

# **Spatial Gradients and Source Apportionment of Volatile Organic Compounds near Roadways**

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## **Abstract**

Concentrations of 55 volatile organic compounds (VOCs) ( $C_2$  to  $C_{12}$ ) are reported near a highway in Raleigh, NC. Thirty-minute samples were collected at eight locations, ranging from approximately 10–100 m perpendicular from the roadway. The highest concentrations of VOCs were generally measured closest to the roadway, and concentrations decreased exponentially with increasing distance from the roadway. The highest mean concentration for individual VOCs were for ethylene (3.10 ppbv) (mean concentration at  $x = 13$  m), propane (2.27 ppbv), ethane (1.91 ppbv), isopentane (1.54 ppbv), toluene (0.95 ppbv), and n-butane (0.89 ppbv). Concentrations at the nearest roadway location ( $x = 13$  m) were generally between 2.0 and 1.5

times those from the farthest roadway location ( $x = 92$  m). The data were apportioned into four source categories using the EPA Chemical Mass Balance Model (CMB8.2): motor vehicle exhaust, compressed natural gas, propane gas, and evaporative gasoline. The majority of the VOCs resulted from motor vehicle exhaust ( $67 \pm 12\%$ ) (% of total VOC at  $x = 13$  m  $\pm$  S.D.). Compressed natural gas, propane gas, and evaporative gasoline accounted for approximately 15%, 7% and 1% of the total VOC emissions, respectively, at  $x = 13$  m.

## 1. Introduction

Motor vehicles constitute a major source of emissions in urban areas, comprising a variety of pollutants, including volatile organic compounds (VOCs) (29% of emissions in the U.S. as estimated in U.S. Environmental Protection Agency, 2001), nitrogen oxides ( $\text{NO}_x$ ) (34%), and carbon monoxide (CO) (51%). Several approaches have been used to estimate the contribution of vehicle emissions to ambient concentrations. These include source tests, where emission factors and/or detailed chemical profiles are developed for different vehicles and operating conditions, typically using a dynamometer under controlled test conditions. For example, source tests have reported that VOCs comprise >95% (by mass) gasoline-powered motor vehicle exhaust (Schauer et al., 2002) and >50% medium-duty truck exhaust (Schauer et al., 1999). Numerous gas-phase organic compounds have been identified and quantified, including aromatic hydrocarbons, alkanes, and alkenes. Because source profiles are limited to the sources and conditions tested, these studies can be supplemented by measurements collected in roadway tunnels (e.g., Legreid et al., 2007; McGaughey et al., 2004) to represent a composite vehicle fleet in an actual urban area. Advances in sampling and analytical techniques have expanded the library of source profiles such that source markers have been widely used in

receptor modeling of PM concentrations (e.g., Schauer et al., 2000; Schauer et al., 1996). In addition, several source apportionment studies (Wittig and Allen, 2008; Hellen et al., 2006; Choi et al., 2004; Mukerjee et al., 2004; Hellen et al., 2003) have estimated the contributions of various sources to ambient VOC levels.

Studies have reported various PM size fractions (nano, ultrafine, fine, coarse) near roadways (e.g., Zhu et al., 2006; Charron and Harrison, 2005; Lin et al., 2005; Zhu et al., 2002), but reports of spatial variability near roadways have generally been limited to surrogate measurements (PM, CO, etc.) as opposed to source markers for receptor models. Particle number concentrations have been reported to decay exponentially with distance from the roadway, e.g., an approximately 5-fold decrease in particle number concentration from 30 m to 300 m near a Los Angeles highway during daytime (Zhu et al., 2006).

Although dozens of organic compounds have been reported from source tests of motor vehicles, studies reporting VOC concentrations in near road environments have been limited. Chan et al. (2002) reported concentrations of VOCs from 16 near roadway sites (21,000-50,000 daily traffic counts) in urban and industrial areas. Concentrations for most VOCs were higher in the industrial as compared with the residential area (e.g., mean benzene concentrations of 31.8 and 17.6  $\mu\text{g m}^{-3}$  in the industrial and residential areas, respectively). Chang et al. (2006) measured VOCs from two roadway sites to evaluate the suitability of different vehicle source markers, including aromatic and aliphatic hydrocarbons.

Exposure to elevated VOC concentrations near roadways may be an important contributor to total VOC exposures for populations that live near major roadways. Data from the U.S. Census indicate that 36 million people in U.S. live within 300 feet of a four-lane highway, railroad, or airport (U.S. Census Bureau, 2005). Recently, the U.S. EPA has incorporated the



influence of living near a major roadway into exposure modeling conducted as part of the National Air Toxics Assessment (NATA) using the limited data available for providing an estimate of roadway impact (U.S. Environmental Protection Agency, 1999a; Rosenbaum and Huang, 2007). The exposure model used in this assessment estimates the relative increase in chemical concentrations based on proximity to roadway. Studies that characterize the spatial pattern of elevated VOC concentrations near roadways are needed to improve exposure and risk assessment for urban populations living near major roadways.

The objective of this study is to quantify spatial differences in VOCs near roadways. Although numerous studies have reported VOC concentrations in urban areas, few have focused on VOC gradients near roadways. Studies have reported spatial variability of bulk parameters (e.g., CO, NO<sub>x</sub>, PM size fractions) in near roadway environments, but none have quantified spatial differences in VOCs. This research reports concentrations of 55 VOCs near a highway in Raleigh, NC using sampling locations at eight different horizontal distances perpendicular to the road (10–100 m) and three vertical distances (0.5–2 m) to examine spatial variability in VOCs near roadways.

## **2. Experimental Methods**

### *2.1. Site description*

VOC measurements were collected at eight horizontal distances and three vertical distances near a highway in Raleigh, NC (Figure 1). U.S. Interstate 440 (I-440) is an 8-lane, limited access highway carrying a daily weekday traffic volume of approximately 125,000 vehicles day<sup>-1</sup>. The highway, which surrounds the perimeter of north Raleigh, predominately carries local traffic. Average heavy-duty truck volume on I-440 was approximately 4% during

the study. A secondary road carrying approximately 200 vehicles day<sup>-1</sup> was located parallel to I-440 (approximately 10 m north of I-440). The site was an open field that extended 120 m north from I-440; the field was at grade with the highway. No physical structures were present at the study location other than a guardrail adjacent to the highway and sparse shrubbery (all <1 m in height). A one-story building (height <10 m) was located at the study site; for all monitoring locations, samples were collected at least 20 m from this building. Fewer than 100 passenger cars per day were estimated to use the parking lot and adjacent access road to the building in a typical day. No other sources of VOCs were identified within 1 km of the study site. Additional details on the site description are given elsewhere (Baldauf et al., 2008).

The eight horizontal distances were located at 13, 19, 25, 31, 43, 58, 74, and 92 m from the roadway (Figure 1); all samples were collected along the same transect perpendicular from the road. One VOC sample was collected at each of the eight sampling locations for each sampling period. Sampling sites located farther from the roadway were not selected so that all samples were collected at grade with the highway and unobstructed from the one-story building. At the 13-m site, samples were also collected at three different vertical distances ( $z = 0.5, 1.0$  and  $1.5$  m). VOC samples were collected for 5 different sampling periods; given the comparatively small number of sampling periods, sample collection focused on rush hour traffic periods on weekdays. Sampling periods included a mix of morning (collected at approximately 8:00 AM) and afternoon (collected at approximately 5:00 PM) samples. Weather conditions during sampling were generally clear with wind speeds ranging from 1 to 1.5 m/s. All measurements were collected during August 2006.

## 2.2. *Sample collection and analytical methods*

Samples were collected for 30 min in 6-L, evacuated, internal surface treated (Summa electropolished), stainless steel canisters; four different sampling days were completed over the course of the study. Canister cleaning and sample preparation were performed using U.S. EPA compendium method TO-14A (U.S. Environmental Protection Agency, 1999b).

Traffic volume was measured using traffic surveillance cameras mounted within 5 m of I-440. Vehicle counts, speed, and size class (motorcycles, light-duty cars, light-duty trucks, and heavy-duty trucks) were estimated using TigerEye software (DTS Inc.). Additional details on traffic measurements are described elsewhere (Baldauf et al., 2008).

Wind speed and wind direction data were collected using sonic anemometers (Model 81000 Ultrasonic Anemometer, R.M. Young Co.). Additional details on meteorological measurements are described elsewhere (Baldauf et al., 2008).

Canister samples were analyzed for C<sub>2</sub> to C<sub>12</sub> VOCs using a gas chromatograph (GC, Hewlett-Packard 5890 Series) equipped with flame ionization detector (FID) with cryogenic preconcentration. Analytical procedures were completed using U.S. EPA compendium method TO-14A (U.S. Environmental Protection Agency, 1999b). A 60-m, 0.32-mm i.d., fused silica capillary column with 1.0- $\mu$ m film thickness (DB-1, J&W Scientific, Rancho Cordova, CA) was used for separation of target analytes. Additional details describing cryogenic concentration of samples, peak identification and quantitation are provided elsewhere (U.S. Environmental Protection Agency, 1999b; Seila et al., 2001). A repeat analysis was completed for each canister sample collected.

A compound list consisting of 55 VOCs was used for all samples described in this study, based on a hydrocarbon target list used at the U.S. EPA Photochemical Assessment Monitoring



Station (PAMS) network sites (U.S. Environmental Protection Agency, 2003). Similar target lists have been used in previous source apportionment studies (e.g., Mukerjee et al., 2004; Fujita, 2001; Watson et al., 2001). Several of the compounds measured in this study are also classified as Hazardous Air Pollutants (HAPs), including 1,3-butadiene, benzene, toluene, ethylbenzene, xylenes, and styrene.

### 2.3. *Data analysis*

Data processing and descriptive statistics were performed using SAS v.8.02 (SAS Institute, Cary, NC). The EPA Chemical Mass Balance Model (CMB8.2) (U.S. Environmental Protection Agency, 2006) was used to determine source contribution estimates of VOCs. The CMB8.2 model uses an effective variance least squares algorithm to apportion the receptor data to source profiles.

Several sources of VOCs were considered for CMB analysis based on previous studies (Mukerjee et al., 2004; Fujita, 2001; Watson et al., 2001). Numerous attempts were made to resolve a variety of source combinations using different fitting species. A four-source solution was selected as it provided the best agreement between measured and predicted concentrations (average  $r^2 = 0.93$ ). The four sources included motor vehicle exhaust, natural gas, propane gas, and evaporative gasoline vapor (Fujita, 2001). Inclusion of additional sources typically resulted in negative source contributions or inconsistent source contribution estimates (e.g., collinearity among sources). Attempts were also made to separate motor vehicle exhaust into gasoline- and diesel-powered vehicles, but both sources did not consistently decay with distance. A composite vehicle profile was used to represent motor vehicle exhaust (96% gasoline vehicle and 4% diesel

vehicle based on truck and total traffic counts during the study period and using source profiles in Fujita, 2001).

### 3. Results

#### 3.1. *Spatial patterns in VOC concentrations*

Table 1 gives a statistical summary of VOC concentrations at all horizontal distances for all species measured in this study. As expected, the highest mean concentrations of VOCs were generally measured at the 13-m sampling location. The highest mean concentration for individual VOCs were for ethylene (3.10 ppbv at  $x = 13$  m), propane (2.27 ppbv), ethane (1.91 ppbv), isopentane (1.54 ppbv), toluene (0.95 ppbv), and n-butane (0.89 ppbv).

Concentrations of VOC species generally decayed exponentially with horizontal distance from the roadway. Figure 2 shows concentrations of selected VOCs (isopentane, toluene, benzene, and n-hexane) as a function of horizontal distance for one sampling event ( $r^2 > 0.9$  for the exponential decay of all compounds in Figure 2; slopes ranging from -0.05 to -0.21 for all compounds in Figure 2). As indicated in Figure 2, concentrations of duplicate canister sample were reasonable, i.e., generally within 10% for most species in Figure 2. The relative concentrations of VOC species are consistent with expected levels. For example, isopentane and toluene concentrations are both approximately twice those of benzene, while benzene concentrations are approximately twice those of n-hexane. These results are similar to existing profiles on gasoline-powered motor vehicles (Fujita, 2001), which report ratios of 2.3 for toluene/benzene, 2.0 for isopentane/benzene, and 1.7 for benzene/hexane.

While concentrations of most species clearly displayed spatial differences horizontally, no spatial differences were evident vertically. For most species, concentrations at the three



vertical distances were generally within 20% of each other. Sufficient vertical mixing over the sampling interval may explain the lack of spatial differences in the vertical direction, or that the range of heights used in this study was too narrow to detect differences in VOC concentrations.

The extent to which near roadway concentrations were elevated when compared with minimum levels is shown in Figure 3. Concentrations of six VOCs (acetylene, propane, 1,3-butadiene, benzene, toluene, and 2,3-dimethylbutane) at each horizontal distance (ranging from 13 m to 92 m) are normalized by the minimum concentration for that compound on the given sample day. Normalized concentrations are shown in this figure to be consistent with previous NATA exposure modeling assessments, where the relative increase in chemical concentrations is estimated for different distances from roadways. Thus, Figure 3 displays both the attenuation of compounds with horizontal distance as well as the variability among sampling events. A complete listing of normalized concentrations with distance is given in Tables S1-S5 (see Supporting Information).

Acetylene ratios are highest at two locations nearest the roadway ( $x = 13$  and  $19$  m), but a clear attenuation pattern across the entire range of distances is not evident. Furthermore, ratios for both acetylene and 1,3-butadiene have the highest variability among sampling events compared with the other compounds in Figure 3. While this discrepancy for acetylene and 1,3-butadiene largely resulted from variability among the different sampling days, no factor (e.g., wind speed, wind direction, temperature, and heavy truck traffic) could explain day-to-day differences for these species. The standard error (standard deviation divided by mean) was  $>100\%$  for the acetylene concentrations shown in Figure 3. As an example using two other compounds of similar reactivity (based on  $k_{OH}$  rate constants as reported in Fujita et al., 1995) and molecular weight as acetylene (n-butane and iso-butane), standard errors for these

compounds were typically 10–20%. Thus, it is unlikely that chemical reactivity can explain the variability seen in acetylene concentrations. As expected, ratios of propane concentrations remain unchanged across the sampling locations, likely the result that background sources of propane (e.g., compressed natural gas) were larger than localized vehicle exhaust emissions from the roadway.

The remaining three compounds in Figure 3 (benzene, toluene, and 2,3-dimethylbutane) decreased with distance from the roadway. The maximum to minimum ratio for these species is generally no more than 2, similar in magnitude to previous studies reporting total particle number concentrations (e.g., an approximately two-fold decrease during daytime from 30 to 90 m as reported in Zhu et al., 2006). In terms of the distance where normalized concentrations were within one standard deviation a ratio = 1, for both acetylene and 1,3-butadiene this occurred at  $x = 19$  m whereas for other compounds this occurred at farther distances (e.g., benzene at  $x = 58$  m, toluene at  $x = 43$  m, and 2,3-dimethylbutane at  $x = 74$  m).

One interesting feature to Figure 3 is that the lowest normalized concentration (indicated by the horizontal line at  $y = 1$ ) typically did not occur at the farthest distance from the roadway. Although differences among the farthest three distances were generally not statistically significant for VOC species, a pattern of increasing concentration for the last distance is evident in Figure 3. While this pattern may be the result of additional sources of VOCs near the study location, a preliminary factor analysis did not indicate any sources other than those considered for CMB analysis (described below). Secondary roads near the study location may have also contributed to ambient VOC levels, although traffic counts for these were several orders of magnitude less than the main highway.

Most of the species in Figure 3 have been used as markers for vehicle exhaust, and a recent study (Chang et al., 2006) has reported that several branched alkanes (2,2-dimethylbutane, 3-methylpentane, methylcyclopentane, 2-methylhexane, and 3-methylhexane) are correlated with known vehicle markers based on samples measured in urban areas. Variability among sampling events for both benzene and toluene was typically lower than other compounds in Figure 3, whereas variability of branched alkanes (2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, methylcyclopentane, 2-methylhexane, and 3-methylhexane) were similar to that seen for 2,3-dimethylbutane (see Figure S1, Supporting Information).

Although several factors were examined (wind speed, wind direction, temperature, and heavy truck traffic) to better describe variability among sampling events, only total traffic counts were found to consistently explain changes in normalized concentrations. In addition, no pattern was evident between morning and afternoon samples. One possible reason that other factors were not important was the comparatively narrow range of conditions for this study (e.g., wind speeds generally from 1 to 1.5 m/s, wind direction averaged across the sampling period that was generally perpendicular to the highway  $\pm 45^\circ$ , etc.) such that these factors only had a negligible effect on downwind concentrations. The effect of traffic was consistent across horizontal distance, especially at sampling distances nearest the roadway (see Figure S2, Supporting Information, where normalized benzene concentrations are given as a function of traffic from  $x = 13$  to 31 m). An example is shown for select VOCs in Figure 4, where normalized concentrations (from the  $x = 19$  m sampling location) are given as a function of traffic counts measured during the sampling period. While all compounds show increased concentrations with increasing traffic, especially strong relationships ( $r^2 > 0.9$ ) were seen for pentane, isopentane, and 2,2-dimethylbutane. Across all sampling events, the following VOCs had highest  $r^2$  values



(correlation coefficient of normalized concentration with traffic averaged across all sampling events): 3-methylhexane ( $r^2 = 0.86$ ), 3-methylpentane (0.84), o-xylene (0.84), acetylene (0.82), p-ethyltoluene (0.81), n-heptane (0.79), 1-butane (0.74), 2,3-dimethylbutane (0.74), 1,2,4-trimethylbenzene (0.65), and toluene (0.65). Although the small number of sampling events ( $n = 5$ ) precludes more detailed statistical comparisons, it is clear that several compounds in addition to traditional vehicle markers (acetylene, benzene, and toluene) show effects from changes in traffic.

### 3.2. Source apportionment results using CMB

Source apportionment results are shown in Figure 5 for the sampling event on 8/3/2006 for the base run scenario. The base run scenario includes the following compounds as fitting species: ethane, ethylene, acetylene, propylene, propane, n-butane, isopentane, n-pentane, n-hexane, benzene, and toluene. The model apportioned the observed data into four sources: motor vehicle exhaust, compressed natural gas, propane gas, and evaporative gasoline vapor. As expected, the majority of VOCs in Figure 5 resulted from motor vehicle exhaust ( $67 \pm 12\%$ ) (% of total VOC at  $x = 13 \text{ m} \pm \text{S.D.}$ ). Compressed natural gas, propane gas, and evaporative gasoline vapor accounted for approximately 15%, 7% and 1% of the total VOC emissions, respectively, at  $x = 13 \text{ m}$ .

As described earlier in the Data analysis section, initial attempts using CMB involved separation of gasoline and diesel sources. The main difficulty in this approach stems from similarity in VOC profiles. As an example, most compounds lighter than  $C_{10}$  are within a factor of two of one another for the gasoline and diesel profiles (Fujita, 2001). Some notable exceptions to this pattern include n-decane, n-undecane, and 1,2,3-trimethylbenzene. These three

compounds were generally below detection for this study, which likely explains the inability to separate gasoline and diesel exhaust sources.

Summary statistics for the base run scenario are presented in Table 2 for all sampling days. Reasonable measures of model performance (average  $r^2 = 0.93$ , average total VOC mass apportioned = 84%) were seen across all sampling events. The highest values for percent mass apportioned and motor vehicle exhaust contribution occur at  $x = 13$  m and these values decrease with increasing distance from roadway. The sampling day on 8/8/2006 provided the best measures of model performance: average total VOC mass apportioned of 93% and an average motor vehicle exhaust contribution of 69%. When the motor vehicle source contribution is normalized by the minimum value (occurring at  $x = 74$  m), concentration ratios are approximately 2.0 at  $x = 13$  m and decay to 1.0 by  $x = 74$ . This pattern is similar to the decays seen for benzene, toluene, and 2,3-dimethylbutane in Figure 3. Additional fitting species, shown to correlate with traffic as indicated in Figure 4, were added to the base run scenario to assess model performance for additional run scenarios: 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane (selection of fitting species given in Table S7). The apportioned sources and performance measures from the additional runs were slightly lower than results from the base run scenario (see Table S6, Supporting Information).

The MPIN matrix (see Table S7, Supporting Information), an indicator of influential species, showed the following marker species for each source: motor vehicle exhaust (toluene, benzene, and n-hexane), natural gas (ethane), propane gas (propane), and evaporative gasoline vapor (n-butane and isopentane). These results are consistent with existing source profiles (Mukerjee et al., 2004; Fujita, 2001; Watson et al., 2001). Moreover, all of the additional fitting

species for Runs 1-3 primarily loaded onto motor vehicle exhaust, except for 2,2-dimethylbutane (see Table S7, Supporting Information).

#### 4. Conclusions

These results provide a more comprehensive assessment of spatial gradients of VOCs near roadways than has been possible with previous studies. Results indicate that concentrations of most VOCs were highest at sampling locations closest to the roadway, and that levels decreased exponentially with distance from the roadway. In addition, a factor of two decrease in concentrations was generally observed for VOCs across the range of sampling locations, a result similar to studies previously reporting changes in bulk components (e.g., PM) near roadways.

Several source markers traditionally used to represent vehicle exhaust (e.g., benzene and toluene) were shown to vary with changes in traffic, whereas other traditional source markers (acetylene and 1,3-butadiene) displayed more unexplained variability in measured concentrations. Consequently, source apportionment results for motor vehicle exhaust were most influenced (as indicated by the MPIN matrix) by species such as benzene, toluene, and n-hexane. A number of additional fitting species were considered based on correlations with traffic: 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane. Except for 2,2-dimethylbutane, the influence on apportioned motor vehicle exhaust from these additional fitting species was similar to that of benzene, toluene, and n-hexane. Thus, future studies need to evaluate a variety of source markers when attempting to apportion motor vehicle exhaust from ambient concentrations of VOCs.



The results of this study provide important information for characterizing the impact of major roadways on VOC exposures. First, spatial variability is species dependent and different attenuation factors (maximum/minimum concentrations) should be used for acetylene and 1,3-butadiene than for benzene and toluene. Concentrations of benzene and toluene were elevated by a factor of 2 at 13 m from the road, but were near the minimum concentration level at 74 m from the road and had much less variability in this pattern than the more reactive species. Second, variability among samples was dependent upon traffic counts for several species, indicating that if a concentration relationship with traffic data could be developed then this could be incorporated into exposure modeling to characterize the day-to-day and diurnal variability in VOC concentrations near roadways.

#### **Disclaimer**

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## References

- Baldauf, R., Thoma, E., Isakov, V., Long, T., Snow, R., Khlystov, A., Hays, M., Shores, R., Kinsey, J., Gullett, B., Kimbrough, S., Weinstein, J., Chen, F.L., Seila, R., Olson, D., Gilmour, I., Cho, S.H., Watkins, N., Rowley, P., Bang, J., 2008. Traffic and meteorological impacts on near road air quality: Summary of methods and trends from the Raleigh near road study. *Journal of the Air and Waste Management Association*, 58, 865–878.
- Chan, C.Y., Chan, L.Y., Wang, X.M., Liu, Y.M., Lee, S.C., Zou, S.C., Sheng, G.Y., Fu, J.M., 2002. Volatile organic compounds in roadside microenvironments of metropolitan Hong Kong. *Atmospheric Environment*, 36, 2039–2047.
- Chang, C.C., Wang, J.L., Liu, S.C., Lung, S.C.C., 2006. Assessment of vehicular and non-vehicular contributions to hydrocarbons using exclusive vehicular indicators *Atmospheric Environment* 40, 6349–6361.
- Charron, A., Harrison, R.M., 2005. Fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particulate matter on a heavily trafficked London highway: Sources and processes. *Environmental Science and Technology* 39, 7768–7776.
- Choi, Y.J., Ehrman, S.H., 2004. Investigation of sources of volatile organic carbon in the Baltimore area using highly time-resolved measurements. *Atmospheric Environment* 38, 775–791.
- Fujita, E. M., 2001. Hydrocarbon Source Apportionment for the 1996 Paso del Norte Ozone Study *Science of the Total Environment* 276, 171–184.
- Fujita, E.M., Lu, Z., Sagebiel, J.C., Robinson, N.F., Watson, J.G., 1995. VOC source apportionment for the coastal oxidant assessment for southeast Texas—final report, Desert Research Institute, Reno, NV.
- Hellen, H., Hakola, H., Laurila, T., 2003. Determination of source contributions of NMHCs in Helsinki (60° N, 25° E) using chemical mass balance and the Unmix multivariate receptor models. *Atmospheric Environment* 37, 1413–1424.
- Hellen, H., Hakola, H., Pirjola, L., Laurila, T., Pystynen, K.H., 2006. Ambient air concentrations, source profiles, and source apportionment of 71 different C2-C10 volatile



- organic compounds in urban and residential areas of Finland. *Environmental Science and Technology* 40, 103–108.
- Legreid, G., Reimann, S., Steinbacher, M., Staehelin, J., Young, D., Stemmler, K., 2007. Measurements of OVOCs and NMHCs in a Swiss highway tunnel for estimation of road transport emissions. *Environmental Science and Technology* 41, 7060–7066.
- Lin, C.C., Chen, S.J., Huang, K.L., Hwang, W.I., Chang-Chien, G.P., Lin, W.Y., 2005. Characteristics of metals in nano/ultrafine/fine/coarse particles collected beside a heavily trafficked road. *Environmental Science and Technology* 39, 8113–8122.
- McGaughey, G.R., Desai, N.R., Allen, D.T., Seila, R.L., Lonneman, W.A., Fraser, M.P., Harley, R.A., Pollack, A.K., Ivy, J.M., Price, J.H., 2004. Analysis of motor vehicle emissions in a Houston tunnel during the Texas Air Quality Study 2000. *Atmospheric Environment* 38, 3363–3372.
- Mukerjee, S., Norris, G. A., Smith, L. A., Noble, C. A., Neas, L. M., Ozkaynak, A. H., Gonzales, M., 2004. Receptor model comparisons and wind direction analyses of volatile organic compounds and submicrometer particles in an arid, binational, urban air shed. *Environmental Science and Technology* 38, 2317–2327.
- Rosenbaum, A., M. Huang, 2007. The HAPEM6 User's Guide: Hazardous Air Pollutant Exposure Model, Version 6. Prepared by ICF, Inc. for the U.S. EPA. [http://www.epa.gov/ttn/fera/hapem6/HAPEM6\\_Guide.pdf](http://www.epa.gov/ttn/fera/hapem6/HAPEM6_Guide.pdf), 2007.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C1-C29 Organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33, 1578–1587.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C1-C32 Organic compounds from gasoline-powered motor vehicles. *Environmental Science and Technology* 36, 1169–1180.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34, 1821–1832.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837–3855.
- Seila, R. L., Main, H. H., Arriaga, J. L., Martinez, G., 2001. Atmospheric volatile organic compound measurements during the 1996 Paso del Norte Ozone Study. *Science of the Total Environment* 276, 153–169.
- U.S. Census Bureau, 2005. Current Housing Reports, Series H150/05, American Housing Survey for the United States: 2005. U.S. Government Printing Office, Washington, DC, 20401, <http://www.census.gov/prod/2006pubs/h150-05.pdf>.



- U.S. Environmental Protection Agency, 1999a. The 1999 National-Scale Air Toxics Assessment. <http://www.epa.gov/ttn/atw/nata1999/>.
- U.S. Environmental Protection Agency, 1999b. Compendium Method TO-14A: Determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography, Cincinnati, OH. EPA/625/R-96/010b.
- U.S. Environmental Protection Agency, 2001. National air quality and emission trends report, 1999. EPA-454/R-01-004, Office of Air Quality Planning and Standards, Research Triangle Park.
- U.S. Environmental Protection Agency, 2003. EPA-Enhance Ozone Monitoring (PAMS). <http://www.epa.gov/air/oaqps/pams/> (updated July 7, 2003; accessed September 21, 2004).
- U.S. Environmental Protection Agency, 2006. [www.epa.gov](http://www.epa.gov) Technology Transfer Network, Support Center for Regulatory Atmospheric Modeling. [www.epa.gov/scram001/receptor\\_cmb.htm](http://www.epa.gov/scram001/receptor_cmb.htm) (updated 28 December 2006; accessed 8 June 2007).
- Watson, J. G., Chow, J. C., Fujita, E. M., 2001. Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment* 35, 1567–1584.
- Wittig, A.E., Allen, D.T., 2008. Improvement of the Chemical Mass Balance model for apportioning—sources of non-methane hydrocarbons using composite aged source profiles. *Atmospheric Environment* 42, 1319–1337.
- Zhu, Y., Hinds, W.C., Kim, S., Sioutas, C., 2002. Concentration and size distribution of ultrafine particles near a major highway. *Journal of the Air and Waste Management Association* 52, 1032–1042.
- Zhu, Y., Kuhn, T., Mayo, P., Hinds, W.C., 2006. Comparison of daytime and nighttime concentration profiles and size distributions of ultrafine particles near a major highway. *Environmental Science and Technology* 40, 2531–2536.

## Figure captions

Figure 1. Map of sampling locations.

Figure 2. Concentrations of isopentane, toluene, benzene, and n-hexane as a function of horizontal distance for one sampling event.

Figure 3. Normalized VOC concentrations as a function of horizontal distance across all sampling events (for x-axis: "1" = 13 m, "2" = 19 m, "3" = 25m, "4" = 31m, "5" = 43 m, "6" = 58 m, "7" = 74 m, "8" = 92 m). Concentration ratio is the VOC concentration at each distance divided by the minimum for that sampling event. The standard deviation (whiskers in figure) is based on variance among all sampling events.

Figure 4. Normalized VOC concentrations for select species as a function of total traffic counts for one sampling event. Concentration ratio is the VOC concentration at each distance divided by the minimum for that sampling event.

Figure 5. Source contribution estimates for four-source solution using CMB for one sampling event. Error bars represent one standard error.

Table 1.

Statistical summary of VOC concentrations (ppbv)<sup>a</sup>

	Mean concentration (standard deviation) with distance from roadway							
	13 m	19 m	25 m	31 m	43 m	58 m	74 m	92 m
Acetylene	0.85 (0.39)	0.73 (0.38)	0.64 (0.34)	0.61 (0.32)	0.63 (0.37)	0.39 (0.25)	0.66 (0.28)	0.55 (0.24)
Ethane	1.91 (0.68)	1.94 (0.90)	1.90 (0.74)	1.97 (0.70)	2.01 (0.66)	2.46 (1.38)	2.19 (0.75)	2.30 (1.23)
Ethylene	3.10 (0.92)	2.54 (0.92)	1.84 (0.78)	1.94 (0.78)	2.10 (0.80)	2.23 (1.05)	1.82 (0.57)	1.95 (0.70)
Propane	2.27 (0.40)	2.21 (0.40)	2.24 (0.37)	2.18 (0.36)	2.15 (0.42)	2.45 (0.42)	2.25 (0.39)	2.27 (0.60)
Propylene	0.72 (0.16)	0.50 (0.25)	0.56 (0.17)	0.55 (0.16)	0.42 (0.15)	0.47 (0.24)	0.32 (0.11)	0.38 (0.11)
Isobutane	0.36 (0.06)	0.32 (0.08)	0.32 (0.07)	0.31 (0.08)	0.27 (0.05)	0.30 (0.11)	0.28 (0.05)	0.34 (0.10)
1-Butene	0.35 (0.07)	0.24 (0.13)	0.29 (0.07)	0.29 (0.07)	0.23 (0.10)	0.32 (0.15)	0.23 (0.12)	0.22 (0.06)
<i>n</i> -Butane	0.89 (0.17)	0.85 (0.22)	0.78 (0.20)	0.79 (0.17)	0.63 (0.16)	0.71 (0.33)	0.68 (0.15)	1.13 (0.77)
1,3-Butadiene	0.11 (0.03)	0.08 (0.04)	0.07 (0.03)	0.07 (0.03)	0.05 (0.02)	0.06 (0.03)	0.04 (0.02)	0.05 (0.02)
Isopentane	1.54 (0.25)	1.30 (0.35)	1.27 (0.32)	1.23 (0.31)	0.98 (0.19)	1.06 (0.39)	0.98 (0.21)	1.49 (0.72)
1-Pentene	0.21 (0.70)	1.30 (2.30)	0.17 (0.23)	0.97 (1.53)	1.68 (2.59)	0.07 (0.05)	1.53 (2.40)	0.43 (0.88)
<i>n</i> -Pentane	0.68 (0.12)	0.57 (0.16)	0.55 (0.13)	0.54 (0.14)	0.43 (0.09)	0.46 (0.16)	0.43 (0.10)	0.69 (0.35)
<i>n</i> -Hexane	0.28 (0.03)	0.24 (0.04)	0.25 (0.04)	0.23 (0.04)	0.19 (0.02)	0.21 (0.05)	0.18 (0.03)	0.25 (0.08)
2,2-Dimethylbutane	0.07 (0.03)	0.06 (0.03)	0.06 (0.03)	0.06 (0.03)	0.05 (0.03)	0.05 (0.03)	0.06 (0.03)	0.05 (0.02)
2,3-Dimethylbutane	0.11 (0.03)	0.09 (0.04)	0.09 (0.03)	0.09 (0.03)	0.07 (0.04)	0.07 (0.03)	0.07 (0.03)	0.09 (0.03)
2-Methylpentane	0.47 (0.12)	0.39 (0.15)	0.38 (0.13)	0.39 (0.13)	0.32 (0.14)	0.30 (0.12)	0.31 (0.15)	0.38 (0.14)
3-Methylpentane	0.28 (0.07)	0.24 (0.09)	0.23 (0.08)	0.23 (0.09)	0.19 (0.09)	0.18 (0.08)	0.19 (0.09)	0.27 (0.18)
Benzene	0.62 (0.12)	0.53 (0.12)	0.51 (0.12)	0.48 (0.12)	0.37 (0.06)	0.48 (0.28)	0.37 (0.10)	0.41 (0.10)
Cyclohexane	0.36 (0.13)	0.34 (0.24)	0.25 (0.09)	0.25 (0.10)	0.20 (0.13)	0.20 (0.06)	0.16 (0.06)	0.24 (0.17)
2-Methylhexane	0.12 (0.02)	0.09 (0.03)	0.10 (0.02)	0.09 (0.03)	0.07 (0.02)	0.07 (0.02)	0.07 (0.01)	0.09 (0.03)
3-Methylhexane	0.13 (0.02)	0.11 (0.03)	0.11 (0.03)	0.10 (0.03)	0.13 (0.16)	0.09 (0.03)	0.08 (0.02)	0.10 (0.03)
<i>n</i> -Heptane	0.18 (0.14)	0.15 (0.14)	0.15 (0.13)	0.17 (0.14)	0.13 (0.14)	0.11 (0.12)	0.15 (0.15)	0.12 (0.11)
Toluene	0.95 (0.16)	0.81 (0.21)	0.81 (0.21)	0.79 (0.19)	0.62 (0.11)	0.64 (0.22)	0.59 (0.11)	0.74 (0.26)
Ethylbenzene	0.19 (0.05)	0.21 (0.06)	0.20 (0.06)	0.18 (0.07)	0.15 (0.06)	0.14 (0.06)	0.15 (0.07)	0.17 (0.09)
<i>m,p</i> -Xylenes	0.52 (0.16)	0.45 (0.28)	0.48 (0.20)	0.48 (0.21)	0.36 (0.23)	0.39 (0.22)	0.36 (0.22)	0.45 (0.23)
Styrene	0.41 (0.26)	0.19 (0.09)	0.32 (0.12)	0.34 (0.17)	0.50 (0.46)	0.34 (0.12)	0.25 (0.14)	0.42 (0.13)
<i>o</i> -Xylene	0.21 (0.05)	0.17 (0.07)	0.18 (0.04)	0.17 (0.04)	0.13 (0.04)	0.15 (0.07)	0.13 (0.04)	0.17 (0.06)
<i>m</i> -Ethyltoluene	0.11 (0.03)	0.07 (0.04)	0.08 (0.03)	0.09 (0.03)	0.07 (0.03)	0.07 (0.02)	0.07 (0.04)	0.11 (0.05)
1,2,4-Trimethylbenzene	0.23 (0.07)	0.18 (0.05)	0.18 (0.06)	0.15 (0.03)	0.16 (0.04)	0.17 (0.04)	0.14 (0.04)	0.23 (0.08)

<sup>a</sup>Mean concentrations of the following compounds were <0.05 ppbv at the majority of sampling locations: Cyclopentane; 2,4-Dimethylpentane; 2,3-Dimethylpentane; Methylcyclohexane; 2,3,4-Trimethylpentane; 2-Methylheptane; 3-Methylheptane; *n*-Octane; *n*-Nonane; *n*-Decane; *n*-Propylbenzene; *o*-Ethyltoluene; 1,3,5-Trimethylbenzene; 1,2,3-Trimethylbenzene; *n*-Undecane; *n*-Dodecane; Isopropylbenzene.



Table 2.  
Summary Statistics for Base CMB Run

Date	Distance (m)	% Mass	MVE <sup>a</sup> (ppbV) and standard error
8/3/2006	13	89.2	16.31 ± 1.47
	19	80.7	11.78 ± 1.1
	25	84.2	11.72 ± 1.1
	31	85.7	10.92 ± 1.03
	43	60.1	9.37 ± 0.9
	58	79.2	11.71 ± 1.1
	74	60.4	7.48 ± 0.74
	92	64.8	8.34 ± 0.82
8/7/2006	13	97.1	11.31 ± 1.05
	19	95.7	7.64 ± 0.74
	25	85.3	8.79 ± 0.84
	31	62.6	8.74 ± 0.84
	43	103.3	6.44 ± 0.64
	58	78.2	8.03 ± 0.77
	74	71.8	6.99 ± 0.69
	92	81.0	8.04 ± 0.78
8/8/2006	13	98.4	17.95 ± 1.59
	19	97.7	16.21 ± 1.45
	25	92.7	14.02 ± 1.27
	31	94.1	13.02 ± 1.19
	43	80.1	9.62 ± 0.91
	58	<sup>b</sup>	<sup>b</sup>
	74	97.4	9.11 ± 0.86
	92	93.1	13.9 ± 1.28
8/10/2006	13	93.4	16.13 ± 1.46
	19	87.3	12.83 ± 1.19
	25	88.2	11.18 ± 1.05
	31	84.8	10.75 ± 1.01
	43	83.1	9.65 ± 0.92
	58	82.1	8.87 ± 0.86
	74	78.0	7.82 ± 0.77
	92	76.6	8.11 ± 0.79
Average		84.1	10.73 ± 1.01

<sup>a</sup>MVE = motor vehicle composite source (96% automobile and 4% diesel emissions)

<sup>b</sup>Data not available for this sample

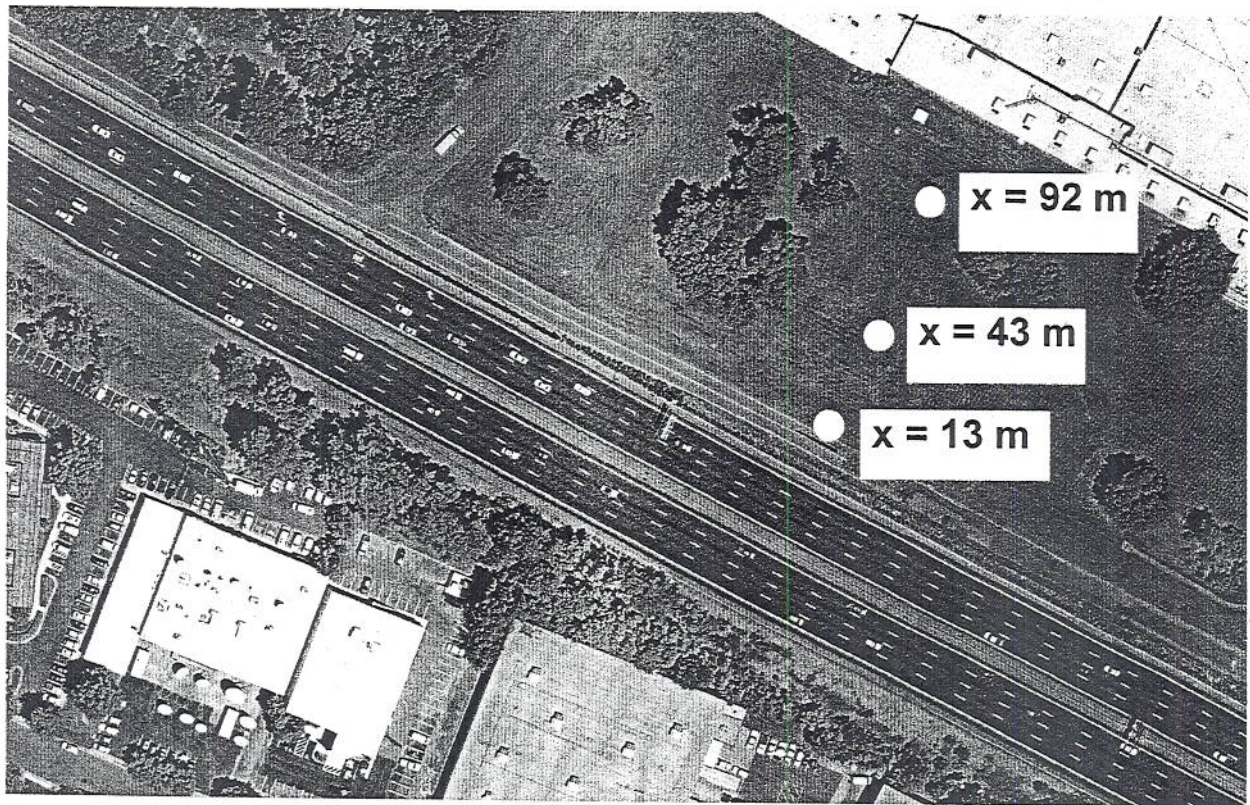


Figure 1.

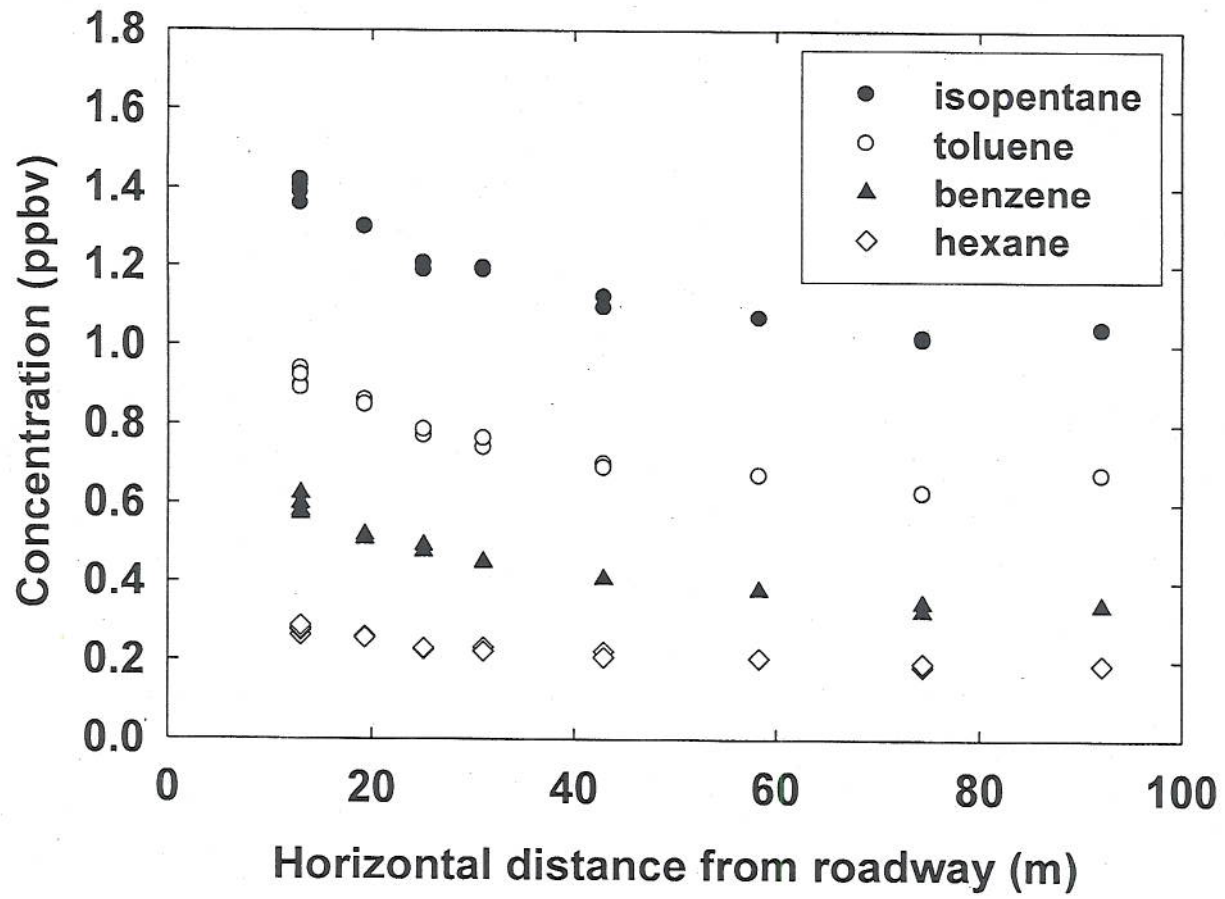


Figure 2.



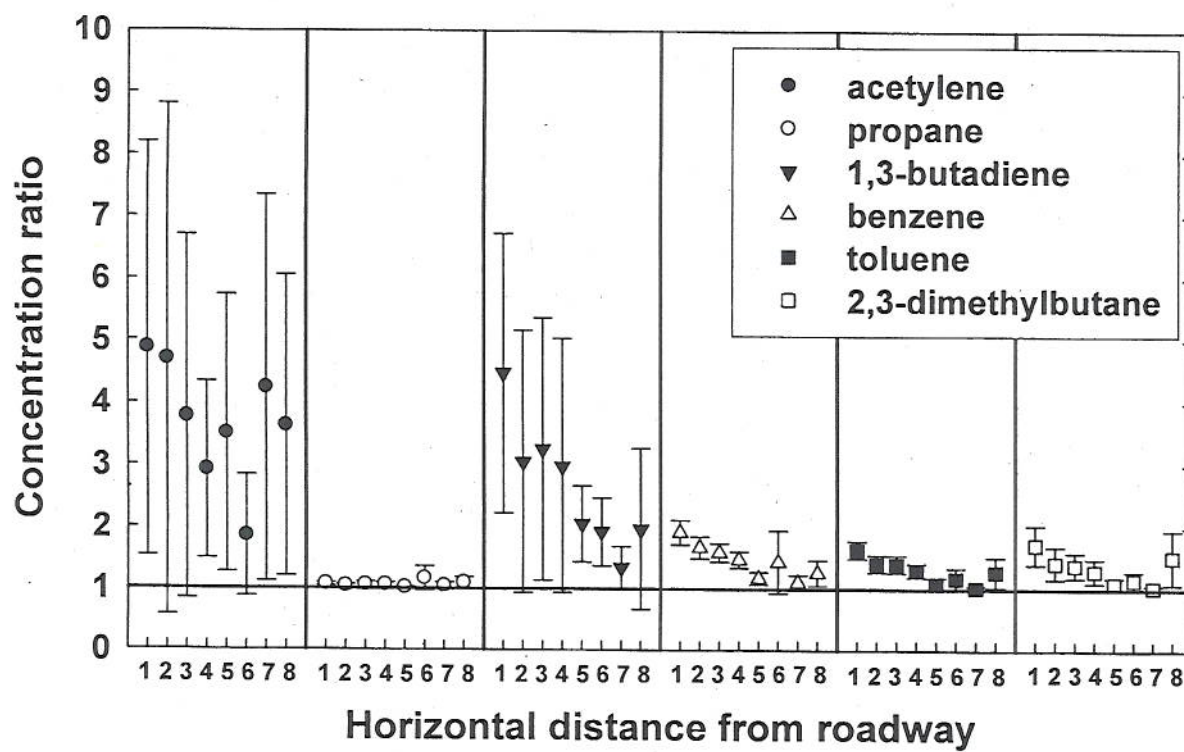


Figure 3.

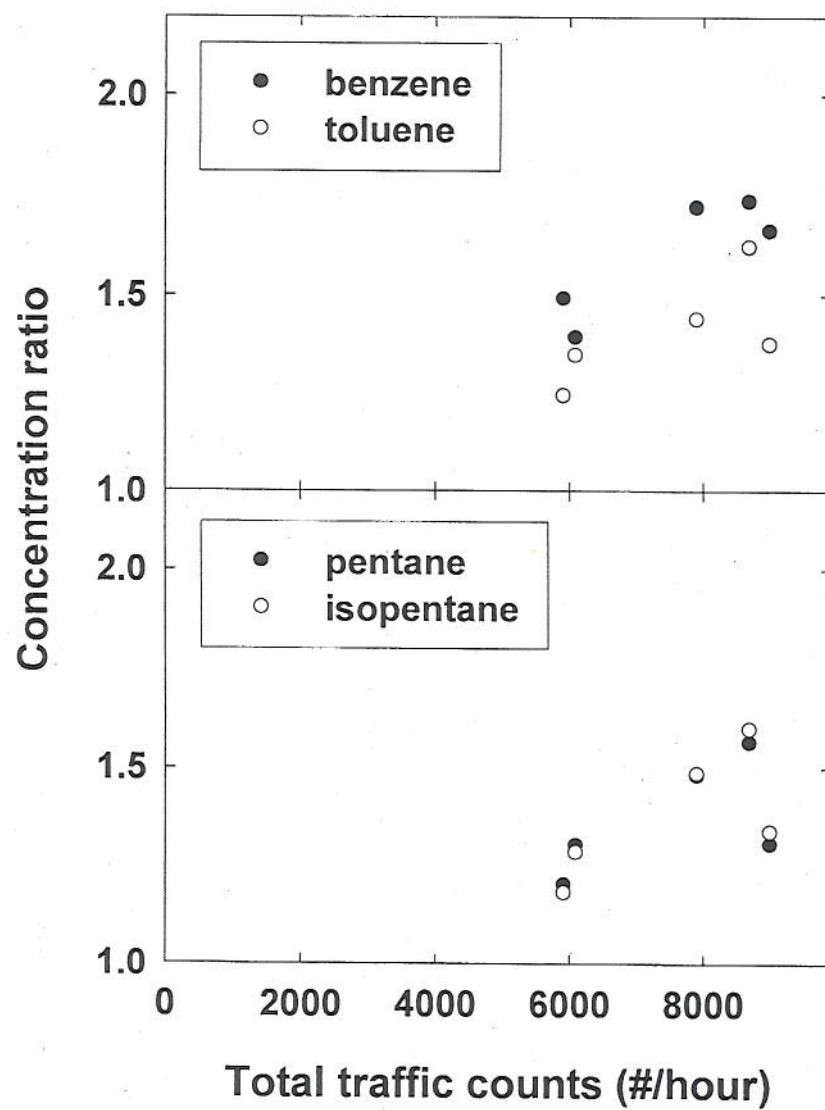


Figure 4.

