

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231290756>

# On-Road Emissions of Particulate Polycyclic Aromatic Hydrocarbons and Black Carbon from Gasoline and Diesel Vehicles

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JANUARY 1998

Impact Factor: 5.33 · DOI: 10.1021/es970566w

---

CITATIONS

324

---

READS

258

3 AUTHORS, INCLUDING:



**Thomas Kirchstetter**

Lawrence Berkeley National Laboratory

**103** PUBLICATIONS **4,485** CITATIONS

SEE PROFILE



**Robert A Harley**

University of California, Berkeley

**150** PUBLICATIONS **5,579** CITATIONS

SEE PROFILE

# On-Road Emissions of Particulate Polycyclic Aromatic Hydrocarbons and Black Carbon from Gasoline and Diesel Vehicles

ANTONIO H. MIGUEL,<sup>†</sup>  
THOMAS W. KIRCHSTETTER, AND  
ROBERT A. HARLEY\*

*Department of Civil and Environmental Engineering,  
University of California, Berkeley, California 94720-1710*

SUSANNE V. HERING

*Aerosol Dynamics Inc., 2329 Fourth Street,  
Berkeley, California 94710*

Motor vehicles are a significant source of fine carbonaceous particle emissions. Fuels have been reformulated and vehicle technologies have advanced, so an updated assessment of vehicular emissions is needed. Gas- and particle-phase pollutant concentrations were measured in the Caldecott Tunnel in the San Francisco Bay Area during the summer of 1996. Separate samples were collected for uphill traffic in two tunnel bores: one bore was influenced by heavy-duty diesel truck emissions; a second bore was reserved for light-duty vehicles. Fine particle black carbon and PAH concentrations were normalized to fuel consumption to compute emission factors. Light-duty vehicles and heavy-duty diesel trucks emitted, respectively,  $30 \pm 2$  and  $1440 \pm 160$  mg of fine black carbon particles per kg of fuel burned. Diesel trucks were the major source of lighter PAH, whereas light-duty gasoline vehicles were the dominant source of higher molecular weight PAH such as benzo[a]pyrene and dibenz[a,h]anthracene. Size-resolved measurements of particulate PAH showed significant fractions of diesel-derived PAH to be present in both the ultrafine size mode ( $<0.12 \mu\text{m}$ ) and the accumulation mode ( $0.12\text{--}2 \mu\text{m}$ ). In contrast, gasoline engine-derived PAH emissions were found almost entirely in the ultrafine mode.

## Introduction

Combustion-derived aerosol consists of solid carbonaceous soot particles (black carbon) that are associated with a complex mixture of organic compounds (1). Black carbon contributes significantly to fine particle mass and is an important cause of atmospheric visibility impairment (2, 3). Of the organic compounds associated with combustion-generated aerosols, polycyclic aromatic hydrocarbons (PAH) are of particular concern because several are potent mutagens and carcinogens (4). Particulate PAH measured in urban air and in roadway tunnels has been found in the respirable size range (5–10).

Characterization of aerosols in motor vehicle exhaust has indicated that PAH emission profiles are distinct for different

vehicle classes. It has been suggested that selected PAH could be used as tracers for particulate emissions from motor vehicles (11). Measurements in roadway tunnels carrying both light-duty gasoline and heavy-duty diesel vehicles indicate that diesel-derived aerosols are enriched in lower molecular weight PAH (e.g., alkylated phenanthrenes, chrysene), whereas higher molecular weight PAH are associated with gasoline engine-derived aerosol (8, 12, 13). Similarly, dynamometer measurements on catalyst-equipped and noncatalyst gasoline cars and diesel trucks show that PAH emissions from diesel trucks are weighted toward lower molecular weight PAH, whereas gasoline engine exhaust shows a greater abundance of higher molecular weight PAH (14). The dynamometer tests also indicate that the total aerosol PAH emission rate per kilometer driven for noncatalyst gasoline-powered cars was 25 times larger than for catalyst-equipped cars, and 7 times larger than for diesel trucks (14).

While emission rates of black carbon and PAH have been characterized in the past, an updated characterization of motor vehicle emissions is needed. Recent changes in the composition of gasoline and diesel fuel and improvements in engine and emission control technologies are likely to have affected vehicle emissions. In California, low-aromatic, low-sulfur diesel fuel (15) and reformulated gasoline (16) have been used year-round since 1993 and 1996, respectively. The introduction of electronic diesel fuel injection systems and the declining fraction of noncatalyst light-duty vehicles on the road are examples of shifts in vehicle technology that would influence emissions.

The goal of this study was to characterize PAH and black carbon emissions from a current on-road fleet of heavy-duty diesel and light-duty gasoline vehicles. Specific objectives were to (a) collect aerosol samples in a roadway tunnel carrying both light-duty gasoline vehicles and diesel trucks, (b) develop PAH emission profiles for gasoline and diesel vehicles, (c) determine the size distribution of PAH emissions, and (d) determine emission rates of black carbon and PAH for light-duty gasoline and heavy-duty diesel vehicles.

## Methods

**Field Sampling Site.** Vehicle emissions were measured in the Caldecott Tunnel. Located east of San Francisco Bay on State Highway 24, the Caldecott Tunnel runs in the east–west direction through the Berkeley hills and connects Oakland and Berkeley with inland communities in Contra Costa County. The tunnel is comprised of three 2-lane traffic bores, is 1.1 km long, and has a roadway grade of 4.2% uphill in the eastbound direction. Fully transverse ventilation is provided by adjustable pitch fans housed in portal buildings at each end of the tunnel.

The northernmost bore (bore 3) of the tunnel always carries westbound traffic, whereas the southernmost bore (bore 1) of the tunnel always carries eastbound traffic. To accommodate larger traffic volumes during weekday rush hour periods, the center bore (bore 2) carries traffic heading westbound toward San Francisco in the morning and eastbound traffic in the afternoon. Heavy-duty vehicles are restricted to bores 1 and 3 of the tunnel and the center bore is reserved for use by light-duty vehicles. Further description of the sampling site, including a schematic of the tunnel, is available in Kirchstetter et al. (17).

Field sampling was conducted at the Caldecott Tunnel on weekdays during the period August 20–28, 1996. Pollutant concentrations were measured in the traffic tubes ~50 m before the tunnel exit and in the background air injected

\* Corresponding author fax: 510-642-7483; e-mail: harley@ce.berkeley.edu.

<sup>†</sup> Present address: CE-CERT022, University of California, Riverside, California 92521-0434.

into the tunnel by the ventilation fans. Sampling was conducted during uphill (eastbound) traffic events in bores 1 and 2 of the tunnel. Measurements in bore 2 (center bore) were made during afternoon rush hours, from 4 to 6 PM, when the fleet was almost entirely light-duty vehicles. Measurements in bore 1, the truck-influenced bore, were made from 1 to 3 PM when the fraction of heavy-duty trucks in the vehicle fleet was largest.

**Pollutant Sampling Methods.** Gas-phase measurements included real time determination of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and oxides of nitrogen (NO<sub>x</sub>) concentrations. Two-hour integrated air samples were collected in stainless steel canisters for subsequent analysis of hydrocarbon concentrations. Reported here are tunnel and background CO and CO<sub>2</sub> concentrations measured by gas-filter correlation spectrometry (Thermo Environmental Instruments, Models 48 and 41H, Franklin MA).

Particle sampling included the collection of time-integrated filter and impactor samples for subsequent analysis of the chemical composition of the fine aerosol and of real-time measurement of particle number concentration and size distribution. Tunnel filter samples were collected for particles in two size fractions: below 1.3  $\mu\text{m}$  (PM<sub>1.3</sub>) and below 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>) aerodynamic diameter. These samples were analyzed for carbon, mass, ions, and trace metals. Additional PM<sub>1.3</sub> samples collected inside the tunnel were analyzed for speciated PAH and organics. PM<sub>2.5</sub> samples were collected at the clean air ventilation intake and analyzed for carbon, mass, ions, and trace metals. PM<sub>2.5</sub> samples were collected using AIHL cyclones operated at 24 L min<sup>-1</sup> (18). PM<sub>1.3</sub> samples were collected using the same type of AIHL cyclone operated at 50 L min<sup>-1</sup> (19). The 50 L min<sup>-1</sup> flow was split between two filter samples to maintain approximately equal face velocity across all filters.

Reported here are results for PM<sub>1.3</sub> black carbon and PM<sub>1.3</sub> PAH. Samples for carbon analysis were collected on pre-fired 47-mm quartz filters (Pallflex QAT, Putnam CT) and analyzed by Sunset Labs Inc. (Forest Grove, OR) using a thermal-optical technique (20). Tandem quartz filters were used to correct for organic vapor adsorption onto the filter media. PM<sub>1.3</sub> samples for determination of PAH were collected using 47-mm diameter Teflon-coated glass fiber filters (Pallflex T60A20, Putnam, CT).

Size-segregated samples for PAH analysis were collected inside the tunnel using a low-pressure impactor with size cuts at 0.05, 0.075, 0.12, 0.26, 0.50, 1.0, 2.0, and 4.0  $\mu\text{m}$  aerodynamic diameter (21, 22). Impactor samples were collected onto glass disks coated with 1  $\mu\text{L}$  of a 2% solution of Vaseline in cyclohexane to prevent particle bounce. The same impactor was used by Venkataraman et al. (8) to measure vehicle-derived PAH. Impactor results are reported for a composite sample collected from 4 to 6 PM on August 20 and 21 in bore 2 and for a single 6-h sample collected from 10 AM to 4 PM on August 27 in the truck-influenced bore (bore 1).

All air flow standards were subjected to a quality assurance audit by the Monitoring and Lab Division of the California Air Resources Board before field sampling began. During sample collection, flow rates were monitored with rotameters and pressure gauges. Each rotameter was calibrated against the audited bubble flowmeter for the complete range of operating pressures used in the tunnel measurements, and final sample volumes have been calculated accordingly. Impactor flow rates were measured at the beginning and end of each sampling period. Filter and impactor samples were placed in containers and put in a freezer within 2 h from the conclusion of each sample period.

**PAH Extraction.** In the laboratory, filter and impactor samples were handled under room light shielded with a yellow filter to avoid photooxidation of PAH. Each 47-mm sample

TABLE 1. Ten Particle-Phase PAH Measured in the Caldecott Tunnel

species name	abbreviation	molecular weight
fluoranthene	FLT	202
pyrene	PYR	202
benz[ <i>a</i> ]anthracene	BAA	228
chrysene	CRY	228
benzo[ <i>b</i> ]fluoranthene	BBF	252
benzo[ <i>k</i> ]fluoranthene	BKF	252
benzo[ <i>a</i> ]pyrene	BAP	252
benzo[ <i>ghi</i> ]perylene	BGP	276
indeno[1,2,3- <i>cd</i> ]pyrene	IND	276
dibenz[ <i>a,h</i> ]anthracene	DBA	278

filter was cut in half, placed in an amber vial, and covered with 5 mL of HPLC-grade dichloromethane. PAH were extracted for 30 min in an ultrasonic bath. The bath water was replaced every 8 min to prevent overheating. Extracts were transferred into a disposable plastic syringe and filtered through a 5- $\mu\text{m}$  Spartan-25 syringe filter into an amber vial. The syringe and filter were washed with dichloromethane and added to the extract. The extracts were reduced to ~0.5 mL under air at reduced pressure and were evaporated to dryness under a gentle stream of helium at room temperature and pressure. Residues were dissolved with 1 mL of HPLC-grade acetonitrile. Vials were sealed with a PTFE-lined cap. A second filter extraction was performed in the same way.

Similarly, each impactor disk was extracted for 24 min in a covered beaker with 5 mL of HPLC-grade dichloromethane. The extract was filtered into amber vials, the volume reduced, and the residue taken up with 250  $\mu\text{L}$  of HPLC-grade dichloromethane. The extract was rotated over the vial walls and sonicated for 3 min. This step was repeated two additional times to ensure quantitative transfer. The extract was then transferred into a 250- $\mu\text{L}$  glass insert, mounted with a spring, and capped with a PTFE-lined screw cap septum.

**PAH Separation and Quantification.** Aerosol extracts were analyzed for the 10 PAH listed in Table 1. Measurements of vehicle exhaust in prior roadway tunnel experiments show that PAH with molecular weights  $\geq 228$  (e.g., benz[*a*]anthracene, chrysene, and larger PAH) are entirely in the particle phase; PAH less volatile than fluoranthene and pyrene have not been found in the gas phase (13). The distribution of fluoranthene and pyrene between the gas and particle phases is affected by ambient temperature. Concentrations of lower molecular weight PAH such as naphthalene, phenanthrene, and anthracene were not quantified in the present study.

PAH were separated using a Supelcosil LC-PAH, 15 cm, 5- $\mu\text{m}$  column that was adapted with a Supelcosil guard-column (Supelco, Bellefonte, PA). A mobile-phase solvent gradient of acetonitrile and water (40–100% acetonitrile over 20 min, held at 100% acetonitrile for 7.5 min) was maintained at a flow rate of 0.9 mL min<sup>-1</sup> using a Waters (Milford, MA) 626 pump and associated 600S controller. PAH were quantified using a McPherson (Acton, MA) FL-spectrophotometer (150 W Xe lamp) in the following configurations: excitation wavelength = 265 nm; emission wavelength = 0.001 (zero order); excitation and emission slits of 2 and 4, respectively; a CF-300 filter in the emission side (no filter in the excitation side); sensitivity ranges (*R*) of 0.03, 0.1, 0.3, and 1.0; time constant = 0.5 s; photomultiplier gain = 904; 10 mV output signal into the Waters SAT/IN module.

The system was calibrated using a Radian (Austin, TX) 16 Priority PAH standard (ERS-010, 10  $\mu\text{g}$  mL<sup>-1</sup> in acetonitrile) that was diluted with HPLC-grade acetonitrile to produce individual standards of 5, 10, 20, and 50 pg  $\mu\text{L}^{-1}$ . Under optimized chromatographic and instrumental conditions, the detection limits (in picograms) for a 20- $\mu\text{L}$  standard

TABLE 2. Measured Pollutant Concentrations and Vehicle Counts at the Caldecott Tunnel

species	bore 2 (4–6 PM)		bore 1 (1–3 PM)		
	Aug 20	Aug 21	Aug 22	Aug 23	Aug 28
tunnel PAH <sup>a</sup> (ng m <sup>-3</sup> )					
FLT	3.11	3.27	16.8	25.4	17.4
PYR	3.20	4.04	22.4	36.7	24.6
BAA	1.81	2.01	5.81	8.08	5.23
CRY	2.85	2.75	3.95	5.31	3.49
BBF	3.14	2.97	2.72	3.75	2.29
BKF	1.11	0.86	0.75	0.85	0.47
BAP	2.89	2.26	1.00	NA <sup>c</sup>	1.08
BGP	7.16	7.29	1.7	2.6	1.2
IND	3.93	3.29	0.6	1.3	0.8
DBA	5.90	7.06	2.2	2.5	1.6
tunnel black carbon <sup>a</sup> (μg m <sup>-3</sup> )	12.1	13.4	59.3	69.3	68.5
background black carbon <sup>b</sup> (μg m <sup>-3</sup> )	0.7	1.0	3.3	4.9	5.9
tunnel CO (ppm)	28.0	26.9	19.6	21.2	20.7
background CO (ppm)	0.8	0.6	1.7	2.4	3.2
tunnel CO <sub>2</sub> (ppm)	1017	1011	719	763	735
background CO <sub>2</sub> (ppm)	347	346	364	383	410
traffic count (vehicles h <sup>-1</sup> )	4400	4300	2100	2200	2100
% HD diesel <sup>d</sup>	0.07	0.2	4.6	4.6	4.8

<sup>a</sup> Pollutant concentrations determined from PM<sub>1.3</sub> samples collected in the tunnel bores. <sup>b</sup> Black carbon concentrations determined from PM<sub>2.5</sub> samples collected in the background air. <sup>c</sup> Not available. The concentration of BAP was not determined for this filter sample because an instability in the spectrophotometer resulted in signal saturation during analysis of this peak. <sup>d</sup> Percentage of heavy-duty diesel trucks in the tunnel vehicle fleet.

injection were FLT, 25; PYR, 26; BAA, 13; CRY, 9; BBF, 9; BKF, 7; BAP, 6; BGP, 35; IND, 35; and DBA, 67. Each extract was injected at least twice and sometimes more when a peak was lost due to saturation in the fluorescence system. Final filter PAH concentrations were calculated taking into consideration secondary extraction yields, which averaged ~6% of the mass found in the primary extractions. Analysis precision for the standard was ~2%; for the samples, it ranged from 2 to 16%. All reported PAH concentrations were blank-corrected.

**Traffic Characterization.** Several methods were used to characterize the vehicles traveling through the tunnel. Visual traffic counts indicated average traffic volumes of 2100 vehicles per hour in bore 1 from 1 to 3 PM and 4300 vehicles per hour in bore 2 from 4 to 6 PM. The vehicle fleet in bore 2 comprised 66% cars; 34% pick-ups, small trucks, and vans; and <0.3% heavy-duty trucks. In bore 1, the traffic composition was 62% cars; 32% pickups, small trucks, and vans; and 6% heavy-duty trucks. A license plate survey of traffic in bore 2 indicated that 1.5% of the light-duty vehicles were diesel fueled. The mean vehicle model year was 1990, and <1% of the vehicles were pre-1975 model year.

The 1992 Truck Inventory and Use Survey (23) was used to determine the fraction of heavy-duty trucks in each axle class that were diesel powered. Census data for California indicate that a negligible fraction of two-axle, four-tire trucks meet the definition of a heavy-duty diesel truck; ~50% of two-axle, six-tire trucks are heavy-duty diesel; and >90% of trucks with three or more axles are heavy-duty diesel. Using these classifications and the traffic counts mentioned above, heavy-duty diesel trucks accounted for 4.7% of total traffic in bore 1 from 1 to 3 PM, whereas the percentage in bore 2 from 4 to 6 PM was <0.2%. Approximately 70% of the heavy-duty diesels in bore 1 were large trucks with three or more axles.

Driving conditions inside the tunnel were determined using an instrumented vehicle equipped to log speed at 1 s intervals. The average speed of traffic in bore 2 during the 4–6 PM sample period was 41 ± 5 mph (*n* = 31). Light-duty vehicles in bore 1 during the 1–3 PM sample period traveled faster, 49 ± 4 mph (*n* = 4), because there was less traffic congestion in the early afternoon. Heavy-duty trucks in bore 1 traveled at an average speed of 42 ± 7 mph (*n* = 16). Average

speed measured inside the tunnel in 60 independent drivethroughs confirmed the instrumented vehicle data. Due to merging traffic and large numbers of vehicles using the tunnel during the 4–6 PM periods, traffic was often backed up before entering bore 2. There was less traffic congestion ahead of the entrance to bore 1 during the 1–3 PM sample periods because traffic flow was lighter earlier in the afternoon. During all sample periods, traffic inside the tunnel flowed smoothly, lacking heavy accelerations and stop-and-go driving.

## Results and Discussion

**Pollutant Concentrations.** Concentrations of PAH (obtained from filter samples), black carbon, CO, and CO<sub>2</sub> measured in the truck-influenced bore (bore 1) and the light-duty vehicle bore (bore 2) of Caldecott Tunnel are presented, together with traffic count data, in Table 2. As indicated in Table 2, the PAH concentration profile was quite different in the two bores. Even though light-duty traffic volumes were higher during sampling in bore 2, concentrations of lower molecular weight PAH (FLT, PYR, and BAA) were much higher in the truck-influenced bore (bore 1) than in the light-duty vehicle bore (bore 2). This suggests that heavy-duty diesel trucks emit much more of these lower molecular weight PAH than do light-duty vehicles. Conversely, concentrations of higher molecular weight PAH (BAP, BGP, IND, and DBA) were higher in bore 2 as compared to bore 1. Concentrations of CRY, BBF, and BKF were similar in both bores.

Average PAH concentrations measured in bore 2 were compared to a PAH profile measured previously for gasoline engine exhaust (24). The profiles were highly correlated (*r* = 0.93), indicating that gasoline engines were the dominant contributor to PAH emissions in bore 2. This is not surprising because light-duty gasoline vehicles comprised ~98% of traffic in bore 2, and most of the remaining vehicles in bore 2 were light-duty diesel.

As shown in Table 2, CO concentrations in bore 2 were higher than in bore 1. This was expected because traffic volumes were higher from 4 to 6 PM when measurements were made in bore 2. Despite the fact that light-duty traffic flow was higher during bore 2 sampling, black carbon concentrations in truck-influenced bore 1 were ~5 times

TABLE 3. Selected Properties of Gasoline and Diesel Engines and Fuels

parameter	gasoline (light-duty)	diesel (heavy-duty)
carbon weight fraction, $w_c$	0.85 <sup>a</sup>	0.87 <sup>b</sup>
density, $\rho$ (g L <sup>-1</sup> )	743 <sup>a</sup>	830 <sup>b</sup>
fuel economy (mpg)	20 <sup>c</sup>	5 <sup>c</sup>

<sup>a</sup> Average properties determined from 36 gasoline samples collected in the San Francisco Bay Area in the summer of 1996 (31). <sup>b</sup> Typical properties for diesel fuel (32). <sup>c</sup> Measured fuel economy for uphill traffic in the Fort McHenry Tunnel (25).

higher than bore 2 values. This implies that heavy-duty diesel trucks emit much more black carbon than light-duty vehicles.

**Emission Factors.** Emission factors for individual PAH and black carbon were calculated from measured pollutant concentrations. By carbon balance, total carbon (mainly CO<sub>2</sub>) concentrations in the tunnel were used to back-calculate the amount of fuel burned. PAH and black carbon concentrations were normalized to fuel consumption as follows:

$$E_p = 10^6 \times \left( \frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \right) w_c \quad (1)$$

where  $E_p$  is the emission factor ( $\mu\text{g}$  emitted per kg of fuel burned) for pollutant P,  $\Delta[P]$  is the increase in the concentration ( $\text{ng m}^{-3}$ ) of pollutant P above background levels,  $\Delta[CO_2]$  and  $\Delta[CO]$  are the increases in the concentrations of CO<sub>2</sub> and CO ( $\mu\text{g of C m}^{-3}$ ) above background levels, and  $w_c$  is the carbon weight fraction in the fuel. Properties of gasoline and diesel fuel used to calculate emission factors are shown in Table 2.

Since the vehicle fleet in bore 2 comprised almost entirely light-duty vehicles (see Table 2), PAH and black carbon emission factors for light-duty vehicles were computed directly using eq 1 and pollutant concentrations measured in bore 2. To compute emission factors for heavy-duty diesel trucks in bore 1, it was necessary to exclude light-duty vehicle contributions to total pollutant concentrations in bore 1.

Prior roadway tunnel studies have shown that heavy-duty diesel trucks and light-duty gasoline-powered vehicles emit comparable amounts of CO per vehicle mile traveled (25). Therefore, a small fraction of  $\Delta[CO]$  in bore 1 was attributed to heavy-duty diesel truck emissions, equal to the fraction of heavy-duty diesel trucks shown in Table 2 for each sample period.

CO<sub>2</sub> concentrations in bore 1 were apportioned using traffic counts and the fuel economies of light-duty gasoline vehicles and heavy-duty diesel trucks with the following equation:

$$\frac{\Delta[CO_2]_D}{\Delta[CO_2]} = \frac{f_D U_D \rho_D w_D}{(f_D U_D \rho_D w_D) + ((1 - f_D) U_G \rho_G w_G)} \quad (2)$$

where  $\Delta[CO_2]_D$  is the component of  $\Delta[CO_2]$  attributable to heavy-duty diesel emissions,  $f_D$  is the fraction of traffic identified as heavy-duty diesel vehicles,  $U$  is the fuel consumption rate per vehicle mile traveled (reciprocal of fuel economy),  $\rho$  is the fuel density, and  $w$  is the carbon weight fraction in the fuel. The subscripts D and G denote diesel and gasoline, respectively. Table 3 presents the fuel economies used to apportion CO<sub>2</sub> together with fuel densities and carbon weight fractions. Using eq 2, heavy-duty diesel trucks were estimated to contribute 18% of the  $\Delta[CO_2]$  measured in bore 1 during 1–3 PM sample periods.

The contribution of heavy-duty diesels to PAH and black carbon concentrations in bore 1 was determined by subtracting the contribution of light-duty vehicles from the PAH

TABLE 4. Fine Particulate<sup>a</sup> PAH and Black Carbon Mass Emitted Per kg of Fuel Burned for Light-Duty Vehicles and for Heavy-Duty Diesel Trucks in the Caldecott Tunnel

species	light-duty vehicles ( $\mu\text{g kg}^{-1}$ )	heavy-duty diesel ( $\mu\text{g kg}^{-1}$ )
FLT	8.0 ± 0.3	480 ± 100
PYR	9.0 ± 1.5	690 ± 170
BAA	4.8 ± 0.4	140 ± 30
CRY	7.0 ± 0.1	66 ± 20
BBF	7.6 ± 0.3	25 ± 17
BKF	2.5 ± 0.4	2.8 ± 2.5
BAP	6.4 ± 1.1	NS <sup>b</sup>
BGP	18.0 ± 0.3	NS
IND	9.0 ± 1.1	NS
DBA	16.2 ± 2.1	NS
black carbon (mg kg <sup>-1</sup> )	30 ± 2	1440 ± 160

<sup>a</sup> The emission factors reported here are for particle phase ( $<1.3 \mu\text{m}$  aerodynamic diameter) PAH and black carbon. <sup>b</sup> Not a significant source. Use of eq 3 to apportion individual PAH in bore 1 indicated that gasoline vehicles could account for 100% of these PAH emissions.

and black carbon concentrations measured in bore 1, using the following equation:

$$\Delta[P]_{D,1} = \Delta[P]_1 - \Delta[CO]_{G,1} \left( \frac{\Delta[P]_2}{\Delta[CO]_2} \right) \quad (3)$$

where  $\Delta[P]$  is the increase in the concentration of pollutant P above background levels and the subscripts 1 and 2 denote that the pollutant was measured in bore 1 and 2, respectively.  $\Delta[CO]_{G,1} = \Delta[CO]_1(1 - f_D)$  is the fraction of  $\Delta[CO]$  in bore 1 attributed to light-duty vehicle emissions. Apportionment of PAH concentrations in bore 1 using eq 3 indicated that the contributions from heavy-duty diesels to individual PAHs decreased with increasing molecular weight. Diesel trucks contributed 80–90% of the FLT, PYR, and BAA in bore 1, whereas all of the BAP, DBA, BGP, and IND in bore 1 could be attributed to light-duty vehicles. Apportionment of black carbon using eq 3 indicated that heavy-duty diesel trucks were responsible for 87% of the black carbon emitted in bore 1 of the tunnel.

An alternate method for apportioning black carbon concentrations between light-duty vehicles and heavy-duty diesel trucks was considered. A PAH source profile was derived for light-duty vehicle emissions using ratios of PAH to black carbon concentrations measured in bore 2 of the tunnel. The Chemical Mass Balance (CMB) model (26) was then applied to determine source contributions to bore 1 black carbon concentrations, using the PAH profile from bore 2 as a fingerprint for light-duty vehicle emissions. The CMB calculations indicated that heavy-duty diesel trucks were responsible for ~93% of the black carbon emissions in bore 1 of the tunnel. This result is consistent with the apportionment of black carbon using eq 3.

Emission factors for PAH and black carbon calculated using eq 1 are reported in Table 4. Emission factors are reported as mass of pollutant emitted per unit mass of fuel burned. When comparing emission factors, it is important to note that by weight, ~6 times more gasoline than diesel fuel is sold for use by on-road vehicles in California. Therefore, in cases where the emission factors shown in Table 4 are comparable, light-duty vehicles are the dominant source. Heavy-duty diesel trucks are the dominant on-road source of black carbon and lighter PAH such as FLT, PYR, and BAA; light-duty vehicles are the major source of heavier PAH including BKF, BAP, DBA, BGP, and IND.

**PAH Size Distributions.** PAH size distributions measured in bores 1 and 2 are shown in Figures 1 and 2, respectively.

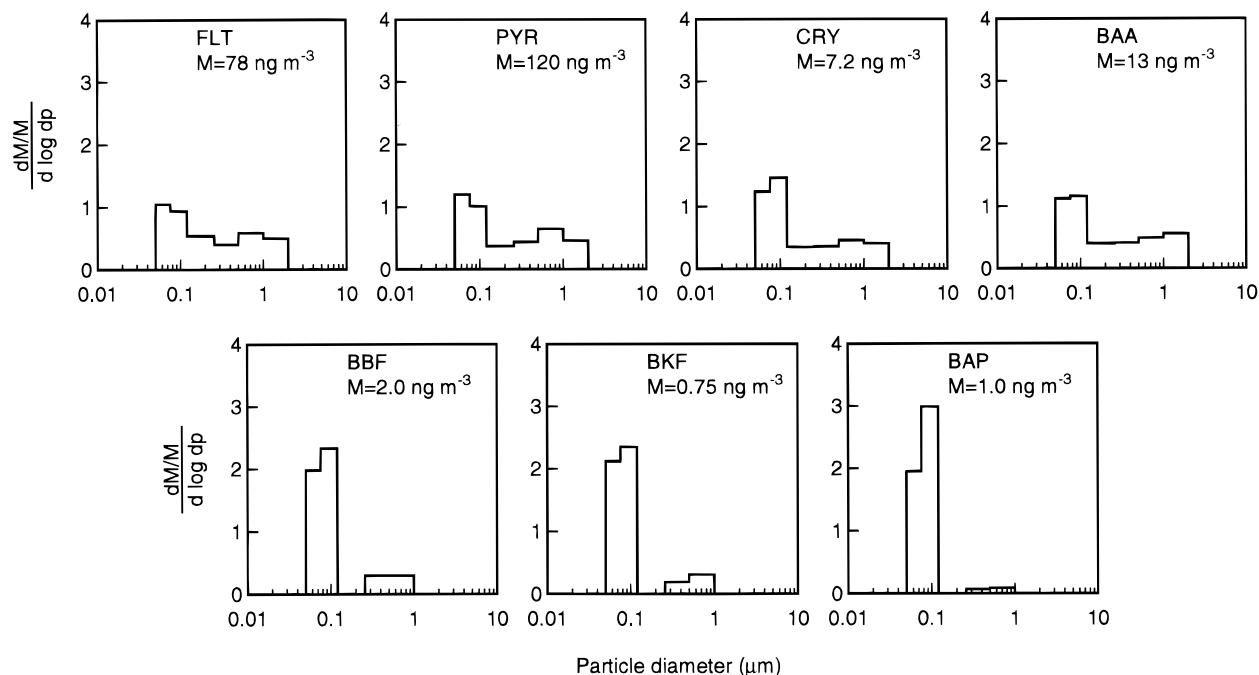


FIGURE 1. Size distribution and total mass concentration ( $M$ ) of seven PAH measured on August 27 with a low-pressure impactor in the truck-influenced bore (bore 1) of the Caldecott Tunnel.

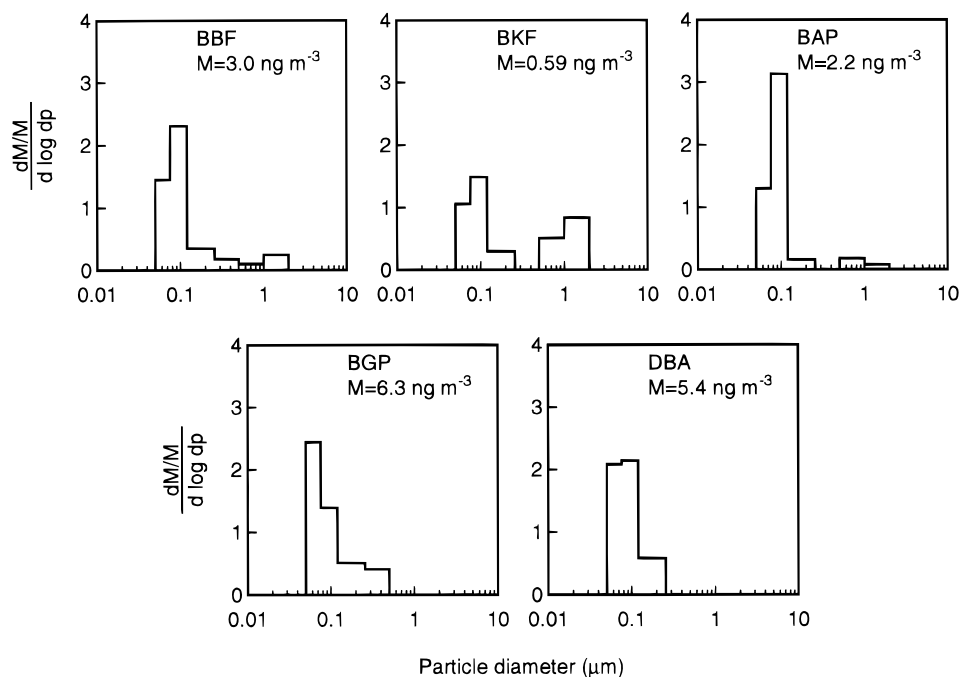


FIGURE 2. Size distribution and total mass concentration ( $M$ ) of five PAH measured on August 20 and 21 with a low-pressure impactor in the light-duty vehicle bore (bore 2) of the Caldecott Tunnel.

Insufficient mass of several PAH (FLT, PYR, BAA, CRY, and IND in bore 2; BGP, IND, and DBA in bore 1) was collected on the low-pressure impactor stages to determine their size distributions. Significant amounts of all PAH shown in Figures 1 and 2 were found in the ultrafine mode (0.05–0.12  $\mu\text{m}$  aerodynamic diameter). PAH with molecular weights of 202–228, including FLT, PYR, BAA, and CRY, were also present in the accumulation mode (0.12–2  $\mu\text{m}$  aerodynamic diameter). Compared to the lower molecular weight PAH, less of the higher molecular weight PAH mass was found in the accumulation mode. The heaviest PAH shown in Figure 2, BGP and DBA, were not found at particle sizes greater than 0.5  $\mu\text{m}$ .

Concentrations of PAH measured using the low-pressure impactor are compared to parallel filter measurements in Figure 3. For BAA and CRY, impactor-derived concentrations were higher than the filter-derived values by a factor of nearly 2. For BBF, BKF, BAP, DBA, and BGP, there was good agreement between the two measurement techniques. Impactor- and filter-derived concentrations of FLT and PYR were much higher on August 27 as compared to other bore 1 samples shown in Table 2. The reason for the higher concentrations of these two PAH during sampling on August 27 is unknown.

Previous measurements in the Caldecott Tunnel (7, 8) showed that black carbon was present only in the ultrafine

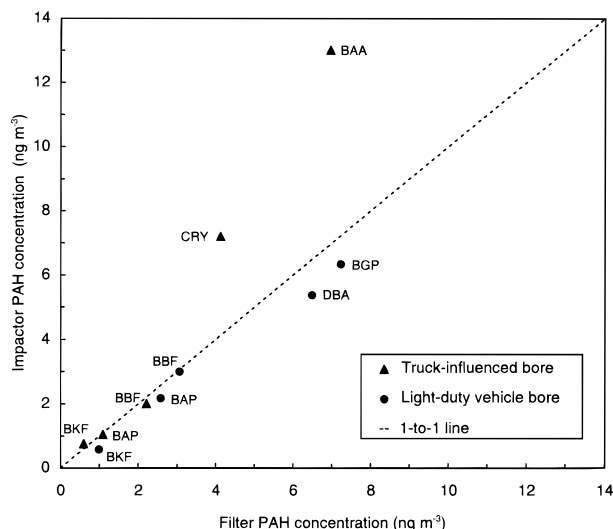


FIGURE 3. Comparison of PAH concentrations measured using a low-pressure impactor and Teflon-coated glass fiber filters.

mode ( $0.05\text{--}0.12\text{ }\mu\text{m}$ ). An overlap of black carbon and PAH in the ultrafine mode is consistent with current understanding of soot formation, which suggests that PAH react first to form soot precursor particles as a result of physical and/or chemical condensation (27). The presence of PAH in the accumulation mode and the absence of black carbon in the accumulation mode suggest that there may be another mechanism that contributes lower molecular weight PAH to the accumulation mode. The low molecular weight PAH may originate from diesel fuel that escapes combustion. Previous studies have shown that the majority of low molecular weight PAH collected in diesel exhaust particulate are derived from unburned fuel and from lubricating oil (28–30). Thus, it appears that two distinct mechanisms lead to the formation of aerosol PAH: a combustion process that leads to the formation of gasoline- and diesel-derived PAH primarily in the ultrafine mode and a noncombustion process associated with diesel-derived PAH that is found mainly in the accumulation mode.

Observations by Venkataraman et al. (8) of the size distributions of the same PAH in the Caldecott Tunnel in 1989 revealed a predominant ultrafine mode, with over 80% of their mass found on particles smaller than  $0.12\text{ }\mu\text{m}$ . In the present study, the ultrafine PAH mass fractions were 62% for bore 1 and 72% for bore 2 (for the PAH that are shown in Figures 1 and 2). Compared with the earlier results, the relatively larger accumulation mode observed in the present study may have resulted from a larger diesel contribution to PAH emissions (especially in bore 1). An increase in the number of catalytic converter-equipped cars and light-duty trucks would have resulted in lower ultrafine mode PAH emissions from these vehicles.

### Acknowledgments

The authors thank Gary Kendall, Graham Scovell, and Mike Traverse of the Bay Area AQMD; Linda Aston, Doug Black, David Dreher, Katharine Hammond, Charles Perrino, and Brett Singer of UC Berkeley; Nathan Kreisberg and Mark Stolzenburg of Aerosol Dynamics; Pablo Cicero and Jim Pederson of the California Air Resources Board; and the Caltrans staff at the Caldecott Tunnel. This research was funded by the California Air Resources Board (Contract 95-330). The statements and conclusions in this paper are those of the authors and not necessarily those of the California Air Resources Board.

### Literature Cited

- (1) Sawyer, R. F.; Johnson, J. H. Diesel emissions and control technology. In *Diesel Exhaust: a critical analysis of emissions,*

*exposure, and health effects*; Health Effects Institute: Cambridge, MA, 1995.

- (2) Larson, S. M.; Cass, G. R.; Gray, H. A. *Aerosol Sci. Technol.* **1989**, *10*, 118–130.
- (3) Larson, S. M.; Cass, G. R. *Environ. Sci. Technol.* **1989**, *23*, 281–289.
- (4) Naus, K. M. Critical issues in assessing the carcinogenicity of diesel exhaust: a synthesis of current knowledge. In *Diesel Exhaust: a critical analysis of emissions, exposure, and health effects*; Health Effects Institute: Cambridge, MA, 1995.
- (5) Miguel, A. H.; Friedlander, S. K. *Atmos. Environ.* **1978**, *12*, 2407–2413.
- (6) Miguel, A. H.; Rubenish, L. M. Submicron size distributions of particulate polycyclic aromatic hydrocarbons in combustion emissions. In *Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects*; Bjorseth, A., Dennis, A. J., Eds.; Battelle Press: Cleveland, OH, 1980; pp 1077–1083.
- (7) Miguel, A. H.; Friedlander, S. K. Size distribution of elemental carbon in atmospheric aerosols. In *Aerosols*; Liu, B. Y. H., Pui, D., Fissan, H., Eds.; Elsevier Science: New York, 1984; pp 407–410.
- (8) Venkataraman, C.; Lyons, J. M.; Friedlander, S. K. *Environ. Sci. Technol.* **1994**, *28*, 555–562.
- (9) Venkataraman, C.; Friedlander, S. K. *Environ. Sci. Technol.* **1994**, *28*, 563–572.
- (10) Allen, J. O.; Dookeran, N. M.; Smith, K. A.; Sarofim, A. F.; Taghizadeh, K.; Lafleur, A. L. *Environ. Sci. Technol.* **1996**, *30*, 1023–1031.
- (11) Daisey, J. M.; Cheney, J. L.; Liou, P. J. *J. Air Pollut. Control Assoc.* **1986**, *36*, 17–33.
- (12) Hering, S. V.; Miguel, A. H.; Dod, R. L. *Sci. Total Environ.* **1984**, *36*, 39–45.
- (13) Benner, B. A.; Gordon, G. E. *Environ. Sci. Technol.* **1989**, *23*, 1269–1278.
- (14) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R. *Environ. Sci. Technol.* **1993**, *27*, 636–651.
- (15) Proposed adoption of regulations limiting the sulfur content and the aromatic hydrocarbon content of motor vehicle diesel fuel. Stationary Source Division, California Air Resources Board, Sacramento, CA, 1988.
- (16) CARF performance and compatibility test program. California Air Resources Board, Sacramento, CA, 1996.
- (17) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Chan, W. *Environ. Sci. Technol.* **1996**, *30*, 661–670.
- (18) John, W.; Wall, S. M.; Ondo, J. L. *Atmos. Environ.* **1988**, *22*, 1627–1635.
- (19) John, W.; Reischl, G. J. *Air Pollut. Control Assoc.* **1980**, *30*, 872–876.
- (20) Birch, M. E.; Cary, R. A. *Aerosol Sci. Technol.* **1996**, *25*, 221–241.
- (21) Hering, S. V.; Flagan, R. C.; Friedlander, S. K. *Environ. Sci. Technol.* **1978**, *12*, 667–673.
- (22) Hering, S. V.; Friedlander, S. K.; Collins, J. J.; Richards, L. W. *Environ. Sci. Technol.* **1979**, *13*, 184–188.
- (23) *Truck inventory and use survey*; United States Census Bureau: Washington, DC, 1992.
- (24) Li, C. K.; Kamens, R. M. *Atmos. Environ.* **1993**, *27A*, 523–532.
- (25) Pierson, W. R.; Gertler, A. W.; Robinson, N. F.; Sagebiel, J. C.; Zielinska, B.; Bishop, G. A.; Stedman, D. H.; Zweidinger, R. B.; Ray, W. D. *Atmos. Environ.* **1996**, *30*, 2233–2256.
- (26) Watson, J. G.; Robinson, N. F.; Chow, J. C.; Henry, R. C.; Kim, B.; Nguyen, Q. T.; Meyer, E. L.; Pace, T. G. *Receptor Model Technical Series Volume III: CMB Users Manual Version 7.0*; U.S. Environmental Protection Agency: Washington, DC, 1990.
- (27) Vanderwal, R. L.; Jensen, K. A.; Choi, M. Y. *Combust. Flame* **1997**, *109*, 399–414.
- (28) Abbass, M. K.; Andrews, G. E.; Williams, P. T. *SAE Tech. Pap. Ser.* **1989**, No. 892079.
- (29) Williams, P. T.; Abbass, M. K.; Andrews, G. E.; Bartle, K. D. *Combust. Flame* **1989**, *75*, 1–24.
- (30) Westerholm, R.; Li, H. *Environ. Sci. Technol.* **1994**, *28*, 965–972.
- (31) McGetrick, J. ARCO Products Co., Los Angeles, CA. Personal communication, 1995.
- (32) Heywood, J. B. *Internal Combustion Engine Fundamentals*; McGraw-Hill Publishing Company: New York, 1988.

Received for review July 1, 1997. Revised manuscript received October 30, 1997. Accepted November 17, 1997.

ES970566W