

Distribution and origin of polycyclic aromatic hydrocarbons in surface sediments from an urban river basin at the Metropolitan Region of Curitiba, Brazil

Natalicio Ferreira Leite¹, Patricio Peralta-Zamora², Marco Tadeu Grassi^{2,*}

1. Instituto de Tecnologia do Paraná (TECPAR), 81350-010 Curitiba, Brazil

2. Departamento de Química, Universidade Federal do Paraná (UFPR), C.P. 19081, 81531-990 Curitiba, Brazil. E-mail: mtgrassi@ufpr.br

Received 21 July 2010; revised 15 October 2010; accepted 01 November 2010

Abstract

The concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) were determined in surface sediment samples from nine sites located at the Iguaçu River Basin in the Metropolitan Region of Curitiba, Brazil to evaluate their distribution and sources. The total concentration of the PAHs was greater for sediments from highly urbanized areas, while the sediments from the Iraí Environmental Protection Area (Iraí EPA) showed significantly low concentrations. The sediments from the Iguaçu and Barigui rivers were classified as highly contaminated, while those from the Cercado and Curralinho rivers were classified as moderately contaminated. The predominance of PAHs containing two to four aromatic rings in most of the samples suggested the direct input of raw sewage into the water resources evaluated. Benzo[*g,h,i*]perylene, dibenzo[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene were predominant in sediments from the areas under the greatest urban and industrial development. The correlation between thermodynamic stability and the kinetics of evolution presented by the isomeric pairs indicated that combustion is the predominant source of PAHs in the sediments because the combustion of fossil fuels affected most of the points evaluated, followed by combustion of biomass and eventually combustion of oil product inputs. In general, the results showed that areas under strong urban influence, as well as the Iraí EPA, receive contributions of PAHs from similar sources.

Key words: PAHs; trace level analysis; river sediment; isomeric ratio; Iguaçu River Basin

DOI: 10.1016/S1001-0742(10)60496-2

Citation: Natalicio F L, Patricio P Z, Marco T G, 2011. Distribution and origin of polycyclic aromatic hydrocarbons in surface sediments from an urban river basin at the Metropolitan Region of Curitiba, Brazil. *Journal of Environmental Sciences*, 23(6): 904–911

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants primarily produced by exposure of organic matter to temperatures exceeding 700°C. Production of PAHs occurs in natural and anthropogenic processes of incomplete pyrolysis and combustion (WHO, 1998) in addition to the geochemical formation of fossil fuels (Yang et al., 1991). Anthropogenic emissions, including domestic and industrial wastes, by-products of incineration of industrial and urban wastes, oil spills and their derivatives and, particularly, the combustion of biomass and fossil fuels (WHO, 1998; Baird and Cann, 2008), are responsible for the most significant contribution of PAHs to the environment. In developing countries like Brazil the burning of vegetation from both forests and agricultural practices represents a significant source of PAHs in the environment (Godoi et al., 2004).

The stationary sources are responsible for approximately 80% of the total emission of PAHs, while the exhaust

of vehicles powered by diesel and gasoline are the most prominent mobile sources (Yang et al., 1991; Mostafa et al., 2009). While most of the physicochemical properties of PAHs vary considerably, the semi-volatile behavior presented by some PAHs makes them highly mobile in the environment, resulting in re-volatilization after deposition and favoring their distribution through air, soil and water bodies. Atmosphere is the environmental compartment that receives most of the discharge of PAHs, which occurs in the gas phase or, predominantly, in association with the particulate material. PAHs are pollutants that are strongly implicated in the degradation of human health in some cities because their concentration in the outdoor air in urbanized areas commonly has a range from 1 to 500 ng/m³. PAH levels can even reach ten times this concentration in heavily polluted environments (WHO, 1998).

Usually, after spending several hours or even days in suspension in the atmosphere, where these compounds can be transported over long distances (Wania and Mackay, 1996), they eventually precipitate by dry or wet deposition (Dickhut et al., 2000; Baird and Cann, 2008). The

* Corresponding author. E-mail: mtgrassi@ufpr.br

occurrence of perennial sources of these pollutants results in their accumulation in soil, vegetation and aquatic environments (Trapido, 1999). Once deposited, a significant fraction of the PAHs is transferred to water bodies throughout the urban runoff. Due to their low aqueous solubility and hydrophobic nature, once in a water body, these compounds occur as colloids, dissolved organic matter or suspended particles and are eventually deposited in the sediment (Guo et al., 2009). Therefore, bottom sediments contain the highest levels of PAHs and represent as an adequate environmental indicator for assessment of the anthropogenic emissions of these contaminants. However, to gain additional information and to determine the most appropriate strategy for monitoring and environmental control, it is necessary to identify the most likely sources of such substances (Yunker et al., 2002).

The positive identification of precursors of PAHs that occur in the environment is a complex task due to the diversity of sources and the dynamics of these substances in the environment (Venturini and Tommasi, 2004). Despite this challenge, some PAHs exhibit comparable thermodynamic stability and kinetic evolution in the environment. Therefore, the ratio of the concentrations of isomers has been demonstrated to be an efficient method to assign the probable sources of PAHs that arise in sediments (Yunker and Macdonald, 1995; Budzinski et al., 1997; Dickhut et al., 2000; Yunker et al., 2002; Cortazar et al., 2008; Guo et al., 2009; Mostafa et al., 2009).

Relatively little is known about the sources and composition of PAHs in sediments from various river systems. This fact is especially true in Brazil, despite having its

Table 1 Description of sampling stations at the study area in the Iguaçu River Basin in the Metropolitan Region of Curitiba

Station No.	Description	Location
1	Curralinho River	25°23'45.1"S, 49°03'17.5"W
2	Cercado River	25°23'3.6"S, 49°04'1.6"W
3	Iraí Dam	25°23'5.0"S, 49°05'1.7"W
4	Timbú River	25°22'15.9"S, 49°05'8.4"W
5	Canguiri River	25°22'39.5"S, 49°07'11.7"W
6	Iraí River	25°26'39.9"S, 49°08'34.2"W
7	Iguaçu River - SJ Pinhais	25°32'16.5"S, 49°13'32.5"W
8	Barigui River	25°33'22.6"S, 49°20'32.6"W
9	Iguaçu River - Araucária	25°35'46.3"S, 49°24'58.1"W

major river basins under strong urban, industrial and agricultural influences. In the state of Rio de Janeiro, Southeast Brazil, Torres et al. (2002) assessed an industrialized area of the Rio Paraíba do Sul, Brito et al. (2005) evaluated the Paraíba do Sul and Guandu rivers in an area under industrial, urban and agricultural influence, while Gomes and Azevedo (2003) studied the Campos dos Goytacazes basin, an agricultural area. Meire et al. (2008) assessed national parks in the states of Espírito Santo, Rio de Janeiro and São Paulo. Meniconi et al. (2002) evaluated the rivers Barigui and Iguaçu at the Metropolitan Region of Curitiba (MRC), South of Brazil, in the influence area of an oil refinery.

Taking all these aspects into consideration, the aim of this study was to determine the concentrations of 16 PAHs in river bottom sediments from the Iguaçu Basin, at the MRC, in Brazil, as well as to assess their possible sources.

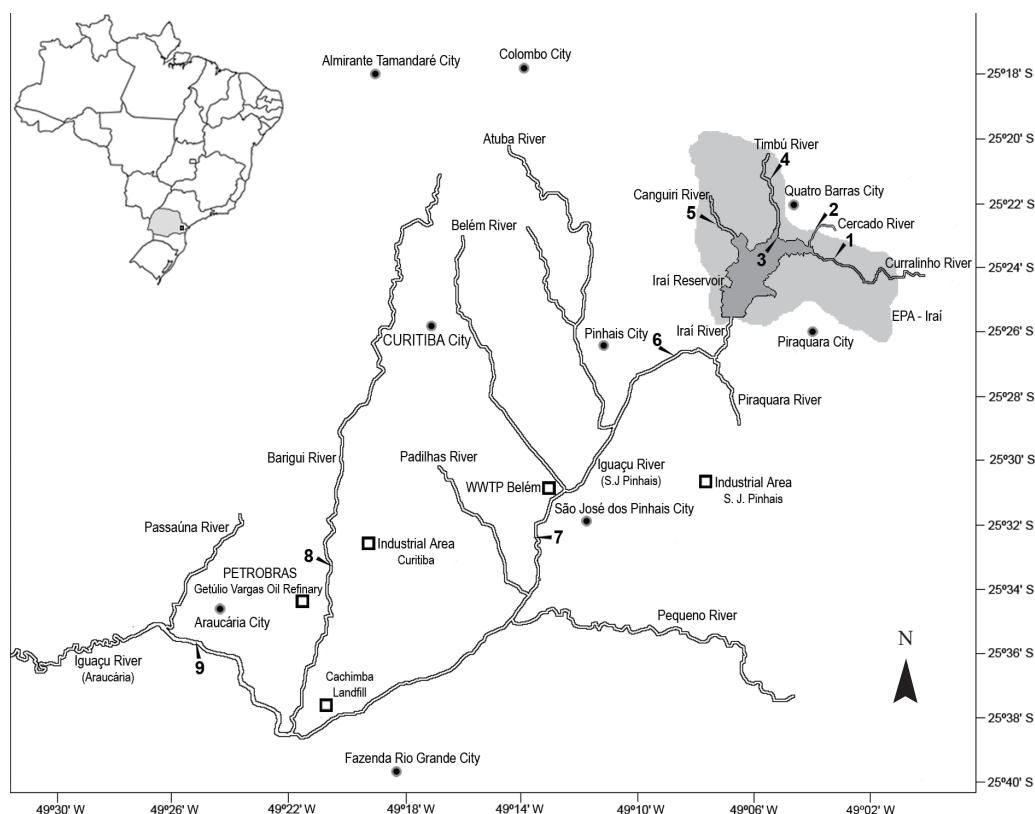


Fig. 1 Study area and sample stations (1–9) in the Iguaçu River Basin in the Metropolitan Region of Curitiba, Brazil.

1 Materials and methods

1.1 Study area

Sediment samples were obtained at the Iguau River Basin located at the MRC (Fig. 1 and Table 1). This basin is among the largest in Brazil, draining an area of 55,024 km² (SUDHERSA, 1997). The sources are located in the vicinity of the MRC and the river extends for 1275 km to its mouth in the Paraná River (COMEC, 1999). The basin has about 3.2 million inhabitants with 2.1 million living in the MRC. The Canguiri, Curralinho, Cercado and Timbú rivers (sample stations No. 5, 1, 2 and 4 respectively) are the main Iguau River tributaries that are located upstream of the MRC and form the Iraí dam (sample station No. 3). The Iraí dam and its main tributaries are located within the Iraí Environmental Protection Area (Iraí EPA), a hotspot area responsible for supplying up to 75% of the drinking water to the MRC.

The Iraí River (sample station No. 6) is located downstream of the dam, near the Iraí EPA region. The Iguau River, located in the cities of São José dos Pinhais/Curitiba and Araucária/Curitiba (sample stations No. 7 and 9 respectively), and the Barigui River, located in the cities of Araucária and Curitiba (sample station No. 8), run through the main urban centers of the MRC and are directly impacted by the high population density in the metropolitan area.

1.2 Sediment sampling and analytical procedures

Nine sediment samples covering representative areas of the MRC were collected from Jun to Nov 2005 using a homemade PVC hand corer (50 mm i.d., 25 cm in depth). The surface sediments were transferred to a solvent cleaned glass jar. The samples were placed in a cooler box and returned to the laboratory where they were stored at –18°C until analyzed. The procedures for preparation, extraction and analysis of the sediment samples were described by Leite et al. (2008). Sediment samples were thawed at room temperature, transferred to a glass tray and air-dried for five days under exhaust in a darkened fume hood. Each sample was then ground in a heavy porcelain mortar and passed through a 149-µm sieve. Foreign objects such as sticks, leaves, and rocks were discarded. The samples were homogenized and stored in a desiccator in the dark at room temperature. Approximately 10 g of the dried sediment was thoroughly mixed with an equal mass of anhydrous sodium sulfate, transferred to a 250-mL screw cap Erlenmeyer flask, wetted with acetone, spiked with 10 ng of each internal standard (²H₁₀]acenaphthene, [²H₁₂]crysene, [²H₈]naphthalene, [²H₁₂]perylene, and [²H₁₀]phenanthrene) and extracted in a shaker apparatus at 120 r/min for 16 hr with 50 mL of dichloromethane. The extract was concentrated in a rota-evaporator to 5 mL, and the solvent was exchanged by addition of 2 mL of cyclohexane. The volume was reduced again to 2 mL in the same evaporator apparatus. The cleanup of the sample extracts was accomplished by passing them through a chromatographic column (11 mm

× 300 mm) which was packed with 0.1 g of activated copper at the bottom to absorb elemental sulfur, 10 g of activated silica gel, and 2 g of anhydrous sodium sulfate on top to absorb residual water. The extract was cleaned up with 15 mL of pentane and the PAH fraction was recovered with 50 mL of dichloromethane/pentane (2:3, V/V) into a Kuderna-Danish concentrator attached to a 5 mL calibrated graduated tube. Then a gentle stream of nitrogen was used to bring the volume of the extract down to 1 mL. The final extract was transferred to an amber vial, sealed and stored at –18°C until the following analysis.

The gas chromatograph-mass spectrometry (GC-MS) analysis was performed on a Varian CP-3800 gas chromatograph (Walnut Creek, USA) equipped with a Varian Saturn 2000 three-dimensional quadrupole ion trap MS. The target compounds were separated on a 30-m length and 0.25 mm i.d. capillary column coated with a 0.25 µm film thickness (diphenyl 5% dimethylsiloxane 95%) stationary phase (Chrompack CP-Sil8). Helium was employed as carrier gas, with a constant column flow of 1.0 mL/min. All injections (1 µL) were carried out through a universal injector (Varian 1177) in the splitless mode and programmed to return to the split mode after 0.75 min from the beginning of a run, and the samples were introduced using a CP-8400 Varian auto-sampler. Split flow was set at 30 mL/min. The GC oven temperature program was: 80°C for 3 min, 20°C/min to 230°C, 10°C/min to 300°C and held for 6.5 min, with a total acquisition program of 24 min. The temperature of the injector was kept constant through all injections at 280°C. By using these chromatographic conditions it was possible to qualitatively distinguish between benzo[a]anthracene/crysene, a pair of isomers that are commonly co-eluted by GC systems.

The target compounds were identified by GC retention times, comparison with authentic standards, and from their recorded mass spectra with the NIST mass spectral program (NIST, 2005). The main prominent ion suggested by the NIST program for each target compound was selected for the MS optimization. These most abundant ions were confirmed through the ion trap mass spectrogram obtained by separated injection of a mixture of 16 target PAHs and a mixture of 5 target deuterated PAHs in the GC-QIT MS operating in full-scan mode.

In general, the MS was operated in the EI mode at 70 eV, 10 µA for emission current, 100 µsec for the prescan ionization time, 4.1 V for the axial modulation voltage, and –1950 V for the electron multiplier set. The mass range was scanned from 90 to 300 mass-to-charge ratio (*m/z*) at 1 sec/scan.

The following PAHs were analyzed: acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), benzo[a]anthracene (BaA), chrysene (Chry), benzo[a]pyrene (BaP), benzo[b,k]fluoranthenes (Bb/kF), benzo[g,h,i]perylene (Bghi), dibenzo[a,h]anthracene (DahA), fluoranthene (Fluo), fluorene (Flu), indene[1,2,3-cd]pyrene (IP), naphthalene (Nap), phenanthrene (Phe) and pyrene (Pyr). All the PAH concentrations are reported on a dry weight (dw) sediment basis.

2 Results and discussion

2.1 Distribution of PAHs

The individual and total concentrations of the 16 PAHs in sediments obtained from the sampling stations are presented in Table 2.

The total concentration of the 16 PAHs ($\Sigma 16\text{PAHs}$) was higher for the sediments of predominantly urban and industrial areas, represented by sampling station No. 7 ($\Sigma 16\text{PAHs} = 1713 \text{ ng/g}$), No. 8 ($\Sigma 16\text{PAHs} = 1206 \text{ ng/g}$) and No. 9 ($\Sigma 16\text{PAHs} = 691 \text{ ng/g}$). Moreover, the sediments from the Iraí EPA showed significantly lower concentrations, with the $\Sigma 16\text{PAHs}$ ranged from 131 to 358 ng/g for the sampling stations No. 1–5. In these cases, the levels of contamination were proportionally lower compared to those in the densely urbanized areas of the MRC. This is probably due to the positive influence of the Iraí EPA and regions of wetlands located in its internal and surrounding areas. These areas remain flooded or semi-flooded most of the year (COMEC, 1999), thus contributing to inhibition of urban sprawl in this region.

Among the sediment samples from the Iraí EPA, higher total concentrations of PAHs were found in stations No. 1 ($\Sigma 16\text{PAHs} = 358 \text{ ng/g}$) and No. 2 ($\Sigma 16\text{PAHs} = 278 \text{ ng/g}$). Despite being located in sparsely urbanized areas, the concentrations may point to the impact of emissions arising from the intense vehicle traffic on the BR-116 highway that crosses the region as well as by commercial and industrial activities located in the vicinities of the highway.

The total PAHs concentration in the Iguaçu River Basin located at the MRC is in agreement with the values cited more frequently in the literature for freshwater sediments under urban influence as can be seen in Tables 2 and 3. Meniconi et al. (2002) reported $\Sigma 16\text{PAHs}$ 532 and 70 ng/g in sediment samples from rivers Barigui and Iguaçu, respectively in 2000, which are in the same order of magnitude with our results obtained in the same region. However, Torres et al. (2002) reported higher concentrations of

total PAHs (40,000 ng/g) in sediments at Paraíba do Sul drainage, Southeast Brazil, which is near a large industrial area. This aspect makes sense due to the concentrations of these compounds in the environment are subjected to wide variations depending on factors such as incidence of biomass burning and fossil fuel combustion in the area of influence.

Based on the correlation between impacted river environments and the occurrence of PAHs in sediments, Johnson and Larsen (1985) and Benlanchen et al. (1997) suggested classification criteria whereby an area is considered “highly contaminated” when concentrations of total PAHs are higher than 500 ng/g, “moderately contaminated” when concentrations range from 250 to 500 ng/g and “slightly contaminated” when concentrations are lower than 250 ng/g. These criteria have often been used to assess the level of contamination of sediments (Notar et al., 2001; Venturini and Tommasi, 2004; Silva et al., 2007). Based on these criteria, the sediments of stations No. 7 ($\Sigma 16\text{PAHs} = 1713 \text{ ng/g}$), No. 8 ($\Sigma 16\text{PAHs} = 1206 \text{ ng/g}$) and No. 9 ($\Sigma 16\text{PAHs} = 691 \text{ ng/g}$), which are within urban and industrial areas, were classified as highly contaminated. Sediments from stations No. 1 ($\Sigma 16\text{PAHs} = 358 \text{ ng/g}$) and No. 2 ($\Sigma 16\text{PAHs} = 278 \text{ ng/g}$) were classified as moderately contaminated, while all the others were classified as slightly contaminated.

Several studies, including those performed by Pérez et al. (2001) in Portugal, Stevens et al. (2003) in the United Kingdom and Blanchard et al. (2004) in France, have demonstrated that the hydrolysis of organic matter originating from municipal sewage in wastewater treatment plants (WWTP) contributes to the desorption of the content of simpler structure PAHs with two to four aromatic rings, which are released to the aqueous phase, while the more complexes PAHs with five and six aromatic rings are preferably adsorbed onto the particles forming the sludge. Among these simpler structure compounds, Phe, Fluo, Pyr, Nap and some methyl derivatives were reported as the most predominant in treated effluents. In fact, the concentrations of Phe, Fluo, Pyr and Nap found in the sediments evaluated

Table 2 PAH concentration of dry weight sediment samples collected from the main water bodies of the Metropolitan Region of Curitiba, Brazil

Station No.	1	2	3	4	5	6	7	8	9
Ace (ng/g)	nd	nd	nd	5.6 (2.3)	nd	4.0 (1.0)	2.9 (0.4)	11.5 (3.5)	10.1 (1.8)
Acy (ng/g)	0.50 (0.14)	0.85 (0.07)	3.7 (0.2)	3.2 (0.4)	0.72 (0.08)	4.1 (0.2)	18.3 (0.4)	14.7 (0.4)	19.9 (1.5)
Ant (ng/g)	9.1 (0.2)	3.9 (0.4)	nd	2.5 (0.6)	4.9 (0.4)	1.1 (0.3)	12.6 (3.5)	9.8 (4.0)	8.9 (2.3)
BaA (ng/g)	16.9 (2.2)	10.8 (2.0)	nd	22.8 (5.1)	6.5 (0.8)	15.8 (1.1)	12.8 (3.1)	45.5 (7.3)	30.4 (7.8)
Cry (ng/g)	22.4 (1.2)	21.9 (9.2)	40.8 (7.4)	42.8 (8.9)	18.7 (4.2)	44.7 (0.1)	34.5 (7.1)	47.3 (17.2)	39.5 (14.2)
BaP (ng/g)	84.0 (4.7)	63.8 (25.0)	21.6 (6.4)	23.1 (10.9)	2.4 (0.9)	28.1 (1.3)	13.6 (4.3)	97.8 (0.9)	36.6 (12.2)
Bb _k F ^a (ng/g)	49.6 (38.1)	27.9 (12.1)	nd	nd	22.2 (10.1)	nd	390.2 (57.9)	47.5 (2.0)	64.3 (13.3)
Bghi (ng/g)	14.3 (1.3)	9.5 (0.5)	nd	18.9 (3.0)	8.6 (1.7)	29.0 (6.2)	10.7 (2.7)	36.2 (6.8)	21.2 (5.9)
DahA (ng/g)	36.9 (18.9)	42.6 (0.2)	nd	nd	24.9 (5.8)	nd	466.5 (34.5)	49.4 (8.7)	15.9 (2.4)
Fluo (ng/g)	24.7 (8.1)	13.7 (2.5)	4.6 (1.7)	24.6 (7.6)	14.9 (2.6)	20.0 (2.3)	99.2 (11.8)	117.2 (20.6)	80.7 (14.0)
Flu (ng/g)	29.4 (17.9)	27.9 (5.9)	15.2 (1.5)	15.5 (8.1)	12.1 (5.3)	21.8 (0.8)	62.5 (12.3)	135.2 (57.8)	65.4 (14.8)
IP (ng/g)	8.3 (0.7)	8.2 (0.1)	13.0 (1.3)	17.4 (0.3)	8.2 (1.8)	16.6 (0.9)	164.3 (46.9)	48.5 (15.9)	27.2 (1.4)
Nap (ng/g)	nd	nd	nd	nd	nd	nd	256.7 (31.3)	88.8 (9.9)	78.7 (11.3)
Phe (ng/g)	51.5 (21.1)	38.0 (4.2)	32.5 (2.3)	19.7 (1.3)	6.2 (0.4)	38.1 (5.7)	63.6 (17.3)	314.6 (61.4)	110.1 (35.1)
Pyr (ng/g)	10.1 (1.3)	8.5 (2.4)	nd	26.3 (3.0)	12.9 (3.6)	20.0 (1.4)	104.7 (31.2)	142.2 (29.1)	82.1 (19.5)
$\Sigma 16 \text{ PAHs}$	358	278	131	222	143	243	1713	1206	691

Data are presented as mean with standard deviation values between parentheses ($n = 4$).

^aBenzo[b]fluoranthene and benzo[k]fluoranthene: isomer co-eluent analytes, quantified as a sole compound.

nd: not detected, is assigned for PAHs having concentration lower than the method detection limit.

Table 3 Comparison of PAHs levels in sediments with other rivers and lakes around the world

Localization	Land type	Σ PAHs (ng/g)	Reference
MRC rivers, Brizal	Industrial and urban areas	131–1713 (16)	This study
Paralba do Sul River, Southeast Brazil	Industrial and urban areas	1–275 (16)	Brito et al., 2005
Paralba do Sul River, Southeast Brazil	Industrial and urban areas	40,000 (13)	Torres et al., 2002
Barigui and Iguaçu rivers, MRC, Brazil	Industrial and urban areas	70–532 (16)	Meniconi et al., 2002
Susquehanna River system, USA	Industrial and urban areas	1547–9847 (37)	Ko et al., 2007
Daliao River system, China	Agricultural, industrial and urban areas	103–3419 (18)	Guo et al., 2009
Lake de Cima, Southeast Brazil	Agricultural area	340 (35)	Gomes and Azevedo, 2003
Several lakes and rivers, Southeast Brazil	Remote areas	4–576 (13)	Meire et al., 2008

Values in parentheses represent the number of PAHs analyzed.

in this work were between 19% and 59% of the total PAHs. The sediments of the rivers under the influence of the Iraí EPA (sampling stations No. 1 to 5) showed concentrations between 32% to 41% for these compounds, while their concentrations were 49% and 59% of the total PAHs at stations No. 8 and 9 respectively. If taking into account that the direct input of raw sewage into the water also contributes to this phenomena and that contamination by raw sewage is a known fact for the urban rivers at the MRC (SUDERHSA, 1997; COMEC, 1999; Sodr  et al., 2005; Grassi et al., 2007; Sodr  and Grassi, 2007a, 2007b). The predominance of Phe, Fluor, Pyr and Nap in most of the sediment samples suggests that municipal sewage may be a significant source of input of PAHs to the Igua u River Basin in the MRC, especially the Ira  dam (station No. 3) and its tributaries.

On the other hand, PAHs with five and six rings were predominant in the sediment at station No. 7 because the sum of the concentrations of Bghi, DahA and IP was 65% of the total PAHs. According to Yunker et al. (2002), these compounds are more common in sediments from urban areas and their occurrence is strongly linked to human activities. Oil products are the predominant sources of these PAHs with molar mass (MM) of 276 and 278. Asphalt, which has the highest concentration, is the main contributor, followed by refined oil products (Yunker et al., 2002). Our results are consistent with this possibility because the sampling station No. 7 is located downstream of the Bel m WWTP at the mouth of the Bel m River. In addition to receiving the discharge of treated effluent the largest sewage treatment plant at the MRC, the sub-basin of the Bel m River has the highest rate of urbanization in comparison to others in this metropolitan region. Therefore its drainage should significantly contribute to the input of more varied sources of PAHs of anthropogenic origin, such as particulate matter from asphaltic surfaces, tire wears, atmospheric deposition and oil spills. Other significant occurrences of these compounds were observed at stations No. 8 and 9, which are under the direct impact of high urban density as well as industrial activities. These compound contributed 15% and 23% of the total PAHs at sampling stations No. 8 and 9, respectively. In the Ira  EPA, stations No. 1, 2 and 5, where sub-basins are under the influence of the heavy traffic from the highway BR-116, showed 24%, 25% and 33% of the total PAHs, respectively.

PAHs of MM 252 (BbkF and BaP) are among the most important in emissions produced by burning of wood, coal and vegetation, as well as combustion of fossil fuels,

especially diesel. However, once in the environment, their concentrations tend to decline rapidly, especially in the atmosphere, due to degradation catalyzed by sunlight (Yunker et al., 2002). Among the PAHs from pyrolytic sources, BaP is the most important because of its carcinogenic potential (WHO, 1998). BaP occurred at comparable concentrations in all samples, ranging from 19 to 47 ng/g. The ubiquity of this compound at equivalent concentrations indicates the contribution of combustion sources, which probably affect all environmental compartments of the MRC.

2.2 Relative distribution of individual PAHs

The ratio between the concentrations of isomers has been demonstrated as an efficient method for identifying sources of PAHs that occur in sediments (Yunker and Macdonald, 1995; Budzinski et al., 1997; Dickhut et al., 2000; Yunker et al., 2002). When human activities or combustion are the primary sources of PAHs, the parent PAHs of lower thermodynamic stability tend to be degraded more quickly in the environment compared to others of the same MM. As a result, there is a decrease of the ratio between a less stable parent PAH and its more stable isomer, depending on the source. This ratio can be expressed as $R_{178} = [\text{Ant}]/[\text{178}]$, $R_{202} = [\text{Flu}]/[\text{202}]$ and $R_{228} = [\text{BaA}]/[\text{228}]$, where [178], [202] and [228] are the sum of the concentrations of isomers Ant and Phe (MM 178); Flu and Pyr (MM 202); and BaA and Chry (MM 228), respectively. These ratios are suitable to represent the pyrogenic and anthropogenic sources of PAHs due to the high stability of these isomers related to other parent PAHs and also due to their great abundance in the environment (Yunker and Macdonald, 1995).

When the ratio R_{178} is less than 0.10, it generally indicates that these compounds are from petrogenic sources. Diesel and lubricants are among the oil products that have this profile. On the other hand, when the ratio is greater than 0.10, it points to the dominance of combustion sources (Budzinski et al., 1997) mainly from coal and shale (Yunker et al., 2002).

The pair of isomers Flu and Pyr shows the transition between the pyrogenic and petrogenic sources at 0.50 for R_{202} and the combustion of kerosene, vegetation, coal and wood tend to have R_{202} higher than 0.50. Emissions of gasoline, diesel and fuel oils by combustion and emissions from cars and diesel trucks usually have values lower than 0.50. The value of 0.40 for R_{202} indicates the transition between oil and the products of combustion. Values lower than 0.40

are generally linked to diffuse sources of lubricating oil products (Yunker et al., 2002).

The isomers BaA and Chry (MM 228) and Bghi and IP (MM 276) are among the constituents that occur in smaller proportions in refined petroleum products, which are usually present in greater concentrations in their heavy fractions, such as asphalt, bitumen and coal (Dickhut et al., 2000; Yunker et al., 2002). These compounds are also produced in the burning of fossil fuels and biomass, and the occurrence of IP and Bghi may be associated with the burning of wood and coal near the site of deposition (Dickhut et al., 2000). A value of R_{228} less than 0.20 has been applied more frequently to the correlation of BaA and Chry with oil, while values up to 0.35 correlate with combustion and oil, and values of more than 0.35 correlate with other sources of combustion (Yunker et al., 2002).

Figure 2 shows the combination between the ratios of the pairs of isomers with MM 178 and 228 versus the pair of isomers with MM 202, which were computed from the concentrations of PAHs obtained in this study. The values for the ratio R_{178} obtained ranged from 0.0 for the sediment sample from Station No. 3, to 0.29 for the sample from Station No. 5 (Fig. 2a; station No. 3 is out of scale). Sediments from stations No. 3, 6 and 8 showed R_{178} less than 0.10, indicating that oil products are the possible source of Ant and Phe in these environments. Sediments from the remaining stations showed R_{178} higher

than 0.10, indicating that in these environments, the parent PAHs Ant and Phe originate mainly from oil combustion. The predominant sources of combustion were higher in sediments from stations No. 1 ($R_{178} = 0.24$) and 5 ($R_{178} = 0.29$), both located in Iraí EPA, which stood out with the highest values of R_{178} . Moreover, station No. 3 showed R_{178} was equal to 0.0 because Ant was not detected in the sediment.

The values for the ratios $[Flu]/[202]$ (R_{202}) obtained for sediment samples (Fig. 2) ranged from 0.37 for stations No. 4 and No. 7 to 1.00 for station No. 3 (out of scale). The R_{202} values indicate that Fluo and Pyr come from the combustion of fossil fuels in sediments at stations No. 5, 7 and 8, whereas at stations No. 4 and 9, R_{202} values less than 0.40 indicate that these parent PAHs are probably from oil products. The sediment of station No. 6 presented a value of R_{202} equal to 0.53, which is slightly above the interface between the combustion sources, but suggests the probable predominance of biomass burning emissions. The higher values of R_{202} obtained for the sediments of the stations No.1 (0.74) and No. 2 (0.77) indicate a high probability that the precursors of Fluo and Pyr in these environments are due to the combustion of biomass.

Figure 2b shows that the ratios of R_{228} obtained ranged from 0.35 for the sediment of station No. 6 to 0.59 for station No. 9. Compared to the results obtained by Yunker et al. (2002), the values of R_{228} obtained in this work

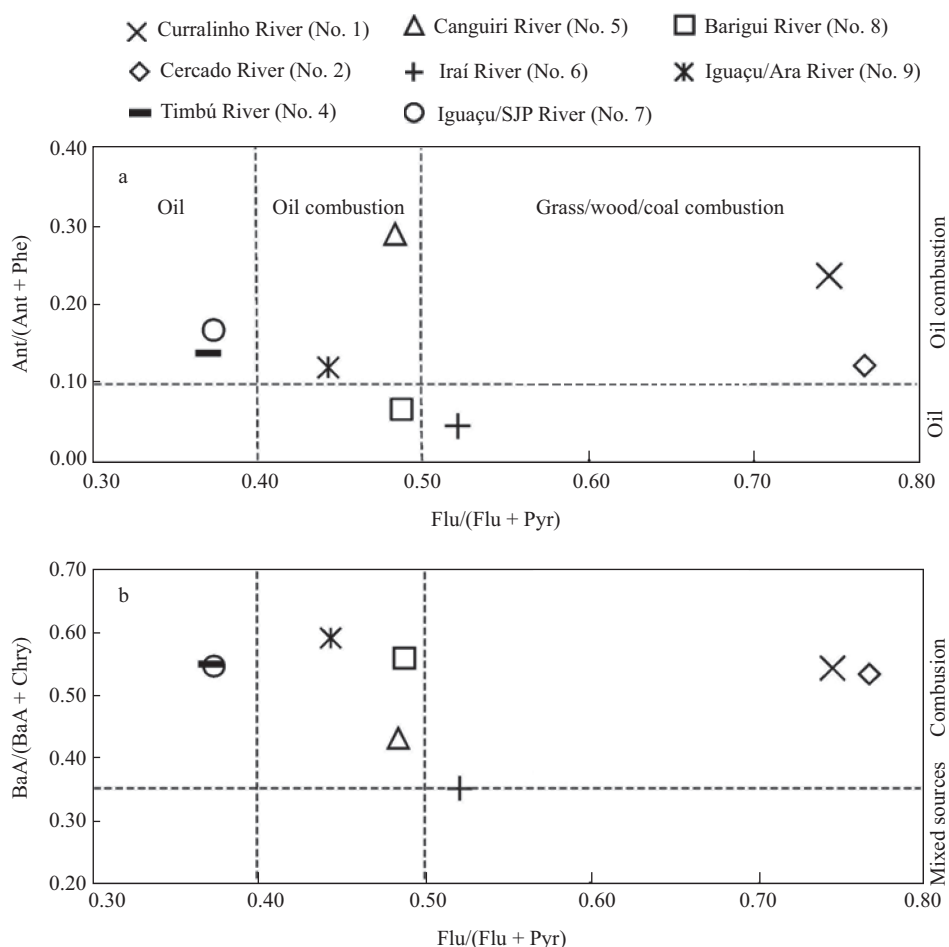


Fig. 2 Cross plots for the values of $[Ant]/[Ant+Phe]$ vs. $[Flu]/[Flu+Pyr]$ (a) and $[BaA]/[BaA+Chry]$ vs. $[Flu]/[Flu+Pyr]$ (b) for sediments of the Iguaçu River Basin in the Metropolitan Region of Curitiba.

indicate that the isomers BaA and Chry in the sediments are predominantly from combustion sources, except at station No. 6, presented an R_{228} value of 0.35 representing the interface between combustion and mixed sources (the origin of parent PAHs can be oil as pyrogenic sources), and station No. 3, where these compounds were not detected.

3 Conclusions

The concentrations of total PAHs were higher for the sediments of urban and industrial areas, represented by the Iguaçu and Barigui rivers, while sediments from the rivers of the Iraí EPA showed significantly lower concentrations. The predominance of Phe, Fluo, Pyr and Nap suggests that municipal sewage may be a significant source of PAHs to the Iguaçu River Basin, especially to the Iraí dam and its tributaries. Bghi, DahA and IP were among the predominant PAHs found in areas receiving the greatest urban and industrial impact, mainly the Iguaçu River in São José dos Pinhais and the Barigui River in Araucária. This indicates that release of oil products such as the asphalt used for paving may be a significant contributor. PAHs derived from combustion probably affect all environmental compartments of the MRC regardless the proximity of urban and industrial centers. The correlation between the thermodynamic stability and the kinetics of evolution presented by the isomeric pairs indicated that combustion is the predominant source of PAHs. Our results suggest that combustion of fossil fuels affects most of the points, followed by combustion of biomass and eventually the input of oil products. This work yielded unprecedented information about the occurrence, distribution and origin of PAHs in sediment from rivers of the Iguaçu River Basin, demonstrating that some water bodies of the Iraí EPA already have moderate contamination by PAHs. This is a warning sign because of the strategic importance of this hotspot area as source of drinking water to the MRC.

Acknowledgements

The authors are thankful to Fundação Araucária de Apoio ao Desenvolvimento Científico e Tecnológico do Paraná, Brazil for financial support.

References

- Baird C, Cann M, 2008. Environmental Chemistry (4th ed.). W H Freeman Co., New York.
- Benlanchen K T, Chaoui A, Budzinski H, Bellocq J, Garrigues Ph, 1997. Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. *Marine Pollution Bulletin*, 34: 298–305.
- Blanchard M, Teil M J, Ollivon D, Legenti L, Chevreuil M, 2004. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in wastewaters and sewage sludges from the Paris area (France). *Environmental Research*, 95: 184–197.
- Brito E M S, Vieira E D R, Torres J P M, Malm O, 2005. Persistent organic pollutants in two reservoirs along the Paraíba do Sul – Guandu River system, Rio de Janeiro, Brazil. *Química Nova*, 28: 941–946.
- Budzinski H, Jones I, Bellocq J, Piérard C, Garrigues P, 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde Estuary. *Marine Chemistry*, 58: 85–97.
- COMEC (Coordenação da Região Metropolitana de Curitiba), 1999. Zoneamento ecológico-econômico proposto para a Área de Proteção Ambiental do Iraí. Curitiba PR, Brazil.
- Cortazar E, Bartolomé L, Arrasate S, Usobiaga A, Raposo J C, Zuloaga O et al., 2008. Distribution and bioaccumulation of PAHs in the UNESCO protected natural reserve of Urdaibai, Bay of Biscay. *Chemosphere*, 72: 1467–1474.
- Dickhut R M, Canuel E A, Gustafson K E, Liu K, Arzays K M, Walker S E et al., 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environmental Science & Technology*, 34: 4635–4640.
- Godoi A F L, Ravindra K, Godoi R H M, Andrade S J, Santiago-Silva M, Vaeck L V et al., 2004. Fast chromatographic determination of PAHs in aerosol samples from sugar cane burning. *Journal of Chromatography A*, 1027: 49–53.
- Gomes A O, Azevedo D A, 2003. Aliphatic and aromatic hydrocarbons in tropical recent sediments of Campos dos Goytacazes, RJ, Brazil. *Journal of Brazilian Chemistry Society*, 14: 358–368.
- Grassi M T, Scheffer E W O, Sodré F F, 2007. Fatores que governam a especiação do cobre em ambientes aquáticos urbanos: evidências da contribuição de sulfetos solúveis. *Química Nova*, 30: 332–338.
- Guo W, He M C, Yang Z F, Lin C Y, Quan X C, Men B, 2009. Distribution, partitioning and sources of polycyclic aromatic hydrocarbons in Daliao River water system in dry season, China. *Journal of Hazardous Materials*, 164: 1379–1385.
- Johnson A C, Larsen P F, 1985. The distribution of polycyclic aromatic hydrocarbons in the surficial sediments of Penobscot Bay (Maine, USA) in relation to possible sources and to other sites worldwide. *Marine Environmental Research*, 15: 1–16.
- Ko F C, Baker J, Fang M D, Lee C L, 2007. Composition and distribution of polycyclic aromatic hydrocarbons in the surface sediments from the Susquehanna River. *Chemosphere*, 66: 277–285.
- Leite N F, Zamora P P, Grassi M T, 2008. Multifactorial optimization approach for the determination of polycyclic aromatic hydrocarbons in river sediments by gas chromatography-quadrupole ion trap selected ion storage mass spectrometry. *Journal of Chromatography A*, 1192: 273–281.
- Meire R O, Azevedo A, Pereira M S, Torres J P M, Malm O, 2008. Polycyclic aromatic hydrocarbons assessment in sediment of national parks in southeast Brazil. *Chemosphere*, 73: 180–185.
- Meniconi M F G, Gabardo I T, Carneiro M E R, Barbanti S M, Silva G C, Massone C G, 2002. Brazilian oil spills chemical characterization - case studies. *Environmental Forensics*, 3: 303–321.
- Mostafa A R, Hegazi A H, El-Gayar M Sh, Andersson J T, 2009. Source characterization and the environmental impact of urban street dusts from Egypt based on hydrocarbon distributions. *Fuel*, 88: 95–104.
- NIST (National Institute of Standards and Technology), EPA (Environmental Protection Agency), NIH (National Institutes of Health), 2005. Mass Spectral Data Base (software version 2.0d). Gaithersburg MD, USA.

- Notar M, Leskovsek H, Faganeli J, 2001. Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. *Marine Pollution Bulletin*, 42: 36–44.
- Pérez S, Guillamón M, Barceló D, 2001. Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants. *Journal of Chromatography A*, 38: 57–65.
- Silva T F, Azevedo D A, Aquino Neto F R, 2007. Distribution of polycyclic aromatic hydrocarbons in surface sediments and waters from Guanabara Bay, Rio de Janeiro, Brasil. *Journal of Brazilian Chemistry Society*, 18: 628–637.
- Sodré F F, Grassi M T, 2007a. Assessing anthropogenic influences on copper complexation by aquatic dissolved organic matter using synchronous fluorescence. *Journal of Brazilian Chemistry Society*, 18: 1136–1144.
- Sodré F F, Grassi M T, 2007b. Changes in copper speciation and geochemical fate in freshwaters following sewage discharges. *Water, Air & Soil Pollution*, 178: 103–112.
- Sodré F F, Prestes E C, Anjos V E, Grassi M T, 2005. Identification of copper sources to urban surface waters using the principal component analysis based on aquatic parameters. *Journal of Environmental Monitoring*, 7: 581–585.
- Stevens L J, Northcott G L, Stern G A, Tomy G T, Jones K C, 2003. PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks and polychlorinated alkanes in U.K. sewage sludge: survey results and implications. *Environmental Science & Technology*, 37: 462–467.
- SUDERHSA (Superintendência de Desenvolvimento de Recursos Hídricos e Saneamento Ambiental), 1997. Qualidade das águas interiores do Estado do Paraná: 1987–1995. Curitiba PR, Brazil.
- Torres J P M, Malm O, Vieira E D R, Japenga J, Koopmans G F, 2002. Organic micropollutants on river sediments from Rio de Janeiro, Southeast Brazil. *Cadernos de Saúde Pública*, 18: 477–488.
- Trapido M, 1999. Polycyclic aromatic hydrocarbons in Estonian soil: contamination and profiles. *Environmental Pollution*, 105: 67–74.
- Venturini N, Tommasi L R, 2004. Polycyclic aromatic hydrocarbons and changes in the trophic structure of polychaete assemblages in sediments of Todos os Santos Bay, Northeastern, Brazil. *Marine Pollution Bulletin*, 48: 97–107.
- Wania F, Mackay D, 1996. Tracking the distribution of persistent organic pollutants. *Environmental Science & Technology*, 30: 390A–396A.
- WHO (World Health Organization), 1998. Selected non-heterocyclic polycyclic aromatic hydrocarbons, Environmental Health Criteria 202. United Nations Environment Programme. International Labour Organization, Geneva. <http://www.inchem.org/documents/ehc/ehc/ehc202.htm> cited 03-28-2007.
- Yang S Y N, Connell D W, Hawker D W, Kayal S I, 1991. Polycyclic aromatic hydrocarbons in air, soil and vegetation in the vicinity of an urban roadway. *The Science of the Total Environment*, 102: 229–240.
- Yunker M B, Macdonald R W, 1995. Composition and origins of polycyclic aromatic hydrocarbons in the Mackenzie River and on the Beaufort Sea shelf. *Arctic*, 48: 118–129.
- Yunker M B, Macdonald R W, Vingarzan R, Mitchell R H, Goyette D, Sylvestre S, 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33: 489–515.