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Preliminary Comparison of PAH in Total Suspended Particulate Samples Taken at Niterói and Rio de Janeiro Cities, Brazil

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PAHs are ubiquitous persistent pollutants which have been described in all environmental compartments. Many of them exhibit mutagenic and/or carcinogenic properties and they have been related to several kinds of cancer (Boffetta et al. 1997; Pereira Netto et al. 2000). Their formation and fate have been reviewed (Baeck et al. 1991; Lopes and De Andrade 1996; Bouchez et al. 1996; IPCS, 1998). PAHs and/or their derivatives are present in the atmosphere even in remote areas of the world (Ciccioli et al. 1996) distributed between particulate and vapour phases, according to their vapour pressures and consequently to their molecular weights. In urban areas, the emission of automotive vehicles seems to be one of their main sources. There are data concerning atmospheric PAHs for many cities and places of the world (Alsberg et al 1985; Menchini 1992; APARG 1995; Ciccioli et al. 1996; IPCS 1998; Anh et al. 1999; Menchini et al. 1999), although data concerning South America are scarce (Daisey et al. 1987; Miguel and De Andrade 1989; Catoggio et al. 1989; Vasconcellos, 1996).

Niterói city (about 460000 inhabitants) is located in the margins of Guanabara Bay in Rio de Janeiro State, Brazil (Figure 1). It belongs to the Metropolitan Area of Rio de Janeiro city (about 5.6 millions inhabitants) and it is the second biggest city of the region. When compared to other Brazilian cities, Niterói is considered to have a high environmental quality and a high standard life quality. Despite its regional importance, there is a complete lack of data on atmospheric PAHs for Niterói (and for almost all Brazilian cities). Even for Rio de Janeiro city, the capital of the state, many of the available data are about 10 to 15 years old (Daisey et al. 1987; Miguel and De Andrade 1989; Fernandes et al. 1999; Azevedo et al. 1999). In this work we compare the atmospheric concentrations of 16 PAHs (Table 1) in samples collected in the summer of 1999 in both cities.

MATERIALS AND METHODS

Solid PAHs standards were purchased from both Aldrich Chemical Co. (WI, USA) and AccuStandard (CT, USA). Dichloromethane (HPLC grade),

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Correspondence to: A. D. Pereira Netto hexane and toluene (both Omnisolv - Residue Analysis) were purchased from E M Science (NJ, USA). SiO_2 Sep Pak cartridges (3 mL; 500 mg) purchased from PR Cola (RJ, Brazil) and a Sep Pak Vacuum Manifold (Waters Corporation, WI, USA) were used to clean-up the samples.

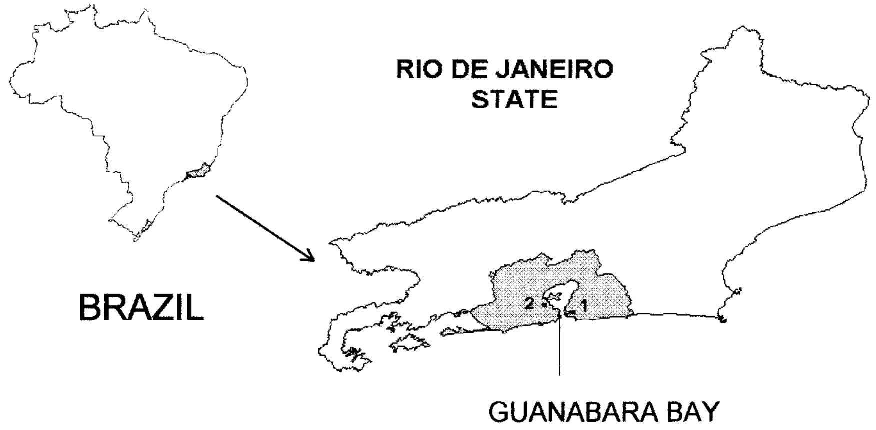

Figure 1. Map showing the localisation of Rio de Janeiro State in Brazil and the approximate localisation of the sampling points at Niterói (1) and at Rio de Janeiro (2). The gray area corresponds to the Metropolitan Area of Rio de Janeiro.

Day-time samples of TSP were collected using a portable high volume air sampler (SIBATA-HVC 500, Japan) and glass fibber filter paper (Advantec Toyo, Japan). They were collected in open areas facing traffic routes at the Campus of Federal Fluminense University located in the center of the Niterói city in a mixed commercial/residential neighbourhood, representative of this city and at the Campus of Oswaldo Cruz Foundation, located in a very intensive traffic area 10 km away of Rio de Janeiro city center, beside the most important route to this city.

One quarter of each filter was extracted by means of ultrasonication in aluminium foil covered amber bechers with 4 portions of 20 mL of CH_2Cl_2 during 20 minutes each. Each combined extract was concentrated up to 10 mL under vacuum in rotary evaporator at temperatures below 40°C and centrifuged at ambient temperature to exclude remaining solids. The solutions were transferred to other test tubes and evaporated under gentle high purity N_2 flow after the addition of 100 μL of toluene as a keeper.

Each extract was transferred onto a SiO_2 Sep Pak cartridge previously activated with 10 mL of CH_2Cl_2. The PAHs rich fraction was eluted with 6 mL of hexane and after addition of 100 μL of toluene, it was evaporated under N_2 flow, transferred to 2 mL vials and kept in refrigerator until analysis by HRGC-MS.

Table 1. Measured PAHs at Niterói and Rio de Janeiro, their abbreviations and monitored ions for SIM.

Compound	Abbreviations	Ion for SIM
Phenanthrene	Phe	178
Anthracene	A	178
2-methyl-phenanthrene	2-MePhe	192
Fluoranthene	Fluo	202
Pyrene	Py	202
Benzo[a]anthracene	BaA	228
Chrysene	Chry	228
Benzo[k]fluoranthene	BkFluo	252
Benzo[b]fluoranthene	BbFluo	252
Benzo[e]pyrene	BeP	252
Benzo[a]pyrene	BaP	252
Perylene	Per	252
Benzo[ghi]perylene	BgP	276
Indene[1,2,3-cd]pyrene	Ind	276
Dibenzo[a,h]anthracene(*)	DiBA	278
Coronene	Cor	300
9-phenylanthracene(#)	FiA	254
2,2'-binaphthalene(#)	BiNA	254
9,10-diphenylanthracene(#)	DiFiA	330

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

(#) internal standards

Chromatographic conditions for PAHs separation were previously optimised by HRGC-FID using a HP-5890 gas chromatograph and a DB5-ms column (30 m; 0.25 μm; 0.25 mm; J&W, CA, USA). Resolutions between A and Phe and between BaP and BeP were used to evaluate the chromatogram.

Qualitative and quantitative analysis were performed by HRGC-MS employing a HP5890 gas chromatograph interfaced to a HP5970 mass selective detector and the same column. 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. The injector was kept at 280°C and all injections were performed in splitless mode with hot needle technique. The transfer line was kept at 280°C and the ionisation was performed by electron impact at 70eV.

For qualitative analysis, mass spectra were obtained from 50 to 350 a.m.u. and the identification was performed by comparison of retention times with true compounds, fragmentograms and in few cases by mass spectra.

Quantitative analysis was performed by selected ion monitoring (SIM) mode using PAHs molecular ions (Table 1) (Tuominen et al., 1986). The calibration solution was prepared by dissolution of solid PAHs and internal standards: 9-phenylanthracene, 2,2'-binaphthalene (Alsberg et al. 1985) and 9,10-diphenylanthracene in toluene and posterior dilution in the same solvent. The concentrations in the calibration solution were adjusted to intermediate values of the linear ranges described for each PAH in a similar equipment (Brindle and Li, 1990).

RESULTS and DISCUSSION

Recoveries between 89 % (Phe) and 103% (BeP) were obtained under the analytical conditions. Relative standard deviations of individual response factors were better than 12 % and are comparable to the previous results of Brindle and Li (1990).

Extracts of all samples taken at Niterói or Rio de Janeiro displayed similar patterns in scan mode. Fragmentograms of specific ions (m/z 71 and 85) showed that aliphatic hydrocarbons were the predominating compounds. All extracts also displayed similar patterns of PAHs under HRGC-MS-SIM.

The atmospheric concentrations of atmospheric PAHs in Niterói and Rio de Janeiro cities are presented in Table 2. Individual PAH concentrations were systematically lower in Niterói (0.03 to 1.45 ng/m^3) than in Rio de Janeiro (0.13 and 4.10 ng/m^3). The PAHs concentrations in Niterói are also comparable to the lowest values previously reported for urban areas (IPCS, 1998). Comparison of total PAH concentrations shows that in Rio de Janeiro they are 3.5 times greater than in Niterói.

Mean individual concentrations of PAHs in Niterói were 2 to 12 times lower than in Rio de Janeiro. BaP, a well known carcinogenic PAH, is a typical example with mean concentrations of 0.33 ng/m^3 and 1.23 ng/m^3. The ratios of the concentrations of BaA and Chry in both cities were the highest among all PAHs (12 and 10 times, respectively). The causes and significance of this fact are unclear and are being studied, but they may be of environmental concern due to the carcinogenic properties of BaA.

Data for Per and diBA in the atmosphere of Rio de Janeiro are here reported for the first time. Although our sampling was done in different place and 15 years later, our results are of the same magnitude of those previously reported by Daisey et al. (1987) and Miguel and De Andrade (1989) for day time samples taken at Rio de Janeiro city.

Table 2. Concentrations (ng/m^3) and means of concentrations of atmospheric PAHs at Niterói and Rio de Janeiro

	Niterói				Rio de Janeiro		
Date	01/25/1999	02/09/1999	02/23/1999	Mean	01/15/1999	02/27/1999	Mean
Phe	0.26	0.35	0.21	0.27	1.07	1.04	1.06
A	0.027	0.035	0.032	0.031	0.14	0.13	0.14
2-MePhe	0.063	0.084	0.070	0.072	0.37	0.40	0.39
Fluo	0.28	0.39	0.22	0.30	1.38	1.30	1.34
Py	0.36	0.44	0.33	0.38	1.63	1.51	1.57
BaA	0.091	0.21	0.094	0.13	2.10	1.31	1.71
Chry	0.19	0.33	0.19	0.24	2.06	3.37	2.72
BbFluo	1.11	1.62	1.30	1.34	3.92	4.10	4.01
BkFluo	0.20	0.24	0.20	0.21	0.50	0.84	0.67
BeP	0.28	0.44	0.31	0.34	1.32	1.99	1.66
BaP	0.30	0.41	0.29	0.33	1.52	0.94	1.23
Per	0.043	0.043	0.038	0.041	0.31	0.19	0.25
Bgp	0.67	1.07	1.23	0.99	2.22	3.34	2.78
DiBA	0.045	0.067	0.070	0.061	0.14	0.28	0.21
Ind	0.68	0.95	0.94	0.86	1.43	2.07	1.75
Cor	0.89	1.20	1.45	1.18	2.34	1.62	1.98
TOTAL	5.48	7.88	6.98	6.78	22.5	24.4	23.4

Our results for BaP are greater than those reported by Fernandes et al. (1999) but the reason may be related to the period of sampling because they collected 24 hours samples and during the night, atmospheric PAHs concentrations decrease due to traffic reduction. Our data for Rio de Janeiro also show consistency with the results of Vasconcellos (1996) for São Paulo, another Brazilian megacity. The predominating PAHs were the same and the ratios BeP/Bap and BgP/Ind are nearly the same for Rio de Janeiro and São Paulo.

Our data also show similarities with those of Azevedo et al. (1999). For example the ratios Fl/Fl+Py and BaA/BaA+Chry+Try are in intermediate values of their results. Those ratios can be used to source assessment (Sicre et al., 1987) and our values are indicatives of same sources in both cities: emission by gasoline fuelled vehicles and used motor oil. Total PAHs concentration at Niterói also is similar to those previously reported for green areas of Rio de Janeiro City (Azevedo et al., 1999).

Considering that low atmospheric concentrations of PAHs are indicative of good environmental quality, our results are consistent with the hypothesis of a good environmental quality of Niterói.

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