

PII: S0045-6535(97)00321-4

## A CHEMICAL MASS BALANCE ANALYSIS OF NONMETHANE HYDROCARBON EMISSIONS IN NORTH CAROLINA

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(Received in USA 19 November 1996; accepted 6 June 1997)

### ABSTRACT

The EPA's Chemical Mass Balance Receptor Model (CMB7) was used for analysis of nonmethane hydrocarbon source-receptor relationships in the Raleigh, North Carolina Metropolitan Statistical Area (MSA). Three hour integrated ambient samples collected 15 km southeast of downtown Raleigh from 5-8 AM weekdays during August, 1993 were analyzed for speciated hydrocarbons and used as inputs in the model. Additional samples collected from 12-3 PM and 5-8 PM were also analyzed. CMB results for four source profiles, i.e. roadway, whole gas, surface coating, and isoprene were compared with the State of North Carolina's seasonally adjusted emission inventory for anthropogenic and biogenic hydrocarbon emissions. The Biogenic Emission Inventory System (BEIS) was used to estimate isoprene emissions for a typical summer day in the Raleigh area. CMB results using average concentrations of the 5-8 AM samples were similar to both the anthropogenic and biogenic emission inventory. Mass balance attributed 50.5% of total nonmethane organic carbon to roadway sources, 17.0% to surface coatings, and 4.0% to isoprene sources during the 5-8 AM sampling period; compared to the emission inventory which apportioned 47.5% to mobile sources, 14.0% to surface coating sources and 6.0% to isoprene sources during the same period. Afternoon and early evening samples were used to determine the diurnal profile for isoprene and roadway sources for comparison with emission inventory profiles. CMB results showed roadway source emissions decrease from morning to the afternoon and remain relatively constant from the afternoon to early evening.

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### 1. INTRODUCTION

To meet the National Ambient Air Quality Standard (NAAQS) for ozone (0.12 ppmv) in urban and rural areas of the United States, ozone abatement strategies have included attempts at reducing nonmethane hydrocarbon (NMHC) emissions from sources such as vehicular traffic, private businesses and public industries. Despite major efforts to reduce ozone in non-attainment areas, many areas of the United States are still out of compliance. One reason suggested for this failure is inaccuracies in perceived VOC/NO<sub>x</sub> ratios resulting from drastic underestimations in NMHC emission inventories (National Research Council, 1991).

The Chemical Mass Balance (CMB) Receptor Model has in the past decade become a popular tool for determining the contribution of hydrocarbon sources to ambient levels and has often been used to validate and further develop existing emission inventories [Scheff and Wadden 1993; O'Shea and Scheff, 1988; Conner et al., 1994; Wadden et al., 1986; Lewis et al., 1993; Dzubay et al, 1991; Kenski et al., 1992]. The CMB model has been used to determine the emissions impact of a variety of sources in many locations. Sources characterized include vehicle tailpipe emissions, gasoline vapor in the form of headspace and whole gas, petroleum refineries, architectural coatings, dry cleaning, graphic arts, wastewater, propane sources, and isoprene sources.

The CMB model quantifies contributions from chemically distinct source types [Watson, 1990] by using a variance weighted least squares solution to the following equation to solve for the mass contribution of each source ( $S_j$ ).

$$C_i = \sum a_{ij} S_j + e_i \quad (1)$$

where  $C_i$  is the concentration of species  $i$  measured at the receptor, and  $a_{ij}$  is the fraction of species  $i$  in source  $j$ .  $e_i$  is the difference between the measured and calculated species concentration [Watson et al., 1984]. The model cannot separate emissions of particular emitters with the same source profiles, such as, for example, Power Plant 1 and Power Plant 2 [Watson et al., 1990]. However, it will estimate the emissions from source categories (e.g., all power plants) impacting individual receptor sites.

#### Experimental Procedures

We used ambient data from three hour integrated samples collected during the 1993 Raleigh Oxidant Study [Lawrimore et al., 1995] as inputs to the USEPA/DRI Chemical Mass Balance Receptor Model - CMB7 [Watson et al., 1990]. The primary objective of this study was to estimate the contribution of individual source types to the local hydrocarbon budget in the Raleigh Metropolitan Statistical Area (MSA) and to compare the results with existing emission inventories.

Twelve hydrocarbon species were used in the analysis; acetylene, n-butane, i-pentane, 2-methylpentane, 3-methylpentane, methylcyclopentane, benzene, toluene, ethylbenzene, m-xylene, p-xylene, and isoprene. These species were chosen because they are major components of the selected sources and they were present in most all ambient samples. Ethane was not used as a fitting species because there were questions about the accuracy of the data for that species.

One assumption of the mass balance model is that selected species concentrations do not significantly change between source and receptor due to factors such as chemical reaction or deposition [Watson et al., 1990]. Although m/p xylene are moderately reactive species, they were included in the model because of the large contribution they make to automobile exhaust emissions. In addition, because of extremely high reactivity with the OH radical, inclusion of isoprene in the model should only be done with the understanding that contribution estimates may be low. Since isoprene is thought to be the most important naturally emitted hydrocarbon in the urban southeast [Chameides et al., 1988], an attempt to estimate the contribution of isoprene was made.

Five sources were initially selected as model inputs based on the species measured at the site and the inventory of hydrocarbon sources in the surrounding area. The sources are gasoline headspace vapor, whole gas, roadway, surface coatings and isoprene. The headspace and whole gas profiles could not be used in analysis of the morning samples because they were found to be collinear with the roadway profile. The headspace profile was also collinear with the roadway profile in the afternoon and evening samples; however, the whole gas profile was not, and was thus used in those analyses.

### Sample Collection

Although ambient data was collected at three levels during the Raleigh Oxidant Study; surface, 250 meters, and 450 meters, only surface data was used for CMB7 analysis. Collection was accomplished weekdays from August 2 to August 27, 1993 from 5-8 AM (period 1). Additional samples collected on August 19 from 12-3 PM (period 2), and 5-8 PM (period 3) were used to study the diurnal variation.

The collection site was located approximately 15 km southeast of downtown Raleigh, the capital of North Carolina. Raleigh is located in the central part of the state and has a population of about 250,000. Six liter electropolished SUMMA canisters and Parker Metal Bellows MB151 pumps were used for collection of three hour integrated ambient air samples. Unattended sampling was achieved with electronic timers and sample time was confirmed with digital meters.

Because the site was closed on Monday, two canisters and electronic timers were connected to one pump for sample collection on Monday and Tuesday mornings. The pump and canisters were housed in a temperature controlled room and samples were collected through 1/8 inch o.d. stainless tubing that extended two meters from the sampling room, three meters above the ground. Except for Monday samples, canisters used for period 1 sampling were picked up the day of collection and returned to North Carolina State University (NCSU) for same day analysis. Period 2 and period 3 canisters were placed at the site two hours prior to sample collection and were analyzed the following day.

### Sample Analysis

C2-C10 hydrocarbons were separated and analyzed at NCSU using a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). An Entech 2000 Automated Concentrator (Entech Laboratory Automation, Simi Valley, California) was used to pre-concentrate 300 ml of sample air prior to injection into the GC system. For a complete discussion of the sample analysis procedures see [Lawrimore et al., 1995] and [Apel et al., 1995].

### Source Profiles

The type and number of source profiles used for model input were determined from a review of the 1990 State of North Carolina source emission inventory data base for the site county (Wake County) and the seven surrounding counties. The largest source of hydrocarbon emissions in the combined counties, as specified in the inventory, is highway mobile sources. The total amount of Nonmethane Organic Carbon (NMOC) emitted by this source category in the eight counties is 126.8 tons per day (TPD), of which 46.6 TPD is emitted in Wake county.

Area sources are responsible for the second largest amount of NMOC emissions (101.4 TPD). Area sources are defined as a collection of stationary and non-road sources of air pollution within a specified geographical area, all emitting less than the minimum level prescribed for point sources. [NCDEHNR, 1993] Area sources are subdivided into individual area source types whose emission levels have been estimated. The largest source type is surface coating sources, which is responsible for emission of more than 44 TPD into the Raleigh area. This amounts to ~44.0% of all area source emissions. Pesticide application, solvent use, and slash burning comprise 9.0%, 8.0%, and 7.0% of all area source emissions respectively. The remaining emissions are made up of a number of sources that include, for example, dry cleaning, graphic arts, roofing, and bakeries.

The last two source categories, point and non-highway mobile, emit comparable amounts of NMOC. Non-highway mobile sources are responsible for about 25 TPD and point sources emit about 23 TPD

NMOC. Non-highway mobile sources consist of a variety of emitters such as lawn mowers, chain saws, farm equipment, construction machinery, railroad locomotives, and aircraft. Point sources consist of individual sources at specific locations that emit an amount of NMOC that exceeds 10 tons per year (TPY). By far, the largest group of point sources in the Raleigh area are a number of gasoline storage facilities located approximately 25 km east of the collection site. These facilities emit more than 5 tons of NMOC each day from gasoline loading racks due to spillage and replacement of gasoline vapor. Other types of point sources such as vegetable oil processing, paper production, tire manufacturing, and surface coating operations emit over 1 TPD of NMOC.

The largest NMOC emitters among mobile, area, and point sources were compared to determine the source profiles needed for CMB analysis. Vehicular mobile sources were found to be the largest emitters (~127 TPD), followed by surface coating sources (~45 TPD).

Because highway mobile source emissions are comprised of running losses and vapor losses due to displacement of vapor laden air and whole gas spillage, we chose 3 source profiles to represent mobile source emissions; roadway, headspace, and whole gas. The chosen source profile for roadway sources (Table 1) is a composite of tailpipe exhaust and running losses produced by warmed-up engines during steady-state driving conditions determined from analysis of ambient data collected in Atlanta, Georgia during the summer of 1990 [Conner et al., 1994]. Although this profile was collected in Atlanta, atmospheric and driving conditions are similar to those in Raleigh. Thus, this automotive profile should be more representative of automotive emissions in Raleigh than that from a generic profile. The headspace and whole gas profiles were also derived by [Conner et al., 1994] from ambient data in Atlanta during 1990.

The source profile for the surface coating sources was taken from the EPA's speciate data base. Because surface coating emissions in the Raleigh area primarily result from solvent-based coating applications, profile 1003 was chosen. It is a composite of lacquer, primer, and enamel profiles. Although profile 1003 was derived from emissions in the California South Coast Air Basin, of the available source profiles it was most representative of the emissions in the Raleigh area. Source uncertainties were not available for this profile. Thus we estimated uncertainties based on the magnitude of the percent abundance [Lewis et al., 1993]:  $<0.1: \pm 10\%$ ;  $0.1$  to  $0.5: \pm 5\%$ ;  $>0.5: \pm 2\%$ .

In addition to the anthropogenic VOC sources discussed above, biogenic VOC sources also play an important role in ozone production in southeastern cities [Chameides et al., 1988] such as Raleigh. Because of extensive vegetation and warm weather, biogenic hydrocarbon emissions approach, and often exceed, those of anthropogenic emissions in North Carolina [NCDEHNR, 1993]. Although biogenic emissions include a large number of hydrocarbon species, isoprene comprises the largest percentage, approximately 50%, of all biogenic hydrocarbons emitted in the southeast U.S. during the summer months [Lamb et al., 1987]. Emissions of isoprene are highly variable and are dependent on factors such as land cover, sunlight intensity, and temperature [Tingey et al., 1979]. Because isoprene emissions are dependent on various uncontrollable factors, a standard daily emission flux cannot be accurately determined. Thus the Biogenic Emissions Inventory System (BEIS) is used to estimate the hourly flux of isoprene.

Not only is isoprene emitted in large abundance in the southeast, but because it is highly reactive with the OH radical, it is thought to be one of the most important naturally emitted hydrocarbons in the urban southeast as a precursor to ozone formation [Lawrimore et al., 1995; Chameides et al., 1988]. Because

Table 1. Source profiles, for CMB analysis, of five hydrocarbon sources in the Raleigh Area.

| Specie                 | a    | b    | c     | d     | e     |
|------------------------|------|------|-------|-------|-------|
| ethylene               | 4.34 | 0.01 | 0.01  | 0.00  | 0.00  |
| acetylene*             | 3.80 | 0.00 | 0.01  | 0.00  | 0.00  |
| ethane                 | 1.55 | 0.02 | 0.14  | 0.00  | 0.00  |
| propane                | 1.05 | 0.08 | 0.97  | 0.00  | 0.00  |
| i-butane               | 1.12 | 0.60 | 5.13  | 0.00  | 0.00  |
| n-butane*              | 4.11 | 3.23 | 21.80 | 0.00  | 0.00  |
| i-pentane*             | 8.64 | 7.37 | 27.90 | 0.00  | 0.00  |
| n-pentane              | 2.66 | 2.76 | 7.40  | 0.00  | 0.00  |
| isoprene*              | 0.32 | 0.04 | 0.07  | 0.00  | 60.94 |
| cyclopentane           | 0.25 | 0.27 | 0.43  | 0.00  | 0.00  |
| 2-methylpentane*       | 2.43 | 2.88 | 3.53  | 0.00  | 0.00  |
| 3-methylpentane*       | 1.42 | 1.79 | 1.93  | 0.00  | 0.00  |
| n-hexane               | 1.09 | 1.50 | 1.20  | 0.00  | 0.00  |
| methylcyclopentane*    | 0.78 | 1.10 | 0.81  | 0.00  | 0.00  |
| benzene*               | 2.73 | 1.53 | 0.86  | 0.00  | 0.00  |
| 2,3 dimethylpentane    | 0.90 | 1.02 | 0.46  | 0.00  | 0.00  |
| 2,2,4 trimethylpentane | 2.51 | 2.82 | 0.99  | 0.00  | 0.00  |
| toluene*               | 6.59 | 8.11 | 1.26  | 37.87 | 0.00  |
| n-octane               | 0.29 | 0.45 | 0.03  | 0.00  | 0.00  |
| ethylbenzene*          | 1.28 | 1.80 | 0.10  | 0.54  | 0.00  |
| m/p-xylene*            | 4.35 | 6.30 | 0.32  | 3.75  | 0.00  |
| o-xylene               | 1.66 | 2.60 | 0.12  | 4.47  | 0.00  |

a - Roadway Source; b - Whole Gas; c - Headspace; d - Surface Coatings; e - Isoprene Sources;  
\* Fitting Species

of its importance, we included a source profile for Isoprene which was also determined from 1990 Atlanta ambient data [Lewis et al., 1993]. Because isoprene is very reactive with the hydroxyl radical, its ambient concentration is most likely reduced between emission and measurement. Thus the CMB emission estimate should only be taken as a lower limit [Lewis et al., 1993].

## 2. RESULTS AND DISCUSSION

Initial analysis consisted of running the model on the average of all 5-8 AM ambient samples (18 samples) with all source profiles and varying the fitting species to achieve the best fit. Ambient uncertainties for individual species were estimated from the expression [Lewis et al., 1993]

$$\Delta C_i \text{ (ppbC)} = (0.2^2 + (0.5 \cdot c_i)^2)^{1/2} \quad (2)$$

There was collinearity between the roadway, headspace and whole gas profiles. The model was rerun without the whole gas profile, and collinearity between the roadway and headspace profiles remained. There was also collinearity between the roadway and whole gas profiles when the headspace profile was omitted from the model. Because automotive running emissions are generally much greater than whole gas

contributions and vapor losses due to displacement and evaporation, we chose to drop the whole gas and headspace profiles from the CMB model even though by not using a whole gas profile, overestimation of roadway emissions could result [Lewis et al., 1993]. The CMB model was then rerun using only roadway, surface coatings, and isoprene source profiles.

The results from the analysis of the average of all 5-8 AM samples using three source profiles and twelve fitting species are shown in Figure 1. Hydrocarbon concentration due to roadway sources was calculated as  $42.7 \pm 2.9$  ppbC which was  $50.5 \pm 3.0\%$  of the total emissions measured during the 5-8 AM time period, based on measurement of every species with an FID response, i.e. total nonmethane organic carbon (TNMOC). Surface coating operations were  $14.4 \pm 1.6$  ppbC or  $17.0 \pm 2.0\%$  of all emissions. Isoprene sources were calculated as

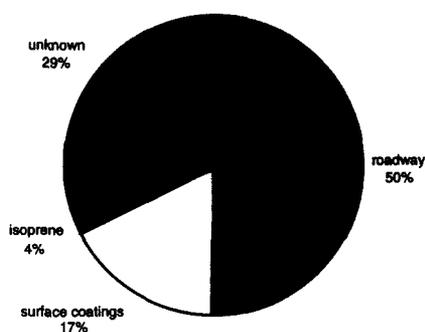


Figure 1. CMB calculated percent contribution of sources, from averaged ambient concentrations, during the 5-8 AM sampling period. ( $r^2 = 0.97$ ,  $\chi^2 = 2.05$ ).

$3.2 \pm 0.4$  ppbC or  $4.0 \pm 0.5\%$ . The combined percentage for the three source profiles was 71.5% with the remaining 28.5% unknown. The chi-square and r-square values were good (2.05 and 0.97 respectively).

Agreement between calculated and measured concentrations was also good for individual fitting species. Ten of the species had calculated/measured ratios between 0.81 and 1.25. Table 2 shows the concentrations for each compound and the corresponding ratio of the calculated to measured values. Ratios greater than 1 suggest possible chemical reaction or deposition of the compound between emission and measurement at the receptor site. Ratios less than 1 suggest that additional sources, not included in the model, may be responsible for a portion of the measured concentration [Lewis et al., 1993]. All species except m/p-xylene had ratios between 0.75 and 1.25. The measured concentration of m/p-xylene was 1.66 ppbC and the calculated value was 2.40 ppbC which resulted in a ratio of 1.45. This large ratio is not unexpected due to the high reactivity of these species.

Collection of additional samples from 12-3 PM and 5-8 PM on August 19 allowed profile analysis through three distinct periods of the day. Headspace and whole gas profiles were added to the model for each period on this day. Both profiles were again collinear to the roadway profile for the period 1 sample. However, the whole gas profile was not collinear in the period 2 and period 3 samples. Thus the model was run using four source profiles for the afternoon and evening samples.

CMB analysis for the period 1 sample on August 19 was similar to the months average results. ( $r^2 = 0.97, \chi^2 = 2.64$ ). The higher  $X^2$  value may be due to dropping the whole gas profile. The roadway source component contributed  $53.6 \pm 3.1$  ppbC ( $54.0 \pm 3.0\%$ ) of the total emissions, surface coating provided  $13.3 \pm 2.2$  ppbC which was  $13.0 \pm 2.0\%$  and isoprene sources contributed  $6.1 \pm 0.4$  ppbC or  $6.0 \pm 0.5\%$  to the total emissions from 5 - 8 AM (Figure 2.). By early afternoon, (Figure 3.) the roadway source contribution had been reduced to  $14.0 \pm 3.0\%$  ( $r^2 = 0.97, \chi^2 = 4.10$ ). However, surface coating and isoprene emissions increased in both mass and percent contribution. Surface coating sources were responsible for  $21.8 \pm 2.2$  ppbC ( $20.0 \pm 2.0\%$ ) of the measured hydrocarbons in period 2. Isoprene sources contributed  $12.2 \pm 0.8$  ppbC or  $11.0 \pm 1.0\%$  of all emissions from 12-3 PM.

Table 2. Measured and calculated concentrations and ratios for averaged values during the 5-8 AM sampling period.

| Species            | Calculated Concentration<br>ppbC | Measured Concentration<br>ppbC | Ratio<br>Calculated/Measured |
|--------------------|----------------------------------|--------------------------------|------------------------------|
| Acetylene          | $1.62 \pm 0.27$                  | $1.30 \pm 0.21$                | $1.25 \pm 0.29$              |
| n-Butane           | $1.76 \pm 0.30$                  | $2.04 \pm 0.22$                | $0.86 \pm 0.18$              |
| Isopentane         | $3.69 \pm 0.36$                  | $4.42 \pm 0.30$                | $0.84 \pm 0.10$              |
| 2-Methylpentane    | $1.04 \pm 0.04$                  | $1.28 \pm 0.21$                | $0.81 \pm 0.14$              |
| 3-Methylpentane    | $0.61 \pm 0.03$                  | $0.70 \pm 0.20$                | $0.87 \pm 0.25$              |
| Isoprene           | $2.08 \pm 0.10$                  | $2.08 \pm 0.23$                | $1.00 \pm 0.12$              |
| Methylcyclopentane | $0.34 \pm 0.02$                  | $0.30 \pm 0.20$                | $1.12 \pm 0.75$              |
| Benzene            | $1.17 \pm 0.08$                  | $1.32 \pm 0.21$                | $0.88 \pm 0.15$              |
| Toluene            | $8.29 \pm 0.31$                  | $8.97 \pm 0.49$                | $0.95 \pm 0.06$              |
| Ethylbenzene       | $0.62 \pm 0.02$                  | $0.65 \pm 0.20$                | $0.96 \pm 0.30$              |
| m/p-Xylene         | $2.40 \pm 0.08$                  | $1.66 \pm 0.22$                | $1.45 \pm 0.20$              |

By late afternoon, (Figure 4.) the contribution of isoprene had increased significantly ( $r^2 = 0.98, \chi^2 = 2.90$ ). Isoprene sources were responsible for  $33.2 \pm 2.0$  ppbC which was  $43.0 \pm 3.0\%$  of all emissions during period 3. The percent contribution from roadway sources remained about the same in period 3,  $11.4 \pm 3.3$  ppbC ( $15.0 \pm 14.5\%$ ). Surface coating operations were responsible for only  $3.3 \pm 1.4$  ppbC or  $4.5 \pm 2.0\%$  during period 3.

The whole gas contribution was greater than the emissions attributed to roadway sources during the 12-3 PM and 5-8 PM sampling periods. CMB analysis attributed  $20.6 \pm 5.3$  ppbC ( $19.0 \pm 5.0\%$ ) and  $23.8 \pm 6.9$  ppbC ( $31.0 \pm 9.0\%$ ) to whole gas sources during both periods respectively. Because only one day of ambient data was analyzed during these periods, it is unclear why whole gas emissions were so influential. It is possible that the prevailing easterly surface winds on August 19 may have transported

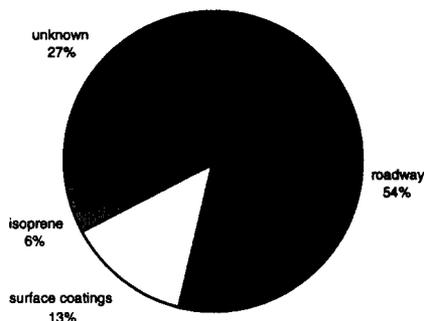


Figure 2. CMB calculated source percent contribution from sample collected from 5-8 AM on August 19, 1993. ( $r^2 = 0.97$ ,  $\chi^2 = 2.64$ ).

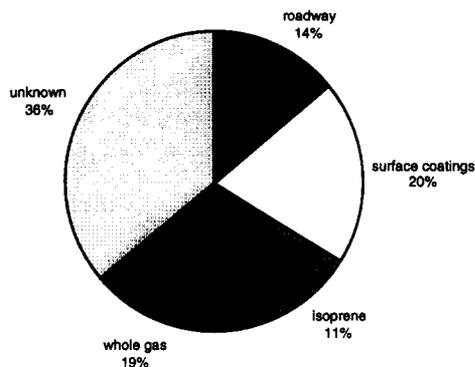


Figure 3. CMB calculated source percent contribution from sample collected from 12-3 PM on August 19, 1993. ( $r^2 = 0.97$ ,  $\chi^2 = 4.10$ ).

significant concentrations of whole gas hydrocarbons from a large number of gasoline storage facilities located 25 km east of the tower during these sampling periods.

#### Comparison with emission inventories

Table 3 gives a summary of the North Carolina seasonally adjusted emissions inventory for Wake county and the combined inventory for Wake and the surrounding counties. As previously mentioned, highway mobile sources emit the largest amount of hydrocarbons, followed by area, non-highway mobile, and point sources. The BEIS model was used to calculate isoprene emissions in each county for a day with typical summertime meteorological conditions. The emission profile for isoprene is shown in Figure 5. Because the sun does not rise until after 6 AM, isoprene emissions during the 5-8 AM period are very low. Total emissions in all counties during this period are only 2.2 tons.

Although 126.8 tons of NMOC are emitted from mobile sources each day, these emissions also vary throughout the day, and thus should not be compared with CMB results until adjusted for their diurnal variation. We adjusted automotive emissions by using the EPA's Vehicle Miles Traveled (VMT) default profile for automotive emissions (Figure 6). Automotive emissions are largest in the morning and evening during the daily commute to and from work. By multiplying the default profile factor for each hour during the 5-8 AM period, automotive emissions were more accurately estimated. Area, point, and non-highway mobile sources were estimated by assuming a constant diurnal profile for each source. The emission inventory fractional contribution of each source was then compared to the CMB calculated emissions as shown in Table 4.

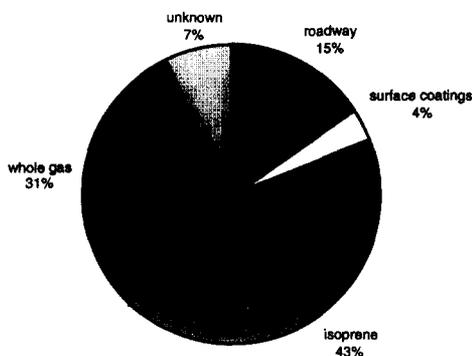


Figure 4. CMB calculated source percent contribution from sample collected from 5-8 PM on August 19, 1993. ( $r^2 = 0.98$ ,  $\chi^2 = 2.90$ ).

Table 3. North Carolina Anthropogenic Emission Inventory (tons per day).

|             | Wake | Combined |
|-------------|------|----------|
| Mobile      | 46.6 | 126.8    |
| Area        | 36.9 | 101.4    |
| Point       | 6.9  | 23.6     |
| Non-highway | 12.0 | 25.0     |

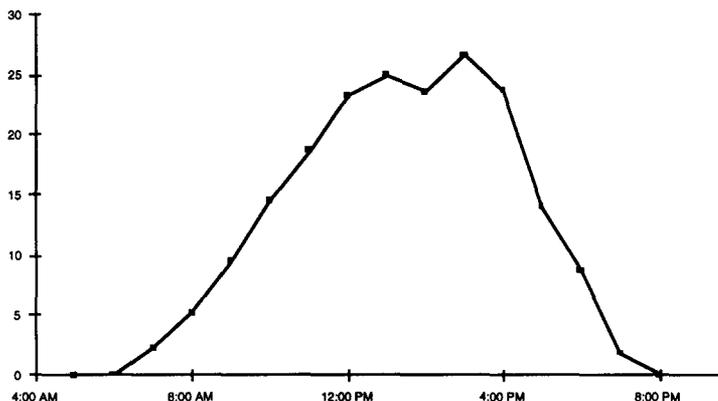


Figure 5. BEIS calculation of average isoprene diurnal flux for a typical summer day in Wake county, NC and the surrounding counties.

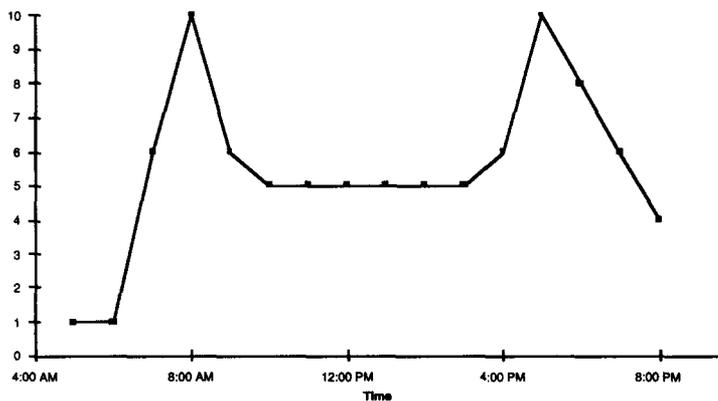


Figure 6. Vehicle Miles Traveled (VMT) default emission profile.

Table 4. Emission Inventory and CMB Results (% of Total NMOC) for the 5-8 AM Sampling Period.

|                 | Inventory | CMB Calculation |
|-----------------|-----------|-----------------|
| Mobile          | 47%       | 50%             |
| Surface Coating | 14%       | 17%             |
| Isoprene        | 6%        | 4%              |

Because highway mobile source inventories are determined using the Mobile 5.0 model, vehicle refueling losses, which include whole gas and vapor losses, also contribute to mobile source emissions. Thus the mobile source inventory is compared with a combination of the whole gas and roadway source profiles for the periods when both had significant source coefficients. Roadway source emissions match up very well with the mobile source inventory during the morning sampling period. Emission inventories estimate 47.5% and the CMB results showed that automotive sources were responsible for  $50.5 \pm 3.0\%$  of total emissions during the 5-8 AM sampling period. The small additional contribution estimated by CMB analysis is within the uncertainty limits.

Surface coating operations were the only area source estimated by CMB analysis. As previously discussed, the North Carolina emission inventory specifies surface coating operations as about 44.0% of all area emissions, which amounts to approximately 14.0% of total NMOC. This was similar to the CMB calculation estimate for surface coating operations of  $17.0 \pm 2.0\%$  of total NMOC. BEIS calculations estimated emission of 2.2 tons of isoprene during the 5-8 AM sampling period. This was 6.0% of total hydrocarbon emissions during this period which was similar to the CMB calculation of  $4.0 \pm 0.5\%$  of TNMOC emissions.

The period 2 and period 3 samples also enabled a diurnal comparison of the emission inventory for highway mobile and isoprene sources with the CMB results. Because data for all three periods was only available for August 19, only the North Carolina emission inventory data for the counties located along the prevailing wind direction were used for this comparison. The wind was from the East/Northeast, thus data for Wake, Nash, and Franklin counties was used.

Figure 7 shows the emissions as a percent of TNMOC for the inventory and CMB calculated emissions. The mobile source inventory was compared to the sum of roadway and whole gas contributions. The inventory profile was similar to the CMB results during all periods. However, the emission inventory after adjustment by the VMT profile, was less than the model estimates. This is probably a result of additional whole gas contributions from the gasoline storage facilities east of the receptor site.

The fractional contribution from isoprene sources, as predicted by BEIS calculations, match closely with CMB results for the early morning and early evening periods (Figure 8). However, there is a very large discrepancy between BEIS and CMB results during the afternoon. Because there are only CMB results for one diurnal profile, it is unclear whether this is an anomaly or actually occurs on a daily basis. But it must be remembered that the CMB model relies on mass conservation, and thus, is limited by the assumption that once released, hydrocarbon species do not significantly react prior to measurement at the receptor location. Because the 12-3 PM sampling period is the time of greatest solar radiation and highest OH radical concentration [Logan et al., 1981] it is possible that the majority of isoprene emitted during this period is converted to radicals. As a result, isoprene concentrations are dramatically reduced, and because CMB analysis is based on measurement of ambient concentrations, its' estimates do not accurately reflect emission fluxes for isoprene. During late afternoon as sunlight intensity decreases, and the pool of available OH radicals decrease, ambient levels of isoprene increase and the CMB results more accurately reflect emission levels.

### 3. CONCLUSION

An analysis of nonmethane hydrocarbon source-receptor relationships in the Raleigh, North Carolina area was performed using the EPA's Chemical Mass Balance Receptor Model, CMB7. Twelve compounds, acetylene, n-butane, i-pentane, 2-methylpentane, 3-methylpentane, methylcyclopentane, benzene, toluene, ethylbenzene, m-xylene, p-xylene, and isoprene, were used as fitting species and four source profiles, roadway, whole gas, surface coating, and isoprene were analyzed for their respective emissions impact at the receptor location.

Three hour integrated samples collected during the month of August as part of the 1993 Raleigh Oxidant Study were used in the analysis. Average hydrocarbon concentrations measured during the 5-8 AM sampling period were used in the principal CMB analysis. Additional samples collected from 12-3 PM and 5-8 PM were also studied as part of a diurnal analysis.

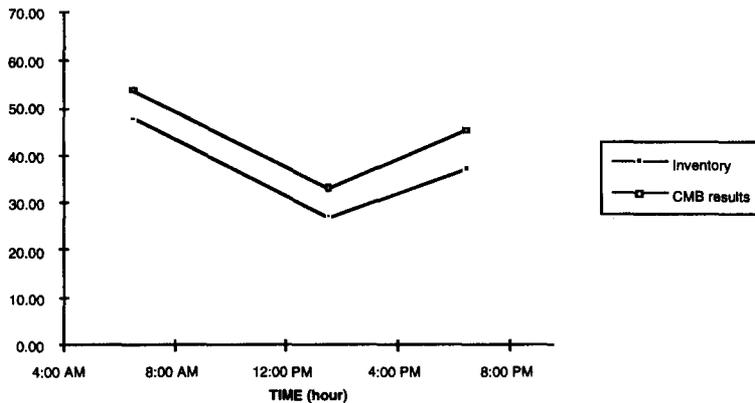


Figure 7. Profile of CMB calculated emissions for roadway and whole gas sources and emissions estimated from the North Carolina mobile source inventory and VMT default profile as a percent of TNMOC.

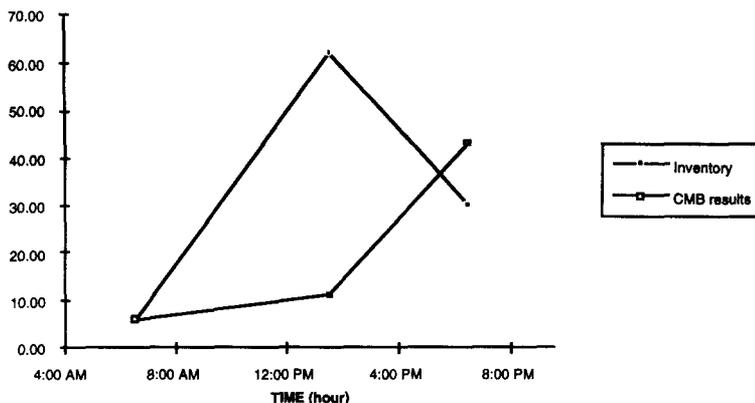


Figure 8. Profile of isoprene CMB calculated emissions and BEIS calculated isoprene emissions as a percent of TNMOC.

CMB7 results were compared with the North Carolina seasonally adjusted hydrocarbon emission inventory for mobile, area, and isoprene sources. The emission inventory for mobile sources was also adjusted for diurnal variation using the EPA's Vehicle Miles Traveled, VMT, profile for automotive traffic. CMB analysis of the average concentrations of all 5-8 AM samples resulted in  $50.5 \pm 3.0\%$  of total nonmethane organic carbon emissions being attributed to roadway sources, while the North Carolina emission inventory specified 47.5% of hydrocarbon emissions from mobile sources during the same period. CMB calculations also attributed  $17.0 \pm 2.0\%$  to surface coatings, and  $4.0 \pm 0.5\%$  to isoprene. The North Carolina adjusted emission inventory specified 14.0% to surface coating sources and 6.0% to isoprene sources during the same period. The sum of the three source profiles constituted 71.5% of the hydrocarbon emissions from 5-8 AM with the remaining 28.5% unknown.

Analysis of samples collected on August 19, during all three periods, revealed a hydrocarbon emission diurnal profile. Mobile source emissions were calculated to be responsible for  $53.5 \pm 3.0\%$  of TNMOC from 5-8 AM,  $14.0 \pm 3.0\%$  from 12-3 PM, and  $15.0 \pm 4.0\%$  from 5-8 PM on August 19. Surface coating sources were found to be responsible for  $14.0 \pm 2.0\%$ ,  $20.0 \pm 2.0\%$ , and  $4.0 \pm 1.0\%$ ; and isoprene sources for  $6.0 \pm 0.5\%$ ,  $11.0 \pm 1.0\%$ , and  $43.0 \pm 3.0\%$  during the same periods. Whole gas sources were calculated to contribute  $19.0 \pm 5.0\%$  from 12-3 PM and  $31.0 \pm 9.0\%$  from 5-8 PM.

Although there are inherent limitations to the Chemical Mass Balance Receptor Model, by selection of appropriate source profiles based on a review of existing emission inventories, the contribution of individual source types to the total hydrocarbon budget can be ascertained. Because the validity of emission inventories and the corresponding control strategies based on those inventories, are sometimes questioned, CMB analysis is a useful tool for verification of existing emission inventories. Additionally, as hydrocarbon source control strategies are implemented, CMB analysis along with ambient monitoring, can be used to assess the effectiveness of emission controls on a year to year basis.

#### 4. ACKNOWLEDGMENTS

This research has been funded by the North Carolina Department of Environment, Health and Natural Resources (NCDEHNR) under contract J-4004. We wish to thank George Murray and Thomas Manuszak of NCDEHNR for their assistance and discussions. We are grateful to W.A. Lonneman of the United States Environmental Protection Agency for his critical review of this paper. Thanks to Mita Das for her assistance with data analysis. Thanks to E. Apel, National Center for Atmospheric Research, for providing the retention time standard and to R. Zika, University of Miami, for providing the mass standard. Thanks to Ms. Brenda Batts and Ms. Mel DeFeo in the preparation of the manuscript.

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