PAHs diagnostic ratios for the distinction of petrogenic and pirogenic sources: applicability in the Upper Iguassu Watershed - Parana, Brazil

Relações diagnósticas de HPAs para distinção de fontes petrogênicas e pirogênicas: aplicabilidade na Bacia do Alto Rio Iguaçu - Paraná, Brasil

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are considered persistent organic pollutants and can cause serious damage in some organisms, including mutagenic and carcinogenic properties. The aim of this study was to evaluate the PAH concentrations in an urban basin and use diagnostic ratios to possible distinguish sources of contamination. The surface water analysis showed predominance of compounds containing 3 to 4 aromatic rings while in suspended particulate matter and sediment there was a predominance of compounds containing 4, 5 and 6 rings. Although present in low concentrations in the sediment, assessment of toxicity equivalent factor (TEF) showed values higher than 3 ng g^{-1} pellet to 50% of the samples with values of up to 125.35 ng g^{-1}. The use of diagnostic ratios allowed verifying that the main source of PAHs in these aquatic environments, are pyrogenic sources. Still, the use of such relations should be done with caution, trying to assess possible interference of degradation factors

Keywords: Diagnostic ratios; Risk assessment; Polycyclic aromatic hydrocarbons; Environmental contamination.

RESUMO

Hidrocarbonetos policíclicos aromáticos (HPAs) são poluentes orgânicos considerados persistentes e que podem causar sérios danos em alguns organismos, incluindo propriedades mutagênicas e carcinogênicas. O objetivo desse estudo foi avaliar as concentrações de HPAs em uma bacia urbanizada e utilizar relações diagnósticas para tentar distinguir fontes de contaminação. A análise de água superficial mostrou um predomínio de compostos de 3 a 4 anéis aromáticos, enquanto que para material particulado suspenso e sedimentos houve uma predominância de compostos com 4, 5 e 6 anéis aromáticos. Apesar de baixas concentrações no sedimento, avaliação de equivalentes de toxicidade mostraram valores superiores a 3 ng g^{-1} de sedimento para 50% das amostras, com valores de até 125.35 ng g^{-1}. O uso de relações diagnósticas permitiu atribuir, nestes ambientes aquáticos, que os HPAs foram provenientes, principalmente, de origem pirogênicas. Mesmo assim, o uso de tais relações deve ser feito com o devido cuidado, tentando avaliar possíveis interferências de fatores de degradação.

Palavras-chave: Relações diagnóstico; Avaliação de risco; Hidrocarbonetos policíclicos aromáticos; Contaminação ambiental.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class that belongs to persistent organic pollutants.

The processes that originate these substances are both natural and anthropogenic (MAGALHÃES; BURNS; VASCONCELLOS, 2007; ACQUAVITA et al., 2014).

Examples of natural sources of PAHs are forest fires, petroleum seeps, post depositional changes of biogenic precursors and also biosynthesis origin of some plants and fungi (AIZENSHTAT, 1973; SUESS, 1976; WAKEHAM; SCHAFFNER; GIGER, 1980; BAUMARD et al., 1998; BETTIN; FRANCO, 2005; WANG et al., 2009; ZHANG et al., 2015). As anthropogenic sources the examples that may be pointed out are combustion of fossil fuels, leaking of petroleum and derivatives, incineration of waste, production of coke, pitch, asphalt, cracking of petroleum and industrial effluents (MCCREADY et al., 2000; CHANG; SHIUNG; YUAN, 2002; MURI; WAKEHAM, 2009; MOSERT; AYOKO; KOKOT, 2010).

A recent increase on concentrations of PAHs in the environment may be associated to economic development and population increase, which leads to a greater number of sources of these compounds (ANDERSON et al., 2014; YANG et al., 2016). The majority of the anthropogenic sources are related to exploration, transformation and combustion of fossil fuels (WITT, 1995).

Regarding toxicity, compounds with two and three aromatic rings exhibit a significant acute toxicity (PEREIRA NETTO et al., 2000) and compounds with a larger number of aromatic rings present a considerable carcinogenic, mutagenic and teratogenic potential (WITT, 1995; CAVALCANTE et al., 2007; HUSSAIN; BALACHANDRAN; HOQUE, 2015; ZHENG et al., 2016). The PAHs may induce growth inhibition, degradation of the lymphatic system, and interference in hematopoietic functions (ZAGHDEN et al., 2007; RUIZ et al., 2011). The main concern about the presence of PAHs in the environment is primary to the bioaccumulation effect, mainly in invertebrates (EUROPEAN COMMISSION, 2002; EEA, 2014).

Considering these environmental harmful effects the United States Environmental Protection Agency (USEPA) classified some PAHs as primary control organic pollutants. These pollutants must be monitored in several environments, like sediments, water, soil and biota. One of the most toxic PAHs is benzo(a)pyrene, which is usually applied as an indicator of PAHs (ALBUQUERQUE; COUTINHO; BORREGO, 2016).

PAHs can be introduced in aquatic ecosystems due to atmospheric deposition, wastewater discharges, navigation activities and oil spills (HEENKEN et al., 2000; GARBAN et al., 2002; MONTELAY-MASSEI et al., 2007; MOUHRI et al., 2008; MASOOD et at., 2016).

Considering their hydrophobic properties, PAHs tend to adsorb to other particles and deposit, contributing to sediment formation. When PAHs bind to other particles they can represent a greater risk to benthic organisms, which can affect the entire food chain (BOULOUBASSI et al., 2012; ADHIKARI et al., 2016) also, in favorable conditions, adsorbed PAHs can be released to water column e become bioavailable in the aquatic ecosystem (CHEN et al., 2013).

Recent studies show that PAHs are a substantial interest in aquatic environments that are influenced by urban areas (BOURGEAULT; GOURLAY-FRANCÉ, 2013) and also in estuarine environments (SANT'ANNA JUNIOR et al., 2010; MIZUKAWA et al., 2015). Due to their extensive environmental distribution and their exposure risk, it became fundamental to identify the main sources of these compounds (BOULOUBASSI et al., 2012).

One of the ways to differentiate contamination sources of PAHs is to employ diagnostic ratios (YUNKER et al., 1996; YUNKER et al., 2002; ZHANG et al., 2004a). Such relations allow differentiating between petroleum related sources and combustion related sources.

The use of these ratios is based on the relative thermodynamic stability of some PAHs isomers. One isomer is formed by fast chemical reactions and exhibits a low stability. These isomers are usually formed during combustion processes or other chemical treatments (BIACHE; MANSUY-HUAULTA; FAUREA, 2014). A higher thermodynamics stability isomer is formed during processes that take longer period of times, like diagenesis or catagenesis, resulting in fossil organic matter such as petroleum or charcoal, defined as petrogenic sources that are enriched with these isomers (YUNKER et al., 2002). Therefore, these ratios can be employed to better understand PAHs distribution and diagnose the main sources in the environment (SOUZA, 2010).

The employment of these ratios is based on the assumption that such PAHs isomers have similar physical and chemical properties and therefore will be transformed and degraded at the same rate, preserving the relation that is present in the emission (MOSERT; AYOKO; KOKOT, 2010; TOBISZEWSKI; NAMIESNIK, 2012; BIACHE; MANSUY-HUAULTA; FAUREA, 2014; CLÉMENT et al., 2015).

These ratios have been widely adopted in several researches (BAUMARD et al., 1998; MAGI et al., 2002; YUNKER et al., 2002; MEDEIROS; BICEGO, 2004; DE LUCA et al., 2005; LI et al., 2006; ZAGHDEN et al., 2007; MONTELAY-MASSEI et al., 2007; MEIRE et al., 2008; BAKHTIARI et al., 2009; BAKHTIARII et al., 2010; PIETZSCH et al., 2010; YUNKER et al., 2011; EVANS et al., 2016), however, they must be used with caution (TOBISZEWSKI; NAMIESNIK, 2012) due to complex mixtures that may happen in the environment and can interfere in the final conclusions (YUNKER et al., 2002; DASKALOU et al., 2009).

The aim of this research was to determine concentrations of some PAHs in aquatic environments inside a strongly urbanized water basin, assessing PAHs distribution between sediments and water column (dissolved fractions and PAHs associated to the suspended particulate material). The distinction between PAHs sources was performed based on the diagnostic ratios.

MATERIALS AND METHODS

Study area

The study area was located in the Upper Iguassu River basin (Figure 1) in the Metropolitan Region of Curitiba (MRC). Curitiba is the capital and biggest city in the Brazilian state of Paraná. This basin is the main source of water supply in the
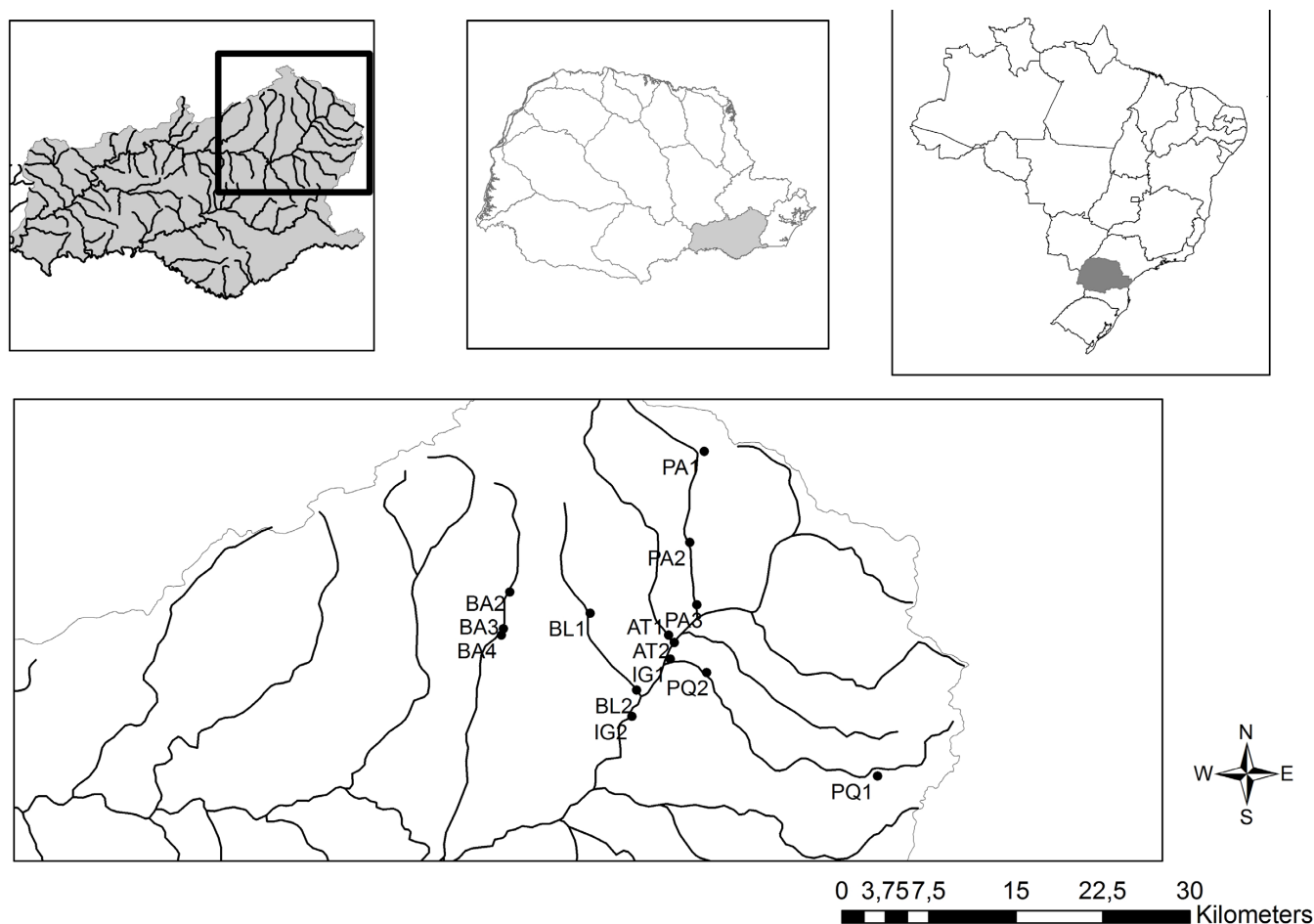
Figure 1. Upper Iguassu River Basin, highlighted, sampling points localization in Atuba River (AT), Barigui River (BA), Belém River (BL), Iraí RIver (IR), Palmital River (PA), Pequeno River (PQ) and Iguassu River (IG) in the Metropolitan Region of Curitiba (MRC).

MRC, corresponding to approximately 60% of the water supply. The unplanned and uncoordinated urban growth in this region also contributes to aquatic environments pollution. The main source of pollution is wastewater, a problem that is aggravated by clandestine sewer connections (ANDREOLI et al., 1999). Currently, this region incorporates 13 neighboring cities of Curitiba. The MRC have an estimated population of 3.5 millions of inhabitants, corresponding to 30% of the Paraná state entire population (IBGE, 2016).

The Upper Iguassu River basin covers an area close to 2882 km² and it is formed by 32 rivers. Among these 32 Rivers the main rivers are Iguassu River (main river), Barigui River, Palmital River, Atuba River, Passaúna River, Iraí River, Belém River, Itaqui River, and Pequeno River. The total length of Iguassu River is nearly 910 km, and of 910 km, approximately 100 km are inside the MRC, which encompasses the Upper Iguassu River basin.

For this research, four sampling events were performed in the Rivers of the MRC (Figure 1).

In Atuba River (AT) samples were collected in two points along the River, both with urban influence from MRC. The sampling point AT1 is located upstream of a Wastewater Treatment Plant (WWTP-South Atuba) and the sampling point AT2 is located downstream the same WWTP.

In Palmital River there were three sampling points. Sampling point PA1 was located in a rural area, PA2 was located in an urbanized area, between the cities of Colombo and Curitiba. Sampling point PA3 is located near the mouth of Palmital River, between the cities of Pinhais and Curitiba, where it suffers a bigger urban influence than the previous sampling points. Palmital River is located in an area that presents less demographic influence, although also shows problems in the treatment and collection of domestic sewage, mainly near Palmital River mouth.

In Belém River (BL) there were two sampling points. The sampling point BL1 was located in the middle of the length of the river, with an expressive urban influence and the second sampling point, BL2, is near the mouth of Belém River, influenced by an extensive and continuous urban area, one of the most degraded sampling points.

In Barigui River there were three sampling points. The sampling point BA2 is after the lake of the Barigui Park, receiving influence from degraded sewage and phytoplankton from the lake. Sampling point BA3 is upstream of a WWTP and sampling point BA4 is downstream the WWTP. Barigui River basin is known by the great quantity and diversity of industrial activities.

The rivers cited above are all located in the right side of the bank of Rio Iguassu. They are currently degraded due to

the high population density and to the irregular occupation on their banks, which imply in clandestine launches of domestic sewage and solid waste (IDE et al., 2013; KRAMER et al., 2015; SANTOS et al., 2016).

Also, there were two sampling points in Iguassu River, the main river of the basin. The first sampling point in Iguassu River (IG1) was after the contributions of Atuba River (AT2) and Iraí River (IR1). The second sampling point (IG2) was located after the contribution of Belém River (BL2). The choice of the sampling points in Iguassu River had the goal to assess the influence of its tributaries.

In the left bank there were also sampling points in Pequeno River. The left bank has less urban influence and less population density. Nevertheless, the two sampling points located in Pequeno River (PQ1 and PQ2) are close to a highway (BR-277), which can be a pollution source, due to an expressive traffic in this highway.

Sample collection

The surface water and sediment samples were collected in 15 points along the Upper Iguassu River basin (Figure 1). The campaigns were performed in Jun/11, Set/11, Nov/11 and Apr/12. Surface water samples were collected in decontaminated amber bottles and were stored in low temperature (4 °C). Afterwards the water samples were filtered on 0.45 μm cellulose acetate membranes and extracted in a maximum of 24 hours after sampling.

Sediment samples were collected with a modified Peterson grab sampler and stored in previously decontaminated aluminum containers (450 °C).

PAHs extraction

Extraction procedures were based in the ones stablished by Mater et al. (2004). The samples were filtered through micro glass fiber filters with a 1.2 μm diameter, to analyze PAHs. The material that was retained in the filters was separated to analyze the suspended particulate matter (SPM). The filtrated water was acidified until pH 3.00 with hydrochloric acid.

To the solid phase extraction the cartridges were washed with 5mL of dichloromethane, 5 mL of methanol, and 5 mL of ultrapure water. A volume of 1000 mL was transferred to the C18 cartridges, with a 6-8mL min⁻¹ flux, so the target compounds could be retained. After, the cartridges were dried under a nitrogen flux and eluted with two portions of 5 mL of dichloromethane and 5 mL of ethyl acetate.

The SPM retained in the filters was lyophilized. After the filters were completely dry, the extraction was performed utilizing ultrasonification. The extraction was executed in three parts. First, the filters were immersed in 20 mL of hexane. In the second part the filters were immersed in 20 mL of a solution containing 10 mL of hexane and 10 mL of dichloromethane and in the last part the filters were immersed in 20 mL of dichloromethane. In each part of the processes the samples were sonified during 20 minutes. The three parts were filtered, reunited and evaporated. The material was then reconstituted in 3 mL of dichloromethane.

In sediments PAHs extraction was performed in sediment samples dried in a temperature of 40 °C. The same procedures applied to the filters containing SPM were applied to 20 g of sediment. Due to the large amount of the sediment the volumes were altered to 40 mL of hexane, 40 mL of hexane and dichloromethane in a 1:1 proportion and 40 mL of dichloromethane.

The reconstituted extract of the dissolved PAHs, and the PAHs present in SPM and in the sediments were cleaned-up in a chromatography column filled with 2 g of silica, 2 g of alumina and 1 g of sodium sulfate. The column was conditioned with 20 mL of hexane and after the samples were inserted, 20 mL of hexane were eluted from the column, eliminating a fraction containing n-alkanes. To the PAHs elution 20 mL of dichloromethane were utilized. After evaporation, the final volume was adjusted to 1 mL.

Chromatographic conditions

PAHs analyses were performed in the gas chromatography GC-431 (Varian). The employed chromatography column was a HO-5Ms (30 m × 0.25 mm × 0.25 μm). The carrier gas was Helium 6.0 (99.9999%) with a 1 mL min⁻¹ flux. The initial temperature of the oven was adjusted to 60 °C with a 20 °C elevation per minute until 120 °C, remaining isothermal for 1 minute. Subsequently the elevation was scheduled to 10 °C per minute until 200 °C and then an elevation of 5 °C per minute until 300 °C, remaining isothermal for 34 minutes. A volume of 1 μL was injected in the gas chromatography (GC-MS). The injector and the transfer line temperatures were adjusted to 280 °C and the trap ion temperature was adjusted to 200 °C. The data acquisition was operated in the 50 to 650 m/z band.

To validate the employed method recover tests were performed in two concentrations with five repetitions (N=5). To assess possible contaminations blank samples were prepared during the analysis. Also, repetition tests were performed (intra-day precision) with five injections in the same day (N=5) of a sample replica with a concentration of 2 μg L⁻¹. To verify precision (inter-day precision) a sample replica with a concentration of 2 μg L⁻¹ was injected 5 times a day, during three consecutive days.

RESULTS AND DISCUSSION

Validation and quality control

Table 1 demonstrates the main variables in the validation and control of the analytical method applied in the PAHs quantification. Detection limits varied from 0.10 to 23.57 ng L⁻¹, according to analytical sensibility of each solute. Recovery rates to water samples in the lower level varied from 86 to 94%. In sediment samples recovery rates varied from 60 to 91% in the lower level. In the precision and repetition tests, the coefficients of variation were below 20%, which are acceptable levels to chromatographic methods destined to trace analysis. PAHs weren´t detected in blank samples during the analyses, confirming that contaminations didn´t occur in the analytical method.

Distribution of dissolved PAHs and PAHs associated to particulate matter

Table 1. Validation parameters of the HPA analytical method employed.

	DL	QL	Water Recover (%)		Sediment Recover (%)		CV (%)	
	ng L⁻¹		10 ng L⁻¹	50 ng L⁻¹	2 ng L⁻¹	20 ng L⁻¹	Intra	Inter
Naphthalene	1.20	3.65	88	91	67	90	6	15
Acenaphtylene	1.18	3.60	89	92	61	90	8	15
2-bromonaphtalene	1.76	5.36	88	94	62	80	10	15
Acenaphtene	1.16	3.54	89	94	73	80	11	12
Fluorene	1.01	3.07	92	89	63	75	10	17
Phenanthrene	0.46	1.40	90	91	61	85	12	12
Anthracene	0.81	2.47	86	92	71	88	9	13
Fluoranthene	0.84	2.57	89	88	60	81	9	15
Pyrene	0.61	1.85	90	91	68	89	9	12
Benzo(a)anthracene	1.00	3.06	89	92	69	88	12	17
Chrysene	1.27	3.88	90	92	75	76	12	13
Benzo(e)acenaphenanthrylene	0.10	0.29	93	94	73	87	9	18
Benzo(a)pyrene	0.38	1.17	88	88	69	77	6	12
Indeno(1,2,3-cd)pyrene	16.11	49.12	93	89	65	82	9	12
Dibenzo(a,h)anthracene	20.38	62.16	86	90	65	75	11	18
Benzo(ghi)perylene	23.57	71.88	86	91	62	91	9	13

PAHs concentrations in the sampling points tend to increase the nearest the sampling point is to intense urban occupation zones, like can be observed in PA2, AT2, BA3 and IG2. This tendency can be confirmed by the concentrations of the dissolved PAHs and PAHs associated to suspended particulate matter (Figures 2 and 3).

In the dissolved fraction PAHs with three or four rings were the largest contribution, with an exception of the Jun/11 campaign, where PAHs with five or six rings were predominant in some rivers. The predominance of small molecular structures occurred, mainly, because their high solubility in water compared to higher molecular mass compounds, which are hydrophobic (Figure 2) and show a tendency to be adsorbed in the SPM.

In the dissolved fraction, the concentrations varied from 250 to 18983 ng L⁻¹, values close to the ones obtained by Wang et al. (2009) and Bourgeault and Goulay-France (2013) in impacted urban areas.

The greater total PAHs concentrations were:

a) In Jun/11, because of the results obtained in the PA1 sampling point (Palmital River). There are indications that the PAHs may be originated from organic matter combustion, since the sampling point is located in a rural area, where the act of burning plants is recurrent;

b) In Sep/11, in the PA2 sampling point (also in Palmital River), presumably due to petroleum combustion or asphaltic residues, since sampling point PA2 is upstream a bridge in a highway (BR 116), which has a high traffic flux that can influence in the PAHs concentration in this environment;

c) In Nov/11 and Apr/12 the greatest dissolved PAHs concentrations were obtained in the BL1 (Belém Rover) and PQ1 (Pequeno River) sampling points. Sampling point BL1 is located inside the city of Curitiba. In this particular case the PAHs must be originated from the traffic in the central area of the city. Sampling point PQ1 is located in a

bridge in a highway (BR 277), which connects Curitiba to the east coast, where the traffic is extensive and continuous.

Due to the lower solubility of compounds with 4, 5 and 6 rings, an increase of these compounds has been observed in the suspended particulate material (Figure 3).

The predominance of higher molecular mass compounds in the suspended particulate material can generate greater adverse effects in the environment, once these compounds tend to induce carcinogenic, mutagenic and teratogenic responses in some organisms, originating chronic effects (WITT, 1995; CAVALCANTE et al., 2007). Otherwise, compounds containing 3 rings are frequently associated to acute effects. However, acute effects occur only in elevated concentrations, superior to the ones observed in the environment (PEREIRA NETTO et al., 2000).

Total PAHs concentrations in suspended particulate material (SPM) varied from 13 ng mg⁻¹ to 675 ng mg⁻¹. The greatest concentration was observed in sample point BA3 (Barigui River) in Nov/11. During the four sample campaigns (Jun/11, Sep/11, Nov/11 and Apr/12) sampling points BA3 e PQ1 were the ones where higher concentrations of total PAHs in SPM were found. In sampling point PQ1, this outcome is probably due to the localization of the sampling point, in a bridge in a highway (BR 277), which connects Curitiba with the Port of Paranaguá and Paraná Coast., with a lot of traffic. Sampling point BA3 is located in an urban area, which also presents a lot of traffic, due to everyday car flux. In both sampling points, the main source of PAHs may be fuel combustion.

PAHs distribution in surface sediments

The spatial distribution of PAHs in sediments of the Upper Iguassu River basin (Table 2), suggests that higher concentrations of total PAHs were detected in environments with intense anthropic influence, like Barigui River, Iguassu River and Belém River
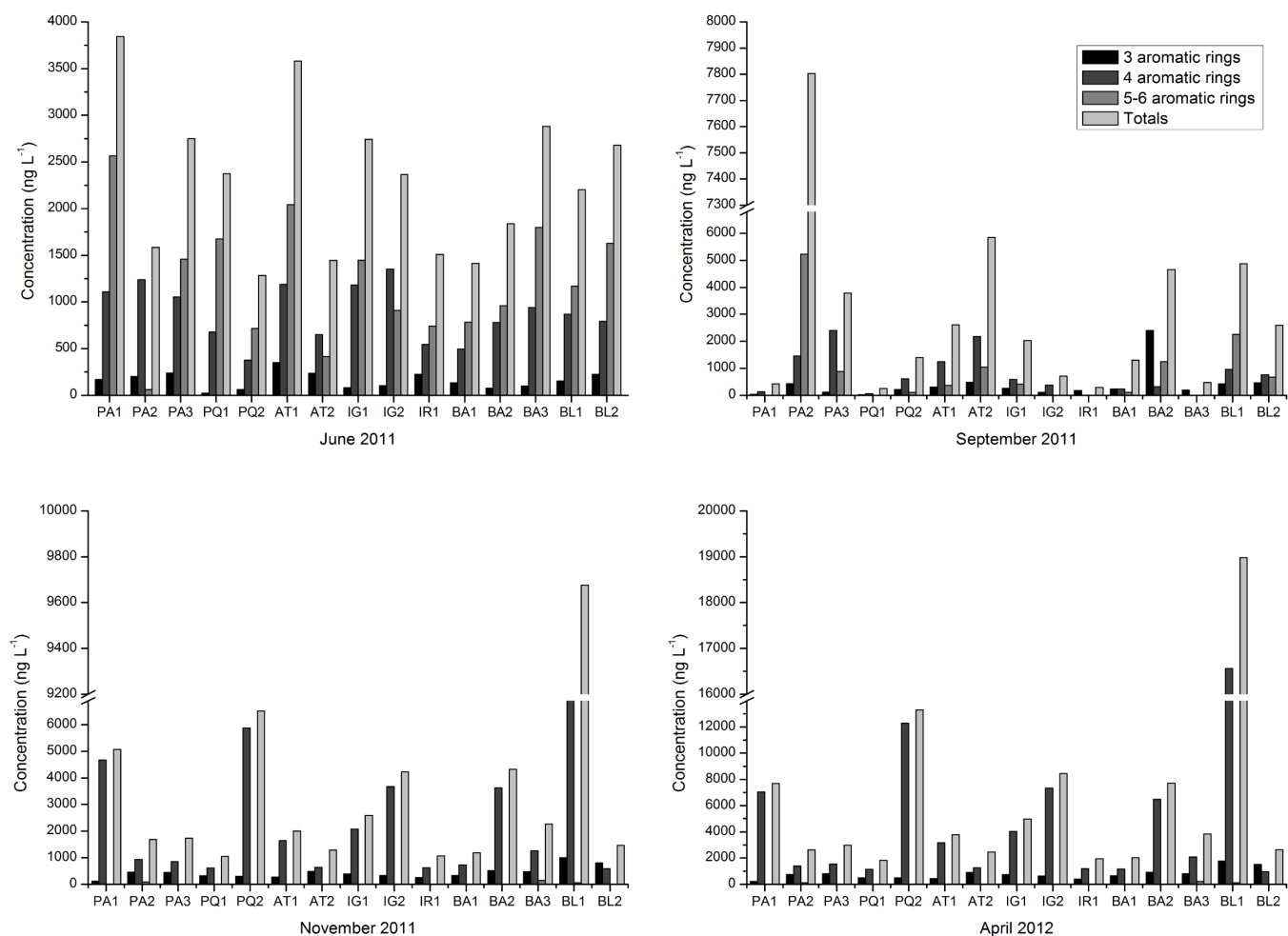
Figure 2. PAHs distribution in samples (Jun/11, Sep/11, Nov/11 and Apr/12) in surface water in the following rivers: Palmital (PA), Pequeno (PQ), Atuba (AT), Iguassu (IG), Iraí (IR), Barigui (BA) e Belém (BL).

Table 2. Concentrations of some PAHs determined in sediment samples of the following rivers: Palmital (PA), Pequeno (PQ), Atuba (AT), Iguassu (IG), Iraí (IR), Barigui (BA) and Belém (BL).

	Acen	Flu	Phen	Ant	Flut	Pyr	Chry	BeA	BaP	Ind	Dib	Beng	Sum
							Sediment PAHs (ng g⁻¹)						
PA1		0.89	1.05	0.14	3.21	4.57		18.97					28.82
PA2	2.95	1.15	2.79	0.80	9.12	3.38	3.11	12.94					36.23
PA3	1.00		1.99	2.19	30.17	7.24		10.49					53.08
PQ2	1.54	0.95	3.94	1.43	12.57		3.08	0.34	78.31	11.17			113.32
AT1	4.14	1.56	2.80	0.82	9.10	4.44		13.93					39.42
AT2	2.56	6.57	1.98	1.63	7.38	0.37		26.31	16.91				64.37
IG1	8.29	6.10	21.95	8.27	22.38	30.35	17.08	96.50	54.70	112.49	345.04	64.29	811.92
IG2	1.57	0.98	3.90	0.83	8.63		1.66	13.19					33.87
IR1	9.10	0.33	0.21	1.91	49.53		6.69	19.89	39.93	21.48		35.70	186.07
BA2	19.23		63.28	23.08	68.40	110.1	33.33	138.82	94.85	101.44	453.94	375.56	1521.22
BA3	3.98	1.80	26.75	10.10	14.87	13.67	3.14	60.09	55.23	174.25	446.61	53.85	867.80
BA4	1.76	0.23	3.81	1.55	18.66	4.69	1.32	10.36					46.72
BL1	4.90	2.29	32.80	7.53	31.22	30.74	5.67	40.54	27.99	61.49	159.59	30.99	445.09
BL2	11.73	1.98	10.36	1.43	7.81	4.32	3.28	14.98					57.38

ACEN: Acenaphtene; FLU: Fluorene; PHEN: Phenanthrene; ANT: Anthracene; FLUT: Fluoranthene; PYR: Pyrene; CRHY: Chrysene; BeA: Benz(e)acephenantryilene; BaP: Benzo(a)pyrene; IND: Indeno(1,2,3-cd)pyrene; DIB: Dibenzo(a,h)anthracene; BghiP: Benzo(ghi)perylene. In Sum was also included: NAPH (naphftalene), ACE (acenaphtalene), NAB (2-bromo-naphtalene) and BEA (benzanthracene).
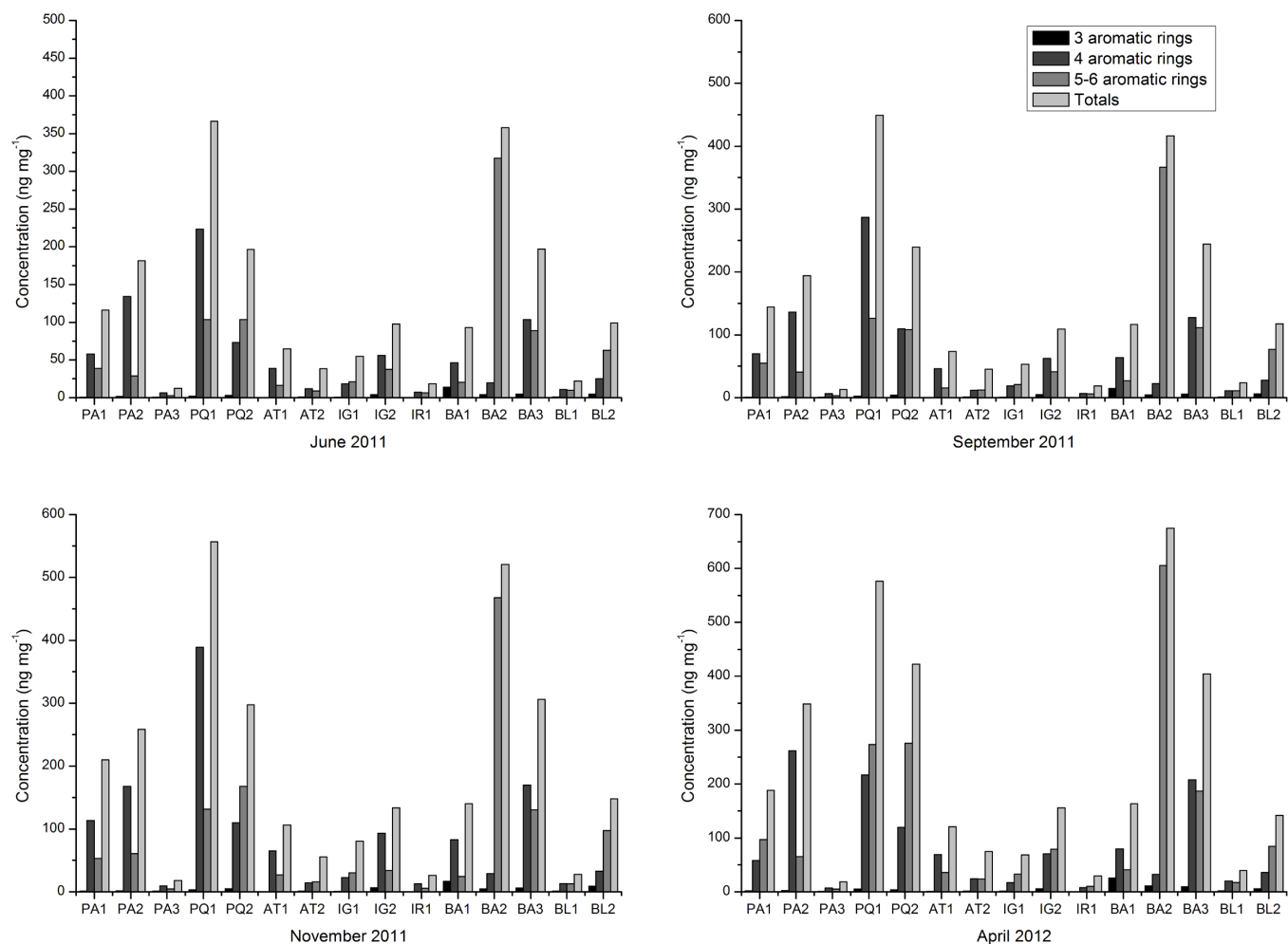
Figure 3. PAHs distribution in samples (Jun/11, Sep/11, Nov/11 e Apr/12) of suspended particulate material in the following rivers: Palmital (PA), Pequeno (PQ), Atuba (AT), Iguassu (IG), Iraí (IR), Barigui (BA) and Belém (BL).

(Figure 4). Compounds that have stable molecular structures, less predisposed to degradation, hydrophobic, with greater number of aromatic rings were predominant in the sediments

Considering the Brazilian resolution CONAMA 344/2004 (BRASIL, 2004), highest values were detected in sampling point BA2, regarding the first level to: phenanthrene, pyrene, benzo(a) pyrene e para o dibenzo(a,h)anthracene. Sampling points BA3 and IG1 also showed superior values to benzo(a)pyrene e para o dibenzo(a,h)anthracene. Sampling points PQ2 and BL1 showed superior values to dibenzo(a,h)anthracene. These values characterize that the sediments offer, even if concentrations of some PAHs are low, a probability of adverse effects in the biota.

Total PAHs concentration varied from 28.82 to 1521.22 ng g^{-1}. These values are relatively lower than the ones observed in other aquatic environments (MA et al., 2001; WU; ZHANG; ZHU, 2003; ZHANG et. al., 2004b; KANNAN et al., 2005; LIU et al., 2009), however, considering their effects and accumulation it is necessary to follow their variations in the environment.

Generally, higher molecular mass compounds, the ones with 4 to 6 aromatic rings (Chrysene to Benzo(ghi)perylene), were found in higher concentrations than the ones with lower molecular mass, with 2 to 4 aromatic rings (Naphtalene to Benzo(a)anthracene). That indicates, in general, mixtures of PAHs originated from high temperature fossil fuels combustion (SOCLO; GARRIGUES; EWALD, 2000; GOGOU; BOULOUBASSI; STEPHANOU, 2000). The average percentage value of PAHs with 4 or more rings, in relation to the total concentration of PAHs was 61.88%. Sampling point BA3 showed the greatest percentage (91%), indicating that the environment may have concentrations of PAHs harmful to the biota.

However, total concentration of PAHs may be intangible about the possibility of negative effects due to the presence of these substances in the environment and many times toxicity related analysis of the compounds should be performed.

One of the ways to assess toxicity of sediments containing PAHs is by toxicity equivalent factor of Benzo(a)Pyrene (TEF(BaP)) (LIU et al., 2009). Of the 14 sampling points, 7 showed concentrations above 3 ng g^{-1} of TEF(BaP) (Figure 5), a recommended value of sediment quality guidelines from Netherlands (VAN DER GAAG et al., 1991). Therefore, even with lower concentrations
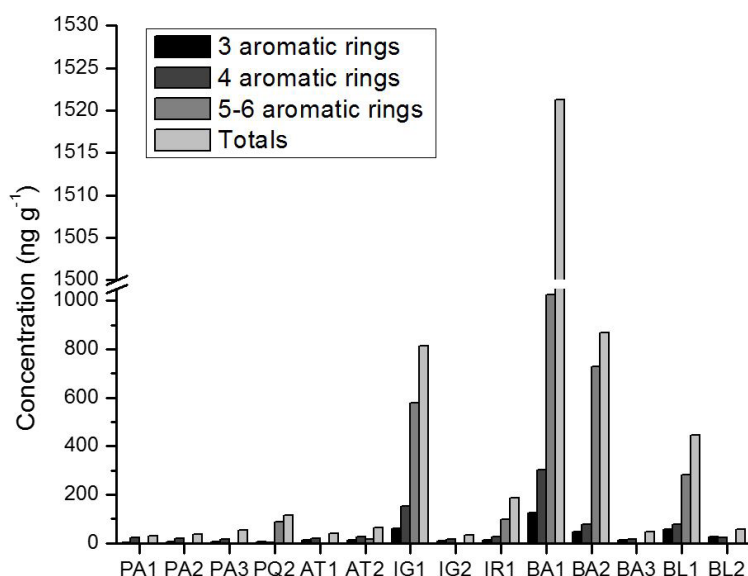
Figure 4. PAHs distribution in sediment samples (Jun/11, Sep/11, Nov/11 e Apr/12) in the following rivers: Palmital (PA), Pequeno (PQ), Atuba (AT), Iguassu (IG), Iraí (IR), Barigui (BA) e Belém (BL).
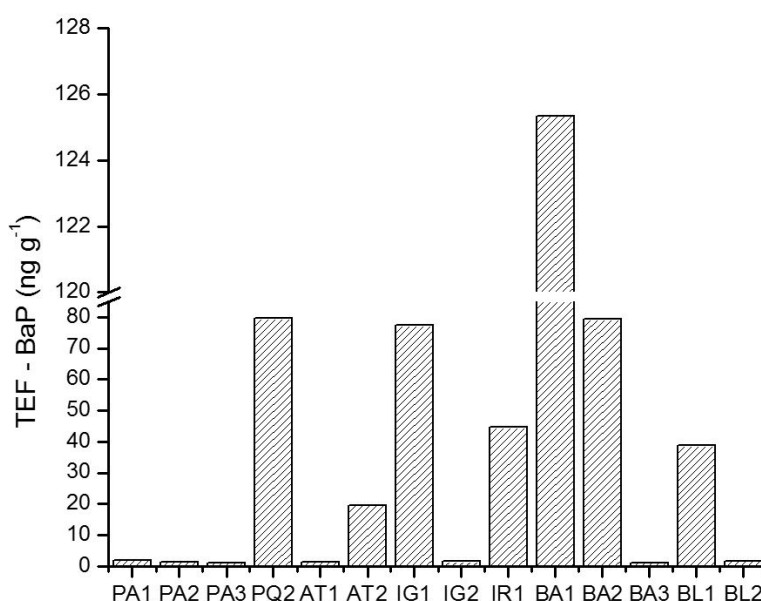

Figure 5. Toxicity equivalent factor (TEF) of Benzo(a)Pyrene (BaP), TEF-BaP, in sediments of the Upper Iguassu River basin in the following rivers: Palmital (PA), Pequeno (PQ), Atuba (AT), Iguassu (IG), Iraí (IR), Barigui (BA) and Belém (BL).

than the ones observed in other environments, PAHs found in sediments of the Upper Iguassu River basin may offer risk to some organisms.

Pyrogenic and petrogenic distinction using diagnostic ratios

To identify possible PAHs sources in the samples (water, SPM and sediments), ratios between PAHs isomers were employed. According to Yunker et al. (2002), these ratios are possible due to thermodynamic characteristics of the PAHs and to the differences in the formation heat of these compounds, distinguishing the most stable isomer from the least stable, making it possible to differentiate the sources.

The ration between phenanthrene/anthracene (PHEN/ANT) was applied to differentiate PAHs of pyrogenic sources from PAHs of petrogenic sources (SOCLO; GARRIGUES; EWALD, 2000; MAGI et al., 2002; CHEN; CHEN, 2011; CHEN et al., 2013). To water, SPM and sediment samples the values of this ratio were lower than 10 (Figure 6A, C, E), indicating that PAHs samples from MRC may be associated to pyrogenic sources (combustion).

In the same Figure 6A, C, E values from Fluoranthene/pyrene (FLUT/PYR) are shown. It was observed that not all sample points, applying FLUT/PYR ratio, had the same results as in the PHEN/ANT ratio, because not all sample points and collected
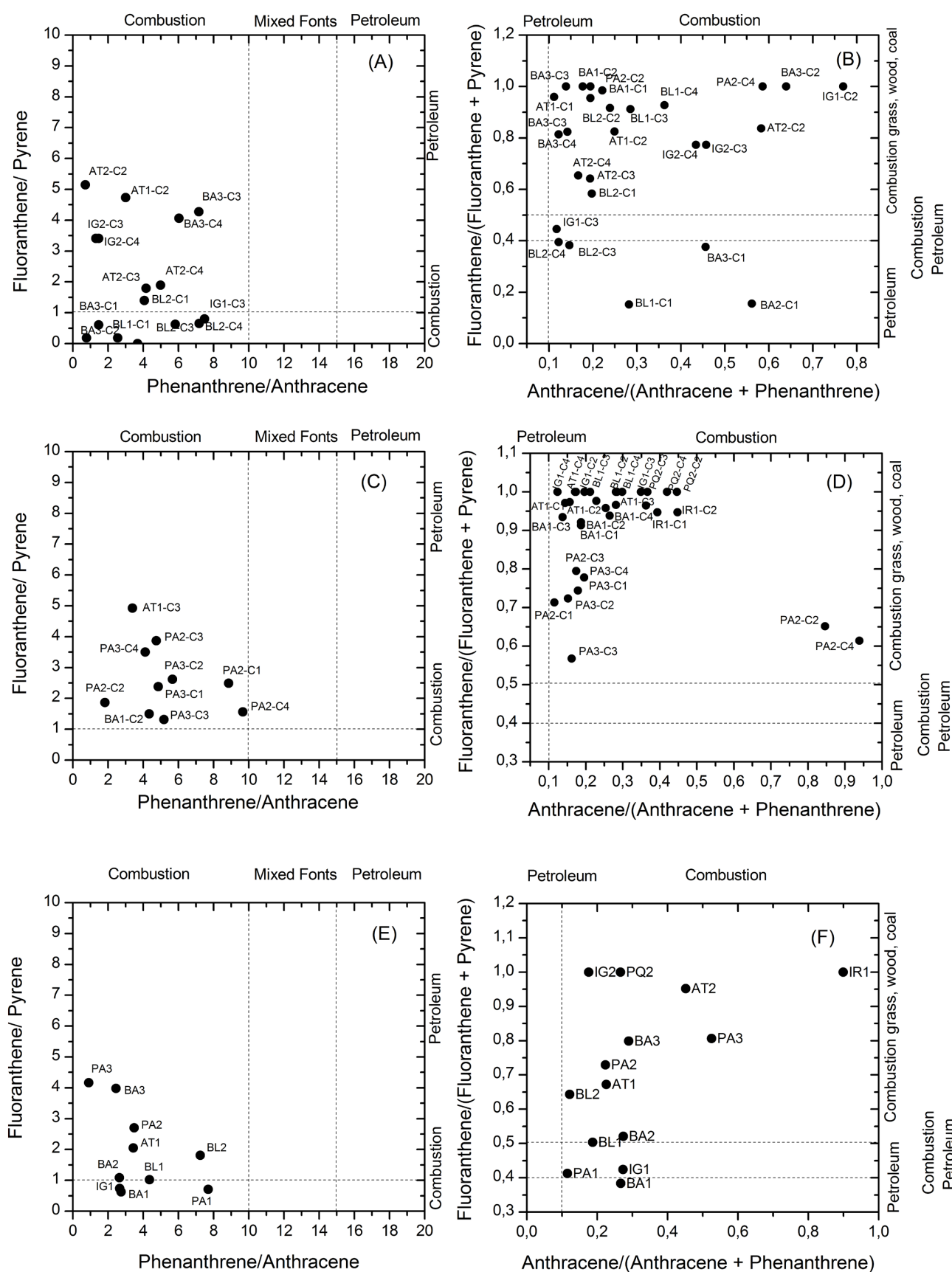
Figure 6. Diagnostic ratios of PAHs to distinguish between pyrogenic and petrogenic sources in water (A and B), suspended particulate material (C and D) and sediments (E na F) in the Upper Iguassu River basin, in the following rivers: Palmital (PA), Pequeno (PQ), Atuba (AT), Iguassu (IG), Iraí (IR), Barigui (BA) and Belém (BL).

samples show PAHs from pyrogenic sources. Some values were more than one, indicating, according to Magi et al. (2002) and Chen and Chen et al. (2011), PAHs from petrogenic sources.

Alternatively to the PHEN/ANT ratio it can be employed the [anthracene/(phenanthrene+anthracene)] [ANT/(PHEN+ANT)] ratio. In this diagnostic, according to author that applied it (YUNKER et al., 2002; ZHANG et al., 2004a; QIAO et al., 2006; CHEN et al., 2013), values superior to 0.10 indicate pyrogenic sources. To water, SPM and sediment samples (Figure 6B, D, F), the ratio indicate that PAHs found in the rivers of the MRC may be associated to pyrogenic sources.

Another ratio employed to distinguish PAHs sources was [fluoranthene/(fluoranthene+pyrene)]. This ratio was already applied in other studies (MAGI et al.; 2002; ZHANG et al., 2004b; LI et al., 2006). The ratio [FLUOR/(FLUOR+PYR)] was employed to assess if the PAHs were originated from the combustion of petroleum byproducts or from the wood, grass and/or coal burning. Values below to 0,40 indicate petrogenic sources, values between 0.40 and 0.50 indicate petroleum combustion and values above 0,50 indicate PAHs from wood, grass or coal burning. With Figure 6B, D, E it was possible to verify that PAHs from wood, grass or coal burning were detected in the samples.

Based on the employment of the diagnostic ratios method (Figure 6), it was possible to confirm the predominance of PAHs originated from pyrogenic sources in practically the entire basin. This phenomenon was observed in all analyzed environmental matrices (water, SPM and sediment).

From the four ratios used, the FLUT/PYR may be considered the most sensitive among the other methods, since its distribution was close to the distinction range. Other factor that may have influenced ratio results was the possible transformation that the PAHs may have suffered in the aquatic environment, mainly photolysis oxidation (BIACHE; MANSUY-HUAULTA; FAUREA, 2014).

CONCLUSION

Monitoring of PAHs may provide interesting data to the understanding of the environmental conditions in the rivers of the Upper Iguassu River basin, in the Metropolitan Region of Curitiba. The observed concentrations in all studied matrices are elevated and potentially harmful to the environment. The concentration of PAHs in surface water, suspended particulate material and sediments indicated that the studied area is under an elevated urban pressure and the human activities are probably affecting the contribution of PAHs. Diagnostic ratios have been shown to be an enlightening tool to distinction of pyrogenic and petrogenic PAHs sources, which may help in the implementation of measures to control emissions of PAHs. In the MRC, in the studied rivers, a predominance of pyrogenic sources was observed.

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