

A Top-Down Emissions Inventory Evaluation for the Upper Midwest

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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. This study is an NREL-funded top-down evaluation of the 2005 emissions inventory that the Lake Michigan Air Directors Consortium (LADCO) is using to conduct regional air quality modeling in the upper Midwest. The on-road mobile source component of the inventories was a special focus of this study.

Several techniques can be used to evaluate the accuracy and representativeness of any emissions inventory 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, this work 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 (see **Figure 1**). The goals of the project were to (1) identify areas of agreement and differences between the ambient data and emissions inventories; (2) identify areas of the emissions inventories that may need improvement, and (3) 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, and in

Roberts et al. (2004) and Chinkin and Reid (2006). 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) 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.



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

2. METHODS

The technical approach for this top-down emissions inventory reconciliation was divided into three elements:

1. Data acquisition and processing;
2. Comparison of emissions inventory and ambient criteria pollutant ratios; and
3. Comparison of emissions inventory and ambient relative hydrocarbon compositions and reactivity.

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 because comparisons

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between emissions and ambient data can be confounded by transported pollution and chemical reactions occurring after pollutants are emitted. To minimize the influence of these effects, we used data from periods when emission rates were high and chemical reaction rates were low (e.g., early morning hours of 0600-0900).

In addition, it should be noted that, because of the inherent uncertainties associated with top-down evaluations, ambient- and emissions inventory-derived pollutant ratios within approximately 25-50% of each other are considered to be in good agreement (California Air Resources Board, 1997).

Additional details on our technical approach are provided in the following sections.

2.1 Data Acquisition and Processing

Available air quality and meteorological data was acquired from the U.S. Environmental Protection Agency's (EPA) Air Quality System (AQS) for eight monitoring sites (see Figure 1). Hourly data for the years 2004-2006 were acquired from AQS for summer (June-August) and winter (December-February) months, and data were validated following established protocols.

STI also acquired 2005 Base M emissions inventory data files and supporting files (e.g., speciation profile libraries) for area, point, nonroad 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.

To prepare the data for analysis, STI speciated (i.e., disaggregated into individual hydrocarbon species) the VOC emissions and matched the individual chemical species from the emissions data with 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. STI also converted the emissions data from mass to molar units prior to comparisons with ambient data.

To gain an understanding of the source mix around each monitoring site, we summarized the emissions data for each site's grid analysis zone. Emissions summaries by source sector for each monitoring site of interest show that on-road mobile source emissions account for 61% to 80% of the January CO emissions. For January and July, on-road mobile sources account for 57% to 73% of the NO_x emissions around each monitoring

site (see Figures 2 and 3 for example winter and summer plots). The exception to the domination of on-road mobile sources was the Gary site, where the point sources contributed the majority of CO and NO_x emissions, as shown in Figure 4. Unlike the other sites, which are in urban or suburban areas, the Gary site is in an industrial area, immediately south of a large steel plant.

For VOC, area sources account for 35% to 57% of the January and July emissions around each site, while on-road mobile sources account for only 15% to 39% of the January and July emissions around each site.

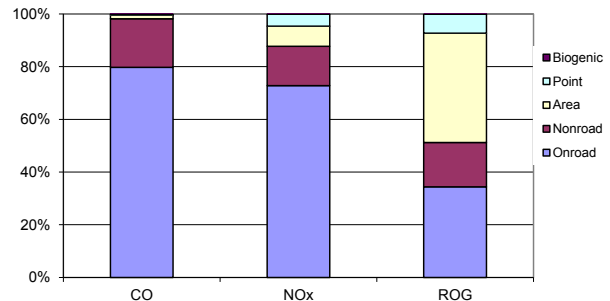


Fig. 2. January weekday emissions by source sector for the grid analysis zone around the Chicago-Mannheim site for hours 0600 to 0900.

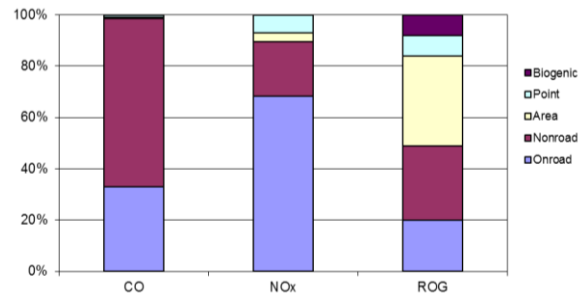


Fig. 3. July weekday emissions by source sector for the grid analysis zone around the Chicago-Mannheim site for hours 0600 to 0900.

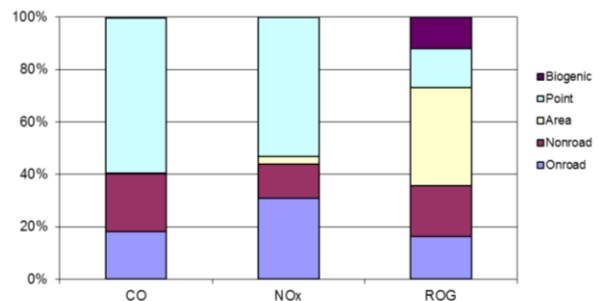


Fig. 4. July weekday emissions by source sector for the grid analysis zone around the Gary site for hours 0600 to 0900.

Once data processing was complete, we evaluated the relative ambient concentrations and emissions densities around each site. For the sites where TNMOC/NO_x ratios were evaluated, we found that VOC emissions were highest around the Chicago-Jardine site and lowest around the Gary and Milwaukee sites. Conversely, 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. These discrepancies suggest that VOC emissions are underestimated at the Gary and East 7 Mile sites in the 2005 inventories. In the case of the Gary site, this underestimate of VOC emissions is likely due to the presence of large industrial sources in the region around the site.

2.2 Comparison of Emissions Inventory and Ambient 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, 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). 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 5** illustrates an example of a full extent grid analysis zone centered on an ambient monitoring site and shows the wind quadrant definitions, whose extents vary according to the observed wind speeds at each site.

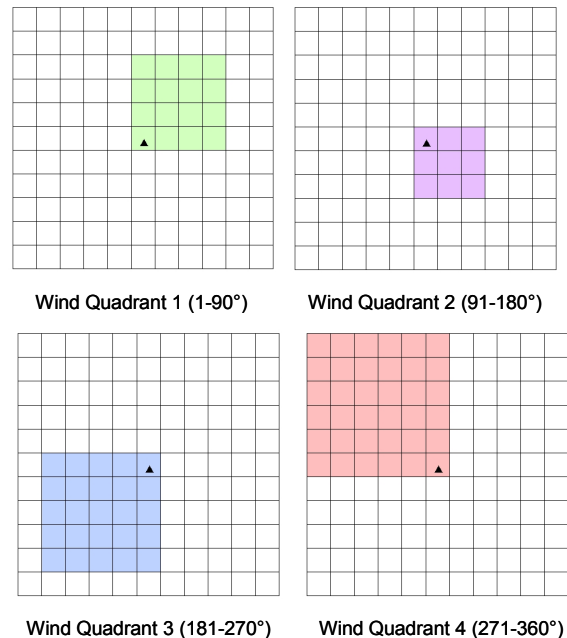


Fig. 5. Example of a full extent grid analysis zone, showing the spatial configuration of grid cells for which ambient- and emission inventory-derived ratio comparisons were calculated. The monitoring site is represented by a small triangle.

2.3 Comparison of Emissions Inventory and Ambient Relative Hydrocarbon Compositions and Reactivity

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, the relative reactivity of the organic species in the emissions inventory and ambient data were computed and compared. 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 is the weighted reactivity, $(MIR)_i$ is the maximum incremental reactivity for species i , and w_i is the 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.

3. RESULTS

To evaluate the relative amounts of TNMOC, 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.

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-August), and wind quadrant. 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.

Figure 6 shows calculated ratios for the full grid extent around each monitoring site for all summer days. These data show good agreement ($\pm 20\%$) 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.

In addition, more detailed analyses of TNMOC/ NO_x ratios at the Chicago sites indicate that the agreement between ambient- and emissions inventory-derived ratios is poorer on weekend days than on weekdays, as shown in **Figures 7 and 8**. This is particularly true for Sundays at the Northbrook site, where the ambient-derived TNMOC/ NO_x ratio is a factor of 2 higher than the emissions inventory-derived ratio,

whereas these ratios agree to within 30% on weekdays.

This increased discrepancy between ambient- and emissions inventory-derived ratios largely occurs because significant decreases in ambient NO_x concentrations from weekdays to weekend days are not reflected in the emissions inventory, where NO_x decreases from weekdays to weekend days are modest. As a result, ambient-derived TNMOC/ NO_x ratios increase sharply from weekdays to weekend days, while emissions inventory-derived TNMOC/ NO_x ratios increase only slightly. For sites dominated by on-road mobile source emissions, such as the Chicago sites, this finding indicates that heavy-duty truck traffic may be lower on weekends than the emissions inventory suggests.

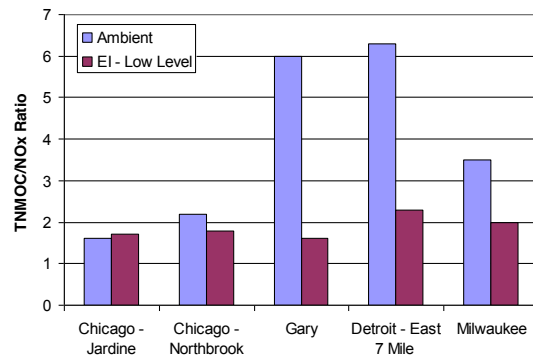


Fig. 6. TNMOC/ NO_x ratios by site for the hours 0600 to 0900 (emission ratios for full grid extent around each site; ambient ratios for 2005 based on 2004-2006 data)

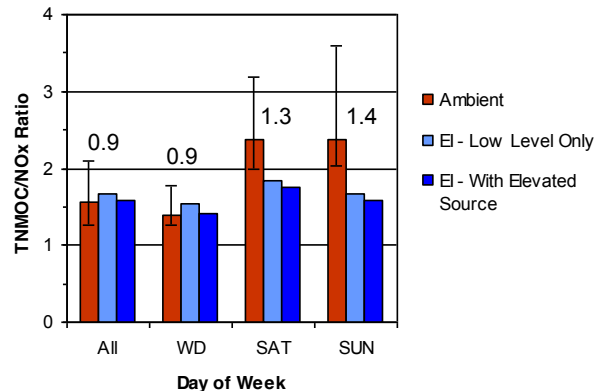


Fig. 7. Summer TNMOC/ NO_x ratios by day of week for the Chicago-Jardine site.

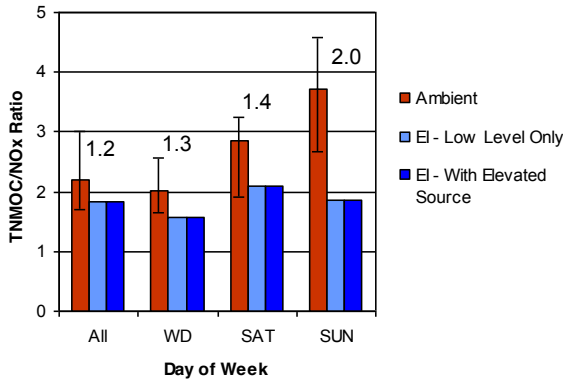


Fig. 8. Summer TNMOC/NO_x ratios for by day of week for the Chicago-Northbrook site.

3.2 CO/NO_x Ratio Comparisons

CO/NO_x ratios were calculated by day of week, month, and season. 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.

Figure 9 shows calculated ratios for the full grid extent around each monitoring site for all winter days. This figure shows that ambient- and emissions inventory-derived ratios have close agreement (within ±20%) at all sites.

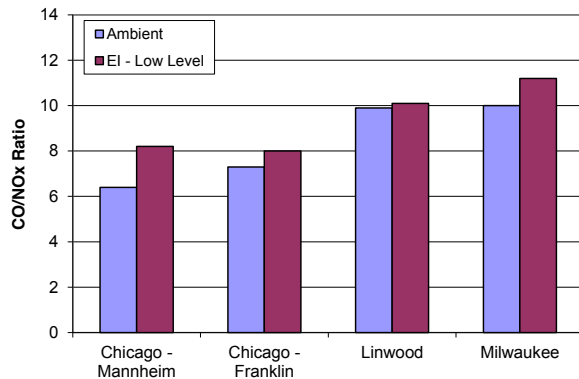


Fig. 9. Winter CO/NO_x ratios by site for the hours 0600 to 0900 (emission ratios for full grid extent around each site; ambient ratios for 2005 based on 2004-2006 data)

However, at the Chicago sites, the agreement between ambient- and emissions inventory-derived CO/NO_x ratios is poorer on Sundays than on Saturdays and weekend days, as shown in **Figures 10** and **11**. This increased discrepancy between ambient- and emissions inventory-derived ratios on Sundays largely occurs

because ambient NO_x concentrations decrease significantly from weekdays to Saturdays, then decrease sharply again from Saturdays to Sundays. However, in the emissions inventory, NO_x emissions show only a modest decrease from Saturdays to Sundays. This finding again points to potential issues with the characterization of heavy-duty truck travel on weekends in the Chicago area.

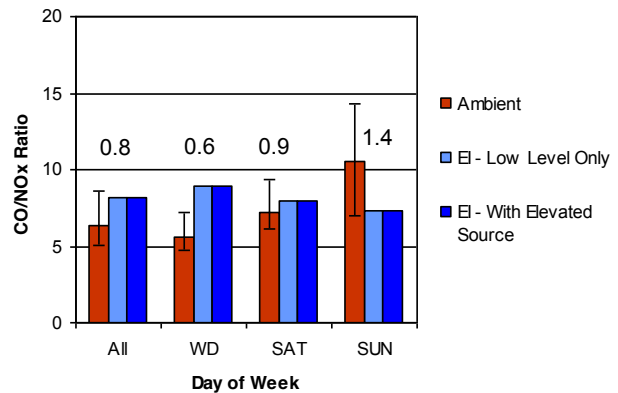


Fig. 10. Winter CO/NO_x ratios by day of week for the Chicago-Mannheim site.

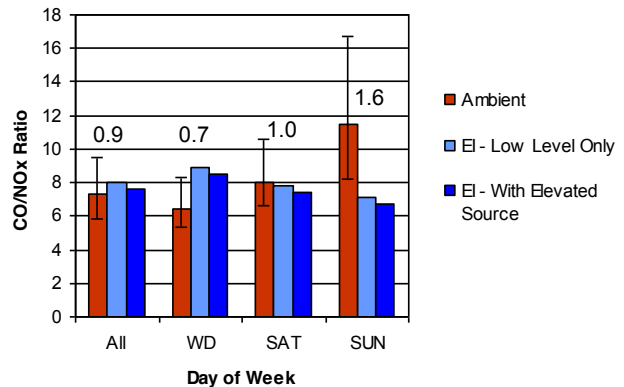


Fig. 11. Winter CO/NO_x ratios by day of week for the Chicago-Franklin site.

3.3 Relative Hydrocarbon Composition Comparisons

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. Relative hydrocarbon composition comparisons were performed by day of week, season, and wind quadrant. Hydrocarbon composition comparisons were performed for five sites: Chicago-Jardine,

Chicago-Northbrook, Gary, Detroit-East 7 Mile, and Milwaukee.

In general, our comparisons of the ambient- and emissions inventory-derived relative hydrocarbon compositions showed that

- There was good agreement for some species (e.g., C4+ alkanes, C8+ aromatics, styrenes, and propylene)
- The contribution of some species is overestimated in the inventory (e.g., acetylene, ethylene, toluene, and isoprene)
- The contribution of some species is underestimated in the inventory (e.g., ethane, propane, and C6-C11 alkanes)

Figure 12 shows an example comparison of ambient- and emissions inventory-derived TNMOC compositions for 15 of the most abundant species in the ambient data.

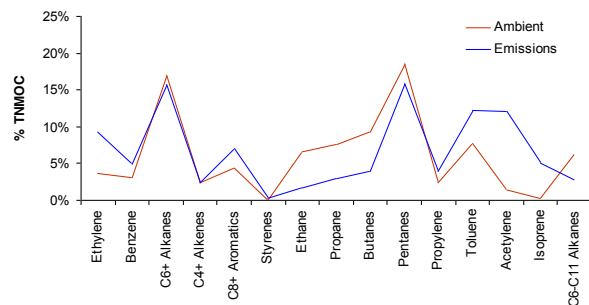


Fig. 12. Comparison of 0600-0900 ambient- and emissions inventory-derived TNMOC compositions for the Chicago-Jardine site.

To investigate the potential impact of these speciation issues on ozone formation in the upper Midwest, the weighted reactivity of the mix of hydrocarbon species in the ambient and emissions inventory data were calculated and compared. Across all sites, the overall weighted reactivity values for the summer season emissions inventory were 16% to 80% higher than the weighted reactivity values for the ambient data. The reactivity values agreed most closely at the Milwaukee site and had the greatest disparity at the Northbrook site in Chicago.

4. CONCLUSIONS

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 ($\pm 20\%$) for wintertime

CO/NO_x ratios (see Figure 9), 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, perhaps due to decreases in on-road mobile source emissions from Saturdays to Sundays, as well as inaccurate temporal characterizations of other source categories.

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.

5. REFERENCES

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