

**Final Report**

**Evaluation of MOBILE for Application to Houston, TX**

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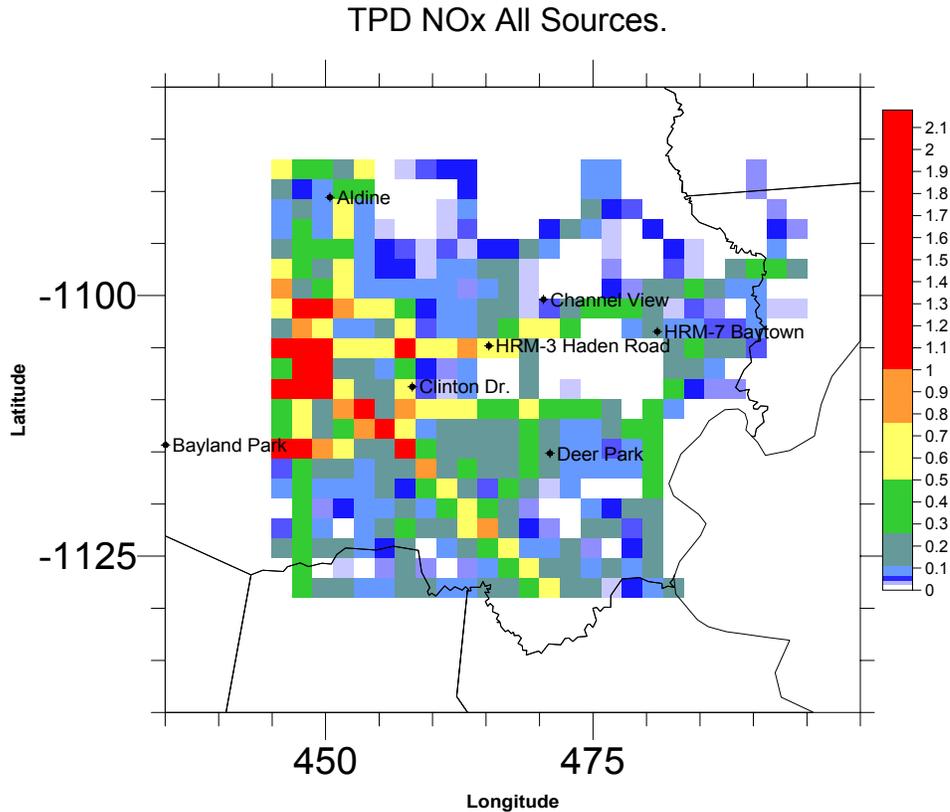
## EXECUTIVE SUMMARY

Emissions from cars and trucks currently account for a significant fraction of total emissions of ozone and particulate matter precursors in most major U.S. cities. As a result, extensive resources have been devoted at national, state, and local levels to development of accurate emission inventories for on-road mobile sources. In Texas as in all other states (except California), mobile source inventories are assembled using the MOBILE emission factor model developed and supported by the U.S. EPA. The EPA recently released a new version of MOBILE; the new model is known as MOBILE6. MOBILE6 replaces MOBILE5 which had been in use prior to 2002. MOBILE6 contains significant revisions to the methodology and supporting data used in prior versions of MOBILE for computing on-road emission factors for non-methane hydrocarbons (NMHC), carbon monoxide (CO), and oxides of nitrogen (NO<sub>x</sub>). While MOBILE6 has thus far undergone peer and stakeholder review, it has not been subjected to a "top down" evaluation via comparisons with ambient air quality data as have earlier versions of MOBILE. Given the significance of on-road mobile sources to air quality issues and the central role of the MOBILE model in development of mobile source emission inventories, a rigorous and thorough validation of the model is extremely important for the continued success of air quality management programs.

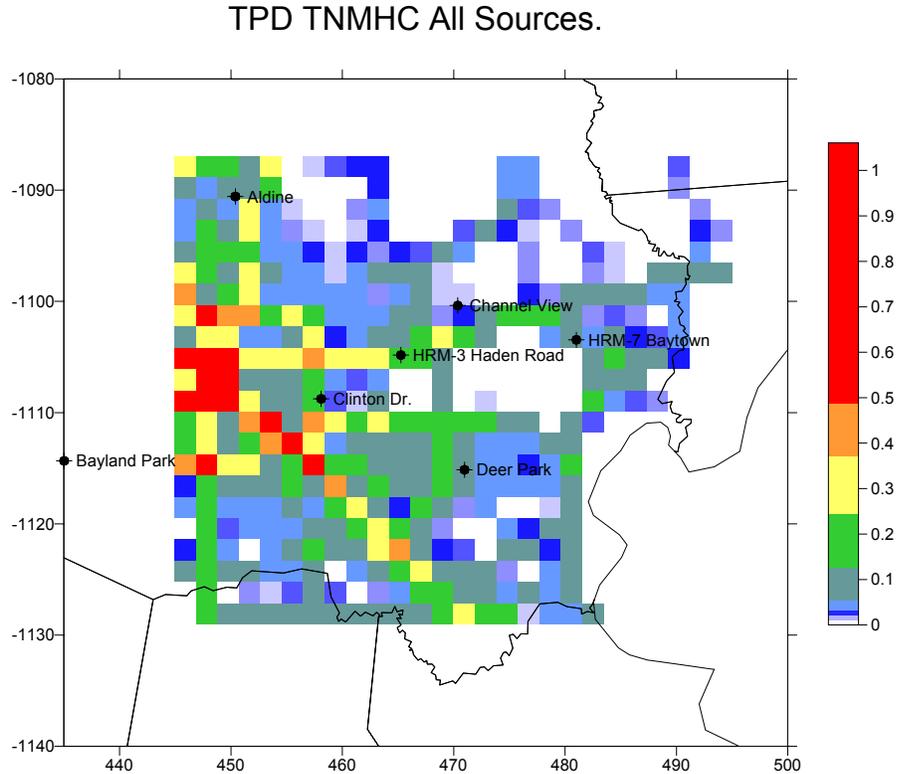
One way of evaluating MOBILE is to compare ratios of species in emission inventories prepared using MOBILE with corresponding ratios in ambient monitoring data. In this study we compared estimates of emission ratios of non-methane hydrocarbon (NMHC) and carbon monoxide (CO) to nitrogen oxides (NO<sub>x</sub>) in a detailed, MOBILE6-based inventory recently developed for Houston, TX with NMHC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios observed at several Houston area monitoring sites for the 1999-2001 summer ozone seasons. Inventory estimates were obtained from speciated, gridded, hourly emission estimates developed by the Texas Natural Resource Conservation Commission (TNRCC).<sup>1</sup> The TNRCC inventory is designed to be representative of emissions on a weekday during late August, 2000. On-road mobile source emissions in this inventory were developed from MOBILE6 using traffic speed and volume estimates for thousands of individual roadway links over the entire metropolitan area. Hourly ambient speciated hydrocarbon, NO<sub>x</sub>, and CO concentration data were obtained from a network of six monitoring sites in Houston. TNRCC's inventory is gridded at 4 km resolution; spatial distributions of NO<sub>x</sub> and NMHC emissions are shown in **Figures ES-1** and **ES-2**, respectively, along with the monitoring site locations.

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<sup>1</sup> On 1 September 2002, the TNRCC was renamed the Texas Commission on Environmental Quality.

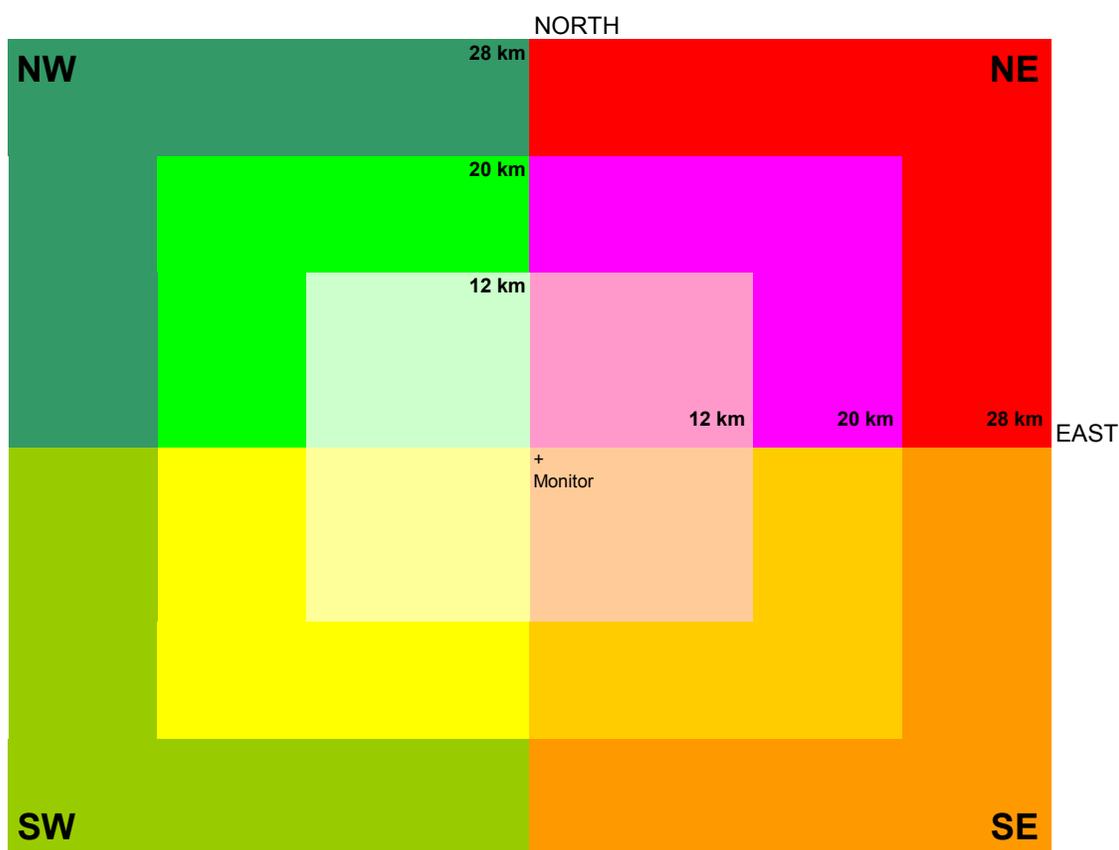


**Figure ES-1.** NOx emissions in tons/day (total of all source categories) with monitoring site locations (Source: Jim MacKay, TNRCC).



**Figure ES-2.** VOC emissions in tons/day (total of all source categories) with monitoring site locations (Source: Jim MacKay, TNRCC).

The speciated NHMC emissions were processed to exclude species which are not included among the PAMS target species detected by the ambient monitoring equipment.<sup>2,3</sup> Emissions data were further processed to compute molar NMHC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios for different sized sectors surrounding each ambient monitoring site. Sectors were defined by dividing the area around the monitor into four directional quadrants and three overlapping downwind distances (12, 20, and 28 km) as shown in **Figure ES-3**. Each sector was characterized by the relative contribution of on-road mobile sources to sector total emissions. The ambient/inventory comparisons were restricted to the early morning weekday commute period (5 – 8 am LST) when mobile source emission impacts at the ambient monitoring sites are maximized and results were stratified by wind direction.



**Figure ES-3.** Orientation of emission quadrants with respect to monitoring site.

<sup>2</sup> For simplicity, we continue to refer to the total of PAMS species as total NMHC in the remainder of this Executive Summary.

<sup>3</sup> A total of 56 hydrocarbon species are targeted for detection under the Photochemical Assessment Monitoring Station (PAMS) program. Ambient data used in this study consisted of 65 reported species, 54 of which are PAMS target species. For the weekday morning observations used in this analysis, the PAMS species accounted for 85% of the total of all reported NMHC species on average.

Ambient NMHC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios were compared with corresponding emissions ratios by computing the so-called “ratio of ratios”: ambient NMHC/NO<sub>x</sub> divided by inventory NMHC/NO<sub>x</sub> and ambient CO/NO<sub>x</sub> divided by inventory CO/NO<sub>x</sub>. Results are summarized in **Table ES-1** and **Table ES-2**, respectively. Quadrants with the highest mobile source contribution to total VOC in the inventory are shaded in these two tables. For these quadrants, ambient NMHC/NO<sub>x</sub> ratios exceed inventory ratios by roughly a factor of 3:1 while the ambient CO/NO<sub>x</sub> ratios are within  $\pm 30\%$  of the inventory ratios, except at Deer Park where the ambient CO/NO<sub>x</sub> ratio exceeds the inventory CO/NO<sub>x</sub> ratio by a factor of 3:1 or more. It is useful to note that point source emissions in the vicinity of Deer Park are a significant fraction of the inventory in the NE and SE quadrants. The presence of point sources in this area may have something to do with the greater discrepancy in the CO/NO<sub>x</sub> ratio at Deer Park. Point sources are a very small portion of the inventory (less than 5%) in the other shaded quadrants.

**Table ES-1.** Average hourly ratio of ratios (ratio of ambient NMHC/NO<sub>x</sub> to emissions NMHC/NO<sub>x</sub>) by site and quadrant (quadrants in which mobile sources represent a substantial fraction of the total inventory are shaded).

Site	Quadrant				
	All	NE	NW	SE	SW
Aldine	3.1	3.5	2.4	3.7	3.2
Channel View	11.7	18.5	5.7	13.7	7.6
Clinton Dr.	5.1	5.8	2.9	12.3	2.8
Deer Park	8.9	12.3	6.7	14.2	4.4

**Table ES-2.** Average hourly ratio of ratios (ratio of ambient CO/NO<sub>x</sub> to emissions CO/NO<sub>x</sub>) by site and quadrant (quadrants in which mobile sources represent a substantial fraction of the total inventory are shaded).

Site	Quadrant				
	All	NE	NW	SE	SW
Aldine	1.3	1.2	1.2	1.2	1.7
Channel View	N/A	N/A	N/A	N/A	N/A
Clinton Dr.	1.6	1.8	1.0	3.4	0.7
Deer Park	7.6	11.9	7.2	9.5	2.9

The discrepancy between ambient and inventory NMHC/NO<sub>x</sub> ratios noted above may be due to one or more factors, including:

- NMHC emissions may be under estimated in the inventory and/or NO<sub>x</sub> emissions may be over estimated. If NO<sub>x</sub> emissions are overestimated, then CO emissions would also have to be overestimated by nearly the same factor since the inventory CO/NO<sub>x</sub> ratios were found to closely match the ambient ratios. NO<sub>x</sub> emission factors for on-road mobile sources are generally regarded as being subject to less uncertainty than hydrocarbon emission factors, further decreasing the likelihood of significant overestimation of inventory NO<sub>x</sub>. On the other hand, a recent analysis of tunnel study data by Tran et al.<sup>4</sup> suggests that MOBILE6 tends to overestimate CO emissions.
- The speciation of HC emissions may be in error, causing a bias in the sum of PAMS target compound emission estimates used in the ambient/inventory comparison. However, the upper bound impact of such speciation errors would be at most to reduce the discrepancy in NMHC/NO<sub>x</sub> ratios from a factor of 3 to a factor of 2 so speciation errors cannot by themselves fully account for the observed discrepancy although they may contribute to it.
- Ambient NO<sub>x</sub> concentrations may be lower than they would otherwise be due to chemical reactions between the time of emission and when material is observed at the monitoring site. The rate of reaction is sensitive to ambient ozone and hydroxyl radical mixing ratios and temperature. However, loss of NO<sub>x</sub> to NO<sub>z</sub> should be minimal during the early morning, high emission periods focused on in our analysis and the ambient NO<sub>x</sub> measurements are typically biased high because some of the NO<sub>z</sub> is included in the reported NO<sub>x</sub>.
- Air parcels sampled at the monitoring site may represent a different source mixture than is contained in the area-wide average emission inventory. This is particularly important for NO<sub>x</sub> emissions from elevated sources such as power plant smoke stacks since the extent to which smoke stack plumes mix to the ground at the monitoring site is highly variable. However, point source emissions were found to be a very small component of the inventory for the locations and wind directions identified as "mobile source dominated" in our analysis and in which the discrepancy between ambient and inventory NMHC/NO<sub>x</sub> noted above is observed. Inventory on-road mobile NMHC/NO<sub>x</sub> ratios are relatively constant across the 40 emission quadrants/hours with the highest mobile source contributions, averaging 1.04 during the morning hours with a range of 0.86 – 1.17. Inventory area plus off-road source NMHC/NO<sub>x</sub> ratios are higher and more variable. Nevertheless, inventory total NMHC/NO<sub>x</sub> ratio still only average 1.40 with a range of 1.02 – 1.83.
- NMHC may accumulate at lower levels overnight to a greater extent than NO<sub>x</sub> and emissions from NMHC rich sources outside the emission source sectors considered in this analysis may travel far enough overnight to impact the monitoring sites. Overnight NMHC concentrations are high in Houston, averaging about 275 ppbC.
- Errors may occur in the ambient measurements due to concentrations below instrumentation detection limits, calibration errors, etc. We sought to minimize problems with detection limits by restricting the ambient samples analyzed to those with NMHC mixing ratios greater than 100 ppbC and NO<sub>x</sub> greater than 10 ppb.

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<sup>4</sup> Tran, C., R. Chi, and A. Pollack, 2002. *Validation of the U.S. EPA MOBILE6 Highway Vehicle Emission Factor Model: Task 1 – On-Road Tunnel Studies*. CRC Project E-64, ENVIRON International Corp., July 29.

- Errors in mobile source emission ratios may be due to errors in mobile source emission factors or to errors in activity data and the spatial and temporal allocation of activity. Examples of the latter include the fleet mix, cold start fractions, and diurnal VMT patterns by vehicle type.

Of course, the discrepancies between ambient and inventory NMHC/NO<sub>x</sub> ratios noted above may be due to errors in characterization of area and off-road source emissions as well as on-road mobile source emissions. Even for emission quadrants/hours dominated by on-road mobile sources, area plus off-road sources account for between one third and one half of total NMHC emissions from all source categories. Thus, errors in area and off-road source emission ratios can significantly impact the ambient/inventory comparisons described above.

In conclusion, we find that NMHC/NO<sub>x</sub> ratios reported in the Houston August, 2000 inventory are about a factor of three less than ratios observed in the ambient air while inventory CO/NO<sub>x</sub> ratios are generally within  $\pm 30\%$  of ambient ratios. This discrepancy in NMHC/NO<sub>x</sub> ratios most likely indicates a significant problem with the inventory which requires further investigation. Although the ambient/inventory comparisons presented here were limited to situations in which on-road mobile source contributions to inventory total emissions are maximized, the contribution of area sources is still fairly significant, especially for NMHC. As a result, errors in area source NMHC/NO<sub>x</sub> ratios could be contributing to the this discrepancy and it is not possible to determine to what extent the on-road mobile source estimates by themselves are in error. It is also not possible to determine from these results if the MOBILE6 emission factors themselves are incorrect or if there is a problem with the mobile source activity data.

## 1.0 INTRODUCTION

Emissions from cars and trucks currently account for a significant fraction of total emissions of ozone and particulate matter precursors in most major U.S. cities. As a result, extensive resources have been devoted at national, state, and local levels to development of accurate emission inventories for on-road mobile sources. In Texas as in all other states (except California), mobile source inventories are assembled using the MOBILE emission factor model developed and supported by the U.S. EPA. The EPA recently released a new version of MOBILE; the new model is known as MOBILE6. MOBILE6 replaces MOBILE5 which had been in use prior to 2002. MOBILE6 contains significant revisions to the methodology and supporting data used in prior versions of MOBILE for computing on-road emission factors for non-methane hydrocarbons (NMHC), carbon monoxide (CO), and oxides of nitrogen (NO<sub>x</sub>). While MOBILE6 has thus far undergone peer and stakeholder review, it has not been subjected to a "top down" evaluation via comparisons with ambient air quality data as have earlier versions of MOBILE. Given the significance of on-road mobile sources to air quality issues and the central role of the MOBILE model in development of mobile source emission inventories, a rigorous and thorough validation of the model is extremely important for the continued success of air quality management programs.

One way of evaluating MOBILE is to compare ratios of species in emission inventories prepared using MOBILE with corresponding ratios in ambient monitoring data. While this "ambient-inventory reconciliation" approach does not allow one to evaluate the accuracy of the estimated absolute magnitudes of emissions, it does allow one to evaluate the ability of MOBILE to reproduce the observed composition of the mobile source pollutant mixture. Obtaining accurate estimates of the relative composition of species in emissions is critical for effective air quality management since predictions of ozone and secondary PM formation are sensitive to species ratios in the inventory. The primary advantage of this method of validating MOBILE is that it provides a direct comparison of the inventory estimates for an area around a given ambient monitoring site with data from that site.

The Texas Natural Resource Conservation Commission has developed a gridded, speciated, temporally resolved emissions inventory for Houston for the summer of 2000 which includes a link-based MOBILE6 inventory component. A linked-based, gridded, hourly inventory for Houston for 1999 had previously been developed using MOBILE5. Hourly, speciated ambient NMHC measurements have been made at several locations in Houston for several years. Other data collection activities and analyses, including a tunnel study, were conducted as part of the overall TexAQS 2000 project carried out in August and September, 2000. The PAMS and TexAQS data sets, together with the detailed emission inventories, provide a valuable opportunity for a top-down evaluation of MOBILE in Houston and a comparison of results from such an analysis with results from other TexAQS-related mobile source studies.

There are, of course, a number of limitations inherent in ambient-inventory reconciliation analyses in addition to the fact that they are limited to an evaluation of species ratios rather than the absolute magnitude of emissions. In the context of the current study, it must be recognized that species ratios in the monitoring data represent a mixture of source categories and are not limited to just on-road mobile sources. Thus, discrepancies between ambient and inventory ratios cannot be definitively tied to inaccuracies in the MOBILE portion of the

inventory. This ambiguity can be minimized by selecting monitoring sites in locations that are dominated by on-road mobile sources.

In general, one must recognize that there are several reasons why ratios of, for example, NMHC/NO<sub>x</sub> in the inventory may differ from ratios in the ambient data:

- NMHC emissions may be over (under) estimated in the inventory.
- NO<sub>x</sub> emissions may be under (over) estimated in the inventory.
- Emissions of NMHC or NO<sub>x</sub> may not be properly spatially allocated across different sources or properly temporally allocated to different times of the day or may not represent actual emissions during the ambient monitoring period (day specific effects). This may be particularly important in the case of diesel truck activity which can strongly influence NO<sub>x</sub> levels and exhibits distinctive diurnal and day-of-week variations.
- The definition of what range of hydrocarbons are included in the inventory definition of “NMHC” may not correspond well with the range of hydrocarbons captured by the ambient NMHC measurement. Previous studies have used mobile source speciation profiles to break down the NMHC calculated by MOBILE into its individual component species and then include in the comparison only the range of species represented in the ambient data (typically the sum of the 55 species targeted for measurement at Photochemical Assessment Monitoring Stations [PAMS] or the “total NMHC” reported from a GC/FID or GC/MS analysis). Care must be taken to use the most appropriate speciation profiles and to estimate the potential uncertainties introduced into the analysis as a result of the speciation.
- Ambient NMHC or NO<sub>x</sub> concentrations may be lower than they would otherwise be due to chemical reactions between time of emissions and when material is observed at the monitoring site. The rate of reaction will in general be different for different chemical species, different pollutant mixtures, and different meteorological conditions.
- Air parcels sampled at the monitoring site may represent a different source mixture than is contained in the area-wide average emission inventory. This is particularly important for NO<sub>x</sub> emissions from elevated sources such as power plant smoke stacks since the extent to which smoke stack plumes mix to the ground at the monitoring site is highly variable.
- Errors may occur in the ambient measurements due to concentrations below instrumentation detection limits, NMHC species misidentification, calibration errors, etc.

### **Previous Ambient/Inventory Reconciliation Studies**

Stoeckenius and Jimenez (2000) prepared a review of ambient/inventory reconciliation studies conducted in the United States over approximately the past decade. Results are summarized in **Table 1-1**. With the exception of the LADCO analysis, these studies (which primarily focussed on the NMHC/NO<sub>x</sub> ratios) concluded that the inventory NMHC/NO<sub>x</sub> ratio was lower than the ambient ratio by factors ranging from 1.2 to 6. Studies which also examined CO/NO<sub>x</sub> ratios concluded that the ambient CO/NO<sub>x</sub> ratio exceeds the inventory ratio by a factor ranging from 1.5 to 2.7.

Fujita et al. (2001) describe the collection and analysis of ambient speciated NMHC, NO, NO<sub>y</sub>, CO and black carbon (BC) data collected from a van driven over various predefined

routes in the Los Angeles area. Samples collected during roadway transits are more likely to be representative of real world on-road emissions from various fleet mixes than samples collected at the typical fixed, neighborhood scale monitoring site where the relative contribution of area sources to the samples are likely to be larger. By regressing NO<sub>x</sub> concentrations against CO and BC, Fujita and co-workers were able to split total NO<sub>x</sub> into CO-related and BC-related fractions. Since diesel exhaust emissions contribute BC but very little CO relative to exhaust from spark ignition engines, this approach allowed the researchers to estimate the contribution of the diesel fleet to observed NO<sub>x</sub>. Fujita and co-workers applied emissions profiles for on-road gasoline and diesel emissions collected during the study to apportion ambient NMHC and NO<sub>x</sub> by Chemical Mass Balance.

**Table 1-1.** Previous inventory reconciliation studies.

Study	Reference	Location	Date	Ambient Data	Inventory Data	Ratio of Ratios: (Ambient NMHC/NO <sub>x</sub> )/ (Inventory NMHC/NO <sub>x</sub> )	Additional Results
MARAMA	Stoeckenius and Jimenez (2000)	Mid-Atlantic	1997	PAMS: McMillan Res., Washington DC; Essex, Baltimore MD	New gridded, speciated, MOBILE5b based inventory (no excess NO <sub>x</sub> adjustment)	Washington: 1.2 to 1.6 Baltimore: 1.5 to 3.7	Relative abundance of aromatics slightly higher in inventory relative to ambient
CA-PAMS	Haste-Funk and Chinkin (1999)	Central and Southern California	1996	PAMS: Fresno, Sacramento	ARB county-level inventory for 1996	NMHC/NO <sub>x</sub> : 1.5 to 4.0 CO/NO <sub>x</sub> : 1.5 to 2	Ambient paraffins slightly higher than in inventory; olefins and aromatics lower
NARSTO-NE	Haste et al. (1998)	Northeastern U.S.	1995	PAMS and NARSTO-NE: Bronx, NY (New York City), Lake Clifton, MD (Baltimore, MD), Lynn, MA (near Boston).	OTAG 1990 grown to 1995 using 1995 OTAG modeling inventory (MOBILE5)	1.5 to 3.5	Ambient NMHC composition similar to composite of mobile and area inventory composition
LADCO	LADCO, 1998	Lake Michigan, New York City, Washington, DC	1995	PAMS (Jardine-Chicago; IITRI-Gary, IN; UWM-North-Milwaukee; Northbrook, IL)	OTAG 1995 modeling inventory with local adjustments (MOBILE5)	1 ± .25	
COAST	Korc et al. (1995)	Southeast TX	1993	PAMS-Houston (Clinton Dr., Galleria)	COAST inventory from TNRCC	2 to 6	
SCAQS	Fujita et al. (1992)	South Coast (Los Angeles)	1987	SCAQS	SCAQS (EMFAC7E)	CO/NO <sub>x</sub> : 1.1 to 2.7 NMOG/NO <sub>x</sub> : 1.8 to 3.2	

## 2.0 DATA PREPARATION

Ambient air quality monitoring data and emissions inventory data for Houston were provided for use in this study by the Texas Natural Resource Conservation Commission (TNRCC). All data quality assurance was performed by the TNRCC; additional detailed quality assurance was not possible within the scope of this study. However, routine checks of data summaries for completeness and any unexpected values or patterns performed within the course of our study did not uncover any problems with the data as delivered.

In the following subsections we briefly summarize the ambient and inventory data provided by the TNRCC and describe procedures used to process the data in preparation for making comparisons of species ratios.

### 2.1 AMBIENT DATA

Hourly speciated non-methane hydrocarbon (NMHC) data have been collected with automated gas chromatographs (Auto-GCs) at seven sites in the Houston area over various time periods (see **Table 2-1**). Note that monitoring equipment was moved from the Bayland Park site to the Audine site in August, 2000. Canister data were also collected at La Port during the TEXAQS 2000 field study period (mid-August to mid-September, 2000). Hourly speciated NMHC, NO<sub>x</sub>, CO, wind direction, wind speed, ambient temperature and humidity data collected at the auto-GC sites were obtained from the TNRCC for the period 1999 – 2001. This period brackets the inventory data (discussed in the next section) which are representative of emissions in the year 2000 while retaining enough data to obtain meaningful averages when samples are stratified by time of day, day of week, and wind direction. Data prior to 1999 were not used to avoid potentially confounding influences of trends in emissions.

**Table 2-1.** Characteristics of Houston area hydrocarbon sampling sites.<sup>1</sup>

NMHC Sampling						
Site ID	Sampling System	Period of Operation <sup>2</sup>	Data Completeness <sup>3</sup>	CO	Major Source Impacts	Comments
Aldine (C08)	Auto GC	8/31/00 – 7/30/01	90%; Data generally incomplete prior to 4 <sup>th</sup> quarter of 2000	High resolution	Mobile (Fwy); School buses	TNRCC/STI have validated data
Deer Park (C35)	Auto GC	1/16/97 – 10/31/01	72%; Data generally complete for 1998, 3 <sup>rd</sup> – 4 <sup>th</sup> quarter 1999, 2 <sup>nd</sup> quarter 2000, and Aug-Oct 2001	High resolution	Mixed Industrial; Ship Channel sources to the N - NE	TNRCC/STI have validated data
La Port	Canisters	8/15/00 – 9/15/00		High resolution	Industrial/Mobile	TXAQS 2000 study site
Clinton Dr. (C403/C113/C304)	Auto GC	8/20/96 – 10/31/01	90%; Data generally complete for 1998-2001 (no completeness statistics for 1996-1997)	Low resolution	Petroleum/Petrochemical to the S, SE, E; Residential and urban to the W and NW. Mobile sources dominate under SW – NW winds.	TNRCC/STI have validated
HRM 3 (Haden)	Auto GC	8/21/01 – 10/31/01	69%	NA		TNRCC/STI have validated data
HRM 7 (Baytown)	Auto GC	8/27/01 – 10/31/01	84%	NA		TNRCC/STI have validated data
Bayland Park (CAMS 53)	Auto GC	5/4/98 – 8/7/2000	Data generally complete between 4 <sup>th</sup> quarter 1998 and 2 <sup>nd</sup> quarter 2000	Yes	Mobile source	TNRCC/STI have validated data
Channel View (C15/115)	Auto GC	8/4/01 – 10/31/01	73%	NA	Large stationary VOC sources to N and NE; School buses parked to W-SW could impact NOx	TNRCC has validated data

Our analysis focussed on data collected during the morning weekday commute period when mobile source emissions are high relative to other sources, mixing and chemical reactivity is limited, and the impact of elevated point sources is reduced. As described in more detail in Section 3, our primary focus was on samples collected between 5 and 8 am local standard time (LST).

Estimates of “unidentified” NMHC were not available from the TNRCC (Jolly, 2001). However, the 65 reported NMHC species in the data included 54 of the 56 species currently

<sup>1</sup> This table is largely based on a table developed by John Jolly of the TNRCC.

<sup>2</sup> As of 10/31/01

<sup>3</sup> Percentages apply to 8/1/01 – 10/31/01 only, include allowance for 2 hours per day for calibration/blanks, and count samples with missing TNMOC data as missing

designated as target compounds by EPA's Photochemical Assessment Monitoring Station (PAMS) program (**Table 2-2**). Thus, the total concentration of these PAMS target compounds (referred to hereafter as "sum-of-PAMS" or simply "PAMS") was selected as the point of comparison with the emissions inventory. For the weekday morning observations used for comparison with the emission inventory as described in Section 3, the PAMS species accounted for 85% of the total of all reported NMHC species, on average.

**Table 2-2.** PAMS target species.

1,2,3-Trimethylbenzene	Isopentane
1,2,4-Trimethylbenzene	Isoprene
1,3,5-Trimethylbenzene	Methylcyclopentane
1-Butene	Methylcyclohexane
1-Pentene	m-Diethylbenzene
2,2,4-Trimethylpentane	m-Ethyltoluene
2,2-Dimethylbutane	m,p-Xylene
2,3,4-Trimethylpentane	n-Butane
2,3-Dimethylbutane	n-Decane
2,3-Dimethylpentane	n-Heptane
2,4-Dimethylpentane	n-Hexane
2-Methylheptane	n-Nonane
2-Methylhexane	n-Octane
2-Methylpentane	n-Propylbenzene
3-Methylheptane	n-Pentane
3-Methylhexane	n-Undecane
3-Methylpentane	o-Ethyltoluene
Acetylene	o-Xylene
Benzene	p-Diethylbenzene
c-2-Butene	p-Ethyltoluene
c-2-Pentene	Propane
Cyclohexane	Propylene
Cyclopentane	Styrene
Ethylbenzene	t-2-Butene
Ethane	t-2-Pentene
Ethylene	Toluene
Isobutane	1-Hexene (not reported by TNRCC)
Isopropylbenzene	N-Dodecane (not reported by TNRCC)

Some sites have been shown in previous analyses to be impacted by emissions from large industrial sources under certain wind directions. A notable example is Clinton Dr. where significant impacts from petroleum refining and petrochemical sources located to the south and east have been observed. However, air parcels sampled under west and north winds at this site have characteristics typical of a mobile-source dominated air mass. Maps of gridded emissions data around each monitoring site were examined to determine dominant source influences under various wind directions. Since the objective of this study was to evaluate the on-road mobile component of the inventory, we focussed our attention on sites and wind

directions for which on-road mobile source emissions represent a significant fraction of the inventory.

Samples with low sum-of-PAMS (less than 100 ppbC) or low NO<sub>x</sub> (less than 10 ppb) concentrations were eliminated from the analysis since such samples are not likely to have TNMOC/NO<sub>x</sub> ratios representative of significant fresh mobile source emissions. Excluding the low NO<sub>x</sub> samples also avoided NO<sub>x</sub> monitor detection limit issues. Overall, 81% of the morning weekday ambient samples simultaneously exceeded both the sum-of-PAMS and NO<sub>x</sub> thresholds.

## 2.2 EMISSIONS INVENTORY

TNRCC developed a detailed hourly, gridded (2 x 2 km), speciated emissions inventory for Houston covering the August 2000 ozone modeling episode. This inventory was developed using 1999 baseline data grown to 2000. TNRCC provided ENVIRON with emissions data representative of 23 August 2000 for the hours from 5 am to 10 am, LST (McKay, 2002). Spatial distributions of total VOC and NO<sub>x</sub> relative to the ambient monitoring sites are shown in **Figures 2-1 and 2-2**, respectively.<sup>4</sup>

Inventory files provided by the TNRCC were broken down into several major source categories:

- Elevated point sources
- Low level point and area sources (including non-road mobile)
- On-road mobile
- Biogenics

On-road mobile source emissions were developed by Texas Transportation Institute (TTI) using MOBILE6 together with link-based VMT and average speed estimates. Details on the mobile source inventory development are provided in TNRCC (2002) and references therein. Biogenic emissions were developed using the GloBEIS model (ENVIRON, 2001). A review of the inventory data supplied by the TNRCC revealed that biogenic emissions were set to zero for hours 5, 6, and 7 (biogenics are non-zero starting in hour 8).<sup>5</sup> Since, as explained in Section 3 below, the focus of our analysis is on this morning commute period, biogenic emissions did not factor into our results.

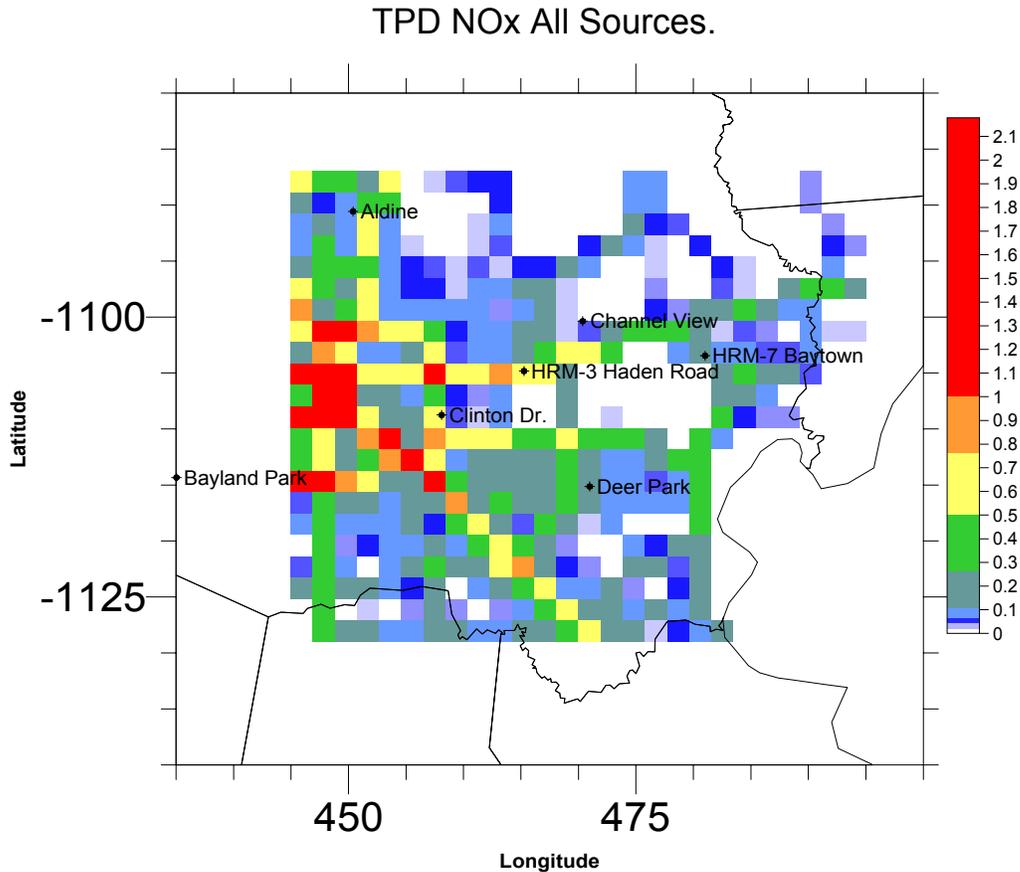
VOC emissions were speciated by TNRCC, using the latest available profiles, including the new on-road mobile source profiles developed by ENVIRON from the Washburn Tunnel study data analyzed by Rob Harley of the University of California, Berkeley (Yarwood, 2002)

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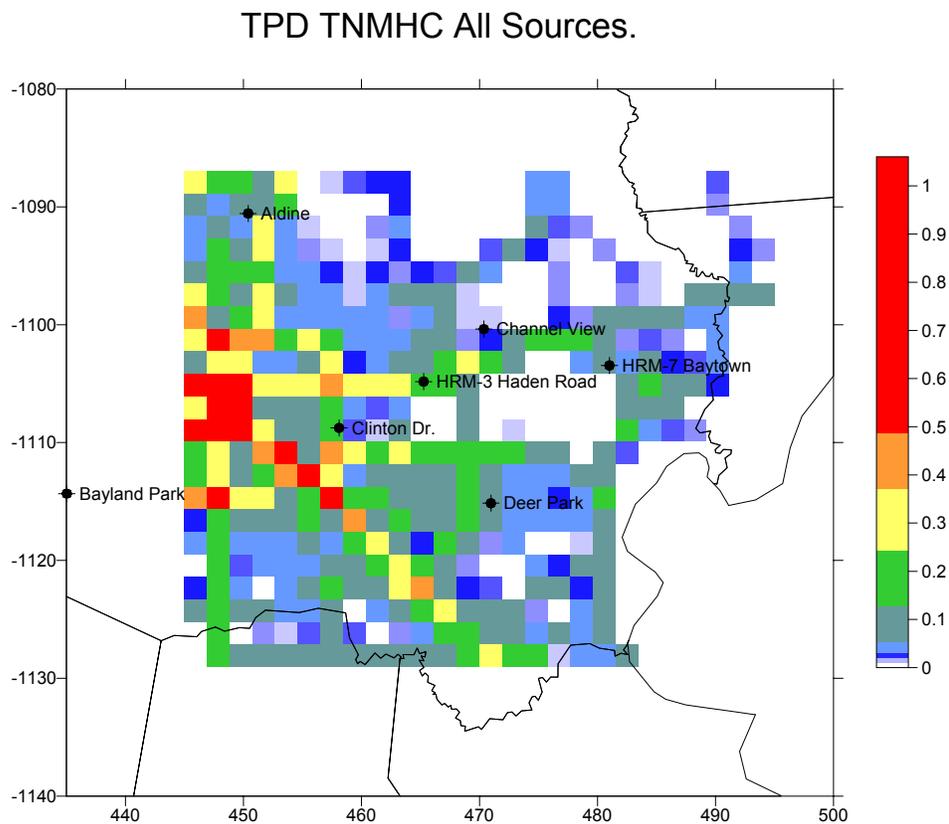
<sup>4</sup> Following standard practice, we refer to the collection of hydrocarbon species reported in the inventory as “VOCs”. Matching of the reported hydrocarbons with the specific hydrocarbons included in the ambient monitoring data is discussed later in this section under **Processing of Emissions Data**.

<sup>5</sup> Emissions supplied by the TNRCC were labeled “hour 5”, “hour 6”, ..., “hour 10” and these designations are used for purposes of this discussion. Temporal alignment of the hourly emissions and ambient data is discussed in Section 3.1.

Day-specific factors used to develop the inventory include day-specific operations for some of the major point sources (e.g., electric generating units) and daily ambient temperatures. Day-of-week factors (temporal profiles, VMT estimates, etc.) representative of weekdays (Monday – Thursday) were used to develop the 23 August 2000 inventory day (a Wednesday).



**Figure 2-1.** NO<sub>x</sub> emissions in tons/day (total of all source categories) with monitoring site locations.



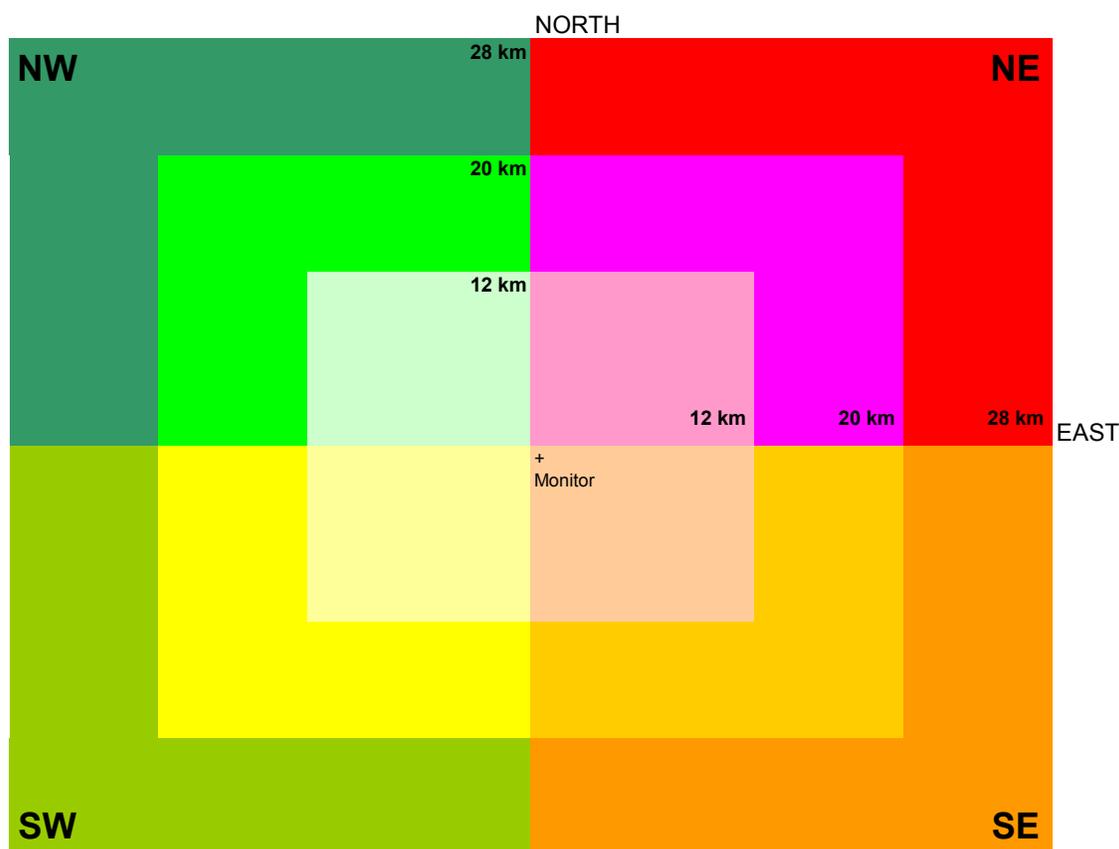
**Figure 2-2.** VOC emissions in tons/day (total of all source categories) with monitoring site locations.

### 2.2.1 Processing of Emissions Data

Speciated, gridded, temporally allocated emissions data provided by TNRCC were prepared for analysis by converting VOC emissions to units of molesC/hour and NO<sub>x</sub> and CO to moles/hour (with NO<sub>x</sub> expressed as NO<sub>2</sub>) for comparison with the ambient data. Since the auto-GC instruments used at the ambient monitoring sites are not designed to detect all of the organic compounds included in the emission inventories, emissions of species not included in the PAMS target list described above were excluded from the comparison. For the inventory as a whole, the sum-of-PAMS species accounted for 67% of the total reported non-methane hydrocarbon emissions (mass basis). The potential impact of the unmonitored non-methane hydrocarbon emissions on ambient/inventory comparisons is discussed in Section 3.4.

For any given time period, meteorological conditions will determine the size and shape of the emissions source region impacting a monitoring site. In addition, chemical transformation and deposition of pollutants between the time they are emitted and subsequently detected at the monitoring site depends on meteorology as well. Application of a photochemical air quality model (e.g., CAMx) to estimate the impact of a group of sources on a monitoring site over a specific time interval (accounting for chemical transformations along the way) was beyond the scope of this study. Instead, we simply defined a square region of grid cells around each monitoring site and divided this region into four wind direction quadrants centered on NE, SE,

SW, and NW compass points. Three different size squares (“subgrids”), with side lengths of 12, 20, and 28 km were used as shown in **Figure 2-3**. Emission were subtotaled for each quadrant for each of the different subgrids and then integrated over all quadrants for each subgrid. The subgrid lengths (12, 20, 28 km) correspond roughly to one hour transport times to the monitoring site under straight-line winds at speeds of 2, 3, and 4 m/s, respectively. Such light winds are typical of ozone episode conditions.



**Figure 2-3.** Orientation of emission quadrants with respect to monitoring site.

**Table 2-3** lists total mobile, area, and point source emissions for hours 5 – 7 within the 28 km box centered on each monitoring site. Note that point source NO<sub>x</sub> emissions represent a significant portion of the inventory around all of the monitoring sites except for Aldine. Point source hydrocarbon emissions are on par with mobile source hydrocarbon emissions around all sites except Aldine and Clinton Drive. Point sources typically have emission characteristics significantly different from area and mobile sources. Furthermore, the impacts of emissions from elevated point sources on a ground-level monitoring site are highly variable and difficult to quantify. These factors make it difficult to use ambient/inventory comparisons to evaluate mobile and area source inventories at locations with significant point source activity.

**Table 2-3.** Sum of pollutant mass emissions between 5 am to 7 am at distance of 28 km in all quadrants.

Monitor Site	Mobile			Area			Point		
	PAMS	NOx	CO	PAMS	NOx	CO	PAMS	NOx	CO
	Units	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr
Aldine	2,037	6,475	50,420	2,812	2,877	18,903	42	448	410
Deer Park	3,754	11,892	92,025	15,613	12,605	55,326	2,676	30,123	13,091
Clinton Dr.	6,703	20,609	158,552	14,545	13,231	65,331	1,374	20,065	9,522
HRM-3 Haden Road	4,108	12,880	99,207	14,294	11,965	51,427	2,101	24,379	12,423
HRM-7 Baytown	1,428	4,975	38,654	9,845	7,396	31,642	3,369	26,694	13,136
Channel View	2,298	7,627	58,983	14,226	10,073	39,168	2,906	29,521	14,217

To help identify locations of interest to our analysis, we calculated the relative contribution of on-road mobile sources to inventory total emissions of PAMS, NOx and CO for each grid quadrant around each monitoring site. Emissions for quadrants with the top 40 mobile source fractions of PAMS (sorted from high to low) are listed in **Table 2-4**. All quadrants around the Aldine monitoring site, and SW and NW quadrants of the Clinton site have some of the highest PAMS mobile source fractions, ranging from just under 50% up to 70%. The SW quadrants of the Deer Park site also have relatively high mobile PAMS fractions. Mobile source fractions in other quadrants at Clinton and Deer Park and all quadrants at the other monitoring sites are lower. Mobile source NOx fractions for the quadrants in Table 2-4 are mostly above 60% and range up to 85%. The highest PAMS and NOx mobile source fractions occur in hour 6; hours 5 and 7 are also represented in the top 40 list. Note that the NOx mobile source fractions are higher at Aldine than at Clinton: there is a greater relative contribution of area source NOx at Clinton. Point sources contribute very little to the inventory for all of the top 40 quadrants listed in Table 2-4.

**Table 2-4.** Monitoring sites, subgrid length, quadrant and hour of day with the highest mobile source fraction of PAMS.

Site	Subgrid Length			Mobile Fraction			Point Fraction		
	(km)	Quadrant	Hour	PAMS	NOx	CO	PAMS	NOx	CO
Aldine	28	NE	6	70.1%	80.1%	93.9%	0.0%	0.0%	0.0%
Aldine	12	NE	6	68.8%	82.1%	93.6%	0.0%	0.0%	0.0%
Aldine	20	NE	6	68.4%	81.1%	93.4%	0.0%	0.0%	0.0%
Clinton Dr.	12	SW	6	68.2%	64.3%	90.9%	0.5%	0.7%	0.0%
Clinton Dr.	28	SW	6	62.3%	67.8%	84.9%	0.1%	1.9%	0.1%
Clinton Dr.	28	NW	6	61.8%	69.8%	89.7%	0.7%	1.1%	0.4%
Clinton Dr.	20	SW	6	61.7%	66.1%	87.8%	0.2%	1.1%	0.0%
Aldine	28	SW	6	59.5%	75.8%	93.8%	0.0%	0.0%	0.0%
Clinton Dr.	20	NW	6	59.4%	63.3%	86.5%	1.4%	1.9%	0.8%
Deer Park	28	SW	6	56.4%	66.9%	74.3%	0.0%	0.3%	0.1%
Clinton Dr.	12	SW	5	56.2%	62.5%	89.2%	0.8%	1.1%	0.0%
Aldine	28	NE	5	55.8%	81.0%	91.8%	0.0%	0.0%	0.0%
Aldine	20	SW	6	55.6%	73.0%	93.4%	0.0%	0.0%	0.0%
Aldine	12	All	6	55.3%	76.3%	92.5%	1.4%	0.0%	0.0%
Aldine	20	All	6	54.5%	72.7%	91.4%	0.9%	0.4%	0.1%
Aldine	12	SE	6	54.5%	74.4%	93.4%	0.0%	0.0%	0.0%
Aldine	28	All	6	54.3%	68.6%	89.9%	0.9%	3.6%	0.6%
Aldine	12	NE	5	54.0%	85.3%	91.4%	0.0%	0.0%	0.0%
Aldine	20	NE	5	53.7%	83.8%	91.2%	0.0%	0.0%	0.0%
Aldine	20	NW	6	53.6%	81.8%	90.9%	5.7%	0.0%	0.0%
Aldine	12	NW	6	53.6%	81.8%	90.9%	5.7%	0.0%	0.0%
Aldine	28	NW	6	53.6%	81.8%	90.9%	5.7%	0.0%	0.0%
Deer Park	20	SW	6	51.8%	64.6%	71.7%	0.0%	0.0%	0.0%
Clinton Dr.	12	NW	6	51.3%	53.6%	79.4%	4.1%	4.1%	2.0%
Clinton Dr.	28	NW	5	50.7%	72.2%	88.1%	1.1%	1.7%	0.7%
Clinton Dr.	28	SW	5	50.0%	70.4%	83.5%	0.2%	3.1%	0.2%
Aldine	20	SE	6	49.9%	66.1%	88.9%	0.0%	1.0%	0.2%
Aldine	12	SW	6	49.5%	68.9%	92.2%	0.0%	0.0%	0.0%
Clinton Dr.	20	NW	5	49.4%	63.7%	83.8%	2.1%	2.8%	1.2%
Clinton Dr.	20	SW	5	48.7%	67.6%	86.3%	0.3%	1.8%	0.0%
Aldine	28	SE	6	47.7%	58.5%	85.1%	0.8%	7.8%	1.4%
HRM-3 Haden Road	28	NW	6	47.7%	58.5%	85.1%	0.8%	7.8%	1.4%
Clinton Dr.	12	SW	7	47.4%	58.0%	67.9%	0.4%	0.8%	0.0%
Aldine	28	NE	7	46.8%	73.9%	66.4%	0.0%	0.0%	0.0%
HRM-7 Baytown	12	NE	6	46.3%	74.7%	77.1%	0.0%	0.0%	0.0%
Aldine	28	SW	5	46.3%	82.4%	94.2%	0.0%	0.0%	0.0%
Deer Park	28	SW	5	45.8%	76.3%	74.0%	0.0%	0.6%	0.1%
Aldine	12	NE	7	44.7%	75.6%	64.8%	0.0%	0.0%	0.0%
Aldine	20	NE	7	44.4%	74.6%	64.6%	0.0%	0.0%	0.0%
Channel View	12	SW	6	44.0%	62.0%	87.0%	1.8%	6.2%	0.6%

### 3.0 AMBIENT/INVENTORY COMPARISONS

Ratios of PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> in the ambient data were compared with corresponding ratios in the emissions inventory. Processing of the ambient and emissions data needed to develop appropriate “apples to apples” comparison was described in Section 2 above. In the following subsection, we analyze the relative temporal alignment of the ambient and inventory data and summarize ratios in the ambient data and the inventory data. This is followed by a summary of results from direct comparisons of the ambient and inventory ratios. In the final subsection, we present some estimates of how different the ambient/inventory comparisons would have been if MOBILE5 had been used to generate the on-road mobile inventory instead of MOBILE6.

#### 3.1 ANALYSIS OF TEMPORAL PATTERNS

Diurnal profiles of ambient and inventory data were prepared to evaluate the temporal alignment of the diurnal profiles used in the inventory processing relative to the time stamps applied to the ambient data. **Figure 3-1** shows the mean weekday (Monday – Friday) diurnal profile of the sum of all identified hydrocarbon species for each ambient monitoring site.<sup>1,2</sup> Concentrations are generally low at night and increase sharply in the morning in response to input of fresh emissions. Concentrations decrease during the middle of the day as morning commute traffic ends, atmospheric mixing increases in response to the onset of solar heating, and the photochemical cycle starts reacting away the more short-lived species. Concentrations increase again during the early evening as the evening commute kicks in and atmospheric mixing decreases in response to lower solar heat flux. This diurnal pattern in VOC concentrations is typical of most urban locations (e.g., Sather et al., 1997; Sather and Kemp, 1998; Main and O’Brien, 2001). The sharp morning peak is centered at the 6 am LST observation (which represents the 6 – 7 am LST average) at most sites and generally extends from the 5 am through the 7 am observations (i.e., from 5 am – 8 am LST). Concentrations are significantly lower on average in the 8 am observations. The pattern for NO<sub>x</sub> is nearly identical (see **Figure 3-2**).

Hourly emissions profiles for hours 5 – 10 of the Houston inventory are shown in **Figure 3-3** (on-road mobile sources only) and **Figure 3-4** (all sources). Both total NO<sub>x</sub> and CO emissions are close to their morning peaks by hour 7, while total PAMS emissions continue to increase in hours 8 and 9 as the biogenics come into play.<sup>3</sup> On-road mobile emissions of all three species peak in hour 6 with the second highest-levels occurring in hour 7. Analysis of the fraction of the total inventory attributable to mobile sources confirms that the mobile source fraction peaks in hour 6 with the second highest contributions in hours 5 and 7.

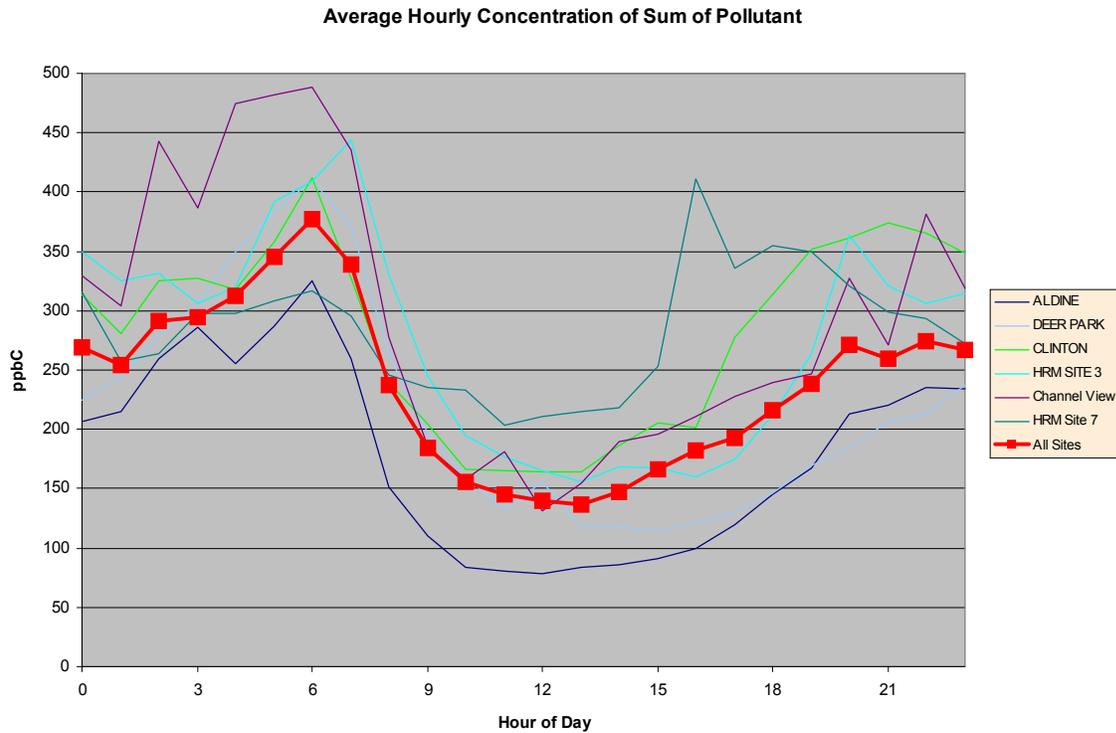
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<sup>1</sup> The Bayland Park monitor is not included in the analysis since the emission inventory provided by TNRCC did not include the area around this site.

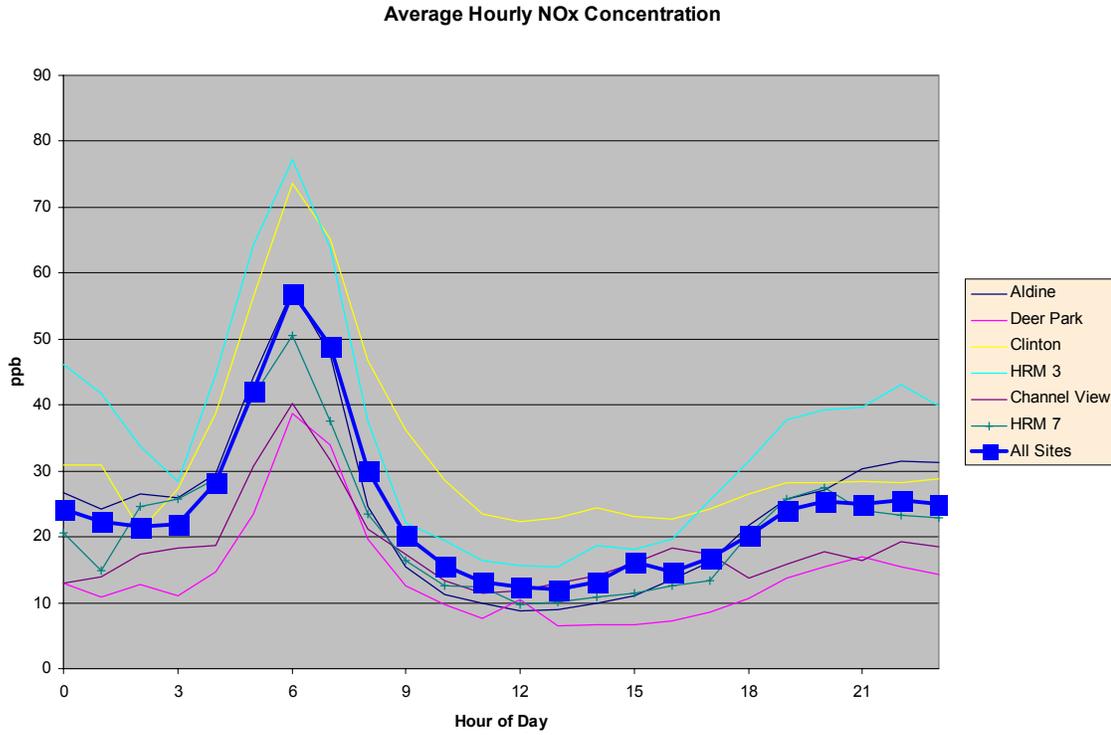
<sup>2</sup> As defined by TNRCC, the “sum of pollutants” measure excludes 1,2,3-trimethylbenzene, m- and p-diethylbenzene, 1,3-butadiene, m-, p-, and o-ethyltoluene, n-decane, and n-undecane.

<sup>3</sup> Biogenic emissions in the Houston inventory are zero until hour 8.

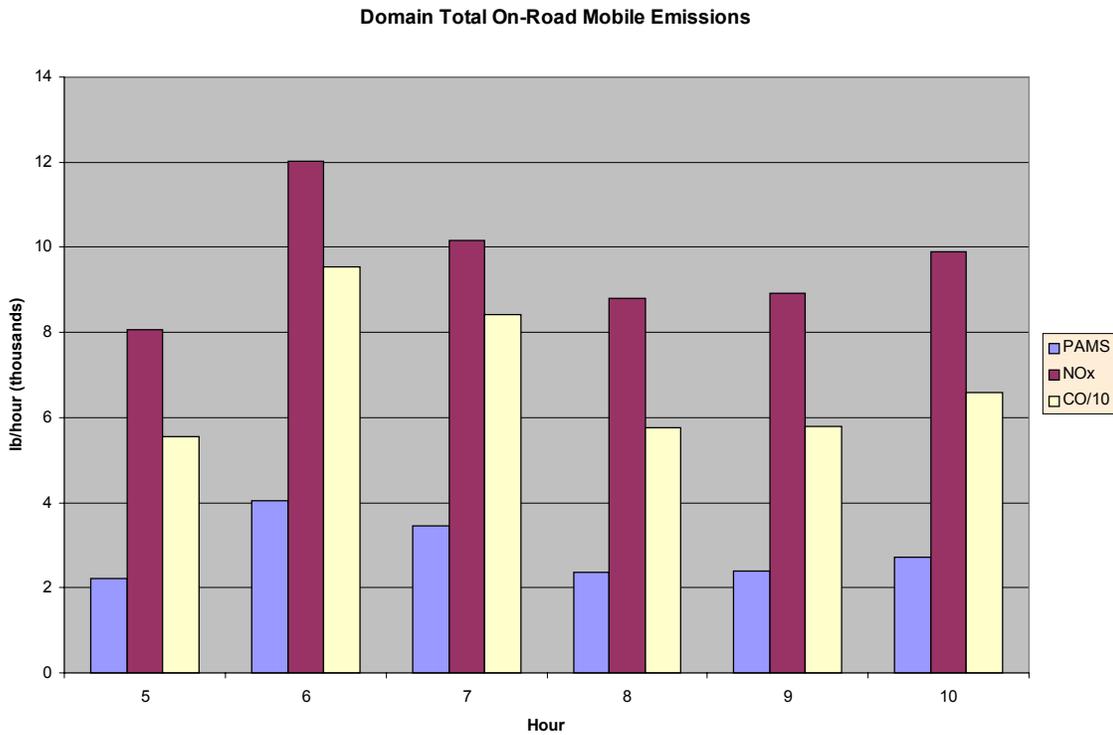
Based on the temporal patterns in ambient and inventory data described above, it appears that the inventory and ambient data are in correct temporal alignment if we assume hour 5 of the inventory corresponds to the ambient sample assigned the 5 am LST time stamp (representing approximately an average over 5 – 6 am LST), and so on. As a result, our comparisons of ambient with inventory ratios will be based on the 5, 6, and 7 am ambient samples and the inventory data for hours 5, 6, and 7.



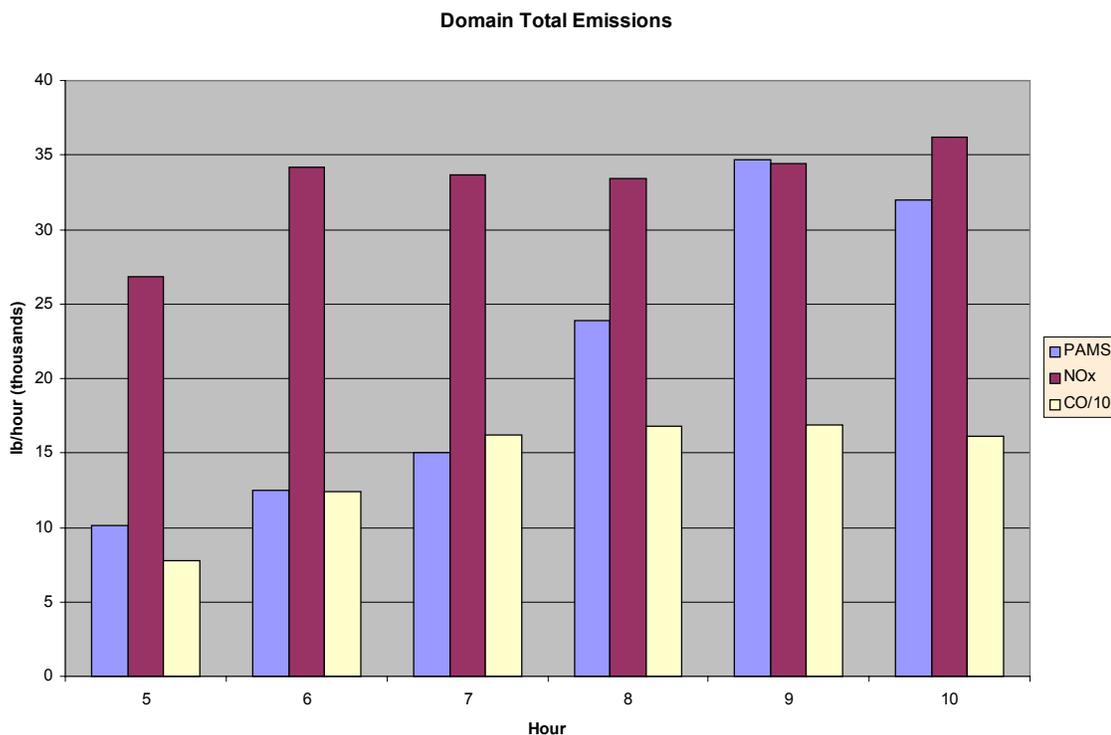
**Figure 3-1.** Average concentration by time of day: sum of identified NMHC.



**Figure 3-2.** Average concentration by time of day: NOx.



**Figure 3-3.** Total emissions by hour of day: on-road mobile sources.



**Figure 3-4.** Total emissions by hour of day: all sources.

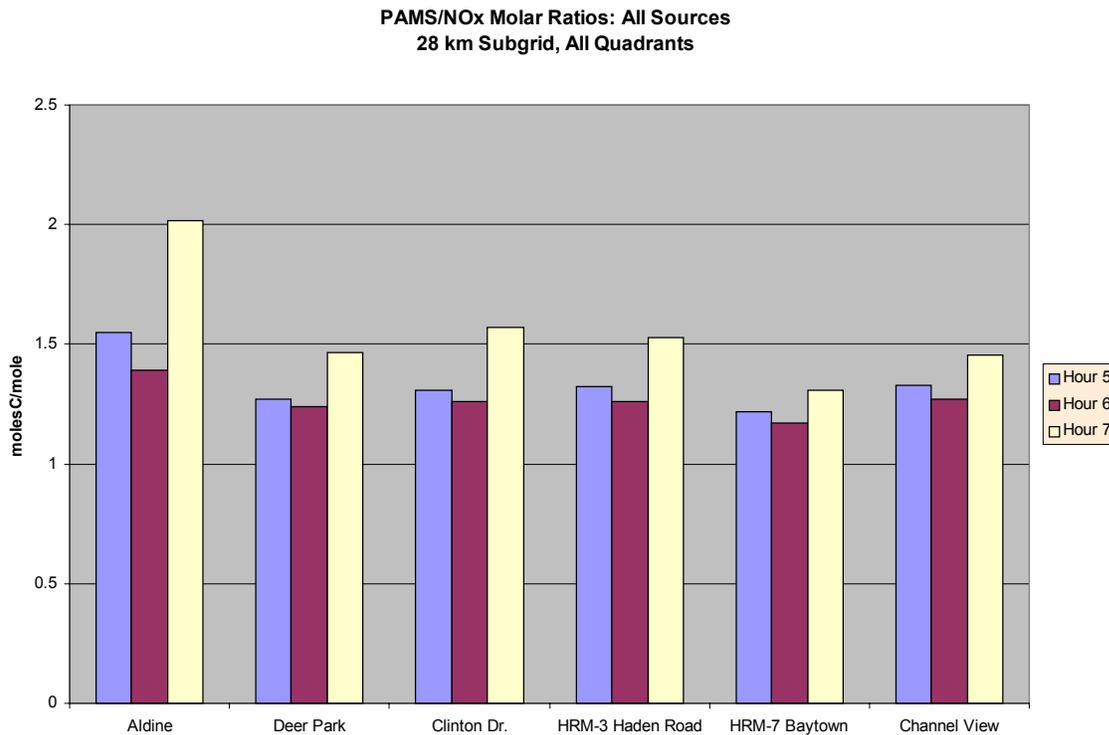
### 3.2 SUMMARY OF EMISSIONS RATIOS

Inventory PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> molar ratios were computed for each quadrant around each ambient monitoring site as described in Section 2 above. For the 28 km subgrids centered on each monitoring site for all source categories combined, the average hourly PAMS/NO<sub>x</sub> ratio for hours 5, 6, and 7 is 2.2 and the average CO/NO<sub>x</sub> ratio is 7.0. Ratios vary widely from hour to hour and between individual quadrants depending on the particular source mix in each quadrant. Since the objective of this study is evaluation of the mobile source component of the inventory, we focussed our attention on quadrants in which emissions are dominated by mobile sources. In Section 2, we identified the 40 quadrants and hours with the highest mobile source PAMS fractions. PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios for these quadrants and hours are listed in **Table 3-1** for both the sum of all source categories and for just the on-road mobile source category. For mobile sources, PAMS/NO<sub>x</sub> ratios average 1.04 with a range of 0.86 to 1.17. Values towards the low end of this range presumably represent areas with a greater than average fraction of heavy-duty diesel activity. Mobile source CO/NO<sub>x</sub> ratios average 12.6 with a range from 11.2 to 13.7. For all source categories combined over the 40 quadrants and hours examined, PAMS/NO<sub>x</sub> ratios range from 1.02 to 1.83 (average = 1.40) and CO/NO<sub>x</sub> ratios range from 7.83 to 16.02 (average = 10.66). PAMS/NO<sub>x</sub> ratios are higher around Aldine than at any of the other sites.

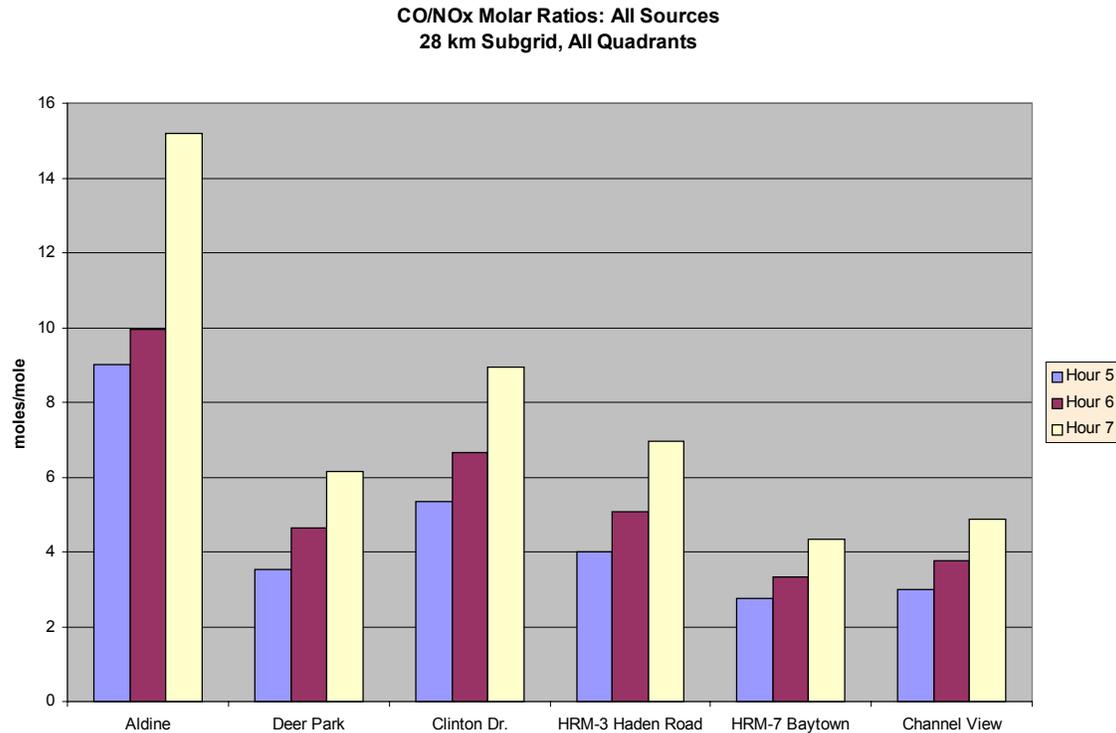
**Table 3-1.** Species ratios at monitoring sites, subgrid length, quadrant and hour of day with the highest mobile source fraction of sum of PAMS species: Total of all source categories and on-road mobile only.

Site	Subgrid Length (km)	Quadrant	Hour	TOTAL		MOBILE	
				PAMS/NO <sub>x</sub>	CO/NO <sub>x</sub>	PAMS/NO <sub>x</sub>	CO/NO <sub>x</sub>
Aldine	28	NE	6	1.26	11.23	1.10	13.16
Aldine	12	NE	6	1.31	11.52	1.09	13.13
Aldine	20	NE	6	1.30	11.41	1.09	13.14
Clinton Dr.	12	SW	6	1.07	9.10	1.13	12.88
Clinton Dr.	28	SW	6	1.28	10.19	1.17	12.76
Clinton Dr.	28	NW	6	1.26	10.10	1.11	12.98
Clinton Dr.	20	SW	6	1.25	9.63	1.16	12.81
Aldine	28	SW	6	1.42	10.52	1.10	13.00
Clinton Dr.	20	NW	6	1.15	9.58	1.08	13.09
Deer Park	28	SW	6	1.38	11.61	1.16	12.88
Clinton Dr.	12	SW	5	1.02	7.83	0.91	11.18
Aldine	28	NE	5	1.31	9.96	0.89	11.30
Aldine	20	SW	6	1.50	10.10	1.13	12.92
Aldine	12	All	6	1.51	10.78	1.08	13.07
Aldine	20	All	6	1.49	10.31	1.10	12.98
Aldine	12	SE	6	1.52	10.33	1.10	12.98
Aldine	28	All	6	1.39	9.94	1.09	13.04
Aldine	12	NE	5	1.40	10.52	0.87	11.28
Aldine	20	NE	5	1.39	10.37	0.88	11.28
Aldine	20	NW	6	1.57	11.91	1.01	13.23
Aldine	12	NW	6	1.57	11.91	1.01	13.23
Aldine	28	NW	6	1.57	11.91	1.01	13.23
Deer Park	20	SW	6	1.44	11.55	1.15	12.83
Clinton Dr.	12	NW	6	1.10	8.89	1.04	13.17
Clinton Dr.	28	NW	5	1.27	9.23	0.88	11.26
Clinton Dr.	28	SW	5	1.32	9.42	0.93	11.17
Aldine	20	SE	6	1.52	9.55	1.13	12.84
Aldine	12	SW	6	1.60	9.68	1.13	12.95
Clinton Dr.	20	NW	5	1.13	8.61	0.87	11.32
Clinton Dr.	20	SW	5	1.30	8.73	0.93	11.16
Aldine	28	SE	6	1.36	8.92	1.10	12.99
HRM-3 Haden Road	28	NW	6	1.36	8.92	1.10	12.99
Clinton Dr.	12	SW	7	1.39	11.52	1.13	13.49
Aldine	28	NE	7	1.74	15.27	1.09	13.73
HRM-7 Baytown	12	NE	6	1.44	12.69	0.88	13.09
Aldine	28	SW	5	1.56	9.85	0.86	11.27
Deer Park	28	SW	5	1.58	11.60	0.94	11.25
Aldine	12	NE	7	1.83	16.02	1.07	13.73
Aldine	20	NE	7	1.82	15.86	1.08	13.73
Channel View	12	SW	6	1.35	9.22	0.95	12.93
			<b>Avg</b>	1.40	10.66	1.04	12.64
			<b>Max</b>	1.83	16.02	1.17	13.73
			<b>Min</b>	1.02	7.83	0.86	11.16

Hourly variations in PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> emission ratios are shown in **Figures 3-5** and **3-6**, respectively, for the 28 km subgrids (all quadrants) around each monitoring site. PAMS/NO<sub>x</sub> ratios are lowest in hour 6 (when cold-start mobile source impacts are at their peak) and highest in hour 7 (when evaporative emissions start to become more important). Hour 6 ratios average approximately 1.3 but are slightly higher at Aldine. CO/NO<sub>x</sub> ratios increase steadily from hour 5 to 6 to 7 and are significantly higher at Aldine than at the other sites. Examination of the inventory indicates that ratios are higher at Aldine primarily because there is less NO<sub>x</sub> from point and area sources around this location than around the other sites.



**Figure 3-5.** PAMS/NO<sub>x</sub> molar ratios: all sources, 28 km subgrid, all quadrants.



**Figure 3-6.** CO/NO<sub>x</sub> molar ratios: all sources, 28 km subgrid, all quadrants.

### 3.3 SUMMARY OF AMBIENT RATIOS

Ambient VOC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios for weekdays were summarized for observation times 5, 6, and 7 am. Average hourly ratios at each monitoring site aggregated by resultant wind direction and over all directions are presented in **Table 3-2** along with bootstrap 95% confidence intervals for the mean ratios over all directions. Wind direction data are not available for the HRM 3 and HRM 7 sites; CO data are not available for either of these sites nor at Channel View. Ratios of the Sum of PAMS species to NO<sub>x</sub> vary widely, from a minimum of 3.8 under SW and NW winds at Clinton Drive to a maximum of 18.7 under SE winds at Channel View. Average ambient CO/NO<sub>x</sub> ratios vary from a minimum of 7.7 under SW winds at Clinton Drive to a maximum of 37.1 under SW winds at Deer Park.

**Table 3-2.** Mean hourly ratios computed from ambient monitoring data (weekdays, 5 - 7 am LST).

Site	Wind Direction	PAMS/NO <sub>x</sub>		CO/NO <sub>x</sub>	
		Mean	95% Conf. Int.	Mean	95% Conf. Int.
Aldine	NE	5.2		14.4	
	SE	6.6		13.1	
	SW	6.0		21.4	
	NW	4.7		15.4	
	ALL	5.6	(5.2, 6.1)	15.4	(14.6, 16.4)
Clinton Drive	NE	8.7		11.9	
	SE	18.4		10.5	
	SW	3.8		7.7	
	NW	3.8		10.1	
	ALL	7.3	(6.6, 8.7)	10.0	(9.5, 10.6)
Deer Park	NE	15.8		27.0	
	SE	9.8		28.3	
	SW	8.1		37.1	
	NW	11.0		30.0	
	ALL	12.0	(11.2, 13.0)	29.9	(28.39, 31.52)
Channel View	NE	15.1		NA	
	SE	18.7		NA	
	SW	12.8		NA	
	NW	9.4		NA	
	ALL	14.5	(12.15, 17.70)	NA	
HRM 3	ALL	8.48	(7.34, 10.38)	NA	
HRM 7	ALL	9.19	(7.69, 11.03)	NA	

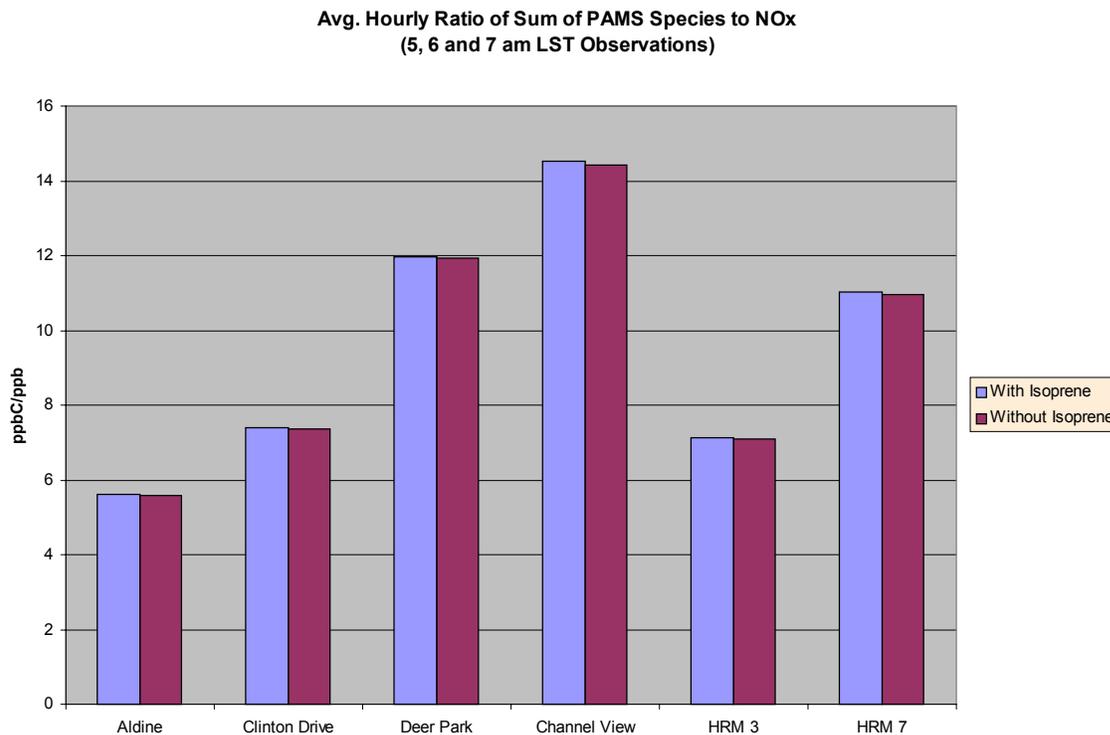
During the mid-day period, biogenics can be an important source of VOCs in Houston but biogenics are expected to have minimal impact on observations taken during the 5 – 8 am period (i.e., the 5, 6, and 7 am LST observations). Of the 54 PAMS species included in the Houston ambient measurements, isoprene is the only biogenic. To verify that biogenics are not a significant contributor to early morning VOCs, we compared ratios of the sum of PAMS to NO<sub>x</sub> with isoprene included to the same ratios with isoprene excluded. Results of this comparison for hourly ratios averaged over the 5, 6, and 7 am LST observations (see **Figure 3-7**) confirm the lack of any significant biogenic impacts during this period.

Ratios of PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> are summarized by hour of day for the 5, 6, and 7 am LST observation times in **Figures 3-8** and **3-9**. These results are averages over all weekday data meeting the minimum PAMS and NO<sub>x</sub> concentration cutoffs (100 ppbC and 10 ppb, respectively) as described in Section 2 above, regardless of wind direction.

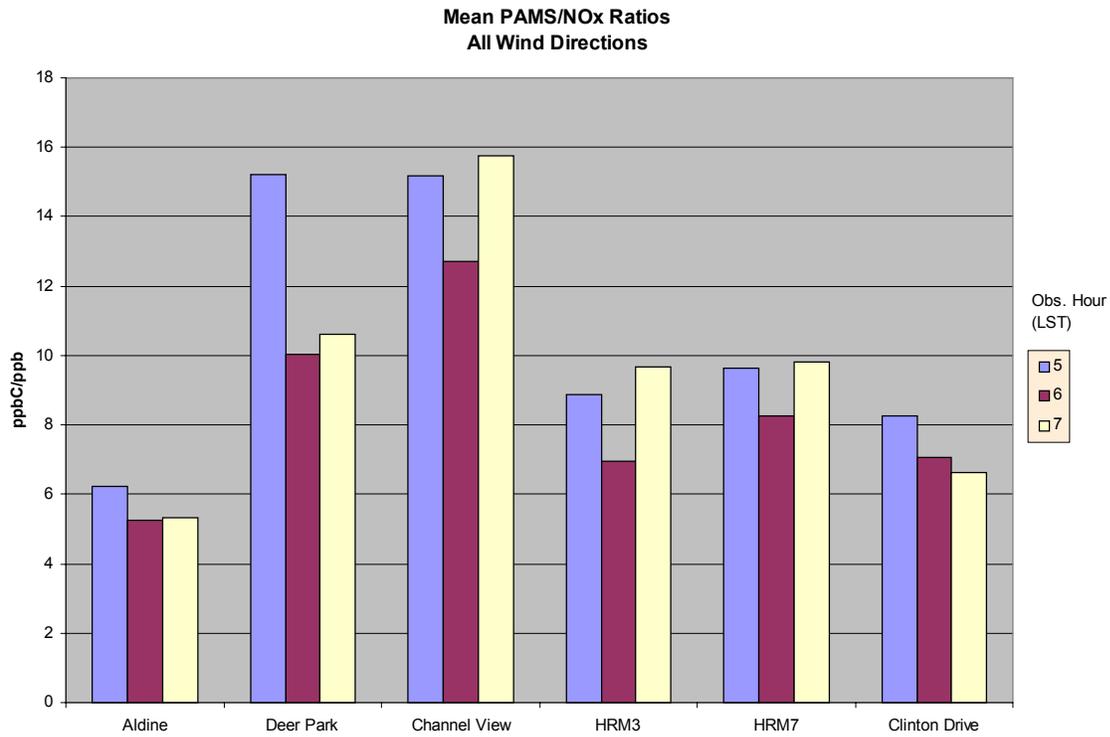
PAMS/NO<sub>x</sub> ratios are lowest at Aldine and vary comparatively little from hour to hour; ratios at the other sites are larger and exhibit more hour-to-hour variability. CO/NO<sub>x</sub> ratios vary little between the 5, 6 and 7 am observations at Aldine and Clinton Drive. As described in the following subsection, the gridded emission inventory data show that the area around the Aldine monitor is dominated by mobile sources in all quadrants whereas the other sites show lower mobile source contributions overall and a greater heterogeneity in mobile source contributions with respect to wind direction.

At Clinton Drive, the SW and NW quadrants have much higher mobile source contributions in the inventory as compared to NE and SE. Similarly, at Deer Park, the SW quadrant has relatively high mobile source contributions as compared to other quadrants. Direction-specific mobile source contributions are relatively smaller at all of the other monitoring sites.

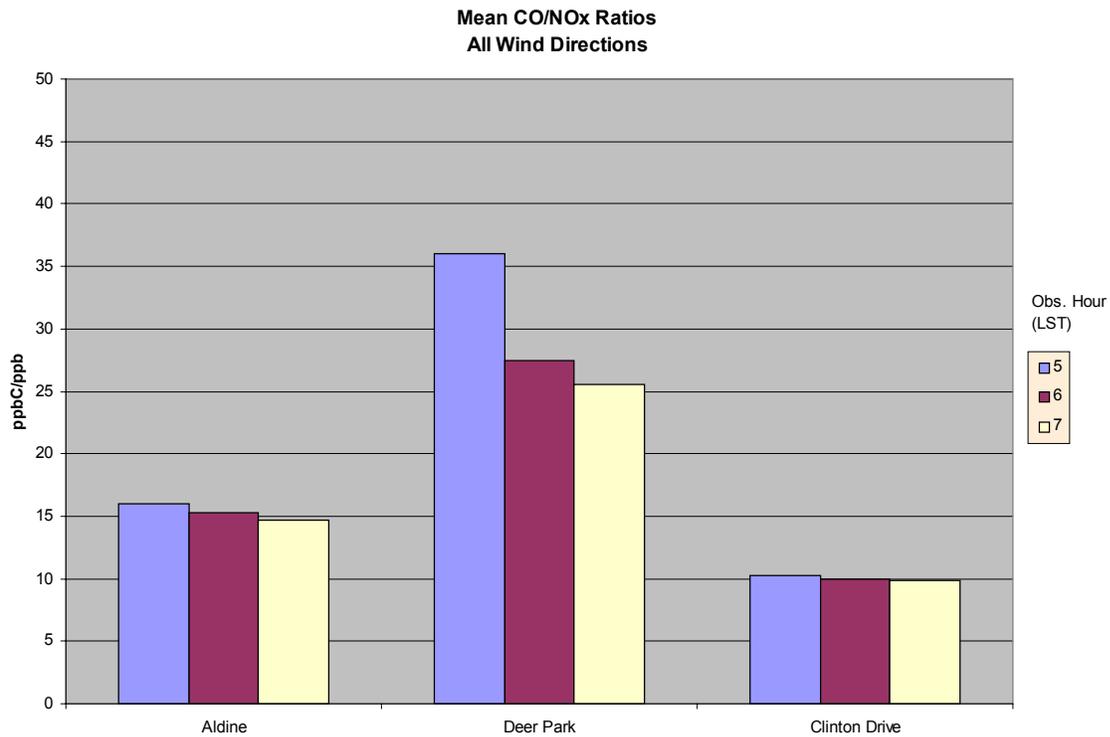
**Figures 3-10 and 3-11** compare mean hourly PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios, respectively, calculated for all wind directions at Aldine but for just SW and NW directions at Clinton Drive and SW winds at Deer Park. Hour-to-hour variations are small at Aldine and Clinton Drive but vary more at Deer Park. Both PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios at Clinton Drive under NW and SW winds are the lowest of any values shown in **Figures 3-8 through 3-11**.



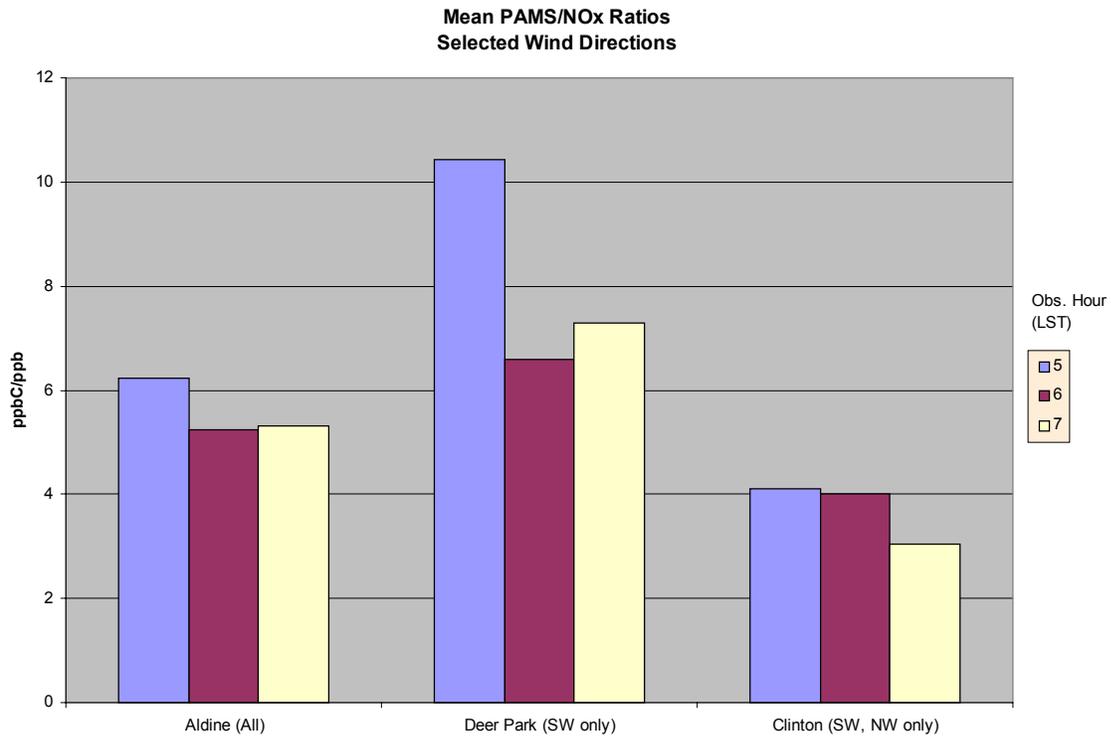
**Figure 3-7.** Average of 5, 6, 7 am LST PAMS/NO<sub>x</sub> ratios at each monitoring site.



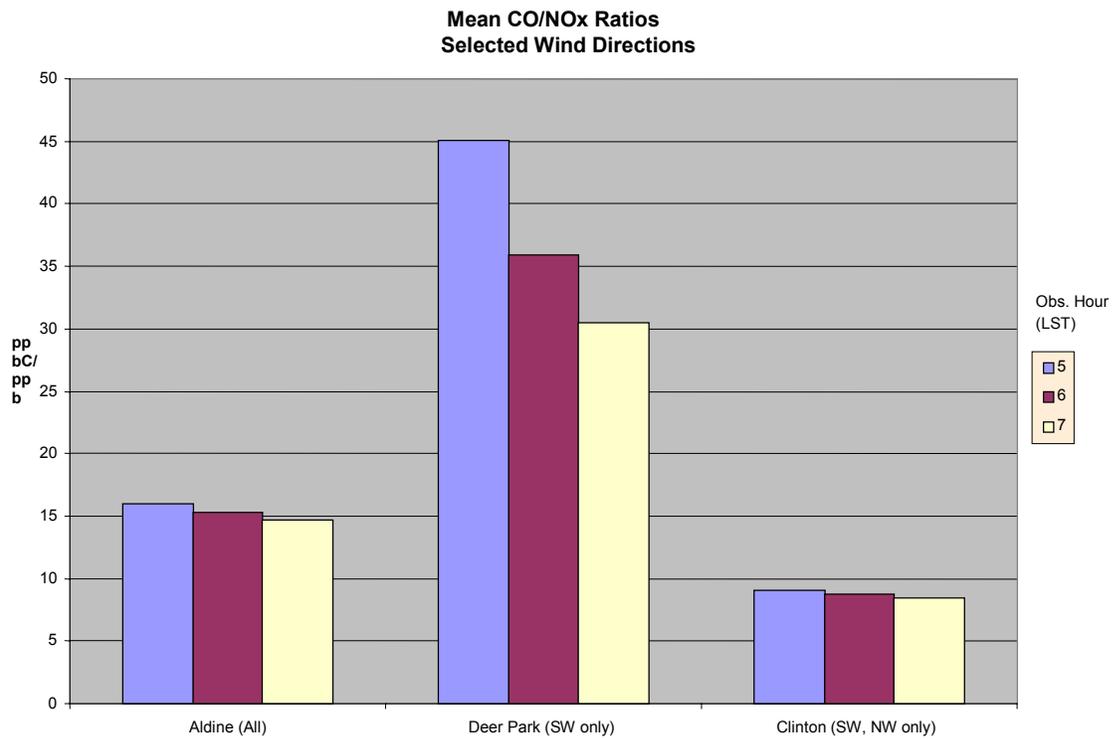
**Figure 3-8.** Average PAMS/NOx ratio by hour at each monitoring site.



**Figure 3-9.** Average CO/NOx ratio by hour at each monitoring site: all wind directions.



**Figure 3-10.** Average PAMS/NOx ratio by hour under selected resultant wind directions.



**Figure 3-11.** Average CO/NOx ratio by hour under selected resultant wind directions.

Generally speaking, there is a difference between an average of hourly ratios (such as those described above) and a ratio of hourly averages. Averages of hourly ratios are useful to our analysis because each ratio can be associated with a particular wind direction. To explore the potential difference between an average of ratios versus a ratio of averages, we compared the ratios described in the previous paragraph with ratios of the 5 – 7 am average PAMS to the 5 – 7 am average NO<sub>x</sub> (and the 5 – 7 am average CO to the 5 – 7 am average NO<sub>x</sub>). These calculations were made only for Aldine since this is the only site where mobile sources dominate in all directions as discussed above. **Table 3-3** lists the average PAMS, NO<sub>x</sub> and CO concentrations at Aldine for weekday mornings, 5 – 8 am along with ratios of the averages.<sup>4</sup> **Table 3-4** lists summary statistics for the daily ratios of morning (5 – 8 am) average PAMS to morning average NO<sub>x</sub> and morning average CO to morning average NO<sub>x</sub>. In the case of the PAMS/NO<sub>x</sub> ratios, the ratio of overall averages in Table 3-3 (5.30) is very close to the mean of the daily morning ratios shown in Table 3-4 (5.39) and to the mean of the hourly ratios for Aldine (all quadrants) listed in Table 3-2 (5.60). Similarly, for CO/NO<sub>x</sub>, the ratio of overall averages (13.92) is similar to the mean of the daily morning ratios (15.28) and to the mean of the hourly ratios (15.4). Thus, on average the ratio of means is similar to mean ratio for both PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub>.

**Table 3-3.** Summary of ratios of average concentrations at Aldine (averages are for weekdays, 5 – 8 am, 1999-2001; days with two or more hours with Sum of PAMS < 100 ppbC or NO<sub>x</sub> < 10 ppb excluded).<sup>5</sup>

Avg. Sum of PAMS	302.2 ppbC
Avg. NO <sub>x</sub>	57.0 ppb
Avg. CO	768.5 ppb
Avg. Sum of PAMS / Avg. NO <sub>x</sub>	5.30
Avg. CO / Avg. NO <sub>x</sub>	13.92

**Table 3-4.** Summary of daily ratios of morning (5 – 8 am) average sum of PAMS to morning average NO<sub>x</sub> and morning average CO to morning average NO<sub>x</sub> at Aldine.

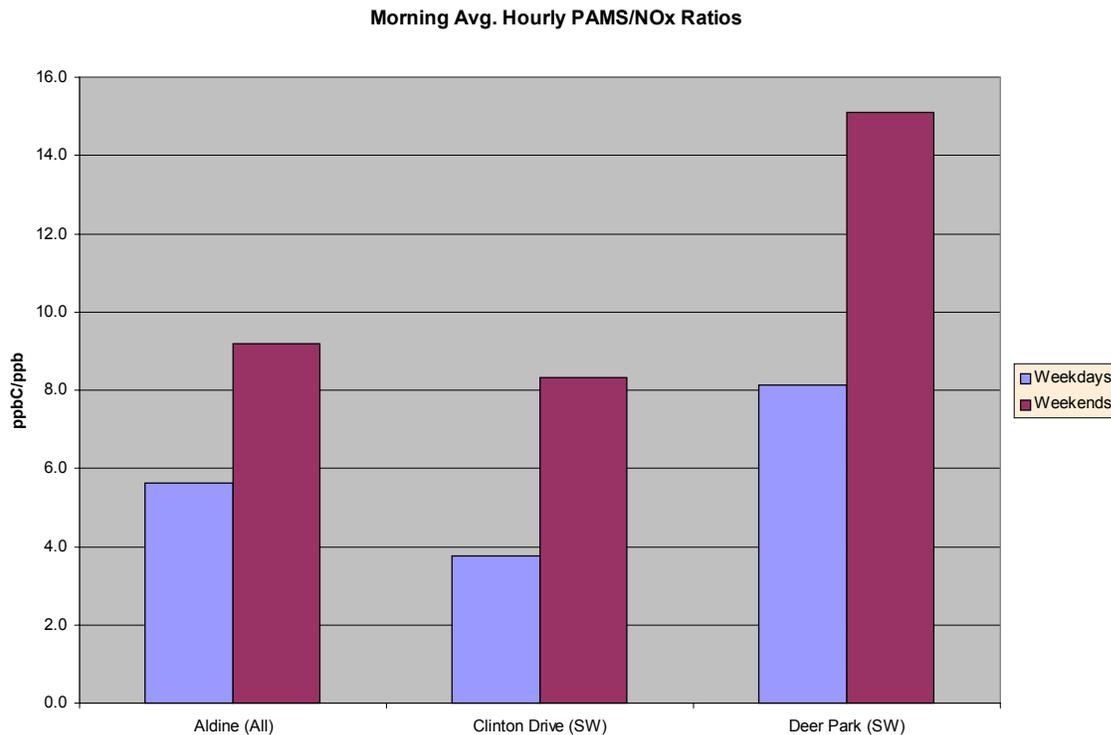
	Mean	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
PAMS/NO <sub>x</sub>	5.39	3.83	5.01	5.91
CO/NO <sub>x</sub>	15.28	12.25	14.48	18.52

Ratios of PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> summarized above are for weekday (Monday – Friday) observations only since the emission inventory supplied by the TNRCC is for an average weekday. Ratios on weekends will generally differ from weekday ratios as a result of changes in the source mix (vehicle fleet mix, stationary source shutdowns on weekends, etc.). **Figures**

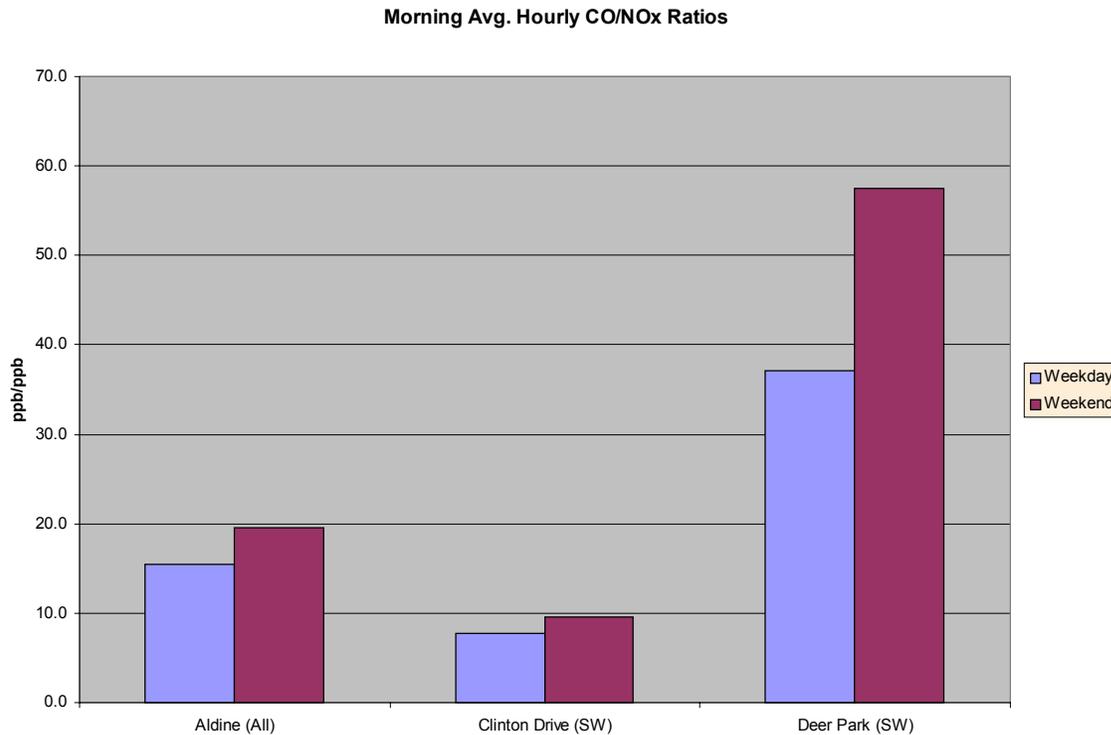
<sup>4</sup> Average concentrations used to form the ratios are averages over only days in which valid values are available for both the species in the numerator and in the denominator of the ratio whereas the averages of each individual species are taken over all days with valid values for that species. A daily average is considered valid if values meeting the minimum concentration thresholds (100 ppbC for PAMS and 10 ppb for NO<sub>x</sub>) are available for two of the three hours making up the 5 – 8 am average.

<sup>5</sup> Averages shown in the first three rows of this table differ slightly from the averages used to compute the ratios in the last two rows due to missing data.

**3-12** and **3-13** compare weekday and weekend ratios of PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub>, respectively, for the Aldine monitor (all wind directions) and for observations under SW winds at Clinton and Deer Park. As discussed above, observations at these location and under these wind directions are most heavily impacted by mobile sources according to the emissions inventory. As expected, both PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios are higher on weekends. This is most likely associated with reduced NO<sub>x</sub> emissions on weekends as a result of less heavy-duty truck traffic and less weekend stationary combustion source activity. Inventory data representative of weekend emissions in Houston are currently unavailable, so comparisons with these ambient ratios will have to be put off to a future study.



**Figure 3-12.** Morning (5 – 8 am LST) average PAMS/NO<sub>x</sub> ratios under selected wind directions on weekdays and weekends.



**Figure 3-13.** Morning (5 – 8 am LST) average CO/NO<sub>x</sub> ratios under selected wind directions on weekdays and weekends.

### 3.4 COMPARISON OF EMISSIONS AND AMBIENT RATIOS

Ambient PAMS/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios were compared with corresponding emissions ratios for the 40 emissions quadrants with the highest mobile source PAMS fractions by computing the so-called “ratio of ratios”: ambient PAMS/NO<sub>x</sub> divided by inventory PAMS/NO<sub>x</sub> and ambient CO/NO<sub>x</sub> divided by inventory CO/NO<sub>x</sub>. Results are summarized in **Table 3-5** for PAMS/NO<sub>x</sub> and **Table 3-6** for CO/NO<sub>x</sub>. Quadrants with the highest mobile source contributions to total VOC in the inventory as discussed in Section 2 above are shaded in these two tables. For these quadrants, ambient PAMS/NO<sub>x</sub> ratios exceed inventory ratios by roughly a factor of 3:1 while the ambient CO/NO<sub>x</sub> ratios are within  $\pm 30\%$  of the inventory ratios, except at Deer Park where the ambient CO/NO<sub>x</sub> ratio exceeds the inventory CO/NO<sub>x</sub> ratio by a factor of 3:1 or more. It is useful to note that point source emissions in the vicinity of Deer Park are a significant fraction of the inventory in the NE and SE quadrants. The presence of point sources in this area may have something to do with the greater discrepancy in the CO/NO<sub>x</sub> ratio at Deer Park.

**Table 3-5.** Average hourly ratio of ratios (ratio of ambient PAMS/NO<sub>x</sub> to emissions PAMS/NO<sub>x</sub>) by site and quadrant (quadrants in which mobile sources represent a substantial fraction of the total inventory are shaded).

Site	Quadrant				
	All	NE	NW	SE	SW
Aldine	3.1	3.5	2.4	3.7	3.2
Channel View	11.7	18.5	5.7	13.7	7.6
Clinton Dr.	5.1	5.8	2.9	12.3	2.8
Deer Park	8.9	12.3	6.7	14.2	4.4

**Table 3-6.** Average hourly ratio of ratios (ratio of ambient CO/NO<sub>x</sub> to emissions CO/NO<sub>x</sub>) by site and quadrant (quadrants in which mobile sources represent a substantial fraction of the total inventory are shaded).

Site	Quadrant				
	All	NE	NW	SE	SW
Aldine	1.3	1.2	1.2	1.2	1.7
Channel View	N/A	N/A	N/A	N/A	N/A
Clinton Dr.	1.6	1.8	1.0	3.4	0.7
Deer Park	7.6	11.9	7.2	9.5	2.9

Various factors may contribute to the discrepancy noted above in PAMS/NO<sub>x</sub> ratio between the ambient measurements and inventory estimates. Of particular interest is the degree to which any errors in speciation of the VOC emissions predicted via application of the MOBILE model into component species may impact the comparison. As noted in Section 2 above, for the inventory as a whole, the PAMS species accounted for 67% of the total inventory TNMHC on a mass basis. For just on-road mobile sources, the corresponding fraction is 64%. Thus, an upper bound on the “actual” inventory PAMS/NO<sub>x</sub> ratio for areas that are dominated by mobile source emissions would be approximately 1.56 times the PAMS/NO<sub>x</sub> ratios computed for this study ( $1.56 = 1/0.64$ ). Using this upper bound on the emissions ratio would reduce the ratio of ratios shown in Table 3-5 by this factor: the ratio of ratios averaged over the mobile source dominated quadrants identified by the shaded entries in this table (excluding the high value at Deer Park) would be reduced from 2.9 to 1.9. Thus the ambient PAMS/NO<sub>x</sub> ratio is still at least double the inventory ratio.

### 3.5 COMPARISON OF RESULTS USING MOBILE5 VS MOBILE6

MOBILE6 represents a significant change from the previous version of MOBILE (MOBILE5b). This raises the question of what impact the model revisions have on VOC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios. TNRCC previously developed a 1999 inventory for Houston using MOBILE5b and has grown this inventory to be representative of the August 2000 episode. Summaries of this inventory and the MOBILE6 inventory used in our study are presented in a technical support document to the Houston-Galveston SIP (TNRCC, 2002). **Table 3-7** compares emission totals from the two inventories for Harris County. *Unfortunately, the MOBILE5 inventory is based on VMT estimates from an older set of travel demand model*

outputs than were used for the new MOBILE6 inventory, thus confounding comparisons between the two inventories. Although VOC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios computed for each inventory are independent of total VMT, these ratios are quite sensitive to differences in the distribution of VMT by vehicle and roadway type. Since different VMT allocations were used for each of these inventories, this will impact comparisons of the emission ratios. Based on the results in Table 3-7, it would appear that MOBILE6 total inventory VOC/NO<sub>x</sub> ratios are about 20% higher than in MOBILE5b while MOBILE6 CO/NO<sub>x</sub> ratios are about double the MOBILE5 values.<sup>6</sup>

EPA Region VI has completed a comparison of MOBILE5 vs. MOBILE6 based emission inventories for 1999 for the four county Dallas-Ft. Worth nonattainment area (Behnam, 2001). This comparison was deliberately designed to use, to the maximum practical extent, the same sets of input parameters for both versions of MOBILE. Thus, the Dallas comparison provides a clearer picture of the differences between the two models than the Houston comparison described above. On the other hand, differences between the two versions of MOBILE in estimated VOC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios in Dallas are not necessarily the same as in Houston due to differences in fleet mix and VMT distributions between the two cities. Furthermore, the Dallas study used an earlier, draft version of MOBILE6 which preceded the officially released version used to generate the current Houston inventory. Nevertheless, the Dallas study does provide another data point for comparing MOBILE5 with MOBILE6. Results from the Region VI study are summarized in **Table 3-8**. Total inventory VOC/NO<sub>x</sub> ratios are about the same for the two versions of MOBILE and the MOBILE6 ratio is very similar to the Houston MOBILE6 VOC/NO<sub>x</sub> ratio shown in Table 3-7. CO emission totals were not included in the Region VI report. Although far from definitive, these results suggest that the inventory total VOC/NO<sub>x</sub> ratio is not strongly impacted by the move from MOBILE5 to MOBILE6: the 20% difference seen in Houston may have at least as much to do with the different VMT allocations as with differences in formulation between the two versions of the model. It is not possible to conclude anything about differences in CO/NO<sub>x</sub> ratios from these results.

**Table 3-7.** Summary of MOBILE5b and MOBILE6 inventories for the 8/30/2000 episode day for Harris County.<sup>7</sup> (Source: TNRCC, 2001)

	MOBILE5b	MOBILE6
VMT	89,631,427	91,855,778
VOC (tons/day)	102.5	107.9
NO <sub>x</sub> (tons/day)	209.2	177.0
CO (tons/day)	790.7	1459.6
VOC/NO <sub>x</sub> (ton/ton)	0.49	0.61
CO/NO <sub>x</sub> (ton/ton)	3.8	8.25

<sup>6</sup> Note that these ratios are mass based and therefore cannot be compared directly with the molar emission ratios described elsewhere in this document.

<sup>7</sup> **Important Note:** Emissions shown in this table for the MOBILE 5b inventory are based not only on a different estimate of total VMT compared to the MOBILE 6 inventory but also on a different distribution of VMT by vehicle type and roadway classification. This, differences in VOC/NO<sub>x</sub> and CO/NO<sub>x</sub> ratios are due not only to differences in the MOBILE model formulation but also differences in VMT distribution.

**Table 3-8.** Summary of 1999 MOBILE5b and MOBILE6 inventories for the Dallas – Ft. Worth nonattainment area. (Source: Behnam, 2001)

	<b>MOBILE5b</b>	<b>MOBILE6</b>
VMT	117,172,669	117,172,669
VOC (tons/day)	137.02	195.4
NOx (tons/day)	196.28	311.5
VOC/NOx (ton/ton)	0.70	0.63

## 4.0 SUMMARY AND CONCLUSIONS

### 4.1 SUMMARY

Results presented in Section 3 indicate a discrepancy in NMHC/NO<sub>x</sub> ratios between emission inventory estimates and ambient air samples in locations in Houston where on-road mobile sources dominate the inventory. For weekday morning ambient samples collected at monitoring sites and under wind directions for which mobile sources are estimated to have their peak impact, the ambient PAMS/NO<sub>x</sub> ratio exceeds the inventory ratio by a factor of 2.9, on average (excluding the relatively high ratios at Deer Park) with a range of 2.8 to 3.7. In contrast, the average ratio of ambient CO/NO<sub>x</sub> to inventory CO/NO<sub>x</sub> is equal to 1.0 (again excluding the much larger average value of 2.9 observed at Deer Park). Ambient samples collected at Deer Park are more likely to exhibit intermittent impacts of large point sources than is the case at the other sites, thus complicating the ambient/inventory comparisons.

The discrepancy between ambient and inventory PAMS/NO<sub>x</sub> ratios (and by extension, NMHC/NO<sub>x</sub> ratios) noted above may be due to one or more factors, including:

- NMHC emissions may be under estimated in the inventory and/or NO<sub>x</sub> emissions may be over estimated. If NO<sub>x</sub> emissions are overestimated, then CO emissions would also have to be overestimated by nearly the same factor since the inventory CO/NO<sub>x</sub> ratios were found to closely match the ambient ratios. NO<sub>x</sub> emission factors for on-road mobile sources are generally regarded as being subject to less uncertainty than hydrocarbon emission factors, further decreasing the likelihood of significant overestimation of inventory NO<sub>x</sub>. On the other hand, a recent analysis of tunnel study data by Tran et al. (2002) suggests that MOBILE6 tends to overestimate CO emissions.
- The speciation of HC emissions may be in error, causing a bias in the sum of PAMS target compound emission estimates used in the ambient/inventory comparison. As noted in the previous section, the upper bound impact of such speciation errors would be at most to reduce the discrepancy in PAMS/NO<sub>x</sub> ratios from a factor of 3 to a factor of 2 so speciation errors cannot by themselves fully account for the observed discrepancy although they may contribute to it.
- Ambient NO<sub>x</sub> concentrations may be lower than they would otherwise be due to chemical reactions between the time of emission and when material is observed at the monitoring site. The rate of reaction is sensitive to ambient ozone and hydroxyl radical mixing ratios and temperature. However, loss of NO<sub>x</sub> to NO<sub>z</sub> should be minimal during the early morning, high emission periods focussed on in our analysis and the ambient NO<sub>x</sub> measurements are typically biased high because some of the NO<sub>z</sub> is included in the reported NO<sub>x</sub>.
- Air parcels sampled at the monitoring site may represent a different source mixture than is contained in the area-wide average emission inventory. This is particularly important for NO<sub>x</sub> emissions from elevated sources such as power plant smoke stacks since the extent to which smoke stack plumes mix to the ground at the monitoring site is highly variable. However, point source emissions were found to be a very small component of the inventory for the locations and wind directions identified as "mobile source dominated" in our analysis and in which the discrepancy between ambient and inventory NMHC/NO<sub>x</sub>

noted above is observed. Inventory on-road mobile PAMS/NO<sub>x</sub> ratios are relatively constant across the 40 emission quadrants/hours with the highest mobile source contributions, averaging 1.04 during the morning hours with a range of 0.86 – 1.17. Inventory area plus off-road source PAMS/NO<sub>x</sub> ratios are higher and more variable. Nevertheless, inventory total PAMS/NO<sub>x</sub> ratio still only average 1.40 with a range of 1.02 – 1.83.

- NMHC may accumulate at lower levels overnight to a greater extent than NO<sub>x</sub> and emissions from NMHC rich sources outside the emission source sectors considered in this analysis may travel far enough overnight to impact the monitoring sites. Overnight NMHC concentrations are high in Houston, averaging about 275 ppbC.
- Errors may occur in the ambient measurements due to concentrations below instrumentation detection limits, calibration errors, etc. We sought to minimize problems with detection limits by restricting the ambient samples analyzed to those with PAMS mixing ratios greater than 100 ppbC and NO<sub>x</sub> greater than 10 ppb.
- Errors in mobile source emission ratios may not be due solely to errors in mobile source emission factors but also to errors in activity data and the spatial and temporal allocation of activity. Examples include the fleet mix, cold start fractions, and diurnal VMT patterns by vehicle type.

Of course, the discrepancies between ambient and inventory PAMS/NO<sub>x</sub> ratios noted above may be due to errors in characterization of area and off-road source emissions as well as on-road mobile source emissions. Even for emission quadrants/hours dominated by on-road mobile sources, area plus off-road sources account for between one third and one half of total PAMS emissions from all source categories. Thus, errors in area and off-road source emission ratios can significantly impact the ambient/inventory comparisons described above.

## 4.2 CONCLUSIONS

NMHC/NO<sub>x</sub> ratios reported in the Houston August, 2000 inventory are about a factor of three less than ratios observed in the ambient air while CO/NO<sub>x</sub> ratios generally agree to within  $\pm 30\%$ . This discrepancy in NMHC/NO<sub>x</sub> ratios most likely indicates a significant problem with the inventory which requires further investigation. Although the ambient/inventory comparisons presented here were limited to situations in which on-road mobile source contributions to inventory total emissions are maximized, the contribution of area sources is still fairly significant, especially for NMHC. As a result, errors in area source NMHC/NO<sub>x</sub> ratios could be contributing to the this discrepancy and it is not possible to determine to what extent the on-road mobile source estimates by themselves are in error. It is also not possible to determine from these results if the MOBILE6 emission factors themselves are incorrect or if there is a problem with the mobile source activity data.

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