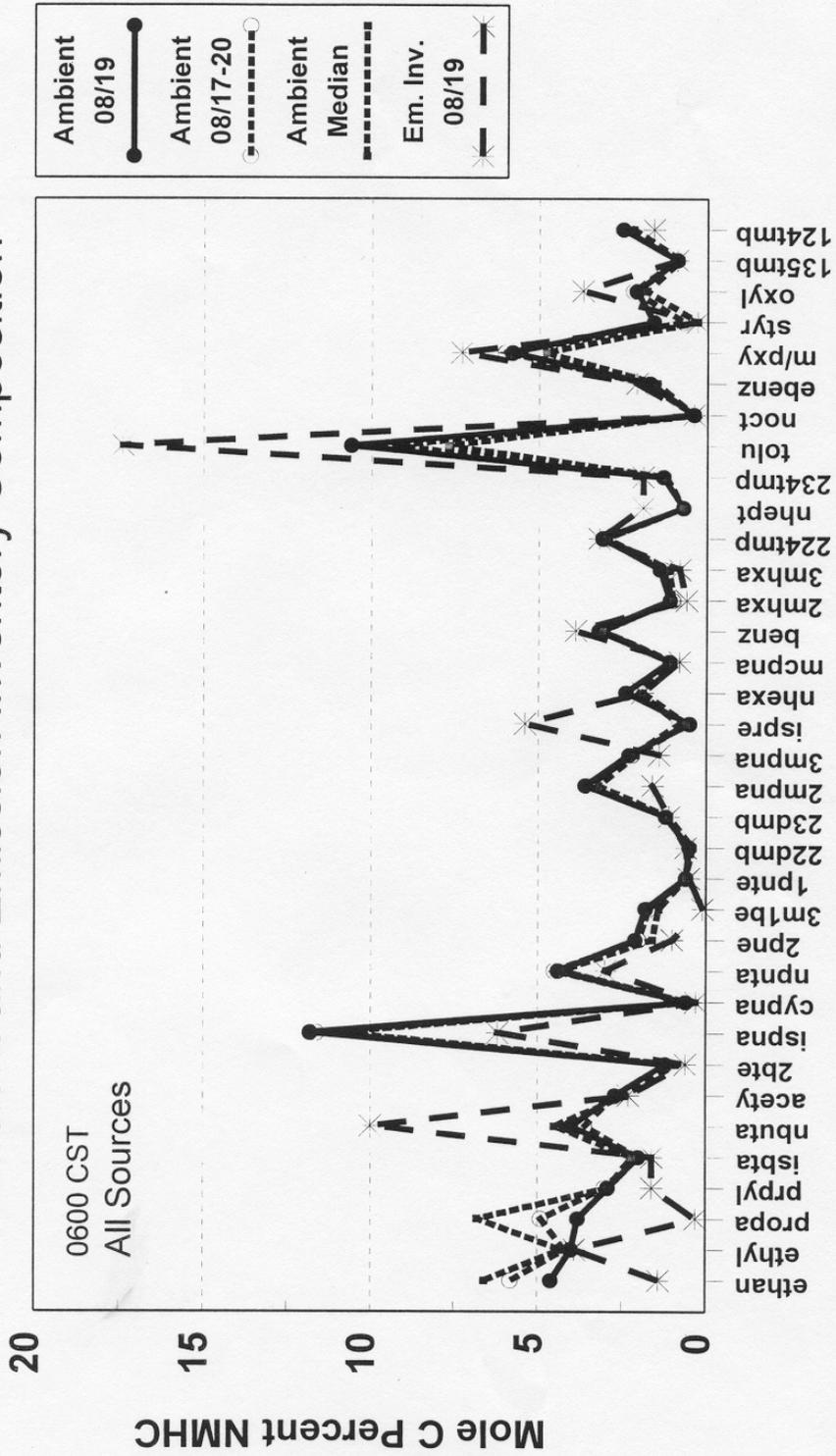


Figures 8 and 9 show data for compound classes. Similar analyses were performed for individual species. For the most abundant chemical species, relative composition data from the EI were compared to similar data from the monitoring. Emissions were converted from a mass basis to a molar basis to place the monitored data and the emissions data on the same basis. Monitoring concentrations at 6:00 am were used for this analysis. The results are shown in Figures 10 and 11 (Korc, 1995; PAMS Data Analysis Workshop, 1996). At the Galleria, the compositions of ethane, propane, and isopentane in the EI were significantly lower than the measured values. For n-butane, isoprene, and toluene the EI values were higher than the measured values. At Clinton the concentrations of ethane, acetylene, isopentane and cyclopentane in the EI are lower than the measured values. For n-butane, isoprene, and benzene the EI values are higher than the measured values. Analysis of the gasoline composition for the time when the monitoring was conducted revealed that a better profile for gasoline should be used. This modification was made to the emissions prior to the development of the final SIP.

Some of the discrepancies between the individual compound emissions reported in the inventory and the compositions of NMOC observed at Clinton and the Galleria can be reconciled. For example, ethane may be under-reported in the inventory because it is not defined as a volatile organic compound (VOC). Since ethane is not a VOC, its emissions are not reported if a plant reports only VOC. Acetylene is also under-reported in the 1993 inventory. A major source of acetylene is mobile source exhaust, so if the values in the emissions inventory are significantly lower than the monitored values it would appear that the mobile source emissions in the inventory are under predicted. Numerous studies have suggested that vehicular NMOC emissions are underestimated by MOBILE (National Research Council, 2000).

Galleria

Ambient and Emission Inventory Composition

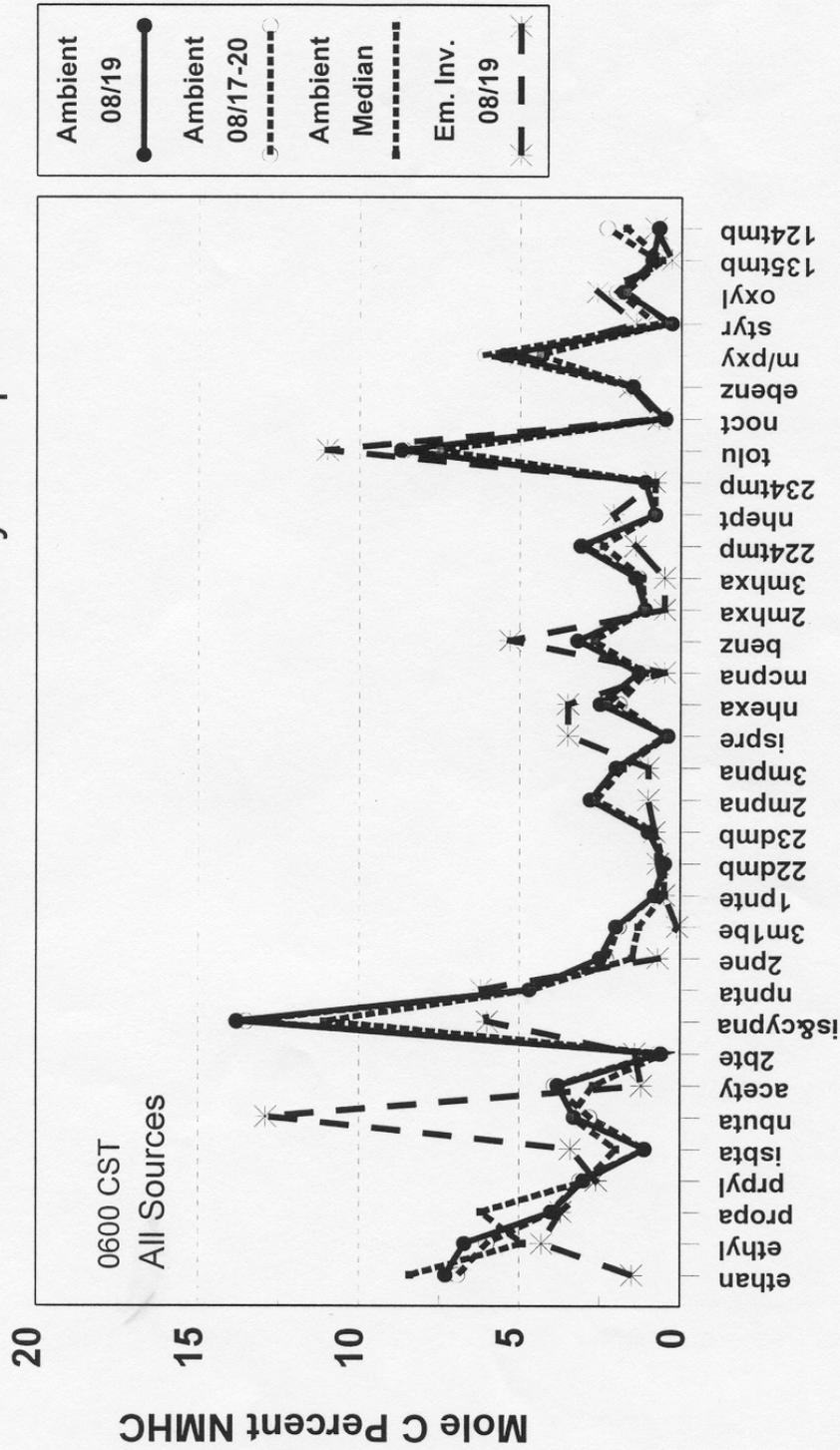


Comparison of the 0600 CST ambient- and total emissions-derived relative compositions of the most abundant chemical species for the 9x9 cell (18x18 km) area surrounding Galleria (Houston), TX. Note that the compositions of ethane, propane, and isopentane in the emission inventory are significantly lower than the ambient composition whereas the compositions of n-butane, isoprene, and toluene are significantly higher. (Ambient data, Level 1 AIRS; 1993 COAST emission inventory data, TNRCC)

Figure 10.

Clinton

Ambient and Emission Inventory Composition



Comparison of the 0600 CST ambient- and total emissions-derived relative compositions of the most abundant chemical species for the 9x9 cell (18x18 km) area surrounding Clinton (Houston), TX. Note that the compositions of ethane, acetylene, isopentane and cyclopentane in the emission inventory are significantly lower than the ambient composition whereas the compositions of n-butane, isoprene, and benzene are significantly higher. (Ambient data, Level 1 AIRS; 1993 COAST emission inventory data, TNRCC)

Figure 11.

Similar analyses have been performed for the period 1998-2001 (Main and Brown, 2002) and the results for the summer of 2000 are shown in Tables 3 and 4. As shown in Tables 3 and 4, the magnitudes of the concentrations observed in 2000 are lower than those observed in 1993, but the composition profiles are virtually identical. (Note that there are slight differences between the total hydrocarbon concentrations reported by Fujita, et al. (1995) and Main, et al. (2001), but the main features are consistent) The dominant hydrocarbons are light alkanes, with some light alkenes and aromatics.

Table 5 provides a more detailed analysis, showing the most abundant hydrocarbons detected during the summers of 1998-2001 at multiple ground stations (Main and Brown, 2002). Again, the profiles are consistent, indicating that while concentration magnitudes have changed over time, the composition profiles, as measured at ground sites, have remained constant.

Table 3. Fifteen most abundant hydrocarbon species detected at the Clinton site during the 1993 COAST Study (Fujita, et al., 1995) and during the summer of 2000 (Main, et al., 2001)

Compound	Summer 1993		Summer 2000
	Average Concentration (ppbC)	Percentage of Non-methane Hydrocarbons	Average Concentration (ppbC)
Isopentane/cyclopentane	43.7	8.2	13
Ethane	29.5	7.4	15
n-butane	27.5	5.1	15.5
n-propane	24.0	5.6	14.5
Toluene	22.9	4.2	6.5
n-pentane	22.3	4.3	6
n-hexane	21.0	3.7	3.5
Isobutane	16.5	2.8	8.5
2-methylpentane	13.8	2.4	4
Propene	12.5	2.2	3.5
Ethene	12.1	2.4	4
Meta- and para-xylene	11.8	2.3	4
3-methylpentane	11.6	2.0	2.5
Benzene	8.7	1.6	3.0
n-heptane	5.8	1.1	2.0

Table 4. Fifteen most abundant hydrocarbon species detected at the Galleria site during the 1993 COAST Study (Fujita, et al., 1995) and at Aldine (also a residential site) during the summer of 2000 (Main, et al., 2001)

Compound	Galleria Summer 1993		Aldine Summer 2000
	Average Concentration (ppbC)	Percentage of Non-methane Hydrocarbons	Average Concentration (ppbC)
Isopentane/cyclopentane	20.7	7.1	6.5
Ethane	21.3	7.7	14
n-butane	16.6	5.5	8.5
n-propane	18.5	6.6	13
Toluene	12.5	3.9	3.5
n-pentane	8.8	3.1	3.5
n-hexane	3.9	1.3	2
Isobutane	8.3	2.6	5
2-methylpentane	5.6	2.0	2
Propene	7.5	2.6	2
Ethene	8.4	2.6	4
Meta- and para-xylene	8.5	2.9	1.5
3-methylpentane	3.6	1.3	1
Benzene	5.0	1.5	2
<i>Species in top 15 at Galleria but not at Clinton in 1993</i>			
2,2,4 trimethylpentane	4.2	1.2	1
acetylene	4.2	1.3	2

Table 5.

Ten most abundant hydrocarbons, ranked by concentration in ppbC, during July-September, by site and year (Main and Brown, 2002)

	ethane	propane	Iso-pentane	n-butane	Iso-butane	ethene	toluene	n-pentane	Trans-2-butene	n-hexane	propene	xylene	2-methyl pentane	acetylene	isoprene	benzene
Deer Park 1998	1	2	3	4	5	6	7	8	9	10						
Deer Park 1999	1	2	3	5	4	6	7	8			9	10				
Deer Park 2000	1	2	3	4	5	7	6	10			8	9				
Deer Park 2001	1	2	5	4	3	6	7	9		10	8					
Clinton 1998	3	2	1	4	6	8	9	7			10	5				
Clinton 1999	3	2	1	4	6	9	8	7			10	5				
Clinton 2000	3	2	1	4	5	>10	6	8				9	10	7		
Clinton 2001	2	1	4	3	5	9	6	7			10	8				
Bayland 1998	1	2	3	4	7	8	5	6				9				
Bayland 1999	1	2	3	5	7	8	4	6				9				
Bayland 2000	1	2	3	4	8	7	6	9				10				
Aldine 2000	1	2	3	4	5	6	7	>10		10		8	9			
Channelview 2001	2	1	5	3	4	6	7	9			8					10
HRM-3 '01	2	1	4	3	5	8	6	9			7	10				
HRM-7 2001	2	1	4	3	5	9	7	6			8	10				

Table 6.

Ten most abundant hydrocarbons measured in NOAA/NCAR aircraft samples, that would also be detected by auto-GC, ranked by concentration in ppbC

	ethane	propane	Iso-pentane	n-butane	Iso-butane	ethene	toluene	n-pentane	Trans-2-butene	n-hexane	propene	xylene	2-methyl pentane	acetylene	isoprene	benzene
Aircraft	1	2	4	5	3	6		7			8				9	10

Aircraft data collected during the Texas Air Quality Study can also be used to examine the mix of hydrocarbon concentrations. As shown in Figure 12 and Table 6, the most abundant hydrocarbon species detected by the NOAA/NCAR Electra, are generally consistent with the ground measurements (note that Figure 12 is reported as ppbv, while the convention for reporting the ground concentrations is ppbC). The same alkenes and alkanes dominate the measurements. Some differences are apparent, but most are readily reconciled. The presence of chlorinated compounds and oxygenated compounds in the NCAR/NOAA data and their absence in the 1993 COAST data are due to differences in analytical methods. The presence of isoprene in the NOAA/NCAR data and its absence among the commonly detected species at the ground sites is likely due to differences in sampling locations. Along with these differences due to methodologies, however, there also appear to be some real differences in the hydrocarbon composition. In particular, aromatic species appear to be detected at higher concentrations at the ground sites than in the NOAA/NCAR aircraft samples.

One method that can be used to quantitatively assess the differences in concentrations of aromatic species in the ground and aircraft samples is to examine the ratios of the concentrations to a relatively inert species, detected at high concentration, such as ethane. For example, the ratios of average ethene to average ethane concentrations are similar for the aircraft samples and the ground samples. For the aircraft, the ratio of the average concentrations is approximately 0.35 (Figure 12), while for the ground samples, the ratio of the average concentrations for the summer of 2000 is approximately 0.3 (see Figure 13). This suggests that the ethene concentrations detected by the aircraft and at the ground sites were consistent. In contrast, the ratio of average concentration of toluene (ppbC) to average concentration of ethane (ppbC) for the summer of 2000 at the ground sites was 0.25-0.4 (Figure 13). A similar ratio for the NOAA/NCAR aircraft would give a concentration for toluene comparable to that observed for n-pentane (see Figure 12).

The differences in average aromatic concentrations observed at ground sites and by the NOAA/NCAR aircraft may be explained by data collected by the DoE G-1 aircraft and the Baylor twin otter aircraft (Daum, et al., 2002). In many samples collected by the G-1 aircraft that were associated with high ozone productivities, the primary contributors to instantaneous hydrocarbon reactivity were alkenes, as observed in the NOAA/NCAR data. However, on some flights, very high concentrations of aromatics and alkanes were observed. In fact, the maximum concentration of toluene observed by the G-1 aircraft (>200 ppbv) was higher than any of the alkene concentrations observed in the high reactivity plumes. This suggests that the average aromatic concentrations observed at the ground sites are consistent with aircraft data, but that extreme values of aromatic concentrations may be strongly influencing average concentrations. In addition, data collected by the Baylor twin otter aircraft, shown in Figure 14, show that in some of the industrial plumes with high reactivity, aromatics and alkanes made significant contributions to the reactivity (as weighted by the hydroxyl radical reactivity).

Figure 12.

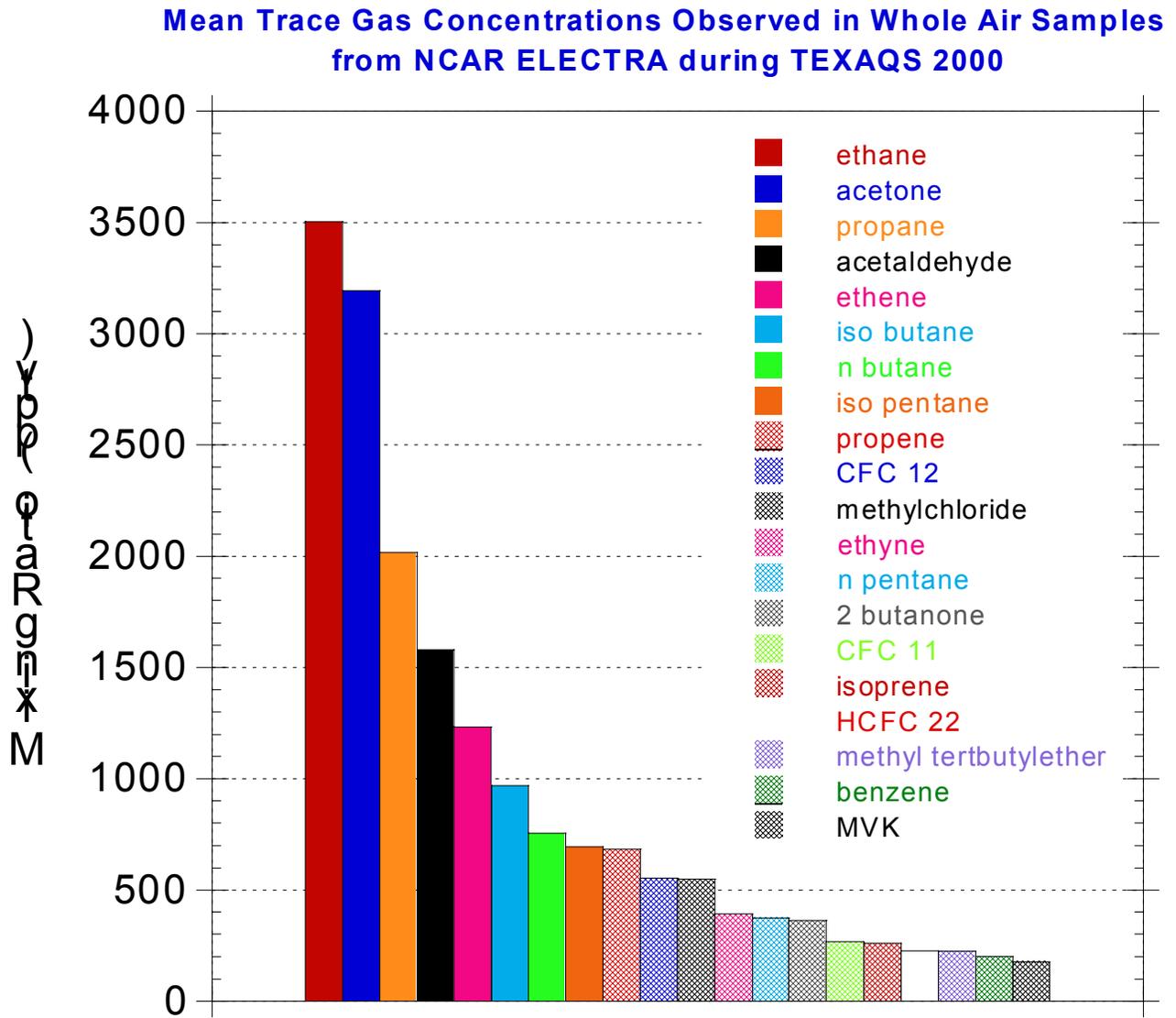


Figure 13. Average hydrocarbon concentrations observed at Clinton during the summer of 2000 (Main, et al., 2001).

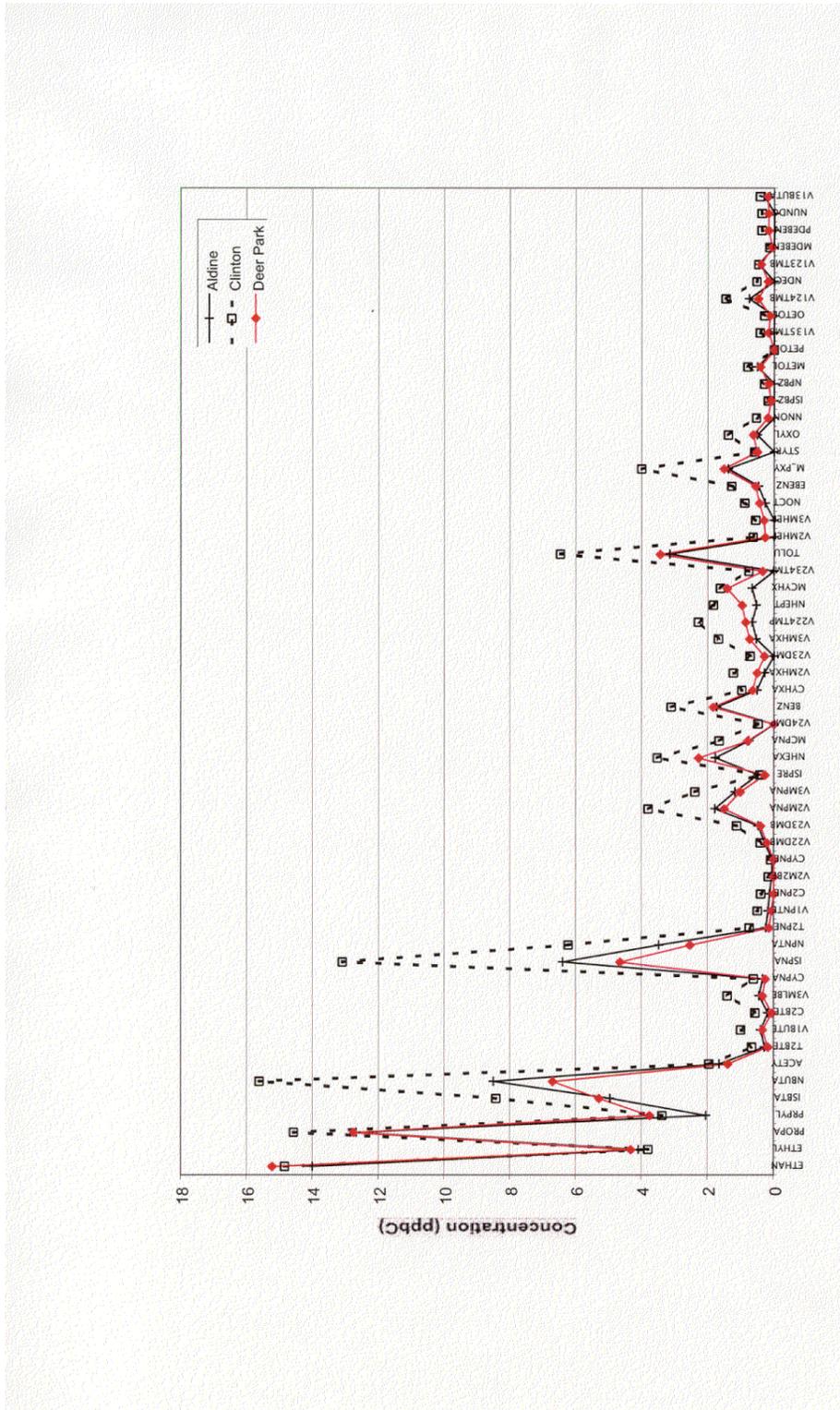
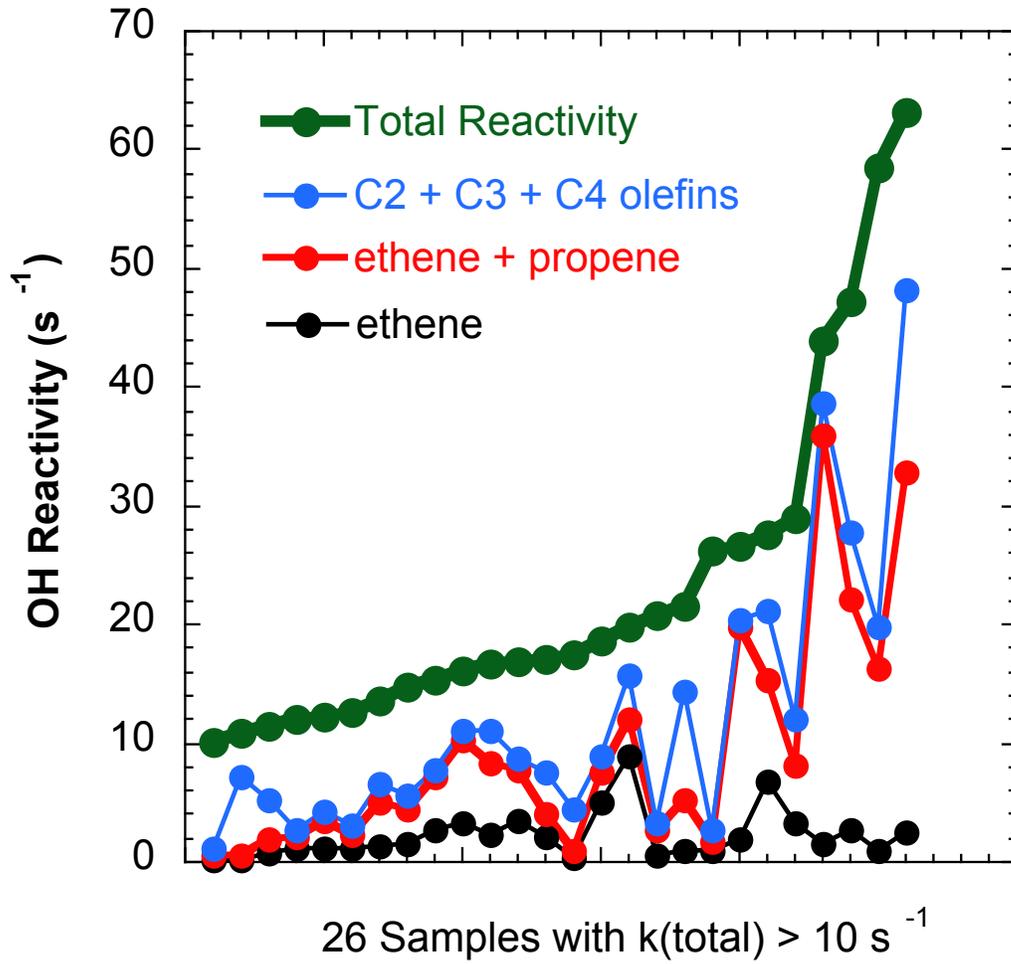
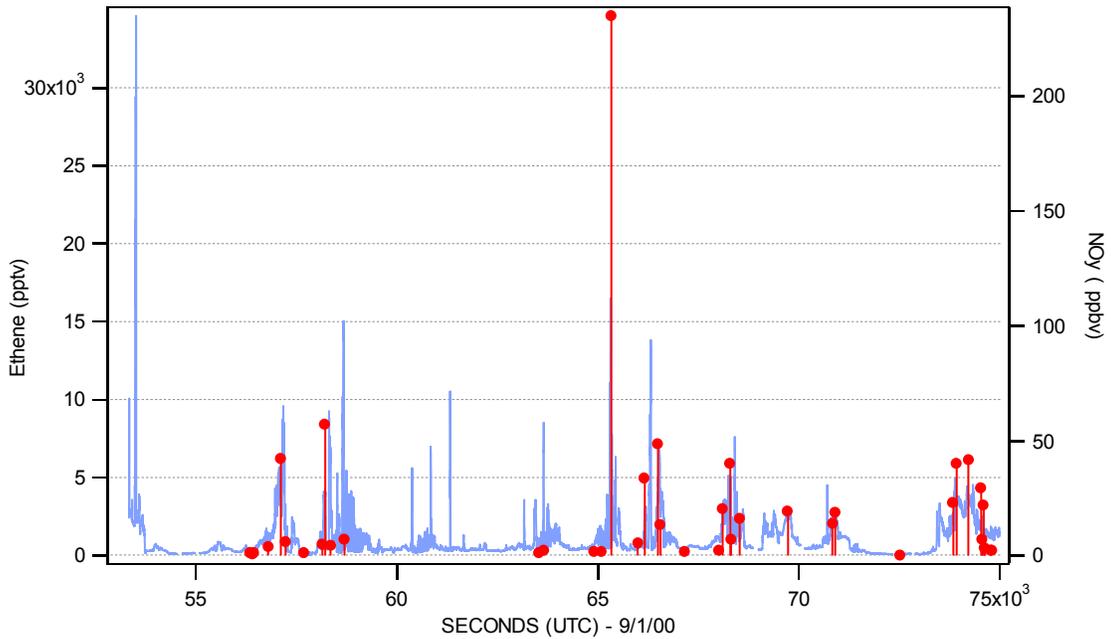


Figure 14. Contributions of hydrocarbon classes to the overall hydrocarbon reactivity (as weighted by hydroxyl radical reactivity) in highly reactive industrial plumes sampled by the Baylor twin otter aircraft



This general phenomenon, of very high concentrations of hydrocarbons in isolated regions, was observed by aircraft at multiple times during the Texas Air Quality Study and in follow-up measurements in 2001. Assuming that these isolated regions of elevated concentrations represent plumes, the plumes can be described as very narrow and are generally confined to industrial source regions. This is shown in Figure 15, which shows the concentration of ethene observed by the NOAA/NCAR Electra on a flight conducted on 9/01/00. Ethene concentrations were generally below 10 ppb, except for one sample, which was in excess of 30 ppb. Concentration measured a few minutes before the high concentration were only about 1 ppb. Since the aircraft flies at 100 m/s, this suggests that this ethene plume was narrow.

Figure 15. Ethene concentrations (dots) observed during the NOAA/NCAR Electra flight of 9/01/00 indicate the presence of a narrow plume of ethene. The aircraft flies at a velocity of approximately 100 m/s, so 100 seconds represents a distance of 10 km.



Similar, but more spatially resolved, data were collected in 2001 by an aircraft operated by Baylor University. The Baylor University twin otter aircraft was equipped with a chemiluminescence monitor that could measure olefins continuously. The instrument was calibrated with propene and would respond to propene, 1,3 butadiene, isoprene and had a moderate response to ethene and other olefins. Continuous measurements of NO_y , ozone, CO and SO_2 were also collected. Samples were collected with canisters for more detailed analysis of NMHC. The flights were made near several chemical plants in the HG area at an elevation of 1000 feet.

The data collected by the Baylor aircraft both confirmed and refined the measurements made during the Texas Air Quality Study. Data confirming the results of the Texas Air Quality Study are shown in Figure 16 and show the co-existence high concentrations of olefins and NO_x in industrial plumes.

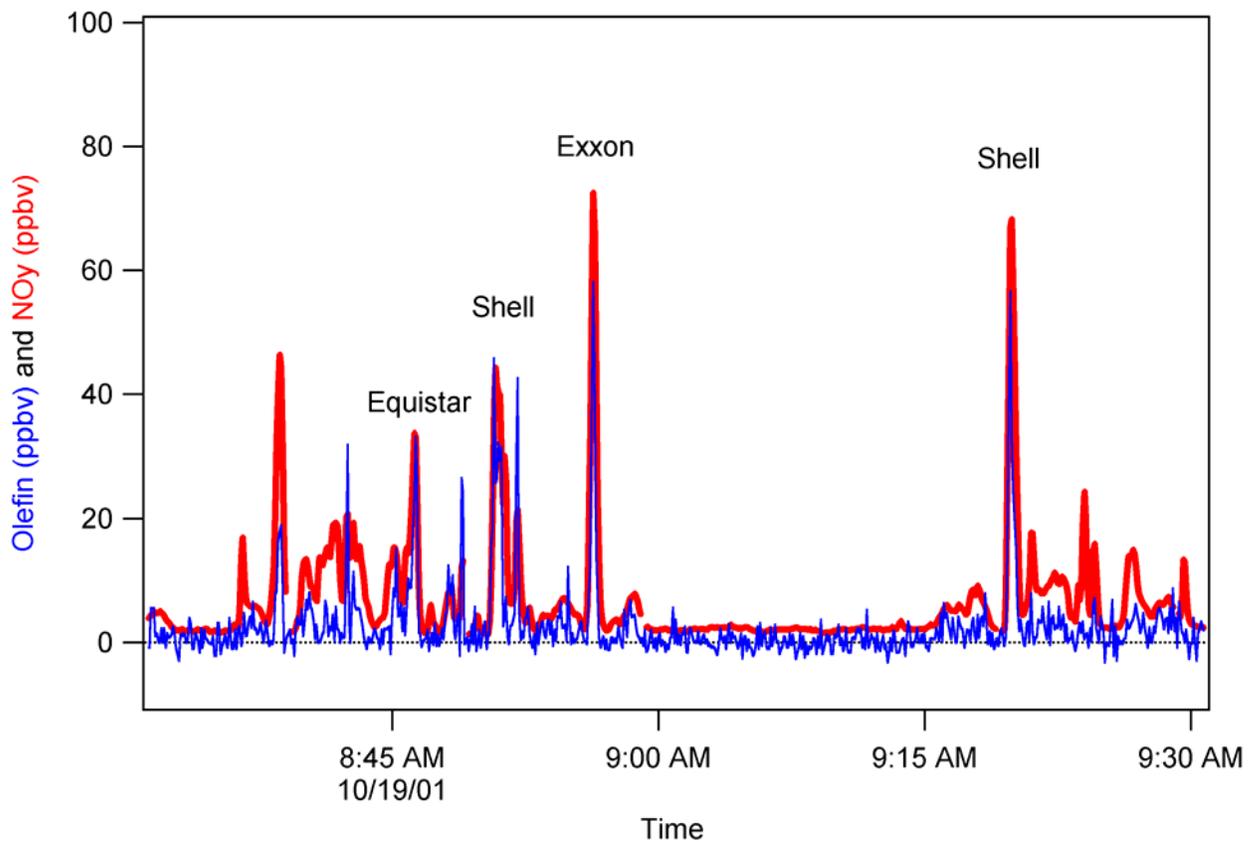


Figure 16 Data from Baylor aircraft showing industrial plumes with high concentrations of both NO_y and olefins (as detected using a chemiluminescent monitor).

However, some data collected by the Baylor aircraft show that plumes can have complex spatial structure. Figure 17 is an example of a time series from a portion of the flight made on the afternoon of October 29, 2001. At about 4:31 a plume was found that had elevated levels of NO_y , but no olefins were measured. Later, at 4:40 a plume was located that had concentrations of olefins that were about twice as high as the concentrations of NO_y . At 4:44 a plume was located that had elevated levels of olefins but not NO_y . At 4:50 a plume was found that had very high levels of olefins, but no significant NO_y was found.

Figure 17. Time series from a portion of the Baylor University twin otter flight made in the afternoon of October 29, 2001.

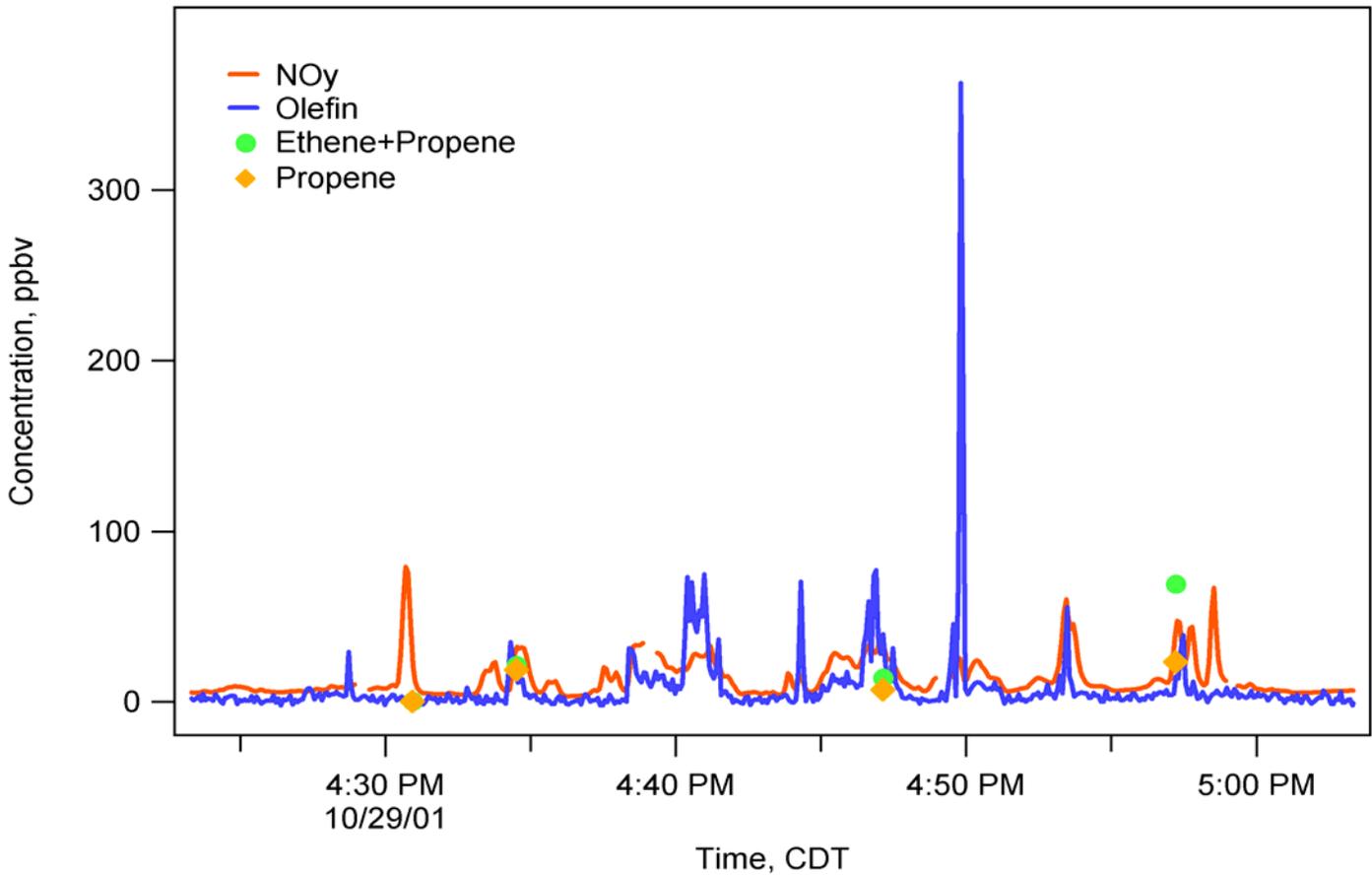
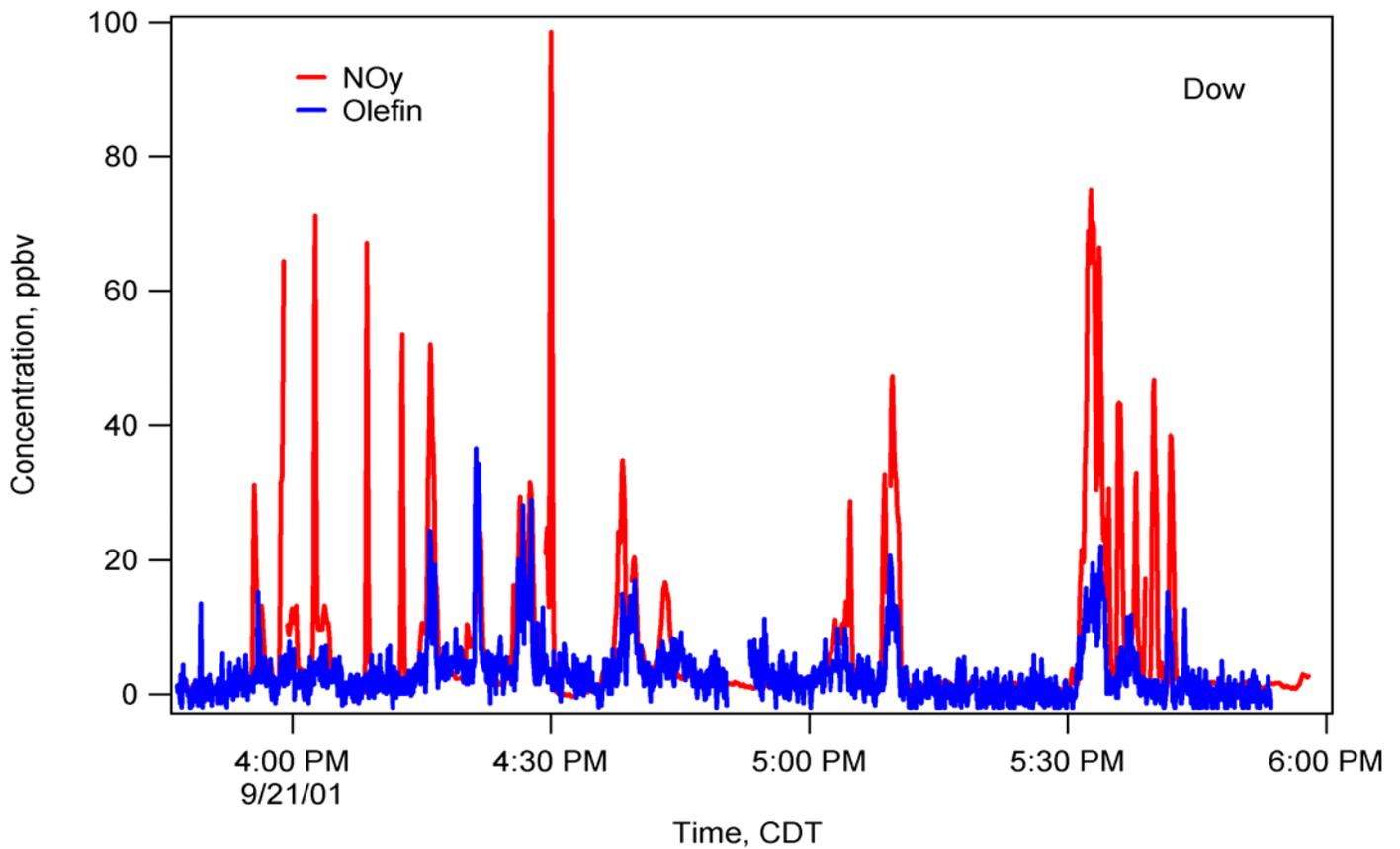


Figure 18 is a time series from a portion of the Baylor University twin otter flight made on the afternoon of October 21, 2001 in the vicinity of Dow Chemical plant in Freeport. A number of plumes were found that had elevated levels of NO_y , but no concentrations of olefins. There were multiple plumes found between 4:15 and 4:30 that had elevated levels of both NO_y and olefins. Additional plumes were located that had elevated levels of both NO_y and olefins and some plumes were located that had elevated levels of only NO_y .

Figure 18. Time series from a portion of the Baylor University twin otter flight made in the afternoon of October 21, 2001.



Figures 16, 17 and 18 show aircraft data indicating the presence of regions of high concentrations of NMOC and/or NO_y . Evidence of sporadic episodes of very high concentrations of individual hydrocarbons is also present in ground observations. Figures 19a, 19b and 19c (Main, et al, 2001) report concentrations of ethylene as a function of time of day at the Clinton, Deer Park and Aldine monitoring sites for 2000. Similar data are available for benzene, toluene, 1,3 butadiene, propane, i-pentane, isoprene and total xylenes. Figures 19a, 19b and 19c indicate that the median ethylene hourly concentration is less than about 10 ppb for all hours and that 75 percent of the concentrations fall in the range of below 20 ppb. However, there are a number of hours when ethylene concentrations are significantly greater than 20 ppb. At Clinton and Deer Park there are a number of hourly concentrations greater than 50 ppb and some approach 300 ppb.

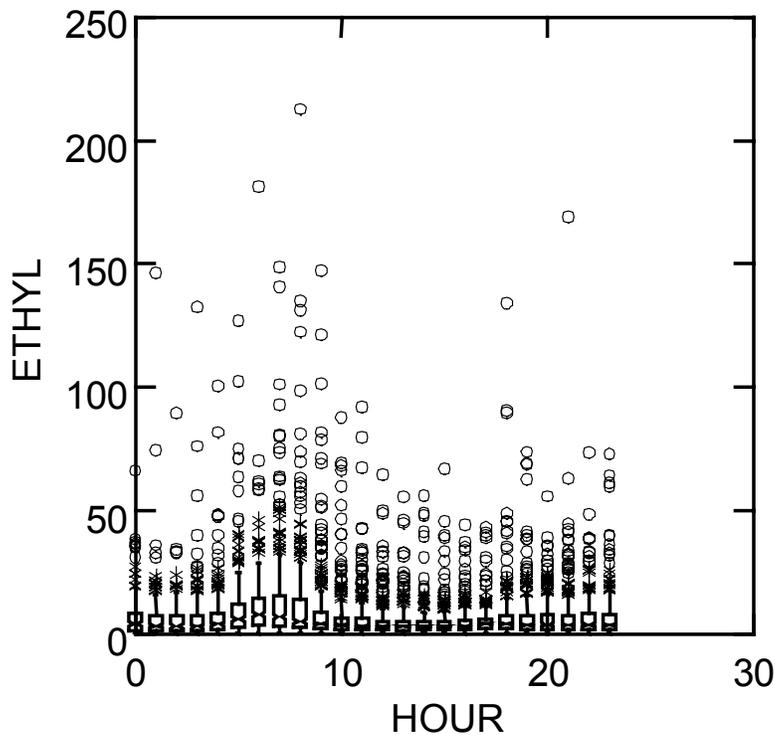


Figure 19a. Notched box plots of ethene concentrations (ppbC) by time of day in 2000 at the Clinton monitoring site. (See appendix for a description of the nomenclature used in Figures 18a, b and c)(Main, et al, 2001).

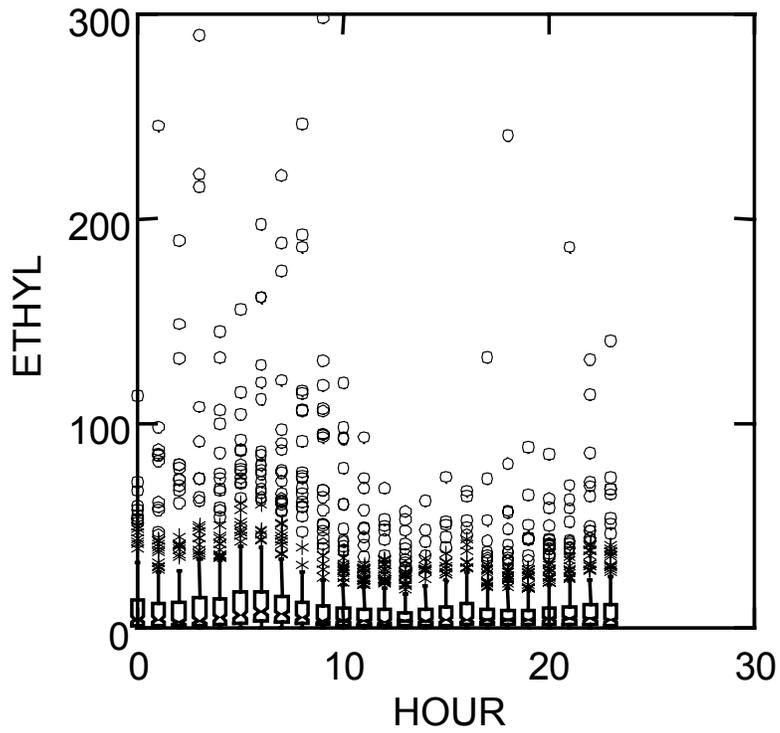


Figure 19b. Notched box plots of ethene concentrations (ppbC) by time of day in 2000 at the Deer Park monitoring site (Main, et al, 2001).

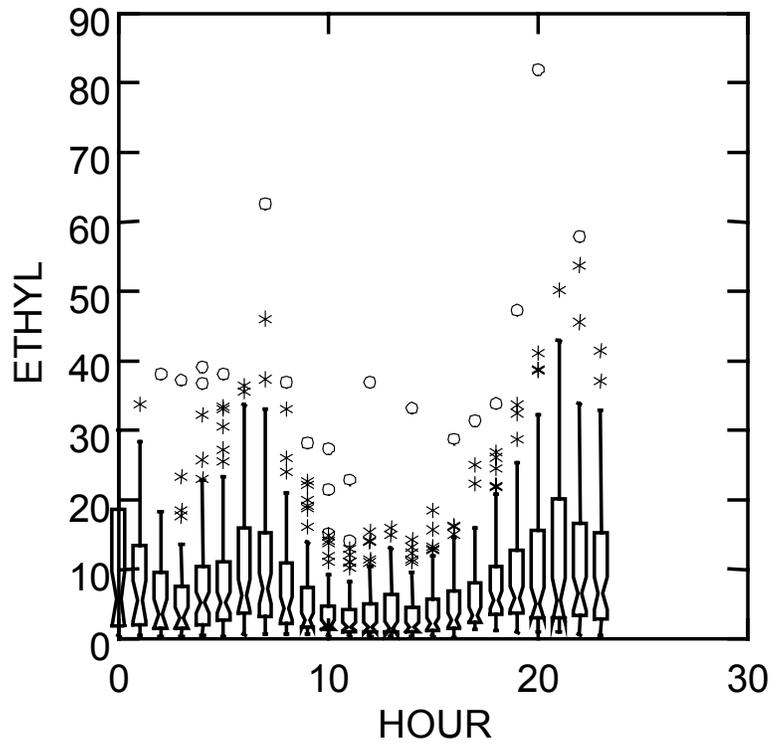


Figure 19c. Notched box plots of Ethene concentrations (ppbC) by time of day in 2000 at the Aldine monitoring site (Main, et al, 2001)

These data showing elevated hydrocarbon concentrations are not typical for U.S. cities. A quantitative comparison (Kleinman, et al., 2002) is shown in Figure 20, which compares the contributions to hydrocarbon reactivity in 5 cities.

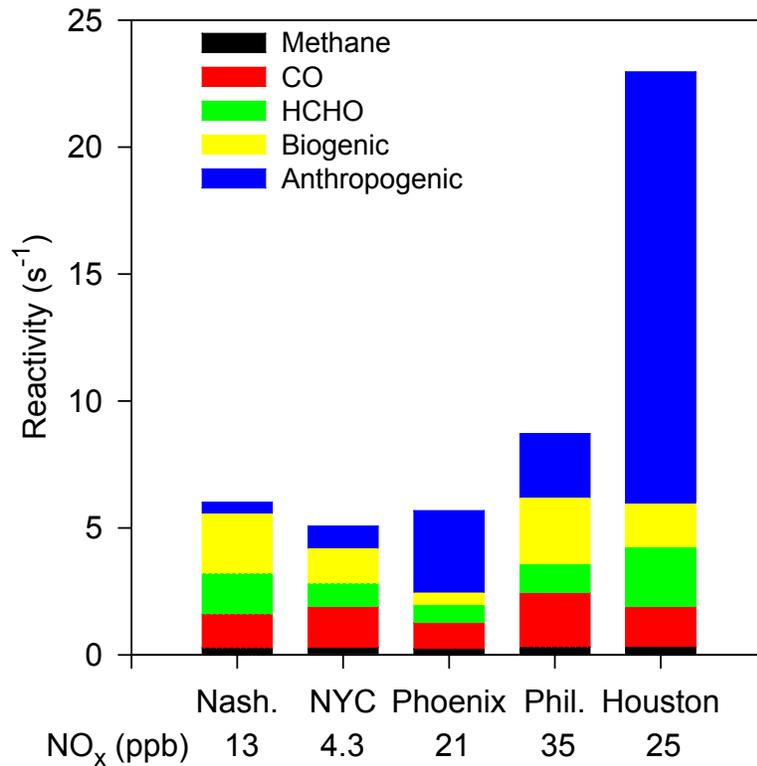


Figure 20. VOC reactivity for 5 cities, averaged over a set of samples with ozone formation rate equal or above the 90th percentile values. One Houston and one Phoenix VOC sample have been removed as outliers with biogenic reactivity (primarily from terpenes) an order of magnitude greater than the 2nd highest value. NO_x concentration is averaged over near-source samples as defined by Kleinman, et al. (2002)

The data presented to this point have focused primarily on absolute concentrations. While the absolute concentrations of hydrocarbons observed in the HG area are clearly higher than observed in other areas, the hydrocarbon measurements alone are not sufficient to evaluate the accuracy of the magnitude of hydrocarbon emissions in the inventory.

The two approaches commonly used to evaluate the accuracy of emission estimates are to (1) employ photochemical models to relate emission estimates to observed concentrations and (2) to examine ratios of NMOC concentrations to NO_x or NO_y concentrations. Both of these approaches have been employed and yield similar results.

Airborne measurements of the concentrations of hydrocarbons and NO_x have been compared to inventory data. Ratios of measured concentrations of propene to measurements of NO_x and measured concentrations of ethene to measurements of NO_x (all measured by aircraft in apparently well mixed plumes) have values of about 1. For sources at Chocolate Bayou, Freeport and Sweeny ratios of alkenes to NO_x using data from the TNRCC point source inventory are 0.3, 0.1 and 0.2 respectively (T. Ryerson et al, 2001). If the emissions of NO_x are correctly characterized, then this would indicate that the emissions for these hydrocarbons have been significantly under estimated at these locations.

Similar NMOC/ NO_x ratios, although with greater variability, have been reported at ground sites. Main et al. (2002) report median values of olefin to NO_x ratios ranging from 0.03 to 0.32, with maximum values generally below 2. These values are generally higher than the ratio of olefins to NO_x in the point source inventory, which has a median value of about 0.03.

Regional photochemical modeling, reported by the TCEQ and Jeffries, indicates reasonable agreement between aircraft observations of light olefin concentrations and model predictions, if the inventory for large point sources of olefins is adjusted so that olefins emissions are set equal NO_x emissions. This represents an increase of olefin emissions by a factor of approximately 6, at large point sources of olefin emissions.

To summarize, aircraft and ground measurements lead to the following findings:

NMOC/ NO_x ratios observed by aircraft in industrial plumes, and at ground monitoring stations, are higher than values observed in other urban areas. NMOC concentrations observed in industrial plumes in Houston are substantially higher than concentrations observed in other urban areas, while observed NO_x concentrations are more typical of other urban areas with significant NO_x point sources.

Observations made by aircraft suggest that plumes from petrochemical facilities are heterogeneous, with NO_x rich regions, NMOC rich regions, and regions rich in both NMOC and NO_x . In addition, data on NMOC/ NO_x ratios, taken over multiple years at ground monitoring stations in industrial source dominated areas, show

substantial temporal variability. Because of this spatial and temporal heterogeneity, individual measurements of NMOC/NO_x ratios must be viewed with caution.

A limited number of measurements made by aircraft downwind of isolated petrochemical facilities suggest that NO_x emission inventories are reasonably accurate, while NMOC emission inventories are underestimated.

The average composition of NMOC in Houston has remained relatively constant for a decade or more. While the average composition of NMOC is well established, the composition of NMOC in individual plumes is variable.

Ground observations, taken over a period of several years, and other data, suggest that emissions exhibit significant temporal variability. The implication of this finding is that NMOC/NO_x ratios will be variable, and individual plumes may have very different ozone formation potentials at different times.

In order to resolve differences between ambient observations and emission inventories, two strategies are being employed. One strategy, commonly referred to as “bottom-up”, is focussing on evaluating the accuracy and completeness of the emission estimates for individual sources. The other strategy is commonly referred to as “top-down”, which focuses on comparisons between ambient observations and emission inventories.

These approaches are synergistic. A top-down approach relies on ground-up estimates of emissions in source regions to evaluate the ambient data. The ground-up estimates rely on the top-down evaluations to assess whether all sources are being captured in the inventory.

Preliminary work on ground-up and top-down inventories from industrial sources indicate that (Chinkin, 2002) emissions from industrial sources of VOC submitted to TCEQ have been calculated using the methods approved by TCEQ and EPA. This suggests that inaccuracies in the emission inventory are likely to be from sources that are missing from the inventory, rather than sources that are estimated incorrectly (although emission estimation methods in some categories can certainly be improved). In addition, the fact that the composition of the inventory is consistent with the average composition observed by monitors suggests that missing sources must be ubiquitous. Finally, the temporal variability of the NMOC ambient observations (relatively frequent observations of very high concentrations) suggests that many of the events are episodic in nature (such as flares, cooling tower leaks and large fugitive leaks from equipment and process vents). These observations, together with the ground-up analyses suggest that

Underestimates of fugitive emissions, emissions from flares and emissions from cooling towers are expected to be the most likely causes of differences between observed NMOC/NO_x ratios and NMOC/NO_x ratios in the inventories.

Projects are underway that will enhance the development of emissions from flares, fugitive leaks, and cooling towers. These and other activities designed to improve emission estimates are described in the next section of this report; the discussion is organized by source category, and covers point, area, on-road, non-road and biogenic sources. For each inventory category, the following key questions will be addressed:

1. Are the magnitudes of the emissions correct?
2. Are the emissions adequately and correctly speciated?
3. Are the emissions correctly distributed spatially and is the spatial resolution sufficient for accurately predicting ozone formation?
4. Are the emissions correctly distributed temporally and is the temporal resolution sufficient for accurately predicting ozone formation?

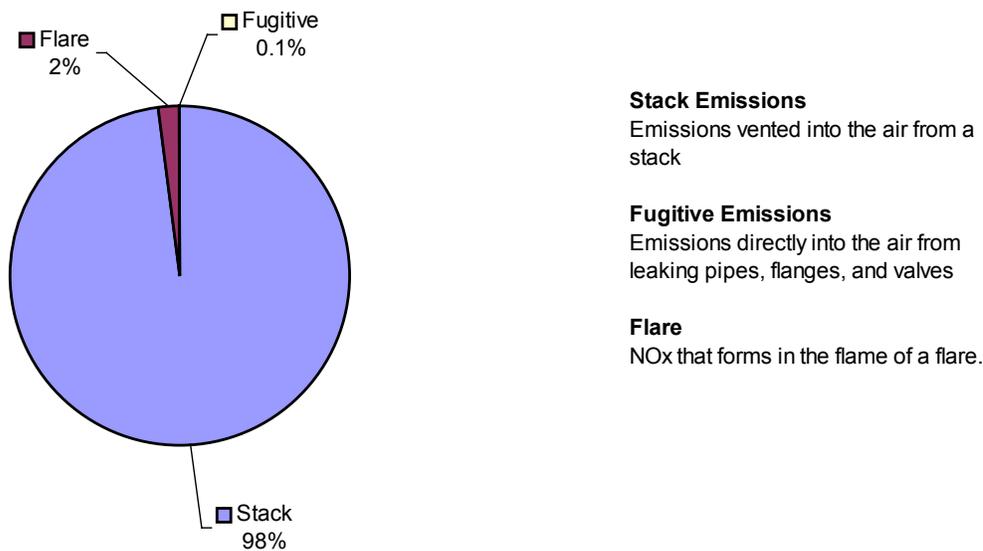
POINT SOURCES

NO_x Point Sources

Emissions Magnitude

As shown in Tables 1 and 2, point sources are a major source of NO_x emissions in the Houston Galveston area. The division of NO_x point source emissions into stack, flare and fugitive sources is shown in Figure 21 (Neece, 2002). Note that 98% of the emissions are from stacks.

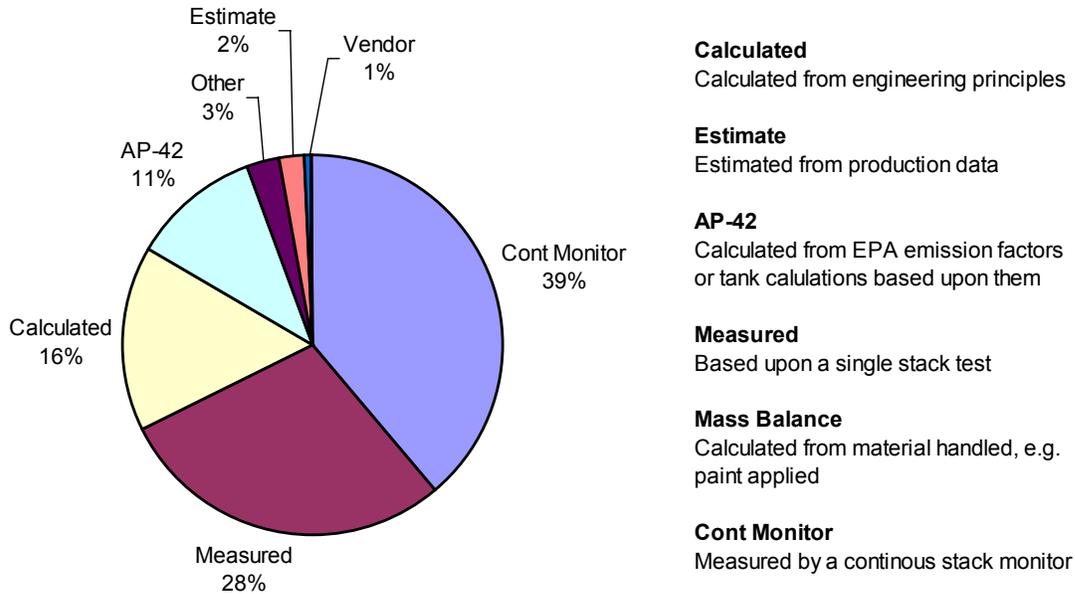
2000 HG NO_x emissions by point type



Dataset: oracle.psd_b_alloc_2000_v10

Figure 21. Distribution of 2000 NO_x Point Source emissions in the Houston/Galveston nonattainment area, Neece, 2002.

2000 HG emissions by NOx EI method



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Figure 22. Methods used to calculate 2000 NO_x Point Source emissions in the Houston/Galveston nonattainment area, Neece, 2002.

The methods used to determine the magnitude of NO_x point source emissions are shown in Figure 22 (Neece, 2002). These methods are described below.

Continuous monitoring directly or indirectly measures emissions from the stack. Permitted emitters of significant quantities of NO_x from stacks are required to continuously measure NO_x emissions. Direct measurements are performed with continuous emissions monitors (CEM). If it is impractical to use a CEM, continuous NO_x emissions are estimated with a predictive emissions monitor (PEM). The PEM is a mathematical model that predicts NO_x emissions based on continuously measured process data (such as furnace temperatures) that influence NO_x emissions. CEM and PEM have the potential for providing accurate estimates of NO_x emissions and these methods were used for determining 39 percent of the NO_x point source emissions in the inventory (Neece, 2002).

The term “measured” is used for methods that use stack testing to determine emissions. These methods were used for calculating 28 percent of the NO_x point source emissions in the inventory (Neece, 2002). Stack testing is normally performed when the plant is well tuned and is running at permitted capacity, so it may not accurately replicate other types of plant operations.

The term “calculated” is used for methods that determine emissions from engineering calculations based on the design of the plant. For example, such methods use specific design characteristics and fuel composition to determine the emissions from a boiler or heater. These calculations are based on source specific information used in permit review. These methods were used for 16 percent of the NO_x point source emissions in the inventory (Neece, 2002)

The term “estimate” was used for methods that calculate emissions based on the actual capacity for which the plant was operated. For example, emissions based on permit allowable capacity are multiplied by ratios of plant actual operating capacity to permit allowable capacity to estimate actual emissions. Estimates were used for about 2 percent of the NO_x point source emissions in the inventory (Neece, 2002).

AP-42 emissions factors (EPA, 2002d) were used for 11 percent of the NO_x point source emissions (Neece, 2002). This process uses an average emission factor for generic types and sizes of sources. There are many potential sources of uncertainty in these measurements, including the effect of humidity. It is well established that humidity level influences NO_s emissions (emissions decrease as humidity increases), and most AP-42 emission factors are based on measurements made in environments with lower humidity than Houston.

To summarize, the data shown in Figures 21 and 22 show that most point source NO_x emissions in the current inventory are from stacks and that CEM/PEM or stack measurement data are available for about half of the emissions documented in the inventory. It should be noted that the existence of PEM data does not ensure that continuous data have been used to develop the emission inventories.

Since approximately half of the point source NO_x emissions documented in the current inventory are not directly measured, there may be a significant amount of uncertainty in the determination of the quantity of the NO_x emissions. At this time it is not possible to establish an error bound on these emissions, but since the error bounds could be significant, it would not be appropriate to a priori assume that the NO_x point source emissions are well known.

Speciation

The composition of the NO_x emissions in the HG area is generally believed to be typical of combustion sources nationally. This is accurate except for a few highly specialized processes (e.g., emissions from the manufacture of adipic acid, which can involve significant emissions of N₂O, and individual source profiles for these processes have

been developed). These unusual situations have been reviewed by the TNRCC and have been addressed in the inventories.

The EPA default speciation of NO_x is 90 percent as NO and 10 percent as NO₂. Some control methods will decrease the total NO_x emissions, but may increase the percentage of NO₂ emitted. (Note for this and all subsequent sections on NO_x speciation that inventories report all NO_x as NO₂; it is in the photochemical modeling that the emissions are speciated)

Spatial resolution

Spatial resolution of ground position is not an issue for NO_x point source emissions since these emissions come from well defined stacks at specific locations. As suggested by the data in Figures 17 and 18, it is important that each emission source be correctly located. TNRCC has performed extensive review of coordinates for each source (TNRCC, 1998).

While ground position is well known, the height at which point source NO_x emissions are effectively released may not be well known. Emissions of NO_x from point sources are often at elevated temperatures, and therefore subject to plume rise. The methods used for determining plume rise should be evaluated.

Temporal resolution

Because of the use of CEMs and PEMs on most significant point sources of NO_x, continuous data on emission rates are available and are generally believed to be very accurate. This can provide valuable information on the diurnal variation of NO_x point source emissions. Especially useful is the information on power plants that may cycle load and therefore vary their emissions during the day. This is especially true of plants that are run for only a few hours for meeting power demand during peak use periods. TNRCC uses hourly emissions from continuous monitoring at all Acid Rain Program facilities (Large Electric Generating Units, EGUs).

Continuous monitoring data have been collected at some non-EGU sites, and these data have generally been incorporated into the total emissions reported in the inventories. However, the detailed temporal distributions from the CEM/PEM data, from non-EGU sites, have not been routinely incorporated into emission inventories for photochemical modeling.

The following activities would improve the accuracy of the point source NO_x emission inventory; they are categorized into operational and scientific issues.

Key Science Issues

1. *Develop an approach that can establish an error bound on the quantity of NO_x emissions in the HG area.*

2. *Develop approaches for modeling effective plume rise in stacks, especially those with non-conventional discharge (e.g., rainhats, horizontal discharge, severe downwash)*

NMOC Point Sources

Emissions Magnitude

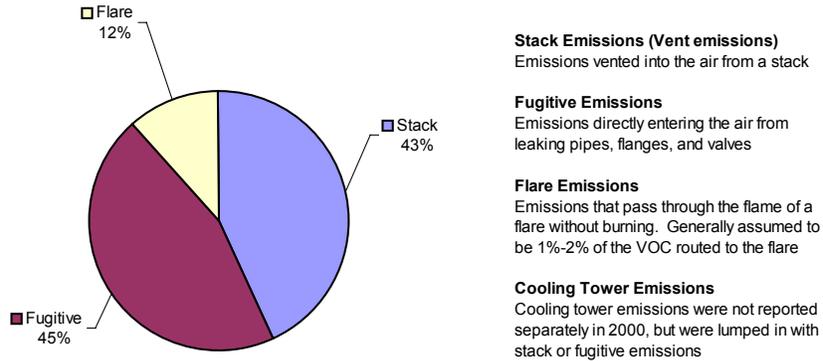
Figure 23 shows the distribution of NMOC point source emissions for the 2000 EI and Figure 24 shows the distribution of methods used to determine NMOC point source emissions for the 2000 EI (Neece, 2002).

A notable feature of Figure 23 is the relatively high fraction of emissions that are due to fugitive emissions due to equipment leaks (45%). The magnitude of these emissions can be highly uncertain. The fugitive emissions defined in Figure 23 are normally estimated by determining the number of valves, flanges and other sources of emissions and using emissions factors. The magnitude of these emission estimates can be a strong function of the specific approach used in estimating the emissions (for a detailed discussion, see Allen and Rosselot, 1997).

There are at least three tiers of analysis that can be used in estimating fugitive emissions. The first approach, requiring the least information, involves counting the total number of valves, flanges, fittings, and other potential sources of leaks. The number of each component type is multiplied by an average emission factor. This average emission factor is based on the assumption that a certain percentage of components (as much as 10%) will leak and that the emission rates for leaking and non-leaking components are known, based on statistical studies done at similar facilities. This approach is often used because the large number of potential leak sources (over 80,000 in a typical, moderately sized refinery) make testing the components a time consuming task.

Because of the uncertainties associated with assuming a certain fraction of components leak, a leak/no-leak analysis of fugitive emission is frequently performed in regions with air quality regulations. In this approach, organic vapor analyzers are used, in regularly scheduled inspections, to determine if a component is leaking. If the organic concentration in vapors surrounding the component exceeds a specified value, the component is classified as leaking. Separate emission factors for leaking and non-leaking components are used to calculate emissions, and the total emission rate is dominated by the contributions from leaking components. For example, the emission rate for leaking refinery valves in gas service is 400 times greater than the emission rate for non-leaking valves (Allen and Rosselot, 1997). If a facility has less leaking components than the facilities used to determine the average emission factors, or if a facility repairs its leaks sooner than the facilities used to determine average emission factors, then using a leak/no-leak approach will lead to lower estimates of fugitive emissions.

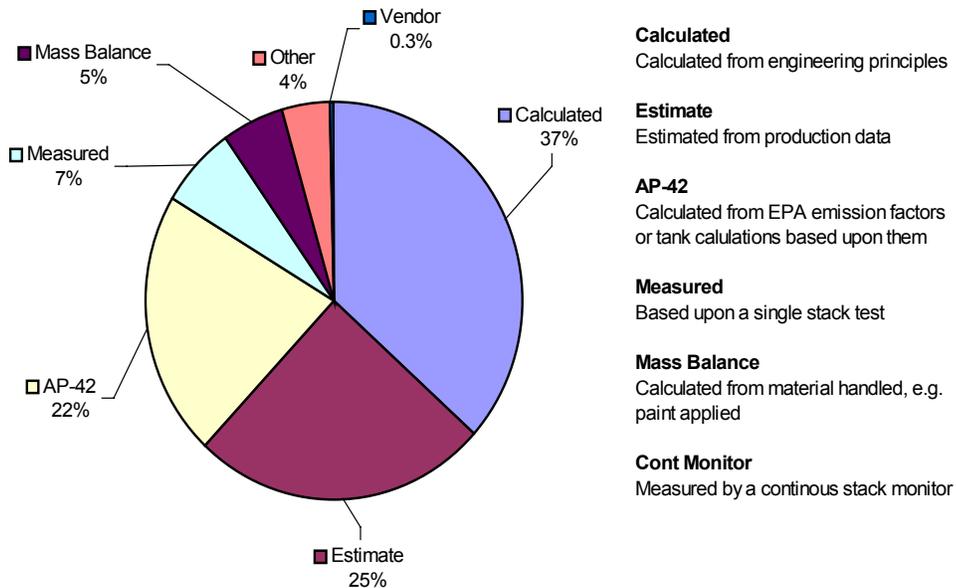
2000 HG VOC emissions by point type



Dataset: oracle.psd_b_alloc_2000_v10

Figure 23. Distribution of 2000 VOC Point Source emissions in the Houston/Galveston nonattainment area, Neece, 2002.

2000 HG emissions by VOC EI method



Dataset: oracle.psd_b_alloc_2000_v10

Figure 24. Methods used to calculate 2000 VOC Point Source emissions in the Houston/Galveston nonattainment area, Neece, 2002. (Calculated emissions include use of programs such as EPA's TANK program (EPA2001e)).

The leak/no-leak approach classifies components into only two categories – leaking and non-leaking. Clearly, however, some leaks will be more severe than others, so a third level of analysis of fugitive emissions correlates emission rate with the concentrations detected by organic vapor analyzers (for a detailed description, see Allen and Rosselot, 1997). An emission rate is estimated for each component and these are summed for the entire facility.

The difference in predictions between these various estimation methods can be extreme, if a facility has operating practices that are either significantly better or significantly worse than the norm. For example, in studies of acrolein manufacturing facilities, Berglund, et al. (1989) found that the three methods could yield estimates of emissions that differed by a factor of 300. Using average emission factors, estimated fugitive emissions for an acrolein facility were 268,000 lb/yr. In contrast, estimates based on organic vapor analyses correlated with emissions yielded fugitive emissions of 900 lb/yr. These facilities may be extreme examples, because the toxicity of acrolein mandates that leaks in an acrolein facility be immediately identified and repaired. Nevertheless, this example provides an indication of the uncertainties inherent in fugitive emissions.

Several studies were conducted during the summer of 2002 to evaluate the uncertainties of fugitive emissions in the HG area. Imaging measurement methods were used to screen for equipment leaks to determine if the numbers of leaking components have been accurately determined in past inventories. The results suggest that some components that are not routinely tested in fugitive emission detection programs, such as sight glasses, can be sources of emissions. Further, it was found that detecting leaks from insulated components could be difficult, because the emissions may exit the insulation at a point far from the leak. Finally, leaks were imaged that were large enough to impinge on nearby components, leading in some cases to misidentification of the leaking component. These preliminary findings suggest that imaging systems hold great promise for identifying and reducing fugitive emissions. Further development of these imaging methods is underway.

Sometimes emissions from cooling towers are considered as fugitive emissions. Emissions from cooling towers occur when other process devices (especially heat exchangers) that use cooling water develop leaks that allow hydrocarbons to enter the cooling water. When this water is processed through the cooling tower and the water evaporates, the hydrocarbons evaporate along with the water, generating emissions. In studies currently being planned, measurements of hydrocarbon concentrations in cooling water at inlet and return locations will be made. Emissions estimates from this sampling will be compared to results from use of AP-42 estimation methods. This process should either provide a greater level of confidence in the current emissions estimates or yield more accurate estimates.

Moving beyond fugitive emissions, additional assumptions and uncertainties are inherent in the NMOC point source emission inventory. An assumption embedded in many of the NMOC point source emission estimates is rule effectiveness. Rule effectiveness

acknowledges that all pollution control equipment does not function at design effectiveness at all times. This approach has been used for a number of years (since the 1980's); the EPA default value for effectiveness is 80%. Reported emissions are increased by the rule effectiveness factor. The rule effectiveness adjustment always increases emissions by a significant amount. TCEQ has developed its own procedure for estimating rule effectiveness (Durrenberger, 1993).

The rule effectiveness adjustment is applied for modeling, but not for the data in the emissions inventory. Rule effectiveness was not used in the August 1993 modeling EI (or EIs based on the August 1993 data) for sources that reported hourly emissions for August 1993. Rule effectiveness is not applied to NO_x emissions, since at present all of these control measures tend to be permanent (burner controls) and not subject to failure.

Non-routine, or upset, start-up, shutdown, and maintenance releases may also constitute a major uncertainty in the magnitude of emissions. As a part of the Texas Air Quality Study, the TCEQ collected special inventory data by surveying the largest sources of NO_x and VOC emissions in the Houston/Galveston and Beaumont/Port Arthur areas. Sources emitting at least 250 tons per year of NMOC or 1000 tons per year of NO_x were requested to participate in the survey. The data collected were specific operating conditions, upsets, start-ups, shutdowns and speciation of VOC emissions during the time period of the study. This information was then used to develop episode-day and hour-specific point source emissions for the EI used for photochemical modeling. Since most of the factors that are considered for rule effectiveness were directly accounted for in the survey, no rule effectiveness adjustments were applied to the EI used for modeling. More information on the specific details of this inventory may be found in TNRCC, 2002.

Speciation

TNRCC requests that facilities report hydrocarbon emissions by species. For the 1999 inventory, approximately half of the total mass of hydrocarbon emissions is reported by species. For the 2000 inventory, this percentage of speciated emissions had increased to 70%. For each source type, TNRCC develops an average default emissions profile based on the speciated emissions that are reported.

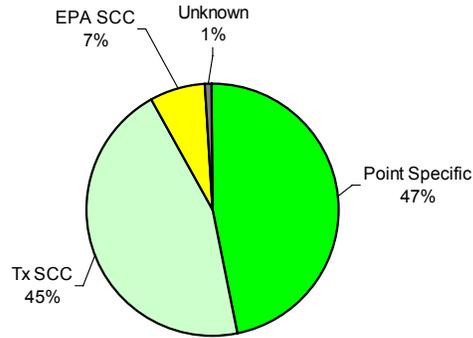
In cases when a facility does not provide speciated emissions, it will provide emissions for total VOC emitted for the year. VOC is defined by regulation and eliminates a number of hydrocarbons that are defined by regulation as not being very reactive. In the TNRCC reporting procedures (TNRCC document RG-360), unreactive emissions are reported separately, and are not inventoried. Ethane is used as the benchmark for determining if a compound is not very reactive and a list of unreactive VOCs is provided in Appendix B.

If total VOC is reported, then TNRCC uses the average default speciation profile for the source type to determine the emissions for each species. If total emissions are reported as VOC, then emissions of the compounds not considered as a VOC will not be quantified for that facility.

Figure 25 shows the distribution of methods used to determine speciation for NMOC point sources for the 2000 EI (Neece, 2001). Figure 26 shows the distribution of species in the 2000 EI (Neece, 2002).

2000 HG emissions by VOC profile type

% of HG VOC Emissions



Point Specific Profile
Industry supplied complete data for each specific point.

TX SCC Average
Industry data for all points in Texas with that particular SCC were averaged together.

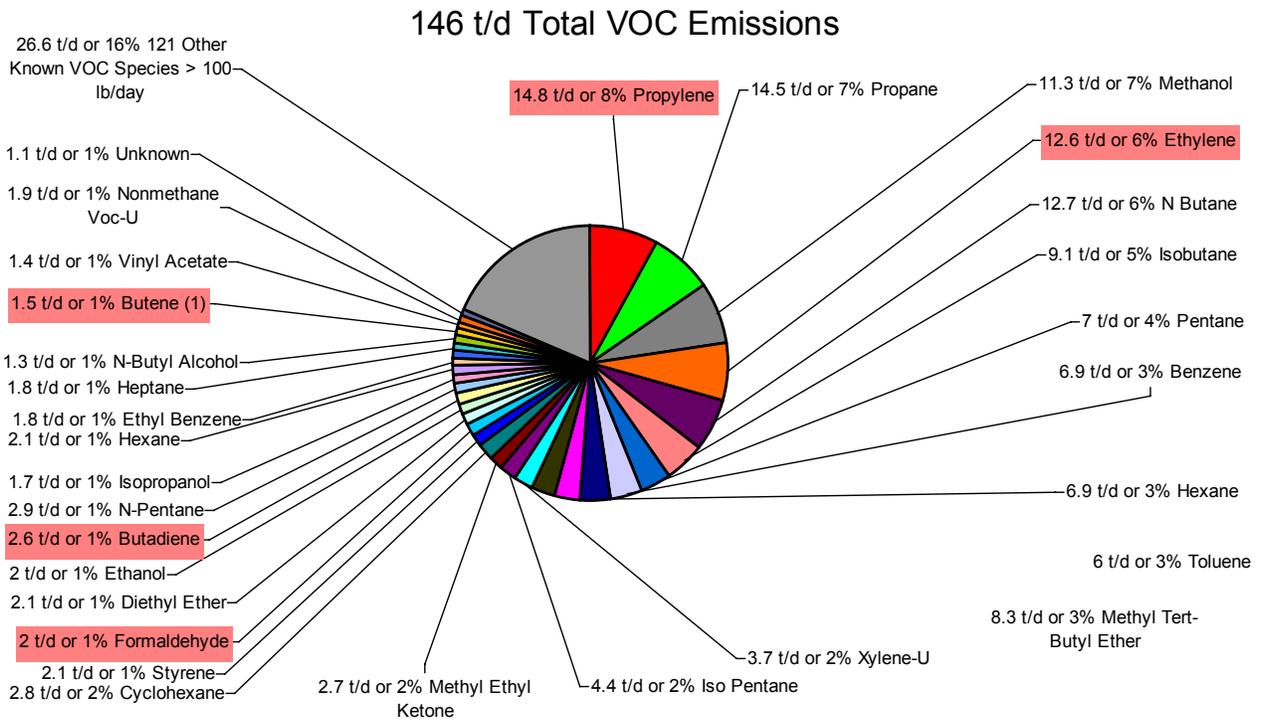
EPA SCC Default
EPA defaults profiles based upon SCC code.

Unknown
SCC code without any known VOC profile.

eset: oracle.psd_b_alloc_2000_v10

Figure 25. Methods used to calculate 2000 VOC Point Source speciated emissions in the Houston/Galveston nonattainment area, Neece, 2002.

Estimated 2000 HG 8 County VOC Speciation



Dataset: oracle.psd_b_alloc_2000_v10

Highly reactive VOC specie

Figure 26. 2000 VOC Point Source speciated emissions in the Houston/Galveston nonattainment area, Neece, 2002.

Spatial resolution

For NMOC point sources these issues are the same as discussed under NO_x point sources, although plume rise may not be as important an issue for most categories of VOC emissions, such as fugitives.

Temporal resolution

There are a number of chemical processes that are episodic in nature. The basic emissions inventory is reported as annual emissions and ozone season daily emissions. The 24-hour average of emissions may be significantly different from the maximum hourly emission rate and the profile of hourly emissions. Examples of episodic emissions include batch processing, loading and unloading activities, cooling tower emissions, wastewater and process vent emissions. Episodic releases may also include events that are non-routine in nature, such as releases due to start-ups, shut-downs and non-routine maintenance activities. To provide an indication of the potential significance of daily and hourly variations of emissions from annual averages, consider non-routine releases.

Table 7 shows a small subset of upset reports that were submitted to TNRCC during the time period of TexAQS. For routine reporting purposes an “upset” is associated with plant startup, plant shutdown or an unplanned emission event. The magnitude of the event that triggers an upset report depends on the compound, but for many hydrocarbons, the reporting threshold is 5,000 pounds. For the emissions inventory for TexAQS smaller reporting levels were used in some cases in an attempt to quantify all significant emission sources during the study. Shown in Table 7 are the upset emissions, the duration of the upset and the ratio of upset emissions to the routine emissions, integrated over the period of the upset. The data indicate that an upset can result in emissions from a facility increasing by a factor of 1000 or more. These releases can range in length from under an hour to more than a week, and the temporal pattern of emissions in the longer events is not recorded in the upset reports.

Table 7. Selected sample of upset reports for the summer of 2000.

<u>Chemical</u>	Release (lbs.)	Duration (hr)	Upset release to routine release ratio
Butadiene	1225	7	34
Cumene	6300	27.5	
Ethylene	5280	1	242
Ethylene	26700	14	87
Ethylene	25000	59	19
Ethylene	5000	19	5
Ethylene	20000	744	6
Isobutylene	581	0.5	
Propylene	1235	0.22	3036
Propylene	2680	4.3	52
Propylene	1295	3	38
Propylene	7108	48	25

These results clearly indicate that annual average, or even daily average data, may not provide accurate information. Data and analyses presented in the Accelerated Science Evaluation report on Photochemical Air Quality Modeling demonstrate that these hourly variations in emissions can result in dramatic changes in ozone productivities. Further, the large increases that these upsets would create in the ratio of NMOC to NO_x emissions is consistent with the observational data collected during the Texas Air Quality Study, that found much higher ratios of NMOC to NO_x in industrial point source plumes than reported in the inventory.

It is not clear, however, that upsets alone can explain the inconsistencies in NMOC to NO_x ratios in the emissions inventory and the observational data sets. High NMOC/NO_x ratios were observed consistently throughout the TexAQS period, which is inconsistent with upsets that are sporadic events.

The magnitude of non-routine releases, and reconciling the observed NMOC to NO_x ratios with the emission inventory is among the most significant issues that must be addressed in the Accelerated Science Evaluation.

Additional issues: Flares

According to Figure 23, flares emissions account for 12 percent of the NMOC emissions. Flare emissions are quantified based on destruction efficiency – usually 98-99 percent, but this may not be the destruction efficiency for all compounds in the flare feed stream, and the combustion process in the flare may generate products of incomplete combustion.

Additional uncertainties are due to potential variations in the combustion efficiency from the design value of 98-99%, the lack of data on the temporal distribution of the emissions, and the lack of data on operating parameters (waste gas flow rate, steam or air assist rate, and other parameters). Figure 27 provides an indication of the extent of temporal variability in flare emissions.

In addition to uncertainties in the magnitude and temporal distribution of flare emissions, the (vertical) location is not well understood. Vertical location depends on flare plume rise. (Tan, 1967; TNRCC, 1999)

Studies are ongoing that may provide better data for determination of flare emissions. Various methods for monitoring waste gas flow rate and measuring composition in flare headers will be evaluated. This information will provide specific data that can be used to determine the spatial and temporal extent, magnitude and speciation of emissions from flare operations.

Flare Flow
(May 2001 - April 2002)

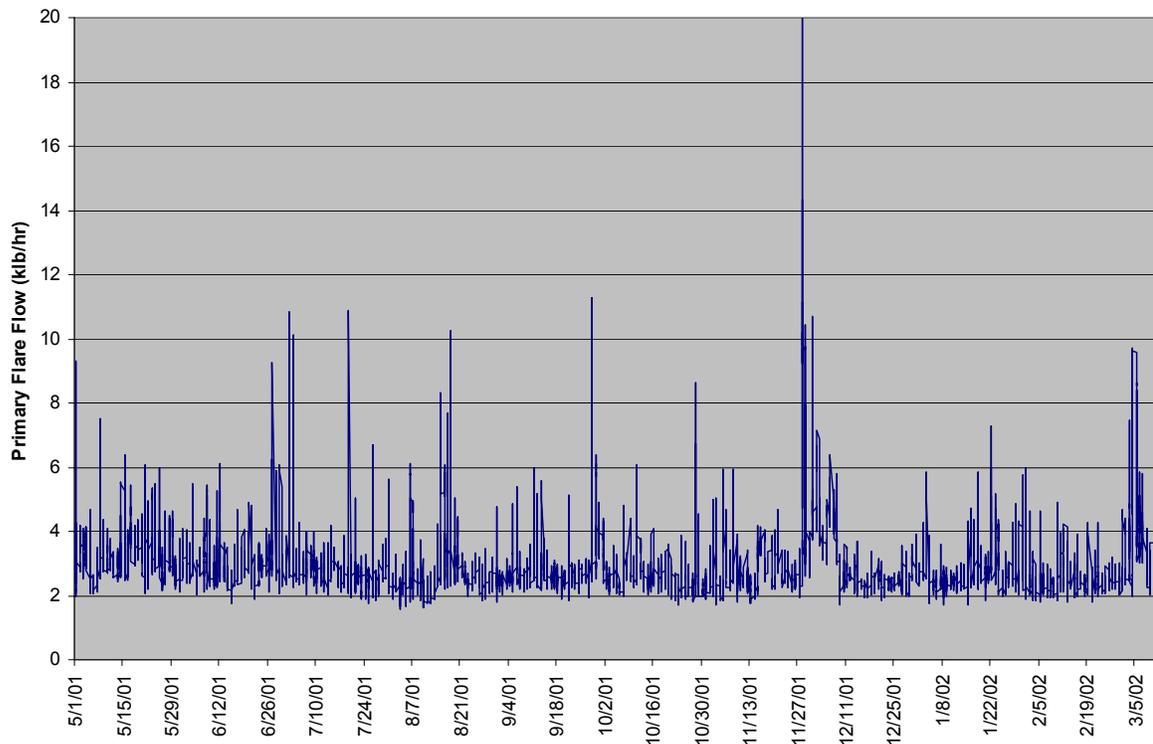


Figure 27. Example of Emission Variability. Plot shows daily flow of VOC to a flare head at an industrial facility. Such data are not generally available to an emissions model, rather, only the total annual flow (area under the curve) is used in the regulatory inventory. This area then is re-allocated as a daily average to the period the model is simulating (Tesche, 2002)

The following activities would improve the accuracy of the NMOC point source emission inventory:

Key Science Issues

3. *Observational data from both the Texas Air Quality Study and previous air quality studies have indicated that NMOC emissions are significantly underestimated. Further, the data from the Texas Air Quality indicate that industrial point sources are the most likely source of these underrepresented*

emissions. Thus, improvements in point source NMOC emission inventories should be aggressively pursued. The areas requiring the most attention are fugitives, flares, start-up/shut-down emissions and emissions from cooling towers and other water handling systems. On-going projects are addressing many of these issues.

- 4. Evaluate methods for obtaining data on the temporal distribution and magnitude of emissions from flares, cooling towers, wastewater units, equipment leaks and start-up/shut-down/maintenance activities. On-going projects are addressing many of these issues.*

AREA SOURCES

NO_x Area Sources

Emissions Magnitude

In general, area source emissions in the HG area have been refined with survey data, but this approach has not been used for all NO_x area sources since the total NO_x emissions from this category are relatively small. Area source NO_x emissions occur mainly from small combustion sources such as small industrial boilers and hot water heaters.

Speciation

The speciation of NO_x area sources is likely to be accurate.

Spatial resolution

The location of area source emissions should be examined by continuing to evaluate emission tile plots to insure that the emissions are not concentrated in areas that are not appropriate.

Temporal resolution

The emissions of area source NO_x are not believed to be significant, so temporal issues are not a major issue. However, to make sure that the distributions are reasonable, the temporal distribution of these emissions should continue to be reviewed with tile plots.

NMOC Area Sources

Emissions Magnitude

In the HG area NMOC area source emissions have been refined with survey data collected for the largest source categories (TNRCC, 1998). In some cases these data are five or more years old and may need to be updated to reflect current activities. Examples are: use and composition of solvents, use of architectural coatings (paint) and use of consumer products.

Spatial resolution

The spatial location of area source emissions should be examined by continuing to evaluate emission tile plots to insure that the emissions are not concentrated in areas that are not appropriate.

Temporal resolution

The temporal distribution of these emissions should continue to be reviewed with tile plots.

ON-ROAD MOBILE SOURCES

NO_x On-road Mobile Sources

On-road mobile source emissions are based on information from local travel demand models and MOBILE emission factors (Perkinson, 2000). Local travel demand models are used to determine speeds and vehicle miles traveled (VMT). VMT is adjusted with data from the HPMS. For the area covered with a travel demand model, the emissions calculations have been based on information on each specific link in the road system. Emission factors are determined from the mix of vehicle classes and model years, the speed and temperature.

Emissions Magnitude

For each link in the road system, emissions are determined by multiplying the emissions factor for the link by the VMT in link. Using monitoring data from the 1993 COAST study at Galleria, it was found that the monitored values of ratios of NMOC to NO_x were a factor of two or more times greater than those estimated in the emissions inventory for on-road mobile sources. (Figure 6, Korc, 1995; PAMS Data Analysis Workshop, 1996). Based on other similar comparisons around the country (National Research Council, 2000), it is likely that the NMOC mobile source emissions are significantly under estimated by the MOBILE model. A similar result was found for the Dallas/Fort Worth area (J. Jolly, 2000). During the TexAQS study, data were collected at a tunnel under the ship channel. These data were used to determine fuel based emission inventories. The results are shown in Table 8, which compares the emission factors developed for the Houston area to those estimated in other tunnel studies (McGaughey, et al., 2002).

The sampled fleets for most of these studies were comprised primarily of light-duty gasoline fueled vehicles. The data for the Fort McHenry and Tuscarora tunnels were analyzed to extract the light-duty and heavy-duty components. Note that all but one of these studies were performed at least five years prior to the Washburn tunnel study. Given the elapsed time, a newer vehicle fleet with improved emission controls might be expected to contribute to slightly lower emission factors. In fact, between 1994 and 1999, emissions of CO and NO_x in the Caldecott Tunnel decreased by 54% and 41%, respectively. In addition to turnover in the vehicle fleet, Kean et al. (1999) attribute this decrease to impacts of California phase 2 reformulated gasoline. For the Washburn Tunnel, the CO emission rate is comparable to that of the other studies, while a relatively lower NO_x emission rate was observed. Surprisingly, however, the NMOC emission rate for the Washburn Tunnel is among the highest of all NMOC emission factors reported in Table 8a. While these differences are important, they do not account for the very large excess of hydrocarbons observed in Houston, compared to other U.S. cities, shown in Figure 20.

Table 8a. Comparison of emission factors measured during representative tunnel studies. Adapted from Sawyer et al. (2000).

Tunnel	Roadway grade	Year sampled	CO (g/L)	NMOC (g/L)	NO_x (g/L)
Tuscarora, Pa ^a	Level	1992	48.1	2.89	3.85
Fort McHenry ^b (Baltimore, MD)	Uphill (+3.3%)/ Dnhill (-1.8%)	1992	55.5/47.4	4.88/5.03	7.77/5.55
Caldecott ^c (Oakland, CA)	+4.2%	1994	77.0	3.70	7.47
Callahan ^d (Boston, MA)	Uphill + Dnhill ^e	1995	45.1	4.51	9.32
Lincoln ^{de} (New York, NY)	Uphill + Dnhill ^e	1995	39.2	5.25	10.95
Deck Park ^{de} (Phoenix, AZ)	Level	1995	45.1	6.14	8.44
Sepulveda ^{de} (Los Angeles, CA)	Level	1995	56.2	5.25	7.33
Sherman Way ^{de} (Van Nuys, CA)	~Level	1995	91.0	6.81	7.55
Caldecott ^f (Oakland, CA)	+4.2%	1999	38.7	1.81	4.85
Washburn (Houston, TX)	Uphill + Dnhill +/- 6%	2000	55	6.9	6.7

^aPierson, et al. (1996)

^bPierson et al. (1996)

^cKirchstetter et al. (1996)

^dSagebiel et al. (1996)

^eGertler et al. (1997b) [Note: Data from Gertler et al. (1997b) for LD and HD vehicles combined. The HD contribution of NO_x is significant, especially in the Lincoln tunnel.

^fKean et al. (2000)

^gUnderwater tunnel; includes both downhill and uphill driving (grade ranges from -3.8% to +3.5%).

The emission factors developed using the tunnel data can also be used to assess the accuracy of the overall magnitude of the emission inventory for on-road sources. Harley (personal communication, 2002) estimated the emissions of VOCs, NO_x, and CO from gasoline vehicles, based on the tunnel emission factors. To use the tunnel emission factors (reported as g/L of gasoline consumed), an estimate of gasoline consumption is necessary. Harley used statewide data on gasoline sales and county data on vehicle miles traveled (VMT) to estimate gasoline consumption by county. He estimated gasoline consumption in Harris county and the 8-county non-attainment area by assuming that county fractions of VMT would be the same as county fractions of gasoline consumption. Harley then multiplied the gasoline consumption by the emission factor from the tunnel to obtain estimates of emissions from gasoline powered vehicles. The results are shown in Table 8b, and are compared to emission estimates obtained using two versions of the EPA MOBILE model.

Table 8b. Comparison of MOBILE 5b, MOBILE 6 and Fuel-based estimates for emissions from gasoline powered vehicles in the 8-county non-attainment area (tons/day)

<i>Pollutant</i>	<i>MOBILE 5b estimate</i>	<i>MOBILE 6 estimate</i>	<i>Fuel based estimate</i>
NO _x	212	148	132" 25
CO	1159	2065	1089" 145
NMOC	134	145	136" 17

The results suggest relatively good agreement between the latest generation MOBILE model (MOBILE 6) and the tunnel data for VOC and NO_x, but an underestimate of a factor of 2 for CO emissions. The apparent underestimate of CO emissions by MOBILE 6 is consistent with observations made by aircraft. CO concentrations observed by aircraft in freeway flyovers during the Texas Air Quality Study in 2000 were consistently lower than concentrations predicted in a photochemical model; agreement between model predictions and observed CO concentrations was much better in regions dominated by industrial CO emissions. These data suggest that the emission estimates generated by MOBILE 6 should be carefully evaluated.

Speciation

Speciation of mobile emissions of NO_x are likely to be accurate.

Spatial resolution

Travel demand models have been used to develop the spatial distribution of emissions over the modeling domain. Since on-road mobile emissions are calculated for each link in the road system, the location of these links is used to distribute these emissions over the modeling domain.

Temporal resolution

Diurnal patterns of emissions based on traffic surveys have been used to develop the temporal distribution of traffic densities used in the travel demand model. The on-road emissions are calculated hourly. Distribution of vehicle class is based on 24-hour averages. Data collected in the Washburn Tunnel (McGaughey, et al., 2002) suggest that this will overestimate the number of heavy duty trucks during the rush periods, and underestimate the number during the late evening and early morning hours.

The following activities would improve the accuracy of the on-road NO_x emission inventory:

Key Science Issues

5. *Compare the total estimated on-road emissions, using the fuel based emission factors developed in the Washburn Tunnel study to the total emissions based on vehicle miles traveled and distance based emission factors.*

NMOC On-road Sources

Only those issues not addressed in the section on NO_x on-road mobile emissions will be described here.

Emissions magnitude

Numerous studies performed throughout the United States suggest that the MOBILE emissions estimation software may significantly underestimate the magnitude of vehicular NMOC emissions (National Research Council, 2000). During the TexAQS study, data on vehicular emissions were collected in the Washburn Tunnel and these data suggest that the NMOC emissions from the Houston light duty fleet are slightly higher than national averages. These data are currently being used to assess the accuracy of the MOBILE emissions estimates with the latest versions of the model.

Speciation

NMOC species for on-road mobile emissions are developed based on national profiles. During the TexAQS study, data on exhaust emission, whole gasoline composition and gasoline vapor composition were collected (McGaughey, et al., 2002). These data have been incorporated into the latest inventory and modeling analyses.

NON-ROAD MOBILE SOURCES

NOx Non-road Mobile Sources

Emissions Magnitude

In 1991, non-road mobile source emissions were quantified by EPA for a number of ozone nonattainment counties (EPA, 1991). These emissions were based on default activity data that in some cases was found to be inaccurate. Since that study, EPA has released the NONROAD model that is designed to calculate non-road mobile emissions (U.S. EPA, 2001b). The model may be used with default data or specific survey data may be used. Non-road mobile emissions in the HG area have been calculated with default values except for categories that have survey data (TNRCC, 2000). An extensive survey was conducted for the Houston port equipment to determine emissions from these sources. Extensive survey data were collected for diesel construction equipment in the HG area and this information used to determine non-road mobile emissions from this source category (TNRCC,2000). Detailed data are available on queuing times for aircraft at some airports in the region and an extensive study of marine activity, including movements of specific vessels and their engine specifications, was conducted in the HG area (TNRCC, 2000). Survey data should be collected for any remaining, significant source categories for which surveys have not been conducted.

In addition to uncertainty in activity data, such as movement of marine vessels and queuing times for aircraft, there are many potential sources of uncertainty in emission factors, including the effect of humidity. It is well established that humidity level influences NO_s emissions (emissions decrease as humidity increases), and most non-road emission factors are based on measurements made in environments with lower humidity than Houston.

Speciation

Speciation of NOx emissions has been based on typical products of combustion.

Spatial resolution

The location of various non-road sources can vary significantly with time. For example large road construction projects will move from one area to another over time. Location of these activities can be determined when developing a historical emissions inventory for photochemical grid model base case development, but it is almost impossible to accurately predict locations for future year inventories. Emissions from commercial marine traffic have been based on traffic counts on waterway links. Emissions from aircraft have been based on landings and takeoff from the various airports in the area.

Temporal resolution

Temporal resolution of emissions is important since some proposed control strategies involve the time that construction equipment is operated. Tile plots should continue to be analyzed to determine if the temporal distribution appears to be appropriate.

Key Science Issues

6. *The sensitivity of non-road emission factors to humidity level should be examined. Observational data from both the Texas Air Quality Study and previous air quality*

NMOC Non-road Sources

See the section on NO_x non-road mobile emissions.

BIOGENIC SOURCES

NO_x Biogenic Sources

Biogenic NO_x emissions have been estimated with the GloBEIS model (ENVIRON, 2001). These emissions are small relative to other sources and will not be discussed in detail.

NMOC Biogenic Sources

Emissions Magnitude

As shown in Table 1, biogenic emissions of hydrocarbons dominate the emission inventory for NMOC in the Houston-Galveston area. Wiedinmyer et al. (2001a) have shown that similar high levels of biogenic NMOC emissions can be expected throughout the eastern half of the state. Because of the magnitude of these emissions, the TNRCC and its contractors have expended great effort over the past 5 years in improving biogenic emission estimates.

A number of detailed reviews of biogenic emissions have been performed in the past several years (for example, Guenther, et al., 2000) and these reviews describe in detail the dependence of biogenic emissions on land cover, leaf biomass densities, temperature and photosynthetically active radiation (PAR). Systematic efforts have been made to collect the data necessary to estimate biogenic emissions in Texas. Detailed data on vegetative land covers have been developed for the entire state (Wiedinmyer, 1999, 2000, 2001a). PAR has been estimated based on data retrieved from satellites, and ground temperatures have been estimated based on interpolations of surface temperatures or the predictions of meteorological models (Vizuet, et al., 2001). These input data have then been used in models that combine leaf emission factors with models of the behavior of the tree canopy to predict emissions. In Texas the GloBEIS (Global Biosphere Emissions and Interactions System) model has been used (ENVIRON, 2001). Nevertheless, despite all of this effort, significant uncertainties may still remain in the inventory.

The magnitude of biogenic emissions predictions depends strongly on the input parameters and on the emission factors and canopy models built into GloBEIS. For example, because species specific emission factors (emissions per unit leaf biomass) can vary over three orders of magnitude, emissions predictions are very sensitive to land cover distributions. Because emissions can change exponentially with temperature, small temperature changes or even changes in the interpolation schemes used in estimating temperatures can cause changes in emissions of 25-50% (Vizuet, et al., 2001).

Because biogenic emissions are so sensitive to these parameters, any biogenic emission inventory will have significant uncertainty associated with it, and field verification of emissions is desirable. In Texas, only limited field studies of emission fluxes have been performed. Wiedinmyer, et al. (2001b) report the results of a field study conducted in

Central Texas (in a region 100-250 km northwest of Houston) in which biogenic emissions and their reaction products were measured. The data suggest that emission rates predicted by the current inventories available for Texas are correct to within a factor of about 2.

Data on aloft concentrations of biogenic hydrocarbon concentrations were obtained by aircraft during the summer of 2000, and these measurements can also be compared to the biogenic emission estimates. Since parallel ground measurements of biogenic hydrocarbon concentrations are not available, emission fluxes cannot be directly estimated based on observational data, however, the concentrations of isoprene observed by the aircraft can be compared to concentrations predicted by photochemical models at the aircraft observation altitude. These comparisons indicate that the current biogenic inventory accurately represents both the magnitude and the geographical distribution of emission fluxes.

An additional complicating factor is that emissions may depend on water availability. In the case of the TexAQS period, the area was very dry compared to normal conditions and temperatures were very high. On many days, temperatures reached historical highs for that date. The biogenic emissions factors may not accurately represent changes in plant metabolism caused by prolonged and extremely hot and dry conditions.

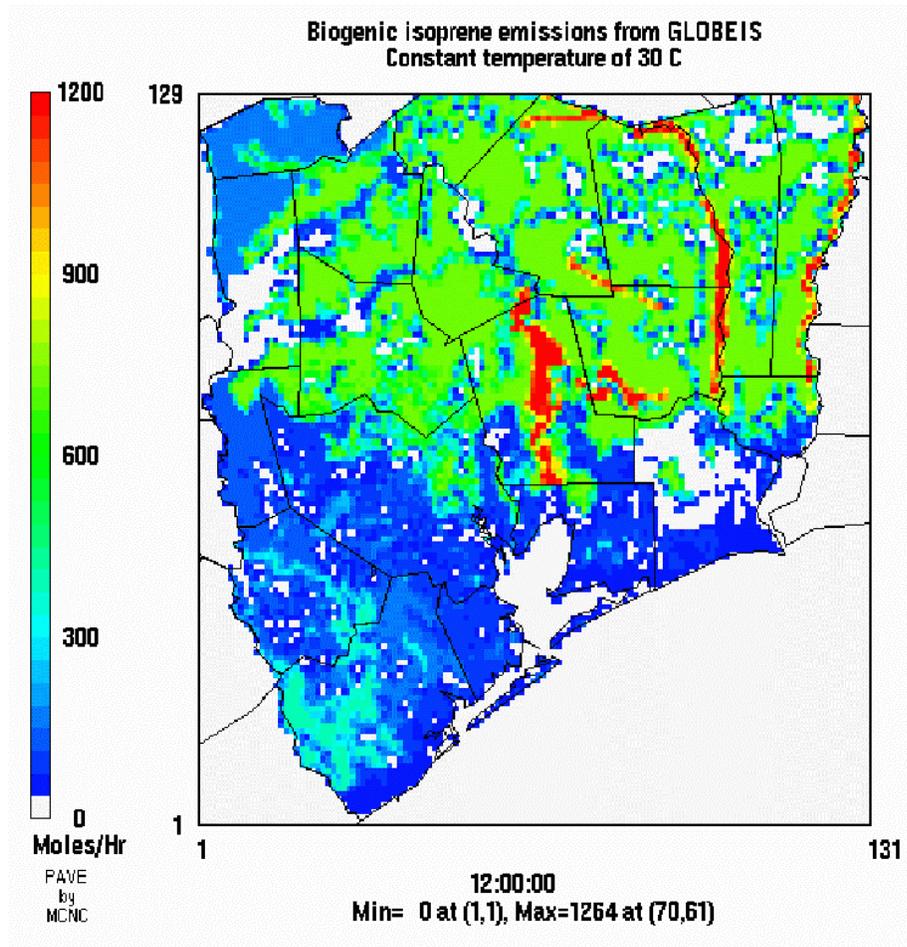
Speciation

Biogenic emissions in Texas are dominated by isoprene, a five carbon diolefin that is very reactive with hydroxyl radical and has a high ozone incremental reactivity (see report on Atmospheric Chemistry; Allen and Price, 2001). Isoprene is emitted primarily by broadleaf tree species. Oaks are the most significant contributor in Texas (Wiedinmyer, et al., 2000, 2001a). Other species are emitted by conifers. Species emitted by conifers include monoterpenes such as α - and β -pinene and sesquiterpenes. These 10 and 16 carbon compounds may be significant in the formation of fine particles. Additional non-terpenoid emissions occur, including large quantities of methanol, but many of these emission rates are not well characterized, particularly for vegetation found in Texas.

Spatial resolution

The spatial distribution of biogenic emissions is influenced by spatial distributions of land cover, PAR and temperature. These parameters can change over relatively short distances. Shown in Figure 28 is the spatial distribution of emissions predicted for southeast Texas if temperature is constant at 30°C and skies are cloudless. Even without variations in temperature or PAR, significant variability in biogenic emissions are possible.

Figure 28. Spatial distribution of isoprene emissions in southeast Texas for a constant temperature of 30°C, based on the land use/land cover data of Wiedinmyer (2001a) and the GloBEIS model (ENVIRON, 2001).



Temporal resolution

Temporal distribution is based on variations in PAR and temperature. This aspect is believed to be accurate in the emissions inventories that have been recently developed.

The following activities would improve the accuracy of the NMOC biogenic emission inventory:

Key Science Issues

7. *Assess the accuracy of the spatial distribution of biogenic emissions by comparing predicted emission fluxes to measurements made by aircraft.*
8. *Assess the response of biogenic emissions to heat and drought stress*
9. *Assess methods for accurately estimating fluxes of photosynthetically active radiation and surface temperature, which are key inputs to biogenic emission estimation models.*
10. *Compare the predictions of the various models available for predicting biogenic emissions, using a consistent set of input data*

Ozone Precursors other than NMOC and NO_x: Chlorine

Recent work indicates that anthropogenic emissions of molecular chlorine and/or hypochlorous acid (which are precursors for atomic chlorine) may have a significant effect on ozone formation in the HG area (Tanaka et al, 2000, 2001). A critical element for the integration of the chlorine chemistry into air quality planning and management is the development of an emissions inventory that can be used for photochemical grid model analysis. The University of Texas has developed a preliminary emission inventory for atomic chlorine precursors (Chang, et al., 2001). The preliminary analysis suggests that several sources may be important. These include volatilization from cooling towers (where chlorine is used as a biocide), volatilization from swimming pools (where chlorine is used as a disinfecting agent), point sources and molecular chlorine released as a result of the reactions of chloride in sea salt.

The following activities would improve the accuracy of the chlorine emission inventory:

Key Science Issues

11. *Analyze chlorine emissions from point sources to insure accuracy of the quantity and diurnal pattern.*
12. *Review cooling towers and swimming pools to determine their locations, the quantity of emissions, the chemical composition of emissions, and the diurnal pattern of emissions.*
13. *Compare the spatial distribution and temporal profiles of the concentrations of chlorine reaction products predicted in photochemical models (based on the emission inventory) to ambient observations; collect additional ambient data if necessary*

Summary of scientific issues and conclusions

In summary, the observational data collected during the Texas Air Quality Study suggest that some components of current emission inventories are incorrect or incomplete. Specifically, measurements of the ratios of non-methane organic compound concentrations to the concentrations of oxides of nitrogen (NMOC/NO_x), especially in industrial plumes, is much higher than documented by inventoried emissions. While high values of NMOC/NO_x have also been observed in previous field studies, the composition of NMOC observed in the Texas Air Quality Study of 2000 appears somewhat different than the compositions reported in previous studies.

Accounting for the dramatic difference between observed concentrations and inventoried emissions is an on-going task, yet there is a need to make immediate policy decisions based on current inventory and observational data. The current body of evidence suggests that the major uncertainties in the inventory are associated with the point source emissions, and that the NMOC emissions from these sources are underestimated. Therefore, a prudent strategy for making immediate policy decisions would be to impute a point source inventory based on available observational evidence. Concurrently, every effort possible should be made to improve existing inventories.

In support of that effort, this document has summarized scientific issues associated with emission uncertainties. A total of 13 scientific issues have been identified. These are listed below.

Key Science Issues

- 1. Develop an approach that can establish an error bound on the quantity of NO_x emissions in the HG area.*
- 2. Develop approaches for modeling effective plume rise in stacks, especially those with non-conventional discharge (e.g., rainhats, horizontal discharge, severe downwash)*
- 3. Observational data from both the Texas Air Quality Study and previous air quality studies have indicated that NMOC emissions are significantly underestimated. Further, the data from the Texas Air Quality indicate that industrial point sources are the most likely source of these underrepresented emissions. Thus, improvements in point source NMOC emission inventories should be aggressively pursued. The areas requiring the most attention are fugitives, flares, start-up/shut-down emissions and emissions from cooling towers and other water handling systems.*
- 4. Evaluate methods for obtaining data on the temporal distribution and magnitude of emissions from flares, cooling towers, wastewater units, equipment leaks and start-up/shut-down/maintenance activities.*

5. *Compare the total estimated on-road emissions, using the fuel based emission factors developed in the Washburn Tunnel study to the total emissions based on vehicle miles traveled and distance based emission factors.*
6. ***The sensitivity of non-road emission factors to humidity level should be examined.***
7. *Assess the accuracy of the spatial distribution of biogenic emissions by comparing predicted emission fluxes to measurements made by aircraft.*
8. *Assess the response of biogenic emissions to heat and drought stress*
9. *Assess methods for accurately estimating fluxes of photosynthetically active radiation and surface temperature, which are key inputs to biogenic emission estimation models.*
10. *Compare the predictions of the various models available for predicting biogenic emissions, using a consistent set of input data*
11. *Analyze chlorine emissions from point sources to insure accuracy of the quantity and diurnal pattern.*
12. *Review cooling towers and swimming pools to determine their locations, the quantity of emissions, the chemical composition of emissions, and the diurnal pattern of emissions.*
13. *Compare the spatial distribution and temporal profiles of the concentrations of chlorine reaction products predicted in photochemical models (based on the emission inventory) to ambient observations; collect additional ambient data if necessary*

Some of these issues clearly are more significant than others. In particular, based on the observational data derived from the Texas Air Quality Study, the issues related to point sources (science issues 1-4) would appear to be most important. As noted in the report, there is an on-going effort to perform a “ground-truth” evaluation of emissions from industrial facilities in the HG area and the results of this activity will be reported in updates to this document.

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APPENDIX A

Spatial and temporal distribution of emissions, by source category for 2000 (TNRCC, 2002)

hg_02km.tx_egu_si4a Total Point Source NO_x Emissions, 08/30/2000

(2x2 Km Grid Cells)

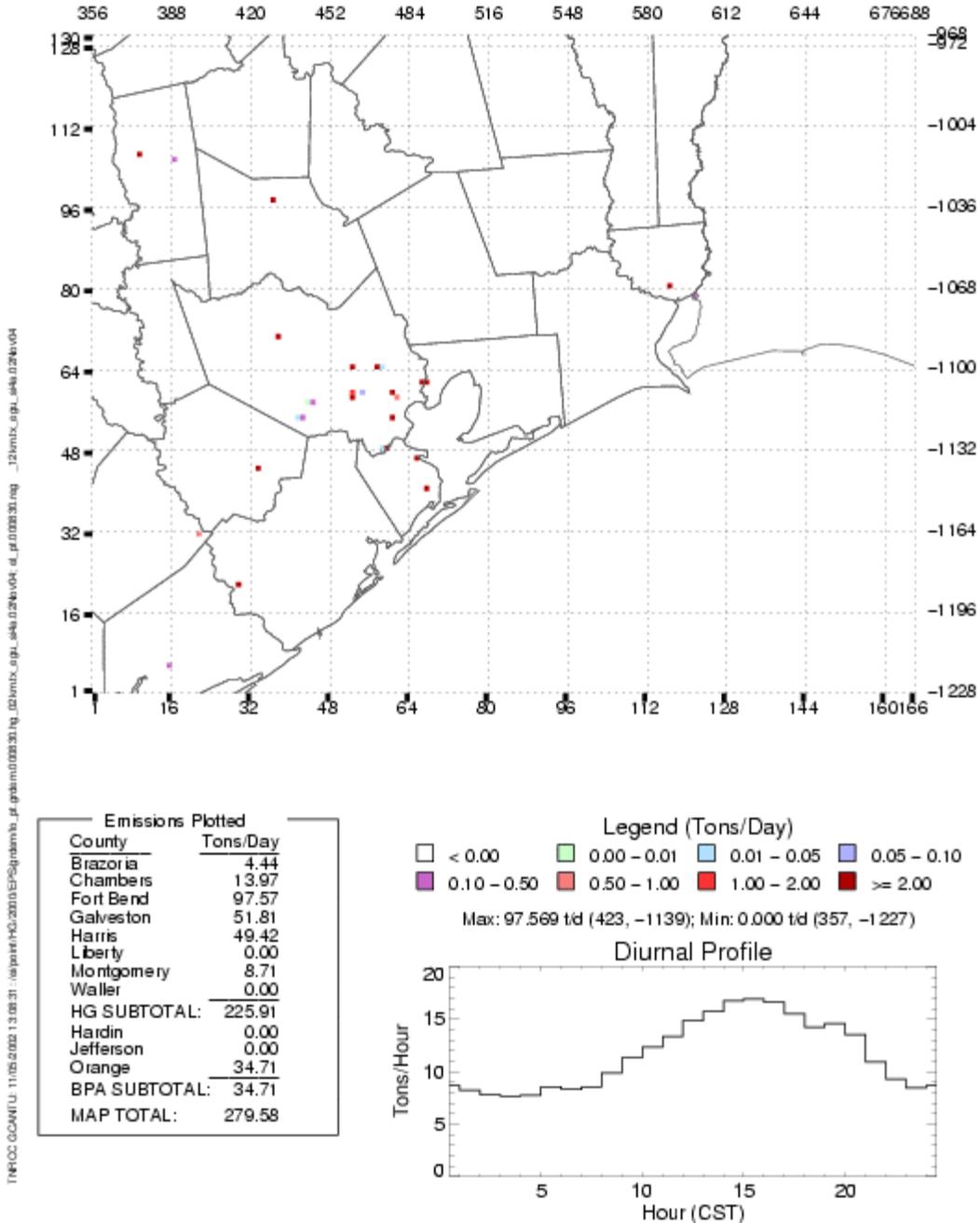


Figure A1. Tile Plot of Electric Generating Utility Point Source NO_x Emissions, Houston/Galveston nonattainment area, August 30, 2000, TNRCC 2002.

hg_02km.tx_negu_si4a Total Point Source NO_x Emissions, 08/30/2000

(2x2 Km Grid Cells)

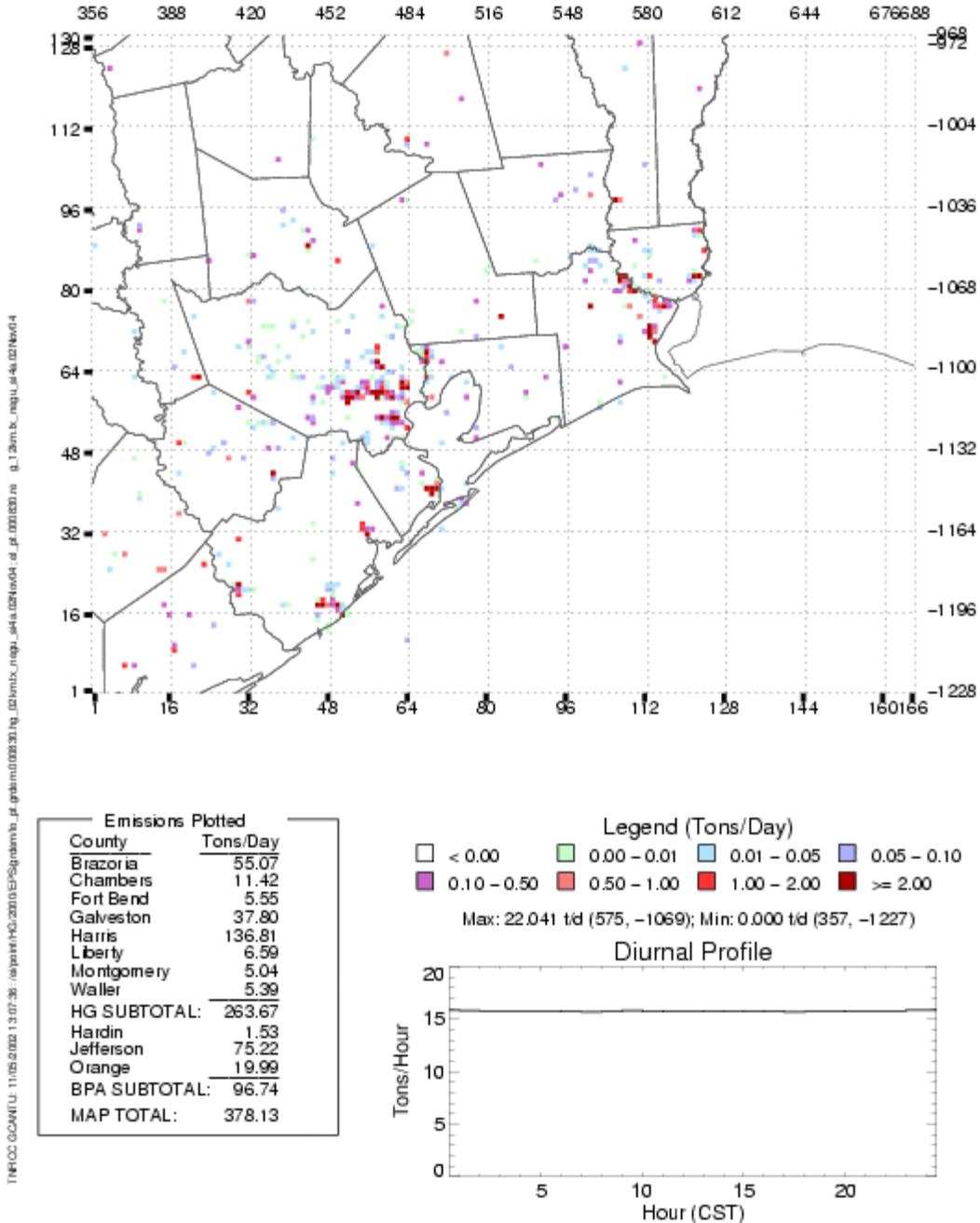


Figure A2. Tile Plot of Non Electric Utility Point Source NO_x Emissions, Houston/Galveston Nonattainment area, August 30, 2000, TNRCC 2002.

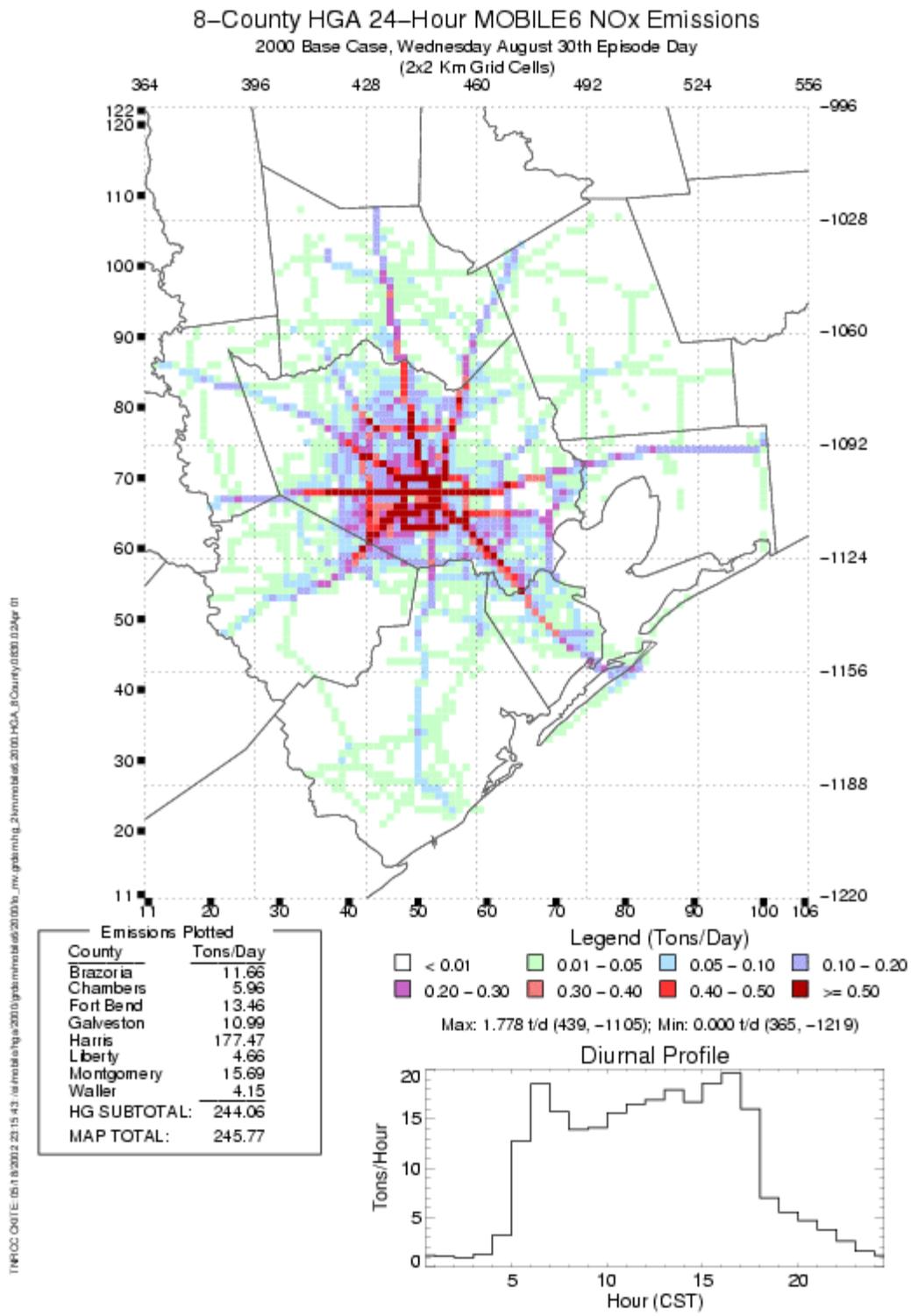


Figure A3. Tile Plot of On-Road Mobile Source NOx Emissions, Houston/Galveston Nonattainment area, August 30, 2000, TNRCC 2002.

hg_02km.tx_egu_si4a Total Point Source CB-IV HC Emissions, 08/30/2000

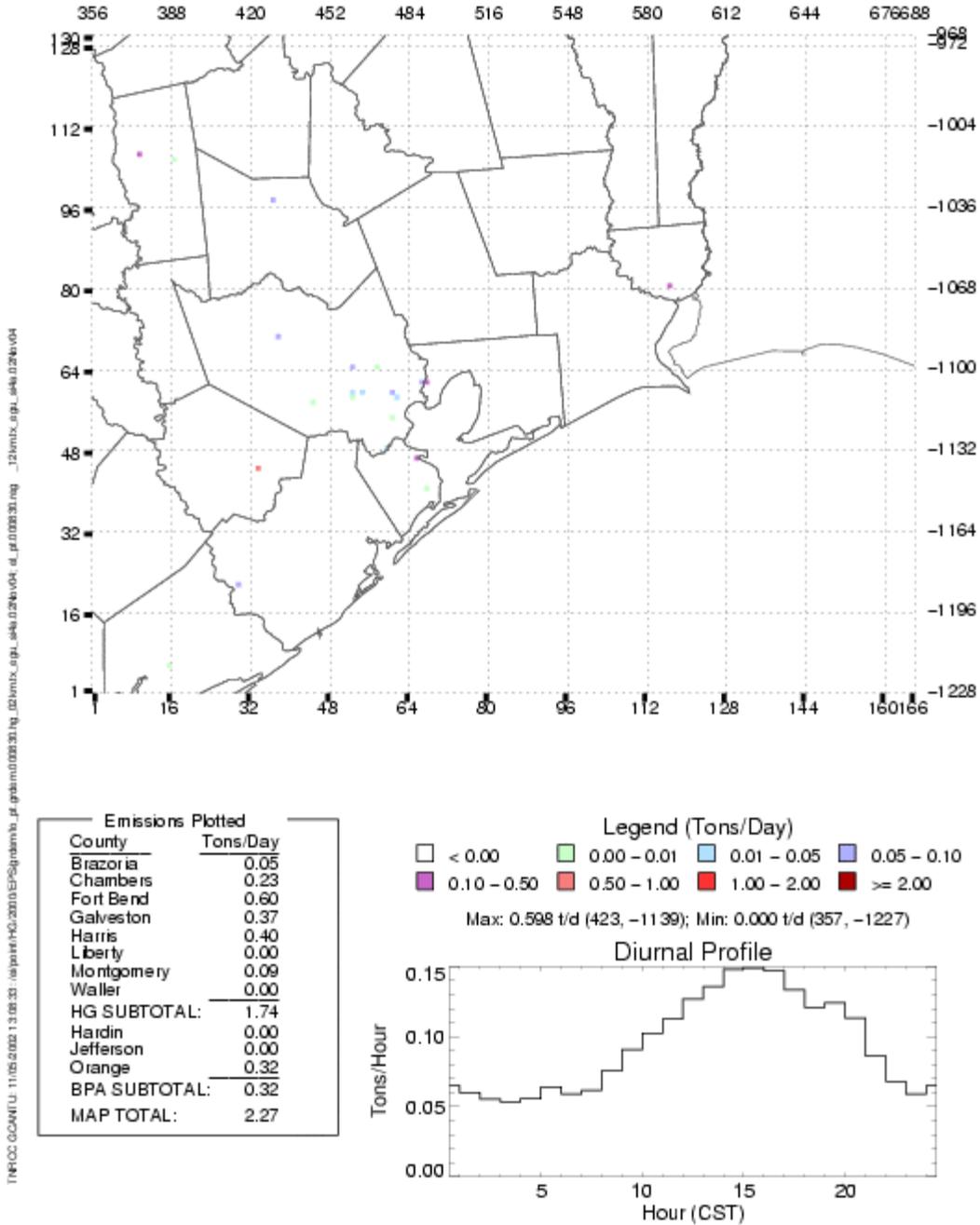


Figure A4. Tile Plot of Electric Generating Utility Point Source VOC Emissions, Houston/Galveston Nonattainment area, August 30, 2000, TNRCC 2002.

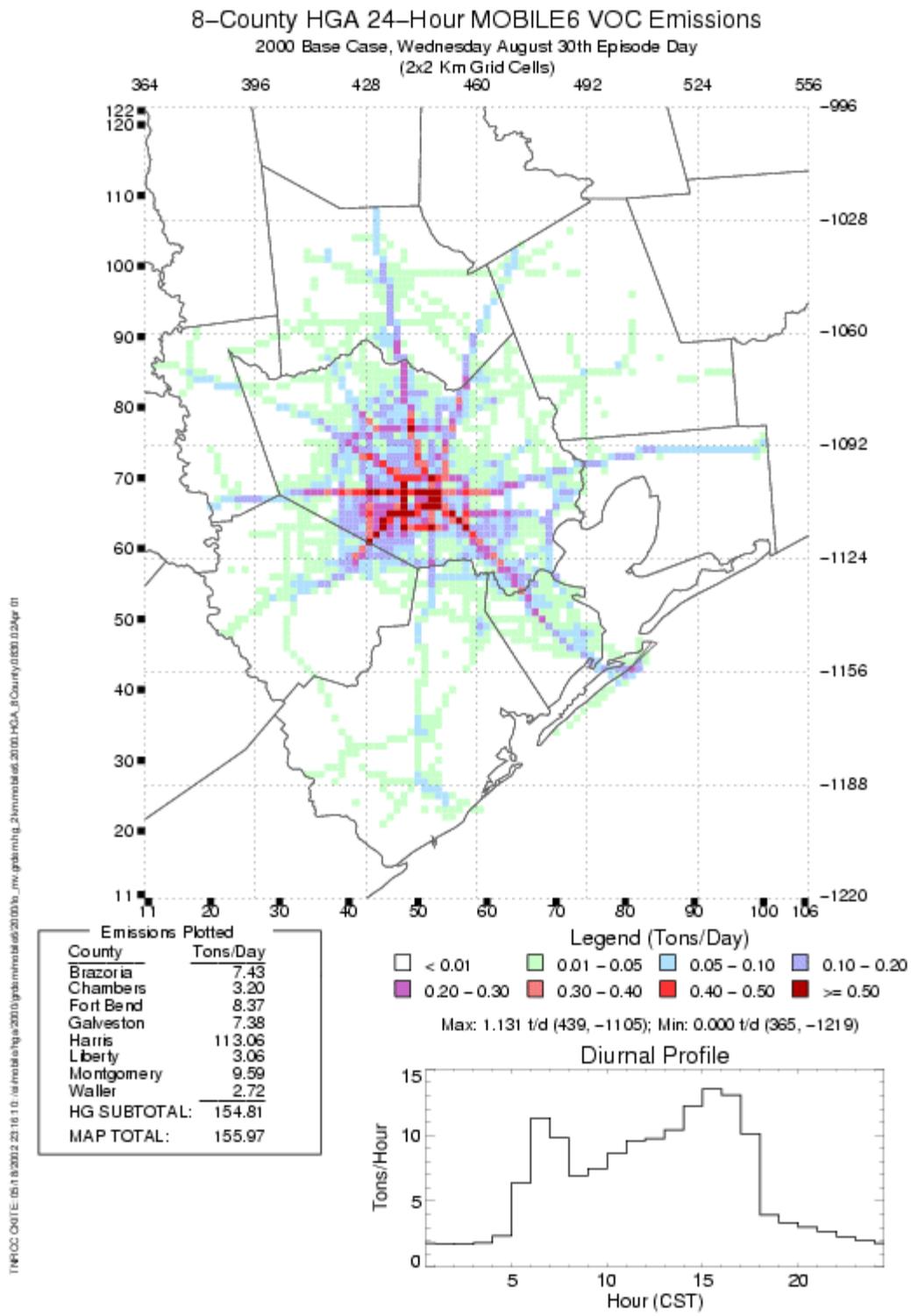


Figure A6. Tile Plot of On-Road Mobile VOC Emissions, Houston/Galveston nonattainment area, August 30, 2000, TNRCC 2002.

APPENDIX B

Volatile organic compounds defined as unreactive for inventory reporting purposes

(TNRCC document RG-360, pages 3-66 and 3-67)

Photochemically Non-reactive VOCs

CONTAM CODE	CAS NO	CONTAM NAME	STATUS *
54020	67641	ACETONE	N
52726	506876	AMMONIUM CARBONATE	N
90100	124389	CARBON DIOXIDE	N
90300	630080	CARBON MONOXIDE	N
53528	75467	CARBON TRIFLUORIDE	N
51060	0	CARBONIC ACIDS-U	N
53298	2837890	CHLORO-1,1,1,2-TETRAFLUOROETHANE, 2-	N
53392	75683	CHLORO-1,1-DIFLUOROETHANE, 1-	N
53314	1615754	CHLORO-1-FLUOROETHANE, 1-	P
53392	75683	CHLORODIFLUOROETHANE	N
53475	75456	CHLORODIFLUOROMETHANE	N
53312	593704	CHLOROFLUOROMETHANE	P
53297	0	DECAFLUOROPENTANE, 1,1,1,2,3,4,4,5,5,5-	N
53295	0	DICHLORO-1,1,1,2,2-PENTAFLUOROPROPANE, 3,3-	N
53296	0	DICHLORO-1,1,2,2,3-PENTAFLUOROPROPANE, 1,3-	N
53313	354234	DICHLORO-1,1,2-TRIFLUOROETHANE, 1,2-	P
53010	1717006	DICHLORO-1-FLUOROETHANE, 1,1-	N
53472	75718	DICHLORODIFLUOROMETHANE	N
53525	1320372	DICHLOROTETRAFLUOROETHANE	N
53294		DIFLUOROETHANE	N
53301	75105	DIFLUOROMETHANE	P
53316	16370208 7	DIFLUOROMETHOXYMETHYL-1,1,1,2,3,3,3- HEPTAFLUOROPROPANE, 2-	P
56550	74840	ETHANE	N
53104	811972	ETHANE, 1,1,1,2,-TETRAFLUORO-	N

53293	306832	ETHANE, 2,2-DICHLORO-1,1,1-TRIFLUORO-	N
53317	16370205 4	ETHOXY-1,1,2,2,3,3,4,4,4-NONAFLUOROBUTANE, 1-	P
53318	16370206 5	ETHOXYDIFLUOROMETHYL-1,1,1,2,3,3,3- HEPTAFLUOROPROPANE, 2-	P
53304	353366	ETHYLFLUORIDE	P
53471	75694	FLUOROTRICHLOROMETHANE	N
53450	0	FREONS-U	N
53310	431630	HEXAFLUOROPROPANE, 1,1,1,2,3,3-	P
53305	690391	HEXAFLUOROPROPANE, 1,1,1,3,3,3-	P
51515		METALLIC CARBIDES-U	N
52550		METALLIC CARBONATES-U	N
60000	74828	METHANE	N
52760	79209	METHYL ACETATE	P
53250	75092	METHYLENE CHLORIDE	N, H
54078	76153	MONOCHLOROPENTAFLUOROETHANE	N
53315	16370207 6	NONAFLUORO-4-METHOXYBUTANE, 1,1,1,2,2,3,3,4,4-	P
53299	98566	PARACHLOROBENZOTRIFLUORIDE	N
53311	406586	PENTAFLUOROBUTANE, 1,1,1,3,3-	P
52443	354336	PENTAFLUOROETHANE	N
53308	431312	PENTAFLUOROPROPANE, 1,1,1,2,3-	P

Table 3-1 continued.

53309	460731	PENTAFLUOROPROPANE, 1,1,1,3,3-	P
53306	679867	PENTAFLUOROPROPANE, 1,1,2,2,3-	P
53307	24270664	PENTAFLUOROPROPANE, 1,1,2,3,3-	P
53360	67721	PERCHLOROETHANE	N, H
56560	67721	PERCHLOROETHANE	N, H
55550	127184	PERCHLOROETHYLENE	N, H
53290	71556	TRICHLOROETHANE, 1,1,1-	N, H
53292	76131	TRICHLOROTRIFLUOROETHANE	N

*This column represents the status of the chemical. A “N” signifies that the chemical is currently considered to be a non-reactive. A “P” signifies that the chemical is listed as a non-reactive in proposed rule revision. A “H” signifies that the chemical is also a hazardous air pollutant (HAP).

APPENDIX C

Graphics Used for Auto-GC Analyses

The following is from the report on analysis of Auto-GC data (Main, et al, 2001). Figure C-1 shows an illustrated box whisker plot. The box shows the 25th, 50th (median), and 75th percentiles. The whiskers always end on a data point, so when the plots show no data beyond the end of a whisker, the whisker shows the value of the highest or lowest data point. The whiskers have a maximum length equal to 1.5 times the length of the box (the interquartile range). If there are data outside this range, the points are shown on the plot and the whisker ends on the highest or lowest data point within the range of the whisker. The “outliers” are also further identified with asterisks representing the points that fall within three times the interquartile range from the end of the box and circles representing points beyond this.

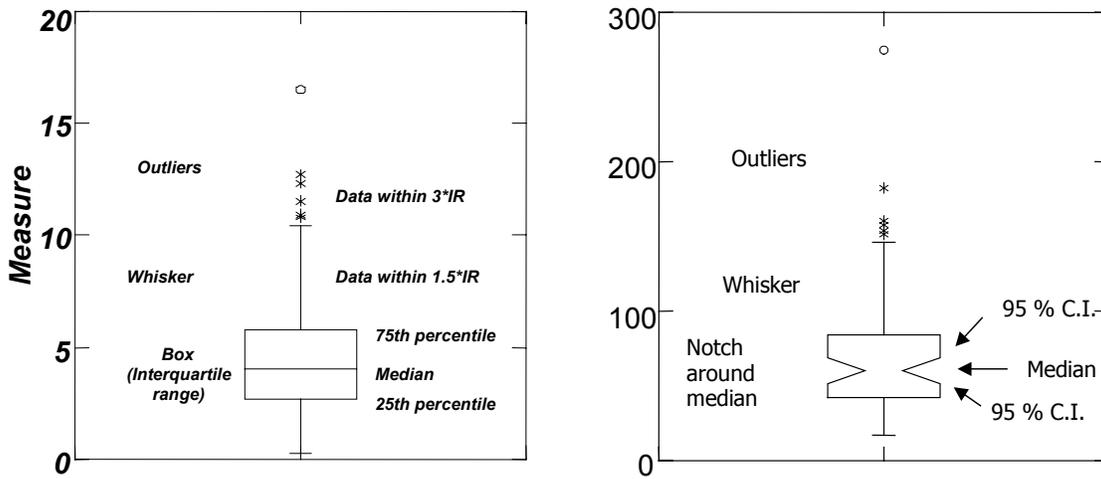


Figure C-1. Illustration of box-whisker plots and notched box whisker plots as defined by SYSTAT statistical software.

Since sample size is also an important consideration when one begins to stratify data, notched box whisker plots have been used to analyze data in this study (see Figure 3.1-1). These plots include notches that mark confidence intervals. The boxes are notched (narrowed) at the median and return to full width at the lower and upper confidence interval values¹. We selected 95% confidence intervals. If the 95% confidence interval is beyond the 25th or 75th percentile, then the notches extend beyond the box (hence the "folded" appearance).

¹ SYSTAT literature uses methodology documented by McGill, Tukey, and Larsen (1978) to show simultaneous confidence intervals on the median of several groups in a box plot. If the intervals around two medians do not overlap, one can be confident at about the 95% level that the two population medians are different.