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Atmospheric Environment 36 (2002) 6059

ATMOSPHERIC ENVIRONMENT

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Corrigendum

Corrigendum to "On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles" [Atmospheric Environment 33 (18) (1999) 2955–2968] ☆

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The authors regret that incorrect entries appear in Table 5 of our published paper. Particle emission rates measured using two different particle number counters and reported in this table are too low by several orders of magnitude for both heavy-duty (HD) diesel trucks and light-duty (LD) vehicles. A revised and corrected version of Table 5 is provided below. The ratios of HD to LD emission rates are correct as originally published, and therefore the conclusions of the study are unchanged. We are grateful to Matthias Ketzel of the National Environmental Research Institute in Roskilde, Denmark, for bringing these problems to our attention. Also note in Table 4 of the published paper that background NO_x concentrations are reported in units of parts per billion (ppb) rather than parts per million (ppm).

Table 5
Light-duty vehicle and heavy-duty diesel truck emission factors[a] (± 1 standard deviation)

Species	Units	HD diesel trucks	LD vehicles	Ratio (HD/LD)
NO_x[b]	($g\,kg^{-1}$)	42 ± 5	9.0 ± 0.2	4.6 ± 0.6
CNC counts[c]	($\#\,kg^{-1}$)	$(6.3 \pm 1.9) \times 10^{15}$	$(4.6 \pm 0.7) \times 10^{14}$	14 ± 5
OPC counts[d]	($\#\,kg^{-1}$)	$(2.5 \pm 0.4) \times 10^{14}$	$(1.34 \pm 0.05) \times 10^{13}$	19 ± 3
$PM_{2.5}$	($g\,kg^{-1}$)	2.5 ± 0.2	0.11 ± 0.01	24 ± 3
BC	($g\,kg^{-1}$)	1.3 ± 0.3	0.035 ± 0.003	37 ± 10
OC[e]	($g\,kg^{-1}$)	0.50 ± 0.04	0.053 ± 0.008	9.4 ± 1.5
SO_4^{2-}	($mg\,kg^{-1}$)	45 ± 8	2.1 ± 0.4	21 ± 6

[a] Emission factors expressed per unit mass of fuel burned, computed using Eq. (1).
[b] NO_x is reported as NO_2 (i.e., a molecular weight of 46 was used to convert measured NO_x concentrations from ppm to $\mu g\,m^{-3}$).
[c] The condensation nucleus counter measured particles $> 0.01\,\mu m$.
[d] The optical particle counter measured particles in the size range of ~ 0.1–$2\,\mu m$.
[e] The mass emission rate of organic carbon was calculated from corrected organic carbon concentrations shown in Table 4.

☆ PII of original article S1352-2310(99)00089-8
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PII: S1352-2310(02)00806-3

PERGAMON

Atmospheric Environment 33 (1999) 2955–2968

ATMOSPHERIC ENVIRONMENT

On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles

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Received 3 August 1998; accepted 8 January 1999

Abstract

An updated assessment of fine particle emissions from light- and heavy-duty vehicles is needed due to recent changes to the composition of gasoline and diesel fuel, more stringent emission standards applying to new vehicles sold in the 1990s, and the adoption of a new ambient air quality standard for fine particulate matter ($PM_{2.5}$) in the United States. This paper reports the measurement of emissions from vehicles in a northern California roadway tunnel during summer 1997. Separate measurements were made of uphill traffic in two tunnel bores: one bore carried both light-duty vehicles and heavy-duty diesel trucks, and the second bore was reserved for light-duty vehicles. Ninety-eight percent of the light-duty vehicles were gasoline-powered. In the tunnel, heavy-duty diesel trucks emitted 24, 37, and 21 times more fine particle, black carbon, and sulfate mass per unit mass of fuel burned than light-duty vehicles. Heavy-duty diesel trucks also emitted 15–20 times the number of particles per unit mass of fuel burned compared to light-duty vehicles. Fine particle emissions from both vehicle classes were composed mostly of carbon; diesel-derived particulate matter contained more black carbon ($51 \pm 11\%$ of $PM_{2.5}$ mass) than did light-duty fine particle emissions ($33 \pm 4\%$). Sulfate comprised only 2% of total fine particle emissions for both vehicle classes. Sulfate emissions measured in this study for heavy-duty diesel trucks are significantly lower than values reported in earlier studies conducted before the introduction of low-sulfur diesel fuel. This study suggests that heavy-duty diesel vehicles in California are responsible for nearly half of oxides of nitrogen emissions and greater than three-quarters of exhaust fine particle emissions from on-road motor vehicles.

Keywords: $PM_{2.5}$; Organic carbon; Black carbon; Reformulated gasoline; Diesel; Tunnel study

1. Introduction

Although heavy-duty diesel trucks currently represent only about 1% of all on-road vehicles in California (ARB, 1996), their emissions contribute significantly to air pollution problems. Cass and Gray (1995) estimated that in the 1980s, on-road diesels contributed 15% of fine particulate carbon and 44% of black carbon emissions in the Los Angeles air basin. California's motor vehicle emission inventory model (MVEI 7G) indicates that in 1995, heavy-duty diesel trucks were responsible for 75% of exhaust particulate matter (PM) and 21% of oxides of nitrogen (NO_x) emissions from on-road vehicles statewide (ARB, 1996). Emissions from off-road diesel engines also contribute significantly to air pollution problems (Sawyer et al., 1998).

Engine dynamometer studies indicate that increasing the cetane index of diesel fuel, a measure of how readily the fuel autoignites, and lowering the aromatic content reduces NO_x and PM emissions (Ullman et al., 1990;

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1352-2310/99/$ – see front matter
PII: S1352-2310(99)00089-8

Nikanjam, 1993). Although carbon monoxide and hydrocarbon emissions from heavy-duty diesel trucks are of less concern, raising fuel cetane index also tends to reduce emissions of these pollutants (Ullman et al., 1990). Lowering fuel sulfur content has been shown to reduce emissions of both sulfur dioxide and particulate sulfate (Wall et al., 1987).

Prior to 1993, typical diesel fuel in California had an aromatic content of 31% by volume and a sulfur content (outside of the Los Angeles area) of 0.28% by mass (ARB, 1988). Effective nationwide in 1993, the composition of diesel fuel used for on-road applications was changed to reduce emissions (CFR, Title 40). Diesel fuel was required to have either a cetane index of at least 40 or a maximum aromatic content of 35% by volume, and sulfur content was limited to 0.05% by mass. Additional requirements applicable to fuel sold in California limited diesel aromatic content to a maximum of 10% by volume (CCR, Title 13; ARB, 1988). However, most refiners in California have chosen to develop alternative diesel fuel formulations having higher aromatic content that are less expensive to refine (e.g., Nikanjam, 1993). Alternative formulations are allowed if they provide equivalent emissions reductions. Use of California reformulated diesel fuel was expected to reduce NO_x, exhaust PM, and sulfur dioxide emissions from diesel vehicles by 7, 25, and 80%, respectively, in addition to reducing the carcinogenicity of diesel exhaust (ARB, 1988).

In recent years, diesel engine manufacturers have met increasingly stringent NO_x and PM emission standards primarily through advances in engine and control technology. Improvements to the fuel injection system including higher injection pressures, improved control of injection rate, and electronic control for precise timing of fuel injection have reduced particulate matter emissions. Improved combustion chamber design and increased intake air swirl have also led to lower particulate emission levels (Sawyer and Johnson, 1995; Sawyer et al., 1998).

Whereas modern light-duty gasoline vehicles equipped with catalytic converters are generally not high emitters of PM, vehicles that burn oil or run very fuel-rich can have high PM emission rates. PM mass emission rates from light-duty vehicles that emit visible smoke (Cadle et al., 1997; Sagebiel et al., 1997), for example, are comparable to measured emission rates from heavy-duty diesel trucks (Hildemann et al., 1991; Lowenthal et al., 1994). Oxygenated gasolines (Kirchstetter et al., 1996,1999a,b) now used in many areas of the country aim to reduce carbon monoxide and hydrocarbon emissions from vehicles that run fuel-rich through enleanment of the air–fuel mixture. Exhaust particulate emissions resulting from fuel-rich operation may also be reduced through the use of these gasolines.

In addition to emitting fine particles directly, motor vehicles emit precursor gases that react in the atmosphere to form secondary particulate matter. In California, secondary ammonium nitrate derived from direct emissions of NO_x comprises a substantial fraction of fine particle mass during the fall and winter seasons, when ambient fine particle concentrations are typically highest (Solomon et al., 1989; Chow et al., 1992,1993,1994,1995; Watson et al., 1994a). In Los Angeles and the San Joaquin Valley, for example, ammonium nitrate constitutes from one-third to more than one-half of particulate mass on days with the highest 24 h average particle concentrations (Solomon et al., 1989; Chow et al., 1992; Watson et al., 1994a).

The recent adoption in the United States of a National Ambient Air Quality Standard for fine particles smaller than 2.5 μm in diameter ($PM_{2.5}$) requires a careful characterization of fine particle emissions from combustion sources such as motor vehicles. Given the introduction of reformulated gasoline in addition to the changes to diesel fuel and engine technology mentioned above, an updated assessment of on-road fine particle emissions is needed. The purpose of this research is (1) to measure on-road $PM_{2.5}$ and NO_x emission factors for light- and heavy-duty vehicles, (2) to determine the chemical composition of $PM_{2.5}$ emissions, and (3) to assess the relative contributions of light- and heavy-duty vehicles to on-road fine particle and NO_x emissions.

2. Methods

2.1. Field sampling site

Vehicle emissions were measured in the Caldecott tunnel. Located east of San Francisco Bay on state highway 24, the Caldecott tunnel connects Oakland, Berkeley, and San Francisco with Contra Costa County. It is comprised of three traffic bores, each about 1100 m long, and has a roadway grade of 4.2%. Forced ventilation along the length of the tunnel is provided by adjustable pitch fans that are located above the entrance and exit of each tunnel bore. A schematic of the tunnel is available elsewhere (Kirchstetter et al., 1996).

Sampling was conducted in two of the traffic bores, both carrying traffic in the uphill direction. One bore (bore 1) was used by both light- and heavy-duty vehicles, whereas the other (bore 2) was reserved for light-duty vehicles only. Measurements were made in bore 1 from 1230 to 1530 h when the percentage of heavy-duty trucks in the vehicle fleet was largest. Vehicle emissions were measured in bore 2 during the afternoon commuter traffic peak, from 1530 to 1830 h, when pollutant concentrations inside the tunnel were highest and traffic consisted almost entirely of light-duty vehicles. Field sampling took place during July and August of 1997, and included four days in bore 1 and four days in bore 2, as indicated in Table 1.

Table 1
Traffic volumes (vehicles h^{-1}) in the Caldecott tunnel, summer 1997

Date	Axle class			% HD diesel[a]
	3 + axles	2-axle/6-tire	2-axle/4-tire	
Bore 1 (1230–1530 h)				
Jul 21	61	90	2040	4.8
Jul 22	43	82	2208	3.7
Jul 23	60	90	2149	4.6
Jul 24	55	85	2377	3.9
Bore 2 (1530–1830 h)				
Jul 31	0	26	3871	0.33
Aug 1	0	24	4115	0.29
Aug 4	2	26	4163	0.36
Aug 5	2	26	4188	0.36

[a]The fraction of heavy-duty diesel trucks in the vehicle fleet was estimated as the sum of all 3 + axle vehicles plus half of the 2-axle/6-tire vehicles, divided by the total vehicle count.

2.2. Traffic characterization

Vehicle attributes and driving conditions inside the tunnel were characterized each day of the study. Traffic volume, composition, age, and fuel type were determined through visual counts and license plate surveys. As shown in Table 1, traffic volumes in bore 1 from 1230 to 1530 h were typically 2200 vehicles h^{-1}, and were about half as large as those in bore 2 from 1530 to 1830 h. Vehicles were counted in three categories according to number of axles and tires: 2-axle/4-tire; 2-axle/6-tire; and 3 + axles. The 1992 Truck Inventory and Use Survey (Bureau of Census, 1992), together with the results of license plate surveys conducted at the tunnel, was used to determine the fraction of vehicles in each axle class that were heavy-duty diesel trucks. Analysis of truck census data for California suggested that almost all (>99%) vehicles with three or more axles are heavy-duty diesel trucks. License plate surveys conducted at the tunnel during this study (see below) and during previous summers indicate that $<2\%$ of 2-axle/4-tire vehicles are diesel-powered; most of those that are diesel-powered are light-duty passenger vehicles. The number of 2-axle/6-tire vehicles that were diesel-powered was less certain. Survey data indicated that 45–68% of these trucks were diesel-powered. The higher value resulted when pickups and vans as well as single-unit trucks were included in the analysis of survey data. For this study, we assumed that 50% of the 2-axle/6-tire vehicles were heavy-duty diesel trucks. Based on these classifications, traffic in bore 1 was estimated to include 4.2% heavy-duty diesel trucks on average. More than half (56%) of these were large trucks with three or more axles. By contrast, heavy-duty diesel trucks comprised only 0.3% of traffic in bore 2, and very few of these were large trucks with three or more axles, as indicated in Table 1. Traffic in bore 2 consisted of about two-thirds cars and one-third light-duty trucks (pickups, vans, and sport utility vehicles).

License plates were recorded as vehicles exited the tunnel and were later matched with vehicle registration data to determine vehicle model year. The average model year of 156 heavy-duty diesel trucks observed in bore 1 was 1988. The average model year of 788 randomly selected light-duty vehicles observed in bore 2 was 1991; fewer than 2% were pre-1975 model year and based on vehicle registration records only 1.8% were diesel-powered. Thus, greater than 95% of the light-duty vehicles in bore 2 were originally equipped with catalytic converters.

Two cars were used to measure the speed of vehicles traveling through the tunnel. One car was equipped with a computer to log vehicle speed at 1 s intervals, and the second car was used to measure average traffic speed based on manually recorded transit time through the tunnel. The average speed of traffic in bore 2 during rush hours (1530–1830 h) on all four sampling days was 59 ± 10 km h^{-1} ($n = 27$). Average vehicle speeds inside bore 1 early in the afternoon (1230–1530 h) were faster because traffic volumes were smaller. Light-duty vehicles traveled through bore 1 at an average speed of 70 ± 9 km h^{-1} ($n = 17$) on 22–24 July and 89 ± 11 km h^{-1} ($n = 8$) on 21 July. The average speed of heavy-duty diesel trucks in bore 1 was 65 ± 11 km h^{-1} ($n = 13$). Traffic was generally smooth flowing; stop-and-go driving and heavy accelerations were rarely observed.

2.3. Gaseous pollutant measurements

Tunnel pollutant concentrations were measured in the traffic tube ~ 50 m before the tunnel exit. Background

pollutant concentrations were measured at the fresh air intake ventilation fans. Concentrations of carbon monoxide (CO), carbon dioxide (CO_2), and NO_x were measured continuously. CO and CO_2 concentrations were quantified using gas filter correlation spectrometers (Thermo Environmental Instruments, Franklin, MA, models 48 and 41 H, respectively), and NO_x was measured with chemiluminescent analyzers (Thermo Environmental Instruments model 42). Analyzers used to measure pollutant concentrations inside the tunnel were located in the fan room above the tunnel exit. A ~ 50 m Teflon sample line was used to draw air samples directly from the traffic tube.

Using traceable gas standards, zero and span checks were performed several times a week on each analyzer. The Quality Assurance Section of the California Air Resources Board conducted a performance audit of the CO and NO_x analyzers, as discussed elsewhere (Kirchstetter et al., 1999a).

2.4. Continuous particle measurements

Particle concentrations in the tunnel were measured continuously and recorded as 15 s averages using a condensation nucleus counter (CNC), an optical particle counter (OPC), and an aethalometer. The CNC (model 3760, TSI Inc., St. Paul, MN) measured particle number concentrations for particles with diameters larger than 0.01 μm. The OPC (model LAS-X, Particle Measuring Systems, Boulder, CO) counted and optically sized particles with diameters between about 0.1 and 2 μm. The optical sizing by the OPC was calibrated with monodisperse fractions of tunnel aerosol selected using a differential mobility analyzer. The aethalometer (Magee Scientific, Berkeley, CA) measured a black carbon mass equivalence by optical attenuation of particles collected on a quartz filter.

The OPC and CNC sampled through 46 m of copper tubing with an inner diameter of 6.3 mm at a flow rate of $5.2\,\mathrm{l\,min^{-1}}$. The transport flow was chosen to minimize particle losses due to turbulence ($Re < 1200$) or sedimentation. The pressure drop across this sampling line was 0.035 atm. All inlet tubes for the real-time instruments, including the sampling line for the gas-phase analyzers, were loosely tied together and inserted down into the vehicle bore through a ceiling vent, penetrating approximately 30 cm and facing the oncoming traffic to maximize aspiration efficiency. The aethalometer was placed inside the tunnel at the same ceiling vent.

A two-stage aerosol dilution chamber was constructed for use with the OPC and CNC to avoid the presence of multiple particles simultaneously passing the instrument's optical sensing region. In each stage, a major portion of the flow (60% for stage one, 99% for stage two) was siphoned off and filtered. The particle-free air was then recombined with the aerosol stream. The OPC siphoned off a small portion of the flow at $0.09\,\mathrm{l\,min^{-1}}$ after the first stage with a dilution factor of 2.6. The CNC sampled at $1.5\,\mathrm{l\,min^{-1}}$ after the second stage with a combined dilution factor of 380.

To simplify comparisons among data from different instruments, a single data acquisition system was used to collect data from the OPC, CNC, and gas analyzers on a common time basis (15 s averages). The difference in transport times between the real-time particle sampling line and the gas sampling line was measured to be ~ 1 s and was accounted for during the averaging of the gas analyzer signals. The aethalometer, which was stationed inside the tunnel, was offset by the sampling line transport time for the OPC and CNC.

Measured particle number concentrations might be biased low due to particle coagulation inside the 46 m sampling line and/or inside the tunnel. Coagulation is important within the vehicle exhaust system where primary particle concentrations are highest and dilution of the exhaust plume has not yet occurred. In the Caldecott tunnel, vehicle exhaust (which initially contains about 14% by volume CO_2) was diluted by a factor of at least 200 : 1 before it was sampled. To determine the significance of coagulation in the tunnel and in the sample line, the characteristic time for coagulation was calculated (Seinfeld and Pandis, 1998). To be conservative, the highest 3-h average particle number concentration measured in the tunnel, $4.0\times10^5\ \mathrm{cm^{-3}}$, and the smallest particle size measured, 0.01 μm, were used in the calculation. Using a typical value of the monodisperse coagulation coefficient, $1.8\times10^{-9}\ \mathrm{cm^3\,s^{-1}}$, the characteristic time for a 50% decrease in particle number concentration was calculated to be 46 min. For polydisperse coagulation with a concentration of $1.4\times10^4\ \mathrm{cm^{-3}}$ of 0.2 μm particles, as indicated by the OPC, the coagulation coefficient is $5.4\times10^{-8}\ \mathrm{cm^3\,s^{-1}}$ and the characteristic time is 15 min. These times are long compared to the residence time of air in the sample line (~ 15 s) and in the tunnel (~ 3 min). Sharp increases (spikes) in particle number concentration were observed in the tunnel over periods of 1–2 min, with the highest values and greatest variability in CNC counts observed in the diesel truck-influenced bore (bore 1). Coagulation rates would have been higher when these spikes in particle number concentration occurred.

2.5. Integrated samples for particle chemistry

Filter samples for chemical characterization of $PM_{2.5}$ particles were collected inside and outside of the tunnel on each sampling day. Teflon filters were collected for determination of mass and inorganic ion concentrations, and were analyzed by the California Air Resources Board laboratory by gravimetry and ion chromatography. Quartz filters were collected for determination of organic (OC) and black carbon (BC) concentrations, and were

analyzed by the thermal optical technique of Birch and Cary (1996; Sunset Laboratories, Beaverton, OR). AIHL cyclones (John and Reischl, 1980) operated at 24 l min^{-1} were used to provide the 2.5 μm precut. All filters were 47 mm in diameter. The Teflon filters were collected at 24 l min^{-1}, with one filter per cyclone. Quartz filters were collected at 12 l min^{-1} by splitting the flow from a single cyclone. The quartz filters were masked with annular stainless-steel shims with an inner diameter of 24.7 mm to provide the same face velocity as for the Teflon filter samples. Tandem quartz filters were used on each sampler leg for analysis of carbon particles.

An experimental activated carbon denuder for scrubbing gas-phase organic compounds was used on one of the quartz filter sampling legs, as shown in Fig. 1. The denuder was 10 cm long with approximately 1000 parallel channels. It was constructed from a block of activated carbon with a square cell structure (product discontinued, Graphite Sales Inc., Chagrin Falls, OH). The flow through each channel was laminar ($Re \sim 10$). The Gormley–Kennedy equations (Fuchs, 1964) predict a removal efficiency of 99.8% for irreversibly depositing gas-phase species, and losses of 3% for particles with a diameter of 0.05 μm (decreasing to less than 1% for 0.1 μm particles). Shedding of carbon from the denuder was tested by drawing filtered air through the denuder at twice the sample flow rate, with the result that no visible darkening was found on a downstream filter. Inside the tunnel, tandem quartz filters were collected downstream of this denuder, in parallel to tandem, undenuded quartz filters. Outside the tunnel, quartz filters were collected with undenuded tandem quartz filters only, with a bypass line in place of the denuder-filter leg. Prior to use, the denuder was baked at 250°C for 2 h. Quartz filters, which were baked before purchase, were again baked at 400–500°C for 2 h prior to use at the tunnel.

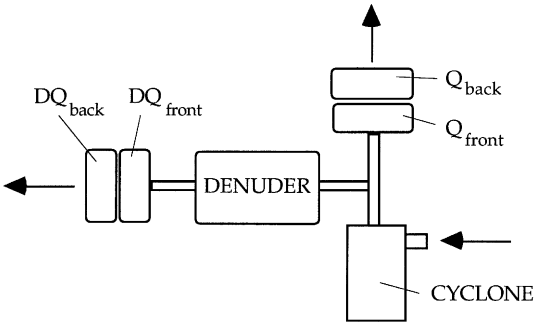

Fig. 1. Schematic diagram showing arrangement of quartz filters used to sample fine particulate carbon concentrations inside the tunnel. Q denotes quartz filter; DQ denotes denuded quartz filter located downstream of an activated carbon denuder.

2.6. Emission factors

Fuel-based pollutant emission factors were computed by relating total carbon emissions in the tunnel (mainly in the form of CO_2) to the carbon content of fuel using the following equation:

$$E_P = 10^3 \left(\frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \right) w_c, \quad (1)$$

where E_P is the emission factor (g emitted per kg of fuel burned) for pollutant P, $\Delta[P]$ is the increase in the concentration of pollutant P(μg m^{-3}) above background levels, $\Delta[CO_2]$ and $\Delta[CO]$ are the increases in the concentrations of CO_2 and CO (μg of carbon m^{-3}) above background levels, and w_c is the weight fraction of carbon in fuel. Carbon weight fractions for gasoline and diesel fuel used to calculate emission factors are reported in Table 2.

Light-duty vehicle emission factors were computed directly with Eq. (1) and pollutant concentrations measured in bore 2. Heavy-duty diesel truck emission factors could not be computed directly from bore 1 measurements because traffic in bore 1 comprised both light-duty vehicles and heavy-duty diesel trucks. Thus, it was necessary to apportion pollutant emissions in bore 1 to the two vehicle classes.

Prior roadway tunnel studies have shown that heavy-duty diesel trucks and light-duty gasoline-powered vehicles emit comparable amounts of CO per unit distance traveled (Pierson et al., 1996). Therefore, a small fraction of Δ[CO] in bore 1 was attributed to heavy-duty diesel truck emissions, equal to the fraction of heavy-duty diesel trucks in the traffic during each sample period.

Table 2
Selected properties of diesel and gasoline fuels

Parameter	Diesel (heavy-duty)	Gasoline (light-duty)
Carbon weight fraction, w_c	0.87[a]	0.85[b]
Density, ρ (g l^{-1})	840[c]	740[b]
Sulfur, (ppm by weight)	135[c]	12[b]
Fuel consumption[d] (l/100 km)	47	12
Fuel sales[e] (l)	8.0×10^9	5.1×10^{10}

[a]Typical properties for diesel fuel (Heywood, 1988).

[b]Average properties determined from 36 gasoline samples collected in the San Francisco Bay Area in summer 1997 (McGetrick, 1997).

[c]Average properties determined from diesel fuel samples collected from five Bay Area refineries (Lum, 1997).

[d]Measured fuel consumption for uphill traffic in the Fort McHenry tunnel (Pierson et al., 1996).

[e]On-road taxable fuel sales in California in 1995 (Board of Equalization, 1997).

CO_2 emissions 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 trucks, U is the fuel consumption rate (reciprocal of fuel economy), ρ is fuel density, and w is the carbon weight fraction in fuel. The subscripts D and G denote diesel and gasoline, respectively. Fuel economies, fuel densities, and carbon weight fractions used to apportion CO_2 are presented in Table 2.

For all other pollutants in bore 1, the portion of total emissions emitted by heavy-duty diesel trucks was determined by subtracting the contribution of light-duty vehicles. Light-duty vehicle emissions in bore 1 were determined using pollutant emission ratios measured in the light-duty vehicle bore (bore 2). The contribution from heavy-duty diesel trucks was expressed as

$$\Delta[P]_D = \Delta[P] - \Delta[CO] \cdot (1-f_D) \cdot \left(\frac{\Delta[P]_2}{\Delta[CO]_2}\right), \quad (3)$$

where $\Delta[P]_D$ is the component of $\Delta[P]$ in bore 1 attributable to heavy-duty vehicle emissions, and $\Delta[CO] \cdot (1-f_D)$ is the fraction of $\Delta[CO]$ in bore 1 attributed to light-duty vehicle emissions. The pollutant emission ratio for light-duty vehicles, $\Delta[P]_2/\Delta[CO]_2$, was measured in bore 2.

3. Results and discussion

3.1. OC sampling artifact

The measurement of particulate organic carbon concentrations with quartz filters is complicated by two sampling artifacts: the adsorption of gas-phase organic compounds onto the filter surface (positive artifact), and the evaporation of organic material from particles on the front filter (negative artifact). These artifacts have been investigated as they pertain to sampling in urban and remote environments (Turpin et al., 1994; Eatough et al., 1995,1996; Novakov et al., 1997).

To address this issue for the tunnel samples, parallel samples of denuded and undenuded pairs of quartz filters were collected, as discussed above and shown in Fig. 1. As reported in Table 3, the average OC mass collected on front filters downstream of the activated carbon denuder (DQ_{front}) was 40% lower than the OC mass collected without the denuder (Q_{front}). In contrast, the BC mass collected on front quartz filters downstream of the denuder was 90%, on average, of the BC mass collected by the undenuded quartz filters. The lower BC mass on denuded quartz filters is attributed to particle losses in the denuder.

Compared to filter samples collected without the denuder, vapor adsorption onto denuded filter samples was diminished. Evaporation of organic aerosol from the front denuded filter was likely enhanced due to the depletion of gaseous carbon constituents in the sample air stream. If the denuder was 100% efficient, then the OC found on the denuded backup filter would be entirely attributable to vaporized organic aerosol from the front filter. Thus, the OC on the denuded backup quartz filter, DQ_{back}, represents the upper limit for collection of evaporated organic particle mass by the backup filter. The upper limit of organic aerosol collected by denuded quartz filters is the sum of the front and back filters, or $DQ_{front} + DQ_{back}$. For this data set, the organic carbon collected on DQ_{back} is small by comparison to that collected by the undenuded backup filter, Q_{back}. Organic carbon mass collected on backup filters below the denuded quartz filters, DQ_{back}, was $\frac{1}{5}$ to $\frac{1}{3}$ of that for the undenuded backup filters, Q_{back}. Since evaporation from the undenuded front filter must be less than from the denuded front filter, most of what is found on the undenuded backup filter, Q_{back}, must be due to adsorption of gas-phase organic compounds not adsorbed by the front filter, or the positive artifact. Thus for the undenuded leg, the particle-phase organic carbon concentration is most closely approximated by the difference between the front and backup filters, $Q_{front} - Q_{back}$. These two measures of organic carbon concentration (undenuded, $Q_{front} - Q_{back}$; and denuded $DQ_{front} + DQ_{back}$) are compared in Fig. 2, with correction for the 10% loss of particles in the denuded leg indicated from the black carbon measurement. Also shown are 1-standard deviation error limits from the analytical method. With the exception of one outlier, these two methods of estimating organic carbon are in reasonable agreement. The bore 1 results fall within the analytical uncertainty of the OC determination; the bore 2 results show a somewhat larger difference, but the two measures of OC agree to within 20%.

Based on these results, corrected particulate organic carbon concentrations inside the tunnel were calculated as the average of these two values, namely $0.5 \times [(Q_{front} - Q_{back}) + f(DQ_{front} + DQ_{back})]$ where $f = 1.1$ accounts for particle losses in the denuder. We note that there may be additional organic carbon lost from the quartz filters by evaporation which is not collected by the backup quartz filters. However, for these experiments, sample times were short, filter samples were at the same temperature as the sampled air, and pressure drop across the filters was small (0.04 atm). These conditions will minimize evaporative losses as compared to that found for most ambient sampling conditions.

Table 3
Organic carbon (OC) and black carbon (BC) concentrations (μg of carbon m^{-3}) measured using quartz filters[a]

		Tunnel				Background	
		OC		BC		OC	BC
Date	Filter	w/o den[b]	denuded[c]	w/o den	denuded	w/o den	w/o den
Bore 1[d] (1230–1530 h)							
Jul 21	Front	43.6	19.9	48.4	50.4	8.4	3.2
	Back	3.2	1.4	0.1	0.1	1.2	0.0
Jul 22	Front	34.6	21.0	61.4	51.2	10.6[f]	4.4
	Back	8.4	3.4	0.0	0.4	3.5	0.5
Jul 23	Front	34.1	21.4	53.7	49.6	6.7	2.3
	Back	7.2	2.4	0.0	0.0	3.8	0.1
Jul 24	Front	33.9	26.0	67.4	57.3	11.5	5.2
	Back	5.6	1.4	0.0	0.1	3.6	0.0
Bore 2[e] (1530–1830 h)							
Jul 31	Front	23.5	15.8	15.5	14.1	6.2	1.7
	Back	3.8	1.3	0.0	0.0	1.8	0.1
Aug 01	Front	22.6	15.4	12.3	11.0	4.9	1.7
	Back	2.8	0.7	0.2	0.1	1.8	0.4
Aug 04	Front	26.8	15.3	16.2	13.5	7.5	2.6
	Back	4.4	0.6	0.0	0.0	2.3	0.4
Aug 05	Front	25.0	13.8	16.8	14.2	7.7	1.7
	Back	4.5	0.8	0.0	0.4	2.8	0.9

[a]The mass of carbon collected was determined using a thermal-optical analytical technique (Birch and Cary, 1996).
[b]These quartz filter samples (*Q*) were collected without the use of an activated carbon denuder.
[c]These quartz filter samples (DQ) were collected downstream of an activated carbon denuder used to scrub gas-phase organic compounds from the air stream (see text for further detail).
[d]Heavy-duty diesel trucks constituted about 4% of traffic in bore 1.
[e]Bore 2 was reserved for use by light-duty vehicles only.
[f]An anomalously high value of 53 μg m^{-3} was measured; sample was probably contaminated. The value shown in the table was determined based on ambient OC/BC ratios and the measured background BC concentration on 22 July.

3.2. Pollutant concentrations

Measured concentrations of CO, CO_2, NO_x, $PM_{2.5}$, BC, OC, SO_4^{2-}, and particle number are reported in Table 4. Concentrations of most pollutants were significantly higher inside the tunnel than in background air. For example, average CO, NO_x, and $PM_{2.5}$ concentrations measured in bore 1 were 17, 25, and 8 times higher than in background air. Particle number concentrations were not measured in background air. However, background levels were estimated from overnight measurements in the tunnel when concentrations of CO, CO_2, and NO_x dropped to typical daytime background levels. Corresponding background particle number concentrations measured using the CNC and OPC were 5500 and 450 cm^{-3}, respectively.

CO and CO_2 concentrations (above background levels) in bore 1 were 60–70% of those measured in bore 2, consistent with the lower total traffic volumes observed earlier in the afternoon in bore 1. In contrast, bore 1 concentrations (again above background levels) of NO_x, $PM_{2.5}$, and BC were 1.1, 2.8, and 3.8 times the corresponding values measured in bore 2. This provides evidence that heavy-duty diesel trucks, which were present in bore 1 but largely absent from bore 2, are much higher emitters of these pollutants than light-duty vehicles.

3.3. Apportionment of pollutant emissions

Eq. (3) was used to apportion emissions in bore 1 for cases where the influence of heavy-duty diesel trucks was evident (i.e., the emission ratio $\Delta[P]/\Delta[CO]$ was significantly higher in bore 1 than in bore 2). The apportionment was not attempted in cases where the influence of diesel trucks on pollutant concentrations in bore 1 was small. Emission factors were computed for the following pollutants: NO_x, $PM_{2.5}$, BC, OC, SO_4^{2-}, and fine particle number concentrations. For these pollutants, measured emission ratios were consistent from one day to the next.

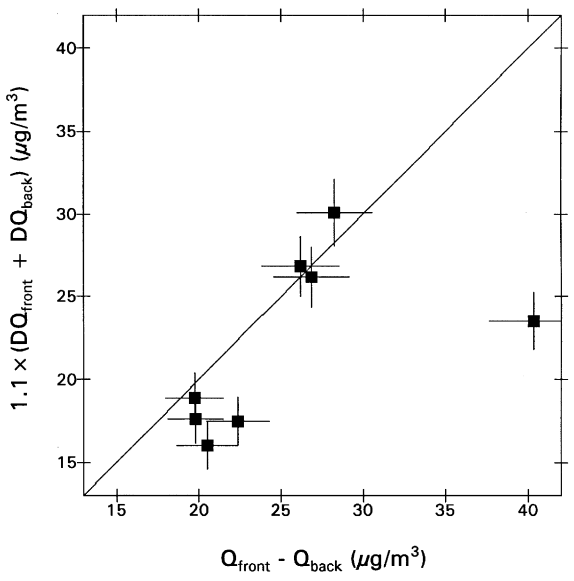

Fig. 2. Plot of fine particulate organic carbon (OC) concentrations (μg of carbon m^{-3}) estimated using denuded quartz (DQ) filters versus OC estimated using undenuded quartz (Q) filters. The factor of 1.1 applied to the denuded filters accounts for particle losses in the denuder (see text).

For example, the average NO_x to CO ratio (± 1 standard deviation) measured in bores 1 and 2 were 0.113 ± 0.003 and 0.071 ± 0.003, respectively. The apportionment indicated that heavy-duty diesels contributed approximately 40% of NO_x, 55% of OC, 70% of fine particles, 75% of $PM_{2.5}$ and SO_4^{2-}, and 85% of BC emissions in bore 1.

Accurate apportionment of emissions with Eq. (3) requires that light-duty vehicle emissions in bore 1 are well characterized by the emission ratio, $\Delta[P]_2/\Delta[CO]_2$, measured for light-duty vehicles in bore 2. Vehicle speeds were typically about 10 km h^{-1} lower in bore 2 during the late afternoon sampling period (1530–1830 h) than in bore 1 during the earlier afternoon sampling period (1230–1530 h). Given that vehicle speed may affect pollutant emission factors, it is necessary to consider how vehicle speed affects the pollutant emission ratio, $\Delta[P]/\Delta[CO]$. As reported by Kirchstetter et al. (1999a), CO emissions in bore 2 of the Caldecott tunnel increased more than NO_x emissions as vehicle speeds increased, so the $\Delta[NO_x]/\Delta[CO]$ ratio for light-duty vehicle emissions was lower earlier in the afternoon, as shown in Fig. 3. Thus, the $\Delta[NO_x]/\Delta[CO]$ ratio measured in bore 2 from 1530–1830 h may overstate the actual $\Delta[NO_x]/\Delta[CO]$ emission ratio for light-duty vehicles in bore 1 earlier in the afternoon.

The fraction of total NO_x emissions (40%) attributed to heavy-duty diesels in bore 1 is therefore a lower bound value. Given the uncertainty in the $\Delta[NO_x]/\Delta[CO]$ ratio and NO_x apportionment due to differences in vehicle speeds, it follows that heavy-duty diesels could be responsible for as much as 48% of total NO_x emissions in bore 1. Thus, the heavy-duty diesel NO_x emission factor may be as much as 20% higher than the value reported below.

Heavy-duty diesel truck emission factors for other pollutants (BC, OC, SO_4^{2-}, $PM_{2.5}$ mass, particle number concentrations) are less sensitive than the NO_x emission factor to uncertainty in the apportionment using Eq. (3). This is because the diesel exhaust contribution to these other pollutants in bore 1 is larger than it is for NO_x. For example, light-duty vehicles in bore 1 were estimated to contribute only 15% of BC versus 60% of NO_x. Therefore, the same level of uncertainty in the light-duty emission ratio ($\Delta[P]_2/\Delta[CO]_2$) leads to a smaller error in the estimation of heavy-duty diesel emissions of BC relative to NO_x.

Carbon dioxide emissions were apportioned using Eq. (2) because the contribution of heavy-duty diesels to CO_2 in bore 1 was too small for Eq. (3) to produce reliable results (i.e., the $\Delta[CO_2]/\Delta[CO]$ ratio in bores 1 and 2 was about equal). Application of Eq. (2) using measured traffic counts and previously published fuel economies (see Table 2) indicated that heavy-duty diesel trucks were responsible for 17%, on average, of CO_2 emissions in bore 1. Based on traffic counts, 4.2% of CO emissions in bore 1 was attributed to heavy-duty diesel trucks.

There are two sources of uncertainty affecting the apportionment of CO_2 emissions in bore 1: use of measured fuel economies from the Fort McHenry tunnel (Pierson et al., 1996) to represent Caldecott tunnel vehicles, and the classification of 2-axle/6-tire trucks as gasoline or diesel-powered. Fuel economies shown in Table 2 were measured for uphill driving on a 3.3% grade, whereas the grade in the Caldecott tunnel is 4.2%. If the ratio of heavy-duty to light-duty fuel economy remains the same as grade changes from 3.3 to 4.2%, this difference will not affect the CO_2 apportionment. However, it is unknown how well the vehicle weight distributions, and therefore fuel economies, match between the two tunnels. As discussed earlier, there are uncertainties about how many of the 2-axle/6-tire trucks were truly heavy-duty diesel. If 68% rather than 50% of these trucks are counted as heavy-duty diesel, then $\Delta[CO_2]_D$ calculated using Eq. (2) would increase, and emission factors shown in Table 5 for heavy-duty diesel trucks would decrease by $\sim 10\%$.

3.4. Fine particle emission rates

Vehicle emission factors, computed as mass of pollutant emitted per kg of fuel burned (Eq. (1)), are reported in Table 5. Compared to light-duty vehicles, heavy-duty diesel trucks have higher emission factors for every

Table 4
Pollutant concentrations measured at the Caldecott tunnel in summer 1997

Date	CO (ppm)	CO_2 (ppm)	NO_x (ppm)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	BC ($\mu g\ m^{-3}$)	OC[c] ($\mu g\ m^{-3}$)	SO_4^{2-} ($\mu g\ m^{-3}$)	CNC[d] ($\#\ cm^{-3}$)	OPC[e] ($\#\ cm^{-3}$)
Bore 1[a] (1230–1530 h) Tunnel concentrations									
Jul 21	19.0	720	2.09	139	48.3	44.7	4.5	4.0×10^5	1.4×10^4
Jul 22	16.9	735	1.93	125	61.4	37.1	3.2	3.7×10^5	1.2×10^4
Jul 23	19.4	747	2.07	130	53.7	37.1	5.2	3.3×10^5	1.2×10^4
Jul 24	19.4	779	2.17	136	67.4	40.8	3.6	2.7×10^5	1.3×10^4
Bore 2[b] (1530–1830 h) Tunnel concentrations									
Jul 31	27.5	1008	1.92	56.1	15.5	27.0	3.0	2.1×10^5	5.7×10^3
Aug 01	26.1	946	1.78	52.5	12.1	26.2	3.3	1.9×10^5	5.1×10^3
Aug 04	27.5	1053	1.94	56.6	16.2	27.9	1.9	1.8×10^5	5.6×10^3
Aug 05	27.6	1090	2.06	53.7	16.8	25.6	2.8	1.6×10^5	5.7×10^3
Bore 1[a] (1230–1530 h) Background concentrations									
Jul 21	1.2	369	85	14.1	3.2	10.1	2.1		
Jul 22	0.9	370	65	19.2	3.9	10.0	1.5		
Jul 23	1.1	366	78	15.3	2.3	4.1	2.5		
Jul 24	1.3	384	103	18.8	5.2	11.0	1.7		
Bore 2[b] (1530–1830 h) Background concentrations									
Jul 31	0.8	365	48	13.4	1.6	6.2	2.4		
Aug 01	0.9	369	58	16.1	1.3	4.4	2.4		
Aug 04	1.3	387	82	11.8	2.3	7.3	1.1		
Aug 05	0.8	384	51	13.6	0.9	6.8	1.8		

[a]Heavy-duty diesel trucks constituted about 4% of traffic in bore 1.
[b]Bore 2 was reserved for use by light-duty vehicles only.
[c]OC concentrations shown here were calculated from measurements presented in Table 3, correcting for sampling artifacts and multiplying by a factor of 1.4 to account for hydrogen and oxygen mass associated with organic carbon (Gray et al., 1986). The method used to correct organic carbon concentrations for sampling artifacts is discussed in the text.
[d]The condensation nucleus counter measured particles $> 0.01\ \mu m$.
[e]The optical particle counter measured particles in the size range 0.1–2 μm.

pollutant listed in Table 5. The greatest differences are for $PM_{2.5}$, BC, and SO_4^{2-}, for which emission factors for heavy-duty diesel trucks were 24, 37, and 21 times higher than for light-duty vehicles. In addition to having higher fine particle mass emissions, heavy-duty diesel engines emit about 15–20 times the number of fine particles larger than 0.01 μm than do light-duty vehicles per unit mass of fuel burned. Note that if emission factors were expressed on a per vehicle km traveled basis, the differences between heavy-duty and light-duty emission factors reported in Table 5 would be four times larger because heavy-duty vehicles burn about four times more fuel per km traveled (see Table 2).

In California, on-road diesel fuel sales are one-sixth the volume of gasoline sales (Table 2). Considering the relative magnitudes of light-duty vehicle and heavy-duty diesel truck emission factors measured in this study, it follows that exhaust emissions of $PM_{2.5}$ and BC from on-road sources are dominated by heavy-duty trucks, which emit about 80 and 90%, respectively, of the total mass. As noted above, however, visibly smoking light-duty vehicles can have fine particle emission rates comparable to heavy-duty diesel trucks. If smoking light-duty vehicles were underrepresented in the present study then light-duty vehicles would contribute a greater portion of fine particle emissions statewide. Furthermore, vehicles driving through the tunnel were operating in a fully warmed-up mode. The possibility of higher exhaust particle emission rates from both cars and trucks under cold-starting/wintertime conditions has not been considered here.

3.5. Chemical composition of fine particles

Carbonaceous material comprised the majority of fine particle emissions. Diesel-derived particulate was more

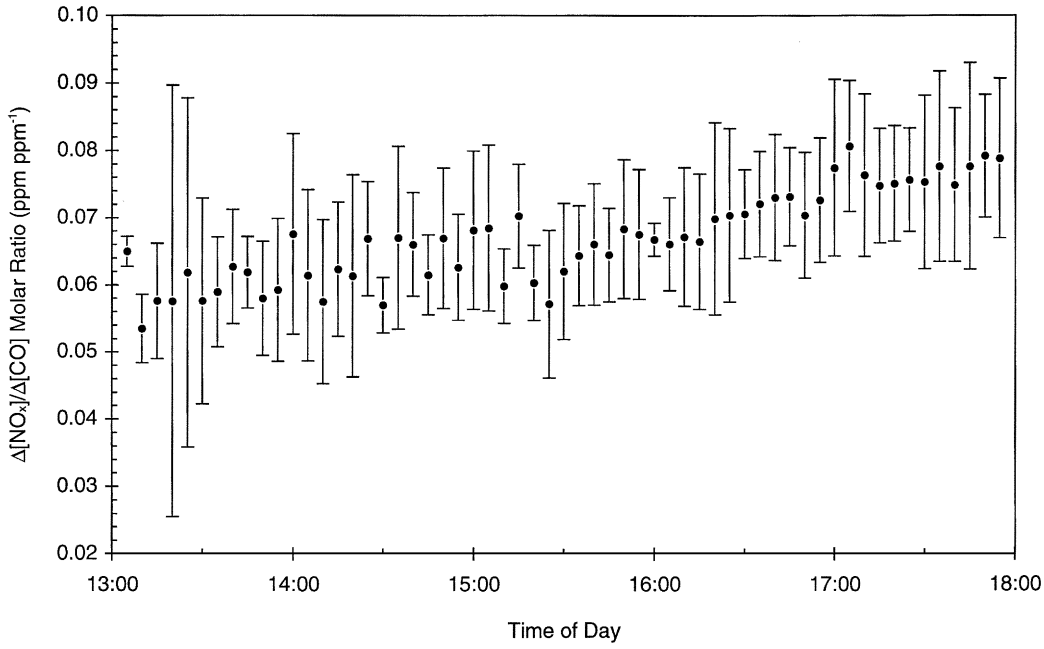

Fig. 3. Average (± 1 standard deviation) NO_x/CO emission ratio measured in bore 2 of the Caldecott tunnel.

Table 5
Light-duty vehicle and heavy-duty diesel truck emission factors[a] (± 1 standard deviation)

Species	Units	HD diesel trucks	LD vehicles	Ratio (HD/LD)
NO_x[b]	(g kg^{-1})	42 ± 5	9.0 ± 0.2	4.6 ± 0.6
CNC counts[c]	(# kg^{-1})	$(6.3 \pm 1.9) \times 10^{12}$	$(4.6 \pm 0.7) \times 10^{10}$	14 ± 5
OPC counts[d]	(# kg^{-1})	$(2.5 \pm 0.4) \times 10^{11}$	$(1.3 \pm 0.05) \times 10^{9}$	19 ± 3
$PM_{2.5}$	(g kg^{-1})	2.5 ± 0.2	0.11 ± 0.01	24 ± 3
BC	(g kg^{-1})	1.3 ± 0.3	0.035 ± 0.003	37 ± 10
OC[e]	(g kg^{-1})	0.50 ± 0.04	0.053 ± 0.008	9.4 ± 1.5
SO_4^{2-}	(mg kg^{-1})	45.1 ± 8.1	2.12 ± 0.43	21 ± 6

[a]Emission factors expressed per unit mass of fuel burned, computed using Eq. (1).
[b]NO_x is reported as NO_2 (i.e., a molecular weight of 46 was used to convert measured NO_x concentrations from ppm to μg m^{-3}).
[c]The condensation nucleus counter measured particles > 0.01 μm.
[d]The optical particle counter measured particles in the size range of ~ 0.1–2 μm.
[e]The mass emission rate of organic carbon was calculated from corrected organic carbon concentrations shown in Table 4.

abundant in black carbon ($51 \pm 11\%$ of $PM_{2.5}$ mass) than light-duty vehicle particulate emissions, which showed a lower BC fraction ($33 \pm 4\%$). Other studies also report black carbon to be more abundant in particle emissions from diesel trucks. Reported BC fractions range from 30 to 50% for heavy-duty diesel trucks (Hildemann et al., 1991; Lowenthal et al., 1994; Watson et al., 1994b), and from 14 to 23% for catalyst equipped light-duty vehicles (Hildemann et al., 1991; Watson et al., 1994b).

Organic carbon comprised $50 \pm 6\%$ of $PM_{2.5}$ mass emissions from light-duty vehicles in the Caldecott tunnel, which agrees with values (30–50%) reported elsewhere (Hildemann et al., 1991; Watson et al., 1994b). Organic carbon constituted only $20 \pm 2\%$ of $PM_{2.5}$ mass emissions from heavy-duty diesel trucks, whereas values ranging from 30 to 40% have been reported in the literature (Hildemann et al., 1991; Lowenthal et al., 1994; Watson et al., 1994b).

Sulfate was a small component of total fine particle emissions, comprising about 2% of total $PM_{2.5}$ mass emissions from both the light- and heavy-duty vehicle fleets. The sulfate emission factor measured for heavy-duty diesel trucks in the Caldecott tunnel (45 ± 8 mg kg^{-1}

of diesel burned) is significantly lower than values reported in earlier studies. Measured heavy-duty diesel sulfate emission rates in the Tuscarora tunnel in 1977 were about 120 ± 15 mg kg^{-1} of diesel burned (Pierson and Brachaczek, 1983; Pierson et al., 1996). Sulfate emission rates measured for heavy-duty trucks in southern California in the late 1980s were approximately 350 ± 60 mg kg^{-1} (Hildemann et al., 1991). Lower sulfate emissions at the Caldecott tunnel were expected due to the reduction in sulfur content of diesel fuel since the time of the earlier studies.

Table 6
Temporal variability in pollutant concentrations within each sampling run

Pollutant	Coefficient of variation[a]	
	Bore 1 (%)	Bore 2 (%)
CO_2	11	7.5
CO	37	25
NO_x	39	18
CNC[b]	58	36
OPC[c]	60	66
BC[d]	102	97

[a]Average coefficient of variation (σ/μ) for time-resolved pollutant concentrations measured inside the tunnel during each 3 h sampling run.
[b]Condensation nucleus counter; particles > 0.01 μm.
[c]Optical particle counter; 0.1–2 μm particles.
[d]Black carbon mass concentrations were measured continuously with an aethalometer.

3.6. Temporal variability

Concentrations of CO, NO_x, black carbon mass, and particle number varied considerably during each 3-h sampling period. Much less variability was observed in the concentration of CO_2, which can be used as a measure of changes in traffic density and the tunnel air ventilation rate. The relative standard deviation in the measured concentration for each of these parameters is given in Table 6. These values reflect the variability in pollutant concentrations during a 3-h sampling period. All pollutant concentrations were measured with 15 s time resolution. Black carbon mass and particle number concentrations were generally more variable than gaseous pollutant concentrations. CNC counts and NO_x concentrations showed greater time variability in bore 1 than in bore 2. The relative variation in OPC and aethalometer (black carbon) readings were similar for both bores.

Sample time series of continuously measured parameters are given in Fig. 4 for bore 1, and Fig. 5 for bore 2. Here the parameters are normalized to

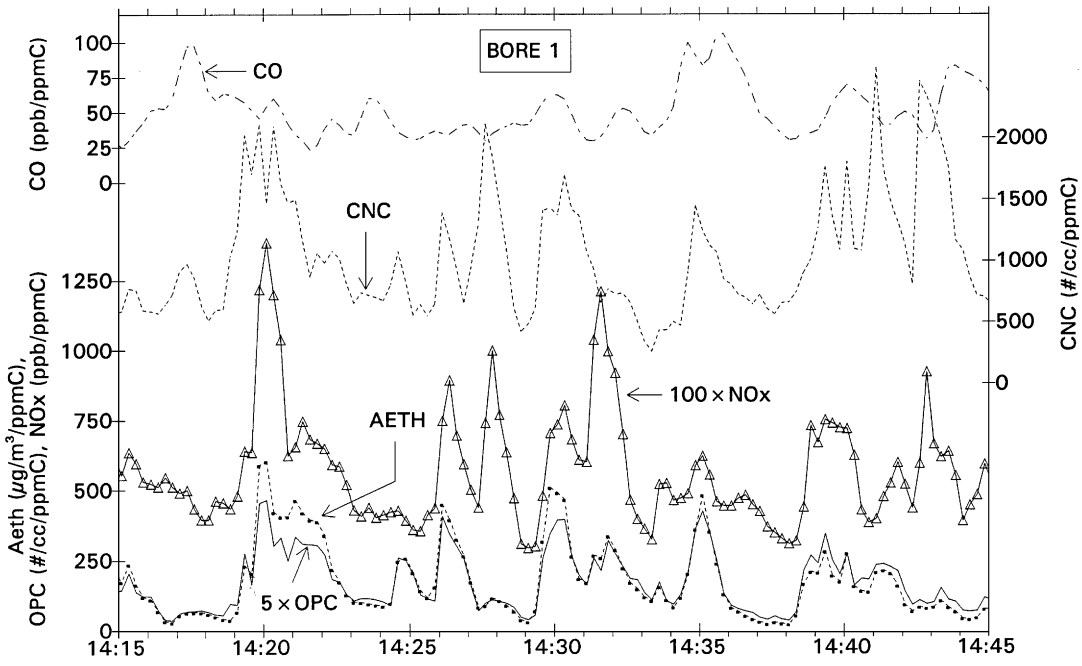

Fig. 4. Time-series plot from 21 July 1997 of pollutant concentrations in the diesel truck-influenced bore (bore 1) of the tunnel. All pollutant concentrations are normalized by $\Delta[CO] + \Delta[CO_2]$.

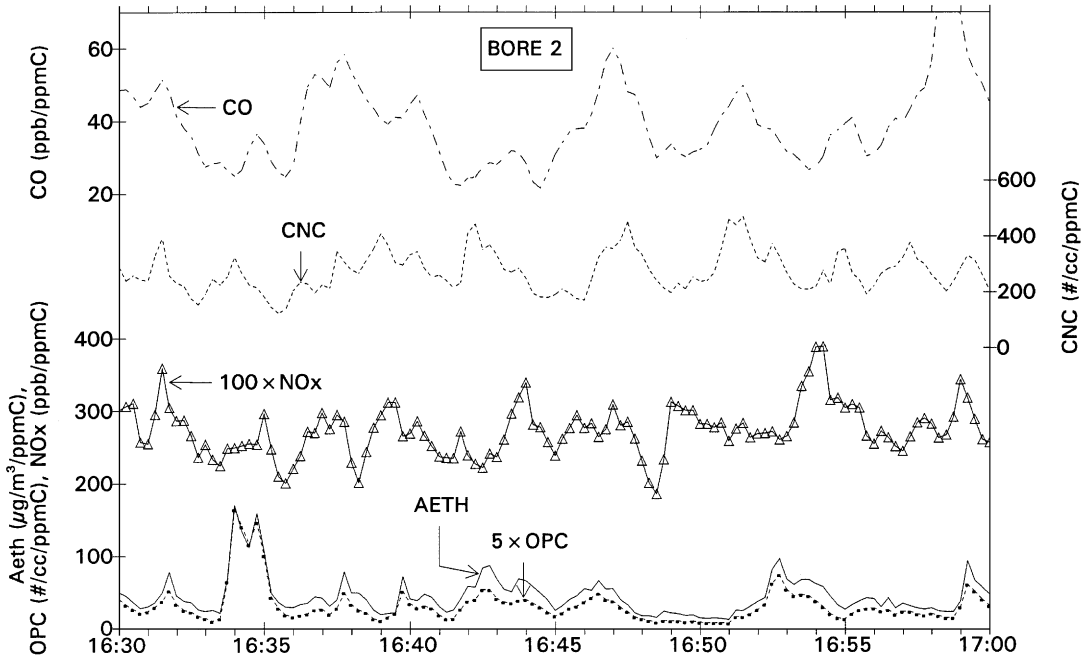

Fig. 5. Time-series plot from 4 August 1997 of pollutant concentrations in bore 2 of the tunnel (reserved for use by light-duty vehicles only). All pollutant concentrations are normalized by $\Delta[CO] + \Delta[CO_2]$.

Table 7
Measured on-road NO_x emissions from heavy-duty vehicles

Study	Year	Roadway grade	Typical speeds (km h^{-1})	NO_x emissions[a] (g kg^{-1})
Tunnel				
Caldecott (this study) Oakland, CA	1997	+ 4.2%	65 ± 11	42 ± 5
Tuscarora[b]	1992	level	87 ± 5	39 ± 3
Tuscarora, PA				
Fort McHenry[b]	1992	+ 3.3%	70–80	37 ± 4
Baltimore, MD		− 1.8%	80	34 ± 2
Cassiar[c]	1995	level	90	48 ± 17
Vancouver, BC				
Remote sensing				
Raleigh-Durham, NC[d]	1997	+ 2.1%	90–110	45 ± 2
Orange County, CA[e]	1997	+ 2.3%	25[f]	31 ± 0.2

[a]Emission factors are reported as mass of NO_x emitted per kg of diesel fuel consumed. NO_x is reported as NO_2 (i.e., a molecular weight of 46 was used to convert measured NO_x concentrations from ppm to μg m^{-3}).
[b]Pierson et al. (1996).
[c]Rogak et al. (1998).
[d]Nelson et al. (1998).
[e]Countess et al. (1998).
[f]Trucks were accelerating on a freeway on-ramp after leaving a weigh station.

$\Delta[CO] + \Delta[CO_2]$, as used in Eq. (1). The sum $\Delta[CO] + \Delta[CO_2]$ is the increase of gas-phase carbon species due to fuel combustion in the tunnel, and is used here to correct for variations in the ventilation rate and traffic density inside the tunnel. The parameters shown are CO, NO_x, black carbon particle mass (AETH), and particle number concentrations in two size ranges. The line labeled CNC counts corresponds to particles above 0.01 μm; that labeled OPC corresponds to particles in the 0.1–2 μm size range.

The time correlation in these parameters was examined to determine whether high NO_x or CO emitters might also be high particle emitters. As is evident from the time series plots, only the OPC counts and the BC measured by the aethalometer are strongly correlated ($r_{OPC,AETH} = 0.89$ in bore 1, and 0.92 in bore 2). This finding is interesting given that the aethalometer measures black carbon, which is found predominantly in the ultrafine mode (below 0.12 μm, Venkataraman et al., 1994), whereas the OPC measures accumulation mode particles.

Other parameters measured in the tunnel are not as well correlated. In bore 1, local peaks in NO_x sometimes correspond to a local peak in CNC counts, and at other times correspond to local peaks in OPC counts. The CNC and OPC both correlate better with NO_x ($r_{NO_x,CNC} = 0.55$ and $r_{NO_x,OPC} = 0.50$, respectively) than with each other ($r_{CNC,OPC} = 0.32$). These correlations are even weaker in bore 2.

3.7. NO_x emissions

On-road NO_x emission factors for heavy-duty trucks measured during several roadway tunnel and remote sensing studies are reported in Table 7. As indicated, truck speeds and roadway grades varied across the different sampling sites. However, measured NO_x emission factors, when expressed on a fuel consumed basis, were consistent from site to site, and did not exhibit a clear trend with roadway grade/speed. The stability of NO_x emission factors when expressed on a fuel consumed basis supports their use in the development of fuel-based emission inventories (e.g., Dreher and Harley, 1998).

When combined with fuel density and on-road fuel sales for the state of California (see Table 2) the NO_x emission factors shown in Table 5 suggest that heavy-duty diesel trucks are responsible for $\sim 45\%$ of total on-road NO_x emissions. Thus, heavy-duty diesels are a significant source of NO_x, nearly equal in importance to light-duty vehicles. As a whole, on-road vehicles are the largest source ($\sim 60\%$) of NO_x emissions in California (ARB, 1997). Therefore, the contribution of heavy-duty diesel truck emissions to secondary (ammonium nitrate) fine particle concentrations is expected to be significant.

Acknowledgements

The authors thank Rex Ganding, Linsey Marr, and Brett Singer of UC Berkeley; Pablo Cicero, Chas Cowell, Bart Croes, Bill Davis, Samantha Kwan, Brian Oxley, and Jim Pederson of the California Air Resources Board; Gary Kendall and Mike Traverse of the Bay Area Air Quality Management District; and Anthony Hansen of Magee Scientific. We also thank Caltrans staff at the Caldecott tunnel. This research was supported 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.

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