Measurements of semivolatile and particulate polycyclic aromatic hydrocarbons in a bus station and an urban tunnel in Salvador, Brazil

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Motor vehicles constitute a significant source of polycyclic aromatic hydrocarbon (PAH) emissions to the atmosphere. Particle-phase priority pollutant PAH concentrations and total suspended particle mass (TSP) were measured in the Lapa bus station and the Americo Simas Tunnel, located in the city of Salvador, Brazil. Separate samples were collected at the bus station at different times of the day, including rush- and non-rush-hour periods. The highest concentrations for nearly all 16 priority PAHs measured at the bus station were observed at 18:30 h, with chrysene showing the highest mean value (26.6 ng m^{-3}). The highest average PAH concentrations measured in the tunnel were observed for pyrene (79.4 $\pm$ 11.5 ng m^{-3}) followed by fluoranthene (39.0 $\pm$ 5.2 ng m^{-3}) and chrysene (28.0 $\pm$ 4.17 ng m^{-3}). TSP levels reached 423 µg m^{-3} in the bus station, and values as high as 2 mg m^{-3} in the tunnel. The measured Salvador tunnel PAH profiles are very similar to the Salvador bus station profiles, and are similar to PAH profiles reported for the Kojouike Tunnel, located in Kurashiki City, Japan, and the Caldecott Tunnel, located in Berkeley, California.

Introduction

Particulate matter plays a significant role in the chemistry of the atmosphere and in human health. The interaction of particles with sunlight interferes with local luminosity and temperatures, affecting thereby the local climate. In addition, depending on their size, particles may settle into different regions of the human respiratory system. Several epidemiological studies have associated daily exposures to particulate matter with increased incidence of premature death, chronic asthma and increased hospital admissions and respiratory problems in children.[1,2] While their constitution may vary from place to place, the sources of particulate matter are numerous, from natural origin—mainly vegetation—to different kinds of human activities, such as disposal of petroleum residues, waste incineration, energy production, vehicular emissions and agricultural slash burning.

Vehicle exhaust aerosols contain carbonaceous particles that are associated with a complex mixture of compounds. Special attention has been given to particles emitted by diesel engines, due to the numerous *in vivo* and *in vitro* studies establishing their adverse effects on human health.[3–5] Among the several organic and inorganic species associated with diesel exhaust particles, which include mono- and polyfunctional organic compounds that result from gas-to-particle conversion mechanisms, the hydrocarbons with high molecular weight, such as polycyclic aromatic hydrocarbons (PAHs) and their oxy- and nitro-derivatives, are of particular interest.[3,4,6] PAHs are an important class of organic compound that includes several potent mutagens and carcinogens.[5,7]

Sources of PAH in motor vehicle exhaust include unburned fuel, lubricating oil and pyrosynthesis from lower molecular weight aromatics. PAH production through pyrolysis is a complex process that depends on variables such as temperature and pressure. At high temperatures and anaerobic conditions, relatively simple mixtures of low molecular weight PAHs are predominantly produced, while at low temperatures methyl- and other alkyl-substituted PAHs become predominant products.[8] In general, combustion PAH profiles are dominated by relatively high molecular weight compounds with three or more condensed rings, whereas mono-, bi- and tricyclic compounds are predominant in fossil fuel mixtures.[9] The particulate PAHs measured in urban air and in roadway tunnels have been found in the respirable size range.[6,10–13]

PAHs are regarded as priority pollutants by both the United States Environmental Protection Agency and the European Community. While no standard currently exists in Brazil for PAH concentrations in ambient air, the UK Government Expert Panel on Air Quality Standards is considering an air quality standard for benzo(*a*)pyrene of 0.25 ng m^{-3}. While PAH concentrations measured in ambient air and in a tunnel have been reported for Rio de Janeiro,[14–16] São Paulo[17] and for the Amazon basin,[18] no results have been previously reported for Salvador, the third largest city of Brazil, in the state of Bahia. We believe this is the first study of PAH concentrations measured in a Brazilian and South American bus station.

In this paper we report the concentrations of 16 particle-phase US EPA priority PAH pollutants and of total suspended particles (TSP), measured at different times and over 4 days in the air of a bus station located in the center of the City of Salvador, Bahia. The concentrations of the target PAHs measured in the bus station are compared with those measured in an urban tunnel of the same city and are discussed in terms of the PAH profiles and diurnal variations.

Experimental

Sample collection

Salvador, the capital of the state of Bahia, Brazil, is located at 13°01′S and 38°31′W on the Atlantic Ocean coast. One of the sampling sites, the Lapa bus station, is located in a downtown region characterized by heavy commercial and service activities, with several stores, small office buildings and a large shopping mall. The bus station has three floors: the first is located underground, the second is at ground level, the two floors have a total area of *ca.* 13,920 m^2, and have five passenger loading/unloading platforms each. The last floor is occupied by some small stores, cafeterias and the administration services. The bus station serves several different bus lines coming from other city districts.

Sample collection was carried out during April, 1991

(Austral fall), over 4 days, from Tuesday to Friday, during time periods of heavy bus traffic—and thus of passengers—that represent rush-hour periods. Twelve samples were collected on quartz fiber filters (Pallflex, 22.8 × 17.7 cm) with a TSP high-volume sampler (Energetica, Rio de Janeiro) at a flow rate of 1.10 m^3 min^{-1} over 120–180 min periods. The ambient temperature during the collection period was 29.5 $\pm$ 1.1 °C. The sampler was set at ground level, alongside a passenger platform. At this site, in addition to departure and arrival bus movements (*ca.* 150 h^{-1} during rush hour), the buses remain idling until departure time.

The other sampling site, the Americo Simas Tunnel, connecting the boroughs of Cidade Alta and Cidade Baixa, is an urban tunnel 300 m long, with four traffic lanes; two in each direction. It is considered representative of the vehicular fleet of Salvador, since it is used by both light duty vehicles (1980 h^{-1} average) using either hydrous ethanol or gasohol (18–22% v/v ethanol in gasoline), and heavy duty diesel vehicles (420 h^{-1} average). Six samples were taken during August, 1991 (Austral winter), at different times during two consecutive days, in the same way as described above. During collection, the temperature in the tunnel was 29.2 + 1.1 °C. After sampling and prior to analysis, filters were placed in a refrigerator, wrapped in aluminium foils and inside "zip-lock" plastic bags.

Filter extraction

Details of the procedure used to extract and quantify the target PAHs are described elsewhere.[19] Briefly, a 5.3 cm^2 section from each filter was cut and placed in a 20 mL amber vial with a Teflon-lined screw cap and extracted with 4 mL of a 3 : 1 acetonitrile : methylene chloride mixture. The extractions were carried out with ultrasonication for 10 min in a water-bath (Fisher Scientific, Atlanta). The PAH recoveries were based on the mean values determined for three extractions of priority pollutant PAHs contained in the Standard Reference Material (SRM) 1649 (Urban dust, organics, NIST, Washington, DC). Mean recoveries ranged from 45% for fluorene to 107% for dibenz[*a,h*]anthracene, with an average recovery of 80%.[19] Following the extraction, the resulting suspensions were filtered through Millex-FG filter units (PTFE membrane, 0.22 μm pore size, 25 mm diameter Millipore, Bedford) directly onto similar amber vials. For the bus station samples, due to the lower PAH concentrations, from each sample, a 1 mL aliquot was transferred to a 1.5 mL micro-centrifuge tube. The extract volume was evaporated to dryness at room temperature under a gentle stream of nitrogen and then recovered with 100 μL of acetonitrile. A 1 μL aliquot of the concentrate was then injected and analyzed; for tunnel samples no preconcentration was needed.

PAH separation and quantification

The priority PAHs measured are listed in Table 1, along with abbreviations, MW and sub-cooled liquid vapor pressures.[20] The GC/MS analysis was performed using a system consisting of an HP1701 column (30 m × 0.25 mm diameter) (Agilent, CA), an HP6890 *Plus* gas chromatograph, an HP6890 GC autosampler and an HP5973 quadrupole mass selective detector (Agilent, CA). The following conditions were employed: (i) oven: 60 °C (1 min) → 280 °C (5 °C min^{-1}) → 280 °C (15 min); (ii) injector: 270 °C, splitless mode; (iii) transfer line: 270 °C; (iv) ion source: 230 °C; (v) analyzer: 150 °C; (vi) electron impact energy: 70 eV. Samples were run in single ion mode (SIM) in order to enhance the sensitivity.

Calibration plots were obtained from external standard solutions prepared by dilution of a PAH standard (ERS-010, Cerilliant, TX) to the range of concentrations expected in the samples. GC/MS quantification of the target PAH ions were as follows: naphthalene (NAP)-128; acenaphthylene (ACY)-152;

Table 1 Sixteen particle-phase priority PAHs measured in the Lapa bus station and the Americo Simas tunnel

PAH	Abbreviation	MW	Log $p^{\ominus}_L{}^a$
Naphthalene	NAP	128	1.57
Acenaphthylene	ACY	152	0.62
Acenaphthene	ACE	154	0.18
Fluorene	FLU	166	-0.15
Phenanthrene	PHE	178	−0.95
Anthracene	ANT	178	−1.11
Pyrene	PYR	202	−1.92
Fluoranthene	FLT	202	−2.06
Benzo[*a*]anthracene	BAA	228	−3.22
Chrysene	CRY	228	−3.97
Benzo[*ghi*]perylene	BGP	276	−4.65
Benzo[*a*]pyrene	BAP	252	−4.67
Benzo[*b*]fluoranthene	BBF	252	−4.99
Benzo[*k*]fluoranthene	BKF	252	−5.39
Dibenz[*a,h*]anthracene	DBA	278	−7.04
Indeno[1,2,3-*cd*]pyrene	IND	276	—^{b}

^{a}Subcooled liquid vapor pressure at 293 K.[20] ^{b}Not available.

acenaphthene (ACE)-154; fluorene (FLU)-166; phenanthrene (PHE)-178; anthracene (ANT)-178; fluoranthene (FLT)-202; pyrene (PYR)-202; benzo[*a*]anthracene (BAA)-228; chrysene (CRY)-228; benzo[*b*]fluoranthene (BBF)-252; benzo[*k*]fluoranthene (BKF)-252; benzo[*a*]pyrene (BAP)-252; indeno[1,2,3-*cd*]pyrene (IND)-276; dibenz[*a,h*]anthracene (DBA)-278 and benzo[*ghi*]perylene (BGP)-276.

Results and discussion

PAH concentrations measured at different sampling time periods at the Lapa bus station and the Americo Simas tunnel are shown in Table 2 (in decreasing log $p^{\ominus}_L$ order) along with measured TSP concentrations. For the bus station samples, the time periods shown represent the intermediary value between the initial and final sampling time. Results of the bus station samples collected on different days but at similar time periods are grouped together. For example, there are two samples grouped at 10:20 h, two at 13:00 h, three at 16:15 h, and two at 18:30 h. For these groups, the results shown represent averages. Other periods shown represent single sample collections. The six tunnel samples listed in Table 2 represent individually collected samples from two different days.

The largest variation in PAH concentrations in the bus station was observed for species with log $p^{\ominus}_L$ in the range from −1.9 to −7.0 (DBA excepted). Except for NAP in the 13:00 h and 21:40 h periods, the highest concentration for nearly all target PAH were observed at 18:30 h, with CRY showing the highest mean value (26.6 ng m^{-3}). The high PAH values measured in the 18:30 h period correspond to the late afternoon rush hour, when there is a substantial increase in the number of buses that take home people employed in nearby offices and shops. The lowest values were found, in general, for samples collected in the 13:00 h period, at the beginning of the afternoon, when the number of buses arriving and departing from the station is relatively small.
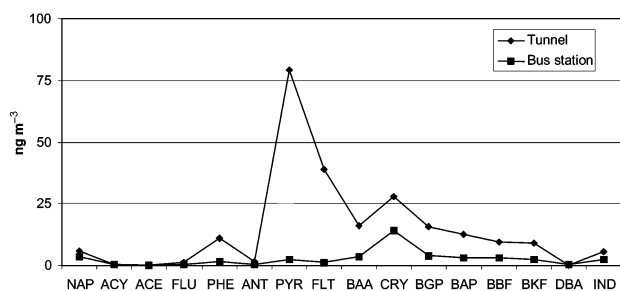
The concentration profiles observed for the PAHs follow closely those of TSP (Table 2), suggesting that vehicular exhaust constitutes their major emission source. The highest mean PAH concentrations measured in the tunnel were observed for PYR (79.4 $\pm$ 11.5 ng m^{-3}) followed by FLT (39.0 $\pm$ 5.2 ng m^{-3}) and CRY (28.0 $\pm$ 4.17 ng m^{-3}). Mean PAH concentrations measured in the bus station and in the tunnel are plotted together in Fig. 1. Except for FLT and PYR, the tunnel PAH profile is very similar to the bus station profile. Albeit at lower concentrations, nearly identical PAH profiles have been reported for the Kojouike Tunnel, located in Kurashiki City, Japan.[21] Also, very similar PAH profiles, but at smaller concentrations, have been reported for the

Table 2 PAH concentrations measured in the Lapa bus station and the Americo Simas tunnel[a]

Lapa bus station

Time	10:20	11:30	13:00	15:00	16:15	18:30	21:40	Mean	SD (1σ)
PAH/ng m^{-3}									
NAP	2.17 ± 0.68	0.23	7.28 ± 4.9	1.65	0.59 ± 0.29	1.41 ± 1.07	10.5	3.40	3.91
ACY	0.31 ± 0.09	0.23	0.5 ± 0.1	0.18	0.48 ± 0.18	0.27 ± 0.02	0.90	0.41	0.25
ACE	0.07 ± 0.07	ND	0.06 ± 0.05	0.19	0.10 ± 0.07	0.12 ± 0.1	0.14	0.11	0.05
FLU	0.33 ± 0.07	0.19	0.45 ± 0.1	0.44	0.38 ± 0.16	0.52 ± 0.21	1.18	0.50	0.32
PHE	1.03 ± 0.22	1.17	1.08 ± 0.3	1.65	1.35 ± 0.18	1.82 ± 0.92	1.57	1.38	0.31
ANT	0.18 ± 0.02	0.22	0.18 ± 0.1	0.31	0.24 ± 0.04	0.35 ± 0.16	0.30	0.25	0.07
PYR	1.39 ± 0.42	2.55	0.47 ± 0.2	3.88	2.5 ± 1.5	5.75 ± 3.48	1.13	2.52	1.81
FLT	0.82 ± 0.24	1.35	0.29 ± 0.1	2.00	1.25 ± 0.71	2.88 ± 1.72	0.53	1.30	0.90
BAA	2.52 ± 0.62	4.00	0.75 ± 0.4	3.90	3.21 ± 1.65	6.85 ± 2.02	3.42	3.52	1.84
CRY	10.2 ± 2.4	16.8	2.99 ± 1.7	16.0	12.4 ± 6.4	26.6 ± 8.62	14.4	14.2	7.17
BGP	3.10 ± 1.16	5.11	1.40 ± 0.6	4.23	3.10 ± 1.41	6.97 ± 1.28	3.10	3.86	1.79
BAP	2.57 ± 0.83	3.53	0.99 ± 0.4	3.18	2.76 ± 1.33	5.82 ± 1.01	2.59	3.06	1.45
BBF	2.49 ± 0.79	3.43	0.89 ± 0.4	3.29	2.8 ± 1.21	5.58 ± 1.01	2.89	3.05	1.39
BKF	1.83 ± 0.55	2.60	0.66 ± 0.3	2.35	2.02 ± 0.89	4.29 ± 0.90	2.17	2.27	1.08
DBA	ND	ND	ND	0.34	0.23 ± 0.17	0.39 ± 0.03	0.55	0.38	0.13
IND	1.86 ± 0.77	3.07	0.77 ± 0.3	2.58	2.05 ± 1.06	4.35 ± 1.01	2.17	2.41	1.11
TSP/μg m^{-3}	225 ± 12	277	186 ± 50	239	242 ± 49	423 ± 30	215	258	77.7

Americo Simas tunnel

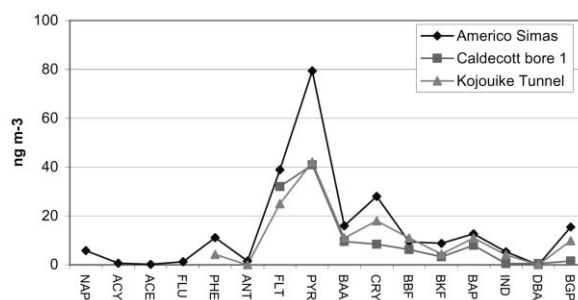|	Sample							
	1	2	3	4	5	6	Mean	SD (1σ)
PAH/ng m^{-3}								
NAP	2.72	3.84	7.36	6.40	7.68	6.48	5.75	2.00
ACY	0.24	0.48	0.72	0.64	0.72	0.64	0.57	0.19
ACE	0.24	ND	ND	ND	ND	0.32	0.28	0.06
FLU	0.72	0.88	1.44	1.36	1.36	1.36	1.19	0.31
PHE	6.56	10.9	13.8	11.6	11.0	12.2	11.0	2.44
ANT	0.88	1.52	1.92	1.52	1.44	1.92	1.53	0.38
PYR	66.0	94.3	87.2	67.4	76.1	85.4	79.4	11.5
FLT	31.2	44.2	42.8	34.2	39.3	42.2	39.0	5.20
BAA	13.3	15.8	17.0	13.6	14.2	22.2	16.0	3.32
CRY	24.6	31.4	30.6	23.6	24.7	33.3	28.0	4.17
BGP	14.3	19.3	13.9	10.5	11.8	23.2	15.5	4.82
BAP	10.4	14.1	11.8	9.30	10.5	19.6	12.6	3.80
BBF	7.80	10.2	9.20	7.40	7.80	13.5	9.31	2.32
BKF	7.68	9.84	8.32	6.80	7.52	12.8	8.83	2.20
DBA	ND	ND	ND	ND	ND	ND		
IND	4.72	6.24	4.72	3.60	4.16	8.48	5.32	1.78
TSP/μg m^{-3}	1959	1020	1351	1111	1036	1278	1293	352

[a] ND = not detected.

"truck-influenced" bore 1 of the Caldecott tunnel, located in Berkeley, California[13] (Fig 2). Although the Americo Simas Tunnel profile represents a mixed vehicular fleet—rather than heavy-duty or light-duty vehicles only—these similarities suggest a predominance of diesel exhaust as the source of the PAHs found in it. For the Caldecott tunnel, chemical mass balance (CMB) calculations revealed that although heavy-duty diesel trucks represented 4.6–4.8% of the passing fleet, they were responsible for ~93% of the black carbon emissions in bore 1 of the tunnel.[6] On the other hand, as sampling in

Salvador occurred in the early 1990s, the high concentrations found, compared with the two other tunnels, reflect higher vehicular emission rates, as the Salvador fleet was older than that of Berkeley and Kurashiki.

Correlations (R^2) between CRY and BAA, BBF, BKF, BAP and BGP determined in the Lapa bus station were, respectively, 0.994, 0.988, 0.983, 0.958 and 0.933, suggesting a unique source for these PAHs. Correlations (R^2) for FLT and PYR with BBF (0.813 and 0.828), BKF (0.790 and 0.806), BAP (0.839 and 0.847), CRY (0.784 and 0.804) and BGP (0.821 and 0.819) are

Fig. 1 Mean PAH concentrations for the Lapa bus station (as Table 2) and the Americo Simas Tunnel in Salvador ($n = 6$).

Fig. 2 PAH profiles for the Americo Simas, Caldecott and Kojouike tunnels (not all PAHs were determined in all samples).

also high. In addition, because the concentrations of FLT and PYR in the bus station correlated well ($R^2 = 0.996$), the differences found in the measured FLT and PYR concentrations in the tunnel and the bus station samples do not necessarily indicate that sources other than heavy-duty diesel vehicles are responsible for the PAHs measured at the Lapa bus station. One possible explanation for the differences in the observed FLT and PYR profiles is that, in ambient air, PAHs with log $p^{\ominus}_{L}$ values in the range from 1.57 to -2.0 are found mostly in the vapor phase,[22] and may partition out of the particle phase after being emitted from diesel engines, while idling, at the bus station. Another possibility that may also account for the different emission profiles of these low MW PAHs would be differences in the composition of the diesel fuel used in Salvador.

For naphthalene, as previously mentioned, a different behavior was observed, with maxima occurring for samples in the 13:00 and 21:40 h periods—with a decrease in the movement of buses and of persons inside the station—and, inversely, a low value for the sample at 18:30 h. This disagreement was also evident in the correlations (R^2) among NAP and BBF, BKF, BAP and BGP, which were mostly low (0.205, 0.185, 0.254 and 0.294, respectively). This fact suggests a different source (*e.g.* petroleum refineries, cigarette smoke, consumer products) that would be influencing naphthalene concentrations at the station. In this case, the effects of these or other sources would be more evident when diesel exhaust diminished as result of decreased bus traffic.

Conclusions

The air concentrations of particulate priority PAHs measured inside the Lapa bus station were strongly influenced by the collection sampling time-period. For almost all 16 PAHs, especially from pyrene to the heaviest, the highest values were measured during the evening rush-hour periods. Conversely, the lowest values were measured in the early afternoon. This behavior was in accordance with the increase and decrease of bus traffic at the passenger loading platforms, suggesting that diesel exhaust is the main source of particulate PAH in the bus station air.

Except for fluoranthene and pyrene, the profiles of the other priority PAHs in the Lapa Station are very similar to the profiles observed in the Salvador urban tunnel for samples collected during field campaigns that were carried out four months later. This corroborates the strong influence of vehicle emissions on the particulate PAHs measured in the bus station, and also that diesel exhaust may be more important than gasoline exhaust as the main source of particle-phase PAHs inside the tunnel. The relatively low concentrations of fluoranthene and pyrene, in comparison to other sites heavily impacted by vehicle emissions, were possibly due to PAH partitioning after emission, or to different emission sources and/or their profiles in the exhaust of idling diesel buses in the station.

Naphthalene, on the contrary, presented a different behavior, with maxima occurring during periods with a decrease in bus movement and, inversely, lower values for evening samples, suggesting other sources (*e.g.* petroleum refineries, cigarette smoke, consumer products) that would be influencing its concentrations at the bus station. As the Lapa station has recently undergone total remodeling, and also due to possible changes in diesel composition from the time of sampling to date, a new sampling campaign is being scheduled for 2002.

Finally, the mean benzo[*a*]pyrene concentration measured in the Lapa bus station (3.06 ng m^{-3}) is about 12 times the annual PAH standard recommended in 1999 by the Expert Panel on Air Quality Standards (EPAQS), UK Department for Environment, Food & Rural Affairs. The EPAQS recommendation for PAHs is 0.25 ng m^{-3} as an annual average, and is based on benzo[*a*]pyrene as a marker for the total mixture of PAH. Although this standard is to be applied at outdoor locations (not for bus stations or tunnels), in the absence of a Brazilian standard, it may serve as an interim practical guide for indoor locations like the bus station, where the exposure is mainly occupational and affects the workers in the small stores, cafeterias, and administration services located inside it. Bus drivers and passengers, on the other hand, are exposed for shorter periods.

Although these levels are already high, the perspective of yearly growth of around 2% for diesel consumption in Brazil, estimated[23] for the period 1999–2020, could aggravate the problem in large urban centers such as Salvador and other cities of Brazil.

Acknowledgements

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