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Concentrations of Air Toxics in Motor Vehicle–Dominated Environments

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and Judith C. Chow



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with a Critique by the HEI Health Review Committee

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ABOUT HEI

The Health Effects Institute is a nonprofit corporation chartered in 1980 as an independent research organization to provide high-quality, impartial, and relevant science on the effects of air pollution on health. To accomplish its mission, the institute

- Identifies the highest-priority areas for health effects research;
- Competitively funds and oversees research projects;
- Provides intensive independent review of HEI-supported studies and related research;
- Integrates HEI's research results with those of other institutions into broader evaluations; and
- Communicates the results of HEI's research and analyses to public and private decision makers.

HEI receives half of its core funds from the U.S. Environmental Protection Agency and half from the worldwide motor vehicle industry. Frequently, other public and private organizations in the United States and around the world also support major projects or certain research programs. HEI has funded more than 280 research projects in North America, Europe, Asia, and Latin America, the results of which have informed decisions regarding carbon monoxide, air toxics, nitrogen oxides, diesel exhaust, ozone, particulate matter, and other pollutants. These results have appeared in the peer-reviewed literature and in more than 200 comprehensive reports published by HEI.

HEI's independent Board of Directors consists of leaders in science and policy who are committed to fostering the public-private partnership that is central to the organization. The Health Research Committee solicits input from HEI sponsors and other stakeholders and works with scientific staff to develop a Five-Year Strategic Plan, select research projects for funding, and oversee their conduct. The Health Review Committee, which has no role in selecting or overseeing studies, works with staff to evaluate and interpret the results of funded studies and related research.

All project results and accompanying comments by the Health Review Committee are widely disseminated through HEI's Web site (www.healtheffects.org), printed reports, newsletters and other publications, annual conferences, and presentations to legislative bodies and public agencies.

ABOUT THIS REPORT

Research Report 156, *Concentrations of Air Toxics in Motor Vehicle–Dominated Environments*, presents a research project funded by the Health Effects Institute and conducted by Dr. Eric M. Fujita, of the Division of Atmospheric Sciences, Desert Research Institute, Reno, Nevada, and his colleagues. This report contains three main sections.

The HEI Statement, prepared by staff at HEI, is a brief, nontechnical summary of the study and its findings; it also briefly describes the Health Review Committee's comments on the study.

The Investigators' Report, prepared by Fujita and colleagues, describes the scientific background, aims, methods, results, and conclusions of the study.

The Critique is prepared by members of the Health Review Committee with the assistance of HEI staff; it places the study in a broader scientific context, points out its strengths and limitations, and discusses remaining uncertainties and implications of the study's findings for public health and future research.

This report has gone through HEI's rigorous review process. When an HEI-funded study is completed, the investigators submit a draft final report presenting the background and results of the study. This draft report is first examined by outside technical reviewers and a biostatistician. The report and the reviewers' comments are then evaluated by members of the Health Review Committee, an independent panel of distinguished scientists who have no involvement in selecting or overseeing HEI studies. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, as necessary, to revise their report. The Critique reflects the information provided in the final version of the report.

PREFACE

HEI's Research Program on Air Toxics Hot Spots

INTRODUCTION

Air toxics comprise a large and diverse group of air pollutants that, with sufficient exposure, are known or suspected to cause adverse effects on human health, including cancer effects on the development of organs and tissues, and damage to the respiratory, immune, neurologic, and reproductive systems. These compounds are emitted by a variety of indoor and outdoor sources and large numbers of people are exposed to them. Therefore, the compounds are a cause for public health concern, even though the ambient levels are generally low. The low ambient levels are one reason that tools and techniques for assessing specific health effects of air toxics are very limited.

Air toxics are not regulated by the U.S. Environmental Protection Agency (EPA) under the National Ambient Air Quality Standards. However, it is required under the Clean Air Act and its amendments to characterize, prioritize, and address the effects of air toxics on public health and the environment, and it has the statutory authority to control and reduce the release of air toxics. The EPA is also required to regulate or consider regulating air toxics derived, at least in part, from motor vehicles (referred to as mobile-source air toxics [MSATs]) by setting standards for fuels, vehicle emissions, or both. In 2001 the EPA identified 21 MSATs that needed to be reduced (U.S. EPA 2001a). However, the EPA did not take any regulatory action because rules mandating the reduction of sulfur in both gasoline and diesel fuels as a way to decrease particulate matter (PM) in emissions were expected to result in the reduction of several MSATs as well (U.S. EPA 2000, 2001b). Subsequently, the EPA identified eight MSATs that, based on their emissions and reported toxicity, pose the greatest risk to health—benzene, 1,3-butadiene, formaldehyde, acrolein, naphthalene, polycyclic organic matter, diesel particulate matter, and diesel exhaust organic gases—and mandated the reduction of benzene in gasoline and of

hydrocarbons (including MSATs) in exhaust (U.S. EPA 2007). In 2007, HEI published a critical review of the literature on exposure to and health effects associated with these highest-priority MSATs (HEI Air Toxics Review Panel 2007).

In trying to understand the potential health effects of exposure to toxic compounds, scientists often turn first to evaluating responses in highly exposed populations, such as occupationally exposed workers. However, workers and their on-the-job exposures are not representative of the general population, and therefore such studies may be somewhat limited in value.

Another strategy is to study populations living in hot spots—areas thought to have high concentrations of these pollutants owing to their proximity to one or more sources. Some hot spots may have sufficiently high pollutant concentrations that they may be studied to determine whether there is a link between exposure to air toxics and an adverse health outcome. Such areas offer the potential to conduct health investigations in groups that are more representative of the general population. Before health effects studies can be initiated, however, actual exposures to pollutants—including their spatial and temporal distributions—in such hot spot areas must be characterized.

DESCRIPTION OF THE PROGRAM

In January 2003, HEI issued a Request for Applications (RFA 03-1) entitled “Assessing Exposure to Air Toxics,” seeking studies aimed at identifying and characterizing exposure to air toxics from a variety of sources in areas or situations where concentrations were expected to be elevated. The rationale for the RFA was that understanding exposures in hot spots, as well as the sources of these exposures, would improve our ability to select the most appropriate sites, populations, and endpoints for subsequent health studies. HEI was particularly interested in studies that focused on MSATs.

Preface

Five studies, including the one by Fujita and colleagues described in this report (Research Report 156), were funded under this RFA to represent a diversity of possible hot-spot locations and air toxics. The studies are summarized below.

**“Assessing Exposure to Air Toxics,”
Eric M. Fujita, Desert Research Institute,
Reno, Nevada (Principal Investigator)**

Fujita and colleagues measured the concentrations of PM and MSATs on major California freeways and compared them with corresponding measurements obtained at fixed monitoring stations. The diurnal and seasonal variations in concentrations of selected pollutants and the contribution of diesel- and gasoline-powered vehicles to selected air toxics and elemental carbon were also determined.

**“Measurement and Modeling of Exposure to
Air Toxics and Verification by Biomarker,”
Roy M. Harrison, University of Birmingham,
Birmingham, United Kingdom
(Principal Investigator)**

In the study described in HEI Research Report 143 (2009), Harrison and colleagues investigated personal exposure to a broad range of air toxics, with the goal of developing detailed personal-exposure models that would take various microenvironments into account. Repeated measurements of exposure to selected air toxics were made for each of 100 healthy nonsmoker adults who resided in urban, suburban, or rural areas of the United Kingdom, among which exposures to traffic were expected to differ; repeated urine samples were also collected for analysis. Harrison and colleagues developed models to predict personal exposure on the basis of microenvironmental concentrations and data from time–activity diaries; they then compared measured personal exposure with modeled estimates of exposure.

**“Assessing Personal Exposure to Air Toxics in
Camden, New Jersey,” Paul Lioy, Environmental
and Occupational Health Sciences Institute,
Piscataway, New Jersey (Principal Investigator)**

Lioy and colleagues measured ambient and personal exposure concentrations of air toxics and fine

PM for 107 nonsmoker participants in two neighborhoods of Camden, New Jersey. One, considered to be a hot spot, had a high density of industrial facilities serviced by truck traffic and nearby busy roads. The other, with no industrial sources but near several highways, was considered an urban reference site. Measurements were made at a central fixed monitoring site in different seasons on weekdays and weekends. To characterize finer spatial variability in pollutant levels, air toxics levels were measured at 16 or 22 sampling sites in each neighborhood during three sampling periods. The investigators also used modeling to estimate the contribution of ambient sources to personal exposure.

**“Air Toxics Exposure from Vehicular Emissions
at a U.S. Border Crossing,” John Spengler,
Harvard School of Public Health, Boston,
Massachusetts (Principal Investigator)**

The study by Spengler and colleagues assessed concentrations of MSATs surrounding the Peace Bridge Plaza, a major border crossing between the United States and Canada, located in Buffalo, New York. Three fixed monitoring sites were used to compare concentrations upwind and downwind of the plaza. Meteorologic measurements and hourly counts of trucks and cars were used to examine the relationship between the concentrations of air toxics and traffic density. To study spatial patterns, members of the investigative team walked along four routes in a residential neighborhood in West Buffalo while making measurements with mobile instruments and global positioning system devices.

**“Air Toxics Hot Spots in Industrial Parks
and Traffic,” Thomas Smith, Harvard School
of Public Health, Boston, Massachusetts
(Principal Investigator)**

The study by Smith and colleagues measured levels of air toxics and PM in truck cabins and in 15 truck terminals across the United States. The HEI study was added to an ongoing study, funded by the National Cancer Institute, of the relationship between exposure to diesel exhaust and mortality from lung cancer among dockworkers and truck drivers at more than 200 truck terminals in the United States. Smith and colleagues measured pollutants at upwind and downwind locations around the perimeter of each terminal

and at loading docks. The degree of variation at various locations and the influence of wind direction were also evaluated with the goal of identifying the potential impact of truck terminals on the surrounding areas. Continuous sampling was performed inside delivery truck cabins during a work shift.

The report on the study of Fujita and colleagues is the second of the five funded under RFA 03-1 to be published. Harrison and colleagues' report was published in 2009. The remaining studies have been completed and are currently at varying stages of the publications process. All are expected to be released this year. HEI is committed to continuing research on air toxics—for example, as part of studies to assess the health outcomes of air quality actions or studies to evaluate the effects of new technologies and fuels.

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HEI STATEMENT

Synopsis of Research Report 156

Concentrations of Air Toxics in Motor Vehicle–Dominated Environments

BACKGROUND

Motor vehicles and other combustion sources emit many air toxics whose levels are not regulated by the U.S. Environmental Protection Agency (EPA), but that are known or suspected, with sufficient exposure, to cause adverse health effects. Among these are mobile-source air toxics (MSATs), compounds the EPA has identified as derived, at least in part, from motor vehicles and whose emissions need to be reduced. Although monitoring has been performed by some state and local agencies in some locations, characterization of ambient levels of and personal exposure to air toxics has been limited. Though their ambient levels are generally low, there may be so-called hot spots where concentrations of one or more air toxics, and exposure of the population, are expected to be elevated. Such elevation may be due to the proximity of the hot spot to one or more pollution sources or to transient or sustained localized conditions that lead to elevated levels of particular pollutants. In 2003, HEI targeted research to identify and characterize potential hot spots.

APPROACH

Dr. Eric M. Fujita and colleagues measured the concentrations of several MSATs and other pollutants on urban highways in Los Angeles County with a varying mix of gasoline- and diesel-powered traffic and at various fixed sites in the vicinity of the roads. The main goals were to compare on-road concentrations with those at fixed sites and those measured at monitoring sites managed by the South Coast Air Quality Management District (SCAQMD) and to estimate the contributions of gasoline- and diesel-powered vehicles to MSATs, particulate matter $\leq 2.5 \mu\text{m}$ in aerodynamic diameter ($\text{PM}_{2.5}$), and elemental carbon (EC).

The pollutants measured were carbon monoxide (CO), oxides of nitrogen (NO_x), MSATs (benzene, toluene, ethylbenzene, xylene, styrene, naphthalene, *n*-hexane, 1,3-butadiene [BD], methyl *tert*-butyl ether, formaldehyde, acetaldehyde, and acrolein) and other volatile organic compounds (VOCs), $\text{PM}_{2.5}$, EC, and black carbon (BC).

The study was conducted in the southern portion of Los Angeles County for several weeks during the summer and fall of 2004. A combination of time-integrated and continuous measurements were made in the following location classes: (1) on roads; (2) at sites at various distances from the roads (referred to as spatial surveys); and (3) at three near-road sites with varying proportions of gasoline- and diesel-powered vehicles. For the on-road sampling, a van equipped with monitoring instruments and operating with windows and vents fully opened and a circulating fan turned on was driven for 1 hour on three commuting routes at peak commuting times and on one freeway loop with a higher fraction of diesel-truck traffic (referred to as the truck route). Spatial surveys were conducted immediately after the morning on-road sampling and immediately before the afternoon on-road sampling by stopping the van for a few minutes at locations at various distances from these routes. The three near-road sites, Long Beach, Lynwood, and Diamond Bar, were located in the same general geographic area as the routes for the on-road measurements and were sampled for 24 hours.

Source apportionment was conducted using the chemical mass balance model to estimate the contributions of gasoline- and diesel-powered vehicles to VOCs, the sum of benzene, toluene, ethylbenzene, and toluene (BTEX), total carbon (the sum of EC and organic carbon), and EC. The model uses measured pollutant concentrations, along with source composition information, to determine the contributions of primary sources to the measured concentrations.

RESULTS AND INTERPRETATION

Measured Concentrations The spatial patterns of on-road concentrations of BC, NO_x, CO, and total VOCs (all measured with continuous monitors) differed. Concentrations of CO and VOCs were higher on the commuting routes, whereas concentrations of BC and NO_x were higher on the truck route. The spatial and temporal variations of on-road concentrations of BTEX and BD were similar to those of corresponding time-averaged continuous CO and total VOC concentrations—higher on the commuting routes in the morning, and in the fall. Formaldehyde and acetaldehyde showed less diurnal variation. The concentrations of MSATs were consistently higher (by about a factor of 2) on the commuting routes than on the truck routes.

The on-road concentrations of nearly all pollutants were higher than those at the survey sites, the near-road sites, and the SCAQMD sites. Unexpectedly, on-road concentrations of acrolein were lower than those at the SCAQMD air toxics sites (but higher than those at the near-road sites).

The findings of higher on-road concentrations are consistent with results of studies that have found that the levels of pollutants decrease with distance from roads. Meteorologic factors (such as wind direction and speed) play a major role in the shape of the decay curves. However, the Review Committee, in its independent review of the study, thought that in the absence of information about the relationship between the roads and the fixed sites, such as the distance between the sites and the sampled roads and other roads, only general qualitative relationships can be inferred from this study. An additional factor that makes comparisons between on-road and near-road measurements difficult to interpret is the different durations of sampling for MSATs (1 hour on road during peak pollution and 24 hours at the near-road sites).

Source Apportionment Apportionment of total VOCs to sources showed that gasoline exhaust was the predominant source for both on-road and near-road concentrations, ranging from 70% for some of the samples at the near-road sites to about 100% for on-road samples. The contribution of diesel exhaust was small (22%) and more significant on the truck route. Apportionment of BTEX showed that gasoline was the dominant source (94% to 100%) for all on-road samples (including those from the diesel-dominated road) as well as those from the near-road sites (83% to 100%).

Apportionment of ambient total particulate carbon (TC) associated with particulate matter to the near-road samples showed a greater contribution from

diesel exhaust (averaging 46% to 52%) than from gasoline exhaust and evaporative emissions, which ranged from 10% to 17% in the summer, but did not show any significant contribution in the fall (0% to 4%). About 40% to 50% of TC was not apportioned to mobile sources. These results are consistent with our knowledge of the emission compositions of gasoline and diesel vehicles when the study was conducted.

Apportionment of EC showed that diesel exhaust contributed 88% to 94% at the three near-road sites. Although the authors interpret these results to be an indication that EC may be a good surrogate for diesel exhaust, the Review Committee noted that the correlation between EC and truck counts was not as good as that with total traffic counts. Overall, the Committee noted that it was difficult to assess the accuracy of the quantitative split between the contributions from diesel- and gasoline-powered vehicles to EC.

CONCLUSIONS

The HEI Health Review Committee thought that Fujita and his colleagues had conducted a comprehensive study focused on the characterization of MSATs and other gaseous pollutants and carbonaceous PM on Los Angeles freeways and roadways and in several locations in the Los Angeles air basin, and that they had collected high-quality data. The study's main conclusions are that (1) on-road concentrations of all pollutants measured, including several MSATs, were higher than those measured at fixed sites away from the roads, (2) gasoline-powered vehicles are the main sources of VOCs (including BTEX) at the near-road sites, and (3) diesel- and gasoline-powered vehicles contribute about 50% to 60% of TC associated with PM.

Though on-road concentrations were higher than near-road concentrations, the question of whether busy highways during commuting hours are hot spots for exposure to MSATs is hard to address, given the design of the in-vehicle sampling, which does not reflect the ventilation conditions in the vehicles of most commuters. However, concentrations as high as those measured in the study may be encountered by commuters if the driving conditions are similar to those examined in this study. The near-road sites were chosen because they were assumed to be affected by traffic, but the investigators do not discuss whether they could be hot spots for exposure. Thus, this question remains unresolved.

Emissions from motor vehicles have been changing rapidly as a result of new emission control technologies and new fuels. The data collected in this study on MSATs and other pollutants on and near roads provide important baseline information for ongoing and future studies.

Concentrations of Air Toxics in Motor Vehicle–Dominated Environments

Eric M. Fujita, David E. Campbell, Barbara Zielinska, William P. Arnott, and Judith C. Chow

Division of Atmospheric Sciences, Desert Research Institute, Reno, Nevada

ABSTRACT

We at the Desert Research Institute (DRI*) measured volatile organic compounds (VOCs), including several mobile-source air toxics (MSATs), particulate matter with a mass mean aerodynamic diameter $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$), black carbon (BC), nitrogen oxides (NO_x), particulate matter (PM), and carbon monoxide (CO) on highways in Los Angeles County during summer and fall 2004, to characterize the diurnal and seasonal variations in measured concentrations related to volume and mix of traffic. Concentrations of on-road pollutants were then compared to corresponding measurements at fixed monitoring sites. The on-road concentrations of CO and MSATs were higher in the morning under stable atmospheric conditions and during periods of higher traffic volumes. In contrast, BC concentrations, measured as particulate light absorption, were higher on truck routes during the midday sampling periods despite more unstable atmospheric conditions. Compared to the measurements at the three near-road sites, the 1-hour averages of on-road BC concentrations were as much as an order of magnitude higher. The peak 1-minute average concentrations were two orders of magnitude higher for BC and were between two and six times higher for $\text{PM}_{2.5}$ mass. The on-road concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) during the summer were 3.5 ± 0.7 and 1.2 ± 0.6 times higher during morning

and afternoon commuting periods, respectively, compared to annual average 24-hour concentrations measured at air toxic monitoring network sites. These ratios were higher during the fall, with smaller diurnal differences (4.8 ± 0.7 and 3.9 ± 0.6 for morning and afternoon commuting periods, respectively). Ratios similar to those for BTEX were obtained for 1,3-butadiene (BD) and styrene. On-road concentrations of formaldehyde and acetaldehyde were up to two times higher than at air toxics monitoring sites, with fall ratios slightly higher than summer ratios.

Chemical mass balance (CMB) receptor model calculations attributed the sum of BTEX almost exclusively to gasoline engine exhaust for on-road samples and all but 5% to 10% of the BTEX at the three near-road sites. CMB analysis attributed 46% to 52% (± 7) of the ambient total particulate carbon (TC) at the three near-road sites to diesel exhaust and 10% to 17% (± 7) to gasoline exhaust; it attributed about 90% of the ambient elemental carbon (EC) concentrations (measured as refractory carbon using the thermal evolution method) to diesel exhaust. Diesel particulate carbon (DPC) concentrations were estimated by multiplying the mean ratio of TC to EC from the source-dominated ambient samples collected on road on Terminal Island (1.30 ± 0.28), which is located between the Long Beach and Los Angeles ports, with the measured ambient EC concentrations at the three near-road sites. DPC estimates from EC measurements correlate well with the diesel source contributions calculated with the CMB model. The indication from these apportionments that BC or EC is a good surrogate for diesel exhaust is further supported by the positive correlation of on-road BC concentrations with volumes of truck traffic.

Traffic counts have been used in past health assessment studies as surrogates for estimating near-road exposure concentrations with appropriate weighting for proximity to the road. However, the results of this study show that it is necessary to account for the proportion of diesel trucks to total vehicular traffic because of the disproportionate contribution of diesel exhaust to BC and to directly emitted PM. Alternatively, easily measured pollutants such as CO and BC can serve as reasonable surrogates for MSATs

This Investigators' Report is one part of Health Effects Institute Research Report 156, which also includes a Critique by the Health Review Committee and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Dr. Eric M. Fujita, 2215 Raggio Parkway, Reno, Nevada 89512; ericf@dri.edu.

Although this document was produced with partial funding by the United States Environmental Protection Agency under Assistance Award CR-83234701 to the Health Effects Institute, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency, and no official endorsement by it should be inferred. The contents of this document also have not been reviewed by private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views or policies of these parties, and no endorsement by them should be inferred.

* A list of abbreviations and other terms appears at the end of the Investigators' Report.

(e.g., BTEX and BD) and DPC, respectively. Measuring CO and BC is a reasonably cost-effective approach to quantifying hot-spot exposure concentrations of MSATs that is perhaps more accurate than what is possible using only data from regional air quality monitoring stations or air quality modeling results.

INTRODUCTION

In this study, we conducted a field measurement program during summer 2004 and fall 2004 to measure the concentrations of MSATs along major highways in Los Angeles County during morning and afternoon commuting periods and to estimate the contributions of gasoline-powered (or spark ignition [SI]) and diesel-powered (compression ignition [CI]) vehicles to the observed concentrations of MSATs. An important aim of the study was to obtain data that would complement the air toxics measurements made by the South Coast Air Quality Management District (SCAQMD) at various fixed monitoring locations during the third Multiple Air Toxics Exposure Study (MATES-III), which was conducted from February 2004 to March 2006. The pollutant concentrations measured on road were compared to corresponding values measured at nearby air quality monitoring stations and at various monitoring locations used in previous health risk assessment studies in the area.

BACKGROUND

Motor vehicles are the largest source of VOCs and fine particulate emissions in urban areas. Of the 33 hazardous air pollutants that the U.S. Environmental Protection Agency (U.S. EPA 2001) has identified as important urban air toxics, 21 are associated with motor vehicles. Additionally, the 1990 Clean Air Act Amendments specified formaldehyde, acetaldehyde, benzene, BD, and polycyclic organic matter (POM) as toxic air pollutants that may be subject to more stringent control. POM consists of polycyclic aromatic hydrocarbons (PAHs), their nitrogen analogs, and a small number of oxygen-containing PAHs. POM compounds are formed primarily from combustion and are present in the atmosphere in particulate form. The U.S. EPA has classified seven PAHs—benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, and dibenzo[*a,h*]anthracene—as probable human carcinogens (U.S. EPA Technology Transfer Network 2000) and has stated that they can be used as a surrogate for POM for the purposes of the Section 112(k) monitoring, emission inventory, and control requirements (U.S. EPA 2002). These priorities are supported by studies such as the MATES-II, which attributed about 70% of all carcinogenic

risk in the Los Angeles Basin in 1998 through 1999 (increased relative risk of cancer for 1400 per million people) to diesel particulate emissions and about 20% to other air toxics associated with mobile sources (including benzene, BD, formaldehyde, and acetaldehyde) (SCAQMD 2000).

Urban and regional air monitoring programs in the United States typically consist of a relatively limited number of widely spaced monitoring stations within a given airshed. While these monitoring networks are generally adequate for characterizing the spatial variations of secondary pollutants such as ozone, nitrogen dioxide (NO₂), and nitrate and sulfate particles, they are less useful for determining the range of exposure to directly emitted pollutants such as CO, diesel PM, and other toxic air contaminants (TACs). Ambient concentrations may vary in space and time, and gradients can be especially sharp near emission sources. These variations may result in significant differences between annual average ambient concentrations measured at fixed-site monitors, which are often used as surrogates for personal exposure, and actual personal exposures, which depend on the amount of time spent in outdoor and indoor environments and in high-exposure microenvironments (e.g., in vehicles during commutes).

Several studies (Wallace 1987; Chan et al. 1991; Weisel et al. 1992; Jo and Choi 1996; Duffy and Nelson 1997; Jo and Park 1999; Leung and Harrison 1999) have found that individuals are exposed to levels of VOCs while commuting that are several-fold higher than the corresponding concentrations measured in ambient air at nearby monitoring sites. In a recent study of ozone precursors in California's South Coast Air Basin (SoCAB), Fujita and colleagues (2003a) found that concentrations of BC* and NO_x were about an order of magnitude higher on roadways relative to regional air monitoring sites, and VOCs and CO were factors of 2 to 4 higher on roadways. Westerdahl and colleagues (2005) also found that concentrations of ultrafine PM (< 100 nm), nitric oxide (NO), BC, and CO on freeways were frequently an order of magnitude higher than on residential streets. Others showed that traffic-related pollutants disperse rapidly downwind of the roadway (Zhu et al. 2002). These results suggest that the exposure to air pollutants for commuters and urban pedestrians would be underestimated by using fixed-site monitoring data or predicted concentrations from grid-based air quality simulation models.

Several studies have linked proximity to traffic to adverse health effects. Most of these studies used data from central

* In this report "BC" refers to carbon that absorbs light, which is measured with instruments such as an aethalometer or a photoacoustic analyzer that measure light absorption. "EC" refers to refractory carbon measured using thermal evolution methods.

monitoring sites or surrogates of exposure to traffic emissions such as proximity and traffic volumes. In a recent example, Wilhelm and Ritz (2003) conducted an epidemiologic case-control study of the effects of residential proximity to traffic and adverse birth outcomes in Los Angeles. They observed a 10% to 20% increase in the risk of pre-term birth and low birth weight in infants born to women potentially exposed to high levels of traffic-related air pollution, as represented by the distance-weighted traffic density at their homes. The weighting was based on a Gaussian decay away from the roadway. Traffic density was based on total traffic and did not account for varying proportions of trucks to total vehicular traffic. Kim and colleagues (2004) conducted a school-based, cross-sectional study of the relationship between measured traffic-related pollutant concentrations outside the schools and respiratory symptoms. They found a modest but significant increase of 5% to 8% in bronchitis and asthma symptoms in children residing at their current address for at least one year in neighborhoods with higher concentrations of traffic pollutants. This study did not examine the relative effects of diesel-truck traffic versus total vehicular traffic.

Diesel particulate matter (DPM) is composed of a center core of EC coated with organic compounds as well as small amounts of sulfate, nitrates, metals, and other trace elements. The EC content of DPM can vary widely depending on engine type, load conditions, and test cycle. Furthermore, EC and organic carbon (OC) are operationally defined and vary with measurement method and protocol. Emission rates of EC are relatively low for gasoline engines but can be higher during cold starts and during hard accelerations. EC measurements were used in MATES-II (SCAQMD 2000) to estimate DPM concentrations according to the relationship of EC to DPM determined by Gray (1986): Approximately 67% of fine EC in the ambient air in the Los Angeles area originated from diesel-engine exhaust, and the average EC fraction of DPM measured was 64%. In MATES-II, SCAQMD estimated DPM concentrations from EC measurements by multiplying a measured EC concentration by 67% and dividing by the fraction of DPM mass accounted for by EC (64%) (SCAQMD 2000). That is, $DPM\ concentration = (EC \times 0.67)/0.64$, or $DPM = EC \times 1.04$. Despite the uncertainties associated with this approach, EC or BC (measured with a continuous optical method) may provide a useful surrogate for estimating DPM in the absence of a more sophisticated receptor modeling analysis for locations where fine-PM EC or BC concentrations are available.

STUDY OBJECTIVES

This study was conducted to measure the concentrations of MSATs on urban highways in Los Angeles County

with a varying mix of gasoline- and diesel-powered vehicles during peak commuting periods and to compare those measurements with the concentrations of air toxics measured at nearby fixed monitoring stations (near-road and neighborhood-scale) and at several locations in Los Angeles County that have been used in past exposure and health risk assessment studies (e.g., schools located near roadways). The purpose of the measurements is explained after each study objective, listed next.

1. Measure concentrations of CO, NO, NO_x, volatile organic air toxics (BTEX, styrene, naphthalene, *n*-hexane, BD, methyl *tert*-butyl ether [MTBE], formaldehyde, acetaldehyde, and acrolein), PM_{2.5}, and BC on highways in Los Angeles County inside a vehicle traveling during the morning and afternoon commuting periods during both summer and fall, and relate the variations in measured concentrations of MSATs to the varying proportions of gasoline and diesel vehicles.

We measured ambient pollutant concentrations on three freeway routes with varying traffic mixes. Two routes had predominantly light-duty gasoline vehicles, and the third route had a greater proportion of diesel vehicles. Measurements were also made after the morning commuting period on a portion of the truck route connecting the port area in the southwest part of the basin to the inland distribution centers in the eastern basin (referred to as the "freeway loop").

Note that these measurements did not reflect the effects of varying ventilation conditions on pollutant concentrations inside the vehicles. Windows and vents in the mobile sampling van were fully opened so that the air inside the vehicle represented the ambient air on the roadway. Therefore, these measurements correspond to the exposure concentrations due to on-road vehicle emissions under maximum ventilation conditions. Estimation of exposure concentrations under varying ventilation conditions was beyond the scope of this work.

2. Compare the MSAT, CO, and NO concentrations on roadways to concentrations measured at fixed air quality monitoring sites (SCAQMD routine monitoring for CO, NO, and air toxics), at MATES-III fixed measurement sites, and at near-road locations used in the California Air Resources Board (ARB) monitoring for the Children's Environmental Health Protection Act (state bill [SB] 25).

We examined the quantitative relationships between the concentrations of MSATs on urban highways in Los Angeles County during peak commuting periods relative to the concentrations of air toxics measured at nearby fixed monitoring stations. The data for MATES-III were under review

by SCAQMD when this report was prepared and were not released to the public until January 2008. Consequently, the comparisons of roadway concentrations of MSATs with the concentrations measured at fixed-site monitors in this report are based on CO and NO_x data from SCAQMD's criteria pollutant monitoring program and data from the routine air toxics monitoring program conducted jointly by SCAQMD and the California ARB.

We also compared the on-road pollutant concentrations to measurements we took at sampling locations that were used in MATES-III and from previous exposure-assessment studies conducted by the California ARB. In addition, we measured pollutant concentrations for several minutes at four to six locations (fixed “survey” sites) along a prescribed route with the continuous monitors on board the mobile sampling van. We conducted these surveys either shortly prior to or after the on-road sampling, in order to compare pollutant levels within the community to the higher on-road pollutant concentrations. We did not intend these surveys to quantitatively examine the gradients in pollutant concentrations near highways. Such studies require saturation monitoring at various distances from the roadway for periods of time that are sufficient for developing quantitative relationships between the measured pollutant gradients and variations in traffic mix and volume and meteorologic conditions. This was beyond the scope of our study.

In response to SB 25, the ARB conducted special studies in Boyle Heights, Wilmington, and four other communities in California at locations where children are typically present and near busy highways and industry sources of pollution. The air quality monitoring study in the residential area of Boyle Heights in Los Angeles was conducted during 2001 and 2002 (California ARB 2003). Hollenbeck Middle School, which is located approximately one-half mile downwind of the convergence of four major Los Angeles area freeways (Interstates 5 and 10, U.S. Route 101, and State Route 60), was chosen by the ARB as the primary air monitoring site. Monitoring sites were also established at the East Los Angeles Mathematics, Science, and Technology Center (Science Center) and the Soto Street Elementary School. The Soto Street School is immediately adjacent to a freeway off-ramp and the intersection of several freeways, and the Science Center is near SR-60. The ARB study found that levels of particulate matter with a mass mean aerodynamic diameter $\leq 10 \mu\text{m}$ (PM₁₀) at the Soto Street School exceeded the state air quality standard for PM₁₀ about three times as often as did the levels of PM₁₀ at the Science Center, the Hollenbeck Middle School, and the two closest long-term monitoring sites in downtown Los Angeles and Burbank. PM₁₀ levels dropped rapidly away from the Soto Street School and the adjacent freeways

and traffic. Average criteria pollutant levels at the Hollenbeck Middle School and the two long-term monitoring sites in downtown Los Angeles and Burbank were similar.

The fixed sampling sites for MATES-III were located in Anaheim, Burbank, *Compton*, Fontana, *Huntington Park*, *North Long Beach*, *Central Los Angeles–North Main Street*, *Pico Rivera*, Rubidoux, and West Long Beach. Microscale sites were located in Sunland, San Bernardino, and *City of Commerce*. (MATES-III sites in italics in the preceding list are located in our study area.) Sampling at each of the MATES sampling sites was conducted every third day, and 24-hour PM_{2.5} samples were collected for mass, OC and EC (using the Interagency Monitoring of Protected Visual Environments–thermal optical reflectance protocol [IMPROVE–TOR]), heavy metals, and particulate polycyclic aromatic hydrocarbons (PAHs). Also, every third day three 8-hour canister samples were collected to measure benzene, BD, naphthalene, and chlorinated hydrocarbons, and 2,4-dinitrophenylhydrazine (DNPH) cartridge samples were collected to measure formaldehyde, acetaldehyde, and acrolein. The MATES-III sites within our study area were included in our spatial surveys of pollutant concentrations. However, data from MATES-III were not available in time for inclusion in this report because of the one-year extension of the study.

The results of this study provide information that will permit estimates of proximity factors used in exposure models such as the Air Pollutants Exposure Model (APEX) and the Hazardous Air Pollutant Exposure Model (HAPEM) (Rosenbaum, 2000).

- Using the CMB receptor model, estimate the contributions of gasoline- and diesel-powered vehicles to VOCs, PM_{2.5}, EC, and MSATs at three near-road locations with varying proportions of diesel- and gasoline-vehicle traffic. Reconcile these results with the spatial patterns of the concentrations of BC (a surrogate of diesel PM) and of CO (a surrogate of gasoline exhaust) observed on nearby commuting routes.

We selected three sites for examining the concentrations of near-road pollutants associated with traffic consisting predominantly of gasoline vehicles, diesel trucks, or a roughly equal mixture of the two. Unlike sampling from the mobile van, sampling at the near-road sites allowed for the collection of sufficient amounts of PM mass on filters for quantitative analysis of speciated organic compounds. The resulting data were used to apportion the relative contributions of the exhaust from diesel and gasoline vehicles to MSATs using source-composition profiles that were recently developed in the SoCAB for VOCs (Fujita et al. 2004) and PM_{2.5} (Fujita et al. 2007b).

The CMB-derived estimates of the contribution of diesel exhaust to fine carbonaceous particles were compared to estimates of DPM concentrations derived from EC. The variations in the source contributions among the three near-road sites were compared to the continuous DustTrak (TSI, Shoreview, MN) photoacoustic analyzer measurements and the photoionization detector (PID) measurements at the three near-road sites and in the mobile sampling van on roadways and at various fixed “survey” sites. Concentrations of MSATs, CO, NO_x, PM_{2.5}, and BC were also related to the average daily truck counts and the total traffic counts on each of three commuting routes and a freeway loop.

4. Develop and implement measures to address sampling and analytic artifacts related to potential loss of BD and acrolein after sample collection. Accurate measurements of BD and acrolein were a priority in this study because they are primarily associated with mobile sources of pollution and are key drivers of health risks. Sampling and analysis artifacts affect the measurements of BD taken using U.S. EPA method TO-14 (collection in stainless steel canisters and analysis by gas chromatography [GC] with flame ionization detection) and also the measurements of acrolein taken using U.S. EPA method 11 (collection on DNPH cartridges and analysis by liquid chromatography with ultraviolet [UV] detection). Therefore, we gave special attention in this study to the choice of sampling and analysis methods and to potential procedures for mitigating the effects of artifacts on measurement accuracy.

STUDY DESIGN AND DATA ANALYSIS

We conducted a field measurement program to determine the range of concentrations of MSATs along major highways in Los Angeles County during morning and afternoon commuting periods and to estimate the contributions of SI vehicles and CI vehicles to the observed concentrations.

DESCRIPTION OF STUDY AREA

We conducted the fieldwork for this study in the southern portion of Los Angeles County. Los Angeles County is the most populous county (about 10 million residents in 2005) in the United States and has the 16th largest economy in the world. The county covers a total area of 4752 square miles and accounts for almost a quarter of the total number of annual vehicle miles traveled in California. Los Angeles County lies within the SoCAB, which also contains Orange County, Riverside County, and part of San Bernardino County. The southern portion of Los Angeles

County is bounded by the Pacific Ocean to the west, the San Gabriel Mountains to the north, and the Santa Ana Mountains to the south. These ranges converge to the east where a relatively narrow opening leads to the inland valley of San Bernardino. The complex terrain in the region adds mesoscale components to the varying synoptic-scale meteorology that affect the movement of pollutants within the SoCAB.

Southern California is in the semipermanent high-pressure zone of the eastern Pacific. Precipitation is rare during the summer. Frequent and persistent temperature inversions often occur during periods of maximum solar radiation; these create mixed daytime atmosphere layers of approximately 1000 m thickness. During the summer, the sea–land breeze is strong during the day, and a land–sea breeze is weak at night. Nocturnal and morning winds are less vigorous than daytime winds. The land surface cools sufficiently to create surface inversions with depths as shallow as approximately 50 m. Surface heating usually erodes the surface and marine layers within a few hours after sunrise each day. Summertime flow patterns are from the west and south during the morning, switching to predominantly westerly winds by the afternoon. The land–sea breeze circulation moves air back and forth between the SoCAB and the Pacific Ocean, as well as along the coast to other air basins. The levels of secondary pollutants such as ozone and formaldehyde are highest during the summer months, but local concentrations of directly emitted pollutants such as CO and MSATs are lower than during the fall due to greater dispersion of pollutants.

The semipermanent high-pressure zone begins to break down in fall. Typically, by late September, the midlatitude transient weather systems start to invade the California coastline, affecting the northern California coast first and, later in the season, beginning to influence the southern California coastline. These transient systems continue to have an impact on the coast until early April. Yet, the very cold and dry penetrations that affect the southern California coast do not typically begin until early December (late fall). These cold and dry penetrations are usually associated with northwesterly flow, and the SoCAB is usually scoured of pollutants during these episodes. The synoptic weather situations that favor increases in pollution (as measured by PM_{2.5} concentrations) appear to occur during the quiescent periods during late fall (mid-October through early December). Typically, few strong cold-front passages occur during this time period, and although the weather is transient (i.e., successive passages of low- and high-pressure systems occur), the high-pressure systems dominate and persist for a longer time over the SoCAB. We conducted the summer phase of the field measurement program during September 2004 and the fall phase during

the fall stagnation period, from November through December 2004.

Mobile sources comprise the single largest source of pollutant emissions in the SoCAB, accounting in 2000 for about 62%, 88%, and 95% of the average daily VOC, NO_x, and CO emissions, respectively (California ARB 2001). Between 1980 and 2000, NO_x emissions from gasoline vehicles decreased by 37% in the SoCAB, while NO_x emissions from diesel vehicles increased by 40%. Consequently, the contribution of diesel trucks to the total NO_x emitted from on-road vehicles increased from 16% to 29%. Vehicle tests have shown that diesel trucks typically have much higher emission rates than gasoline vehicles on a gram per fuel or distance traveled basis for NO_x (20 to 30 times higher) and BC (100 to 1000 times higher) (Fujita et al. 2007a). In contrast, the CO and VOC emission rates of diesel trucks are comparable to those of gasoline vehicles. The proportion of diesel vehicles to the total vehicle population in Los Angeles County is small, but the diesel vehicles are concentrated in the port areas and along truck routes to container transfer facilities and warehouse distribution centers. The county's two main seaports are the Port of Los Angeles and the Port of Long Beach. Together they handle over a quarter of all container traffic entering the United States, making the complex the largest port in the county and the fifth largest port complex in the world. The port generates about 30,000 truck trips daily along I-710 and the Terminal Island Freeway (SR-103) between the port and the container transfer facilities located at the northern terminus of SR-103 and off I-710 in the city of South Gate. A higher concentration of diesel traffic also travels on the truck routes (I-710, SR-91, I-605, and SR-60) that connect the ports to the distribution centers in San Bernardino and Riverside.

MEASUREMENT APPROACH AND METHODS

Three sets of measurements were made using different combinations of time-integrated and continuous measurements: (1) on-road measurements, (2) spatial surveys from roadways to MATES-III and other fixed air quality monitoring sites, and (3) near-road measurements close to roads with varying proportions of gasoline and diesel vehicles.

Figure 1 shows the locations of sampling sites and routes for on-road measurements as well as the MATES-III and other nearby monitoring sites. In addition, integrated samples were collected on highways with either predominantly diesel-truck or gasoline-vehicle traffic. Data about the composition of these source-oriented ambient samples were compared to the source-composition data from the dynamometer tests performed for the Department of Energy's 2001 Gasoline/Diesel PM Split Study (reported in Fujita et al. 2007a,b). Table 1 lists all the sampling sites at which

data were collected for this study and other sites mentioned in this report. Table 2 summarizes the four sampling combinations that we used in the study. Measurements were made at each of the three near-road sites for 1 week during the summer field study, from September 9, 2004, to October 1, 2004, and again during the fall field study, from November 8, 2004, to December 13, 2004. On-road measurements were made on each commuting route over a period of 1 week. In addition, on-road samples were collected on a freeway loop with high numbers of diesel trucks. Table 3 and Table 4 summarize the data collected during the two sampling periods.

On-Road Sampling

The concentrations of air toxics were measured along roadways using a minivan driven in traffic on several routes during the morning (7–8 AM) and evening (5–6 PM) commuting periods. The actual duration of the sampling depended on traffic speed, but was typically between 45 and 60 minutes. A sampling route was selected in the general area of the three near-road sites. Measurements were made on the truck route during the summer study following the morning commuting period (approximately 9–10 AM) and preceding the evening commuting period (approximately 3–4 PM). All truck route measurements were made at midday (11 AM–1 PM) during the fall study.

On-road measurements were made along the following three commuting routes and one freeway loop with a higher fraction of diesel-truck traffic:

- Commuting route #1 — Westbound on SR-60 from Diamond Bar to Boyle Heights or downtown Los Angeles, depending on average speed during morning commutes. The reverse eastbound direction was driven during evening commutes starting at Boyle Heights and ending at Diamond Bar. Diesel-truck traffic is greater on SR-60 east of I-605.
- Commuting route #2 — Northbound on I-405 from the intersection of I-405 and I-710 to northbound I-110 to downtown Los Angeles during morning commutes and the reverse direction during evening commutes. The traffic consisted of predominantly light-duty gasoline vehicles, and the roads were heavily congested between I-105 to the downtown area. Most of I-110 between I-105 and I-10 is below the adjacent surface street level, which can restrict mixing and result in higher pollutant concentrations, especially during fall mornings.
- Commuting route #3 — Northbound on I-405 from the intersection of I-405 and I-710 to La Tierra Boulevard or Culver Boulevard; the return route depended on the average speed during the morning and evening

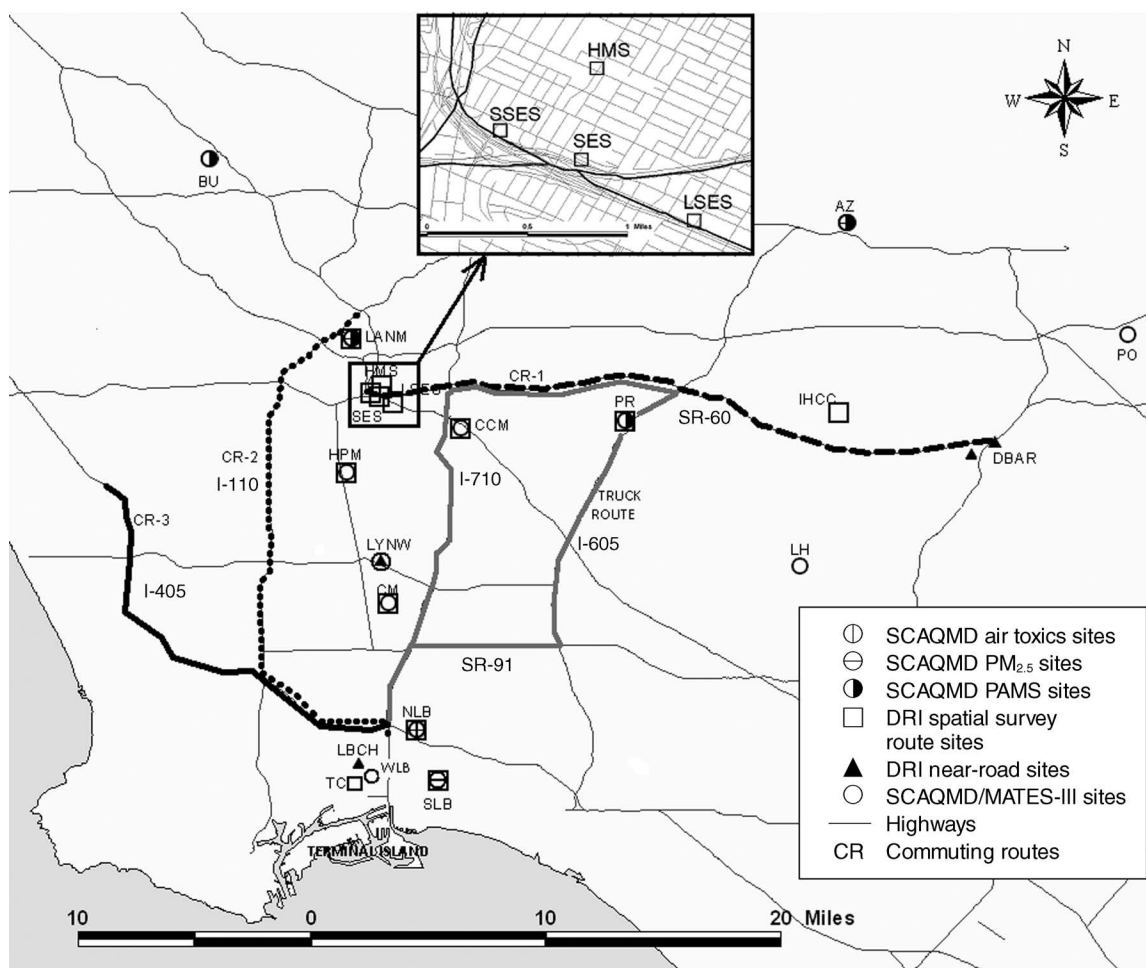


Figure 1. Location of fixed sampling sites and routes for on-road measurements.

commutes. The traffic consisted of predominantly light-duty gasoline vehicles, and the roads were heavily congested approaching the Marina Freeway (SR-90). I-405 is above ground, and afternoon on-shore winds are perpendicular to the highway.

- Truck route—Northbound I-710 from the Willow Street on-ramp to eastbound SR-60 to southbound I-605 to westbound SR-91. Truck traffic on I-710, SR-91, and I-605 from 10 AM to noon is three times higher than on I-110 or I-405 from 7 to 8 AM and about four times higher from 5 to 6 PM. The percentages of truck traffic to total traffic on this route as compared to the other three routes were about five to eight times greater.

The commuting routes were sampled three times during the week on different weekdays (typically Monday, Wednesday, and Friday). A total of 27 sets of time-integrated canister and DNPH cartridge samples (plus 5 blanks) were

collected in each season over the entire driving route and analyzed for hydrocarbons and carbonyl compounds, respectively. Continuous instruments, with 10-second time resolutions, in the sampling van were used to determine variations in concentrations of CO, VOCs (estimated by PID), NO and NO_x, PM_{2.5} (light scattering), and BC. All sampling lines were positioned near the driver's breathing zone. The sampling van traveled in the second lane from the highway median, and most heavy-duty diesel trucks were in the third and fourth lanes. The speed of the sampling van and its proximity to other vehicles were consistent with the prevailing flow of traffic.

Windows and vents were fully opened and a circulating fan was turned on in order to measure concentrations of air toxics on the road. Thus, the measured concentrations represent the ranges in maximum potential exposure levels during typical commutes in Los Angeles County and do not account for varying ventilation conditions. Consideration

Table 1. Monitoring Locations for Which Data Are Presented or That Are Cited in the Report

Sampling Sites Used in the Study	HEI Study Sampling Locations					SCAQMD Monitors (Regulated Pollutants)	SCAQMD Air Toxics Monitors	SCAQMD PM Monitors	PAMS Sites	ARB 55 VOCs
	On-Road Sampling	Spatial Survey Sites	Near-Road Sites	Source-Dominated Ambient Samples	MATES-III Sites					
Commuting Route #1: SR-60	✓									
Survey #1: Industry Hill Conf Center (IHCC)		✓								
Survey #1: Pico Rivera (PR)		✓			✓	✓			✓	
Survey #1: Soto Street School (SSES)		✓								✓
Survey #1: Hollenbeck Middle School and Roosevelt High School (HMS)		✓								✓
Survey #1: Sunrise Elementary School (SES)		✓								
Survey #1: Lorena Street School (LSES)		✓								
Commuting Route #2: I-110	✓									
Survey #2: Los Angeles Leroy Street ^a		✓								
Survey #2: City of Commerce (CCM)		✓			✓					
Survey #2: Huntington Park (HPM)		✓			✓					
Survey #2: Compton (CM)		✓			✓					
Commuting Route #3: I-405	✓									
Survey #3: North Long Beach (NLB)		✓			✓	✓	✓	✓		
Survey #3: Long Beach City College (SLB)		✓				✓				
Survey #3: Long Beach State University Tech Center (TC) ^b		✓								
Truck Route: I-710/SR-60/I-605/SR-91 (or freeway loop)	✓									
Long Beach: Buddhist Temple, 2100 Willow Street (near roads with high diesel traffic, i.e., SR-103)			✓			✓				
Lynwood: 11220 Long Beach Boulevard, north of I-105 (light-duty vehicles)			✓			✓				
Diamond Bar: 21865 Copley Drive (mix of gasoline and diesel traffic, i.e., SR-60)			✓							
Terminal Island (SR-47)				✓						
Gasoline-dominated roads (I-405, I-110)				✓						
Asuza						✓	✓	✓	✓	
Burbank–W Palm Ave						✓	✓		✓	
La Habra						✓	✓			
Pomona						✓				
Riverside–Rubidoux							✓	✓		

^a 500 m southwest of the Central Los Angeles–N Main St (LANNM) MATES-III site.^b 300 m south of the West Long Beach (WLB) MATES-III site.

Table 2. Time Resolution for On-Road and Near-Highway Exposure Measurements

Species Measured	Sampling/Analysis Method	Mobile Van		Mobile Laboratory	
		Commuting Routes	Spatial Surveys	Source Samples	Near-Road Sites
Continuous instruments					
CO	Monitor Labs 9830				1 min
CO/CO ₂	TSI Q-Trak Plus (Model 8554)	10 sec	10 sec	10 sec	
NO only	Horiba APNA-360E	10 sec	10 sec	10 sec	
NO and NO _x	TEI 17C				1 min
Total VOCs (photoionization)	RAE systems ppbRAE	10 sec	10 sec	10 sec	1 min
BC	DRI photoacoustic	10 sec	10 sec	10 sec	1 min
PM _{2.5} mass (light scattering)	TSI DustTrak	10 sec	10 sec	10 sec	1 min
BC plus PM _{2.5} mass (light scattering)	DRI photoacoustic with light-scattering sensor			10 sec	1 min
Time-integrated samples					
Volatile hydrocarbons	Canister, GC–MS	45–60 min		~ 4 hours	24 hours
Carbonyl compounds	DNPH, HPLC-UV	45–60 min		~ 4 hours	24 hours
PM _{2.5} mass	Teflon filter, gravimetric mass			~ 4 hours	24 hours
OC and EC	Quartz filter, IMPROVE-TOR			~ 4 hours	24 hours
Particulate and semivolatile organic compounds	TIGF/XAD-4, GC–MS			~ 4 hours	24 hours

Table 3. Data Collected During Summer Field Sampling

Location	Exposure Type	Sample Type	Sampling Start Time	Sampling Period	Number of Integrated Samples			
					PM _{2.5} Mass and Carbon	PM _{2.5} Organic Speciation	VOCs and Carbonyls	Continuous CO, NO _x , BC, VOCs, PM
Diamond Bar	Near-road residential	24 hour	Midnight	9/9 to 9/15	7	7	7	Yes
Lynwood	Near-road residential	24 hour	Midnight	9/17 to 9/23	7	7	7	Yes
Long Beach	Near-road residential	24 hour	Midnight	9/25 to 10/1	6	7	7	Yes
SR-60	On-road	1 hour	7 AM, 5 PM	9/10 to 9/15			8	Yes
	Spatial survey	1 hour	8 AM, 4 PM					
I-110	On-road	1 hour	7 AM, 5 PM	9/17 to 9/27			6	Yes
	Spatial survey	1 hour	8 AM, 4 PM					
I-405	On-road	1 hour	7 AM, 5 PM	9/27 to 10/1			5	Yes
	Spatial survey	1 hour	8 AM, 4 PM					
Truck route	On-road	1 hour	9 AM, 3 PM	9/28 to 9/30			4	Yes
Terminal Island/ I-710	Diesel dominated	2.5 hour	8 AM, noon	9/20 to 9/21	3	3	3	Yes
I-405/I-110/ U.S. Route 101	Gasoline dominated	3 hour	Various	9/18 to 9/21	3	3	3	Yes

Table 4. Data Collected During Fall Field Sampling

Location	Exposure Type	Sample Type	Sampling Start Time	Sampling Period	Number of Integrated Samples			
					PM _{2.5} Mass and Carbon	PM _{2.5} Organic Speciation	VOCs and Carbonyls	Continuous CO, NO _x , BC, VOCs, PM
Diamond Bar	Near-road residential	24 hour	Midnight	12/7 to 12/13	7	7	7	Yes
Lynwood	Near-road residential	24 hour	Midnight	11/8 to 11/14	7	7	7	Yes
Long Beach	Near-road residential	24 hour	Midnight	11/16 to 11/22	7	7	7	Yes
SR-60	On-road	1 hour	7 AM, 5 PM	12/8 to 12/13			7	Yes
	Spatial survey	1 hour	8 AM, 4 PM					
I-110	On-road	1 hour	7 AM, 5 PM	11/10 to 11/17			7	Yes
	Spatial survey	1 hour	8 AM, 4 PM					
I-405	On-road	1 hour	7 AM, 5 PM	11/8 to 11/16			6	Yes
	Spatial survey	1 hour	8 AM, 4 PM					
Truck route	On-road	1 hour	11 AM	11/8 to 12/13			5	Yes
Terminal Island/ I-710	Diesel dominated	2.5 hour	10:30 AM	11/8 to 11/10	3			No
I-405/I-110/ U.S. Route 101	Gasoline dominated	3 hour	7 AM	11/8 to 11/10	3			No

of other factors that can affect exposures of individual commuters, such as ventilation conditions, emission rates of leading vehicles, and following distances, was beyond the scope of this study. Consequently, this report uses the term “on-road” rather than “in-vehicle.”

In a separate study, we examined the effect of vehicle ventilation conditions on in-vehicle pollutant concentrations and found that CO and VOC pollutant concentrations were more variable under high ventilation (Zielinska et al. 2007). These variations occurred as the vehicle moved into and out of the exhaust plume of the leading vehicles, with in-vehicle values changing rapidly under high ventilation. Under low ventilation, however, the concentrations of pollutants that were trapped in-cabin as the vents were closed stayed relatively constant during the remainder of the low-ventilation conditions.

We also conducted mobile sampling along a freeway loop with a higher fraction of diesel-truck traffic. Table 5 shows the annual average daily traffic (AADT) counts (vehicles per day), the annual average hourly traffic (AAHT) counts in 2004 for the relevant freeway segments (California Department of Transportation 2005), and the percentages of trucks to total vehicles. Hourly traffic profiles (Gao and Niemier 2003), also shown in the table, were used to

estimate the percentage of the average hourly total vehicle and truck traffic and the percentages of average truck traffic during the morning, midday, and afternoon sampling periods relative to the total daily traffic. The spatial distribution of diesel-truck traffic in the basin is largely related to the movement of goods from the ports of Los Angeles and Long Beach to the rail yards in South Gate and to the distribution facilities in the Inland Empire (Ontario, San Bernardino, Redlands, Upland, and Riverside). Thus, truck traffic is heaviest on I-710 from the ports to South Gate and from the ports to the Inland Empire along I-710, SR-91, I-605, and SR-60.

Spatial Surveys

The continuous instruments on the sampling van were used to determine the spatial variations in the concentrations of CO, VOCs (estimated by PID), NO and NO_x, PM_{2.5} (light scattering), and BC from the highway to the MATES-III sampling sites, to SCAQMD air quality monitoring stations, and to sampling locations that were used in previous measurement studies. The surveys utilized continuous measurements only and were done during the hour immediately after the morning commute or prior to the evening commute. The sampling van stopped at various fixed sampling

Table 5. Total Vehicle and Truck Traffic Counts

Route	Direction	2004 AADT ^a (vehicles/day)			2004 AAHT ^b (vehicles/hour)			Weekday Distribution by Hour ^c		
		Total	Trucks	% Trucks	Total	Trucks	% Trucks	Time	Total (%) ^d	Trucks (%) ^e
Commute #1	SR-60 W to I-605	228,000	18,113	8.0	15,550	857	5.5	7–8 AM	6.8	4.7
	SR-60 W from I-605	224,000	13,154	5.8	15,277	622	4.1	7–8 AM	6.8	4.7
	SR-60 E to I-605	226,667	13,966	6.1	15,776	489	3.1	5–6 PM	7.0	3.5
	SR-60 E from I-605	262,250	22,416	8.7	18,253	785	4.3	5–6 PM	7.0	3.5
Commute #2	I-405 N, I-110 N	261,000	12,631	4.7	17,800	597	3.4	7–8 AM	6.8	4.7
	I-110 S, I-405 S	259,500	13,375	4.9	18,061	468	2.6	5–6 PM	7.0	3.5
Commute #3	I-405 N	289,167	13,110	4.5	19,721	620	3.1	7–8 AM	6.8	4.7
	I-405 S	276,857	12,755	4.6	19,269	446	2.3	5–6 PM	7.0	3.5
Truck route	I-710 N	190,571	28,502	14.5	12,959	1,348	10.4	7–8 AM	6.8	4.7
	SR-60 E	249,333	16,775	6.7	16,955	793	4.7	7–8 AM	6.8	4.7
	I-605 S	266,000	26,124	9.9	18,088	1,236	6.8	7–8 AM	6.8	4.7
	SR-91 W	234,667	27,691	11.5	15,957	1,310	8.2	7–8 AM	6.8	4.7
	I-710 N	190,571	28,502	14.5	9,548	2,132	22.3	11–noon	5.0	7.5
	SR-60 E	249,333	16,775	6.7	12,492	1,255	10.0	11–noon	5.0	7.5
	I-605 S	266,000	26,124	9.9	13,327	1,954	14.7	11–noon	5.0	7.5
	SR-91 W	234,667	27,691	11.5	11,757	2,071	17.6	11–noon	5.0	7.5
	I-710 N	190,571	28,502	14.5	13,264	998	7.5	5–6 PM	7.0	3.5
	SR-60 E	249,333	16,775	6.7	17,354	587	3.4	5–6 PM	7.0	3.5
	I-605 S	266,000	26,124	9.9	18,514	914	4.9	5–6 PM	7.0	3.5
	SR-91 W	234,667	27,691	11.5	16,333	969	5.9	5–6 PM	7.0	3.5

^a California Department of Transportation, 2005. Annual average daily total and truck traffic counts include trucks with 2 through 5 axles. The class of two-axle trucks includes 1.5-ton trucks with dual rear tires and excludes pickups and vans with only four tires.

^b Annual average hourly total and truck traffic counts were estimated from the hourly traffic profiles in Gao and Niemier (2003) from the 1996–2000 weigh-in-motion data from twelve weigh-in-motion systems in Caltrans District 7 (greater Los Angeles area).

^c Estimated from the AADT and the AAHT.

^d Percent of total vehicles during the sampling hour.

^e Percent of total truck traffic during the sampling hour.

locations (with engine off) where it remained stationary long enough for all continuous measurements to reach stable readings (typically several minutes). The following sampling locations were associated with the three commuting routes.

- Spatial survey route #1—Industry Hills Conference Center (IHCC), Pico Rivera SCAQMD air monitoring station (PR; also a MATES-III fixed site), Soto Street Elementary School (SSES), Hollenbeck Middle School and Roosevelt High School (HMS), Lorena Street Elementary School (LSES), and Sunrise Elementary School (SES).
- Spatial survey route #2—Los Angeles–Leroy St., 500 m southwest of the Central Los Angeles–North Main Street SCAQMD air monitoring station (LANM; also a MATES-III fixed site), City of Commerce MATES-III microscale

site (CCM), Huntington Park MATES-III fixed site (HPM), and Compton MATES-III fixed site (CM).

- Spatial survey route #3—North Long Beach SCAQMD air monitoring station (NLB; also a MATES-III fixed site), Long Beach City College SCAQMD air monitoring station (SLB), and Long Beach State University Tech Center (TC), which is 300 m southwest of the West Long Beach (WLB) MATES-III site.

The intent was to gather “snapshot” data for comparison with monitoring data collected by others at these locations, to provide some additional context for the on-road measurements. Unfortunately, we were unable to obtain concurrent data from the MATES-III study stations as planned. As a result, no speciated PM or EC data from fixed sites near the study driving routes are available for comparison with the study’s on-road BC measurements.

Near-Road Sites with Varying Contributions of Gasoline and Diesel Exhaust

Concentrations of several pollutants were measured from the DRI mobile monitoring laboratory by a combination of 24-hour integrated sampling of $PM_{2.5}$ and organic gases and continuous monitoring of CO, NO and NO_x , total VOCs (estimated by PID), and BC. A total of 21 sets of samples—canister, DNPH, Teflon-impregnated glass fiber (TIGF) with backup XAD-4 resin, Teflon, and quartz—plus 3 sets of field blanks (excluding canisters) were collected and analyzed per season. We selected the following three near-road neighborhood sites based upon their potential for varying pollutant concentrations as a result of differing proportions of diesel-truck and gasoline-vehicle traffic.

Long Beach The I-710 freeway to the port area and the Terminal Island Freeway (SR-103) that connects the Port of Long Beach and the Port of Los Angeles to the Intermodal Container Transfer Facility (ICTF) have high volumes of diesel-truck traffic. The northern terminus of SR-103 is at Willow Street in a residential area in West Long Beach near the ICTF. At the Khemara Buddhikaram Cambodian Buddhist Temple at 2100 West Willow Street, sampling was conducted in 2004 from September 25 to October 1 and from November 16 to November 22. The temple is located at the southeast corner of Willow Street and SR-103. The

DRI mobile monitoring laboratory was located about 100 m east of SR-103 in the temple parking lot (Figure 2). The queue of trucks at the northern terminus of SR-103 was typically 5 to 15 trucks long during the day but occasionally stretched to over 1 km. Prevailing winds were from the south or west during the afternoon.

Lynwood We placed the sampling equipment from the DRI mobile monitoring laboratory in the SCAQMD air monitoring station in Lynwood, located on 11220 Long Beach Boulevard, one block north of I-105 (Figure 3). Long Beach Boulevard is a main arterial with traffic consisting of predominantly light-duty gasoline vehicles. The Lynwood station is located in a one-story commercial building that fronts Long Beach Boulevard. Sampling inlets are located on the roof of the building about 10 to 20 m east of the street edge. This monitoring station has historically recorded the highest CO concentrations in the basin, which is partly due to how close the sampling inlet is to traffic and the tendency for vehicles in this neighborhood to be older than in other parts of the basin. Sampling was conducted at this site in 2004 from September 17 to September 23 and from November 8 to November 14.

Diamond Bar The SCAQMD district headquarters is located at 21865 Copley Drive in Diamond Bar. DRI's mobile



Figure 2. DRI's near-road monitoring site in Long Beach near roads with a high volume of diesel trucks. The mobile monitoring laboratory (white star) was located in the parking lot of the Khemara Buddhikaram Cambodian Buddhist Temple, which is at the southeast corner of Willow Street and SR-103.



Figure 3. DRI's near-road site at the SCAQMD air monitoring station in Lynwood, at 11220 Long Beach Boulevard, one block north of I-105. Long Beach Boulevard is a main arterial with traffic consisting of predominantly light-duty gasoline vehicles.



Figure 4. DRI's near-road site at the SCAQMD district headquarters, at 21865 Copley Drive in Diamond Bar. The mobile monitoring laboratory was located at the west end of the parking area on a hill about 50 m above and 125 m south of SR-60 and SR-57. The traffic on SR-60 is a mix of gasoline and diesel vehicles.

monitoring laboratory was located in the west end of the parking area near the intersection of SR-60 and SR-57 (Figure 4). The site sits on a hill and is about 50 m above and 125 m south of SR-60. Traffic is a mix of gasoline and diesel vehicles. Sampling was conducted at this site in 2004 from September 9 through September 15 and from December 7 through December 13.

We expected the Long Beach and Lynwood sites to contribute the greatest amounts of diesel and gasoline exhaust to ambient concentrations of volatile and particulate MSATs, respectively. We recognized that sharp gradients in pollutant concentrations occur as distance from the roadway is increased and that the magnitude of pollutant exposures can depend greatly upon the volume of traffic and proximity of sampling equipment to the roadway. Our main objective for sampling at these sites was to determine whether there were significant differences in the relative concentrations of specific air toxics that could be associated with varying contributions of diesel or gasoline exhaust.

The wind roses in Figure 5 show that winds in the Wilmington and West Long Beach areas are almost exclusively from 135° (southeast) to 315° (northwest) throughout the year. Winds are most frequently from the northwest during winter, southeast during summer, and west during spring and fall. Winds are typically calm overnight and

switch from the south during the morning to the north in the afternoon with a pronounced increase in the westerly component in the afternoon. The diurnal variations in the northerly component are due to the convergence of air flows from north and east of the Palos Verdes Peninsula. Winds elsewhere in the study area are predominantly in the westerly direction with stronger onshore afternoon winds and a weak offshore breeze at night.

Source-Dominated Ambient Samples

Samples were collected in the DRI mobile laboratory on Teflon and quartz filters, on TIGF filters with backup XAD-4 resin, in canisters, and in DNPH cartridges on roadways in traffic that was dominated by either gasoline vehicles (e.g., on-road samples collected on weekends or on a commuter-dominated freeway) or diesel vehicles (weekday samples collected on road on Terminal Island). The chemical compositions of these samples were determined for comparison with the composition profiles obtained for diesel and gasoline exhaust in the Gasoline/Diesel PM Split Study (see the next section). PM_{2.5}, CO, and BC were continuously measured concurrently with the integrated samples. The contributions of gasoline and diesel exhaust to these samples were estimated by CMB and compared to the source contributions, also estimated by CMB, and ratios of BC to PM observed at the three near-road sites. These results may be used to evaluate the use of BC as a surrogate for diesel PM.

Ambient Air Quality Monitoring in the SoCAB

Within California's SoCAB are a total of 35 state and local air monitoring stations that monitor one or more criteria pollutants (ozone, CO, NO₂, PM, sulfur dioxide, and lead). Subsets of these monitoring stations are also photochemical assessment monitoring stations (PAMS) and air toxics monitoring stations. The Figure 6 map indicates the 15 SoCAB stations located within Los Angeles County. SCAQMD monitors speciated VOCs at five PAMS sites in Los Angeles County (Azusa, Burbank, Hawthorne, Pico Rivera, and Santa Clarita) from June through September. The VOCs monitored include 55 C₂-to-C₁₁ hydrocarbons, formaldehyde, and acetaldehyde. Eight 3-hour samples are collected daily at Burbank and Pico Rivera and every third day at the other three sites. The air toxics monitoring program in the SoCAB consists of five monitoring stations, with four stations located in Los Angeles County (Azusa, Burbank–West Palm Avenue, North Long Beach, and Central Los Angeles–North Main Street) and one in Riverside–Rubidoux. The air toxics monitored include various volatile hydrocarbons and aldehydes, metals, and particulate PAHs, and the stations collect 24-hour integrated samples every sixth

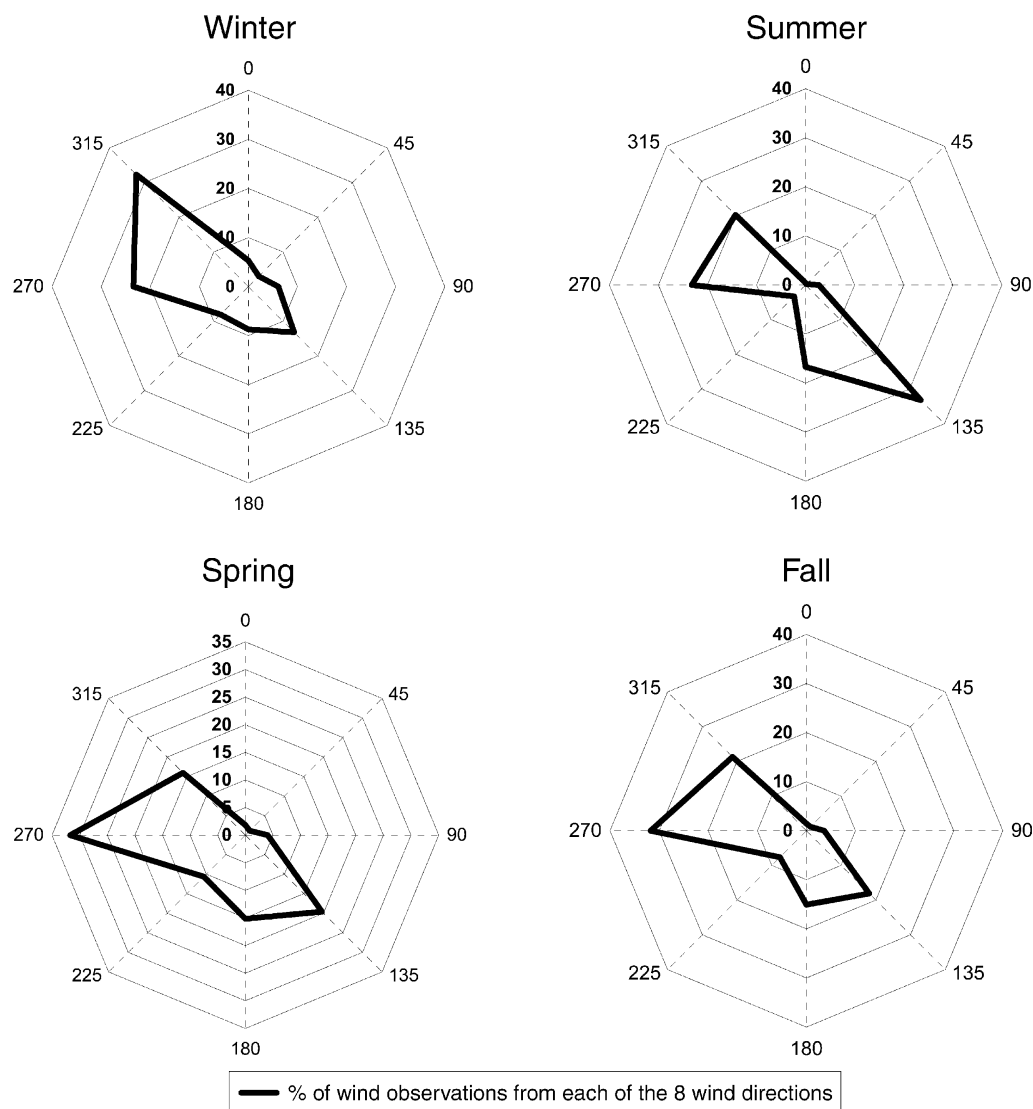


Figure 5. Seasonal wind patterns at Wilmington and West Long Beach area, August 2001 to July 2002. Source: California Air Resources Board.

day throughout the year. In addition, 24-hour average $PM_{2.5}$ mass is measured daily throughout the year at the Anaheim, Azusa, Central Los Angeles–North Main Street, North Long Beach, and Riverside–Rubidoux stations. $PM_{2.5}$ mass (24-hour) is also measured every third day at 10 other locations. Twenty-four-hour integrated samples are chemically speciated at several sites on an every-third-day schedule. We also used the CO and NO_x data from several of these sites as well as from the Pomona and La Habra sites.

EXPERIMENTAL METHODS

Pollutant concentrations were measured using time-integrated monitors that collected samples over periods

ranging from 1 to 24 hours and continuous monitors with time resolutions ranging from 10 to 60 seconds. The time-integrated sampling included the following: canisters for BTEX, styrene, BD, MTBE, and *n*-hexane; DNPH cartridges for formaldehyde, acetaldehyde, and acrolein; Teflon filters for gravimetric $PM_{2.5}$ mass; quartz filters for OC and EC; and TIGF filters with backup XAD-4 resin for speciated particulate and semivolatile PAHs. Continuous methods included both an active nondispersive infrared (NDIR) analyzer and a passive electrochemical cell device for CO, a portable NDIR analyzer for carbon dioxide (CO_2), a chemiluminescence analyzer for NO and NO_x , a photoacoustic analyzer for BC, and an active PID for VOCs with ionization potentials below 10.6 eV (principally olefins

previous 10 samples were reweighed. At least 30% of the weights were checked by an independent technician, and samples were reweighed if the checked weights were not within ± 0.015 mg of the original weights. Pre- and post-weights, check weights, and reweights (if required) were recorded on data sheets and were directly entered into a database via an RS232 connection. All PM_{2.5} Teflon filters were analyzed for mass.

EC and OC were measured by the TOR method using the IMPROVE temperature/oxygen cycle (IMPROVE-TOR) (Chow et al. 1993, 2001). PM_{2.5} samples were collected using this method on quartz filters. A section of the filter sample was placed in the carbon analyzer oven such that the optical reflectance or transmittance of helium-neon laser light (632.8 nm) could be monitored during the analysis process. The filter was first heated under oxygen-free helium purge gas. The volatilized or pyrolyzed carbonaceous gases were carried by the purge gas to the oxidizer catalyst where all carbon compounds were converted to CO₂. The CO₂ was then reduced to methane, which was quantified by a flame ionization detector. The carbon evolved during the oxygen-free heating stage was defined as OC. The sample was then heated in the presence of helium gas containing 2% oxygen, and the carbon evolved during this stage was defined as EC. The organic compounds that pyrolyzed when heated during the oxygen-free stage of the analysis and that produced additional EC were defined as pyrolyzed carbon (PC). The formation of PC was monitored during the analysis by the sample reflectance. EC and OC were thus distinguished based upon the refractory properties of EC, which were measured using a thermal-evolution carbon analyzer with optical correction to compensate for the pyrolysis (charring) of OC. Carbon fractions identified with the IMPROVE-TOR method correspond to temperature steps of 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in a nonoxidizing helium atmosphere, and to 550°C (EC1), 700°C (EC2), and 850°C (EC3) in an oxidizing atmosphere. The IMPROVE-TOR method uses variable hold times of 150 through 580 seconds at each heating stage so that carbon responses return to baseline values. The sum of the particulate EC and OC is what is referred to in this report as "TC."

Particulate-Bound and Semi-VOCs We used the DRI sequential fine particulate and semivolatile organic compounds sampler (PSVOC sampler) for the collection of samples on TIGF filters and backup XAD-4 resin cartridges. The air sample was drawn through a Bendix 240 cyclone separator with a cut-off diameter of 2.5 μ m operating at 113 L/min. The flow was set using a calibrated rotameter on the inlet side of the copper sampling line and was maintained by a flow controller.

The samples on the TIGF filters and the backup XAD-4 cartridges were extracted and analyzed together. Prior to

extraction, the following deuterated internal standards were added to each filter and cartridge pair: naphthalene-*d*₈, acenaphthylene-*d*₈, phenanthrene-*d*₁₀, anthracene-*d*₁₀, chrysene-*d*₁₂, pyrene-*d*₁₀, benz[*a*]anthracene-*d*₁₂, benzo[*a*]pyrene-*d*₁₂, benzo[*e*]pyrene-*d*₁₂, benzo[*k*]fluoranthene-*d*₁₂, benzo[*g,h,i*]perylene-*d*₁₂, coronene-*d*₁₂, cholestane-*d*₅₀, and tetrocosane-*d*₅₀. The samples on filters and XAD-4 cartridges were extracted with dichloromethane, followed by acetone, using the Dionex Accelerated Solvent Extractor. The extracts were then combined and concentrated by rotary evaporation at 20°C under gentle vacuum to ~1 mL and filtered through a 0.45-mm Acrodisc filter (Gelman Scientific, Pensacola, FL). The extract was concentrated to 1 mL and split into two fractions. The first fraction was precleaned by the solid-phase extraction technique (Wang et al. 1994a,b) using Supelclean LC-Si SPE cartridges (Supelco) with sequential elution with hexane and hexane:benzene (1:1). The hexane fraction contained the nonpolar aliphatic hydrocarbons, and hopanes and steranes, and the hexane:benzene fraction contained the PAHs. These two subfractions were combined and concentrated to ~100 μ L and analyzed by a GC-mass spectrometry (MS) technique for hydrocarbons, hopanes, steranes, PAHs, and oxy-PAHs. The second fraction was utilized for the polar compound analysis without precleaning. It was derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide and pyridine to convert the polar compounds into their trimethylsilyl derivatives, evaporated to 100 μ L under moisture-filtered, ultra-high-purity nitrogen, and transferred to 300- μ L silanized glass inserts (National Scientific Company, Rockwood, TN). Samples were further evaporated to 50 μ L and 25 μ L pyridine (Pierce, Rockford, IL), 25 μ L internal standard mixture (succinic acid *d*-4, myristic acid *d*-27, and 1,2,4-butanetriol), and 150 μ L N,O-bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane (Pierce) was added. The glass insert containing the sample was put into a 2-mL vial and sealed. The sample was then placed onto a thermal plate (custom made) containing individual vial wells and heated at 70°C for 3 hours. The calibration solutions were freshly prepared and derivatized just prior to the analysis of each sample set, and then all samples were analyzed by GC-MS within 18 hours to avoid degradation. Analysis of the polar organic compounds and the internal standards added are described elsewhere (Rinehart et al. 2006; El-Zanan et al. 2009).

Samples were analyzed by GC-MS using a Varian CP-3800 gas chromatograph equipped with a Varian CP-8400 AutoSampler that was interfaced to a Varian Saturn 2000 Ion Trap operating in electron-impact ionization mode (Zielinska et al. 2004). Concentrations were quantified by comparing the response of the deuterated internal standards to the analyte of interest (Zielinska et al. 2004).

VOCs Whole air samples were collected in pressurized canisters and analyzed with a Varian CP-3800 gas chromatograph coupled to a Varian Saturn 2000 Ion Trap (U.S. EPA method TO-15) for BTEX, styrene, *n*-hexane, BD, MTBE, and all other VOCs measured at PAMS sites. BD is unstable in canisters in the presence of NO_x . Atkinson and colleagues (1984) showed that a mixture of NO and NO_2 produces a series of reactions that result in hydroxyl radicals being formed in the dark. Hydroxyl radicals react rapidly with BD, resulting in rapid BD removal from the sample at higher NO levels. Using concentrations that may be encountered during on-road sampling on a congested freeway (300 ppb NO; 30 ppb NO_2 , and 2 ppbV BD), theoretical calculations resulted in a 3-day decay rate for BD of 3.5%. Because of the expected time between sample collection and laboratory analysis of about 5 to 10 days and the possibility of occasionally encountering higher NO_x levels, we decided to remove NO_x from the on-road canister samples using a cobalt-oxide-coated diffusion denuder previously developed by DRI for vehicle testing. Appendix A provides additional information on the development and application of the NO_x denuder in sampling BD in canisters. At the conclusion of the summer field study, the denuder was tested in the laboratory by passing 50 ppm NO through it and monitoring the postdenuder NO_x levels. No significant level of NO was detected, and the removal efficiency was confirmed to be nearly 100%. The NO_x denuder was used for near-highway samples during fall only.

It is known that measurements of BD by U.S. EPA method TO-14 and of acrolein by U.S. EPA method 11 are affected by sampling and analysis artifacts. Both of these measurement issues were addressed in this study. BD reacts with NO_x in the canister, and the rate of BD decay is concentration dependent. To determine whether removal of NO_x is necessary for on-road samples, BD decay rates were estimated for the levels of NO_x and BD that were expected in the SoCAB during the study. Using summer ambient levels (75 ppb NO; 30 ppb NO_2 ; 1 ppm CO; and 2 ppbV BD) and fall ambient levels (200 ppb NO; 40 ppb NO_2 ; 3 ppm CO; and 5 ppbV BD) at a typical regional monitoring station in the SoCAB yielded decay rates of 1.1% and 2.5%, respectively, after 3 days. Using a range of higher concentrations that may be encountered during on-road sampling on a congested freeway resulted in 3-day decay rates of 3.5% and 17% for low (300 ppb, 30 ppb, and 2 ppb) and high (1000 ppb, 100 ppb, and 5 ppb) ambient levels, respectively. These decay rates are not inconsequential given the expected time between sample collection and laboratory analysis of about 5 to 10 days. Therefore, we concluded that NO_x had to be removed from the on-road canister samples. NO_x was removed from the samples using a cobalt oxide denuder during the fall only. The preparation and

testing of this denuder and additional background information are provided in Appendix A.

Formaldehyde, Acetaldehyde, and Acrolein Formaldehyde, acetaldehyde, and acrolein were collected on Sep Pak cartridges that had been impregnated with an acidified DNPH reagent (Waters; U.S. EPA method TO-11A). Carbonyl compounds collected in the cartridges (as hydrazones) were eluted with acetonitrile (high-pressure liquid chromatography [HPLC]-grade) and analyzed by HPLC with photodiode array detection. A reverse-phase HPLC column was used. Identifications were made based on matching the HPLC retention times with those of authentic standards. A three-level calibration curve (plus a blank) was constructed for each quantified hydrazone.

Acrolein is known to rearrange on DNPH cartridges to an unknown degradation product (acrolein-x) (Tejada 1986). The rearrangement of acrolein occurs over time periods of days, so it was not logistically possible to avoid the effect of this artifact in this study. The sum of acrolein and acrolein-x provides an estimate of total acrolein that was originally present in the samples. However, the UV spectra from the photodiode array detector showed that the chromatographic retention time of acrolein-x substantially overlapped that of butyraldehyde. Thus, the sum of acrolein and butyraldehyde represented an upper-bound estimate of acrolein that was originally present in the sample. An accurate quantification of acrolein was not possible with the DNPH methods because of the mixture of both aldehydes in the samples and lack of a specific response factor for acrolein-x.

For this study, we developed a way to more accurately quantify acrolein using method TO-11A. The response factor for DNPH-acrolein-x was first determined by diluting a known amount of acrolein in a Tedlar bag and sampling it through a DNPH cartridge. Several mixtures of DNPH-butyraldehyde and DNPH-acrolein-x with different proportions of both compounds were analyzed. The ultraviolet-visible (UV-VIS) spectra of coeluting compounds were recorded, and a linear least-squares method was used to relate the proportion of both compounds to the appearance of spectrum maxima for each compound. The correction procedure was applied to the stored UV-VIS spectra for this study. Appendix B provides additional details on the development of the correction procedure.

Continuous Sampling Methods

Continuous methods included both an active NDIR analyzer and a passive electrochemical cell device for CO, an NDIR analyzer for CO_2 , a chemiluminescence analyzer for NO and NO_x , a photoacoustic analyzer for BC, and an active PID for VOCs. Continuous CO and PID measurements were

related to time-integrated measurements, and the resulting correlations were applied to the continuous measurements to reconstruct the time-series values for the target species (e.g., BTEX and BD).

We used a ppbRAE Model PGM-7240 PID monitor (RAE Systems, San Jose, CA) to continuously monitor ambient VOC levels. The monitor is equipped with a 10.6-eV PID detector and responds to gases with an ionization potential of less than 10.6 eV, which include aromatic hydrocarbons, olefins, and higher-molecular-weight alkanes. It does not respond to light hydrocarbons, such as methane, ethane, and propane, or to acetylene, formaldehyde, or methanol. The monitor has < 5-second response and a lower detection limit of 1 ppbV. Because the total response of the PID depends upon the specific mix of VOCs, the response must be calibrated to the expected mix of VOCs. Isobutylene is the calibration gas, and the PID response can be adjusted to one of several specific VOC species or to standard mixtures of VOCs, such as gasoline.

CO and CO₂ were continuously monitored with a TSI Q-Trak Plus (Model 8554) during on-road sampling. This portable instrument measures CO₂ with an NDIR optical absorption method with a resolution of 1 ppm and an accuracy of \pm (3% of reading + 50 ppm), and it measures CO with an electrochemical cell with a resolution of 0.1 ppm and an accuracy of \pm 3% of reading or 3 ppm, whichever is greater. This instrument also records ambient temperature and relative humidity. CO was monitored continuously at the near-road sites by a Monitor Labs 9830 NDIR CO analyzer. This instrument is a gas-filter correlation NDIR optical monitor certified by the U.S. EPA. It has a lower detectable limit of 0.05 ppm and a precision of 0.1 ppm or 1%. Comparisons of this monitor with the TSI 8554 indicated an accuracy of about 0.5 ppm for the TSI 8554, which is substantially better than the specifications for the analyzer.

NO and NO₂ were monitored using a Horiba APNA-360E instrument based on the chemiluminescence NO-ozone method. This method mixes ambient air with a high concentration of ozone so that any NO in the air sample will react to form NO₂, which produces light. The light intensity is measured with a photomultiplier and converted into an electronic signal that is proportional to the NO concentration. To measure NO_x concentrations, the sum of NO and NO₂, the air sample is first directed through a heated catalyst (molybdenum or gold in the presence of CO) where NO₂ is reduced to NO, adding to the NO already present in the sample; then the NO is passed into the reaction chamber for measurement as described above. The NO₂ concentration is derived by subtracting the NO concentration from the NO_x concentration. Standard sensitivity instruments such as the APNA-360E have detection limits of about 0.5 to 3 ppb (60-second averaging times).

The TSI DustTrak nephelometer monitored forward light scattering that was interpreted as PM mass. The DustTrak is a portable, battery-operated, laser photometer that measures 90° light scattering (which is different from the total light scattering measured by an integrating nephelometer) and reports it as PM mass concentration. The laser diode used by the DustTrak has a wavelength of 780 nm, and as a result the smallest particle it can detect is about 0.1 μ m. The reported PM mass concentration is factory calibrated using the respirable fraction of an Arizona Road Dust standard (International Organization for Standardization [ISO] 12103-1, A1). The mass-scattering efficiency depends on the shapes, size distribution, and composition (index of refraction) of the particles. The ISO 12103-1, A1 standard consists of primarily silica particles (70%) that are provided with some particle-size specifications. By volume, the standard consists of 1% to 3% of particles with diameters smaller than 1 μ m, 36% to 44% of particles with diameters smaller than 4 μ m, 83% to 88% of particles with diameters smaller than 7 μ m, and 97% to 100% of particles with diameters smaller than 10 μ m. This standard contains a larger quantity of coarse particles (> 2.5 μ m) than are usually found in ambient aerosol. PM_{2.5} has a higher mass-scattering efficiency, so the DustTrak overestimates PM_{2.5} for smaller, chain aggregate soot particles. In the recent Gasoline/Diesel PM Split Study, the DustTrak data were found to exceed gravimetric mass concentrations of the motor vehicle-dominated ambient samples by a factor of 2.24 with an r^2 value of 0.75 (Fujita et al, 2007b). The DustTrak data were corrected in the final report based on this factor. Comparisons of DustTrak data with gravimetric data obtained in the present study showed similar, but less consistent differences.

Particle light absorption was monitored with a photoacoustic instrument (Arnott et al. 1999, 2000). Light from a 1047-nm laser is power-modulated at the operating frequency of an acoustical resonator. Light absorbing aerosols (BC) drawn continuously through the resonator absorb some of the laser power, slightly heating the aerosol. The heat transfers rapidly from the aerosol to the surrounding air, and the local pressure increases, contributing to the standing acoustic wave in the resonator. The acoustic wave is measured with a microphone as a measure of the light absorption, which is linearly proportional to the mass concentration of the BC aerosol in the sample air. Light absorption (in Mm^{-1}) can be interpreted as BC and converted to $\mu\text{g}/\text{m}^3$ when divided by an assumed mass absorption efficiency (in m^2/g). A mass absorption efficiency of 5 m^2/g was assumed for these conversions, based on previous comparisons of EC measured by the IMPROVE-TOR method with photoacoustic absorption of aerosol in exhaust from diesel-powered vehicles (Arnott et al. 2005). Based on the

instrument's assumed absorption efficiency, its resolution for the 10-second averaging time used in the study was approximately $0.2 \mu\text{g}/\text{m}^3$. The photoacoustic instrument used at the near-road sites incorporated a sensor that also measured light scattering, to estimate $\text{PM}_{2.5}$ mass. The photoacoustic instrument in the mobile sampling van did not, and a TSI DustTrak aerosol monitor was used for all on-road measurements.

A Delorme global positioning system receiver connected to a computer running map software tracked the position, speed, and heading of the mobile sampling van at 1-second intervals (less often when the van was stationary). The resulting track was used with geographic information systems (GIS) software to create spatial data maps of pollutants. A Davis Instruments Weather Monitor II meteorology package was used to measure wind speed, wind direction, relative humidity, and temperature during sampling at the fixed monitoring locations. A dedicated data logger recorded time-integrated data at 10-minute intervals. The anemometer was mounted on a mast extending 12 feet above the level of the location of the parked van.

DATA ANALYSIS

The data analysis presented in this report consists of the following:

- Statistical summaries of the concentrations of $\text{PM}_{2.5}$, BC, NO, NO_x , CO, and MSATs on roadways in Los Angeles County during morning and afternoon commutes and other times with greater numbers and proportions of diesel trucks.
- Ratios of NO_x and CO concentrations measured on road to corresponding measurements at nearby SCAQMD monitoring stations and the three near-road sites used in source apportionment.
- Ratios of MSAT concentrations measured on road to the seasonal mean 24-hour concentrations measured by SCAQMD at air toxics monitoring sites.
- Estimation of the contributions of gasoline- and diesel-powered vehicles to on-road and near-road concentrations of specific gaseous air toxics and carbonaceous PM.

Characterization of On-Road Concentrations and Their Relationship to Pollutant Concentrations at Nearby Fixed Monitoring Sites

Ambient pollutant concentrations were characterized using descriptive statistics, regression analysis of correlations, and graphical displays of the spatial and temporal variations in pollutant concentrations (e.g., box-and-whisker plots and GIS maps of pollutant concentrations). We report the means and standard deviations of the on-road, 1-minute

continuous data and the minima, maxima, and means of the corresponding time-integrated data for specific MSATs for each freeway route by time of day and season.

We examined the relationships between on-road concentrations of pollutants and ambient concentrations of pollutants at nearby fixed monitoring sites by comparing the means and ranges of on-road CO and NO_x measurements with the corresponding hourly means of the measurements collected at the SCAQMD air quality monitoring stations and at our three near-road sites. One objective of the study was to compare the on-road concentrations of PM and specific volatile organic air toxics to the annual and seasonal average pollutant concentrations at MATES-III fixed and microscale sites. However, data from MATES-III were not available for inclusion in this report.

As a substitute for the MATES-III data, we obtained all available 24-hour air toxics data from SCAQMD sites in the greater Los Angeles area for the periods when our field study was in progress and averaged the reported concentrations of BTEX, BD, styrene, formaldehyde, acrolein, and acetaldehyde. In addition, the annual average values were also obtained. Although these data were not expected to be directly comparable to our on-road and near-road measurements due to differences in sampling duration and sampling schedules, they do represent the type of data normally available for use in exposure models.

Source Apportionment by CMB

The ambient source apportionments were obtained by applying U.S. EPA version 8.0 of the CMB receptor model. The CMB model (Friedlander 1973; Watson 1984; Watson et al. 1991) consists of a least-squares solution to a set of linear equations that expresses each receptor concentration (x) of a chemical species as a linear sum of products of source profile species (f) and source contributions (g). The general mass balance receptor model can be stated in terms of the contribution from p independent sources in relation to all measured chemical species in a given sample as follows:

$$x_{ik} = \sum_{j=1}^p g_{ij} f_{jk} + \epsilon_{ik}$$

where, for airborne particles or VOCs, x_{ik} is the k th specie concentration measured in the i th sample, g_{ij} is the particulate or VOC mass concentration ($\mu\text{g}/\text{m}^3$) from the j th source contributing to the i th sample, f_{jk} is the k th specie mass fraction of particles or VOCs emitted from the j th source, and ϵ_{ik} is the model residual. The source profile species (the fractional amount of the species in the emissions from each type of source) and the receptor concentrations, each with uncertainty estimates, are the input data for the CMB model. The output consists of the contributions from each type of source to the total ambient PM or VOCs as well as

to individual species concentrations. The model calculates values for contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the relative importance of the input data to the model solution and to estimate uncertainties in the source contributions. VOCs and PM were apportioned separately using available source-composition profiles and procedures used in recent apportionment studies in the SoCAB (Fujita et al. 2003b, 2007a).

VOC Apportionment Gasoline and diesel exhaust VOC profiles were derived from samples collected during the National Renewable Energy Laboratory Weekend Ozone Study (Fujita et al. 2003b) along the Harbor Freeway (where trucks are prohibited) in downtown Los Angeles and at the truck stop near I-10 and I-15 in Ontario. Each roadside sample was corrected for surrounding background VOC concentrations by subtracting a background sample that preceded each roadside sample. The background site was located 500 m southwest of the freeway roadside sampling site, near the east entrance to Dodger Stadium. The two weekday roadside samples generally reflected vehicle operation in stop-and-go traffic, and the two weekend samples reflected free-flow conditions. Each truck-stop sample was corrected for background VOC concentrations by subtracting from it the average of the overnight samples that were collected on a hillside at the Industry Hills Conference Center, located about midway between Diamond Bar and downtown Los Angeles. The background correction was adjusted in order to yield zero MTBE in the background-corrected diesel profile.

Gasoline liquid and vapor compositions were derived for this study from analysis of two grades of gasoline samples (regular and premium) for five brands (ARCO, Union 76, Shell, Chevron, and Mobil). An overall composite liquid gasoline profile was constructed based on the relative weighting of 68% regular and 32% premium gasoline. The compositions of gasoline vapors were predicted from the measured composition of liquid gasoline by correcting the partial pressure of the pure species by the mole fraction of that species in gasoline.

The commercial natural gas and liquefied petroleum gas VOC profiles are based on profiles reported by Mayrsohn and colleagues (1976, 1977). The contribution of aged emissions is a plausible alternative interpretation of these two sources. The combination of the two profiles accounts for the excess ethane and propane that typically exist in most urban areas. We used the profiles for surface coatings reported by Censullo and colleagues (1996) and a composite of various consumer products compiled by the U.S. EPA. Biogenic nonmethane hydrocarbon emissions are highly reactive in the atmosphere, and biogenic source contributions derived from CMB modeling supply only a lower limit to the actual contributions from biogenic emissions.

A prerequisite for using receptor models is that the relative proportions of chemical species change little between source and receptor. Most ambient VOCs are oxidized in the troposphere with lifetimes ranging from hours to several months. Nominal afternoon summertime residence times for a reactive environment (e.g., Los Angeles) are estimated in Table 6. These estimates provide indications

Table 6. Fitting Species Used in CMB Source Apportionment of VOCs

Name	Formula	Group ^a	k_{OH}^b at 298 K	Lifetime Hours	CMB Fitting Species		
					Urban AM	Urban PM	Downwind
Ethene	C2H4	O	8.52	6.52	*		
Acetylene	C2H2	Y	0.90	61.73	*	*	*
Ethane	C2H6	P	0.27	207.30	*	*	*
Propene	C3H6	O	26.30	2.11			
<i>n</i> -Propane	C3H8	P	1.15	48.31	*	*	*
Isobutane	C4H10	P	2.34	23.74	*	*	*
1-Butene	C4H8	O	31.40	1.77			
<i>n</i> -Butane	C4H10	P	2.54	21.87	*	*	*
<i>t</i> -2-Butene	C4H8	O	64.00	0.87			
<i>c</i> -2-Butene	C4H8	O	56.40	0.99			

(Table continues next page)

^a A indicates aromatic, O indicates alkene (olefin), P indicates paraffin, Y indicates alkyne.

^b Rate constant k ($10^{12} \times k \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 298 K for the reaction of OH radicals with VOCs.

^c Single species source profile for biogenic emissions sources. The true contribution of these sources will be underestimated due to the high reactivity of these species.

Table 6 (Continued). Fitting Species Used in CMB Source Apportionment of VOCs

Name	Formula	Group ^a	k_{OH}^{b} at 298 K	Lifetime Hours	CMB Fitting Species		
					Urban AM	Urban PM	Downwind AM or PM
Isopentane	C5H12	P	3.90	14.25	*	*	*
1-Pentene	C5H10	O	31.40	1.77			
<i>n</i> -Pentane	C5H12	P	3.94	14.10	*	*	*
Isoprene ^c	C5H8	O	101.00	0.55	*	*	*
<i>t</i> -2-Pentene	C5H10	O	67.00	0.83			
<i>c</i> -2-Pentene	C5H10	O	65.00	0.85			
2,2-Dimethylbutane	C6H14	P	2.32	23.95	*	*	*
Cyclopentane	C5H10	P	5.16	10.77	*	*	
2,3-Dimethylbutane	C6H14	P	6.20	8.96	*		
2-Methylpentane	C6H14	P	5.60	9.92	*	*	
3-Methylpentane	C6H14	P	5.70	9.75	*	*	
2-Methyl-1-pentene	C6H12	O	31.40	1.77			
<i>n</i> -Hexane	C6H14	P	5.61	9.90	*	*	
Methylcyclopentane	C6H12	P	8.81	6.31	*		
2,4-Dimethylpentane	C7H16	P	5.10	10.89	*	*	
Benzene	C6H6	A	1.23	45.17	*	*	*
Cyclohexane	C6H12	P	7.49	7.42	*		
2-Methylhexane	C7H16	P	6.79	8.18	*		
2,3-Dimethylpentane	C7H16	P	4.87	11.41	*	*	
3-Methylhexane	C7H16	P	7.16	7.80	*	*	
2,2,4-Trimethylpentane	C8H18	P	3.68	15.10	*	*	*
<i>n</i> -Heptane	C7H16	P	7.15	7.77	*		
Methylcyclohexane	C7H14	P	10.40	5.34	*		
2,3,4-Trimethylpentane	C8H18	P	7.00	7.94	*		
Toluene	C7H8	A	5.96	9.32	*	*	
2-Methylheptane	C8H18	P	8.18	6.80	*	*	
3-Methylheptane	C8H18	P	8.56	6.49	*		
<i>n</i> -Octane	C8H18	P	8.68	6.40	*		
Ethylbenzene	C8H10	A	7.10	7.82	*		
<i>m</i> - & <i>p</i> -Xylenes	C8H10	A	18.95	4.71			
Styrene	C8H8	A	58.00	0.96			
<i>o</i> -Xylene	C8H10	A	13.70	4.06			
<i>n</i> -Nonane	C9H20	P	10.20	5.45	*		
Isopropylbenzene	C9H12	A	6.50	8.55	*		
<i>n</i> -Propylbenzene	C9H12	A	6.00	9.26	*		
<i>m</i> -Ethyltoluene	C9H12	A	19.20	2.89			
<i>p</i> -Ethyltoluene	C9H12	A	12.10	4.59			
1,3,5-Trimethylbenzene	C9H12	A	57.50	0.97			
<i>o</i> -Ethyltoluene	C9H12	A	12.30	4.52			
1,2,4-Trimethylbenzene	C9H12	A	32.50	1.71			
<i>n</i> -Decane	C10H22	P	11.60	4.79	*		
1,2,3-Trimethylbenzene	C9H12	A	32.70	1.70			
<i>m</i> -Diethylbenzene	C10H14	A	14.20	3.90			
<i>p</i> -Diethylbenzene	C10H14	A	14.20	3.90			
<i>n</i> -Undecane	C11H24	P	13.20	4.20	*		

^a A indicates aromatic, O indicates alkene (olefin), P indicates paraffin, Y indicates alkyne.^b Rate constant k ($10^{12} \times k \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 298 K for the reaction of OH radicals with VOCs.^c Single species source profile for biogenic emissions sources. The true contribution of these sources will be underestimated due to the high reactivity of these species.

of which components are likely to remain relatively stable between source and receptor and can be used as fitting species for CMB source apportionment. An exception is isoprene, which was included as a fitting species despite its high reactivity, because it serves as a marker for biogenic emissions. The source contribution estimates underestimated the actual source contributions of biogenic emissions, i.e., they provide a lower limit to biogenic contributions. Table 6 lists three sets of default fitting species, which we have used in past CMB analysis (Fujita et al. 2003b). VOC samples collected during the morning from urban sites contain largely unreacted VOCs; samples collected during the afternoon contain a mixture of relatively fresh and photochemically aged VOC emissions. The 36 hydrocarbons listed in Table 6 were used as fitting species in the CMB analysis for samples collected at urban sites in the morning hours prior to 9 AM, and a shorter list of more stable species (20 species) was used for samples collected between 9 AM and 6 PM or over a 24-hour period. The short list of 11 default fitting species was not used in the study as none of the samples in this study were collected in far downwind areas. Though the reactive species do not influence the CMB calculations, they were retained in the CMB modeling as “floating species,” which provide useful diagnostic information. Since the CMB model calculations are based on nonreactive fitting species, the predicted concentrations for reactive species exceed the measured values by margins that increase with increasing reactivity of the species.

Particulate TC Apportionment The source profiles used in the source apportionment analysis were obtained from the Gasoline/Diesel PM Split Study (Fujita et al. 2007a). That study was conducted during the summer of 2001 to assess the sources of uncertainties in quantifying the relative contributions of tailpipe emissions from gasoline-powered motor vehicles and from diesel-powered motor vehicles to ambient $PM_{2.5}$ concentrations in the urbanized region of California’s SoCAB. Groups participating in the study included California’s Bureau of Automotive Repair; SCAQMD; the U.S. EPA; Bevilacqua-Knight, Inc., Research Triangle Park, North Carolina; West Virginia University; the University of Wisconsin at Madison; and the DRI.

Source testing of 59 light-duty vehicles (including two diesel vehicles) was completed in June 2001; ambient measurements were taken in July 2001, and the testing of 34 heavy-duty vehicles was completed in September 2001. Source samples were analyzed for gravimetric mass, elements, ions, OC, EC (by both TOR with the IMPROVE protocol) PAHs, hopanes, steranes, alkanes, and polar organic compounds. Samples were also collected and analyzed for speciated VOCs. The analyses were performed on site by

GC-MS in order to minimize loss of BD due to reactions with NO and NO_2 in the canisters.

The study examined the range of uncertainties that may be associated with the methods and procedures for sample collection, chemical analysis, and source apportionment using a CMB receptor model based on organic compounds. The source composition profiles from the Gasoline/Diesel PM Split Study were used in this study to estimate the contributions of gasoline and diesel exhaust to ambient PM levels at the near-road sampling sites and for the ambient samples from roadways dominated by either gasoline or diesel vehicles.

Profiles for CI and SI exhaust created for the Gasoline/Diesel PM Split Study (Fujita et al. 2007a) were applied to the 24-hour near-road ambient samples to determine the contributions of diesel and gasoline-vehicle exhaust to ambient TC. Since those source profiles were derived specifically for apportionment of motor vehicle exhaust PM in the Los Angeles basin, and were tested and evaluated extensively as part of that study, we applied the same fitting species and default source profiles from that study to this project. The single CI vehicle profile and the four SI vehicle profiles in this study were derived from the 14 CI and 26 SI individual or composite profiles in the Gasoline/Diesel PM Split Study. HDD is the composite exhaust profile for heavy-duty trucks on the city-suburban and highway driving cycles. The light-duty SI vehicle composite profiles consist of high (H) and low (L) emitters for both the “cold” (SI_LC and SI_HC) and “warm” (SI_LW and SI_HW) portions of the unified test cycle.

The final apportionments were obtained by applying the composite profiles in percentage of weight, normalized to total carbon (determined using IMPROVE-TOR). Uncertainties consisted of either the one-sigma variations in fractional abundances among members of the composite or the propagated root mean squares of the analytical uncertainties, whichever were larger. The analytical uncertainties were calculated from the square roots of the sum of the squares of the product of the replicate precision and analyte concentration plus the minimum detection limit. Table 7 identifies the species that were included in the default set of fitting species. This list includes EC (determined with IMPROVE-TOR analysis), seven particulate PAHs, four hopanes, and eight steranes. These 20 species are known components of motor-vehicle exhaust, are usually present in both ambient and source samples at analytically significant levels, and are sufficiently stable in the atmosphere for receptor modeling.

After apportioning particulate TC to engine exhaust, a significant fraction of TC measured at the near-road sites was apportioned to other emission sources or secondary

Table 7. Fitting Species Used in CMB Source Apportionment of Particulate Carbon

Elemental carbon
Anthracene
Fluoranthene
Methylpyrenes and methylfluoranthenes
Chrysene
Indeno[1,2,3- <i>cd</i>]pyrene
Benzo[<i>g,h,i</i>]perylene
Coronene
C27-20(<i>R</i>)5 α (H),14 β (H)-Cholestane
ster45+40(cholestane)
C28-20(<i>S</i>)5 α (H),14 β (H),17 β (H)-Ergostane
C28-20(<i>R</i>)5 α (H),14 α (H),17 α (H)-Ergostane
C29-20(<i>S</i>)5 α (H),14 α (H),17 α (H)-Stigmastane
C29-20(<i>R</i>)5 α (H),14 β (H),17 β (H)-Stigmastane
C29-20(<i>S</i>)5 α (H),14 β (H),17 β (H)-Stigmastane
C29-20(<i>R</i>)5 α (H),14 α (H),17 α (H)-Stigmastane
17 α (H),21 β (H)-30-Norhopane
17 α (H),21 β (H)-Hopane
22(<i>S</i>)-17 α (H),21 β (H)-30-Homohopane
22(<i>R</i>)-17 α (H),21 β (H)-30-Homohopane

organic aerosols. Direct sources that might contribute to this unexplained fraction include meat cooking and wildfires. Excluding these and other sources of TC from the CMB analysis can result in overestimation of the contributions of motor-vehicle exhaust to TC if the excluded sources contain species in common with engine exhaust. In this study, the apportionments of engine exhaust and the split between gasoline and diesel contributions were determined by the abundances of EC, hopanes, steranes, and particulate PAHs in the source profiles relative to their presence in the ambient samples. Restricting the apportionment calculation to the fitting species shown in Table 7 tended to minimize the potential for overestimation of the contribution of diesel and gasoline exhaust TC resulting from the presence of nonengine sources in the ambient sample.

Source Apportionment of CO, NO, PM_{2.5}, and BC Using Multivariate Analysis and Traffic Counts

While the CMB model can provide useful source apportionments, it requires detailed speciation of ambient air samples and source emissions. Since such data are costly and difficult to obtain, the CMB approach is generally applied to a very limited set of observations. An alternative method for source apportionment that can be applied using widely available data for criteria pollutants is the much simpler multivariate analysis. With this method, we look for consistent relationships between the concentrations of a measured pollutant, such as CO, and observed

variations in emissions parameters, for example, traffic volume, to evaluate whether such surrogates can be used to estimate on-road pollutant concentrations.

Although multivariate methods typically require larger data sets as inputs than those compiled for this study, we applied a multivariate method to our on-road in-cabin measurements and traffic-count data from an earlier project as a test to determine whether the approach had potential for application to future epidemiological modeling efforts. AADT counts for numerous locations along Los Angeles-area freeways are available from the California Department of Transportation (2005). To estimate the number of trucks and total vehicles per hour traveling on each of the freeway segments where our on-road measurements were made, we combined the AADT data with data on hourly traffic distribution compiled by Gao and Neimier (2003) using the on-highway weigh-in-motion system. To relate these traffic counts to the observed on-road concentrations of pollutants derived from vehicle exhaust, we proposed the following simple relationship:

$$[P_e] = aV_D + bV_G$$

where P_e = estimated on-road pollutant concentration, V_D = heavy-duty truck counts per hour (a metric of diesel-engine emissions), and V_G = light- and medium-duty vehicle counts per hour (a metric of gasoline-engine emissions).

We applied this equation to each freeway segment using the same values for the constants a and b (emission factors), and we calculated the differences in percentage between the resulting estimated concentrations of a pollutant and the mean measured on-road concentrations of that pollutant. Using an iterative solution process (with the Excel Solver tool), we then adjusted the constants to yield the minimum value of the root mean square of the percentage differences for all freeway legs. Since we applied the model to directly emitted pollutants associated with mobile sources, we used a zero intercept in the regression to improve the stability of the solution.

Estimation of DPM from EC

DPM is composed of a center core of elemental carbon EC coated with organic compounds, as well as small amounts of sulfate, nitrates, metals, and other trace elements. There is no direct method for measuring DPM in ambient air as it contains many of the chemical components that are also emitted by other combustion sources (e.g., gasoline vehicles). Ambient concentrations of EC in the SoCAB have been primarily attributed to diesel exhaust (Fujita et al. 2007b; Lough et al. 2007). In the MATES-II study for the SoCAB (SCAQMD 2000), EC measurements were used to estimate DPM concentrations using the following relationships:

Approximately 67% of EC in the ambient air in the Los Angeles area originates from diesel-engine exhaust (Gray 1986), and the average EC fraction of diesel particles is 64%. Therefore, in the MATES-II study, SCAQMD calculated DPM concentrations from EC measurements by multiplying a measured EC concentration by 67% and dividing by the fraction of DPM mass accounted for by EC (64%). That is, $\text{DPM concentration} = (\text{EC} \times 0.67)/0.64$, or $\text{DPM} = \text{EC} \times 1.04$.

Using a 1998 emissions inventory for the SoCAB, the conversion from EC to DPM was a factor of 1.24 (SCAQMD 2000).

In this study, DPC concentrations for each site were estimated by multiplying the measured EC concentrations by the slope of the correlation between particulate TC and EC in the source-dominated ambient samples collected on road on Terminal Island at the ports of Long Beach and Los Angeles (i.e., 1.3, as shown later in the report), based on the assumption that TC in this scenario is equal to DPC. The upper-bound ambient concentrations of DPC were estimated using the regression results and the average EC concentrations at each site. The estimates of DPC derived from this EC-surrogate approach are compared in this study to the CMB source contribution estimates of diesel exhaust to particulate TC. The DPM mass concentrations can be estimated from the following relationship:

$$\text{DPM} = \text{EC} + 1.46 (\text{DPC} - \text{EC})$$

where 1.46 is the ratio of diesel particulate organic matter to DPC from the Gasoline/Diesel PM Split dynamometer testing of diesel trucks in the Riverside, California, area (Fujita et al. 2007a; El-Zanan et al. 2009). Metals are minor contributors to DPM and can be excluded in the above calculation. The solution of this equation is $\text{DPM} = \text{EC} \times 1.438$.

RESULTS

CHARACTERIZATION OF ON-ROAD CONCENTRATIONS OF POLLUTANTS

The concentrations of CO, VOCs, NO, NO_x, PM_{2.5}, BC, and various MSATs were measured along roadways during the peak morning and evening commuting hours and during other times of the day on freeways with greater numbers of diesel trucks. Continuous and time-integrated data were used to determine the average concentrations of MSATs and other pollutants over commuting periods of about an hour. The continuous data were also used to characterize

the spatial variations in pollutant concentrations in relation to variations in volumes of light-duty vehicles and diesel trucks.

The on-road continuous BC, PM_{2.5}, CO, and VOC data are graphically displayed in a series of GIS maps in Appendix G (available on the HEI Web site). The maps show the 1-minute average concentrations of pollutants; these are plotted as circles that are proportional to the measured concentrations. Two of these plots illustrate the contrasting spatial variations of BC and CO concentrations relative to the average hourly traffic counts for trucks and all vehicles, which are listed in Table 5 by relevant road segment. The spatial pattern of higher BC concentrations, shown in Figure 7, for the summer sampling period is consistent with the higher truck counts on I-710, I-605, SR-60, and SR-91. BC concentrations were generally lower on I-405 and I-110 during the morning and afternoon peak commuting periods, when the proportion of trucks to total vehicle traffic during the day was lowest. Figure 8 shows that the spatial pattern of CO is the opposite of that of BC, with the highest concentrations on I-405 and I-110 during peak commuting periods. Higher CO concentrations were measured at intersections and when the mobile sampling van was following gasoline vehicles with high emissions.

Tables 8 and 9 summarize the means and standard deviations of on-road, continuous 1-minute concentrations of CO₂, CO, NO, NO_x, VOCs, PM_{2.5}, and BC by freeway routes and sampling periods for summer and fall, respectively. On-road concentrations of CO and VOCs were higher during the morning than during the afternoon periods. This was likely due to more stable atmospheric conditions since traffic counts are comparable during the two periods. The highest CO levels were measured during morning commutes on the below-grade sections of I-110 between I-105 and I-10. In contrast, BC and NO_x concentrations were higher on truck routes during sampling periods with the more unstable atmospheric conditions relative to the early morning commuting periods. The ratios of the mean on-road pollutant concentrations on commuting routes to truck routes in Table 10 are indicative of the combined effects of varying atmospheric stability and traffic volumes on the ambient levels of various pollutants. The ratios were consistently lowest for BC (0.3 to 0.6). The ratios for NO, NO_x, and PM_{2.5} were also lower than 1. For these pollutants, the ratios tended to be lower due to higher truck-traffic volumes and higher exhaust emission rates from diesel rather than gasoline engines, which resulted in higher concentrations of pollutants. In contrast, ratios for CO and VOCs were generally between 1.5 and 2 during the morning and near 1 during rest of the day.

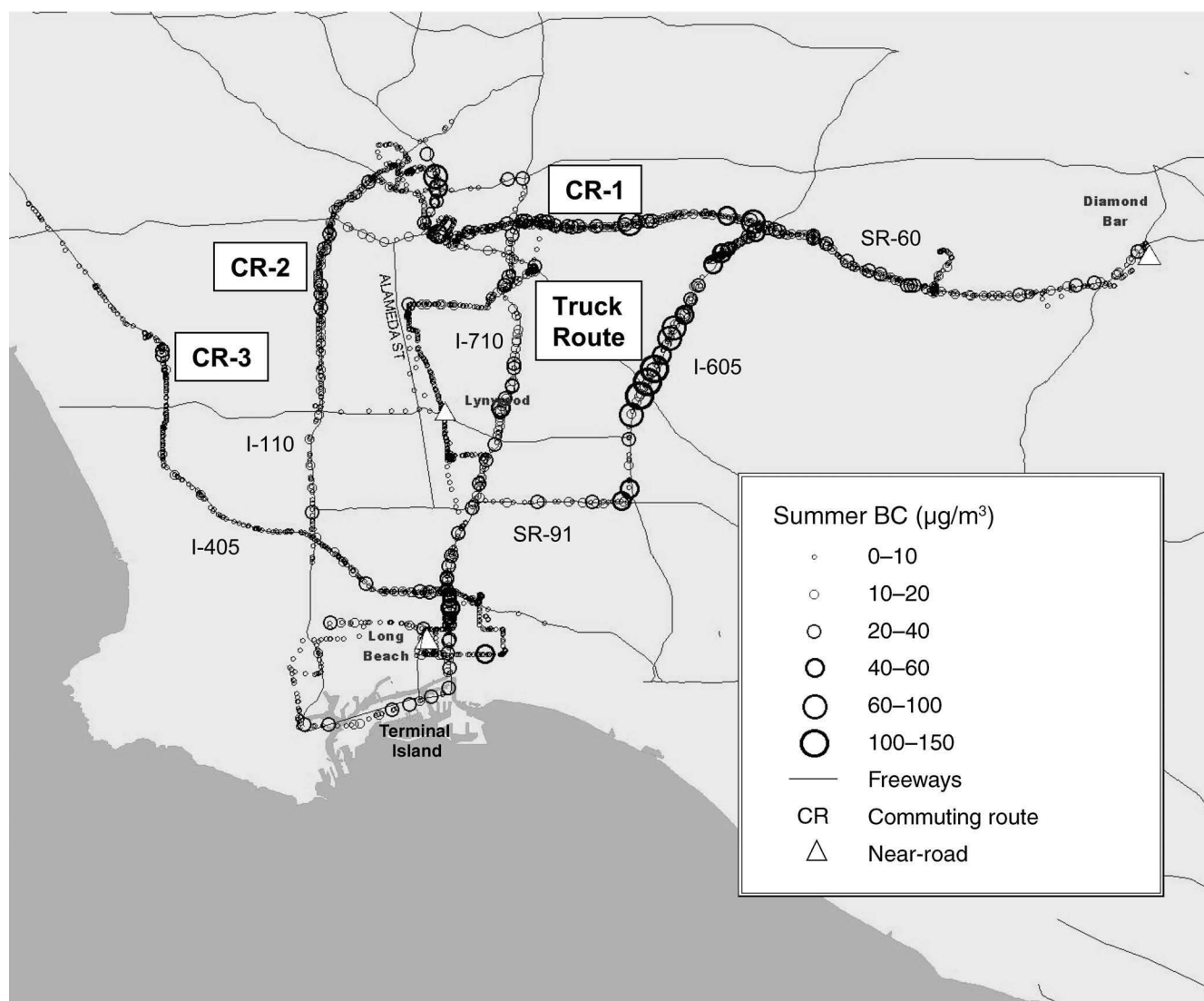


Figure 7. Spatial display of all 1-minute, on-road BC concentrations during the summer field study. The highest concentrations occur at Terminal Island and along truck routes (i.e., I-710, SR-91, I-605, and SR-60).

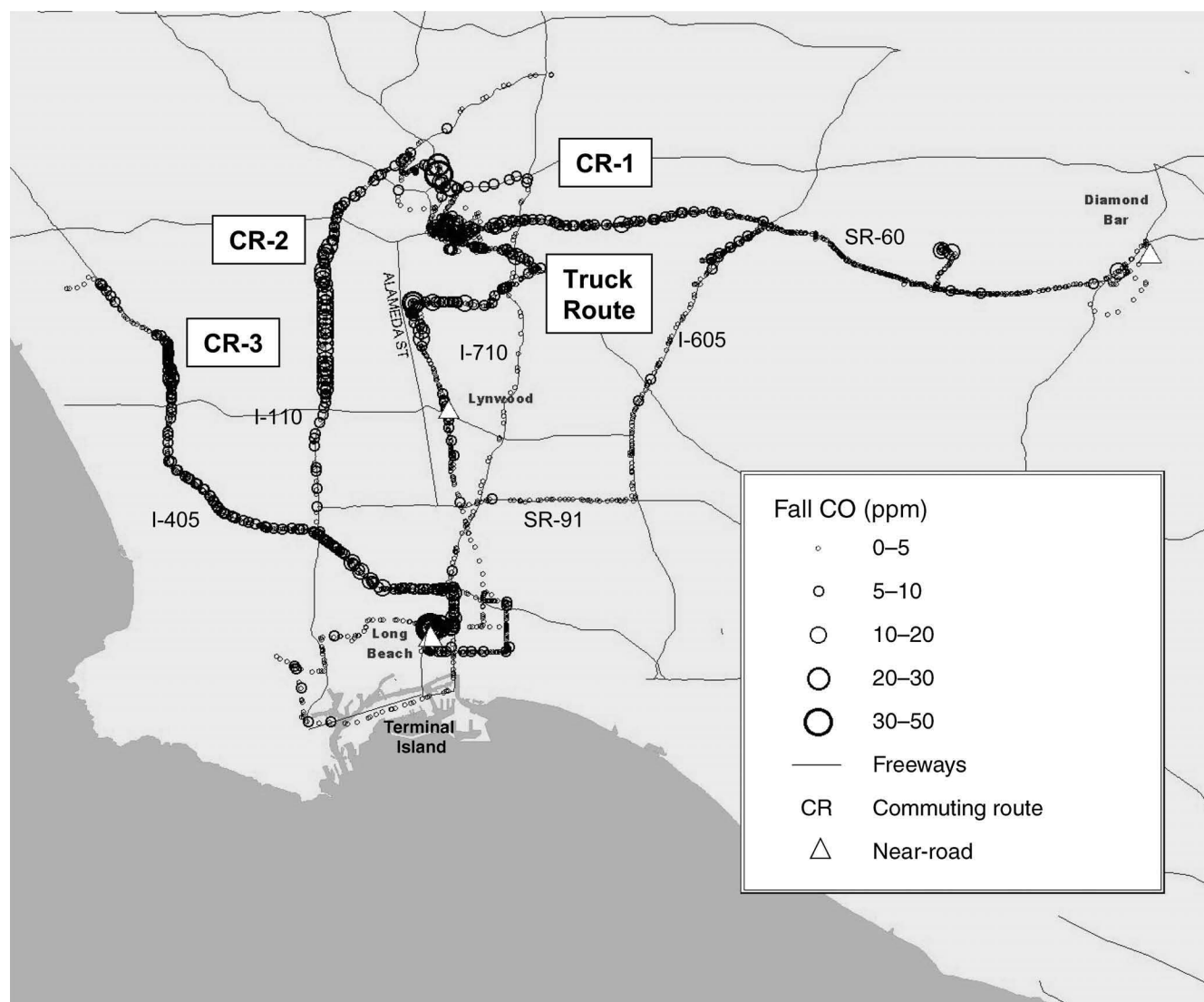


Figure 8. Spatial display of all 1-minute, on-road CO concentrations during the fall field study. Higher exposures typically occurred during congested commuter traffic, at intersections, or when the mobile sampling van was following gasoline vehicles with high emissions.

Table 8. On-Road, Continuous 1-Minute Pollutant Concentrations During Summer^a

Route	Time	Statistic	CO ₂ (ppm)	CO (ppm)	NO (ppb)	NO _x (ppb)	VOCs ^b (ppbV)	PM _{2.5} ^c (µg/m ³)	BC ^d (µg/m ³)	T_CABIN (°C)	T_OUT (°C)	RH (%)	Speed (mph)
I-110	AM	Mean	476	4.9	347	411	88	63	8.8	24	23	50	22
		SD	43	2.3	235	250	44	33	6.3	2	2	16	14
		<i>n</i>	68	68	147	147	99	147	143	147	147	147	147
I-405	AM	Mean	481	3.1	198	245	57	22	5.7	21	22	59	23
		SD	41	1.1	94	100	28	7	4.9	2	2	6	20
		<i>n</i>	135	135	107	107	134	134	54	107	107	107	135
SR-60	AM	Mean	519	4.7	329	388	95	38	11.9	26	27	55	14
		SD	40	1.7	114	120	25	8	7.1	2	4	6	9
		<i>n</i>	61	61	122	122	61	122	120	82	122	82	83
Truck route	AM	Mean	432	2.3	361	426	50	43	20.8	23	26	51	39
		SD	26	1.3	143	154	23	32	24.1	1	1	3	16
		<i>n</i>	55	55	106	106	106	106	105	106	106	106	106
I-110	PM	Mean	433	1.8	95	148	30	17	3.5	27	32	32	23
		SD	50	1.3	49	62	7	8	2.8	2	3	16	14
		<i>n</i>	136	136	136	136	136	136	131	136	136	136	136
I-405	PM	Mean	424	2.2	98	140	26	25	2.7	25	26	49	33
		SD	28	1.7	56	64	5	16	3.2	1	2	6	20
		<i>n</i>	173	173	173	173	173	173	171	173	173	173	173
SR-60	PM	Mean	407	2.0	112	170	44	22	3.7	26	34	53	20
		SD	25	1.2	55	65	38	8	1.7	3	2	8	10
		<i>n</i>	98	98	99	99	98	98	97	99	99	99	99
Truck route	PM	Mean	438	3.1	258	321	34	24	11.1	28	33	39	31
		SD	34	1.3	114	125	9	8	8.3	2	5	4	16
		<i>n</i>	125	125	125	125	120	125	122	125	125	125	125

^a *n* indicates the number of observations.^b Based on the ppbRAE PID monitor. The monitor responds to gases that have an ionization potential of less than 10.6 eV, which include aromatic hydrocarbons, olefins, and higher-molecular-weight alkanes.^c Based on TSI DustTrak light-scattering measurements. Raw data were divided by 2.24 ratio of DustTrak to gravimetric mass.^d Based on raw photoacoustic light absorption measurements divided by a mass absorption efficiency of 5 m²/g.

Concentrations of Air Toxics in Motor Vehicle–Dominated Environments

Table 9. On-Road, Continuous 1-Minute Pollutant Concentrations During Fall^a

Route	Time	Statistic	CO ₂ (ppm)	CO (ppm)	NO (ppb)	NO _x (ppb)	VOCs ^b (ppbV)	PM _{2.5} ^c (µg/m ³)	BC ^d (µg/m ³)	T_CABIN (°C)	T_OUT (°C)	RH (%)	Speed (mph)
I-110	AM	Mean	628	7.8	490	548	92	103	4.2	20	20	48	29
		SD	111	3.7	191	212	39	34	2.1	2	3	6	18
		<i>n</i>	108	108	163	163	163	163	162	163	163	163	163
I-405	AM	Mean	576	5.4	350	398	98	72	3.1	21	18	54	15
		SD	68	1.9	121	132	30	23	1.5	2	2	10	11
		<i>n</i>	154	154	154	154	154	154	134	154	154	154	154
SR-60	AM	Mean	550	2.5	386	427	94	119	5.0	21	15	46	25
		SD	146	1.4	130	130	55	48	2.8	3	2	7	16
		<i>n</i>	159	159	159	159	115	159	156	159	159	159	159
I-110	PM	Mean	543	4.0	242	298	58	42	2.2	27	21	35	13
		SD	49	1.6	99	108	17	14	1.6	2	1	2	14
		<i>n</i>	164	164	115	115	164	164	113	164	164	164	164
I-405	PM	Mean	482	2.3	162	203	44	38	1.6	23	21	50	17
		SD	57	1.6	76	83	13	15	1.3	1	1	3	14
		<i>n</i>	166	166	168	168	166	166	150	168	168	168	168
SR-60	PM	Mean	555	3.5	367	417	61	120	4.7	23	21	44	18
		SD	50	1.9	121	123	15	40	1.8	3	3	9	8
		<i>n</i>	169	169	169	169	168	169	164	169	169	169	169
Truck route	Midday ^e	Mean	463	2.4	456	517	49	124	6.9	24	28	40	43
		SD	39	1.4	175	189	10	68	3.7	3	4	7	12
		<i>n</i>	285	285	286	286	285	280	280	286	286	286	286

^a *n* indicates the number of observations.

^b Based on the ppbRAE PID monitor. The monitor responds to gases that have an ionization potential of less than 10.6 eV, which include aromatic hydrocarbons, olefins, and higher-molecular-weight alkanes.

^c Based on TSI DustTrak light-scattering measurements. Raw data were divided by 2.24 ratio of DustTrak to gravimetric mass.

^d Based on raw photoacoustic light absorption measurements divided by a mass absorption efficiency of 5 m²/g.

^e Between 11 AM and 1 PM.

Table 10. Ratios of Mean On-Road Pollutant Concentrations on Commuting Routes to Mean On-Road Concentrations on Truck Routes

	Time	CO ₂ (ppm)	CO (ppm)	NO (ppb)	NO _x (ppb)	VOCs (ppbV)	PM _{2.5} (µg/m ³)	BC (µg/m ³)
Summer								
Concentrations								
Commuting routes SR-60, I-110, I-405	AM	492	4.2	291	348	80	41	8.8
Commuting routes SR-60, I-110, I-405	PM	421	2.0	102	153	34	22	3.3
Truck route	AM	432	2.3	361	426	50	43	20.8
Truck route	PM	438	3.1	258	321	34	24	11.1
Ratios								
Commuting/truck routes ratio	AM	1.14	1.82	0.81	0.82	1.61	0.94	0.43
Commuting/truck routes ratio	PM	0.96	0.65	0.39	0.48	0.99	0.88	0.30
Fall								
Concentrations								
Commuting routes SR-60, I-110, I-405	AM	585	5.2	408	458	95	98	4.1
Commuting routes SR-60, I-110, I-405	PM	527	3.3	257	306	54	67	2.8
Commuting routes SR-60, I-110, I-405	Mean AM and PM	556	4.2	333	382	74	82	3.5
Truck route	Midday ^a	463	2.4	456	517	49	124	6.9
Ratio								
Commuting/truck routes ratio	Mean AM and PM	1.20	1.76	0.73	0.74	1.52	0.67	0.50

^a Between 11 AM and 1 PM.

The on-road data from the time-integrated canister and DNPH samples for individual MSATs are summarized in Table 11 for the summer and in Table 12 for the fall sampling periods. The spatial and temporal variations of BTEX and BD were consistent with corresponding time-averaged CO and VOC levels (Table 11), with on-road concentrations higher in the morning than the afternoon and higher in the fall than the summer. Formaldehyde and acetaldehyde showed less diurnal variation in on-road pollutant concentrations, in comparison to BTEX and BD, because these carbonyl compounds are also formed by photochemical reactions during the day. Concentrations of MSATs were consistently about a factor of 2 higher on commuting routes than on truck routes. The ratios of the mean concentrations of on-road MSATs measured on commuting routes to the mean concentrations

measured on truck routes were substantially greater than 1 for all MSATs during the morning sampling period and for most species during the afternoon sampling period (Table 13).

One-minute concentrations were estimated for BTEX, BD, formaldehyde, and acetaldehyde based on correlations of the time-integrated canister and DNPH data with the time-averaged continuous CO (see Appendix D). The reconstructed, on-road 1-minute data are summarized in Table 14 for the summer sampling period and in Table 15 for the fall sampling period. The standard deviations indicate the range of concentrations during each sampling period attributable to factors such as variations in emission rates of vehicles traveling ahead of the mobile sampling van, the following distance of the van, and traffic density and speed.

Concentrations of Air Toxics in Motor Vehicle–Dominated Environments

Table 11. On-Road Time-Integrated Canister and DNPH Measurements of MSATs During Summer^a

Route	Time	Statistic	BD ^b	Benzene ^b	Toluene ^b	Ethyl- benzene ^b	Xylenes ^b	Hexane ^b	Styrene ^b	Form- aldehyde ^c	Acrolein ^c	Acet- aldehyde ^c
I-110	AM	Mean	1.28	3.9	8.5	1.2	5.3	13.2	0.4	8.51	0.40	4.39
		Min	0.52	2.1	4.4	0.7	3.3	1.2	0.3	7.87	0.24	3.66
		Max	1.89	6.7	15.9	2.1	8.8	34.8	0.5	9.68	0.53	5.62
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
I-405	AM	Mean	0.52	2.1	4.0	0.6	3.1	0.8	0.3	4.46	0.22	1.90
		Min	0.49	2.0	3.6	0.6	3.0	0.5	0.1	4.29	0.18	1.63
		Max	0.56	2.3	4.4	0.6	3.1	1.1	0.4	4.63	0.27	2.18
		<i>n</i>	2	2	2	2	2	2	2	2	2	2
SR-60	AM	Mean	0.62	1.8	3.6	0.7	3.6	0.6	0.2	6.98	0.30	3.88
		Min	0.50	1.3	1.6	0.5	2.4	0.4	0.2	5.02	0.20	3.20
		Max	0.74	2.4	5.7	1.0	4.8	0.9	0.2	8.94	0.40	4.56
		<i>n</i>	2	2	2	2	2	2	2	2	2	2
Truck route	AM	Mean	0.57	1.5	3.7	0.5	2.1	1.0	0.1	5.66	0.25	2.74
		Min	0.52	1.4	3.7	0.4	1.9	1.0	0.1	4.38	0.18	1.66
		Max	0.63	1.6	3.8	0.5	2.3	1.0	0.1	6.95	0.33	3.82
		<i>n</i>	2	2	2	2	2	2	2	2	2	2
I-110	PM	Mean	0.29	1.5	2.3	0.2	0.5	0.9	0.0	5.56	0.34	1.67
		Min	0.14	0.9	0.4	0.0	0.0	0.6	0.0	4.73	0.19	1.59
		Max	0.37	2.2	4.0	0.3	1.1	1.2	0.0	6.77	0.49	1.79
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
I-405	PM	Mean	0.34	0.9	1.9	0.2	0.8	0.4	0.1	4.52	0.20	1.87
		Min	0.33	0.6	1.5	0.2	0.6	0.3	0.0	3.83	0.15	1.18
		Max	0.34	1.0	2.2	0.2	0.9	0.5	0.1	5.56	0.25	2.93
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
SR-60	PM	Mean	0.36	1.2	2.4	0.3	1.4	0.6	0.1	5.63	0.27	2.77
		Min	0.32	0.9	1.9	0.3	1.1	0.5	0.0	4.76	0.22	2.51
		Max	0.40	1.4	2.8	0.4	1.7	0.7	0.1	6.51	0.32	3.03
		<i>n</i>	2	2	2	2	2	2	2	2	2	2
Truck route	PM	Mean	0.45	1.3	3.1	0.2	0.6	0.7	0.0	5.57	0.26	2.50
		Min	0.41	1.1	2.0	0.2	0.6	0.6	0.0	4.54	0.20	1.93
		Max	0.49	1.4	4.2	0.2	0.6	0.8	0.0	6.60	0.33	3.08
		<i>n</i>	2	2	2	1	1	2	2	2	2	2

^a Compounds are expressed as ppbV. *n* indicates the number of observations.

^b Canister measurement.

^c DNPH measurement.

Table 12. On-Road Time-Integrated Canister and DNPH Measurements of MSATs During Fall^a

Route	Time	Statistic	BD ^b	Benzene ^b	Toluene ^b	Ethyl- benzene ^b	Xylenes ^b	Hexane ^b	Styrene ^b	Form- aldehyde ^c	Acrolein ^c	Acet- aldehyde ^c
I-110	AM	Mean	1.50	4.9	11.7	1.8	10.2	3.0	1.5	11.61	0.32	4.59
		Min	1.01	3.1	7.0	1.0	6.2	1.7	0.8	8.82	0.25	3.31
		Max	2.37	7.4	17.8	3.0	16.2	5.1	2.7	15.41	0.45	6.84
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
I-405	AM	Mean	1.12	4.3	9.9	1.5	8.7	2.8	1.1	6.87	0.21	2.66
		Min	1.02	4.0	8.8	1.3	7.5	2.4	0.6	4.98	0.13	1.07
		Max	1.26	4.7	11.2	1.8	10.3	3.0	1.6	8.46	0.27	3.63
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
SR-60	AM	Mean	0.44	1.4	3.0	0.5	2.1	0.7	0.2	6.04	0.22	2.02
		Min	0.20	0.8	2.0	0.3	1.2	0.4	0.1	5.60	0.18	1.54
		Max	0.74	1.9	3.9	0.7	3.2	1.0	0.4	6.51	0.30	2.61
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
I-110	PM	Mean	1.00	3.4	8.0	1.1	6.1	2.1	0.3	10.81	0.30	3.59
		Min	0.86	3.3	7.3	1.0	5.2	2.0	0.2	8.37	0.19	2.77
		Max	1.10	3.6	8.3	1.3	7.1	2.3	0.3	13.06	0.45	4.69
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
I-405	PM	Mean	0.62	2.2	4.1	0.5	3.0	0.9	0.2	7.00	0.16	2.37
		Min	0.40	1.5	2.7	0.3	1.8	0.6	0.1	4.90	0.12	1.75
		Max	1.05	3.2	6.0	0.9	4.6	1.3	0.2	8.35	0.21	2.93
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
SR-60	PM	Mean	0.82	2.6	6.3	1.2	5.6	1.6	0.2	8.16	0.23	3.59
		Min	0.38	2.1	5.2	1.0	4.6	1.3	0.1	6.97	0.21	2.99
		Max	1.35	3.4	8.6	1.5	7.5	2.0	0.2	9.37	0.26	4.48
		<i>n</i>	3	3	3	3	3	3	3	3	3	3
Truck route	Midday ^d	Mean	0.46	1.4	3.1	0.5	2.1	0.7	0.2	6.01	0.19	1.91
		Min	0.39	1.0	2.7	0.3	1.0	0.5	0.1	4.46	0.15	0.80
		Max	0.53	1.7	3.7	0.6	2.7	0.9	0.2	7.51	0.24	3.25
		<i>n</i>	5	5	5	5	5	5	5	5	5	5

^a Compounds are expressed as ppbV. *n* indicates the number of observations.^b Canister measurement.^c DNPH measurement.^d Between 11 AM and 1 PM.

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Table 13. Ratios of Mean On-Road Volatile Organic MSAT Concentrations on Commuting Routes to Mean On-Road Concentrations on Truck Routes^a

	Time	BD	Benzene	Toluene	Ethyl- benzene	Xylenes	Hexane	Styrene	Form- aldehyde	Acrolein	Acet- aldehyde
Summer											
Concentrations											
Commuting routes SR-60, I-110, I-405	AM	0.81	2.62	5.39	0.85	4.00	4.89	0.30	6.65	0.31	3.39
Commuting routes SR-60, I-110, I-405	PM	0.33	1.18	2.20	0.23	0.89	0.63	0.04	5.24	0.27	2.10
Truck route	AM	0.57	1.54	3.72	0.48	2.09	1.01	0.08	5.66	0.25	2.74
Truck route	PM	0.45	1.25	3.12	0.20	0.62	0.70	0.00	5.57	0.26	2.50
Ratios											
Commuting/truck routes ratio	AM	1.41	1.71	1.45	1.76	1.91	4.86	3.67	1.17	1.20	1.24
Commuting/truck routes ratio	PM	0.72	0.94	0.71	1.17	1.44	0.90	12.70	0.94	1.04	0.84
Fall											
Concentrations											
Commuting routes SR-60, I-110, I-405	AM	0.94	3.25	7.51	1.15	6.40	1.98	0.81	7.86	0.25	2.98
Commuting routes SR-60, I-110, I-405	PM	0.81	2.71	6.15	0.94	4.87	1.55	0.20	8.66	0.23	3.19
Commuting routes SR-60, I-110, I-405	Mean AM and PM	0.88	2.98	6.83	1.05	5.63	1.77	0.51	8.26	0.24	3.08
Truck route	Midday ^b	0.46	1.37	3.13	0.47	2.10	0.73	0.15	6.01	0.19	1.91
Ratio											
Commuting/truck routes ratio	Mean AM and PM	1.92	2.17	2.18	2.23	2.68	2.43	3.30	1.37	1.30	1.62

^a All data are expressed as ppbV.

^b Between 11 AM and 1 PM.

Table 14. On-Road, Reconstructed 1-Minute Concentrations for Summer^{a,b}

Route	Time	Statistic	BD	BTEX	Formaldehyde	Acrolein
I-110	AM	Mean	—	—	—	—
		SD	—	—	—	—
		<i>n</i>	—	—	—	—
I-405	AM	Mean	0.54	10.28	4.61	0.22
		SD	0.27	5.13	1.72	0.10
		<i>n</i>	134	134	135	135
SR-60	AM	Mean	—	—	8.94	0.40
		SD	—	—	3.14	0.14
		<i>n</i>	—	—	61	61
Truck route	AM	Mean	0.57	7.91	4.38	0.18
		SD	0.24	3.45	2.38	0.10
		<i>n</i>	106	106	55	55
I-110	PM	Mean	0.29	4.48	5.46	0.33
		SD	0.13	2.63	3.48	0.24
		<i>n</i>	136	136	136	136
I-405	PM	Mean	0.34	3.76	4.57	0.20
		SD	0.07	0.80	4.01	0.18
		<i>n</i>	173	173	173	173
SR-60	PM	Mean	0.36	5.29	4.45	0.21
		SD	0.22	3.09	2.81	0.13
		<i>n</i>	98	98	97	97
Truck route	PM	Mean	0.45	—	5.55	0.26
		SD	0.12	—	2.48	0.13
		<i>n</i>	120	—	125	125

^a Estimated from correlations between time-averaged continuous CO measurements and time-integrated canister and DNPH measurements. Compounds are expressed as ppbV. *n* indicates the number of observations.

^b Dashes indicate missing data.

Table 15. On-Road, Reconstructed 1-Minute Concentrations for Fall^a

Route	Time	Statistic	BD	BTEX	Formaldehyde	Acrolein
I-110	AM	Mean	1.51	28.80	12.18	0.35
		SD	0.74	13.87	4.80	0.14
		<i>n</i>	163	163	108	108
I-405	AM	Mean	1.13	24.66	6.80	0.21
		SD	0.37	8.26	2.06	0.08
		<i>n</i>	154	154	154	154
SR-60	AM	Mean	0.55	6.92	6.04	0.22
		SD	0.32	4.24	2.66	0.11
		<i>n</i>	115	115	159	159
I-110	PM	Mean	1.01	18.59	10.81	0.32
		SD	0.26	4.56	4.53	0.18
		<i>n</i>	164	164	164	164
I-405	PM	Mean	0.62	9.81	6.97	0.16
		SD	0.36	4.56	3.80	0.12
		<i>n</i>	166	166	166	166
SR-60	PM	Mean	0.82	15.72	8.19	0.23
		SD	0.47	5.47	3.68	0.10
		<i>n</i>	168	168	169	169
Truck route	Midday ^b	Mean	0.46	7.04	6.02	0.19
		SD	0.09	1.69	3.55	0.11
		<i>n</i>	285	285	285	285

^a Estimated from correlations between time-averaged continuous CO measurements and time-integrated canister and DNPH measurements. Compounds are expressed as ppbV. *n* indicates the number of observations.

^b Between 11 AM and 1 PM.

RELATIONSHIPS BETWEEN ON-ROAD POLLUTANT CONCENTRATIONS AND CONCENTRATIONS AT NEARBY FIXED MONITORING SITES

Studies have shown that traffic-related pollutants disperse rapidly downwind of the roadway (Zhu et al. 2002). In addition to meteorologic conditions and traffic density, on-road concentrations depend on pollutant emission rates and the proximity and speed of the vehicles traveling ahead of the sampling van. Based on the simulations by Jiang and colleagues (2005) of unconfined dilution of exhaust plumes in ambient air, we estimated that the exhaust-dilution ratios would be about 400 after 1 second at a vehicle speed of 65 mph (29 m following distance) and about 150 at a vehicle speed of 25 mph (11 m following distance). Given such rapid dispersion of vehicle emissions, pollutant concentrations are potentially much higher on a roadway than in the adjacent residential neighborhood. This section examines the variations in concentrations of MSATs and related pollutants measured on Los Angeles freeways relative to the corresponding concentrations at nearby SCAQMD monitoring stations and other locations away from the highway,

including two of our near-road sites, MATES-III fixed sites and temporary microscale sites, and several schools in the Boyle Heights area of East Los Angeles.

Figure 9 and Figure 10 are box-and-whisker plots of the 1-minute averages of on-road NO_x concentrations during the summer and fall, respectively. They show large variations in on-road concentrations of NO_x, especially on routes with higher proportions of trucks. Figure 11 and Figure 12 show similar plots for CO. On-road CO levels also show large variations, but the highest concentrations of CO were generally related to congested traffic or times when we followed gross polluters (data not shown). The below-grade sections of I-110 may have also contributed to the higher average CO levels on that freeway during the morning commutes, as a result of restricted dispersion of pollutants. Figures 9, 10, 11, and 12 also show the corresponding hourly average levels of NO_x or CO at nearby SCAQMD monitoring stations and at two near-road sites (Diamond Bar and Lynwood): Data for monitoring stations closest to each of the on-road-measurement locations are plotted to the right of each box-and-whisker plot. Note that

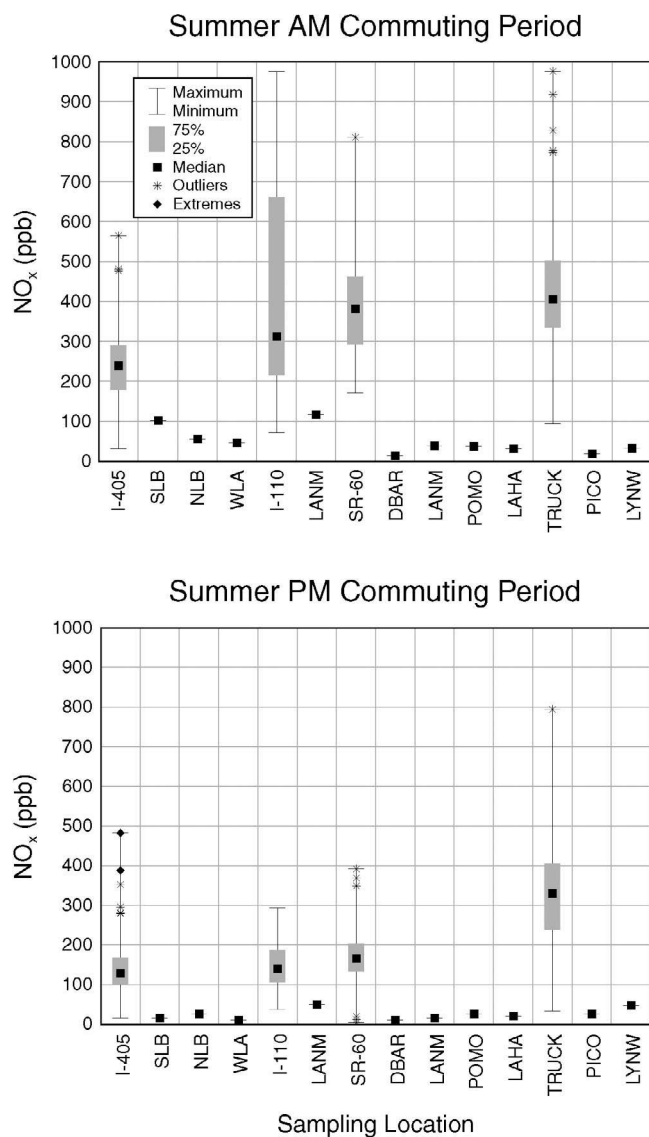


Figure 9. One-minute averages of on-road NO_x concentrations during morning and afternoon commutes (summer field studies) and corresponding hourly averages at near-road and SCAQMD monitoring stations. Data from the near-road Long Beach site are not shown. Outliers and extremes are defined as individual points that are more than 1.5 or 3 times, respectively, the 25% to 75% interquartile range.

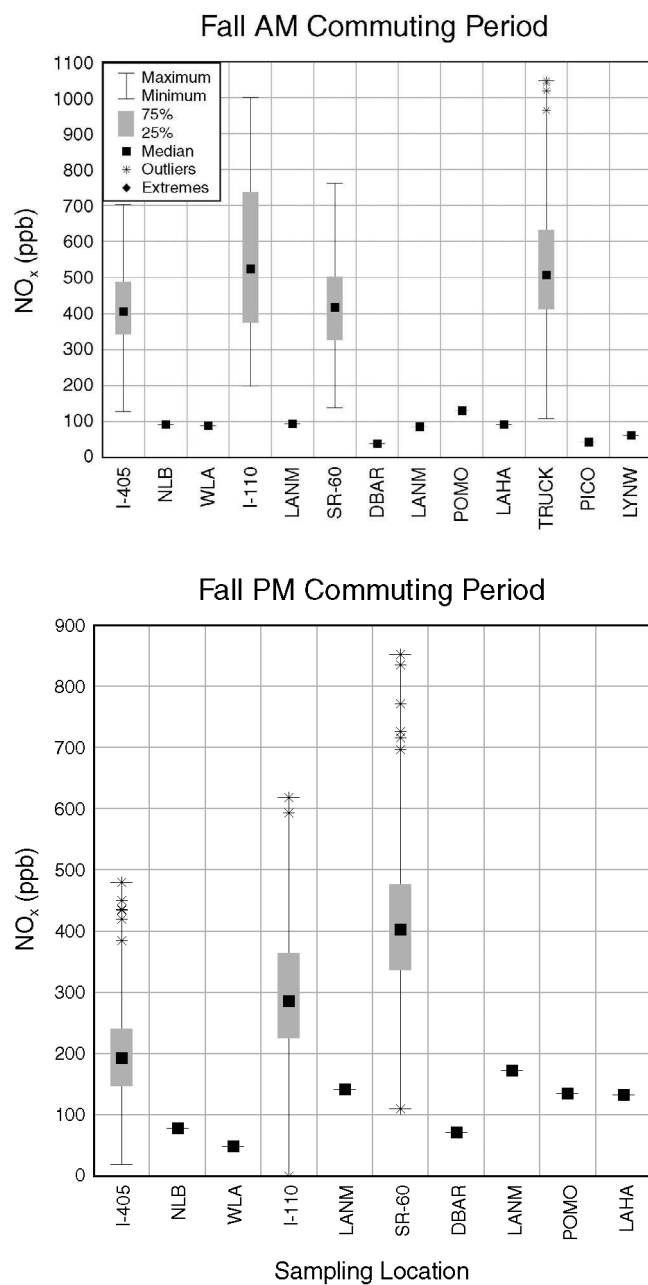


Figure 10. One-minute averages of on-road NO_x concentrations during morning and afternoon commutes (fall field studies) and corresponding hourly averages at near-road and SCAQMD monitoring stations. Data from the near-road Long Beach site are not shown. Outliers and extremes are defined as individual points that are more than 1.5 or 3 times the 25% to 75% interquartile range beyond the end of the box, respectively.

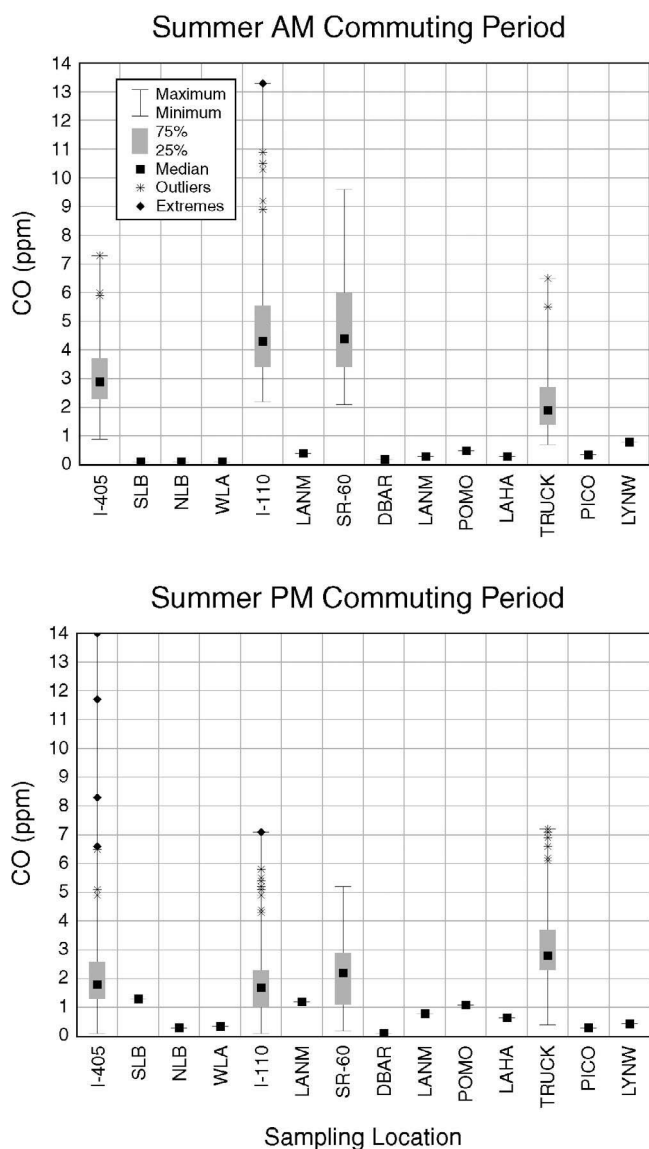


Figure 11. One-minute averages of on-road CO concentrations during morning and afternoon commutes (summer field studies) and corresponding hourly averages at near-road and SCAQMD monitoring stations. Data from the near-road Long Beach site are not shown. Outliers and extremes are individual points that are greater than 1.5 and 3 times the 25% to 75% interquartile range beyond the end of the box, respectively.

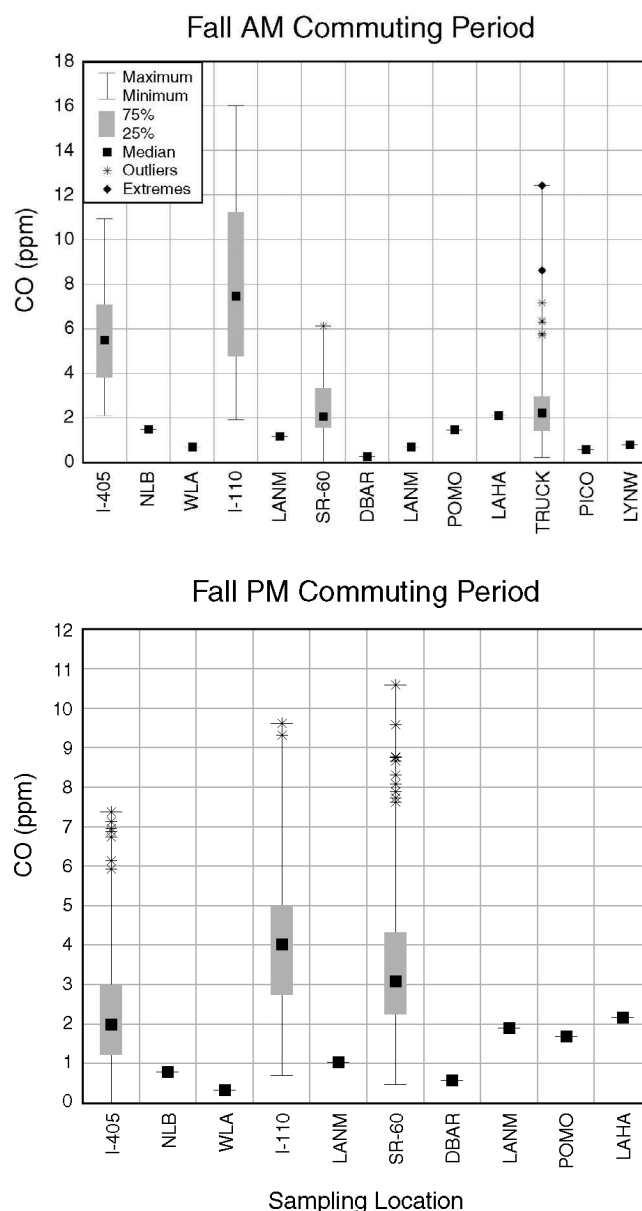


Figure 12. One-minute averages of on-road CO concentrations during morning and afternoon commutes (fall field studies) and corresponding hourly averages at near-road and SCAQMD monitoring stations. Data from the near-road Long Beach site are not shown. Outliers and extremes are individual points that are greater than 1.5 and 3 times the 25% to 75% interquartile range beyond the end of the box, respectively.

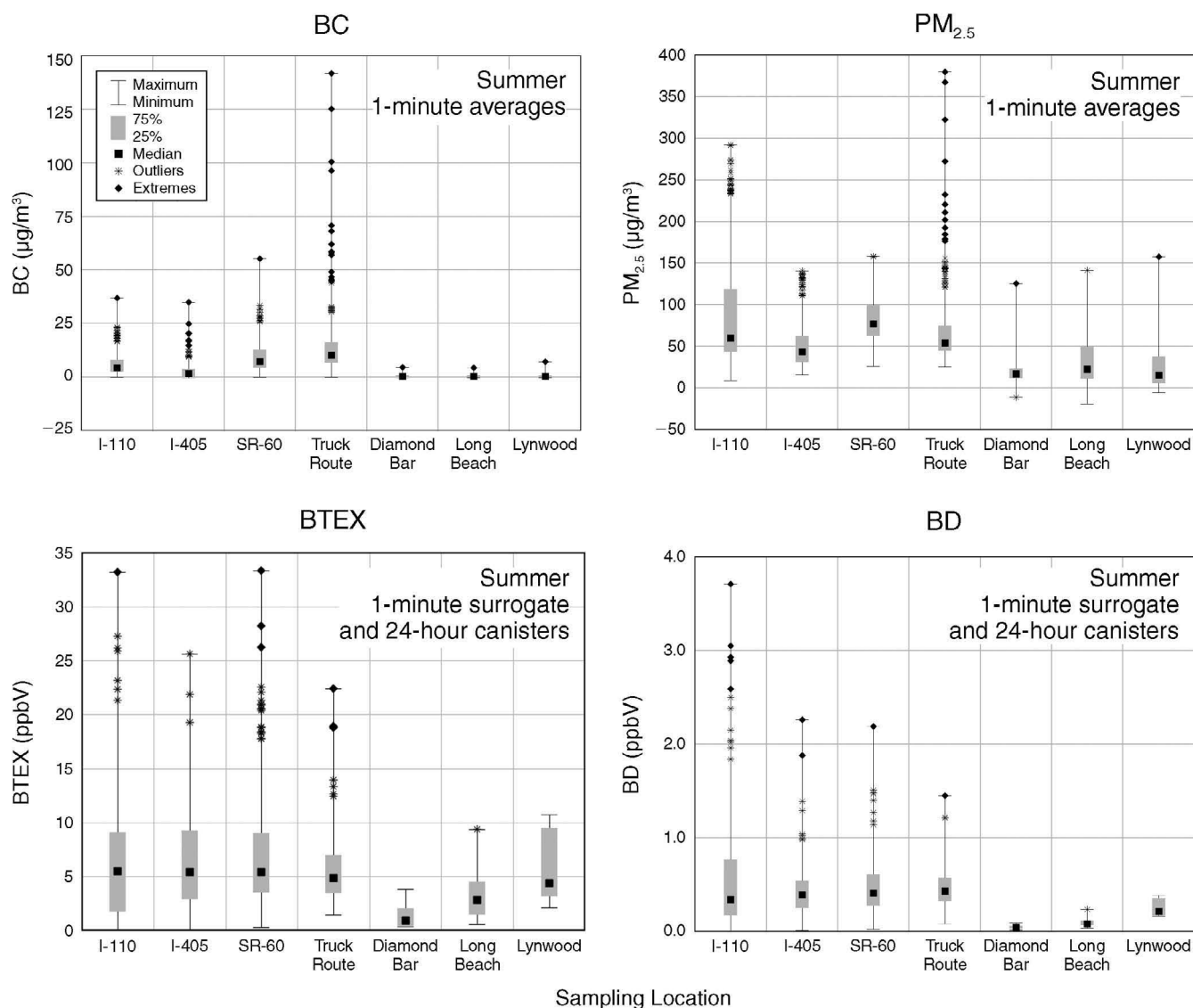


Figure 13. One-minute on-road and near-road BC, PM_{2.5}, BTEX, and BD concentrations. DustTrak PM_{2.5} data are unadjusted raw and exceed gravimetric mass by a factor of 2 to 2.5. Correlations of time-averaged PID and canister measurements were used to reconstruct 1-minute BTEX and BD concentrations. The BC and PM_{2.5} data for all locations are 1-minute averages. The BTEX and BD data are estimated 1-minute concentrations for on-road routes and 24-hour integrated canister measurements for the three near-road sites.

the minima of the plots are about equal to the hourly average values at the nearby monitoring stations.

As noted in the discussion of Figures 7 and 8, which show 1-minute average on-road measurements for BC and CO (see the preceding section, Characterization of On-Road Concentrations of Pollutants), higher concentrations of BC were associated with higher proportions of trucks, and higher CO concentrations were associated with commuter traffic consisting predominantly of gasoline-powered vehicles. In addition to higher rates of BC emissions, diesel trucks also had higher rates of NO_x and PM emissions than

gasoline-powered vehicles. The associations among these copollutants are apparent in the box-and-whisker plots in Figure 13 of 1-minute BC and PM_{2.5} concentrations at various locations. The average and upper range of BC concentrations were highest on the truck route. This figure also compares the ranges of on-road concentrations to those of the pollutants measured at each of the near-road sites. The average concentration ranges for BC were as much as an order of magnitude higher on road than at the three near-road sites, and the peak 1-minute average concentrations on roadways with high amounts of truck traffic were as

Table 16. Average Summer AM and PM On-Road NO_x and CO Concentrations, Corresponding Mean Hourly Ambient Concentrations Reported at SCAQMD Air Toxics Monitoring Sites, and Ratios of the Average Concentrations^a

Route	Time	Statistic	NO _x (ppb)		On-Road / SCAQMD	CO (ppm)		On-Road / SCAQMD
			On-Road	SCAQMD		On-Road	SCAQMD	
I-110	AM	Min	245	49	3.5	5.1	0.6	5.0
		Avg	379	110		5.1	1.0	
		Max	724	155		5.1	1.4	
I-405	AM	Min	200	96	2.3	3.0	0.5	5.0
		Avg	232	103		3.0	0.6	
		Max	264	109		3.0	0.7	
SR-60	AM	Min	331	71	2.6	2.9	1.0	2.1
		Avg	366	143		4.0	1.9	
		Max	444	300		4.7	3.1	
Truck route	AM	Min	360	46	8.2	2.3	0.0	6.6
		Avg	429	53		2.3	0.4	
		Max	497	59		2.3	0.7	
I-110	PM	Min	141	24	2.9	1.3	0.4	3.0
		Avg	149	51		1.9	0.6	
		Max	164	77		2.6	0.9	
I-405	PM	Min	129	37	3.7	2.1	0.1	21.6
		Avg	140	38		2.2	0.1	
		Max	149	39		2.3	0.1	
SR-60	PM	Min	157	55	2.7	1.9	1.0	2.7
		Avg	168	64		2.8	1.1	
		Max	179	72		3.8	1.1	
Truck route	PM	Min	308	75	4.2	2.8	1.3	2.4
		Avg	321	76		3.1	1.3	
		Max	333	76		3.5	1.3	

^a The mean on-road concentrations are compared to mean concentrations measured at the nearby monitoring stations according to the following association: I-110 with Los Angeles, N Main; I-405 with N Long Beach and W Los Angeles; SR-60 with Los Angeles, N Main, La Habra, and Pomona; and the truck route with Lynwood and Pico Rivera.

much as two orders of magnitude higher than peak concentrations at near-road sites. The average 1-minute PM_{2.5} mass concentrations on road were about two to six times higher than at the three near-road sites. The highest concentrations of PM_{2.5} were measured on the truck route, but they were not as high relative to the concentrations measured at the near-road sites as the concentrations of BC were, due to higher urban background concentrations of PM_{2.5} and contributions of other sources to ambient PM_{2.5} concentrations.

Gasoline-powered vehicles account for the majority of CO and VOC emissions in the emissions inventory and, by association, should also account for a larger fraction of MSATs such as BTEX and BD. The reconstructed 1-minute

BTEX and BD values are also shown in Figure 13 and compared to the 24-hour canister measurements from the three near-road sites. In contrast to particle measurements, the ranges of on-road concentrations of MSATs were greater for the gasoline-vehicle-dominated commuting routes. Also note that the concentrations of BTEX and BD were higher at Lynwood than at the other two near-road sites. The Lynwood monitoring station has historically recorded the highest CO concentrations in the SoCAB due in part to the close proximity to traffic of the sampling inlet.

We compared the on-road CO and NO_x concentrations to the corresponding mean hourly values at the nearby SCAQMD monitoring sites during the summer sampling period (Table 16) and during the fall (Table 17). Ratios of

Table 17. Average Fall AM and PM On-Road NO_x and CO Concentrations, Corresponding Mean Hourly Ambient Concentrations Reported at SCAQMD Air Toxics Monitoring Sites, and Ratios of the Average Concentrations^a

Route	Time	Statistic	NO _x (ppb)		On-Road / SCAQMD	CO (ppm)		On-Road / SCAQMD
			On-Road	SCAQMD		On-Road	SCAQMD	
I-110	AM	Min	434	58	5.2	4.8	0.6	9.7
		Avg	547	105		7.8	0.8	
		Max	772	162		10.7	1.1	
I-405	AM	Min	380	80	3.8	3.7	0.7	5.5
		Avg	399	105		5.4	1.0	
		Max	412	142		7.4	1.4	
SR-60	AM	Min	348	61	3.4	1.5	0.8	1.7
		Avg	422	124		2.5	1.4	
		Max	524	201		3.4	2.4	
Truck route	Midday ^b	Min	475	43	8.4	1.4	0.5	3.4
		Avg	519	62		2.4	0.7	
		Max	558	90		3.0	1.1	
I-110	PM	Min	272	67	2.0	3.7	0.8	3.0
		Avg	293	148		4.0	1.3	
		Max	323	236		4.7	1.9	
I-405	PM	Min	185	25	3.2	1.5	0.7	2.8
		Avg	203	63		2.3	0.8	
		Max	230	101		3.5	1.1	
SR-60	PM	Min	338	122	2.7	2.4	1.5	1.9
		Avg	415	152		3.5	1.8	
		Max	466	185		4.8	2.2	

^a The mean on-road concentrations are compared to mean concentrations measured at the nearby monitoring stations according to the following association: I-110 with Los Angeles, N Main; I-405 with N Long Beach and W Los Angeles; SR-60 with Los Angeles, N Main, La Habra, and Pomona; and the truck route with Lynwood and Pico Rivera.

^b Between 11 AM and 1 PM.

on-road concentrations to corresponding measurements at the nearby monitoring stations ranged from 2 to 5 for both CO and NO_x during peak commuting periods. Exceptions were higher ratios for CO on I-405 during the afternoon commute due to near zero values at nearby monitoring stations and on I-110 during the fall on the below-grade sections of the freeway, likely because of reduced dispersion of pollutants. The ratios for NO_x on the truck route tended to be higher than those for the gasoline-vehicle-dominated commuting routes.

Table 18 and Table 19 show the average fall concentrations of MSATs on road and at nearby fixed monitoring locations during the morning and afternoon commuting periods, respectively. The data from these surveys were

intended to characterize the differences in concentrations of MSATs within the adjacent neighborhoods relative to the on-road concentrations rather than to develop quantitative relationships between pollutant concentrations and proximity to highways. The results generally show much higher on-road concentrations relative to the sites away from the highway, about an order of magnitude higher for CO, NO, and NO_x, and about factors of 2 to 5 higher for VOCs and PM_{2.5}. For the most part, the concentrations away from the highway were uniformly lower, which is consistent with other studies that have found that the concentration falls to the surrounding background levels within several hundred meters of highways (Zhu et al. 2002).

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Table 18. Average Fall Morning Concentrations of MSATs On Road and at Nearby Survey Locations

Site		CO ₂ (ppm)	CO (ppm)	NO (ppb)	NO _x (ppb)	VOCs (ppbV)	PM _{2.5} (µg/m ³)	BC (µg/m ³)
I-110 On road	Avg	628	7.8	490	548	92	103	4
	SD	111	3.7	191	212	39	34	2
	Max	980	16.0	895	1001	187	244	11
City of Commerce (MATES-III Site)	Avg	203	0.4	53	65	20	35	8
	SD	223	0.6	65	78	22	38	9
	Max	416	1.3	135	161	43	76	20
Compton (MATES-III Site)	Avg	214	0.7	51	69	24	41	8
	SD	236	0.9	67	88	27	46	10
	Max	477	2.3	165	215	57	96	25
Huntington Park (MATES-III Site)	Avg	216	0.8	46	60	25	38	8
	SD	240	1.0	51	68	28	42	9
	Max	501	2.0	110	146	62	84	17
LA North (Leroy St)	Avg	236	0.5	46	58	22	25	6
	SD	260	0.7	58	69	24	27	7
	Max	518	1.7	120	143	47	53	15
I-405 On road	Avg	576	5.4	350	398	98	72	3
	SD	68	1.9	121	132	30	23	1
	Max	751	11.0	644	703	251	145	11
SCAQMD Long Beach (MATES-III Site)	Avg	197	0.4	33	43	28	39	5
	SD	218	0.9	50	64	40	56	8
	Max	432	2.0	119	151	103	122	18
Long Beach City College	Avg	188	0.2	27	35	40	38	5
	SD	207	0.5	36	48	68	55	7
	Max	410	1.1	83	107	175	128	15
Long Beach State Univ Tech Center	Avg	197	0.8	67	81	52	46	9
	SD	220	1.8	133	150	84	66	16
	Max	455	4.0	336	381	215	153	40
SR-60 On road	Avg	550	2.5	386	427	94	119	5
	SD	146	1.4	130	130	55	48	3
	Max	1593	6.1	714	762	273	266	17
IHCC	Avg	192	0.0	29	46	13	34	2
	SD	210	0.1	34	53	15	54	3
	Max	399	0.2	71	120	33	139	8
Pico Rivera (MATES-III Site)	Avg	226	0.0	35	50	17	29	3
	SD	252	0.1	39	55	20	41	4
	Max	494	0.2	85	115	43	105	10
Soto St School	Avg	257	0.4	35	50	21	36	3
	SD	282	0.5	39	55	25	49	4
	Max	548	1.1	77	105	58	123	10
Hollenbeck Middle School	Avg	226	0.3	31	44	20	38	3
	SD	248	0.4	35	50	21	53	4
	Max	472	1.1	78	109	39	134	10
Lorena St School	Avg	300	0.8	69	86	29	50	7
	SD	276	1.0	66	81	27	54	8
	Max	544	2.3	145	178	54	130	15
Sunrise Elementary School	Avg	258	0.3	34	47	21	34	2
	SD	286	0.5	38	52	25	48	3
	Max	570	1.1	73	97	60	124	7

Table 19. Average Fall Afternoon Concentrations of MSATs On Road and at Nearby Survey Locations

Site		CO ₂ (ppm)	CO (ppm)	NO (ppb)	NO _x (ppb)	VOCs (ppbV)	PM _{2.5} (µg/m ³)	BC (µg/m ³)
I-110 On road	Avg	543	4.0	242	298	58	42	2
	SD	49	1.6	99	108	17	14	2
	Max	685	9.6	522	619	121	127	9
City of Commerce (MATES-III Site)	Avg	202	0.3	15	33	20	12	4
	SD	223	0.5	21	44	22	13	6
	Max	443	1.2	47	93	47	27	15
Compton (MATES-III Site)	Avg	280	0.4	7	15	16	12	1
	SD	318	0.4	7	18	19	15	2
	Max	680	0.9	15	45	44	37	5
Huntington Park (MATES-III Site)	Avg	243	0.4	12	28	20	12	2
	SD	267	0.6	16	31	23	14	3
	Max	524	1.2	34	66	48	35	6
LA North (Leroy St)	Avg	263	0.5	31	27	18	10	2
	SD	296	0.9	47	34	20	12	2
	Max	614	2.2	121	81	48	26	5
I-405 On road	Avg	482	2.3	162	203	44	38	2
	SD	57	1.6	76	83	13	15	1
	Max	826	7.4	399	480	92	89	10
SCAQMD Long Beach (MATES-III Site)	Avg	192	0.2	23	35	14	18	3
	SD	212	0.2	46	65	15	22	6
	Max	417	0.6	117	165	30	50	15
Long Beach City College	Avg	187	0.3	9	19	13	13	2
	SD	205	0.4	13	27	14	15	5
	Max	394	1.0	33	68	30	36	12
Long Beach State Univ Tech Center	Avg	194	0.2	15	28	16	14	4
	SD	215	0.4	28	44	18	17	7
	Max	438	1.0	71	113	34	43	15
SR-60 On road	Avg	555	3.5	367	417	61	120	5
	SD	50	1.9	121	123	15	40	2
	Max	687	10.6	795	852	110	189	12
IHCC	Avg	185	0.1	2	14	11	23	2
	SD	203	0.2	4	17	12	41	4
	Max	402	0.3	9	42	27	105	8
Pico Rivera (MATES-III Site)	Avg	240	0.8	30	52	28	39	6
	SD	275	1.1	37	59	31	46	6
	Max	626	2.6	80	124	63	98	12
Soto St School	Avg	315	1.5	93	118	32	37	15
	SD	350	2.1	121	146	38	52	21
	Max	726	5.2	280	330	89	132	50
Hollenbeck Middle School	Avg	251	1.6	98	787	26	41	9
	SD	282	2.8	153	1783	32	51	11
	Max	616	7.1	390	4422	76	125	25
Lorena St School	Avg	221	1.2	67	83	20	34	10
	SD	311	1.8	96	115	27	51	14
	Max	652	4.2	206	227	54	115	30
Sunrise Elementary School	Avg	296	1.5	103	129	30	42	10
	SD	324	2.1	134	160	34	54	11
	Max	603	5.3	330	385	76	133	25

RATIOS OF ON-ROAD CONCENTRATIONS OF MSATs TO SEASONAL MEAN 24-HOUR CONCENTRATIONS MEASURED AT AIR TOXICS MONITORING SITES

We also determined the ratios of the mean concentrations of MSATs, measured during commutes, to the average, 24-hour MSAT concentrations—either seasonal or annual—measured at the SCAQMD air toxics monitoring sites. Comparisons were also made with measurements from our three near-road sites. These comparisons show the extent to which the on-road concentrations were greater than the seasonal and annual average concentrations. Specifically, we compared the data for MSATs from the on-road samples to the near-road, time-integrated data from canister and DNPH samples and to the corresponding seasonal and annual averages derived from data that was routinely collected every sixth day in 2004 at these air toxics monitoring sites: Azusa, Burbank–West Palm Avenue, Central Los Angeles–North Main Street, North Long Beach,

and Riverside–Rubidoux. As noted earlier, MATES-III data were not available in time for inclusion in this report because of the one-year extension of the study. The data from the 24-hour time-integrated samples from the three near-road sites are summarized in Table 20; the on-road data are summarized in Tables 11 and 12. The seasonal mean and maximum 24-hour average concentrations of MSATs measured at the air toxics monitoring sites are summarized in Table 21. The corresponding annual averages are summarized in Table 22. Ratios of on-road concentrations of MSATs averaged over the commuting sampling period to the averages of 24-hour measurements taken at air toxics monitoring sites are shown in Table 23 for the summer sampling period and in Table 24 for the fall period.

Compared to the annual, average 24-hour concentrations measured at the air toxics monitoring sites, on-road concentrations of BTEX in the summer were about 3.5 ± 0.7 and 1.2 ± 0.6 times higher during the morning and afternoon commuting periods, respectively. These ratios were higher

Table 20. 24-Hour Time-Integrated Pollutant Concentrations at Near-Road Sites

Near-Road Sites		PM _{2.5} (µg/m ³)	EC (µg/m ³)	BD (ppbV)	Benzene (ppbV)	Formal- dehyde (ppbV)	Acrolein (ppbV)	Acetal- dehyde (ppbV)	POM Surrogates (ng/m ³)	Volatile PAHs (ng/m ³)	Semivol PAHs (ng/m ³)	Particle PAHs (ng/m ³)	nitro- PAHs (ng/m ³)
Summer													
Diamond Bar	Min	6.2	0.6	0.02	0.05	1.81	0.05	0.18	0.3	213	7.1	0.8	3.5
	Median	12.3	1.3	0.05	0.19	2.81	0.06	0.58	0.9	299	7.5	1.9	
	Max	18.2	2.7	0.09	0.49	5.79	0.27	1.72	15.3	1221	62.2	37.4	
Lynwood	Min	7.3	0.5	0.16	0.43	1.60	0.05	0.06	0.1	474	9.7	0.5	1.2
	Median	12.4	2.3	0.21	0.67	3.38	0.15	1.49	0.3	791	18.3	1.6	
	Max	16.0	2.9	0.39	1.33	4.33	0.26	2.55	1.3	2247	24.1	5.4	
Long Beach	Min	18.3	1.3	0.03	0.13	0.82	0.04	0.02	0.1	676	8.7	0.2	1.7
	Median	29.9	2.0	0.08	0.48	1.26	0.06	0.37	0.3	837	11.4	0.6	
	Max	48.8	4.1	0.24	1.48	2.56	0.13	0.59	0.6	1365	18.3	1.1	
Fall													
Diamond Bar	Min	6.0	0.7	0.07	0.32	1.94	0.04	0.59	0.2	316	8.2	1.2	23.8
	Median	11.3	1.2	0.10	0.45	2.62	0.06	1.00	0.7	519	8.6	2.0	
	Max	27.7	2.6	0.14	0.70	3.70	0.12	1.79	0.9	630	11.7	2.9	
Lynwood	Min	11.4	1.6	0.40	1.38	4.38	0.09	1.40	1.3	700	12.3	3.9	5.0
	Median	14.3	2.3	0.51	1.79	5.30	0.14	2.12	3.2	1046	15.9	6.7	
	Max	16.6	3.2	0.89	3.47	6.44	0.18	2.97	4.3	1960	20.4	9.6	
Long Beach	Min	4.9	0.0	0.06	0.24	1.31	0.04	0.47	0.5	492	18.0	2.0	2.9
	Median	20.4	2.5	0.17	0.72	2.69	0.07	1.04	1.7	1044	20.0	4.6	
	Max	30.6	5.4	0.29	1.46	7.39	0.20	2.97	6.5	1507	26.9	10.1	

Table 21. Seasonal Mean and Maximum Concentrations of MSATs: 24-Hour Data Collected Every Sixth Day^a

Site	BD	Benzene	Toluene	Ethyl- benzene	Xylenes	Styrene	Form- aldehyde	Acrolein	Acet- aldehyde
Summer Mean									
Azusa	0.13	0.72	2.55	0.34	1.56	0.27	6.60	0.75	3.25
Burbank–W Palm Ave	0.20	0.90	2.95	0.45	2.09	0.23	3.35	0.60	1.15
Los Angeles–N Main St	0.33	1.10	3.80	0.56	2.46	0.21	14.00	0.87	1.30
North Long Beach	0.12	0.45	1.28	0.19	0.93	0.20	3.35	0.56	0.75
Riverside–Rubidoux	0.15	0.63	2.20	0.27	1.43	0.27	5.65	0.76	2.75
Summer Maximum									
Azusa	0.17	0.81	3.10	0.41	1.90	0.42	7.20	0.85	3.50
Burbank–W Palm Ave	0.30	1.20	4.30	0.63	2.97	0.40	3.50	0.69	1.20
Los Angeles–N Main St	0.33	1.10	3.80	0.56	2.46	0.21	15.00	0.87	2.20
North Long Beach	0.15	0.63	1.90	0.28	1.36	0.34	3.60	0.56	0.90
Riverside–Rubidoux	0.25	0.90	3.20	0.44	2.06	0.49	6.40	0.76	3.40
Fall Mean									
Azusa	0.09	0.35	1.25	0.10	0.75	0.13	1.37	0.40	0.83
Burbank–W Palm Ave	0.25	1.06	3.20	0.48	2.27	0.30	4.33	0.57	1.63
Los Angeles–N Main St	0.26	0.74	1.95	0.30	1.38	0.16	5.73	1.20	1.13
North Long Beach	0.25	0.77	2.00	0.27	1.39	0.41	2.30	0.44	1.23
Riverside–Rubidoux	0.17	0.70	2.67	0.25	1.32	0.27	1.93	0.44	1.07
Fall Maximum									
Azusa	0.10	0.39	1.50	0.10	0.84	0.15	2.00	0.42	1.00
Burbank–W Palm Ave	0.29	1.40	4.50	0.62	3.07	0.43	7.90	0.70	2.00
Los Angeles–N Main St	0.36	0.87	2.20	0.30	1.58	0.17	8.40	1.50	1.40
North Long Beach	0.34	0.92	2.30	0.34	1.75	0.60	3.00	0.52	1.30
Riverside–Rubidoux	0.32	1.00	2.80	0.40	2.02	0.41	2.50	0.52	1.40

^a All data are expressed as ppbV.

during the fall with smaller diurnal differences (4.8 ± 0.7 and 3.9 ± 0.6 for morning and afternoon commuting periods, respectively).

These ratios were higher for the morning than for the afternoon commuting hours and for the fall than for the summer because of greater atmospheric stability. Additionally, the ratios were lower for summer afternoons for the more reactive compounds consistent with their atmospheric lifetimes, as shown in Table 6 for reaction with hydroxyl radical. Benzene is the most stable, with a lifetime of 45 hours; it therefore has the highest ratios. Styrene is the least stable, with a lifetime of 1 hour; the other BTEX species have lifetimes ranging from 5 to 9 hours.

On-road concentrations of formaldehyde and acetaldehyde were up to two times higher than those measured at

air toxic monitoring sites, with fall ratios slightly higher than summer ratios. On-road concentrations of acrolein were unexpectedly lower than their annual, average 24-hour concentrations at the air toxic monitoring sites. Secondary formation of acrolein from the oxidation of BD provides a potential explanation. However, if this had been the case, the concentrations of formaldehyde should also have been higher at the fixed sites relative to the on-road concentrations. Acrolein is measured in the air toxics monitoring program by the California ARB using EPA method TO-15, in which sample air is collected in canisters and analyzed by gas chromatography with mass spectrometry. Other investigators have also obtained measurements of acrolein that were much lower than those obtained by the California ARB (Cahill et al. 2010).

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Table 22. Annual Mean Concentrations of MSATs: 24-Hour Data Collected Every Sixth Day at the SCAQMD Air Toxics Monitoring Sites^a

	Annual Average					
	Azusa	Burbank– W Palm	Los Angeles– N Main St	North Long Beach	Riverside– Rubidoux	5-Site Mean
BD	0.08	0.19	0.19	0.15	0.12	0.14
Benzene	0.45	0.77	0.67	0.56	0.54	0.60
Toluene	1.86	2.50	2.00	1.48	1.81	1.93
Ethylbenzene	0.18	0.37	0.30	0.20	0.19	0.25
Xylenes	0.94	1.77	1.37	1.02	1.01	1.22
Styrene	0.13	0.14	0.10	0.17	0.18	0.14
Formaldehyde	3.06	3.86	5.74	2.84	3.43	3.79
Acrolein	0.54	0.52	0.73	0.57	0.53	0.58
Acetaldehyde	1.57	1.83	1.29	1.23	1.57	1.50
CO	530	800	770	560	740	680
NO	10	40	40	30	20	28
NO _x	30	70	70	60	40	54

^a All data are expressed as ppbV.

Table 23. Ratios of Summer On-Road 1-Hour Concentrations of MSATs to Seasonal, Mean 24-Hour Measurements Taken at the SCAQMD Air Toxics Monitoring Sites^a

Route	Time	Statistic	BD	Benzene	Toluene	Ethyl- benzene	Xylenes	Styrene	Form- aldehyde	Acrolein	Acet- aldehyde
I-110	AM	Mean	8.85	6.53	4.42	4.78	4.32	2.98	2.25	0.68	2.93
		Min	3.59	3.45	2.29	2.72	2.68	1.99	2.08	0.41	2.45
		Max	13.12	11.21	8.25	8.52	7.22	3.65	2.56	0.92	3.75
I-405	AM	Mean	3.61	3.56	2.07	2.54	2.52	1.79	1.18	0.39	1.27
		Min	3.36	3.30	1.89	2.49	2.48	0.99	1.13	0.31	1.09
		Max	3.86	3.81	2.26	2.59	2.55	2.59	1.22	0.47	1.45
SR-60	AM	Mean	4.29	3.09	1.88	2.91	2.97	1.57	1.84	0.52	2.59
		Min	3.43	2.09	0.82	1.85	1.98	1.50	1.33	0.35	2.13
		Max	5.15	4.08	2.95	3.98	3.97	1.63	2.36	0.69	3.04
Truck route	AM	Mean	3.95	2.57	1.93	1.94	1.71	0.58	1.50	0.44	1.83
		Min	3.57	2.40	1.91	1.75	1.52	0.38	1.16	0.31	1.11
		Max	4.34	2.74	1.95	2.13	1.90	0.77	1.84	0.57	2.55
I-110	PM	Mean	1.99	2.56	1.21	0.62	0.41	0.05	1.47	0.60	1.11
		Min	0.96	1.49	0.22	0.00	0.00	0.00	1.25	0.33	1.06
		Max	2.53	3.69	2.07	1.26	0.87	0.13	1.79	0.84	1.19
I-405	PM	Mean	2.33	1.43	0.99	0.80	0.63	0.35	1.19	0.35	1.25
		Min	2.30	1.07	0.80	0.73	0.52	0.10	1.01	0.26	0.79
		Max	2.36	1.73	1.11	0.85	0.70	0.85	1.47	0.43	1.96
SR-60	PM	Mean	2.47	1.95	1.22	1.40	1.14	0.39	1.49	0.47	1.85
		Min	2.21	1.47	1.00	1.30	0.89	0.21	1.26	0.39	1.67
		Max	2.74	2.42	1.44	1.50	1.39	0.57	1.72	0.56	2.02
Truck route	PM	Mean	3.13	2.10	1.62	0.80	0.51	0.02	1.47	0.45	1.67
		Min	2.85	1.91	1.05	0.80	0.51	0.01	1.20	0.35	1.29
		Max	3.41	2.29	2.18	0.80	0.51	0.03	1.74	0.56	2.05

^a The mean on-road concentrations are compared to mean concentrations measured at the nearby monitoring stations according to the following association: I-110 with Los Angeles, N Main; I-405 with N Long Beach and W Los Angeles; SR-60 with Los Angeles, N Main, La Habra, and Pomona; and the truck route with Lynwood and Pico Rivera.

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Table 24. Ratios of Fall On-Road Concentrations of MSATs to Seasonal, Mean 24-Hour Measurements Taken at the SCAQMD Air Toxics Monitoring Sites^a

Route	Time	Statistic	BD	Benzene	Toluene	Ethyl- benzene	Xylenes	Styrene	Form- aldehyde	Acrolein	Acet- aldehyde
I-110	AM	Mean	8.64	6.79	5.01	5.94	6.82	8.11	2.81	0.54	2.84
		Min	3.30	2.44	1.86	1.91	2.15	1.21	2.05	0.43	2.18
		Max	16.39	12.43	9.20	12.03	13.27	18.85	4.07	0.79	4.57
I-405	AM	Mean	7.78	7.16	5.13	6.10	7.14	7.41	1.82	0.37	1.78
		Min	7.05	6.78	4.58	5.31	6.11	4.06	1.32	0.22	0.71
		Max	8.71	7.91	5.79	7.08	8.44	11.22	2.23	0.47	2.43
SR-60	AM	Mean	3.02	2.36	1.54	1.93	1.75	1.44	1.60	0.39	1.35
		Min	1.38	1.42	1.02	1.21	0.94	0.56	1.48	0.32	1.03
		Max	5.14	3.25	2.02	2.66	2.64	2.83	1.72	0.53	1.74
I-110	PM	Mean	6.94	5.70	4.13	4.50	4.95	1.89	2.86	0.53	2.39
		Min	5.92	5.54	3.79	4.10	4.29	1.39	2.21	0.32	1.85
		Max	7.63	5.99	4.31	5.16	5.78	2.32	3.45	0.79	3.13
I-405	PM	Mean	4.28	3.62	2.14	2.21	2.42	1.11	1.85	0.28	1.58
		Min	2.78	2.50	1.42	1.36	1.49	0.69	1.29	0.21	1.17
		Max	7.28	5.34	3.11	3.43	3.79	1.71	2.20	0.37	1.95
SR-60	PM	Mean	5.70	4.31	3.29	4.66	4.58	1.20	2.15	0.39	2.40
		Min	2.61	3.44	2.67	3.92	3.76	0.96	1.84	0.36	2.00
		Max	9.36	5.66	4.45	6.11	6.11	1.62	2.47	0.44	2.99
Truck route	Midday ^b	Mean	3.15	2.30	1.62	1.89	1.72	1.07	1.59	0.32	1.27
		Min	2.68	1.75	1.42	1.27	0.85	0.73	1.18	0.26	0.53
		Max	3.64	2.81	1.92	2.53	2.17	1.38	1.98	0.42	2.17

^a The mean on-road concentrations are compared to mean concentrations measured at the nearby monitoring stations according to the following association: I-110 with Los Angeles, N Main; I-405 with N Long Beach and W Los Angeles; SR-60 with Los Angeles, N Main, La Habra, and Pomona; and the truck route with Lynwood and Pico Rivera.

^b Between 11 AM and 1 PM.

SOURCE APPORTIONMENT OF VOCs AND TC

Source Apportionment of VOCs by CMB

We applied CMB version 8.0 to the VOC data collected at the near-road fixed sites and to the data collected from the mobile van; we used the default set of source composition profiles described in the section VOC Apportionment, under Data Analysis. Source contribution estimates in percentage of the sum of the measured concentrations of the 55 species of hydrocarbons measured at PAMS sites are given in Table 25 for the on-road samples and in Table 26 for samples from the near-road fixed sites. The uncertainties provided in the tables for the average values for each route or site are expressed as either the standard deviation of the seven daily source apportionment results at the

fixed sites or, in the case of the freeway driving routes, the average deviation from the mean of the results for the smaller numbers (from 1 to 5) of individual samples.

Gasoline exhaust was the predominant source in all samples, ranging from nearly 100% for on-road samples to about 70% for samples taken at more regionally representative samples during the summer. The mean contributions attributed to gasoline vehicles for the fall samples were somewhat lower for the on-road samples and slightly higher for the near-road samples, but the differences were within the range of variation of the results. The relative contributions of diesel exhaust were generally insignificant, except for the fall samples from the freeway routes with heavy truck traffic. This may be explained in part by the difficulty in identifying diesel emissions without the

Table 25. On-Road Source Contributions to the Sum of 55 PAMS Hydrocarbons^a

					Mean Source Contribution Estimates (% of Concentrations at PAMS) and Avg Deviation					
Route	Time	Concentration (µg/m ³)	<i>n</i>	<i>r</i> ^{2b}	Gasoline Exhaust	Diesel Exhaust	Consumer Products	Coatings	CNG/ LPG ^c	Biogenic
Summer										
I-110	AM	572 ± 299	2	0.88	93 ± 27	0 ± 0	2 ± 2	0 ± 0	9 ± 1	0 ± 0
I-405	AM	204 ± 51	2	0.90	94 ± 33	21 ± 21	0 ± 0	1 ± 3	3 ± 2	0 ± 1
SR-60	AM	252 ± 91	2	0.80	80 ± 10	5 ± 7	1 ± 1	0 ± 2	4 ± 1	0 ± 1
Truck route	AM	215 ± 5	1	0.88	96 ± 61	0 ± 0	1 ± 1	0 ± 0	9 ± 2	0 ± 1
SR-60	Midday	177 ± 21	3	0.85	90 ± 7	7 ± 5	1 ± 1	0 ± 0	7 ± 4	0 ± 1
I-110	PM	164 ± 47	3	0.78	106 ± 20	0 ± 0	1 ± 1	0 ± 0	5 ± 3	0 ± 1
I-405	PM	111 ± 20	3	0.78	101 ± 42	2 ± 3	2 ± 2	0 ± 0	2 ± 2	0 ± 1
SR-60	PM	142 ± 16	2	0.80	99 ± 9	1 ± 2	0 ± 0	0 ± 0	2 ± 1	0 ± 1
Truck route	PM	146 ± 14	2	0.76	108 ± 9	4 ± 4	2 ± 2	0 ± 0	2 ± 1	0 ± 1
Source-dominated ambient samples		133 ± 74	3	0.76	81 ± 32	3 ± 3	4 ± 2	0 ± 0	11 ± 3	0 ± 1
		237 ± 151	2	0.82	102 ± 9	0 ± 1	0 ± 1	0 ± 0	5 ± 3	0 ± 1
Fall										
I-110	AM	716 ± 299	3	0.85	90 ± 18	0 ± 0	3 ± 2	0 ± 0	7 ± 0	0 ± 0
I-405	AM	589 ± 51	3	0.84	85 ± 22	0 ± 21	3 ± 0	0 ± 2	8 ± 2	0 ± 1
SR-60	AM	183 ± 91	3	0.85	77 ± 7	13 ± 5	4 ± 1	0 ± 1	10 ± 1	0 ± 0
Truck route	AM	174 ± 1	5	0.84	74 ± 12	22 ± 0	6 ± 0	0 ± 0	6 ± 0	0 ± 0
I-110	PM	461 ± 47	2	0.73	106 ± 30	0 ± 0	2 ± 1	0 ± 0	2 ± 3	0 ± 1
I-405	PM	261 ± 20	4	0.78	97 ± 31	1 ± 3	3 ± 2	0 ± 0	2 ± 2	0 ± 1
SR-60	PM	358 ± 16	3	0.83	93 ± 9	0 ± 2	1 ± 0	0 ± 0	5 ± 1	0 ± 1

^a Mean estimated percent contribution and average deviation from the mean (or root mean square uncertainty, if larger) are shown for each route. *n* indicates the number of observations.

^b CMB model performance parameter.

^c CNG and LPG source contributions can also include aged exhaust that is enriched in stable hydrocarbons such as methane, ethane, and propane, abundant species in CNG and LPG.

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Table 26. Source Contributions to the Sum of 55 PAMS Hydrocarbons at Near-Road Sites

				Mean Source Contribution Estimates (% of Concentrations at PAMS) and Avg Deviation					
Site	Day	Concentration ($\mu\text{g}/\text{m}^3$)	r^2 ^a	Gasoline Exhaust	Diesel Exhaust	Consumer Products	Coatings	CNG/ LPG ^b	Biogenic
Summer									
Diamond Bar	Sun	26.1	0.82	69 ± 38	0 ± 0	9 ± 8	0 ± 0	25 ± 10	2 ± 3
	Mon	20.9	0.34	30 ± 11	3 ± 4	4 ± 3	3 ± 7	12 ± 4	1 ± 2
	Tue	21.4	0.85	75 ± 22	0 ± 0	7 ± 8	0 ± 0	23 ± 8	1 ± 4
	Wed	37.0	0.91	78 ± 43	0 ± 0	8 ± 9	0 ± 0	21 ± 11	0 ± 4
	Thu	88.8	0.81	62 ± 19	0 ± 0	7 ± 7	4 ± 13	16 ± 7	1 ± 3
	Fri	97.9	0.91	71 ± 21	0 ± 0	5 ± 8	4 ± 15	13 ± 7	0 ± 4
	Sat	72.2	0.84	76 ± 22	0 ± 0	8 ± 8	0 ± 0	19 ± 8	1 ± 4
Long Beach	Sun	164.1	0.75	61 ± 34	0 ± 0	13 ± 7	0 ± 0	19 ± 9	0 ± 0
	Mon	125.1	0.73	63 ± 35	0 ± 0	11 ± 7	0 ± 0	18 ± 9	0 ± 0
	Tue	43.2	0.79	67 ± 37	0 ± 0	10 ± 8	0 ± 0	22 ± 10	0 ± 3
	Wed	39.9	0.9	79 ± 44	0 ± 0	5 ± 9	0 ± 0	18 ± 11	0 ± 4
	Thu	351.8	0.72	69 ± 32	0 ± 0	11 ± 8	0 ± 0	13 ± 5	0 ± 0
	Fri	127.3	0.8	81 ± 24	0 ± 0	5 ± 9	0 ± 0	14 ± 8	0 ± 0
	Sat	196.7	0.84	75 ± 42	0 ± 0	10 ± 9	0 ± 0	16 ± 11	0 ± 0
Lynwood	Sun	67.1	0.78	92 ± 26	0 ± 0	0 ± 0	0 ± 0	7 ± 9	0 ± 5
	Mon	113.9	0.9	92 ± 227	0 ± 0	1 ± 9	0 ± 0	10 ± 13	0 ± 4
	Tue	227.6	0.91	90 ± 200	0 ± 0	2 ± 8	0 ± 0	11 ± 11	0 ± 4
	Wed	268.1	0.91	85 ± 189	0 ± 0	3 ± 7	0 ± 0	13 ± 11	0 ± 3
	Thu	255.3	0.91	89 ± 26	0 ± 0	4 ± 10	0 ± 0	10 ± 9	0 ± 4
	Fri	95.4	0.87	100 ± 27	0 ± 0	0 ± 0	0 ± 0	8 ± 6	0 ± 5
	Sat	85.8	0.86	100 ± 30	0 ± 0	1 ± 11	0 ± 0	7 ± 10	0 ± 5
Diamond Bar	Avg ± SD	52 ± 33	0.78 ± 0.20	66 ± 17	0 ± 1	7 ± 2	2 ± 2	19 ± 5	1 ± 1
Long Beach	Avg ± SD	150 ± 106	0.79 ± 0.06	71 ± 8	0 ± 0	9 ± 3	0 ± 0	17 ± 3	0 ± 0
Lynwood	Avg ± SD	159 ± 87	0.88 ± 0.05	92 ± 6	0 ± 0	2 ± 1	0 ± 0	9 ± 2	0 ± 0

(Table continues on next page)

^a CMB model performance parameter.

^b CNG and LPG source contributions can also include aged exhaust that is enriched in stable hydrocarbons such as methane, ethane, and propane, abundant species in CNG and LPG.

Table 26 (Continued). Source Contributions to the Sum of 55 PAMS Hydrocarbons at Near-Road Sites

				Mean Source Contribution Estimates (% of Concentrations at PAMS) and Avg Deviation					
Site	Day	Concentration (µg/m ³)	r ^{2a}	Gasoline Exhaust	Diesel Exhaust	Consumer Products	Coatings	CNG/ LPG ^b	Biogenic
Fall									
Diamond Bar	Sun	121.5	0.84	55 ± 134	6 ± 26	4 ± 5	0 ± 0	22 ± 8	0 ± 2
	Mon	113.4	0.74	47 ± 79	6 ± 5	10 ± 4	0 ± 0	14 ± 3	0 ± 1
	Tue	66.0	0.49	136 ± 38	0 ± 0	0 ± 0	0 ± 0	6 ± 8	0 ± 0
	Wed	50.9	0.92	74 ± 44	2 ± 11	7 ± 9	0 ± 0	15 ± 11	0 ± 4
	Thu	87.2	0.91	86 ± 51	0 ± 12	4 ± 10	0 ± 0	12 ± 12	0 ± 4
	Fri	46.5	0.88	92 ± 26	0 ± 0	5 ± 10	0 ± 0	9 ± 6	0 ± 5
	Sat	99.3	0.8	90 ± 42	0 ± 0	6 ± 10	0 ± 0	9 ± 6	1 ± 5
Long Beach	Sun	46.5	0.65	62 ± 29	0 ± 0	10 ± 7	0 ± 0	13 ± 5	0 ± 3
	Mon	166.5	0.78	99 ± 28	0 ± 0	16 ± 11	2 ± 21	9 ± 6	0 ± 0
	Tue	179.6	0.83	72 ± 40	0 ± 0	7 ± 8	0 ± 0	14 ± 11	0 ± 0
	Wed	196.5	0.79	71 ± 34	0 ± 0	8 ± 8	0 ± 0	13 ± 5	0 ± 0
	Thu	109.1	0.79	66 ± 37	0 ± 0	9 ± 8	0 ± 0	16 ± 10	0 ± 0
	Fri	350.7	0.7	48 ± 28	0 ± 0	10 ± 6	0 ± 0	14 ± 8	0 ± 0
	Sat	119.4	0.73	63 ± 36	0 ± 0	9 ± 8	0 ± 0	13 ± 9	0 ± 0
Lynwood	Sun	558.8	0.87	84 ± 39	0 ± 0	9 ± 9	0 ± 18	7 ± 5	0 ± 0
	Mon	214.5	0.89	80 ± 37	0 ± 0	6 ± 9	1 ± 18	8 ± 5	0 ± 0
	Tue	213.0	0.87	89 ± 25	0 ± 0	4 ± 10	0 ± 0	14 ± 6	0 ± 0
	Wed	313.1	0.86	92 ± 43	0 ± 0	4 ± 10	0 ± 0	8 ± 6	0 ± 0
	Thu	326.9	0.89	85 ± 47	0 ± 0	3 ± 10	0 ± 0	15 ± 12	0 ± 0
	Fri	353.6	0.86	92 ± 43	0 ± 0	4 ± 10	0 ± 0	7 ± 6	0 ± 0
	Sat	246.9	0.87	90 ± 25	0 ± 0	5 ± 10	0 ± 0	8 ± 5	0 ± 0
Diamond Bar	Avg ± SD	84 ± 30	0.80 ± 0.15	83 ± 29	2 ± 3	5 ± 3	0 ± 0	13 ± 5	0 ± 0
Long Beach	Avg ± SD	167 ± 96	0.75 ± 0.06	69 ± 15	0 ± 0	10 ± 3	0 ± 1	13 ± 2	0 ± 0
Lynwood	Avg ± SD	318 ± 120	0.87 ± 0.01	87 ± 5	0 ± 0	5 ± 2	0 ± 0	9 ± 3	0 ± 0

^a CMB model performance parameter.^b CNG and LPG source contributions can also include aged exhaust that is enriched in stable hydrocarbons such as methane, ethane, and propane, abundant species in CNG and LPG.

inclusion of heavier hydrocarbon species ($> C_{12}$) in the data. Contributions of commercial natural gas (CNG) and liquefied petroleum gas (LPG), which may also represent aged mobile-source emissions, were the largest component after gasoline engine exhaust, contributing 5% to 10% to the on-road samples and 10% to 20% to the near-road samples. Consumer products contributed up to 10%, on average, to the near-road samples, but were negligible in the on-road samples. No variations related to the day of the week were apparent in the source apportionments.

The source apportionments for the sum of BTEX are shown in Table 27 and Table 28 for the on-road and near-road-site samples, respectively. As expected, these compounds were apportioned almost exclusively to gasoline-engine exhaust for the on-road samples. Only about 5% to 10% of the BTEX was attributed to other categories of sources measured at the fixed sites, confirming the dominance of mobile sources. The contribution of the largest nonmobile source, consumer products, was notably lower at Lynwood than at Diamond Bar or Long Beach where the distance to the roads was greater.

Source Apportionment of TC by CMB

To estimate the relative contribution of gasoline and diesel-vehicle exhaust to ambient PM at the three near-road sites, we applied the PM source composition profiles from the Gasoline/Diesel PM Split Study. The results of CMB analysis for the daily samples collected at the three near-road sites are shown in Figure 14 and Figure 15 for the summer and fall sampling periods, respectively. Apportionment of TC, rather than total $PM_{2.5}$, is shown because very little of the noncarbonaceous component of urban PM is directly emitted by vehicles. The results are presented as percentages of TC because the absolute amounts for each day are dependent on meteorology and traffic patterns. Averages of the seven daily samples for each site are provided in Table 29, which also includes the CMB performance statistics r^2 and χ^2 to indicate the overall “goodness of fit.”

The contributions from diesel exhaust to TC in this study were consistently much greater than those from gasoline

exhaust at all sites, averaging from 46% to 52% of total carbon for both seasons. Gasoline exhaust contributions averaged from 10% to 17% for the three sites in September, but did not contribute significantly during the November/December period. This was probably because particulate PAH composition in exhaust varies with vehicle operating temperatures. In the Kansas City PM Characterization Study (U.S. EPA 2008), we observed seasonal differences in the relative abundance of the three important gasoline marker species: benzo[*g,h,i*]perylene, indeno[1,2,3-*cd*]pyrene, and coronene. Since our source profiles were developed from emissions measurements made in summer only, they may not be appropriate for fall emissions. This is consistent with the observation that only the “cold start” gasoline profiles were identified as sources by the CMB model for the November/December ambient data. Because diesel engines typically operate at higher temperatures than gasoline engines, diesel exhaust composition is generally less affected by lower ambient temperatures.

About 40% to 50% of the carbonaceous PM was not apportioned to either gasoline or diesel exhaust. We expect this unidentified portion to be higher for the September period because of the increased formation of secondary organic aerosol during that period, but in this case the inability to apportion the gasoline exhaust during the fall months results in about the same fraction apportioned to sources other than mobile sources. The better performance statistics for the fall months are attributable to the dominance of a single source profile (diesel exhaust) for most samples.

The source apportionments for the three near-road sites are similar to those estimated for the Gasoline/Diesel PM Split Study at the Azusa and the Central Los Angeles–North Main Street monitoring stations, but with somewhat larger contributions from both diesel and gas vehicles. This is to be expected since these locations are not as close to freeways or busy arterials as the sites selected for this project. The uncertainties in the Gasoline/Diesel PM Split Study averages were lower than those for this study because in that study 3 weeks of samples were collected at each site and the samples were composited by day of the week to reduce the analytical error.

Table 27. On-Road Source Contributions to BTEX^a

Route	Time	Concentration ($\mu\text{g}/\text{m}^3$)	n	$r^{2\text{b}}$	Mean Source Contribution Estimates (% of BTEX) and Avg Deviation					
					Gasoline Exhaust	Diesel Exhaust	Consumer Products	Coatings	CNG/ LPG ^c	Biogenic
Summer										
I-110	AM	86 \pm 45	2	0.88	98 \pm 11	0 \pm 0	2 \pm 2	0 \pm 0	0 \pm 0	0 \pm 0
I-405	AM	39 \pm 2	2	0.90	95 \pm 9	3 \pm 3	0 \pm 0	2 \pm 2	0 \pm 0	0 \pm 0
SR-60	AM	39 \pm 16	2	0.80	96 \pm 12	3 \pm 2	1 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
Truck route	AM	30 \pm 2	1	0.88	99 \pm 10	0 \pm 0	1 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0
SR-60	Midday	21 \pm 6	3	0.85	95 \pm 10	4 \pm 2	1 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
I-110	PM	17 \pm 8	3	0.78	99 \pm 9	0 \pm 0	1 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
I-405	PM	14 \pm 1	3	0.78	97 \pm 7	1 \pm 2	2 \pm 2	0 \pm 0	0 \pm 0	0 \pm 0
SR-60	PM	21 \pm 1	2	0.80	100 \pm 13	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0
Truck route	PM	18 \pm 3	2	0.76	97 \pm 14	1 \pm 2	1 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
Source-dominated ambient samples		11 \pm 6	3	0.76	94 \pm 12	2 \pm 8	6 \pm 3	0 \pm 0	0 \pm 0	0 \pm 0
		37 \pm 25	2	0.82	99 \pm 13	0 \pm 0	1 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
Fall										
I-110	AM	114 \pm 45	3	0.85	96 \pm 7	0 \pm 0	4 \pm 2	0 \pm 0	0 \pm 0	0 \pm 0
I-405	AM	97 \pm 2	3	0.84	96 \pm 6	0 \pm 3	4 \pm 0	0 \pm 2	0 \pm 0	0 \pm 0
SR-60	AM	28 \pm 16	3	0.85	92 \pm 8	3 \pm 1	5 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
Truck route	AM	28 \pm 0	5	0.84	86 \pm 2	7 \pm 0	7 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0
I-110	PM	70 \pm 8	2	0.73	98 \pm 13	0 \pm 0	2 \pm 1	0 \pm 0	0 \pm 0	0 \pm 0
I-405	PM	49 \pm 1	4	0.78	96 \pm 5	0 \pm 1	3 \pm 2	0 \pm 0	0 \pm 0	0 \pm 0
SR-60	PM	63 \pm 1	3	0.83	99 \pm 9	0 \pm 0	1 \pm 0	0 \pm 0	0 \pm 0	0 \pm 0

^a Mean estimated percent contribution and average deviation from the mean (or root mean square uncertainty, if larger) are shown for each route. *n* indicates the number of observations.

^b CMB model performance parameter.

^c CNG and LPG source contributions can also include aged exhaust that is enriched in stable hydrocarbons such as methane, ethane, and propane, abundant species in CNG and LPG.

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Table 28. Source Contributions to BTEX at Near-Road Sites

			Mean Source Contribution Estimates (% of BTEX) and Avg Deviation					
Site	Day	Concentration (µg/m³)	Gasoline Exhaust	Diesel Exhaust	Consumer Products	Coatings	CNG/LPG ^a	Biogenic
Summer								
Diamond Bar	Sun	1.2	88 ± 45	0 ± 0	12 ± 1	0 ± 0	0 ± 0	0 ± 0
	Mon	1.3	77 ± 39	3 ± 4	9 ± 1	11 ± 4	0 ± 0	0 ± 0
	Tue	1.4	92 ± 46	0 ± 0	8 ± 1	0 ± 0	0 ± 0	0 ± 0
	Wed	3.3	91 ± 46	0 ± 0	9 ± 1	0 ± 0	0 ± 0	0 ± 0
	Thu	10.4	81 ± 41	0 ± 0	10 ± 1	9 ± 4	0 ± 0	0 ± 0
	Fri	15.5	85 ± 43	0 ± 0	7 ± 1	8 ± 3	0 ± 0	0 ± 0
	Sat	6.0	91 ± 46	0 ± 0	9 ± 1	0 ± 0	0 ± 0	0 ± 0
Long Beach	Sun	10.9	83 ± 42	0 ± 0	17 ± 2	0 ± 0	0 ± 0	0 ± 0
	Mon	7.0	85 ± 43	0 ± 0	15 ± 1	0 ± 0	0 ± 0	0 ± 0
	Tue	1.9	87 ± 44	0 ± 0	13 ± 1	0 ± 0	0 ± 0	0 ± 0
	Wed	4.1	94 ± 48	0 ± 0	6 ± 1	0 ± 0	0 ± 0	0 ± 0
	Thu	37.4	86 ± 44	0 ± 0	14 ± 1	0 ± 0	0 ± 0	0 ± 0
	Fri	15.4	94 ± 48	0 ± 0	6 ± 0	0 ± 0	0 ± 0	0 ± 0
	Sat	20.7	88 ± 45	0 ± 0	12 ± 1	0 ± 0	0 ± 0	0 ± 0
Lynwood	Sun	8.2	100 ± 51	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	Mon	17.5	99 ± 44	0 ± 0	1 ± 0	0 ± 0	0 ± 0	0 ± 0
	Tue	35.7	98 ± 39	0 ± 0	2 ± 0	0 ± 0	0 ± 0	0 ± 0
	Wed	42.9	96 ± 38	0 ± 0	4 ± 0	0 ± 0	0 ± 0	0 ± 0
	Thu	40.3	96 ± 49	0 ± 0	4 ± 0	0 ± 0	0 ± 0	0 ± 0
	Fri	13.5	100 ± 51	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	Sat	11.1	99 ± 50	0 ± 0	1 ± 0	0 ± 0	0 ± 0	0 ± 0
Diamond Bar	Avg ± SD	6 ± 6	86 ± 59	0 ± 0	9 ± 6	5 ± 7	0 ± 0	0 ± 0
Long Beach	Avg ± SD	14 ± 12	87 ± 62	0 ± 0	13 ± 10	0 ± 0	0 ± 0	0 ± 0
Lynwood	Avg ± SD	24 ± 15	98 ± 49	0 ± 0	2 ± 3	0 ± 0	0 ± 0	0 ± 0

(Table continues on next page)

^a CNG and LPG source contributions can also include aged exhaust that is enriched in stable hydrocarbons such as methane, ethane, and propane, abundant species in CNG and LPG.

Table 28 (Continued). Source Contributions to BTEX at Near-Road Sites

Site	Day	Concentration ($\mu\text{g}/\text{m}^3$)	Mean Source Contribution Estimates (% of BTEX) and Avg Deviation					
			Gasoline Exhaust	Diesel Exhaust	Consumer Products	Coatings	CNG/LPG ^a	Biogenic
Fall								
Diamond Bar	Sun	17.3	85 ± 30	9 ± 2	7 ± 1	0 ± 0	0 ± 0	0 ± 0
	Mon	14.0	80 ± 24	3 ± 5	17 ± 1	0 ± 0	0 ± 0	0 ± 0
	Tue	5.5	100 ± 51	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	Wed	7.1	91 ± 46	1 ± 1	8 ± 1	0 ± 0	0 ± 0	0 ± 0
	Thu	13.7	96 ± 48	0 ± 0	4 ± 0	0 ± 0	0 ± 0	0 ± 0
	Fri	5.9	95 ± 48	0 ± 0	5 ± 1	0 ± 0	0 ± 0	0 ± 0
	Sat	11.4	94 ± 48	0 ± 0	6 ± 1	0 ± 0	0 ± 0	0 ± 0
Long Beach	Sun	5.6	85 ± 43	0 ± 0	15 ± 1	0 ± 0	0 ± 0	0 ± 0
	Mon	34.0	83 ± 42	0 ± 0	14 ± 1	3 ± 1	0 ± 0	0 ± 0
	Tue	22.8	91 ± 46	0 ± 0	9 ± 1	0 ± 0	0 ± 0	0 ± 0
	Wed	23.2	89 ± 45	0 ± 0	11 ± 1	0 ± 0	0 ± 0	0 ± 0
	Thu	10.1	88 ± 44	0 ± 0	12 ± 1	0 ± 0	0 ± 0	0 ± 0
	Fri	31.1	83 ± 42	0 ± 0	17 ± 1	0 ± 0	0 ± 0	0 ± 0
	Sat	12.5	87 ± 44	0 ± 0	13 ± 1	0 ± 0	0 ± 0	0 ± 0
Lynwood	Sun	101.4	90 ± 46	0 ± 0	10 ± 1	0 ± 0	0 ± 0	0 ± 0
	Mon	40.0	92 ± 46	0 ± 0	7 ± 1	1 ± 1	0 ± 0	0 ± 0
	Tue	35.0	96 ± 49	0 ± 0	4 ± 0	0 ± 0	0 ± 0	0 ± 0
	Wed	56.5	96 ± 49	0 ± 0	4 ± 0	0 ± 0	0 ± 0	0 ± 0
	Thu	48.6	96 ± 49	0 ± 0	4 ± 0	0 ± 0	0 ± 0	0 ± 0
	Fri	62.6	95 ± 48	0 ± 0	5 ± 0	0 ± 0	0 ± 0	0 ± 0
	Sat	43.8	94 ± 48	0 ± 0	6 ± 0	0 ± 0	0 ± 0	0 ± 0
Diamond Bar	Avg ± SD	11 ± 5	92 ± 30	2 ± 4	6 ± 5	0 ± 0	0 ± 0	0 ± 0
Long Beach	Avg ± SD	20 ± 11	86 ± 41	0 ± 0	13 ± 8	1 ± 2	0 ± 0	0 ± 0
Lynwood	Avg ± SD	55 ± 22	94 ± 34	0 ± 0	6 ± 5	0 ± 0	0 ± 0	0 ± 0

^a CNG and LPG source contributions can also include aged exhaust that is enriched in stable hydrocarbons such as methane, ethane, and propane, abundant species in CNG and LPG.

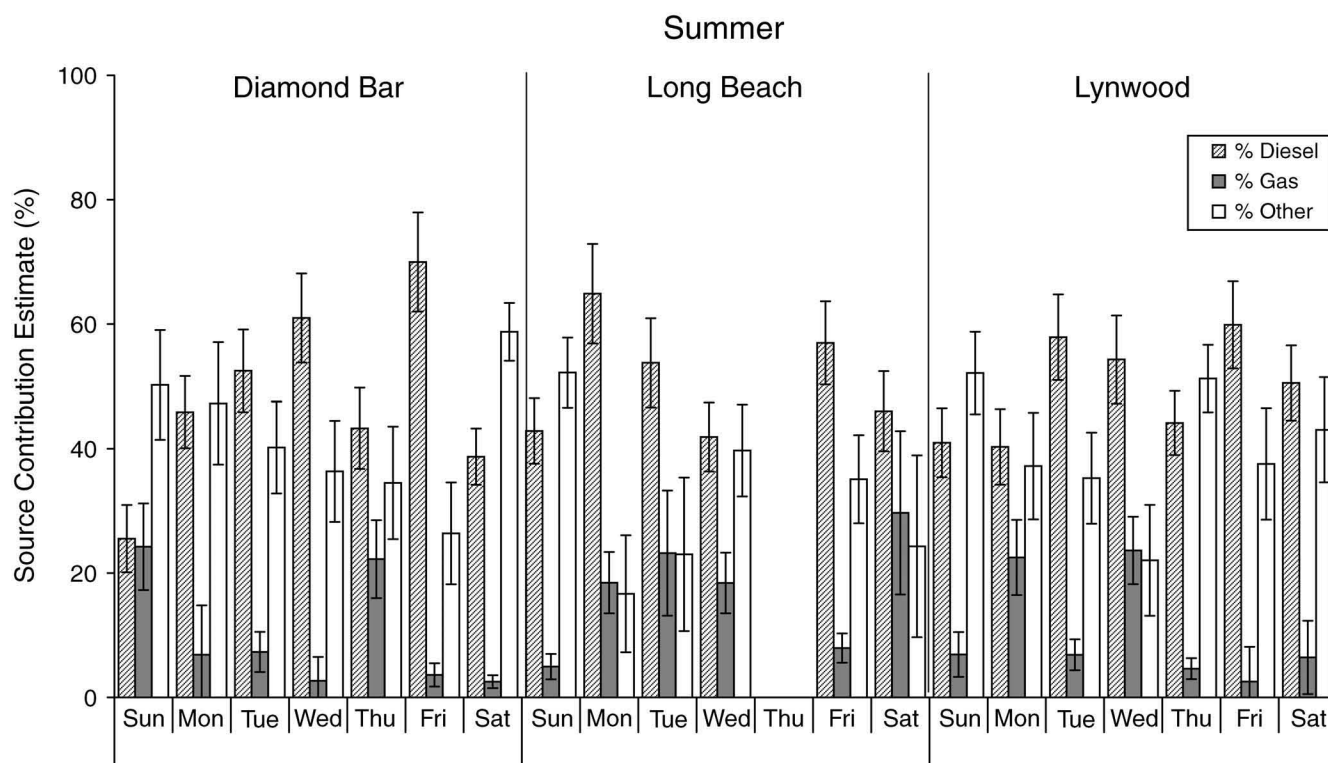


Figure 14. Relative apportionment of TC at the three near-road sites during the summer 2004 sampling period.

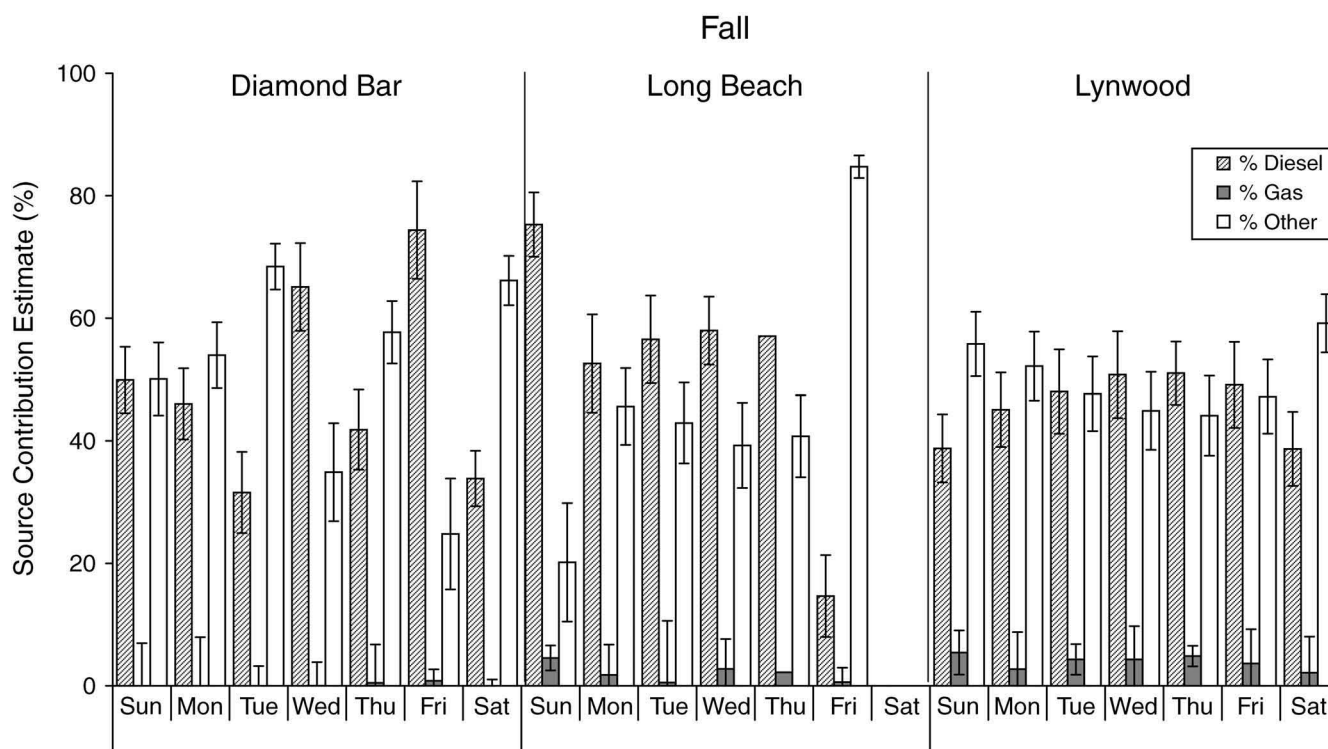


Figure 15. Relative apportionment of TC at the three near-road sites during the fall 2004 sampling period.

Table 29. Means and Uncertainties of Estimates of Source Contributions to TC and CMB Performance Statistics for the Near-Road Sites by Season^a

	% of TC			CMB Performance Statistics	
	Diesel	Gasoline	Other	r^2	χ^2
Summer 2004					
Diamond Bar	48 ± 6	10 ± 4	42 ± 4	0.72	2.75
Long Beach	51 ± 4	17 ± 4	32 ± 5	0.80	1.64
Lynwood	50 ± 3	11 ± 3	40 ± 4	0.92	0.54
Azusa (Gasoline/Diesel PM Split Study) ^b	38 ± 2	5 ± 1	57 ± 2		
Los Angeles (Gasoline/Diesel PM Split Study) ^b	40 ± 2	8 ± 1	52 ± 3		
Fall 2004					
Diamond Bar	49 ± 6	0 ± 0	51 ± 6	0.92	0.38
Long Beach	52 ± 8	2 ± 1	46 ± 9	0.87	0.73
Lynwood	46 ± 2	4 ± 0	50 ± 2	0.83	1.10

^a Uncertainties shown are the SE of the mean of the individual apportionment uncertainties calculated by CMB for each daily sample.

^b Results from the Gasoline/Diesel PM Split Study are included for comparison.

Estimation of DPC from EC

To estimate DPC concentrations from BC or EC concentrations, the following are necessary: (1) the mean ratio of DPC to BC or EC in diesel exhaust from vehicle tests or diesel-dominated ambient samples and (2) the mean ambient EC or BC concentrations. This approach assumes that EC comes predominately from diesel exhaust. As described earlier in this report, we found that BC concentrations were substantially higher on truck routes. The mean source

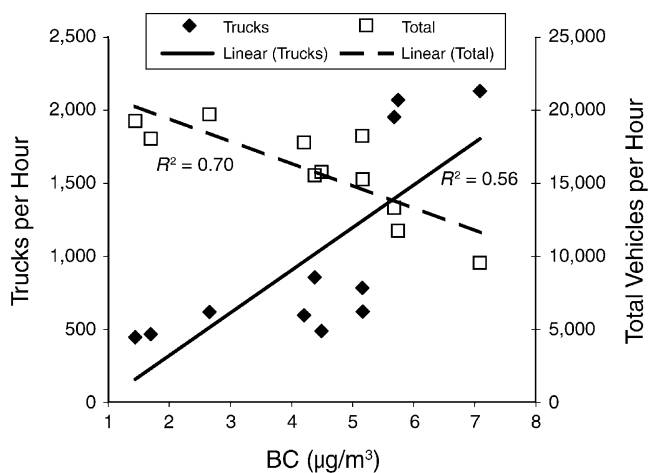
contribution estimates for EC in Table 30 show that about 90% of the ambient EC concentrations were attributed to diesel exhaust, and Figure 16 shows the positive correlation of on-road BC concentrations with truck traffic. These apportionments suggest that BC and EC are good surrogates for diesel exhaust.

We used the source-dominated ambient samples collected on road at Terminal Island (see Tables 3 and 4 for details) to obtain the mean ratio of DPC to EC (based on the

Table 30. Means and Uncertainties of Estimates of Source Contributions to EC for the Near-Road Sites by Season^a

	% of EC		
	Diesel	Gasoline	Other
Summer 2004			
Diamond Bar	93 ± 2	8 ± 3	-1 ± 1
Long Beach	88 ± 1	8 ± 1	4 ± 1
Lynwood	91 ± 3	6 ± 2	3 ± 2
Fall 2004			
Diamond Bar	91 ± 2	0 ± 0	9 ± 2
Long Beach	90 ± 1	2 ± 0	8 ± 2
Lynwood	94 ± 2	4 ± 0	2 ± 2

^a Uncertainties shown are the SE of the mean of the individual apportionment uncertainties calculated by CMB for each daily sample.

**Figure 16.** Correlation of on-road BC with number of trucks or total vehicles per hour.

assumption that in this scenario particulate TC = DPC). Samples were collected for 2.5 hours in the morning in traffic that was predominantly diesel trucks. Figure 17 shows the correlation of TC with EC (determined with IMPROVE-TOR analysis) for the three summer and three fall samples combined. EC correlates well with TC, with a slope of 1.3, an intercept of $6.7 \mu\text{g}/\text{m}^3$, and an r^2 value of 0.84. We estimated the DPC concentrations at the three near-road sites by applying a factor of 1.30 ± 0.28 to the measured EC concentrations. Figure 18 shows that the DPC estimates based on the EC measurements correlate well with estimates based on the CMB results.

Note that the factor we applied to estimate concentrations was derived for vehicles in the SoCAB that use current technologies. Exhaust from diesel engines using new technologies has greater DPC/EC ratios than exhaust from older diesel engines. Additionally, the greater contribution of cold-start emissions from gasoline vehicles in areas with colder climates may result in a lower contribution of diesel exhaust to total ambient EC.

Source Apportionment of CO, NO, PM_{2.5}, and BC Using Multivariate Analysis and Traffic Counts

We related the on-road measurements of these pollutants to a linear combination of the counts of light- and medium-duty vehicles and heavy-duty trucks. We applied multivariate analysis, described earlier, to each freeway segment to estimate the concentrations of CO, NO, PM_{2.5}, and BC as a function of the average hourly traffic density. The resulting estimated concentrations were not well correlated with the measured concentrations, as shown in Figure 19, but the model gave reasonable estimates of the relative source contributions of diesel and gasoline vehicles, as shown in Figure 20 and Figure 21. These apportionments of the contributions of gasoline and diesel vehicles to the observed pollutant levels were calculated by dividing the values of aV_D and bV_G from the equation shown earlier by the measured on-road concentrations.

These results suggest that with a sufficiently large set of on-road measurements and actual corresponding traffic counts, rather than estimates from annual averages as used here, it may be possible to derive robust time-specific relationships between traffic density and roadway pollutant concentrations that could be used to estimate near-road concentrations. Once developed, such relationships would provide a means to quantify exposure to pollutants derived from mobile-source emissions on a much larger scale, and perhaps with better accuracy than is possible using only data from regional air quality monitoring stations.

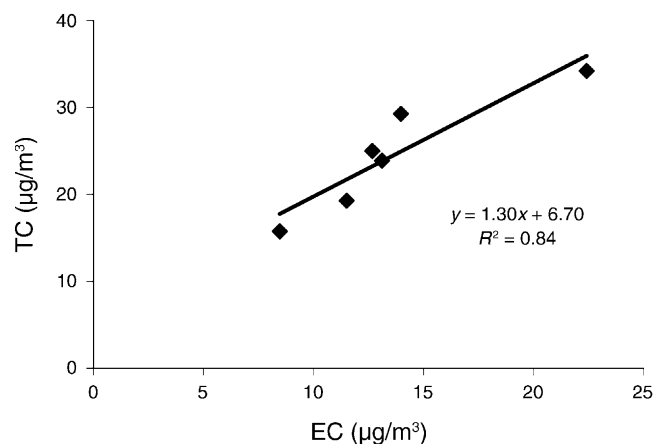


Figure 17. Correlation of TC with EC for PM_{2.5} filter samples collected on road at Terminal Island (where traffic is dominated by diesel trucks) during both summer and fall.

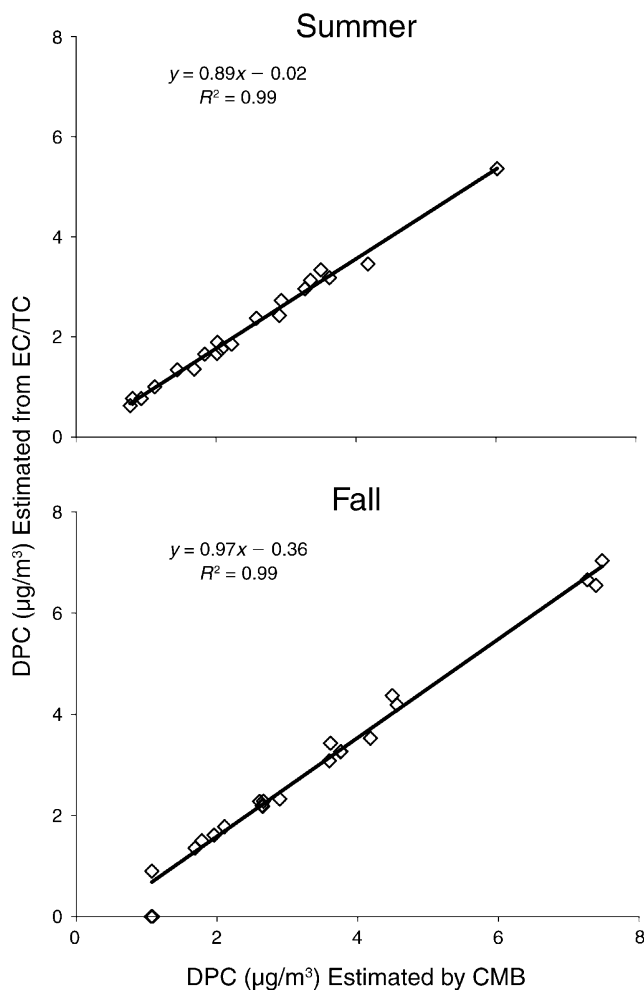


Figure 18. Correlations between DPC ($\mu\text{g}/\text{m}^3$) estimated from CMB and estimates from ambient EC/TC ratios in diesel-dominated ambient environments for samples collected at the three near-road monitoring sites.

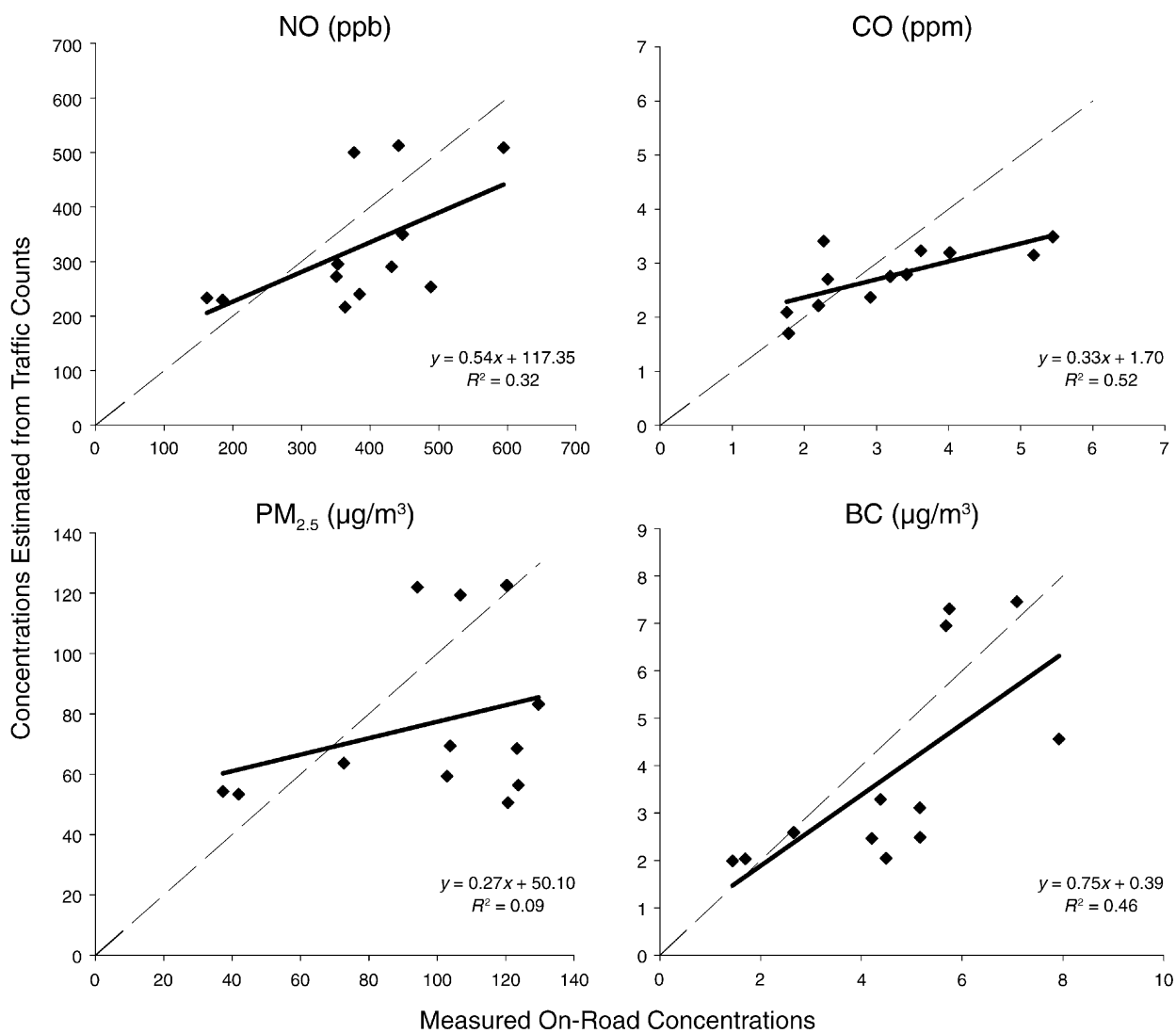


Figure 19. Measured on-road pollutant concentrations compared to values estimated from traffic counts using a multivariate method. The dashed line represents the 1:1 correlation.

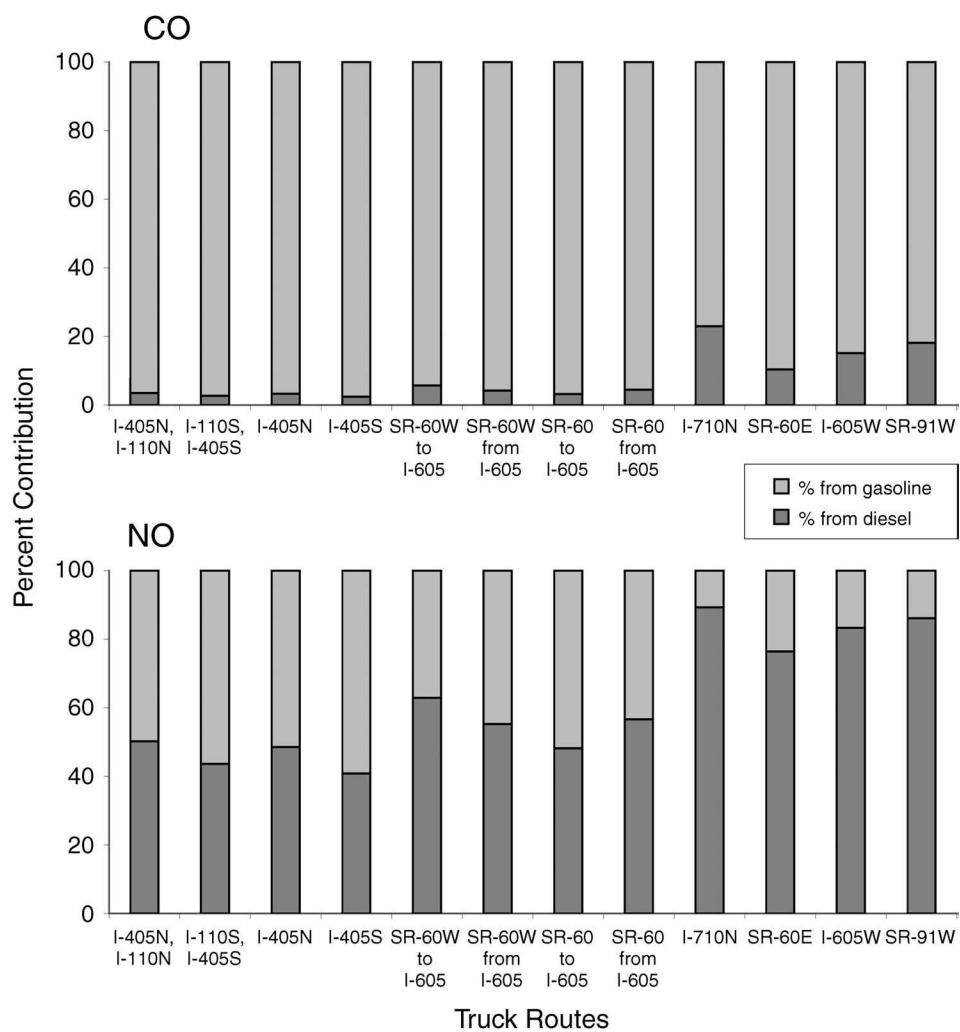


Figure 20. Relative contributions of diesel- and gasoline-vehicle exhaust to on-road CO and NO concentrations estimated from traffic counts.

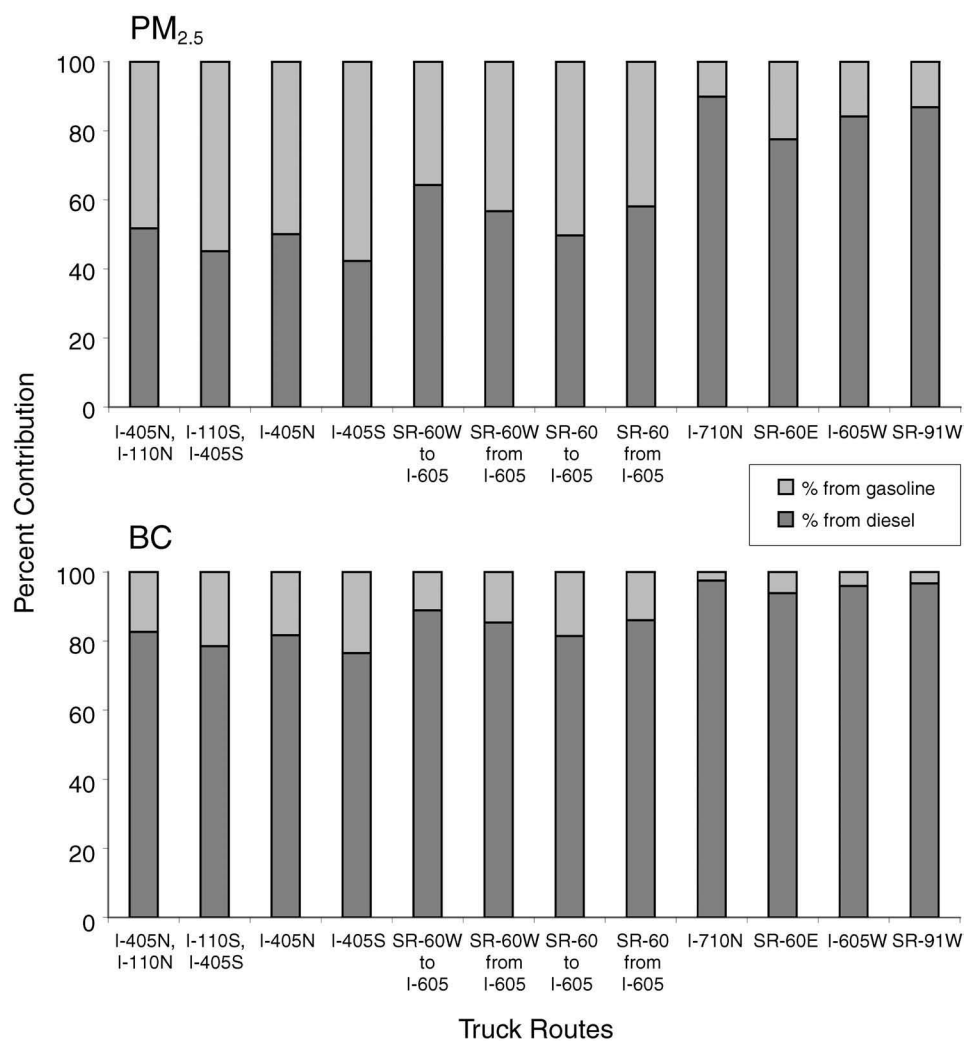


Figure 21. Relative contributions of diesel- and gasoline-vehicle exhaust to on-road PM_{2.5} and BC concentrations estimated from traffic counts.

DISCUSSION AND CONCLUSIONS

Spatial patterns of annual average cumulative exposures were determined in the California MATES studies by supplementing fixed-site monitoring data with the results of dispersion modeling. While model results for annual average pollutant concentrations have compared reasonably well with observations at fixed monitoring sites (SCAQMD 2000; Ching et al. 2004), other studies suggest that such estimates underestimate on-road and near-road exposures (Wallace 1987; Chan et al. 1991; Weisel et al. 1992; Jo and Choi 1996; Duffy and Nelson 1997; Jo and Park 1999; Leung and Harrison 1999; Westerdahl et al. 2005). The purpose of this study was to determine the concentrations of MSATs on urban highways and to characterize the diurnal and seasonal variations in measured concentrations in relation to the volume and mix of traffic. This study also compared the concentrations of MSATs on urban highways to the measurements at fixed monitoring stations. It also showed the disproportionate contributions of diesel vehicles to directly emitted carbonaceous particles and examined the use of EC as a surrogate for estimating ambient concentrations of DPC.

The spatial variations in the concentrations of various MSATs on the interstate highways in the SoCAB were consistent with the average hourly traffic counts for trucks and total vehicles. BC concentrations were generally lower on I-405 and I-110 during the morning and afternoon peak commuting periods when the proportion of trucks to total vehicle traffic during the day was lowest. The spatial pattern for CO was the opposite of that for BC, with the highest concentrations of CO on I-405 and I-110 occurring during peak commuting periods. Higher CO levels also occurred while the mobile sampling van stopped at intersections or when it followed a high-emitting gasoline vehicle. The spatial and temporal variations of BTEX and BD were consistent with corresponding time-averaged CO and VOC levels: On-road concentrations were higher during the morning than the afternoon and during the fall than the summer. On-road concentrations of formaldehyde and acetaldehyde showed less diurnal variation because these carbonyl compounds are also formed by photochemical reactions during the day. The average and upper range of BC concentrations were highest on the truck route. Compared to the concentrations measured at the three near-road sites, on-road BC concentrations were as much as an order of magnitude higher for 1-hour averages and two orders of magnitude higher for peak 1-minute averages. The average, 1-minute mass concentrations of on-road $PM_{2.5}$ were about two to six times higher than at the three near-road sites. In contrast to $PM_{2.5}$ measurements, which were higher on the

truck route, the on-road concentrations of MSATs were higher for the gasoline-dominated commuting routes.

Compared to the average 24-hour concentrations in the summer at the SCAQMD air toxics monitoring sites, on-road concentrations of BTEX, measured during the morning and afternoon commuting periods, were about 3.5 ± 0.7 and 1.2 ± 0.6 times higher, respectively. These ratios were higher during the fall and exhibited less diurnal difference (4.8 ± 0.7 and 3.9 ± 0.6 for morning and afternoon commuting periods, respectively). The variations in the ratios were consistent with greater atmospheric stability during the morning than the afternoon and during the fall than the summer. Ratios were lower for more photochemically reactive species, such as styrene. On-road concentrations of formaldehyde and acetaldehyde were up to two times higher than at air toxic monitoring sites, with slightly higher ratios during the fall than summer. However, on-road concentrations for acrolein were unexpectedly lower than the annual average 24-hour values from the air toxic monitoring network.

In lieu of planned comparisons of our on-road measurements with SCAQMD data from MATES-III, we used mobile surveys that were conducted before or after the on-road measurements. The data from these surveys were used to characterize differences between the pollutant concentrations at locations in the vicinity of the roads where the on-road concentrations were measured. These surveys were not intended to be a quantitative study of pollutant concentration gradients near highways, which was beyond the scope of this study. The results generally showed that on-road concentrations were much higher than those at the sites away from the highway, about an order of magnitude higher for CO, NO, and NO_x , and about factors of 2 to 5 higher for VOCs and $PM_{2.5}$. For the most part, the concentrations away from the highway were uniformly lower, which is consistent with other studies that have found that the concentrations fall to the surrounding background levels within several hundred meters from the highway (Zhu et al. 2002).

CMB receptor model calculations attributed the sum of BTEX almost exclusively to gasoline-engine exhaust for the on-road samples. Only about 5% to 10% of the BTEX was attributed to other source categories at the near-road sites, confirming the dominance of exhaust from gasoline-powered vehicles. CMB attributed 46% to 52% (± 7) of the ambient total particulate carbon at the three near-road sites (Diamond Bar, Lynwood, and Long Beach) to diesel exhaust and 10% to 17% (± 7) to gasoline exhaust. About 90% of the ambient EC concentrations were attributed to diesel exhaust. DPC concentrations were estimated by multiplying the mean ratio of TC to EC measured in source-dominated ambient samples (1.30 ± 0.28) and the ambient EC concentrations

measured at the three near-road sites. DPC estimates from EC measurements correlated well with the diesel source contributions calculated with CMB. These apportionments indicate that BC and EC are good surrogates for diesel exhaust; this conclusion is further supported by the positive correlation of the concentration of on-road BC with the volume of truck traffic.

We explored the potential application of a multivariate approach that relates on-road concentrations to average hourly traffic volumes for heavy-duty trucks and light- and medium-duty vehicles. The coefficients in the multivariate analysis were proportional to the relative contributions of diesel- and gasoline-vehicle exhaust to the observed pollutant concentrations. The pollutant concentrations predicted by the multivariate analysis did not correlate well with the measured concentrations, likely due to the use of the annual average rather than actual traffic counts. However, the model provided estimates of the relative source contributions of diesel and gasoline vehicles that are consistent with the CMB analysis and the 2005 emission inventory estimates of SoCAB (California ARB 2010).

The use of widely available traffic counts as a surrogate for measured exposure concentrations has obvious application in epidemiologic studies of the relationship between ambient air pollution and adverse health effects. Besides suitably weighting for proximity to roads, this approach should specifically account for the proportions of diesel trucks to total vehicular traffic because of the disproportionate contributions of diesel exhaust to BC and directly emitted PM. Easily measured pollutants such as CO and BC can serve as reasonable surrogates for MSATs (e.g., BTEX and BD) and DPC, respectively. These measurements provide a reasonably cost-effective approach to quantifying hot-spot exposure concentrations of MSATs and perhaps an approach that is more accurate than is possible using only data from regional air quality monitoring stations or the results of air quality modeling.

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APPENDIX A. Measurement of BD

Care must be taken in measuring BD because it reacts with NO_x . Atkinson and colleagues (1984) showed that BD reacts with NO_2 , but at a relatively slow rate ($3.1 \times 10^{-20} \text{ cm}^3/\text{molecule}\cdot\text{sec}$). The same work showed that a mixture of NO and NO_2 produces a series of reactions that result in hydroxyl radicals being formed in the dark. The hydroxyl radical reacts rapidly with BD (at a constant rate of $6.8 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{sec}$) resulting in rapid removal of BD from the sample at higher NO levels. While the rate of reaction of BD is around 10^9 faster with the hydroxyl radical than with NO_2 , the concentration of the hydroxyl radical is much lower than that of NO_2 . Table A.1 shows the calculated decay rate (calculated using the reaction rates reported by others) of BD for sampling under source testing and ambient sampling conditions. Theoretical calculations indicated that the loss of BD would be rapid in a canister sample of diluted exhaust from a typical high- NO_x emitter, an engine or a vehicle (sampled from the dynamometer constant volume sampler). At an NO_2 concentration of 1 ppm, BD decays linearly at a rate of 25.3% over 3 days. An NO concentration of 10 ppm results in a loss rate of 92.5% over 3 days. These results show why it is necessary to remove NO_x from whole air samples collected during source tests.

To determine whether such measures are necessary for ambient samples, BD decay rates were estimated using the

SBOX photochemical box model (Seefeld and Stockwell 1999) for levels of NO_x and BD that were expected in the SoCAB during this HEI project (Table A.1). Using ambient pollutant levels at a typical regional monitoring station in the SoCAB for the summer (75 ppb NO, 30 ppb NO_2 , 1 ppm CO, and 2 ppbV BD) and fall (200 ppb NO, 40 ppb NO_2 , 3 ppm CO, and 5 ppbV BD) yielded decay rates of 1.1% and 2.4%, respectively, after 3 days. Using a range of higher concentrations that may be encountered either during sampling in an underground garage or during on-road sampling on a congested freeway yielded 3-day decay rates of 3.4% and 17%, respectively, for low (300 ppb NO, 30 ppb NO_2 , 8 ppm CO, and 2 ppbV BD) and high (1000 ppb NO, 100 ppb NO_2 , 40 ppm CO, and 5 ppbV BD) ambient levels. These decay rates are not inconsequential given the expected time between sample collection and laboratory analysis of about 5 to 10 days. We concluded, therefore, that NO_x had to be removed from the on-road canister samples.

Several papers have discussed the use of cobalt oxide denuders for removal of NO_x . The first such report (Braman et al. 1986) provided a method for producing the required oxide of cobalt to form the denuder. DRI recently applied a slight modification of this method to construct a NO_x denuder for use in an EPA-funded study to characterize exhaust emissions from in-use light-duty gasoline vehicles in the Kansas City metropolitan area. Stainless steel tubes (3/8-inch outer diameter) were coated with a saturated solution of cobalt(II) nitrate in water and dried. The tubes were packed inside a larger stainless steel pipe of approximately 2.5-inch inner diameter and capped with tapped end caps with 1/4-inch fittings. The entire package was heated to approximately 400°C with a flow of air through it of approximately 300 mL/min for 8 to 10 hours. The oxidation of the cobalt could be confirmed by the elution of NO_2 from the denuder.

The newly constructed NO_x denuder was tested during the pilot study phase of the Kansas City Study with funding provided by the U.S. Department of Energy through the National Renewable Energy Laboratory. The results of these tests were recently reported (Fujita et al. 2004) and are briefly summarized here. The denuder was first challenged with a standard of 50 ppm NO in nitrogen and the effluent was monitored with a chemiluminescence NO_x analyzer. Approximately 30 ppb NO_x remained downstream of the denuder. A stock gas solution of BD in humidified zero air was prepared and confirmed against a gas standard prepared by Eric Apel of National Center for Atmospheric Research. This standard was then diluted into three sets of duplicate test canisters with NO, NO_2 , or no NO or NO_2 . The concentrations of BD, NO, and NO_2 were based on the mean values from the higher-emitting vehicles tested in

Table A.1. Simulated Loss Rates of BD in Canister Samples Because of Reactions with NO and NO₂^a

	Initial Conditions					Loss Rate of BD (%)		
	BD (ppbV)	VOCs ^b (ppbC)	NO (ppb)	NO ₂ (ppb)	CO (ppm)	6 Hours	24 Hours	72 Hours
Control								
BD only	43	0	0	0	0	0	0	0
With high NO only	43	0	10,000	0	0	11.4	52.4	92.5
With high NO ₂ only	43	0	0	1,000	0	2.4	9.3	25.3
High-exposure environments								
Underground garage	5	3,000	1,000	100	40	0.5	3.9	17.0
Congested freeway	2	750	300	30	8	0.1	0.7	3.4
SoCAB monitoring								
Summer	1	250	75	30	1	0.1	0.3	1.1
Fall	1	500	200	40	3	0.1	0.6	2.4

^a Source: Kansas City LDGV Characterization Study; Fujita et al. 2004.^b Typical ambient concentrations used in the box model simulations.

the 2001 Gasoline/Diesel PM Split Study. To establish baseline concentrations, the test canisters were made over the course of 2 days, to ensure that each canister could be analyzed immediately after it was made. The canisters were analyzed again at approximately 3 days, 1 week, and 3 weeks after preparation. The BD in the air samples was stable over the 3 weeks. The BD in the samples with NO showed a very dramatic exponential decay (Figure A.1, top left panel). By 3 days, the BD was reduced to 2.5% (first sample) and 9.8% (second sample) of the initial value. After 3 weeks, the level of BD was undetectable in these samples. The BD samples with NO₂ showed a linear decay that was significant but not as rapid as it was in those canisters with NO (Figure A.1, top right panel). This relatively slow reaction did reduce the concentration of BD at 3 days to 39.9% and 49.2%, for samples 1 and 2, respectively, of the initial concentration.

Testing of the denuder in the field was performed in conjunction with the vehicle sampling in Kansas City. On two separate occasions, parallel samples were collected during a dynamometer test run, one through the denuder and one without the denuder. The samples were shipped overnight to DRI and analyzed as soon as they were received. The first sample was analyzed within 24 hours of collection and the second within 32 hours. At the time of the first analysis, the concentration of BD in the sample had declined to 16.6% of that of the denuded one (37.8 versus 228.3 ppbV), which represented a significant loss of BD in the nondenuded sample (Figure A.1, lower left panel). The concentration of the nondenuded sample after 3 weeks showed a loss of over 96% of BD, as compared to the denuded

sample. The 3-week analysis of the denuded sample found a BD concentration that was approximately 83% of the initial concentration, or a loss of 17%. This suggests that the denuder was not 100% efficient and some NO and possibly some NO₂ passed into the canister, but clearly much less than in the nondenuded sample. In contrast to BD, propene was stable in both denuded and nondenuded samples (Figure A.1, lower right panel).

The NO_x denuder was used in the sampling van for in-cabin sampling during this HEI study. At the conclusion of the summer field study, the denuder was tested in the laboratory by passing 50 ppm of NO through the denuder and monitoring the postdenuder NO levels. No significant level of NO was detected, and the removal efficiency was confirmed to be nearly 100%. A scatterplot correlating propene and BD levels for about 50 in-cabin samples yielded a slope of 7.39 ($R^2 = 0.92$) (Figure A.2, left panel), which was essentially identical to the regression results for the dynamometer tests from the Gasoline/Diesel PM Split Study: a slope of 7.33 ($R^2 = 0.84$) (Figure A.3). The correlation of BD and propene for the in-cabin measurements is tighter than for the dynamometer data because in-cabin measurements combine the exhaust from thousands of vehicles. Figure A.2 (right panel) shows the scatterplot of BD and propene for 24-hour samples from the near-road sampling locations at Long Beach, Lynwood, and Diamond Bar; the slope is similar to that for the on-road and dynamometer samples. The consistent slope of the three regressions indicates that NO_x concentrations were reduced to inconsequential levels by the denuder and BD was stable in the canister samples collected for this HEI project.

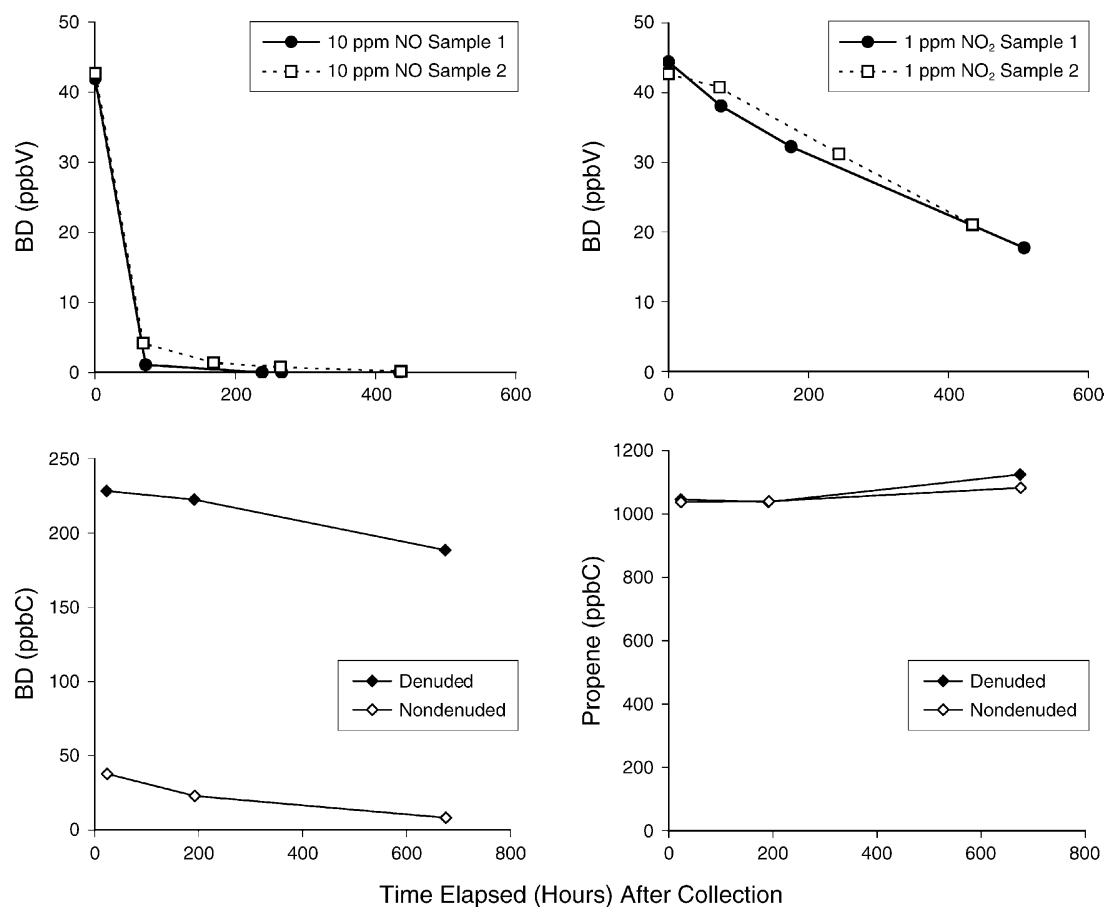


Figure A.1. Stability of BD in canister samples. The top panels show the loss of BD in laboratory test samples with 43 ppbV BD and 10 ppm NO (top left panel) or 1 ppm NO₂ (top right panel). The bottom panels show the loss in the vehicle-emission test samples of BD (bottom left panel) and of propene (bottom right panel) in NO_x denuded and nondenuded dynamometer samples. ppbC is defined as parts per billion carbon and is equal to ppbV of a compound times the number of carbon atoms. Source: Kansas City LDGV Characterization Study (Fujita et al. 2004).

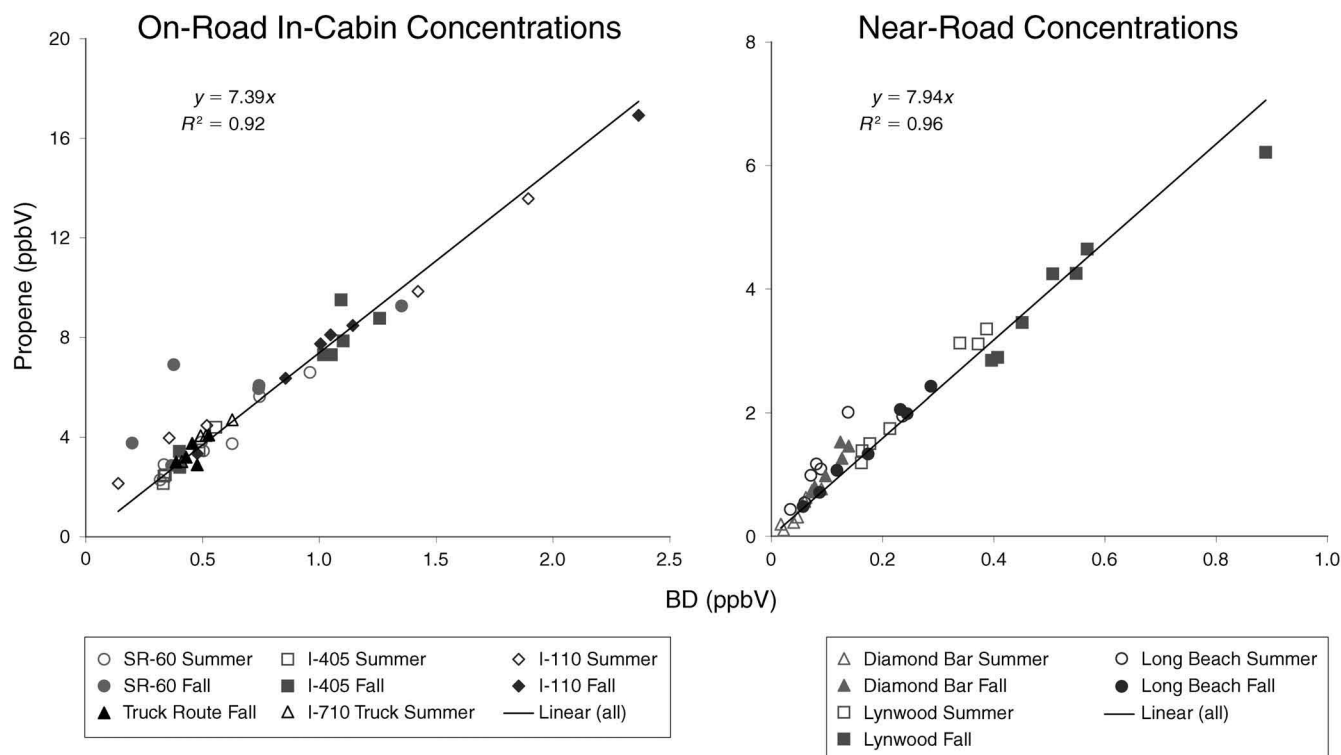


Figure A.2. Correlations between mean concentrations of BD and propene for on-road, in-cabin one-hour samples and 24-hour near-road samples, respectively. A denuder was used to remove NO_x from all on-road samples. The NO_x denuder was used for near-road samples during the fall only.

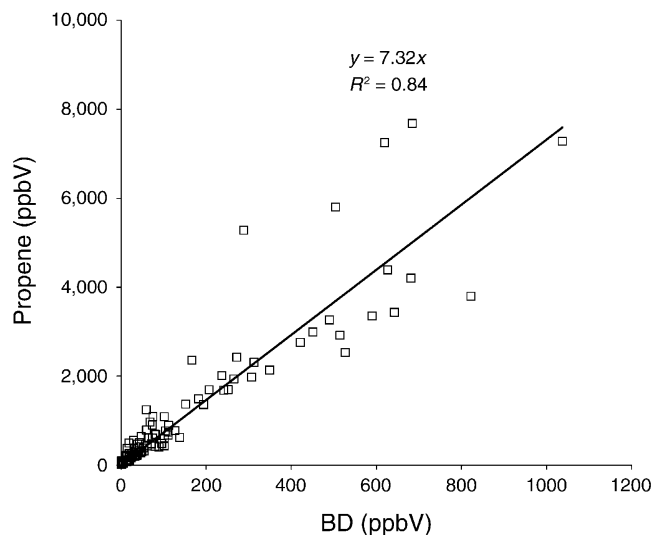


Figure A.3. Correlations of propene and BD in dynamometer test samples over phases 1 and 2 of the LA92 driving cycle for 57 light-duty gasoline vehicles. Canister samples were analyzed on site by GC-MS immediately after collection. Source: Gasoline/Diesel PM Split Study.

APPENDIX B. Corrections of DNPH Measurements of Acrolein

Although acrolein is an important air toxic, it is difficult to measure accurately. Acrolein is known to rearrange on DNPH cartridges to an unknown degradation product (acrolein-x) (Tejada 1986). The disappearance of the acrolein hydrazone in the analytical sample matrix correlates quantitatively almost on a mole-for-mole basis with the growth of acrolein-x, and the sum of acrolein and acrolein-x appears to be invariant with time (Tejada 1986). This process of rearrangement is sufficiently rapid that most of the acrolein may convert to acrolein-x unless the sample is analyzed within a few hours. The problem is compounded by the fact that acrolein-x coelutes in the HPLC analysis with another common carbonyl compound, butyraldehyde. The UV spectra from the photodiode array detector show that the chromatographic retention time of acrolein-x and butyraldehyde overlap substantially. Thus, the sum of acrolein and butyraldehyde represents an

upper-bound estimate of the acrolein that was originally present in the sample. To circumvent this problem, DRI's Organic Analytical Laboratory recently performed experiments to determine if a more accurate measurement of acrolein concentration could be obtained by postanalysis reprocessing of the HPLC spectra. To do this, an acrolein-x standard was generated by collecting a known concentration of acrolein onto a DNPH cartridge and letting it remain in the sample matrix long enough for all of the acrolein to convert to acrolein-x. Subsequent analysis of the sample confirmed that the conversion was complete: No acrolein was detected in that analysis. If there was no significant loss of material in the sampling process, it followed that the concentration of acrolein-x (from the peak identified as butyraldehyde) detected in the analysis would have been equivalent to the concentration of acrolein collected on the DNPH cartridge. This is how we generated a "standard" for acrolein-x.

The next step was to create several mixtures of acrolein-x and butyraldehyde, containing different relative amounts of the two compounds, and to analyze them to obtain spectra for which the correct proportions were known. Then, using a simple iterative solution process (the MS Excel Solver tool), peaks from the spectra of the two pure compounds were added together to obtain the match closest to

the spectrum of each mixture, as shown in Figure B.1. The scaling factors applied to the spectra of acrolein-x and butyraldehyde to obtain the best fit indicated the estimated amounts of each compound in the mixture.

Results from this experiment were quite good, yielding agreement to within 20% of the actual concentrations for all mixtures except those for which the concentration of butyraldehyde was much higher (e.g., 10 times higher) than that of acrolein. Based on this success, we applied the same technique to the previously analyzed HPLC data from this study to estimate the concentrations of acrolein and butyraldehyde in each sample. We compared the sum of the two separated compounds to the original concentrations of unresolved acrolein-x and butyraldehyde for each sample and found very strong correlations and good agreement, but there was some indication of bias due to variations in the instrument response over time. Although chemical standards were analyzed during each analysis run, to compensate for variations in detector response, no standard for acrolein-x was available for routine use. As a result, some uncertainty was associated with the reprocessing of the spectra using standards analyzed at a later time. However, Figure B.2 indicates that the effect was relatively small even over a period of many months.

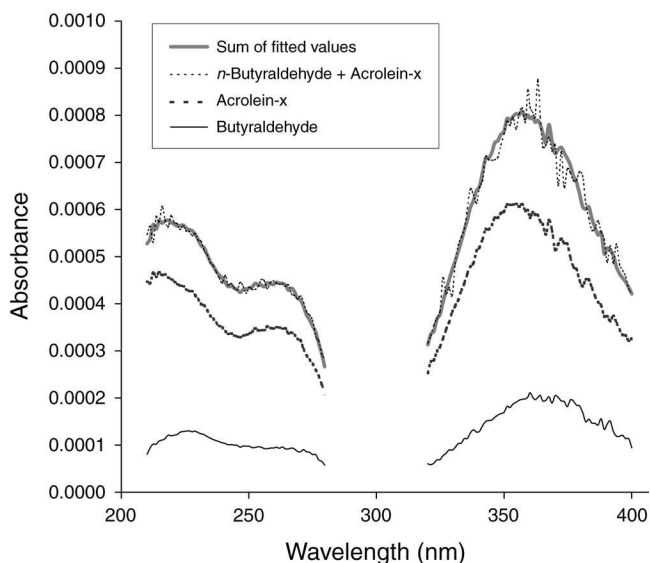


Figure B.1. Sample results from a curve-fitting program for reconstructing acrolein data from the original spectra of acrolein-x and butyraldehyde.

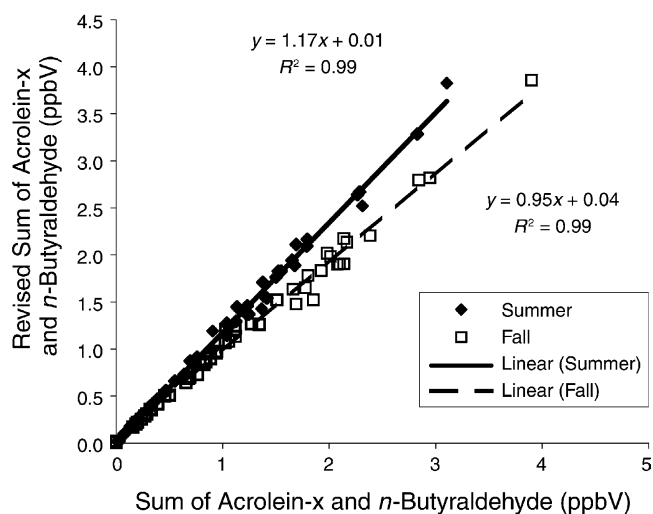


Figure B.2. Regression plot comparing reconstructed sum of acrolein-x and butyraldehyde to original, unresolved total. Data from the two field sampling periods are grouped separately because of differences in instrument calibration.

APPENDIX C. Correlations of Integrated PM_{2.5} Gravimetric Mass Measurements and Continuous DustTrak Measurements

To collect time-resolved fine PM data, and to allow estimates of the PM_{2.5} concentration in the on-road in-cabin samples when filter-sample collection was not possible, continuous PM monitoring instruments were used in the mobile sampling van and at the near-road sites. Two types of instruments were used: a TSI DustTrak aerosol monitor in the van and a sensor that measures light scattering incorporated into the photoacoustic instrument at the near-road sites. Both instruments direct a laser along the long axis of a column of ambient air, and a photodetector measures the light scattered at a 90° angle to the laser beam. The Beer-Lambert transmittance function

$$C = a \ln(I_0/I)$$

is used to estimate aerosol mass concentration (C) from the ratio of the initial beam intensity (I_0) to the scattered light intensity (I). The constant a (the mass-scattering efficiency) is a function of various factors such as the laser wavelength, particle size distribution, aerosol composition, and detector geometry.

The advantages of such a measurement method are high time resolution and precision (limited only by electronic detector noise) and low power consumption and portability of the instruments (typically diode lasers). The major disadvantage is reduced sensitivity to particles much larger or smaller than the laser wavelength, which is generally about 700 nm. As a result of the size-specific response of

the system, variations in particle-size distribution affect the accuracy of the measurement. The greater the departure of the aerosol-size distribution from that of the reference aerosol for which the constant was initially determined, the less accurate the estimated mass concentration will be. Since the DustTrak instrument is factory calibrated using a standard particle mixture known as “Arizona Road Dust” and has an inlet with a PM₁₀-size cutoff inlet, it is not expected to yield highly accurate mass concentrations in situations in which the PM consists of a large fraction of freshly emitted exhaust particles, such as our in-cabin exposure tests.

To correct for this discrepancy, we reduced the indicated mass concentrations from the DustTrak data by a factor of 2.3. This adjustment is an empirical factor derived from the correlation between time-averaged DustTrak data and gravimetric mass measurement of Teflon filter samples in similar on-road driving tests during the August 2000 Gasoline/Diesel PM Split Study. As part of that study, a mobile laboratory with sufficient on-board power systems to operate medium-volume filter samplers collected 23 on-road samples on various freeways and surface streets in the greater Los Angeles area. The correlation of the resulting mass concentrations with the DustTrak data that was collected simultaneously is shown in Figure C.1, left panel.

The measurements of light scattering from the photoacoustic instrument were converted to mass concentrations by dividing the measured scattering coefficient by 2, based on the correlation shown in Figure C.1, right panel. This adjustment was applied to all data in the main body of this report and in the report database.

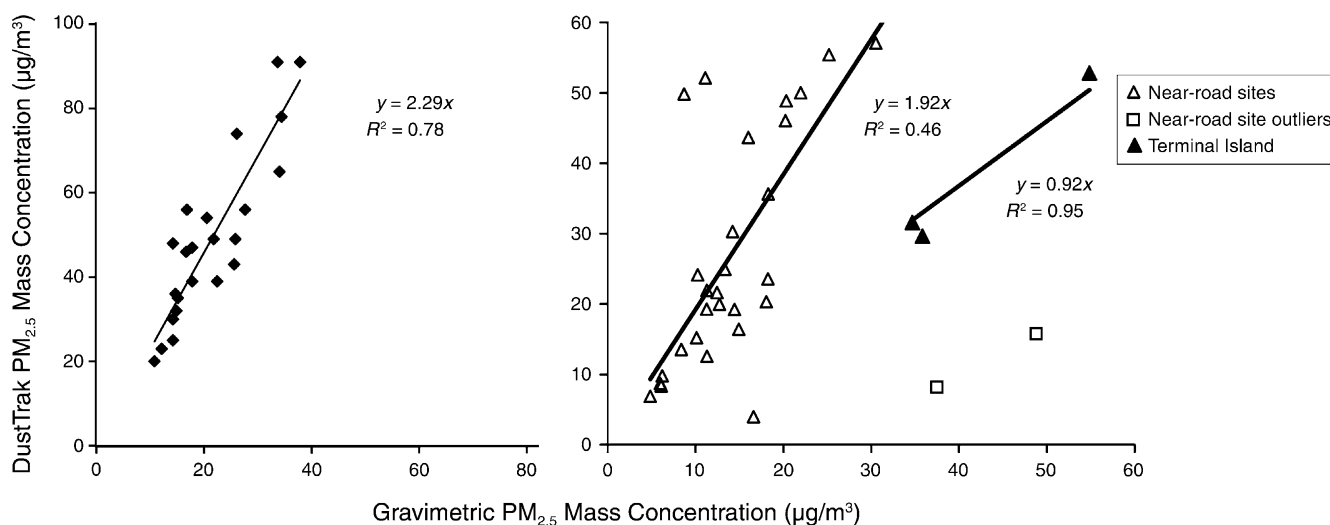


Figure C.1. Correlation of time-averaged DustTrak measurements of PM_{2.5} (by light scattering) with gravimetric mass measurements of PM_{2.5} from Teflon filter samples. The two data points indicated by square symbols in the right plot were excluded from the regression line. Left panel: Data obtained on road in August 2000 in Los Angeles (Gasoline/Diesel PM Split Study). Right panel: Data obtained in this study from three near-road sites and on road in diesel-dominated traffic on Terminal Island.

APPENDIX D. Correlations of Time-integrated MSATs Measurements and Time-Averaged PID and CO Measurements

Time series of concentrations of specific MSATs (BTEX, BD, formaldehyde, and acrolein) were reconstructed from sample-specific ratios of the time-integrated speciated data to the corresponding time-averaged continuous CO or PID measurements. Scatterplots of time-integrated BTEX, BD, formaldehyde, and acrolein measurements for the summer samples and the time-averaged continuous data are shown in Figure D.1 as a function of CO, and in Figure D.2 as a function of PID measurements. BTEX and BD correlate better with PID than CO, and formaldehyde correlates better with CO than PID. Thus, CO data were used to reconstruct time-series concentrations of formaldehyde, and

PID data were used to reconstruct time-series concentrations of BTEX and BD. The reconstructed 1-minute BTEX and BD values are plotted in the bottom left and bottom right panels of Figure 13, respectively. In contrast to particle measurements, the ranges of on-road concentrations are higher for the gasoline-dominated commuter routes. Also note that, based on the 24-hour integrated data, the concentrations of BTEX and BD are higher at Lynwood than at the other two near-road sites, which is probably because the sampling inlet is closer to traffic at Lynwood compared to the other sites. The highest CO concentrations have historically been measured at Lynwood. The average 1-minute reconstructed concentrations for selected VOCs are reported in Tables 14 and 15. Table 20 reports the concentrations for the time-integrated samples from the near-road sites.

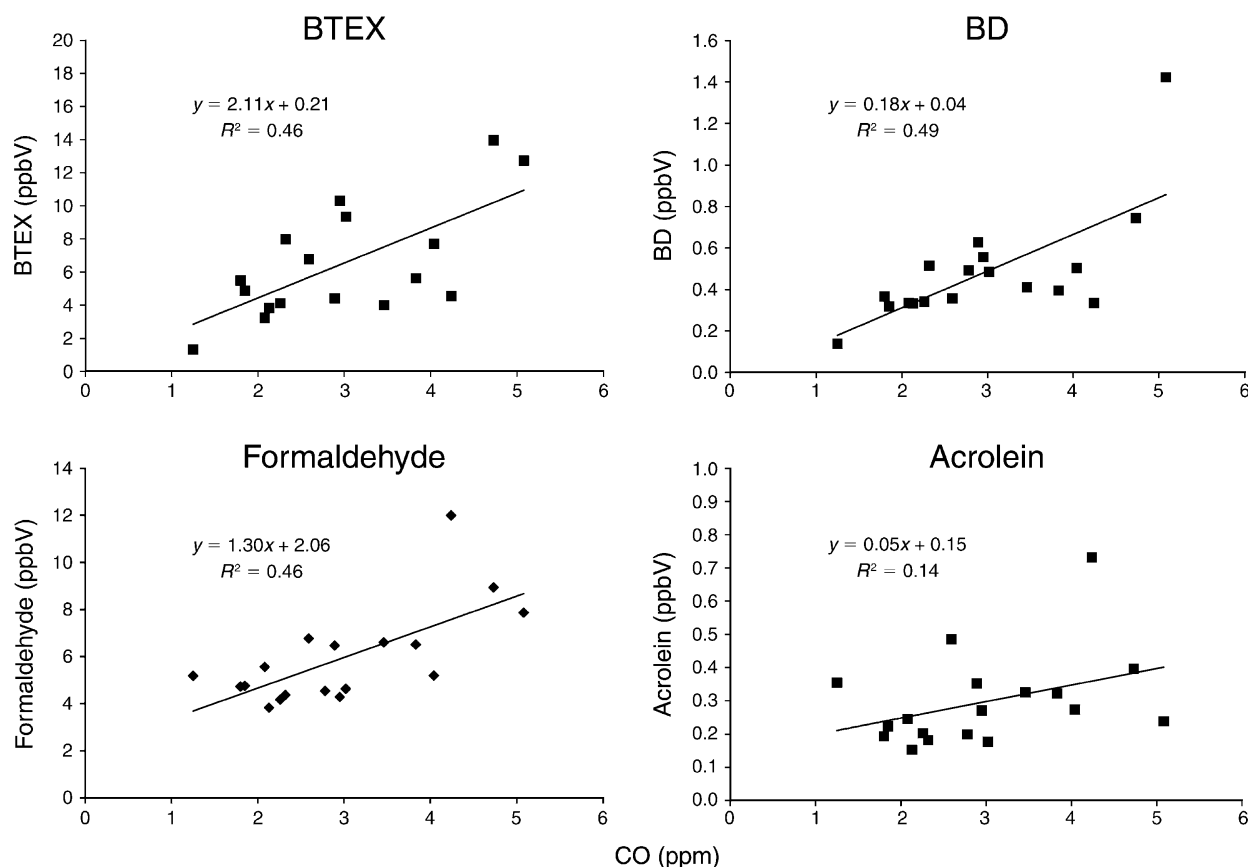


Figure D.1. One-hour time-averaged CO concentrations and time-integrated BTEX, BD, formaldehyde, and acrolein concentrations for summer on-road samples.

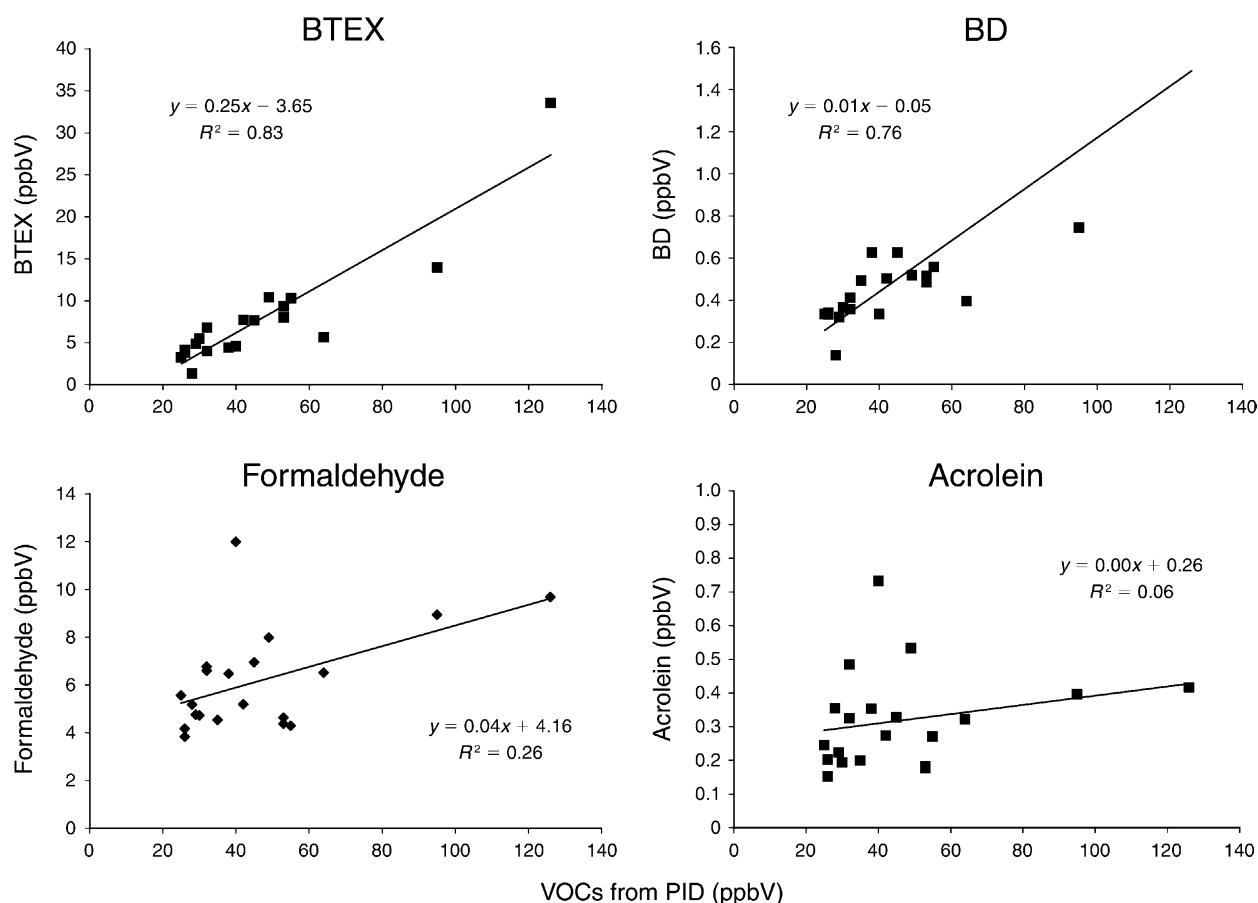


Figure D.2. One-hour time-averaged PID values and time-integrated BTEX, BD, formaldehyde, and acrolein exposures for summer on-road samples.

APPENDIX E. Quality Assurance Data

Prior to and after the end of each seasonal field study, three-point calibrations with NIST-traceable gas standards were performed on the NO and NO₂ and CO analyzers. The portable PID instrument was calibrated with zero air and a mixture of aromatic VOCs that had been analyzed by GC-MS. Although the DustTrak device provides only semi-quantitative values for PM_{2.5} mass concentration, because of the highly variable light-scattering efficiency of aerosol mixtures, its response has been extensively compared to those of gravimetric and other optical methods in ambient, source, and laboratory tests. We compared the gravimetric mass measured from the colocated Teflon filters to the time-integrated DustTrak data to derive a reasonably accurate calibration and uncertainty estimate (Appendix C).

During the field study, daily zero and span checks were conducted. Zero air was supplied from a cylinder. An

EnviroNics calibrator was used to dilute the NIST-traceable NO standard with zero air to appropriate levels, and to convert the NO to NO₂ to check the NO_x response. The CO response was checked with a mixture of 11.5 ppm CO in air. Whenever possible, all zero and span checks were performed automatically between midnight and 1:00 AM to minimize data interruptions. If the results indicated excessive drift, the checks were performed more frequently. Since the concentrations measured by the PID are affected by the composition of the ambient VOC mixture, and are therefore quite variable, no regular span checks were performed on that instrument, and the data it collected are considered qualitative. Both the PID and DustTrak received weekly zero checks, which were performed with activated charcoal or HEPA inlet filters, respectively. Before and after each sampling period, a set of Teflon and quartz filters were loaded into all filter samplers (used in the mobile monitoring laboratory) for 24 hours and then removed. No

airflow was allowed through these samplers, and the filters were retained to be weighed for blank subtraction.

The TEI17C analyzer used to measure NO and NO_x at the fixed sites and during the on-road source characterizations was found to have a low response factor, possibly due to a weak UV source or faulty ozonator. By examining the daily three-point span checks, we were able to adjust for the low response. Figure E.1 shows the unadjusted and adjusted daily span data.

Flow audits on all samplers with internal mass/flow meters were performed weekly, or more often if necessary, using a Gillibrator primary flow standard electronic bubble meter. A rotameter that had been cross-calibrated with a Roots meter was used to measure the flow rates of the stationary filter samplers.

Data from the continuous analyzers were continuously retrieved by a computer or data logger and backed up daily. Instrument and data-logger clocks were synchronized daily to match the time on the computer. Once during each field study period, the mobile sampling van was

parked next to the mobile monitoring laboratory (in the temple parking lot in Long Beach) with all instruments operating, in order to compare results. Figure E.2 shows the results of the NO_x analyzer for one of the comparisons. Higher values measured by the van during the afternoon hours may be due to local vehicle traffic at the site.

The data collected during this study were assembled into a master database for subsequent data analysis and receptor modeling. Validation checks were performed on the continuous data during the field study by reviewing diurnal patterns that would be expected and confirming that all related species followed similar diurnal patterns. After the field study, time-averaged BC and PM_{2.5} mass data were compared to the corresponding time-integrated data. Invalid data resulting from instrument malfunctions were identified and removed from the final database. Other than the corrections to the data discussed in this appendix, the corrections to the acrolein data discussed in Appendix B, and the adjustments to the DustTrak data discussed in Appendix C, no other corrections to the data were made.

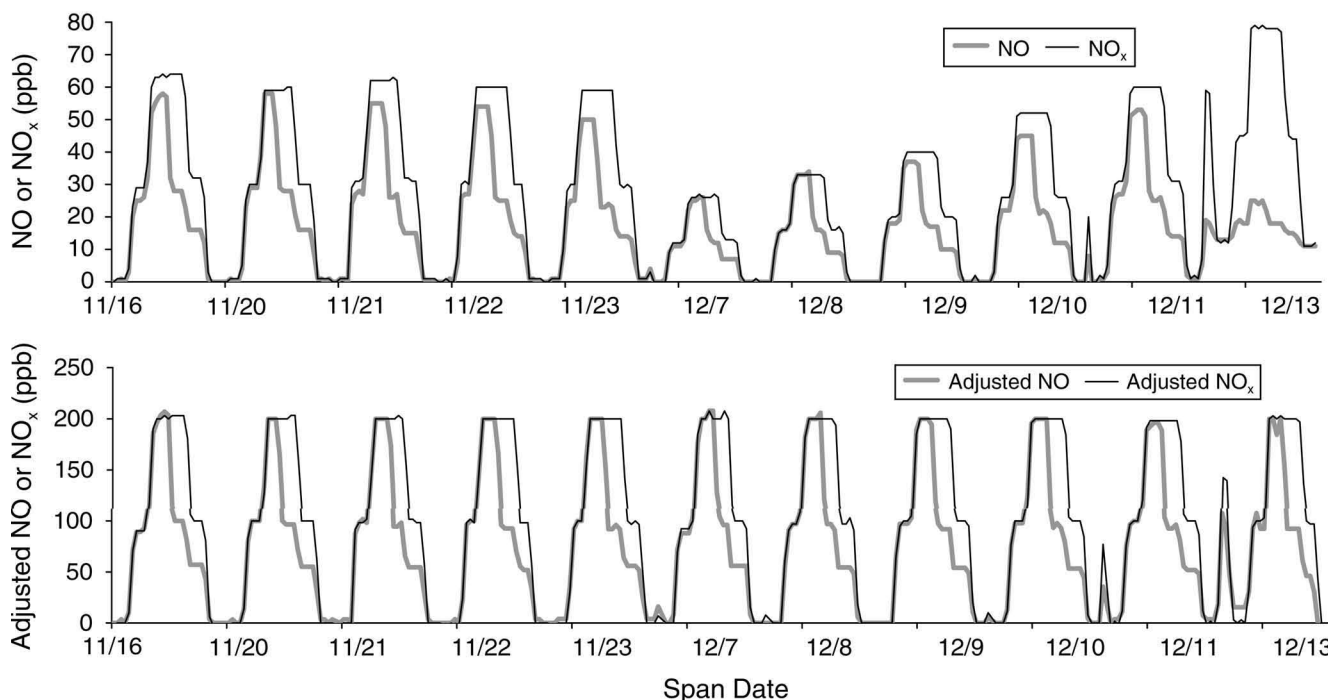


Figure E.1. NO and NO_x daily span data, measured by the TEI17C analyzer, before and after adjustment for a low response factor.

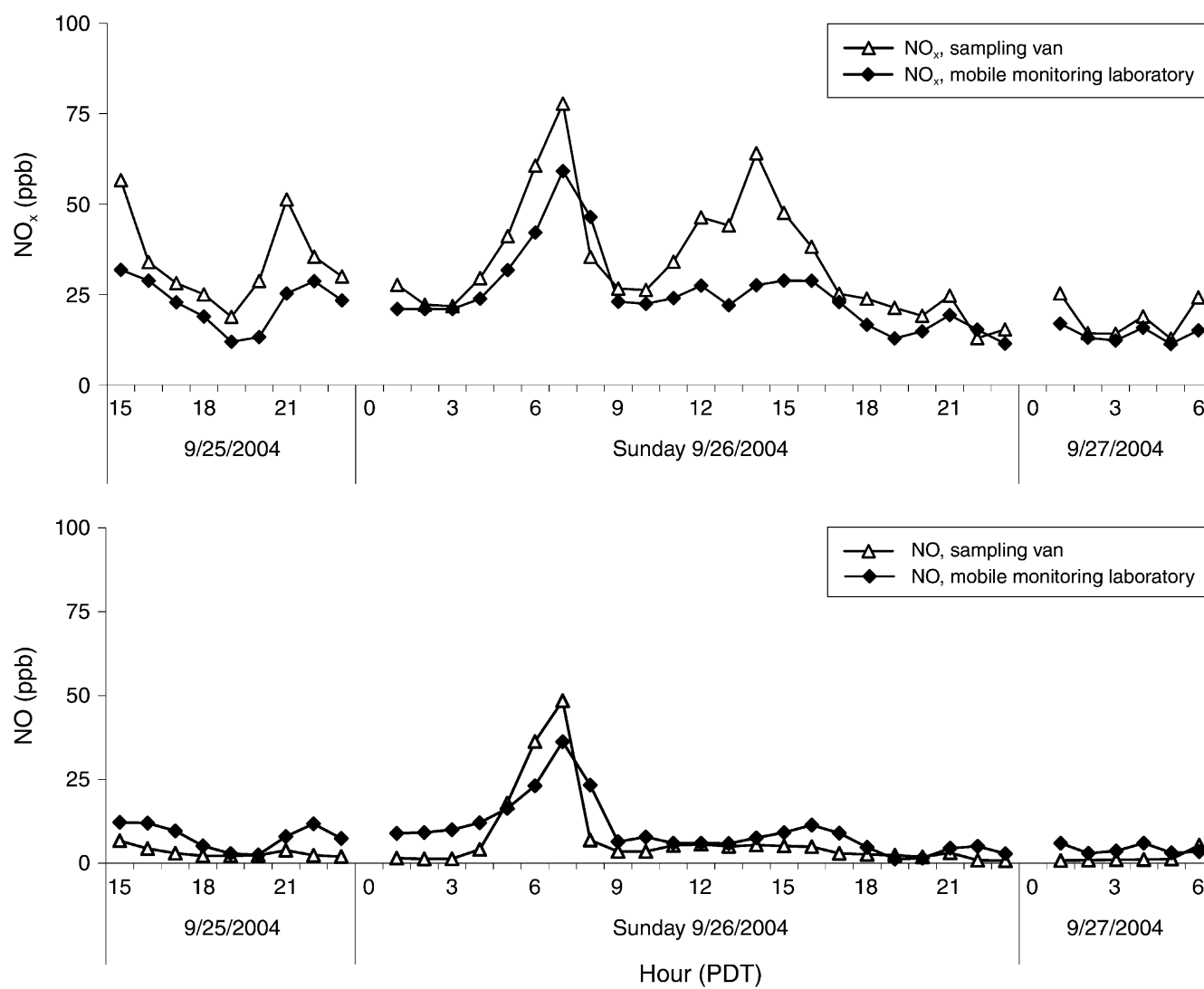


Figure E.2. Comparison of hourly averaged NO_x and NO data from analyzers in the mobile sampling van and in the mobile monitoring laboratory at a near-road site, the temple parking lot in Long Beach. The inlets for the sampling instruments in the sampling vehicles were at different heights and separated by eight feet.

APPENDICES AVAILABLE ON THE WEB

Appendices F and G contain supplemental material not included in the printed report. They are available on the HEI Web site, <http://pubs.healtheffects.org>.

Appendix F. List of Measured Parameters

Appendix G. Spatial Plots

ABOUT THE AUTHORS

Eric M. Fujita received his doctorate in environmental science and engineering from the University of California, Los Angeles, and is currently a research professor in the Division of Atmospheric Sciences of the DRI. Dr. Fujita's research includes chemical characterization of motor-vehicle exhaust and other combustion sources; source apportionment; reconciliation of emission inventory estimates for VOCs, NO_x, and PM with long-term trends in ambient ozone and PM; and measurement and characterization of exposure to TACs. He was the principal author of the field study plans for the 2000 Central California Ozone Study and the 1997 Southern California Ozone Study (SCOS97-NARSTO).

David E. Campbell received his master's degree in ecology from the University of California, Davis, and is currently an assistant research scientist in the Division of Atmospheric Sciences of the DRI. His current research includes the characterization and apportionment of gaseous and aerosol pollutants from mobile sources and the evaluation of human exposure to pollutants from mobile sources.

Barbara Zielinska received her Ph.D. in chemistry from the Polish Academy of Sciences and is currently a research professor in the Division of Atmospheric Sciences of the DRI and is director of DRI's Organic Analytical Laboratory. Dr. Zielinska's research includes characterization of trace atmospheric organic species present in both the gas and particle phases, and development of analytical methods.

William "Pat" Arnott received his Ph.D. in physics from Washington State University and is currently an associate professor in the Physics Department of the University of Nevada, Reno. Dr. Arnott's research includes measurement of BC emissions from vehicles in source sampling and in studies of ambient air quality. These measurements are often combined with the measurements of other real-time particulate emissions to establish detailed knowledge of the conditions giving rise to most of the BC and particulate emissions in the atmosphere and their environmental impacts.

Judith C. Chow received her Sc.D. in environmental science from Harvard University and is currently a research

professor in the Division of Atmospheric Sciences of the DRI and is director of DRI's Environmental Analysis Facility. Dr. Chow's research includes characterization of PM from emission sources and in ambient air, source apportionment, and the relationship between PM and public health.

ABBREVIATIONS AND OTHER TERMS

AADT	annual average daily traffic
AAHT	annual average hourly traffic
ARB	Air Resources Board
BC	black carbon
BD	1,3-butadiene
BTEX	benzene, toluene, ethylbenzene, and xylenes
CI	compression ignition (diesel)
CMB	chemical mass balance
CNG	compressed natural gas
CO	carbon monoxide
CO ₂	carbon dioxide
DNPH	2,4-dinitrophenylhydrazine
DPC	diesel particulate carbon
DPM	diesel particulate matter
DRI	Desert Research Institute
EC	elemental carbon
eV	electron volt
GC	gas chromatography
GC–MS	gas chromatography–mass spectrometry
GIS	geographic information systems
HAPEM	Hazardous Air Pollutant Exposure Model
HPLC	high-pressure liquid chromatography
ICTF	Intermodal Container Transfer Facility
IHCC	Industry Hills Conference Center
IMPROVE–TOR	Interagency Monitoring of Protected Visual Environments–thermal optical reflectance
LPG	liquefied petroleum gas
MATES	Multiple Air Toxics Exposure Study
MS	mass spectrometry
MSAT	mobile-source air toxics
MTBE	methyl <i>tert</i> -butyl ether
NDIR	nondispersive infrared
NO	nitric oxide

NO ₂	nitrogen dioxide	POM	polycyclic organic matter
NO _x	nitrogen oxides	SCAQMD	South Coast Air Quality Management District
OC	organic carbon	SFS	sequential filter sampler
PAH	polycyclic aromatic hydrocarbon	SI	spark ignition
PAMS	photochemical assessment monitoring stations	SoCAB	South Coast Air Basin
PC	pyrolyzed carbon	TAC	toxic air contaminant
PID	photoionization detector	TC	ambient total particulate carbon
PM	particulate matter	TIGF	Teflon-impregnated glass fiber
PM _{2.5}	particulate matter with a mass mean aerodynamic diameter $\leq 2.5 \mu\text{m}$	U.S. EPA	U.S. Environmental Protection Agency
PM ₁₀	particulate matter with a mass mean aerodynamic diameter $\leq 10 \mu\text{m}$	UV	ultraviolet
		UV-VIS	ultraviolet-visible
		VOC	volatile organic compound

Research Report 156, *Concentrations of Air Toxics in Motor Vehicle-Dominated Environments*, E.M. Fujita et al.

INTRODUCTION

Motor vehicles and other combustion sources emit many air toxics whose levels are not regulated by the U.S. Environmental Protection Agency (U.S. EPA) but that are known or suspected, with sufficient exposure, to cause adverse health effects. Although some state and local agencies have performed limited monitoring of air toxics, characterization of ambient levels of, and personal exposure to, air toxics has been challenging, in part as a result of the low ambient levels of individual compounds. HEI has had a longstanding commitment to and involvement in improving methods for measuring selected air toxics and understanding exposure and health effects.

The Preface to Research Report 156 describes the regulatory actions the U.S. EPA has taken to regulate emissions of air toxics in general and of mobile-source air toxics (MSATs) specifically. It also includes the rationale for HEI's issuing of Request for Applications (RFA) 03-1, "Assessing Exposure to Air Toxics," which was to support research to identify and characterize exposure to air toxics at so called hot spot areas, where the concentrations of one or more air toxics and the exposures of the population are expected to be elevated.

In response to this RFA, Dr. Eric M. Fujita, of the Desert Research Institute in Reno, Nevada, submitted an application, "Assessing Exposure to Air Toxics," proposing to measure the concentrations of a set of MSATs (including benzene, 1,3-butadiene [BD], formaldehyde, toluene, acetaldehyde, and acrolein), fine particulate matter (particulate matter [PM] with a mass median aerodynamic diameter $\pm 2.5 \mu\text{m}$ [$\text{PM}_{2.5}$]), elemental carbon (EC), nitrogen oxides

(NO_x), and carbon monoxide (CO) in several mobile source-dominated environments, such as commuting routes, street canyons, and parking garages, in southern California. In addition, Fujita proposed to determine the concentration gradients from fixed monitoring stations to roadways for measured MSATs and to compare his measurements with those collected in local monitoring programs. He also proposed to examine the contributions of diesel- and gasoline-powered vehicles to MSATs and particulate carbon in some environments.

The HEI Research Committee thought that Fujita's proposed measurements would be valuable and of high quality, but it was concerned about the lack of an identified study population and of a clear definition of the sampling plan. In response, Fujita suggested two possible populations, commuters who typically spend 2 hours a day on southern California roadways and residents living near major roadways. He also proposed defining the sampling scheme during a pilot phase and better coordinating his sampling with local monitoring programs, in particular the one that was planned by the South Coast Air Quality Management District (SCAQMD) as part of the third Multiple Air Toxics Exposure Study (MATES-III). Based on Fujita's response, the Research Committee recommended the proposed study for funding.

In their report of the pilot phase, Fujita and colleagues outlined plans to conduct two sampling campaigns in 2004, one in the summer (August–September) and one in the fall (November–December) in three types of locations: in a mobile sampling van driving in commuter traffic, in three communities near major highways and surface roads, and at sites at different distances from the highways. The proposed communities (referred to in the report as near-road sites) were Lynwood, the Long Beach Port area, and Boyle Heights (this site was changed to Diamond Bar after the study started).

This critique is intended to aid HEI sponsors and the public by highlighting the strengths and limitations of the study and discussing the interpretation of the results.

SCIENTIFIC BACKGROUND

When the study was started, it was known that the concentrations of pollutants to which people are exposed vary

Dr. Eric Fujita's 3-year study, "Assessing Exposure to Air Toxics," began in January 2004. Total expenditures were \$485,653. The draft Investigators' Report from Fujita and colleagues was received for review in August 2006. A revised report was received in February 2007. A second revised report was received in January 2008 and was accepted for publication in June 2008. During the review process, the HEI Health Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in both the Investigators' Report and the Review Committee's Critique.

This document has not been reviewed by public or private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views of these parties, and no endorsements by them should be inferred.

* A list of abbreviations and other terms appears at the end of the Investigators' Report.

significantly across locations and that the concentrations of several pollutants (including CO, nitrogen dioxide [NO₂], and EC) measured on road or at the edge of the road decrease with distance from the road. The decay gradients are affected by meteorologic factors (especially wind direction) (Zhu et al. 2002). Very limited information existed about the decay gradients of MSATs (HEI Panel on the Health Effects of Traffic-Related Air Pollution 2010).

In southern California, SCAQMD had conducted a series of MATES studies, to provide a comprehensive database of air toxics levels and exposures, characterize the health risk for the population, and address environmental-justice issues. MATES-II was conducted in 1999 and included 10 monitoring sites within the South Coast Air Basin (SoCAB). The results were published in 2000 (SCAQMD 2000). The MATES-II report notes that monitoring locations were based on the U.S. EPA's guidelines for neighborhood-scale monitoring and "may also be representative of adjacent communities." A new MATES study (MATES-III) was being planned at the outset of the study by Fujita and colleagues. It included two years of monitoring (April 2004 to March 2005 and April 2005 to March 2006; for results, see SCAQMD 2008). All but one of the MATES-II sites were used in the MATES-III study.

In addition, SCAQMD has been operating a large number of routine monitoring sites for measuring regulated pollutants and air toxics. A number of the sites at which Fujita and colleagues made measurements were MATES-III or routine sites or both.

The concentrations of MSATs and other pollutants such as EC and NO_x are influenced by the proportion of gasoline- and diesel-powered vehicles on roadways and the age of the vehicle fleet. Compared with gasoline vehicles, the fleet of diesel vehicles and trucks on U.S. highways has traditionally had higher per-vehicle emissions of PM (including EC and several polycyclic aromatic hydrocarbons [PAHs] and metals) and NO_x. At the time the study was conducted (2004), the motor-vehicle fleet on the road also had higher emission rates of pollutants than the current (2010) fleet because several regulations had been implemented since 2004.

Regulations to reduce exhaust emissions of PM and NO_x from light-duty vehicles and trucks (both gasoline and diesel) were phased in beginning with model year 2004 vehicles and were fully phased in by 2007 as part of the Tier 2 standards (U.S. EPA 2000). In addition, as part of an ongoing program to reduce emissions of MSATs, in 2007 the EPA set more stringent exhaust and evaporative hydrocarbon controls and mandated a reduction in benzene content in gasoline fuel (U.S. EPA 2007). It was expected that the fuel changes and some of the technologies used for

reducing PM emitted from diesel-powered vehicles (such as an oxidation catalyst and catalyst-coated PM filters) would effectively reduce emissions of several MSATs (U.S. EPA 2001b).

Phase 1 NO_x emission standards for heavy-duty diesel engines started to be phased in with model year 2004 (U.S. EPA 1997, 2000), and Phase II PM standards (reducing PM emissions by 90% relative to models from previous years) started to be phased in with model year 2007 (U.S. EPA 2001a). Additional NO_x emission reductions (by 95% of the pre-2004 standards) are taking effect with model year 2010 engines (U.S. EPA 2001a).

To achieve further emissions reductions and enable the introduction of improved emission control technologies, the U.S. EPA has mandated the use of low sulfur gasoline and diesel fuel, which became widely available by mid-2006.

Much work has been conducted to apportion the contribution of diesel-vehicle exhaust to total PM with the goal of improving assessment of exposure to that exhaust, but this effort has been hampered by the lack of unique tracers for diesel. One tracer that has often been used is EC, but it is not unique to diesel-exhaust particles. Another approach has been to supplement EC with molecular markers of diesel emissions (such as hopanes, steranes, and certain PAHs). HEI reviewed the approaches to improving the assessment of exposure to diesel exhaust at a workshop held in 2002 and concluded that these markers cannot sharply distinguish emissions from diesel and gasoline engines because of the similarity of their emission profiles, but they can help to separate diesel and gasoline engines from other combustion sources (2003). Source apportionment of MSATs has been more limited because source emission profiles are scarce.

The U.S. Department of Energy's Gasoline/Diesel PM Split Study used molecular markers to fingerprint PM emissions from 57 gasoline and 34 heavy-duty diesel vehicles (Fujita 2007a,b). The study began in the summer of 2001 with the overall objective of quantifying the relative contributions of tailpipe emissions from gasoline- and diesel-powered motor vehicles to ambient concentrations of PM_{2.5} in the urbanized region of southern California using an organic-compound-based chemical mass balance (CMB) model. Another goal of the study was to obtain a better understanding of the uncertainties associated with the CMB model. The main findings of the study were that the apportionment of gasoline-vehicle exhaust was most sensitive to indeno[1,2,3-*cd*]pyrene, benzo[*g,h,i*]perylene, and coronene and, to a lesser extent, steranes and hopanes, and that spatial and temporal variations in the relative diesel- and gasoline-vehicle apportionments were large. Diesel vehicles were the dominant source of EC and of ambient

total particulate carbon (TC, the sum of EC and organic carbon [OC]) in some locations. A significant fraction of the OC during the summer in the SoCAB could not be apportioned to directly emitted PM from motor vehicles. Data on emission profiles obtained from the Gasoline/Diesel PM Split Study were used by Fujita and colleagues for apportioning the contribution of the exhaust from diesel and gasoline vehicles to particulate carbon in the HEI study.

STUDY AIMS

This study was conducted to measure the concentrations of MSATs on urban highways in Los Angeles County with a varying mix of gasoline and diesel traffic and to compare them to the concentrations of air toxics measured at various sites in the vicinity of the roads and at several other locations in the county, many of which were used as monitoring sites by SCAQMD. The study had four major aims:

1. To measure concentrations of CO, nitrogen oxide (NO), NO_x, MSATs (benzene, toluene, ethylbenzene, and xylene [BTEX], styrene, naphthalene, *n*-hexane, BD, methyl *tert*-butyl ether [MTBE], formaldehyde, acetaldehyde, and acrolein), PM_{2.5}, and black carbon (BC) on roadways during peak commuting periods, and to relate the variations in the measured concentrations to the varying proportions of gasoline and diesel vehicles.
2. To compare the concentrations of MSATs, CO, and NO on roadways to those measured at near-road locations, spatial survey locations, and SCAQMD fixed monitoring sites.
3. To apply the CMB receptor model to estimate the contributions of gasoline- and diesel-powered vehicles to MSATs, PM_{2.5}, and EC at three near-road sites.
4. To develop and implement measures to address sampling and analytical artifacts related to potential loss of BD and acrolein.

STUDY DESIGN

This study was conducted in the southern portion of Los Angeles County for several weeks during the summer and fall of 2004. Measurements were made during each period using different combinations of time-integrated and continuous measurements. They were made on road on three commuting routes and one truck route, at various sites away from the sampled roads (referred to as spatial surveys), at three near-road sites with varying proportions of gasoline and diesel vehicles, and on roads dominated by either gasoline- or diesel-powered vehicles. The sites and the specific measurements are described briefly below. The

pollutant concentrations measured in the study were compared with those measured at several SCAQMD sites. Initially, the investigators planned to compare their results with those of the MATES-III study, but the MATES data were not available by the time the final report was submitted. A list of all the sites for which data are included in the Investigators' Report is provided in Table 1 of the Investigators' Report.

ON-ROAD SAMPLING

The goal of this sampling was to determine the concentration of pollutants along roadways. The investigators measured the concentrations of PM_{2.5}, CO, NO, NO_x, EC, and MSATs using a mobile van equipped with monitoring instruments that was driven with windows and vents fully opened and a circulating fan turned on. MSATs, PM_{2.5}, EC, and OC concentrations were measured using time-integrated samplers. Continuous monitoring instruments were used for measuring CO, total volatile organic compounds (VOCs), NO and NO_x, PM_{2.5}, and BC. The routes sampled, the pollutants measured, and the sampling methods are listed in Critique Table 1.

The van was driven on three commuting routes and one freeway loop with a higher fraction of diesel-truck traffic (referred to as the truck route) going in one direction in the morning and in the reverse direction in the afternoon. Ambient air was sampled for 1 hour during one week on different weekdays (typically Monday, Wednesday, and Friday in the summer and fall) during the morning (7–8 AM) and evening (5–6 PM) commuting periods on the commuting routes and from approximately 9 to 10 AM and 3 to 4 PM on the truck route in the summer and between 11 AM and 1 PM on the truck route in the fall. Each route covered at least one highway or major roadway: Commuting route #1 followed SR-60, which also had some diesel traffic (especially in one direction). Commuting route #2 followed a portion of I-405 and I-110 to downtown Los Angeles (it is referred to as I-110 in the tables in the Investigators' Report). Commuting route #3 primarily followed I-405. Both routes #2 and #3 were dominated by gasoline-vehicle traffic. The truck route consisted of a loop that included I-710, SR-60, I-605, and SR-91. One part of SR-60 on commuting route #1 was part of the truck route. Figure 1 of the Investigators' Report, a map of the area, shows the routes. The percentage of trucks per hour relative to the total number of vehicles per hour (estimated from the annual average daily traffic obtained from the California Department of Transportation) ranged between 2.3% and 5.5% for the commuting routes and between 3.4% and 22.3% for the truck route (as shown in Table 5 of the Investigators' Report).

SPATIAL SURVEYS

The goal of the spatial surveys was to determine the spatial variations of pollutants relative to the on-road measurements. A number of sites at various locations away from the roads where the on-road samples were collected were sampled using the mobile van immediately after the morning on-road sampling and immediately before the afternoon on-road sampling. Fujita and colleagues did not provide the distances of these sites from the roads. These sites included some MATES-III sites and some SCAQMD routine monitoring sites. The mobile van stopped at each location for a few minutes. The surveys utilized continuous monitors only. The pollutants measured were CO, total VOCs, NO, NO_x, PM_{2.5}, and BC. The survey locations associated with each of the three commuting routes, the pollutants measured, and the sampling methods are listed in Critique Table 1.

NEAR-ROAD SITES

The goal of this sampling was to determine variations in pollutant concentrations at three sites located near

neighborhoods in the general geographic area of the routes for the on-road sampling. The sites, Long Beach, Lynwood, and Diamond Bar, were selected based on their potential for having different proportions of diesel-truck and gasoline-vehicle traffic. The Long Beach and Diamond Bar sites were expected to have a mix of diesel and gasoline vehicles; the Lynwood site was near traffic dominated by gasoline vehicles. Long Beach is located south of I-405 and was sampled during the same week that route #3 was, Diamond Bar is located near one end of the SR-60 route and was sampled during the same week route #1 was, and Lynwood is located east of I-110 and was sampled during the same week route #2 was. (The Investigators' Report indicates that Lynwood is one block north of I-105, but this road does not seem to be included in route #2.) The investigators used a mobile monitoring laboratory stationed at each site for 5 days (with the exception of Lynwood, where the sampling equipment was colocated with the SCAQMD equipment on the roof of the building). They measured concentrations of pollutants using a combination of 24-hour integrated sampling (for MSATs and other VOCs routinely measured at U.S. EPA's photochemical assessment

Critique Table 1. Overview of On-Road Sampling Routes and Survey Sites

Location	Duration of Sampling	Type of Sampling	
		Integrated	Continuous
On-Road Sampling			
Route #1 (SR-60)	60 min; 7–8 AM and 5–6 PM September and November (mobile van)	MSATs (canisters for BTEX, BD, and hexane; cartridges impregnated with 2,4-dinitrophenylhydrazine for formaldehyde, acetaldehyde, and acrolein)	CO
Route #2 (I-110)			VOCs (photoionization detector)
Route #3 (I-405)			NO and NO _x PM _{2.5} (DustTrak) BC (photoacoustic)
Truck route (I-710, SR-60, I-605, SR-91)	60 min; 9–10 AM and 3–4 PM in September; 11 AM–1 PM in November		
Spatial Surveys			
Route 1: Industry Hill Conference Ctr., Pico Rivera, Soto Street Elementary School, Hollenbeck Middle School, and Sunrise Elementary School	A few minutes; 8–9 AM and 4–5 PM; same periods as corresponding on-road sampling (mobile van stopped at each location)	None	CO
Route 2: Los Angeles (Leroy Street), City of Commerce, Huntington Park, Compton			VOCs (photoionization detector) NO and NO _x PM _{2.5} (DustTrak) BC (photoacoustic)
Route 3: North Long Beach, Long Beach City College, Long Beach State University Technical Center			

monitoring stations [PAMS], PM_{2.5}, EC, OC, and 20 semivolatile and PM-associated organic compounds) and continuous monitoring (for CO, NO and NO_x, total VOCs, and BC). See Critique Table 2 for a list of these sites, the pollutants measured, and the sampling methods.

SOURCE-DOMINATED AMBIENT SAMPLES

The goal of sampling was to measure pollutant concentrations on source-dominated roadways. Two routes were sampled using the mobile van for 2.5 to 3 hours: a gasoline vehicle-dominated freeway (not specified) and a roadway with diesel vehicles (on Terminal Island). Integrated measurements of PM_{2.5}, EC, OC, MSATs, and other PAMS VOCs, and 20 semivolatile and PM-associated organic compounds were obtained. Continuous measurements were also taken, as was done at the near-road sites (see Critique Table 2).

AMBIENT AIR QUALITY MONITORING IN THE SoCAB

SCAQMD operates several air monitoring stations in the SoCAB, to measure, with differing frequency, one or more criteria pollutants (such as ozone, CO, NO₂, and PM) and air toxics (including various VOCs, aldehydes, metals, and particulate PAHs). A list of all the sites whose measurements were used by the investigators for comparisons with the measurements collected in this study is provided in Table 1 of the Investigators' Report.

EXPERIMENTAL METHODS

SAMPLING METHODS

Pollutant concentrations were measured concurrently (unless otherwise indicated) using time-integrated samples collected over periods ranging from 1 to 24 hours and continuous monitors with time resolutions ranging from 10 to 60 seconds, with the data averaged over the same periods of time.

Integrated Samplers

The time-integrated samplers included the following: canisters for BTEX, styrene, BD, MTBE and *n*-hexane (and other VOCs routinely measured at PAMS sites); Sep Pak cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) for aldehydes (formaldehyde, acetaldehyde, and acrolein); DRI sequential filter samplers with Teflon filters for gravimetric PM_{2.5} mass and with quartz filters for OC and EC; a DRI sequential fine particulate and semivolatile organic compounds sampler with Teflon-impregnated glass fiber (TIGF) filters and a backup XAD-4 resin cartridge for speciated particulate and semivolatile PAHs, hopanes, and steranes.

Continuous Samplers

Continuous samplers included an electrochemical monitor for CO and carbon dioxide, a chemiluminescence

Critique Table 2. Overview of Near-Road Sites and Source-Dominated Routes

Location	Duration of Sampling	Type of Sampling	
		Integrated	Continuous
Near-Road Sites			
Long Beach (impacted by diesel trucks), near I-405	24 hours; 1 week in September and November or December (fixed mobile laboratory)	MSATs (canisters for BTEX, BD, hexane, and other VOCs measured at PAMS; ^a cartridges impregnated with 2,4-dinitrophenylhydrazine for formaldehyde, acetaldehyde, and acrolein) PM _{2.5} (Teflon filter) EC and OC (quartz filter) 20 organic compounds (PAHs, hopanes, steranes; semivolatile organic compound sampler with glass fiber filter and XAD-4 resin cartridges)	CO VOCs (photoionization detector) NO and NO _x (chemiluminescent) PM _{2.5} (DustTrak) BC (photoacoustic)
Lynnwood (impacted primarily by gasoline vehicles), near I-110			
Diamond Bar (impacted by a mix of gasoline and diesel vehicles), near SR-60			
Source-Dominated On-Road Sampling			
Commuter-dominated freeway (not specified)	2.5 hours; 10:30 AM–1 PM, November (mobile van)		
Terminal Island, diesel dominated	3 hours; 7–10 AM, November (mobile van)		

^a PAMS: 55 C₂-to-C₁₁ aliphatic and aromatic hydrocarbons plus formaldehyde and acetaldehyde (see list in Table 6 of the Investigators' Report).

analyzer for NO and NO_x (and NO₂ calculated as NO_x minus NO), a photoacoustic analyzer measuring light absorption for BC, an active photoionization detector for total VOCs (olefins and aromatic hydrocarbons), and the TSI DustTrak nephelometer for PM_{2.5}. The DustTrak data were corrected based on comparison with gravimetric data. At the fixed sites, CO was monitored continuously by an active nondispersive infrared analyzer.

ANALYSES OF INTEGRATED SAMPLES

VOCs were analyzed by gas chromatography–mass spectrometry (GC–MS). Because BD in canisters in the dark is degraded by hydroxyl radicals generated by high concentrations of NO_x, NO_x was removed from the on-road samples using a cobalt oxide denuder upstream of the sampler inlet. The denuder was developed by the investigators as part of an earlier study (U.S. EPA 2006).

Carbonyls were extracted from the Sep Pak cartridges impregnated with an acidified DNPH reagent and analyzed by high-pressure liquid chromatography. The DNPH cartridges used for collecting carbonyls are not generally considered adequate for collecting acrolein because the product of the reaction of DNPH with acrolein (a hydrazone adduct) is very unstable (Zhang et al. 2000). To improve the measurement of this species using DNPH cartridges, the investigators investigated the degradation product of the hydrazone adduct and found that a new species, which they referred to as acrolein-x, was formed. The sum of this species and the acrolein from the chromatographic analysis was constant over time. When analyzing a mixture of aldehydes, the investigators found that acrolein-x coeluted with butyraldehyde. They isolated acrolein-x (by allowing the acrolein hydrazone adduct to completely convert to acrolein-x) and then generated mixtures of varying proportions of acrolein-x and butyraldehyde as calibration standards to which to compare the spectra from the ambient samples that had already been analyzed. They note in the Investigators' Report that there is some uncertainty to this correction because the standards were not analyzed at the same time as the ambient samples and there are variations in the detector response over time.

The EC and OC in PM_{2.5} collected on quartz filters were measured using the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal-optical reflectance (TOR) method (Chow et al. 1993 and 2001). Although both EC measured by the TOR method and BC measured by light absorption define a comparable portion of the carbonaceous fraction of PM, they have different thermal, optical, and physical properties, and measurements of the two are not always in agreement (Venkatachari et al. 2006).

Particulate and semi-VOCs were extracted from TIGF filters and backup XAD-4 cartridges and analyzed by GC–MS. Concentrations in the combined extracts were quantified by correcting for the response of the corresponding deuterated internal standards.

DATA ANALYSIS

Analyses of the Measured Concentrations

Summary statistics are presented in tabular and graphic form in the Investigators' Report and include the averages of continuous and integrated measurements of pollutants collected at the various sampling locations, listed by time of day and season. For some of the pollutants, ratios of on-road concentrations to the concentrations at fixed sites (using measurements obtained in this study or measurements available from routine monitors operated by SCAQMD) are provided.

The spatial patterns of BC and CO on-road concentrations along the commuting and truck routes are presented in maps created using geographic information systems information on the position, speed, and direction of the mobile sampling van.

Analyses to Apportion the Contribution of Sources

Source apportionment was conducted using the CMB model for VOCs, TC, and EC. The model uses measured pollutant concentrations, along with source composition information, to apportion the contributions of primary sources to the measured concentrations.

VOCs and BTEX The investigators apportioned VOCs and BTEX to the on-road and near-road locations using the ambient measurements made in their study and available source composition profiles used in another study conducted by the investigators in southern California (the National Renewable Energy Laboratory Weekend Ozone Study conducted in 1997 and described in Fujita et al. 2003). The VOC profiles consisted of the 55 PAMS hydrocarbons. The sources of the VOC emission profiles included tailpipe emissions from gasoline and diesel vehicles, evaporative emissions of gasoline, natural gas and liquefied petroleum combustion, surface coatings, gasoline vapors, and consumer products. The U.S. EPA defines consumer and commercial products as exterior and interior paints and wood coatings, cleaning and personal care products, and auto refinishing coatings. The report cites the studies from which the emission profiles for the various sources (with the exception of consumer products) were taken.

Particulate TC and EC The investigators determined the contribution to TC of the exhaust of diesel and gasoline

vehicles in samples collected on roads dominated by either gasoline or diesel vehicles and at the three near-road sites. They used the source profiles for EC, selected PAHs, hopanes, and steranes (see Table 7 of the Investigators' Report) created for the Gasoline/Diesel PM Split Study conducted in 2001 (described in Fujita et al. 2007b). From these analyses, they estimated the concentration of TC derived from diesel particulate carbon (DPC). The investigators also determined the contribution to EC of diesel and gasoline exhaust at the three near-road sites using the EC emission inventories used for apportioning TC.

DETERMINATION OF DPC AT NEAR-ROAD SITES

Estimates of DPC concentrations were calculated by multiplying the EC measurements at the near-road sites by 1.3 (the ratio of EC to TC on the diesel-dominated route) and were compared with the DPC estimates obtained using the CMB approach summarized above.

Source Apportionment of CO, NO, PM_{2.5}, and BC Using Multivariate Analysis and Traffic Counts

The investigators used hourly traffic counts (as an indicator of motor-vehicle emissions) in a multivariate model to derive an estimate of the pollutant concentrations of CO, NO, PM_{2.5}, and BC. Hourly counts of diesel and gasoline vehicles were derived from 2004 annual average daily vehicle data from the California Department of Transportation and data on hourly traffic distribution determined by Gao and Niemeier (2003) using data collected from 1996 through 2000. The model assumes that the pollutant concentration is proportional to the sum of the heavy-duty trucks per hour and the light- and medium-duty vehicles per hour. The proportionality constants used in the model are not described in the Investigators' Report. The investigators compared the estimated pollutant concentrations with the measured concentrations, and they determined the contribution of diesel- and gasoline-vehicle exhaust to each pollutant.

RESULTS

ON-ROAD POLLUTANT CONCENTRATIONS

The results show that the spatial patterns of BC, CO, NO_x, and total VOCs (all measured with continuous monitors) differed. Concentrations of CO and VOCs were higher on the commuting routes, while concentrations of BC and NO_x were higher on the truck route. The ratios of the mean on-road pollutant concentrations on the commuting routes to those concentrations on the truck route were between 0.3 to 0.5 for BC, between 0.5 and 0.8 for NO_x, and generally

between 1.5 and 2 in the morning and near 1 during the rest of the day for CO and VOCs (as shown in Table 10 of the Investigators' Report). These results are consistent with the patterns of 1-minute concentrations along the routes shown in Figures 7 and 8 of the Investigators' Report. The NO_x ratios for the truck route were generally higher than those for the commuting routes. The spatial pattern of CO and NO_x shows that concentrations varied along the routes.

The spatial and temporal variations of on-road integrated concentrations of BTEX and BD were similar to those of the corresponding time-averaged continuous CO and total VOC concentrations—higher on the commuting routes and higher during the morning and in the fall. Formaldehyde and acetaldehyde showed less diurnal variation. The concentrations of MSATs were consistently higher (by about a factor of 2) on commuting routes than on the truck route. The ratio of the species mean concentrations on commuting routes to those on the truck route was greater than 1 for all volatile species in the morning and for most species in the afternoon (see Table 13 of the Investigators' Report).

Relationships Between Pollutant Concentrations Measured On Road and at Fixed Monitoring Sites

The investigators compared the 1-minute average (AM and PM) on-road concentrations of NO_x and CO and the 1-minute average concentrations measured at near-road sites and sites operated by SCAQMD and found that all on-road concentrations were higher than those measured at the fixed sites. For the summer and fall, the majority of the ratios of the on-road NO_x and CO concentrations to those measured at the SCAQMD site near each route (reported in Tables 16 and 17 of the Investigators' Report) ranged from 2 to 5.

The investigators compared the ranges of the 1-minute average concentrations of BC measured on road and those measured at the near-road sites and found higher ranges of BC on the roads (by as much as an order of magnitude); the peak concentrations on the truck route were up to 2 orders of magnitude higher (shown in Figure 13 of the Investigators' Report). The average continuous 1-minute PM_{2.5} concentrations measured on road were also higher than those at the near-road sites. The ranges of all on-road concentrations of BTEX and BD (and also aldehydes) were higher than those at the near-road sites.

The comparison of the average on-road concentrations with those at nearby survey locations (measured with continuous monitors) during the morning and afternoon commute showed generally much higher on-road concentrations relative to sites away from the highways—about

2-fold higher for CO, NO, and NO_x and 2- to 5-fold higher for VOCs and PM_{2.5} (see Tables 18 and 19 of the Investigators' Report).

Ratios of On-Road Concentrations of MSATs to Mean 24-Hour Concentrations Measured at SCAQMD Air Toxics Sites

The 1-hour average on-road concentrations of BTEX were 3.5-fold higher (morning sampling) and 1.2-fold higher (afternoon sampling) than the 24-hour seasonal concentrations at the SCAQMD air toxics sites; on-road concentrations of formaldehyde and acetaldehyde were 2-fold higher. The ratios tended to be higher in the fall than the summer. On-road concentrations of acrolein were lower than those at the SCAQMD air toxics sites, but higher than those at the near-road sites.

Source Apportionment by CMB

VOCs Apportionment of total VOCs to sources showed that gasoline exhaust (including evaporative emissions) was the predominant source for both on-road and near-road concentrations, ranging from 70% for some of the samples at the near-road sites (primarily Diamond Bar and Long Beach) to about 100% for on-road samples. The contribution of diesel exhaust was small and more significant on roads with a higher proportion of trucks (commuting route #1 and the truck route) in the fall (13% and 22%, respectively). The contribution of compressed natural gas and liquefied petroleum gas was between 2% and 11% for on-road samples and between 7% and 25% for samples from the near-road sites. Consumer products contributed up to 16% of the VOCs in the samples taken at the near-road sites, and up to 6% of the VOCs in the on-road samples. The results are shown in Tables 25 and 26 of the Investigators' Report.

BTEX Apportionment of BTEX to the on-road samples showed that gasoline was the dominant source (86% to 100%) for all routes (including the diesel-dominated road). Apportionment to the near-road sites also showed that gasoline exhaust was the predominant source at all sites (77% to 100%), while the contribution of diesel was negligible. The only other source contributing to BTEX at the near-road sites was consumer products (0% to 17%). The results are shown in Tables 27 and 28 of the Investigators' Report.

Particulate TC and EC Apportionment of TC associated with PM to the near-road samples showed a greater contribution of diesel exhaust (averaging from 46% to 52%) for both summer and fall samples (Table 29 of the Investigators' Report). Gasoline exhaust and evaporative emissions

contributed, on average, 10% to 17% percent of TC in the summer samples, but did not appear to contribute to the fall samples to any significant extent (0% to 4%). About 40% to 50% of the TC was not apportioned to mobile sources. The TC concentration contributed by diesel exhaust, estimated by CMB analysis, was compared with DPC concentrations, which were estimated by multiplying EC concentrations by 1.3. The investigators concluded that there is good agreement between these two estimates (shown in Figure 18 of the Investigators' Report).

Apportionment of EC alone, to separate the contributions of diesel and gasoline exhaust at the near-road sites, showed that 88% to 94% was from diesel vehicles (Table 30 of the Investigators' Report). The contribution of gasoline exhaust was 6% to 8% in the summer and 0% to 4% in the fall.

As part of this analysis, the investigators report the correlations of BC with hourly truck traffic and total vehicular traffic. The total traffic count showed a better fit ($R^2 = 0.70$) than the truck count ($R^2 = 0.56$).

Source Apportionment of CO, NO, PM_{2.5}, and BC Using Multivariate Analysis and Traffic Counts

The results of the multivariate regression showed that the estimated on-road concentrations of these pollutants did not correlate well with the measured concentrations (shown in Figure 19 of the Investigators' Report).

HEI HEALTH REVIEW COMMITTEE'S EVALUATION OF THE STUDY

The HEI Health Review Committee, in its independent review of the study, thought that Fujita and colleagues had conducted a comprehensive study on the characterization of MSATs and other gaseous pollutants and carbonaceous PM on Los Angeles freeways and roadways and in several locations in the Los Angeles air basin and that they had collected high-quality data. However, the Committee noted that, although the specific goals of the study were addressed, the extent to which the concentrations measured can be used to identify hot spots of population exposure, which was the overall objective of the HEI research program, was not addressed. The Committee's evaluation of specific parts of the study is provided below.

METHODS

The Committee thought that a strength of the study was the careful approach to sample collection and analysis. Though largely standard methods were used, the investigators made notable improvements in their analytic strategy.

In particular, the correction for the degradation of acrolein in the DNPH cartridges (described in Appendix B of the Investigators' Report) represents a thoughtful approach to dealing with the limitations of the DNPH-based sampler. However, the investigators do not explain whether internal standards were added to account for the recovery of the various aldehydes. The use of a NO_x denuder to prevent degradation of BD by NO_x -generated hydroxyl radicals (described in Appendix A) is also commendable. The denuder was used for the on-road sampling based on field experiments conducted as part of another study showing that high NO_x concentrations cause the degradation of BD in canister samples.

The investigators compared several measurements with each other: the DustTrak measurements with the gravimetric data, to determine the correction factor to apply to the DustTrack data (Appendix C); the time-integrated BTEX and BD concentrations with the continuous CO measurements, to reconstruct the 1-minute concentrations of these species (Appendix D); and the measurements from the colocated mobile van with those from the mobile monitoring laboratory (data on NO_x are presented in Appendix E). Overall, the Review Committee thought that the methods employed were appropriate and care was taken in explaining the correction factors applied. However, comparisons of the results in this study with those of other studies should be undertaken with caution because of differences in sampling and analytic methods, instrument response, and correction factors across studies.

RESULTS

On-Road Concentrations

The investigators note that the concentrations measured inside the vehicles with windows open and maximum ventilation reflect on-road concentrations rather than the in-vehicle exposures of commuters; these conditions generally do not reflect the ventilation in the vehicles of commuters. The Committee agreed with the investigators' decision to refer to these measurements as on-road concentrations. However, the model used to derive the concentrations is not described and the investigators did not elaborate on how vehicle speed might have affected the ventilation rate inside the vehicles and the measured concentrations and whether this was taken into account.

The variations among pollutant concentrations on the various routes are consistent with the described vehicular patterns, with concentrations of MSATs higher on the commuting routes, and BC and NO_x higher on the truck route. The traffic data the investigators provided confirmed that

the truck counts were higher on the truck route, but the proportion of trucks did not exceed 22% on any of the routes.

The investigators hypothesized that the concentrations of many pollutants were generally higher in the morning because they were associated with differences in atmospheric stability. However, the possibility that diurnal variations in traffic volume and possibly in traffic speed were responsible, at least in part, for this difference, cannot be ruled out. The finding from the continuous measurements that the concentrations along roads were variable is important because most epidemiologic studies treat roads as having constant levels of pollutants.

Westerdahl and colleagues (2005) conducted a study in 2003 using an electric car with a sampling outlet located at the rear window (behind the passenger seat) that was driven at different times of day for two hours on some of the same roads sampled by Fujita and colleagues. They found a similar correlation between BC and NO and diesel-vehicle traffic, but they did not measure any MSATs. Despite differences in the sampling times and seasons between their study and the current study by Fujita and colleagues, the BC concentrations they measured on I-710 (one of the freeways on Fujita's truck route) were within the range reported by Fujita and colleagues ($12 \mu\text{g}/\text{m}^3$ versus $6.9\text{--}20.8 \mu\text{g}/\text{m}^3$). An earlier study by Fruin and colleagues (2004) on Los Angeles and Sacramento freeways reported a range of in-vehicle concentrations of BC that depended on the type of vehicle in front of the sampling vehicle; they concluded that the type of vehicle being followed was the most important predictor of in-vehicle BC concentrations.

Measurement at Different Sites Away from Roads

Because one of the original goals of the investigators was to study residents living near roadways, quantitative information on the proximity of the selected sampling sites to the roads where the measurements were made and to possible exposed populations would have been useful. A map provided in the Investigators' Report shows that the three near-road sites are at various distances from the sampled roadways. The Committee agreed with the investigators' general conclusions that on-road concentrations of the measured pollutants were higher than the concentrations at the fixed monitoring sites (both those that were sampled by the investigators and those that were sampled by SCAQMD). This is not an unexpected finding and is consistent with results of studies that have measured pollutant gradients away from roads. These studies have explored the gradients of $\text{PM}_{2.5}$, ultrafine PM (PM with a mass mean aerodynamic diameter of $0.1 \mu\text{m}$ or less), BC, NO_2 , benzene, and VOCs (for recent reviews of these studies, see Zhou and Levy 2007 and Karner et al. 2010) and have found that,

with the exception of PM_{2.5} (which is fairly well mixed in the atmosphere), the levels of all these pollutants decrease with distance from roads and that meteorologic factors (such as wind direction and speed) play a major role in the shape of the decay curves. Since information on the distance from the monitoring sites to the roads and data on meteorology are not provided in this study, ratios between on-road and fixed-site concentrations in this study are difficult to interpret; however, they can be useful for describing the results.

The finding that on-road concentrations of acrolein were lower than those at the SCAQMD air toxics sites is unexpected. The concentrations of acrolein measured at the near-road sites were also lower than those measured at the air toxics sites (and lower than the on-road concentrations). The investigators state that SCAQMD uses U.S. EPA method TO-15, which involves collection of air samples in canisters and analysis by GC-MS and was specifically developed for analysis of acrolein. Because the investigators corrected for the degradation of acrolein in their samples, one would have expected the concentrations of acrolein to be more comparable to those measured with method TO-15. The fact that internal standards were not used to account for possible losses may in part explain the differences, but without a side-by-side comparison of the two methods it is hard to explain the reason for this finding. The investigators mention the possibility that acrolein could have formed from the photooxidation of BD in the air at the SCAQMD sites, but BD was also present during this study's sampling periods.

Overall, the results of the spatial surveys would be much more informative for epidemiologic studies if some variables could be identified to use in models to predict levels of various pollutants given a distance away from the highway, but this was beyond the scope of the study.

Source Apportionment

The main conclusions of the CMB modeling are that gasoline vehicles are the main sources of VOCs (including BTEX) and that diesel vehicles contribute more than gasoline vehicles to the TC associated with PM at the near-road sites. Although these findings are reasonable and consistent with what would be expected from the emission profiles, the Committee had some concerns about the conclusion that 90% of EC is derived from diesel vehicles at the near-road sites. The authors interpret these results to indicate that EC may be a good surrogate for diesel exhaust; however, the Committee noted that the correlation between EC and truck counts was not as good as its correlation with total traffic counts (see Figure 16 of the Investigators' Report). Moreover, the Committee noted that the source contribution of gasoline vehicles to EC at Diamond Bar in the

fall of 0% \pm 0 was not plausible based on the real-world traffic conditions in the Los Angeles area. These issues limit the conclusions that can be drawn about EC as a surrogate for diesel-exhaust PM. While the investigators found that DPC calculated directly from EC correlated well with estimates based on the CMB modeling, both approaches are driven by the EC observations.

The Committee thought that the multivariate analysis using traffic counts was not convincing. First, the model is not presented in sufficient detail. In particular, the values of the proportionality coefficients, *a* and *b*, were not provided. Second, the agreement between the measured and the modeled concentrations was not very good (as shown in Figure 19 of the Investigators' Report). Thus, the Committee was not convinced of the value of using this model to predict pollutant concentrations from mobile sources even if, as the investigators suggested, one were to use a larger set of on-road measurements and actual traffic counts.

SUMMARY AND OVERALL CONCLUSIONS

The study's main conclusion is that on-road concentrations of all pollutants measured, including several MSATs, were higher than those measured at near-road sites. This finding is consistent with other studies. However, in the absence of information about the relationship between the roads and the near-road sites, such as the distance between the sites and the sampled roads and other roads, only qualitative relationships can be drawn. Another factor that makes comparisons between on-road and near-road measurements difficult to interpret is the different duration of sampling for MSATs (1-hour during peak pollution on road and 24 hours at the near-road sites).

Though on-road concentrations were higher than near-road concentrations, the question of whether busy highways during commuting hours are hot spots for exposure to MSATs is hard to address, given the design of in-vehicle sampling. However, concentrations as high as those measured in the study may be encountered by commuters if the driving conditions are similar to those examined in this study. The near-road sites were chosen because they were assumed to be affected by traffic, but the Investigators' Report does not discuss whether they could be hot spots for exposure. Thus, this question remains unresolved.

The source-apportionment results are consistent with our knowledge of the emission compositions of gasoline and diesel vehicles at the time the study was conducted, with gasoline vehicles contributing primarily to MSATs and CO, and diesel vehicles to particulate carbon (TC and EC). However, it is difficult to assess the accuracy of the quantitative split between the contributions of diesel- and gasoline-exhaust vehicles to EC.

Emissions from motor vehicles have been changing rapidly as a result of new emission control technologies and new fuels. The data collected in this study on MSATs and other pollutants on roads and at nearby locations provide important baseline information for ongoing and future studies.

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