Particle emission from heavy-duty engine fuelled with blended diesel and biodiesel

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Abstract In this study, particulate matter (PM) were characterized from a place impacted by heavy-duty vehicles (Bus Station) fuelled with diesel/biodiesel fuel blend (B3) in the city of Londrina, Brazil. Sixteen priority polycyclic aromatic hydrocarbons (PAH) concentrations were analyzed in the samples by their association with atmospheric PM, mass size distributions and major ions (fluorite, chloride, bromide, nitrate, phosphate, sulfate, nitrite, oxalate; fumarate, formate, succinate and acetate; lithium, sodium, potassium, magnesium, calcium and ammonium). Results indicate that major ions represented 21.2% particulate matter mass. Nitrate, sulfate, and ammonium, respectively, presented the highest concentration levels, indicating that biodiesel may also be a significant source for these ions, especially nitrate. Dibenzo[*a,h*]anthracene and indeno[1,2,3,-*cd*]pyrene were the main PAH found, and a higher fraction of PAH particles was found in diameters lower than 0.25 μm in Londrina bus station. The fine and ultrafine particles were dominant among the PM evaluated, suggesting that biodiesel decreases the total PAH emission. However, it does also increase the fraction of fine and ultrafine particles when compared to diesel.

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Introduction

It is well known that vehicular emissions significantly contribute to air contamination in urban areas and that heavy-duty vehicles are the main contributors to particle emissions. The large increase in internal combustion vehicles in big cities has intensified atmospheric pollution and consequently the harmful effects on human health. Among the harmful compounds emitted from vehicular emissions into the atmosphere, polycyclic aromatic hydrocarbons (PAHs) can be highlighted, as they can be found in both vapor and particle phases. Human exposure to PAH in the air is concerning because many of them are mutagenic and carcinogenic (IARC 1983). Thus, some approaches aimed at reducing pollutant emissions, such as switching fuels, introducing new control technologies, and improving energy efficiency, are likely to have the joint benefit of also reducing other pollutant emissions that are of concern mainly because of their health effects.

Polycyclic aromatic hydrocarbons can be found in small particulate matter (PM) fractions emitted by incomplete combustion in waste incineration, motor vehicles, oil refining, domestic heating and biomass burning. The PAH content is strongly influenced by emissions from heavy-duty diesel vehicles on highways. As a result, several papers have been published on PAH emissions from mobile sources, with some studies being carried out in locations highly affected by diesel emissions. Vasconcellos et al. (2003) proposed a PAH profile from motor vehicles in São Paulo, where pyrene followed by chrysene and fluoranthene were emitted mainly from gasohol fuel burning, while chrysene, pyrene and benzo[a]anthracene were emitted mainly from gasohol and diesel burning. They also found that vehicular emissions were the most important PAH sources in the urban site. More recently, Machado et al. (2009) and Da Rocha et al. (2009) determined the atmospheric PM levels for 16 US EPA priority PAH present in

some urban areas. Machado et al. (2009) observed that total PAH in the particle phase at a bus station was 2.59 ng m^{-3} and the contribution of carcinogenic US EPA priority PAH in PM was of 6.73 μg g^{-1} (54% from the total PAH). Da Rocha et al. (2009) determined PAH in three sites in Salvador, Bahia (Brazil). These results indicated that chrysene presented higher concentration in those sites, which were strongly impacted by heavy-duty diesel vehicles.

Water-soluble ionic species and their PM size distribution have been highlighted by Lin et al. (2007) as species that have seldom been studied, particularly those emitted from vehicles. They also mention that PM mass has received less attention than nanoparticle number concentration studies. However, the issues concerning the PM characteristics (mass, number, surface area and chemical composition) in causing adverse health effects still remain. Limbach et al. (2007) draws attention to the importance of PM chemical composition, since health effects can be dependent on chemical and catalytic properties.

Recently, greater attention has been given to the development of cleaner alternative fuels that, in addition to helping improve air quality, contribute to reducing the dependence on fossil fuels, regarded as non-renewable sources of energy (Ribeiro et al. 2007; Guarieiro et al. 2008, 2009; Liaquat et al. 2010). Historically, diesel specifications in Brazil have changed. Until 1994, Brazilian diesel had 13,000 ppm of sulfur. Then, in 1994, two types of diesel—Metropolitan and Rural diesel—were introduced. Nowadays, Metropolitan diesel has been commercialized in large urban areas with less sulfur (500 ppm), while Rural diesel has been commercialized in other parts of the country, with 1,600 ppm of sulfur. In 2005, there was another significant change in Brazilian diesel through the Biodiesel Program, which determined an addition of up to 5% (in volume) of biodiesel to diesel fuel, to be implemented within the following 8 years. In 2007, diesel had 2% of biodiesel (B2); in 2008, this percentage was 3% of biodiesel (B3) and in mid-2009, it increased to 4% of biodiesel (B4). Currently, the Brazilian Government adopts the addition of 5% of biodiesel (B5) to diesel (ANP 2010).

The addition of biodiesel to diesel might bring some advantages as reported by Sharp (1998) and Swanson et al. (2007). These studies showed that pure biodiesel fuel (B100) decreases PM emissions in up to 30%. However, the PM soluble organic fractions increase in about 40%, when compared to the emissions of those using pure diesel. Although it might produce less PM, biodiesel emissions have shown higher NO_x emission levels, which might cause a fourfold increase in cytotoxic effects in biological assays when compared to diesel fuel (Bunger et al. 2000; Chung et al. 2008).

Particle size is also an important variation in terms of vehicular emissions, as it has been associated with the increase of health conditions. Ultrafine particles, generated in great amounts by diesel exhaust, have special toxicity due to their ability to penetrate into the cardiovascular system and other organs (Burtscher 2005; Oberdörster et al. 2005; Martins et al. 2010). According to Chung et al. (2008), particles emitted by biodiesel burning were morphologically different from those produced using diesel fuel, having high elemental carbon content in its particle emissions. In addition, the small particle number increased when heavy-duty vehicles were fueled with biodiesel, in comparison to low-sulfur diesel fuel (Tsolakis 2006; Lin et al. 2008).

However, there are few studies about the emission characterization when biodiesel fuel is used in diesel engines, some of them being divergent (Rantanen et al. 1993; Sharp et al. 2000; Zou and Atkinson 2003; Allen et al. 2008; Guarieiro et al. 2008; Borrás et al. 2009). Emissions obtained from measurements at bus stations represent the bulk of the emissions from a large number of vehicles in real operation conditions. Moreover, these emissions can be useful as reference points in discussions regarding emission inventories and vehicular emission control strategies. In this manner, the present study reports the results of field measurements for air pollutants released in a bus station in the South of Brazil. The aims of this study were to identify the characteristics of PM emitted by heavy-duty vehicles in real operation fueled with diesel/biodiesel fuel blend (B3) and to characterize the size distribution in terms of mass and PAH major ion concentrations emitted by those vehicles.

Experiment

Description of sampling site

Field measurements were carried out inside a bus station in the city of Londrina from July 3rd to 24th during the winter of 2008. During this year, all buses were fueled with B3, whose specifications are presented in Table 1. The bus station is located in the downtown area of Londrina, at 23.308°S and 51.161°W. The sampling site selection took into consideration the place where the buses frequently entered and exited the terminal and where there were many passengers waiting for it. On workdays, about 100,000 people pass through this bus station. The bus station is a two-storey building, and the samples were collected on the ground floor. This place is semi-closed with little air circulation and about 85 buses enter and exit the ground floor of the station during the weekend (46 on Saturdays and 29 on Sundays). In Londrina's bus station ground floor there are no restaurants, snack bar or other facilities like these.

Table 1 Diesel (B3/B4) and biodiesel (B100) specifications used in Brazil in 2008 (ANP resolutions N. 15/2006 and N. 07/2008; ANP:2010)

Characteristic	*Diesel sold (3–4% biodiesel)	Biodiesel
Density at 20°C (kg m^{-3})	820–880	850–900
Viscosity at 40°C (CST)	2.0–5.0	3.0–6.0
Water (mg kg^{-1})	–	500
Carbon residue (wt%)	0.25	0.050
Cetane index	42	–
Sulfur (mg kg^{-1})	1,800	50
Corrosiveness (copper, 3 h at 50°C)	1	1
Flash point (°C)	38	100
Total glycerol (wt%)	–	0.25

*Diesel characteristics in the countryside in 2008

Sampling procedure

Air samples were collected for the analysis of PM_{10} mass concentration, major ions concentration, PAH concentration in PM size distribution, and PM size distribution from 0.01 μm to 18.0 μm. Thus, different pieces of equipment were used to collect PM from the air as well as to perform the methodological analysis. A PM_{10} low-vol (PM_{10}-LV) impactor (built at *ZUF*—Frankfurt University), a high volume (PM_{10}-HV) air sampler (Hi-vol, Energética, Brazil) model, a Sioutas Cascate Impactor (SKC) and NanoMoudi equipment (NanoMoudi™ II, model 125A, MSP Corporation, MN, USA) were used to obtain PM_{10}, major ions concentration, PAH concentrations in the PM size distributions, and PM size distribution, respectively.

Samples of PM_{10} were collected using PM_{10}-LV system by drawing air using 47-mm Teflon filters with a 2-μm pore size at a 20 L min^{-1} rate, used to investigate daily PM_{10} mass emission. In addition, PM_{10} samples were also collected using a PM_{10}-HV air sampler at a 1.3 m^3 min^{-1} rate to obtain major ions concentration. For this collection, quartz fiber filters (20 × 25 cm^2) were used, pre-cleaned with deionized water, and dried at 800°C for 8 h. After each sampling, the filters were wrapped in aluminum foil envelopes and kept in a refrigerator inside sealed plastic bags until being weighed and analyzed. Both PM_{10} systems worked in 24-h intervals.

The Sioutas impactor operated at 9.0 L min^{-1} rate and separated PM in five different stages. Size intervals were as follows: <0.25 μm (after-filter); from 0.25 to 0.50 μm; from 0.50 to 1.00 μm; from 1.00 to 2.50 μm, and from 2.50 to 10.0 μm (Sioutas et al. 2002). Teflon filters with a 0.5 μm pore size and a 25-mm diameter (SKC) were used from the 0.25 μm stage to the inlet, and a 2-μm pore size Teflon-backed filter with a 37-mm diameter was used at the after-filter stage (Sioutas et al. 2003). Five substrate sets were used to perform PAH concentration sampling in PM size distributions. All samplings were conducted over 24-h periods, and the sampling temperature varied from 18°C to 26°C, with humidity ranging from 11% to 40%.

In the PAH study, sampling is a critical step due to possible losses for both volatilization and chemical reactions (Miguel et al. 1986). Possible artifacts in sampling procedures might occur with PAH in particulate and gas phase. In the particulate phase, a negative artifact (underestimation) is a result of PAH volatilization from filters and oxidation processes (Goriaux et al. 2006; Ravindra et al. 2008). Thus, in order not to have problems during the PAH analysis, these compounds were analyzed only in Sioutas filters, which were immediately extracted (Sioutas et al. 2003). Some studies have used sampling methodology similar to the ones used in this paper (e.g., Wingfors et al. 2001; Allen et al. 2008; Dallarosa et al. 2008).

Finally, in order to investigate PM size distribution emitted by engines in real operation fueled with B3 fuel, NanoMoudi equipment was used. This is a single-nozzle impactor with rotating impactor plates providing nearly uniform deposits over circular impaction areas. It operated at a 10.0 L min^{-1} rate and separated PM in 14 different stages, with the following equivalent cutoff diameters (dp, at 50% efficiency): <10.0 nm (after-filter); 14.0 nm; 25.0 nm; 44.0 nm; 78.0 nm; 140 nm; 250 nm; 440 nm; 780 nm; 1.40 μm; 2.50 μm; 4.40 μm; 7.80 μm and 14.0 μm. Teflon filters (SKC) with a 47-mm diameter and 1-μm pore size were used from the 0.01 μm stage to the inlet. The NanoMoudi operated in 7-day intervals (168 h) in the period between July 3rd and 24th of 2008, corresponding to three cycles.

Analysis procedure

Gravimetric analysis was performed by weighing the filters before and after sampling. In order to control humidity, filters were conditioned for 24 h. The PM mass was obtained using an analytical Microbalance Metter (Metter Toledo AX26) with 1 μg sensitivity (IO-3 1999 Method).

For the extraction of ionic compounds, both the sample and the blank quartz filters (47 mm diameter) were extracted using a shaker for 90 min with 20 ml deionized water (18 MΩ) (Wang et al. 2007). After passing through Millipore Millex GV (PVDF 0.22 μm pore size; 33 mm diameter) microporous membranes, ionic concentrations in aqueous extracts were determined by ion chromatography (Metrohm AG, Herisau, Switzerland) with chemical suppression (50 mM H_2SO_4) and

conductivity detector. For anion detection (SO_4^{2-}, Cl^-, NO_2^-, NO_3^-, F^-, PO_4^{3-} including $C_2O_4^{2-}$), samples were injected via a 20-μL loop through a Metrosep A Supp 5 250/4.0 mm analytical column. The mixture of 1.0 mM $NaHCO_3$ and 3.2 mM Na_2CO_3 was used as eluent. The suppressor system was regenerated by a 50 mM H_2SO_4 solution pumped through the suppressor unit simultaneously with deionized water.

Organic acid determination was performed by injecting the samples via a 20 μL loop using a Metrosep Organic acids 250/7.8 mm analytical column. The system was run in isocratic mode with a solution of perchloric acid (0.5 mM) as eluent and the chemical suppressor system was regenerated by a 10.0 mM LiCl solution pumped through the suppressor unit simultaneously with deionized water.

Metrosep C2-150 150/4.0 mm analytical column was used for cation detection (K^+, NH_4^+, Ca^{2+}, Mg^{2+} and Na^+) and a solution of 2.7 mM oxalic acid was used as eluent. The system ran in isocratic mode.

The recoveries ranged from 109% to 118% for inorganic anions, from 80% to 101% for cations and from 87% to 107% for carboxylic acids. The detection limits ($S/N = 4$) ranged between 3–45 ng m^{-3} (inorganic anions), 4–24 ng m^{-3} (cations) and 13–35 ng m^{-3} (organic acids). Blank values were subtracted from sample determinations (Vasconcellos et al. 2010).

The analysis of PAH was carried out for every collected sample and blank filters from the Sioutas equipment, which were extracted with 100-μL acetonitrile and shaken for 30 min. The extracts were then centrifuged for 10 min and kept at 4°C until analysis. The PAH concentrations were determined by HPLC-UV-FLU (Perkin Elmer, model 200) with a Fluorescence selective detector. The chromatography column used was a LC-PAH (2.1 cm × 250 mm × 5 μm) Supelcosil. For the analysis, a gradient system was used with mixture A, containing 35% acetonitrile and 65% ultra-pure water, and solvent B (100% acetonitrile). The program performed by the system consisted in ramps with mobile phase variation during retention time. For the first 20 min, a ramp from 90% to 0% mixture A and from 10% to 100% of B was used as the mobile phase; from minutes

20 to 32.5, 0% mixture A and 100% B was used; from minutes 32.5 to 35.5, a ramp from 0% to 93% mixture A and 100% to 7% B was used. A flow rate of 0.5 mL min^{-1} and 20 mL aliquots were used for PAH analysis. The fluorescence selective detector worked with variable excitation (from 220 to 289 nm) and emission (from 330 to 480 nm) wavelengths during analysis time (Miguel and De Andrade 1989).

A standard certificate (Supelco, Bellefonte, PA, USA) of sixteen PAH was used to quantify the samples from the Sioutas equipment. This standard contains naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CRY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenzo[a,h]anthracene (DBA), benzo[a]pyrene (BaP), indeno[1,2,3,-cd]pyrene (IND) and benzo[ghi]perylene (BgP). Blank values were subtracted from sample determinations, and the recovery efficiency of PAH species was performed in triplicate, using the standard certificate solution. Only nine PAHs were found in the samples and their recovery ranged from 80% to 90%. Detection limits ranged from 0.4 to 5.0 μg L^{-1} and quantification limits ranged from 1.2 to 15.0 μg L^{-1} for samples analyzed using HPLC-UV-FLU. Relative standard deviations for the nine PAH found in the samples were between 1.3% and 4.7%.

Results and discussion

Measurement concentrations for PM_{10} emitted by diesel engine exhausts in real operation fueled with B3 fuel are shown in Fig. 1. It shows the comparison between PM_{10} measured by PM_{10}-LV and Sioutas instruments. Both measurements were in agreement except for the one on July 5th, because sampling with Sioutas started on July 5th. Therefore, it was not possible to start the Sioutas instrument at the same time that PM_{10}-LV for the first sample. On the weekends (July 5th, 6th, 12th and 13th), the number of buses in operation decreased and PM_{10} concentrations were

Fig. 1 Comparison of PM_{10} mass concentration measured through PM_{10}-LV and Sioutas instruments at the bus station in Londrina in 2008
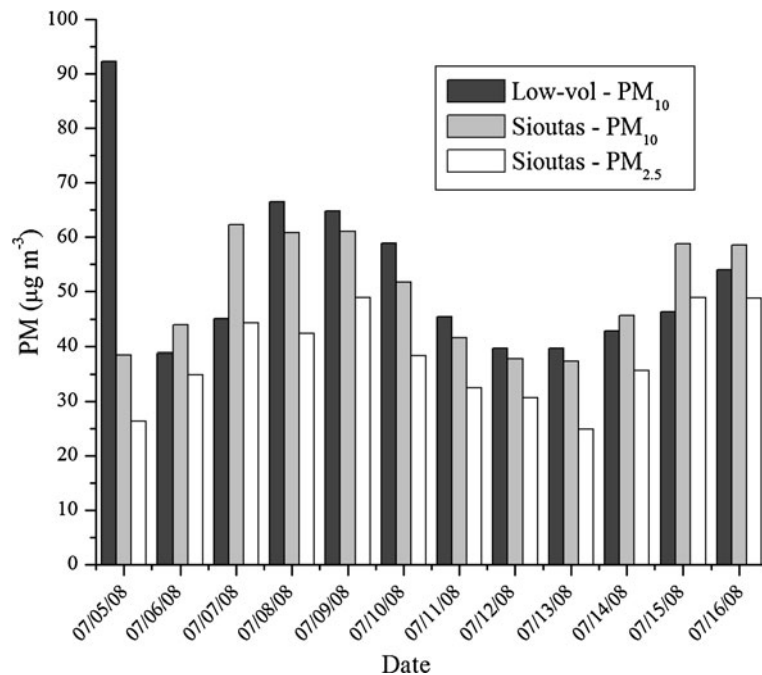
consequently lower than those observed on week-days. As the bus station is a semi-closed place, PM from this location might have some effects such as particle accumulation inside of the station, resulting in higher concentrations in the middle of the week; the contribution of meteorological conditions, mainly humidity and wind, which may result in the increase of particle concentration due to their resuspension; influence of other local sources like smoking and particles being brought in from outside of the bus station.

PM_{10} concentration found in this study was lower (38.8–92.2 μg m^{-3}) than the Brazilian air quality standard of 150 μg m^{-3} for 24 hours. However, when mass size distributions were analyzed (Fig. 2), a large fraction of fine particles in mass could be observed. The PM mean concentrations on five Sioutas size ranges are shown in Fig. 3. Seventy-six percent of PM_{10} particles emitted were below 2.5 μm ($PM_{2.5}$), in agreement with the works from Freitas and Solci (2009), which were of 70%; and 30% of this $PM_{2.5}$ were below 0.25 μm, with a large fraction of soot, according to data provided by Sioutas equipment. This data agrees with measurements performed in a tunnel in the city of São Paulo (Sánchez-Ccoyllo et al.

2009). Furthermore, in Brazil the PM_{10} air quality standards are much higher than those recommended by the World Health Organization and there is no standard established for fine particles ($PM_{2.5}$).

The PM size distribution from 0.01 μm to 18.0 μm was also investigated using NanoMoudi system. Figure 4 shows PM size distribution of mass concentration averages emitted by engines in real operation using B3 fuel. Two modes could be clearly identified in Fig. 4: an accumulation mode ($D_{50} = 0.25$ μm), and a coarse mode ($D_{50} = 14.0$ μm). A less pronounced mode could be identified in sizes smaller than 10 nm. The sum of PM concentrations from all size intervals obtained in every sampling cycle were 53.5 μg m^{-3} in the first cycle (from July 3rd to 9th); 34.1 μg m^{-3} in the second cycle (from July 10th to 16th) and 44.1 μg m^{-3} in the third cycle (from July 17th to 23rd).

The total average concentrations of water-soluble ions found in the samples at Londrina bus station were over 11 μg m^{-3}. In Fig. 5 and Table 2, it can be observed that the most abundant species were nitrate (8 μg m^{-3}), sulfate (1.4 μg m^{-3}) and ammonium (0.3 μg m^{-3}). These results are in agreement with studies performed in

Fig. 2 Particulate matter concentration at five size interval ranges sampled with Sioutas equipment at the bus station in Londrina in 2008
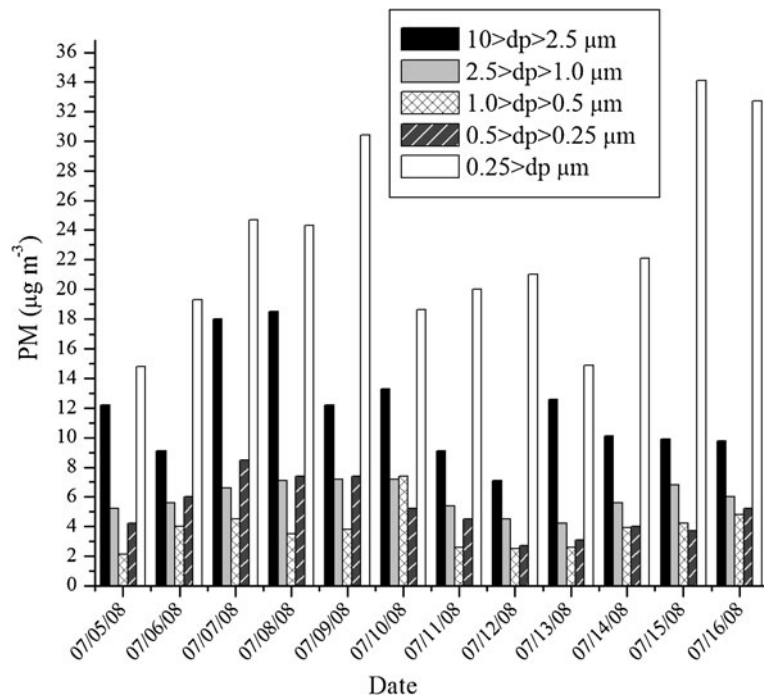
urban sites, except for the contaminant levels (Lin et al. 2007; Kai et al. 2007; Vasconcellos et al. 2007). Notably, nitrate and sulfate presented the highest concentrations on weekdays (July 3rd, 7th and 14th for nitrate, and July 10th and 16th for sulfate). This fact can be associated with diesel engine emissions, which emit significant amounts of nitrogen compounds. Also, the nitrate emission factors are 2.7 times higher than sulfate, as reported by Kerminen et al. (1997). On weekends the flow of buses at the station decreases when compared to the flow during weekdays, as previously mentioned.

The presence of sulfate and nitrate is usually attributed to anthropogenic activities such as vehicle and industry emissions. Zhang et al. (2009) found that sulfate and nitrate had higher emission rates for B20 (20% biodiesel and 80% diesel) than those for pure diesel. However, different results were observed by Wall et al. (1987), which reported that lowering fuel sulfur content could reduce emissions for both sulfur dioxide and particulate sulfate. Thus, sulfate levels and mainly nitrate concentrations from PM found in this work could be attributed to the presence of biodiesel to diesel fuel (B3), which can emit higher NO_x

concentrations when compared to diesel emission (Chung et al. 2008; Cheung et al. 2009).

Ammonia is found in animal and human waste, and is also emitted during combustion processes, fertilizer production and sugarcane
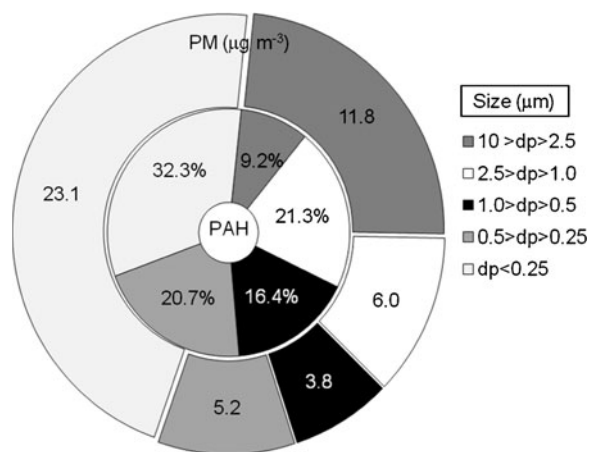

Fig. 3 Mean particulate matter (PM) concentration in each size range (external circle) and percentage of PAH mass obtained from air samples collected using Sioutas equipment at the bus station in Londrina in 2008
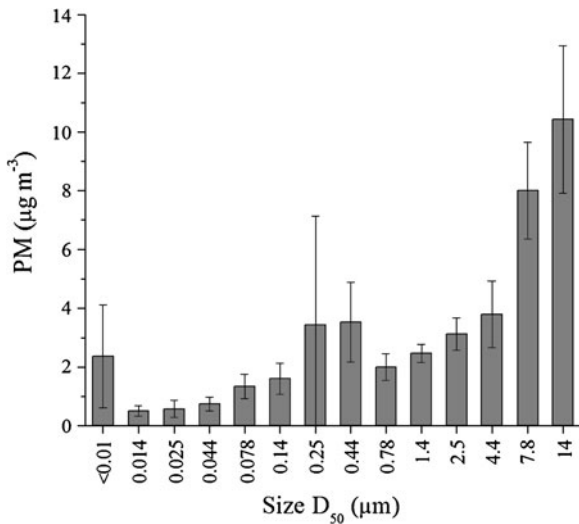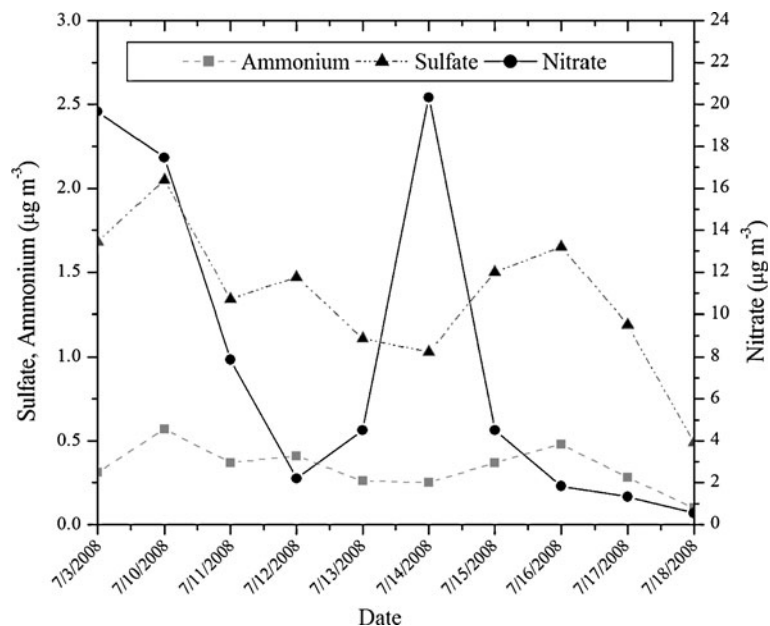
Fig. 4 Mean size distribution of mass concentration sampled with NanoMoudi equipment at the bus station in Londrina in 2008

burning (Allen et al. 2008; Vasconcellos et al. 2007; Viana et al. 2008). Other ammonia sources include industrial and vehicular emissions, as well as in a wide range of transportation. Differently, potassium average concentration (0.33 μg m^{-3}) is widely found in biomass burning plumes around the world and can, eventually, be trans-

ported. Magnesium (0.08 μg m^{-3}) and calcium (0.38 μg m^{-3}) have both been attributed to soil resuspension.

Among acids studied in this present work, oxalic (0.13 μg m^{-3}), formic (0.04 μg m^{-3}) and succinic (0.04 μg m^{-3}) acids were the most abundant in the PM from Londrina bus station. Oxalic acid contributed to 52% of the acids studied. Kawamura and Kaplan (1987) have suggested that primary vehicular emission is responsible for the dicarboxylic acids in urban atmosphere. The major ions concentrations found in this work represented 21.2% PM mass in the filters (see Table 2; fluorite, nitrite, bromide and lithium were below detection limit), representing the particle characteristics emitted mainly by biodiesel (B3) engines in real operation.

Sixteen PAH compounds were analyzed in five PM size ranges, which are included in the list of priority in US EPA due to their characteristics. PAH compounds with low molecular weight were not detected in the PM samples collected, because they are mostly found in gaseous phase. In this sense, PAH with two rings exist solely in the gas phase, those with two to three rings are present in both gas and particle phases, and PAH with five or more rings are predominantly adsorbed in PM (Corrêa and Arbilla 2006). According to

Fig. 5 The most abundant ion concentrations found at the bus station in Londrina in 2008

Table 2 Mean PAH concentration in five size intervals and mean ion concentrations collected at the bus station in Londrina from July 05 to July 16, 2008

PAH	ng m^{-3} (n = 12)											
	$10 > D_{50} >$ 2.5 μm		$2.5 > D_{50} >$ 1.0 μm		$1.0 > D_{50} >$ 0.5 μm		$0.5 > D_{50} >$ 0.25 μm		>0.25 μm		Total	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PYR	<DL		0.17	0.09	0.16		<DL		0.20	0.06	0.24	0.13
BaA	0.02	0.01	0.08	0.08	0.06	0.09	0.05	0.05	0.09	0.07	0.20	0.14
CRY	0.03	0.02	0.06	0.06	0.06	0.08	0.06	0.04	0.10	0.09	0.25	0.13
BbF	0.04	0.03	0.07	0.06	0.04	0.05	0.10	0.07	0.05	0.07	0.22	0.13
BkF	0.02	0.01	0.03	0.02	0.02	0.03	0.04	0.02	0.03	0.03	0.08	0.04
DBA	0.04	0.01	0.17	0.21	0.19	0.20	0.09	0.06	0.53	0.02	0.43	0.21
BaP	0.03	0.02	0.04	0.04	0.03	0.04	0.06	0.05	0.05	0.05	0.11	0.06
IND	0.03	0.01	0.09	0.12	0.13	0.11	0.10	0.09	0.28	0.16	0.34	0.15
BgP	0.02	<0.01	0.03	0.01	0.09	0.06	0.04	0.02	0.09	0.03	0.10	0.04

Mean ions concentrations (μg m^{-3}), $n = 10$

Chlorite	Nitrate	Phosphate	Sulfate	Formate	Succinate	Fumarate
0.08	8.02	0.04	1.35	0.04	0.04	0.01
Acetate	Oxalate	Sodium	Ammonium	Potassium	Magnesium	Calcium
0.03	0.13	0.15	0.34	0.33	0.08	0.38

*DL* detection limit; *SD* standard deviation

ATSDR/US EPA, ACE and ACY are present in gas phase while FLT, ANT, PHE, PYR are in both particle and gas phase (Ravindra et al. 2008).

PAH concentrations collected with Sioutas are shown in Table 2. The major PAH findings were DBA and IND with mean total concentrations of 0.43 ± 0.21 and 0.34 ± 0.15 ng m^{-3}, respectively. The total PAH mean concentrations were 2.21 ±

1.22 ng m^{-3} and the sum of all daily PAH concentrations varied between 0.08 and 3.10 ng m^{-3}, with mean value of 1.69 ± 0.93 ng m^{-3}.

Figure 6 shows the mean concentration for each PAH studied in the size intervals from measurements performed with Sioutas equipment. The results indicated the relevance of total PAH content bound to fine particles (between 2.5 and 1.0 μm)

Fig. 6 Mean concentration and respective standard deviation for each PAH in the size distributions sampled with Sioutas equipment at the bus station in Londrina in 2008
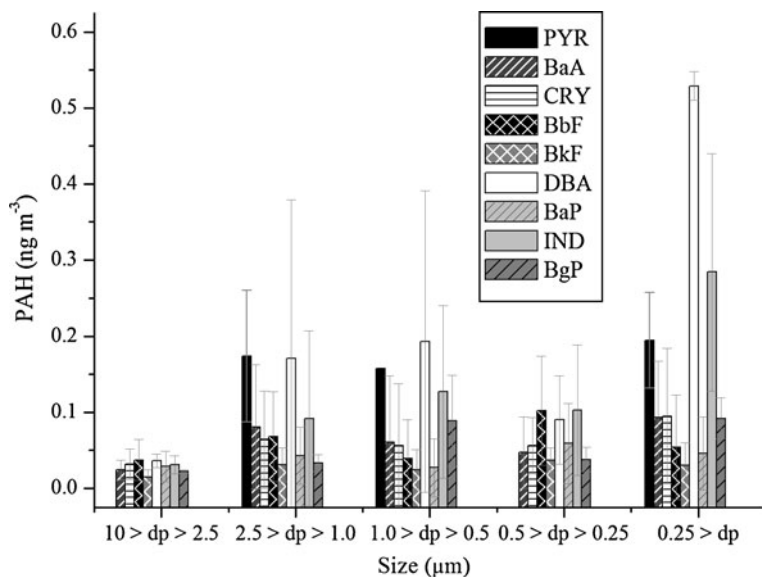
and particles lower than 0.25 μm, which resulted in a contribution of 53.7% in PM mass from all PAH studied during the sampling period. The contribution of PAH in mass percentage for each size interval is shown in the internal circle in Fig. 3. The PAH concentrations were higher for diameters lower than 0.25 μm and the PAH showing the highest concentration in this size distribution was DBA (0.53 ± 0.02 ng m^{-3}). This result was in agreement with others studies performed with laboratory engine, which suggests that the use of biodiesel can increase fine particle emissions when compared to diesel fuel (Krahl et al. 2001).

It is important to mention that both fine and ultrafine particles (<100 nm) have been considered relevant factors contributing to a series of health problems, including premature deaths, aggravated asthma, chronic bronchitis, and a number of social consequences (Sioutas et al. 2005; Ostiguy et al. 2006; Asgharian and Price 2007). Recent studies suggest that the population has been exposed to health risks in levels well below those allowed by the current air quality standard (USEPA 2007;

Baldauf et al. 2009). Martins et al. (2010) investigated the relationships among air quality, aerosol size distribution, meteorological conditions using data from aerosol number size distribution (9.82–414 nm) and numerical modeling in the highly polluted megacity of São Paulo. They suggested that the period characterized as clean, based on PM$_{10}$ measurements, could not be considered a period presenting low health impacts, when using ultrafine particle concentration as a criterion.

Schnelle-Kreis et al. (2001) investigated particle size fractions for PAH distributions in PM next to a road. About 40% of PAH were found in the particle fraction with 0.06–0.13 μm diameters. Some research found that in regions near vehicular sources, the PAH can be associated with particles whose size is less than 180 nm. Therefore, the size intervals of both nucleation and accumulation modes could be found far from the source (Eiguren-Fernandez et al. 2004; Miguel et al. 2005). Since particles with diameters <0.1 μm coagulate relatively fast, with life-times <1 h (Pui and Chen 1997), differences in particle size dis-

Table 3 Mean PAH concentration from different studies in urban locations

PAH	This work (ng m^{-3})	At same site[a] (ng m^{-3})	Brazil[b] (ng m^{-3})	South America[c] (ng m^{-3})	Europe[d] (ng m^{-3})	Asia[e] (ng m^{-3})
NAP	–	97.7	0.29	–	–	7.40
ACY	–	83.9	0.07	–	–	–
ACE	–	61.4	0.11	–	–	–
FLU	–	140.2	0.13	–	–	1.40
PHE	–	348	0.80	–	0.32	7.90
ANT	–	31.1	0.19	0.04	0.05	1.30
FLT	–	37.9	0.73	0.16	0.47	20.70
PYR	0.24	39.8	1.32	0.24	0.83	26.50
BaA	0.20	1.4	1.00	0.23	0.52	5.20
CRY	0.25	3.8	2.63	0.29	0.61	6.00
BbF	0.22	–	1.30	0.07	0.35	1.20
BkF	0.08	–	0.49	–	0.13	0.34
DBA	0.43	–	0.36	0.04	0.23	0.30
BaP	0.11	–	1.05	0.06	0.13	1.30
IND	0.34	–	0.73	0.04	<0.3	0.15
BgP	0.10	–	1.06	0.07	0.97	–
ΣPAH	1.97	–	12.26	1.24	4.61	79.69

[a]Measurements at bus station performed in 2002 (100% diesel) in vapor phase (Tavares et al. 2004)

[b]Measurements in 2005 at a bus station in Salvador, Bahia, Brazil, in particle phase (Da Rocha et al. 2009)

[c]Measurements in-tunnel in particle phase, average at Maria Maluf tunnel (Vasconcellos et al. 2003)

[d]Measurements in-tunnel at the entrance of a tunnel and in PM$_{10}$ (Wingfors et al. 2001)

[e]Measurements in-tunnel on summer weekday in particle phase (Ho et al. 2009)

tributions versus the distance of the sampling site from major sources are expected.

In 2004, PAH measurements in particle phase were performed at the same bus station where this research took place. The methodology, operation conditions, age of fleet and the fuel used were different from those used in this work. Therefore, the concentrations found before were much higher than the ones presented in this paper (Ferraz et al. 2006). In addition, Tavares et al. (2004) in 2002 (see Table 3), performed PAH measurements at the same bus station, when the diesel being burned did not contain biodiesel, and also found higher PAH concentrations than those shown in this paper. Although PAH concentrations obtained by Tavares et al. (2004) were analyzed in vapor phase, these results indicated that biodiesel can decrease PAH emission. Turrio-Baldassarri et al. (2004) also found that biodiesel blend seems to result in small reductions of PAH emissions.

Table 3 shows mean PAH concentrations from different places collected and analyzed using different techniques. A large range of PAH concentrations were observed, which can be attributed to different sampling characteristics for each site, such as addition of biodiesel to diesel; engine operation conditions; presence of other sources near the sampling site when measurements were performed in real situation (in-tunnel, bus station or others); analysis methodology, engine power and fleet age (Lim et al. 2005). Karavalakis et al. (2010), for example, found that the addition of biodiesel to diesel can increase PAH emission of low molecular weight (phenanthrene and anthracene) and both increases and reductions in emission for large PAH.

Compared to Lapa bus station in the city of Salvador (Bahia, Brazil; Da Rocha et al. 2009), those PAH concentrations are much higher than the ones found in this research. The Lapa bus station is strongly impacted by heavy-duty diesel vehicles and its PAH concentrations are shown in Table 2.

The major PAHs in that station were CRY (2.63 ng m^{-3}), PYR (1.32 ng m^{-3}), BbF (1.30 ng m^{-3}), and BgP (1.06 ng m^{-3}), while the PAHs that were mainly found in the present study were DBA (0.43 ng m^{-3}), IND (0.34 ng m^{-3}), CRY (0.25 ng

m^{-3}), and PYR (0.24 ng m^{-3}). These differences (in concentration and major species) can be due to both the use of different fuels (pure diesel at Lapa station and B3 at Londrina bus station) and the flow of buses in each station.

Conclusions

In this study, PAH associated with small particles were determined using an impactor system to investigate these compound emissions from heavy-duty vehicles in real operation running on diesel/biodiesel fuel blend (B3). Particulate size distributions and major ions were also evaluated from B3 fuel combustion. Among major ions, nitrate and sulfate were the highest, representing 21.2% of PM mass. Nine PAH were determined and quantified at the bus station with pronounced DBA concentration in smaller sizes. In general, from all PAH found in the air samples at Londrina bus station, particles with diameter lower than 0.25 μm were the most abundant. Additionally, particulate mass size distribution presented these modes: coarse, accumulation and ultrafine modes, the latter being less significant in terms of total mass. Thus, this study verified that both fine and ultrafine particles were dominant among the evaluated PM, and these particles can contain some chemical species with mutagenic characteristics, such as PAH. Finally, the results suggest that biodiesel decreases the total PAH emission. However, it increased the fraction of fine and ultrafine particles when compared to diesel fuel. It has also shown evidence that levels of particulate sulfate and mainly nitrate found in this study may also be attributed to the emission from diesel/biodiesel fuel blend (B3).

It is well known that particles can cause human health problems, although further studies concerning the health effects of biodiesel exhausts are still needed. Hence, this work is expected to help establish legislation about this issue in Brazil.

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