



## Characterization of polycyclic aromatic hydrocarbon levels in the vicinity of a petrochemical complex located in a densely populated area of the Rio de Janeiro, Brazil

Rafael Lopes Oliveira, Luciana Varandas, Graciela Arbilla

Instituto de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Predio A, Sala 408, Cidade Universitária, 21949–900, Rio de Janeiro–RJ, Brazil

### ABSTRACT

The Petrochemical Complex of Duque de Caxias, Rio de Janeiro, is situated on a coastal strip between Guanabara Bay and a mountainous region covered with tropical forest. The complex comprises a refinery, a thermal power plant and several petrochemical industries. Higher rates of particulate-matter emissions are found in the region, mainly due to diesel emissions and the industrial activities of this area. In 2009 and 2010, samples were collected in three sites, and the 16 polycyclic aromatic hydrocarbons (PAHs) that are designated as priority pollutants by the US Environmental Protection Agency were determined. The sites are located in the vicinity of the Petrochemical Complex, one of them is on a roadside and the others are urban areas around the industrial complex. Multivariate analyses and diagnostic ratios show that the three studied areas were different, and the emissions seemed to be due to both gasoline and diesel vehicles. The carcinogenic PAHs represented the main fraction of the total PAHs determined in the particulate matter, and because the region is densely populated, these values may represent a health concern. The results indicate that regarding PAHs, the principal impact of the petrochemical complex is the high increase in the traffic of diesel vehicles and related tailpipe emissions.

**Keywords:** Polycyclic aromatic hydrocarbons, particulate matter, petrochemical complex, vehicle emissions



**Corresponding Author:**

**Graciela Arbilla**

☎ : +55-21-2562-7755

☎ : +55-21-2562-7265

✉ : gracielaia@gmail.com

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and may represent a health hazard for humans. Sources related to energy production are the most important ones releasing PAHs. PAHs can be classified as either pyrogenic (mainly from the incomplete combustion of organic materials, such as coal, oil, vegetation or fossil fuels) or petrogenic inputs (Vasconcellos et al., 2003; Machado et al., 2009; Maioli et al., 2010). In areas under the influence of urban and industrial activities, the major contributors to anthropogenic emissions are vehicular sources, mainly due to the combustion of gasoline and diesel, and emissions related to industrial processes.

In Brazil, most of the studies on PAHs have been conducted in urban centers, and many reports have been published in the last few decades. Lopes and de Andrade (1996) reviewed the sources, reactivity and analytical methods used to determine PAH levels and the main results obtained up to that date. The PAH concentrations in total suspended particles (TSP), inhalable particles ( $PM_{10}$ ) and, to a lesser extent,  $PM_{2.5}$  were reported for the cities of Sao Paulo (De Martinis et al., 2002; Vasconcellos et al., 2003; Bourotte et al., 2005; Vasconcellos et al., 2010; Vasconcellos et al., 2011), Rio de Janeiro (Azevedo et al., 1999; Fernandes et al., 2002; Oliveira et al., 2002; Machado et al., 2009), Porto Alegre (Dallarosa et al., 2005; Dallarosa et al., 2008), Campo Grande (Re-Poppi and Santiago-Silva, 2005; Stroher et al., 2007), Niteroi (Pereira Netto et al., 2001; Pereira Netto et al., 2002a; Pereira Netto et al., 2002b;

Pereira Netto et al., 2002c; Pereira Netto et al., 2006; Lima and Pereira Netto, 2009), Campos dos Goytacases (dos Santos et al., 2002; Maioli et al., 2009), and Salvador (Pereira et al., 2002; da Rocha et al., 2009).

The impact of industrial and biomass burning has also been studied for a few Brazilian regions. Results were obtained in different matrices for areas impacted by sugarcane–monoculture practices (Maioli et al., 2009; Maioli et al., 2010; Maioli et al., 2011). In 2007 (Vasconcellos et al., 2010), the levels of PAHs as well as other organic compounds and soluble ions were determined and compared in three sites with different characteristics in Sao Paulo State: an urban area with intense traffic of heavy and light vehicles, a clean area in the Mata Atlantica (Atlantic Forest) with primarily biogenic hydrocarbon emissions and a region characterized by intense sugar–cane burning during the dry season. The PAH abundances were higher in the urban area, but tracers of biomass burning were found in the site influenced by biomass burning and in the city, most likely due to long–distance air transport.

In 2008, measurements were taken of the 16 PAHs designated as priority pollutants by the US Environmental Protection Agency in the Cubatao industrial complex in southeast Brazil (Allen et al., 2008). Using the characteristic concentration ratios for emission sources, the authors concluded that tailpipe emissions from diesel vehicles were the main source of the compounds. Recently, PAHs were determined in fine ( $PM_{2.5}$ ) and coarse particles ( $PM_{2.5-10}$ ) in an urban and industrial area in the Metropolitan Area of Porto

Alegre (Teixeira et al., 2012). Based on the diagnostic ratios and principal component analysis, the authors concluded that the major contributors to the PAH levels were vehicular sources (diesel and gasoline), especially for the  $PM_{2.5}$  fraction, as well as coal and wood burning.

To our knowledge, the PAH-concentration data for the metropolitan area of Rio de Janeiro (RJMA), Brazil, are in general related to urban areas where the main contribution to air pollution is due to vehicular emissions. In the present study, the PAH concentrations in a suburban area under the impact of an intensely trafficked road and industrial activities were characterized. The data required for the study were collected from different sampling sites to allow the comparison of areas with different emission characteristics.

## 2. Experimental Method

### 2.1. Sampling site

The sampling was conducted in the suburban area of Duque de Caxias near a petrochemical complex that is strongly affected by vehicular and industrial emissions. The area is located in the Air Basin III, which belongs to the Rio de Janeiro Metropolitan Area (RJMA). Air Basin III is located in the northern region, with an area of 700 km<sup>2</sup>, and has the most severe air-pollution problems of the RJMA, mainly involving particulate matter levels. The highest rates of particulate matter emissions in Air Basin III are found in the downtown area of the city of Rio de Janeiro, mainly due to diesel emissions, and in the region of Campos Eliseos (Duque de Caxias), due to the industrial activities in this area. The most recent emission inventory for RJMA shows that approximately 58% of the particulate matter is emitted from stationary sources (INEA, 2009). According to Pires (2005), the refineries, energy plants and petrochemical industries account for 42%, 31% and 10%, respectively, of the total emissions from stationary sources. The particulate matter emission rates were estimated at 5–10 ton km<sup>-2</sup> y<sup>-1</sup> and 10–100 ton km<sup>-2</sup> y<sup>-1</sup> for the downtown area and Campos Eliseos, respectively.

The Petrochemical Complex comprises a refinery, a thermal power plant, and several petrochemical industries. The refinery, with an area of 13 km<sup>2</sup> and an installed capacity of 242 000 barrels d<sup>-1</sup>, produces gasoline, lubricants, diesel fuels, aviation kerosene, liquefied petroleum gas, bunker and the petrochemical naphtha. This refinery was inaugurated in 1961 and since then has undergone modernization processes focusing on quality and environmental protection. The thermal power plant is natural gas-fired and generates 2 025 MW d<sup>-1</sup>. The activities of the petrochemical plants comprise the development, manufacture and sale of plastics, rubber, resins, solvents, fluids and oils, specialty chemicals and intermediates.

Samples were collected at three monitoring stations located in Duque de Caxias that were implemented and are operated by ASSECAMPE (Campos Eliseos Companies Association): Federal Road Police (FRP), Cora Coralina State School (CC) and Adelina de Castro State School (AC). The FRP station (22°40' S, 43°17' W) is a roadside site, located by the Washington Luiz Highway, and is approximately 5 km from the Petrochemical Complex. The Washington Luiz Highway is the part of the BR-040 road that links the cities of Rio de Janeiro and Petropolis, and the vehicular traffic on this highway contributes approximately 3% of the particulate matter and volatile organic compounds (VOCs) emitted by mobile sources in the RJMA (Loureiro, 2005). The CC station (22°42' S, 43°18' W) is an urban area located in a neighborhood approximately 4 km from the Petrochemical Complex and 2.5 km from the Washington Luiz Highway. The AC station (22°42' S, 43°16' W) is a mixed urban-industrial area approximately 1.5 km from the Petrochemical Complex. It was not possible to perform a vehicular count, but clearly, the diesel (trucks and buses) and light-vehicle

movement is very intense in the vicinity of this monitoring station. A map of the studied area is provided in the Supporting Material (SM) (Figure S1).

Climatological evaluations of the wind patterns near the city of Rio de Janeiro show a larger frequency of south-southeast to north-northwest winds in virtually every month of the year, with an average wind speed of 8 km h<sup>-1</sup>. Data collected from the Aeronautical Meteorology Services Network website (REDEMET, 2010) during the sampling period showed a predominance of weak winds in the southeast and northwest directions. The frequencies of winds over the sampling period were plotted according to the wind directions to show the direction with the greatest frequency. The plots show that the AC and CC stations were heavily affected by the industrial emissions, mainly in the early hours of the day. Atmospheric trajectory models show that changes in wind directions occur due to the area's geographical location on a coastal plain at the base of a mountain range (Mata Atlantica), frequently, a sea breeze predominates from the south-southeast direction during the day, and air flows from the continent to the ocean at night (Godoy et al., 2009; INEA, 2009). Because the studied area is located near the coast, polluted air emitted by the vehicular and industrial facilities is carried into the continent during the daytime. The wind rose and some illustrative trajectories obtained with the NOAA HYSPLIT model are shown in the SM (Figures S2 and S3).

### 2.2. Sampling

For the particulate matter, the selection of the points and the sampling procedures took into account the minimum sampler-siting criteria, calibration and filter-handling procedures recommended by the Environmental Protection Agency (U.S. EPA, 2007). Briefly, following the EPA recommendations, the height above ground should be 2 to 7 m, the distance from the samples to obstacles should be at least twice the height of the obstacle, and the air flow around the sampler inlet should be unrestricted. In this work,  $PM_{10}$  and  $PM_{2.5}$  were collected over 24 h using high-volume samplers (Hi-vol-Energetica) that were equipped with an impactor-design size-selected inlet (Andersen, model G1200-2.5) and quartz-fiber filters (Millipore filters with an area of 20x25 cm and a thickness of 0.5 mm). The flow rate was 1.15 m<sup>3</sup> min<sup>-1</sup>. The samplers were placed at a height of 3 m. Preceding the sampling, the filters were cleaned by thermal treatment (at 800 °C) for 24 h and weighed in an analytical balance after conditioning in a desiccator at constant temperature, (24±2) °C, and relative humidity, (55±3)%, conditions. The loaded filters were similarly conditioned and weighed for gravimetric determination of the particle mass concentration. Then, the filters were wrapped in aluminum foil and kept refrigerated (-20 °C), inside sealed plastic bags, until extraction and analysis (<4 days).

Samples were collected from June 2009 to August 2010 as indicated in Table 1. The samplings were done only on weekdays without rainfall. No attempt was done to collect samples during Saturdays and Sundays because it was not the objective of this study to assess comparisons between different periods such as weekdays and weekends. Because only two  $PM_{2.5}$  samplers were available, simultaneous sampling in the three locations was not possible.

Additionally, PAHs in the gas phase were collected using XAD-2 cartridges (SKC 226-30-06, 400/200 mg) and an air pump with a flow rate of 1.0 L min<sup>-1</sup>. These samples were collected at the FRP and CC monitoring stations during the same period as the  $PM_{2.5}$  sample collection.

### 2.3. Extraction procedure and analysis

The levels of  $PM_{10}$  and  $PM_{2.5}$  were determined by gravimetry using an electronic microbalance with a 1 µg sensitivity. Organic

matter was recovered from the filters using the EPA 3550B Method (U.S. EPA, 1996a). The filters were extracted by ultrasonification in 50 mL dichloromethane (HPLC grade) for 15 min. The extraction procedure was repeated three times thereafter. Then, a further extraction by ultrasonification in 100 mL dichloromethane for 20 min was performed. The filtrate was then concentrated on a rotary evaporator followed by a stream of nitrogen gas to a reduced volume. The concentrated extracts were fractionated using a 16 cm x 1.4 cm column containing 2.5 g of pre-cleaned silica gel (24 h, at 120 °C). The column was first eluted with 10 mL of hexane, further with 10 mL of hexane:dichloromethane (Hx:DCM; 4:1; v:v) and finally with 20 mL of dichloro-methane:methanol (DCM:MeOH; 9:1; v:v). The extracts were concentrated using a rotary evaporator and transferred to an auto-sampler microvial (250 µL).

The extraction of the PAHs in the cartridges was performed by ultrasonification in 5 mL of a 4:1 solution of dichloromethane and methanol over a period of 30 min. The extract was then applied to a cleanup column, which was eluted with 5 mL of the extraction solution. The filtrate was then concentrated to a reduced volume using a rotary evaporator followed by a stream of nitrogen, transferred to vials and stored at –20 °C until analysis.

The samples were then analyzed using high-resolution gas chromatography–mass spectrometry (CG–MS) following the 8270C Method (U.S. EPA, 1996b). The operating conditions were as follows: an Agilent 6890N gas chromatograph and an Agilent 5973 mass spectrometer, with an ionization of 70 eV, a 30 m x 0.25 mm i.d. x 0.25 mm film thickness capillary column (DB–5, J&W Scientific, Folsom, CA), and a temperature program of 60 °C to 300 °C at 8 °C min<sup>–1</sup>, held at 300 °C for 40 min. Helium was used as the carrier gas (1.1 mL min<sup>–1</sup>). The injector temperature was 290 °C using the splitless injection mode. The detection and identification of each PAH was achieved using selective ion monitoring (SIM) of the most abundant ions: naphthalene (NAF)–128, 102; acenaphthylene (ACY)–152, 76; acenaphthene (ACE)–153, 76; fluorene (FLU)–166, 82; phenanthrene (PHE)–178, 152; anthracene (ANT)–178, 89; fluoranthene (FLT)–202, 101; pyrene (PYR)–202, 101; benzo[*a*]anthracene (BaA)–228, 114; chrysene (CRY)–228, 114; benzo[*b*]fluoranthene (BbF)–252, 126; benzo[*k*]fluoranthene (BkF)–252, 126; benzo[*a*]pyrene (BaP)–252, 126; indeno[1,2,3-*c,d*]pyrene (IND)–276, 138; dibenz[*a,h*]anthracene (DBA)–278, 139; and benzo[*g,h,i*]perylene (BgP)–276, 139. The quantification was carried out based on external calibration curves constructed with eight different concentration levels of a standard reference solution containing the 16 EPA priority PAHs. The calculated correlation coefficients of the linear fits were greater than 0.99. The limits of the detection and quantification were calculated using the standard deviation of the noise. The limits of detection (LOD) ranged from 0.19 (NAF) to 24.02 (PHE) pg m<sup>–3</sup> in the particulate-matter samples and from 0.06 (NAF) to 7.21 (PHE) pg m<sup>–3</sup> in the XAD–2 samples. The limits of quantification (LOQ) ranged from 0.65 (NAF) to 82.86 (PHE) pg m<sup>–3</sup> in the particulate-matter samples and from 2.15 (NAF) to 276.2 (PHE) pg m<sup>–3</sup> in the XAD–2 samples. The accuracy of the method was previously evaluated using samples spiked with reference standards and the same experimental conditions and equipment (Maioli et al., 2011). All of the samples were measured in triplicate, and a difference of less than 1% was considered to be acceptable. The PAH contents in the filter and reagent blanks were below the detection limits.

#### 2.4. Statistical analysis

The experimental data was analyzed using STATISTICA 7.0 (Statsoft). The data was analyzed using descriptive statistics before extended analyses. After removing outliers, a multivariate statistical analysis was performed that included cluster analysis

(CA) based on Euclidian distances and Ward's method and principal component analysis (PCA). The calculations (CA and PC) were achieved using the individual experimental values of each of the 16 PAHs (ng m<sup>–3</sup>) for each sample and sampling site. Diagnostic parameters were also calculated to investigate the possible origins of the PAHs.

### 3. Results and Discussion

#### 3.1. PM<sub>2.5</sub> and PM<sub>10</sub>

As shown in Table 1, considering all the samples, the PM<sub>2.5</sub> levels ranged from 10.8 to 80.3 µg m<sup>–3</sup>. The mean concentration for all of the samples was lower at the FRP station (25.5 µg m<sup>–3</sup>). A direct comparison between the experimental values should not be made because the number of samples and the sampling period were not the same. However, it was an expected result since the diesel contribution, mainly buses and trucks, is higher in the vicinity of CC and AC stations.

Because the PM<sub>10</sub> and PM<sub>2.5</sub> samples were collected simultaneously at the AC station, their levels may be compared directly. The PM<sub>2.5</sub>/PM<sub>10</sub> ratios calculated for the same sampling date were in the range of 0.22 to 0.67, with an average value of 0.46. The main contribution to particulate matter in the PM<sub>10</sub> range is probably due to re-suspension of dust and particles from natural sources (plants and ocean spray), unpaved roads, building construction, and wind erosion from open areas which are common in this area. The proximity of Guanabara Bay may lead to an important contribution of sea-spray (Godoy et al., 2009). Fine particles are probably due to combustion processes, mainly related to vehicular emissions. Marine aerosols may also contain a small fraction of fine particles. In a previous study, Godoy et al. (2009) found that the sea-spray had a contribution of 4–6% for two sampling sites located in the coastal area of Rio de Janeiro.

Table S1 (see the SM) shows a comparison of the present values with some studies published in the literature involving a similar sampling methodology. PM<sub>2.5</sub> and PM<sub>10</sub> mass concentrations are in a similar range of reported values for other urban locations with a high vehicular traffic, but they are higher than the values reported by Godoy et al. (2009) for ten urban sampling sites in the RJMA.

#### 3.2. Levels of PAHs

All of the 16 EPA-priority PAHs were determined in the samples. The medians, mean concentrations, standard derivations, minima and maxima are shown in Table 1. In all sites, the PAHs with higher relative molar mass and lower vapor pressure (those with 5–6 benzene rings, namely, BbF, BkF, BaP, IND, DBA and BgP) reached higher particle-phase concentrations, and those with 2–3 rings, such as ACY, ACE and FLU, were scarcely found in the particulate matter and presented higher concentrations in the gas-phase. This was an expected result because the literature data show that most of the volatile PAHs are preferentially present in the gas-phase (Tavares et al., 2004; Marques et al., 2009) and Rio de Janeiro has a sub-tropical climate, with intense solar radiation and elevated temperatures.

In PM<sub>2.5</sub>, the most abundant PAHs were also those with 4–6 rings. IND and BgP were the most abundant in AC and CC locations. In the roadside sampling point (FRP), CRY levels were higher, indicating that pyrogenic contributions are predominant. A similar result was previously obtained in the Lapa bus station in Salvador (Brazil) where CRY accounted for 20% of PAHs in PM<sub>10</sub> (da Rocha et al., 2009). The NAF, ACY and ACE concentrations were under the detection limit in all samples.



Table 1. Summary statistics of concentrations of PAH determined in  $PM_{2.5}$ ,  $PM_{10}$  and gaseous phase (GF) samples.

Sampling site	PAH (ngm <sup>-3</sup> )										PM(μg m <sup>-3</sup> )							
	NAF	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CRY	BbF	BkF	BaP	IND	DBA	BgP	PM <sub>2.5</sub>	PM <sub>10</sub>
Adelina de Castro PM <sub>2.5</sub> n=22 June 2009-December 2009	Mean	<LOD	<LOD	0.006	0.085	0.014	0.142	0.141	0.173	0.214	0.386	0.379	0.473	0.817	0.082	0.505	37.0	
	Median	<LOD	<LOD	0.0038	0.0335	0.0056	0.0341	0.0647	0.0283	0.0262	0.0243	0.0143	0.0865	0.0833	0.0112	0.0804	30.8	
	SD	<LOD	<LOD	0.006	0.090	0.016	0.258	0.163	0.401	0.437	0.904	0.951	1.018	2.153	0.203	1.158	18.4	
	Max	<LOD	<LOD	0.019	0.279	0.049	1.147	0.530	1.804	1.780	3.830	3.712	4.535	8.356	0.884	4.347	75.0	
	Min	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	11.4	
Adelina de Castro PM <sub>10</sub> n=22 June 2009-December 2009	Mean	<LOD	<LOD	0.023	0.137	0.023	0.197	0.228	0.454	0.579	0.869	0.745	1.234	2.135	0.159	1.170	80.7	
	Median	<LOD	<LOD	0.0103	0.1556	0.0178	0.1888	0.2056	0.2003	0.3160	0.3600	0.1946	0.4129	0.4265	0.0201	0.3521	81.0	
	SD	<LOD	<LOD	0.065	0.094	0.019	0.144	0.168	0.620	0.740	1.047	0.970	1.758	3.323	0.303	1.703	32.6	
	Max	<LOD	<LOD	0.315	0.374	0.057	0.512	0.648	2.269	2.536	3.491	3.298	5.149	10.562	1.069	5.955	136.0	
	Min	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	27.2	
Cora Coralina PM <sub>2.5</sub> n=34 June 2009-March 2010	Mean	<LOD	<LOD	0.032	0.049	0.006	0.042	0.059	0.027	0.038	0.047	0.066	0.052	0.126	0.010	0.076	40.2	
	Median	<LOD	<LOD	0.0075	0.0399	0.0056	0.0348	0.0516	0.0119	0.0125	0.0190	0.0127	0.0152	0.0169	0.0087	0.0232	25.9	
	SD	<LOD	<LOD	0.080	0.040	0.004	0.036	0.055	0.033	0.051	0.093	0.161	0.083	0.384	0.013	0.170	17.3	
	Max	<LOD	<LOD	0.402	0.169	0.015	0.139	0.226	0.126	0.207	0.514	0.806	0.371	2.062	0.069	0.900	80.3	
	Min	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10.8	
Federal Road Police PM <sub>2.5</sub> n=14 March 2010-July 2010	Mean	<LOD	<LOD	0.003	0.041	0.005	0.060	0.098	0.074	0.725	0.246	0.183	0.586	0.540	0.017	0.264	25.5	
	Median	<LOD	<LOD	0.0017	0.0251	0.0051	0.0474	0.0990	0.0490	0.1036	0.1520	0.0989	0.3253	0.2733	0.0034	0.1060	18.3	
	SD	<LOD	<LOD	0.003	0.041	0.004	0.060	0.076	0.077	2.189	0.275	0.176	0.581	0.611	0.029	0.279	6.2	
	Max	<LOD	<LOD	0.011	0.137	0.013	0.200	0.246	0.246	8.000	0.947	0.486	1.644	1.928	0.086	0.773	39.1	
	Min	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.002	0.001	0.005	14.0	
Federal Road Police Gas phase n=12 March 2010-July 2010	Mean	1.176	4.896	4.617	3.077	1.949	1.337	6.464	3.839	1.060	0.452	<LOD	<LOD	<LOD	<LOD	<LOD		
	Median	1.176	4.896	4.6170	3.0770	1.9490	1.3370	6.4640	3.8390	1.0600	0.4520	<LOD	<LOD	<LOD	<LOD	<LOD		
	SD	2.050	1.528	0.860	1.238	0.719	0.454	3.071	2.344	0.465	0.342	<LOD	<LOD	<LOD	<LOD	<LOD		
	Max	7.414	6.614	7.095	4.478	3.223	2.130	13.986	9.146	2.005	1.229	<LOD	<LOD	<LOD	<LOD	<LOD		
	Min	0.2679	2.966	3.843	0.768	1.159	0.274	1.823	0.646	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		
Cora Coralina Gas phase n=26 June 2009-March 2010	Mean	1.067	4.785	4.785	3.002	5.213	0.680	5.894	3.254	2.212	1.714	<LOD	<LOD	<LOD	<LOD	<LOD		
	Median	0.4043	4.8961	4.5395	3.1312	17.1176	1.3545	6.1842	3.7720	0.9612	0.3959	<LOD	<LOD	<LOD	<LOD	<LOD		
	SD	1.411	5.344	2.861	6.304	3.822	0.872	8.121	5.202	4.670	3.938	<LOD	<LOD	<LOD	<LOD	<LOD		
	Max	5.518	30.412	18.551	32.536	14.968	4.132	37.338	20.062	23.603	16.200	<LOD	<LOD	<LOD	<LOD	<LOD		
	Min	0.274	2.947	3.808	0.561	0.217	0.136	0.764	<LOD	0.674	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		

n: number of samples

&lt;LOD: under detection limit

The results are of the same order of magnitude as those determined in other locations of the State of Rio de Janeiro in different matrices (TSP, PM<sub>10</sub> and/or PM<sub>2.5</sub>) (Miguel and De Andrade, 1989; Azevedo et al., 1999; Lima and Pereira Netto, 2009; Marques et al., 2009). Tables S2 and S3 (see the SM) show a comparison of the present values with some studies recently published in the literature for urban and industrial areas. Individual values and the total PAHs are in the same order of magnitude with other studies undertaken in other countries except for those reported for Beijing (China) for urban and industrial areas which are more than ten times higher (Wang et al., 2008) than those measured in the present study.

The carcinogenic PAHs (BaA, BbF, BkF, BaP, DBA, and IND) represented an important fraction of the total PAHs determined in the particulate matter. For PM<sub>2.5</sub> samples contributions were 44% (CC), 50% (AC), and 63% (FRP). For PM<sub>10</sub> samples collected at AC the contribution of carcinogenic PAHs was 71% which may suggest serious health concerns.

The value for AC PM<sub>10</sub> was similar to those determined in other Brazilian industrial areas. In Aratu Harbor in Todos os Santos Bay, approximately 50 km away from Salvador (Brazil), which possesses approximately 60% of the total port operations in the Salvador region by supporting the transportation of manufactured products from both the Industrial Center of Aratu and the Petrochemical Complex of Camacari, the contribution of carcinogenic species in PM<sub>10</sub> was relatively high (70%) (da Rocha et al., 2009). In Cubatao, Sao Paulo State, in the southeastern region of Brazil, which is the largest industrial center in this state, the contribution was 59% (Allen et al., 2008).

Estimated risk assessment for each polycyclic aromatic hydrocarbons in relation to benzo[a]pyrene in the sampling sites are presented in Table S4 (see the SM). For PM<sub>10</sub>, values are between  $1.2 \times 10^{-3}$  (benzo[a]pyrene) and  $2.3 \times 10^{-8}$  (fluorene). For PM<sub>2.5</sub>, values are in the range of  $5.9 \times 10^{-4}$  (benzo[a]pyrene) to  $3.0 \times 10^{-9}$  (fluorene). No specific guideline values have been recommended for PAHs (WHO, 2000), but the calculated values (see the SM, Table S4) seems rather high and the population of these areas may be subjected to health risks. A similar result was previously obtained for other areas in Rio de Janeiro (Rainho et al., 2013).

In the gas-phase, the total PAH values were similar for both of the locations, and the 4-ring compounds represented about 40% of the total PAH content. For the two sites, gas-phase and PM<sub>2.5</sub> samples were collected during the same period. The total concentration (in ng m<sup>-3</sup>) of 2-, 3- and 4-ring compounds was clearly higher than the total concentration of ANT, BgP, BkF, BbF, PYR and BaP, which are the major species in gasoline emissions. The high contribution (over 90%) of 3- and 4-ring compounds indicated a predominant contribution of diesel emissions in the gas-phase samples.

### 3.3. Statistical analysis

A multivariate statistical approach was applied to identify the relationships between the determined PAHs. A combination of cluster analysis and principal component analysis (PCA) was used.

As previously stated, the PM<sub>2.5</sub> and PM<sub>10</sub> samples were collected simultaneously at the AC station. The principal component analysis showed three main components, which accounted for a total of 82.4% of the data variability. Factor 1 included BbF, BkF, BaP, IND and BgP (5–6 rings), while factor 2 included PHE, ANT, FLT and PYR (3 rings). Factor 3 included FLU with a high factor loading (0.994). FLU (3-rings) may be due to diesel emissions or also to petroleum-refinement processes (Ravindra et al., 2008). Also, as it is mainly associated to the gas phase, it could also be separated in factor 3 due to its low concentration in particulate matter. A plot of factor 2 versus factor 1 (Figure S4 in the SM)

clearly suggests that the most volatile compounds were the main contributors to PM<sub>10</sub>, while the PAHs with higher molar mass and lower vapor pressure were mainly associated with the fine particulate matter. As previously noted, 3–4-ring compounds are predominant species in diesel emissions, while 5–6-ring compounds are the major species in gasoline emissions.

The results suggest that the main contributions to the fine and coarse particulate matter are different; diesel emissions mainly contributed to PM<sub>10</sub>, whereas gasoline combustion was mainly associated with the fine particulate matter. The high factor loading of FLU for factor 3 may indicate the presence of a stationary source, most likely associated with the petrochemical industries.

Then, PCA was applied to the PAHs associated with PM<sub>2.5</sub> in the three sites. The first two PC explained 71% of the variance in the original data set, and a score plot obtained from those first two PC visualizes the differences in the profile of PAHs (Figure S5 in the SM). The samples seem to be divided into two groups by PC1 (55.5%). On the left-hand side of the score plot, the samples from the AC and CC stations were predominant, whereas almost all of the samples from the FRP station were found on the right-hand side of the score plot. The data separation is not conclusive but suggests that the samples from FRP are most likely different from the samples from AC and CC.

Factor 1 was associated with BkF, IND and BgP, usually due to gasoline power-fuel emissions. Factor 2 was related to PHE, ANT, FLT and PYR, characteristic of diesel emissions (Ravindra et al., 2008). Again, factor 3 was related to FLU. The results suggest that the AC monitoring station was more impacted by the industrial activities and diesel emissions due to the transport of supplies and several bus lines. The proximity of the sampling sites to the Petrochemical Complex and the predominant wind direction (southeast to northwest, which is from the Petrochemical Complex to the continent) leads to the transport of the atmospheric air in the direction of the monitoring stations. The FRP and CC sites are mainly impacted by the vehicular traffic (diesel and gasoline).

The same analysis was applied to the samples collected using XAD-2 cartridges. The first two PC accounted for 82% of the variance in the original data set. A score plot obtained from those first two PC shows the differences in the PAH profile (see the SM, Figure S6).

The samples were divided into two groups: on the left-hand side of the score plot, the samples from the CC site predominated, whereas most of the samples from the FRP station were found on the right-hand side of the score plot. PC1 was related to ACE, ACY, FLU and ANT and FLT, and PC2 was related to BaA and CRY. The different profiles in the two sets of data suggest that the diesel contribution was more important on the Washington Luiz Highway. The cluster analysis gave similar results and is not presented here.

### 3.4. Diagnostic ratios

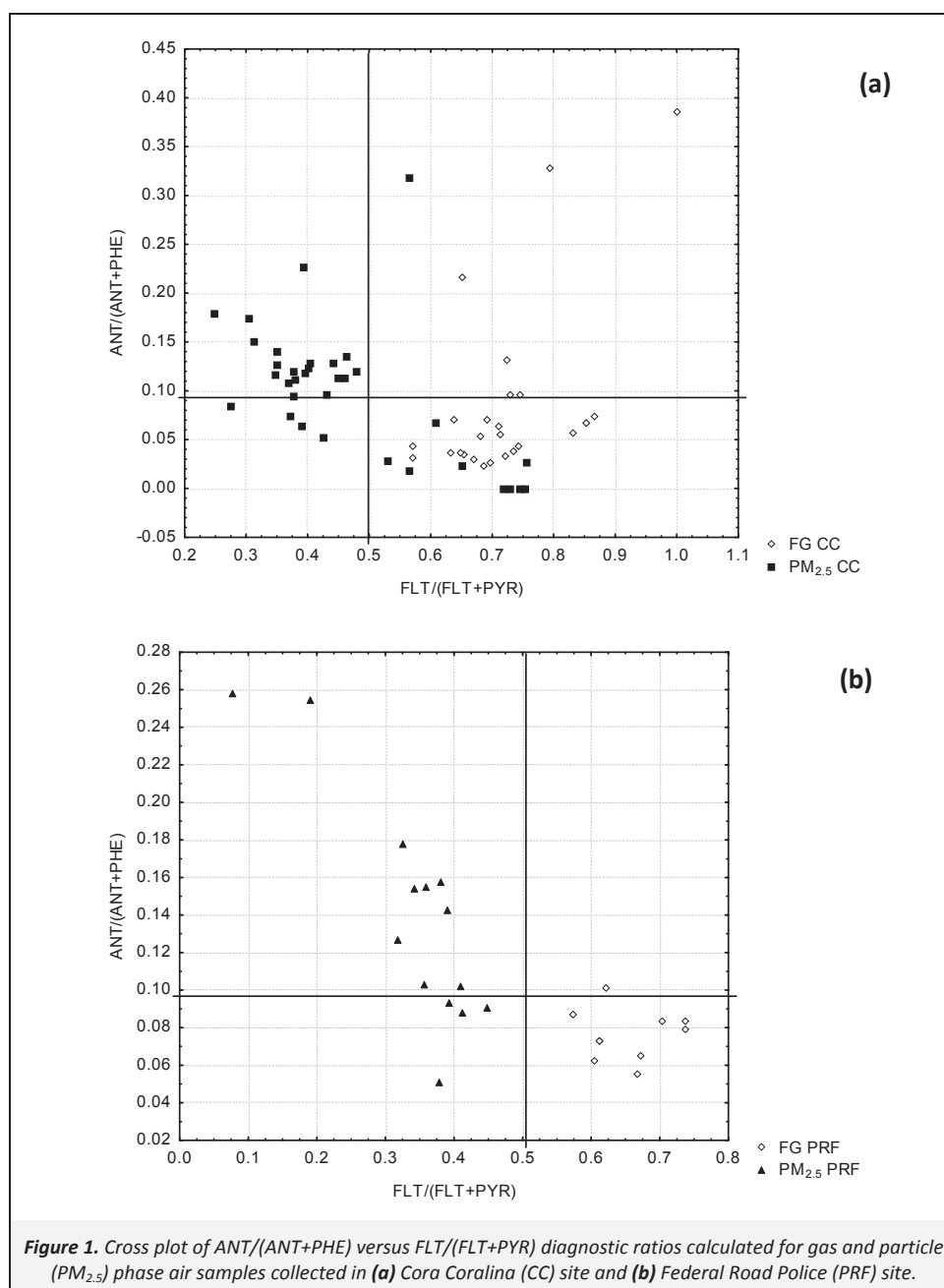
The ratios of the individual PAH species in the ambient samples and source emissions are frequently employed as diagnostic tools to identify the origin of PAHs in ambient air (Manoli et al., 2004; Ravindra et al., 2008). However, diagnostic ratios should be used with caution because a significant overlap is frequently observed between them, and they can be altered due to the reactivity and volatility of some PAH species (Manoli et al., 2004). As stated by Galarneau (2008) and by Tobiszewski and Namiesnik (2012), diagnostic ratios are not definitive and may show inter-source similarity and intra-source variability, which could lead to ambiguous conclusions. The diagnostic ratios calculated in the present study (see the SM, Table S5) are compared with those found in source samples and the literature in an attempt to identify similarities/dissimilarities between ambient-and literature-source PAH profiles.

From the comparison of our data with literature values it can be concluded that more than one source is contributing to the aerosol PAH mixture. The average BaP/BgP ratios calculated at the three sites ranged from 0.93 to 1.89 and did not provide a clear characterization of the samples. The BaA/(BaA+CRY) ratios were similar in all of the samples and indicated the possible contribution of both gasoline and diesel exhaust (Ravindra et al., 2008; da Rocha et al., 2009). The IND/(IND+BgP) ratios were compatible with diesel exhaust, and the FLU/(FLU+PYR) ratios were lower than 0.5, indicating gasoline combustion. The values are in the range of those reported by Manoli et al. (2004) for vehicle exhaust pipe. These results are in contrast with those obtained in Cubatao industrial area (Allen et al., 2008), where the FLU/(FLU+PYR) mean ratio was 0.52, indicating the contribution of diesel. On the other hand, the ratios PHE/(PHE+ANT) are close to values found for crude oil and used motor oil (Sicre et al., 1987).

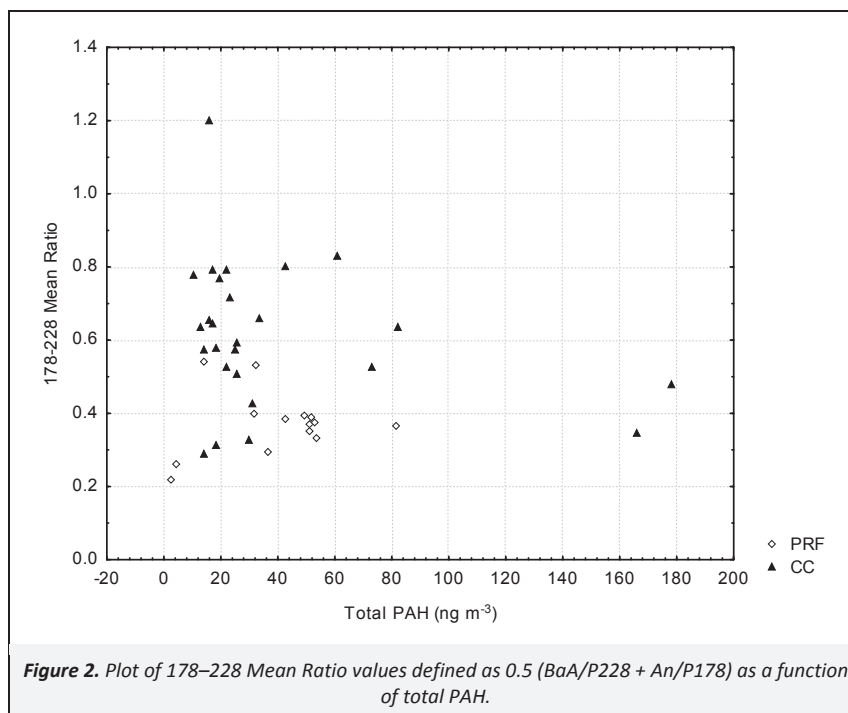
More useful information may be obtained from the plot of diagnostic ratios involving isomer compounds (Yunker et al., 2002; Rajput et al., 2013). Bi-variate plots of several diagnostic PAH ratios for PM<sub>2.5</sub>, PM<sub>10</sub> and gas-phase samples were constructed,

but none of them were useful to discriminate between petroleum and combustion sources. Additionally, these plots did not provide a clear discrimination among the sampling sites. The isomer ratios ANT/(ANT+PHE) versus FLT/(FLT+PYR) are shown in Figures 1a and 1b. For PM<sub>2.5</sub> samples ANT/(ANT+PHE) are compatible with diesel emissions and FLT/(FLT+PYR) with gasoline emissions.

Diagnostic ratios for gas-phase samples are clearly different than those calculated for PM<sub>2.5</sub> samples. As suggested by Tobiszewski and Namiesnik (2012), the total (gas+particle) concentrations of atmospheric PAHs should be used to calculate the diagnostic ratios. Following Sofowote et al. (2010), a linear combination of BaA/(BaA+CRY) and ANT/(ANT+PHE), called the 178–228 mean ratio, *versus* the total PAH for individual samples is presented in Figure 2. The total concentrations (PM<sub>2.5</sub> plus the gas phase) for CC and FRP are represented. Lower 178–228 mean ratios were observed for the FRP samples, but most of the values were higher than 0.25, suggesting combustion sources. The lower values for the FRP samples reinforce the previous conclusion that the diesel contributions on the Washington Luiz Highway were significant.



**Figure 1.** Cross plot of  $ANT/(ANT+PHE)$  versus  $FLT/(FLT+PYR)$  diagnostic ratios calculated for gas and particle (PM<sub>2.5</sub>) phase air samples collected in (a) Cora Coralina (CC) site and (b) Federal Road Police (PRF) site.



#### 4. Conclusions

The levels of PAHs in the vicinity of the Petrochemical Complex seem to be due to vehicular emissions from both gasoline and diesel vehicles. Multivariate analyses and diagnostic ratios show that the three studied areas are different, but the differences seem to be related to the composition of the vehicular fleet. Industrial emissions related to the petrochemical facilities were not identified in the urban area, and further studies are necessary to characterize the emissions due to the petroleum refinery or petrochemical industries. Emissions of PAHs from industrial sources within the Petrochemical complex seem to be small, compared to road transport emissions (including transport sources within the industrial park).

Diagnostic ratios considering both the particulate and gas-phase PAHs were different. The determination of the total PAH concentration (gas+particle) seems to be extremely important to obtain conclusive diagnostic ratios, mainly in this tropical area where factors such as air temperature and photodegradation would modify the air–particle distribution.

Carcinogenic PAHs represent the main fraction of the total PAHs determined in the particulate matter. Because the present area is highly urbanized, these compounds may have large negative effects on human health, including pulmonary, cardiac, vascular and neurological impairments. The region is also subjected to high concentrations of volatile organic compounds and ozone and has adverse topographic and meteorological conditions, which impede pollutant dispersion.

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#### Supporting Material Available

Mean PM<sub>2.5</sub> and PM<sub>10</sub> levels. Comparison between the results obtained in this work and values obtained worldwide using similar sampling conditions (Table S1), Mean concentrations for PAHs determined in PM<sub>10</sub>. Comparison between the results obtained in this work and values obtained worldwide using similar sampling conditions (Table S2), Mean concentrations for PAHs determined in PM<sub>2.5</sub>. Comparison between the results obtained in this work and values obtained worldwide using similar sampling conditions (Table S3), Estimated risk assessment for each polycyclic aromatic hydrocarbons in relation to Benzo[a]pyrene in the sampling sites (Table S4), Diagnostic ratios for PAH in PM<sub>2.5</sub> and PM<sub>10</sub> samples collected in the three sites (Table S5), Location of the sampling sites and the Petrochemical Complex (Figure S1), Wind rose for sampling period showing the wind direction with the greatest frequency (Figure S2), Trajectories obtained with the NOAA HYSPLIT model (Figure S3), Score plot of the first two PC on PAH concentrations in PM<sub>2.5</sub> and PM<sub>10</sub> collected in the AC station (Figure S4), Score plot of the first two PC on PAH concentrations in PM<sub>2.5</sub> collected in the three sampling sites (Figure S5), Score plot of the first two PC on PAH concentrations in gas phase collected in the CC and PRF sampling sites (Figure S6). This information is available free of charge via the internet at <http://www.atmospolres.com>.

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