APPENDIX D –

Emissions Inventory Evaluation by Sonoma Technology, Inc.

Sonoma Technology, Inc.
Air Quality Research and Innovative Solutions

A Top-Down Emissions Inventory Evaluation for the Upper Midwest

Final Report

Prepared for
National Renewable Energy Laboratory
Golden, CO

May 2011

A Top-Down Emissions Inventory Evaluation for the Upper Midwest

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Cover graphic illustrates the locations of monitoring sites included in the top-down emissions inventory evaluation. See Section 1 for more information.

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Glossary

Term	Definition
AQS	Air Quality System – the U.S. Environmental Protection Agency's repository of ambient air quality data
CAMx	Comprehensive Air Quality Model with extensions
CO	Carbon monoxide
CONCEPT	Consolidated Community Emissions Processing Tool
DRI	Desert Research Institute
EGU	Electrical generating units
EPA	Environmental Protection Agency
HC	Hydrocarbon
LADCO	Lake Michigan Air Directors Consortium
MIR	Maximum incremental reactivity
NO	Nitric oxide
NO_x	Oxides of nitrogen
NREL	National Renewable Energy Laboratory
PAMS	Photochemical Assessment Monitoring Stations
PAMSHC	Hydrocarbon species measured at Photochemical Assessment Monitoring Stations
PAR	Paraffin carbon bond
PMF	Positive matrix factorization
ppb	Parts per billion
ppbC	Parts per billion carbon
TNMOC	Total nonmethane organic compounds
VOC	Volatile organic compounds
VOCDat	Volatile Organic Compound Data Validation and Analysis Software

1. Introduction

The Health Impacts Program of the National Renewable Energy Laboratory (NREL) is responsible for quantifying the effects of new vehicle technologies and fuels on air quality and human health and, as such, is interested in the quality of on-road mobile source emissions inventories. Under funding from the U.S. Department of Energy Office of Vehicle Technologies through NREL, Sonoma Technology, Inc. (STI) performed a top-down evaluation of the 2005 and 2008 emissions inventories that the Lake Michigan Air Directors Consortium (LADCO) is using to conduct regional air quality modeling in the Upper Midwest, with a special focus on the on-road mobile source component of the inventories.

Several techniques can be used to evaluate the accuracy and representativeness of any emissions inventory that is intended for use in air quality modeling: "common sense" review of the data; bottom-up evaluations that start with emissions activity data to estimate corresponding emissions; and top-down evaluations that compare emissions estimates to ambient air quality data or use ambient data to estimate emissions profiles. As a top-down emissions inventory evaluation, the work described in this report was focused on comparing the LADCO emissions inventories to ambient monitoring data collected at four urban areas in the region of interest: Chicago, Illinois; Milwaukee, Wisconsin; Gary, Indiana; and Detroit, Michigan. The goals of the project were to identify areas of agreement and differences between the ambient data and emissions inventories, to identify areas of the emissions inventories that may need improvement, and to demonstrate the usefulness of top-down emissions inventory evaluation techniques.

The basic approaches used to perform the top-down evaluation followed methods developed by Fujita et al. (1992) and outlined in a 2005 Desert Research Institute (DRI) report (Desert Research Institute, 2005) and elsewhere (Chinkin and Reid, 2006; Roberts et al., 2004). The approaches include comparisons of pollutant ratios (e.g., total non-methane organic carbon [TNMOC]/oxides of nitrogen [NO_x] and carbon monoxide [CO]/NO_x) that are derived from ambient data (ambient-derived) with those derived from the emissions inventory (emissions inventory-derived), as well as comparisons of ambient- and emissions inventory-derived relative hydrocarbon compositions. Results of these comparisons were used to address the reliability and completeness of, and to make recommendations for improving, the LADCO emissions inventories.

1.1 Background

The objective of this project is to evaluate the hourly emissions inventory for different urban areas in the Upper Midwest, using ambient data collected from 2004 through 2006 and 2008 through 2010. This work focuses on assessing recent (2005 and 2008) emissions estimates and how well they represent real-world pollutant concentrations in the areas of interest.[1] Ambient-derived and emissions inventory-derived primary pollutant ratios (TNMOC/NO_x and CO/NO_x) and relative hydrocarbon compositions were spatially and temporally compared for ambient site locations in Chicago, Milwaukee, Gary, and Detroit. In addition, analyses were

[1] The initial focus of the project was comparing 2004–2006 ambient data with 2005 emissions estimates; however, analyses of 2008 ambient and emissions data were included once 2008 emissions inventories became available.

performed on 2009-2010 ambient data to evaluate ambient measurement trends during the current economic downturn.

Comparison of ambient- and emissions inventory-derived primary pollutant ratios has proven to be a useful tool for assessing and then improving emissions estimates. However, these types of comparisons are confounded by the fact that ambient concentrations are influenced not only by fresh pollutants emitted in the vicinity of a monitor, but also by aged pollutants transported from sources farther away and chemical reactions that may have occurred after the pollutants were emitted. The influence of these effects on comparisons can be minimized (but not eliminated) by selecting ambient data collected at times when emission rates are high and chemical reaction rates are low. Morning sampling periods offer the best potential to minimize the effects of pollutant transport and other influences in the ambient/emissions inventory comparisons. During early morning hours, because of low mixing heights, emissions from elevated sources may be injected above the mixed layer and may not affect surface-level ambient concentrations. Pollutant ratios were calculated with and without elevated sources to evaluate the potential effects of this phenomenon.

1.2 Overview of Technical Approach

STI used techniques outlined by DRI (Desert Research Institute, 2005) to perform this top-down emissions inventory evaluation. These techniques have been previously applied by STI to emissions inventories for several other geographic areas, including central California (Chinkin and Reid, 2006), Southern California (Fujita et al., 1992; Chinkin et al., 2005), and Houston, Texas (Roberts et al., 2004). The technical approach for this top-down emissions inventory reconciliation was divided into three elements:

1. Site selection and data processing;
2. Comparison of emissions inventory and ambient criteria pollutant ratios; and
3. Comparison of emissions inventory and ambient relative hydrocarbon compositions.

The approach used to carry out each work element is described in the following sections.

1.2.1 Site Selection and Data Processing

To support a top-down emissions inventory evaluation for the cities of Chicago, Milwaukee, Gary, and Detroit, STI acquired available air quality and meteorological data from the U.S. Environmental Protection Agency's (EPA) Air Quality System (AQS) for eight monitoring sites, as shown in **Table 1-1 and Figure 1-1**. To effectively evaluate on-road mobile source emissions estimates, an effort was made to focus on monitoring sites that are likely to be impacted by fresh mobile source emissions. However, some of the sites included in these analyses were in the vicinity of other emissions sources, including non-road mobile sources (e.g., the Jardine and Mannheim sites in Chicago) and industrial sources (e.g., the Gary site), as described in Section 2.2. Hourly data for the years 2004–2006 and 2008–2010[2] were acquired

[2] It should be noted that 2008–2010 data were not available for several sites that reported 2004–2006 data, as documented in Section 2.1.1.

from AQS for summer (June-August) and winter (December-February) months, and data were validated following established protocols.

Table 1-1. Monitoring sites included in the top-down emissions inventory evaluation.

Site Name	AQS Code	Site Type[a]	Latitude	Longitude
Chicago, IL – Jardine	17-031-0072	PAMS II	41.8958	-87.6077
Chicago, IL – Northbrook	17-031-4201	PAMS	42.1400	-87.7992
Chicago, IL – Franklin	17-031-0063	SLAMS/Other	41.8770	-87.6343
Chicago, IL – Mannheim	17-031-3103	SLAMS/Other	41.9652	-87.8763
Gary, IN	18-089-0022	PAMS II	41.6067	-87.3047
Detroit, MI – E7Mile	26-163-0019	SLAMS/Other	42.4308	-83.0001
Detroit, MI – Linwood	26-163-0016	SLAMS/Other	42.3578	-83.0960
Milwaukee, WI	55-079-0026	PAMS II	43.0611	-87.9125

[a] PAMS = Photochemical Assessment Monitoring Stations; SLAMS = State/Local Air Monitoring Stations.

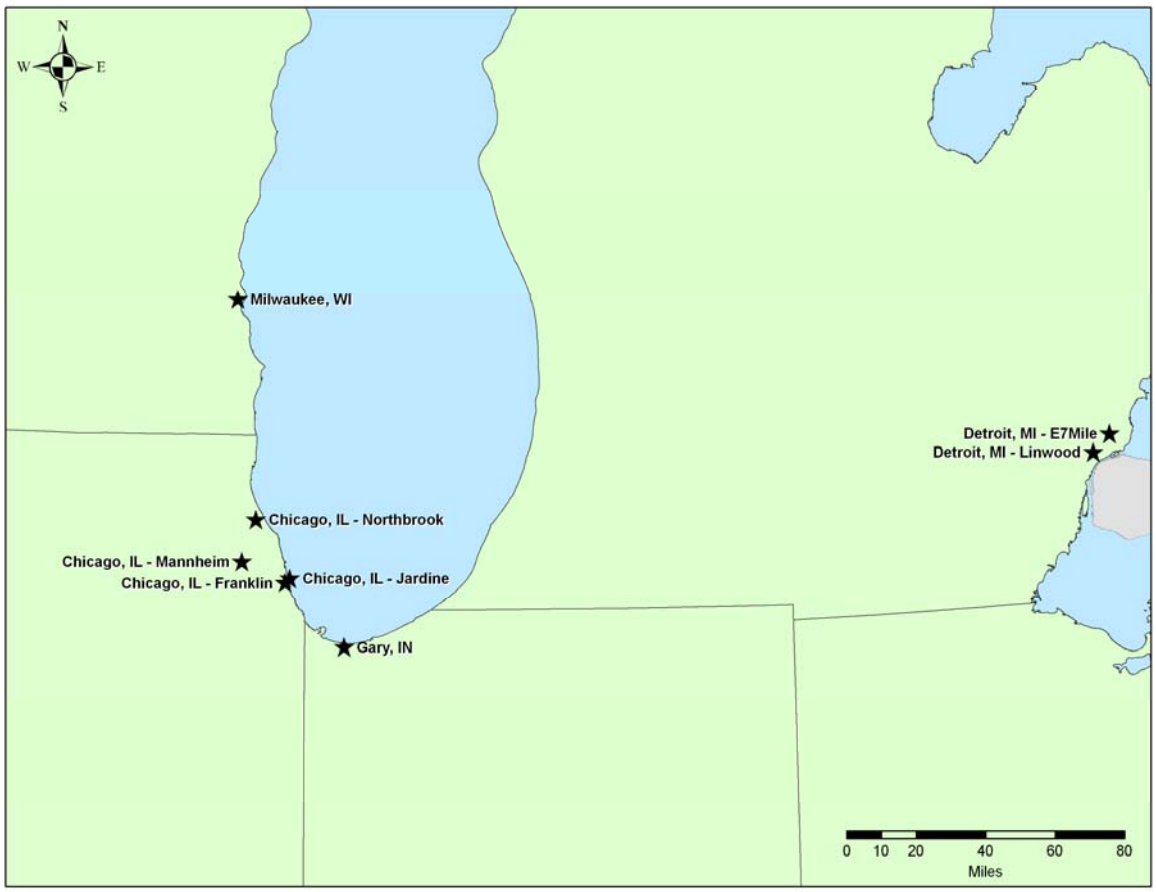

Figure 1-1. Locations of monitoring sites included in the top-down emissions inventory evaluation.

STI also acquired 2005 Base M and 2008 Base B/C emissions inventory data files and supporting files (e.g., speciation profile libraries) for area, point, non-road mobile, on-road mobile, and biogenic sources from LADCO. In general, LADCO provided hourly, gridded criteria pollutant (e.g., volatile organic compounds [VOC], NO_x, and CO) emissions data representing an average weekday, Saturday, and Sunday for each month of 2005 and 2008.[3] Emission file formats varied by source sector[4], so to prepare the emissions data for use in subsequent analyses, STI converted all data files to a common comma-separated-values (CSV) format and extracted data records for the grid cells included in the grid analysis zones around each monitoring site of interest (see Section 1.2.2 for a description of how grid analysis zones were defined for each site). In addition, STI speciated anthropogenic VOC emissions using speciation profiles and cross-reference files provided by LADCO, then matched individual chemical species in the speciated inventories to those species measured in the ambient data (i.e., PAMS hydrocarbons). The compounds reported in the emissions inventory that were not measurable in the ambient samples were excluded from the analysis. Finally, STI converted the speciated inventories from mass to molar units to place the emissions and ambient data on a common basis.

1.2.2 Comparison of Ambient- and Emissions Inventory-Derived Criteria Pollutant Ratios

For the selected sites, TNMOC/NO_x and CO/NO_x ratios from the ambient and emissions inventory data were computed by day-of-week (weekday[5], Saturday, and Sunday), month (June, July, and August), and summer season (June-August). Because CO data were available for winter and summer months, CO/NO_x ratios were also calculated for individual winter months (December, January, and February) and the winter season (December-February). Ambient-derived ratios were compared with emissions inventory-derived ratios by spatially matching ambient data to corresponding groups of 4-km x 4-km grid cells surrounding each ambient monitoring site. These groups of grid cells were identified for each site based on predominant wind speeds during the early morning hours (0600–0900).

Because meteorological factors can affect differences between ambient- and emissions inventory-derived ratios, several different ratio comparisons were considered, each representing a different spatial configuration of wind quadrants and grid cells around each site. The extent of each quadrant-grid cell configuration, or analysis zone, was based on the maximum distance an air parcel could travel during the 3-hour sampling period, given average wind speeds during that period. **Figure 1-2** illustrates an example of a full extent grid analysis zone[6] centered on an ambient monitoring site and shows the wind quadrant definitions, whose extents vary according

[3] For on-road mobile sources, emissions were provided for January and July only. For biogenic sources, emissions were provided for each day of 2005. Additional details on the processing of emissions data for these source categories are provided in Section 2.2.1.

[4] For 2005, biogenic emissions were provided as CAMx-ready binary files, on-road emissions were provided as PostgreSQL files, and the remaining source sectors were provided as SAS files. All 2008 data were provided as SAS files.

[5] For pollutant ratio comparisons and all remaining analyses, ambient data from Tuesday–Thursday were considered "weekday." Emissions inventory data were not provided for individual weekdays.

[6] The full extent grid analysis zone surrounding each site is based on the quadrant analysis zone with the highest average wind speed.

to the observed wind speeds at each site. The center point of the grid represents the ambient monitoring site, the hollow grid represents the entire grid analysis zone, and the colored regions represent the wind quadrant analysis zones. The individual wind quadrant analysis zones are larger for quadrants where wind speeds are greater and smaller for quadrants where wind speeds are light. For the Gary site and three of the Chicago area sites, the grid analysis zone consists of a 9 x 9 grid cell region[7] with the monitoring site in the center cell. For the Northbrook site in Chicago and the sites in Detroit and Milwaukee—where average morning wind speeds were lower—the grid analysis zone consists of a 7 x 7 grid cell region around each monitoring site (see **Table 1-2**).

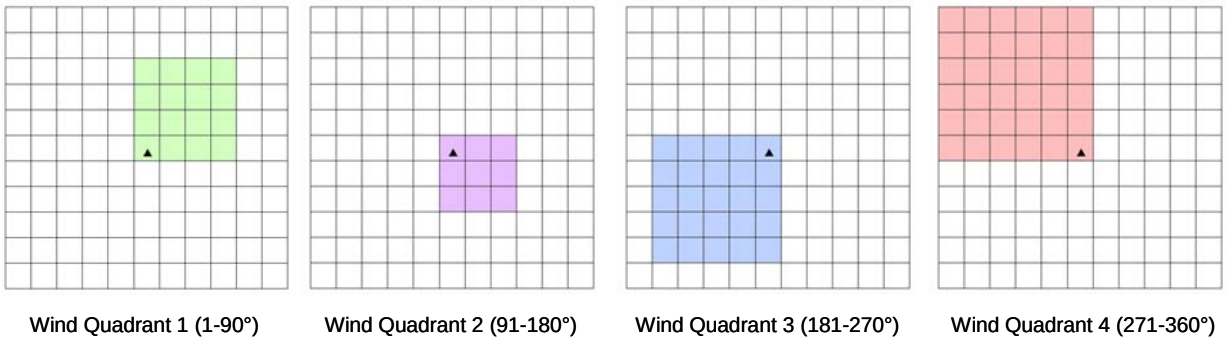

Figure 1-2. Example of a full extent grid analysis zone, showing the spatial configuration of grid cells for which ambient- and emissions inventory-derived ratio comparisons were calculated. The monitoring site is represented by a small triangle.

Table 1-2. Dimensions of the full grid analysis zone around each monitoring site of interest.

Site Name	Dimensions of Grid Analysis Zone	Area of Grid Analysis Zone (km^2)
Chicago, IL – Jardine	9 x 9 cells	1,296
Chicago, IL – Northbrook	7 x 7 cells	784
Chicago, IL – Franklin	9 x 9 cells	1,296
Chicago, IL – Mannheim	9 x 9 cells	1,296
Gary, IN	9 x 9 cells	1,296
Detroit, MI – E7Mile	7 x 7 cells	784
Detroit, MI – Linwood	7 x 7 cells	784
Milwaukee, WI	7 x 7 cells	784

To make consistent comparisons of total hydrocarbons between the ambient data and the emissions inventory, the emissions inventory data were converted from mass to molar units. In

[7] Note that each individual grid cell measures 4 km x 4 km, so the total area of a 9 x 9 grid cell region is 1,296 km^2, as shown in Table 1-2.

addition, the individual chemical species reported in the emissions inventory were matched to those in the ambient data, and only TNMOC species that are identified by the PAMS program (i.e., PAMSHC, or the sum of PAMS-identified hydrocarbons) were included in the analyses. **Appendix A** contains the detailed chemical species cross-reference list that was used to match emissions inventory species to the ambient species.

1.2.3 Comparison of Ambient- and Emissions Inventory-Derived Hydrocarbon Compositions

In addition to ratio comparisons, the chemical composition of hydrocarbons reported in the emissions inventory was compared to the chemical composition of the ambient air at individual monitoring sites. These "fingerprint" analyses were used to determine how accurately the speciation of the emissions inventory compares to the data measured at the ambient monitoring sites. Fingerprint analyses were performed for each site by day of week (weekday, Saturday, and Sunday), month (June, July, August), and wind quadrant.

As a further review of the speciation of the emissions inventory, STI also computed and compared the relative reactivity of the organic species in the emissions inventory and ambient data. The reactivity of each species was estimated using published maximum incremental reactivity (MIR) values that represent the ozone formation potential of various organic compounds (Carter, 2003). Weighted reactivity values for the emissions inventory and ambient data will be calculated as follows:

$$R = \sum_{i=1}^{n} (MIR)_i w_i$$

where:

R = weighted reactivity
$(MIR)_i$ = maximum incremental reactivity for species i
w_i = weight fraction of species i in the emissions inventory or ambient data

Reactivity comparisons were performed by day of week (weekday, Saturday, and Sunday), month (June, July, August), and wind quadrant for each monitoring site.

1.3 Uncertainty Issues

Understanding the uncertainties associated with comparisons of ambient- and emissions inventory-derived pollutant ratios is essential to assess the suitability of top-down evaluation analyses. Three general categories of uncertainty issues are associated with top-down emissions reconciliation analyses: (1) accuracy of the emissions inventory, (2) accuracy of the ambient concentration measurements, and (3) suitability of comparisons.

1.3.1 Emissions Inventory Uncertainties

To compare ambient pollutant ratios to emissions inventory ratios, it is important to accurately characterize, to the extent possible, the magnitude, spatial distribution, chemical composition, and diurnal pattern of emissions. Uncertainties and inaccuracies associated with emissions inventory data generally stem from (1) emissions estimation techniques and

(2) emissions processing techniques. Inaccuracies and uncertainties associated with emissions estimation techniques include misclassification or exclusion of major emissions sources, the use of incorrect emissions activity data, the use of incorrect emission factors, and the use of incorrect chemical speciation profiles. For on-road mobile sources, which are key emissions sources impacting the monitoring sites addressed in the project—particularly during the morning periods evaluated—emissions estimates have historically been prepared using EPA's MOBILE6.2 model. The MOBILE6.2 model, which was used in the development of LADCO's 2005 Base M inventory, calculates gram per mile emission rates for on-road mobile sources operating under various conditions, and though model outputs have been compared to data from tunnel studies and other "real-world" data (Pollack et al., 2004), EPA does not provide estimates of its uncertainty. Recently, EPA has replaced MOBILE6.2 with the MOVES model, which is based on updated emissions test results (U.S. Environmental Protection Agency, 2010). LADCO's 2008 emissions inventory was developed using MOVES.

To perform a top-down emissions inventory evaluation, emissions estimates must be spatially and temporally resolved for the region surrounding the ambient monitoring sites. To accomplish this task, hourly gridded emissions estimates of VOC, NO_x, and CO were acquired from LADCO. The methods used to disaggregate annual average countywide total emissions estimates into gridded, hourly data can introduce inaccuracies into the emissions inventory data. For example, spatial surrogate data that are not representative of the locations of emissions sources can result in misrepresentation of the geographic location of emissions sources. Similarly, temporal profiles that are not representative of the monthly, weekly, and diurnal distribution of emissions source activity can result in misrepresentation of the diurnal activity patterns for sources within the vicinity (grid cells) of the ambient monitor.

To perform a top-down emissions inventory evaluation, emissions estimates must also be chemically resolved, with VOC emissions disaggregated into individual chemical species. STI used speciation profiles and cross-reference files provided by LADCO to perform this step. Emissions inventory uncertainties can be introduced during the speciation process through the incorrect assignments of speciation profiles to emissions sources and/or by speciation profiles that do not represent the chemical source composition.

1.3.2 Ambient Measurement Uncertainties

Uncertainties associated with ambient measurements include instrument detection limits, precision of measurements, and sampling and handling losses. Prior to conducting an emissions inventory evaluation, the ambient data measurement methods should be assessed to ensure that the collection methods yield adequate data for this type of analysis. Furthermore, the ambient data sets intended for use must be quality-assured to eliminate invalid samples. For this study, ambient data were subjected to a data validation process that followed established protocols.

1.3.3 Uncertainties Associated with the Comparisons

Uncertainties associated with the comparison of ambient and emissions inventory data arise from the spatial and temporal matching of ambient and emissions inventory data, meteorological factors, and atmospheric reactions. To minimize differences between ambient- and emissions inventory-derived ratios due to mismatches in time and space, it is best

to use emissions estimates as close to the vintage of the ambient data as practical. For this study, emissions estimates representative of the winter and summer of 2005 were compared to ambient data for the winters and summers of 2004, 2005, and 2006, and emissions estimates representative of the winter and summer of 2008 were compared to ambient data for the winter and summer of 2008.[8]

A major premise of the top-down evaluation is that only monitoring sites and sampling periods that are dominated by fresh emissions should be considered in the analysis. It is possible that temporal uncertainties may be caused by early morning ambient ratios that include carryover emissions in which PAMSHC and/or NO_x have been preferentially removed by chemical conversion overnight. Spatial uncertainties due to different influences of surface and aloft emissions may arise. For example, PAMSHC, CO, and NO_x emissions from nearby elevated sources may be injected aloft and, as a result, may not mix into the surface air sample.

Meteorological factors such as wind speed, direction, and mixing depth determine the spatial distribution of emissions and thus determine which emissions are sampled. Atmospheric reactions modify the species distribution and mass of midday and afternoon ambient samples. Thus, comparisons from midday and afternoon periods are likely to be less reliable than morning comparisons.

1.4 Summary of Results

The on-road mobile source component of LADCO's 2005 emissions inventory was developed using EPA's MOBILE6.2 model and link-level activity data. The top-down evaluation for the 2005 emissions inventory indicates that, in general, on-road mobile sources are represented accurately in the emissions data. This conclusion is based on the fact that agreement between ambient- and emissions-inventory-derived pollutant ratios was closest (±20%) for wintertime CO/NO_x ratios, and on-road mobile sources accounted for 57% to 80% of wintertime CO and NO_x emissions at all sites for which ratios were calculated. For sites in the Chicago area, agreement between ambient- and emissions inventory-derived pollutant ratios was as close as could be expected, given the limitations of the analysis techniques. However, comparisons with ambient data indicate that the emissions inventory for Sundays may not be representative of actual activity patterns on that day of the week, perhaps due to decreases in on-road mobile source emissions from Saturdays to Sundays, as well as inaccurate temporal characterizations of other source categories. In addition, sources of VOC emissions appear to be missing or underrepresented in the emissions inventory near sites that are influenced by industrial and residential emissions, such as the Gary site and the East 7 Mile site in Detroit.

The on-road mobile source component of LADCO's 2008 emissions inventory was developed using EPA's MOVES model with default input data, and county-level outputs from MOVES were spatially allocated using spatial surrogate data.[9] For the 2008 inventory, agreement between ambient- and emissions-inventory derived pollutant ratios was generally

[8] Ambient data from 2009-2010 were also evaluated as part of this project but were not compared directly with emissions data.

[9] LADCO plans to update the 2008 inventory with state-specific MOVES inputs and link-level activity data. The 2008 inventory used in this analysis was the most current version as of April 29, 2011.

poorer than was observed for the 2005 inventory. The greater discrepancy between ambient- and emissions inventory-derived pollutant ratios primarily results from large decreases in on-road NO_x emissions from 2005 to 2008 that outpaced reductions in ambient NO_x concentrations. However, the Saturday-to-Sunday differences in pollutant ratio comparisons observed for the 2005 inventory were not observed for the 2008 inventory, as there was no variation between Saturday and Sunday on-road mobile source emissions in the 2008 inventory (as was the case for 2005).

For both 2005 and 2008, the speciation of the VOC emissions inventory at all sites does not compare well with the hydrocarbon composition of the ambient data, resulting in a VOC emissions inventory that is more reactive (i.e., prone to contribute to ozone formation) at all sites than the corresponding ambient data. As a result, ozone modeling efforts for the region may be influenced by "compensating errors," as the underestimated magnitude of VOC emissions is offset by the overestimated reactivity of those emissions. Key findings that support these conclusions include:

- For 2005, the agreement between overall ambient- and emissions inventory-derived CO/NO_x ratios is good (±30%) across all sites, particularly for winter months, and on-road mobile sources dominate the wintertime CO and NO_x inventories for all sites.
- For 2008, the agreement between overall ambient- and emissions inventory-derived CO/NO_x ratios is poorer (±60%) across all sites, and on-road mobile sources continue to dominate the CO and NO_x inventories for all sites.
- For both 2005 and 2008, the agreement between overall ambient- and emissions inventory-derived $TNMOC/NO_x$ ratios is good (±20%) for Chicago's Jardine (2005 only) and Northbrook sites.
- For 2005, the agreement between overall ambient- and emissions inventory-derived $TNMOC/NO_x$ ratios is poorest at the Detroit East 7 Mile site and the Gary site, which are likely to be affected by industrial and residential emissions sources.
- For 2005, the agreement between ambient- and emissions inventory-derived $TNMOC/NO_x$ and CO/NO_x ratios is generally better on weekdays and Saturdays than on Sundays. For 2008, the agreement between ambient- and emissions inventory-derived pollutant ratios is generally similar across all days.
- Comparison with the ambient data shows that the speciation of the emissions inventory tends to overestimate the contribution of some species (e.g., acetylene, ethylene, toluene, and isoprene) and underestimate the contribution of other species (e.g., ethane, propane, and C6-C11 alkanes).
- Across all sites, the overall weighted reactivity of the species present in the emissions inventory for the summer season is 16% to 80% higher than the weighted reactivity of the species present in the ambient data.

A detailed description of the analysis techniques and results that served as the basis for these conclusions and recommendations is provided in the sections that follow.

2. Data Acquisition and Processing

Preparing ambient concentration, meteorological, and emissions inventory data for use in a top-down emissions inventory evaluation involves several steps. This section presents a detailed discussion of the data preparation and processing performed for this emissions evaluation.

2.1 Ambient Monitoring Data

2.1.1 Ambient Data Acquisition

To support this top-down emissions evaluation, air quality and meteorological data for the years 2004–2006 and 2008–2010 were acquired from AQS for eight monitoring sites in the Upper Midwest. To effectively evaluate on-road mobile source emissions estimates, an effort was made to focus on monitoring sites that are likely to be impacted by fresh mobile source emissions. However, some of the sites included in these analyses were in the vicinity of other emissions sources, including non-road mobile sources (e.g., the Jardine and Mannheim sites in Chicago) and industrial sources (e.g., the Gary site), as described in Section 2.2.

Hourly data for summer (June–August) and winter (December–February) months were acquired from AQS for speciated hydrocarbons (HC), TNMOC, carbonyl compounds, CO, NO_x, wind speed, and wind direction. For the 2004–2006 period, hourly HC data are available for summer months at only five sites in the region. Available winter HC data are limited to 24-hour measurements of a small number of species (e.g., benzene and toluene) collected every six days, making these data insufficiently time-resolved for further analyses.[10] For CO and NO_x, hourly data are available for summer and winter months for all cities except Gary, for which wintertime CO data are unavailable (see **Table 2-1**).

Hourly HC data for 2008 and 2009 are available for summer months at the Chicago-Northbrook site, and for 2008 only at the Milwaukee site. Hourly CO and NO_x data are available for 2008, 2009, and the first quarter of 2010 at three sites in the Chicago area (see Table 2-1).

[10] Comparisons between ambient data and emissions data are generally limited to morning hours, when ambient concentrations are most likely to be influenced by fresh pollutants (i.e., emission rates are high and chemical reaction rates are low).

Table 2-1. Hourly data available at individual monitoring sites (S=summer; W=winter).

Site Name	HC	NO_x	CO	Wind Data
2004-2006 Data Availability				
Chicago-Jardine	S	S/W		S/W
Chicago-Northbrook	S	S/W		S/W
Chicago-Mannheim		S/W	S/W	S/W
Chicago-Franklin		S/W	S/W	
Gary	S	S/W		S/W
Detroit-Linwood		S/W	S/W	
Detroit-E7Mile	S	S/W		S/W
Milwaukee	S	S/W	S/W	S/W
2008 Data Availability				
Chicago-Jardine[a]		S		S/W
Chicago-Northbrook[b]	S	S/W	S/W	S/W
Chicago- Mannheim		S/W	S/W	S/W
Chicago-Franklin		S/W	S/W	
Gary[a]		S/W		S/W
Milwaukee	S	S/W		S/W
2009[c] Data Availability				
Chicago-Jardine[a]		S		S/W
Chicago-Northbrook	S	S/W	S/W	S/W
Chicago-Mannheim		S/W	S/W	S/W
Chicago-Franklin		S/W	S/W	
Detroit-E7Mile		S/W		S/W
Gary, IN[a]		S/W		S/W
Milwaukee		S/W		S/W

[a] Though 2008–2009 TNMOC data for the Jardine and Gary sites were not found in AQS, these data may be available from state agencies. However, the data were not available for use in these analyses.
[b] The only winter data available for Northbrook are from December 2008 (no January/February data available).
[c] Data available for January and February of 2010 were included in 2009 winter analyses. At the time analyses were conducted, NO_x and CO data were available for the first quarter of 2010 at the Northbrook, Mannheim, and Franklin sites in Chicago.

2.1.2 Ambient Data Validation

Data validation was performed to identify a representative data set for each monitoring site of interest. Ambient data from 2004–2006 and 2008–2010 were brought into a Microsoft Access database, sorted, and imported into the Volatile Organic Compound Data Validation and Analysis Software (VOCDat) for validation. VOCDat allows visual inspection of the data and application of screening criteria. To ensure quality data for analysis, established protocols for

validation of the VOC data were followed. Data validation methods included inspection of time series (e.g., TNMOC with total alkanes, alkenes, aromatics, carbonyl compounds, NO_x and ozone), scatter plots (e.g., benzene/acetylene, benzene/toluene, ethane/propane, TNMOC/groups of species) and fingerprint plots (i.e., plots showing the concentration of each species in a sample). Data quality issues identified during the validation process included:

- **Data outliers –** Data outliers were defined as a single sample spike in concentration observed in a species or group of species. These high values were excluded from analysis because, even if the measurements were truly representative of ambient conditions during that hour, the values are not representative of the typical influence of emissions sources around the monitoring site and would skew the overall average. An example of a single sample high value from the Gary, Indiana, PAMS site is shown in **Figure 2-1**. This propane measurement may have been real but was more than 10 times higher than typical measurements at this site; this value was not included in subsequent analyses.
- **Low concentration values –** Abnormally low concentration values were also addressed by the data validation. For example, ethane and propane typically correlate well with one another, but there were samples at the Chicago-Jardine site in which ethane values were low relative to propane. Therefore, measurements were flagged as suspect when ethane values were less than 1 ppbC while propane values were greater than 2 ppbC. Typically, ethane concentrations drop below 2 ppbC only when there are problems with the analytical system. This problem occurred only at the Jardine site for the time period of interest.

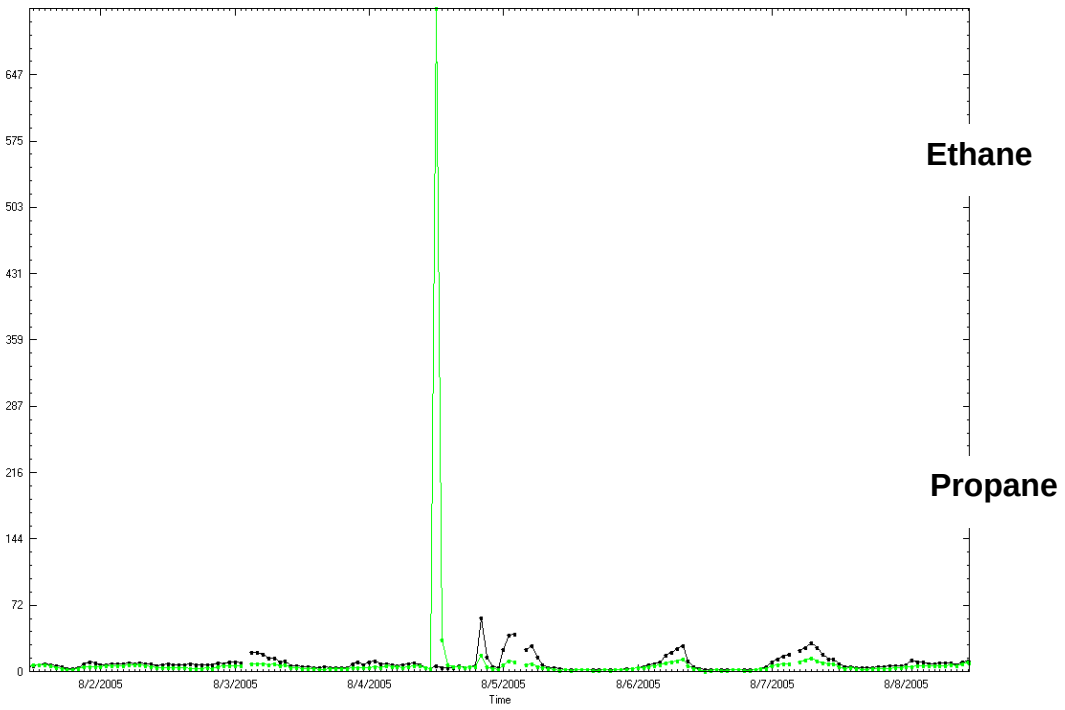

Figure 2-1. Time series of propane and ethane concentrations (ppbC) at Gary, IN.

- **Shifts in species patterns –** In some cases, shifts in measurements for a given species were unlike measurements during the previous and following weeks. For example, the CO baseline at Detroit Linwood site typically falls in the range between 100 ppb to 300 ppb. However, CO concentrations dropped to zero from July 22 to July 26, 2006 (see **Figure 2-2**). Data from this anomalous period were excluded from subsequent analyses. In addition, TNMOC measurements at the Northbrook site in Chicago increased sharply from 2005 to 2009. However, these increases were largely associated with the unidentified portion of TNMOC (see **Figure 2-3**), which may indicate changes in instrument sensitivity post-2005. The higher TNMOC measurements for 2008 and 2009 were included in our analyses but should be viewed with caution.[11]

Data quality issues identified during the validation process resulted in data being flagged as suspect and excluded from subsequent analyses. For the 2004–2006 time period, only about 10% of the data were flagged as suspect for summer months, and only about 8% of the data were flagged as suspect for winter months. For the 2008–2010 time period, only about 4% of the data were flagged as suspect for summer months, and only about 1% of the data were flagged as suspect for winter months.

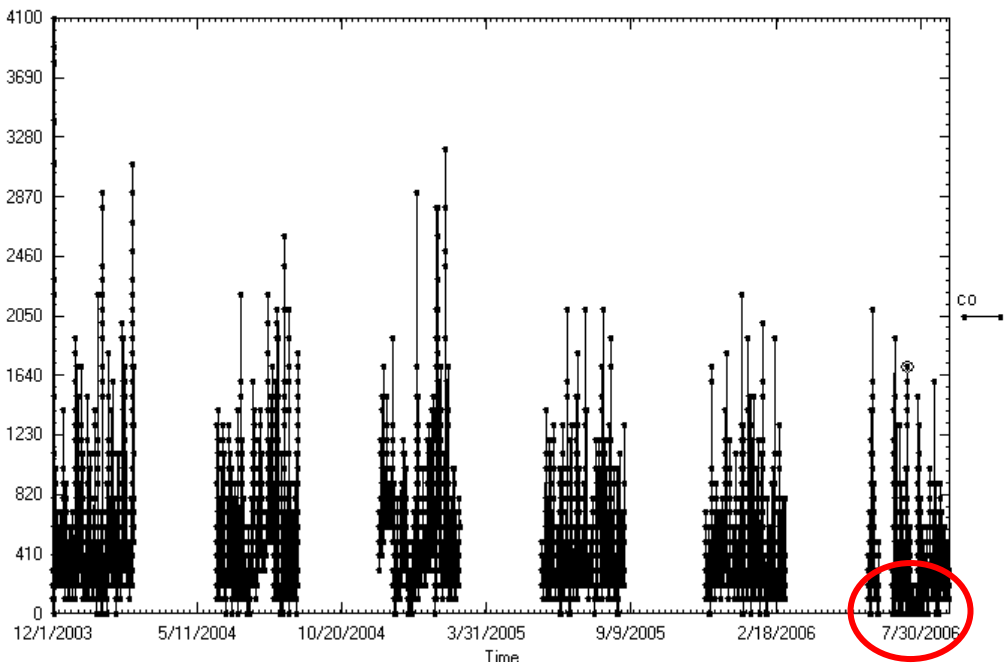

Figure 2-2. Time series of CO concentrations (ppb) for Linwood site in Detroit, MI.

[11] It should also be noted that a significant amount of repair work occurred at the Northbrook site during 2008 and 2009. though this work did not directly involve the TNMOC instrument (auto-GC).

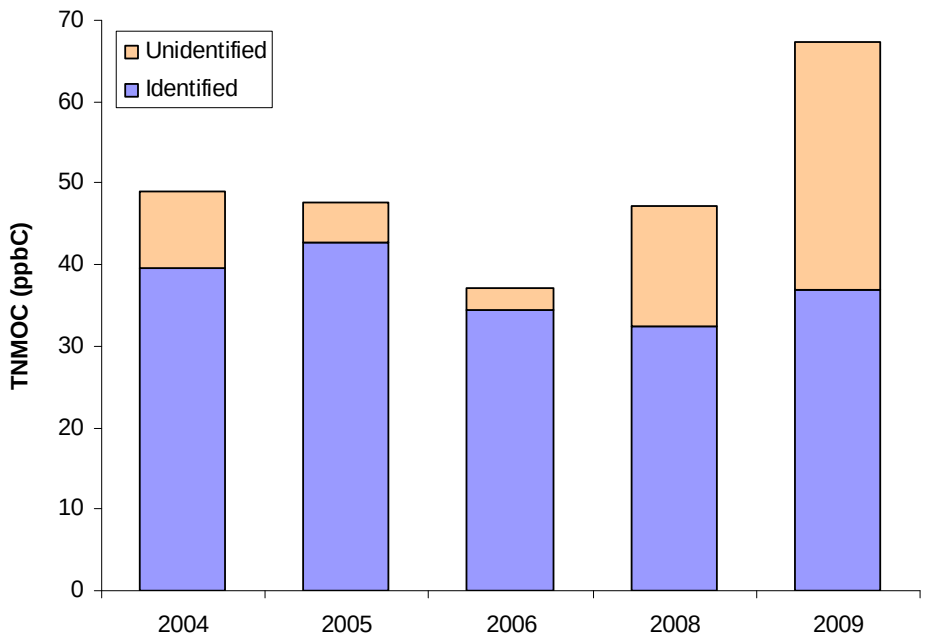

Figure 2-3. Yearly variations in summer weekday TNMOC concentrations (ppbC) at the Northbrook site in Chicago, IL.

2.1.3 Ambient Site Characterization

To help characterize the land use patterns and emissions sources surrounding each ambient monitoring site and to verify that all sites were likely to be significantly impacted by mobile source emissions, digital images of the 5 km x 5 km area around each site were generated using Google Earth. In addition, photographs taken around several of the monitoring sites are provided in **Appendix B**, as well as digital images of a larger area (28 km x 28 km)[12] around each site. A description of the area around each monitoring site appears below.

[12] The grid analysis zones around individual monitoring sites were all at least 7 x 7 grid cells, or 28 km x 28 km.

Chicago – Jardine and Franklin

The Chicago-Jardine site is located at the Jardine Water Filtration Plant on the shore of Lake Michigan. The site is east of downtown Chicago and about 0.7 km from Highway 41, making it subject to significant emissions from pleasure craft and commercial marine vessels, especially during summertime. The Chicago-Franklin site is in downtown Chicago about 3 km southwest of the Jardine site and about 0.2 km north of the Eisenhower Expressway (see **Figure 2-4**), making it an ideal site for capturing the effects of fresh downtown mobile emissions.

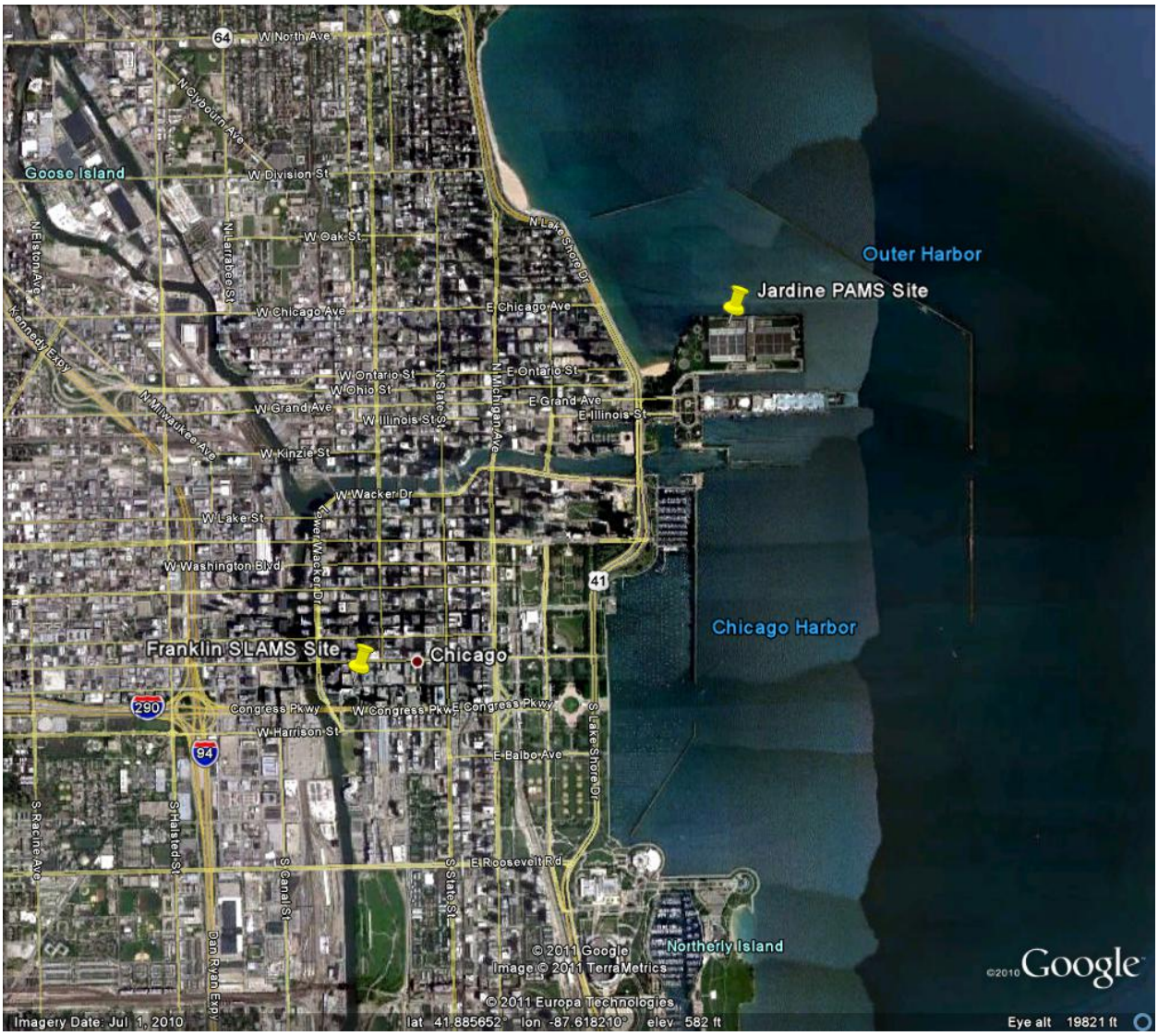

Figure 2-4. Image of the area around the Jardine and Franklin sites in Chicago.

Chicago – Northbrook

The Chicago-Northbrook site is located at the Northbrook Water Plant in a northern suburb of Chicago. The site is about 0.7 km south of the Tri-State Tollway and about 0.7 km west of a major highway (see **Figure 2-5**).

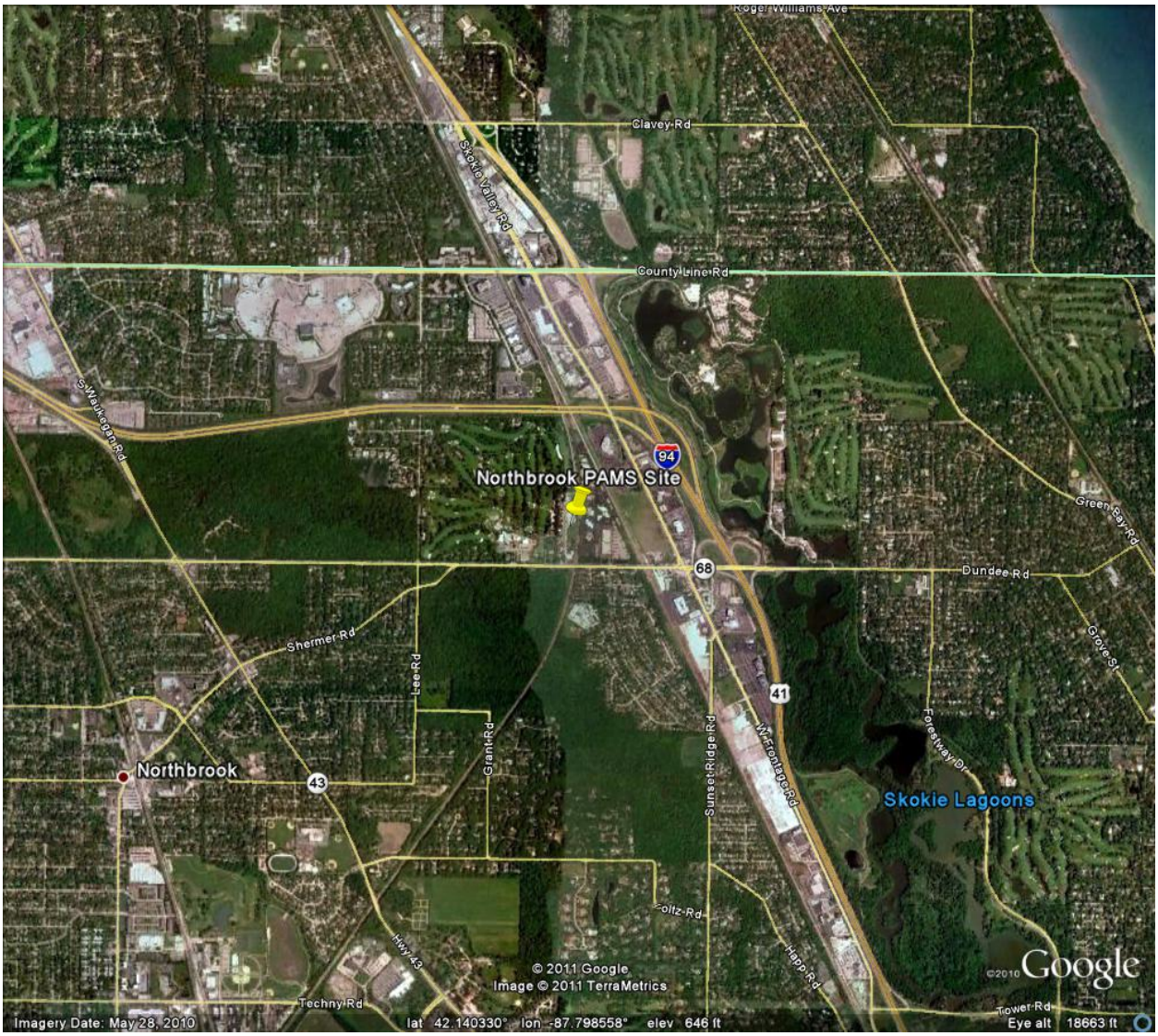

Figure 2-5. Image of the area around the Northbrook site in Chicago.

Chicago – Mannheim

The Chicago-Mannheim site is about 22 km northwest of downtown Chicago adjacent to O'Hare International Airport (see **Figure 2-6**) and subject to significant aircraft and airport-related emissions. The site is 0.2 km north of a toll booth on the Tri-State Tollway.

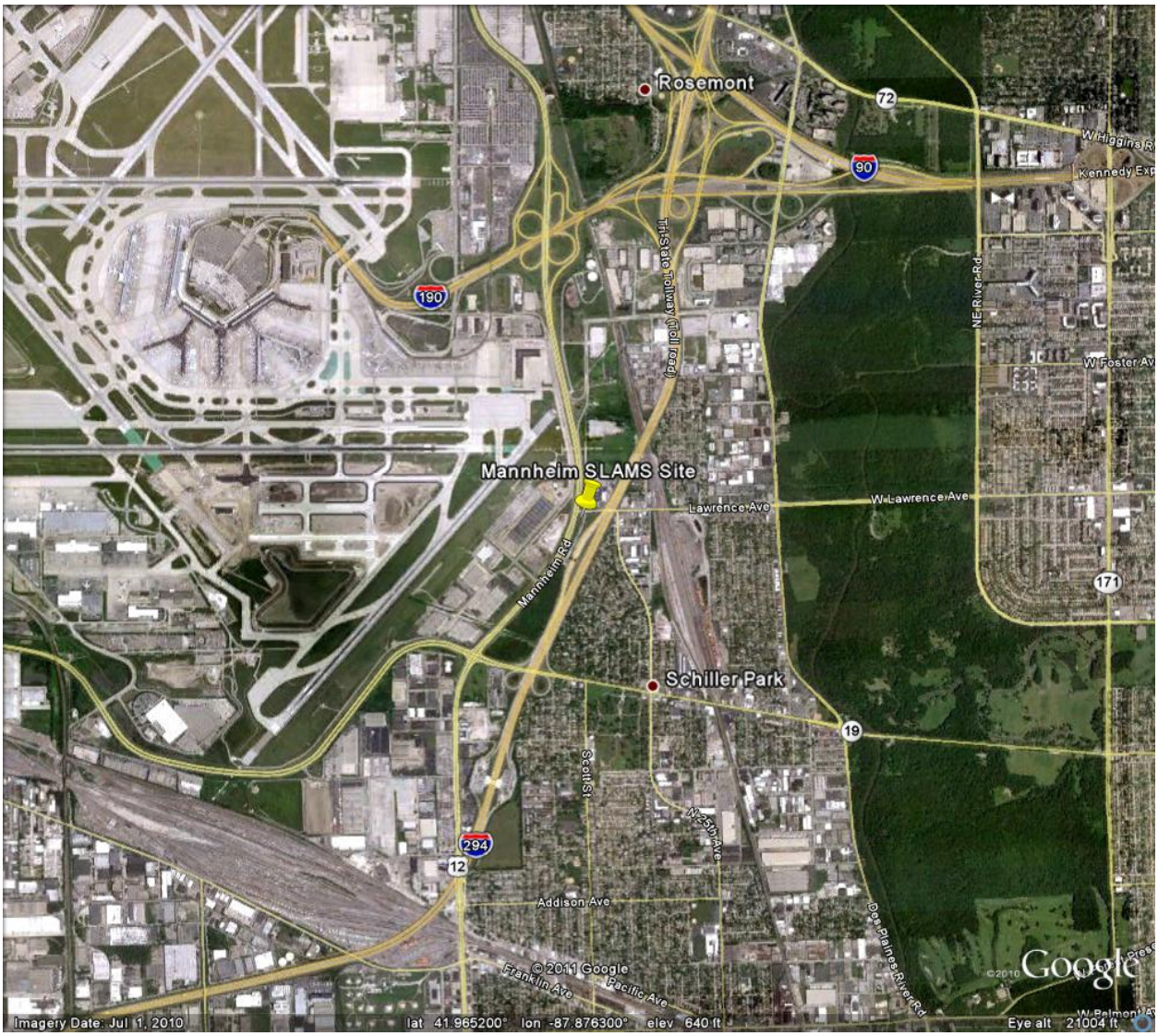

Figure 2-6. Image of the area around the Mannheim site in Chicago.

Gary

The Gary site is just south of the Mittal Steel Works and about 1.5 km northeast of downtown Gary. The site is about 0.6 km north of the interchange that connects two interstate highways (see **Figure 2-7**).

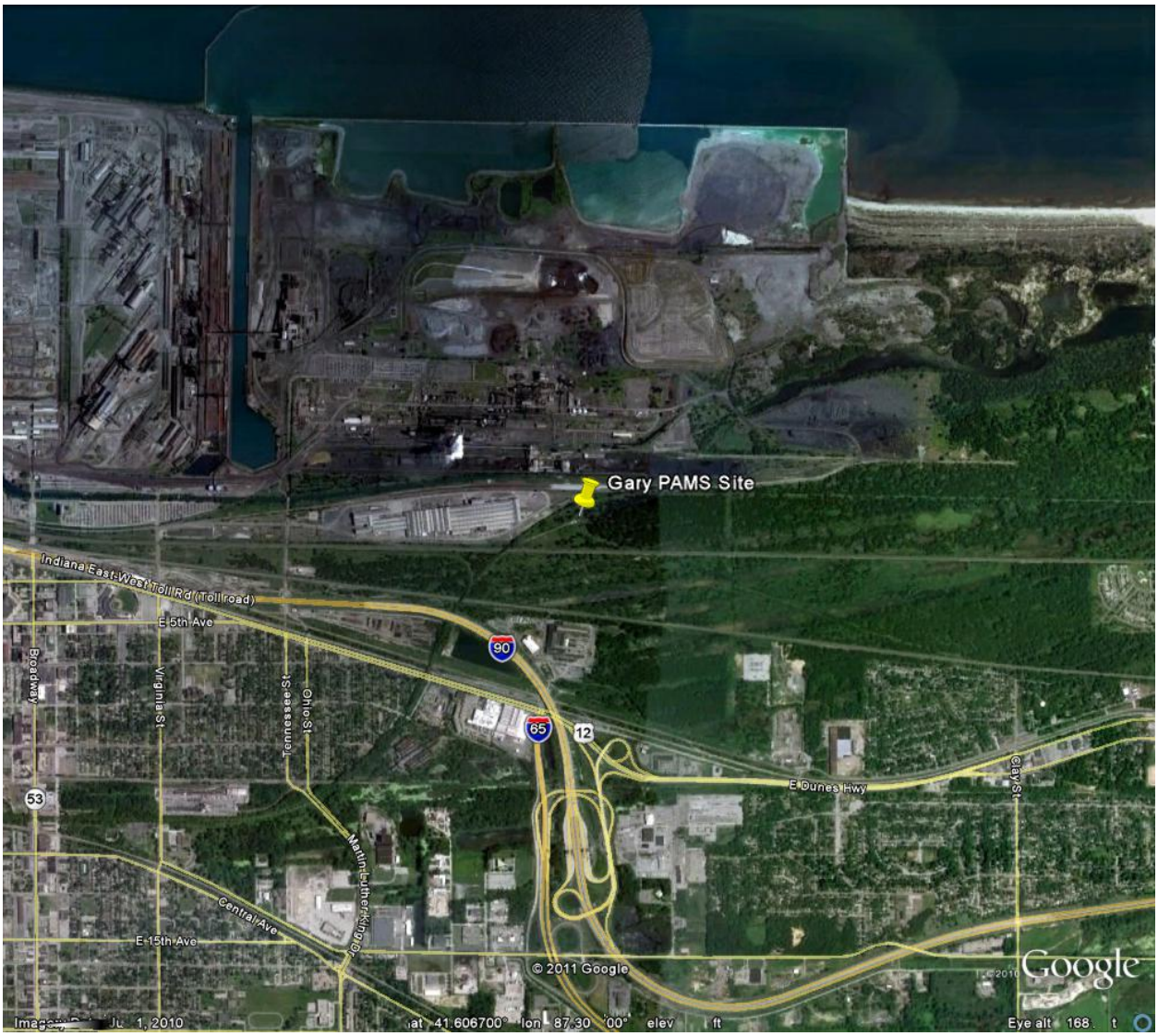

Figure 2-7. Image of the area around the Gary site.

Detroit – East 7 Mile and Linwood

The East 7 Mile and Linwood sites are both located in residential areas. The East 7 Mile site is about 11 km northeast of downtown Detroit, 4 km north of Interstate 94, and 4 km southeast of the Daimler Chrysler Warren Plant. The Linwood site is about 3 km northwest of downtown Detroit and is adjacent to several arterial roads, including the Rosa Parks Memorial Highway (see **Figure 2-8**).

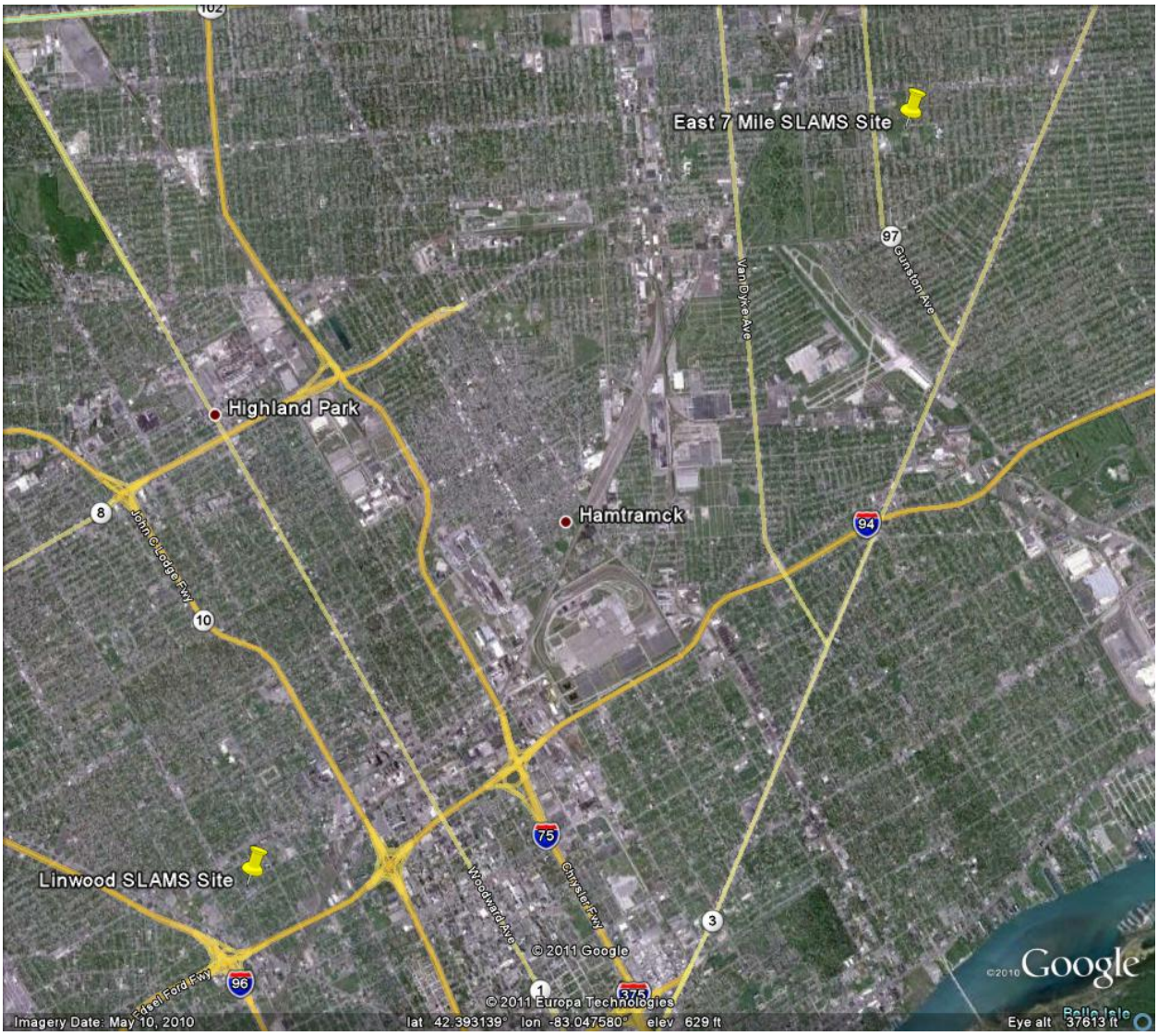

Figure 2-8. Image of the area around the East 7 Mile and Linwood sites in Detroit.

Milwaukee

The Milwaukee site is located in a largely urban and residential area about 2.5 km north of downtown Milwaukee and 3 km west of Lake Michigan. The site is about 0.5 km east of

Highway 43 and about 3 km northeast of the Marquette Interchange that connects Interstates 94 and 43 near downtown Milwaukee (see **Figure 2-9**).

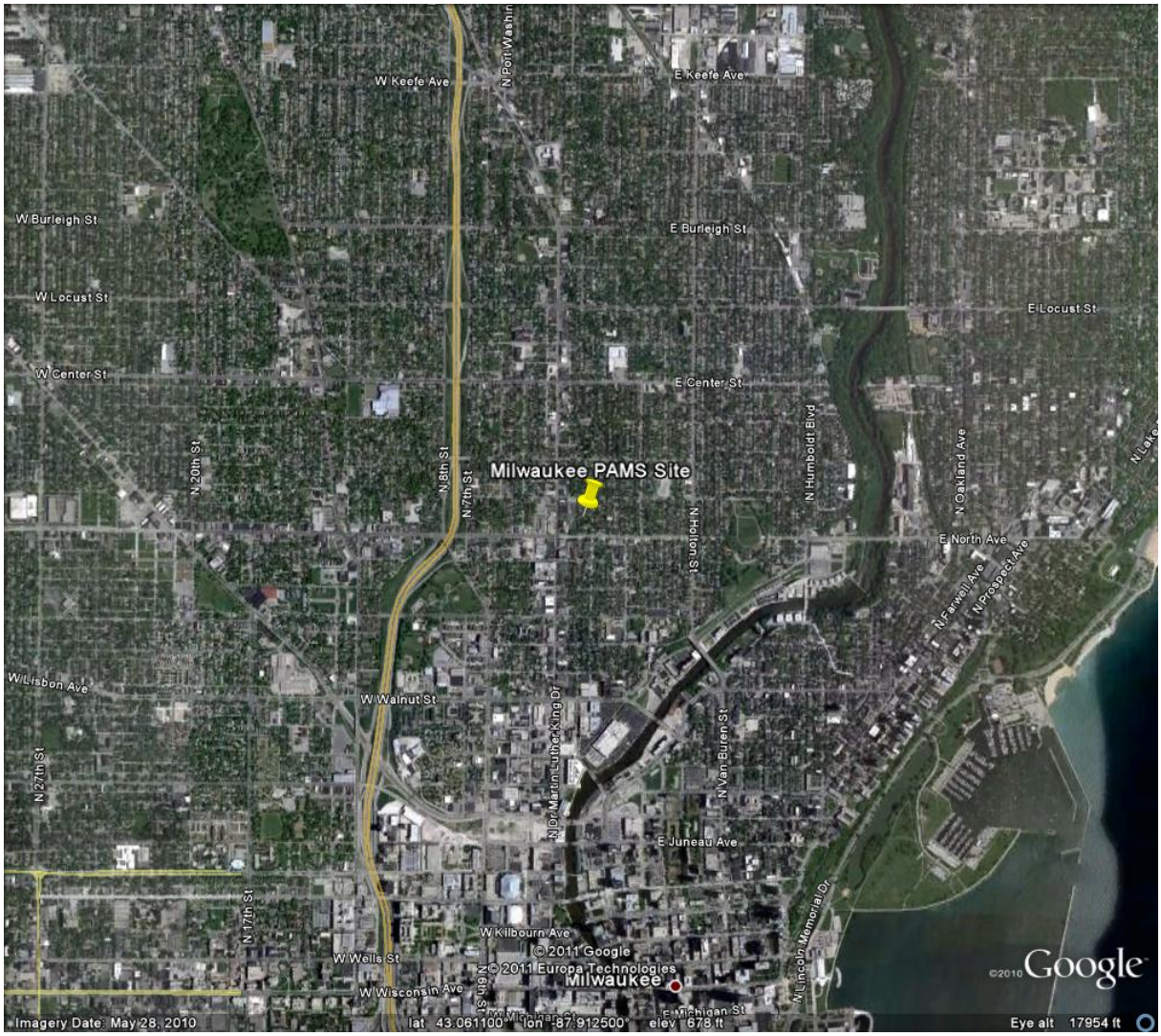

Figure 2-9. Image of the area around the Milwaukee site.

2.1.4 Ambient Concentration Data

For sites with summer TNMOC measurements, morning (0600–0900) concentrations of TNMOC and NO_x were summarized by day of week for data from 2004–2006 and 2008–2009 (see **Table 2-2**). For 2005, mean morning TNMOC concentrations were highest at the Gary site and the East 7 Mile site in Detroit, which is likely due to a greater density of industrial emissions sources around those sites. TNMOC concentrations were 13% to 34% lower on weekend days relative to weekdays, with the Chicago-Jardine and Milwaukee sites having the largest weekend decreases in TNMOC concentrations. At all sites except the Milwaukee site, Sunday TNMOC concentrations were about the same as or higher than Saturday TNMOC concentrations in 2005.

Although mean morning NO_x concentrations did not vary among sites as widely as mean TNMOC concentrations did, NO_x concentrations were also lower on weekend days, decreasing by 11% to 53% on Saturdays and Sundays relative to weekdays. At all sites except the Jardine site, Sunday NO_x concentrations were lower than Saturday NO_x concentrations by 16% to 40%. At the Gary site, Saturday NO_x concentrations were more similar to weekday concentrations than to Sunday concentrations.

For 2008, ambient TNMOC measurements were only available at the Northbrook and Milwaukee sites. At Northbrook, TNMOC concentrations were slightly higher in 2008 than in 2004–2006, while weekday NO_x concentrations were 13% lower in 2008 than in 2004–2006.[13] At the Milwaukee site, weekday TNMOC concentrations were 24% higher in 2008 than in 2004-2006, while weekday NO_x concentrations decreased by 16% in 2008 (see Table 2-2).

For 2009, ambient TNMOC measurements were only available at the Northbrook site, where 2009 TNMOC concentrations were significantly higher than in previous years (see Table 2-2). However, it should be noted that there were potential instrument issues at Northbrook, as described in Section 2.1.2 above.

Table 2-2. Mean summer TNMOC and NO_x concentrations.

Site	TNMOC (ppbC)			NO_x (ppb)		
	Weekday	Saturday	Sunday	Weekday	Saturday	Sunday
2004-2006 Data						
Chicago-Jardine	43.9	30.1	37.5	30.3	14.3	16.7
Chicago-Northbrook	45.6	36.9	39.7	23.5	16.2	11.8
Milwaukee	74.8	59.8	49.7	21.9	13.1	11.0
Gary	142.4	122.0	119.2	26.2	23.2	13.8
Detroit-E7 Mile	157.8	131.6	132.3	22.2	14.4	10.4
2008 Data						
Chicago-Northbrook	47.3	37.8	43.9	20.5	10.2	10.1
Milwaukee	92.5	81.8	69.9	18.3	11.3	6.8
2009 Data						
Chicago-Northbrook	67.3	61.9	74.6	14.2	8.9	6.7

For sites with summer and winter CO measurements, morning (0600–0900) concentrations of CO and NO_x were summarized by day of week for data from 2004–2006 and 2008–2009 (see **Tables 2-3 and 2-4**). In general, mean morning CO and NO_x concentrations were higher in winter than in summer, which is likely due to both meteorological conditions (e.g., lower mixing heights in winter) and increased CO emissions from light-duty vehicles in

[13] Weekend NO_x concentrations for 2008 at Northbrook showed a sharper decrease on Saturdays than on Sundays relative to data from 2004–2006, but note that the use of data from only one summer limits the sample size for individual days of the week.

winter.[14] CO and NO_x concentrations for both summer and winter were highest at the Franklin and Mannheim sites in Chicago. Across all years, CO concentrations were 5% to 45% lower on weekend days relative to weekdays, with the Chicago-Franklin site having the largest weekend decrease in CO concentrations. NO_x concentrations were 15% to 77% lower on weekend days relative to weekdays, with the Chicago-Franklin site again having the largest weekend decrease in concentrations.

Ambient data from the Chicago-Mannheim site showed that summer and winter CO concentrations decreased by about 40% in 2008 compared to 2004–2006. Measurements of NO_x concentrations in 2008 showed a decrease of about 13% in the winter and little change in the summer compared to 2004–2006. At the Chicago-Franklin site, winter CO concentrations in 2008 decreased by about 20% compared to 2004–2006 (see Table 2-4).

For 2009, CO concentrations at the Mannheim site increased relative to 2008, particularly for summer months, while NO_x concentrations continued to decrease. At the Franklin site, both CO and NO_x concentrations decreased between 2008 and 2009. At the Northbrook site, CO and NO_x concentrations generally increased between 2008 and 2009 for winter months and decreased for summer months. It should also be noted that 2009 wintertime NO_x concentrations decreased by 45% on Saturdays at the Franklin and Mannheim sites relative to 2008, while weekday and Sunday concentrations decreased by less than 20%. This sharper decrease on Saturdays may be due to reduced heavy-duty truck traffic on Saturdays as a result of the recent economic downturn. However, at the Northbrook site, weekend NO_x concentrations rose sharply between 2008 and 2009, while weekday NO_x concentrations were virtually unchanged.

Table 2-3. Mean summer (June–August) CO and NO_x concentrations.

Site	CO (ppb)			NO_x (ppb)		
	Weekday	Saturday	Sunday	Weekday	Saturday	Sunday
2004-2006 Data						
Chicago-Franklin	643	371	417	85.9	37.7	25.0
Chicago-Mannheim	541	440	384	76.4	44.5	27.1
Milwaukee	306	266	263	21.9	13.1	11.0
Detroit-Linwood	414	304	318	34.9	21.8	16.3
2008 Data						
Chicago-Franklin	641	439	389	88.2	40.3	20.1
Chicago-Mannheim	331	255	212	73.1	44.4	30.0
Chicago-Northbrook	227	196	198	21.0	10.5	9.2
2009 Data						
Chicago-Franklin	471	335	313	57.9	31.8	20.4
Chicago-Mannheim	388	304	283	55.6	26.8	19.5
Chicago-Northbrook	210	184	178	14.2	8.9	6.7

[14] Note that the Franklin site was an exception to this pattern in 2008, when summer weekday CO concentrations were 11% higher than corresponding winter concentrations.

Table 2-4. Mean winter (December–February) CO and NO_x concentrations.

Site	CO (ppb)			NO_x (ppb)		
	Weekday	Saturday	Sunday	Weekday	Saturday	Sunday
2004-2006 Data						
Chicago-Franklin	742	520	411	119.1	61.3	38.9
Chicago-Mannheim	745	560	487	132.6	75.1	55.4
Milwaukee	448	425	338	49.5	41.6	21.6
Detroit-Linwood	510	476	429	57.1	48.3	39.8
2008 Data						
Chicago-Franklin	579	433	350	111.8	66.0	40.8
Chicago-Mannheim	436	310	283	115.6	68.0	47.8
Chicago-Northbrook[a]	282	199	199	42.8	11.9	16.4
2009[b] Data						
Chicago-Franklin	524	422	360	90.7	36.3	39.4
Chicago-Mannheim	463	304	331	93.5	36.2	41.7
Chicago-Northbrook	335	256	269	41.9	18.9	28.7

[a] Wintertime concentrations listed for the Northbrook site represent the month of December 2008 only.
[b] Wintertime concentrations listed for 2009 include available data from January and February 2010.

Diurnal patterns of TNMOC, NO_x, and CO concentrations were explored using notched box whisker plots (**Figure 2-10**). Across all years, weekday TNMOC, NO_x, and CO concentrations generally showed a morning peak, consistent with traffic activity, and an afternoon decrease, which could be a function of both decreased traffic activity and increased atmospheric mixing. Diurnal plots of pollutant concentrations for 2004–2006 are shown in **Figures 2-11 through 2-18**, and diurnal plots for additional years are provided in **Appendix C**. On weekend days, a small increase in concentrations is generally observed for both TNMOC and NO_x just after noon, consistent with delayed traffic activity on weekends compared to weekdays (also seen by Chinkin et al., 2002). At Jardine (Figure 2-11), the diurnal profile for TNMOC on weekend days is much flatter than on weekdays (i.e., concentrations vary less from hour to hour). However, at Northbrook, the weekend and weekday diurnal profiles for TNMOC are very similar (Figure 2-12). For CO, diurnal variations are somewhat dampened by the resolution of the data. In addition, the instrument used at the Gary site appears to have a detection limit of 250 ppb, so there are no data below that value.

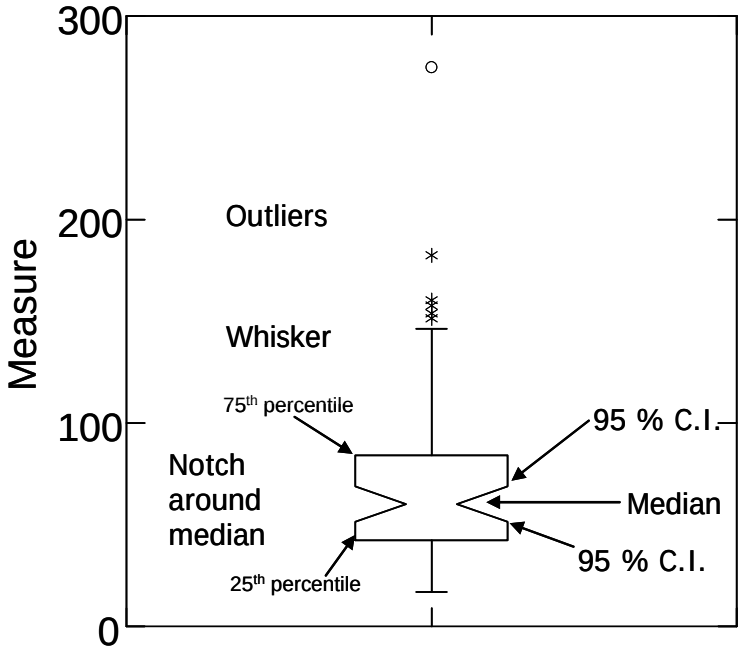

Figure 2-10. Interpretation of notched box whisker plots produced by SYSTAT. Boxes show the 25th to 75th percentiles (interquartile range, or IQR); whiskers extend to 1.5IQR; and concentrations beyond the whiskers are designated by asterisks. Concentrations beyond 3IQR are designated with open circles. The median and 95% confidence intervals (C.I.) are shown by a notch.

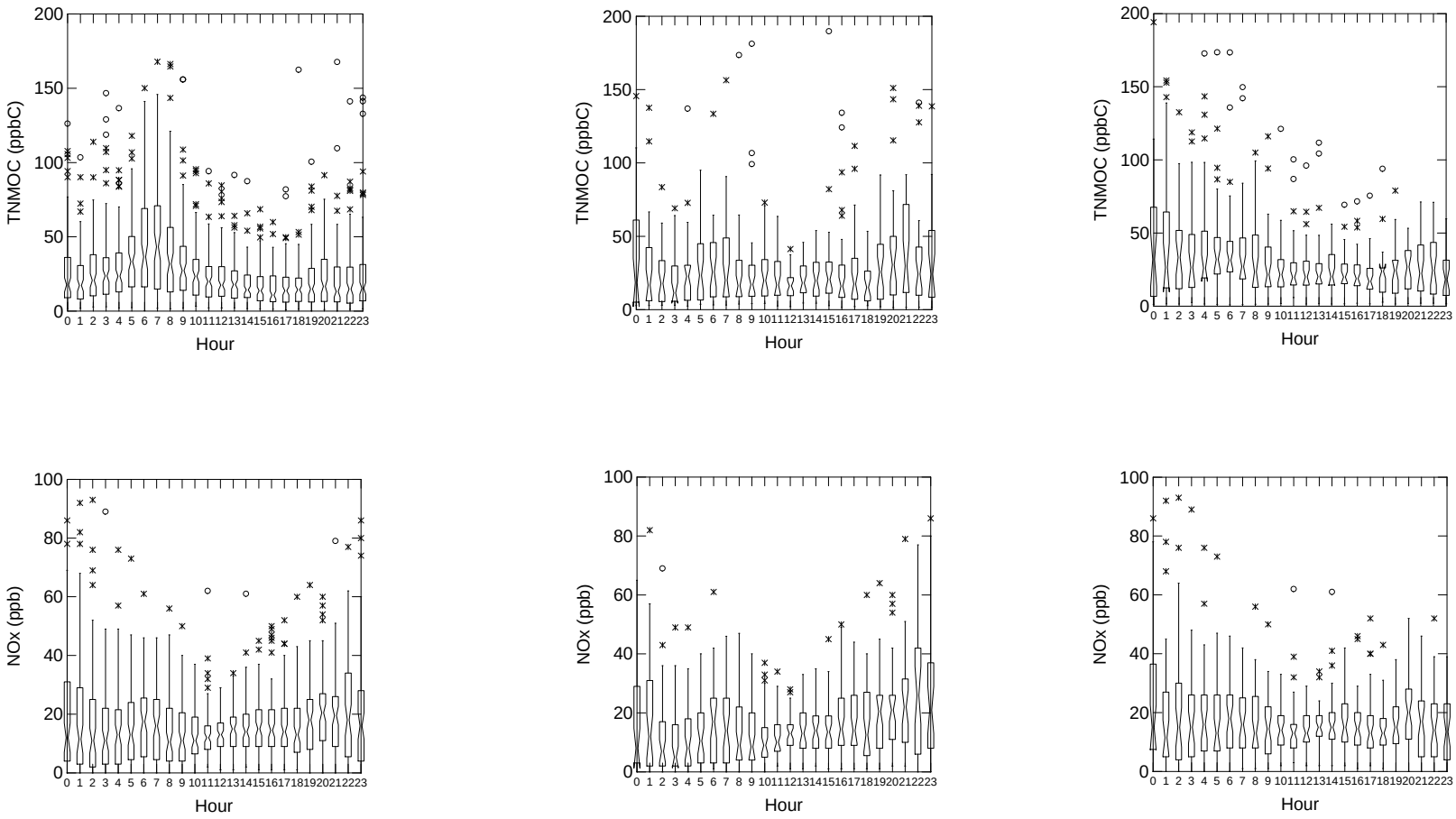

Figure 2-11. Hourly TNMOC and NO_x concentrations for the Chicago-Jardine site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

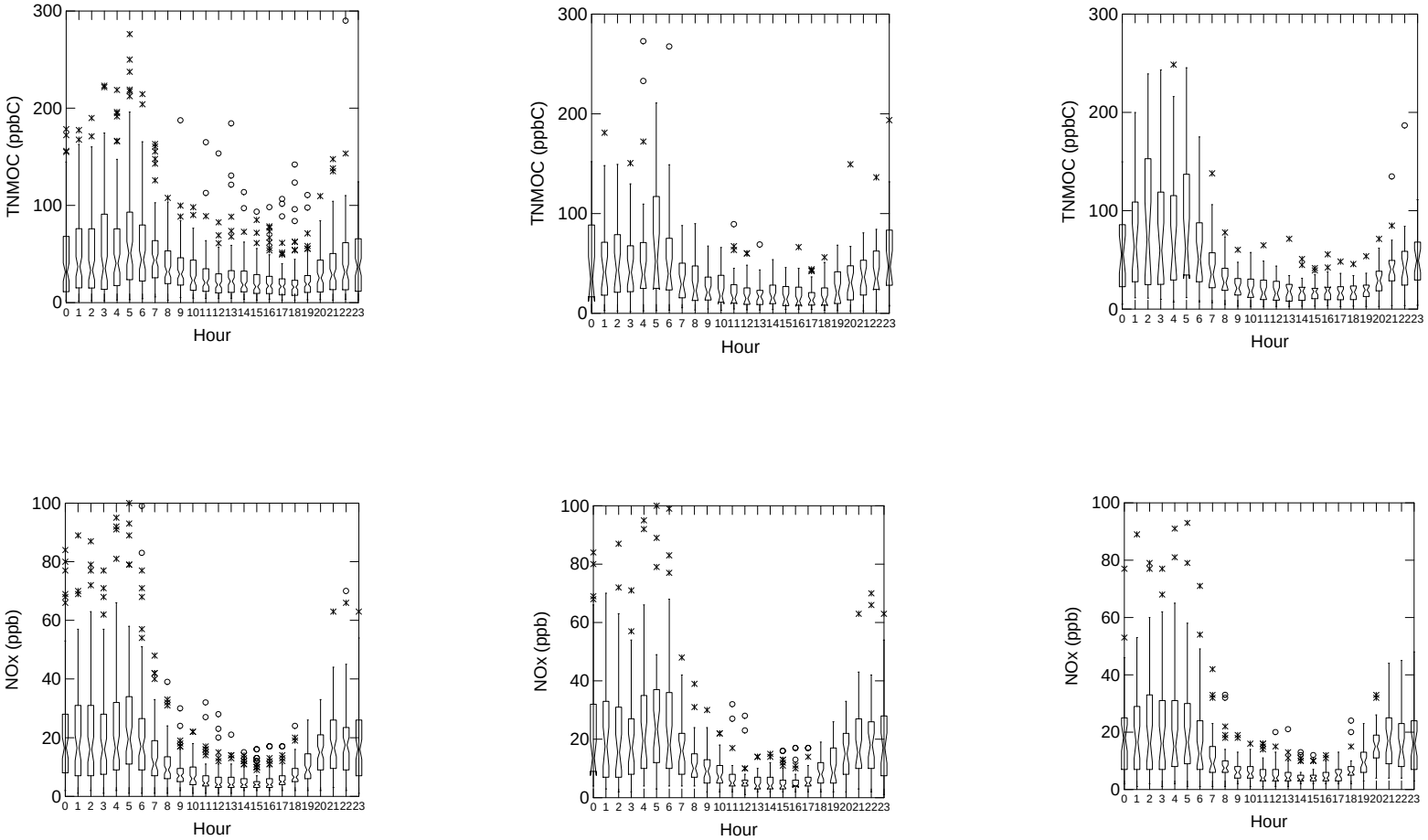

Figure 2-12. Hourly TNMOC and NO_x concentrations for the Chicago-Northbrook site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

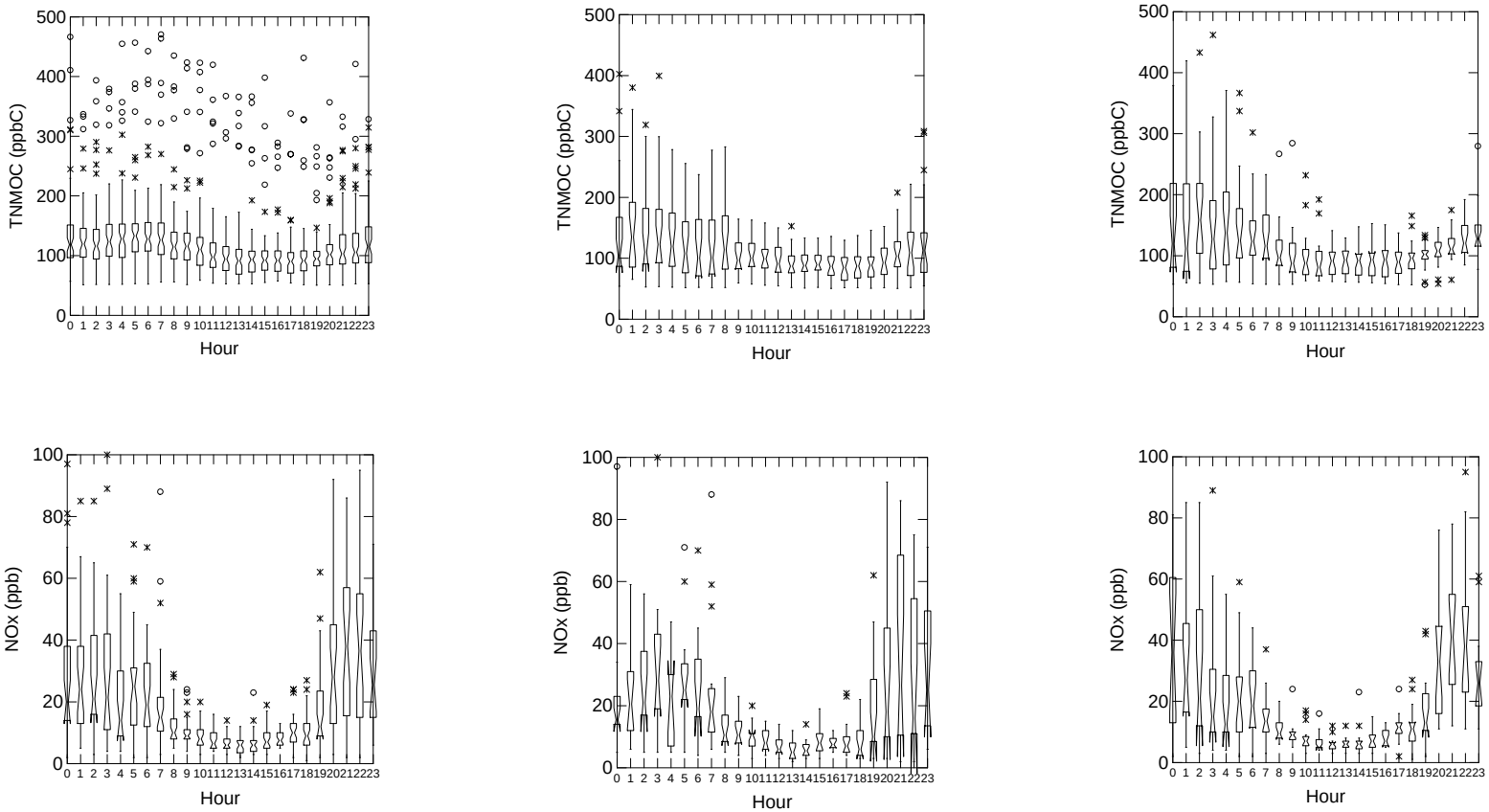

Figure 2-13. Hourly TNMOC and NO_x concentrations for the Gary site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

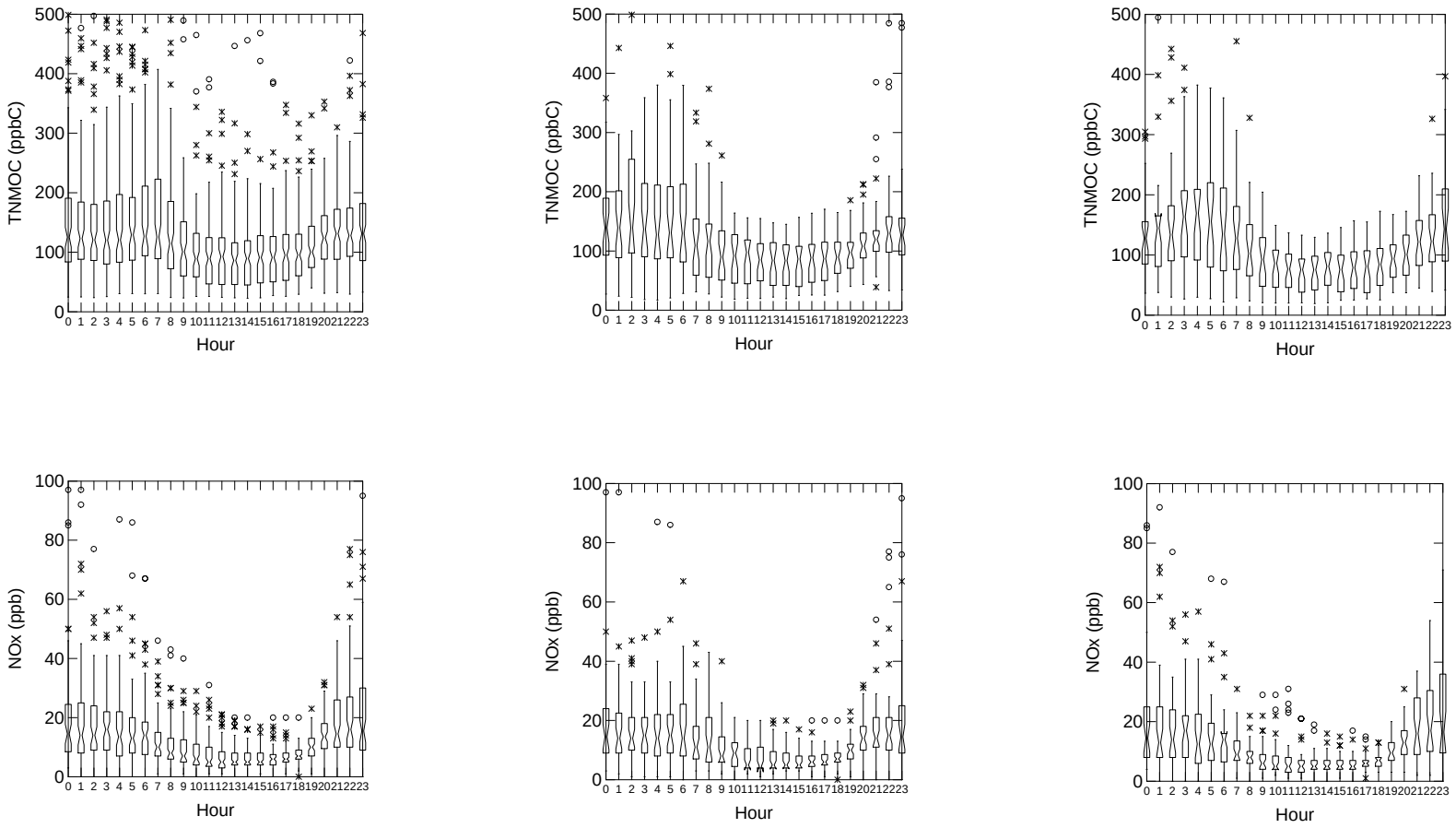

Figure 2-14. Hourly TNMOC and NO_x concentrations for the Detroit-East 7 Mile site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

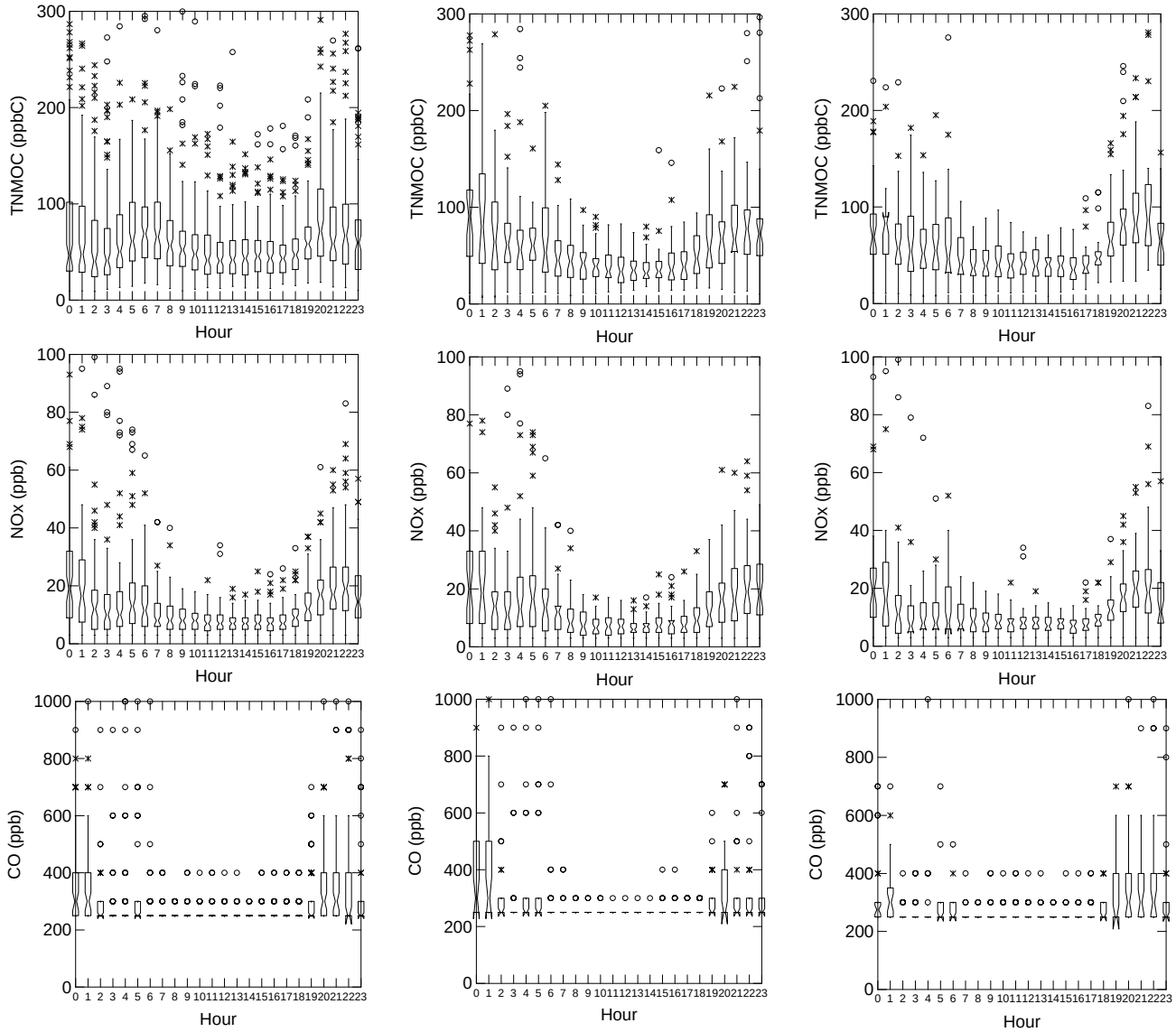

Figure 2-15. Hourly TNMOC, NO_x, and CO concentrations for the Milwaukee site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

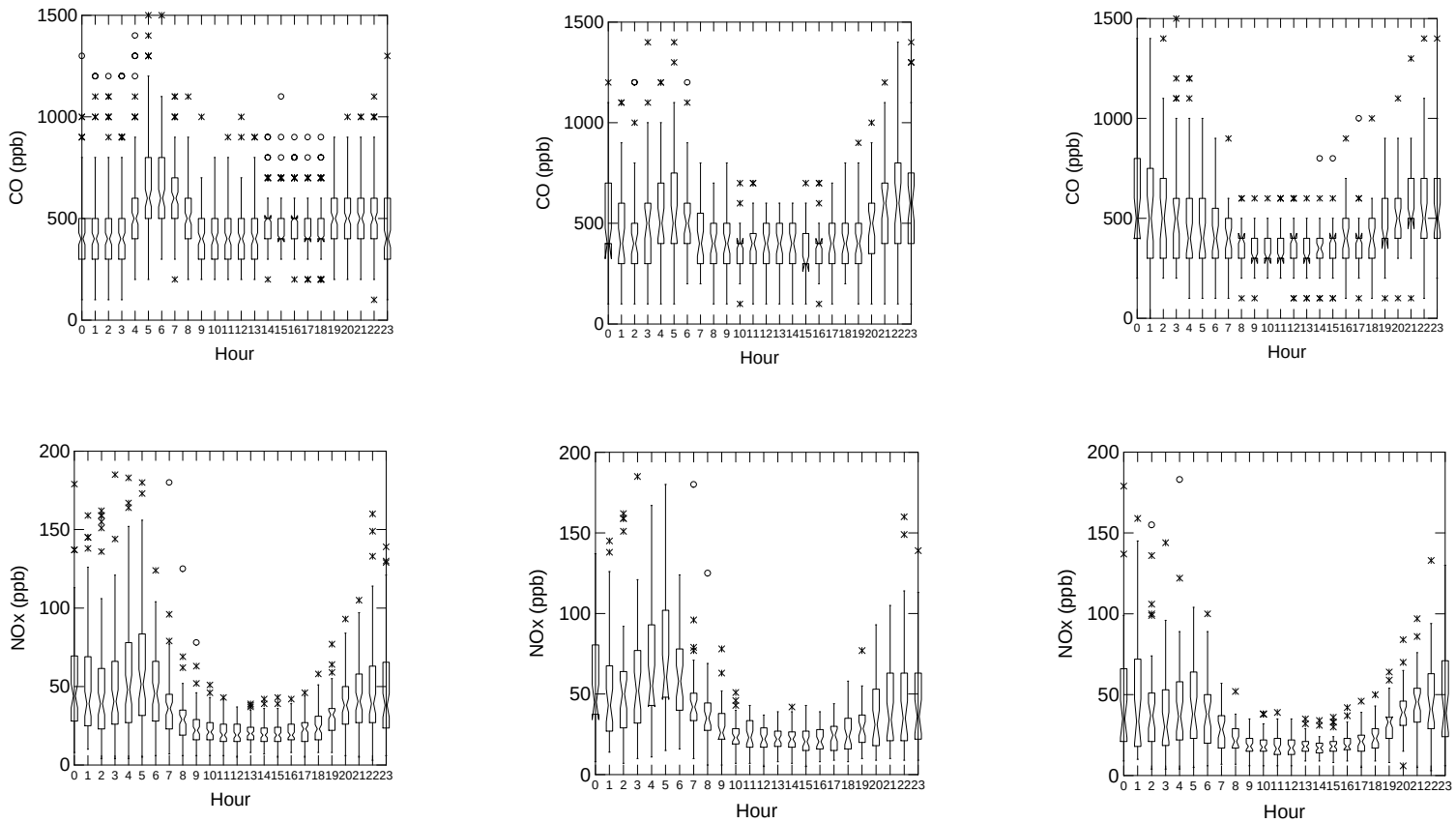

Figure 2-16. Hourly CO and NO_x concentrations for the Chicago-Mannheim site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

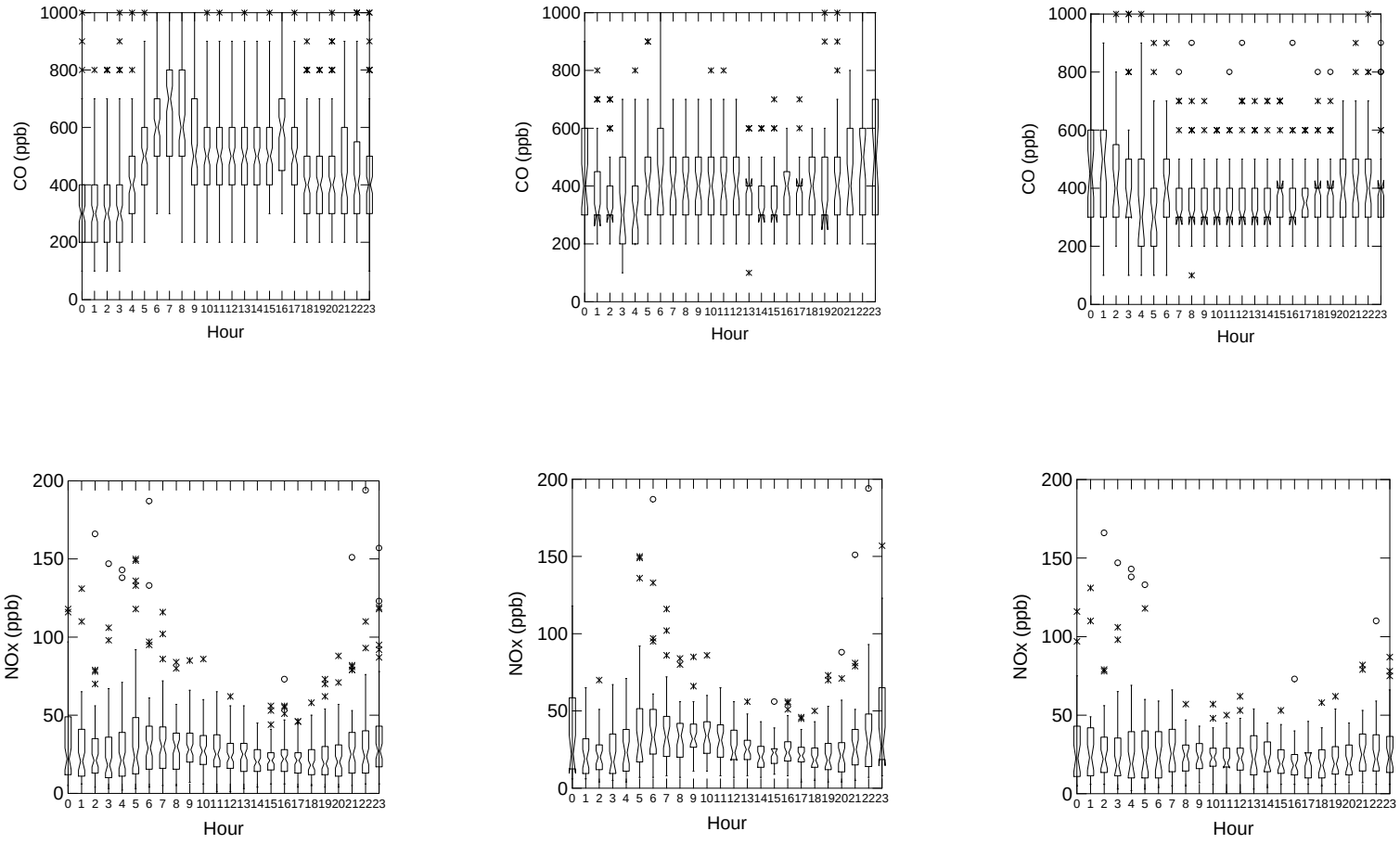

Figure 2-17. Hourly CO and NO_x concentrations for the Chicago-Franklin site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

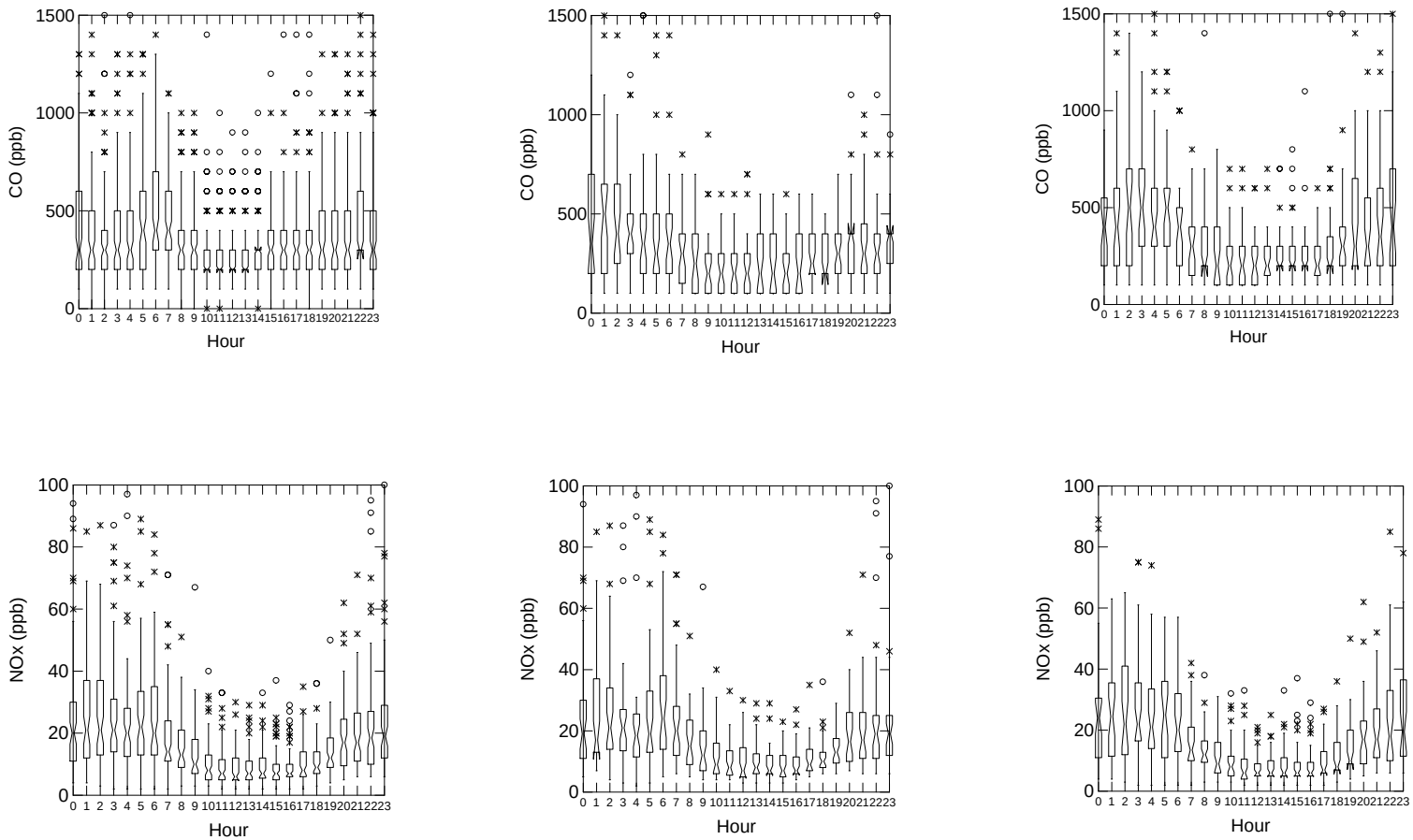

Figure 2-18. Hourly CO and NO_x concentrations for the Detroit-Linwood site for summer weekdays (left), Saturdays (center), and Sundays (right), 2004–2006.

2.1.5 Ambient Data Screening

As described in Section 1.3.3, a major premise of the top-down evaluation is that only monitoring sites and sampling periods that are dominated by fresh emissions are considered in the analysis. Therefore, ambient measurements that do not exceed background thresholds were not included in the data sets used to calculate pollutant ratios. For this analysis, we used concentration thresholds of VOC > 50 ppbC, NO_x > 10 ppb, and CO > 0.150 ppm (Chinkin and Reid, 2006; LADCO, 1998).

2.2 Emissions Inventory Data

2.2.1 Emissions Data Acquisition and Processing

LADCO provided 2005 Base M emissions inventory data files and supporting files (e.g., speciation profile libraries) for area, point, non-road mobile, on-road mobile and biogenic sources. LADCO's anthropogenic emission files contain criteria pollutant emissions that have been spatially resolved to a 4-km grid resolution and temporally resolved to an hourly basis. For all anthropogenic source sectors other than on-road mobile sources, emissions data were provided for a representative weekday, Saturday, and Sunday in each month of 2005. For on-road sources, gridded criteria pollutant emissions were provided for a January weekday, Saturday, and Sunday, and air quality model-ready emission inputs were provided for January and July weekdays, Saturdays, and Sundays. For biogenic sources, hourly emissions data for isoprene and other air quality model-ready biogenic species were provided at a 12-km grid resolution for each day of 2005. Emissions grid domains and file formats varied by source sector (see **Figure 2-19** and **Table 2-5**), with file formats including SAS, PostgreSQL, and CAMx binary.

For 2008, LADCO provided Base B (on-road and non-road mobile sources) and Base C (area and point sources) anthropogenic[15] inventories at the same spatial (4-km) and temporal (hourly) resolution as the 2005 emissions inventories. All 2008 emissions were provided in SAS format for the innermost grid domain shown in Figure 2-19, and files for a representative weekday, Saturday, and Sunday in each month were again made available. For on-road mobile sources, 2008 emissions were generated by running the MOVES model with county-level default data for the region, then gridding the county-level emissions using spatial surrogate data.[16] By contrast, the 2005 on-road inventory was developed at the link level using MOBILE6.2 emission factors within the Consolidated Community Emissions Processing Tool (CONCEPT).[17] As a result, some differences between the 2005 and 2008 on-road inventories result from this change in models, rather than from changes in vehicle fleets and activities alone.

[15] Biogenic emissions for 2008 were not available, so emissions from this source sector were held constant from 2005.

[16] For light-duty vehicles, LADCO used a hybrid surrogate that combined vehicle miles traveled (weighted 75%) with population data (weighted 25%). For trucks, LADCO used miles traveled on rural secondary roads as the spatial surrogate.

[17] For subsequent versions of the 2008 on-road inventory, LADCO will replace MOVES default data with local information on vehicle characteristics and activities and will generate link-level emissions using CONCEPT.

Figure 2-19. Emissions grid domains for the LADCO 2005 Base M inventories.

Table 2-5. LADCO emissions inventory files for January 14, 2005.

File Name	Description
areaemis.sas7bdat.050114.other_baseM_v3_4km	SAS file for area source emissions
areaemis.sas7bdat.050114.mar_baseM_4km	SAS file for marine, aircraft, and rail emissions
areaemis.sas7bdat.050114.nonroad_baseM_v3_4km	SAS file for non-road mobile source emissions other than marine, aircraft, and rail
ptemis.sas7bdat.050114.egu_baseM_4km	SAS file for electrical generating units (EGUs)
ptemis.sas7bdat.050114.pt_nonutil_baseM_4km	SAS file for non-EGU point sources
ocin_[network]_01142005_01.mv_emissions_raw.sql	PostgreSQL file for on-road mobile source emissions (files provided for transportation networks covering Chicago, Milwaukee, Gary, and Detroit)
camx_mv.[network]_01142005_01.base.out.200514.bin	CAMx-ready on-road emissions file
biog.20050114.upmw.12.megan.ld.bin	CAMx-ready biogenic emissions file

To prepare the emissions data for use in subsequent analyses, we converted all data files to a common CSV format. We then extracted data records for the grid cells included in the grid analysis zones around each of the eight monitoring sites of interest. These grid analysis zones were identified for each site on the basis of predominant wind speeds during the early morning hours (0600–0900), as described in Section 1.2.2. For the Gary site and three of the Chicago area sites, the grid analysis zone consists of a 9 x 9 grid cell area with the monitoring site in the center cell. For the Northbrook site in Chicago and the sites in Detroit and Milwaukee—where average morning wind speeds were lower—the grid analysis zone consists of a 7 x 7 grid cell area around each site.

Additional pre-processing was required for 2005 on-road mobile and biogenic sources because it was necessary to use emissions data that had been prepared for the Comprehensive Air Quality Model with extensions (CAMx). For 2005, gridded, hourly criteria pollutant emissions for on-road mobile sources were available only for January, so gridded hourly emissions for July were developed on the basis of CAMx-ready emissions.[18] The CAMx-ready files for January and July contain gridded, hourly emissions, but the emissions for organic species are grouped together by carbon bond mechanisms rather than reported by individual hydrocarbon species (as required for comparisons with ambient data). As a result, scaling factors were derived from the January and July CAMx emissions data that could be used to convert January criteria pollutant emissions data to July emissions data. Specifically, CAMx-ready species CO, nitric oxide (NO), and paraffin carbon bond (PAR[19]), were extracted for the grid analysis zone around each monitoring site; the ratio of January and July morning hour (0600–0900) emissions for each site was used to scale January criteria pollutant emissions that had been extracted from PostgreSQL files. For other months of interest, on-road emissions data were prepared by performing a linear interpolation on January and July emissions, in keeping with the method LADCO has used to develop emissions estimates for on-road sources for months other than January and July.

For biogenic sources, CAMx-ready emission inputs were provided at a 12-km resolution for each day of 2005. Emissions data from these files were averaged across months of interest (December–February and June–August), and isoprene[20] emissions for each monitoring site's grid analysis were then extracted from each monthly average file. Because biogenic emissions data were reported at a 12-km resolution, gridded emissions were disaggregated to a 4-km resolution by evenly distributing the emissions for each 12-km grid cell across the nine 4-km grid cells contained within the larger 12-km cell.

Once pre-processing of the emissions data was complete, STI speciated (i.e., disaggregated into individual hydrocarbon species) anthropogenic VOC emissions using the speciation profiles and cross-reference files provided by LADCO. At LADCO's direction, the same speciation data was applied to both the 2005 and 2008 inventories, and this process resulted in a speciated inventory with hundreds of chemical species. However, the ambient data collection and analysis method is capable of quantifying only hydrocarbons containing between approximately 2 and 12 carbon atoms (i.e., PAMS hydrocarbons). To ensure that the same

[18] This step was unnecessary for the 2008 inventories, as gridded, hourly on-road emissions data was available for all months.
[19] PAR is the dominant organic species in the on-road emissions inventories and was used as a surrogate for VOC emissions.
[20] Isoprene is the dominant biogenic species and is the only biogenic species measured at PAMS sites.

chemical compounds are being compared in the ratio comparisons, the individual chemical species reported in the emissions inventory were matched to those measured in the ambient data. The compounds reported in the emissions inventory that were not measurable in the ambient samples were excluded from the analysis. To compare the emissions inventory data to ambient data, the emissions inventory data were converted from mass to molar units.

2.2.2 Emissions Data Characterizations by Site

To gain an understanding of the source mix around each monitoring site, we summarized the 2005 and 2008 emissions data for each site's grid analysis zone. **Tables 2-6 through 2-8** summarize morning (0600-0900) emissions for sites where TNMOC/NO_x and CO/NO_x ratios were evaluated, while **Figures 2-20 and 2-21** break down morning emissions by source sector and year for all sites. These tables and figures show that, in general, CO and NO_x emissions decreased more sharply from 2005 to 2008 than VOC emissions. This difference was largely driven by the on-road mobile source sector, as 2008 CO and NO_x emissions from the MOVES model were 28% to 78% lower for winter months than corresponding 2005 estimates generated with MOBILE6.2, while 2008 on-road VOC emissions were comparable to (and, in some cases, higher) than corresponding 2005 emissions for both summer and winter months (see **Figure 2-22**). It should be noted that the sharp decreases in on-road NO_x emissions around the monitoring sites was driven, in part, by differences in the spatial distributions of emissions for 2005 and 2008. For example, **Figure 2-23** shows the spatial distribution of on-road NO_x emissions for 2005 and 2008 for Cook County, and emissions have clearly been shifted from the lakefront area to the northwestern part of the county.[21] However, the total on-road NO_x emissions for Cook County decreased by 32% from 2005 to 2008 (for January weekdays), so the significant NO_x emissions reductions around the Chicago-area monitoring sites was not solely due to spatial differences in the 2005 and 2008 inventories.

The 2008 inventories also show less of an emissions decrease from Saturdays to Sunday than the 2005 inventories, which is again driven by differences in the on-road mobile source sector. The 2008 MOVES-based inventories treat Saturdays and Sundays the same and also show less of a decrease from weekdays to weekend days than the 2005 inventories (see **Figure 2-24**). However, it should be noted that this feature of the 2008 on-road emissions data results from using MOVES default day-of-week profiles.

Emissions summaries by source sector for each monitoring site of interest (see Figures 2-20 and 2-21) show that on-road mobile source emissions account for 61% to 80% of the January CO emissions in both 2005 and 2008. For 2005, on-road mobile sources account for 50% to 73% of the January and July NO_x emissions around each monitoring site except for the Gary site, where the point source CO and NO_x inventories were more dominant than at the other sites. However, for 2008, on-road mobile sources account for only 29% to 54% of the January and July NO_x emissions around the non-Gary sites due to sharp reductions in on-road NO_x emissions between the 2005 and 2008 inventories. For VOC, area sources account for 35% to

[21] These differences in the spatial distribution of on-road NO_x emissions result from the use of link-level vehicle activity data for the 2005 inventory vs. the gridding of county-level 2008 emissions using spatial surrogate data (e.g., rural secondary roads for truck activity).

57% of the January and July emissions around each site in both 2005 and 2008,[22] while on-road mobile sources account for only 15% to 39% of the January and July emissions around each site.

For the sites where TNMOC/NO_x ratios were evaluated, VOC emissions were highest around the Chicago-Jardine site and lowest around the Gary and Milwaukee sites for both 2005 and 2008 (see Table 2-6). Conversely, 2005 ambient TNMOC concentrations were highest at the Gary and Detroit-East 7 Mile sites, and lowest at the Jardine site. In addition, VOC emissions around the East 7 Mile site were 18% lower than VOC emissions around the Jardine site (see Table 2-6). These discrepancies suggest that VOC emissions are underestimated at the Gary and East 7 Mile sites in the 2005 inventories.

For 2008, weekday VOC emissions decreased by 26% at the Milwaukee site relative to 2005, while 2008 ambient TNMOC concentrations increased by 24% relative to 2004. At the Chicago-Northbrook site, both VOC emissions and ambient TNMOC concentrations showed little change from 2005 to 2008 (Milwaukee and Northbrook were the only two sites for which 2008 ambient TNMOC measurements were available).

For sites where CO/NO_x ratios were evaluated, 2005 and 2008 emissions were highest at the Franklin and Mannheim sites in Chicago and lowest at the Milwaukee site (see Tables 2-7 and 2-8). Across all sites and years, emissions decreased more sharply relative to weekdays on Sundays than on Saturdays, though this effect was much more pronounced in the 2005 data than the 2008 data because Saturday and Sunday emissions were identical in the 2008 MOVES-based on-road inventory (as discussed above).

Table 2-6. Summary of summer (July) VOC and NO_x emissions for hours 0600 to 0900 for the grid analysis zone around each monitoring site analyzed.

Site	VOC (tons/day)			NO_x (tons/day)		
	Weekday	Saturday	Sunday	Weekday	Saturday	Sunday
2005 Data						
Chicago-Jardine	43.7	41.3	34.3	43.0	37.1	32.2
Chicago-Northbrook	19.0	19.9	15.9	16.6	15.1	12.7
Milwaukee	18.3	12.2	9.7	19.5	9.9	6.0
Gary	13.1	15.9	12.0	22.3	21.8	19.3
Detroit-E7 Mile	35.9	25.2	18.2	29.0	13.0	9.4
2008 Data						
Chicago-Jardine	40.2	40.5	40.3	28.0	24.5	23.9
Chicago-Northbrook	19.6	19.8	19.7	12.3	10.5	10.2
Milwaukee	13.6	13.2	13.2	11.6	9.9	9.4
Gary	11.6	13.8	13.8	17.3	17.3	16.0
Detroit-E7 Mile	26.1	22.8	22.7	15.7	12.8	12.5

[22] Key area sources of VOC include architectural coatings and consumer products.

Table 2-7. Summary of summer (July) CO and NO_x emissions for hours 0600 to 0900 for the grid analysis zone around each monitoring site analyzed.

Site	CO (tons/day)			NO_x (tons/day)		
	Weekday	Saturday	Sunday	Weekday	Saturday	Sunday
2005 Data						
Chicago-Franklin	237.1	279.4	193.7	46.4	40.6	35.5
Chicago-Mannheim	324.1	386.5	254.5	56.3	49.3	41.6
Milwaukee	91.0	75.1	46.4	19.5	9.9	6.0
Detroit-Linwood	169.5	147.4	102.2	35.7	18.3	14.1
2008 Data						
Chicago-Franklin	178.3	162.1	159.9	28.1	25.1	24.5
Chicago-Mannheim	225.0	197.0	194.4	28.1	23.8	23.2
Milwaukee	73.5	65.0	64.3	11.6	9.9	9.4
Detroit-Linwood	130.8	113.6	112.4	19.6	16.5	15.8

Table 2-8. Summary of winter (January) CO and NOx emissions for hours 0600 to 0900 for the grid analysis zone around each monitoring site analyzed.

Site	CO (tons/day)			NO_x (tons/day)		
	Weekday	Saturday	Sunday	Weekday	Saturday	Sunday
2005 Data						
Chicago-Franklin	255.9	178.5	139.9	48.2	39.4	34.2
Chicago-Mannheim	332.5	235.1	181.1	59.7	47.7	39.8
Milwaukee	152.3	40.8	42.0	23.4	7.9	6.8
Detroit-Linwood	241.6	130.9	99.1	43.8	20.4	18.4
2008 Data						
Chicago-Franklin	181.9	144.9	143.4	30.5	26.9	26.5
Chicago-Mannheim	206.7	164.0	162.2	29.4	25.3	24.8
Milwaukee	77.6	63.0	62.5	12.3	10.7	10.3
Detroit-Linwood	123.5	101.1	100.3	21.1	18.3	17.7

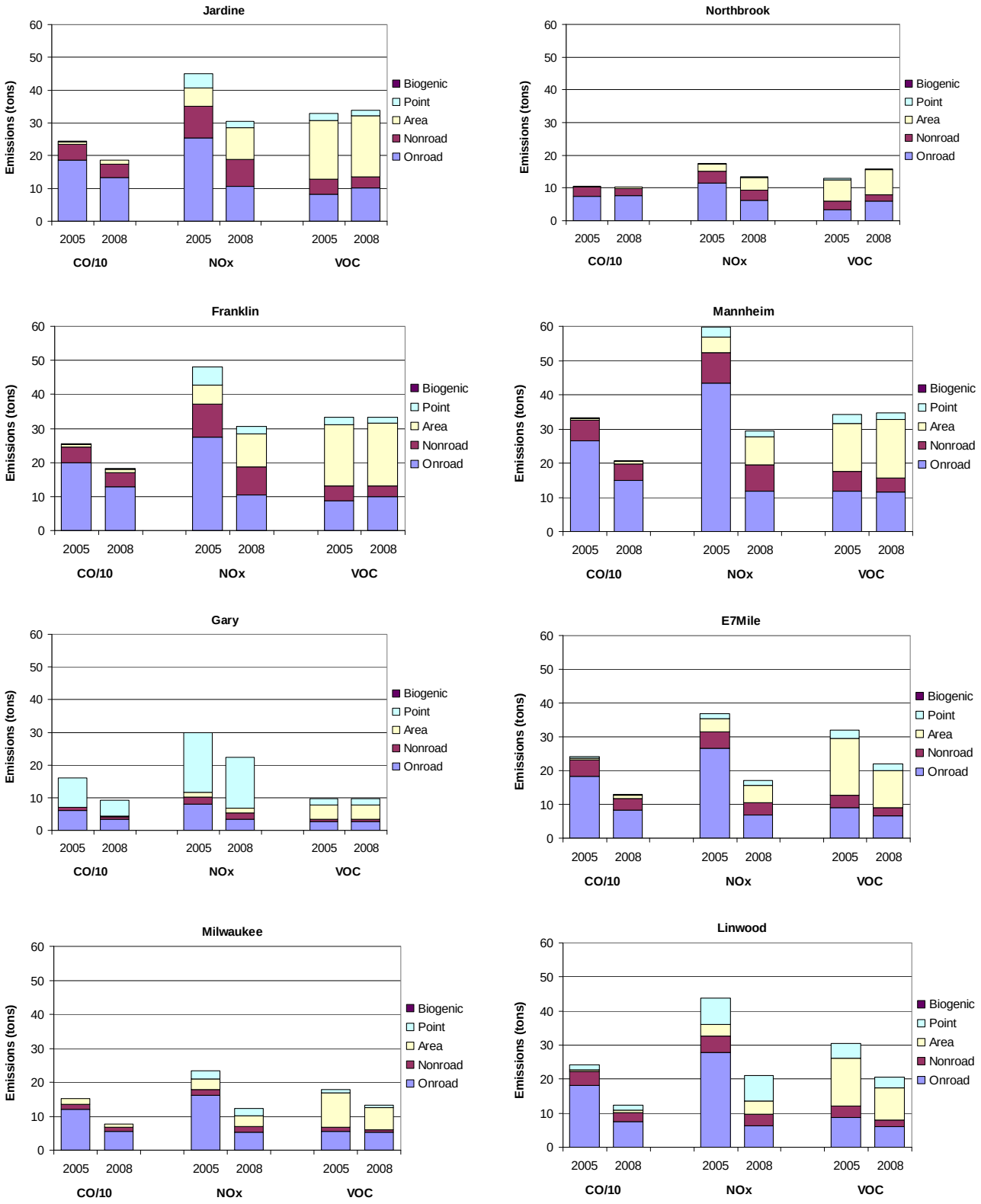

Figure 2-20. January weekday emissions by source sector for the grid analysis zone around each monitoring site for hours 0600 to 0900.

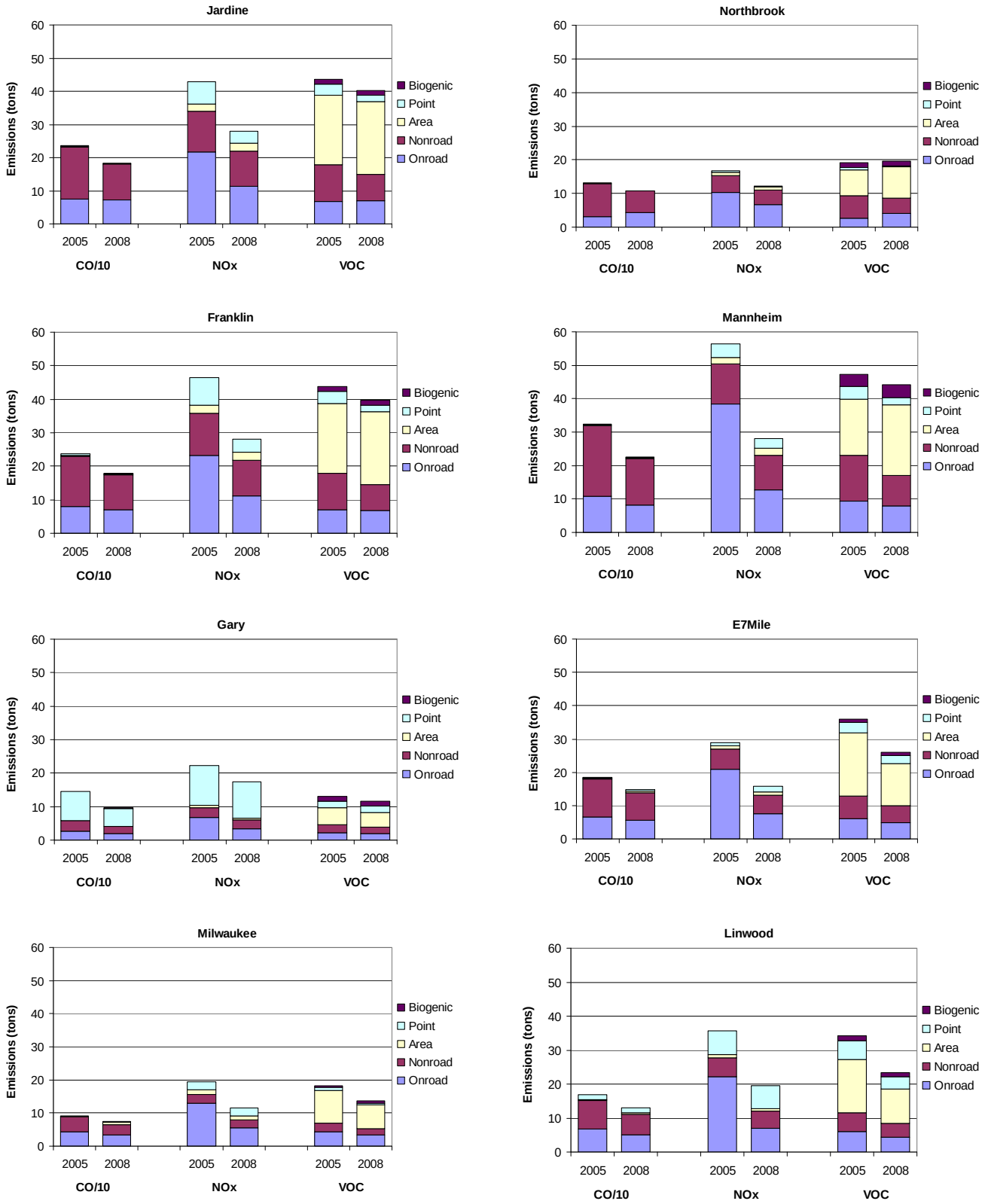

Figure 2-21. July weekday emissions by source sector for the grid analysis zone around each monitoring site for hours 0600 to 0900.

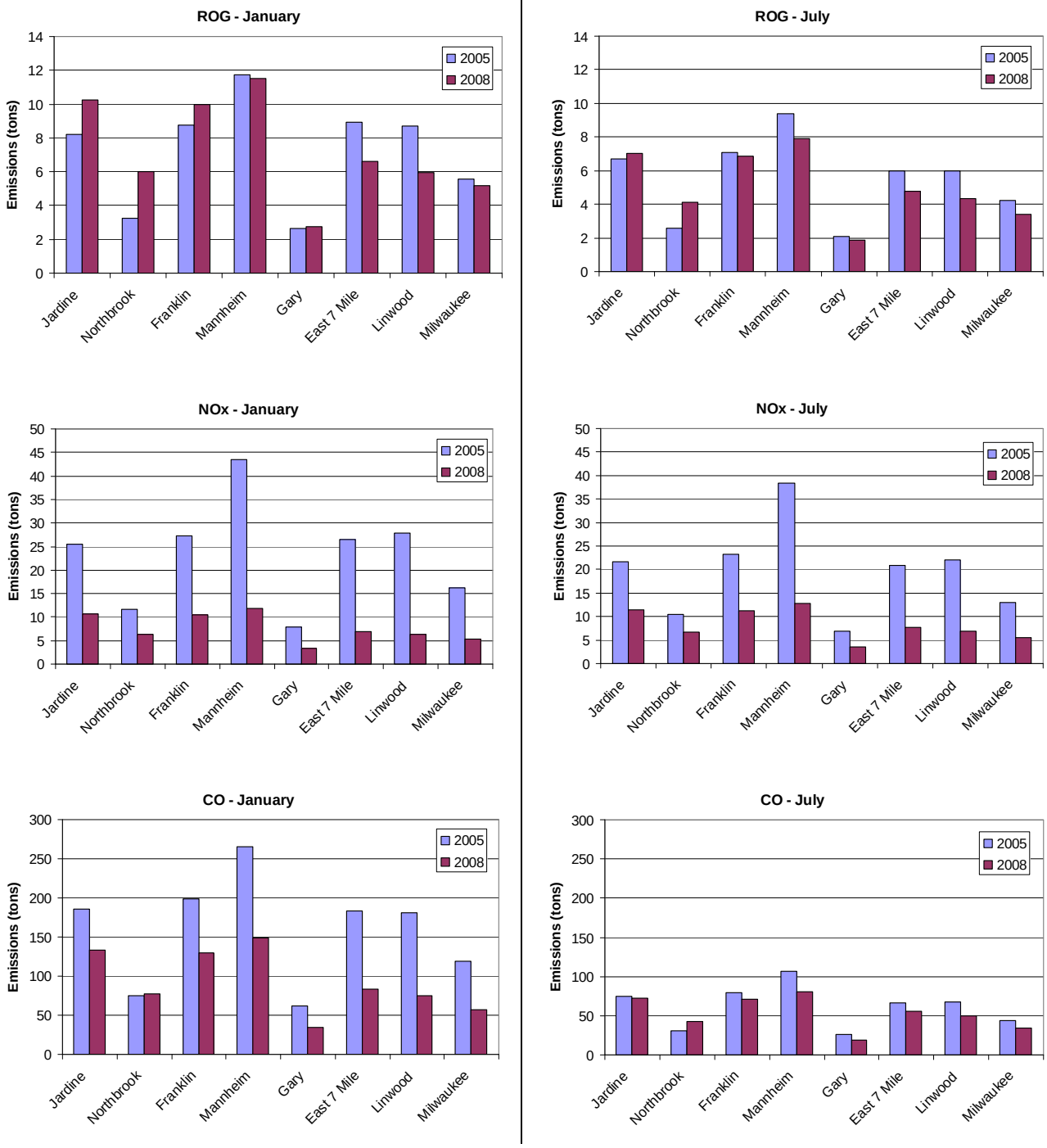

Figure 2-22. January (left) and July (right) weekday on-road mobile source emissions for the grid analysis zone around each monitoring site for hours 0600 to 0900.

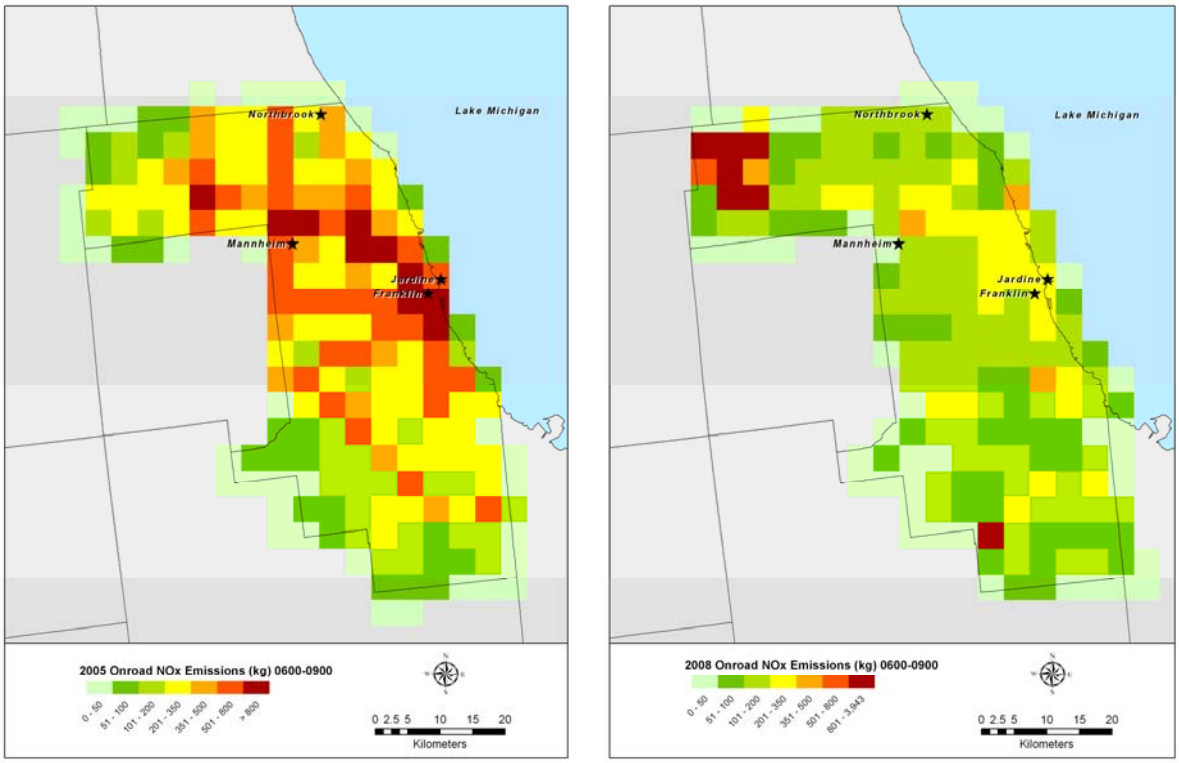

Figure 2-23. Spatial distributions of NO_x emissions from on-road mobile sources in Cook County for LADCO's 2005 (left) and 2008 (right) inventories.

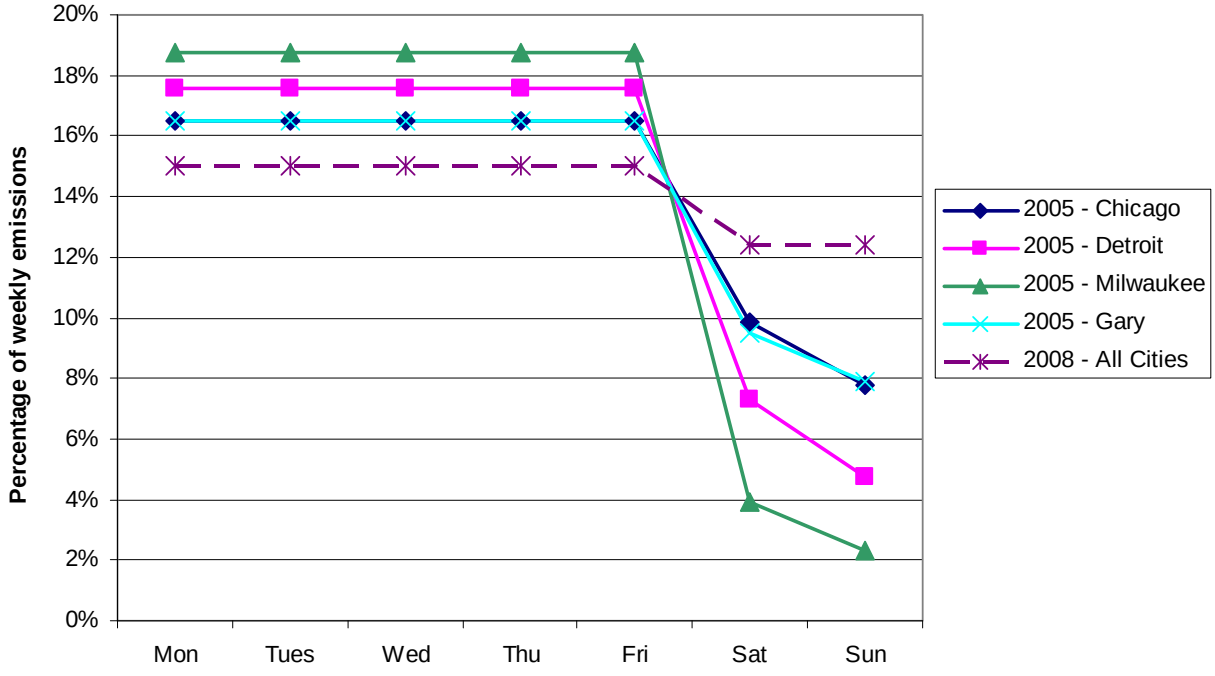

Figure 2-24. Day-of-week emissions profiles for on-road mobile sources.

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3. Pollutant Ratio Comparison Results

To evaluate the relative amounts of TNMOC (PAMSHC), NO_x, and CO in the urban areas of interest, ambient- and emissions inventory-derived TNMOC/NO_x and CO/NO_x ratios were compared. Comparisons were made for the full extent grid analysis zone surrounding each monitoring site and for each individual wind quadrant within the analysis zone. Ambient data average and median ratios were calculated, and ratios were calculated for the emissions inventory with and without elevated sources.[23]

3.1 TNMOC/NO_x Ratio Comparisons

TNMOC/NO_x ratios for the summer months were calculated by day of week (weekday, Saturday, and Sunday), month (June, July, and August), summer season (June through August), and wind quadrant. For 2005, comparisons between ambient- and emissions-inventory-derived TNMOC/NO_x ratios were made for five sites: Chicago-Jardine, Chicago-Northbrook, Gary, Detroit-East 7 Mile, and Milwaukee. For 2008, comparisons were made for the two sites for which ambient TNMOC measurements were available: Chicago-Northbrook and Milwaukee.

Table 3-1 shows calculated ratios for the full grid extent around each monitoring site (previously shown in Table 1-2) for all summer days. For both 2005 and 2008, these data show good agreement[24] (±20%) between ambient- and emissions inventory-derived ratios at the Chicago sites. However, at the remaining sites, ambient-derived ratios were higher than emissions inventory-derived ratios by a factor of 1.8 or more, although the ratios showed somewhat closer agreement when elevated sources were excluded from the analysis.

Across all sites, emissions inventory-derived TNMOC/NO_x ratios were higher in 2008 than in 2005, which resulted from decreases in on-road NO_x emissions that were greater than decreases in on-road VOC emissions. At the two sites for which both 2005 and 2008 data were available, ambient-derived TNMOC/NO_x ratios were also higher in 2008 than in 2005. The following sections show TNMOC/NO_x ratio charts by wind quadrant and day of week and discuss the results of the analysis for each site. Additional charts (e.g., TNMOC/NO_x ratios by month) can be found in **Appendix D**.

[23] Emissions from elevated sources may be injected above the mixed layer and, hence, may not affect surface-level ambient concentrations—especially during morning hours. Pollutant ratios were calculated with and without elevated sources to characterize the potential effects of this phenomenon.

[24] Because of the inherent uncertainties associated with this analysis method, ambient- and emissions inventory-derived ratios that are within approximately 25-50% of each other are considered to be in good agreement (California Air Resources Board, 1997).

Table 3-1. TNMOC/NO_x ratios by site for the hours 0600 to 0900 (emission ratios for full grid extent around each site; ambient ratios for 2005 based on 2004–2006 data).

Site	Ambient Ratios	Emissions Inventory Ratios		Ambient/EI (Low Level)	Ambient/EI (Low Level + Elevated)
		Low Level Only	Low Level + Elevated		
2005 Data					
Chicago-Jardine	1.6	1.7	1.6	0.9	1.0
Chicago-Northbrook	2.2	1.8	1.8	1.2	1.2
Gary	6.0	1.6	1.1	3.6	5.4
Detroit-E7 Mile	6.3	2.3	2.2	2.7	2.9
Milwaukee	3.5	2.0	1.5	1.8	2.3
2008 Data					
Chicago-Jardine	--	2.5	2.2	--	--
Chicago-Northbrook	2.6	2.9	2.9	0.9	0.9
Gary	--	1.8	1.1	--	--
Detroit-E7 Mile	--	2.7	2.4	--	--
Milwaukee	5.1	2.1	1.7	2.4	2.9

3.1.1 Ratio Comparison Results for Chicago-Jardine

Figure 3-1 shows 2005 TNMOC/NO_x ratios by wind quadrant[25] and day of week for the Jardine site in Chicago, Illinois. Overall, there is good agreement between the ambient- and emissions inventory-derived ratios at this site across all wind quadrants and days of week. For wind quadrant 1, however, the agreement between ambient- and emissions inventory-derived ratios is poorer than for the remaining wind quadrants, with the emissions inventory-derived ratio about 40% higher than the ambient-derived ratio. However, it should be noted that because wind quadrant 1 lies northeast of the site, over Lake Michigan (see Figure 2-4), emission levels in that quadrant are very low compared to the other wind quadrants.

Also, the agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios is poorer on weekend days than on weekdays. This is particularly true for Sundays, when the ambient-derived TNMOC/NO_x ratio is about 40% higher than the corresponding emissions-derived ratio. Sunday TNMOC and NO_x concentrations at Jardine are both about 20% higher than Saturday concentrations, making the ambient-derived TNMOC/NO_x ratios at that site virtually the same on Saturdays and Sundays. However, the emissions inventory shows decreases in both VOC and NO_x emissions on Sundays relative to Saturdays, and the somewhat sharper decrease in VOC emissions lowers the emissions inventory-derived TNMOC/NO_x ratio.

[25] On all bar charts, the ambient value represents the median, and error bars represent the 25th and 75th percentiles.

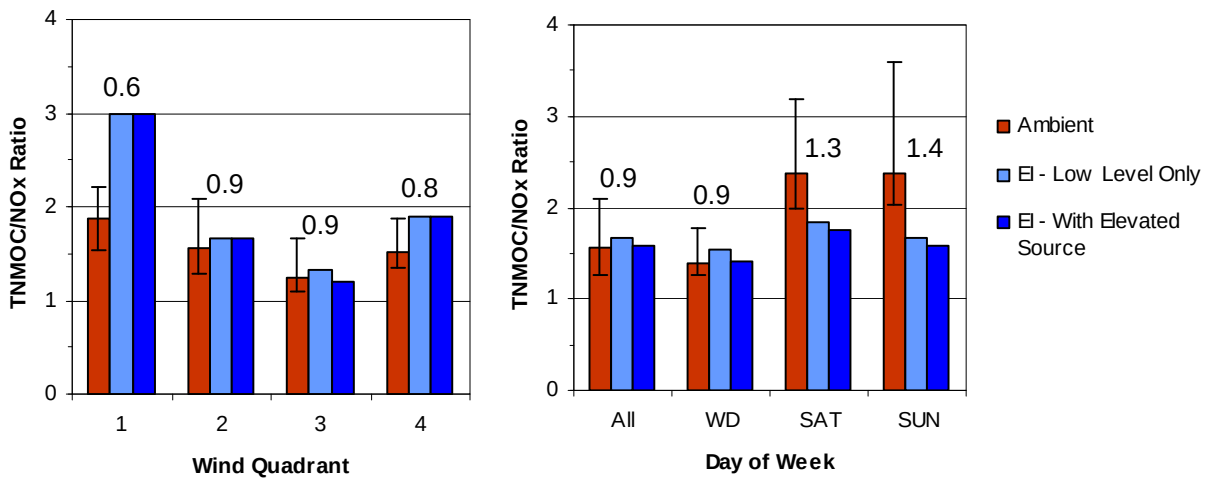

Figure 3-1. TNMOC/NO_x ratios by wind quadrant and day of week for the Jardine site, 2004-2006 (note that for this figure and subsequent ratio comparison figures, values above each ratio group represent the ambient ratio divided by the low-level emissions only ratio).

3.1.2 Ratio Comparison Results for Chicago-Northbrook

Figure 3-2 shows 2005 TNMOC/NO_x ratios by wind quadrant and day of week for the Northbrook site in Chicago, Illinois. Generally, there is good agreement between the ambient- and emissions inventory-derived ratios at this site; however, the agreement between ambient- and emissions inventory-derived ratios is poorer for wind quadrants 1 and 3 than for the remaining wind quadrants. Much of wind quadrant 1 lies over Lake Michigan (see Figure 2-5), and emission levels are thus relatively low in that quadrant. For wind quadrant 3, NO_x emission levels are 40% higher than in neighboring wind quadrant 2, while VOC emission levels are virtually identical for those two wind quadrants. These higher NO_x emissions in wind quadrant 3 are driven by heavy-duty mobile source emissions, suggesting that emissions from this source may be overestimated in wind quadrant 3.

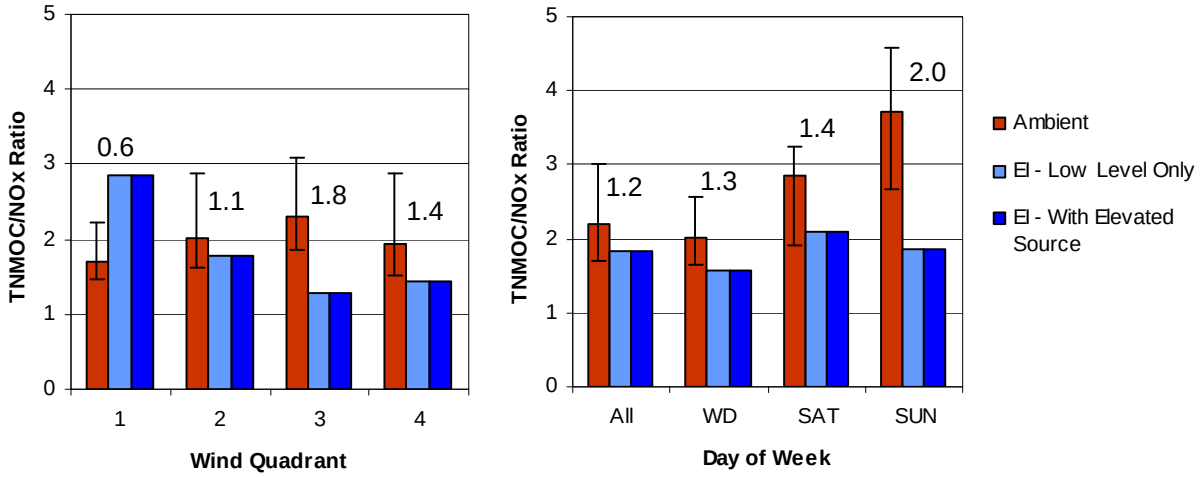

Figure 3-2. TNMOC/NO_x ratios by wind quadrant and day of week for the Northbrook site, 2004–2006.

The ambient-derived TNMOC/NO_x ratio for Sundays is a factor of 2 higher than the emissions inventory-derived ratio for Sundays at the Northbrook site, whereas the ambient-derived ratio for weekdays and Saturdays are only about 30% higher than the emissions inventory-derived ratios. Because TNMOC concentrations are higher (by about 10%) and NO_x concentrations are lower (by about 30%) on Sundays than on Saturdays, the ambient-derived TNMOC/NO_x ratio is higher on Sundays than on Saturdays. However, the emissions inventory-derived ratios do not capture this trend, as both VOC[26] and NO_x emissions decrease on Sundays relative to Saturdays, with VOC decreasing somewhat more sharply and lowering the emissions inventory-derived TNMOC/NO_x ratio.

Ambient- and emissions inventory-derived TNMOC/NO_x ratios for the Northbrook site were also prepared using 2008 data (see **Figure 3-3**), and the overall (all days and wind quadrants) ambient-derived TNMOC/NO_x ratio for this site increased from 2.2 in 2004–2006 to 2.6 in 2008 (an 18% increase). This higher 2008 ratio reflects the increasing TNMOC concentrations and decreasing NO_x concentrations at this site (see Section 2.1.4). The emissions data for Northbrook showed a small VOC increase from 2005 to 2008 and a large NO_x decrease. As a result, the emissions inventory-derived TNMOC/NO_x ratio increased by 61%, and the ambient- and emissions inventory-derived ratios showed somewhat closer agreement for 2008 than for 2005.

It should also be noted that, when examined by day of week and wind quadrant, the 2008 TNMOC/NO_x ratios show a sharper increase relative to 2004–2006 ratios in wind quadrants 1 and 4 and on weekdays.[27]. These results suggest that the increase in TNMOC emissions around this site between 2004–2006 and 2008 largely came from the area north of the site.

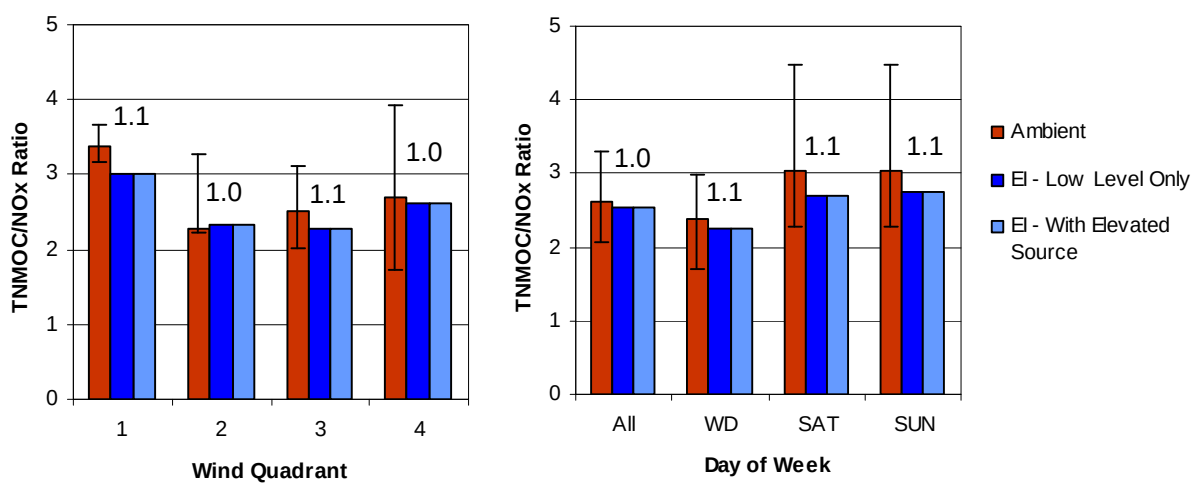

Figure 3-3. TNMOC/NO_x ratios by wind quadrant and day of week for the Northbrook site, 2008.

[26] The organic species in the ambient data are referred to as TNMOC and in the emissions inventory as VOC. For simplicity, all hydrocarbon-to-NO_x ratios are referred to as "TNMOC/NO_x."
[27] For analyses involving 2008 data, Saturdays and Sundays were grouped together as weekend days because of the relatively small number of Saturday/Sunday samples.

3.1.3 Ratio Comparison Results for Gary

Figure 3-4 shows 2005 TNMOC/NO_x ratios by wind quadrant and day of week for the Gary, Indiana, site. Agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios is poor at the Gary site, with the ambient-derived ratios 3.4 to 5.0 times higher than the emissions-based ratios across all wind quadrants and days of week. This discrepancy may largely be driven by an underestimate of VOC emissions around the Gary site (see Section 2.2.2), which is near several large industrial sources—including the Burns Harbor Steel Plant. Among days of the week, agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios is poorest on Sundays, as the 40% decrease in ambient NO_x concentrations between Saturdays and Sundays is not reflected in the emissions data.

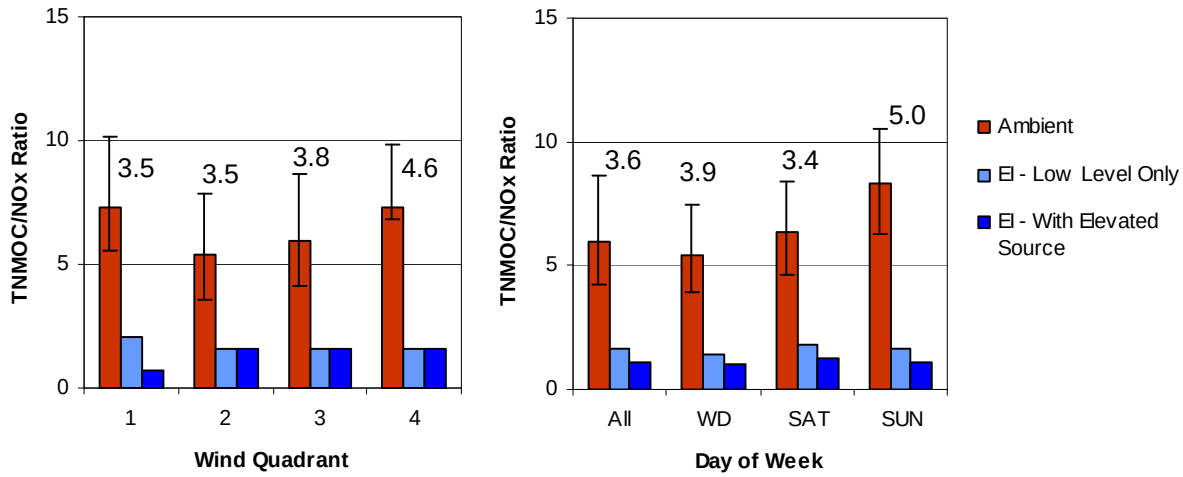

Figure 3-4. TNMOC/NO_x ratios by wind quadrant and day of week for the Gary site, 2004–2006.

3.1.4 Ratio Comparison Results for Detroit-East 7 Mile

Figure 3-5 shows the 2005 TNMOC/NO_x ratios by wind quadrant and day of week for the East 7 Mile site in Detroit, Michigan. Agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios is poor at the East 7 Mile site, with the ambient-derived ratios 2.5 to 4.0 times higher than the emissions-based ratios across all wind quadrants and days of week. Ambient-derived TNMOC/NO_x ratios are lowest when winds are from wind quadrant 3, reflecting the impact of large industrial sources of NO_x southwest of this site (Brown, 2006).

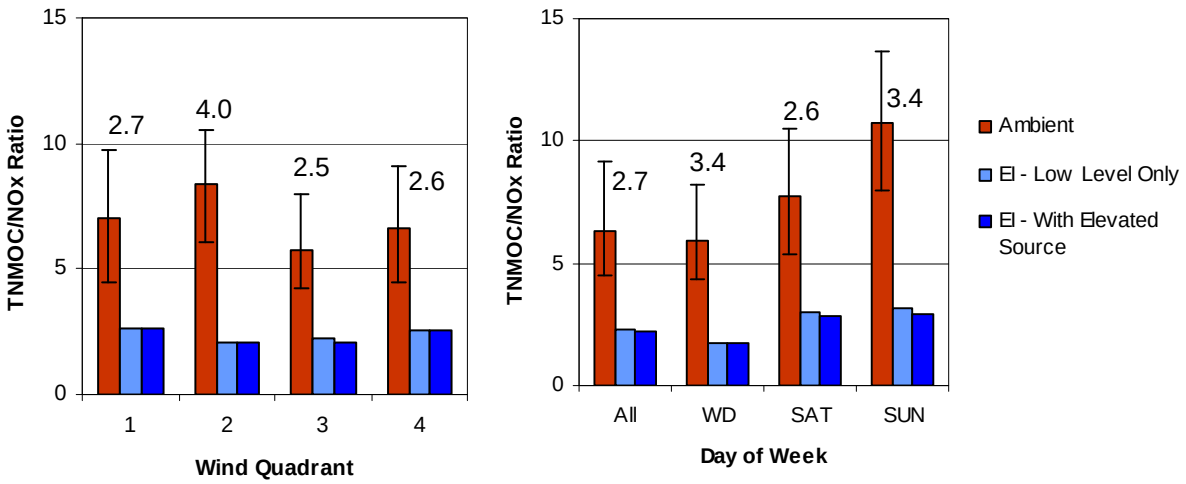

Figure 3-5. TNMOC/NO_x ratios by wind quadrant and day of week for the East 7 Mile site, 2004–2006.

Ambient TNMOC concentrations are highest at the East 7 Mile site among all sites, although VOC emissions levels around the East 7 Mile site are 18% lower than they are around the Chicago-Jardine site (see Table 2-6). This discrepancy suggests that VOC emissions are underestimated around the East 7 Mile site.

3.1.5 Ratio Comparison Results for Milwaukee

Figure 3-6 shows the 2005 TNMOC/NO_x ratios by wind quadrant and day of week for the Milwaukee, Wisconsin, site. Agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios is mediocre at the Milwaukee site, with the ambient-derived ratios 1.5 to 2.2 times higher than the emissions-based ratios across all wind quadrants and days of week. Milwaukee was the only site where agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios was better on Sundays than on weekdays or Saturdays, as Milwaukee was the only site with lower TNMOC concentrations on Sundays than on Saturdays (reflected in the VOC emissions levels for the site).

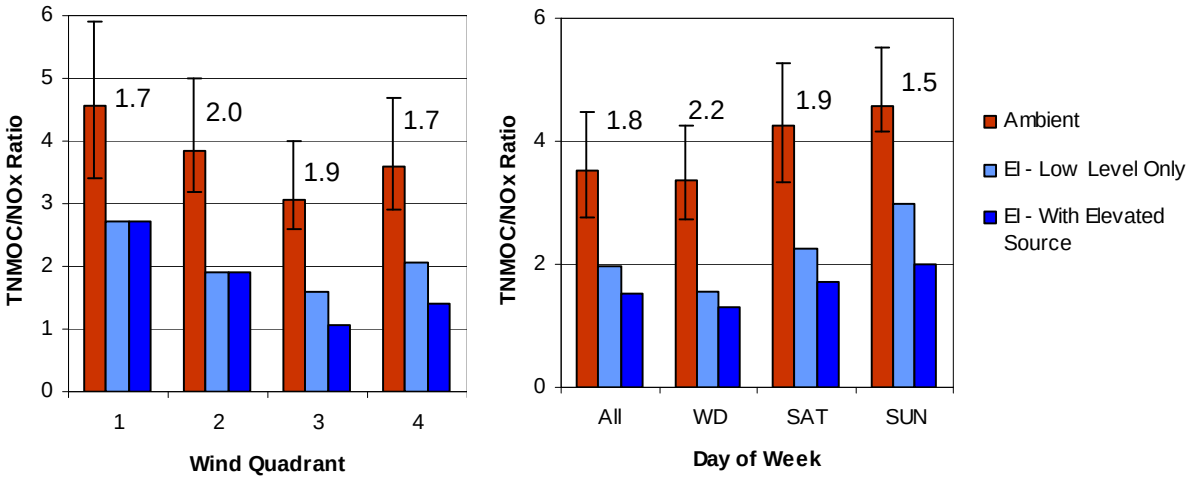

Figure 3-6. TNMOC/NO_x ratios by wind quadrant and day of week for the Milwaukee site, 2004–2006.

Ambient- and emissions inventory-derived TNMOC/NO_x ratios for the Milwaukee site were also prepared using 2008 data (see **Figure 3-7**), and the overall (all days and wind quadrants) ambient TNMOC/NO_x ratio for this site increased from 3.5 in 2004–2006 to 5.1 in 2008 (a 46% increase). This higher 2008 ratio reflects the increasing TNMOC concentrations and decreasing NO_x concentrations at this site (see Section 2.1.4). The emissions data for Milwaukee showed significant decreases in both VOC and NO_x emissions from 2005 to 2008, and emissions-inventory derived TNMOC/NO_x ratios were slightly higher for 2008 than for 2005. As a result, the ambient- and emissions inventory-derived ratios showed poorer agreement for 2008 than for 2005.

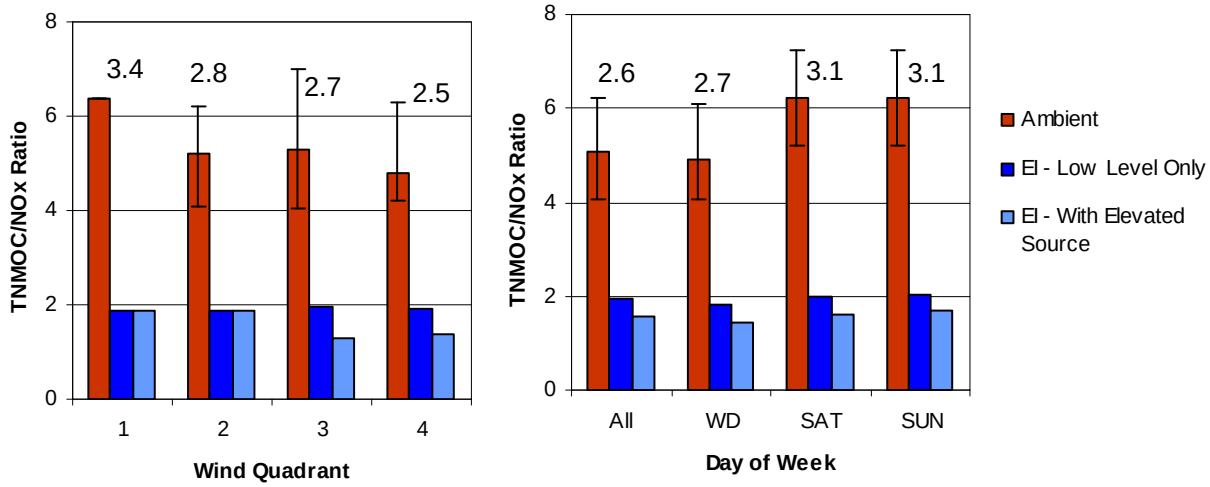

Figure 3-7. TNMOC/NO_x ratios by wind quadrant and day of week for the Milwaukee site, 2008.

3.2 CO/NO_x Ratio Comparisons

CO/NO_x ratios were calculated by day of week, month, and season. For 2005, comparisons between ambient- and emissions inventory-derived CO/NO_x ratios were made for four sites: Chicago-Mannheim, Chicago-Franklin, Detroit-Linwood, and Milwaukee. Also, CO/NO_x ratios were calculated by wind quadrant at the Milwaukee and Chicago-Mannheim sites[28]. For 2008, comparisons were made for the three sites for which ambient CO measurements were available: the Mannheim, Franklin, and Northbrook sites in Chicago (and emissions inventory-derived ratios were calculated for the remaining sites as well).

Table 3-2 shows calculated ratios for the full grid extent around each monitoring site for all summer and winter days. For 2005, these calculations show that ambient- and emissions inventory-derived ratios agree within ±30% at all sites. Agreement is generally closer for winter months when CO concentrations are much higher than in summer months, and agreement is also generally closer when elevated sources are excluded from the calculations. For 2008, ambient-derived CO/NO_x ratios at the Mannheim and Franklin sites were 5% to 39% lower than for 2005; however, emissions inventory-derived CO/NO_x ratios increased by up to 35% at those sites. As a result, the ambient- and emissions-inventory derived ratios show poorer agreement for 2008 than for 2005.

The following sections show CO/NO_x ratio charts by wind quadrant and day of week and discuss the results of the analysis for each site. Additional charts (e.g., CO/NO_x ratios by wind quadrant) can be found in **Appendix D**.

[28] The meteorological data needed to support this analysis are not available at the other sites.

Table 3-2. CO/NO_x ratios by site (emission ratios for full grid extent around each site; ambient ratios for 2005 based on 2004–2006 data).

Site	Season	Ambient Ratios	Emissions Inventory Ratios		Ambient/EI (Low Level)	Ambient/EI (Low Level + Elevated)
			Low Level Only	Low Level + Elevated		
2005 Data						
Chicago-Mannheim	Winter	6.4	8.2	8.2	0.8	0.8
	Summer	8.2	11.2	11.2	0.7	0.7
Chicago-Franklin	Winter	7.3	8.0	7.6	0.9	1.0
	Summer	8.6	10.9	10.3	0.8	0.8
Linwood (Detroit)	Winter	9.9	10.1	8.0	1.0	1.2
	Summer	12.5	11.6	9.1	1.1	1.4
Milwaukee	Winter	10.0	11.2	8.9	0.9	1.1
	Summer	13.6	11.9	9.3	1.2	1.5
2008 Data						
Chicago-Mannheim	Winter	4.2	11.1	10.9	0.4	0.4
	Summer	5.0	15.0	13.6	0.3	0.4
Chicago-Franklin	Winter	5.9	9.6	9.2	0.6	0.6
	Summer	8.2	11.6	10.3	0.7	0.8
Chicago-Northbrook	Winter	8.6	11.9	11.9	0.7	0.7
	Summer	16.7	16.0	16.0	1.0	1.0
Linwood (Detroit)	Winter	--	11.5	9.2	--	--
	Summer	--	12.7	9.5	--	--
Milwaukee	Winter	--	11.3	9.8	--	--
	Summer	--	12.0	9.8	--	--

3.2.1 Ratio Comparison Results for Chicago-Mannheim

Figure 3-8 shows 2005 CO/NO_x ratios by season, wind quadrant, and day of week for the Mannheim site in Chicago, Illinois. Overall, there is good agreement between the ambient- and emissions inventory-derived ratios at this site across all wind quadrants and days of week.

However, there is poorer agreement between ambient- and emissions inventory-derived CO/NO_x ratios on Sundays than on weekdays or Saturdays, as the magnitude of the decrease in NO_x concentrations from Saturdays to Sundays is not completely reflected in the emissions data.

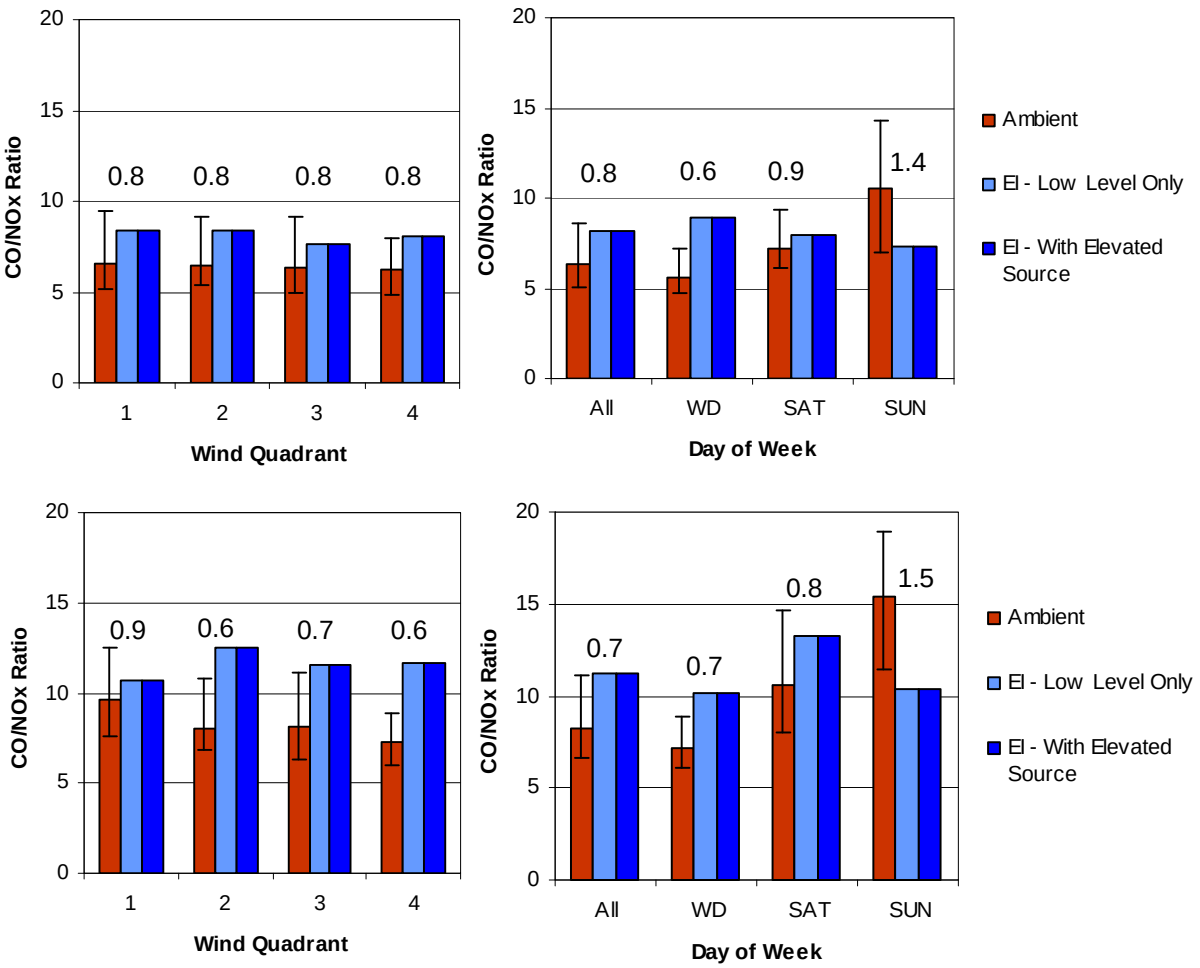

Figure 3-8. CO/NO_x ratios by season (top is winter and bottom is summer), wind quadrant, and day of week for the Chicago-Mannheim site, 2004–2006.

Ambient- and emissions inventory-derived CO/NO_x ratios for the Mannheim site were also prepared using 2008 data (see **Figure 3-9**), and for ambient data, the overall (all days and wind quadrants) wintertime CO/NO_x ratio for this site decreased from 6.4 in 2004–2006 to 4.2 in 2008 (a 34% decrease). This lower 2008 ratio reflects the decreasing CO concentrations at this site (see Section 2.1.4). However, the wintertime emissions inventory-derived CO/NO_x ratios for this site increased by 35% from 2005 to 2008; as a result, the agreement between ambient- and emissions inventory-derived CO/NO_x ratios is much poorer for 2008 than for 2005. Because 2005 to 2008 reductions in CO emissions are similar to reductions in CO concentrations (both around 40%) while NO_x emission reductions (50%) are much larger than NO_x concentration reductions (13%), this discrepancy indicates that NO_x reductions from 2005 to 2008 in the emissions inventory are too large.

It should also be noted that the ambient-derived CO/NO_x ratios for 2008 increase on weekend days, as was the case with the ratios calculated from 2004–2006 ambient data. However, the 2008 emissions inventory-derived CO/NO_x ratios show little variation from weekdays to weekend days (see Figure 3-9).

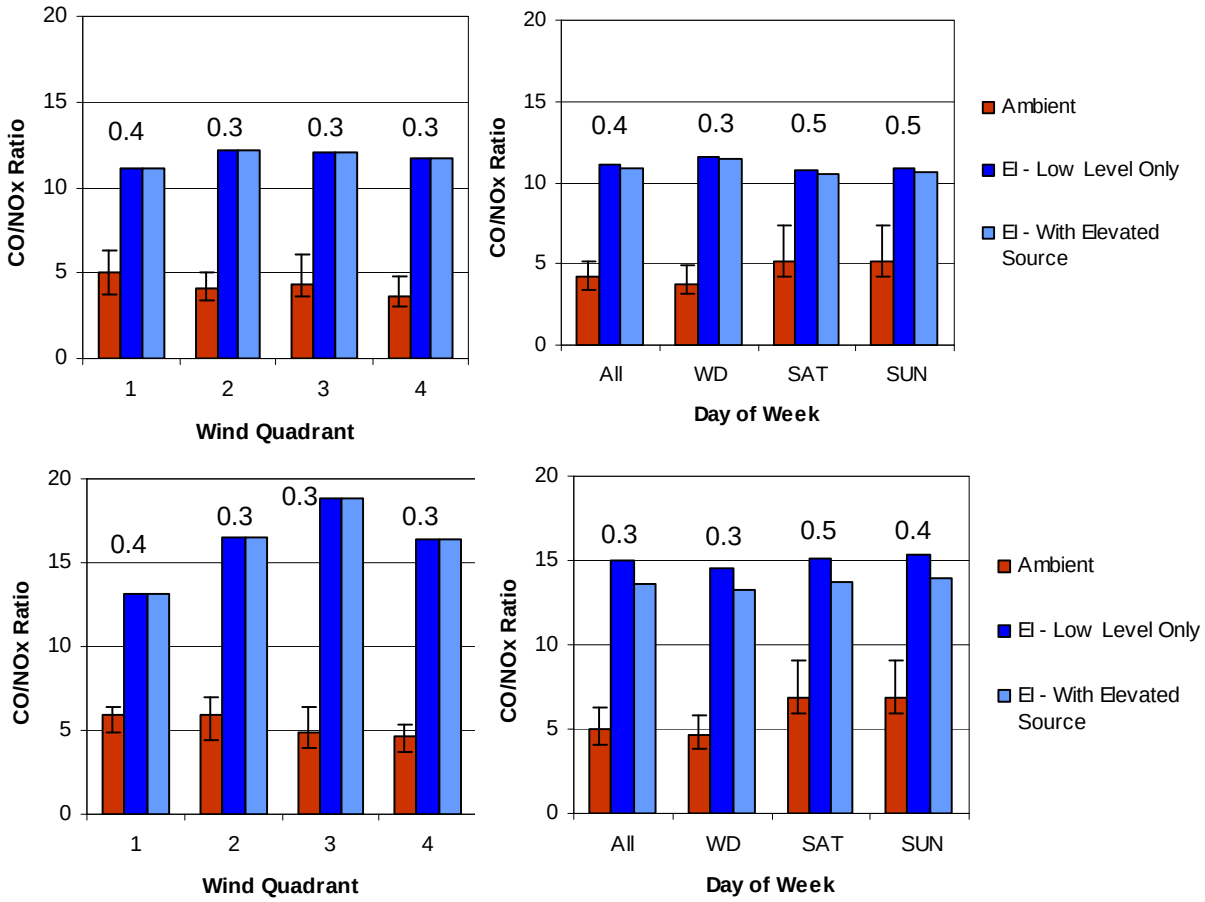

Figure 3-9. CO/NO_x ratios by season (top is winter and bottom is summer), wind quadrant, and day of week for the Chicago-Mannheim site, 2008.

3.2.2 Ratio Comparison Results for Chicago-Franklin

Figure 3-10 shows 2005 CO/NO_x ratios by season and day of week[29] for the Franklin site in Chicago, Illinois. Overall, there is good agreement between the ambient- and emissions inventory-derived ratios at this site across all days of week. However, there is poorer agreement between ambient- and emissions inventory-derived CO/NO_x ratios on Sundays than on weekdays or Saturdays, as the magnitude of the decrease in NO_x concentrations from Saturdays to Sundays is not completely reflected in the emissions data.

[29] Pollutant ratios by wind quadrant could not be calculated for the Franklin site because of a lack of wind data.

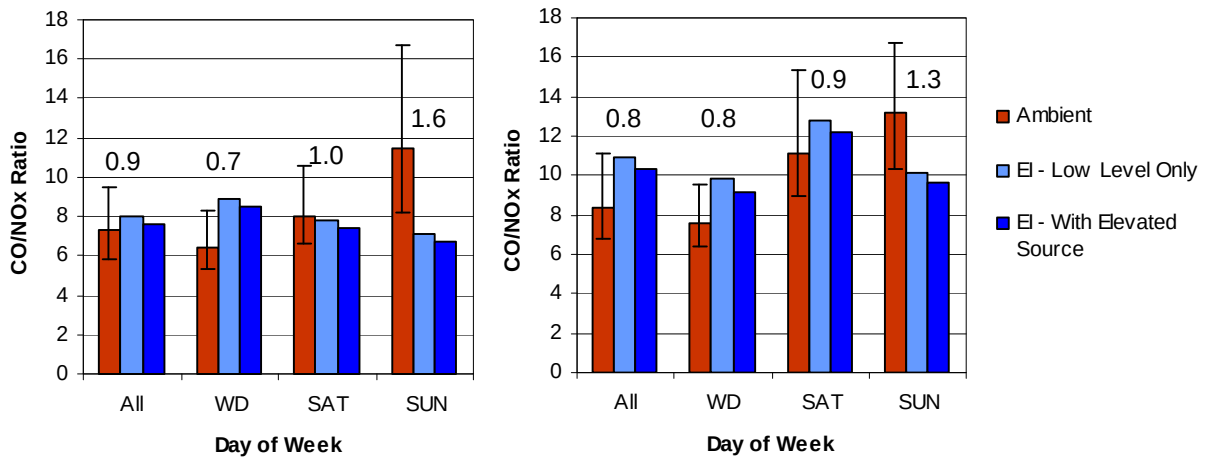

Figure 3-10. CO/NO_x ratios by season (left is winter and right is summer) and by day of week for the Chicago-Franklin site, 2004–2006.

Ambient- and emissions inventory-derived CO/NO_x ratios for the Franklin site were also prepared using 2008 data (see **Figure 3-11**); for ambient data, the overall (all days and wind quadrants) wintertime CO/NO_x ratio for this site decreased from 7.3 in 2004–2006 to 5.9 in 2008 (a 19% decrease). This lower 2008 ratio reflects the decreasing CO concentrations at this site (see Section 2.1.4). However, the wintertime emissions inventory-derived CO/NO_x ratios for this site increased by 20% from 2005 to 2008; as a result, the agreement between ambient- and emissions inventory-derived CO/NO_x ratios is generally poorer for 2008 than for 2005. Although 2005 to 2008 reductions in CO emissions are similar to reductions in CO concentrations (both around 25%), reductions in NO_x emissions (37%) are much larger than reductions in NO_x concentrations (6%). This discrepancy indicates that NO_x reductions from 2005 to 2008 in the emissions inventory are too large.

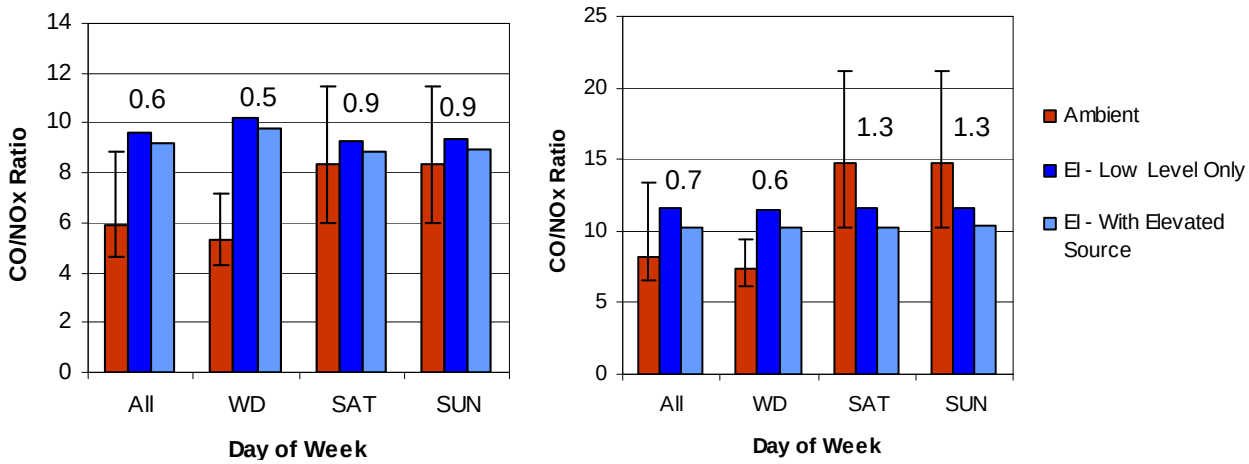

Figure 3-11. CO/NO_x ratios by season (left is winter and right is summer) and by day of week for the Chicago-Franklin site, 2008.

It should be noted that CO/NO_x ratios calculated for Sundays are an exception to the trend described above, as emissions inventory-derived ratios show closer agreement with ambient-derived ratios for 2008 than for 2005, particularly for winter months (see Figure 3-11). This occurs, in part, because ambient-derived CO/NO_x ratios for 2008 do not increase sharply from Saturdays to Sundays, as was the case with the ratios for 2005.

3.2.3 Ratio Comparison Results for Chicago-Northbrook

Figure 3-12 shows 2008 CO/NO_x ratios by season, wind quadrant, and day of week for the Northbrook site in Chicago, Illinois (no ambient CO measurements were available for this site from 2004–2006). Generally, the ambient- and emissions inventory-derived ratios at this site show good agreement (±50%) across all wind quadrants and days of week. However, the ambient- and emissions inventory-derived CO/NO_x ratios show poorer agreement on weekend days than on weekdays, particularly during summer months. During both winter and summer months, the ambient-derived CO/NO_x ratios increase sharply on weekend days compared to weekdays, while the emissions inventory-derived ratios remain relatively constant from weekdays to weekend days. Although weekday to weekend reductions in CO emissions are similar to reductions in CO concentrations (both around 25% for winter months), NO_x emission reductions (14% for winter months) are much smaller than NO_x concentration reductions (72% for winter months). This discrepancy indicates that NO_x reductions from weekdays to weekend days in the emissions inventory are too small.

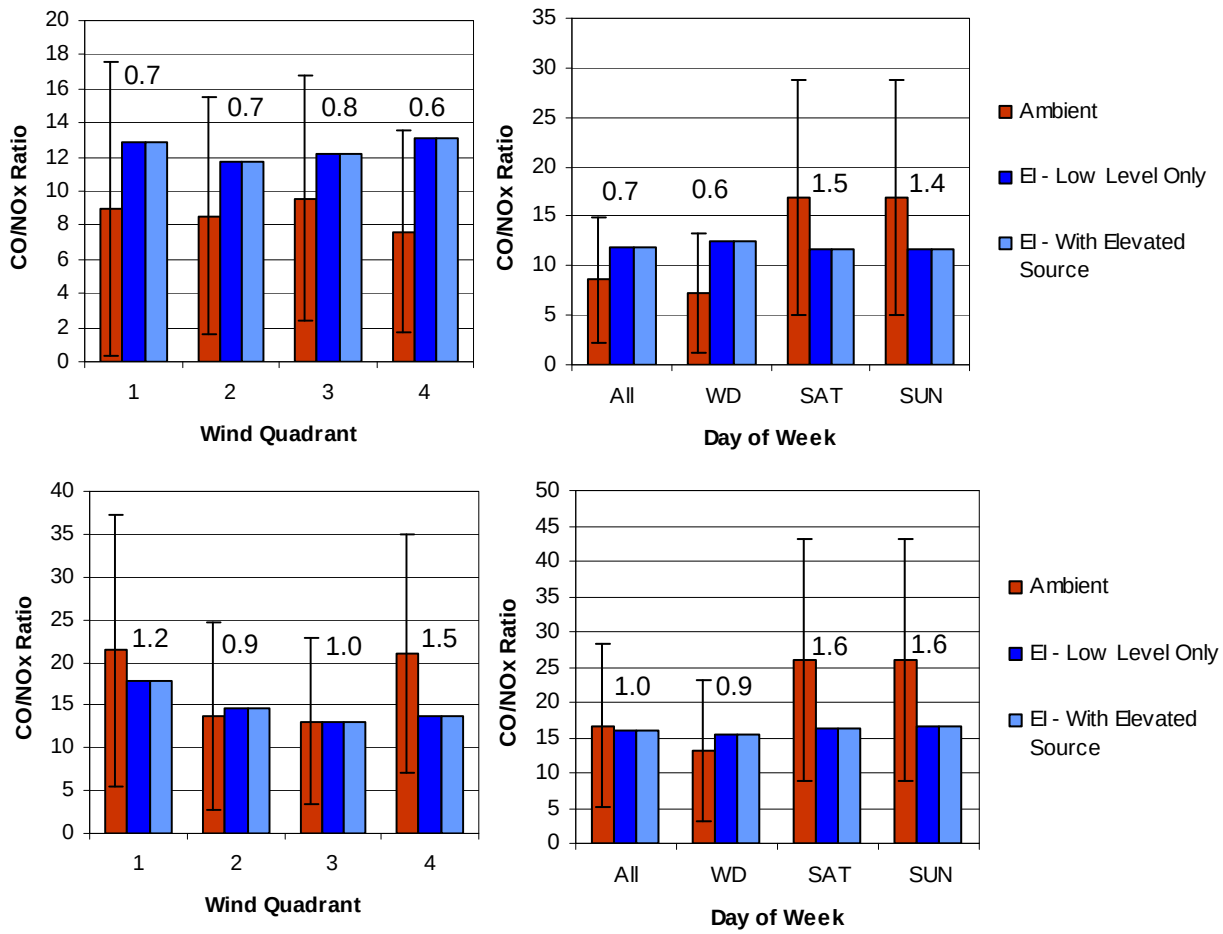

Figure 3-12. CO/NO_x ratios by season (top is winter and bottom is summer), wind quadrant, and day of week for the Chicago-Northbrook site, 2008.

3.2.4 Ratio Comparison Results for Detroit-Linwood

Figure 3-13 shows CO/NO_x ratios by season and day of week[30] for the Linwood site in Detroit, Michigan. Overall, there is good agreement between the ambient- and emissions inventory-derived ratios at this site across all days of week, particularly during winter months.

[30] Pollutant ratios by wind quadrant could not be calculated for the Linwood site because of a lack of wind data.

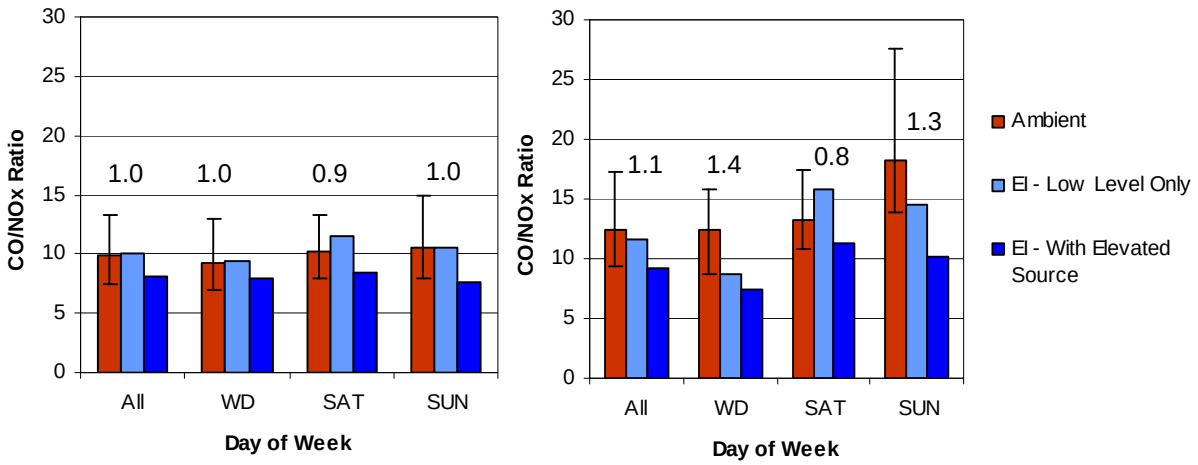

Figure 3-13. CO/NO_x ratios by season (left is winter and right is summer) and by day of week for the Detroit-Linwood site, 2004–2006.

3.2.5 Ratio Comparison Results for Milwaukee

Figure 3-14 shows CO/NO_x ratios by season, wind quadrant, and day of week for the Milwaukee site in Wisconsin. Overall, there is good agreement between the ambient- and emissions inventory-derived ratios at this site across all wind quadrants and days of week for both winter and summer months.

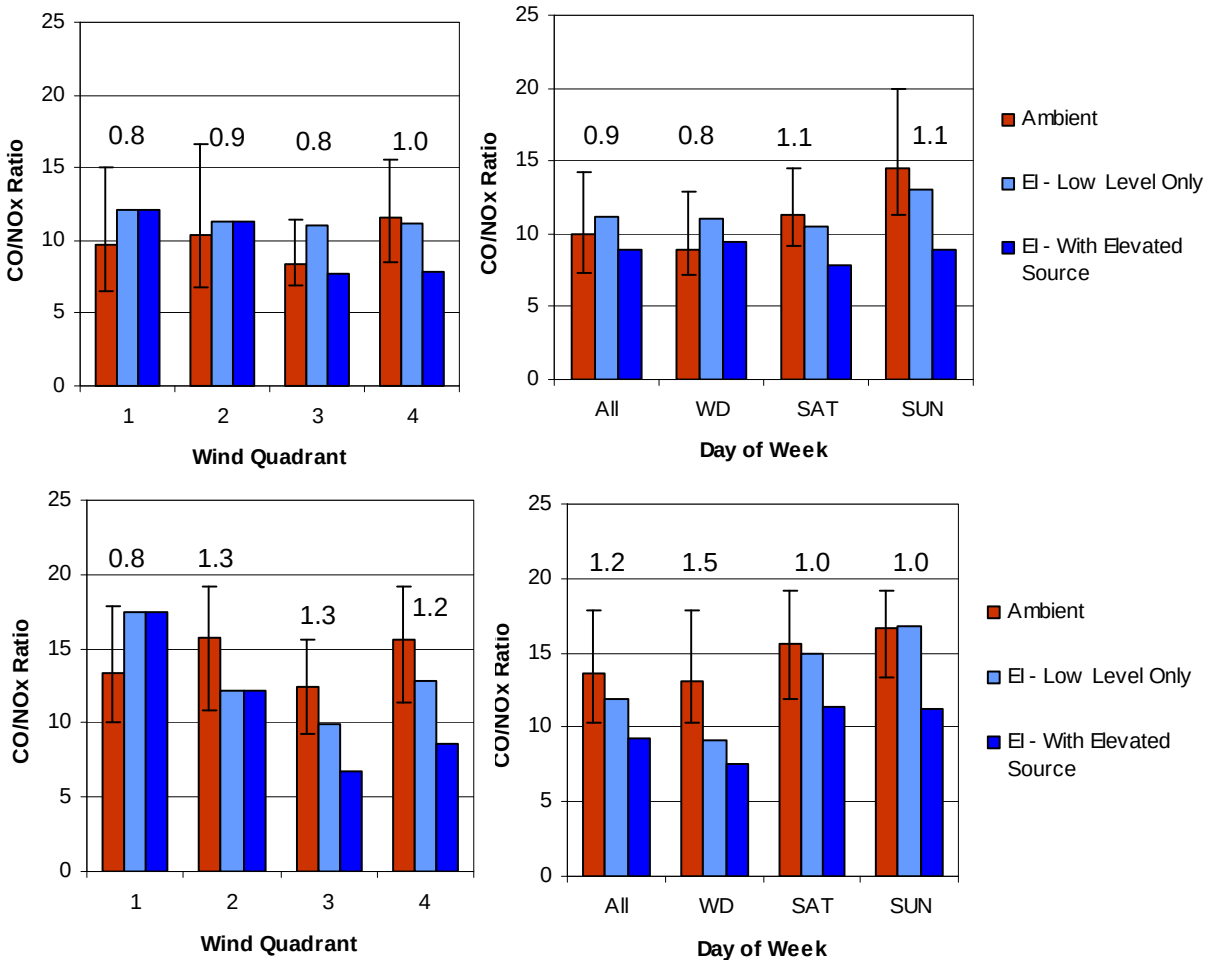

Figure 3-14. CO/NO_x ratios by season (top is winter and bottom is summer), wind quadrant, and day of week for the Milwaukee site, 2004–2006.

4. Hydrocarbon Composition Comparison Results

Comparisons of ambient- and emissions inventory-derived hydrocarbon compositions were based on the 55 individual species that were detected and identified by the ambient measurement systems. In addition, STI also computed and compared the relative reactivity of the organic species in the emissions inventory and ambient data. The reactivity of each species was estimated according to published MIR values that represent the ozone formation potential of various organic compounds (Carter, 2003).

4.1 Relative Hydrocarbon Composition Comparisons

Relative hydrocarbon composition comparisons were performed by day of week, season, and wind quadrant. For 2005, hydrocarbon composition comparisons were performed for five sites: Chicago-Jardine, Chicago-Northbrook, Gary, Detroit-East 7 Mile, and Milwaukee. For 2008, comparisons were made for the two sites for which ambient TNMOC measurements were available: Chicago-Northbrook and Milwaukee.[31] **Figures 4-1 through 4-5** show comparisons of the ambient- and emissions inventory-derived relative compositions of 15 of the most abundant species in the ambient data. These hydrocarbon composition plots show that:

- The speciation of the emissions inventory is representative of the TNMOC composition detected by ambient monitoring sites for some species groups, including C4+ alkanes, C8+ aromatics, styrenes, and propylene.
- The speciation of the emissions inventory is representative of the TNMOC composition detected by ambient monitoring sites for C6+ alkanes at the Chicago and Milwaukee sites; however, this species is overestimated in the emissions inventory at the Gary and Detroit sites. C6+ alkanes are present in gasoline exhaust and evaporative emissions.
- The speciation of the emissions inventory tends to overestimate the contribution of acetylene, ethylene, toluene, and isoprene compared to the ambient data. Isoprene is highly reactive and short-lived in the atmosphere, and therefore it may be under-represented in the ambient data. The dominant source of acetylene and toluene[32] in the summer emissions inventory is gas-powered lawn and garden equipment, and the contribution of these species to overall hydrocarbon emissions increases on weekends, when lawn and garden equipment are most active (see day of week plots in **Appendix E**). The speciation profile assigned to this source in the LADCO inventories is based on a 1997 study on emissions from four-stroke lawn mower emissions covering ten mowers with two types of gasoline (Battye and Harris, 2005), and the same profile is assigned to lawn and garden equipment in the latest version of EPA's SPECIATE database (U.S. Environmental Protection Agency, 2008). Commercial aircraft are the dominant source of ethylene in the LADCO emissions data. A 1984 EPA speciation profile for turbine engine exhaust is assigned to this source category in the LADCO inventories.

[31] Per LADCO's instructions, the same speciation profiles were assigned to both the 2005 and 2008 inventories, so the speciation of the emissions data did not change from year to year. The hydrocarbon composition of the ambient data also showed little year-to-year variation.

[32] For the Gary site, petroleum storage evaporative losses are another significant source of toluene. This is not true at the other sites.

- Compared to the ambient data, the speciation of the emissions inventory overestimates the contribution of pentanes at some sites, especially Detroit East 7 Mile. At the Detroit site, surface coating solvents are the dominant source of pentane emissions.
- The speciation of the emissions inventory underestimates the contribution of ethane, propane, and C6-C11 alkanes at all sites and butane at the Chicago sites. However, ethane and propane are long-lived in the atmosphere and tend to accumulate; therefore, it is likely that the ambient monitors detected aged ethane and propane emissions.

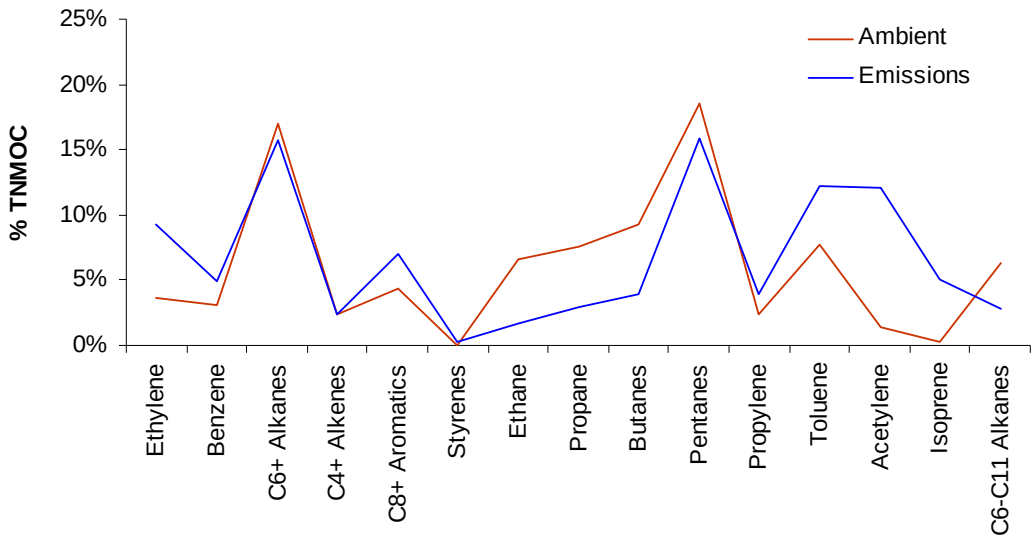

Figure 4-1. Comparison of 0600–0900 ambient- and emissions inventory-derived TNMOC compositions for the Chicago-Jardine site.

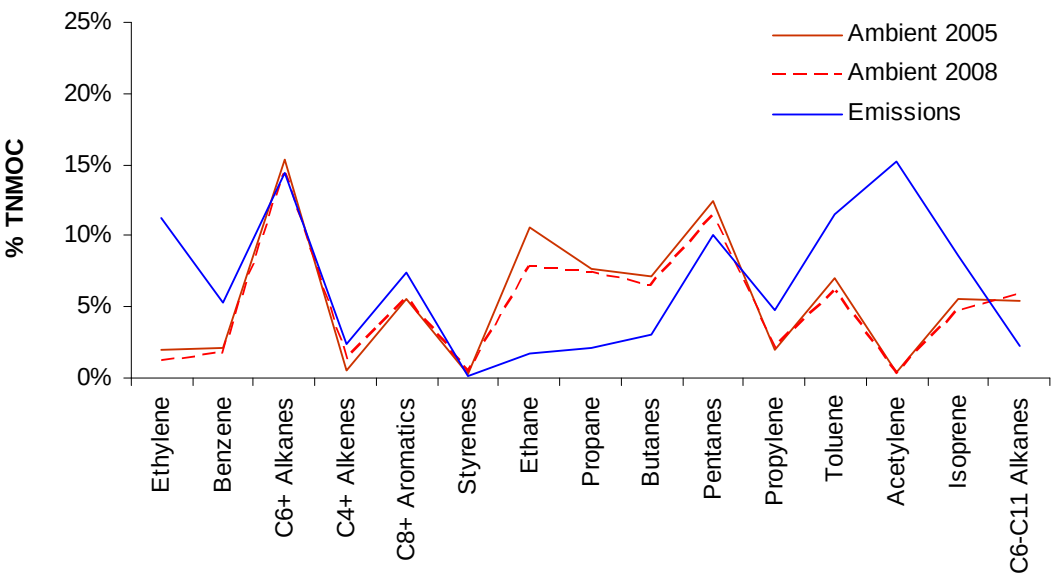

Figure 4-2. Comparison of 0600–0900 ambient- and emissions inventory-derived TNMOC compositions for the Chicago-Northbrook site.

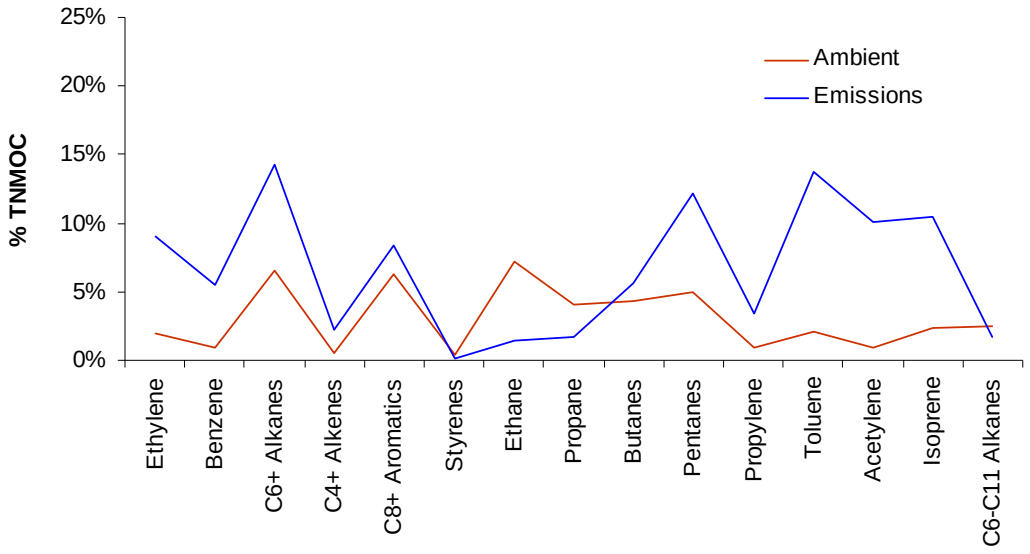

Figure 4-3. Comparison of 0600–0900 ambient- and emissions inventory-derived TNMOC compositions for the Gary site.

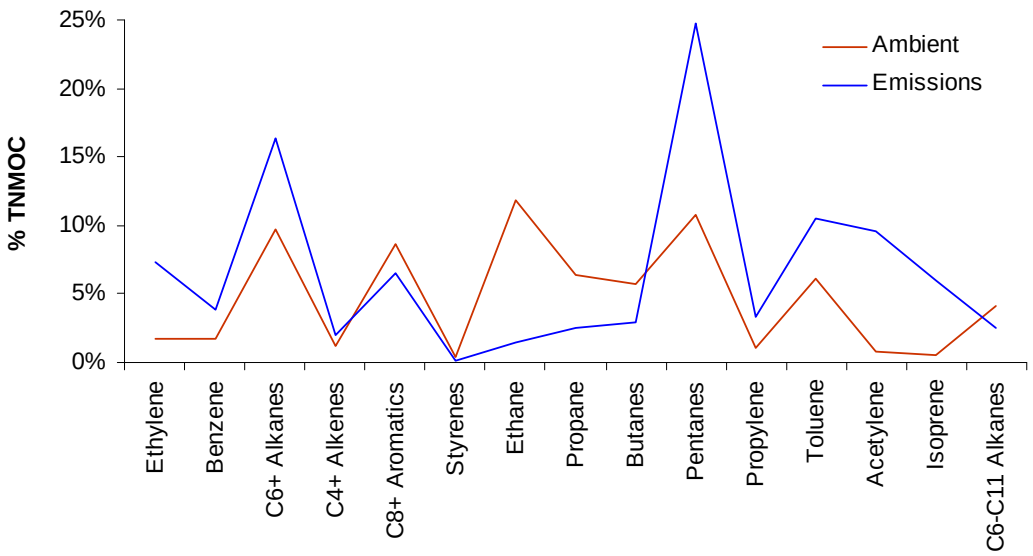

Figure 4-4. Comparison of 0600–0900 ambient- and emissions inventory-derived TNMOC compositions for the Detroit-East 7 Mile site.

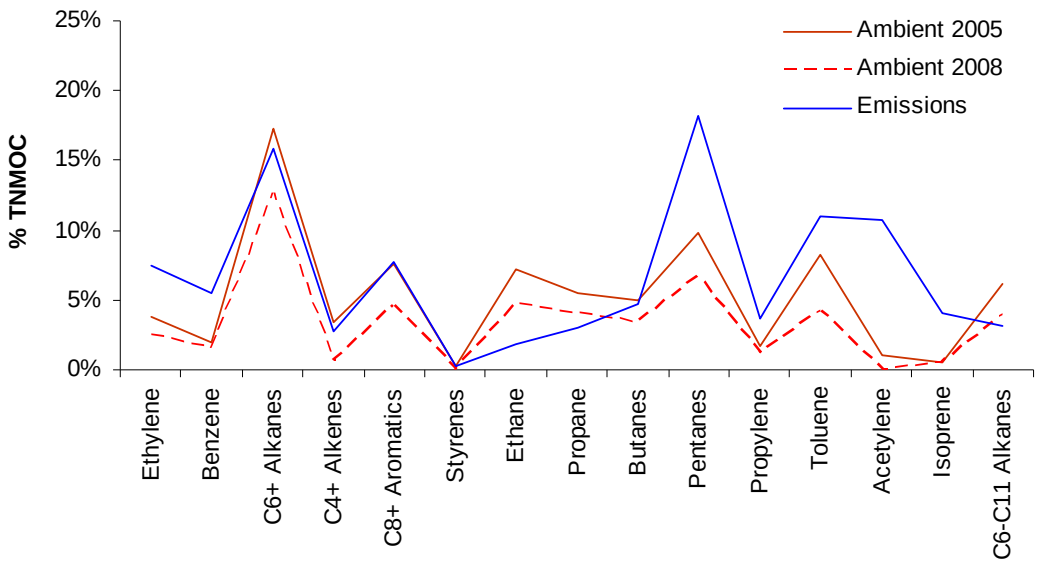

Figure 4-5. Comparison of 0600–0900 ambient- and emissions inventory-derived TNMOC compositions for the Milwaukee site.

4.2 Hydrocarbon Reactivity Comparisons

Hydrocarbon reactivity comparisons were performed by day of week, month, season, and wind quadrant for five sites using 2004–2006 ambient data and 2005 emissions data:[33] Chicago-Jardine, Chicago-Northbrook, Gary, Detroit-East 7 Mile, and Milwaukee. Across all sites, the overall weighted reactivity values for the emissions inventory for the summer season are 16% to 80% higher than the weighted reactivity values for the ambient data. The ambient- and emissions inventory-derived reactivity values show the closest agreement at the Milwaukee site and the greatest disparity at the Northbrook site. The emissions inventory-derived reactivity values are consistently higher for Saturday and Sunday emissions data than for weekday emissions data, while the ambient-derived reactivity values show little change across days of the week. **Tables 4-1 and 4-2** show reactivity data for the five sites.

The hydrocarbon composition analysis in the previous section showed that the emissions inventory and the ambient data differ significantly between several species or group of species. At all sites, ethane and propane make up a higher percentage of the TNMOC concentration in the ambient data than in the emissions inventory, while the more reactive ethylene and acetylene make up a higher percentage in the emissions inventory. (Ethane and propane have MIR values of 0.3 and 0.6, respectively, while ethylene and acetylene are far more reactive, with MIR values of 9.1 and 1.2, respectively.) These differences result in higher weighted reactivity values for the emissions data than for the ambient data.

[33] These analyses were not repeated for 2008 because the 2008 hydrocarbon compositions were very similar to the 2005 versions for both the ambient and emissions data.

Table 4-1. Reactivity values by site, day of week, month, and season.

Site Name	Month	Overall		Weekday		Saturday		Sunday	
		Emissions Inventory	Ambient	Emissions Inventory	Ambient	Emissions Inventory	Ambient	Emissions Inventory	Ambient
Chicago-Jardine	June	3.9	2.8	3.7	2.8	4.0	3.0	4.0	2.9
	July	3.9	2.7	3.7	2.7	4.0	2.9	3.9	2.7
	August	3.7	2.7	3.6	2.6	3.8	2.8	3.8	2.6
	Summer	3.8	2.7	3.7	2.7	3.9	2.9	3.9	2.7
Chicago-Northbrook	June	4.5	2.5	4.3	2.5	4.5	2.4	4.6	2.4
	July	4.4	2.5	4.3	2.6	4.5	2.5	4.5	2.4
	August	4.4	2.5	4.1	2.5	4.3	2.4	4.3	2.3
	Summer	4.5	2.5	4.2	2.5	4.4	2.5	4.4	2.4
Gary	June	4.5	3.3	4.2	2.6	4.3	2.5	4.7	2.5
	July	4.5	3.3	4.2	2.8	4.3	2.9	4.7	2.8
	August	4.3	3.2	4.0	2.8	4.1	2.8	4.4	2.7
	Summer	4.3	2.8	4.0	2.7	4.2	2.7	4.5	2.7
Detroit-E7Mile	June	3.7	2.5	3.4	2.5	3.9	2.5	4.0	2.3
	July	3.7	2.5	3.4	2.6	3.8	2.5	4.0	2.6
	August	3.5	2.5	3.3	2.6	3.7	2.5	3.8	2.5
	Summer	3.6	2.5	3.4	2.6	3.8	2.5	3.9	2.5
Milwaukee	June	3.7	3.1	3.4	3.1	3.8	3.0	3.9	3.0
	July	3.7	3.0	3.4	2.9	3.8	2.9	3.9	3.0
	August	3.6	3.1	3.4	3.0	3.7	3.0	3.7	3.0
	Summer	3.6	3.1	3.4	3.0	3.8	3.0	3.8	3.0

Table 4-2. Reactivity values by wind quadrant (all summer months included).

Site Name	WQ1		WQ2		WQ3		WQ4	
	Emissions Inventory	Ambient	Emissions Inventory	Ambient	Emissions Inventory	Ambient	Emissions Inventory	Ambient
Chicago-Jardine	3.9	2.7	3.7	2.7	3.9	2.8	3.8	2.7
Chicago-Northbrook	4.2	2.5	3.9	2.6	4.6	2.5	4.6	2.4
Gary	4.4	2.8	4.3	2.8	4.1	2.7	3.9	2.6
Detroit-E7Mile	3.4	2.7	3.5	2.5	3.7	2.5	3.8	2.5
Milwaukee	3.5	3.0	3.5	3.1	3.7	3.1	3.6	2.9

5. Findings and Recommendations

The on-road mobile source component of LADCO's 2005 emissions inventory was developed using EPA's MOBILE6.2 model and link-level activity data. The top-down evaluation for the 2005 emissions inventory indicates that, in general, on-road mobile sources are represented accurately in the emissions data. This conclusion is based on the fact that agreement between ambient- and emissions-inventory-derived pollutant ratios was closest (±20%) for wintertime CO/NO_x ratios, and on-road mobile sources accounted for 57% to 80% of wintertime CO and NO_x emissions at all sites for which ratios were calculated. For sites in the Chicago area, agreement between ambient- and emissions inventory-derived pollutant ratios was as close as could be expected, given the limitations of the analysis techniques. However, comparisons with ambient data indicate that the emissions inventory for Sundays may not be representative of actual activity patterns on that day of the week, perhaps due to decreases in on-road mobile source emissions from Saturdays to Sundays, as well as inaccurate temporal characterizations of other source categories. Also, sources of VOC emissions appear to be missing or underrepresented in the emissions inventory near sites that are influenced by industrial and residential emissions, such as the Gary and Detroit-East 7 Mile sites. These results are consistent with previous top-down emissions evaluations for other regions, which show closest agreement between ambient- and emissions inventory-derived pollutant ratios on weekdays and at sites heavily impacted by on-road mobile source emissions (Chinkin and Reid, 2006).

The on-road mobile source component of LADCO's 2008 emissions inventory was developed using EPA's MOVES model with default input data, and county-level outputs from MOVES were spatially allocated using spatial surrogate data.[34] For the 2008 emissions inventory, agreement between ambient- and emissions-inventory derived pollutant ratios was generally poorer than was observed for the 2005 inventory. The greater discrepancy between ambient- and emissions inventory-derived pollutant ratios from 2005 to 2008 primarily results from large decreases in on-road NO_x emissions that outpaced reductions in ambient NO_x concentrations. However, the Saturday-to-Sunday differences in pollutant ratio comparisons observed for the 2005 inventory were not observed for the 2008 inventory, as there was no variation between Saturday and Sunday on-road mobile source emissions in the 2008 inventory (as was the case for 2005).

For both 2005 and 2008, the speciation of the VOC emissions inventory at all sites does not compare well with the hydrocarbon composition of the ambient data, resulting in a VOC emissions inventory that shows significantly more reactivity at all sites than the corresponding ambient data. As a result, ozone modeling efforts for the region may be influenced by "compensating errors," as the underestimated magnitude of VOC emissions is offset by the overestimated reactivity of those emissions. The following key findings support these conclusions.

[34] LADCO plans to update the 2008 inventory with state-specific MOVES inputs and link-level activity data. The 2008 inventory used in this analysis was the most current version as of April 29, 2011.

TNMOC/NO_x Ratios

For both 2005 and 2008, the agreement between overall ambient- and emissions inventory-derived TNMOC/NO_x ratios is good (±20%) for the Jardine (2005 only) and Northbrook sites in Chicago. However, agreement is mediocre for the Milwaukee site, where the ambient-derived ratio is higher than the emissions-derived ratio by a factor of 1.8 in 2005 and a factor of 2.4 in 2008. Agreement is poor at the Detroit-East 7 Mile and Gary sites for 2005, where ambient-derived ratios were higher than emissions inventory-derived ratios by factors of 2.7 and 3.6, respectively.

- For 2005, ambient TNMOC concentrations are highest at the Gary and Detroit-East 7 Mile sites. However, VOC emissions are lowest around the Gary site and are 18% lower at the East 7 Mile site than at the Jardine site (which has the lowest ambient TNMOC concentrations among all sites). These results suggest that some VOC sources are missing or underrepresented at Gary and East 7 Mile. At the Gary site, which is in a heavily industrialized area, point source TNMOC emissions may be underestimated. At the East 7 Mile site, which is in a suburban area, both residential sources of TNMOC and industrial sources, which impact the site when winds are from the southwest, may be underestimated.
- For 2005, the agreement between ambient- and emissions inventory-derived TNMOC/NO_x ratios is generally better on weekdays and Saturdays than on Sundays. The increased discrepancy between ambient- and emissions inventory-derived ratios on Sundays largely occurs because ambient TNMOC concentrations are similar on Saturdays and Sundays at most sites, while VOC emissions are consistently lower on Sundays than Saturdays.
- At the Chicago-Northbrook and Milwaukee sites, overall TNMOC/NO_x ratios derived from 2008 ambient data are higher than ratios derived from 2004–2006 data by 18% and 46%, respectively. The higher 2008 ratios reflect increasing TNMOC concentrations and decreasing NO_x concentrations at these sites.
- For 2008, the overall emissions inventory-derived TNMOC/NO_x ratio for Chicago-Northbrook increased by 61% relative to 2005 and showed somewhat closer agreement to the ambient-derived ratio than in 2005. However, the overall emissions inventory-derived TNMOC/NO_x ratio for the Milwaukee site was virtually unchanged from 2005 to 2008, resulting in poorer agreement with the ambient-derived ratio in 2008 than in 2005.

CO/NO_x Ratios

For 2005, the agreement between overall ambient- and emissions inventory-derived CO/NO_x ratios is good (±30%) across all sites. However, at the Franklin and Mannheim sites in Chicago, the agreement between ambient- and emissions inventory-derived CO/NO_x ratios is better on weekdays and Saturdays than on Sundays, as the emissions data do not completely account for the magnitude of the decrease in NO_x concentrations from Saturdays to Sundays at those sites.

For 2008, the agreement between overall ambient- and emissions inventory-derived CO/NO_x ratios is mediocre (±30%) across all sites. At the Mannheim and Franklin sites in

Chicago, ambient-derived CO/NO_x ratios were 5% to 39% lower than for 2005; however, emissions inventory-derived CO/NO_x ratios increased by up to 35% at those sites. As a result, the ambient- and emissions-inventory derived ratios show poorer agreement for 2008 than for 2005. The large increases in emissions inventory-derived CO/NO_x ratios at these sites resulted from sharp decreases in on-road NO_x emissions between 2005 and 2008.

Speciation and Reactivity

- The speciation of the emissions inventory tends to overestimate the contribution of acetylene, ethylene, toluene, and isoprene compared to the ambient data. Isoprene is highly reactive and short-lived in the atmosphere, and it therefore may be under-represented in the ambient data. The non-road mobile sector of the emissions inventory is the dominant source of acetylene, ethylene, and toluene emissions.
- The speciation of the emissions inventory underestimates the contribution of ethane, propane, and C6-C11 alkanes at all sites and butane at the Chicago sites. However, ethane and propane are long-lived in the atmosphere and tend to accumulate; therefore, it is likely that the ambient monitors detected aged ethane and propane emissions.
- Across all sites, the overall weighted reactivity value of the emissions inventory for the summer season is 16% to 80% higher than the weighted reactivity value of the ambient data.

Based on the findings from this study, we recommend that the following steps be taken to further investigate the LADCO 2005 and 2008 emissions inventories and to make specific improvements to those inventories:

- Improve the accuracy of weekend emissions estimates by collecting and analyzing day-specific on-road, non-road, and area source activity data to better characterize differences in weekday, Saturday, and Sunday activity levels.
- Collect bottom-up emissions activity data for residential and industrial sources around the Gary, Detroit-East 7 Mile, and Milwaukee sites to “ground truth” the current VOC emissions inventories for these locations.
- Employ source apportionment techniques, such as positive matrix factorization (PMF), to further evaluate the inventory around the Gary, Detroit-East 7 Mile, and Milwaukee sites and to identify specific source types that may be underestimated in the VOC inventories.
- Evaluate the source(s) of large decreases in on-road NO_x emissions in the 2008 MOVES-based inventory relative to the 2005 MOBILE6.2-based inventory.
- Review the speciation profiles assigned to on-road mobile sources and key off-road sources, such as lawn and garden equipment and aircraft.
- Redo the 2008 pollutant ratio comparisons with additional ambient data (e.g., TNMOC measurements from the Jardine and Gary sites) and revised on-road mobile source inventories (i.e., on-road emissions developed using link-level activity data and state-specific MOVES inputs).

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APPENDIX A

Chemical Species Cross-Reference List

Table A-1. List of PAMS species used to match emissions and ambient data.

SAROAD Code	CAS Code	Species Name	Molecular Weight	MIR Value
43203	74-85-1	Ethylene	28.054	9.07
45201	71-43-2	Benzene	78.114	0.81
43229	107-83-5	2-Methylpentane	86.178	1.78
43230	96-14-0	3-Methylpentane	86.178	2.06
43248	110-82-7	Cyclohexane	84.162	1.44
43261	108-87-2	Methylcyclohexane	98.189	1.97
43262	96-37-7	Methylcyclopentane	84.162	2.4
43271	108-08-7	2,4-Dimethylpentane	100.205	1.63
43274	565-59-3	2,3-Dimethylpentane	100.205	1.53
43275	591-76-4	2-Methylhexane	100.205	1.36
43276	540-84-1	2,2,4-Trimethylpentane	114.232	1.43
43279	565-75-3	2,3,4-Trimethylpentane	114.232	1.22
43291	75-83-2	2,2-Dimethylbutane	86.178	1.33
43295	589-34-4	3-Methylhexane	100.205	1.84
43298	589-81-1	3-Methylheptane	114.232	1.33
98001	79-29-8	2,3-Dimethylbutane	86.178	1.13
98140	592-27-8	2-Methylheptane	114.232	1.18
43213	106-98-9	1-Butene	56.108	10.22
43216	624-64-6	Trans-2-Butene	56.108	13.9
43217	590-18-1	cis-2-Butene	56.108	13.22
43224	109-67-1	1-Pentene	70.135	7.73
43226	646-04-8	Trans-2-Pentene	70.135	10.23
43227	627-20-3	cis-2-Pentene	70.135	10.23
98005	592-76-7	1-Heptene	98.189	4.2
45107	25551-13-7	Trimethylbenzene	120.195	9.9
45113	141-93-5	1,3-Diethylbenzene	134.222	8.39
45114	105-05-5	1,4-Diethylbenzene	134.222	3.36
45203	100-41-4	Ethylbenzene	106.168	2.79
45204	95-47-6	o-Xylene	106.168	7.48
45207	108-67-8	1,3,5-Trimethylbenzene	120.195	11.22
45208	95-63-6	1,2,4-Trimethylbenzene	120.195	7.18
45209	103-65-1	N-Propylbenzene	120.195	2.2
98043	98-82-8	Isopropylbenzene (Cumene)	120.195	2.32
99914	622-96-8	1-Methyl-4-Ethylbenzene	120.195	3.75
99915	611-14-3	1-Methyl-2-Ethylbenzene	120.195	6.61
43551	67-64-1	Acetone	58.0804	0.43

Table A-1. List of PAMS species used to match emissions and ambient data.

SAROAD Code	CAS Code	Species Name	Molecular Weight	MIR Value
45220	100-42-5	Styrene	104.152	1.94
43502	50-00-0	Formaldehyde	30.0264	8.96
43202	74-84-0	Ethane	30.07	0.31
43204	74-98-6	Propane	44.097	0.56
43212	106-97-8	n-Butane	58.124	1.32
43214	75-28-5	Isobutane	58.124	1.34
43220	109-66-0	n-Pentane	72.151	1.53
43242	287-92-3	Cyclopentane	70.135	2.67
98132	78-78-4	Isopentane	72.151	1.67
43205	115-07-1	Propylene	42.081	11.57
45202	108-88-3	Toluene	92.141	3.97
43503	75-07-0	Acetaldehyde	44.0534	6.83
43206	74-86-2	Acetylene	26.038	1.24
43243	78-79-5	Isoprene	68.119	10.68
43231	110-54-3	n-Hexane	86.178	1.43
43233	111-65-9	n-Octane	114.232	1.09
43235	111-84-2	n-Nonane	128.259	0.93
43238	124-18-5	n-Decane	142.286	0.81
43241	1120-21-4	n-Undecane	156.313	0.72

APPENDIX B

Monitoring Site Photographs

Looking North

Looking East

Looking West

Looking South

Figure B-1. Photographs taken around the Chicago-Jardine monitoring site.

Looking North

Looking East

Looking West

Looking South

Figure B-2. Photographs taken around the Chicago-Northbrook monitoring site.

Looking North

Looking East

Looking West

Looking South

Figure B-3. Photographs taken around the Chicago-Mannheim monitoring site.

Looking North

Looking East

Looking West

Looking South

Figure B-4. Photographs taken around the Gary, Indiana, monitoring site.

Looking North

Looking East

Looking West

Looking South

Figure B-5. Photographs taken around the Milwaukee, Wisconsin, monitoring site.

Looking North

Looking East

Looking West

Looking South

Figure B-6. Photographs taken around the Detroit-East 7 Mile monitoring site.

Looking Northwest

Looking Northeast

Looking Southwest

Looking Southeast

Figure B-7. Photographs taken around the Detroit-Linwood monitoring site.

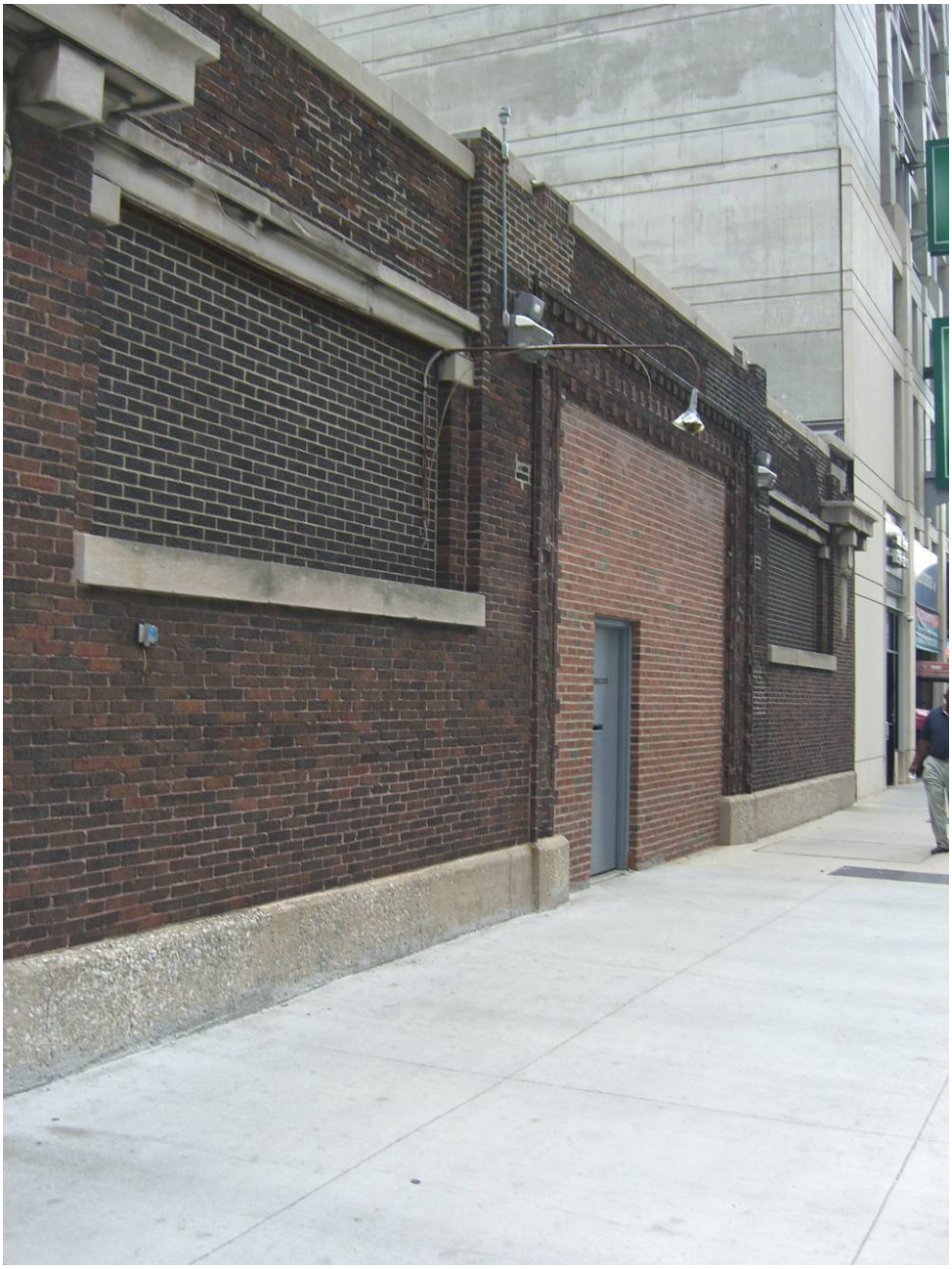

Figure B-8. Photograph of the Chicago-Franklin monitoring site.

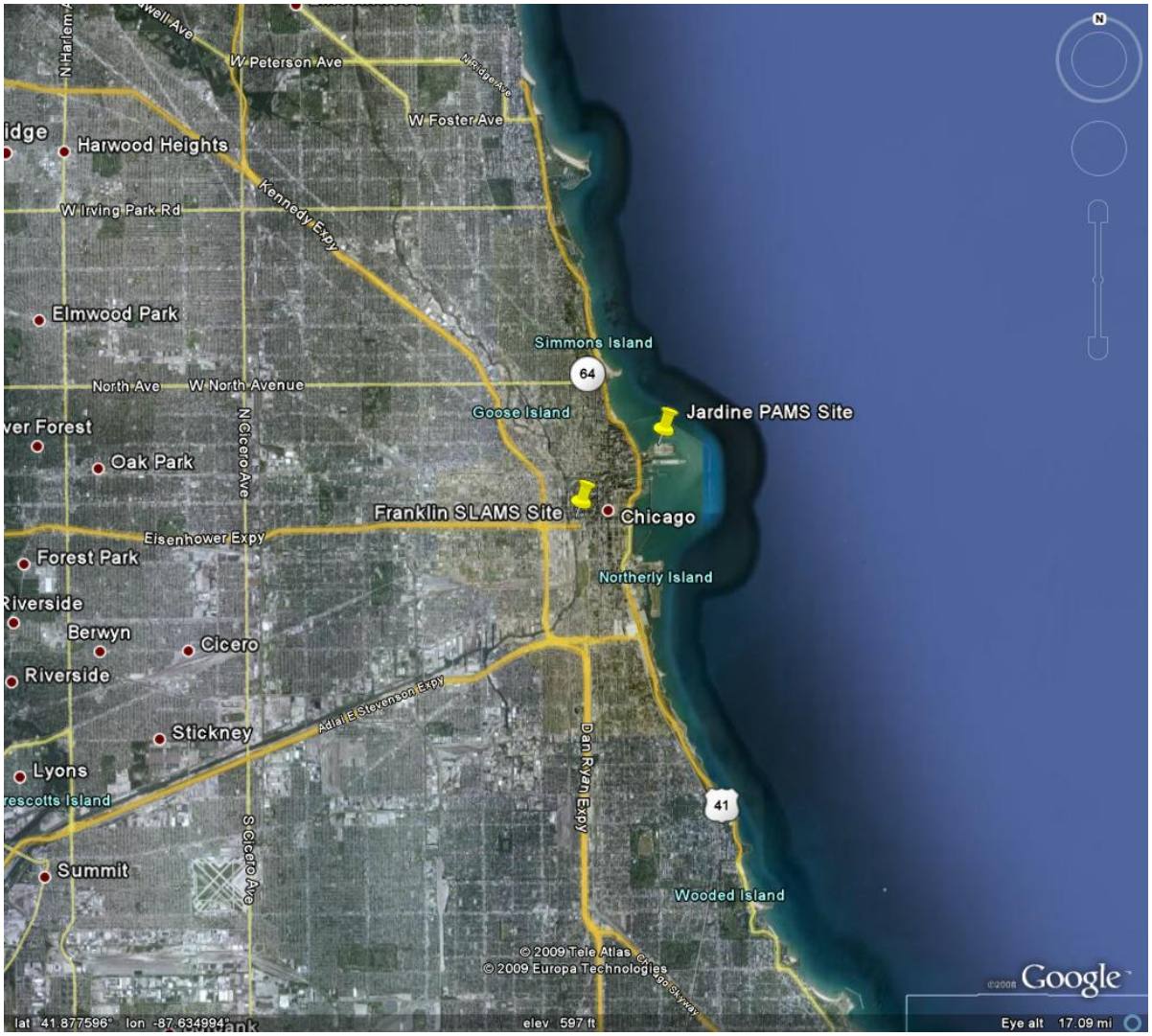

Figure B-9. Image of the area around the Jardine and Franklin sites in Chicago.

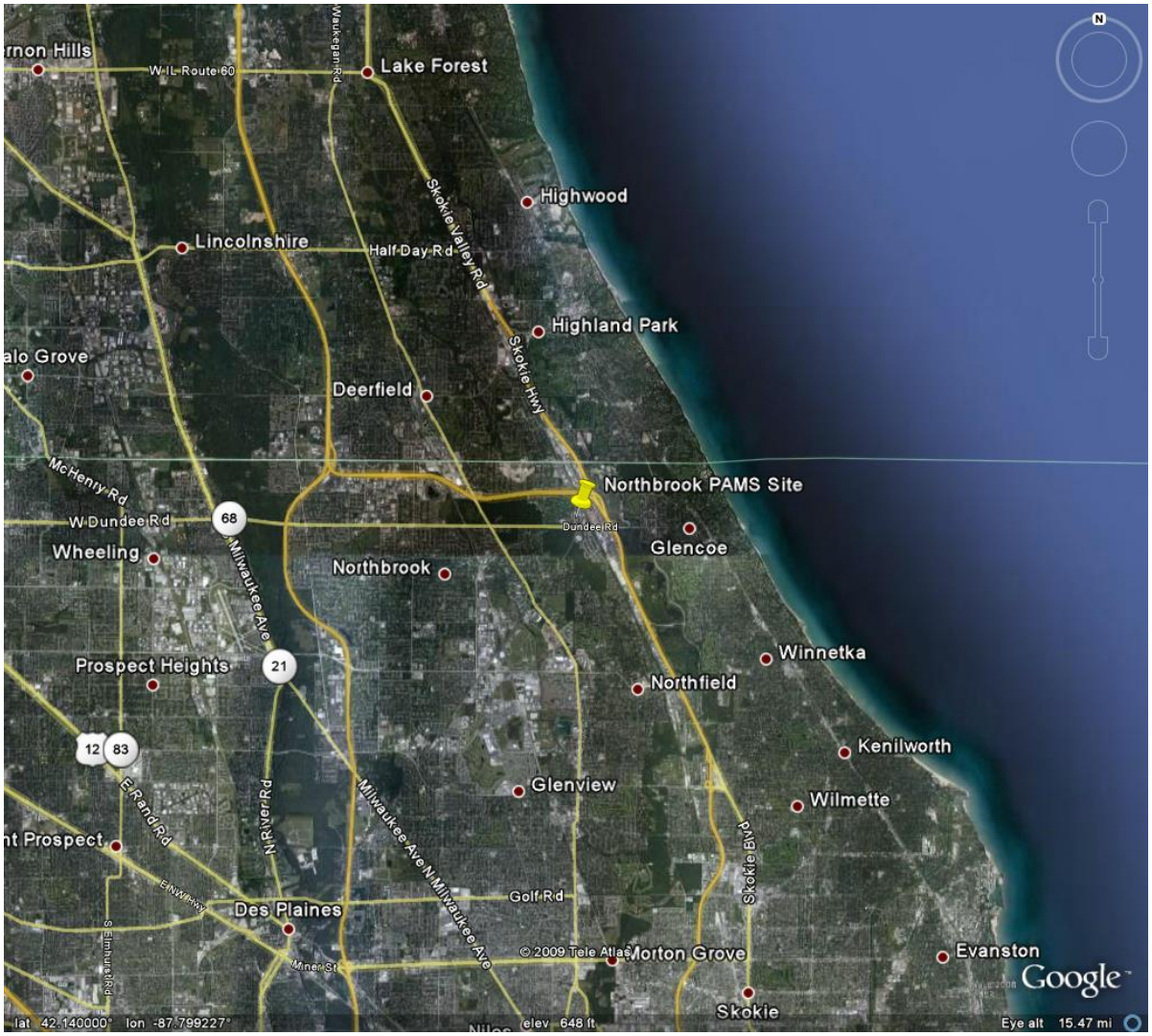

Figure B-10. Image of the area around the Northbrook site in Chicago.

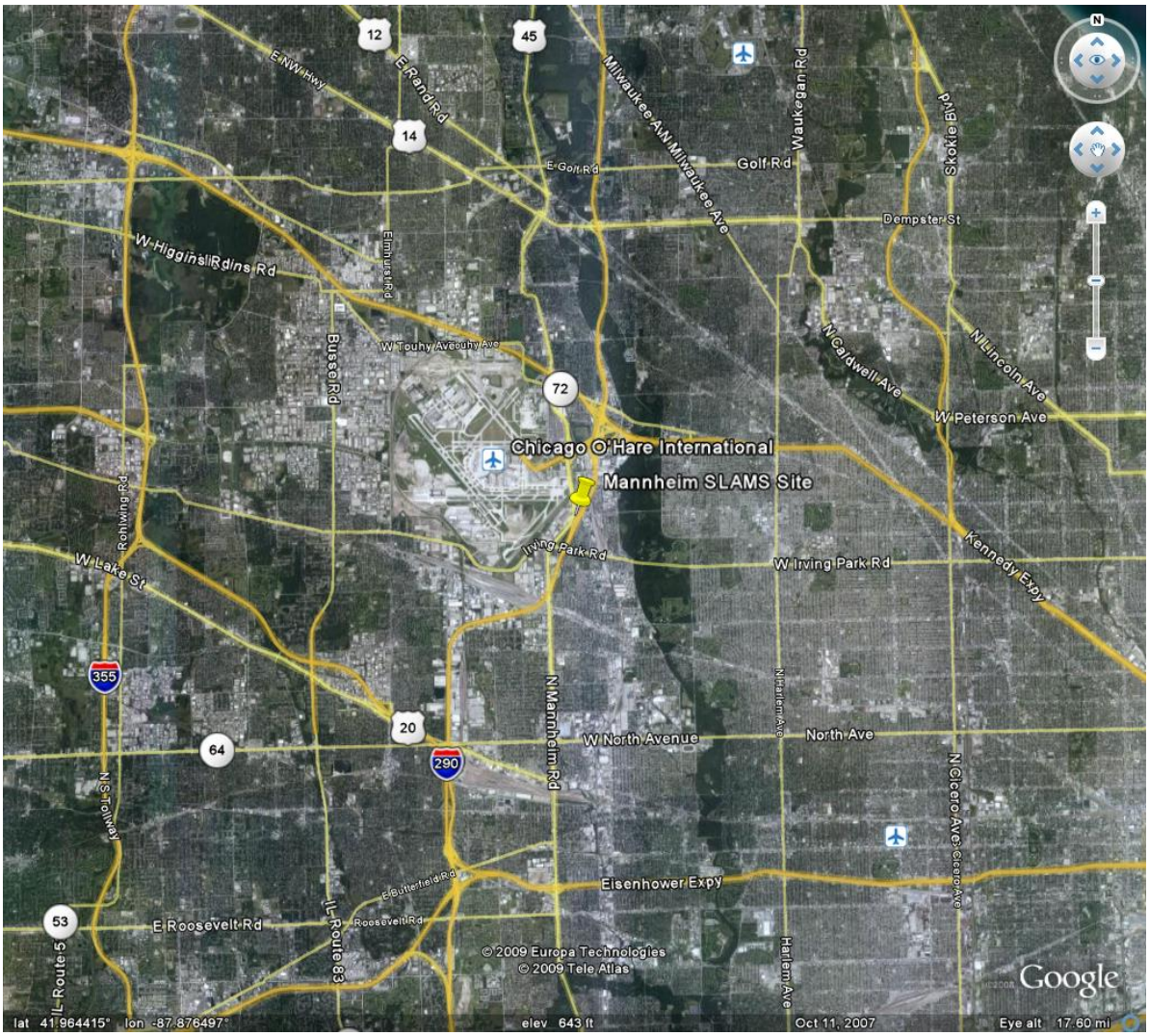

Figure B-11. Image of the area around the Mannheim site in Chicago.

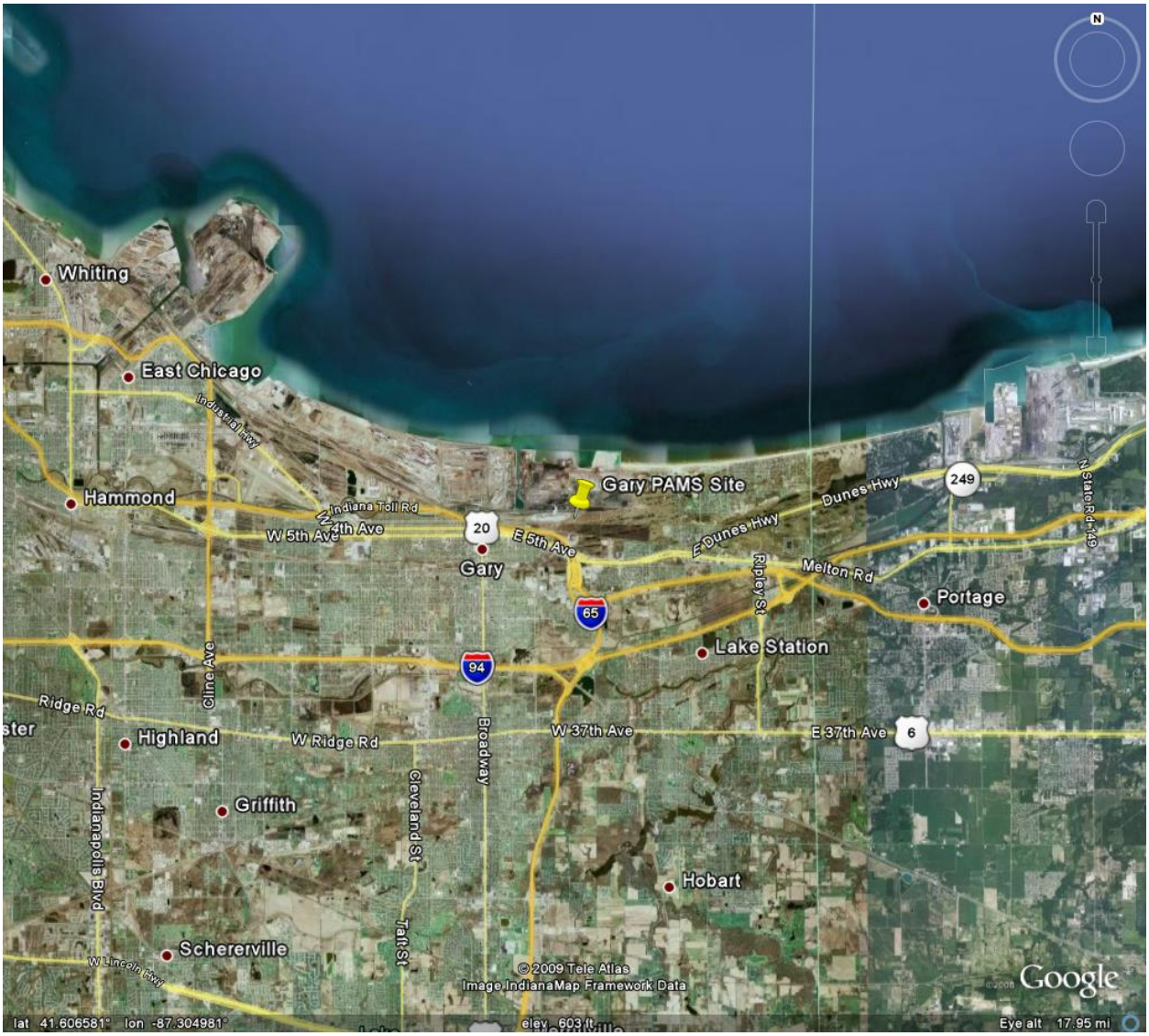

Figure B-12. Image of the area around the Gary site.

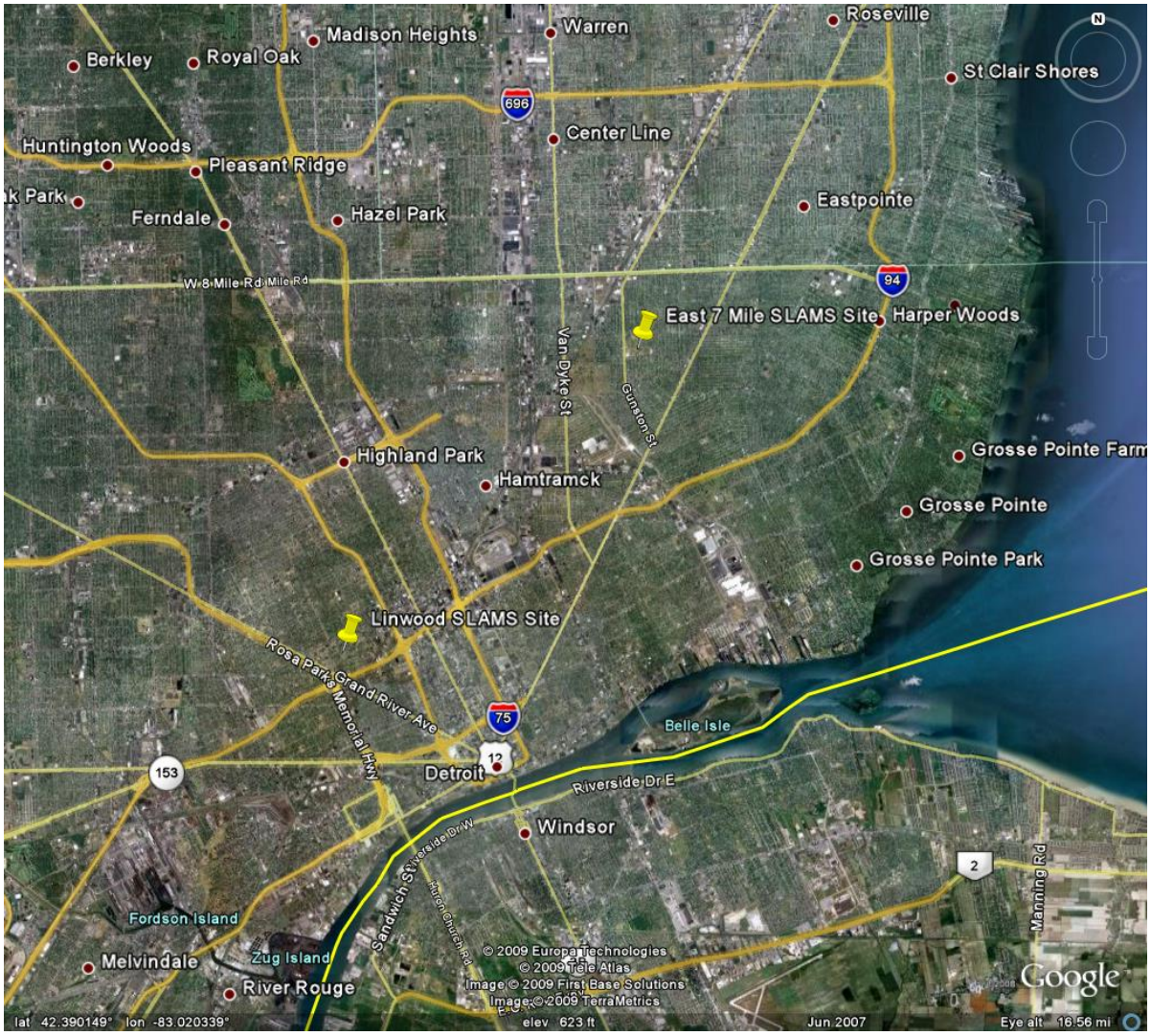

Figure B-13. Image of the area around the East 7 Mile and Linwood sites in Detroit.

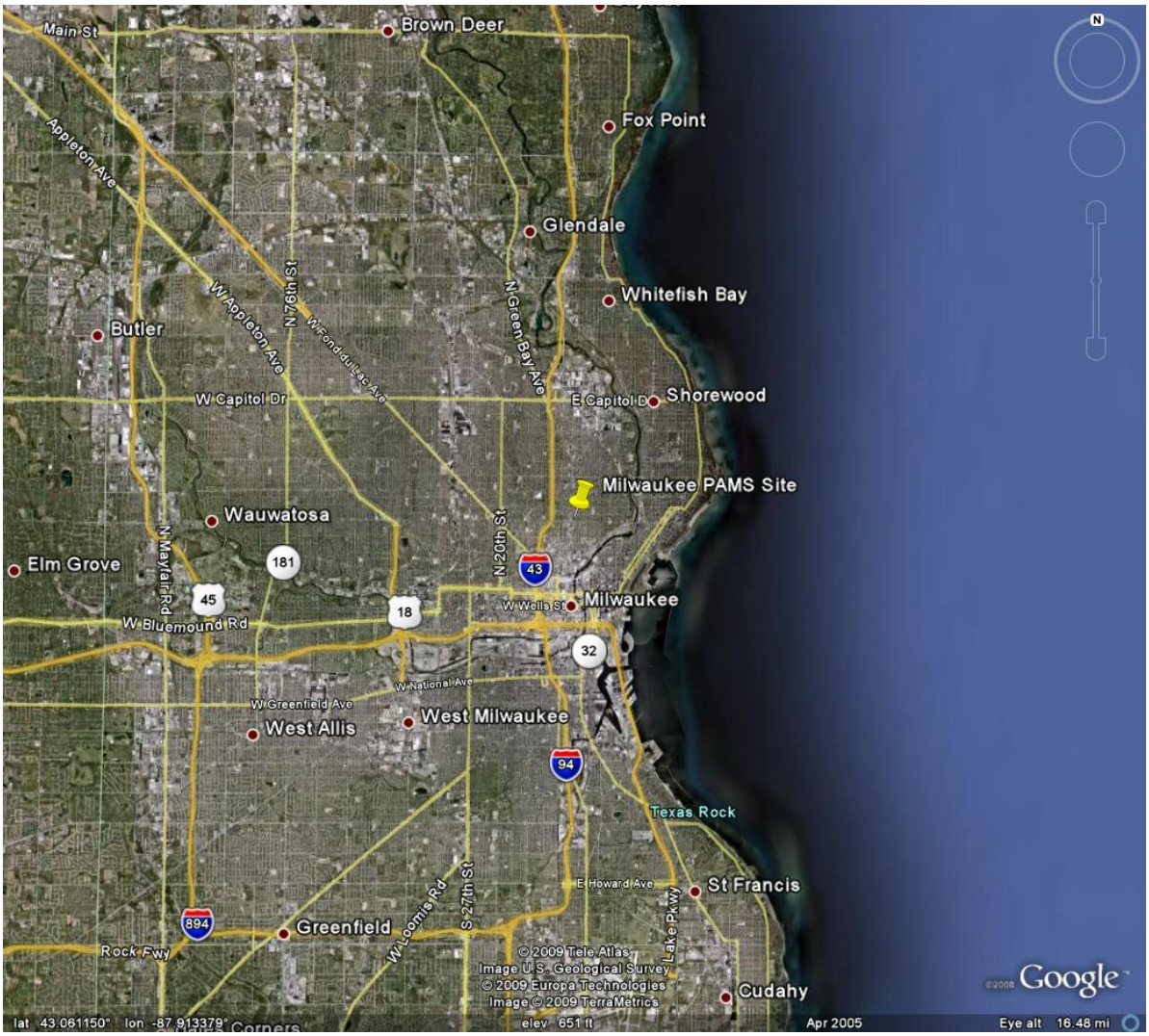

Figure B-14. Image of the area around the Milwaukee site.

APPENDIX C

Diurnal Concentration Plots for 2008 and 2009

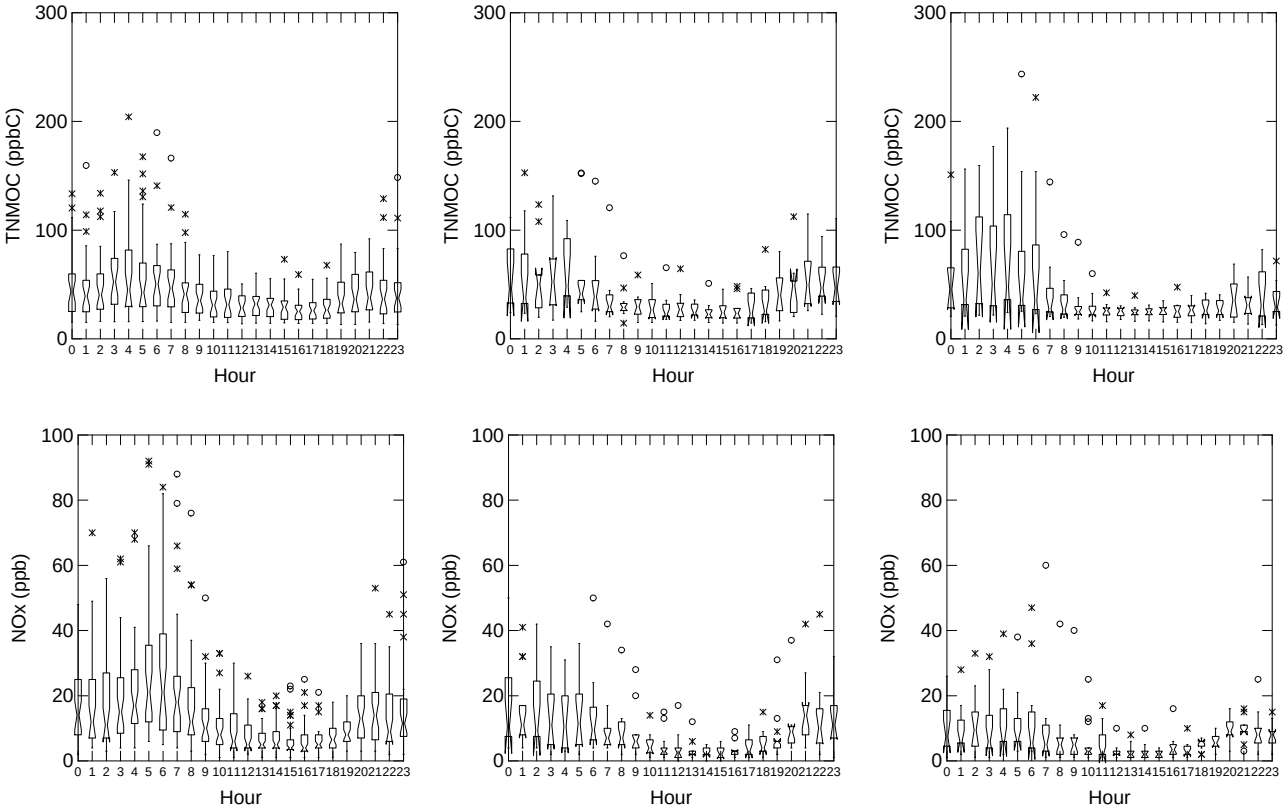

Figure C-1. Hourly TNMOC and NO_x concentrations for the Chicago-Northbrook site for summer weekdays (left), Saturdays (center), and Sundays (right), 2008.

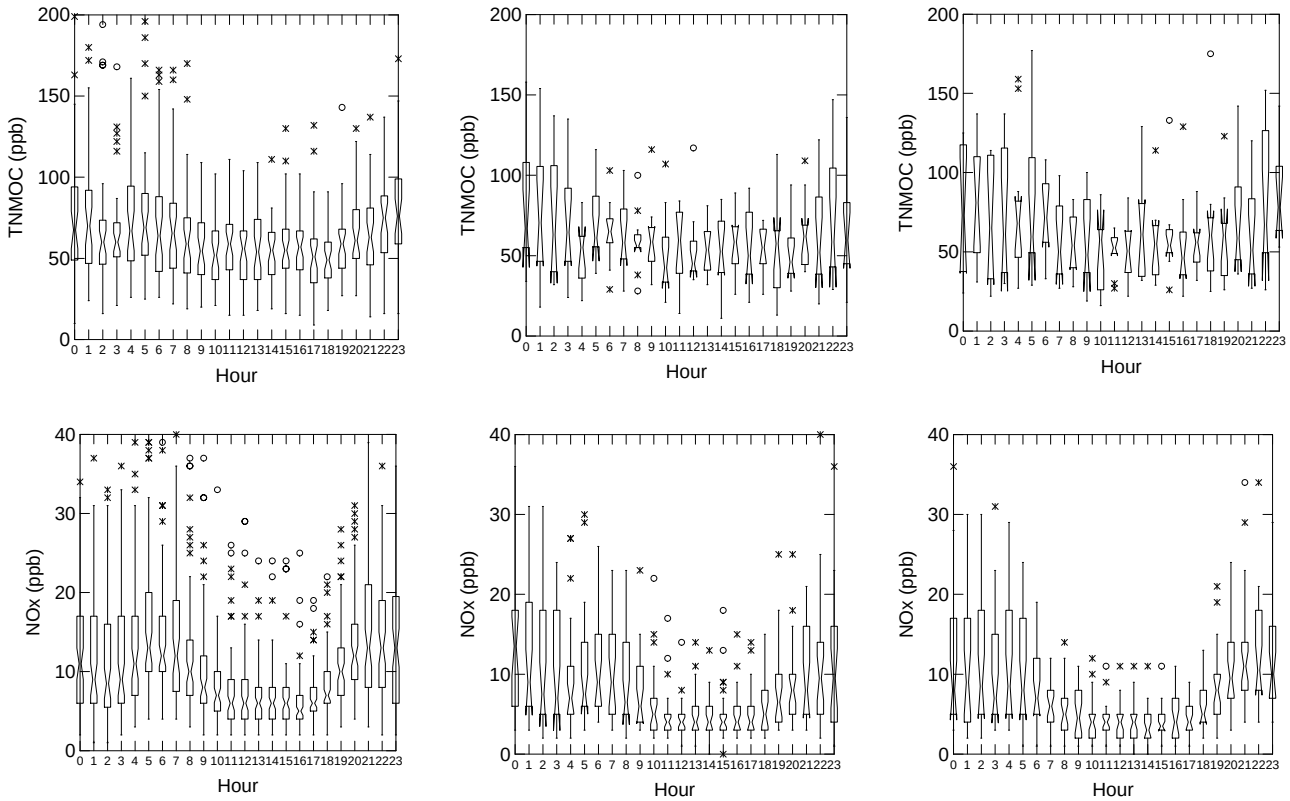

Figure C-2. Hourly TNMOC and NO_x concentrations for the Chicago-Northbrook site for summer weekdays (left), Saturdays (center), and Sundays (right), 2009.

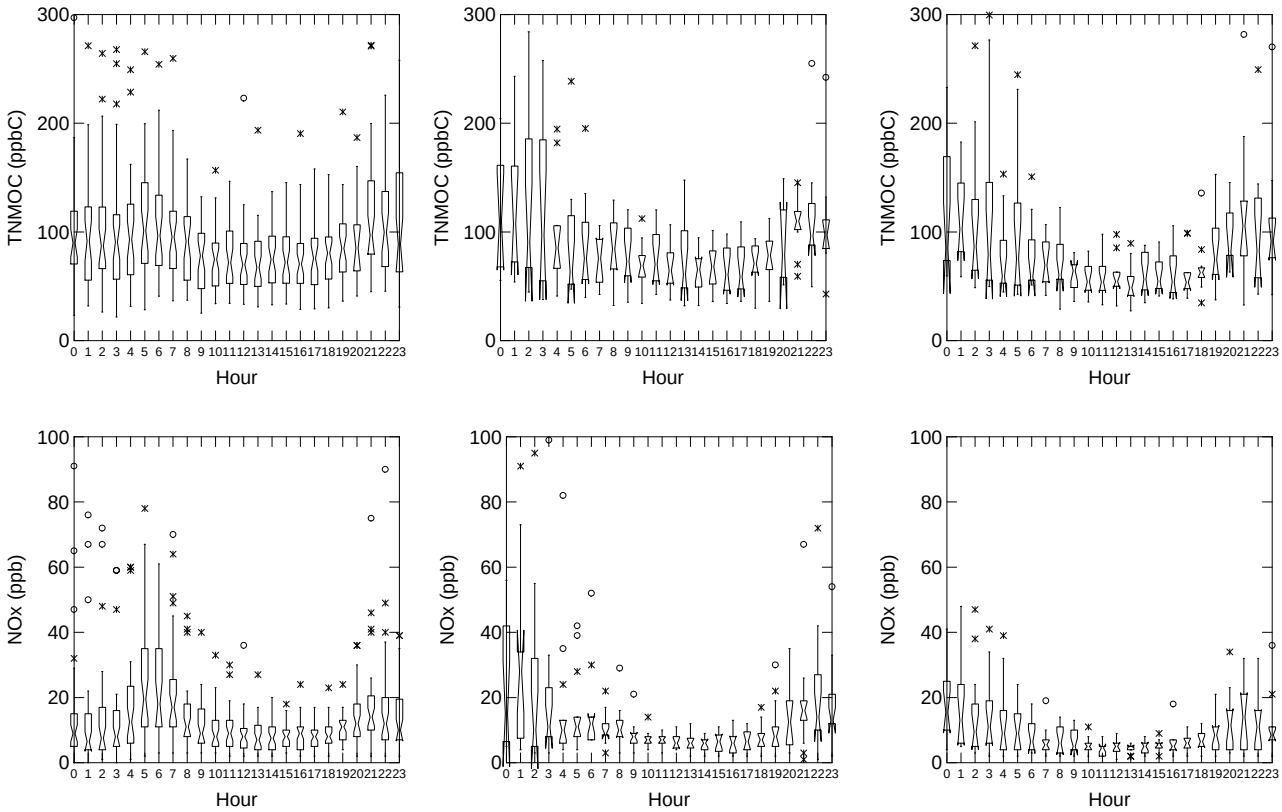

Figure C-3. Hourly TNMOC and NO_x concentrations for the Milwaukee site for summer weekdays (left), Saturdays (center), and Sundays (right), 2008.

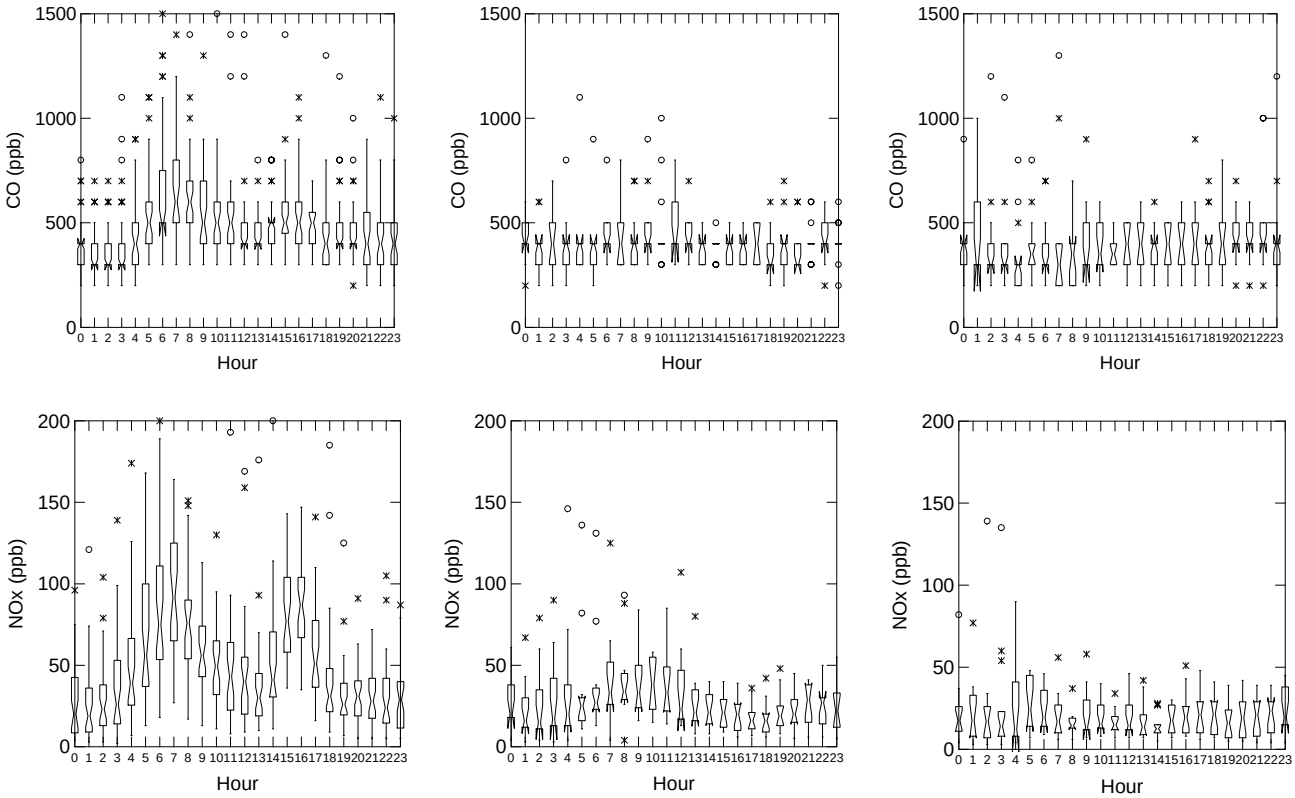

Figure C-4. Hourly CO and NO_x concentrations for the Chicago-Franklin site for summer weekdays (left), Saturdays (center), and Sundays (right), 2008.

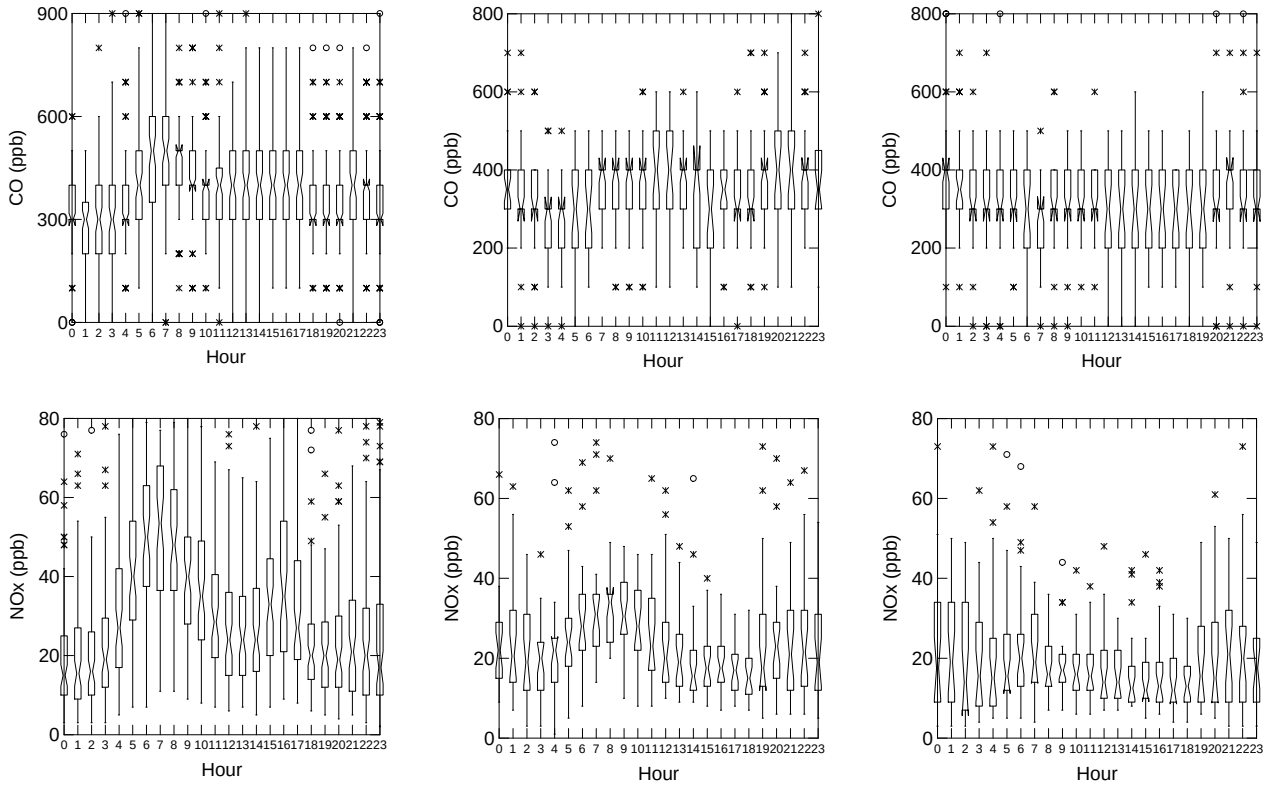

Figure C-5. Hourly CO and NO_x concentrations for the Chicago-Franklin site for summer weekdays (left), Saturdays (center), and Sundays (right), 2009.

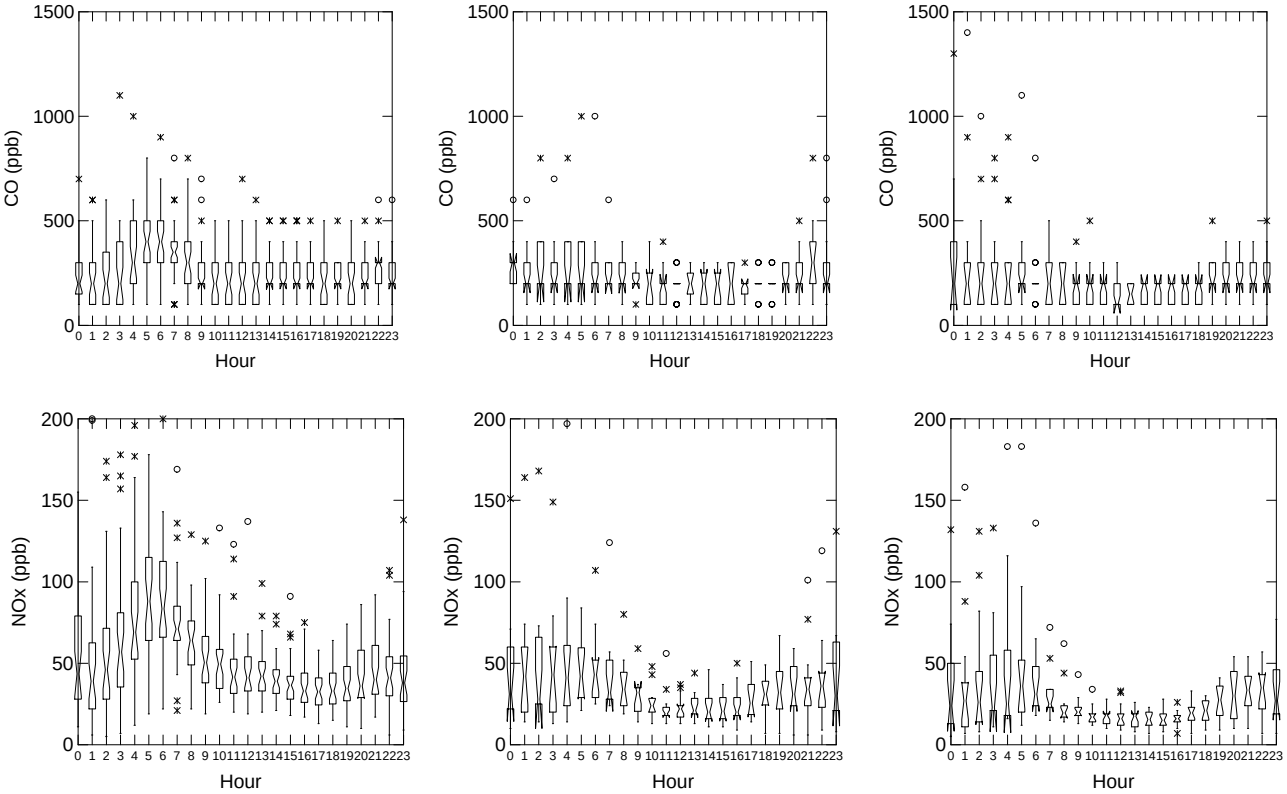

Figure C-6. Hourly CO and NO_x concentrations for the Chicago-Mannheim site for summer weekdays (left), Saturdays (center), and Sundays (right), 2008.

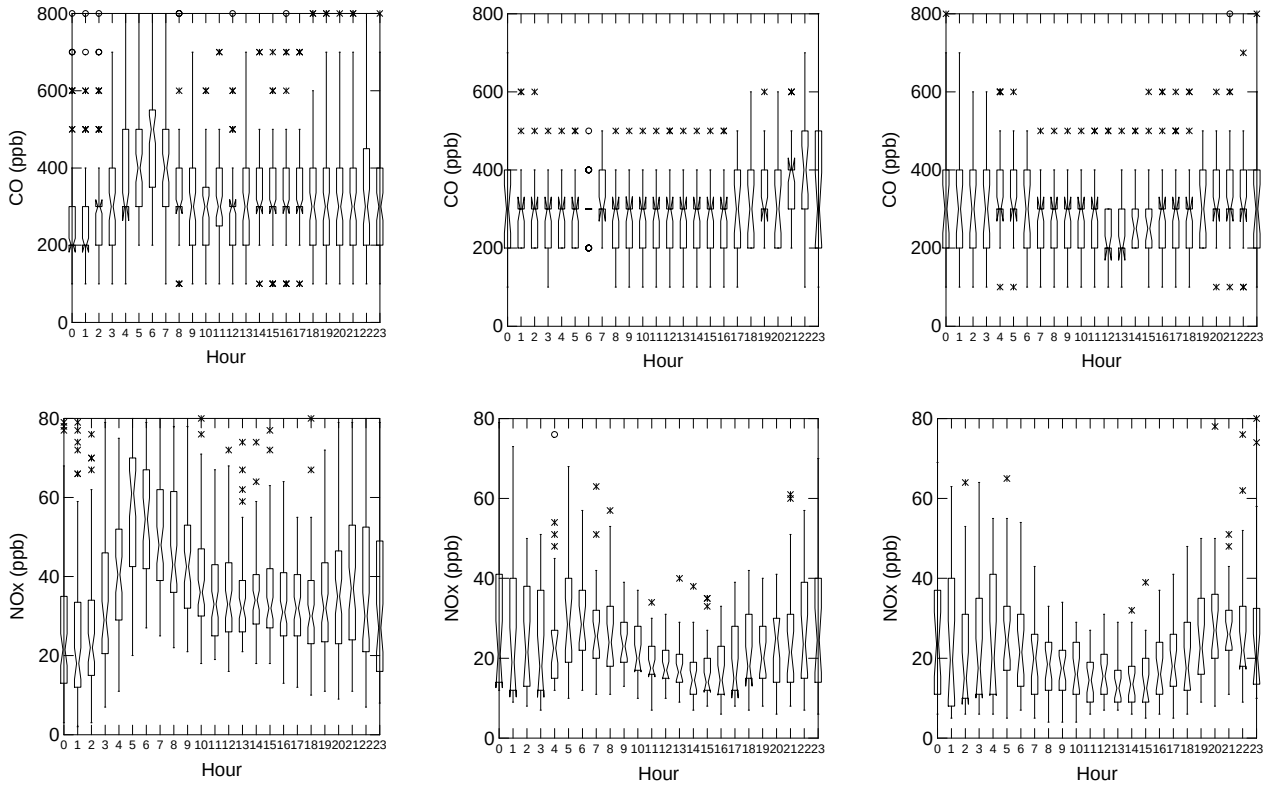

Figure C-7. Hourly CO and NO_x concentrations for the Chicago-Mannheim site for summer weekdays (left), Saturdays (center), and Sundays (right), 2009.

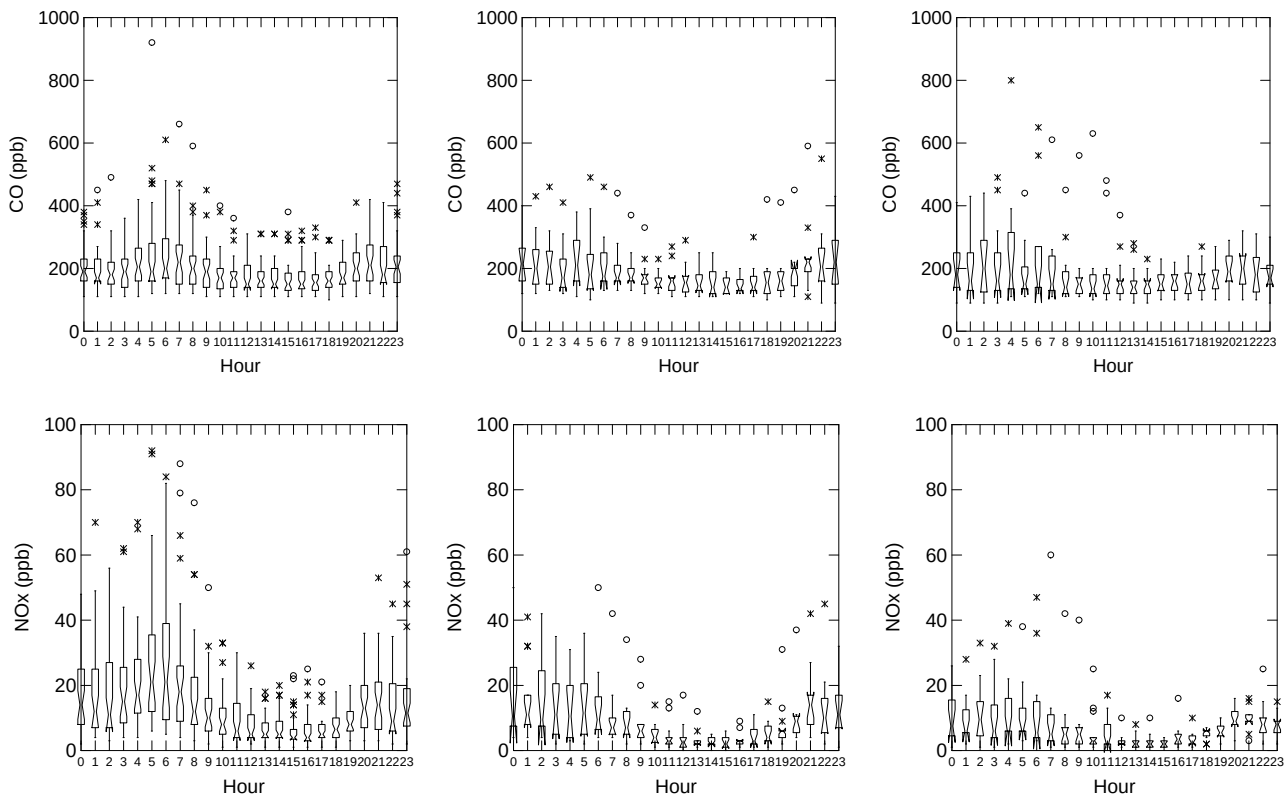

Figure C-8. Hourly CO and NO_x concentrations for the Chicago-Northbrook site for summer weekdays (left), Saturdays (center), and Sundays (right), 2008.

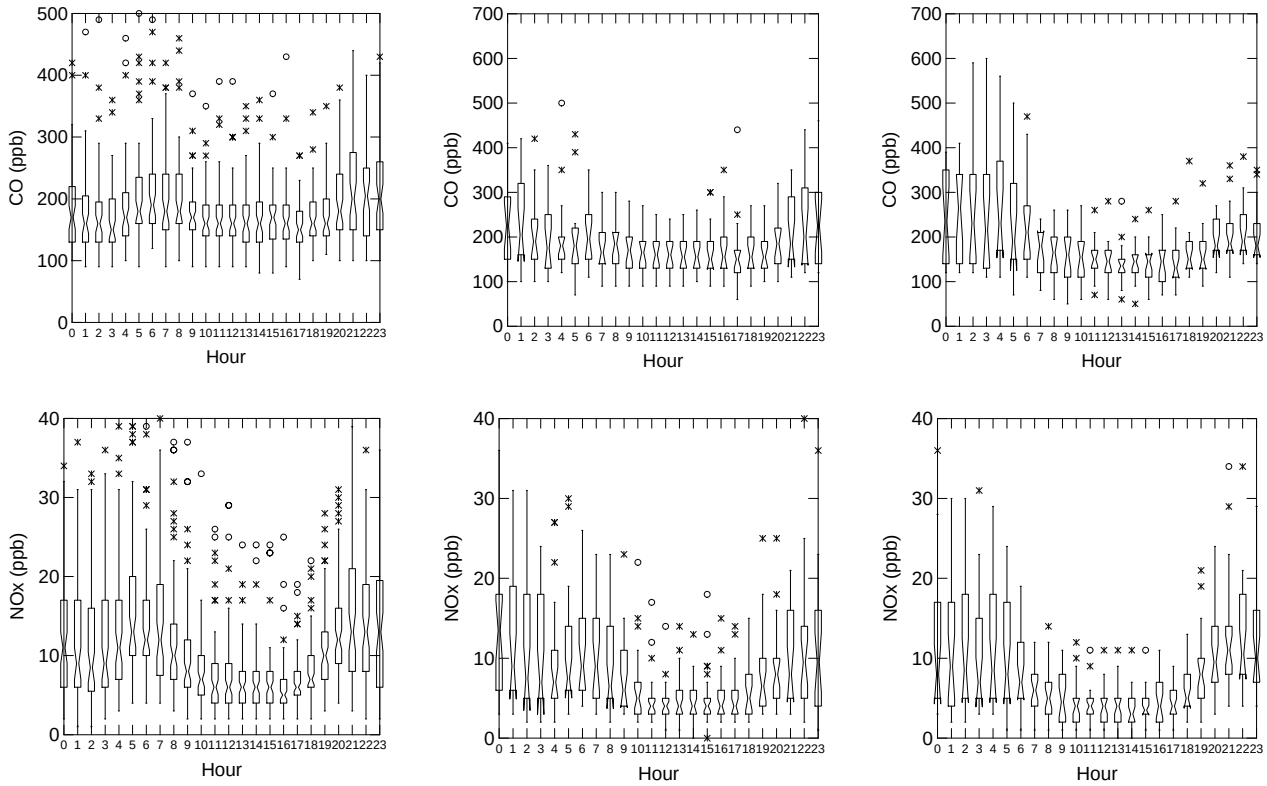

Figure C-9. Hourly CO and NO_x concentrations for the Chicago-Northbrook site for summer weekdays (left), Saturdays (center), and Sundays (right), 2009.

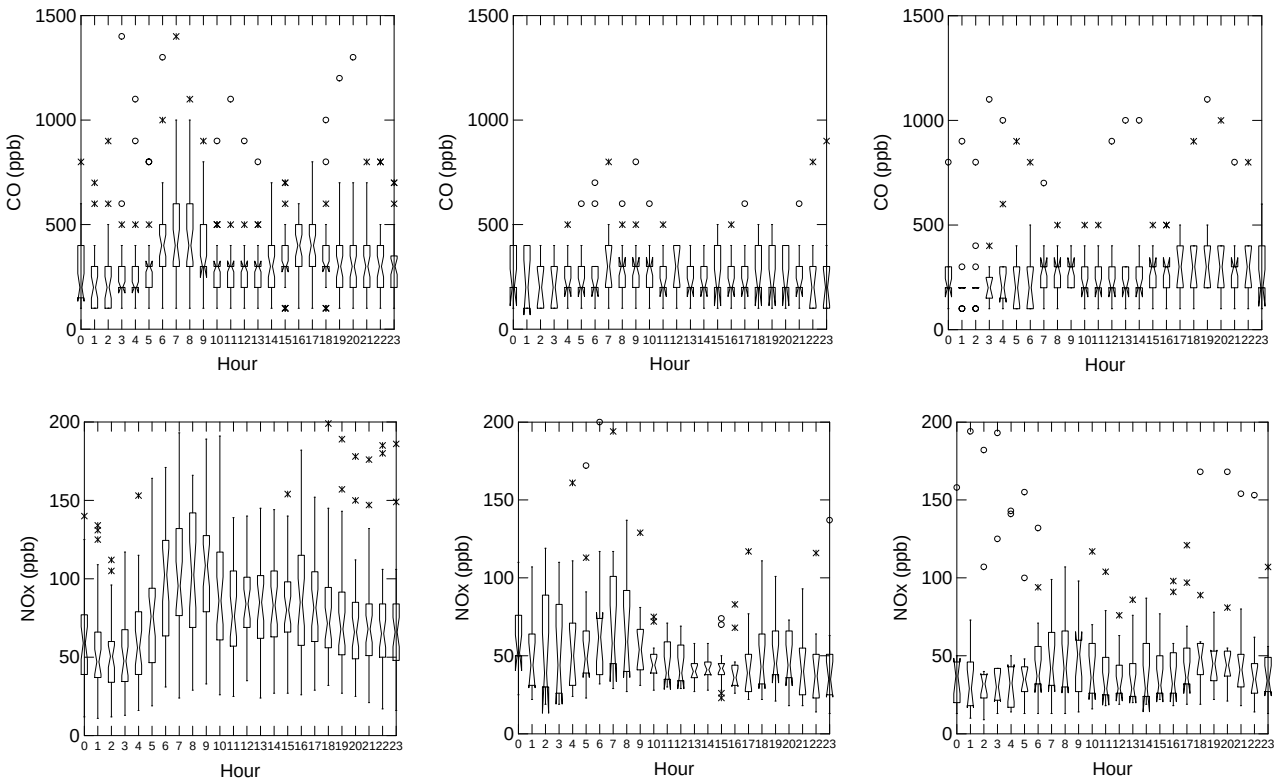

Figure C-10. Hourly CO and NO_x concentrations for the Chicago-Mannheim site for winter weekdays (left), Saturdays (center), and Sundays (right), 2008.

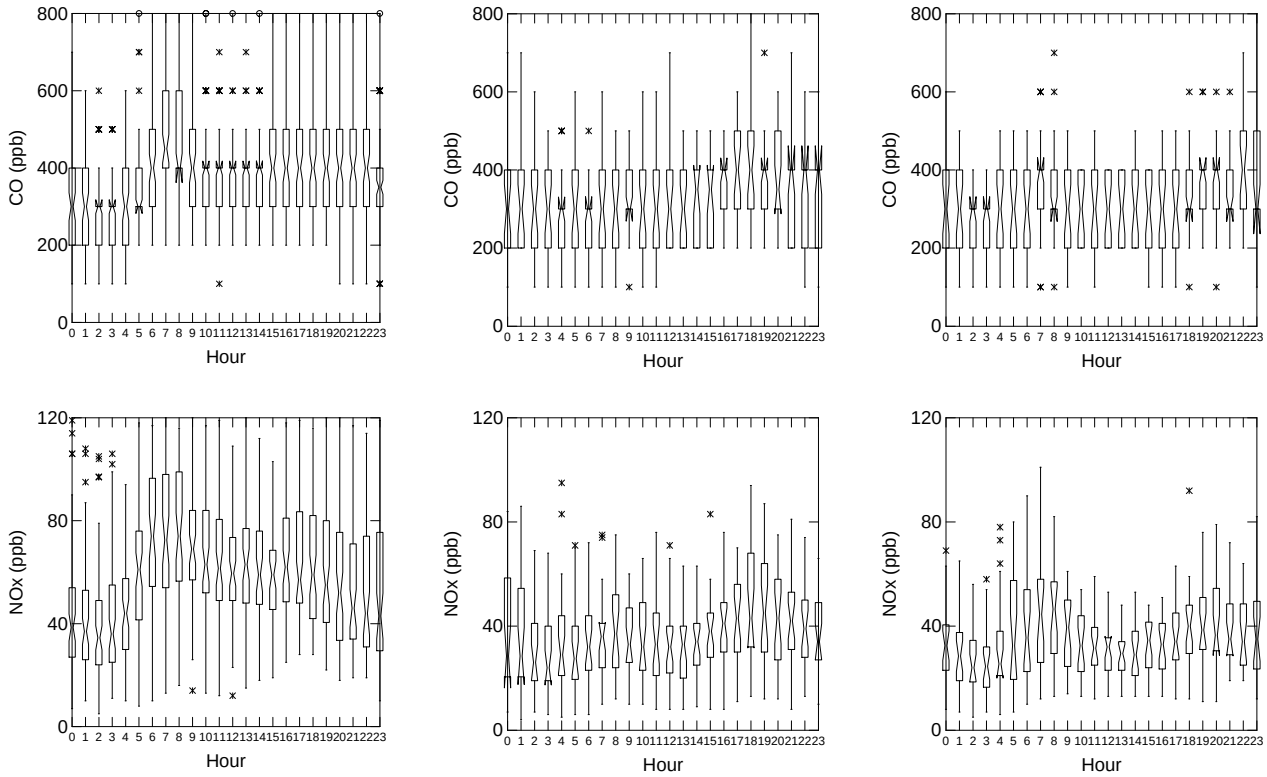

Figure C-11. Hourly CO and NO_x concentrations for the Chicago-Mannheim site for winter weekdays (left), Saturdays (center), and Sundays (right), 2009.

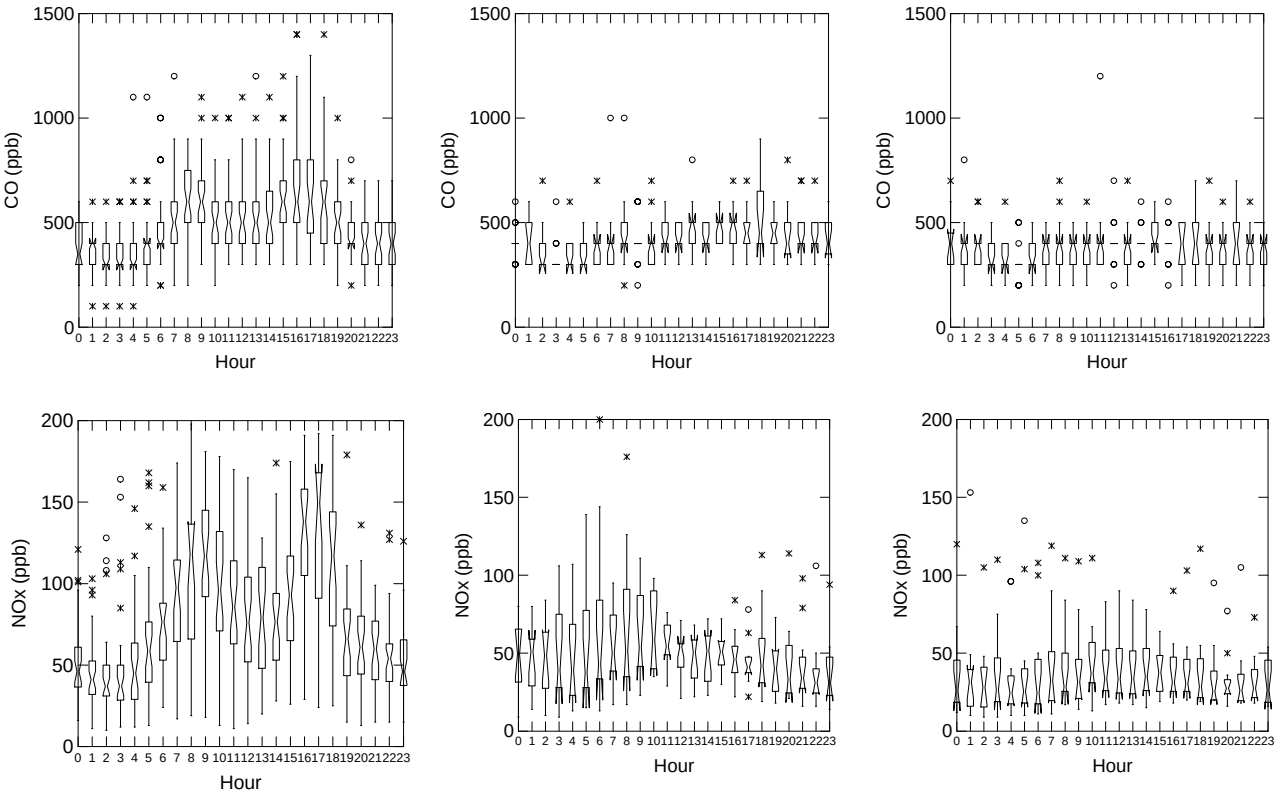

Figure C-12. Hourly CO and NO_x concentrations for the Chicago-Franklin site for winter weekdays (left), Saturdays (center), and Sundays (right), 2008.

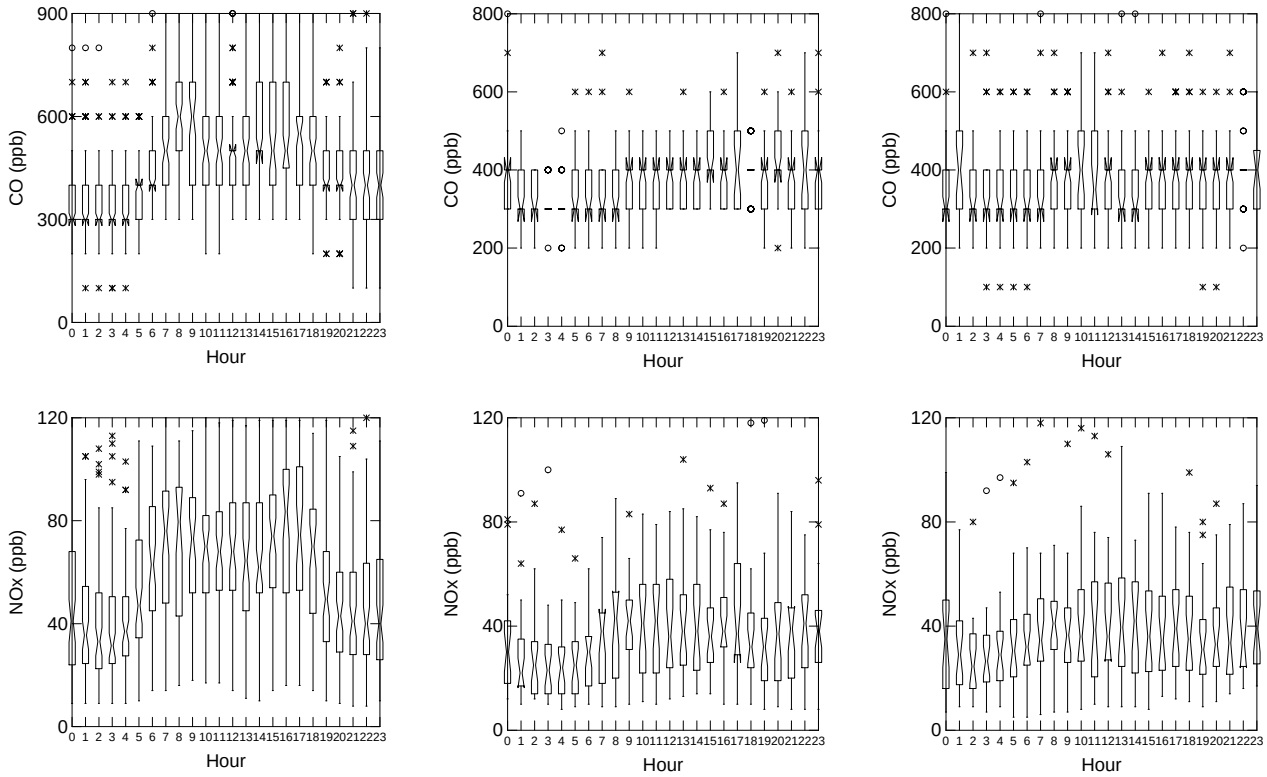

Figure C-13. Hourly CO and NO_x concentrations for the Chicago-Franklin site for winter weekdays (left), Saturdays (center), and Sundays (right), 2009.

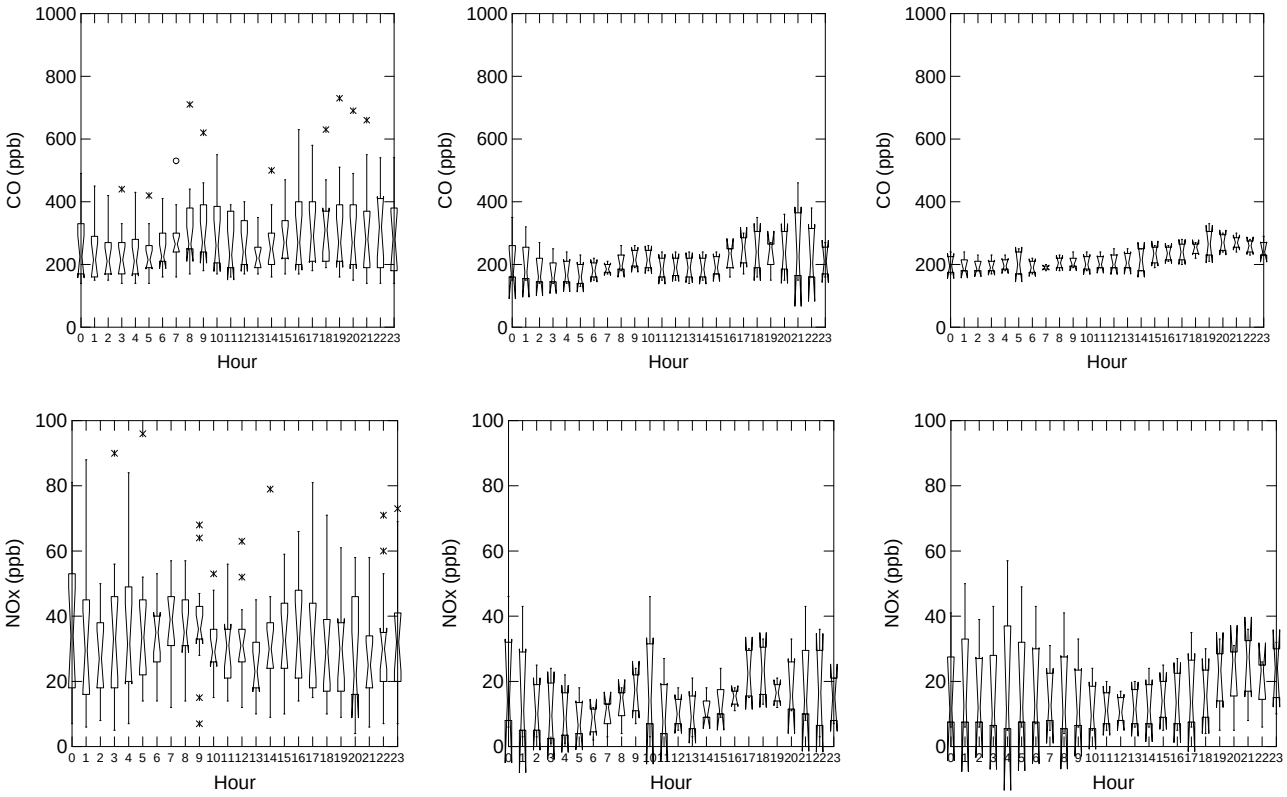

Figure C-14. Hourly CO and NO_x concentrations for the Chicago-Northbrook site for winter weekdays (left), Saturdays (center), and Sundays (right), 2008.

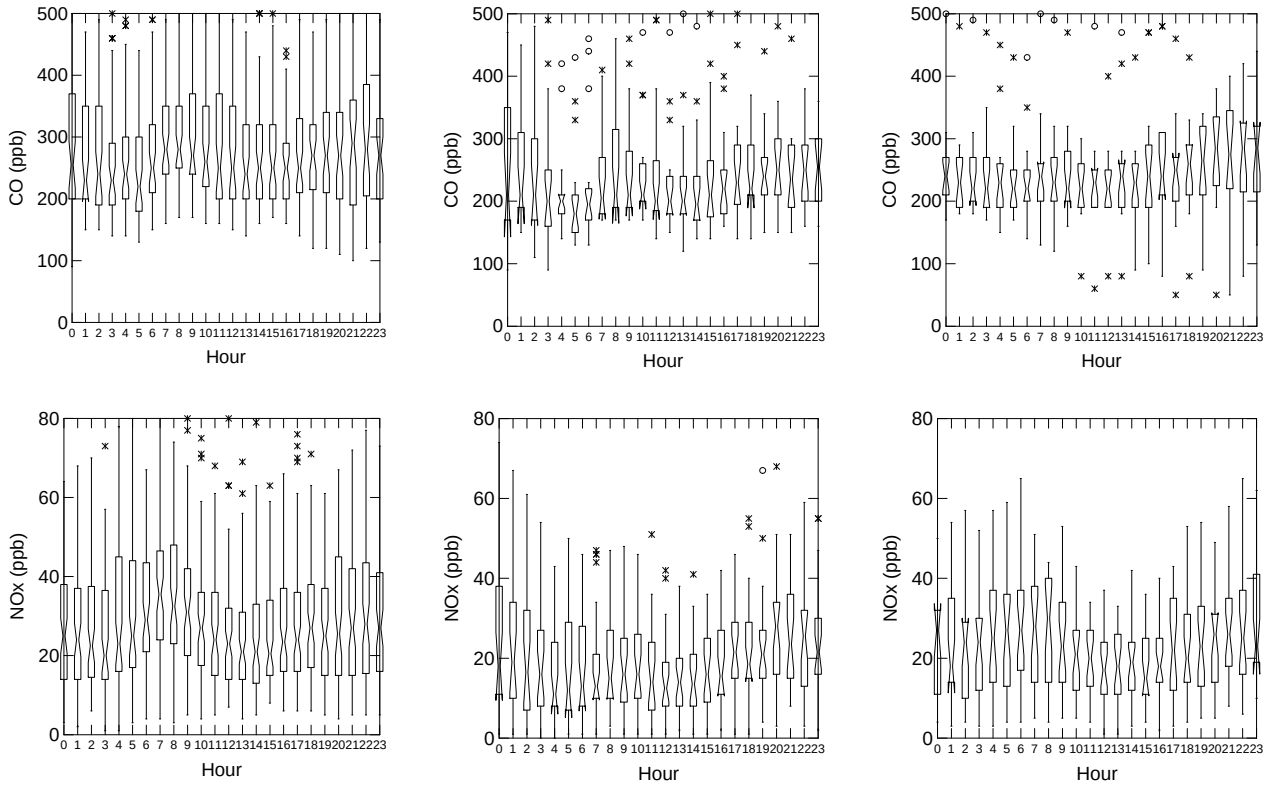

Figure C-15. Hourly CO and NO_x concentrations for the Chicago-Northbrook site for winter weekdays (left), Saturdays (center), and Sundays (right), 2009.

APPENDIX D

Additional Comparisons of Pollutant Ratios

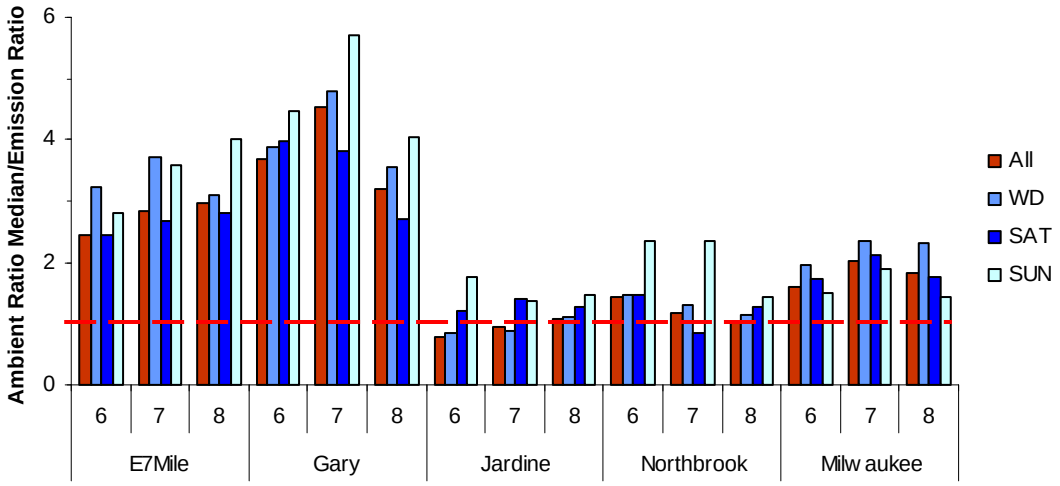

Figure D-1. Ratios of ambient-derived TNMOC/NO_x ratios to emissions-derived TNMOC/NO_x ratios by month and day of week for 2005[1] (the 1:1 agreement line is shown as a dashed red line).

[1] Because the 2005 emissions inventory was compared to ambient data from a three-year period (2004-2006), the large number of ambient samples allowed for month-specific (and other) analyses that were not possible with the 2008 ambient-to-emissions comparisons.

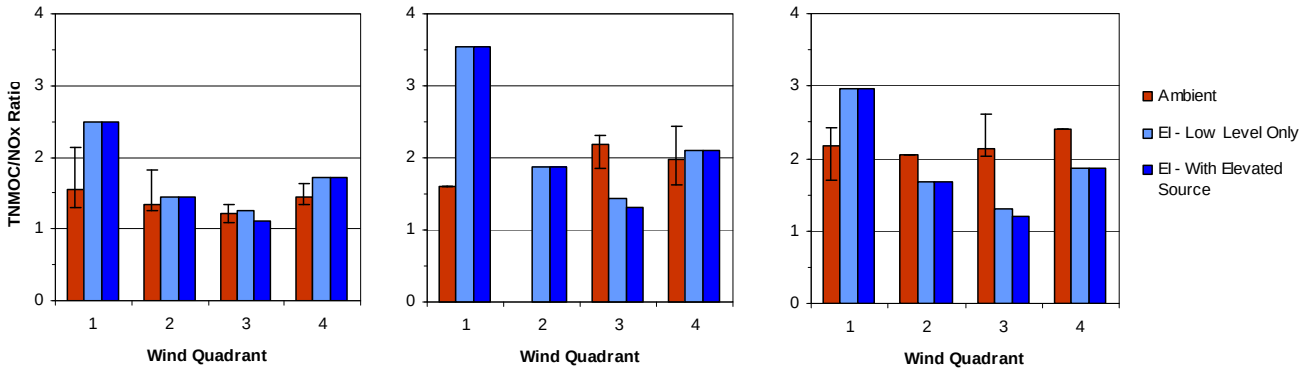

Figure D-2. Summer 2005 TNMOC/NO_x ratios by wind quadrant for the Chicago-Jardine site on weekdays (left), Saturdays (center), and Sundays (right).

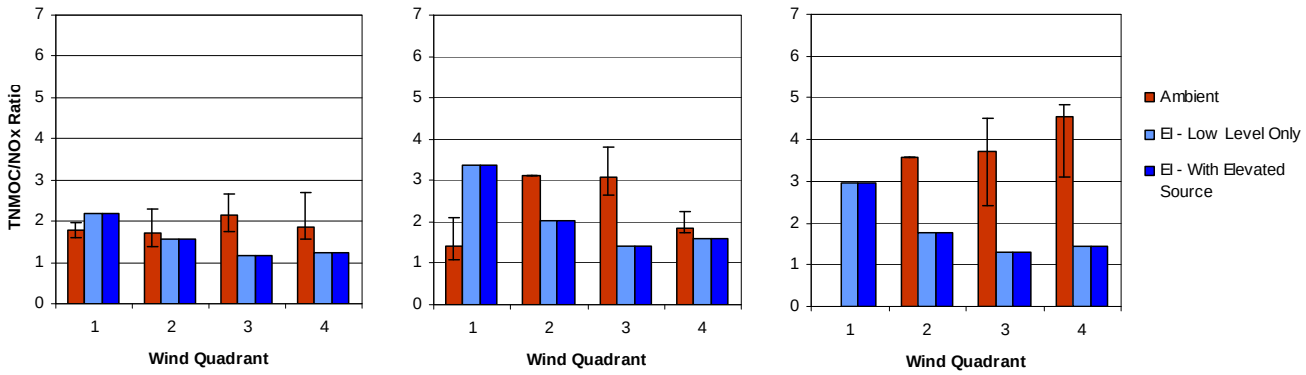

Figure D-3. Summer 2005 TNMOC/NO_x ratios by wind quadrant for the Chicago-Northbrook site on weekdays (left), Saturdays (center), and Sundays (right).

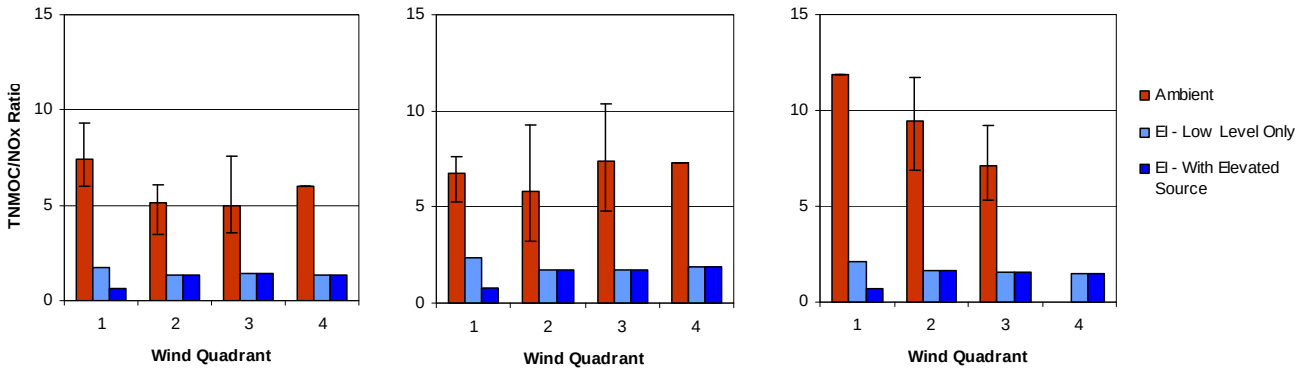

Figure D-4. Summer 2005 TNMOC/NO_x ratios by wind quadrant for the Gary site on weekdays (left), Saturdays (center), and Sundays (right).

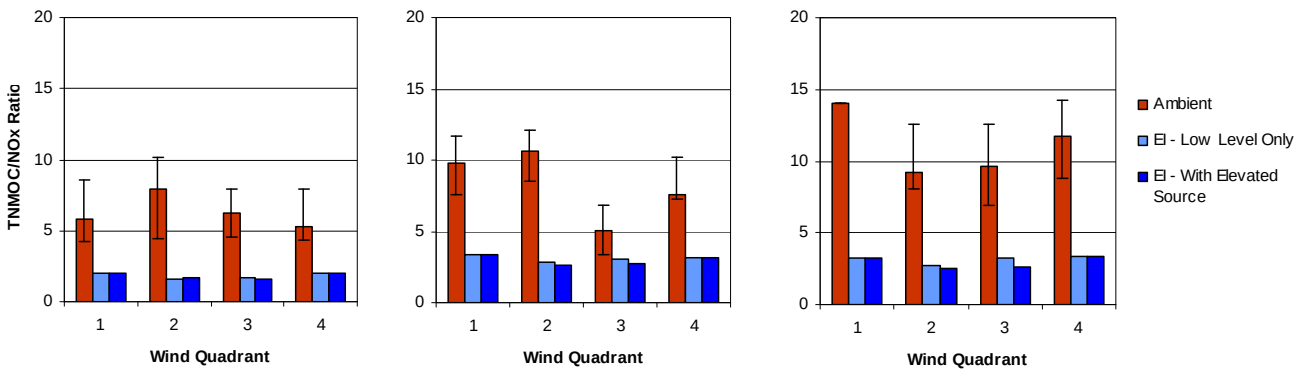

Figure D-5. Summer 2005 TNMOC/NO_x ratios by wind quadrant for the Detroit – East 7 Mile site on weekdays (left), Saturdays (center), and Sundays (right).

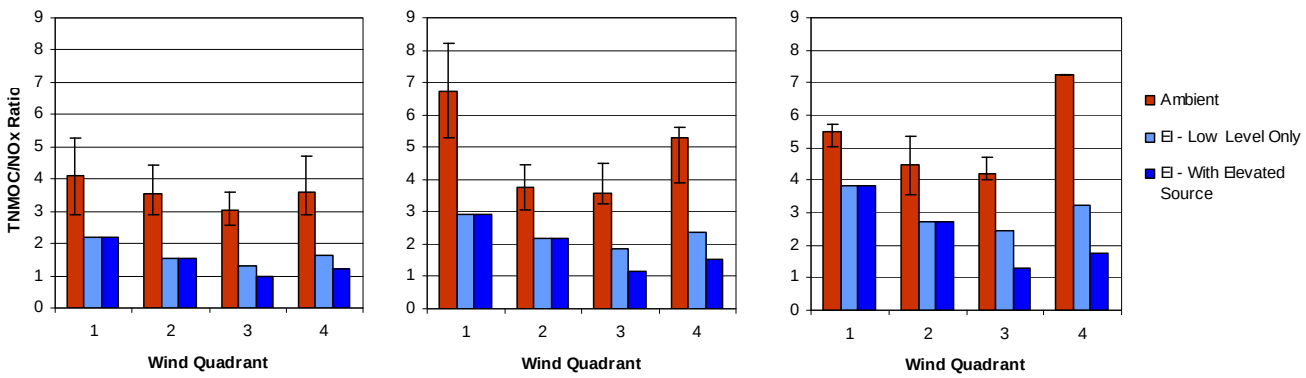

Figure D-6. Summer 2005 TNMOC/NO_x ratios by wind quadrant for the Milwaukee site on weekdays (left), Saturdays (center), and Sundays (right).

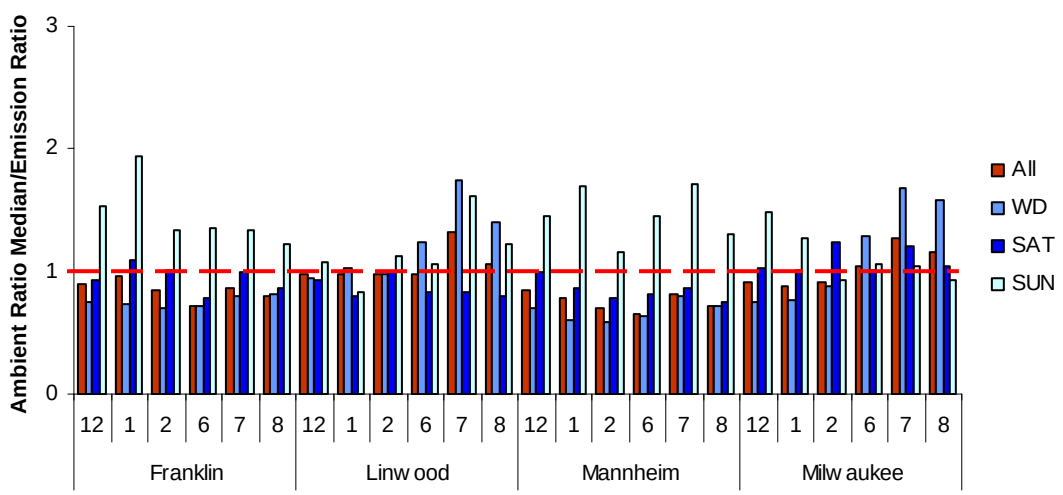

Figure D-7. Ratios of ambient-derived CO/NO_x ratios to emissions-derived CO/NO_x ratios by month and day of week for 2005 (the 1:1 agreement line is shown as a dashed red line).

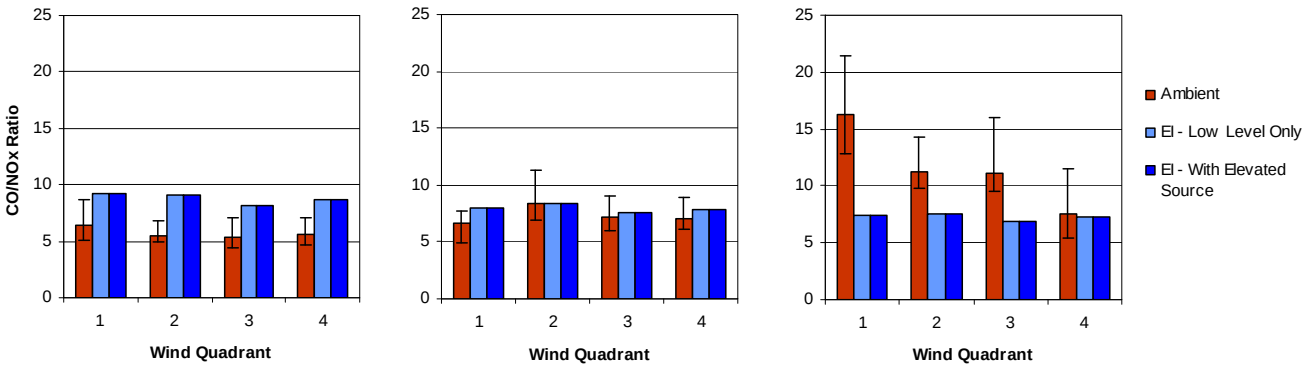

Figure D-8. Winter 2005 CO/NO_x ratios by wind quadrant for the Chicago-Mannheim site on weekdays (left), Saturdays (center), and Sundays (right).

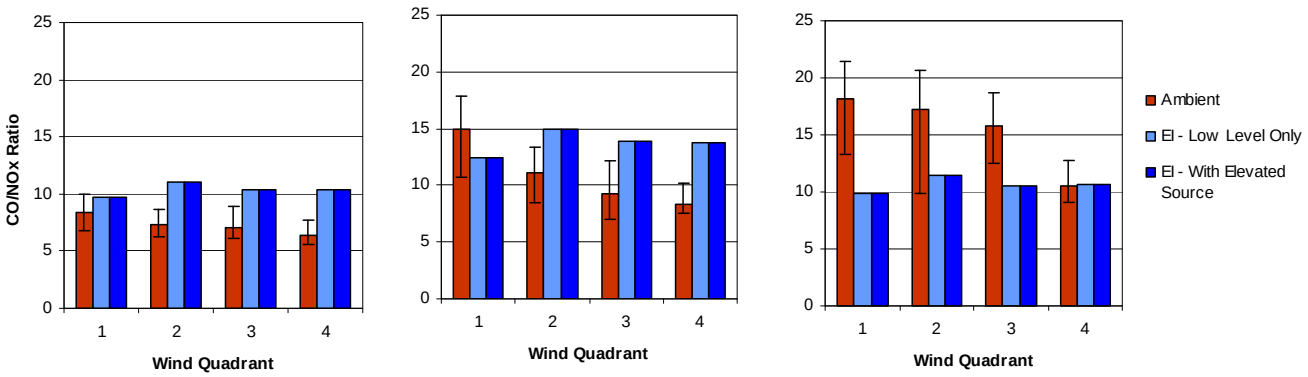

Figure D-9. Summer 2005 CO/NO_x ratios by wind quadrant for the Chicago-Mannheim site on weekdays (left), Saturdays (center), and Sundays (right).

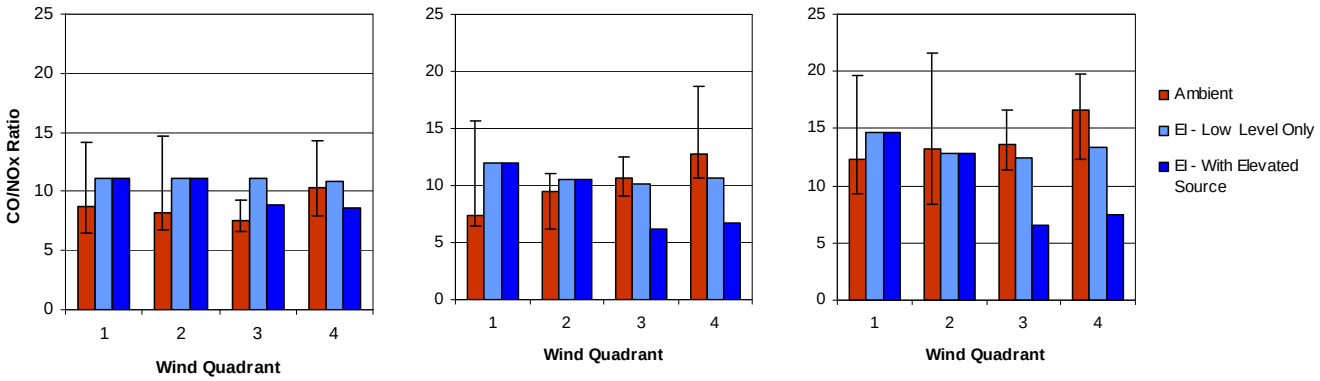

Figure D-10. Winter 2005 CO/NO_x ratios by wind quadrant for the Milwaukee site on weekdays (left), Saturdays (center), and Sundays (right).

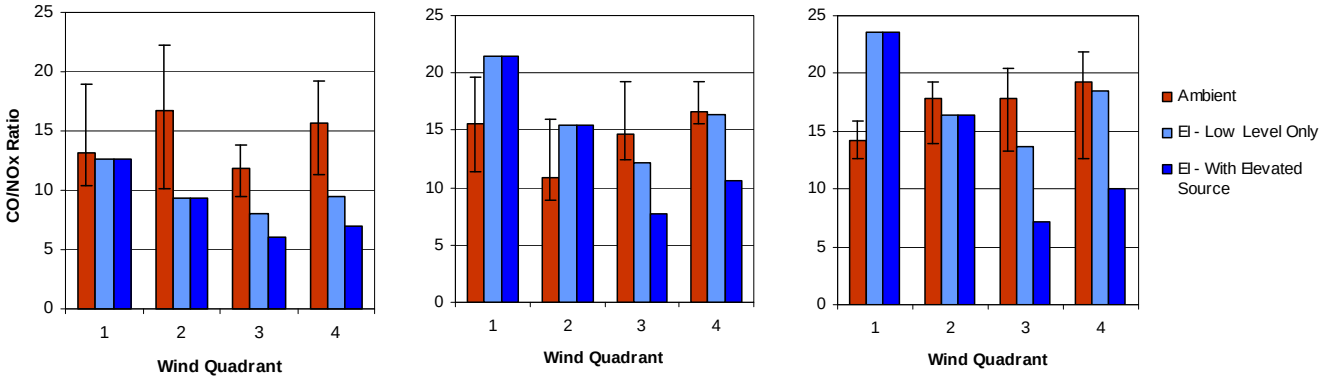

Figure D-11. Summer 2005 CO/NO_x ratios by wind quadrant for the Milwaukee site on weekdays (left), Saturdays (center), and Sundays (right).

APPENDIX E

Additional Comparisons of Hydrocarbon Compositions

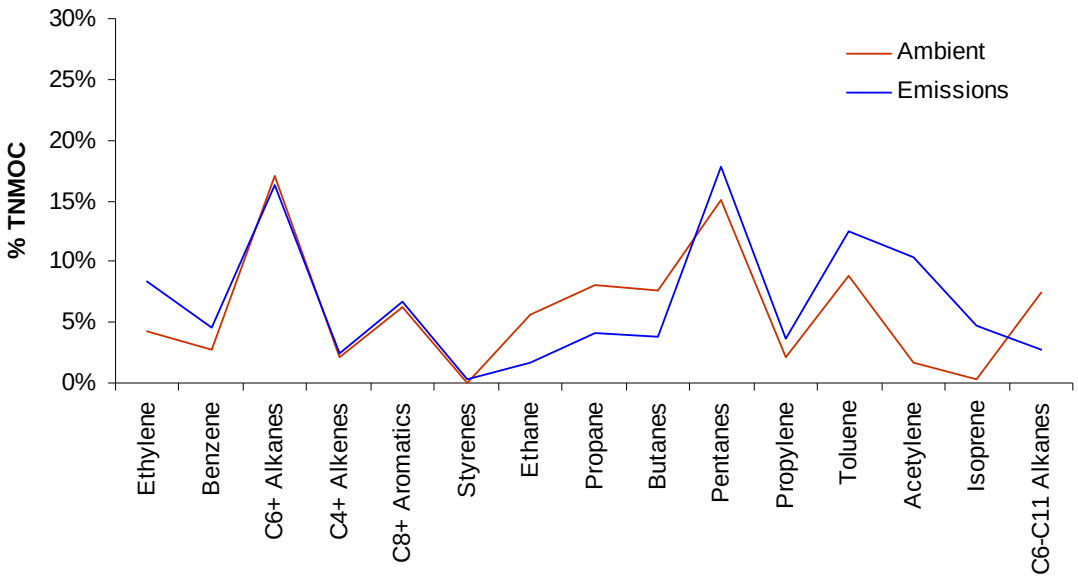

Figure E-1. Comparison of 2005 summer weekday ambient- and emissions-derived hydrocarbon compositions for the Chicago-Jardine site.

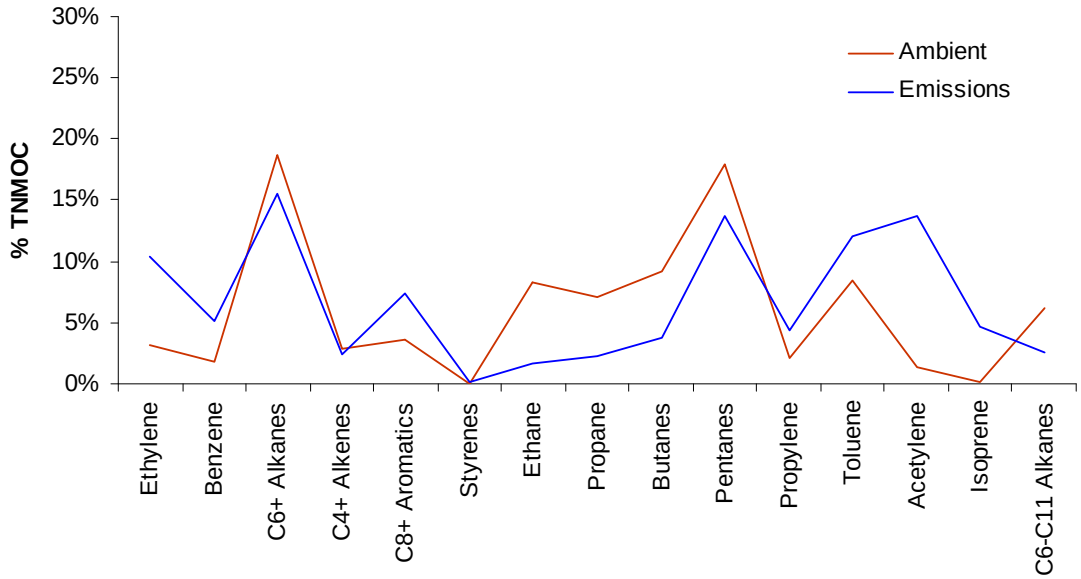

Figure E-2. Comparison of 2005 summer Saturday ambient- and emissions-derived hydrocarbon compositions for the Chicago-Jardine site.

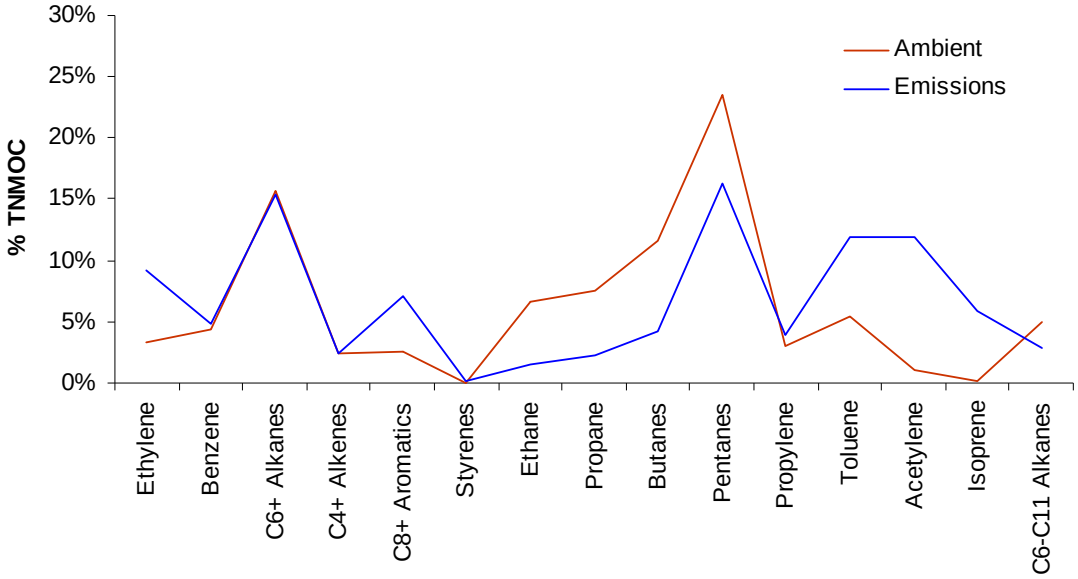

Figure E-3. Comparison of 2005 summer Sunday ambient- and emissions-derived hydrocarbon compositions for the Chicago-Jardine site.

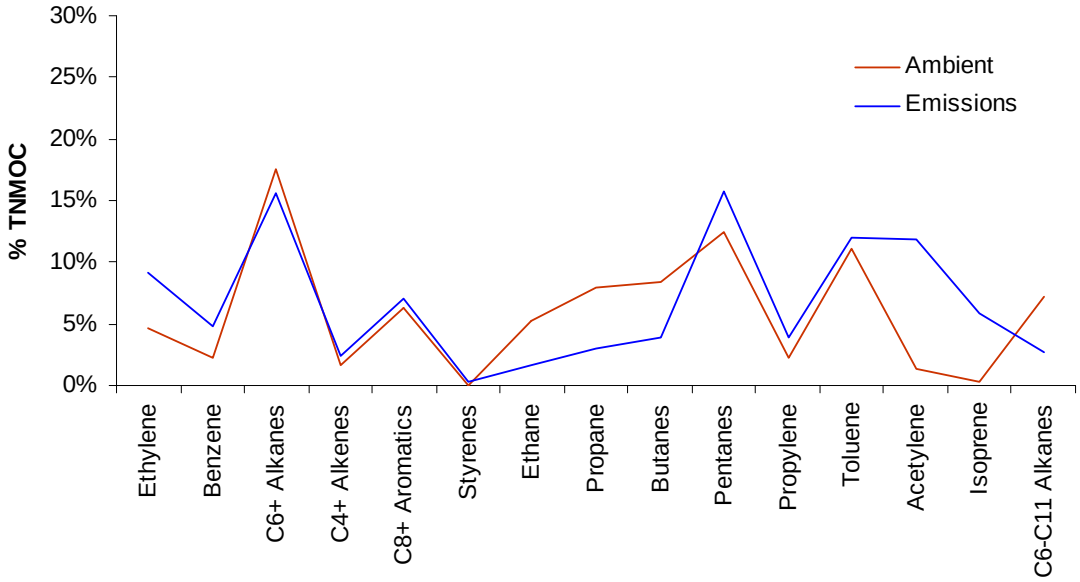

Figure E-4. Comparison of June 2005 ambient- and emissions-derived hydrocarbon compositions for the Chicago-Jardine site.

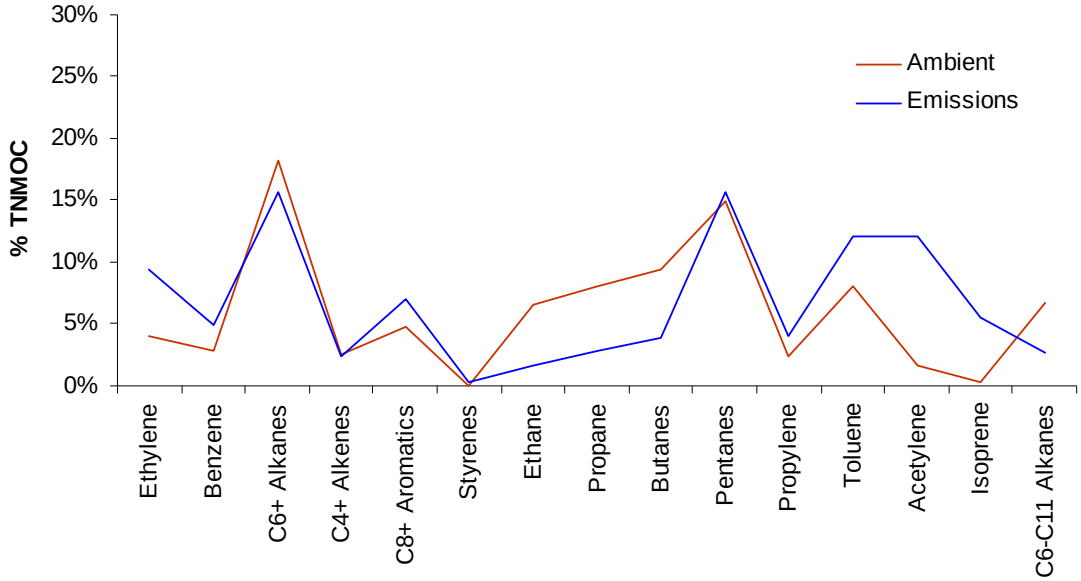

Figure E-5. Comparison of July 2005 ambient- and emissions-derived hydrocarbon compositions for the Chicago-Jardine site.

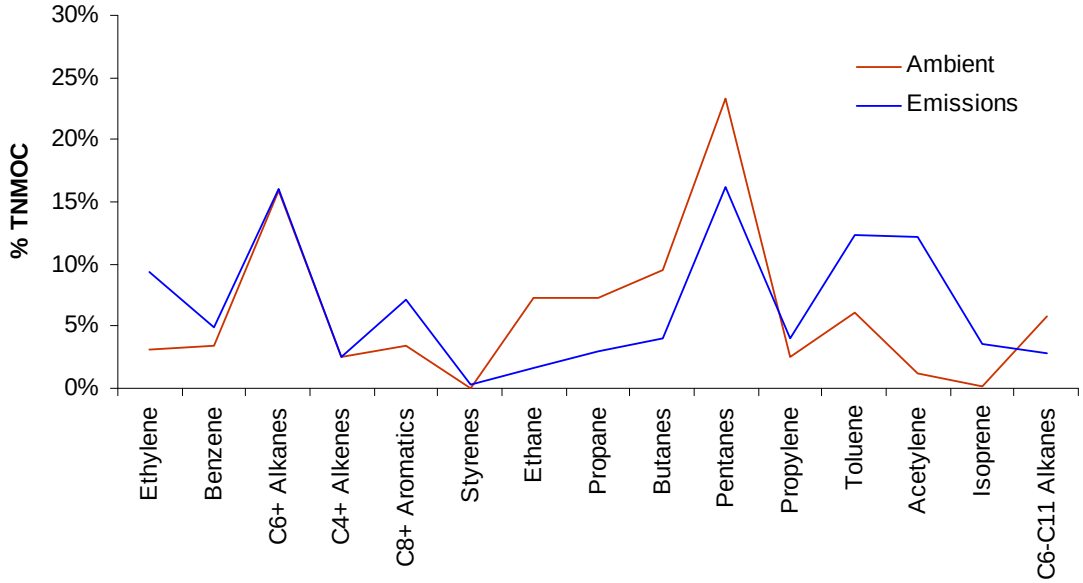

Figure E-6. Comparison of August 2005 ambient- and emissions-derived hydrocarbon compositions for the Chicago-Jardine site.

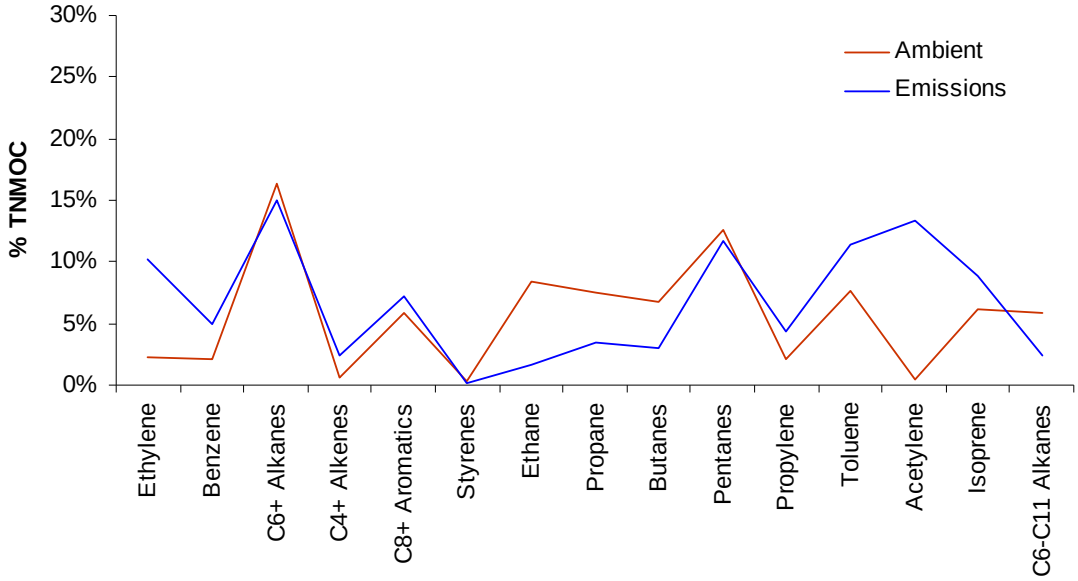

Figure E-7. Comparison of 2005 summer weekday ambient- and emissions-derived hydrocarbon compositions for the Chicago-Northbrook site.

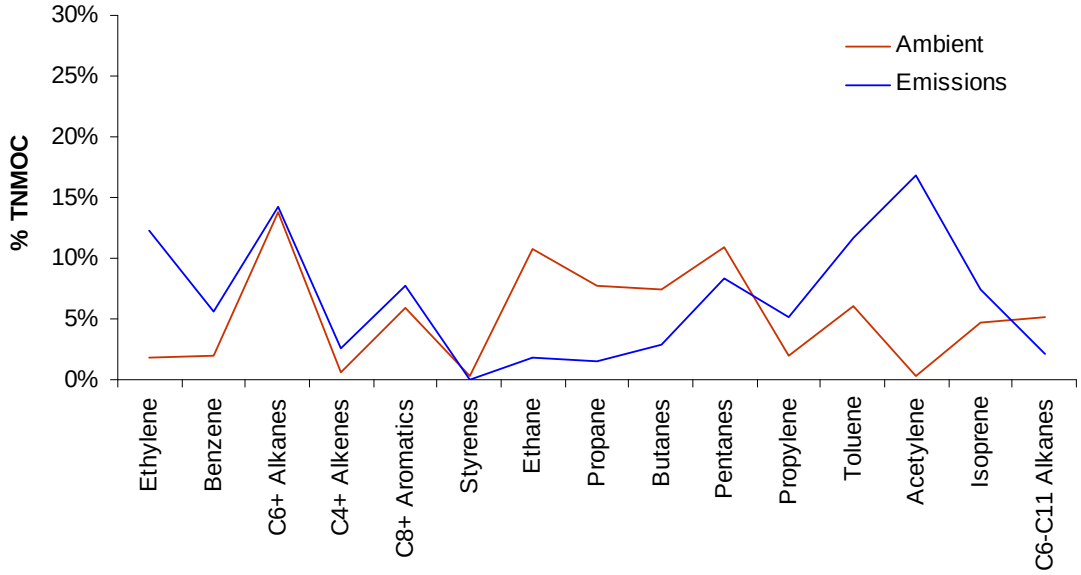

Figure E-8. Comparison of 2005 summer Saturday ambient- and emissions-derived hydrocarbon compositions for the Chicago-Northbrook site.

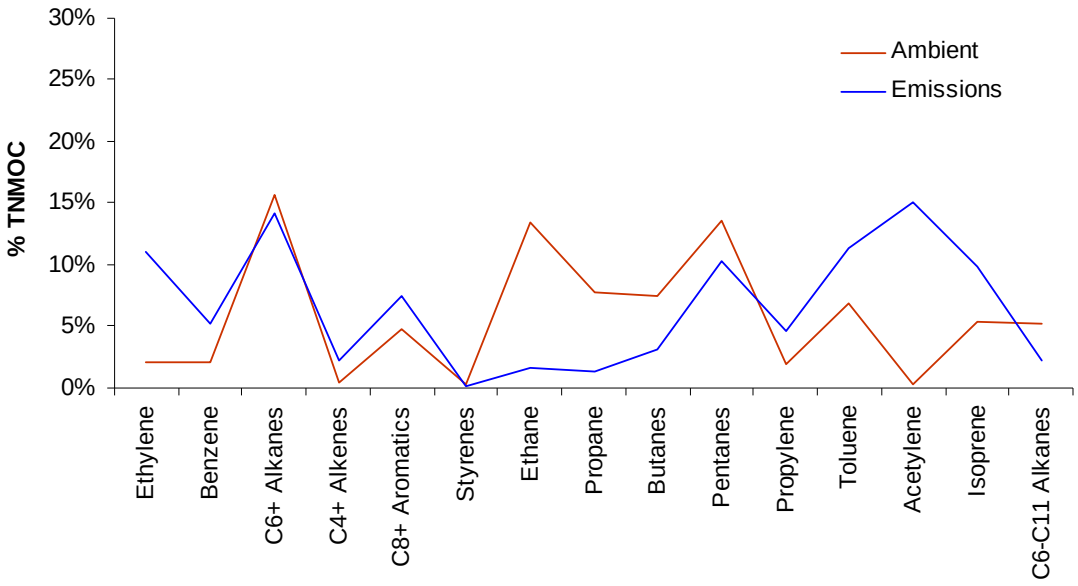

Figure E-9. Comparison of 2005 summer Sunday ambient- and emissions-derived hydrocarbon compositions for the Chicago-Northbrook site.

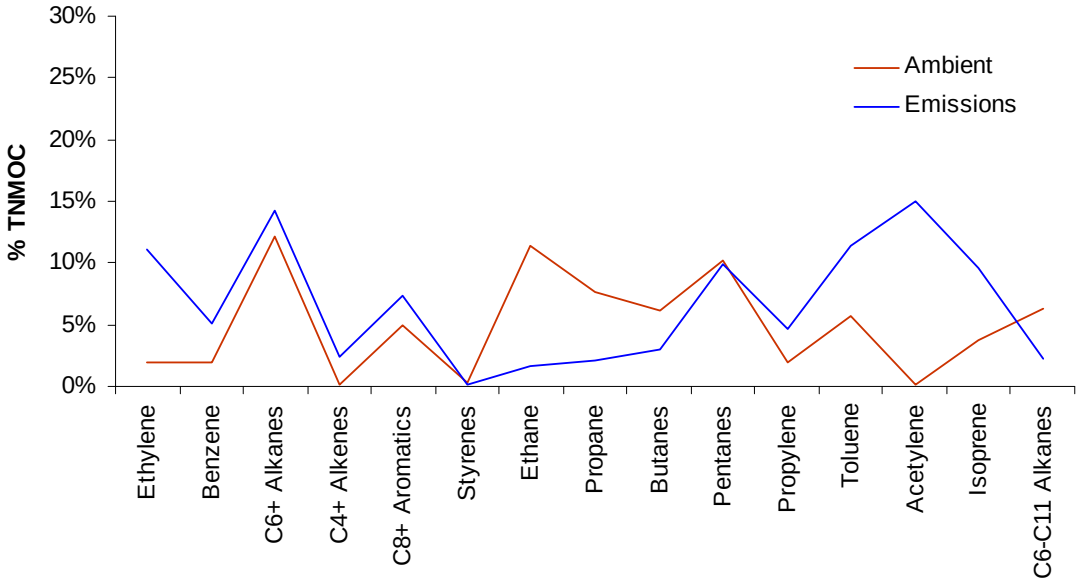

Figure E-10. Comparison of June 2005 ambient- and emissions-derived hydrocarbon compositions for the Chicago-Northbrook site.

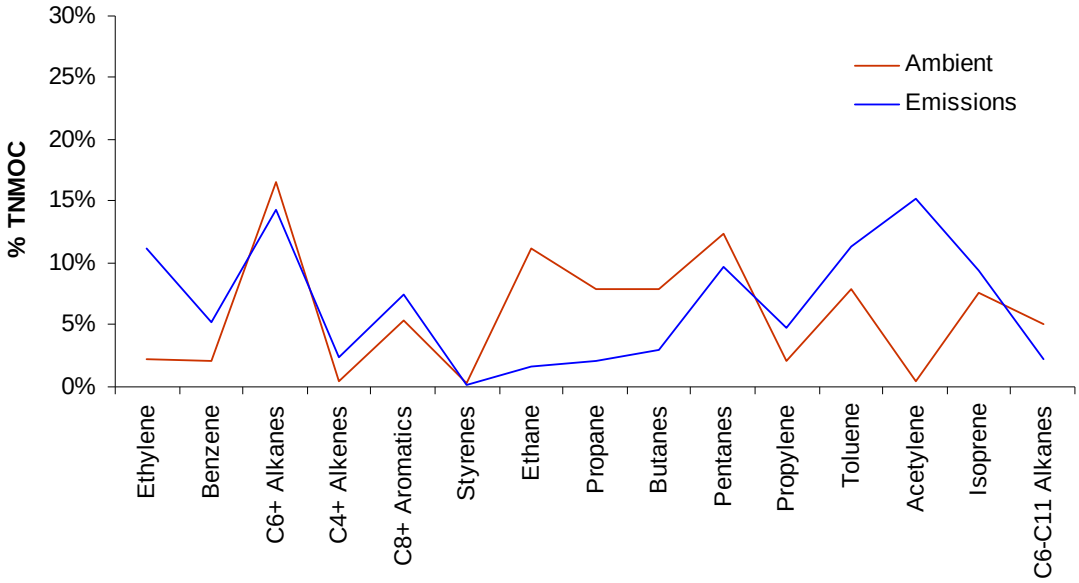

Figure E-11. Comparison of July 2005 ambient- and emissions-derived hydrocarbon compositions for the Chicago-Northbrook site.

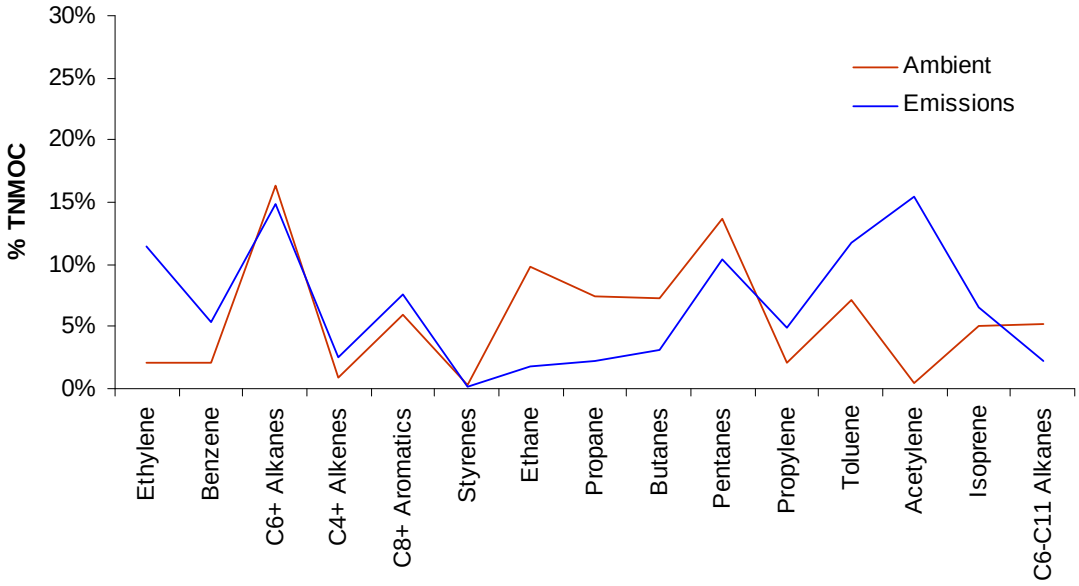

Figure E-12. Comparison of August 2005 ambient- and emissions-derived hydrocarbon compositions for the Chicago-Northbrook site.

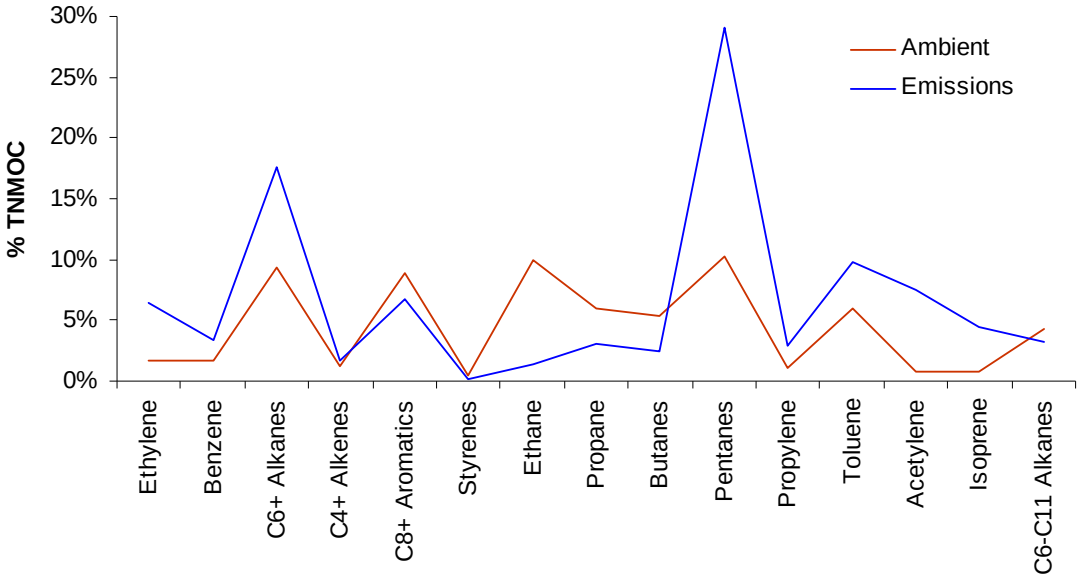

Figure E-13. Comparison of 2005 summer weekday ambient- and emissions-derived hydrocarbon compositions for the Detroit-East 7 Mile site.

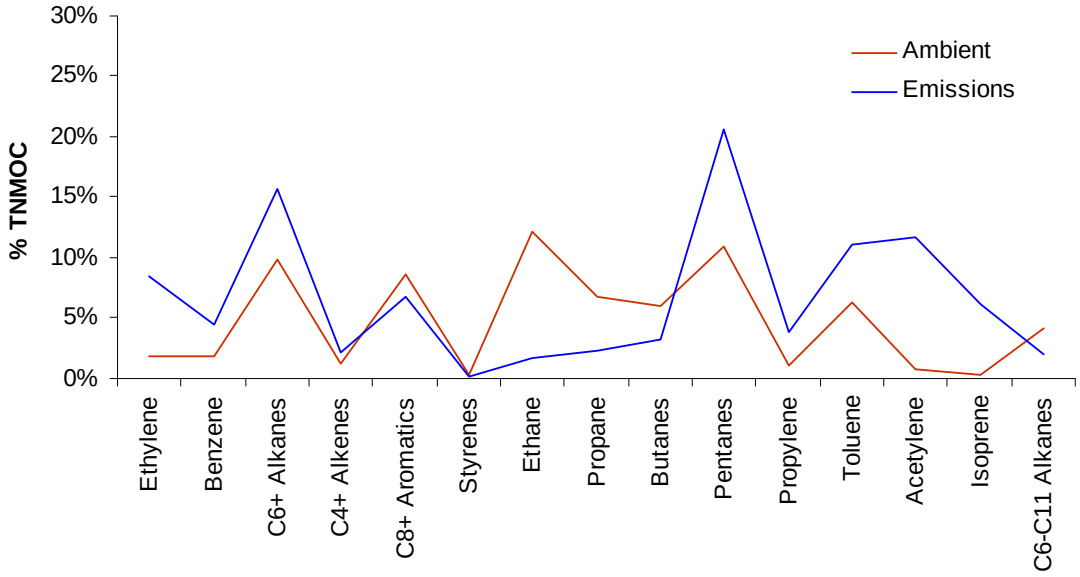

Figure E-14. Comparison of 2005 summer Saturday ambient- and emissions-derived hydrocarbon compositions for the Detroit-East 7 Mile site.

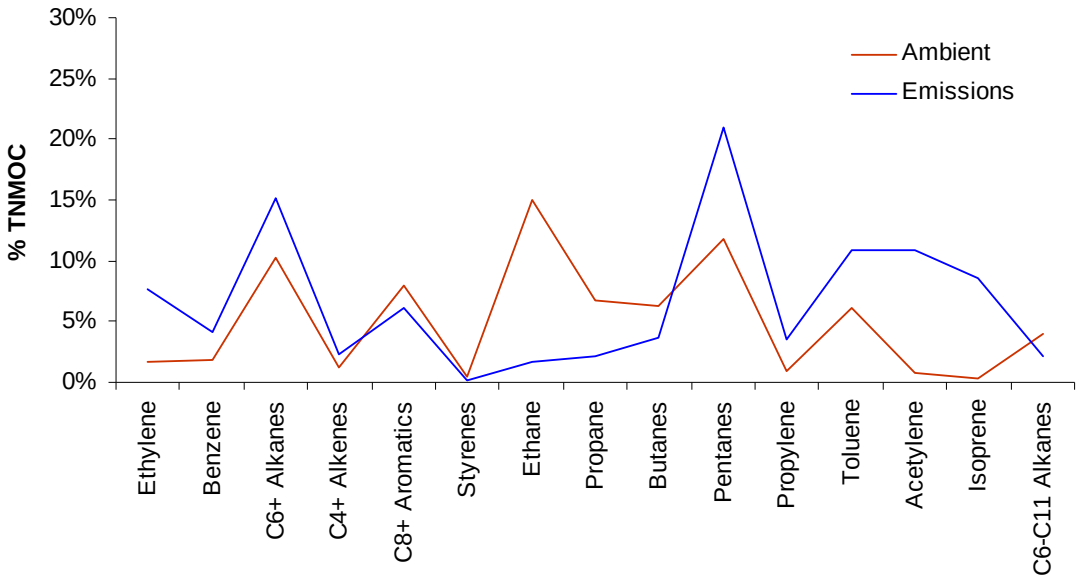

Figure E-15. Comparison of 2005 summer Sunday ambient- and emissions-derived hydrocarbon compositions for the Detroit-East 7 Mile site.

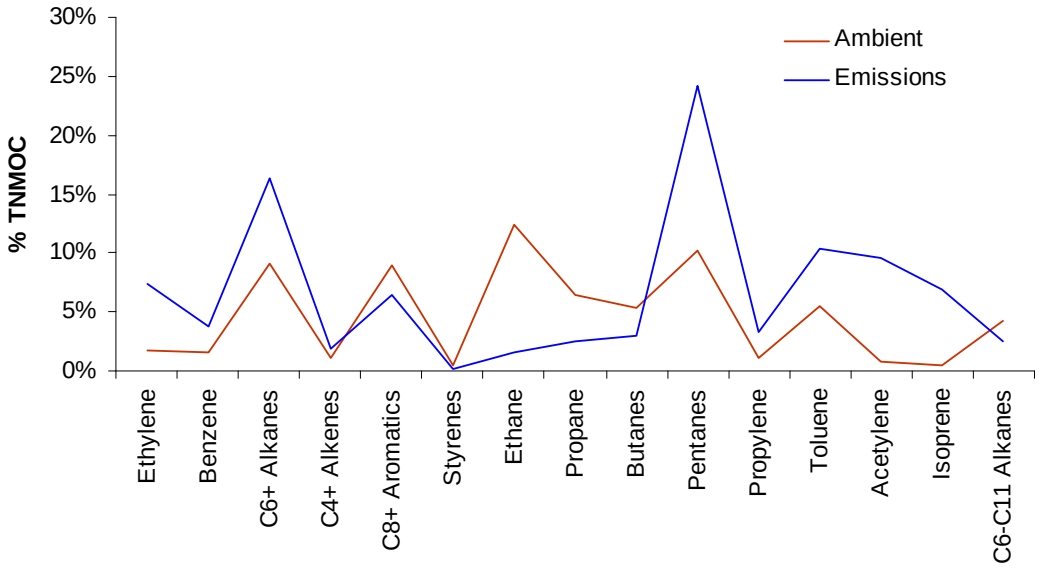

Figure E-16. Comparison of June 2005 ambient- and emissions-derived hydrocarbon compositions for the Detroit-East 7 Mile site.

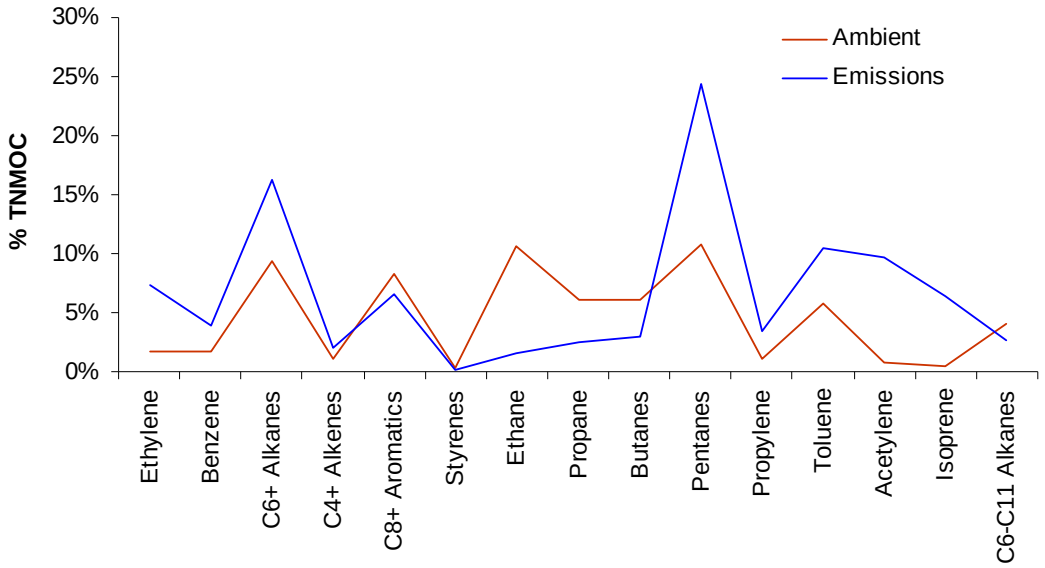

Figure E-17. Comparison of July 2005 ambient- and emissions-derived hydrocarbon compositions for the Detroit-East 7 Mile site.

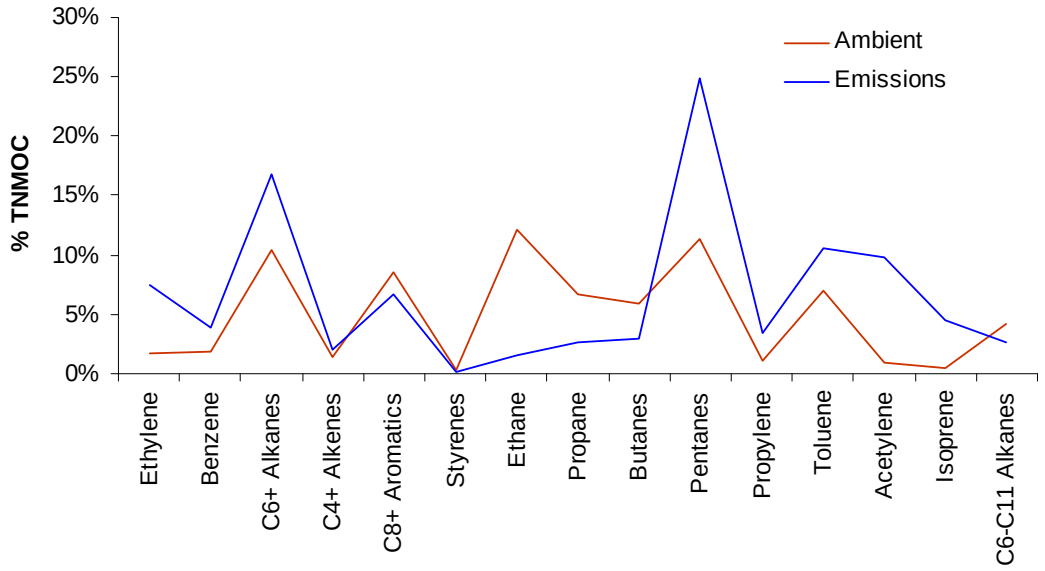

Figure E-18. Comparison of August 2005 ambient- and emissions-derived hydrocarbon compositions for the Detroit-East 7 Mile site.

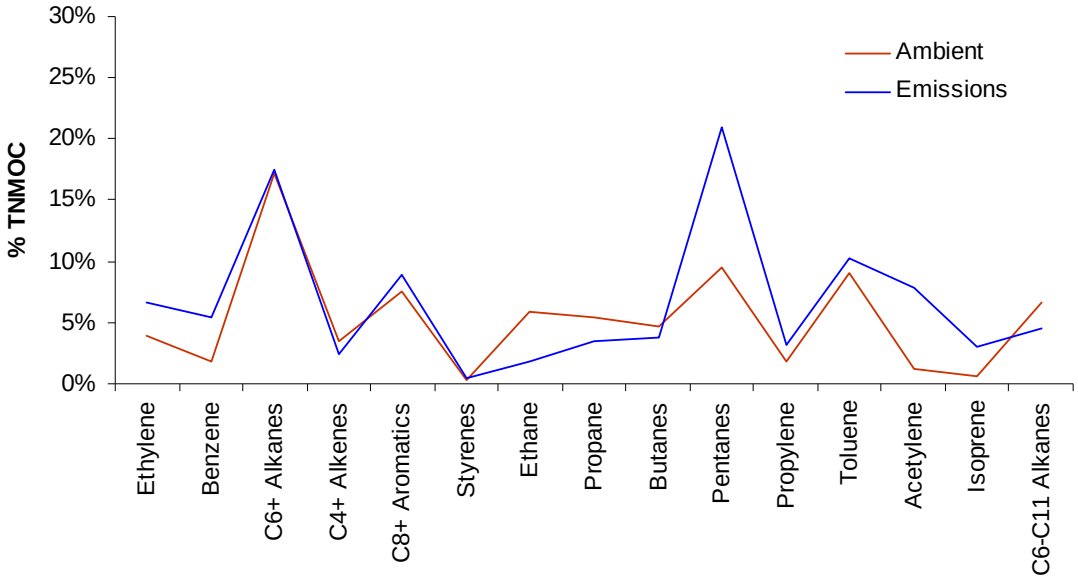

Figure E-19. Comparison of 2005 summer weekday ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

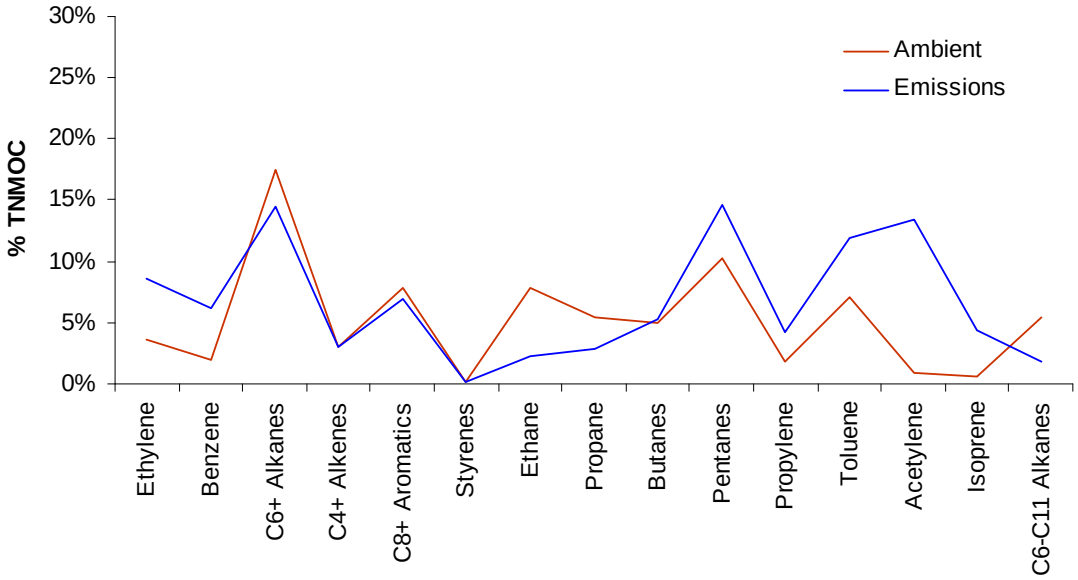

Figure E-20. Comparison of 2005 summer Saturday ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

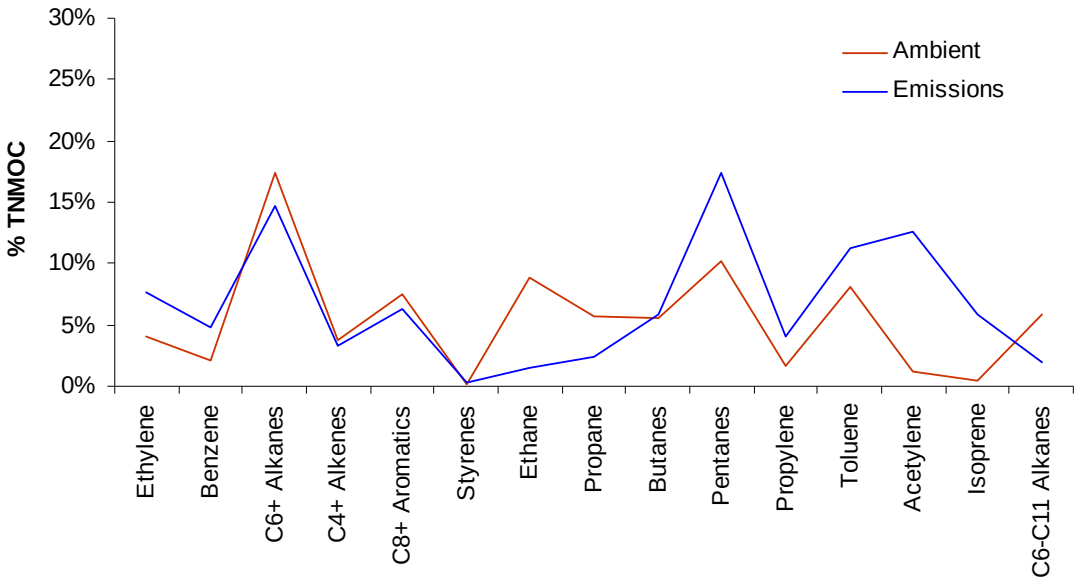

Figure E-21. Comparison of 2005 summer Sunday ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

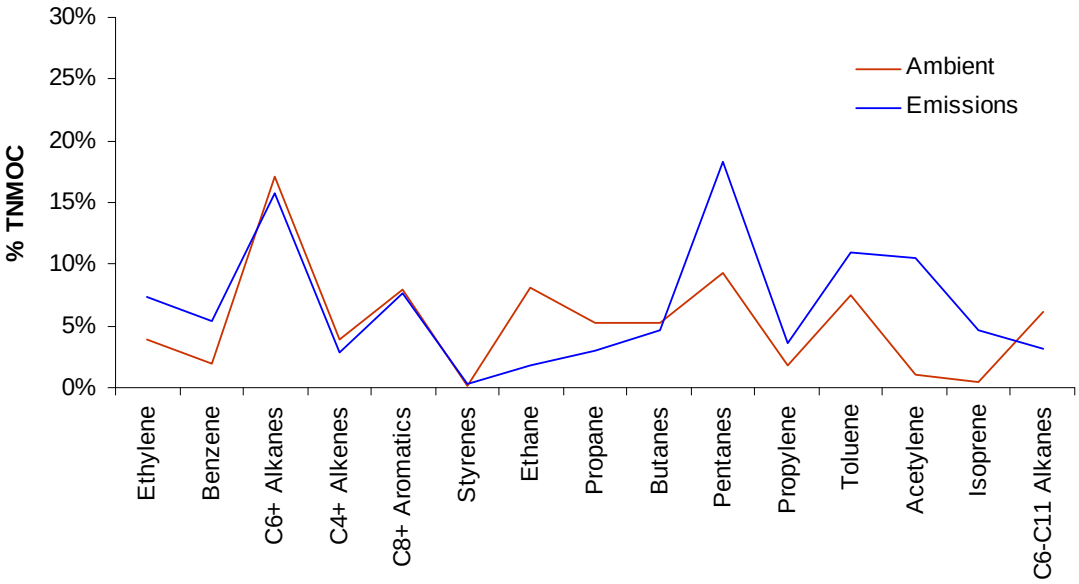

Figure E-22. Comparison of June 2005 ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

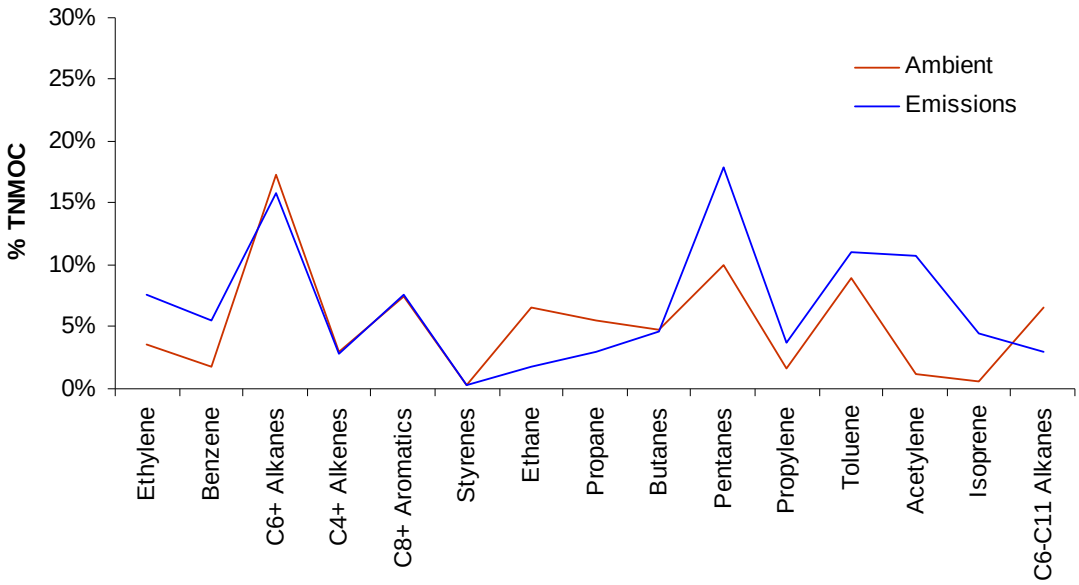

Figure E-23. Comparison of July 2005 ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

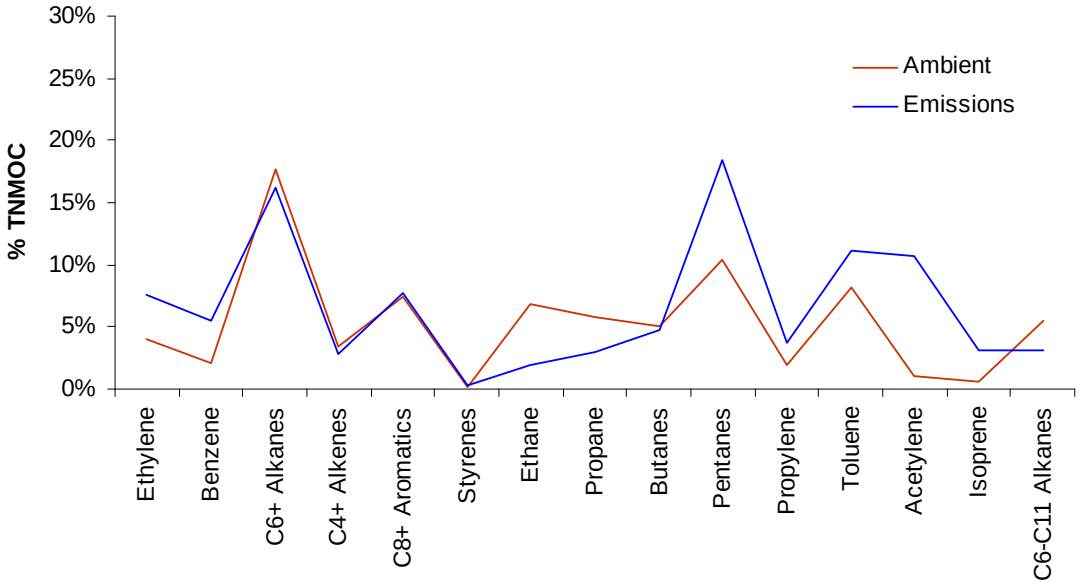

Figure E-24. Comparison of August 2005 ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

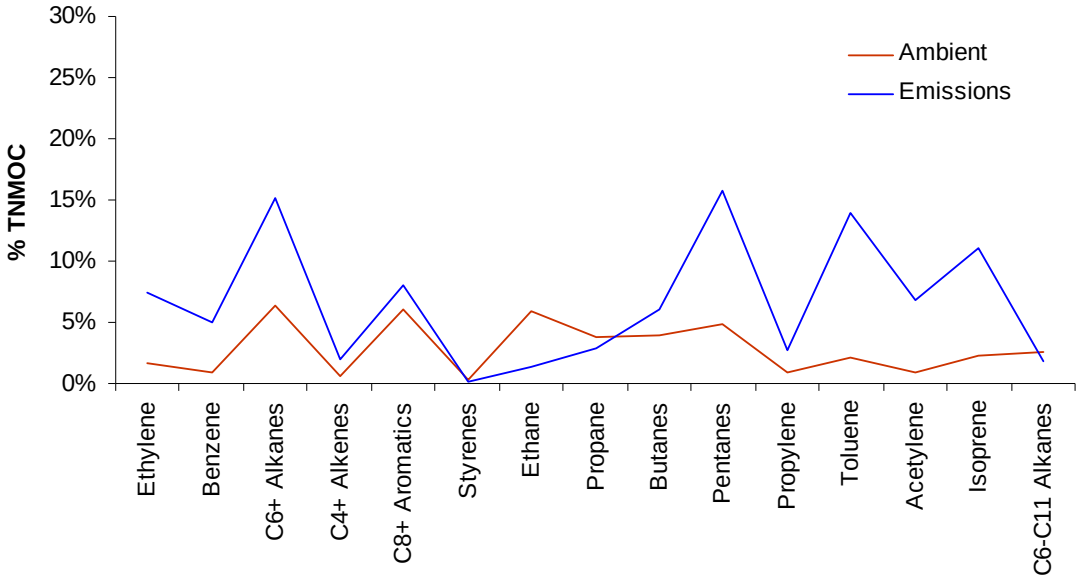

Figure E-25. Comparison of 2005 summer weekday ambient- and emissions-derived hydrocarbon compositions for the Gary site.

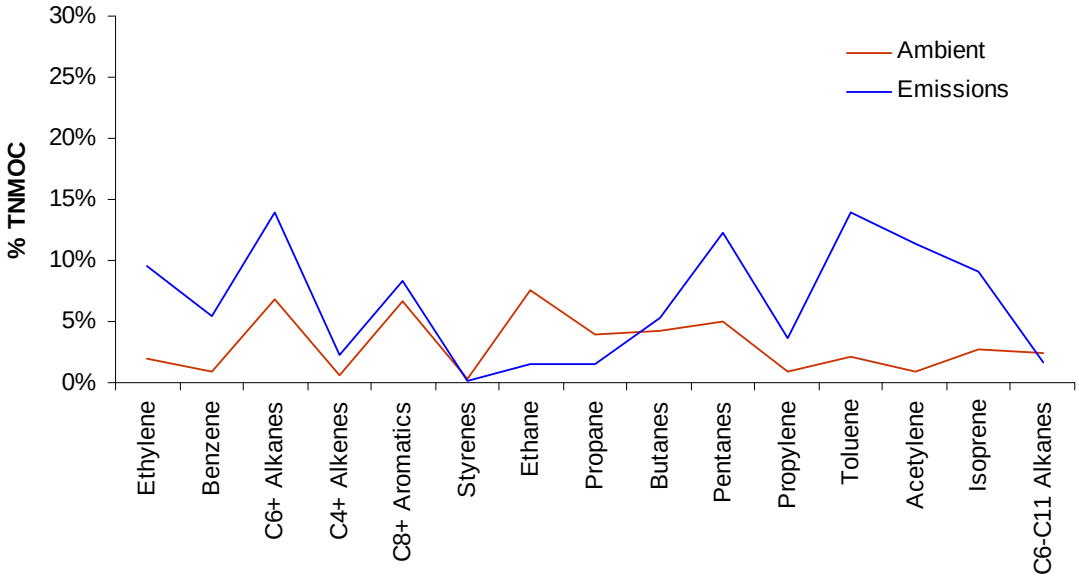

Figure E-26. Comparison of 2005 summer Saturday ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

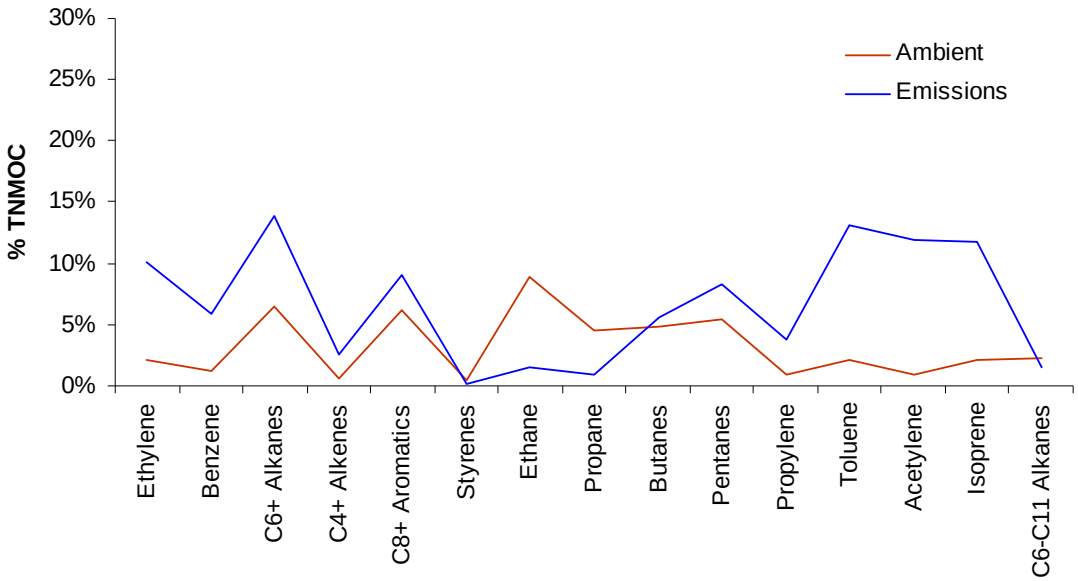

Figure E-27. Comparison of 2005 summer Sunday ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

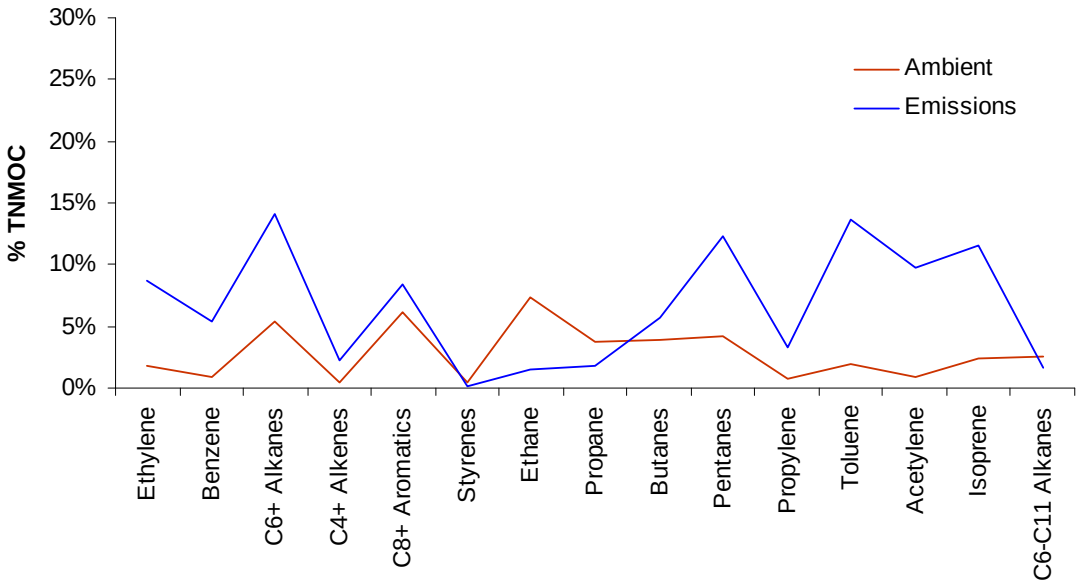

Figure E-28. Comparison of June 2005 ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

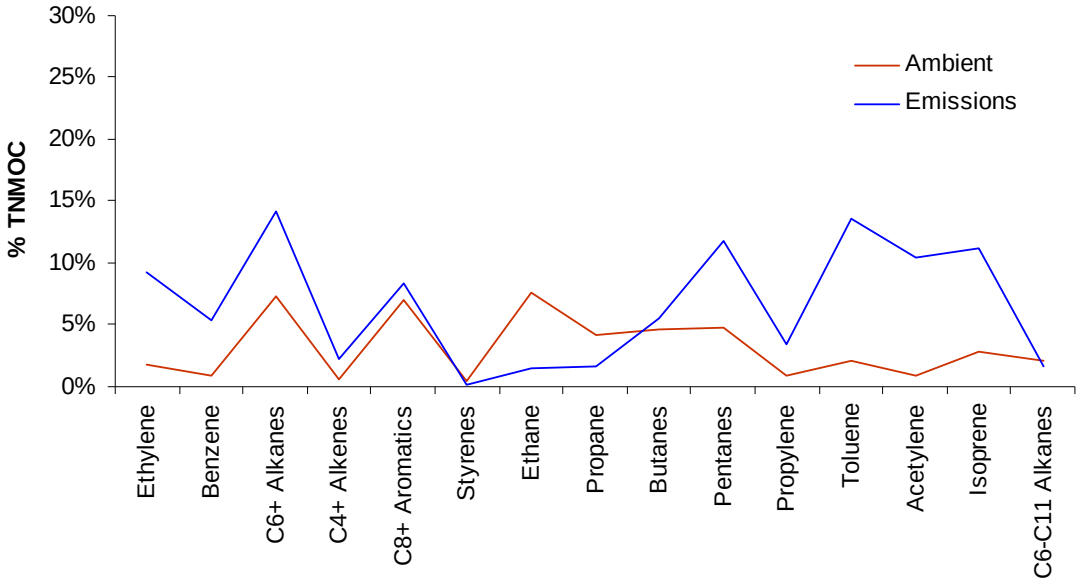

Figure E-29. Comparison of July 2005 ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.

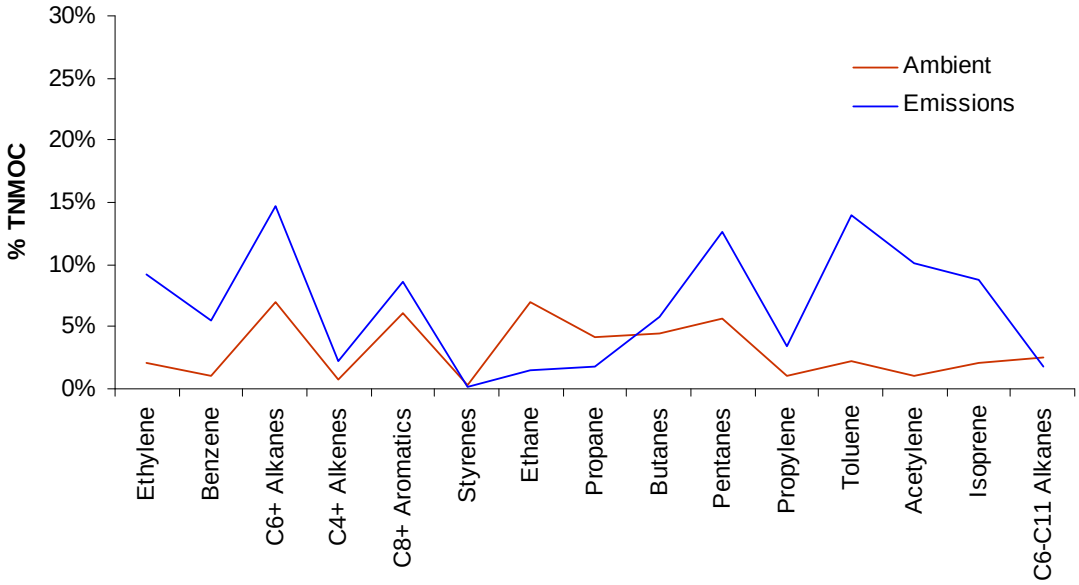

Figure E-30. Comparison of August 2005 ambient- and emissions-derived hydrocarbon compositions for the Milwaukee site.