

PAHs in Diurnal and Nocturnal Samples of Total Suspended Particulate in a Highly Trafficked Area of Rio de Janeiro City, Brazil

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent pollutants that have been described in all environmental compartments. Many of them are well-known pro-carcinogenic and/or mutagenic substances that have been related to several kinds of human cancer (Boffetta et al., 1997; IPCS, 1998; Pereira Netto et al., 2000). The sources, formation and fate of PAHs have been reviewed (Baek et al., 1991; Lopes and Andrade, 1996; Bouchez et al., 1996; IPCS, 1998). In the atmosphere, PAHs are distributed between the gaseous phase and particulate according to their vapour pressures and to the temperature (Valerio and Pala, 1991). PAH concentrations in total suspended particulate (TSP), in suspended particles of different diameters and/or in the gaseous phase have been used to assess air pollution. There are data concerning atmospheric PAHs for many places and cities in the world (for example: Alsberg et al., 1985; Menchini, 1992; IPCS, 1998; Menchini et al., 1999; Panther et al., 1999) but there are relatively few data on atmospheric PAHs in South American cities (Catoggio et al. 1989; Didyk et al., 2000; Kavouras et al., 1999). For Brazilian cities, most of the available data on atmospheric PAHs are restricted to the Megacities of São Paulo and Rio de Janeiro (Daisey et al. 1987; Miguel and Andrade 1989; Miguel and Pereira, 1989; Ciccioli et al., 1996; Vasconcellos et al., 2003; Vasconcellos, 1996; Fernandes et al., 1999; Azevedo et al., 1999) although the medium city of Niterói has also been studied (Pereira Netto et al., 2001, 2002). Vehicular emission plays a major role in urban areas and the levels of atmospheric PAHs varies widely during the day according to traffic (Nielsen, 1996). Kakimoto et al. (2000) observed that the concentrations of atmospheric PAHs varied between day and night in Japanese cities. The only data comparing day periods in Brazilian cities is due to Daisey et al. (1987) when the levels of selected PAHs were studied in inhalable particulate matter (IPM).

This work compare nocturnal and diurnal levels of PAHs in TSP from a highly trafficked area of Rio de Janeiro City, the capital of Rio de Janeiro State, Brazil. This city is located in the margins of Guanabara Bay and its metropolitan area has about 11 million inhabitants. In the area of study, automotive fleet has contributions of both heavy-duty and light-duty diesel-fuelled and gasoline/ethanol fuelled vehicles. This work also partly addresses to fill the lack on data on atmospheric PAHs in diurnal and nocturnal periods from Rio de Janeiro City and tropical cities.

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MATERIALS AND METHODS

PAHs were purchased from AccuStandard (CT, USA) or Aldrich Chemical Co. (WI, USA). Dichloromethane (HPLC grade), hexane and toluene (both Omnisolv - Residue Analysis) were purchased from E M Science (NJ, USA). SiO₂ Sep Pak cartridges (3 ml; 500 mg) from PR Cola (RJ, Brazil) and a Sep Pak Vacuum Manifold (Waters Corporation, WI, USA) were used to clean-up sample extracts.

Samples were collected on the Campus of the Fundação Oswaldo Cruz, a green area located in a very intensive trafficked area about 10 km away from Rio de Janeiro City Center, Brazil. The sampling points were located in open areas facing the twelve lane Brasil Avenue (AB), the main highway to Rio de Janeiro City (245,000 vehicles/day) and the six lane Leopoldo Bulhões (LB) Avenue that cross along several districts of the city. Both sites are partially influenced by other major highways of the city: Yellow Line (181,000 vehicles/day) and Red Line (130,000 vehicles/day). Automotive emission is the main source of PAHs in both points although they may be eventually influenced by industrial emissions. TSP sampling was performed 3 m above ground in Brasil Avenue (AB) and 2 m above ground in Leopoldo Bulhões Avenue (LB) in open areas facing both avenues. TSP samples were collected with a high volume air sampler (SIBATA-HVC 500, Japan) and glass fiber filter paper (Advantec Toyo, Japan). Sampling periods were established by sunrise and sundown. Samples in both points were collected in parallel while nocturn and diurnal periods corresponded to immediate periods of sampling. After sampling, loaded filters were transported to the laboratory, equilibrated and weighted. Filters were kept in freezer inside glass petri dishes wrapped with aluminium foil until extraction (Pereira Netto et al., 2001).

Further details of the methodology were presented elsewhere (Pereira Netto et al., 2001). Briefly, one quarter of each filter was extracted by ultrasonication with 4 portions CH₂Cl₂ (20 ml; 20 minutes each). Combined extracts were concentrated in rotary evaporator, centrifuged and evaporated under gentle high purity N₂ flow after addition of toluene (100 µl). Concentrated extracts were transferred onto SiO₂ Sep Pak cartridges previously activated with CH₂Cl₂. The PAH rich fraction was eluted with hexane (6 ml), evaporated under N₂ flow after addition of toluene, transferred to vial and kept in refrigerator until analysis by HRGC-MS.

Samples were analysed in a HP5890 gas chromatograph interfaced to a HP5970 mass selective detector with a DB5-ms column (30 m; 0.25 µm; 0.25 mm; J&W Scientific, CA, USA). The oven temperature was kept at 95°C during 1 min, increased to 120°C at 10°C/min, hold at this temperature for 2 min and heated to 300°C at 4°C/min with 10 min final hold. Transfer line and injector were kept at 280°C. Sample extracts and standards were manually injected in splitless mode. Ionisation was performed by electron impact at 70eV and mass spectra were recorded between 50 and 350 a.m.u.. Comparison of retention times with true compounds, fragmentograms and in few cases mass spectra allowed PAH identification. Quantitative analysis was performed by selected ion monitoring

with molecular ions of PAHs and internal standards (Tuominen et al., 1986). The calibration solution was prepared by dissolution of internal standards and PAHs in toluene with posterior dilution in the same solvent (Pereira Netto et al., 2001).

RESULTS AND DISCUSSION

Total ion current (TIC) chromatograms showed a large peak due to unresolved complex mixtures (UCM) as expected for extracts of TSP. The fragmentograms of $m/z = 85$ (aliphatic hydrocarbons) and of $m/z = 95$ (naphthenic hydrocarbons) showed that those classes of hydrocarbons predominated in all extracts while the fragmentogram of $m/z = 191$ indicated the presence of tri- and tetra-terpanes and of hopanes in all extracts. Our data showed that vehicular exhaust is a major source of hydrocarbons in that area of Rio de Janeiro City. Our data are also similar to the previous results obtained in two highly trafficked areas of the city: Rebouças Tunnel and Cinelândia (downtown) (Azevedo et al., 1999).

Mean PAH concentrations between 0.01 and 3.06 ng/m³ were found (Table 1). Chrysene, benzo[b]fluoranthene, benzo[g,h,i]perylene, indene[1,2,3-cd]pyrene and coronene predominated in both sampling points and periods. Some of them are considered gasoline or diesel exhaust markers reinforcing the role of automotive emission in the area of study. Our data suggest that large amounts of PAHs are emitted in the studied area. Although this fact has to be taken with caution due to the differences between sampling points, periods, analytical methodologies and automotive fleet. Indene[1,2,3-cd]pyrene and benzo[ghi]perylene were also previously found as the predominant PAHs in TSP samples taken in Rio de Janeiro City (Daisey et al, 1987) and in São Paulo City, the other Brazilian Megacity (Vasconcelos, 1996). The concentrations of pyrene and fluoranthene considered markers of emission by gasoline fuelled vehicles, found in this work were lower than those previously reported in the Rebouças Tunnel (Azevedo et al., 1999) possibly due to the predominance of gasoline fuelled vehicles in the tunnel and to the lowest air circulation when compared to open areas. However, for almost all studied PAHs, the levels found in this work were larger than those previously reported by Daisey et al. (1987).

Total PAH concentration (Σ PAHs) between 8.25 and 24.19 ng/m³ were found in LB and AB (Figure 1). Σ PAHs in diurnal (D) samples were larger than in nocturnal (N) samples in both sampling points. Σ PAHs decreased in the order ABD > ABN > LBD > LBN that is compatible to the automotive fleet decrease observed during the night and to the difference of automotive fleet between AB and LB. When considering the same compounds, Σ PAHs found in this work were lower than those previously reported in Cinelândia and in the Rebouças Tunnel but greater than the values found in green areas of the city (Azevedo et al., 1999). This fact may be attributed to the reduced air circulation in the tunnel and in Cinelândia (in this case due to the buildings) that increase PAH levels. The comparison of our data with those previously reported for Niterói, a medium city of the Metropolitan Area of Rio de Janeiro City, shows that the PAH levels in Rio de Janeiro City were 2 - 12 times higher than the values observed in Niterói

Table 1. Mean levels of individual PAHs (ng/m³) in samples of TSP from Rio de Janeiro, Brazil.

PAHs	Place and Period of the day			
	ABD	ABN	LBD	LBN
Fluorene	0.08 ± 0.02	0.03 ± 0.01	0.03 ± 0.02	0.01 ± 0.01
Phenanthrene	1.41 ± 0.42	0.52 ± 0.12	0.39 ± 0.21	0.13 ± 0.06
Anthracene	0.16 ± 0.05	0.06 ± 0.01	0.04 ± 0.02	0.02 ± 0.01
2-methyl-phenanthrene	0.47 ± 0.11	0.16 ± 0.05	0.11 ± 0.07	0.05 ± 0.03
Fluoranthene	1.72 ± 0.52	0.70 ± 0.31	0.63 ± 0.43	0.17 ± 0.10
Pyrene	2.02 ± 0.59	0.70 ± 0.28	0.59 ± 0.36	0.18 ± 0.11
Benzo[a]anthracene	1.38 ± 0.33	0.82 ± 0.47	0.33 ± 0.18	0.24 ± 0.15
Chrysene	2.73 ± 0.33	1.54 ± 0.80	0.75 ± 0.56	0.54 ± 0.44
Benzo[b]fluoranthene	2.85 ± 0.85	3.06 ± 0.79	1.66 ± 1.54	1.46 ± 1.06
Benzo[k]fluoranthene	0.68 ± 0.11	0.79 ± 0.18	0.37 ± 0.29	0.38 ± 0.25
Benzo[e]pyrene	1.43 ± 0.41	1.47 ± 0.42	0.79 ± 0.72	0.72 ± 0.51
Benzo[a]pyrene	1.17 ± 0.23	1.44 ± 0.30	0.43 ± 0.27	0.62 ± 0.43
Perylene	0.17 ± 0.09	0.30 ± 0.09	0.08 ± 0.05	0.14 ± 0.09
Indene[1,2,3-cd]pyrene	2.36 ± 1.35	1.81 ± 1.20	2.20 ± 1.73	1.56 ± 0.80
Dibenzo[a,h]anthracene ^(*)	0.17 ± 0.12	0.34 ± 0.16	0.17 ± 0.18	0.18 ± 0.11
Benzo[ghi]perylene	2.53 ± 0.45	1.56 ± 0.31	1.21 ± 0.77	0.95 ± 0.47
Coronene	2.88 ± 1.23	1.38 ± 0.28	1.35 ± 0.73	0.89 ± 0.54
TSP (ug/m ³)	382 ± 50	120 ± 54	179 ± 91	121 ± 25

(*) coeluted with dibenzo[a,c]anthracene under our analytical conditions

(Pereira Netto et al., 2001). A comparison with data of Panther et al (1999) shows that our results are in the range of the values found in other tropical cities.

The total concentration of carcinogenic PAHs (Σ CARC), here considered as those classified by IARC as probably carcinogenic (2A) (namely benzo[a]anthracene, benzo[a]pyrene and dibenzo[a,h]anthracene) and those classified as possibly carcinogenic (2B) (namely benzo[b]fluoranthene, benzo[k]fluoranthene and indene[1,2,3-cd]pyrene) ranged from 4.44 to 8.60 ng/m³ (Figure 1). Similar values of Σ CARC were found in each point independent of the period of the day but the value found in AB was nearly twice that of LB (Figure 1). However, when the percentage of carcinogenic PAHs (% CARC) is considered it is shown that it corresponded to almost 50% of Σ PAHs in both sampling points and periods except for ABD. This may be related to the largest concentrations of certain PAHs (pyrene, fluoranthene and coronene) found in ABD samples and also to dust resuspension, that can be evaluated by the high levels of TSP found there (Table 1).

A comparison of Toxic Equivalent Factors (TEF) calculated according to the data reported by Nisbet and LaGoy (1992) and by Malcolm and Dobson (1994) and compiled in IPCS (1998) is also shown in Figure 1. This approach was successfully applied in the study of PAHs associated with TSP (Castellano et al., 2003).

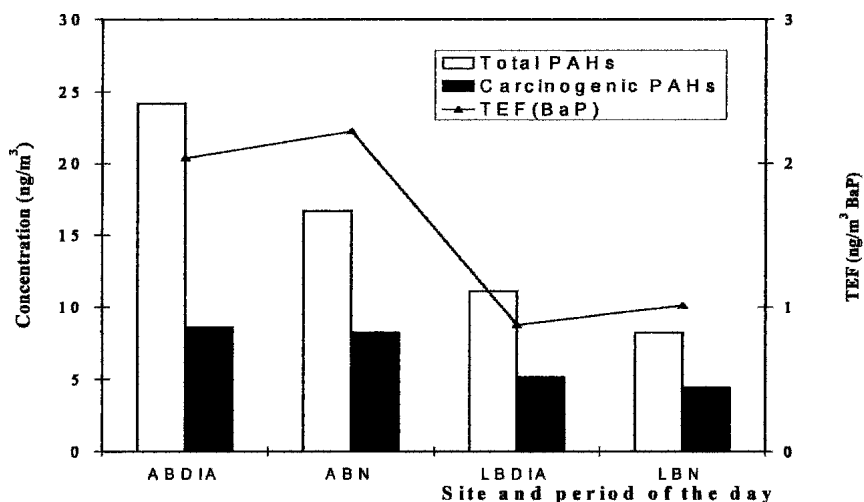


Figure 1. Comparison of the concentration of total PAHs (Σ PAHs - ng/m³), the concentration of carcinogenic PAHs (Σ CARC - ng/m³) and of TEFs from in TSP samples from Rio de Janeiro City, Brazil.

The TEF values for nocturnal samples were larger than the values calculated for diurnal samples: 9 % for AB and 15 % for LB (Figure 1). Those results are certainly dependent on the increase of BaP levels observed during the night in that area of the city, since the TEF of BaP (1.0) is the largest value among all PAHs. It was also observed in both sampling points that the ratios of the mean concentrations of BaP and BeP increased during night, possibly reflecting the lower photochemical stability of BaP when compared to BeP. Our results also reinforce the importance of BaP as a surrogate in atmospheric pollution studies.

For Brazilian cities the only data set comparing day periods is due to Daisey et al. (1987) when the diurnal and nocturnal levels of PAHs in samples of IPM were determined. It was found that during the night the levels of IPM were reduced to about 73% of the diurnal levels. Meanwhile since discrete reductions or even an increase of individual PAH levels were observed during the night; the combination of those results led to an increase of PAHs associated with IPM.

Similar results were observed in this study in ABN sample since the reduction of the levels of both Σ PAHs and Σ CARC were proportionally lower than the reduction of TSP increase (Table 1). This result suggest that if human health is of concern, the exposition to TSP in that area during the night is more dangerous than during the day despite Σ PAHs reduction. The relative increase of PAH levels in the particulate can be attributed to condensation since there is a decrease of about 10°C during the night and to the reduction of photochemical reactions that tend to consume many atmospheric PAHs.

The levels of primary atmospheric pollutants are dependent on the sampling site location, meteorological conditions and temperature, making difficult a direct

comparison of results from different studies. Nevertheless the ratios of individual PAH concentrations found in this study were compared with the ratios calculated from previous data of Daisey et al. (1987) and Kakimoto (2000) (Table 2). From the data of Kakimoto et al. (2000) it can be seen that the ratios of the levels of different PAHs in diurnal and nocturnal samples differ by factors of 0.89 up to 3.55. These ratios also differ in winter and summer samples and seem to depend on site location and on the PAH of concern. Apparently, patterns of PAH ratios were not observed when samples from different sites but in the same season were compared.

Table 2. Ratios of selected PAHs in Rio de Janeiro City and in Japanese cities.

PAHs	Rio de Janeiro			Kanazawa ³		Sapporo ³		Tokyo ³	
	AB ¹	LB ¹	1984 ²	W	S	W	S	W	S
Fluoranthene	2.47	3.74	1.19	1.20	3.08	2.07	1.12	1.29	1.47
Pyrene	2.88	3.25	1.16	1.30	3.55	2.34	1.27	1.18	1.64
Benzo[a]anthracene	1.68	1.36	0.86	1.81	3.00	2.16	1.49	0.88	1.49
Chrysene	1.77	1.39	0.92	1.35	2.91	2.17	1.50	0.90	1.36
Benzo[b]fluoranthene	0.93	1.14	0.98	1.23	2.10	2.34	1.39	0.94	1.24
Benzo[k]fluoranthene	0.86	0.96	0.99	1.19	2.00	2.33	1.37	0.89	1.22
Benzo[a]pyrene	0.81	0.68	0.92	1.49	2.46	2.24	1.40	0.79	1.11
Benzo[ghi]perylene	1.30	1.41	1.12	nd	nd	nd	nd	Nd	nd
Indene[1,2,3-cd]pyrene	1.63	1.27	1.08	nd	nd	nd	nd	Nd	nd

W = winter samples; S = summer samples; nd = not determined

¹This Study; ²Daisey et al., 1987; ³Kakimoto et al., 2000

Our data show that the concentrations of all PAHs were higher during the day than during the night except for some five membered PAHs benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[e]pyrene that showed comparable concentrations in both periods of the day and for benzo[a]pyrene and perylene that displayed larger concentrations during the night. Those results follow the same tendency previously observed by Daisey et al (1987) and it probably reflects a combination of factors such as the reduction of PAH emission, the reduction of the temperature and also the reduction of photochemical reactions. Despite of the fact that no correlation between sunshine levels and seasonal trends of PAH concentrations have been found in other tropical cities (Panther et al, 1999) our data indicate that in Rio de Janeiro City sunshine levels may be of importance at least to the degradation of certain five membered PAHs such as BaP. However, from a toxicological point of view, our results suggest that the particulate would carry a larger amounts of carcinogenic PAHs during the night than during the day in that area of Rio de Janeiro City.

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