

Determination of PAHs in Surface Waters from the Doce and Piracicaba Rivers in Brazil

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Abstract

Sixteen polycyclic aromatic hydrocarbons were determined in water samples from the Piracicaba River and the Doce River in the municipality of Ipatinga, Minas Gerais State, Brazil. The polycyclic aromatic hydrocarbons were extracted by solid-phase extraction and were analyzed by high-performance liquid chromatographic with diode-array detector. The limit of detection was as low as 1.3 ng·L⁻¹. All polycyclic aromatic hydrocarbons were found above the limit of quantification in water from at least four of the eight sampling points. Benzo[a]pyrene and chrysene were found at concentrations up to 80% above the limit set by Brazilian and European environmental legislation (0.05 µg·L⁻¹). The isomer ratios of the compounds indicated that crude oil and combustion processes were the main sources of the polycyclic aromatic hydrocarbons.

Keywords

Monitoring, Polycyclic Aromatic Hydrocarbons, Water Quality

1. Introduction

Biogenic and anthropogenic polycyclic aromatic hydrocarbons (PAHs), mainly derived from fossil fuel combustion, incineration, production of coke and asphalt, oil refining, aluminium manufacture, and burning of agricultural and forest biomass fuels, can reach water bodies and contaminate rivers due to storm water runoff and dis-

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charges of domestic sewage and industrial effluents. In Brazil, which possesses 12% of the global supply of fresh water, the contamination of surface waters is of concern in many regions, including Minas Gerais State, where there is extensive agricultural and mining activity and PAHs are by-products of pyrolysis processes. Sixteen PAHs are listed as priority pollutants for monitoring by the United States Environmental Protection Agency (US EPA) and seven of them are recognized as being carcinogenic to animals and to humans by the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC). According to Brazilian environmental legislation [1], water intended for human consumption should not contain concentrations higher than $0.05 \mu\text{g}\cdot\text{L}^{-1}$ of pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene. European Union legislation is even more rigorous and the sum of annual average concentrations should not exceed $0.03 \mu\text{g}\cdot\text{L}^{-1}$ for the isomers benzo[b]fluoranthene and benzo[k]fluoranthene, and $0.002 \mu\text{g}\cdot\text{L}^{-1}$ for the isomers benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene [2].

The determination of PAHs at such low concentrations requires highly sensitive analytical methods with analyte concentration steps such as solid-phase extraction (SPE) and analysis by chromatographic techniques such as HPLC/FL (fluorescence), HPLC/UV-Vis with or without diode arrays, and GC-MS [3]-[6].

The objective of this study was to evaluate the presence of 16 PAHs listed in the US EPA priority pollutant list in water samples collected in 2008 at eight sampling sites along 10.5 km of the Piracicaba River and the Doce River during two periods, summer and winter of 2008. The PAHs were extracted by SPE and analyzed by high-performance liquid chromatographic with diode-array detector (HPLC/DAD). The concentration ratios between 3, 4 and 5-ring PAH were used to identify the possible sources of the PAHs.

2. Material and Methods

2.1. Chemicals

A stock standard solution containing the sixteen PAHs (naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP)), purchased from Supelco (Kit 610-N), was prepared in HPLC grade acetonitrile with individual concentrations of $200 \text{ mg}\cdot\text{L}^{-1}$. The internal standard (IS) was 1,1'-binaphthyl (BNP, 99%), purchased from Aldrich. All solvents used were purchased from JT Baker. The ultra-pure water was obtained from a LAB-UPW system provided by TKA.

2.2. Sampling of Surface Water

Briefly, water samples (1 L) were collected in triplicate in January 2008, at about 30 cm from the surface at four locations along the Piracicaba River and four locations along the Doce River (Figure 1), in the municipality of Ipatinga (19.46°S , 42.53°W) by using amber glass bottles that had been cleaned with nitric acid solution (2.5%, v/v). The sampling was repeated in June 2008.

The width and depth of the rivers at the sampling sites were 50 m and 0.8 m, respectively, for the Doce River, and 40 m and 0.5 m, respectively, for the Piracicaba River. The mean water temperature was 20°C and the water samples presented high contents of particulate matter in summer. After sampling, the samples were maintained below 4°C and were immediately transported to the laboratory for analysis.

2.3. PAHs Extraction and Analysis

Before analysis, the samples were filtered using cellulose filter (Quanty, $8.0 \mu\text{m}$ pore size, 90 mm diameter) and glass fiber filter (Prefilter, $0.45 \mu\text{m}$ pore size, 47 mm diameter). The filtrates (800 mL) were passed through 3 mL Strata C18-E cartridges (Phenomenex) containing 200 mg of C18 adsorbent, previously conditioned by passing 3 mL of dichloromethane, methanol and deionized water at a flow rate of $5 \text{ mL}\cdot\text{min}^{-1}$. Clean ambient air was then passed through the cartridge for 20 min, and the PAHs were eluted with 3 mL of dichloromethane. An aliquot of $50 \mu\text{L}$ of IS solution ($1000 \mu\text{g}\cdot\text{L}^{-1}$ BNP in acetonitrile) was added to the extracts, the solvent was evaporated to dryness with nitrogen gas, and the extract was resuspended in $500 \mu\text{L}$ of acetonitrile.

Aliquots ($20 \mu\text{L}$) of the extract were injected, in triplicate, into a liquid chromatography system (Model 20A, Shimadzu) equipped with an automatic injection module (Model SIL-20AC) and a UV-Vis-DAD detector (Model SPM-M20A). The column (Lichrospher PAH, C18, $250 \text{ mm} \times 3 \text{ mm}$, $5 \mu\text{m}$, Agilent) was maintained at

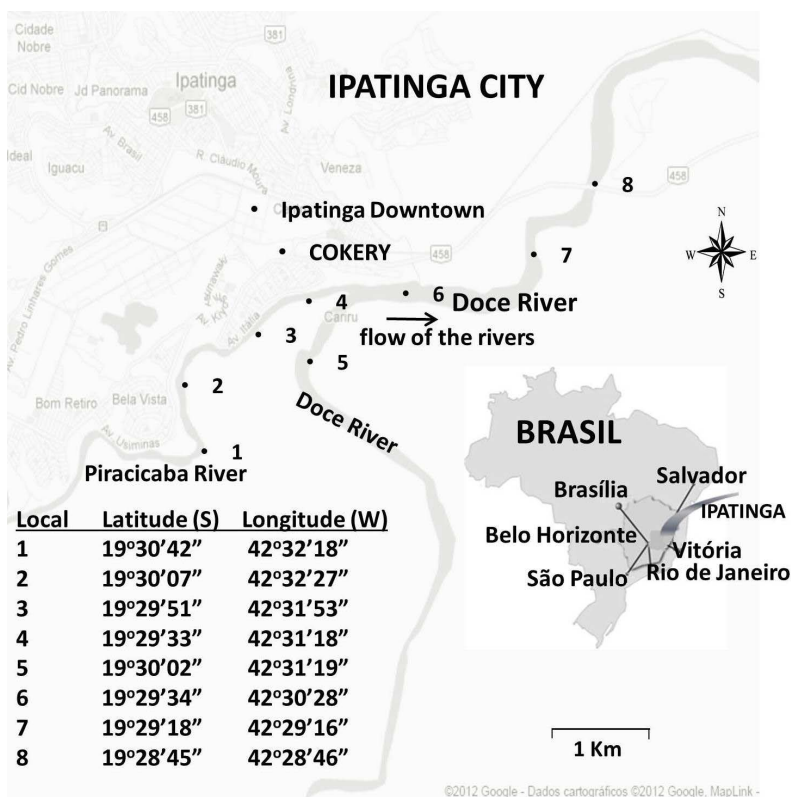


Figure 1. Surface water sampling sites for analysis of PAHs.

40°C. The mobile phase was acetonitrile/water, with an initial concentration of 60:40 for 5 min, followed by a change to 85:15 over 10 min, then to 95:05 over 10 min, with a hold for 9 min, then to 60:40 over 4 min, with a hold for 2 min. The mobile phase flow rate was 0.6 mL·min⁻¹. The chromatograms were obtained using the maximum absorbance wavelength of each PAH: Nap (254 nm), Acy (220 nm), Ace and Flu (226 nm), Phe (250 nm), Ant (250 nm), Flt (235 nm), Pyr (240 nm), BaA (285 nm), Chr (266 nm), BbF (254 nm), BkF (254 nm), BaP (295 nm), DahA (295 nm), BghiP (295 nm), and IcdP (249 nm).

2.4. Method Validation

The linearity of the method was evaluated using the analytical curves obtained by analyzing standard solutions of PAHs in acetonitrile at concentrations ranging from 5 to 400 µg·L⁻¹.

For each PAH, the limit of detection (LOD) was considered as the sample concentration corresponding to three times the standard deviation of the areas obtained in seven injections of the solution with the lowest concentration used for the calibration curve. The estimated limit of quantification (LOQ) was considered to be three times the LOD.

The accuracy was determined from the recovery of the PAHs added to samples of river water, using three PAH concentration levels (6.0, 24.0, and 62.0 ng·L⁻¹) and seven additions for each level. The precision was calculated using the coefficient of variation obtained from the standard deviations of the mean concentrations of the seven spiked samples at each concentration level.

3. Results and Discussion

3.1. Chromatographic Analysis

A standard solution containing 100 µg·L⁻¹ of the sixteen PAHs was injected under different chromatographic conditions in order to optimize the separation of the PAHs. The compounds were identified by comparison of the retention times with those of PAH standards, by spiking with individual PAH standards, and by comparison

of the UV-Vis molecular absorption spectra.

It was not possible to resolve Flu and Ace using any of the chromatographic conditions evaluated. The results for samples with measurable peaks at the retention times of these compounds were therefore presented as the sum of the individual compounds. Under the best chromatographic conditions, the PAHs were completely eluted from the column in less than 35 min (**Figure 2**).

3.2. Method Validation

The pre-concentration factor (the ratio of the sample volume (800 mL) and the extract volume (500 μ L)) was 1600. For all the PAHs studied, the determination coefficients of the calibration curves were higher than 0.99. The LOD and LOQ values (**Table 1**) were lower than those obtained in other studies using UV-Vis detection, and were similar to those obtained using fluorescence detection [7]-[9].

An advantage of UV-Vis detection is that it can be used for a wide range of analytes, while only fluorescent analytes can be determined using a fluorescence detector. The UV-Vis detector is also less expensive than the fluorescence detector and is more frequently available in analytical laboratories.

The accuracy of the method was evaluated based on recovery of the PAHs from spiked samples. The precision was based on the coefficient of variation (CV) of the means of the measured PAH concentrations, following the recommendations of the US EPA [10].

A sample containing low concentrations of PAHs was spiked with PAH standards at three concentration levels (6.0, 24.0, and 62.0 $\text{ng}\cdot\text{L}^{-1}$). Seven replicates of the samples (spiked or without spiking) were subjected to the same extraction process, and a total of 28 extracts were injected into the HPLC system (in triplicate). For all PAHs, the CV values were less than 10% at the three levels of enrichment, with the exception of Nap and BaA spiked with 24.0 $\text{ng}\cdot\text{L}^{-1}$ (**Table 2**). These values are below the 20% recommended by the US EPA for this type of matrix [10]. The recovery of most PAHs was between 70% and 130%, as recommended by the US EPA [10]. Only Acy showed recovery greater than 130%, while BbF was the only PAH with more than four rings that showed recovery greater than 70% at all levels of enrichment. A low recovery of higher molecular weight PAHs from surface waters is expected, because they tend to adhere strongly to colloidal and particulate matter present in the medium, which reduces the percentage of analyte extracted [11]. Similar results have been obtained in other studies [12].

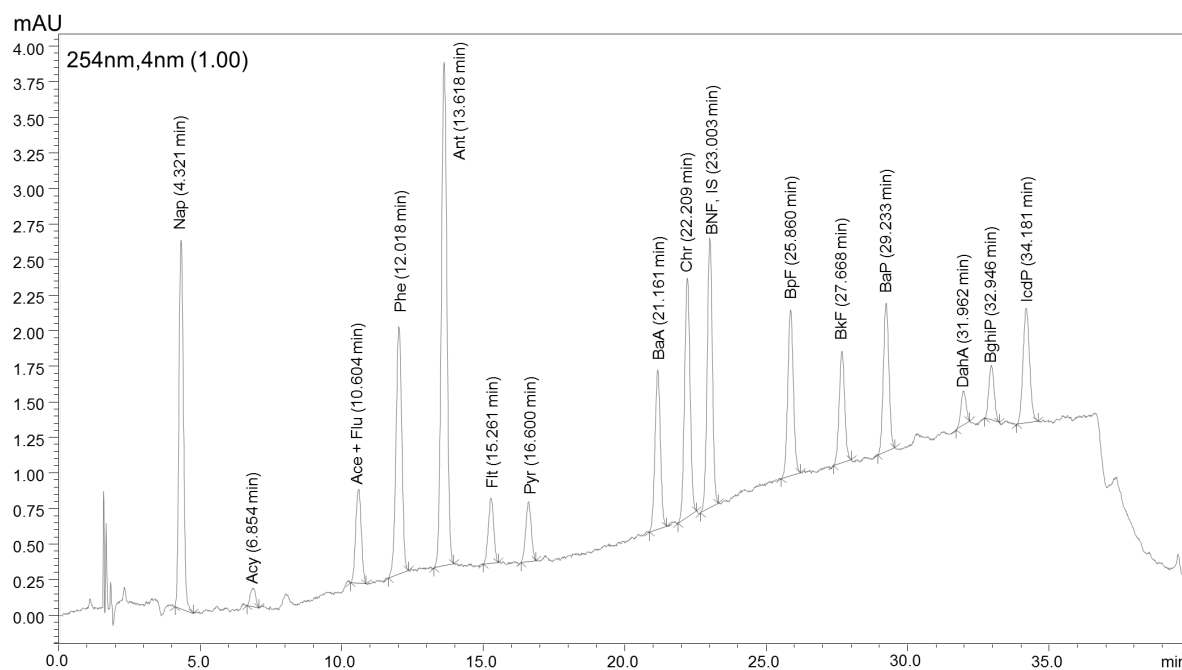


Figure 2. Chromatogram of the 40 $\mu\text{g}\cdot\text{L}^{-1}$ mixed PAHs standard in acetonitrile, using the optimum chromatographic conditions and detection at 254 nm.

Table 1. Parameters of the PAH analytical curves: slopes, intercepts, coefficients of determination (r^2), and limits of detection (LOD) and quantification (LOQ)*.

PAH	Slope	Intercept	r^2	LOD (ng·L ⁻¹)	LOQ (ng·L ⁻¹)
Nap	0.0051	0.0625	0.9934	0.7	2.1
Acy	0.0522	0.0244	0.9968	0.1	0.4
Ace + Flu	0.0488	0.1020	0.9971	0.3	0.9
Phe	0.0090	0.0132	0.9979	0.3	0.8
Ant	0.0211	-0.0522	0.9979	0.3	1.0
Flt	0.0150	-0.0392	0.9969	0.9	2.7
Pyr	0.0147	-0.0309	0.9978	0.6	1.9
BaA	0.0473	-0.2702	0.9912	1.0	3.2
Chr	0.0287	-0.0748	0.9969	0.6	1.8
BbF	0.0043	-0.0106	0.9975	1.0	3.1
BkF	0.0030	-0.0139	0.9967	1.2	3.5
BaP	0.0186	0.0317	0.9947	1.3	3.9
DahA	0.0503	-0.1665	0.9952	0.8	3.4
BghiP	0.0166	-0.0264	0.9969	1.2	3.7
IcdP	0.0060	0.0164	0.9976	1.3	3.9

*For surface waters, using a pre-concentration factor of 1600.

Table 2. Precision (coefficient of variation) and accuracy (recovery) values for the determination of PAHs at three levels of enrichment.

PAH	Sample without enrichment (ng·L ⁻¹)	Recovery					
		6.0 ng·L ⁻¹		24.0 ng·L ⁻¹		62.0 ng·L ⁻¹	
		Mean (%)	CV (%)	Mean (%)	CV (%)	Mean (%)	CV (%)
Nap	53.6	82	6.0	75	17.9	108	3.3
Acy	22.2	112	9.9	75	5.0	131	4.7
Ace + Flu	36.5	101	4.4	103	7.3	103	9.0
Phe	157.1	103	4.7	92	4.2	113	4.0
Ant	15.0	89	6.8	87	8.2	95	5.6
Flt	278.5	106	2.1	104	3.8	117	6.8
Pyr	159.1	109	7.9	92	7.9	93	6.7
BaA	10.5	94	9.7	86	14.6	84	7.2
Chr	28.6	105	6.3	93	9.2	106	3.9
BbF	36.5	105	5.1	95	3.8	88	5.8
BkF	9.3	97	8.7	54	8.6	49	3.3
BaP	5.3	96	9.6	73	7.7	57	6.8
DahA	ND	76	5.6	33	9.3	24	8.9
BghiP	6.2	92	8.6	62	5.1	71	9.9
IcdP	3.9	57	8.3	35	8.1	31	5.8

3.3. PAHs in Surface Waters from the Doce River and the Piracicaba River

The eight sampling sites were located within the municipality of Ipatinga, Minas Gerais, in southeastern Brazil, an area of rainforest at an altitude of 235 m above sea level, with a tropical semi-humid climate. In summer, the average relative humidity is 84%, the average maximum temperature is 29.0°C, and average precipitation is 200.5 mm (in January). In winter, the average relative humidity is 78.2%, the average minimum temperature is 11.5°C, and average precipitation is 11.4 mm (in July). The city of Ipatinga occupies an area of 165 km² and has 240,000 inhabitants. Urban development is above the national average, and all sewage is treated in the city. The main economic activity is industry, representing 54% of the local economy (the average values for Minas Gerais State and Brazil are 32% and 29%, respectively). This is because the urban area hosts one of the largest steel mills in Brazil, which is responsible for the presence of many other industries in the region. Ipatinga has 63,000 vehicles and is the sixth largest city in Minas Gerais State in terms of the number of vehicles.

The PAHs evaluated in this study were found above the LOD in water from at least four of the sampling sites (Table 3). In most samples, PAHs with five and six rings were not detected or were found below the LOQ.

Among the four-ring PAHs, Flu and Pyr were found at higher concentrations. However, of the seven PAHs regulated by Brazilian environmental legislation, only Chr (one sample) and BaP (three samples) were found at levels above the 50 ng·L⁻¹ maximum permissible concentration in surface waters intended for human contact [1].

The samples collected during the rainy season (January) showed concentrations of total PAHs (ΣPAHs) were well above the levels in the dry period (June). This difference could have been due to greater amounts of PAHs transferred to the rivers from the atmosphere and dry surfaces following rainfall.

PAHs with three rings represented more than 50% of the PAHs in all samples, with the exception of the sample collected at Site 2 in January. These three-ring PAHs (Ace, Flu, Phe, and Ant), together with Nap, represent the most volatile compounds of this class of substances. The presence of Nap in environmental samples is related to vehicular and industrial emissions from the combustion of fuels derived from oil. Here, the Nap concentrations were well below the levels found elsewhere; concentrations as high as 9100 ng·L⁻¹ were reported by

Table 3. Concentrations of PAHs (ng·L⁻¹) found in samples collected from the Piracicaba River and the Doce River in January and June 2008.

Sites	1	2	3	4	5	6	7	8	3	4	5	6	7	
PAHs	January 2008 (rainy season)							June 2008 (dry period)					Mean	
Nap	2.1	4.2	<LOQ	6.5	22.9	<LOQ	7.2	8.4	18.8	73.4	67.0	26.0	28.7	24.1
Acy	31.7	25.9	135.1	69.6	58.5	391.3	126.1	59.2	53.3	62.8	26.7	60.8	63.8	89.6
Ace + Flu	6.6	4.3	11.3	7.5	8.3	12.5	14.2	15.7	10.3	16.4	8.3	3.6	13.4	10.2
Phe	331.3	136.7	873.9	610.2	631.2	353.4	402.0	473.4	71.4	43.5	63.4	36.9	27.8	311.9
Ant	10.4	8.6	16.8	16.1	18.8	11.3	12.7	20.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.4
Flt	87.8	81.3	180.9	99.4	129.6	157.2	131.7	130.4	15.3	16.5	12.4	10.0	10.8	81.8
Pyr	76.3	76.1	147.7	93.4	119.2	197.8	209.6	174.6	10.1	19.8	9.7	9.5	11.1	88.8
BaA	5.7	3.4	4.7	4.3	4.3	4.0	4.8	9.5	<LOD	<LOD	<LOD	<LOD	<LOD	5.1
Chr	19.4	13.2	36.9	16.0	25.5	3.8	21.3	71.1	5.1	5.7	4.5	4.4	4.7	17.8
BbF	ND*	4.9	4.8	7.2	<LOD	<LOD	<LOD	<LOD	3.8	4.1	3.4	5.0	3.5	4.6
BkF	12.8	10.4	12.2	6.7	16.0	18.1	27.3	15.5	<LOD	<LOD	3.6	<LOD	<LOD	13.6
BaP	10.9	11.9	54.5	40.9	87.3	90.9	15.4	46.2	<LOD	<LOQ	<LOD	<LOD	<LOQ	44.7
DahA	<LOD**	<LOD	<LOD	<LOD	8.1	10.6	9.9	8.3	<LOD	<LOD	<LOD	<LOD	<LOD	9.2
BghiP	<LOQ***	<LOQ	<LOD	<LOD	29.1	78.6	83.3	23.4	<LOD	<LOD	<LOD	<LOD	<LOD	53.6
IcdP	<LOQ	<LOQ	<LOD	<LOD	17.2	23.9	28.4	17.1	<LOD	<LOD	<LOD	<LOD	<LOD	21.7
ΣPAHs	595.1	380.7	1478.9	977.8	1175.9	1353.3	1093.9	1073.4	188.2	242.2	199.1	156.2	163.7	677.5

*not determined; **below the limit of detection; ***below the limit of quantification.

Doong and Lin [13], who evaluated 48 water samples collected at 12 sites along the Gao-Ping River. In the present case, the low Nap concentrations were probably related to the large number of cars fitted with catalytic converters in the municipality. Acy, Phe, Flt, and Pyr were found at higher concentrations, and the average concentration of Phe was more than three times greater than the concentrations of the other compounds. Emissions from diesel combustion, coal stoves, vehicle exhaust, and urban dusts are the likely sources of these PAHs [14].

Similar results have been reported by other authors who evaluated PAHs in rivers with similar characteristics to the Doce and Piracicaba Rivers [15] [16]. However, the concentrations measured here were much lower than found previously. Ardag *et al.* [6] described high concentrations of PAHs in water samples collected at eight sites along the Menderes River in a highly industrialized region of Turkey (Σ PAHs between $1800 \text{ ng}\cdot\text{L}^{-1}$ and $24,900 \text{ ng}\cdot\text{L}^{-1}$). The highest concentration of BbF ($6600 \text{ ng}\cdot\text{L}^{-1}$) was almost one thousand times greater than the highest concentration of BbF found in the present study. These results show that the impact of PAHs in the Menderes River in Turkey is much higher than in the Doce and Piracicaba Rivers in Brazil.

In another Brazilian study, Brum & Netto [17] evaluated the same PAHs in surface waters of the Tripuí River, near a large aluminium factory located in the urban area of Ouro Preto city. The concentrations of PAHs were higher than those found here, with a maximum Σ PAHs value of $6500 \text{ ng}\cdot\text{L}^{-1}$ and the highest individual PAH concentration for Flu ($2960 \text{ ng}\cdot\text{L}^{-1}$).

It is difficult to accurately identify the sources of PAHs found in the samples from the Piracicaba and Doce Rivers. In general, higher molecular weight PAHs originate from incomplete pyrolysis at high temperatures, such as during the burning of coal for energy production or the manufacturing process of coke, while the lower molecular weight PAHs originate from oil or the products of its refining. Therefore, PAH isomer ratios can be used to assess the likely emission sources [14]. The ratios of the isomers with three rings are used for sources related to oil, while ratios between the 4 and 6 ring isomers are used for pyrolytic sources. Some of the ratios used are: $[\text{Ant}/(\text{Ant} + \text{Phe})]$, $[\text{Flt}/(\text{Flt} + \text{Pyr})]$, $[\text{BaA}/(\text{BaA} + \text{Chr})]$, and $[\text{IcdP}/(\text{BghiP} + \text{IcdP})]$ [18]. Of these four isomer ratios, the ratio of PAHs with 6 rings was not used, because these PAHs were not quantified in four of the 13 samples. The ratios $[\text{Ant}/(\text{Ant} + \text{Phe})]$ and $[\text{BaA}/(\text{BaA} + \text{Chr})]$ could only be used with the results of the first campaign because Ant and BaA were not quantified in any sample collected during the second campaign. For the first campaign, the values of $[\text{Ant}/(\text{Ant} + \text{Phe})]$ were below 0.1, indicating that petroleum-derived compounds were more important, compared to those originating from combustion processes [15]. However, the ratios of 4-ring PAH isomers indicated that combustion processes also contributed to the origin of these PAHs. For half of the sites evaluated, the values obtained for $[\text{BaA}/(\text{BaA} + \text{Chr})]$ were between 0.20 and 0.35, and at one site, the value was above 0.35. This indicates that in addition to crude oil compounds, combustion was also an important source of the PAHs [15]. Moreover, in many samples the concentration of Flt was slightly higher than that of Pyr, and the ratio $[\text{Flt}/(\text{Pyr} + \text{Flt})]$ was greater than 0.5, indicating that pyrolytic combustion may also have been a source of these PAHs [15]. For samples collected at Sites 7 and 8 during the rainy season, all the isomer ratios used in this study indicated that the PAHs mainly originated from petroleum products. However, for the samples collected at Site 7 during the dry period, the $[\text{Flt}/(\text{Flt} + \text{Pyr})]$ values were lower than 0.5, suggesting that combustion processes were also important in this case. These sites were located downstream of the discharge of a small river (the Ipanema River) into the Doce River, and this small river could have received inputs of runoff water contaminated with oil products, since it flowed through the urban area. During the dry period, this contribution was less important due to lack of rainfall, so that the contribution from deposition of air-borne particulate matter, rich in various products of combustion, was more important.

4. Conclusions

The method used in this study provided satisfactory figures of merit for the determination of PAHs in surface water samples from urban areas impacted by heavy industry and traffic.

Although the concentrations of PAHs found in water samples from the Piracicaba River and the Doce River in the municipality of Ipatinga were lower than those found in similar studies in other regions, it was possible to infer the likely sources of the PAHs.

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