Bull. Environ. Contam. Toxicol. (2002) 69:173–180

DOI: 10.1007/s00128-002-0044-3

Bulletin of Environmental Contamination and Toxicology

# Polycyclic Aromatic Hydrocarbons in Total Suspended Particulate of Niterói, RJ, Brazil: A Comparison of Summer and Winter Samples

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Received: 21 July 2001/Accepted: 22 April 2002

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent organic pollutants, which have been described in all environmental compartments. Many of them exhibit carcinogenic and/or mutagenic properties and have been related to several kinds of cancer (Boffetta et al. 1997; Pereira Netto et al. 2000). Their formation, sources and fate have been reviewed (Baeck et al. 1991; Lopes and Andrade 1996; Bouchez et al. 1996; IPCS, 1998). In the atmosphere, PAHs are distributed between suspended particles and the gaseous phase according to their vapor pressures and to temperature (Valerio and Pala, 1991). There are data on atmospheric PAHs for many places and cities in the world (Alsberg et al. 1985; Menchini, 1992; APARG 1995; Ciccioli et al. 1996; IPCS 1998; Anh et al. 1999; Menchini et al. 1999; Panther et al. 1999). Seasonal trends were observed in temperate and cold climates (Rocha and Duarte 1997; Menchini et al. 1999) but there are few data on seasonal trends for tropical cities (Panther et al. 1999).

Moreover data on atmospheric PAHs for urban areas of South America are relatively scarce (Daisey et al. 1987; Catoggio et al. 1989; Miguel and Andrade 1989; Vasconcellos 1996; Azevedo et al. 1999; Fernandes et al. 1999; Kavouras et al. 1999; Didyk et al. 2000; Pereira Netto et al. 2001). Furthermore, most of available data for urban areas of Brazil are restricted to the two Brazilian Megacities: Rio de Janeiro and São Paulo (Daisey et al. 1987; Miguel and Andrade 1989; Vasconcellos, 1996; Azevedo et al. 1999; Fernandes et al. 1999; Pereira Netto et al. 2001). As a consequence there is few information concerning PAHs in the atmospheres of medium or small Brazilian cities (Pereira Netto et al., 2001).

Niterói City is a tropical city located in the margins of Guanabara Bay in Rio de Janeiro State, Brazil. It belongs to the Metropolitan Area of Rio de Janeiro City. When compared to other Brazilian cities, it is considered to have a high environmental quality and a high standard life quality. The aim of this work is to present data on 16 PAHs (Table 1) concentrations in diurnal samples of TSP collected in the summer and in the winter of 1999 in Niterói City in order to evaluate for seasonal differences. It is also a contribution that partly addresses to

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fill the lack of data on atmospheric PAHs in tropical urban areas and in medium Brazilian cities.

## MATERIALS AND METHODS

Further details on sampling site description, sample collection and processing and of PAH analysis were presented elsewhere (Pereira Netto et al. 2001). Briefly, diurnal samples of TSP were collected in open areas facing traffic routes using a portable high volume air sampler (SIBATA-HVC 500, Japan) and glass fibber filter paper (Advantec Toyo, Japan).

**Table 1.** Measured PAHs at Niterói, their abbreviations and monitored ions for selected ion monitoring (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 | IndP | 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 conditions
(#) internal standards

One quarter of each filter was ultrasonically extracted in aluminium foil covered amber bechers (4 portions of 20 mL of $CH_2Cl_2$; 20 minutes each). Each combined extract was evaporated and centrifuged. The solution was transferred to a test tube. After addition of toluene (100 µL), it was further evaporated under $N_2$ flow and transferred onto $SiO_2$ SPE cartridges (500 mg; 3 mL) previously activated with $CH_2Cl_2$. The PAH rich fraction was eluted with hexane. After addition of toluene, it was evaporated under $N_2$ flow, transferred to 2 mL vial and kept in refrigerator until analysis.

Qualitative and quantitative analysis were performed by HRGC-MS with a HP5890 gas chromatograph interfaced to a HP5972 mass selective detector and a DB5-ms column (30 m; 0.25 μm; 0.25 mm - J&W Scientific, CA, USA). 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. Ionization was performed by electron impact at 70eV. Retention times of true compounds and fragmentograms were used for PAH identification. Quantitative analysis was performed by selected ion monitoring (SIM) using molecular ions of PAHs and internal standards (Tuominem et al. 1986) (Table 1).

## RESULTS AND DISCUSSION

Concentrations of atmospheric PAHs in diurnal samples of Niterói are shown in Table 2 (summer samples) (Pereira Nettto et al. 2001) and in Table 3 (winter samples). Individual concentrations between 0.021 and 1.62 ng/m$^3$ were found and total PAH concentrations varied from 5.12 to 9.27 ng/m$^3$. PAHs of 5 or more rings (BbFluo, Cor, IndP and BgP) predominated in all samples.

**Table 2.** Concentrations (ng/m$^3$) and means of concentrations of atmospheric PAHs during the summer of 1999 at Niterói (Pereira Netto et al. 2001).

| Date | 01/25 | 02/09 | 02/23 | Mean |
|---|---|---|---|---|
| Phe | 0.26 | 0.35 | 0.21 | 0.27 |
| A | 0.03 | 0.04 | 0.03 | 0.03 |
| 2-MePhe | 0.06 | 0.08 | 0.07 | 0.07 |
| Fluo | 0.28 | 0.39 | 0.22 | 0.30 |
| Py | 0.36 | 0.44 | 0.33 | 0.38 |
| BaA | 0.09 | 0.21 | 0.09 | 0.13 |
| Chry | 0.19 | 0.33 | 0.19 | 0.24 |
| BbFluo | 1.11 | 1.62 | 1.30 | 1.34 |
| BkFluo | 0.20 | 0.24 | 0.20 | 0.21 |
| BeP | 0.28 | 0.44 | 0.31 | 0.34 |
| BaP | 0.30 | 0.41 | 0.29 | 0.33 |
| Per | 0.04 | 0.04 | 0.04 | 0.04 |
| Bgp | 0.67 | 1.07 | 1.23 | 0.99 |
| DiBA | 0.04 | 0.07 | 0.07 | 0.06 |
| IndP | 0.68 | 0.95 | 0.94 | 0.86 |
| Cor | 0.89 | 1.20 | 1.45 | 1.18 |
| TOTAL PAHs | 5.48 | 7.88 | 6.98 | 6.78 |

Individual atmospheric PAHs concentrations at Niterói are comparable to the lowest values previously reported for urban areas (IPCS, 1998). They are lower than those reported for Rio de Janeiro City (Daisey et al. 1987; Miguel and Andrade 1989; Azevedo et al. 1999) and comparable to the values measured in green areas of Rio de Janeiro City (Azevedo et al. 1999). A comparison of the concentrations of atmospheric PAHs during the summer of 1999 has shown that they were systematically lower in Niterói (0.03 to 1.45 ng/m$^3$) than in Rio de Janeiro City (0.13 and 4.10 ng/m$^3$) (Pereira Netto et al. 2001).

**Table 3.** Concentrations (ng/m$^3$) and means of concentrations of atmospheric PAHs during the winter of 1999 at Niterói.

| Date | 07/26 | 08/23 | 08/30 | Mean |
|---|---|---|---|---|
| Phe | 0.48 | 0.24 | 0.23 | 0.32 |
| A | 0.04 | 0.02 | 0.02 | 0.03 |
| 2-MePhe | 0.10 | 0.07 | 0.07 | 0.08 |
| Fluo | 0.79 | 0.34 | 0.34 | 0.49 |
| Py | 0.76 | 0.43 | 0.44 | 0.54 |
| BaA | 0.44 | 0.21 | 0.25 | 0.30 |
| Chry | 0.77 | 0.48 | 0.52 | 0.59 |
| BbFluo | 1.20 | 0.62 | 0.86 | 0.89 |
| BkFluo | 0.29 | 0.16 | 0.22 | 0.22 |
| BeP | 0.61 | 0.36 | 0.49 | 0.49 |
| BaP | 0.54 | 0.28 | 0.39 | 0.40 |
| Per | 0.10 | 0.06 | 0.08 | 0.08 |
| Bgp | 1.34 | 0.79 | 1.05 | 1.06 |
| DiBA | 0.08 | 0.05 | 0.07 | 0.07 |
| IndP | 0.89 | 0.59 | 0.81 | 0.76 |
| Cor | 0.84 | 0.42 | 0.60 | 0.62 |
| TOTAL PAHs | 9.27 | 5.12 | 6.45 | 6.94 |

The mean individual PAH concentrations for both seasons are compared in Figure 1. In winter, the mean concentrations of all PAHs except A, BbFluo, IndP and Cor were greater than in summer. Among all PAHs, the concentrations of Chry and BaA showed the greatest variations (about 2.5). Concentrations of some PAHs (Fluo, Py and BeP) were increased by about 1.5 while Per concentration is nearly twice in winter than in summer. The decrease of the mean concentrations of A, BbFluo, IndP and Cor in winter samples is unexpected since the reduction of mean temperature would imply in increase of their concentrations in TSP (Valerio and Pala 1991) as observed for all other PAHs. The reason for this fact is unclear but it will receive further attention during undergoing study.

When the mean individual and total PAHs concentrations of both seasons were compared by Student's t test, it was verified that there were no significative

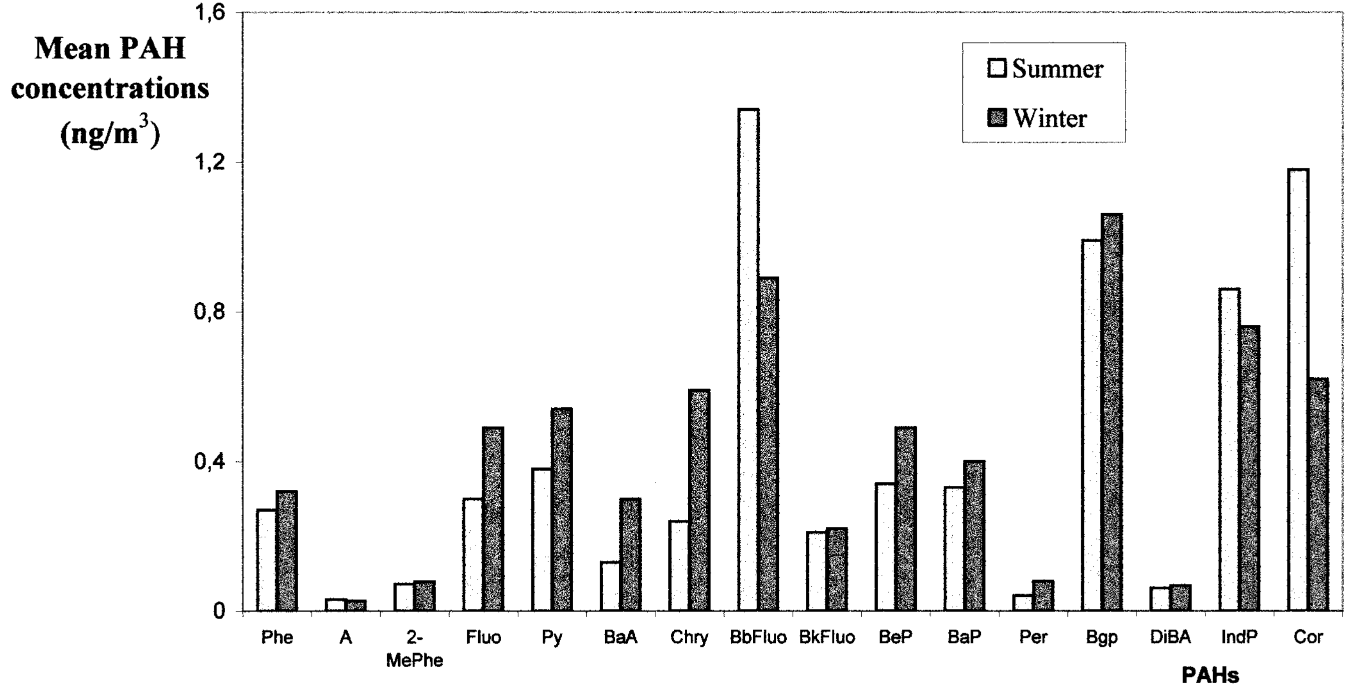


**Figure 1.** Comparison of mean atmospheric PAH concentrations (ng/m$^3$) in summer and winter TSP samples collected in Niterói City.

differences between winter and summer mean concentrations indicating that there were no (significative) seasonal effects.

However, for Niterói City, the difference between summer and winter mean daytime temperatures are relatively small (about 15°C) and consequently there would be few temperature effects on PAHs concentrations. This is consistent with the results of Panther et al. (1999) for other tropical cities, where it was observed that besides temperature other factors had to be considered. Our data also confirm this point: when considering all collected samples, maximum and minimum total PAHs concentrations where obtained in winter, indicating that during the same season individual concentrations can vary widely.

This addresses to the importance of other factors to the interpretation of our data. First of all, in Niterói City summer is typically a rainy season while winter is a dry season. This leads to a decrease of removal rates due to atmospheric processes (scavenging). Second, since heating systems are not used in Niterói City emission is not increased during winter. Third, photochemical reactions are enhanced during summer. Finally, since relatively few data are available this can lead to a misinterpretation of the natural phenomena.

Finally our data are consistent with the hypothesis of good environmental quality in Niterói since atmospheric PAHs concentrations are comparable to the lowest values previously reported for urban areas (IPCS, 1998). Probably lower concentrations will be observed in the residential areas of Niterói during the undergoing study of seasonal and spatial variations of PAH concentrations.

*Acknowledgments.* We thank Dr. Thomas M. Krauss for helpful support in the initial development of HRGC-MS methods. JCM and GA thank CNPq/Brazil for financial support and RPB thanks CNPq/Brazil for a PIBIC undergraduate grant. The authors also thank CAPES for financial support.

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