

IMPORTANT COPYRIGHT INFORMATION

The following PDF article was originally published in the *Journal of the Air & Waste Management Association* and is fully protected under the copyright laws of the United States of America. The author of this article alone has been granted permission to copy and distribute this PDF. Additional uses of the PDF/article by the author(s) or recipients, including posting it on a Web site, are prohibited without the express consent of the Air & Waste Management Association.

If you are interested in reusing, redistributing, or posting online all or parts of the enclosed article, please contact the offices of the *Journal of the Air & Waste Management Association* at

Phone: +1-412-232-3444, ext. 6027

E-mail: journal@awma.org

Web: www.awma.org

You may also contact the Copyright Clearance Center for all permissions related to the *Journal of the Air & Waste Management Association*: www.copyright.com.

Development of Molecular Marker Source Profiles for Emissions from On-Road Gasoline and Diesel Vehicle Fleets

Glynis C. Lough and Charles G. Christensen

Environmental Chemistry and Technology Program, University of Wisconsin–Madison, Madison, WI

James J. Schauer

Environmental Chemistry and Technology Program, University of Wisconsin–Madison, Madison, WI; and Wisconsin State Laboratory of Hygiene, Madison, WI

James Tortorelli and Erin Mani

Wisconsin State Laboratory of Hygiene, Madison, WI

Douglas R. Lawson

National Renewable Energy Laboratory, Golden, CO

Nigel N. Clark

West Virginia University, Morgantown, WV

Peter A. Gabele

U.S. Environmental Protection Agency (Retired), Research Triangle Park, NC

ABSTRACT

As part of the Gasoline/Diesel PM Split Study, relatively large fleets of gasoline vehicles⁵³ and diesel vehicles³⁴ were tested on a chassis dynamometer to develop chemical source profiles for source attribution of atmospheric particulate matter in California's South Coast Air Basin. Gasoline vehicles were tested in cold-start and warm-start conditions, and diesel vehicles were tested through several driving cycles. Tailpipe emissions of particulate matter were analyzed for organic tracer compounds, including hopanes, steranes, and polycyclic aromatic hydrocarbons. Large intervehicle variation was seen in emission rate and composition, and results were averaged to examine the impacts of vehicle ages, weight classes, and driving cycles on the

variation. Average profiles, weighted by mass emission rate, had much lower uncertainty than that associated with intervehicle variation. Mass emission rates and elemental carbon/organic carbon (EC/OC) ratios for gasoline vehicle age classes were influenced most by use of cold-start or warm-start driving cycle (factor of 2–7). Individual smoker vehicles had a large range of mass and EC/OC (factors of 40 and 625, respectively). Gasoline vehicle age averages, data on vehicle ages and miles traveled in the area, and several assumptions about smoker contributions were used to create emissions profiles representative of on-road vehicle fleets in the Los Angeles area in 2001. In the representative gasoline fleet profiles, variation was further reduced, with cold-start or warm-start and the representation of smoker vehicles making a difference of approximately a factor of two in mass emission rate and EC/OC. Diesel vehicle profiles were created on the basis of vehicle age, weight class, and driving cycle. Mass emission rate and EC/OC for diesel averages were influenced by vehicle age (factor of 2–5), weight class (factor of 2–7), and driving cycle (factor of 10–20). Absolute and relative emissions of molecular marker compounds showed levels of variation similar to those of mass and EC/OC.

IMPLICATIONS

The Gasoline/Diesel PM Split Study provides a quantitative measure of the uncertainty in molecular marker source profiles for motor vehicle tailpipe emissions. To develop accurate source profiles for tailpipe emissions of particulate matter from gasoline and diesel vehicles, it is necessary to understand the variability of emissions from an individual vehicle and the factors that effect differences in emissions. As seen in this study, high-emitting gasoline vehicles can have large variations in particulate matter composition. The composition of particulate matter from diesel vehicles was found to depend predominately upon vehicle driving cycle rather than on age or weight class.

INTRODUCTION

Profiles of organic compounds in particulate matter emissions from various sources are becoming more widely used for apportionment modeling to investigate the

Table 1a. Tested gasoline vehicles.

Tested Vehicles	No. of Vehicles
Nonsmokers 1995–2001	15
Nonsmokers 1985–1994	24
Nonsmokers 1975–1984	7
Smoker 1: 1989 Toyota pickup	1
Smoker 2: 1990 Volkswagon Jetta	1
Smoker 3: 1978 Chevy Caprice	1
Smoker 4: 1988 Mazda pickup	1
Smoker 5: 1969 Chevy Malibu	1
Smoker 6: 1984 Toyota pickup	1
Smoker 7: 1980 Toyota Celica	1

sources contributing to ambient particulate matter levels.¹ Several studies have been performed to characterize tailpipe emissions of gasoline-powered and diesel-powered vehicles,^{2–8} many with the goal of developing representative profiles for on-road vehicle tailpipe emissions. Most of these studies have investigated a small number of vehicles but have seen variation in emission rate and composition related to vehicle age, fuel type, driving cycle, engine temperature, and engine repair.^{9–12} With so many factors contributing to differences in emissions, it is necessary to understand the relationships between emissions of tested vehicles and the emissions of an actual on-road fleet of vehicles in an area.

This study was conducted with a relatively large number of gasoline and diesel vehicles, in several age groups and weight classes, to represent average fleet emissions and to assess the uncertainty in average vehicle emissions profiles. With emissions measurements for a larger number of vehicles, average profiles were created that are representative of on-road gasoline and diesel vehicle fleets in the Los Angeles (LA) area in 2001. Although the intervehicle and intertest variability in both the total mass emission rate of particulate matter and the composition of particulate matter are very large, weighted averaging of these measurements to reflect the known composition of vehicle fleets in the area provides a sense of the actual variability in emissions from the fleet. The uncertainty in these profiles and their sensitivity to changes in the fleet composition were explored by varying the composition of the constructed fleet profiles in terms of vehicle age distribution, the fraction of the fleet that was high-emitting

smokers, vehicle weight distribution, and tested vehicle driving cycle.

The focus in these measurements was on organic compounds previously used as tracers for vehicle exhaust in particulate matter apportionment studies,¹ including hopanes, steranes, and polycyclic aromatic hydrocarbons (PAHs).

METHODS

Gasoline Vehicle Testing

A total of 53 gasoline-powered spark-ignition (SI) vehicles were recruited by the California Bureau of Automotive Repair and the South Coast Air Quality Management District (SCAQMD) for testing. The tested vehicles fit into several age groups (1975–1984, 1985–1994, and 1995–2001) plus five recruited high-emitting visible smokers, and one light-duty diesel vehicle (discussed here with diesel vehicles). After testing, two additional vehicles with emissions of elemental carbon (EC) of more than 50 mg·mi⁻¹ were also classified as smokers because their EC emission rates were higher than most tested recruited smokers, and an order of magnitude higher than any other tested nonsmoker. The tested gasoline and smoker vehicles and their ages are summarized in Table 1a.

Vehicle driving simulation was conducted on a chassis dynamometer (Clayton Model CTE-50-0). Particulate matter samples were collected for both cold-start and warm-start engine conditions over the same driving cycles. After an engine-off period of at least 12 hr, vehicles were operated with the Unified Driving Cycle.¹³ The cold-start samples were taken over the first two phases of the Unified Driving Cycle, for a total sample time of 1436 sec and an average speed of 24.6 mph. After a 600-sec engine-off period, warm-start samples were collected over identical cycles.

Diesel Vehicle Testing

Thirty-three diesel-powered compression-ignition (CI) vehicles were recruited by West Virginia University (WVU) and identified by model year and weight class in testing, as summarized in Table 2a. All heavy-heavy duty vehicles were tested at a test weight of 46,000 lb and all other vehicles were tested with a test weight of 70% of the gross vehicle weight rating (maximum weight the vehicle is

Table 1b. Gasoline vehicle fleet averages.

Fleet Averages	No. of Vehicles in Average	Fraction of Fleet Represented by Age Group			
		1995–2001	1985–1994	1975–1984	1965–1974
Tested vehicles	49	0.28	0.51	0.19	0.019
Tested vehicles, excluding smokers	46	0.31	0.50	0.19	0.00
LA age distribution, excluding smokers	46	0.44	0.46	0.074	0.033
LA age distribution, assuming 5% smokers	49	0.41	0.47	0.077	0.034
LA age distribution, assuming 25% smokers	49	0.44	0.46	0.074	0.033
LA age distribution, assuming 50% smokers	49	0.44	0.46	0.070	0.030
New vehicles, 1995–2001 model years only	15	1.00	0.00	0.00	0.00
High smoker area, assuming 75% smokers	49	0.28	0.58	0.094	0.042

Table 2a. Tested diesel vehicles.

Tested Vehicles	1998–2001	1994–1997	1990–1993	Pre-1990	No. of Vehicles in Average
PC = diesel autos	0	0	0	2	2
Class I = under 14,000 lb	3	2	1	1	7
Class II = 14,000–33,000 lb	3	3	0	1	7
Class III = >33,000 lb	4	7	3	2	16
Bus = transit buses	0	0	1	1	2
Total	10	12	5	7	34
No. in average (exclude PC, bus)	10	12	4	4	30
Driving Cycle Averages					

designed to bear). The tests were conducted on two dynamometers owned and operated by West Virginia University. The WVU Heavy-Duty Vehicle Chassis Dynamometer, with two rollers, was used for vehicles over 22,000 lb, and the single-roller WVU Medium-Duty Vehicle Chassis Dynamometer was used for smaller vehicles. The vehicles were tested with three driving cycles, including an engine idle cycle, the city/suburban heavy vehicle route (CSHVR) for low speeds, and the highway cycle for higher speeds. Additionally, subsets of vehicles were operated with a cold-start CSHVR, a CSHVR with the engine brake enabled, a CSHVR with federal fuel (instead of California reformulated fuel), and a heavy-duty urban dynamometer driving schedule (UDDS).¹⁴ Two of the vehicles were buses, and were operated on a CSHVR, a vehicle idle, and on the Manhattan cycle, which approximates slow speeds in stop-and-go traffic. One vehicle was a passenger car, and was operated through cold-start and warm-start Unified Driving cycles like the gasoline-powered passenger cars described above.

Sample Collection and Analysis

Vehicle exhaust was sampled using a dilution-sampling tunnel. Dilution air was charcoal treated and HEPA filtered to remove gaseous and particulate contaminants. Exhaust and dilution air were well mixed in the tunnel. For gasoline vehicle tests, a probe downstream drew diluted exhaust through stainless steel tubing to fine particulate matter (PM_{2.5}) cyclones and filter holders (University Research Glassware). For diesel exhaust tests, the primary dilution tunnel was a full-scale dilution tunnel operated with HEPA-filtered dilution air. A sample probe drew diluted exhaust into a secondary dilution chamber,

Table 2b. Diesel fleet averages.

Description	Abbreviation for Driving Cycle	No. of Vehicles in Average
Vehicle idle	IDLE	32
CSHVR, hot start	HCS	32
Highway cycle	HW	30
CSHVR, cold start	CCS	10
Urban dynamometer schedule	UD	1
Manhattan cycle	MC	2
CSHVR, engine brake	CSJ	1
CSHVR, federal fuel	CCSF	2

and particulate matter samples were collected with cyclones and filter holders attached to the secondary dilution chamber.

PM_{2.5} samples were collected on pre-baked quartz fiber filters (Pall) for organic compound speciation and EC and organic carbon (OC), and on preweighed Teflon membrane filters (Pall) for mass determination. EC and OC were analyzed with the National Institute for Occupational Safety and Health 5040 method, chosen to be parallel to the ACE-Asia study¹⁵ and other recent climate change studies. Mass was determined gravimetrically from conditioned filters with a microbalance (Mettler-Toledo).

Organic compounds were quantified with solvent extraction and gas chromatography (GC)–mass spectroscopy (GCMS). Details of sample preparation¹⁶ and GCMS analysis¹⁷ have been described elsewhere. Before extraction, filters were spiked with internal standards across a range of molecular weights and volatility to enable quantification of a wide range of compounds. Two sequential extractions were performed with a Soxhlet apparatus (one with dichloromethane and one with methanol) and the two extracts were combined. Extracts were rotary evaporated to approximately 10 mL and further evaporated with nitrogen down to 0.25 mL. The GC column was 30 m long with a diameter of 0.25 mm and a film thickness of 0.25 mm. The injector and GCMS interface temperatures were held at 300 °C. The initial oven temperature was held at 65 °C for 10 min, then ramped at 10 °C per minute to 300 °C and held for 26.5 min. The carrier gas was helium, flowing at 1 mL·min⁻¹.

Blank samples were collected to measure background levels in the dilution air and sampling system when vehicles were not running. Blank tests were conducted at intervals during vehicle tests, which allowed blank correction to account for drift in system background over tests of vehicles with high and low emission rates. Tests were corrected using the relevant blank test results from the same test interval, and uncertainty of the blank test measurements was included with vehicle test measurement uncertainty (square root of the sum of the squares of uncertainties). The gasoline and diesel emissions measurements of mass, EC, OC, and organic compounds were corrected for blanks, which represented an overall average of 14% of vehicle test mass, 32% of OC, and 9% of EC. Few of the relevant individual organic compounds (hopanes, steranes, and PAHs) were detectable in blank tests,

and those few represented less than 8% of average vehicle test measurements. The exception was benzofluoranthene, which represented an average of 9–22% of vehicle test concentrations. Blank corrected measurements were converted to per-mile species emission rates. Concentrations measured in the diluted exhaust were multiplied by the total volume of diluted exhaust (dilution air plus exhaust), and divided by the total distance driven in the test period. Diesel vehicle engine idle tests had no distance driven, and the results are presented in units of mass per minute.

Fleet Averaging

To better represent the composition of emissions from on-road fleets of gasoline vehicles and to understand the uncertainty associated with creation of emissions profiles, averaging schemes incorporating vehicle ages and smokers were applied to gasoline vehicles, as listed in Table 1b. All averaging was mass-weighted because the total average composition of real-world fleet emissions, on a mass basis, is more influenced by one high-emitting vehicle than by one low-emitting vehicle. This is analogous to the influence of high emitting vehicles on average emissions of volatile organic compounds, nitrogen oxides, and carbon monoxide observed in other studies.^{18,19} Two of the averaging schemes used were simple mass emission rate-weighted averages of the tested vehicles. One of these included all vehicles tested, and the other included only tested nonsmoking vehicles. These two schemes may not represent the emissions of actual on-road fleets because this study tested a larger percentage of older vehicles and smoker vehicles than is present in the LA area. To construct emissions profiles that more closely reflect actual

fleets, data on vehicle miles traveled (VMT) of vehicle age groups were obtained from the California Air Resources Board (CARB) for 2001. Four averaging schemes used the VMT of vehicles in LA of different ages and the mass-emission-rate weighted average emissions data from vehicles of the same age classes in this study. One of these schemes assumes that no smokers were present in the LA area, and three assume that 5%, 25%, or 50% of vehicles in the total fleet are smokers. The profile for the smoker fraction of the fleet had an average composition from three of the measured smokers that had high OC and low EC, as expected from “normal” oil-burning smoker vehicles. Two additional averages were created to represent emissions in extreme cases. One of these represented only new vehicles (model years 1995–2001), which could represent the future as emissions standards increase and adequate reduction of smoker vehicles is achieved. The second had very high proportions of older vehicles and smokers in the fleet (75% smokers in fleet), which could approximate cities in the United States or areas of the world with a high proportion of old and poorly functioning vehicles.

RESULTS

Mass Emission Rate and EC/OC Ratio

Total mass emission rates and the ratio of EC to OC varied widely between individual vehicles. To develop emissions profiles, emissions measurements from individual vehicle tests were averaged, weighted by mass emission rate. Measurements of emissions for non-smoker gasoline vehicles were averaged according to vehicle model year. The three average categories, as

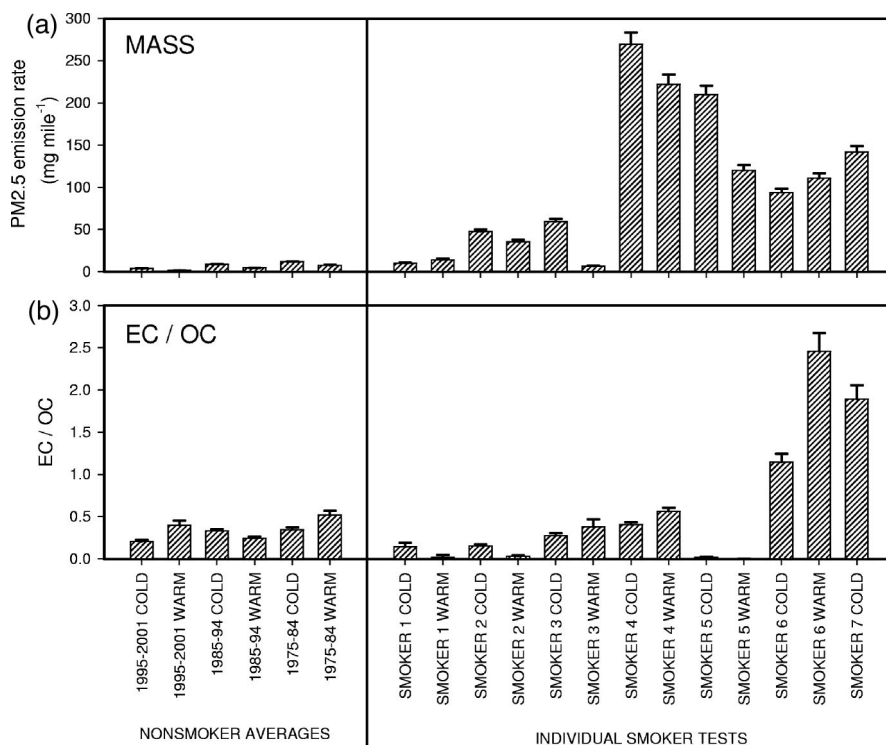


Figure 1. (a) Gasoline vehicle PM_{2.5} mass emissions (mg·mi⁻¹) and (b) EC/OC ratios for average nonsmoker vehicle age groups and for individual smoker vehicles.

listed in Table 1b, were nonsmokers from model years 1975–1984, 1985–1994, and 1995–2001. The seven gasoline vehicles identified as high-emitting smoker vehicles included five identified before testing as smokers, plus two vehicles with measured EC emission rates of more than $50 \text{ mg}\cdot\text{mi}^{-1}$. The mass emission rates ($\text{mg}\cdot\text{mi}^{-1}$) and EC/OC ratios for cold-start and warm-start tests of these three average nonsmoker categories and seven individual smokers are shown in Figure 1. No warm-start data were available for smoker 7. Mass emission rates for average nonsmoker categories were between 4.10 ± 0.085 and $11.7 \pm 0.51 \text{ mg}\cdot\text{mi}^{-1}$ for cold-start tests, and between 1.68 ± 0.047 and $7.64 \pm 0.41 \text{ mg}\cdot\text{mi}^{-1}$ for warm-start tests. Smoker vehicle mass emission rates spanned two orders of magnitude, between 9.91 ± 1.03 and $270 \pm 13.7 \text{ mg}\cdot\text{mi}^{-1}$ for cold-starts, and between 6.56 ± 0.92 and $222 \pm 11.3 \text{ mg}\cdot\text{mi}^{-1}$ for warm-start tests. These gasoline and smoker vehicle mass emission rates are similar to previous work.^{5,10,12,20}

Ratios of EC to OC in particulate matter showed patterns similar to mass emission rate and to previous work.^{12,20} Like mass emission rate, EC/OC ratios were fairly consistent among the nonsmoking vehicle fleet averages. All of the cold-start and warm-start model year EC/OC averages were in the range of 0.20 ± 0.021 to 0.52 ± 0.051 , and showed a general increase with vehicle age. Among smoker vehicles, the EC/OC range was much greater, between 0.00 ± 0.0038 and 2.5 ± 0.22 . As seen in Figure 1, these extremes were not correlated with total mass emission rate, as smokers 4–7 had the highest mass emission rates and the greatest

variation in proportion of EC to OC in exhaust particulate matter.

Diesel vehicle emission measurements were averaged, like gasoline vehicles, by vehicle model year in the categories pre-1990, 1990–1993, 1994–1997, and 1998–2001, with the number of vehicles in each average listed in Table 2a. Weight class was also recorded for diesel vehicles, providing a second method for averaging results to understand total fleet emissions, and the multiple driving cycles tested for diesel vehicles provided a third averaging scheme (Table 2b), which is indicative of microenvironments where vehicles are operated similarly (stop-and-start Manhattan Cycle, for example). Average mass emission rates for all tests on the basis of model year categories were between 178 ± 11.9 and $1130 \pm 21.5 \text{ mg}\cdot\text{mi}^{-1}$, with older vehicles having higher emission rates (Figure 2). For weight classes, emission rates averaged 100 ± 8.67 to $674 \pm 10.9 \text{ mg}\cdot\text{mi}^{-1}$, with heavier vehicles showing higher emissions. The greatest variation was seen in the emissions averaged by tested driving cycle. It must be noted that these averages contained generally fewer vehicle tests than weight class or model year averages (Table 2b). The lowest measured emissions were in the engine idle tests, $17.4 \pm 2.69 \text{ mg}\cdot\text{min}^{-1}$, which cannot be converted to per-mile basis but are shown for comparison in Figure 2. For driving cycles based on miles driven, averages ranged from $270 \pm 6.17 \text{ mg}\cdot\text{mi}^{-1}$ in the highway cycle (30 vehicles in average) to $2600 \pm 144 \text{ mg}\cdot\text{mi}^{-1}$ in the Manhattan Cycle (two vehicles tested). The range of measured mass emission rates is similar to previous studies.^{5,12}

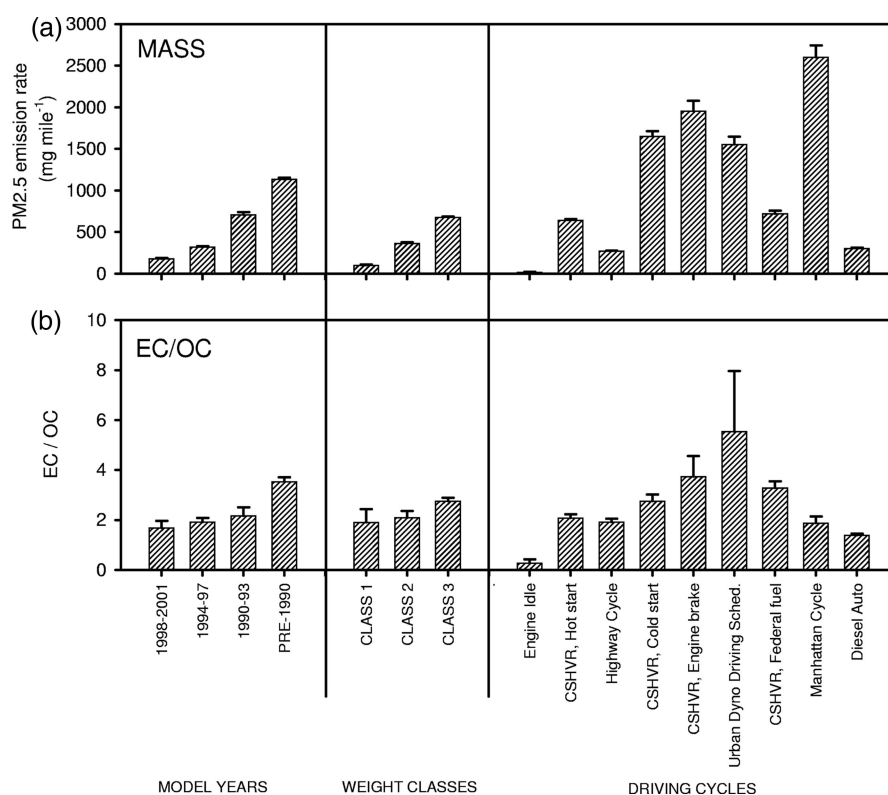


Figure 2. (a) Diesel vehicle $\text{PM}_{2.5}$ mass emissions ($\text{mg}\cdot\text{mi}^{-1}$) and (b) EC/OC ratios for average vehicle age groups, weight classes, and driving cycles. Engine idle tests are presented in units of $\text{mg}\cdot\text{min}^{-1}$.

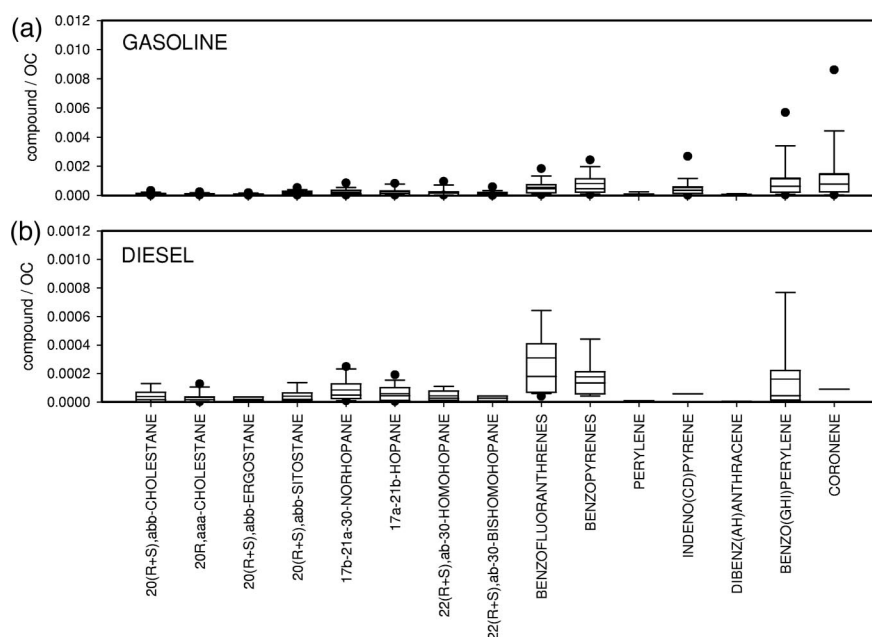


Figure 3. (a) Gasoline and (b) diesel vehicle emissions of hopanes, steranes, and PAHs in individual tests, normalized to OC. Dots are 95% confidence, whiskers 90%, and boxes 75%. Darker line represents the median; thin line represents the mean.

The average ratios of EC to OC measured in diesel particulate matter emissions had similar patterns to the average mass emission rates in this study and to EC/OC ratios in previous work.^{3,5,12} In model year averages, the EC/OC ratio was between 1.7 ± 0.29 for newer vehicles and 3.5 ± 0.19 for older vehicles. For weight class averages, lighter vehicles had somewhat lower EC ratios (1.9 ± 0.53) than heavier vehicles (2.7 ± 0.14). Again, the greatest variation was seen in driving cycles, where EC/OC ratio ranged from 0.27 ± 0.14 (engine idle) to 5.5 ± 2.4 (UDDS, 1 vehicle). There was no trend between mass emission rate and EC/OC ratio for driving cycles, with the cycles with highest and lowest mass emission rates, highway cycle and Manhattan Cycle, both having EC/OC ratios of 1.9.

Molecular Marker Source Profiles

The measured ranges in this study of 15 focus compounds, hopanes, steranes, and PAHs, are shown in Figure 3, normalized to OC emission rate (mass compound per mass OC) in individual vehicle tests. These molecular marker compounds are tracers for vehicle exhaust, but comprise a small fraction of the total OC.¹ Ratios of these compounds to OC were an order of magnitude lower in diesel emissions than in gasoline emissions, similar to previous work.^{3–5,7,21} A plot with expanded scale is included as Figure A (published as supplemental data at http://secure.awma.org/journal/pdfs/2007/10/10.3155-1047-3289.57.10.1190_supplmaterial.pdf). Molecular marker profiles developed in this work are summarized in Table A of the supplemental data.

Emissions of organic compounds normalized to OC emissions for gasoline vehicles are shown in Figure 4. Hopanes and steranes are in the top plot, and PAHs in the bottom plot, with different scales. These OC-normalized

molecular marker compounds in model year averages show somewhat greater variation than the EC/OC ratio. Among smoker vehicles, smokers 1–3 had lower mass emission rates and EC/OC ratios, but have the highest proportion of hopanes and steranes and lowest PAHs, indicating that lube oil combustion is the source of much of the emitted particulate matter from those vehicles. The higher emitting smokers (4–7) had several different results, including low hopanes, steranes, and PAHs, higher hopanes and steranes with lower PAHs, and very high PAHs with very low hopanes and steranes. The specific differences in engine function that caused hopanes, steranes, and PAHs in the OC-normalized emissions profiles of these four smokers to vary by more than an order of magnitude are expected to be linked to combustion-related problems with the vehicles. As these vehicles had the highest measured emission rates of gasoline vehicles tested, the composition of their emissions will have a significant impact on the average composition of particulate matter emitted from a fleet, an impact which must be understood to construct representative emissions profiles.

The emission rates of organic compounds from diesel vehicles, normalized to OC emission rates, were approximately an order of magnitude lower than those from gasoline vehicles. Average OC-normalized organic compounds from diesel vehicles are shown in Figure 5. The scale on the PAH plot (bottom) is half that of the hopane plot (top). Hopanes and steranes are generally low in all model year and weight class averages, with the highest measured fraction of hopanes and steranes in the diesel-powered passenger car (Unified Driving Cycle). In the emissions of the passenger vehicle, PAHs were similar in magnitude to hopanes and steranes. For all compound types, greater proportions relative to OC were seen in emissions from heavier vehicles (Weight Class 3 average) and from older vehicles (pre-1990 average).

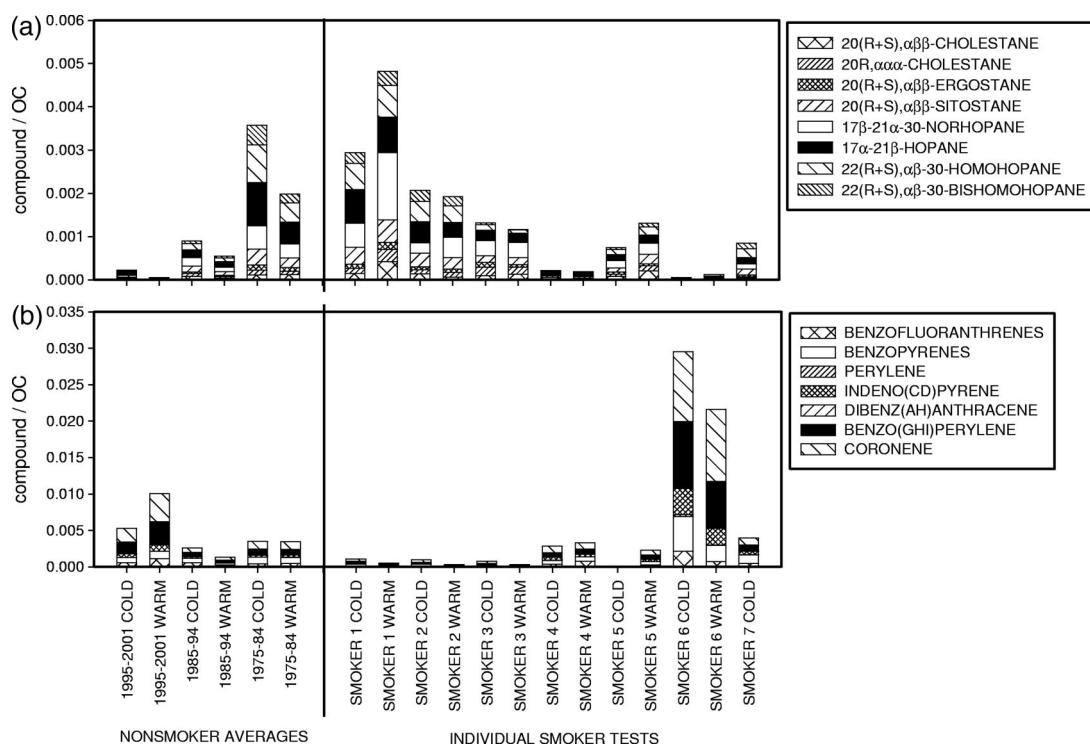


Figure 4. Gasoline vehicle emissions of (a) hopanes and steranes and (b) PAHs normalized to OC. Nonsmoker vehicle age group averages and individual smoker vehicle tests.

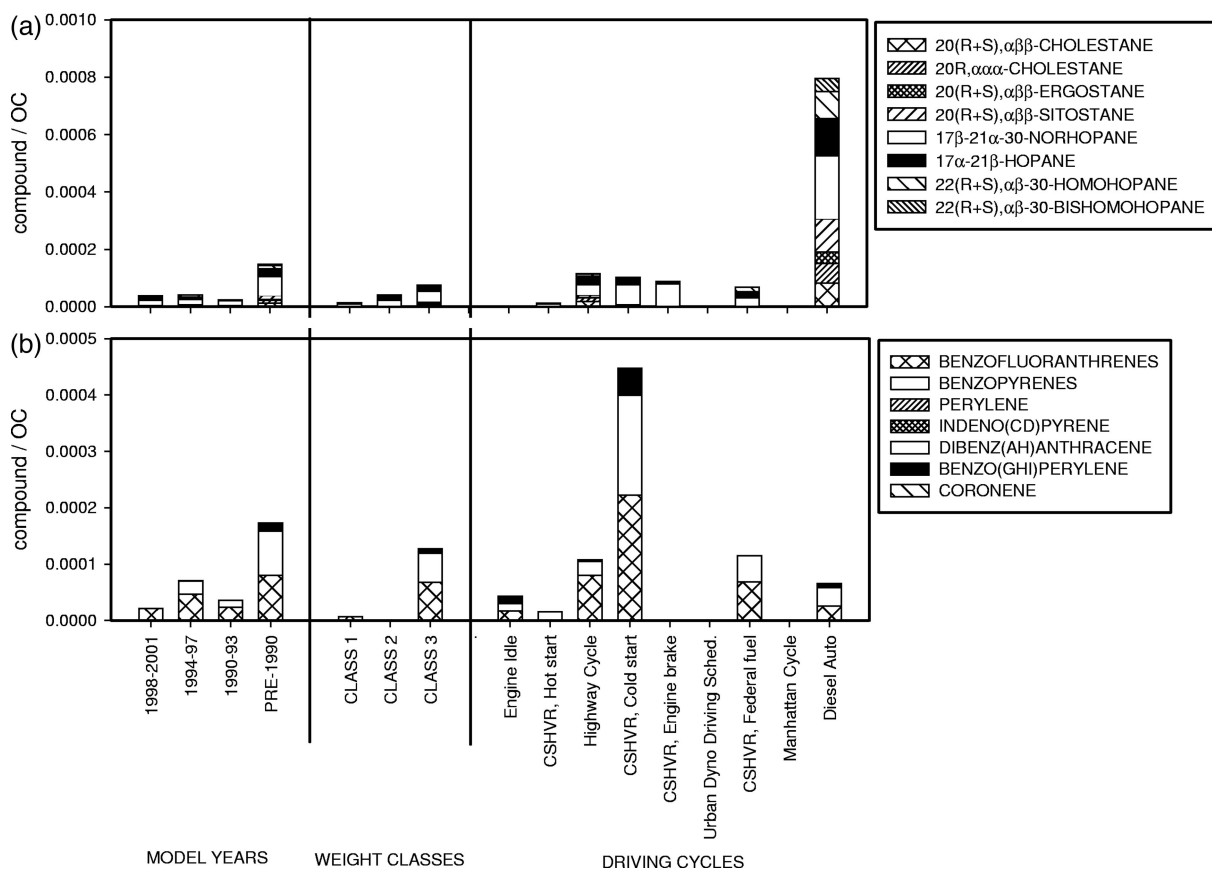


Figure 5. Diesel vehicle emissions of (a) hopanes and steranes and (b) PAHs normalized to OC. Average vehicle age groups, weight classes, and driving cycles.

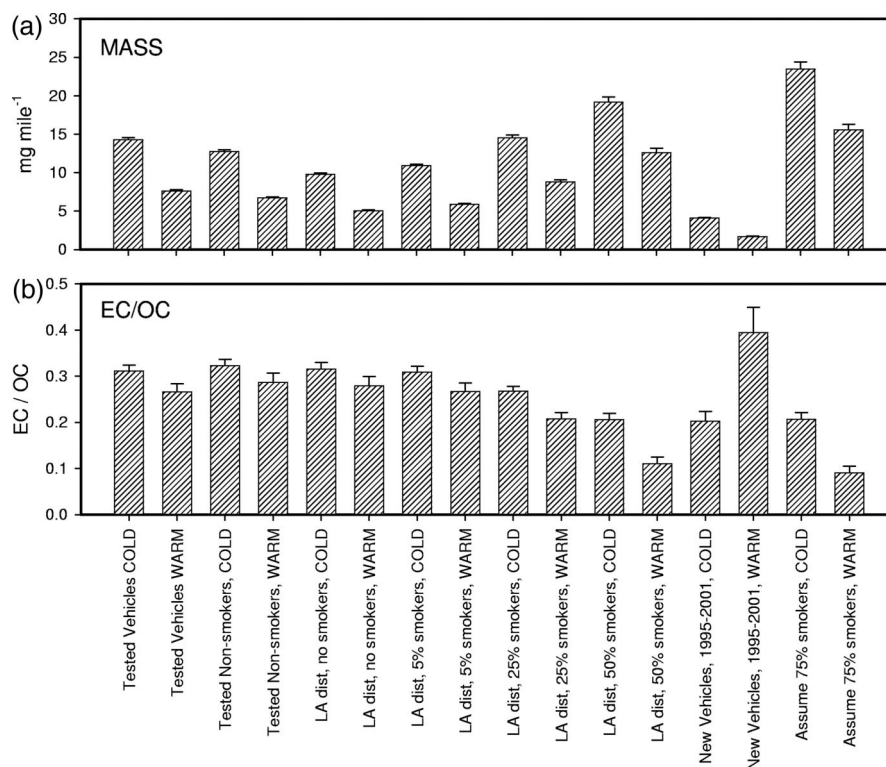


Figure 6. (a) Average gasoline vehicle fleet PM_{2.5} mass emission rates and (b) EC/OC ratios. Fleet averages based on vehicle age and VMT data for the LA area.

Fleet Averaging

The representative averaging schemes were constructed to apply the measurements made in this study to creating emissions profiles for on-road vehicles. The principal goal was determining the sensitivity of the emissions profile to the composition of the vehicle fleet, or how much the profile changed with inclusion of different age distributions and different fractions of smoker vehicles. For the representative gasoline vehicle averaging schemes, the mass emission rates and EC/OC ratios are shown in Figure 6. In general, cold-start averages have slightly higher mass emission rates and slightly higher EC/OC ratios than warm-start tests. These cold-warm differences are greater than the differences between cold profiles and warm profiles for most averages (tested vehicles, tested nonsmoker vehicles, LA age distribution with no smokers, LA age distribution with 5% smokers, and LA age distribution with 25% smokers). For the three profiles which are more extreme (LA age distribution with 50% smokers, high-smoker environment with 75% smokers, and the profile with new vehicles only), larger differences in mass emission rate and EC/OC ratio can be seen, with higher proportions of smokers in the fleet resulting in higher average mass emission rates and lower ratios of EC to OC.

Like mass emission rate and EC/OC ratio, the comparison of the OC-normalized hopanes, steranes, and PAHs in the various average profiles in Figure 7 shows that the uncertainty between the cold-start and warm-start profiles is in most cases larger than interfleet differences. At high percentages of smokers, or when only new vehicles are present, the profiles show the greatest differences.

The two profiles with the greatest fraction of smokers have the highest proportion of hopanes and steranes, because the three normal smokers (oil burners with PM_{2.5} emissions less than 60 mg·mi⁻¹) were used as the average smoker for these profiles. It is important to note that, whereas profiles were constructed for the LA age distribution assuming zero smokers and assuming 5% normal smokers, and the actual representation of these vehicles in the on-road fleet in the area may be less than 5%, the differences between cold-start and warm-start for those profiles are greater than the differences due to 0% or 5% smokers.

These fleet averages do not account for the huge differences in composition between the higher-emitting smokers 4–7. The rate of occurrence of similar vehicles in on-road fleets is not known, but the high observed emission rates (94 ± 5 to 270 ± 14 mg·mi⁻¹) and variation in OC-normalized EC, hopanes, steranes, and PAHs of an order of magnitude or more could have a significant impact on the overall average composition of fleet emissions.

CONCLUSIONS

In developing chemical source profiles for average emissions from fleets of gasoline and diesel vehicles, several factors were observed to have large influences on mass emission rates, and on emissions of EC, hopanes, steranes, and PAHs normalized to OC. For diesel fleet emissions averages, the tested vehicle driving cycle introduced the greatest variations, whereas for gasoline fleet emissions averages, the most important factors were the number of smoker vehicles in the fleet, the composition

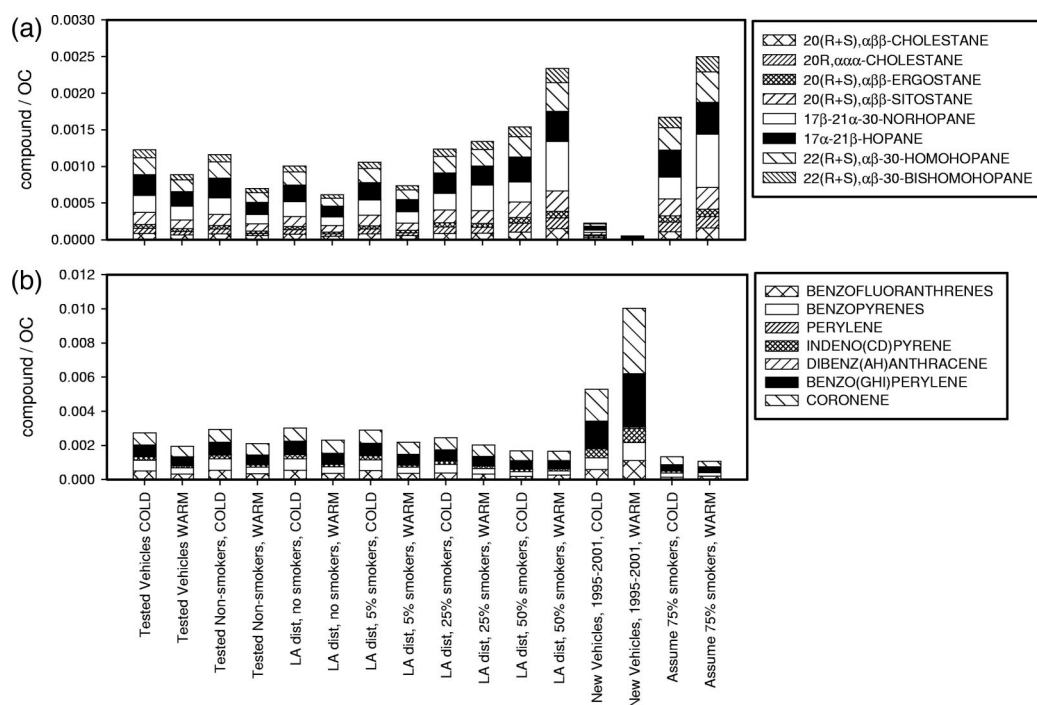


Figure 7. Average gasoline vehicle fleet emissions of (a) hopanes and steranes and (b) PAHs normalized to OC. Fleet averages based on vehicle age and VMT data for the LA area.

of smoker vehicles' emissions, and the use of cold-start or warm-start driving cycles. To further understand the impacts of high-emitting smoker vehicles on average fleet emissions, it is necessary to gain a better understanding of their prevalence in on-road fleets and to describe the causes of the great variation in composition of emissions from these high emitting vehicles. Additionally, because tailpipe emissions of particulate matter from motor vehicles are influenced by a wide range of factors, other studies are needed to determine whether the source profiles from this study are applicable in areas with different fleet compositions, driving patterns, climate conditions, and fuel compositions. The profiles developed in this work were relevant to the LA area vehicle fleet in 2001, but application of any study to understand the impacts of motor vehicle emissions in an area must consider the changes in the vehicle fleet over time, including technological changes, vehicle ages, and the number of poorly performing vehicles.

ACKNOWLEDGMENTS

The authors thank Hector Maldonado of the CARB for providing the EMFAC model data. Funding was provided by the U.S. Department of Energy's Office of FreedomCAR and Vehicle Technologies through the National Renewable Energy Laboratory and the U.S. Environmental Protection Agency. Dave Campbell and Eric Fujita of Desert Research Institute and Richard Snow and William Crews of Clean Air Vehicle Technology Center (CAVTC) were instrumental in the design and implementation of the vehicle testing operations. Jeff DeMinter of the Wisconsin State Laboratory of Hygiene performed the EC/OC analyses. The California

Bureau of Automotive Repair and the SCAQMD were responsible for recruiting vehicles for testing.

REFERENCES

- Schauer, J.J.; Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers; *Atmos. Environ.* **1996**, *30*, 3837-3855.
- Miguel, A.H.; Kirchstetter, T.W.; Harley, T.W.; Hering, S.V. On-Road Emissions of Particulate Polycyclic Aromatic Hydrocarbons and Black Carbon from Gasoline and Diesel Vehicles; *Environ. Sci. Technol.* **1998**, *32*, 450-455.
- Schauer, J.J.; Kleeman, M.J.; Cass, G.R.; Simoneit, B.R.T. Measurement of Emissions from Air Pollution Sources. 2. C₁ through C₃₀ Organic Compounds from Medium Duty Diesel Trucks; *Environ. Sci. Technol.* **1999**, *33*, 1578-1587.
- Schauer, J.J.; Kleeman, M.J.; Cass, G.R.; Simoneit, B.R.T. Measurement of Emissions from Air Pollution Sources. 5. C-1-C-32 Organic Compounds from Gasoline-Powered Motor Vehicles; *Environ. Sci. Technol.* **2002**, *36*, 1169-1180.
- Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of Fine Organic Aerosol. 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks; *Environ. Sci. Technol.* **1993**, *27*, 636-651.
- Kerminen, V.M.; Makela, T.E.; Ojanen, C.H.; Hillamo, R.E.; Vilhunen, J.K.; Rantanen, L.; Havers, N.; VonBohlen, A.; Klockow, D. Characterization of the Particulate Phase in the Exhaust from a Diesel Car; *Environ. Sci. Technol.* **1997**, *31*, 1883-1889.
- Khalili, N.R.; Scheff, P.A.; Holsen, T.M. PAH Source Fingerprints for Coke Ovens, Diesel and Gasoline Engines, Highway Tunnels, and Wood Combustion Emissions; *Atmos. Environ.* **1995**, *29*, 533-542.
- Kleeman, M.J.; Schauer, J.J.; Cass, G.R. Size and Composition Distribution of Fine Particulate Matter Emitted from Motor Vehicles; *Environ. Sci. Technol.* **2000**, *34*, 1132-1142.
- Kweon, C.B.; Foster, D.E.; Schauer, J.J.; Okada, S. *Detailed Chemical Composition and Particle Size Assessment of Diesel Engine Exhaust*; SAE Technical Paper 2002-01-2670; Society of Automotive Engineers: Warrendale, PA, 2002.
- Cadle, S.H.; Mulawa, P.; Groblicki, P.; Laroo, C.; Ragazzi, R.A.; Nelson, K.; Gallagher, G.; Zielinska, B. In-Use Light-Duty Gasoline Vehicle Particulate Matter Emissions on Three Driving Cycles; *Environ. Sci. Technol.* **2001**, *35*, 26-32.
- Cadle, S.H.; Mulawa, P.A.; Ball, J.; Donase, C.; Weibel, A.; Sagebiel, J.C.; Knapp, K.T.; Snow, R. Particulate Emission Rates from In Use

- High Emitting Vehicles Recruited in Orange County, California; *Environ. Sci. Technol.* **1997**, 31, 3405-3412.
12. Cadle, S.H.; Mulawa, P.A.; Hunsanger, E.C.; Nelson, K.; Ragazzi, R.A.; Barrett, R.; Gallagher, G.L.; Lawson, D.R.; Knapp, K.T.; Snow, R. Composition of Light-Duty Motor Vehicle Exhaust Particulate Matter in the Denver, Colorado Area; *Environ. Sci. Technol.* **1999**, 33, 2328-2339.
 13. Ho, J.; Winer, A.M. Effects of Fuel Type, Driving Cycle, and Emission Status on In-Use Vehicle Exhaust Reactivity; *J. Air & Waste Manage. Assoc.* **1998**, 48, 592-603.
 14. Clark, N.N.; Wayne, W.S.; Nine, R.D.; Buffamonte, T.; Hall, T.; Rapp, B.L.; Thompson, G.; Lyons, D.W. *Emissions from Diesel-Fueled Heavy-Duty Vehicles in Southern California*; SAE Technical Paper 2003-01-1901; Society of Automotive Engineers: Warrendale, PA, 2003.
 15. Schauer, J.J.; Mader, B.T.; Deminter, J.T.; Heidemann, G.; Bae, M.S.; Seinfeld, J.H.; Flagan, R.C.; Cary, R.A.; Smith, D.; Huebert, B.J.; Bertram, T.; Howell, S.; Kline, J.T.; Quinn, P.; Bates, T.; Turpin, B.; Lim, H.J.; Yu, J.Z.; Yang, H.; Keywood, M.D. ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon; *Environ. Sci. Technol.* **2003**, 37, 993-1001.
 16. Sheesley, R.J.; Schauer, J.J.; Smith, N.D.; Hays, M.D. Development of a Standardized Method for the Analysis of Organic Compounds Present in PM_{2.5}. In *Proceedings of the A&WMA Annual Meeting 2000*. A&WMA: Pittsburgh, PA, 2000.
 17. Sheesley, R.J.; Schauer, J.J.; Bean, E.; Kenski, D. Trends in Secondary Organic Aerosol at a Remote Site in Michigan's Upper Peninsula; *Environ. Sci. Technol.* **2004**, 38, 6491-6500.
 18. Zhang, Y.; Stedman, D.H.; Bishop, G.A.; Beaton, S.P.; Guenther, P.L.; McVey, I.F. Enhancement of Remote Sensing for Mobile Source Nitric Oxide; *J. Air & Waste Manage. Assoc.* **1996**, 46, 25-29.
 19. Zhang, Y.; Stedman, D.H.; Bishop, G.A.; Guenther, P.L.; Beaton, S.P. Worldwide On-Road Vehicle Exhaust Emissions Study by Remote Sensing; *Environ. Sci. Technol.* **1995**, 29, 2286-2294.
 20. Sagebiel, J.C.; Zielinska, B.; Walsh, P.A.; Chow, J.C.; Cadle, S.H.; Mulawa, P.A.; Knapp, K.T.; Zweidinger, R.B. PM-10 Exhaust Samples Collected during IM-240 Dynamometer Tests of In-Service Vehicles in Nevada; *Environ. Sci. Technol.* **1997**, 31, 75-83.
 21. Zielinska, B.; Sagebiel, J.; McDonald, J.D.; Whitney, K.; Lawson, D.R. Emission Rates and Comparative Chemical Composition from Selected In-Use Diesel and Gasoline-Fueled Vehicles; *J. Air & Waste Manage. Assoc.* **2004**, 54, 1138-1150.

About the Authors

James J. Schauer is an associate professor in Civil and Environmental Engineering at the University of Wisconsin-Madison. Glynis C. Lough was a postdoctoral scholar in the Environmental Chemistry and Technology Program at the University of Wisconsin-Madison. Charles Christensen was a researcher in the Environmental Chemistry and Technology Program at the University of Wisconsin-Madison. James Tortorelli and Erin Mani are scientists at the Wisconsin State Laboratory of Hygiene. Douglas R. Lawson is a principal scientist at the National Renewable Energy Laboratory. Nigel N. Clark is a professor of mechanical and aerospace engineering at West Virginia University. Peter A. Gabele is retired from the U.S. Environmental Protection Agency. Please address correspondence to: James J. Schauer, University of Wisconsin-Madison, 660 N. Park Street, Madison, WI, 53706; phone: +1-608-262-4495; fax: +1-608-262-0454; e-mail: jjschauer@wisc.edu.