

## Vehicular particulate matter emissions in road tunnels in Sao Paulo, Brazil

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**Abstract** In the metropolitan area of São Paulo, Brazil, ozone and particulate matter (PM) are the air pollutants that pose the greatest threat to air quality, since the PM and the ozone precursors (nitrogen oxides and volatile organic compounds) are the main source of air pollution from vehicular emissions. Vehicular emissions can be measured inside road tunnels, and those measurements can provide information about emission factors of in-use vehicles. Emission factors are used to estimate vehicular

emissions and are described as the amount of species emitted per vehicle distance driven or per volume of fuel consumed. This study presents emission factor data for fine particles, coarse particles, inhalable particulate matter and black carbon, as well as size distribution data for inhalable particulate matter, as measured in March and May of 2004, respectively, in the Jânio Quadros and Maria Maluf road tunnels, both located in São Paulo. The Jânio Quadros tunnel carries mainly light-duty vehicles, whereas the Maria Maluf tunnel carries light-duty and heavy-duty vehicles. In the Jânio Quadros tunnel, the estimated light-duty vehicle emission factors for the trace elements copper and bromine were 261 and 220  $\mu\text{g km}^{-1}$ , respectively, and 16, 197, 127 and 92  $\text{mg km}^{-1}$ , respectively, for black carbon, inhalable particulate matter, coarse particles and fine particles. The mean contribution of heavy-duty vehicles to the emissions of black carbon, inhalable particulate matter, coarse particles and fine particles was, respectively 29, 4, 6 and 6 times higher than that of light-duty vehicles. The inhalable particulate matter emission factor for heavy-duty vehicles was 1.2 times higher than that found during dynamometer testing. In general, the particle emissions in São Paulo tunnels are higher than those found in other cities of the world.

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## Introduction

Located in southeastern Brazil, the Metropolitan Area of São Paulo (MASP) has approximately 18 million inhabitants and is considered a megacity. It has an unconventional mixture of vehicle types, burning a variety of fuel blends, including oxygenated fuels. In 2005, the MASP fleet consisted of approximately 6 million vehicles, including diesel-powered heavy-duty vehicles (HDVs) as well as light-duty vehicles (LDVs) that burn gasohol (consisting of 75–78% gasoline, by volume, and 22–25% anhydrous ethanol), or hydrated ethanol. Some of the LDVs, the so-called flex-fuel vehicles, are capable of running on either gasohol or ethanol.

On-road vehicle emissions are considered the main source of air pollution in the MASP. According to the São Paulo State Environmental Protection Agency, CETESB (Companhia de Tecnologia de Saneamento Ambiental), 97% of all hydrocarbon emissions are emitted by vehicles, and 40% of all inhalable particulate matter (PM<sub>10</sub>) emissions come from mobile sources (CETESB 2005). The CETESB data also shows that ozone and particulate matter are the air pollutants that pose the greatest threat to air quality in the MASP; both the hourly ozone air quality standard (82 ppbv) and the warning level (102 ppbv) are frequently exceeded. In addition, 24-h concentrations of inhalable particulate matter—that with an aerodynamic diameter of less than 10 μm (PM<sub>10</sub>)—consistently exceed the National Ambient Air Quality Standard of 50 μg m<sup>-3</sup> at several monitoring stations in the urban area of the MASP (Alonso et al. 1997). This study has been indicated that the main source for fine particulate matter (PM<sub>2.5</sub>) is the emission from heavy-duty diesel vehicles and being the black carbon its main tracer. Although the number of vehicles was less than 1 million in 1980 and now it is more than 7 millions, Pro-Alcohol and PROCONVE programs (national program for vehicular improvement of emissions factors—for instance it was 54 g km<sup>-1</sup> CO emission before 1980 and it is now 0.82 g km<sup>-1</sup>), prevented the deterioration of the air quality in Brazil. Pro-Alcohol and PROCONVE have been the major programs that effectively control air pollutants emissions through legal actions, such as increase fuels quality (desulfurization, substitution of tetraethyl lead by ethanol), and implement electronic injection and catalytic converters in the new cars (<http://www.cetesb.sp.gov.br>).

Obtaining accurate information regarding road vehicle emissions is crucial to evaluating the contribution of road traffic to environmental pollution (Colberg et al. 2005a). To that end, many researchers now calculate emission factors (EFs), which describe the emitted mass (g) of a compound, per distance (km) driven or per volume of fuel consumed (Colberg et al. 2005b). The emission of primary air pollutants have been described using EFs (Staehelin et al. 1998). These EFs can be calculated for single vehicles or for an entire fleet, as well as for categories of vehicles. The EF depends on many variables: vehicle size, type, cylinder capacity, fuel mode (gasohol or diesel), type of exhaust technology (with/without catalytic converter); driving style (acceleration and speed); road gradient; and vehicle maintenance (Colberg et al. 2005a). The EFs of single vehicles can be measured using chassis dynamometers or simple engine emission measurements (Lim et al. 2006; Yang et al. 2005; Hausberger et al. 2003; Schmitz et al. 2000). However, dynamometer tests cannot accurately reflect the potential importance of on-road factors such as actual driving conditions and evaporative emissions from fuel tanks (Kawaashima et al. 2006). Measurements of air pollutants in road tunnels can be used to quantify on-road traffic emissions. Tunnel studies can provide collective information on in-use vehicles, and such information can be used to describe actual traffic emissions. The main advantage of tunnel studies is that they provide an opportunity to calculate on-road EFs for a large number of vehicles (Colberg et al. 2005a).

Emission inventories are essential to our understanding of air quality and climate change issues on local scales, as well as on regional and global scales. The inventories catalog and quantify the pertinent data regarding the atmospheric emissions of all relevant species. The relevant species are those that either directly affect changes in air quality/climate or are precursors of atmospheric species of concern. These emissions are difficult to accurately estimate, since such estimations must integrate the EFs for a diverse, constantly evolving vehicle fleet multiplied by highly variable activity factors (e.g., average kilometers driven per unit time for each vehicle type under varying vehicle operating conditions; Parrish 2006).

In this study, the EFs were calculated from measurements taken in March and May of 2004 in

two tunnels located in the MASP: the Jânio Quadros (JQ) tunnel and the Maria Maluf (MM) tunnel. Many previous studies were performed related to the aerosol characterization in Sao Paulo. Substantial effort was applied in the air pollution source identification. After applying receptor modeling to the aerosol mass concentration data set observed in Sao Paulo, emission sources were characterized as vehicles, solid waste incineration, vegetation, suspended soil dust, and burning of fuel oil (Orsini et al. 1986; Andrade et al. 1994; Alonso et al. 1997; Castanho and Artaxo 2001; Sánchez-Ccoyllo and Andrade 2002). According to Landulfo et al. (2003), the LIDAR profiles measurement revealed the existence of important quantities of aerosols concentration at altitudes between 2,500 and 5,550 m above the LIDAR site, as well as in the altitude range between 1,500 and 2,000 m over the city of Sao Paulo. Also, Colón et al (2001) surveyed the ambient air to identify and quantify the volatile organic compound (VOCs). They demonstrated for Sao Paulo that the mean concentrations of single-ring aromatics are two to three times and volatile aldehydes are five to ten times higher as compared in the Los Angeles, USA. Their results can be used as input for urban air quality dispersion models used in the MASP, as well as to corroborate the official emission inventory for the particulate matter emitted by vehicles.

In the present study, we report the results of in-tunnel field measurements of atmospheric aerosols. The main objectives of this study were to calculate on-road particulate matter EFs for in-use vehicles and to characterize the particle size distribution of vehicle emissions. Gaseous EFs in the same tunnels experiments were calculated and presented by Martins et al. (2006). Vasconcellos et al. (2003) presented the polycyclic aromatic hydrocarbons (PAHs) measurements in the same tunnels in a previous experiment performed in 2001. They showed that pyrene, chrysene and benzo[*a*]anthracene were emitted from gasohol and diesel vehicular motor exhausts, while fluoranthene was emitted mainly from light duty vehicles.

### Measurement of particulate matter

Field measurements were carried out in the JQ and MM tunnels in order to quantify the emissions of

particulate-phase aerosols from different types of vehicles. The JQ tunnel is 1,900 m in length and is located approximately 8 km from downtown São Paulo. Emissions in the JQ tunnel are primarily from LDVs (running on gasohol or ethanol). The MM tunnel is 845 m in length, is located 18 km from the JQ tunnel and carries both vehicle types (LDVs and HDVs). Simultaneous in-tunnel and ambient (external) air measurements were taken to determine the concentrations of the following: nitrogen oxide species ( $\text{NO}_x$ ); carbon monoxide (CO); carbon dioxide ( $\text{CO}_2$ ); fine particles, defined as particulate matter with an aerodynamic diameter of less than  $2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ); and coarse particles, defined as particulate matter with an aerodynamic diameter between 2.5 and  $10 \mu\text{m}$  ( $\text{PM}_{2.5-10}$ ). Samplings were performed simultaneously inside the tunnel and in the ambient air (outside the tunnel) on working days from 08:00 LT (local time) to 18:00 LT, divided into 2-h segments. In the JQ tunnel, sampling was carried out from March 23 to March 26, 2004. In the MM tunnel, sampling was carried out on May 5 and May 6, 2004.

The vehicles were classified as belonging to one of four different groups: LDVs (cars, etc.); HDVs (diesel-powered trucks and buses); motorcycles; and taxis (powered by natural gas).

### Methodology

The ambient and in-tunnel measurements of  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  were taken simultaneously using a Mini-Vol<sup>TM</sup> Air Sampler (Airmetrics, Eugene, OR, USA) operated at a rate of  $7 \text{ l min}^{-1}$  (Baldauf et al. 2001). For the chemical species used to calculate EFs in this study, 2-h samplings (five per day) were performed (Tables 1 and 2). Only the tunnel size distribution of particulate matter, which was determined only inside the tunnel, was measured using a single-nozzle impactor, the micro-orifice uniform deposit impactor (MOUDI<sup>TM</sup>; MSP Corporation, Shoreview, MN, USA), which separates the particulate matter in ten different stages. The nominal 50% cutoff point ( $D_{50}$ ) sizes are as follows:  $<0.1 \mu\text{m}$  (after-filter);  $0.1 \mu\text{m}$ ;  $0.32 \mu\text{m}$ ;  $0.56 \mu\text{m}$ ;  $1.0 \mu\text{m}$ ;  $1.8 \mu\text{m}$ ;  $3.2 \mu\text{m}$ ;  $5.6 \mu\text{m}$ ;  $10 \mu\text{m}$ , and  $18 \mu\text{m}$  (inlet cut point; Marple et al. 1991). The MOUDI has rotating impaction plates that provide nearly uniform deposits over circular impaction areas (Marple et al. 1991).

**Table 1** Traffic volumes (total vehicles) and percentage of HDVs in the JQ tunnel by sampling period

Date	Time (LT)	LDVs	HDVs	Motorcycles	Taxis	Total	% HDVs
Number of vehicles							
3/23/2004	08:00–10:00	4,128	52	342	188	4,710	1.1
	10:00–12:00	4,244	136	334	222	4,936	2.8
	12:00–14:00	4,866	194	328	252	5,640	3.4
	14:00–16:00	5,004	234	446	182	5,866	4.0
	16:00–18:00	6,804	442	604	260	8,110	5.5
3/24/2004	08:00–10:00	4,358	100	384	204	5,046	2.0
	10:00–12:00	4,008	122	390	250	4,770	2.6
	12:00–14:00	5,790	214	418	234	6,656	3.2
	14:00–16:00	5,250	384	492	254	6,380	6.0
	16:00–18:00	6,998	528	674	230	8,430	6.3
3/25/2004	08:00–10:00	4,404	110	392	208	5,114	2.2
	10:00–12:00	4,116	202	424	230	4,972	4.1
	12:00–14:00	5,376	168	384	220	6,148	2.7
	14:00–16:00	5,104	244	548	248	6,144	4.0
	16:00–18:00	6,834	226	622	284	7,966	2.8
3/26/2004	08:00–10:00	4,116	208	386	180	4,890	4.3
	10:00–12:00	4,120	300	450	222	5,092	5.9
	12:00–14:00	5,632	426	486	278	6,822	6.2

LDVs Light-duty vehicles (gasohol), HDVs heavy-duty vehicles (diesel), Taxis (natural gas)

Nucleopore filters with a pore-size of 8  $\mu\text{m}$  (Corning CoStar, Cambridge, MA, USA) were used from the 0.32- $\mu\text{m}$  stage to the inlet, and a 1- $\mu\text{m}$  pore-size Teflon-backed filter with a diameter of 37 mm was used at the after-filter stage. More details about measurements performed in-tunnel are described in Martins et al. (2006).

Mass concentrations were obtained gravimetrically using an electronic microbalance with a sensitivity of 1  $\mu\text{g}$  (CP2P; Sartorius, Gettingen, Germany). Assess-

ments were performed in a controlled-atmosphere room. Filters were equilibrated for 24 h prior to weighing. Electrostatic charges were controlled with radioactive  $^{210}\text{Po}$  sources (Castanho and Artaxo 2001). One quarter of each Nucleopore filter was submitted to particle-induced X-ray emission (PIXE) analysis method (Johansson and Campbell 1988) in order to determine the elemental composition, from aluminum to the heavier elements. The typical precision of the elemental concentration analysis is

**Table 2** Traffic volumes (total vehicles) and percentage of HDVs in the MM tunnel by time of day

Date	Time (LT)	LDVs	HDVs	Motorcycles	Taxis	Total	% HDVs
Number of vehicles							
5/5/2004	08:00–10:00	5,374	942	598	— <sup>a</sup>	6,914	13.6
	10:00–12:00	5,442	1,222	806	— <sup>a</sup>	7,470	16.4
	12:00–14:00	5,532	1,102	660	— <sup>a</sup>	7,294	15.1
	14:00–16:00	6,002	1,290	834	— <sup>a</sup>	8,126	15.9
	16:00–18:00	7,250	1,092	968	— <sup>a</sup>	9,310	11.7
5/6/2004	08:00–10:00	4,620	844	422	198	6,084	13.9
	10:00–12:00	4,112	726	812	198	5,848	12.4
	12:00–14:00	5,246	1,258	784	132	7,420	17.0
	14:00–16:00	5,590	1,282	888	104	7,864	16.3
	16:00–18:00	6,562	1,074	872	116	8,624	12.5

LDVs Light-duty vehicles (gasohol), HDVs heavy-duty vehicles (diesel), Taxis (natural gas)

<sup>a</sup> Taxis were not counted on 05/05/2004

4–8% (Artaxo et al. 1999). A tandem nuclear accelerator, located in the Laboratory for the Analysis of Ion Conducting Material at the University of Sao Paulo, was used for the PIXE analysis (Artaxo et al. 2000; Artaxo and Orsini 1987; Tabacniks et al. 1987). In addition, concentrations of black carbon (BC) and elemental carbon (EC) were evaluated through reflectance analysis of each sampling filter (Artaxo and Hansson 1995) using a smoke stain reflectometer (model 43; Diffusion Systems Ltd., London, UK).

Concentrations of CO and NO<sub>x</sub>, the latter comprising nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), were measured using two CETESB-supplied automatic air pollution monitoring stations, one located at the tunnel exit (ambient air) and the other inside the tunnel.

NO<sub>x</sub> was analyzed by Chemiluminescence method using a Thermo Electron 42B analyzer with 0.5 ppbv of detection limit. For CO, nondispersive infrared technique was used and the analyzer was a Thermo Electron 48B, with 0.1 ppm of detection limit. The calibration of monitors is executed everyday at a specific hour.

Ambient-air and in-tunnel CO<sub>2</sub> concentrations were measured using a portable infrared gas analyzer (Environmental Gas Monitor-EGM-2; PP Systems, Amesbury, MA, USA).

Emission factors

Through the use of traffic counts, the exhaust pipe emission factors were separated by pollutant source (vehicle type). Emission factors for heavy-duty vehicles and light-duty vehicles were derived from measurements of fine particles, coarse particles, carbon monoxide and carbon dioxide. Particle-phase EFs for LDVs were calculated directly from the measurements of particulate matter, CO<sub>2</sub> and CO concentrations for LDVs using the following equation (McGaughey et al. 2004):

$$E_{pm} = 1000x \left( \frac{\Delta[p]}{\Delta[CO_2] + \Delta[CO]} \right) w_c, \tag{1}$$

where:  $E_{pm}$  is the EF (mass of particulate matter emitted per kg of fuel burned);  $\Delta[p]$  is the background-subtracted concentration of particle-phase particulate matter inside the tunnel ( $\mu\text{g m}^{-3}$ );  $\Delta[CO_2]$  and  $\Delta[CO]$  are the background-subtracted concentrations of CO<sub>2</sub> and CO given in micrograms of carbon per cubic meter

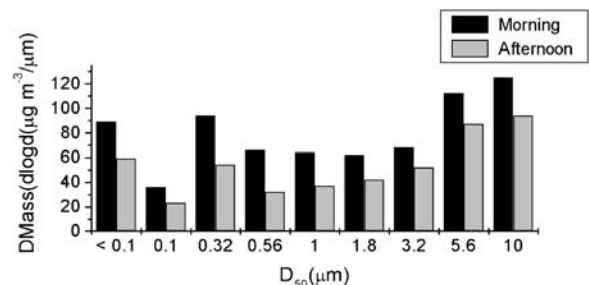
(i.e., when converting concentrations of CO<sub>2</sub> and CO from mol fraction to mass units, a molecular weight of 12 g mol<sup>-1</sup> was used instead of 44 and 28 g mol<sup>-1</sup> for CO<sub>2</sub> and CO, respectively); and  $w_c$  is the carbon weight fraction of the fuel (0.87 for diesel and 0.85 for gasohol).

In the MM tunnel, the contribution from diesel-powered HDVs could not be calculated directly from the in-tunnel measurements, since the traffic in this tunnel consisted of a combination of LDVs and HDVs (diesel-powered buses and trucks; Marr et al. 1999). To exclude the contribution of LDVs to the particulate matter concentration in the MM tunnel, pollutant concentrations were apportioned using the EFs measured in the JQ tunnel (gasohol). Concerning the uncertainties associated with using a constant carbon monoxide emission factor as a tracer for both gasoline and diesel engine emissions, 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 (Kristensson et al. 2004).

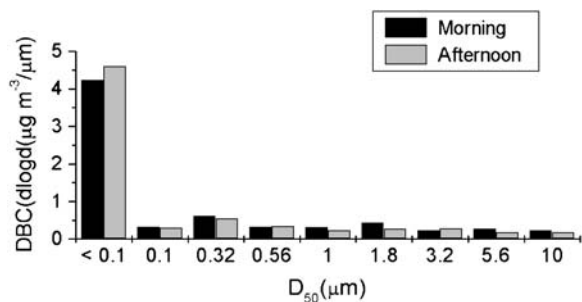
The CO<sub>2</sub> emissions were apportioned based on traffic counts and type of fuel (gasohol or diesel) using the following equation:

$$\frac{\Delta[CO_2]_D}{\Delta[CO_2]} = \frac{f_D U_D \rho_D \omega_D}{(f_D U_D \rho_D \omega_D) + ((1 - f_D) U_G \rho_G \omega_G)} \tag{2}$$

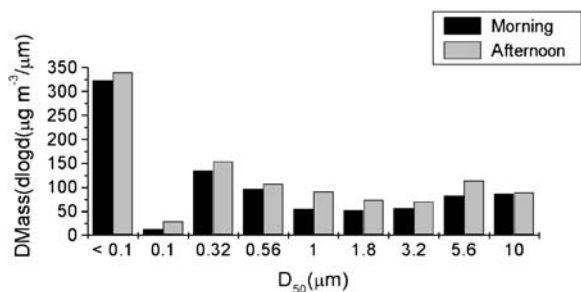
where  $\Delta[CO_2]_D$  is the component of  $\Delta[CO_2]$  attributable to HDV diesel emissions,  $f_D$  is the fraction of traffic identified as heavy-duty diesel trucks,  $U$  is the fuel consumption rate,  $\rho$  is fuel density,  $\omega$  is the



**Fig. 1** Size distribution of average mass concentration measured in the MOUDI impactor stages in the JQ tunnel. Morning values are defined as the averages of measurements taken from 10:00 to 14:00 LT, whereas afternoon values are defined as the averages of those taken from 14:00 to 18:00 LT



**Fig. 2** Size distribution of average black carbon concentrations measured in the MOUDI impactor stages in the JQ tunnel. Morning values are defined as the averages of measurements taken from 10:00 to 14:00 LT, whereas afternoon values are defined as the averages of those taken from 14:00 to 18:00 LT

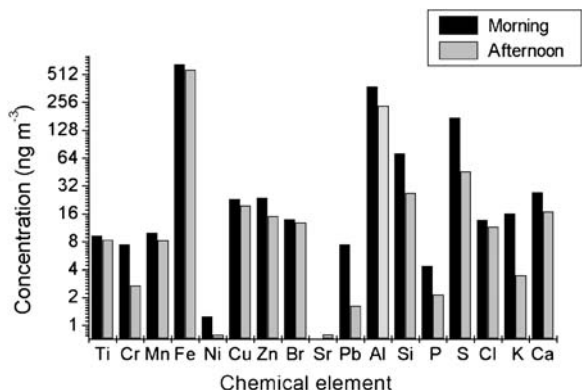


**Fig. 4** Size distribution of average mass concentrations measured in the MOUDI impactor stages in the MM tunnel. Morning values are defined as the averages of measurements taken from 10:00 to 14:00 LT, whereas afternoon values are defined as the averages of those taken from 14:00 to 18:00 LT

carbon weight fraction in fuel,  $f_D$  is diesel, and  $f_G$  is gasohol. For other pollutants in the MM tunnel, the contribution made by HDVs was expressed as:

$$\Delta[PM]_D = \Delta[PM] - \Delta[CO](1 - f_D) \left( \frac{\Delta[PM]_{LD}}{\Delta[CO]_{LD}} \right) \quad (3)$$

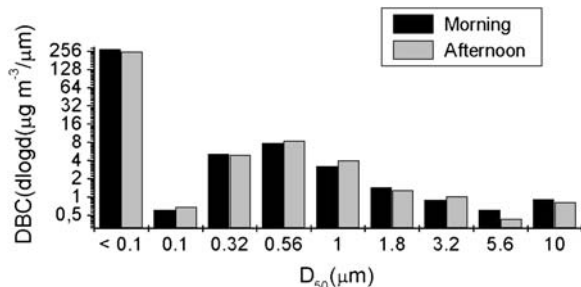
where  $\Delta[PM]_D$  is the component of  $\Delta[PM]$  attributable to HDV emissions in the MM tunnel,  $\Delta[CO] \times (1 - f_D)$  is the fraction of  $\Delta[CO]$  attributed to LDV emissions in the MM tunnel, and  $\frac{\Delta[PM]_{LD}}{\Delta[CO]_{LD}}$  is the pollutant emission ratio measured in the JQ tunnel. Equation 1 was then used to calculate the EFs for HDVs, with  $\Delta[CO_2]$  and  $\Delta[CO]$  calculated from Eqs. 2 and 3, respectively, and carbon weight fractions in the fuels (Miguel et al. 1998; Kirchstetter et al. 1999).



**Fig. 3** Chemical element concentrations measured in the MOUDI impactor stages in the JQ tunnel. Morning values are defined as the averages of measurements taken from 10:00 to 14:00 LT, whereas afternoon values are defined as the averages of those taken from 14:00 to 18:00 LT

**Results**

Table 1 presents the traffic counts by vehicle type (LDV, HDV, motorcycle and taxi), together with the total traffic volume and percentage of HDVs, for each 2-h sampling period in the JQ tunnel. In this tunnel, the fleet consisted of cars (mean, 84.7%; 5064 vehicles), motorcycles (mean, 7.5%; 450 vehicles), taxis (mean, 3.9%; 230 vehicles), and HDVs (mean, 3.8%; 238 vehicles, vans and light trucks). As can be seen in Table 2, the distribution in the MM tunnel was different, the mean percentages being 74% (cars), 12.5% (motorcycles), 1.5% (taxis) and 12.3% (HDVs, buses and trucks). Traffic volume through the MM and JQ tunnels was counted manually four times during each sampling period (15-min counts at 30-min intervals). In both tunnels, the traffic flow velocity was lower during the first hours of the morning, resulting in fewer numbers of vehicles than those counted in mid-afternoon, when the velocity was greater.



**Fig. 5** Size distribution of average black carbon concentration measured in the MOUDI impactor stages in the MM tunnel. Morning values are defined as the averages of measurements taken from 10:00 to 14:00 LT, whereas afternoon values are defined as the averages of those taken from 14:00 to 18:00 LT



**Table 3** Calculated EFs (and standard deviation) in the JQ and MM tunnel and EF ratio between heavy-duty and light-duty

	BC (mg km <sup>-1</sup> )	PM <sub>10</sub> (mg km <sup>-1</sup> )	PM <sub>2.5–10</sub> (mg km <sup>-1</sup> )	PM <sub>2.5</sub> (mg km <sup>-1</sup> )	NO <sub>x</sub> (g km <sup>-1</sup> )	CO (g km <sup>-1</sup> )
Light-duty JQ tunnel	16 (5)	197 (118)	127 (67)	92 (20)	1.6 (0.3)	15 (2)
Heavy-duty MM tunnel	462 (112)	755 (401)	715 (585)	588 (364)	22 (10)	21 (5)
Ratio HDVs/LDVs tunnel	29	4	6	6	14	1.4

The concentration size distribution obtained from the MOUDI data is presented in Figs. 1, 2 and 3 for the JQ tunnel and in Figs. 4 and 5 for the MM tunnel. As stated in the legends, morning values for mass concentrations were defined as the averages of those measured from 10:00 to 14:00 LT, whereas afternoon values were defined as the averages of those measured from 14:00 to 18:00 LT. In Fig. 1, it can be observed that the mass concentrations, in all MOUDI stages, were higher in the morning than in the afternoon. Figure 2 shows that the BC concentrations have a nucleation mode ( $D_{50} < 0.1 \mu\text{m}$ ) in the morning and afternoon periods. This result is in good agreement with the ambient BC measured by Ynoue and Andrade (2004). The slightly higher concentrations of BC in the afternoon are related to the higher number of HDVs counted during that time (Fig. 2). The PIXE analysis of MOUDI data for the mean chemical element concentrations (ng m<sup>-3</sup>) of aerosol particles in the JQ tunnel is presented in Fig. 3.

Figure 4 shows the MOUDI data for mass size distribution in the MM tunnel. In contrast to what was observed for the JQ tunnel, the mass concentrations, in all MOUDI stages, were higher in the afternoon than in the morning. The difference in mass concentrations between the tunnels is probably related to the differences between the two tunnels in terms of the morning and afternoon traffic counts, indicating that the particle emission rate is velocity dependent. Other factors, such as fleet composition and road gradient, could also contribute to differences in particle emission rates. Figure 4 also shows that there are three modes of mass size distribution: nucleation mode ( $D_{50} < 0.1 \mu\text{m}$ ), accumulation mode ( $D_{50} = 0.32 \mu\text{m}$ ), and coarse mode ( $D_{50} = 6.2 \mu\text{m}$ ). Figure 5 shows the MOUDI data for BC particle size distribution. It is noteworthy that the BC nucleation mode was more pronounced during the morning and afternoon periods. This indicates that virtually all of the particulate emissions were produced by diesel-powered vehicles. The accumulation mode appeared as a secondary peak at  $0.56 \mu\text{m}$ .

The EFs were calculated using carbon balance for each 2-h sampling period (Tables 3 and 4).

Compared to the EFs for LDVs, those for HDVs were higher for every pollutant in particulate phase studied (Table 3). The LDV EFs estimated for BC, PM<sub>10</sub>, PM<sub>2.5–10</sub> and PM<sub>2.5</sub> in the JQ tunnel were 16, 197, 127 and 92 mg km<sup>-1</sup>, respectively. The mean contributions made by HDVs to the emissions of BC, PM<sub>10</sub>, PM<sub>2.5–10</sub> and PM<sub>2.5</sub> were 29, 4, 6, and 6 times higher than those made by LDVs. For the gaseous pollutant the emission factors were 14 and 1.4 times higher for the HDV compared to the LDV (Table 3). Kristensson et al. (2004) found an average HDV EF of 236 mg km<sup>-1</sup> for PM<sub>10</sub> in the Stockholm tunnel, Switzerland. For LDVs, the authors observed minimum and maximum EFs for PM<sub>2.5</sub> of 216 and 18.2 mg km<sup>-1</sup>, respectively.

Table 3 clearly shows that virtually all of the particulate emissions were produced by diesel-powered vehicles. Other studies have also shown BC to be more abundant in particle emissions from diesel-powered trucks, reporting a HDVs/LDVs ratio of 37:1 for BC (Kirchstetter et al. 1999). A great fraction of the fine particle concentrations is composed of BC (Fig. 5 and Table 3), associated to the diesel emission. It is also important to point out that most of the BC mass is in

**Table 4** Average (±standard deviation) EFs for trace elements determined by PIXE (in  $\mu\text{g km}^{-1}$ ) in the JQ tunnel

Species	EF ( $\mu\text{g km}^{-1}$ )
Ti	46.6±0.8
Mn	96.3±0.1
Fe	7762±1
Ni	2.40±0.02
Cu	261.0±0.1
Zn	167.4±0.2
Br	220.0±0.1
Zr	13.9±0.1
Pb	14.1±0.1
Al	1036±2
Si	118.3±0.3
S	465.7±0.5

the lower stages of the cascade impactor, in size fractions that have more access to the lower respiratory system.

Table 4 presents the LDV EFs in micrograms per kilometer for trace elements sampled in the JQ tunnel. Only mini-vol sampled filters were submitted to PIXE analysis. During the MM tunnel sampling, background concentrations (measured outside the tunnel) of trace elements were higher than inside tunnel concentrations which did not allow further comparisons. Known trace elements for LDVs as Cu ( $261 \mu\text{g km}^{-1}$ ) and Br ( $220 \mu\text{g km}^{-1}$ ) were calculated in this study. This result presents a good agreement with Castanho and Artaxo (2001) that described that copper is associated with ethanol fuel used in the MASP. The elements iron, aluminum, silicon, titanium and manganese sampled inside the JQ tunnel can be associated also to soil dust emission, not only with vehicular exhaust emission.

## Conclusion

Particulate matter was measured in two tunnels in the MASP from March 23 to March 26, 2004 in the JQ tunnel, as well as on May 5 and May 6, 2004 in MM tunnel. Fine particle BC, as well as  $\text{PM}_{10}$ ,  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$ , were analyzed in order to calculate the EFs. Road tunnel measurements allow EFs to be calculated by vehicle type. Compared to the LDVs (JQ tunnel), the HDVs (MM tunnel) presented higher EFs for every pollutant studied. The LDV EFs estimated in this study for BC,  $\text{PM}_{10}$ ,  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  in the JQ tunnel were 16, 197, 127 and  $92 \text{ mg km}^{-1}$ , respectively. The mean contributions of HDVs to emissions of BC,  $\text{PM}_{10}$ ,  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  were 29, 4, 6, and 6 times higher than were those of LDVs. The main constituent of diesel exhaust particles was found to be BC. The calculated EFs are going to be used in air quality models in the estimative of vehicular impacts on air quality. Due to the significant participation of BC in HDVs emissions, it can be used as a tracer for this source. The diesel emission is an important source of fine particles to the atmosphere, mainly very fine particles, which are related to impacts on human health and atmospheric radiative process. The particles composed mainly of elemental carbon (measured as black carbon) are related to an increase in the radiative forcing of the atmosphere. The adequate

evaluation of the emission profile is important for local and regional air quality modeling and to the establishment of public policies.

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