Bull. Environ. Contam. Toxicol. (2004) 72:829–835

Bulletin of Environmental Contamination and Toxicology

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

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Received: 15 April 2003/Accepted: 7 January 2004

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants of concern since many of them and many PAH mixtures exhibit mutagenic and/or pro-carcinogenic properties (Boffetta et al. 1997; Pereira Netto et al. 2000). PAHs have been described in all environmental compartments and their formation, sources and fate have been reviewed (Baek et al. 1991; Lopes and Andrade 1996; Bouchez et al. 1996; IPCS, 1998; Vo Dinh, 1998). It is well known that the combustion of organic matter is an important source of PAHs to the environment. After formation, they get dispersed in the atmosphere, distributed between the gaseous and particulate phases according to their vapor pressures. PAHs can be transported and dispersed over large areas or they can also be deposited in soil by dry and wet processes (IPCS, 1998; Vo Dinh et al. 1998). Sources of PAHs to street dust (SD) include atmospheric deposition and direct deposition (crankcase oil, for example). There is concern about PAHs in SD since through runoff they can be transported into water bodies contaminating sediments (Herrmann, 1981) and consequently the food chain. Walker et al. (2000) showed that urban runoff was an important source of PAHs to river sediments while Boxall and Maltby (1997) showed that PAHs were responsible for most of sediment toxicity. Krein and Schorer (2000) observed that runoff composition depended on carried particle sizes and that SD was reloaded for its PAH contents in few days. Latimer et al. (1990) suggested that used crankcase oil was the major source of hydrocarbons to runoff but the role of atmospheric deposition in the PAH budget of runoff was also demonstrated by its chromatographic pattern which resembled that of atmospheric total suspended particulate (TSP) (Ngabe et al. 2000). The levels of PAHs in SD are also directly related to urban use and in more trafficked streets they seem to be greater than in less trafficked areas. The patterns of PAHs in SD samples from a residential street and from a heavily trafficked street of Tokyo were compared. In the trafficked street the main PAH source was automobile exhaust while in the residential street PAHs were mainly derived from stationary sources (Takada et al. 1990). PAH concentrations in SD samples from German cities and places were also studied. Spatial and seasonal variations of PAH levels were observed according to site localization (Yang and Baumann, 1995).

There is an almost complete lack of data on PAHs in SD in Brazil except our

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previous results (Pereira Netto et al. 2002). This paper aims to present some quantitative data on PAHs in SD samples collected in the central area of Niterói City, Rio de Janeiro State, Brazil. This tropical city is located in the margins of Guanabara Bay, which consequently receives most of the rainwater drainage from Niterói. Present results are part of a study that aims to evaluate and characterize the seasonal and spatial variations of PAH levels in SD in Niterói. These data will possibly allow the assessment of the importance of SD as a source of PAHs to Guanabara Bay.

MATERIALS AND METHODS

A standard solution containing all 16 EPA target PAHs at concentrations of 0.2 mg/mL (AccuStandard, CT, USA) and solid PAHs from Aldrich Chemical Co. (WI, USA) or AccuStandard were employed. Perdeuterated PAHs were from Isotech (OH, USA) or Cambridge Isotope Laboratories (MA, USA). Hexane and toluene (both Omnisolv – Residue Analysis - E M Science, NJ, USA) and dichloromethane (Absolv – Tedia, RJ, Brazil) were employed. SiO_2 SPE cartridges (3 mL; 500 mg, PR Cola, RJ, Brazil) and a SPE Vacuum Manifold from J.T BAKER (NJ, USA) were used to clean up sample extracts.

Sample collection and extraction were described elsewhere (Pereira Netto et al. 2002a). Briefly, about 10 g of SD were collected near the curb and kept in amber flasks in freezer until analysis. Samples were sieved before extraction. Approximately 1 g of the fraction < 1 mm^2 was submitted to ultrasonic extraction as previously described for TSP and SD samples (Pereira Netto et al. 2001, 2002b). Concentrated extracts were submitted to clean up on SiO_2 SPE cartridges previously activated with CH_2Cl_2. The PAH rich fraction was eluted with hexane, evaporated under N_2 flow and kept in 2-mL vials.

Extracts were analyzed by HRGC-MS using an AutoSystem TurboMass (Perkin Elmer, USA) as previously described (Pereira Netto et al. 2002a). A DB5-ms column (30 m; 0.25 μm; 0.25 mm; J&W, CA, USA) in optimized chromatographic conditions. 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 manually performed in splitless mode with hot needle technique (Pereira Netto et al. 2002a).

Extracts were analyzed in full scan mode and by selected ion monitoring (SIM). Ionization was performed by electron impact at 70eV. Mass spectra were obtained between 50 and 350 a.m.u.. Molecular ions (Tuominem et al. 1986) were used to draw reconstructed chromatograms and in SIM mode. PAHs were identified by combining data from SIM and comparison of retention times with true compounds. Quantitative analysis was performed in the SIM mode. Perdeuterated PAHs were used as internal standards and calibration was performed by external standards. Table 1 summarizes the studied PAHs and the used internal standards.

Table 1. Measured PAHs in SD samples from Niterói City, their abbreviations and monitored ions for SIM.

PAHs	Abbreviations	Ions for SIM
Naphthalene	N	128
Acenaphthylene	Acy	152
Acenaphthene	Ace	154
Fluorene	Fl	166
Phenanthrene	Phe	178
Anthracene	A	178
2-methyl-phenanthrene	2-MePhe	192
Fluoranthene	Fluo	202
Pyrene	Py	202
Benzo[b]fluorene	BbFl	216
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
Indene[1,2,3-cd]pyrene	IndPy	276
Benzo[ghi]perylene	BgPer	276
Dibenzo[ah]anthracene(*)	DiBA	278
Coronene	Cor	300
Perdeuterated naphthalene(#)	ND_8	136
Perdeuterated pyrene(#)	PyD_{10}	212
Perdeuterated chrysene(#)	$ChryD_{12}$	240
Perdeuterated benzo[a]pyrene(#)	$BaPD_{12}$	264
Perdeuterated perylene(#)	$PerD_{12}$	264

(*) Coeluted with dibenzo[a,c]anthracene under our analytical conditions
(#) Internal standards

RESULTS AND DISCUSSION

All extracts displayed similar total ion current chromatograms (TIC) showing large peaks due to unresolved complex mixtures (UCM). Reconstructed chromatograms showed that alkanes (m/z = 85) and cycloalkanes (m/z = 83) predominated in the extracts but an intense fragmentogram of m/z = 95 which also corresponds to branched or cyclic hydrocarbons was also observed (Ziemann and McMurry, 2000). The fragmentogram of m/z = 191 showed that terpanes with 3 to 5 rings (hopanes) were also present in the extract. Those results are similar to our previous conclusions for SD samples collected in Niterói City (Pereira Netto et al. 2002).

Qualitative results led to the identification of 21 PAHs with molecular weights

between 128 Dalton (naphthalene) and 300 Dalton (coronene) in all SD samples. Our results are in good agreement with previous data obtained for PAHs in SD samples (Takada et al. 1990; Yang and Baumann, 1995; Pereira Netto et al. 2002). Those results also agree well with data of related samples such as total suspended particulate (TSP) from Niterói City (Pereira Netto et al. 2002), soils (Sptizer and Kuwatzuka, 1993) and runoff (Ngabe et al. 2000). The combination of such HRGC-MS evidences of the presence of other classes of hydrocarbons in all SD samples with data on PAH identification and quantification clearly shows the role of petroleum hydrocarbons (from combustion residues and lubricating oils) to the hydrocarbon budget found in SD samples from the central area of Niterói City.

The ranges (ng/g) and the geometric means of PAHs found in SD samples from the central area of Niterói City are shown in Table 2. PAH levels between 3.4 ng/g (Fl) and 720 ng/g (BkFluo) were found, with geometric means between 6.8 ng/g (Fl) and 343 ng/g (BgPer). BkFluo and BgPer with mean concentrations of respectively 299 and 343 ng/g were the predominating PAHs. However many other PAHs showed mean levels greater than or as large as 200ng/g. This is the case of Fluo (246 ng/g) and Py (217 ng/g) which were previously found to be the predominant PAHs in SD samples collected in Germany (Yang and Baumann, 1995) and also were found to be responsible for significant part of runoff toxicity (Boxall and Maltby, 1997).

Although relatively low concentrations (3.4 to 23 ng/g) of Ace, Acy and Fl were found, the level of the most volatile naphthalene was at least one order of magnitude higher thus indicating that besides the high vapor pressures of those PAHs other factors such as source emission factors would play important and determinant roles in the PAHs levels found in SD samples.

Mean total PAH concentrations (ΣPAHs) ranged between 2119 and 5063 ng/g with a geometric mean of 3112 ng/g. These results are comparable to the previous levels found in German sites (Yang and Baumann, 1995) although samples from the most contaminated sites of Germany contained ΣPAHs an order of magnitude greater than our results.

Total carcinogenic PAHs here considered as those classified by IARC as probably carcinogenic to humans (namely benzo[a]anthracene, benzo[a]pyrene and dibenzo[ah]anthracene) and as possibly carcinogenic to humans (namely benzo[b]fluoranthene, benzo[k]fluoranthene and indene[1,2,3-cd]pyrene) accounted for 21 to 41 % of ΣPAHs with a geometric mean of 35 %. This mean value is larger than the percentage of carcinogenic PAHs previously found in TSP from the central area of Niterói City (Pereira Netto et al. 2002) and also greater than the levels of carcinogenic PAHs found in used crankcase oil (Wong and Wang, 2001). Those results suggest that SD can concentrate carcinogenic PAHs coherently with the lowest vapor pressures of those 4-ringed or higher carcinogenic PAHs.

Table 2. Ranges and geometric means of individual PAH concentrations (ng/g) in SD samples from the central area of Niterói City, Rio de Janeiro, Brazil.

PAHs	Ranges	Geometric means
N	181 to 297	217
Acy	7.3 to 23	13
Ace	4.9 to 21	9.1
Fl	3.4 to 14	6.8
Phe	71 to 226	111
A	18 to 41	27
2-MePhe	15 to 46	29
Fluo	68 to 617	246
Py	80 to 470	217
BbFl	17 to 51	28
BaA	90 to 394	184
Chry	25 to 210	88
BbFluo	39 to 525	191
BkFluo	101 to 720	299
BeP	131 to 366	215
BaP	54 to 313	142
Per	25 to 91	44
BgPer	234 to 462	343
IndPy	35 to 253	112
DibA's	43 to 82	56
Cor	115 to 537	207
Total PAH concentration (ΣPAHs)	2119 to 5063	3112
Total of carcinogenic PAHs(*)	439 to 2054	1251
% of carcinogenic PAHs	21 to 41	35

(*) Sum of the concentrations of the PAHs classified as 2A and 2B by IARC. See text for details

Further studies of seasonal and spatial variations of PAH levels in SD in the central area of Niterói City are being carried out and this data will possibly allow the assessment of the role of SD as a pollution source to Guanabara Bay.

Acknowledgments. We thank FAPERJ/Brazil (Project E-26/170.827/2000) and CNPq/Brazil (Project 478346/01-8) for financial support. I.F Cunha and F.C. Muniz thank CNPq/Brazil for PIBIC undergraduate grants.

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