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Fine particle emission factors from vehicles in a highway tunnel: Effects of fleet composition and season

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Abstract

In-use, fuel-based motor vehicle emission factors were determined using measurements made in a highway tunnel in Pittsburgh, Pennsylvania. Concentrations of $PM_{2.5}$ mass, CO, CO_2, and NO_x were measured continuously. Filter-based measurements included $PM_{2.5}$ mass, organic and elemental carbon (OC and EC), inorganic ions and metals. Fuel-based emission factors for each pollutant were calculated using a fuel-carbon balance. The weekday traffic volume and fleet composition varied in a consistent diurnal pattern with the estimated fraction of fuel consumed by heavy-duty diesel vehicle (HDDV) traffic ranging from 11% to 36%. The emission rate of most species showed a significant dependence on sample period. NO_x, $PM_{2.5}$, EC and OC emission factors were significantly larger during the early morning, truck-dominated period. Emissions of particulate metals associated with brake wear (Cu, Sb, Ba and potentially Ga) were emitted at higher rates during the rush-hour period, which is characterized by slower, stop-and-go traffic. Emission rates of crustal elements (Fe, Ca, Mg, Li), Zn and Mn were highest during the early-morning period when there was more heavy-truck traffic. A seasonal shift in average OC/EC ratio for the rush-hour period was observed; fall and summer OC/EC ratios are 1.0 ± 0.6 and 0.26 ± 0.06, respectively. Potential causes for this shift are increased partitioning of semi-volatile organic compounds into the gas phase during the summer months and/or effects of seasonal changes in fuel formulation. Emission factors for HDDV and light-duty vehicles (LDV) classes were estimated using a linear regression of emission factor as a function of fleet composition. The extrapolated emission factors generally agree with previously published measurements, though a substantial range in published values is noted.

Keywords: $PM_{2.5}$; Organic carbon; Elemental carbon; Trace metals; Emission inventories

1. Introduction

Motor vehicles are among the most important sources of gas- and particle-phase pollutants in the urban atmosphere. Experiments in roadway tunnels provide information about pollutant emissions from

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a large sample of in-use vehicles. Tunnel experiments have been used to measure vehicle emission rates in a range of geographic locations (see, e.g., Pierson et al., 1996; Kirchstetter et al., 1999; Gertler et al., 2002; Chellam et al., 2005; Lough et al., 2005). Substantial prior work has been done to quantify gas-phase emissions on the East Coast (Pierson et al., 1996), but fine particle emissions have not been as well characterized, and there is more disagreement between measured emission factors and those derived from regulatory models (Kuhns et al., 2004). Geographical variation in fleet age and condition are important issues; for instance, high-emitting or 'smoker' light-duty vehicles (LDV) can emit large amounts of particulate matter (Zielinska et al., 2004), and their portion of the fleet can vary significantly with geographical location (Mazzoleni et al., 2004).

The goal of this paper is to measure in-use motor vehicle emissions in a highway tunnel in Pittsburgh, Pennsylvania. Fleet average emission factors were determined for gaseous species and PM mass, organic carbon (OC), elemental carbon (EC) and elemental metals. Measurements are combined with traffic data to investigate the impact of vehicle fleet composition and operating mode on emission rates. Data taken during both fall and summer periods allows the examination of seasonality in emissions.

2. Experimental methods

2.1. The Squirrel Hill Tunnel

The experiments were conducted in the two-lane westbound bore of the Squirrel Hill Tunnel on Interstate 376 in Pittsburgh, Pennsylvania. The tunnel is 1.3 km long and has a 2.5% up-grade in the westerly direction. The tunnel is ventilated mechanically through ducts situated in the tunnel ceiling and by the effects of traffic motion. The sampling location was roughly 50 m from the tunnel exit; at this position the mechanical ventilation system was under positive pressure and thus pushing fresh air into the tunnel. The sample inlets were inserted through an otherwise sealed ventilation slit in the tunnel ceiling; several slits up- and down-stream of the sample location were also blocked. The majority of the measurements were made during a two-week period in November of 2002. A more limited study was also performed in the summer of 2004 to examine seasonal dependence of organic aerosol emissions.

Traffic count and speed data were gathered via a Remote Traffic Microwave Sensor (RTMS) operated for the Pennsylvania Department of Transportation (PennDOT). Fleet composition was determined from PennDOT video by manually counting heavy-duty (HD) vehicles. HD vehicles include tractor-trucks, large single-unit trucks and buses. City buses did not regularly pass through the tunnel. While this approach separates vehicles by size and not fuel-type, the assumption that most large vehicles are diesel-powered and smaller ones gasoline-powered is reasonable. Less than 5% of HD vehicles with more than three axles in the US fleet are gasoline-powered (VIUS, 2002). The portion of LDV powered by diesel fuel is similarly small; around 1% of vehicles in US households were diesel powered (EIA, 1994) and at most 15% of light-duty trucks are diesel powered (VIUS, 2002). Therefore, we assume that all of the HD vehicles are diesels (HDDV) and LDV are gasoline powered.

The portion of fuel use in the tunnel by HDDV was calculated based on the HD vehicle number counts from the video,

$$\%\text{fuel}_{\text{HD}} = \frac{f_{\text{HD}} U_{\text{HD}}}{f_{\text{HD}} U_{\text{HD}} + (1 - f_{\text{HD}}) U_{\text{LD}}}, \quad (1)$$

where f_{HD} is the fraction of traffic identified as HD and U_{HD} and U_{LD} are the fuel consumption rates for HDDV and cars, respectively. Fuel consumption values for cars and HDDV on an incline were assumed to be 12 ± 2 and 47 ± 91 $(100\,\text{km})^{-1}$, respectively (Pierson et al., 1996). Fuel consumption rates of the US LDV and HD vehicle fleets have remained essentially unchanged over the past 15 years (BTS, 2001; USDOT, 2004). Therefore, these values represent a best estimate of in-use fuel consumption rates as they were derived from measurements taken under similar conditions (in-use vehicles under load).

2.2. Air-quality measurements

The suite of continuous instruments and manual samplers used to measure pollutant species concentrations during the November 2002 study is listed in Table 1. Continuous instruments measured CO, CO_2, NO, NO_2 and $PM_{2.5}$ mass. The Tapered Element Oscillating Microbalance (TEOM) operated at 30 °C with a $PM_{2.5}$ cyclone and Sample Equilibration System that incorporates a Nafion dryer on the inlet. The CO_2 monitor was the only

Table 1
Instrumentation used in tunnel sampling site

Species measured	Method	Instrument	Time resolution
CO_2	Non-dispersive infrared	Li-Cor LI-820	1 min
NO_X/NO	Chemiluminensce	API 200A	1 min
$PM_{2.5}$	TEOM with SES	R&P 1400a	5 min
CO	Non-dispersive infrared	API 300A	1 min
Elemental and organic carbon	Quartz/quartz-behind teflon	Sunset Laboratory TOT	2/4/6.5 h
Size resolved mass and OC/EC	MOUDI with Teflon/foil filters	Sunset Laboratory TOT	2/4/6.5 h
Inorganic ions	Teflon/nylon/cellulose filters with denuder	Dionex DX-600/120 IC	2/4/6.5 h
$PM_{2.5}$ metals	Teflon/cellulose filters	Agilent 4500 ICP-MS	6.5/8/12 h

continuous instrument used during the summer 2004 study.

Integrated filter samples were collected to characterize $PM_{2.5}$ levels inside the tunnel. Based on the diurnal patterns in tunnel traffic (discussed below), three manual sampling periods (12–6 AM, 7–9 AM and 10 AM to 4:30 PM) were defined to characterize variation in emissions with fleet composition and traffic characteristics. All manual sampling was carried out during these time periods.

$PM_{2.5}$ OC and EC were measured with a two-channel sampler: one channel consisted of a quartz filter (Bare-Q) and the other of a backup quartz filter behind a Teflon (QBT) membrane filter (Subramanian et al., 2004). The quartz filters were analyzed using a modified version of the NIOSH 5040 thermal-optical transmittance (TOT) protocol in a Sunset Laboratory OC/EC Analyzer (Subramanian et al., 2004). OC measured by the backup quartz filter (QBT) is used to correct for positive sampling artifact (Turpin et al., 2000). Unless otherwise noted, all OC data reported in the paper is artifact-corrected by subtracting the OC on the backup filter from the bare quartz filter (Q−QBT).

Samples to measure $PM_{2.5}$ and gas-phase inorganic ions were collected using a two-channel sampler with each channel consisting of a filter pack with a PTFE Teflon membrane filter, a nylon filter, and a backup citric-acid-coated cellulose-fiber filter in series; one channel operated with MgO and citric acid denuders and the second channel operated without the denuders (Takahama et al., 2004). Ion chromatography was performed using the method of Chow and Watson (1998) to yield concentrations of $PM_{2.5}$ Na, K, Mg, Ca, Cl, ammonium, nitrate and sulfate and gas-phase ammonia, hydrochloric acid, and nitric acid. Gas-phase measurements were determined by taking the difference of semi-volatile inorganic species concentrations between the two sampling lines.

$PM_{2.5}$ samples for elemental analysis were collected using a two-channel sampler with one channel containing a Teflon filter and the other a cellulose filter. Exposed filters were processed using microwave-assisted digestion in a solution containing HNO_3, HF, and H_2O_2. Digested samples were then analyzed by inductively coupled plasma mass spectrometry (ICP-MS). This method was used to quantify the airborne concentrations of Ag, Al, As, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Ni, Pb, Rb, Se, Sb, Sr, Ti, Tl, V, and Zn as described by Pekney and Davidson (2005).

To measure particle size distribution, two 8-stage Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corp.) were operated during the study. One MOUDI was operated with aluminum foil substrates and a quartz-fiber after-filter, and the second with Teflon substrates. The Teflon filters were used for gravimetric analysis followed by elemental analysis by ICP-MS using the procedures described above. The aluminum substrates were used for OC/EC analysis as described by Cabada et al. (2004).

2.2.1. *Calculating fuel-based emission factors*

Emission factors are calculated on a fuel basis using a carbon balance of the major carbon-containing exhaust constituents (Miguel et al., 1998; Kirchstetter et al., 1999):

$$\mathrm{EF}_P = \left[\frac{\Delta[P]}{\Delta[\mathrm{CO_2}] + \Delta[\mathrm{CO}]}\right]\left[\frac{\mathrm{MW}_p}{\mathrm{MW}_C}\right] w_\mathrm{c}, \qquad (2)$$

where EF_P is the emission factor of pollutant P in grams $(\mathrm{kg\,fuel})^{-1}$, $\Delta[P]$, $\Delta[\mathrm{CO_2}]$ and $\Delta[\mathrm{CO}]$ are the background-corrected pollutant, CO_2 and CO concentrations measured in the tunnel, MW_P and MW_C are the molecular weights of the pollutant

and carbon, and w_c is the weight fraction of carbon in fuel. VOCs and particulate carbon were assumed to contribute negligibly to the overall carbon mass balance. The carbon weight fractions for gasoline and diesel fuel were assumed to be 0.85 and 0.87, respectively; a weighted average value for w_c was determined based on fleet fuel use for mixed fleet conditions.

2.2.2. Background pollutant concentrations

All measurements in the tunnel were background corrected using measurements made at the Pittsburgh Air Quality Study (PAQS) main site on the Carnegie Mellon University (CMU) campus and other sampling sites operated throughout Allegheny County, none of which were strongly impacted by local sources. Although the PAQS main site was approximately 2 km to the northwest of the tunnel sampling location, the strong regional character of fine particle concentrations in the Pittsburgh area supports the use of regional background measurements to correct the tunnel data (Tang et al., 2004). In addition, tunnel concentrations were typically much higher than background concentrations, minimizing uncertainty associated with the background correction. For example, the average diurnal profiles of in-tunnel and regional background $PM_{2.5}$ mass concentrations are shown in Fig. 1. Tunnel concentrations are significantly above background levels throughout the day.

Background $PM_{2.5}$ mass was measured with a TEOM operated at the CMU site. Background $PM_{2.5}$ OC and EC data were measured with 24-h quartz and quartz-behind-Teflon filters collected at the CMU site. OC and EC levels during traffic sampling periods were estimated by scaling the 24-h background filter results with the time-resolved TEOM data (Weitkamp et al., 2005).

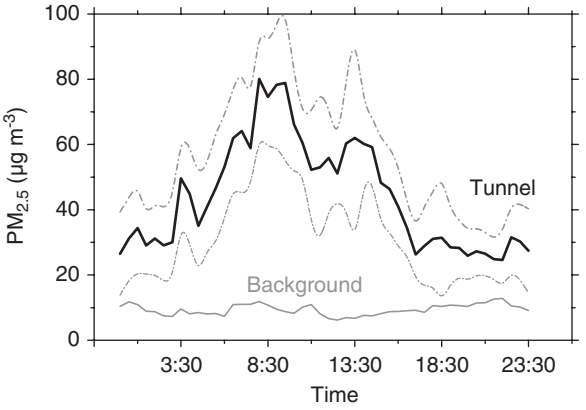

Fig. 1. Average diurnal profile of in-tunnel (heavy solid line) and background (light solid line) $PM_{2.5}$ mass concentrations. Dashed lines indicate ± one standard deviation of tunnel concentration.

Background metal levels were estimated using the average ambient concentrations from PAQS daily measurements taken during November and December 2001 with obvious plume-impaction events removed. Elements with tunnel concentrations that were not significantly above detection limits or background levels were removed from the analysis; tunnel concentrations of the species considered were, on average, a factor of 7 higher than in the background. Tunnel data for trace metals that had concentrations less than the mean background concentration plus two times the background standard deviation were discarded.

Background levels of inorganic ion concentrations were estimated based on averages of US EPA's Speciation Trends Network (STN) measurements from two sites in Pittsburgh taken during the study period. Concentrations of inorganic ions in tunnel $PM_{2.5}$ were not consistently significantly elevated relative to the variable background levels.

Background NO, NO_2, and CO mixing ratios were taken as the average values of monitors operated at 5 sites in Allegheny County (Weitkamp et al., 2005); NO_x concentrations in the tunnel were at least a factor of 14 above background levels. A composite diurnal profile for background CO_2 was constructed based on measurements taken periodically from the ventilation air.

3. Results and discussion

3.1. Fleet composition and traffic characteristics

The average diurnal traffic flow rate, vehicle speed and fleet-fuel usage are shown in Fig. 2a–c. A consistent, weekday diurnal traffic pattern was evident throughout the study. Average traffic characteristics for the specific periods selected for manual sampling are listed in Table 2. These periods encompass a range of fleet compositions and vehicle operating conditions. The morning rush-hour period (6:30–9:00 AM) was dominated by slow-moving light-duty traffic; on a number basis trucks comprised only 3% of vehicles, which is equivalent to 11% of fuel use (Eq. (1)). During the mid-day period from 10 AM to 4:30 PM, the traffic volume decreased slightly and both the average speed and the proportion of HDDV increased. HDDV were

most prevalent during the early morning hours (between 12 and 6 AM); during this period traffic flow thinned to a quarter of its daytime level and average speed increased to 57 mph. The data indicate that the diurnal variation in fleet composition was largely due to changes in LDV volume; the HDDV traffic volume was relatively constant throughout the day.

Adequate video data for fleet composition identification were available for slightly more than half of the manual sampling periods. In cases where direct counting of vehicles was not possible (for example when it was raining), fleet composition was defined using the ratio of background-corrected NO_x and CO_2 mixing ratios measured in the tunnel. A linear regression of NO_x/CO_2 data from high traffic periods onto HDDV fuel consumption fraction yielded an excellent fit ($R^2 = 0.92$). This regression equation was then used to derive estimated fleet fuel use for those periods when video data were not available.

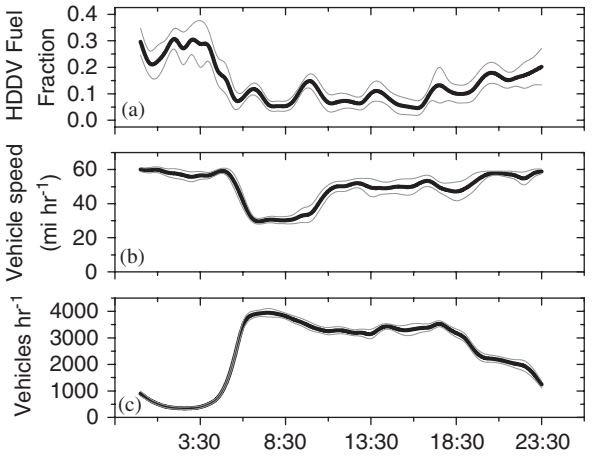

Fig. 2. Average diurnal profile of (a) heavy duty fuel use, (b) vehicle speed and (c) traffic volume in the Squirrel Hill Tunnel during the November 2002 study. In-use fleet fuel use is expressed as a fraction of fuel consumed by diesel vehicles and was estimated from traffic composition data using Eq. (1). Heavy line indicates average profile with light lines indicating ± one standard deviation.

3.2. Period average emission characteristics

Aggregated fuel-based emission factors for each sampling period were calculated by averaging emission factors weighted with the average fuel consumption during the individual sample periods. The sum of the background-corrected CO and CO_2 concentrations was used as the measure of fuel consumption.

Period average fleet fuel use and emission factors for $PM_{2.5,}$ OC (with and without positive artifact correction), EC and elemental metals are shown in Table 3. Background-corrected fine particle mass in the tunnel was largely carbonaceous in nature, with study average composition of 44% organic material (OM = artifact-corrected OC × 1.2 (Turpin and Lim, 2001)), 42% EC, 5% sulfate, 2% ammonium, 2% chloride, 1% other inorganic and 4% elemental metals. Filter measurements for speciated fine particle concentrations collected in the tunnel exhibited good mass closure with gravimetric mass measurements with the sum of background-corrected $PM_{2.5}$ components accounting for an average of 97 ± 18% of the gravimetrically determined $PM_{2.5}$ mass. The OC positive artifact correction for each sampling period was 18 ± 6% of the total OC mass measured on the bare quartz filter.

The results in Table 3 indicate that the emission factors for many pollutants depend on fleet composition. For example, the fleet-wide fuel-based $PM_{2.5}$ emission factor is two times higher during the HDDV dominated early-morning hours than during the LDV-dominated rush-hour period. EC and OC emissions show a similar trend. Therefore, the emission factors for HDDV are significantly higher than those for LDV. Variability between measurements made on different days during the same sampling period is relatively small compared to the variations between sampling periods.

Table 2
Summary of sampling period traffic conditions

Period	Time	Speed (miles h^{-1})	Traffic volume (vehicles h^{-1})	% HDDV (count basis)	% HDDV (fuel basis)
Early morning (high truck)	12 AM–6 AM	56.5 ± 1.5	860 ± 70	14.5 ± 4.0	36 ± 8
Rush hour (low speed)	7 AM–9 AM	30.4 ± 3.0	3860 ± 180	3.4 ± 0.5	11.0 ± 1.6
Mid-day (high speed)	10 AM–4:30 PM	49.3 ± 3.8	3290 ± 150	6.0 ± 1.1	19.2 ± 2.1

Table 3
Measured tunnel emission factors

	Units	High-speed (mid-day)	Low-speed (Rush-hour)	High truck (early morning)
% HDDV	% fuel	**19±2**	**11±2**	**36±8**
$PM_{2.5}$	mg (kg fuel)$^{-1}$	**158±29**	**189±23**	**437±76**
EC	mg (kg fuel)$^{-1}$	**110±44**	**74±27**	**153±27**
OC (Q-QBT)	mg (kg fuel)$^{-1}$	**64±28**	**61±7**	**115±21**
OC (Bare Q)	mg (kg fuel)$^{-1}$	**82±29**	**74±5**	**139±12**
NO_X	G (kg fuel)$^{-1}$	**11±2**	**8±1**	**18±4**
NH_3	mg (kg fuel)$^{-1}$	**183±87**	**274±72**	**272±46**
Al	μg (kg fuel)$^{-1}$	**1660±930**	**850±690**	N/A
As	μg (kg fuel)$^{-1}$	N/A	2.3±1.0	5±13
Ba	μg (kg fuel)$^{-1}$	**360±50**	**450±110**	**250±50**
Ca	μg (kg fuel)$^{-1}$	**1270±240**	**840±490**	**2200±1200**
Ce	μg (kg fuel)$^{-1}$	**2.9±0.7**	**2.3±1.2**	**4.4±2.1**
Cs	μg (kg fuel)$^{-1}$	**4.0±1.0**	**2.2±1.0**	**4.1±2.8**
Cu	μg (kg fuel)$^{-1}$	**145±19**	**209±54**	**98±65**
Fe	μg (kg fuel)$^{-1}$	**5400±800**	**4900±1300**	**7000±2100**
Ga	μg (kg fuel)$^{-1}$	**15.1±1.8**	**24.7±5.3**	6.7±9.9
Li	μg (kg fuel)$^{-1}$	N/A	4.1±2.4	**47±26**
Mg	μg (kg fuel)$^{-1}$	**163±20**	**590±150**	**1100±300**
Mn	μg (kg fuel)$^{-1}$	**48±7**	**92±25**	**400±90**
Mo	μg (kg fuel)$^{-1}$	**42.4±5.1**	**10.5±2.4**	3.9±8.0
Pb	μg (kg fuel)$^{-1}$	N/A	19±6	45±54
Rb	μg (kg fuel)$^{-1}$	N/A	3.0±0.6	3.6±8.0
Sb	μg (kg fuel)$^{-1}$	**31±4**	**57±12**	**17±8**
Sr	μg (kg fuel)$^{-1}$	**11.2±1.4**	**11.1±2.8**	**10.6±5.3**
Ti	μg (kg fuel)$^{-1}$	**53.7±7.0**	**89.6±23.3**	**54.9±37.8**
Zn	μg (kg fuel)$^{-1}$	70±9	**290±70**	**2100±820**

Emission factors that are statistically significant relative to inter-sample variation and background concentrations are in underlined, bold text. N/A = tunnel concentrations below background.

3.2.1. Metals emissions

Fig. 3 and Table 3 indicate that fine particle metal emissions were dominated by Fe, Ca, Al, Zn and Mg. Concentrations of Ba, Cu, Mn, Ti, Ce, Cs, Ga, Li, Mo, Sb and Sr were also significantly above background levels during all sampling periods, while Ga, Li and Mo were not significantly elevated relative to background levels during some sampling periods.

Fe, Ca, Al and Mg are associated with crustal components of road dust (Lough et al., 2005). Ca, Ti, Fe, Zn, Ba, Cu, Sr and Sb particles have been associated with brake-wear (Garg et al., 2000; Sternbeck et al., 2002), but there is large variation in reported emission rates due to variations in sampling conditions and brake-pad compounds. Rb, Pt, and Pd emissions are associated with degradation of catalytic converters (Lough et al., 2005); Rb and Pd were not elevated relative to background, and Pt was not measured.

Fig. 3 shows that Ca, Mg, Zn, Mn, Mo, Sb, and to a lesser extent Fe, emissions all exhibit significant variation with sample period and thus appear influenced by the fleet composition and/or vehicle speed. Emissions of Ca, Mg, Zn and Mn were significantly higher during the early-morning, HD-vehicle-dominated testing period. Gertler et al. (2002) found HD vehicles to emit significantly more Ca and Fe than LD vehicles. However, they also report a lower Mg emission factor for HD vehicles than LDV—the opposite of what was observed here. Zn in particular has been has been found to be emitted in larger quantities by HDDV in other studies (Lowenthal et al., 1994; Gillies et al., 2001).

Ba, Cu and Sb are associated with brake wear particles (Garg et al., 2000); emissions of these elements were all significantly higher during the morning rush-hour period. Average speed during this period was 30 mph and is much more variable, indicating more brake usage than other periods. The ratio of Cu and Sb measured in the tunnel match the diagnostic criteria of 4.6±2.3 proposed by Sternbeck et al. (2002) for brake wear. Ga emissions were also highest during this period.

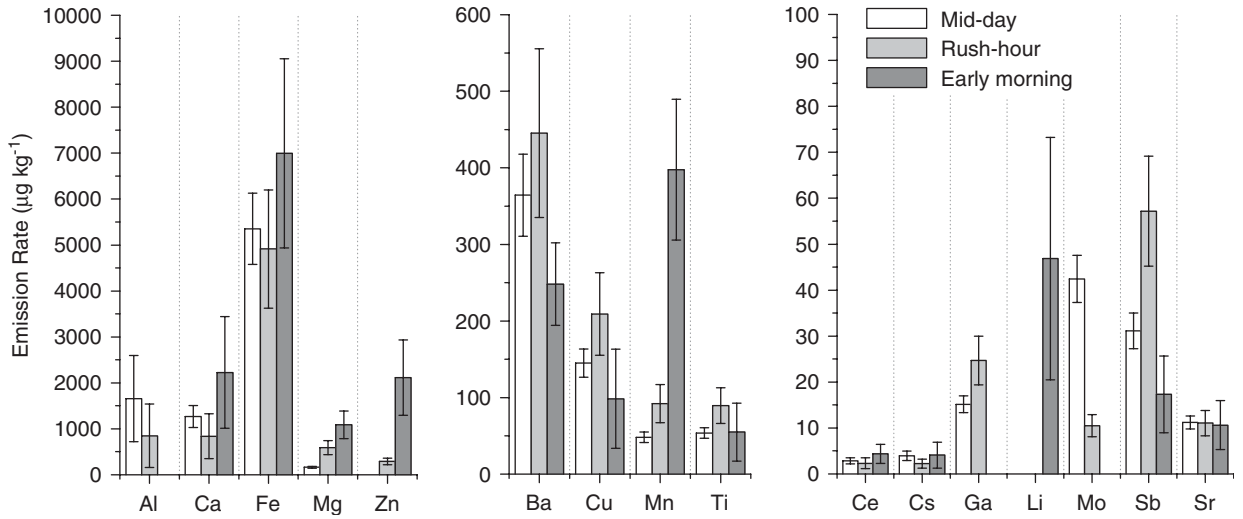

Fig. 3. Period-average emission factors for elemental metals from the three different manual sampling periods. Error bars represent the standard deviation of samples collected on different days.

Table 4
$PM_{2.5}$, EC and OC emission factors measured during the rush-hour period in November 2002 and July/August, 2004

		Nov. 2002	July/Aug. 2004
	Temp. (°C)	9±3	26±2
	N	3	14
	$PM_{2.5}$ (mg (kg fuel $^{-1}$)	188±23	213±31
	EC (mg-C (kg fuel) $^{-1}$)	74±27	111±19
Artifact-corrected (Q-QBT)[a]	OC (mg-C (kg fuel) $^{-1}$)	61±7	29±4
	OC/EC	1.0±0.6	0.29±0.05
Not artifact-corrected (BareQ)[b]	OC (mg-C (kg fuel)$^{-1}$)	74±5	60±5
	OC/EC	1.2±0.6	0.48±0.08
Artifact Correction	QBT/Q	18±6%	35±7%

[a]Artifact-corrected OC is determined by subtracting the OC measured on quartz backup filter (QBT) from the OC measured on the Bare Q filter.
[b]Bare quartz filter (Bare Q)–OC measurement includes positive artifact gas-phase material adsorbed onto filter.

The Mo emission rate is significantly higher during the mid-day sampling period—a period of higher speed, more car-dominated traffic than other periods. Mo is used as a component of automotive catalysts and as an anti-friction additive in lubricating oils.

3.2.2. Seasonal shift in particle OC emissions

Comparing the measurements of $PM_{2.5}$ mass, EC and OC emissions made during the November 2002 and the July 2004 studies provides insight into seasonal changes in emissions. Both studies measured emissions during the early morning rush-hour period (6:30–9:30 AM). Fleet composition and traffic flow during this period were similar in both studies.

Emission factors and OC sample characteristics for the fall and summer studies are compared in Table 4. The overall $PM_{2.5}$ emission rate is fairly consistent between the summer and fall periods, but there is a significant shift in the composition of the emissions. EC emissions are modestly higher in the summer, but artifact-corrected OC emissions are reduced by a factor of 2. During the summer the OC/EC ratio of emissions was 0.26±0.06 versus 1.0±0.6 in the fall.

A potential explanation for this shift in emissions is that changes in ambient temperature influence the gas-particle phase partitioning of the OC emissions. The average temperature during the summer study was 16 °C higher than during the fall study. The hypothesis is that under cooler fall conditions a

larger fraction of the semi-volatile emissions exists in the particle phase compared to summer conditions. Recent dilution sampling measurements have shown that sampling conditions can cause large shifts in the partitioning of semi-volatile organics in engine emissions (Lipsky and Robinson, 2006). A roadside study also found significant volume loss of volatile material from freshly emitted particles upon heating (Kuhn et al., 2005).

Careful examination of the quartz filter OC data provides evidence that supports the hypothesis that there are significant seasonal differences in the gas-particle partitioning of the OC emissions. As is seen in Table 4, little seasonal dependence exists in the OC emission factors calculated with non-artifact-corrected bare quartz filters; however, a factor of 2 more OC is collected by the back up quartz filter (QBT) during the summer than during the fall. This is consistent with a much larger fraction of the emitted organic material remaining in the gas phase during the summer sampling period. The sampling flow rates, total sample volumes and filter loadings were essentially the same in both sets of measurements, minimizing potential biases due to the dependence of sampling artifacts on collection time, face velocity, and OC loading on the filter (Subramanian et al., 2004). While artifact corrections are imperfect measures of gas-particle partitioning of organic matter (Turpin et al., 2000), the data strongly suggests that ambient conditions are having a significant impact on the partitioning of freshly emitted particles.

A comparison of the $PM_{2.5}$ mass measured with the TEOM and MOUDI during the fall study provides additional evidence for the loss of semi-volatile mass with increased temperature. A linear regression analysis of data from the two instruments indicates that the TEOM operating at 30 °C measured 13% less $PM_{2.5}$ mass than the MOUDI during the November 2002 period ($R^2 = 0.81$, $N = 9$). The average temperature inside the tunnel was 9 °C versus 30 °C in the TEOM. Roughly half the $PM_{2.5}$ mass in the tunnel is organic material, while only 3% is ammonium nitrate. Therefore, a significant fraction of the mass discrepancy between the TEOM and the MOUDI data is likely due to loss of semi-volatile organic matter in the TEOM. Assuming all mass lost in the TEOM is volatilized OM explains the seasonal discrepancy in measured OC emission rates.

Another potential explanation for the seasonal shift in OC/EC emissions is changes in fuel composition. Regulations require gasoline sold in southwestern Pennsylvania to have substantially lower Reid vapor pressure (RVP) during the May–September ozone season (EPA, 2003). Reformulated gasoline (RFG) has been demonstrated to have a large impact on gaseous emissions (Kirchstetter et al., 1996). However, Norbeck et al. (1998) found little difference in the fine particle emissions from LDVs operating on California Phase 2 summer time RFG and pre-reformulation gasoline.

3.2.3. Gas-phase species emission rates

NO_x and NH_3 emission factors for each sample period are given in Table 3. Concentrations of both of these pollutants inside the tunnel were significantly higher than background levels. Fleet composition has a significant impact on NO_x emission factors; the early-morning (high-truck) period emission factor is twice that during the rush-hour period. The emission factor for gas-phase NH_3 was relatively constant across testing periods (Table 3). The study average ammonia emission factor is 243 ± 122 mg (kg fuel)$^{-1}$, which is significantly lower than values reported in a recent tunnel study conducted in California by Kean et al. (2000).

3.3. LDV and HDDV emission rates

Table 3 indicates there is a strong dependence of overall emission factors of several species on the fleet composition in the tunnel, with HDDV emitting significantly more on a fuel basis than LDV. Previous studies have performed linear regressions of emission data as a function of fleet composition to estimate HDDV and LDV emission factors (Gertler et al., 2002; Fraser et al., 2003). Results from a similar analysis of the Squirrel Hill tunnel data are summarized in Figs. 4a–d.

Fig. 4a shows NO_x emission factors plotted versus HDDV fuel use; a least-squares linear regression fit to the data is used to estimate HDDV and LDV emission factors. The results show that NO_x emission factor is well correlated with estimated diesel and gasoline fuel consumption ($R^2 = 0.74$). The extrapolated value for HDDV agrees well with values from the literature shown in Fig. 4a. The extrapolated value for LDV NO_x emission factor is somewhat lower than many published values but similar to those found by Durbin et al. (1999) in a dynamometer study of model-year 1991–97 gasoline vehicles.

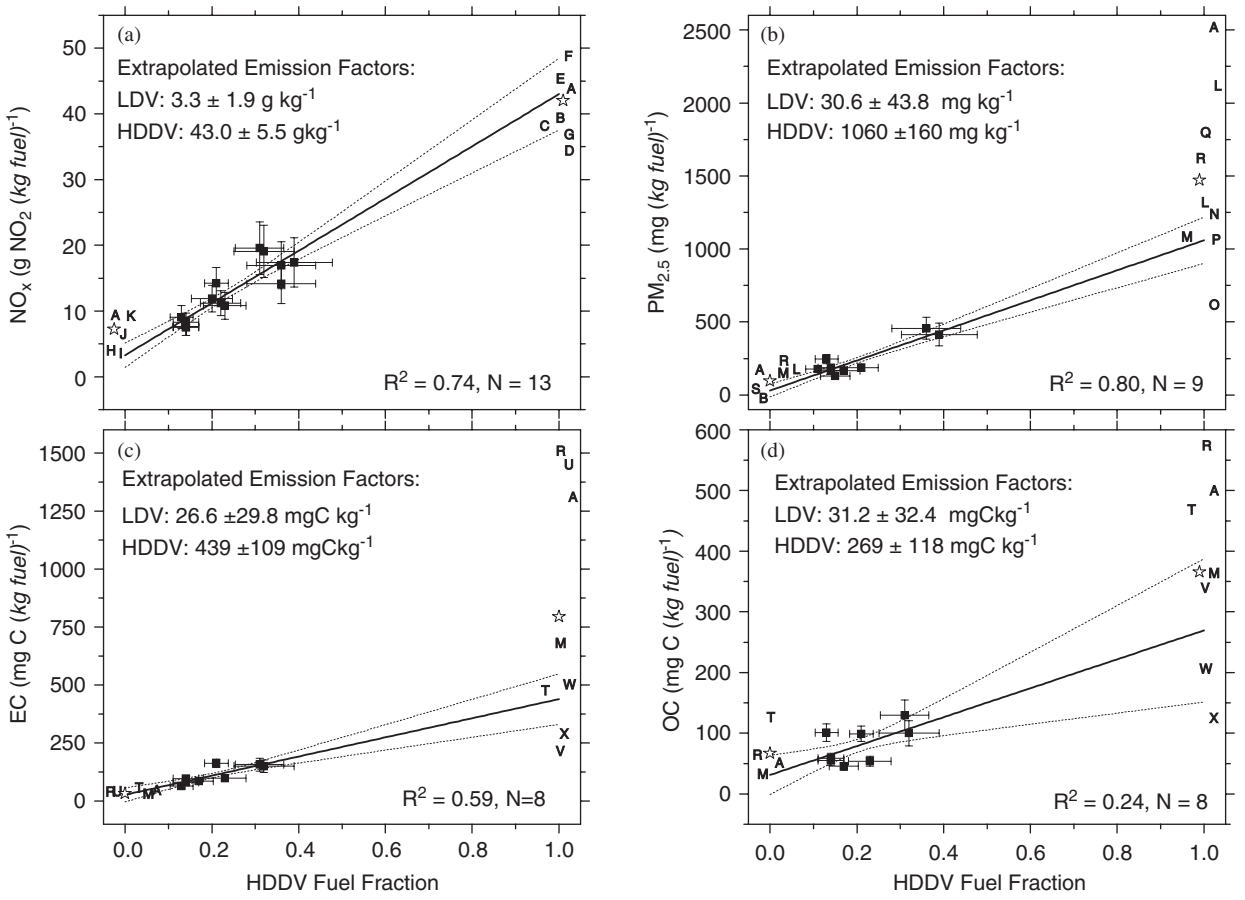

Fig. 4. (a) NO_x, (b) $PM_{2.5}$, (c) EC, and (d) OC emission factors as a function of the fraction of fuel used by HDDV. Best-fit linear regression line is shown along with 69% confidence intervals for the fit. OC is artifact-corrected OC. Letters indicate emission factors reported in the literature: (A) (Kirchstetter et al., 1999), (B) (Pierson et al., 1996) Tuscarora Tunnel, (C) (Pierson et al., 1996) Ft. McHenry Uphill, (D) (Pierson et al., 1996) Ft. McHenry Downhill, (E) (Jimenez et al., 2000), (F) (Rogak et al., 1998), (G) (Yanowitz et al., 1999), (H) (Cadle et al., 1999), (I) (Durbin et al., 1999), (J) (Kean et al., 2003), (K) (McGaughey et al., 2004), (L) (Mazzoleni et al., 2004), (M) (Allen et al., 2001), (N) (Lowenthal et al., 1994), (O) (Morris et al., 1998), (P) (Fraser et al., 2002), (Q) (Yanowitz et al., 2000), (R) (Hildemann et al., 1991), (S) (Zielinska et al., 2004), (T) (Rogge et al., 1993), (U) (Miguel et al., 1998), (V) (Shah et al., 2004) Creep, (W) (Shah et al., 2004) Transient, (X) (Shah et al., 2004) Cruise. Average of published emission factors for gasoline and diesel vehicles are shown with stars.

The agreement of the emission factors estimated here with those from others' work suggests that vehicle classes are being accurately separated using traffic count and video data.

Similar regressions for $PM_{2.5}$, EC and OC emission factors versus fleet composition yield estimates for LDV and HDDV emission factors; in all cases the fuel-based emission factors for HDDV are significantly larger than for LDV. Fig. 4b shows that the $PM_{2.5}$ mass emission factors based on the MOUDI measurements are well correlated with fleet fuel use ($R^2 = 0.80$). On a fuel basis, HDDV emit a factor of 25–40 more $PM_{2.5}$ mass than LDV.

EC emission factors, shown in Fig. 4c, are modestly correlated with fleet fuel usage ($R^2 = 0.58$). The extrapolated LDV EC emission factor is highly uncertain but significantly smaller than the extrapolated HDDV EC emission factor. Under the hot-stabilized operating conditions inside the tunnel, LDV EC emissions are a factor of 10–20 lower than HDDV EC emissions.

Fig. 4d shows OC emission factors based on the positive-artifact-corrected (Bare Q−QBT) filter measurements. Again HDDV emissions are higher, but the correlation between OC emission rate and diesel fuel fraction is poor ($R^2 = 0.24$), significantly worse than for other species. This indicates wider

variability in OC emissions from vehicles and/or inconsistent artifact corrections. OC emission rates calculated based on Bare-Q data (not-artifact-corrected) are modestly higher but do not provide better correlations with fuel use, suggesting that variation in OC emission rates is not associated with artifact correction.

Comparison of the estimated vehicle-class $PM_{2.5}$, EC and OC emission factors to values from the literature show that they generally fit within the wide range of published values. Fig. 4b–d plot a selection of published $PM_{2.5}$, EC and OC emission factors for LDV and HDDV. The LDV $PM_{2.5}$ emission factor estimated here is a factor of 2 lower than many of the literature values shown in Fig. 4b, while the estimated HDDV $PM_{2.5}$ emission factor shows better agreement with prior work. The extrapolated LDV EC emission factor shown in Fig. 4c is consistent with values from the literature, but the extrapolated HDDV EC emission factor is roughly a factor of 3 lower than that found in many other studies. Extrapolated LDV and HDDV OC emission factors are both lower than values reported in many studies, the value for HDDV significantly so. The seasonal variation in measured OC emission factors discussed above provides a potential explanation for large variability in the published values.

4. Conclusions

This study was carried out to provide a detailed characterization of motor vehicle emissions in conjunction with the Pittsburgh Air Quality Study. Emission factors were determined from tunnel data collected during three distinct periods: early morning (high proportion of heavy-duty vehicles), midday (high speed, mixed fleet) and rush hour (low speed, low proportion of heavy-duty vehicles). Emissions of NO_x, $PM_{2.5}$, OC and EC had a strong dependence on sample period, as did many of the metals sampled, indicating a strong influence of fleet composition and operating conditions on emissions. Estimates for emission factors for light-duty gasoline vehicles and heavy-duty diesel vehicles were determined by performing a linear regression on the emissions and fleet composition data.

OC emissions were more variable than other pollutants. Measurements made in the summer also indicate a significant seasonality in OC emission factors. There is evidence that these changes may be due to changes in partitioning of semi-volatile organic compounds associated with seasonal changes in ambient temperature. If this is the case, the impact of ambient conditions on sampling of organic particulate matter must be considered when measuring and interpreting emissions data. Further work in this area is necessary to elucidate the nature and evolution of organic PM from vehicles and other combustion sources.

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References

Allen, J.O., Mayo, P.R., et al., 2001. Emissions of size-segregated aerosols from on-road vehicles in the Caldecott Tunnel. Environmental Science & Technology 35 (21), 4189–4197.

BTS, 2001. Transportation Indicators Report, Bureau of Transportation Statistics.

Cabada, J.C., Rees, S., et al., 2004. Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh supersite. Atmospheric Environment 38 (20), 3127–3141.

Cadle, S.H., Mulawa, P.A., et al., 1999. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. Environmental Science & Technology 33 (14), 2328–2339.

Chellam, S., Kulkarni, P., et al., 2005. Emissions of organic compounds and trace metals in fine particulate matter from motor vehicles: a tunnel study in Houston, Texas. Journal of the Air & Waste Management Association 55 (1), 60–72.

Chow, J.C., Watson, J.G., 1998. Guideline on Speciated Particulate Monitoring, DRI.

Durbin, T.D., Norbeck, J.M., et al., 1999. Particulate emission rates from light-duty vehicles in the South Coast air quality management district. Environmental Science & Technology 33 (24), 4401–4406.

EIA, 1994. Residential Transportation Energy Consumption Survey. US Energy Information Administration.

EPA, 2003. Guide on Federal and State Summer RVP Standards for Conventional Gasoline Only. US Environmental Protection Agency.

Fraser, M.P., Buzcu, B., et al., 2003. Separation of fine particulate matter emitted from gasoline and diesel vehicles using chemical mass balancing techniques. Environmental Science & Technology 37 (17), 3904–3909.

Fraser, M.P., Lakshmanan, K., et al., 2002. Variation in composition of fine particulate emissions from heavy-duty vehicles. Journal of Geophysical Research 107 (D21).

Garg, B.D., Cadle, S.H., et al., 2000. Brake wear particulate matter emissions. Environmental Science & Technology 34 (21), 4463–4469.

Gertler, A.W., Gillies, J.A., Pierson, W.R., Rogers, C.F., Sagebiel, J.C., Abu-Allaban, M., et al., 2002. Real-world particulate matter and gaseous emissions from motor vehicles in a highway tunnel. Health Effects Institute, 1–92.

Gillies, J.A., Gertler, A.W., et al., 2001. On-road particulate matter ($PM_{2.5}$ and PM_{10}) emissions in the Sepulveda Tunnel, Los Angeles, California. Environmental Science & Technology 35 (6), 1054–1063.

Hildemann, L.M., Markowski, G.R., et al., 1991. Chemical-composition of emissions from urban sources of fine organic aerosol. Environmental Science & Technology 25 (4), 744–759.

Jimenez, J.L., McRae, G.J., et al., 2000. Remote sensing of NO and NO_2 emissions from heavy-duty diesel trucks using tunable diode lasers. Environmental Science & Technology 34 (12), 2380–2387.

Kean, A.J., Harley, R.A., et al., 2000. On-road measurement of ammonia and other motor vehicle exhaust emissions. Environmental Science & Technology 34 (17), 3535–3539.

Kean, A.J., Harley, R.A., et al., 2003. Effects of vehicle speed and engine load on motor vehicle emissions. Environmental Science & Technology 37 (17), 3739–3746.

Kirchstetter, T.W., Singer, B.C., et al., 1996. Impact of oxygenated gasoline use on California light-duty vehicle emissions. Environmental Science & Technology 30 (2), 661–670.

Kirchstetter, T.W., Harley, R.A., et al., 1999. On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles. Atmospheric Environment 33 (18), 2955–2968.

Kuhn, T., Biswas, S., et al., 2005. Physical and chemical characteristics and volatility of PM in the proximity of a light-duty vehicle freeway. Aerosol Science and Technology 39 (4), 347–357.

Kuhns, H.D., Mazzoleni, C., et al., 2004. Remote sensing of PM, NO, CO and HC emission factors for on-road gasoline and diesel engine vehicles in Las Vegas, NV. Science of the Total Environment 322 (1–3), 123–137.

Lipsky, E.M., Robinson, A.L., 2006. Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke. Environmental Science & Technology 40 (1), 155–162.

Lough, G.C., Schauer, J.J., et al., 2005. Emissions of metals associated with motor vehicle roadways. Environmental Science & Technology 39 (3), 826–836.

Lowenthal, D.H., Zielinska, B., et al., 1994. Characterization of heavy-duty diesel vehicle emissions. Atmospheric Environment 28 (4), 731–743.

Mazzoleni, C., Kuhns, H.D., et al., 2004. On-road vehicle particulate matter and gaseous emission distributions in Las Vegas, Nevada, compared with other areas. Journal of the Air & Waste Management Association 54 (6), 711–726.

McGaughey, G.R., Desai, N.R., et al., 2004. Analysis of motor vehicle emissions in a Houston tunnel during the Texas Air Quality Study 2000. Atmospheric Environment 38 (20), 3363–3372.

Miguel, A.H., Kirchstetter, T.W., et al., 1998. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environmental Science & Technology 32 (4), 450–455.

Morris, J.A., Bishop, G.A., et al., 1998. On-road remote sensing of heavy-duty diesel truck emissions in the Austin—San Marcos Area. University of Denver, Denver, CO.

Norbeck, J.M., Durbin, T.D., et al., 1998. Characterization of particulate emissions from gasoline-fueled vehicles. California Air Resources Board.

Pekney, N.J., Davidson, C.I., 2005. Determination of trace elements in ambient aerosol samples. Analytica Chimica Acta 540 (2), 269–277.

Pierson, W.R., Gertler, A.W., et al., 1996. Real-world automotive emissions—summary of studies in the Fort McHenry and Tuscarora Mountain Tunnels. Atmospheric Environment 30 (12), 2233–2256.

Rogak, S.N., Pott, U., et al., 1998. Gaseous emissions from vehicles in a traffic tunnel in Vancouver, British Columbia. Journal of the Air & Waste Management Association 48 (7), 604–615.

Rogge, W.F., Hildemann, L.M., et al., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science & Technology 27 (4), 636–651.

Shah, S.D., Cocker, D.R., et al., 2004. Emission rates of particulate matter and elemental and organic carbon from in-use diesel engines. Environmental Science & Technology 38 (9), 2544–2550.

Sternbeck, J., Sjodin, A., et al., 2002. Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. Atmospheric Environment 36 (30), 4735–4744.

Subramanian, R., Khlystov, A.Y., et al., 2004. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. Aerosol Science and Technology 38, 27–48.

Takahama, S., Wittig, A.E., et al., 2004. Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study. Journal of Geophysical Research-Atmospheres 109 (D16).

Tang, W., Raymond, T., et al., 2004. Spatial variations of $PM_{2.5}$ during the Pittsburgh air quality study. Aerosol Science and Technology 38, 80–90.

Turpin, B.J., Lim, H.J., 2001. Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass. Aerosol Science and Technology 35 (1), 602–610.

Turpin, B.J., Saxena, P., et al., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmospheric Environment 34 (18), 2983–3013.

USDOT, 2004. Summary of Fuel Economy Performance. US Department of Transportation.

VIUS, 2002. Vehicle Inventory and Use Survey. US Census Bureau.

Weitkamp, E., Lipsky, E., et al., 2005. Fine particle emission profile for a large coke production facility based on highly time resolved fence line measurements. Atmospheric Environment 39 (36), 6719–6733.

Yanowitz, J., Graboski, M.S., et al., 1999. Chassis dynamometer study of emissions from 21 in-use heavy duty diesel vehicles. Environmental Science & Technology 33 (2), 209–216.

Yanowitz, J., McCormick, R.L., et al., 2000. In-use emissions from heavy-duty diesel vehicles. Environmental Science & Technology 34 (5), 729–740.

Zielinska, B., Sagebiel, J., et al., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. Journal of the Air & Waste Management Association 54 (9), 1138–1150.