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Sensitivity of Source Apportionment of Urban Particulate Matter to Uncertainty in Motor Vehicle Emissions Profiles

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ABSTRACT

A sensitivity analysis was conducted to characterize sources of uncertainty in results of a molecular marker source apportionment model of ambient particulate matter using mobile source emissions profiles obtained as part of the Gasoline/Diesel PM Split Study. A chemical mass balance (CMB) model was used to determine source contributions to samples of fine particulate matter ($PM_{2.5}$) collected over 3 weeks at two sites in the Los Angeles area in July 2001. The ambient samples were composited for organic compound analysis by the day of the week to investigate weekly trends in source contributions. The sensitivity analysis specifically examined the impact of the uncertainty in mobile source emissions profiles on the CMB model results. The key parameter impacting model sensitivity was the source profile for gasoline smoker vehicles. High-emitting gasoline smoker vehicles with visible plumes were seen to be a significant source of PM in the area, but use of different measured profiles for smoker vehicles in the model gave very different results for apportionment of gasoline, diesel, and smoker vehicle tailpipe emissions. In addition, the contributions of gasoline and diesel emissions to total ambient PM varied as a function of the site and the day of the week.

INTRODUCTION

Motor vehicles are a major source of particulate matter (PM) to the urban atmosphere. However, results of studies investigating the contributions of vehicle tailpipe emissions to urban PM have often differed, especially concerning the relative impacts of gasoline and diesel vehicles.[1–3] The range of results suggests that the chemical mass balance (CMB) models used for source apportionment are sensitive to variation in the methods used to create chemical source profiles for vehicle emissions. One source of variation in source profiles and models results is the use of different methods for measurement of the operationally defined organic carbon (OC) and elemental carbon (EC) fractions, which has been explored previously.[4] The other major source of uncertainty in vehicle emissions source profiles are the relationships between representative vehicle profiles and actual on-road fleets of vehicles.

Vehicle tailpipe emissions profiles are developed through testing vehicle emissions on chassis dynamometers. The uncertainty in source profiles arises from testing of a small number of vehicles to represent a large fleet in an area, from applicability of tested driving cycles to on-road driving patterns, and from the unknown numbers of high-emitting or poorly-functioning vehicles in on-road fleets that are not adequately represented in testing. Compared with other combustion sources, it is difficult to develop representative profiles for emissions from gasoline and diesel vehicles. Other sources, such as coal burning or open wood burning, have a relatively limited set of possible combustion conditions, and therefore a limited range of emissions compositions. Alternatively, motor vehicle emissions are dependent upon such factors as fuel, engine condition, ambient temperature, driving cycle, and lubricating oil age.[5–10] These factors vary not only between vehicles of different ages and weight classes, but also for an individual vehicle in different circumstances.[11] Therefore, developing useable source emissions profiles that are representative of the actual on-road emissions from a fleet of vehicles requires understanding of the variability of emissions profiles.

In this study, a large number of gasoline and diesel vehicles were tested on chassis dynamometers over several driving cycles. The chemical compositions of the PM emissions were averaged to create profiles for gasoline and diesel tailpipe emissions for source apportionment of ambient PM collected in Los Angeles. Profiles were developed for the most realistic vehicle fleets possible, using data on vehicle ages and weight classes for the Los Angeles area. To investigate the impact of a variety of emissions conditions on the model results, additional profiles were developed for different vehicle ages, for different driving cycles, and for gasoline smoker vehicles with visible plumes. The vehicle profiles were also used to conduct CMB source

IMPLICATIONS

The Gasoline/Diesel PM Split Study provides an assessment of the uncertainty in molecular marker source apportionment of motor vehicle tailpipe emissions that results from the uncertainty associated with the profiles for gasoline and diesel vehicles. These results demonstrate that the largest uncertainty associated with the molecular marker source apportionment models is the characterization of smoking vehicles. When the average composition of emissions from smoking vehicles is constrained, the apportionment of primary emissions from gasoline and diesel vehicles is not greatly altered by changes in their profiles. This study further emphasizes the need to better characterize the frequency of smoking vehicles and the average composition of their PM emissions.

Table 1. Tested gasoline vehicles by age class and fraction of tested fleet.

	1995–2001		1985–1994		1975–1984		1965–1974		Total	
	Number of Vehicles Tested	Fraction of Tested Fleet	Number of Vehicles Tested	Fraction of Tested Fleet	Number of Vehicles Tested	Fraction of Tested Fleet	Number of Vehicles Tested	Fraction of Tested Fleet	Number of Vehicles Tested	Fraction of Tested Fleet
Nonsmokers	15	0.28	24	0.45	7	0.13	0	0.00	46	0.87
Smokers	0	0.00	3	0.06	3	0.06	1	0.02	7	0.14
Total	15	0.28	27	0.51	10	0.19	1	0.02	53	1.00

Notes: Tested high emitting vehicles: Smoker 1, 1989 Toyota Pickup; Smoker 2, 1990 VW Jetta; Smoker 3, 1978 Chevy Caprice; Smoker 4, 1988 Mazda Pickup; Smoker 5, 1969 Chevy Malibu; Smoker 6, 1984 Toyota Pickup; Smoker 7, 1980 Toyota Celica.

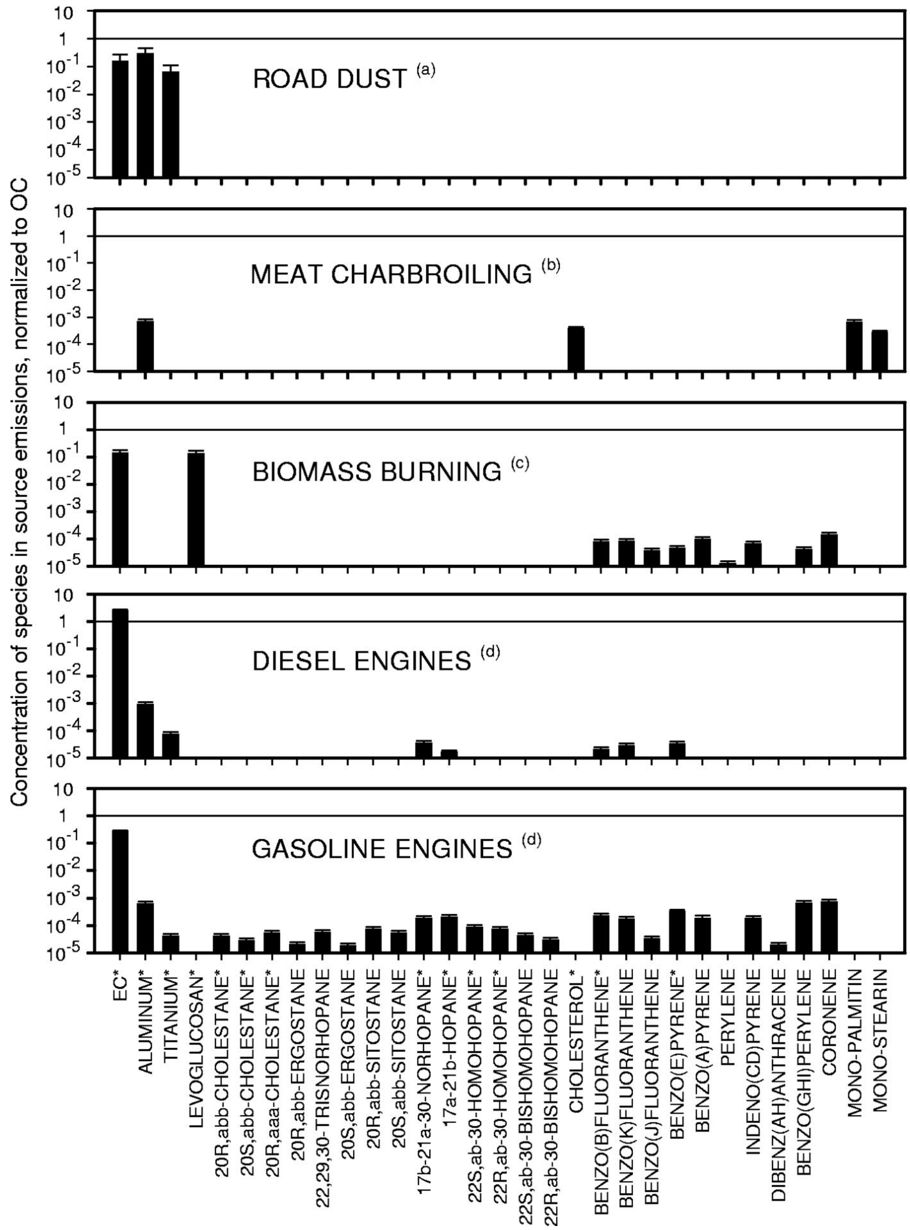

Figure 1. Source profiles used for apportionment with CMB model. Mass of species normalized to mass of OC. Stars denote CMB fit species. References: (a) Schauer 1996[23] (organic compound ratios) and this study (metals and EC/OC); (b) Schauer 1999[25] and Nolte 1999[26]; (c) Fine 2002[24] average woodsmoke profile; and (d) this study.

Table 2. Diesel vehicle fleet averages.

Model	No. Vehicles in Average
1998–2001 model years	10
1994–1997 model years	12
1990–1993 model years	4
Pre-1990 model years	4
CSHVR,*a* hot Start	32
Highway cycle	30
CSHVR,[a] cold start	10
Urban dynamometer schedule	1

Notes: [a]City-suburban heavy vehicle route.

apportionment of day-of-week composite samples of ambient PM to observe changes in the contribution of gasoline and diesel vehicles to ambient concentrations with the day of the week.[12]

METHODS

Ambient Samples

Ambient samples were collected at two sites in Los Angeles (LA), CA, over 3 weeks in July 2001.[13] The first site was located in Azusa, a suburb of LA, in an area that is residential and industrial. The second site was in downtown LA, near a main highway in an industrial area. Daily 24-hr $PM_{2.5}$ (PM that is 2.5 μm in size or smaller) samples were collected with a 92-LPM cyclone

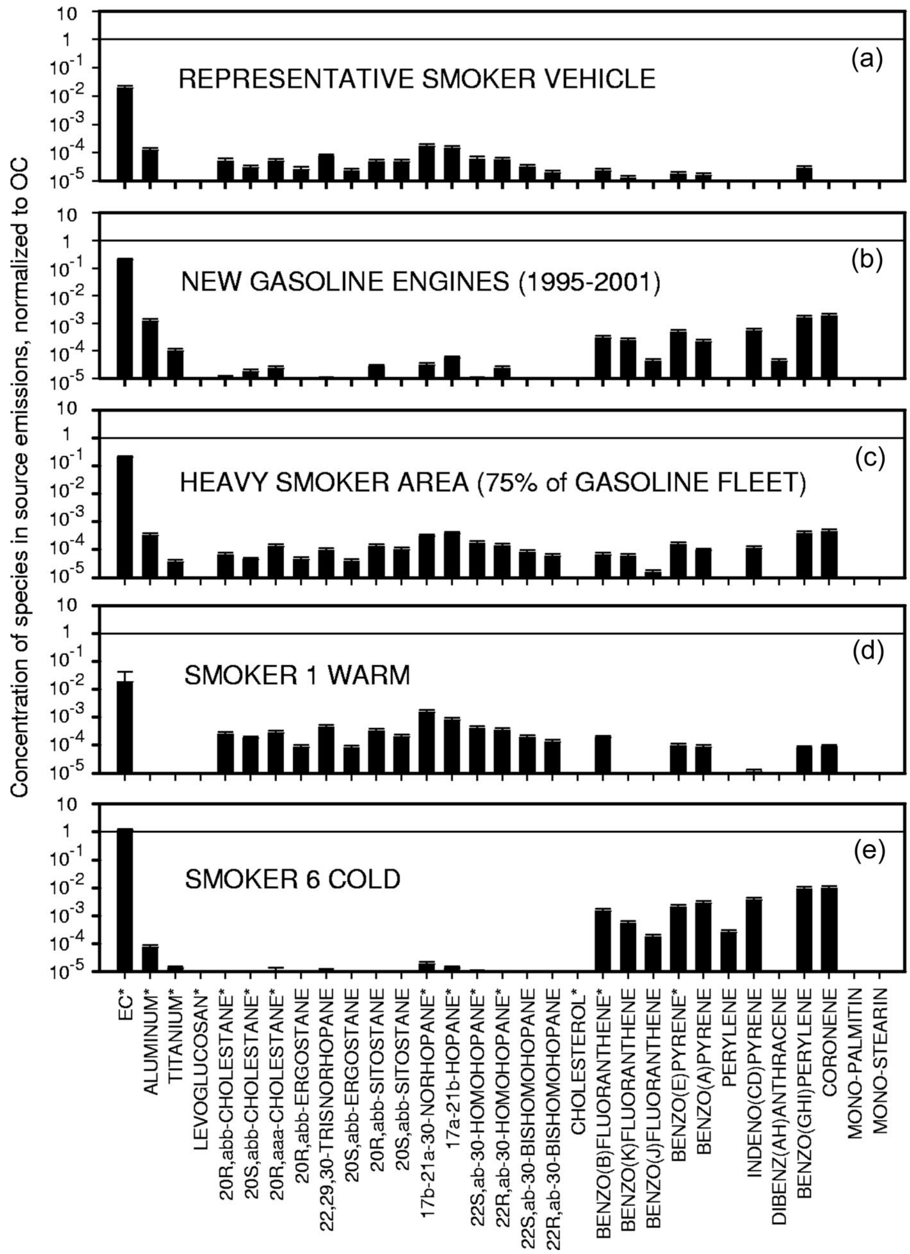

Figure 2. Source profiles used for apportionment with CMB model. Profiles for representative smoker vehicle (base case), new gasoline engines, an environment with 75% of vehicles smokers, and two individual smoker tests. Mass of species normalized to mass of OC. Stars denote CMB fit species. References: all profiles developed in this study. (a) Representative smoker vehicle, (b) new gasoline engines, (c) heavy smoker area, (d) Smoker 1 warm, and (e) Smoker 6 cold.

Table 3. Vehicle fleet averages for source profiles.

Gasoline Fleet Average Profiles	No. Vehicles in Average	Fraction of Fleet Represented by Age Group							
		1995–2001	1995–2001 Smokers	1985–1994	1985–1994 Smokers	1975–1984 Smokers	1975–1984 Smokers	1965–1974	1965–1974 Smokers
Base case: LA passenger cars distribution,[a] 5% smokers	49	0.41	0.00	0.43	0.043	0.07	0.007	0.00	0.00
LA passenger cars distribution,[a] 25% smokers	49	0.44	0.00	0.23	0.23	0.04	0.037	0.00	0.017
LA passenger cars distribution,[a] 50% smokers	49	0.44	0.00	0.00	0.46	0.00	0.070	0.00	0.030
New cars only, 1995–2001 model years	15	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
High smoker environment, 75% smokers	49	0.28	0.00	0.00	0.58	0.00	0.094	0.00	0.042
Diesel Fleet Average Profiles		Pre-1990	1990–1993	1994–1997	1998–2001				
Base Case: LA diesel vehicle age distribution[a]	32	0.42	0.14	0.18	0.26				

Notes: [a]Data from CARB EMFAC model. Distribution of vehicle ages present in 2001.

and 90-mm filter holder (URG Inc.) on prebaked quartz fiber filters. A punch of each filter was taken for analysis of EC and OC using the National Institute for Occupational Safety and Health 5040 method.[14] The remainder of the filters were composited by the day of the week for detailed organic compound analysis, resulting in seven composites of three filters at each site (i.e., the three Monday Azusa filters were composited). These day-of-week composites were extracted with solvents and analyzed by GC–mass spectroscopy (GCMS). Details of sample preparation[15] and GCMS analysis[16] have been described elsewhere.[13] Filters were spiked with a set of

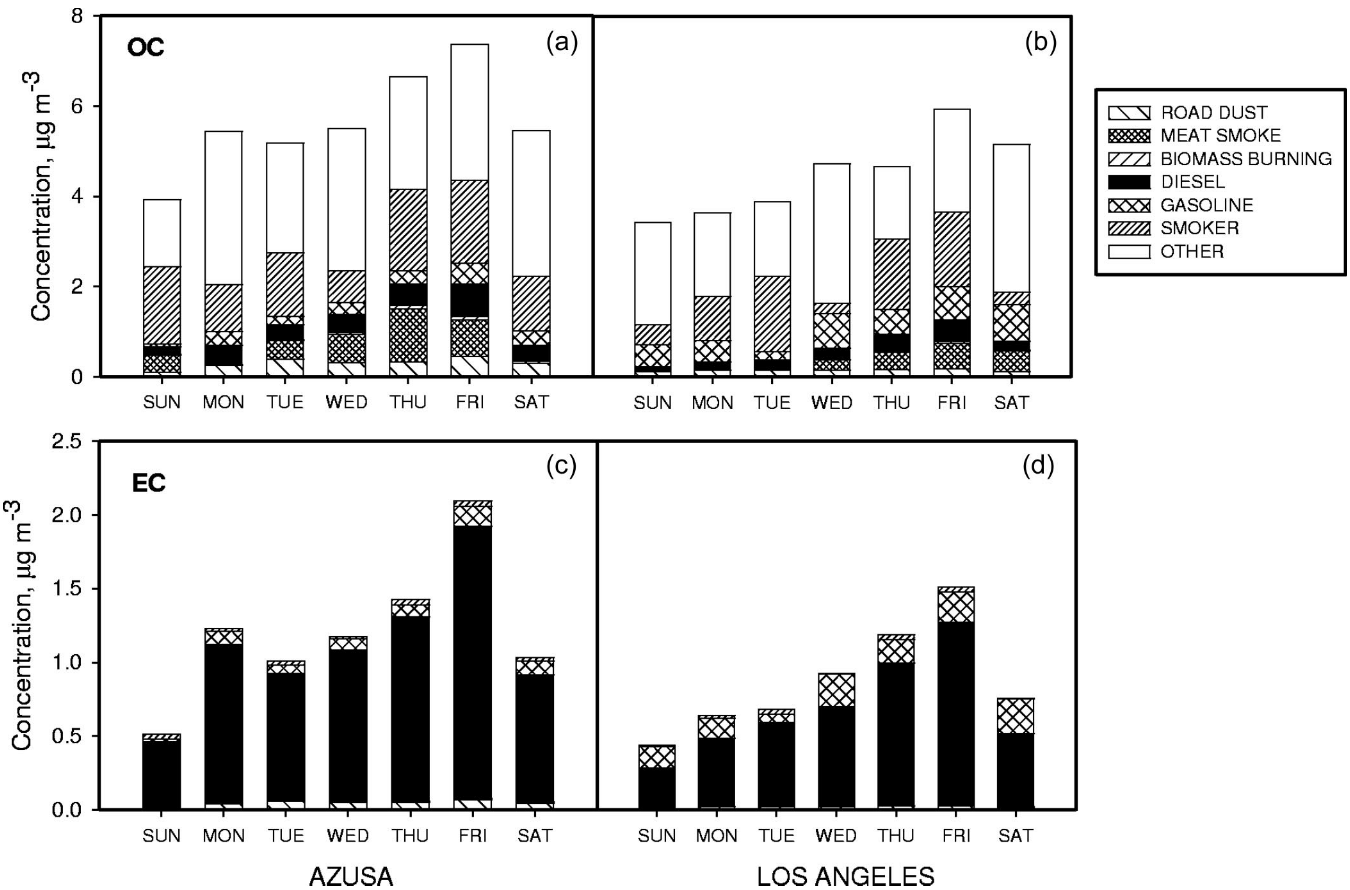

Figure 3. Calculated source contributions to (a and b) OC and (c and d) EC concentrations ($\mu g \cdot m^{-3}$) in (a and c) Azusa and (b and d) LA by day of the week. Daily ambient data are average of 3 days in July 2001.

Table 4. OC results for base case: OC in ambient sample due to each source, $\mu g \cdot m^{-3}$.

	Resuspended Soil (μg OC m^{-3})	Meat Charbroiling (μg OC m^{-3})	Biomass Burning (μg OC m^{-3})	Diesel (μg OC m^{-3})	Gasoline (μg OC m^{-3})	Smoker (μg OC m^{-3})	Total Apportioned (μg OC m^{-3})	Other (μg OC m^{-3})
Azusa								–
Sunday	0.098	0.388	0.004	0.176	0.059	1.716	2.441	1.477
Monday	0.256	0.000	0.016	0.419	0.310	1.045	2.046	3.395
Tuesday	0.383	0.414	0.016	0.336	0.186	1.413	2.749	2.428
Wednesday	0.314	0.627	0.039	0.402	0.270	0.704	2.355	3.147
Thursday	0.333	1.171	0.073	0.486	0.279	1.810	4.152	2.502
Friday	0.449	0.818	0.066	0.722	0.464	1.841	4.360	3.005
Saturday	0.295	0.000	0.055	0.338	0.327	1.217	2.232	3.225
Los Angeles								–
Sunday	0.110	0.000	0.003	0.106	0.497	0.435	1.152	2.276
Monday	0.149	0.000	0.000	0.182	0.473	0.978	1.782	1.855
Tuesday	0.148	0.000	0.008	0.222	0.187	1.668	2.232	1.657
Wednesday	0.151	0.222	0.000	0.265	0.761	0.232	1.631	3.097
Thursday	0.163	0.387	0.014	0.378	0.550	1.567	3.059	1.604
Friday	0.184	0.569	0.036	0.480	0.729	1.660	3.657	2.270
Saturday	0.118	0.458	0.010	0.196	0.818	0.278	1.879	3.269

internal standard compounds before extraction. Two sequential extractions were performed with a Soxhlet apparatus, one with dichloromethane and one with methanol, and the two extracts were combined. Rotary evaporation and nitrogen blowdown decreased total extract volume to 0.25 mL. Derivatization of an aliquot of the extract with diazomethane allowed quantification of organic acids as their methyl ester analogs. A portion of this methylated aliquot was then silylated to allow quantification of very polar compounds as their trimethylsilyl derivatives. All three aliquots of extract were analyzed with the same GCMS conditions.

Data for ambient mass, ionic species (sulfate, nitrate, and ammonium), and trace metals were obtained from measurements made by Desert Research Institute (DRI).[17,18]

Field blanks were collected at regular intervals, and all sample data were corrected by subtraction of blank results. Mass of a species on a filter or in a filter composite, after blank correction, was divided by the total volume of air sampled to obtain concentrations in mass per volume of air.

Source Profiles

Gasoline Engine Emissions. Emissions profiles for gasoline and diesel vehicles were developed in this work. Sample collection has been described completely elsewhere,[10] and briefly described here. To develop the gasoline profile, PM emissions from 54 gasoline vehicles (Table 1) operated on a chassis dynamometer were sampled from diluted exhaust. Emissions were sampled from each vehicle over cold-start and warm-start phases of the

Table 5. EC results for base case: EC in ambient sample due to each source, $\mu g \cdot m^{-3}$.

	Resuspended Soil (μg EC m^{-3})	Meat Charbroiling (μg EC m^{-3})	Biomass Burning (μg EC m^{-3})	Diesel (μg EC m^{-3})	Gasoline (μg EC m^{-3})	Smoker (μg EC m^{-3})	Total Apportioned (μg EC m^{-3})	Other (μg EC m^{-3})
Azusa								–
Sunday	0.015	0.000	0.001	0.448	0.016	0.033	0.514	0.000
Monday	0.039	0.000	0.002	1.079	0.089	0.021	1.230	0.000
Tuesday	0.059	0.000	0.002	0.866	0.054	0.027	1.007	0.003
Wednesday	0.048	0.000	0.006	1.030	0.077	0.014	1.175	0.000
Thursday	0.051	0.000	0.010	1.246	0.081	0.036	1.424	0.004
Friday	0.069	0.000	0.010	1.845	0.133	0.035	2.093	0.000
Saturday	0.045	0.000	0.008	0.862	0.094	0.024	1.034	0.000
Los Angeles								–
Sunday	0.017	0.000	0.000	0.269	0.144	0.008	0.438	0.000
Monday	0.023	0.000	0.000	0.464	0.136	0.019	0.642	0.000
Tuesday	0.023	0.000	0.001	0.570	0.054	0.032	0.680	0.003
Wednesday	0.023	0.000	0.000	0.678	0.219	0.005	0.925	0.000
Thursday	0.025	0.000	0.002	0.970	0.158	0.031	1.186	0.002
Friday	0.029	0.000	0.005	1.237	0.210	0.032	1.512	0.000
Saturday	0.019	0.000	0.002	0.497	0.234	0.005	0.756	0.000

Table 6. Mass results for base case; mass in ambient sample due to each source, $\mu g \cdot m^{-3}$.

	Resuspended Soil (μg Mass m^{-3})	Meat Charbroiling (μg Mass m^{-3})	Biomass Burning (μg Mass m^{-3})	Diesel (μg Mass m^{-3})	Gasoline (μg Mass m^{-3})	Smoker (μg Mass m^{-3})	Total Apportioned (μg Mass m^{-3})	Other (μg Mass m^{-3})
Azusa								–
Sunday	0.75	0.69	0.00	0.43	0.08	2.06	4.01	10.03
Monday	1.95	0.00	0.02	1.03	0.40	1.26	4.66	11.59
Tuesday	2.92	0.73	0.02	0.83	0.24	1.70	6.44	11.72
Wednesday	2.39	1.11	0.05	0.99	0.35	0.85	5.73	12.56
Thursday	2.54	2.07	0.09	1.19	0.36	2.18	8.43	11.79
Friday	3.43	1.44	0.08	1.77	0.60	2.21	9.54	13.23
Saturday	2.25	0.00	0.07	0.83	0.42	1.46	5.03	15.39
Los Angeles								–
Sunday	0.84	0.00	0.00	0.26	0.64	0.52	2.27	11.32
Monday	1.14	0.00	0.00	0.45	0.61	1.18	3.37	10.98
Tuesday	1.13	0.00	0.01	0.54	0.24	2.01	3.93	12.92
Wednesday	1.16	0.39	0.00	0.65	0.98	0.28	3.46	12.25
Thursday	1.25	0.68	0.02	0.93	0.71	1.88	5.47	10.10
Friday	1.40	1.01	0.04	1.18	0.94	1.99	6.56	13.49
Saturday	0.90	0.81	0.01	0.48	1.05	0.33	3.60	12.07

unified driving cycles. Analysis for EC, OC, and speciated organic compounds was the same as for ambient samples. The cold-start and warm-start results were averaged by model year class, using data on the age distribution of vehicles in the LA area in 2001 provided by the California Air Resources Board (CARB). The cold-start and warm-start profiles were then averaged on a mass-weighted basis to create a single profile for gasoline vehicle emissions. All species were normalized to OC, and the profile is presented in units of mass species per mass OC. This profile is shown in Figure 1. In all vehicle profiles, uncertainties for each species represent the total measurement uncertainties in the averaged vehicle tests, propagated through the mass-weighted averaging as the square root of the sum of the squares.

Diesel Engine Emissions. Development of the profile for diesel emissions was similar to that of gasoline emissions. A total of 33 diesel vehicles (Table 2) were operated on a chassis dynamometer through several driving cycles. The results from all driving cycles and vehicle weight classes were averaged based on vehicle age data for the LA area, as discussed in other work.[10] The resulting source profile, normalized to OC, is shown in Figure 1. The diesel profile contains a large fraction of EC, which the model relies on to apportion to this source. Whereas EC/organic carbon ratios in the emissions of individual diesel vehicles have been observed in this[10] and other studies[19,20] to vary over more than an order of magnitude, the robust approach taken in this study to average measured emissions to represent on-road vehicle fleets decreased the EC/OC variability.

Smoker and Microenvironment Profiles. Seven smoker vehicles with either visible emission plumes or emissions of greater than 50 $mg \cdot mi^{-1}$ were also tested during testing of gasoline vehicles (Table 1).[10] Three of the vehicles had emissions profiles similar to what is expected of a "normal" oil-burning smoker vehicle, with high mass fractions of OC, high concentrations of hopane and sterane

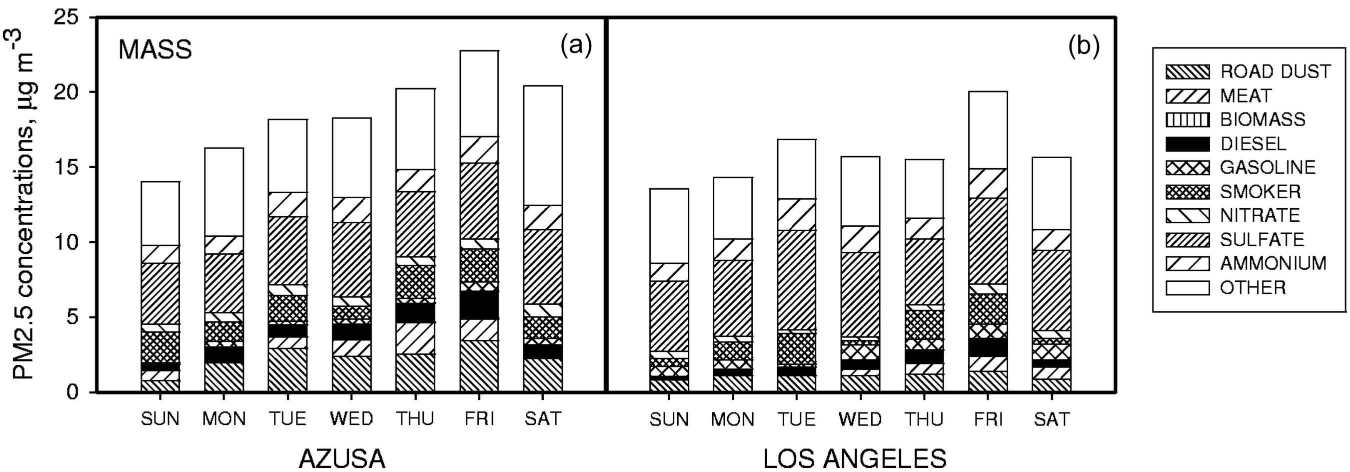

Figure 4. Calculated source contributions to $PM_{2.5}$ Mass concentrations ($\mu g \cdot m^{-3}$) in (a) Azusa and (b) LA by day of the week. Daily ambient data is average of 3 days in July 2001. Sulfate, nitrate, and ammonium are shown as measured concentrations.

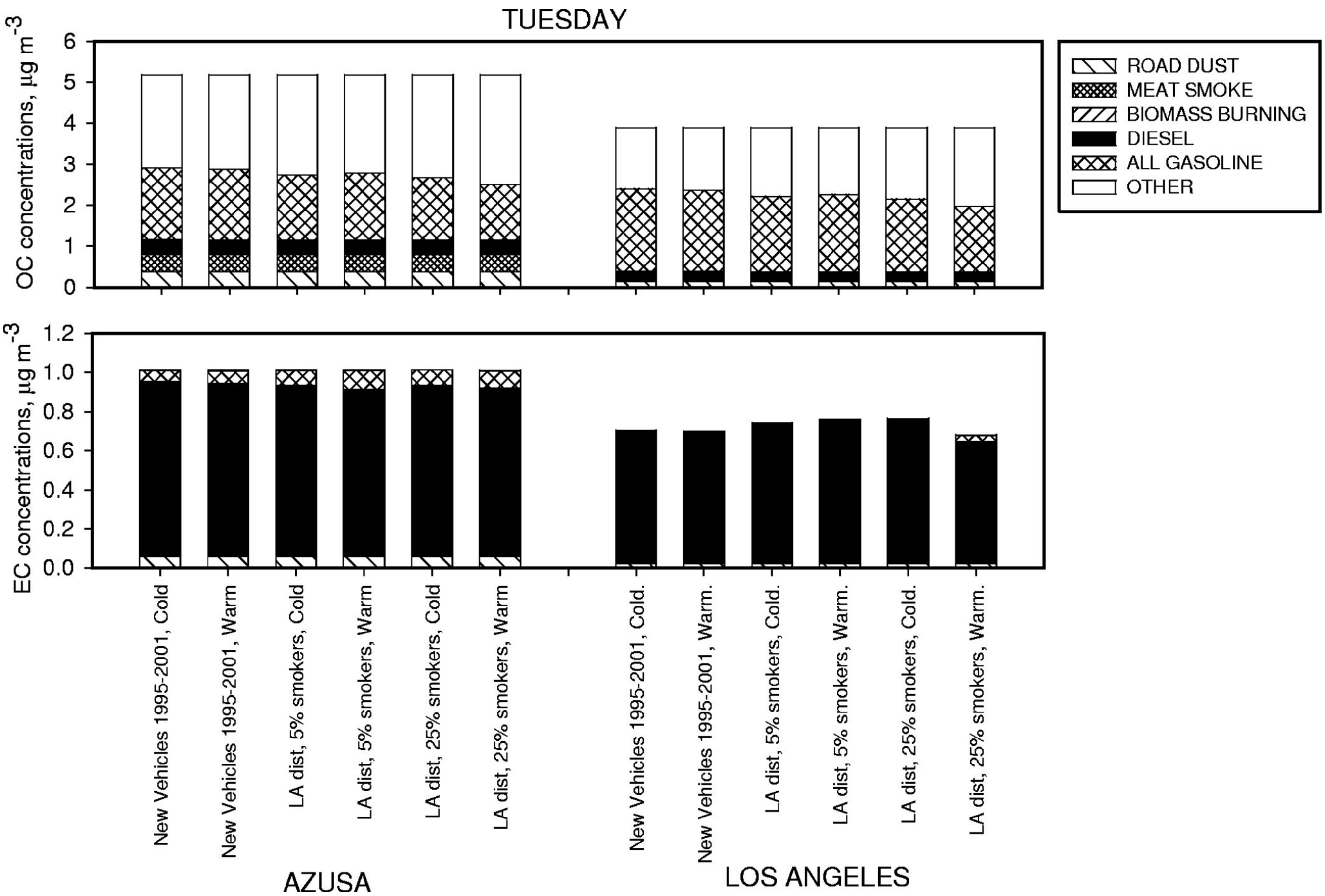

Figure 5. Sensitivity of calculated source contributions to use of different gasoline source profiles. Calculated contributions to OC and EC concentrations ($\mu g{\cdot}m^{-3}$) in Azusa and LA (Tuesday average ambient data).

compounds, and low concentrations of polycyclic aromatic hydrocarbons (PAHs).[10] The other four tested smoker vehicles had a wide range of emission compositions and rates, reflecting the fact that a number of mechanisms other than oil burning can cause a vehicle to be a smoker. A profile of smoker vehicle emissions similar to the normal oil-burning smoker profile was used as the base case in the model, and is shown at the top of Figure 2.

Also shown in Figure 2 are two profiles for microenvironments, potential areas in which gasoline vehicles would not have the LA age distribution. The two possibilities investigated here were new vehicles, with all gasoline vehicles assumed newer than model year 1995, and the opposite, an area where smoker vehicles make up 75% of the total gasoline vehicle fleet (Table 3).[10] These "microenvironment" profiles could be similar to emissions in other areas of the world as vehicle emissions are decreased or as many vehicles fall into disrepair.

The final two plots in Figure 2 demonstrate extremes in the variation observed between individual smoker vehicles. The two cycles shown, for the warm-start cycle of Smoker 1 and the cold-start cycle of Smoker 6, demonstrate the big differences in emission composition for individual smoker vehicles with similar emission rates. One has high OC and high hopanes and steranes, and the other has more EC than OC and very high PAH concentrations.

As with other average vehicle profiles, uncertainties for each species in smoker profiles represent total measurement uncertainties propagated through the mass-weighted averaging. Because the modeling was focused on determining the sensitivity of model results to different profiles, individual smoker profiles that are used in the model include propagated measurement uncertainties for the single test.

Resuspended Road Dust Profile. The profile for resuspended road dust was partially created through this work. Samples of road dust from eight sites in the LA area were collected and later resuspended using a dilution chamber similar to that described and illustrated by Hildemann et al.[21,22] The sample dust was placed in a flask, and clean zero air carried the suspended sample through stainless steel tubing into the dilution chamber, a stainless steel cylinder ~0.3 m in diameter and 1.5 m high. $PM_{2.5}$ samples were collected by drawing air from the chamber through cyclone separators (Thermo Anderson, Smyrna, GA) and filters (Pall Corp., Ann Arbor, MI). The size separation and filter collection were parallel to collection methods for ambient aerosols and other samples to ensure direct comparability of the data. The road dust profile

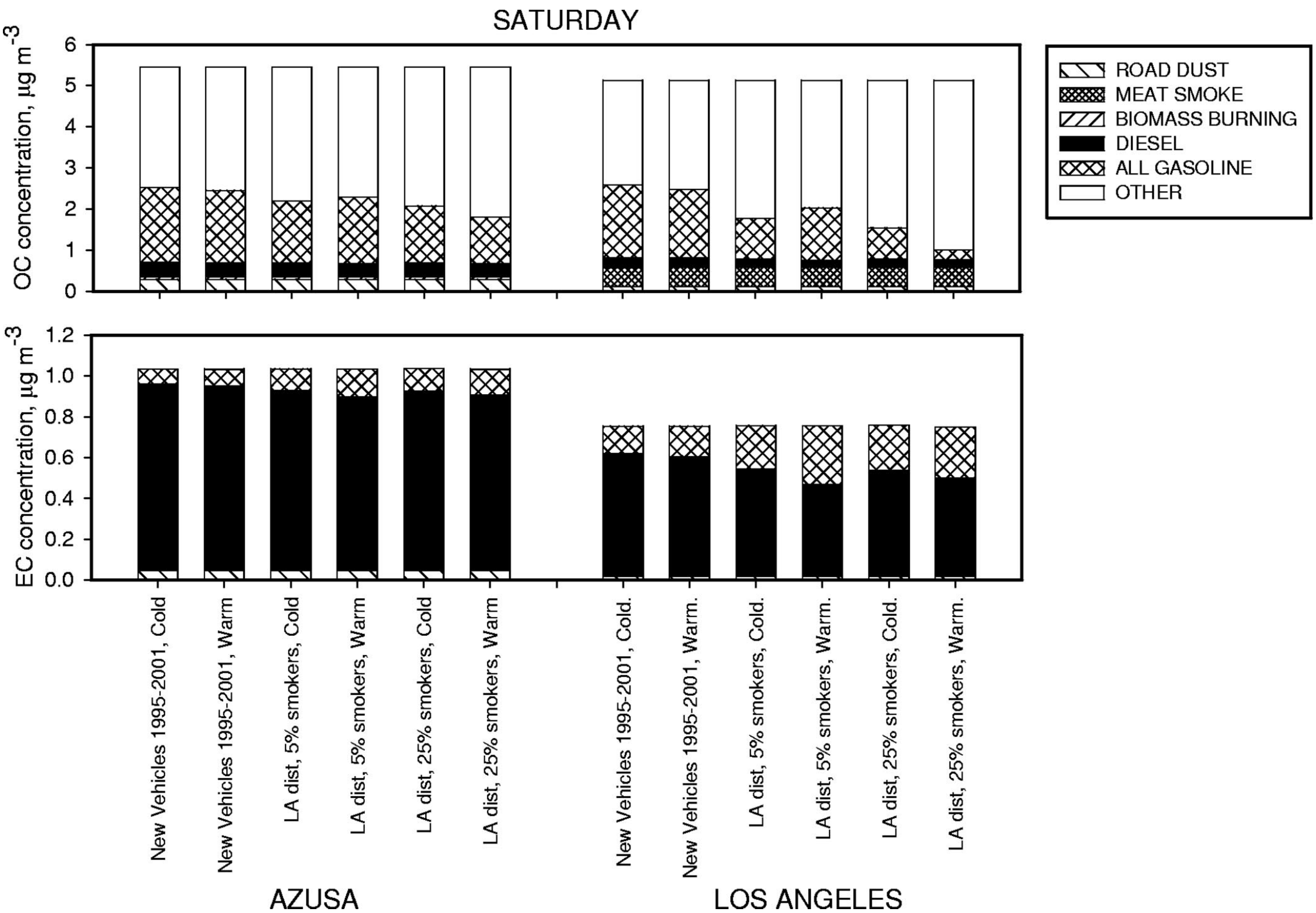

Figure 6. Sensitivity of calculated source contributions to use of different gasoline source profiles. Calculated contributions to OC and EC concentrations ($\mu g \cdot m^{-3}$) in Azusa and LA (Saturday average ambient data).

used in this work had the average EC content and metals data from the LA samples, but because organic analysis was not performed on the samples, data on organic compounds in LA area soils were taken from previously published work.[23] Because a soil dust profile was not included in the model, the road dust apportionment likely includes some resuspended soil, but this distinction does not impact the results because the road dust profile contains no measurable hopanes or steranes and only a few PAHs at very low concentrations.

Other Source Profiles. Profiles for other sources were taken from previous work, and are shown in Figure 1. The biomass burning profile was taken as an average of four types of wood burning quantified by Fine.[24] Meat cooking was taken from Schauer et al.,[25] with very polar compounds from Nolte.[26] Several additional profiles were included in preliminary analysis of these data, but tracer compounds unique to those sources were not detected (or had high uncertainty) in this ambient dataset, and were therefore not used in the model. Those profiles included cigarette smoke and vegetative detritus. The cigarette smoke profile was taken from work by Rogge et al.,[27] with mass and OC conversion factors from Hildemann et al.[22] Green and dead vegetative detritus emissions were taken from Rogge et al.[28] with conversion factors from the same Hildemann work.

CMB Modeling

Based on previous source apportionment work, the model used was CMB8.2 created by the U.S. Environmental Protection Agency.[29] The CMB model solves for an effective variance least squares fit of known source profiles to describe the composition of an ambient sample.[1,29,30] Because the principal goal of the modeling was investigating the sensitivity of the model results to changes in the vehicle fleet emissions profiles, the modeling was focused on application of a variety of profiles for gasoline, diesel, and smoker vehicle emissions. The base case model used best-estimate profiles[10] for gasoline and diesel vehicles plus a normal oil-burning smoker profile, all of which were consistent with previous work.[8,31,32] The sensitivity modeling used the base case conditions, but replaced one profile (gasoline, diesel, or smoker vehicle) with an alternate profile from this work. In addition to motor vehicles, profiles for road dust, biomass burning, and meat cooking were used when an ambient sample contained detectable levels of tracer species for that source.

RESULTS AND DISCUSSION

Base Case

The base case for the CMB model used the profiles considered to be the best estimates[10] for on-road diesel vehicle, gasoline vehicle, and smoker vehicle emissions (Table

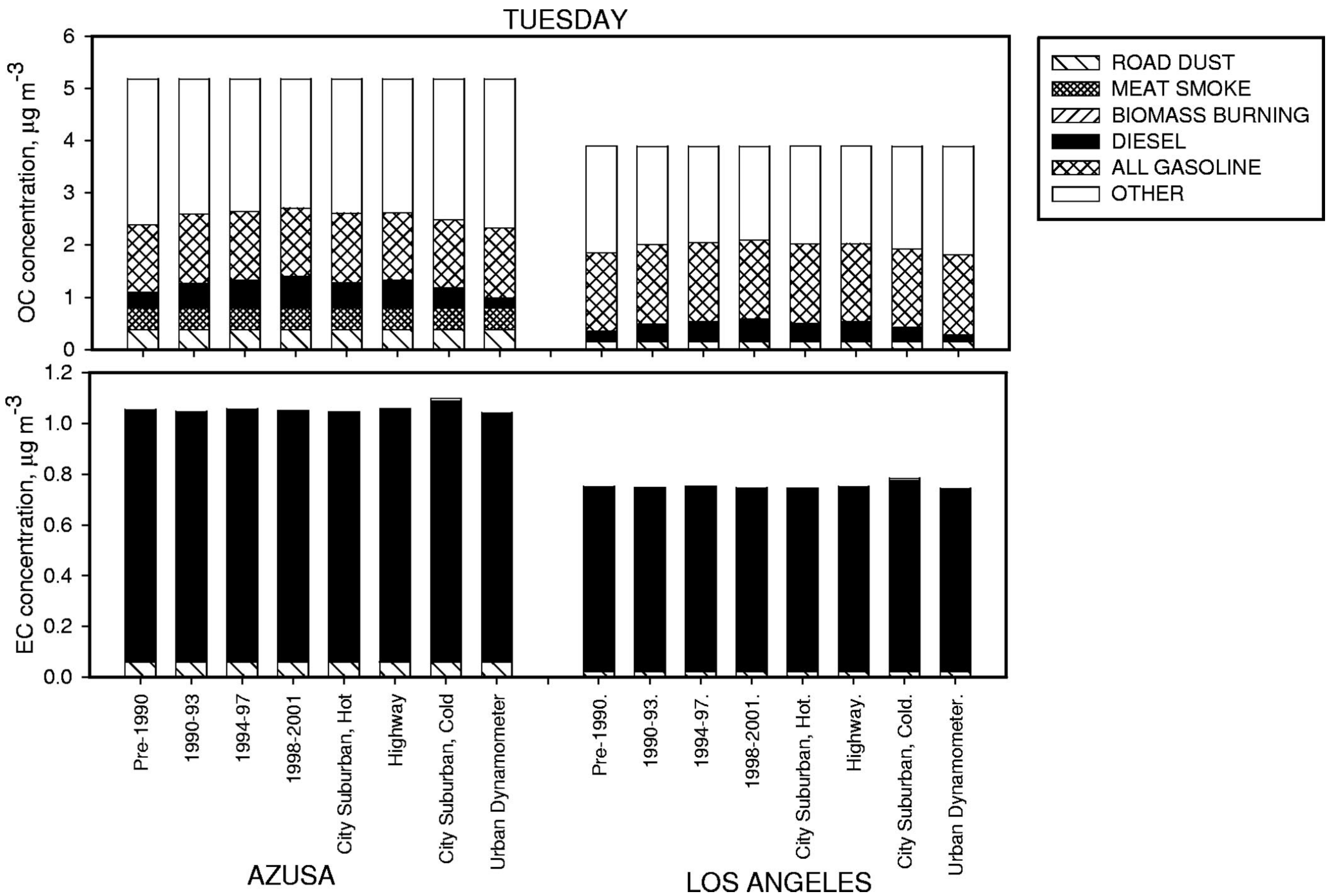

Figure 7. Sensitivity of calculated source contributions to use of different diesel source profiles. Calculated contributions to OC and EC concentrations ($\mu g \cdot m^{-3}$) in Azusa and LA (Tuesday average ambient data).

3). The diesel profile was an age-averaged profile representing averages of all weight classes and driving cycles tested. The gasoline profile was an average of the cold-start and warm-start profiles for a fleet with the age distribution of the LA area assuming 5% of the fleet to be high-emitting smoker vehicles. It is important to note that the gasoline vehicle fleets in the LA area may have less than 5% high-emitting smoker vehicles. However, the differences between the cold-start and warm-start profiles for the average fleet with 5% smokers were much greater than the differences between the average cold-warm profiles with 5% smokers and with no smokers.[10] For example, the differences between OC-normalized hopanes, steranes, and PAHs in the cold-start and warm-start profiles were often greater than 50% for each fleet average, but were always less than 10% between the average cold-warm profile for the 5% smoker fleet and the average cold-warm profile assuming no smokers. Because the average cold-warm profiles were so similar, the profile for the average gasoline fleet with 5% normal oil-burning smokers was used as the base case to ensure representation of smoker vehicles in the fleet. However, in modeling, use of only the gasoline (including 5% smoker vehicles) and diesel profiles did not allow the model to resolve all of the EC or motor vehicle tracer species measured in the ambient samples. Therefore, an additional smoker profile was necessary to explain ambient concentrations of molecular marker compounds from motor vehicles. The additional smoker profile was assigned the average composition of normal oil-burning smoker vehicles (Figure 2). The contributions of each source reported are for the independent profiles of gasoline vehicles, diesel vehicles, and smoker gasoline vehicles. No attempt was made to further identify the specific contribution of the 5% of smoker vehicles included in the base case gasoline profile.

Although the profiles for gasoline vehicles, smokers, and diesel vehicles contain many similar compounds, the model was able to distinguish the three sources. In Figure 3, the contributions of each modeled source to measured ambient concentrations of OC and EC are shown (CMB statistics in Supplementary Table 1 of supplemental data published at http://secure.awma.org/journal/pdfs/2007/10/10.3155-1047-3289.57.10.1190_supplmaterial.pdf). A portion of OC (37.5–66.5%) in each ambient composite was not apportioned by the model because of the fact that the model only included primary sources. The unapportioned OC mass is labeled "other". This observation is consistent with other work in the LA area[2] and with work showing that unapportioned OC is consistent with secondary organic aerosol in the summer months in LA.[30] Because of this, the validity of CMB model runs was determined using the fit parameters of χ^2 and R^2 rather than the fraction of mass apportioned.

Results for the ambient composites (Tables 4–6) show trends in source contributions related to the site and the

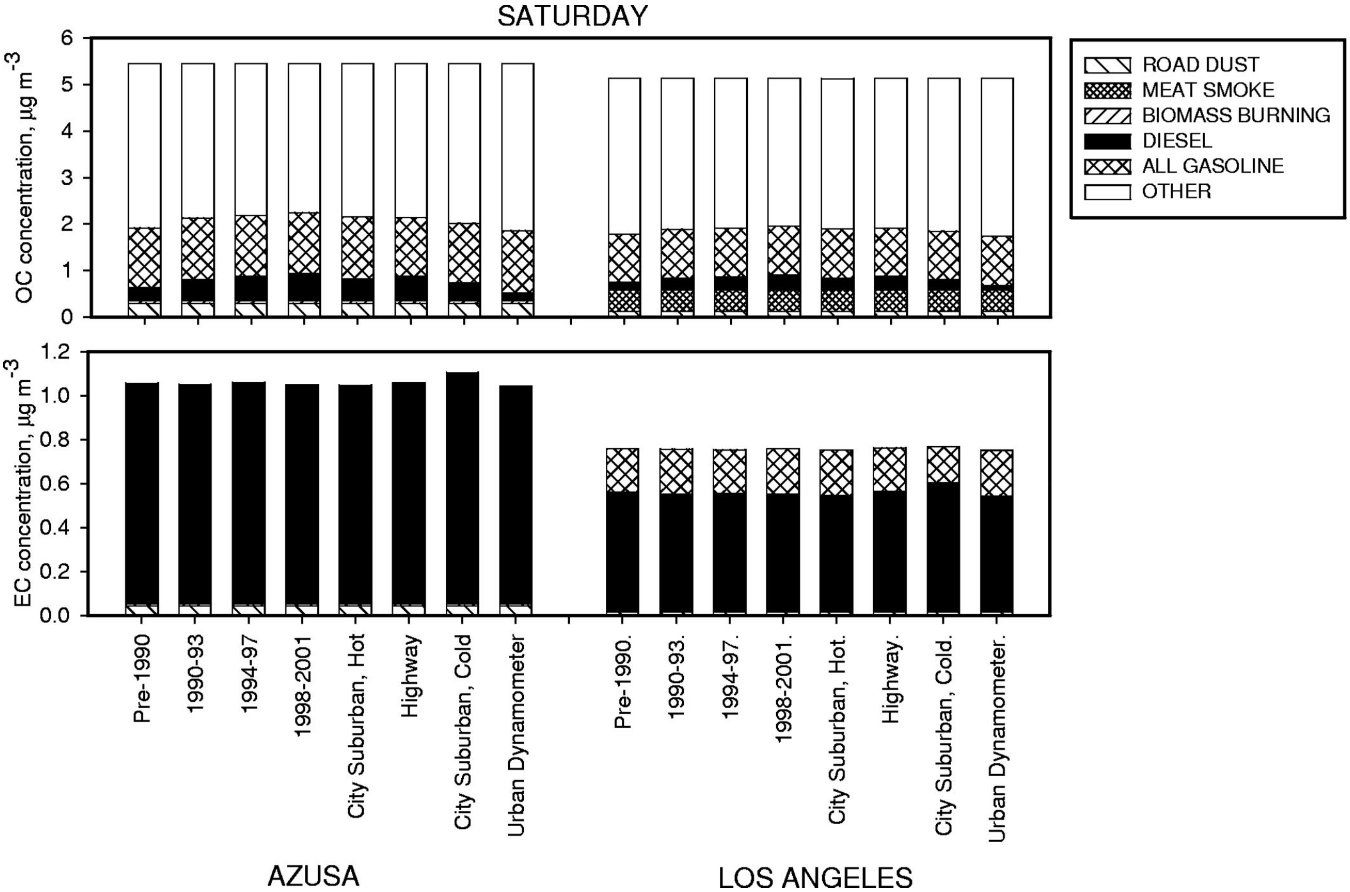

Figure 8. Sensitivity of calculated source contributions to use of different diesel source profiles. Calculated contributions to OC and EC concentrations ($\mu g \cdot m^{-3}$) in Azusa and LA (Saturday average ambient data).

day of the week. The contribution of diesel vehicles generally increased at both sites throughout the weekdays, and decreased over the weekend. This corresponds to trends in diesel vehicle activity patterns in the area that is higher on weekdays,[33,34] and to observed Monday–Friday increases in ambient concentrations of motor vehicle tracer species in these samples.[13] Similar weekly patterns in diesel activity have been seen in other data.[12] The EC at each site was apportioned predominately to diesel vehicles, with smaller amounts due to gasoline vehicles and smoker vehicles. Concentrations of EC and the fraction of EC due to diesel vehicles were both higher in Azusa.

In Azusa, the contribution of resuspended road dust (soil, minerals) was higher than in LA and was higher on weekdays than on the weekend. These observations are probably related to a quarry and trucking activity near the Azusa site because crustal elements were higher in the Azusa ambient samples.[13] At each site, for samples with statistically significant concentrations of meat smoke tracers, the contributions of meat smoke were lowest early in the week and increased later in the week,[13] related to activity patterns with increased late-week cookouts[33] and restaurant business. Very little ambient OC mass was apportioned to biomass burning at either site, which agrees with expected low use of wood burning in summer months in an urban area.

Source contributions to the total ambient $PM_{2.5}$ mass are shown in Figure 4. Sulfate, which was assumed to be formed wholly through secondary processes, was a major portion of $PM_{2.5}$ mass at both sites. Secondary species ammonium and nitrate also contributed. As expected for all these secondary species, which are formed regionally in the airshed and are less subject to daily fluctuations in emissions, no patterns dependent upon the day of the week were observed. Road dust was a larger contributor to mass than to OC at each site. As in contributions to OC, the Monday–Friday increases in diesel contributions to $PM_{2.5}$ mass were seen at both sites, and diesel contributions decreased over the weekends.

Sensitivity to Gasoline Vehicle Profile

The sensitivity of the source apportionment to different gasoline fleet profiles was investigated. The base case gasoline profile representing the average of cold-start and warm-start emissions for the age distribution of vehicles in the LA area was replaced with six different profiles, three for cold-start and three for warm-start gasoline emissions. Two profiles, one cold-start and one warm-start, represented the LA age distribution with assumed 5% smokers; two profiles represented the cold- and warm-starts of the LA age distribution with 25% smokers in the gasoline fleet; and two further profiles investigated the impact of using cold- and warm-start emissions from only new vehicles of model years 1995–2001. The results of these apportionments are shown for Tuesday and Saturday at each site in Figures 5 and 6 (CMB statistics in

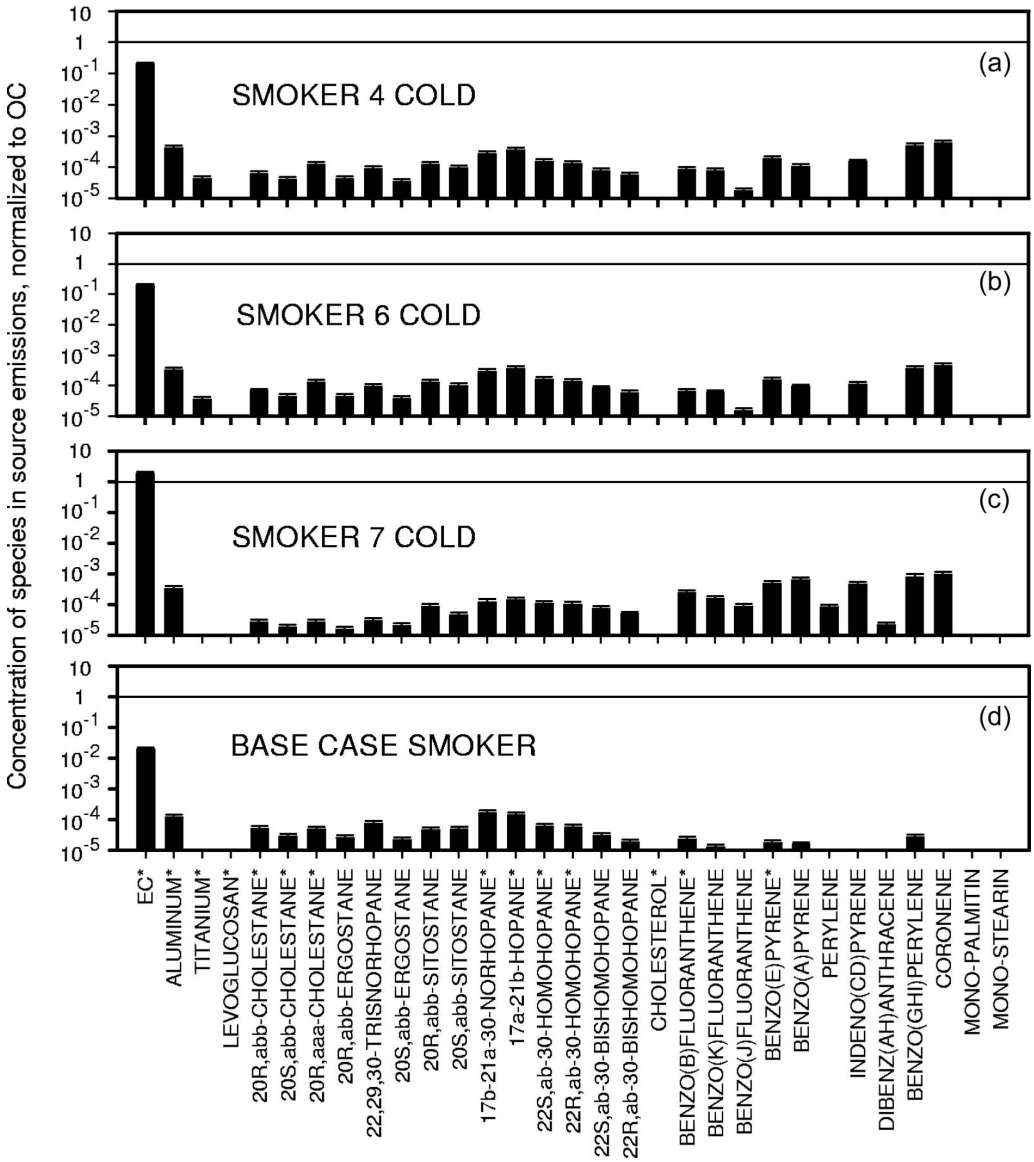

Figure 9. Source profiles for gasoline smoker vehicles used for apportionment with CMB model. Mass of species normalized to mass of OC. Stars denote CMB fit species. References: all profiles developed in this study. (a) Smoker 4 cold, (b) Smoker 6 cold, (c) Smoker 7 cold, and (d) base case smoker.

Supplementary Table 2). Compared with the base case, using the different gasoline profiles caused the model to be less able to distinguish between the gasoline profile and the smoker vehicle profile. Therefore, the OC and $PM_{2.5}$ mass apportioned to nonsmoker and smoker profiles were added together to create one result for all gasoline engines. Although there were differences in the results between the Azusa and LA sites, and between Tuesday and Saturday, the differences in apportionment due to various gasoline vehicle fleet profiles were small. The use of different fleet profiles did not impact the apportionment of road dust, meat cooking, or biomass burning. The most variability in model results was seen for gasoline vehicles in LA on Saturday (Figure 6), when the apportionment of OC to gasoline vehicles ranged from 0.23 to 1.6 $\mu g \cdot m^3$ (RSD 52%), and apportionment of OC to diesel vehicles ranged from 0.18 to 0.23 (RSD 11%). For the other days and locations shown in Figures 5 and 6, the RSD of apportionment of ambient OC using different gasoline profiles was less than 17% for gasoline vehicles, and less than 3% for diesel vehicles. The larger variability in model results in LA on Saturday is likely due to unusual relative impacts of mobile sources, which is also apparent in the apportionment of twice as much EC to gasoline and smoker vehicles on Saturday in LA than on other days and locations in Figures 5 and 6.

One important observation from the model results with different gasoline fleet profiles is the similarity of results using profiles with 5% smoker vehicles and with no smoker vehicles (new vehicles only, 1995–2001). As shown in Figures 5 and 6, the apportionment results of OC and EC for each site and day were very similar whether the gasoline fleet profile with only the newest vehicles or the profile with the LA age distribution and 5% assumed smokers was used. Even for LA on Saturday,

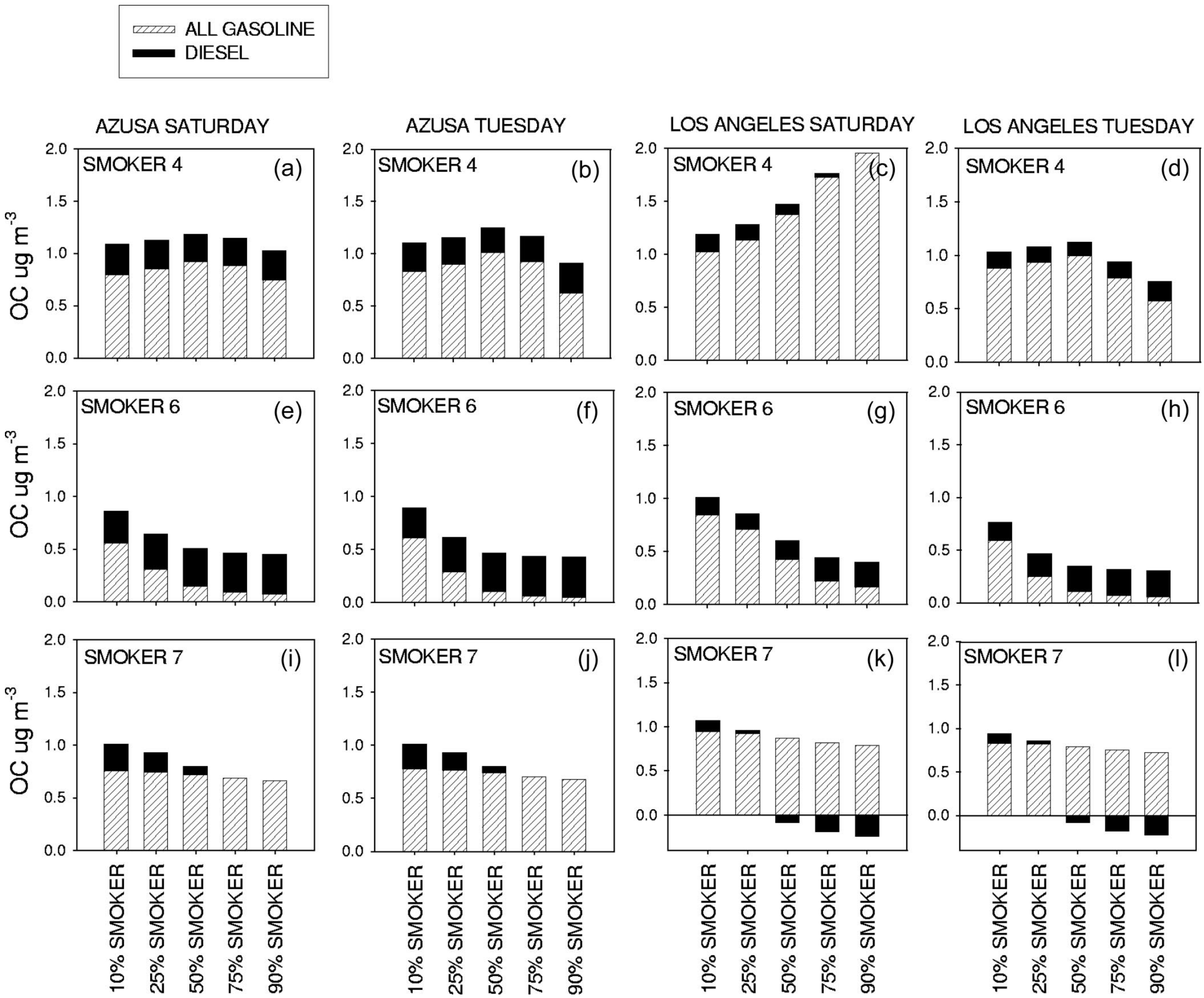

Figure 10. Average calculated OC contributions ($\mu g{\cdot}m^{-3}$) of gasoline and diesel vehicles, with five different gasoline profiles, each using different proportions (10%, 25%, 50%, 75%, 90%) of one of three smoker vehicles (Smoker 4, 6, or 7). (a, e, and i) Saturday at Azusa; (b, f, and j) Tuesday at Azusa; (c, g, and k) Saturday at LA; and (d, h, and l) Tuesday at LA.

which had the greatest variability in model results in Figure 6, using only the new vehicle profile and the 5% smokers profile decreases the variation (RSD of apportionment of OC to gasoline vehicles is 25%, instead of 52%). This result is further indication that although the representation of smoker vehicles in the LA gasoline vehicle fleet may be less than 5%, the use of the average cold-warm profile with 5% smokers as the base case profile does not affect the conclusions.

Sensitivity to Diesel Fleet Profile

Like gasoline vehicles, the impact of diesel fleet was investigated. Profiles of different age groups of diesel vehicles were used, including vehicles older than model year 1990, 1990–1993, 1994–1997, and 1997–2001 model years. Additionally, four profiles for different vehicle driving cycles were used, including the City Suburban Cycle, cold and hot starts, the Highway Cycle, and the Urban Dynamometer Driving Schedule. This study did not address the potential contributions of smoking or poorly functioning diesel vehicles. The results for Tuesday and Saturday at both sites are shown in Figures 7 and 8 (CMB statistics in Supplementary Table 3). Use of different diesel fleet profiles made small differences in the apportionment of ambient PM to diesel emissions. Although the profiles had significantly different proportions of tracer species and EC, the model results were minimally sensitive to changes in profile. The RSD of apportionment of OC to diesel vehicles for dates and locations in Figures 7 and 8 were very similar, ranging only from 32.1% to 32.5%. Of that, the RSD due to changes in age profile averaged 28.3%, whereas the RSD due to changes in driving cycle profile averaged 39.4%. The two profiles for vehicles older than model year 1990 and the Urban Dynamometer driving cycle contributed the most variability; excluding those two profiles resulted in an RSD of OC apportionment of only 13.5–14.9%. The RSD of apportionment of EC to diesel vehicles and of OC to gasoline vehicles due to these profile changes were much lower, ranging from 1.5 to 3.5% and 0.8 to 1.7%, respectively. As expected, no changes were seen in apportionment of nonmobile sources with different diesel emissions profiles.

Smoker Impacts

Although the model results were very stable with different gasoline and diesel emissions profiles, they were very sensitive to the gasoline smoker vehicle profile. The cold-start and warm-start emissions profiles for each of the seven smoker vehicles were used in the model to investigate the sensitivity. Compared with the normal oil-burning smoker profile used as the base case smoker, many of the smoker vehicles tested had much higher fractions of EC, hopanes, steranes, and PAHs. Smokers 4, 6, and 7, especially, had higher fractions of EC and PAHs, as seen in Figure 9.

Because the nonsmoker gasoline and smoker profiles contain many of the same compounds in different proportions, the model often became unstable because it was unable to separate the nonsmoker gasoline profile from the smoker profile. To determine how the smoker profile impacted the model results, the model was run with blends of several profiles averaged together in different proportions. These blended profiles allowed the model to reach a solution. Figure 10 shows the model results using emissions from smokers 4, 6, and 7. In the figure, the smoker profile was combined with the base case nonsmoker gasoline profile in different proportions (10% smoker, 25% smoker, 50% smoker, 75% smoker, and 90% smoker). The model results were very sensitive to these changes. Compared with the very small changes seen using different gasoline and diesel profiles, the changes in model results from including a different weight of a single smoker profile were much larger and more variable. For instance, the RSD of the apportionment of OC to all gasoline vehicles for a given day, location, and smoker in different proportions in Figure 10 ranged from 5.6% (Azusa, Tuesday, smoker 6) to 106% (Azusa, Tuesday, Smoker 7). For a single date and location using the 3 different smokers shown, the RSD for apportionment of OC to all gasoline vehicles and to all diesel vehicles ranged from 49.3 to 53.7% and 50.8 to 204%, respectively. Clearly, this sensitivity is notable for its unpredictability. For illustration, smokers 4 and 6 had very similar emissions profiles (Figure 9). However, using each of those two smokers in the model caused model instability, and the blended profiles created from smokers 4 and 6 with the gasoline profile behaved very differently in the model for a given ambient sample (Figure 10).

SUMMARY

The apportionment of ambient PM to various sources using a CMB model was stable and affected very little by use of different emissions composition profiles for nonsmoking gasoline or diesel vehicle fleets. However, smoker gasoline vehicles, which had high emission rates and very variable emission composition, were very difficult for the model to handle. In many cases, the model became unstable as a result of the similarities between the smoker profiles and other profiles. This instability clouded the results and made interpretation of the actual apportionments to gasoline vehicles, gasoline smoker vehicles, and diesel vehicles more complex. Overall, the key factor identified in uncertainty of source apportionment of urban PM using motor vehicle profiles was smoker vehicles, with their varied emission composition of emissions, and an uncertain representation in on-road fleets. Therefore, developing a better understanding of the range of compositions of gasoline smoker vehicle emissions will be vital to reducing uncertainty of modeled source contributions to ambient PM concentrations. Future studies also must investigate the composition and emissions of smoking and poorly functioning diesel vehicles.

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