

Identification of Polycyclic Aromatic Hydrocarbons in Street Dust of Niterói City, RJ, Brazil

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PAHs are ubiquitous persistent organic pollutants. Many of them exhibit carcinogenic or mutagenic properties (Boffetta et al. 1997; Pereira Netto et al. 2000). PAHs formation and fate have been reviewed (Baek et al. 1991; Lopes and Andrade 1996; Bouchez et al. 1996; IPCS, 1998) and they have been described in all environmental compartments. There is concern about PAHs in street dust (SD) since through runoff they can be transported into water bodies contaminating sediments (Herrmann, 1981) and consequently the food chain. Walker et al. (1999) showed that urban runoff was a main PAH source to river sediments. Latimer et al. (1990) suggested that used crankcase oil was the main hydrocarbon source to runoff. Ngabe et al (2000) showed that atmospheric deposition also played an important role in the PAHs content of runoff since its chromatographic pattern resembled that of atmospheric total suspended particulate (TSP). Krein e Schorer (2000) showed that runoff composition depended on carried particle sizes and that SD was reloaded for its PAH content in few days. Takada et al. (1991) compared SD samples from a residential street and from a very trafficked street of Tokyo. In the residential street, PAHs were mainly from stationary sources while automobile exhaust was their main source in the trafficked street. Yang and Baumann (1995) studied spatial and seasonal variations of PAH concentrations in SD from some German cities.

The aim of this paper is to present results on the identification of 15 PAHs in SD samples collected in the summer of 2000/2001 in Niterói City, Rio de Janeiro State, Brazil, which is located in the margins of Guanabara Bay. The seasonal and spatial variations of PAH concentrations in SD are being studied. Our work will allow the assessment of SD as a PAH source to this water body, which receives most of the rainwater from Niterói. As far as we know, there are no data on PAHs in either SD or runoff in Brazil.

MATERIALS AND METHODS

Solid PAHs were purchased from AccuStandard (CT, USA) and Aldrich Chemical Co. (WI, USA). Hexane and toluene (both Omnisolv - Residue Analysis - E M Science, NJ, USA) and dichloromethane (Absolv – Tedia, RJ, Brazil) were

employed. SiO₂ SPE cartridges (3 mL; 500 mg) and a SPE Vacuum Manifold from Waters Corporation (WI, USA) were used to clean up sample extracts.

SD samples were collected using a car cleaner in the sidewalk, near the curb. Typically, areas of 0.5 – to 1 m² were sampled. About 10 g of SD were collected and kept in amber flasks in freezer until analysis. Results presented here correspond to samples collected at 2 different points of Niterói City: in front of the Boat Station, in the city center, about 30 meters from seashore and at the University Campus, in front of our laboratory building, about 400 m away from seashore.

Samples were sieved before extraction. Approximately 1 g of the fraction < 1 mm² was weighted to 0,1 mg and submitted to extraction as previously described for TSP samples (Pereira Netto et al, 2001). Briefly, SD samples were ultrasonically extracted in aluminium foil covered amber bechers (4 portions of 20 mL of CH₂Cl₂, 20 minutes each). Combined extracts were concentrated up to 10 mL in rotary evaporator (T < 40 °C) and centrifuged at ambient temperature to exclude solids. Solutions were transferred to test tubes and evaporated under gentle high purity N₂ flow after addition of toluene (100 µL). Concentrated extracts were transferred onto SiO₂ SPE cartridges previously activated with CH₂Cl₂. The PAHs rich fraction was eluted with hexane, further evaporated with N₂ flow and kept in 2 mL vials.

Extracts were analysed by HRGC-MS using an AutoSystem TurboMass (Perkin Elmer, USA). Separation conditions were previously optimised in a DB5-ms column (30 m; 0.25 µm; 0.25 mm; J&W, USA) with a solution containing 25 PAHs including the 16 EPA target PAHs. Oven temperatures were: 80°C during 0.5 min, heated to 120°C at 20°C/min, kept at this temperature for 2 min and increased to 290°C at 4°C/min, with 15 min final hold. Transfer line was kept at 260°C and injector was kept at 300°C. Injections were performed with automatic sampler in splitless mode.

Extracts were analysed in full scan mode and by selected ion monitoring (SIM). Ionisation was performed by electron impact at 70 eV. Mass spectra were obtained from 50 to 350 a.m.u. Molecular ions were used to draw reconstructed chromatograms and in SIM mode (Tuominen et al., 1986). Retention times obtained with the known solution were used to construct a table for SIM acquisition. Combination of data from SIM, fragmentograms and retention times led to PAH identification. Mass spectra represented limited tools for PAH identification due to extract complexity.

RESULTS AND DISCUSSION

All extracts displayed total ion current (TIC) chromatograms showing large peaks due to unresolved complex mixtures (UCM). This is illustrated by the TIC chromatogram of the sample collected in front of the Boat Station in 02/13/01

(Figure 1a). The reconstructed chromatogram of $m/z = 85$ (Figure 1b) showed that as expected aliphatic hydrocarbons predominated in the extract.

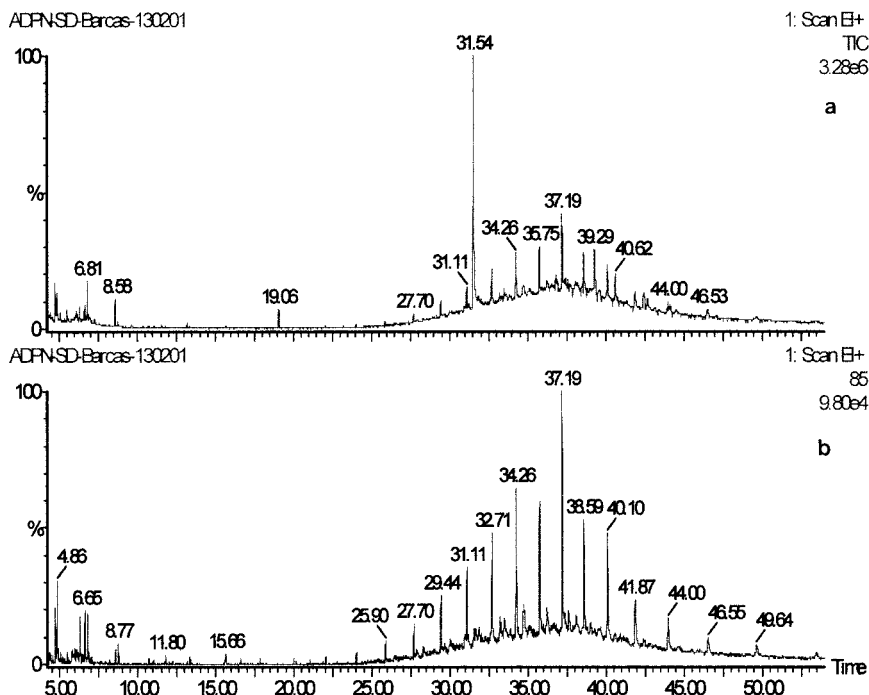


Figure 1. TIC chromatogram (a) and fragmentogram of $m/z = 85$ (aliphatic hydrocarbons) (b) of SD extract.

Two large peaks were also present in the TIC chromatogram (Figure 1a). Fragmentogram of $m/z=149$ indicated that they were due to phthalates. Interpretation of mass spectra led to identification of butylphthalate (19.06 min) and of diisooctylphthalate (31.55 min). The sources of phthalates to SD samples are unclear. However their presence can be attributed to their environmental ubiquity or even to extract contamination during handling.

SIM chromatograms for that sample are shown in Figure 2a-f. Fifteen PAHs were identified: phenanthrene (17.40 min) and anthracene (17.64 min) (Figure 2a); 2-metilphenanthrene (19.94 min) (Figure 2b); fluoranthene (23.14 min) and pyrene (24.17 min) (Figure 2c); benzo[a]anthracene (30.18 min) and chrisene (30.28 min) partly resolved from tryphenylene (30.34 min) (Figure 2d). Benzo[b]fluoranthene (34.26 min), benzo[k]fluoranthene (35.12 min), benzo[e]pyrene (36.22 min), benzo[a]pyrene (36.42 min) and perylene (37.19 min) are shown in Figure 2e. Indeno[1,2,3-cd]pyrene (41.08 min), benzo[ghi]perylene (42.28 min) and coronene (52.19 min) are shown in Figure 2f.

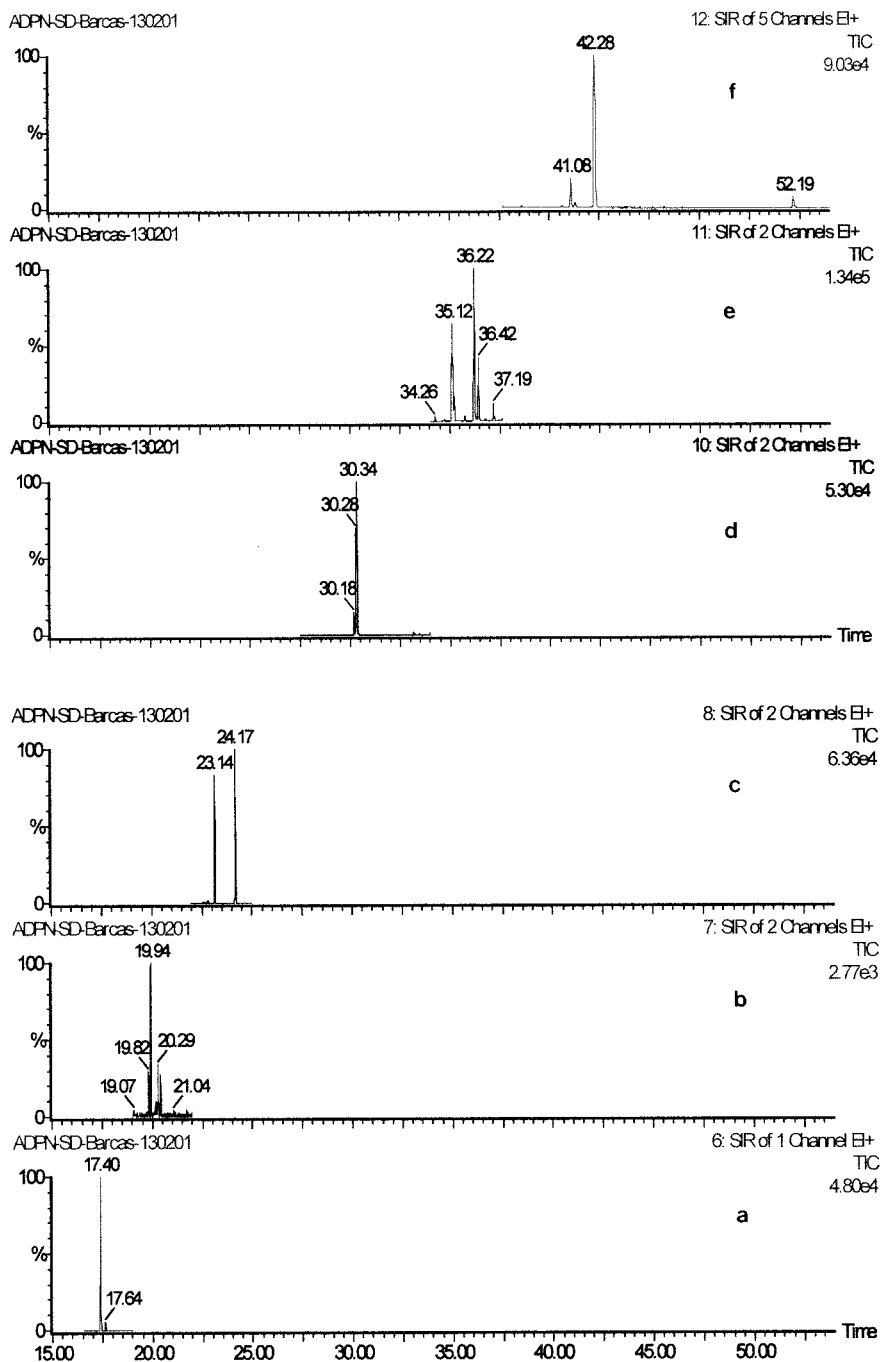


Figure 2. SIM chromatograms showing the peaks of the PAHs identified in SD samples from Niterói City. See text for details.

Samples collected in front of the Boat Station in 01/15/01 and in the car park in front of our laboratory building in the University Campus in 11/21/00 displayed similar results: a complex UCM peak mainly due to aliphatic hydrocarbons; the same phthalates and PAHs also were identified.

However and considering sample origin, an surprising fact was observed during the analysis of the sample collected in 11/20/2000 in the car park in front of our laboratory building in the University Campus: benzo[a]pyrene (BaP) was absent in this sample.

Parts of the SIM chromatograms of $m/z = 252$ obtained with the 3 samples are compared in Figure 3a-c. The peaks corresponding to BaP and benzo[e]pyrene (BeP) can be respectively observed in Figures 3a and 3b. In contrast, in the sample collected in the car park (Figure 3c) the peak corresponding to BaP is practically absent.

The causes for BaP absence in this sample are unclear, but possibly, they can be attributed to a combination of many factors. First, the sampled area in the University Campus is frequently swept. Second, PAHs deposition is relatively limited due to the restricted automotive traffic and to trees which, limit atmospheric deposition. This would imply that at this point, SD is an "old" unswept deposit hold inside pavement pores submitted to both runoff and solar radiation. Finally it is necessary to consider that BaP is more photosensitive than BeP. As a conclusion, the reload rate of BaP (Krein and Schorer, 2000) would be slow implying in very low concentrations in SD at this point.

Nevertheless, the absence of BaP in this sample does not reduce its environmental concern and importance since other carcinogenic PAHs such as benzoanthracene were found on it. Moreover phenanthrene, fluoranthene and pyrene, which according to Boxall and Maltby (1997) are responsible to a great part of sediment toxicity were also identified in all SD samples. However, the absence of BaP can be used to distinguish between those samples if SD is supposed to be used as a passive sampler in future air pollution studies.

The absences of naphthalene, acenaphthene, acenaphthylene and fluorene in all samples may be due to 2 factors, related to their elevated vapour pressures and consequently to their evaporation. Firstly: environmental temperature was relatively high (35 to 40°C) during sampling; secondly they may have been lost in any evaporation step during sample handling.

PAHs identified in this work are summarised in Table 1 together with those previously described in samples from related environmental compartments. Considering the relationships among those media or compartments, very good agreement is found between our data and the previously reported.

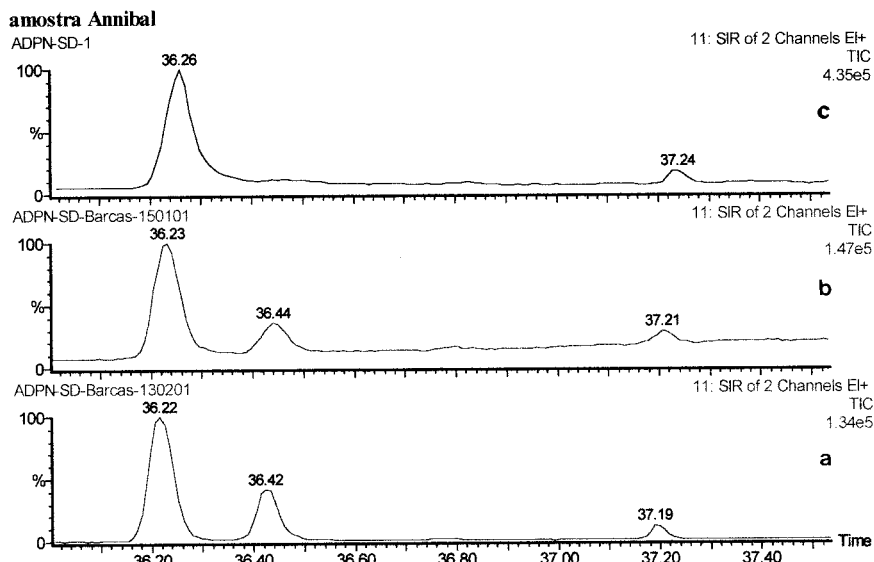


Figure 3. Part of the SIM chromatograms ($m/z=252$) of SD samples. Note that benzo[a]pyrene peak is missing in Figure 3c. See text for details.

Table 1. Comparison of the PAHs identified in this work and in related or similar samples.

	This work (2001)	Yang and Baumann (1995)	Ngabe et al. (2000)	Spitzer and Kuwatsuka (1993)	Pereira Netto et al. (2001)
PAHs	SD Niterói	SD Germany	Runoff USA	Soil Germany	TSP Niterói
Fluorene	-	+	+	nm	nm
Phenanthrene	+	+	+	+	+
Anthracene	+	+	+	-	+
2-methyl-phenanthrene	+	+	+	nm	+
Fluoranthene	+	+	+	+	+
Pyrene	+	+	+	+	+
Benzo[a]anthracene	+	+	+	+	+
Chrysene	+	+	+	+	+
Benzo[k]fluoranthene	+	nm	+\$	+\$	+
Benzo[b]fluoranthene	+	nm			+
Benzo[e]pyrene	+	nm	+	+	+
Benzo[a]pyrene	+	nm	+	+	+
Perylene	-	nm	nm	+	-
Benzo[ghi]perylene	+	nm	+	nm	+
Indene[1,2,3-cd]pyrene	+	nm	+	nm	+
Coronene	+	nm	nm	nm	+

(\$) benzo[b]fuoranthene + benzo[k]fluoranthene

nm = not mentioned in the reference

PAH quantification and the study of seasonal and spatial variations of their concentrations are being carried out. This will allow the assessment of the role of SD as a pollution source to Guanabara Bay, which receives most of the rainwater from Niterói City.

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