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Receptor Model Evaluation for Lake Michigan Ozone Study
Measurements for VOC

by

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INTRODUCTION

The questions surrounding emission inventories are becoming increasingly important as regulatory pressures mount to resolve ozone nonattainment. Large-scale studies like the Lake Michigan Ozone Study have focused more attention on quantifying and speciating inventories for volatile organic compounds (VOCs) because of their need for accurate input to photochemical models like the Urban Airshed Model (UAM). One tool available to assist researchers in their efforts to relate ambient measurements with emission inventories is chemical mass balance (CMB) receptor modeling. This technique uses the pattern of speciated emissions from major sources to determine the contribution of those sources to a given sample of ambient air. Because the method uses data from ambient measurements, it offers an independent check on emission inventories developed by more traditional permit, survey, emission factor, and source-test techniques.

This study reports preliminary results of an application of the CMB model to a subset of the VOC data from the Lake Michigan Ozone Study. Contributions of vehicles and gasoline vapor (sources of gasoline vapor include service stations and bulk storage terminals) to ambient NMOC are estimated at 8 sites in the Lake Michigan region. Other sources included in the CMB model are oil refineries, architectural coating, graphic arts processes, and wastewater treatment. The CMB model is applied to each individual sample. The resulting estimates of source contributions are for sources upwind of the receptor, since those are the sources that lie in the wind's path before it reaches the receptor. As wind direction changes, source contributions will change to reflect this source-receptor geometry. Changes in vehicle coefficients are examined in light of these changes in wind direction.

DATA SUMMARY

The purpose of the Lake Michigan Ozone Study was to collect sufficient air quality and meteorological data to accurately characterize the periods of elevated ozone concentrations experienced every summer in the Lake Michigan area. Intensive monitoring was performed on 7 days in June and July of 1991. Data analyzed in this study are a subset of the LMOS data, consisting of NMOC samples collected at 5 Illinois sites and 3 boats on Lake Michigan. The Chicago site was in a typical city canyon, Kankakee is at the southern boundary of the study area, Rockford is at the western boundary of the study area, Aurora is a far western suburb of Chicago, and Zion is a far northern suburb of Chicago. The south lake boat was stationed just offshore at the Illinois/Wisconsin state line, the midlake boat was about 30 km east of it, and a transect boat traveled just offshore between downtown and the south side of Chicago. At each site, a canister of air was collected from 7 to 9 am and again from 10 am to noon. A total of 60 compounds were targeted for identification. The collection and analysis of these data have been documented in a number of Lake Michigan Ozone Study reports.

METHODOLOGY

The CMB model extends the concept of the chemical tracer. Instead of using a single chemical to quantify emissions from a particular source category, the CMB model uses the unique chemical pattern of emissions for each source type as a tracer to quantify the contribution of each to ambient NMOC.

The CMB general equation is

$$Y = BZ + E$$

where:

- Y** = vector of *i* molecular concentrations in the ambient air (i.e., the speciated ambient concentrations of VOCs)
- Z** = composition matrix (*i* x *j*) of molecular compounds for each of the *j* sources modeled (the fingerprints),
- B** = vector of VOC concentrations from the modeled sources that are predicted at the receptor, and
- E** = vector of *i* errors (measured concentration minus predicted concentration).

Because the gas chromatograph data (ambient concentration measurements) errors vary inversely with concentration, each observation is weighted by its measurement error in order for observations with greater error to have less influence on the solution. In this application the weighting factor was 10% of the ambient concentration. Weighted least squares regression was performed to solve equation 1 for each sample using SAS, a commercial statistical analysis package. Each of the values of **B** represents the contribution of hydrocarbon, in ug/m³, from a given source.

Several model assumptions are important to note. Because the model is a mass balance, we assume that the species being modeled do not react or selectively deposit between the sources and the receptor--i.e., mass is conserved. Species used as fitting compounds are chosen to have similar low reactivities. When travel times between the sources and receptor are on the order of a few hours, previous studies have shown that reactivity does not significantly alter the source fingerprint (Wadden et al., 1986).

Other requirements are that the compositions of source emissions are relatively constant, that all major sources are included in the model, and that source compositions

are linearly independent. Experience with receptor models has shown that applications to NMOC are robust; deviations in these requirements are well tolerated (Kenski et al., 1993, Scheff and Wadden 1993).

FINGERPRINTS

Fingerprints are the pattern of species emitted from a source category, expressed as percent of total NMOC. They constitute the independent variables in the model. Consequently, accurately speciated fingerprints that reliably reflect source emissions are crucial to the success of the CMB model. Table 1 gives the source fingerprints used in this model. Highly reactive organics (e.g., acetylene, propylene) are not used as fitting compounds, but emissions of these compounds can be estimated once the model is fit with more stable compounds. The following sections summarize the formation of the fingerprints used in this study.

Vehicles. The vehicle fingerprint is a composite of data from several sources. Roadway measurements were collected in Atlanta in 1990 as part of 1990 Atlanta Precursor Study (Lonneman, et al. 1991). A total of 9 canister samples were collected in morning rush-hour traffic in a 'minitunnel' formed by the intersection of Interstates 20, 75, and 85. Chicago area data were from three sites: 4 samples from Lower Wacker Dr. were collected during rush hour traffic (Doskey et al., 1992); 5 samples were collected in the Hubbard cave, a section of the I-94 expressway near downtown Chicago that is covered by a number of bridges and thus resembles a tunnel; and 3 samples were collected in the Grant Park underground parking garage. The Chicago sampling was part of an air toxics study. Finally, the fingerprint also includes the tailpipe measurements documented in Sigsby's 1987 study of 46 in-use cars (Sigsby et al., 1987).

The final vehicle fingerprint was formed by first combining the Chicago data in a weighted average, where weight equaled the number of samples, then averaging the Atlanta data, the Chicago data, and the Sigsby data (Lin 1993).

Gasoline Vapor. The gasoline vapor fingerprint is a composite of data from two sources, Lonneman's 24°C headspace (Lonneman 1991) and regular, plus, and super headspace measurements in Chicago (Doskey 1992). All were summer-blend gasolines. The Chicago data were combined in a weighted average by sales (6:1:3), then averaged with Lonneman's data for the final fingerprint (Lin 1993).

Refinery. The refinery source fingerprint is a composite of three studies: a refinery plume study by Sexton and Westberg (1983) that included 6 ground-level samples and 2 samples aloft; a personal sampling study of refinery operators (Rappaport, 1987), and another plume study (Doskey et al., 1992) that consisted of 6 ground-level

samples. Data from the three studies were averaged together for a final fingerprint (Lin 1993).

Sewage Treatment. An average of 23 fenceline and on-site samples collected at a Chicago sewage treatment facility (Scheff 1992).

Coke Ovens. An average of 8 fenceline samples were collected downwind of a Chicago area coke oven (Scheff 1992).

Graphic Arts. A lithography fingerprint was derived from samples collected by UIC at three printing plants (Wadden et al. 1993). A total of 68 hourly air samples were collected at a print shop with both sheet- and web-fed, nonheatset presses. Twenty-four hourly samples were collected at a shop with heatset, webfed presses. Twelve hourly samples were collected at a sheetfed, nonheatset pressroom. The fingerprint from each location was averaged together to form the lithography fingerprint. Fingerprints for rotogravure, letterpress, and flexography processes were used as published in Scheff, et al. (1989). The four process fingerprints were combined in a weighted average according to estimates made for ink useage in Ramus (1992). We assume that solvent use is the primary VOC source in all printing operations. Estimates of solvent use by the different industry sectors were not available, but estimates of ink use are published, and solvent use is proportional to ink use. Ink use estimates were 1019×10^6 lbs for lithography, 519×10^6 lbs for rotogravure, 385×10^6 lbs for flexography, 145×10^6 lbs for letterpress, and 95×10^6 lbs for other processes.

RESULTS

Table 2 gives the average CMB allocation of ambient NMOC to vehicle and gasoline vapor sources for the 7-9 am samples in $\mu\text{g}/\text{m}^3$. Of the land sites, downtown Chicago averaged $124 \mu\text{g}/\text{m}^3$ of NMOC from vehicles (33% of the total). The other sites averaged 15-25 $\mu\text{g}/\text{m}^3$ from vehicles (23-35%). Gasoline vapor contributions were small- -26 $\mu\text{g}/\text{m}^3$ in Chicago (8%) and 1-3 $\mu\text{g}/\text{m}^3$ (2-3%) at the suburban and boundary sites. On the boats, vehicle and gasoline vapor contributions fell between those at boundary sites and downtown, and were highest on the transect boat that traveled up and down the lake between downtown and the south side of Chicago.

Table 3 gives the average CMB allocations for the 10-12 am samples. They are generally distributed similarly to the 7-9 am samples, but with smaller contributions from vehicles (5-15 $\mu\text{g}/\text{m}^3$ at the boundary sites, 100 $\mu\text{g}/\text{m}^3$ downtown) and lower total NMOC. Gasoline vapor contributions are slightly larger than the earlier samples. A similar pattern of diurnal variations has been noted in other studies--vehicle contributions falling during the midday and gasoline vapor contributions rising (Kenski et al. 1993).

In addition to looking at average contributions, it is sometimes useful to examine the variation in coefficients at a given site as wind direction changes. Figure 1 shows the vehicle coefficients and total NMOC for each site modeled on two days, July 17 and 18, when the wind speed and direction were very similar. Vehicle contributions at each site are similar on both days. In contrast, Figure 2 shows vehicle coefficients and total NMOC for June 26 and 27, when the wind direction changed sharply from one day to the next. Vehicle coefficients exhibit a similar sharp change--for example, from 148 $\mu\text{g}/\text{m}^3$ at the downtown site on June 26 to 60 $\mu\text{g}/\text{m}^3$ on June 27.

CONCLUSIONS

CMB evaluations of ambient hydrocarbon data provide a sample-specific allocation of emissions to particular source categories. This preliminary CMB evaluation showed that vehicles contributed 100-150 $\mu\text{g}/\text{m}^3$ of total NMOC (30-40%) downtown Chicago over these seven days of study. On the boundary of the study area, vehicle contributions are typically 10-20 $\mu\text{g}/\text{m}^3$. These estimates incorporate both exhaust and running losses. These values are higher for early morning samples, perhaps because of rush-hour traffic. The CMB evaluation is consistent for samples when the wind is from the same direction; allocations differ when the wind direction changes, as expected because of the changing source-receptor geometry.

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TABLE 1 Source Fingerprints (Weight Percent of Total NMOC)

SPECIES	VEHICLES	GAS VAPOR	REFINERY	WASTE WATER	GRAPHIC ARTS	COKE OVENS	ARCH. COAT.
ethylene	6.173	0	1.453	0	0	0	0
ethane	1.49	0	4.946	0	0	0	0
propane	1.035	0.96	11.126	0	0	0	0
cis-2-butene	0.524	1.3	0.618	0	0	0	0
isobutene	0	0	0	0	0	0	0
n-butane	5.4	23.69	13.204	0.74	0	2.03	0
isobutane	1.108	5.43	4.238	0.52	0	0.27	0
trans-2-butene	0.425	1.74	1.746	0	0	0	0
1-pentene	0.701	2.13	0.23	0.11	0	0.01	0
2-methyl-2-butene	1.039	2.99	2.104	0	0	0	0
3-methyl-1-butene	0	0.53	0.028	0	0	0	0
cyclopentane	0.552	0.79	0.161	0	0	0	0
cyclopentene	0.177	0.37	0	0	0	0	0
cis-2-pentene	0.44	1.33	0	0	0	0	0
isoprene	0	0	0	0	0	0	0
n-pentane	2.88	9.2	4.519	1.32	0	0.47	0
isopentane	7	26.82	12.983	3.14	0	0.69	0
trans-2-pentene	0.8	2.43	0	0	0	0	0
2-Methpentane	2.512	3.16	3.081	1.27	0	0.39	0
2,2-DMbutane	0.744	0.72	0	0.8	0	0.18	0
2,3-DMbutane	0.979	1.22	1.095	0.7	0	0	0
2-Me-1-penten	0.174	0.29	0	0	0	0	0
3-methylpentane	1.51	1.81	1.965	0.98	0	0.42	0
4-methyl-1-penten	0	0	0	0	0	0	0
benzene	3.378	0.78	1.076	1.4	2.35	10.5	0.09
cyclohexane	0.938	0.13	0.538	0.27	0	0.02	0
cis-2-hexene	0.132	0.17	0	0	0	0	0
methylcyclopentan	1.345	0.82	1.505	0	0	0	0
n-hexane	1.239	1.76	2.209	1.78	0.73	0.47	0
trans-2-hexene	0.263	0.31	0	0	0	0	0
2,3-DMpentane	1.37	0.53	1.26	0.59	0	3.51	0
2,4-DMpentane	0.895	0.51	0.924	0.97	0	0.19	1.09
3-methylhexane	1.113	0.5	1.309	0.58	0	0.93	0
methylcyclohexane	0.647	0.14	0.984	0	0	0.65	0
n-heptane	0.704	0.22	1.201	0	0	0.96	2.22
toluene	7.915	1.32	2.943	10.19	13.66	2.03	25.9
2,2,4-TMpentane	2.547	0.54	2.721	0	0	1.27	0
2,3,4-TMpentane	0.713	0.15	0.395	0.3	0	0.1	0
2-methylheptane	0.41	0.07	0.717	0	0	0	0
3-methylheptane	0.408	0	0.401	0.35	0	0.08	0
ethylbenzene	1.14	0.1	0.405	2.7	0.328	0.87	0.45
n-octane	0.406	0.04	0.546	0	0	0.21	0
o-xylene	1.69	0.1	0.575	1.61	0.54	1.35	2.86
m&p-xylene	3.619	0.31	1.421	2.96	0.975	1.23	2.67
styrene	0	0	0	0	0	0	0
1,2,4-TMbenzene	1.428	0.06	0.277	0.41	2.09	0.08	0
1,3,5-TMbenzene	0.669	0.02	2.021	0.82	1.29	0.38	0
isopropylbenzene	0.154	0.04	0.491	0.57	0.36	0.94	0
n-nonane	0.24	0	0.764	0.49	0	3.14	0
n-propylbenzene	0	0.01	0.098	1	0.9	0.66	0
CO	825.54	0	3.25	0	0	401.43	0
NOx	54.53	0	133.13	0	0	600.5	0

TABLE 2 Average CMB Allocation to Vehicle and Gasoline Vapor Sources, 7 a.m. samples, in ug/m³
(percent of total NMOC given in parentheses)

Source Type	NMOC Sampling Sites							
	Rockford	Aurora	Kankakee	Zion	Chicago	Mid-Lake Boat	South Lake Boat	Transect Boat
Vehicles	19.2 (35%)	16.3 (24%)	21.1 (24%)	25.7 (23%)	123.7 (33%)	35.5 (41%)	22.9 (22%)	93.5 (26%)
Gasoline Vapor	1.0 (2%)	1.3 (3%)	3.1 (3%)	1.9 (2%)	25.9 (8%)	7.8 (12%)	1.9 (1%)	12.7 (1%)
Total NMOC	50.9	68.4	99.1	106.1	350.1	83.2	144.3	397.1

TABLE 3 Average CMB Allocation to Vehicle and Gasoline Vapor Sources, 10 a.m. samples, in ug/m³
(percent of total NMOC given in parentheses)

Source Type	NMOC Sampling Sites							
	Rockford	Aurora	Kankakee	Zion	Chicago	Mid-Lake Boat	South Lake Boat	Transect Boat
Vehicles	5.8 (20%)	9.4 (29%)	16.6 (21%)	8.1 (16%)	106.4 (29%)	26.4 (38%)	23.5 (28%)	20.7 (32%)
Gasoline Vapor	1.6 (6%)	2.6 (7%)	3.3 (3%)	1.1 (3%)	28.1 (7%)	4.8 (7%)	1.6 (3%)	5.3 (6%)
Total NMOC	30.3	28.0	100.0	54.5	384.7	70.4	68.6	58.0

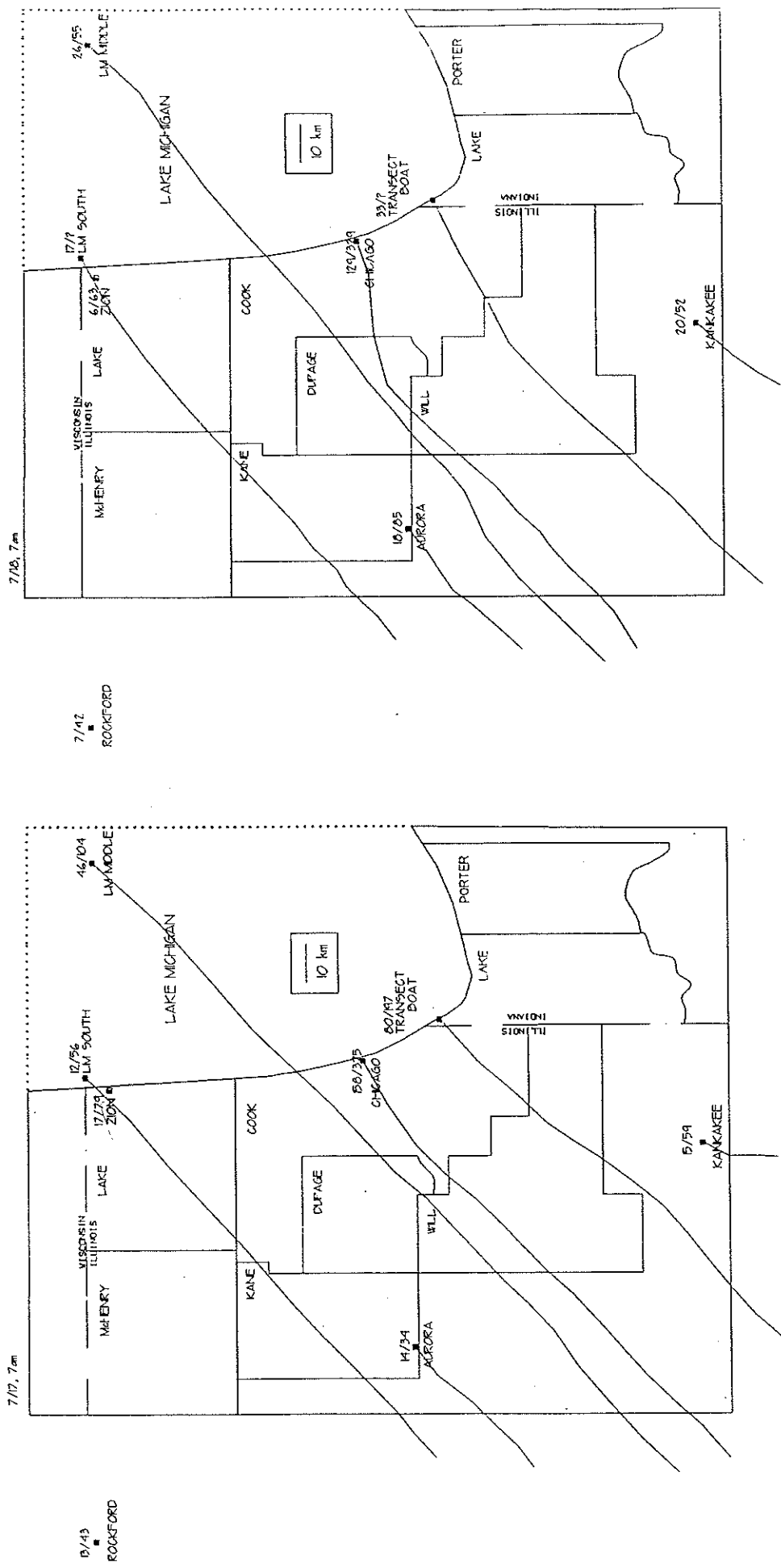


FIGURE 1 Vehicle Contributions (numerator) and Total NMOC (denominator) when Wind Speed and Direction are Similar

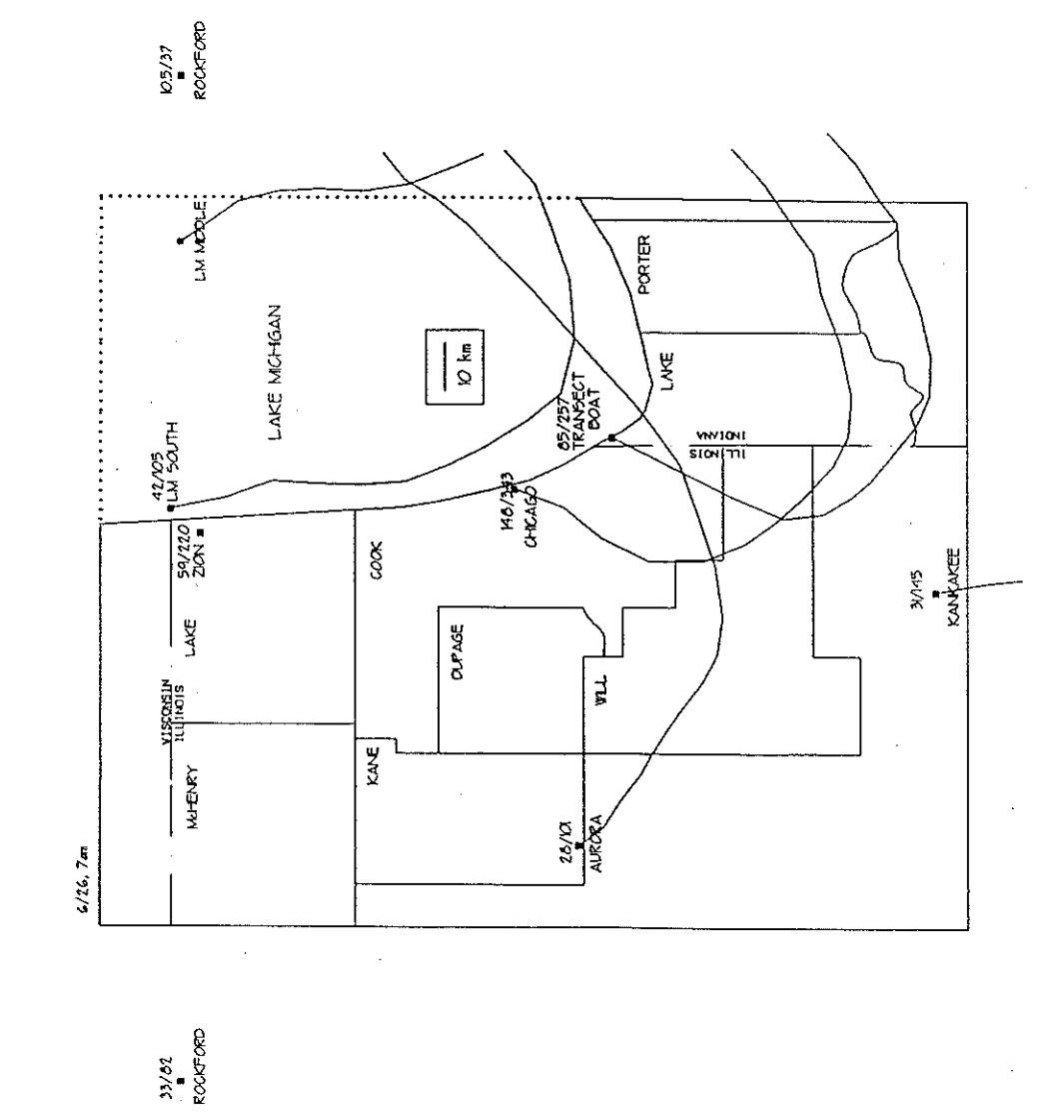
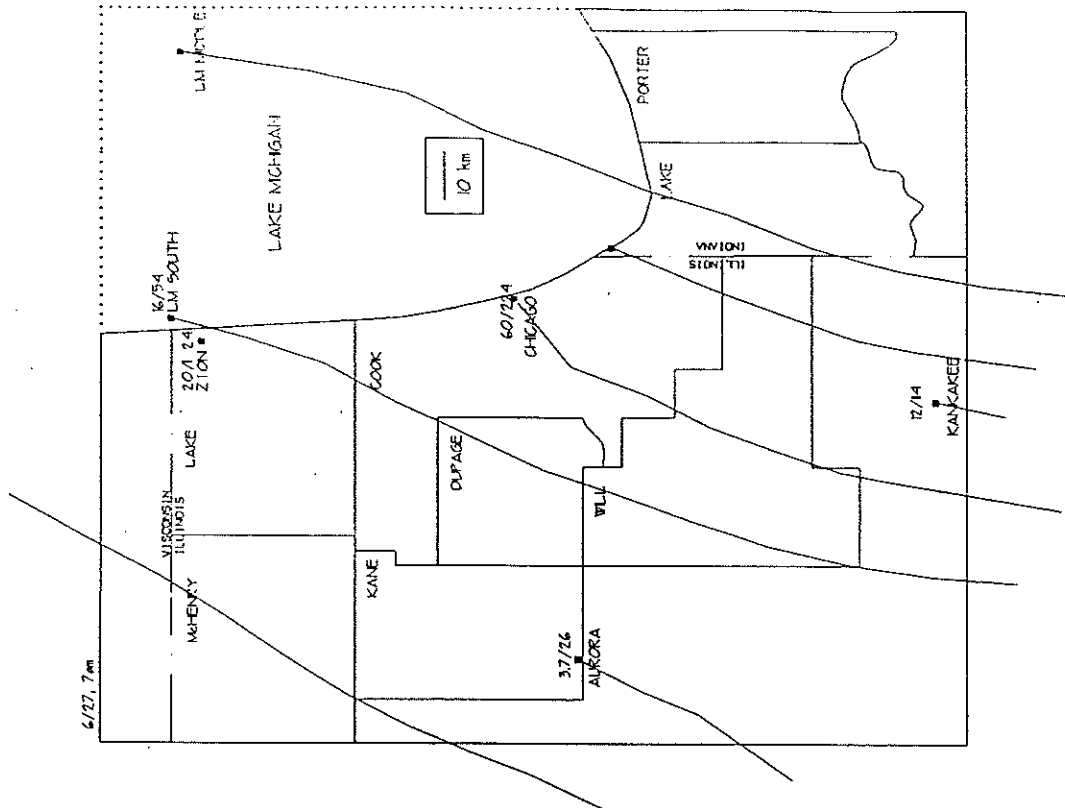


FIGURE 2 Vehicle Contributions (numerator) and Total NMOC (denominator) when Wind Speed and Direction are Different