

# Hydrocarbon concentration and source appraisal in atmospheric particulate matter (PM<sub>2.5</sub>) of an urban tropical area

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**Abstract** Polycyclic aromatic (46 PAHs) and aliphatic hydrocarbons (C<sub>12</sub>–C<sub>40</sub>) were studied in atmospheric particulate matter sampled in Rio de Janeiro Metropolitan Area (RJMA). In total, 236 samples from six different sites were collected simultaneously and weekly over 1 year (January–December 2011) allowing a robust atmospheric characterization of fine particulate matter (PM<sub>2.5</sub>). Hydrocarbon concentration was in general low compared to previous studies in the area (PAHs range 0.25–19.3 ng m<sup>-3</sup>), possibly due to changes in fuel composition over time. Precipitation is the main meteorological parameter that rules particulate and hydrocarbon concentration, modifying PAH typology by scavenging. Aliphatic and aromatic diagnostic ratios gave indications conflicting with combustion features. However, ratios showed differences among sites. Principal component analysis (PCA) associated to multiple linear regressions (MLR) allowed quantitative estimate of sources and effectively indicated vehicular emission as the main hydrocarbon source in the atmospheric particulate matter.

**Keywords** PM<sub>2.5</sub> · Atmospheric pollution · Rio de Janeiro Metropolitan Area · Hydrocarbon sources · Diagnostic ratios · PCA-MLR

## Introduction

Rare are the studies addressing the time-space variability in hydrocarbon nature and concentration over extended periods of time and representative geographic scope (Panther et al. 1999; Manoli et al. 2004). Such approach is extremely relevant for understanding source strength and concentration changes in the very dynamic atmospheric compartment. In this context, polycyclic aromatic hydrocarbons, which are of especial concern due to their toxicity, have been altered in relative concentration of individual compounds by worldwide changes in fuel matrix (Abrantes et al. 2004).

The Rio de Janeiro Metropolitan Area (RJMA) includes 14 municipalities comprising the second most populated area (10<sup>7</sup> inhabitants) in Brazil. The area houses the second largest industrial district in the country and serves as a base for the expanding offshore oil and gas exploration industry. With the intense population growth in the last 30 years, rural activities moved away giving place to urbanization. The Rio de Janeiro Environmental Agency (INEA) classifies the air quality in the southern region of Rio de Janeiro city as “good”; however, in the north region, air quality parameters surpass the limits of the Brazilian legislation (CONAMA 1990).

In Rio de Janeiro State, motor vehicles are responsible for most of the hydrocarbon and aldehyde emissions (Souza et al. 2013) and for fine aerosol mass in the atmosphere (Godoy et al. 2009). These emissions have been considered as the main route of aromatic hydrocarbon release into the atmosphere in Rio de Janeiro (Fernandes et al. 2002) and Niterói (Lima 2006) cities.

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Despite the several reports on hydrocarbons in atmospheric particulate matter (PM) from RJMA, understanding temporal trends and space distribution is difficult since data were obtained for different sampling periods, locations, particle size, and methodologies (Lopes and Andrade 1996; Lima 2006; Fernandes et al. 2002; Azevedo et al. 1999; Pereira-Netto et al. 2001, 2002; Quitério et al. 2007). None of these studies were performed over a larger time span or embracing a wider diversity of sampling stations.

The presence of particulate matter and pollutants in the atmosphere is affected by several factors. Variations have been associated with rain, temperature, solar radiation, and wind speed (Lopes and Andrade 1996; Panther et al. 1999; Esen et al. 2008).

The present work addresses the time and space variability of hydrocarbons in the RJMA and the contribution from different sources. For this, aliphatic and aromatic hydrocarbons were determined in fine particulate matter (PM<sub>2.5</sub>) sampled weekly in six sites over the period of 1 year. The general objective was to obtain reliable data for future trend evaluation and improve hydrocarbon source evaluation and characterization. Several tools as typology analysis, diagnostic ratios, and statistical analysis were applied. This study compiles literature data to support field observations and evaluates source diagnostic tools in this tropical environment.

## Methods

### Sampling

The sites were selected based on the State Environmental Institute (INEA) atmospheric sampling grid. Six sites were chosen for simultaneous sampling of atmospheric fine particulate matter (PM<sub>2.5</sub>) as to obtain the most representative distribution of atmospheric contaminants, considering the different features of RJMA.

The sampling sites were grouped according to their characteristics as follows: area 1 (rural)—Seropédica (SE), area selected as control; area 2 (industrial/urban)—São João de Meriti (SJ) and Campos Eliseos (CE), a blend of industrial activities and heavy vehicular traffic; and area 3 (urban)—Rio de Janeiro Downtown (D), Copacabana shoreline (CP), and a major road in Niterói (NT), all of them subjected to heavy traffic conditions (Fig. 1).

Samples were collected according to Brazilian standard procedure (ABNT, NBR 13412/95), consistent with the US-EPA methods. The collectors were placed at a height of approximately 2 m in a large open area. Samples were collected over 24 h every 6 days using fiberglass filters (203×254 mm, 0.21-mm thickness, 0.3- $\mu$ m diameter, Millipore, USA) in high-volume samplers (AGVMP252, Energética S. A., Brazil) at an average flow rate of 1.13 m<sup>3</sup> min<sup>-1</sup>. Mass

concentrations were determined gravimetrically from filter samples by means of an analytical balance (model SA 2.0; Scientech, USA;  $\pm$ 0.0001 g). Due to occasional setback in INEA sampling system, collected few sampling gaps occurred which, however, do not compromise temporal and spatial data analysis.

### Meteorological data

Hydrocarbon data interpretation made use of meteorological data obtained from monitoring networks of the Meteorology National Institute (INMET), Rio de Janeiro Alerta-Rio System (GEORIO), and from airports (Santos Dumont National Airport and Antonio Carlos Jobim International Airport). Meteorological parameters considered as of relevance to hydrocarbons and particulate matter concentration alterations in the atmosphere were wind speed (m s<sup>-1</sup>) and direction (°), temperature (°C), precipitation (mm), solar radiation (kJ m<sup>-2</sup>), and relative humidity (%).

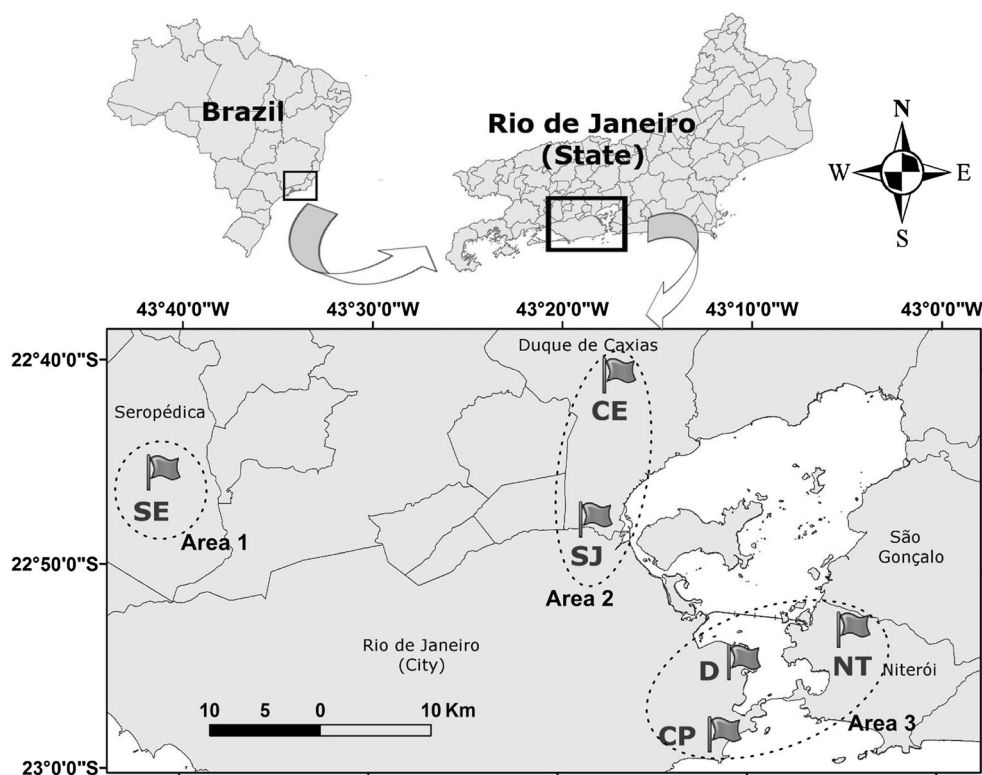
### Chemical analysis

Hydrocarbon determinations were based on the EPA 8015C (2007a) method for aliphatic hydrocarbons and the EPA 8270D (2007b) method for polycyclic aromatic hydrocarbons (PAHs). In brief, 2500 ng of *n*-C<sub>30</sub>d<sub>62</sub> and 100 ng of *p*-terphenyl-d<sub>14</sub> were added to the filters as surrogate standards for *n*-alkanes and PAHs, respectively. Samples were Soxhlet extracted in dichloromethane over 24 h.

Clean up proceeded in a glass column (1.3 i.d. and 30-cm height) packed in the top with 2 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>, 10 g of silica gel, and 7 g of alumina. The aliphatic fraction was eluted with 50 mL of hexane followed by PAH elution with 75 mL of a 1:1 (*v/v*) hexane and dichloromethane mixture. The PAH determinations were performed in an ion trap GC/MS system (Finnigan Trace gas chromatographer coupled to a Finnigan Polaris mass spectrometer—DB5MS 30 m×0.25 mm×0.25  $\mu$ m) system while *n*-alkanes (C<sub>12</sub>–C<sub>40</sub>), isoprenoids, and unresolved complex mixture (UCM) were determined by GC/FID (Focus GC—Thermo—HP-5 30 m×0.25 mm×0.25  $\mu$ m).

Quantification included the following PAH compounds: naphthalene (N), acenaphthylene (Acen), acenaphthene (Ace), fluorene (F), phenanthrene (Ph), anthracene (A), fluoranthene (Fl), chrysene (Ch), pyrene (Py), benzo(a)pyrene (BaPy), benzo(e)pyrene (BePy), benz(a)anthracene (BaA), benzo(b)fluoranthene (BbFl), benzo(k)fluoranthene (BkFl), indeno(1,2,3-cd)pyrene (IP), dibenz(a,h)anthracene (DBahA), benzo(ghi)perylene (BghiPe), perylene (Pe), dibenzothiophene (DBT), alkylated naphthalenes (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>), fluorenes (C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>), phenanthrenes (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>), dibenzothiophenes (C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>), chrysenes (C<sub>1</sub> and C<sub>2</sub>), and pyrenes (C<sub>1</sub> and C<sub>2</sub>).

Fig. 1 Sampling map



Quantification of the alkylated PAHs was based on the calibration curve of the non-alkylated homolog, except in the case of 1 and 2 methyl-naphthalene for which calibration curves were obtained, and of C<sub>2</sub> naphthalenes that were quantified based on the 2,3-dimethylnaphthalene. For *n*-alkanes, retention times were determined using a standard solution containing all compounds of interest and quantification was based on response factors obtained for individual *n*-alkane relative to *n*-C<sub>24</sub>d<sub>30</sub>. For PAHs, instrumental calibration standard solutions were used that containing in addition to the deuterated standards (100 ng mL<sup>-1</sup>), the 16 US-EPA priority PAHs, 2-methylnaphthalene, 1-methylnaphthalene, dibenzothiophene, 2,3-dimethylnaphthalene, and perylene. Only calibration curves with linear correlation coefficients higher than 0.990 were accepted. For each group of 10 analyzed samples, a standard solution was injected to check instrumental calibration conditions.

In search for other source indicators to be used in this study, the following compounds were identified and quantified: acephenanthrylene (Act), benzo(c)phenanthrene (BcPh), dibenz(a,j)anthracene (DBaJA), pentaphene (Pt), benzo(b)chrysene (BbCh), picene (Pi), indeno(7,1,2,3-cd)chrysene (Ich), and retene (Rt). These PAHs were not considered in the reported total PAH concentration, being used only as indicators of process and sources appointment.

The identification of these compounds was based on literature data (Wise et al. 1988; Yunker et al. 2002), on a Standard Reference Material (SRM 1597) for burning coal tar, and on

expected retention times based on each compound retention index. The quantification was conducted using the calibration curve of a compound of equal relative mass/charge ratio (*m/z*) and closest retention time, excepted for Rt which was quantified based on C<sub>4</sub>-alkylated phenanthrene. Considering filter mass extraction, volume sampled (approx. 1630 m<sup>3</sup> day<sup>-1</sup>), and analytical quality procedures, the quantification limit was 0.18 ng m<sup>-3</sup> for *n*-alkanes and 0.007 ng m<sup>-3</sup> for PAHs.

Blank samples and filters were also extracted as part of analytical control and presented mean results below 1 % of sample extract concentration. Average surrogate recovery in samples extracts was 77.6±18.5 % for aliphatic hydrocarbons (*n*-C<sub>30</sub>d<sub>62</sub>) and 91.1±17.5 % for aromatic hydrocarbons (*p*-terphenyl-d<sub>14</sub>).

### Statistical analysis

Parametric and non-parametric statistical tests, such as Shapiro-Wilk test and Box-Cox transformation technique, were applied to aliphatic and aromatic concentration data as to identify differences among sampling sites. When parametric statistical tools were inappropriate, differences were determined based on Kruskal-Wallis analysis followed by Wilcoxon-Mann-Whitney post hoc method, where *p* (probability) values were adjusted according Bonferroni correction. In multiple comparisons, there is a higher chance of type I error and Bonferroni correction is one the most simple and conservative method to avoid this problem. Where

parametric statistical methods could be applied, ANOVA and honestly significant difference (HSD) from Tukey's test were used. All statistical considerations for significance, parametric and non-parametric, were evaluated considering 95 % of confidence level ( $\alpha=0.05$ ).

Ratios of specific PAHs, known as diagnostic ratios, provide, at most, qualitative information about sources (Li et al. 2012). Quantitative assessment of PAHs can be obtained by principal component analysis in association with multiple linear regressions (PCA-MLR). This approach was initially proposed for source apportioning in urban atmosphere (Larsen and Baker 2003) but has also been applied to data for other environment matrices (Sofowote et al. 2008; Li et al. 2012).

The first step of this method consists in a PCA based on a correlation matrix followed by varimax rotation, retaining principal components whose eigenvalues is greater than one (1). The distribution of PAHs in each factor is evaluated and the probable corresponding source identified. Multiple linear regressions (MLR) of the factor scores are used to quantify the source contribution. The regression model was performed employing absolute factor scores as independent variables and the sum of PAHs concentration as the dependent variable, both standardized prior to the analysis. The regression coefficients obtained by MLR were used to estimate each source (factor) contribution to total PAH concentration in the samples.

## Results and discussion

### Atmosphere and hydrocarbon concentration

#### *Particulate matter*

Variance analysis of particulate matter concentration indicates higher concentrations in the industrial/urban area (SJM and CE) and D (Downtown—urban area) while NT and CP (urban area) have concentrations in the same range of the rural area (Seropédica). This geographic pattern for hydrocarbon concentration in the atmosphere concurs with the road grid density and industry distribution (Table S1—supplementary material).

Figure 2a shows the accumulated rain precipitation during the sampling period and Figure 2b, c gives medians for  $PM_{2.5}$  in CE. There is a particulate matter removal from the atmosphere by precipitation events as highlighted in Fig. 2c. Zeri et al. (2011) reported results for  $PM_{10}$  in Rio de Janeiro City revealing a relationship with air temperature which varies in time scales of 1–8 days typical of the short-term cold fronts occurring between October and May. From May to September, due to high pressure system in Rio de Janeiro region, periods of atmospheric stagnation frequently occur, causing elevated pollution levels (INEA 2009).

Although there is evidence of association between rain and atmospheric particulate matter (Fig. 2), no significant statistical correlation was proved. The seasonal pattern produced by rain frequency is better observed through a qualitative approach such as shown in Fig. 2c. In this figure, samples are grouped in boxes for wet and dry periods considering incidence or not, respectively, of any precipitation event within 48 h before sampling termination.

In all sampling sites, there was difference in particulate matter concentration between sunny and rainy periods, except for Copacabana (CP) where differences were not statistically significant.

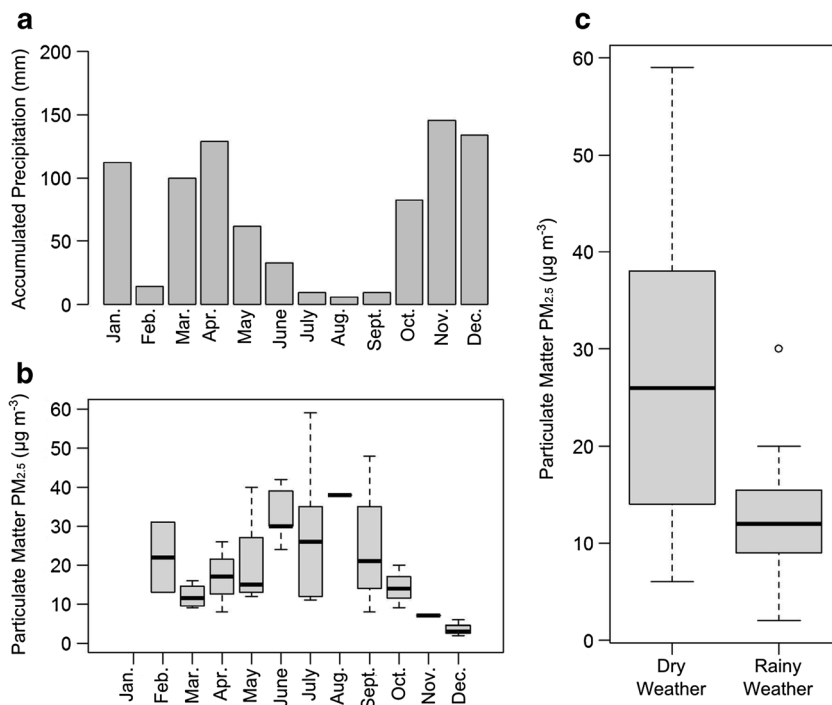
#### *Hydrocarbon concentration*

Hydrocarbon concentrations in Rio de Janeiro Metropolitan Area (RJMA) are summarized in Table 1. Some extreme concentration, denominated outliers, influenced data distribution and statistical analysis. These outliers are especially important in the aliphatic fraction, leading to larger difference between mean and median values, and higher relative standard deviation. These data were not removed for interpretation since extreme concentration events occur naturally in the environment.

The variance analysis of the aromatic and of the aliphatic compounds gave similar information: (1) Industrial/urban area (São João de Meriti and Campos Elíseos) and Downtown (urban area) are distinct from other sampling areas due to higher concentration and (2) Niterói and Copacabana (urban area) showed concentrations similar to the rural area (Seropédica), used as the control site. Figures 3 and 4 show the difference in concentrations among sites for aliphatic and aromatic hydrocarbons, respectively. This geographic pattern concurs with road grid density and industry distribution already discussed for particulate matter in “Particulate matter” section.

Some important factors limit the comparison with literature data. Few studies in Brazil report observations carried out over longer period of time as in the present case. Not all studies followed ABNT (NBR 13412/95) procedures, and most of them collected atmospheric fraction higher than  $PM_{2.5}$ . Sampling site also must be carefully evaluated since in some cases, samples were taken in restricted areas such as tunnels in Rio de Janeiro (Azevedo et al. 1999). In as much, most atmospheric studies report concentration for only a limited number of PAHs, usually the 16 priority US-EPA PAHs. The inclusion of alkylated homologs was especially relevant for source appraisal in D and CP stations, as will be further discussed in the section “Particulate matter.” In these stations, the 16 US-EPA PAHs represent 45 and 56 % of total concentration, respectively, while in the other sites, these compounds made up to 70 % of the total concentration based on 38 PAHs.

**Fig. 2** Annual accumulated precipitation for Irajá station from ALERTA-RIO system (a), annual particulate matter concentration in Campos Eliseos (b), and concentration box-plot related to rainy events (c)



In spite of these limitations, association between road proximity and hydrocarbons concentration has also been found by other authors (Pereira-Netto et al. 2001; Quitério et al. 2007) confirming the importance of vehicular sources in Rio de Janeiro Metropolitan Area.

Regardless of the specificity and limitations of existing studies (Pereira-Netto et al. 2005 and other references cited therein), when comparing the concentrations found in this paper with literature data, it is possible to identify a decreasing trend in hydrocarbon concentration in RJMA. The concentrations in the studied area are also lower than those reported for other Brazilian regions (Allen et al. 2008; Vasconcellos et al. 2011) and for other sites in the globe (Bi et al. 2003; Manoli et al. 2004). As for the decreasing concentration trend, Lima (2006) suggested a possible relation to increasing governmental incentive for ethanol consumption. Abrantes et al. (2009)

described mean PAH emissions 92 % lower for ethanol compared to gasoline. Vasconcellos et al. (2011) also indicate fuel composition change as responsible for temporal variation in hydrocarbon concentration for São Paulo and Rio de Janeiro cities acknowledging, however, that differences in sampling sites and methodologies preclude a detailed assessment.

As observed for particulate matter, in all sampling sites, there was a difference in hydrocarbon concentration between sunny and rainy periods. However, there is no significant correlation between concentration and rain precipitation frequency. This is due to the influence of other variables acting in synergy to modify hydrocarbon concentration in the atmosphere. Panther et al. (1999) among others which worked in several regions of different climate also observed PAH alterations associated to rain periods, without significant correlation.

Precipitation seems to be the principal phenomenon in tropical environment influencing hydrocarbon concentration. High temperatures are usually associated to elevate atmospheric concentrations (Esen et al. 2008), however, under tropical conditions is of lesser importance. Pereira-Netto et al. (2002) proposed that relatively small temperature variation in tropical regions is not enough to induce the significant concentration changes observed in temperate zones (Akyüz and Çabuk 2008; Manoli et al. 2004; Esen et al. 2008).

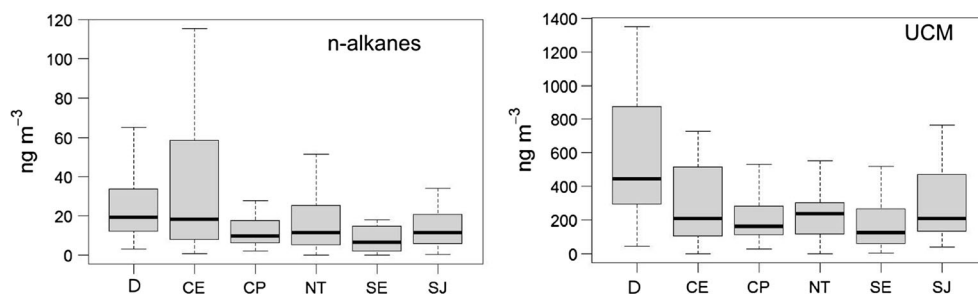
In the present work, rain precipitation also induces change in PAH concentration but principally in typologies (see Fig. 5). Strong scavenging effects upon typology was observed in two sampling sites from urban area (area 3), in Downtown and in Copacabana. In other sites, there was no

**Table 1** Mean, standard deviation, median, and range to hydrocarbon concentrations (ng m<sup>-3</sup>) in fine aerosol (PM<sub>2.5</sub>) of Rio de Janeiro Metropolitan Area

	Mean	Stand. Dev.	Median	Range
<i>n</i> -Alkanes	27.8	60.3	12.4	nd–697
Resolved peaks	91.3	230	42.3	nd–2935
UCM	299	596	174	nd–7935
Total aliphatics	390	769	225	0.43–9413
16 US-EPA PAH	2.83	2.39	2.18	0.15–15.5
Total PAH	4.42	3.25	3.52	0.27–19.3

nd not detected

**Fig. 3** *n*-Alkane and UCM concentrations in Rio de Janeiro Metropolitan Area (data without outliers)



significant change in PAH typology. A significant change in PAH typology, however, was observed only in Downtown and Copacabana where more abundant LMW PAH scavenging was observed during rain periods. In all stations, including in D and CP, HMW PAHs were more effectively removed during rain period.

### Diagnostic tools

#### Aliphatic hydrocarbons

Several tools have been used to infer possible sources of *n*-alkanes in environmental samples (see Table 2). Determination of the most abundant alkane ( $C_{max}$ ) for a given range of homologous compounds can also provide an indication of relative source strength.

Examples of typical *n*-alkane typology are shown in Figure S1 (supplementary material) for different sampling sites, and they highlight the very similar distribution with predominance of molecules containing odd number of carbon atoms in the range of  $C_{23}$  to  $C_{33}$ . The incidence of short-chain *n*-alkanes in CP and D is higher than that in SE or SJ, while in CE and NT, these compounds are almost undetected. The occurrence of lower molecular weight *n*-alkanes has been related to multiple emissions from anthropogenic sources (Souza et al. 2013).

Individual sources of *n*-alkanes cannot be correctly estimated solely by examining the distribution histogram since there are large variations in gas/particulate partitioning as molecular weight rises. Reported concentrations refer only to

hydrocarbon associated to particulate matter; therefore, it is difficult to link such data to the original emissions and those of light compounds can be underestimated.

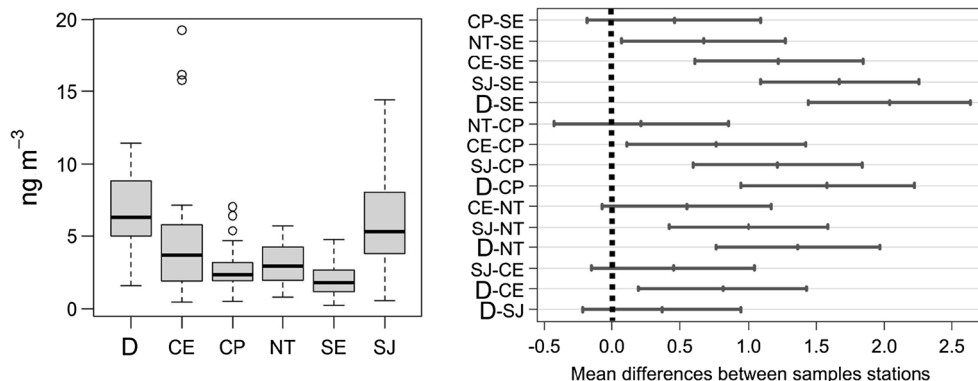
Carbon preference index (CPI) has been used (Table 2) as an additional tool for source diagnosis. Figure 6 shows CPI found in all stations characterizing predominant anthropogenic contribution to the aliphatic pool. CPI values for D (area 3—urban) and industrial/urban area sites (area 2—CE and SJ) showed lesser variations than in other stations due to the high concentrations derived from constant anthropogenic input. Conversely, as observed here, for the control site (area 1—rural), wide ranges of CPI values have been reported for rural and forested areas (Vasconcellos et al. 1998).

Different from temperate zones where CPI values are distinctly low in winter due to higher emissions and lower natural contributions, in the region of the present work (lower tropics), no seasonal pattern was verified. As most diagnostic ratios, CPI must be applied with caution to distinguish natural from petrogenic contribution since biomass combustion can also produce CPI values higher than 4 and  $C_{max}$  distribution similar to natural contribution (Oros et al. 2006).

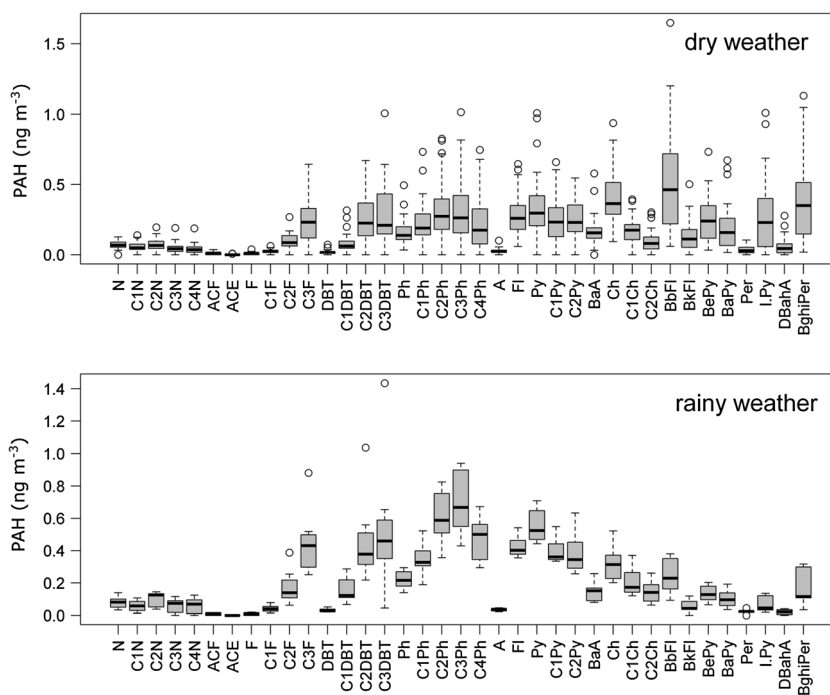
An additional tool widely used to distinguish sources is based on *n*-alkane contribution from cuticular plant waxes (Simoneit et al. 1991a, b). The wax normal alkanes (WNA) is calculated using higher molecular weight *n*-alkanes ( $>C_{23}$ ), where negative values are replaced by zero (Eq. 1):

$$WNA C_n = [C_n] - \frac{[(C_{n+1}) + (C_{n-1})]}{2} \quad (1)$$

**Fig. 4** PAHs concentrations in Rio de Janeiro Metropolitan Area and results of honestly significant difference (HSD) from Tukey's test



**Fig. 5** Box-plot of PAH profiles to Downtown samples collected in 2011 related to precipitation occurrence within 48 h before end of sampling



Relative median WNA contributions were 12 % in D, 18 % in CE, 18 % in SJ, 21 % in CP, 25 % in Niterói, and 29 % in SE (Fig. 6). These results emphasize the gradient of anthropic inputs already discussed above. WNA values are higher than those observed by Nascimento (2006) in São Paulo (10 %), Bogota (6 %), and Buenos Aires (8 %), possibly due to the proximity of the Tijuca Forest and other forested mountains in Rio de Janeiro.

The ratio of the unresolved complex mixture to resolved peaks (UCM/RP) has been used to examine petroleum product contribution in aerosols. UCM presence in the atmosphere originates mainly from fossil fuel combustion (Rogge et al. 1993a, b; Simoneit and Mazurek 1982). Plant-derived emissions do not show UCM and emissions from different biomass burning produce ratios close to 1 (Oros et al. 2006). The

UCM/RP ratio >4 can be used to confirm presence of weathered oil (Simoneit and Mazurek 1982).

In Rio de Janeiro Metropolitan Area, UCM/RP assumes, especially in Downtown and São João de Meriti, high values (>4), as expected for vehicular emissions (Fig. 6). Vasconcellos et al. (2010) describe for São Paulo higher values of the ratio as compared to Bogota and Buenos Aires possibly due to the fuel mixture in Brazil. The addition of about 20 % of ethylic alcohol to the gasoline seems to reduce the resolved peak concentration, thereby increasing the ratio in urban centers.

The above discussion of the results suggests the presence in the PM<sub>2.5</sub> of a strong aliphatic component from vehicle emission which is emphasized by the UCM values. Accurate source appraisal is critical to understand emission patterns, since diversity of vehicular fleet in association to environmental conditions results in fingerprints substantially different from those obtained in controlled emission assays which support the establishment of diagnostic ratio thresholds.

**Table 2** Aliphatic diagnostic ratios to atmospheric samples

Ratio	Source evaluation		
$C_{max} \text{ alkane}^a$	Odd $\geq n-C_{27}$ Natural terrestrial	$\leq n-C_{24}$ Diesel combustion	even $\leq n-C_{36}$ Light fuel combustion
CPI <sup>b</sup>	$\geq 4$ unpolluted		$< 4$ polluted
WNA <sup>c</sup>	Relative contribution from cuticular plant waxes (%)		
UCM/RP <sup>d</sup>	$< 4$ unpolluted		$\geq 4$ polluted

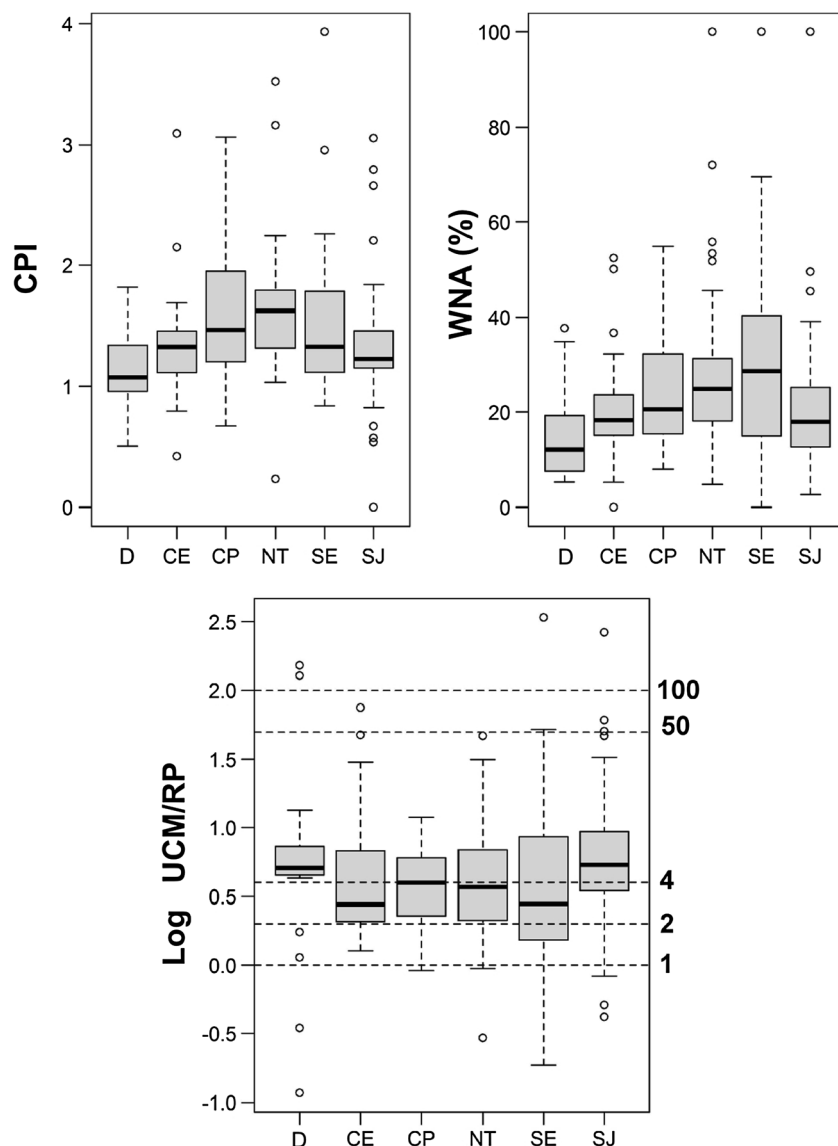
<sup>a</sup> Simoneit et al. (1991b); Omar et al. (2007); Mazurek et al. (1989)  
<sup>b</sup> Rogge et al. (1993a,b); Gogou et al. (1996)  
<sup>c</sup> Simoneit et al. (1991b,a)  
<sup>d</sup> Rogge et al. (1993a); Simoneit and Mazurek (1982); Kavouras et al. (2001)

*Aromatic hydrocarbons*

The medians and deviations for PAH concentration in the different stations shown in Figure S2 (supplementary material) highlight predominance of specific compounds useful for source identification. Most sites show high predominance of compounds with  $m/z$  252+276, especially the benzo(k)fluoranthene. In D, and in lesser intensity in CP, the low molecular weight PAHs are significantly abundant.

The relevance of compounds in the above  $m/z$  range is also found in other studies performed in Rio de Janeiro

**Fig. 6** Carbon preference index (CPI), wax normal alkane (WNA), and unresolved complex mixture over resolved peaks (UCM/RP) diagnostic ratios to Rio de Janeiro Metropolitan Area atmospheric samples



Metropolitan Area and elsewhere (Pereira-Netto et al. 2001, 2002; Dallarosa et al. 2008; Manoli et al. 2004).

Fluoranthene and pyrene are considered as effective molecular markers of diesel emissions while benzo(ghi)perylene and indeno(1,2,3-cd)pyrene have been used as gasoline molecular markers (Ho et al. 2009; Rogge et al. 1993a, b). Light PAHs can also derive from coal burning (Oros and Simoneit 2000) as well as biomass burning (Oros et al. 2006). Biodiesel burning also produces light PAHs but due to its reduced use shall not be considered here. Different sources often have similar or overlapped PAH typologies, which result in difficulty to identifying the major sources.

Evaluation of sources through typology analysis suggests that all sampled sites are principally affected by gasoline combustion due to the predominance of  $m/z$  252 and 276 compounds. In D and CP, the low molecular weight compounds suggest diesel contribution. In spite of the fact that biomass

and coal combustion also produces low molecular weight PAHs, it is an unlikely source in both the above sites. PAHs derived from biomass burning can be transported over long distances, as observed in other Brazilian sites (Dallarosa et al. 2008), hence being able to influence PAH typology over a large geographic setting. Distinct patterns, as occurred in Rio de Janeiro Metropolitan Area, most probably derive from local sources and heavy vehicular traffic.

The commonly used diagnostic ratios to infer sources of aromatic compounds in atmospheric samples and the associated thresholds are shown in Table 3. Figure 7 shows the results as box and whiskers for each sampling site.

Two major inferences can be drawn from data in Table 3 and Fig. 7: (1) there is little agreement among ratios as for the source indication and (2) thresholds used to establish sources in the literature are not adequate as will be shown later.



**Table 3** Aromatic diagnostic ratios to atmospheric samples

Ratio	Source evaluation	
IP/(IP+BghiPe)	0.18 <sup>a</sup>	Gasoline combustion
	<0.4 <sup>b</sup>	
	0.21–0.22 <sup>c</sup>	
	0.37 <sup>a</sup>	Diesel combustion
	0.35–0.70 <sup>b,c</sup>	
FI/(FI+Py)	≈0.5 <sup>d</sup>	
	0.56 <sup>a</sup>	Coal burning
	0.62 <sup>a,e</sup>	Biomass burning
	<0.5 <sup>f</sup>	Gasoline combustion
	<0.4 <sup>g</sup>	Petroleum
BaA/(BaA+Ch)	0.4–0.5 <sup>g</sup>	Petroleum combustion
	>0.5 <sup>f</sup>	Diesel combustion
	0.60–0.70 <sup>h</sup>	
	>0.5 <sup>g</sup>	Grass, wood, and coal combustion
	0.2–0.35 <sup>i</sup>	Coal burning
BaPy/(BaPy+Ch)	>0.35 <sup>h,i</sup>	Vehicle emissions
	>0.35 <sup>g</sup>	Combustion
	<0.2 <sup>g</sup>	Petroleum
	≈0.5 <sup>j</sup>	Diesel combustion
	≈0.73 <sup>j</sup>	Gasoline combustion
BbFl/BkFl	>0.5 <sup>k</sup>	Diesel combustion
	>0.73 <sup>k</sup>	Gasoline emissions
BaPy/BghiPe	0.5–0.6 <sup>k</sup>	Vehicle emissions
	<0.5 <sup>l</sup>	High traffic conditions
CPAHs <sup>o</sup> /16PAHs	≈1 <sup>e,m</sup>	Mainly combustion
	0.41 <sup>b</sup>	Non-catalyst vehicle emissions
	0.51 <sup>b</sup>	Catalyst vehicle emissions
	0.30 <sup>b</sup>	Heavy-duty diesel emissions
BaPy/(BaPy+BePy)	≈0.5 <sup>n</sup>	Fresh particles
	<0.5 <sup>n</sup>	Photolysis (aging)

<sup>a</sup> Grimmer et al. (1983); Ho et al. (2009)

<sup>b</sup> Rogge et al. (1993a)

<sup>c</sup> Kavouras et al. (2001)

<sup>d</sup> Khalili et al. (1995)

<sup>e</sup> Gogou et al. (1996)

<sup>f</sup> Ravindra et al. (2008a)

<sup>g</sup> Yunker et al. (2002)

<sup>h</sup> Sicre et al. (1967)

<sup>i</sup> Akyüz and Çabuk (2008)

<sup>j</sup> Guo et al. (2003)

<sup>k</sup> Pandey et al. (1999); Park et al. (2002)

<sup>l</sup> Manoli et al. (2004)

<sup>m</sup> Gogou et al. (1996); Ravindra et al. (2008b)

<sup>n</sup> Oliveira et al. (2011); Tobiszewski and Namiehnik (2012)

<sup>o</sup> CPAHs=FI+Py+BaA+Ch+BbFl+BkFl+BaPy+IP+BghiPe

Benzo(ghi)perylene is considered a gasoline marker; therefore, lower values of IP/(IP+BghiPe) should infer higher contribution from gasoline emissions. Figure 7a shows an increasing trend of IP/(IP+BghiPe) from D to SJ. The ratios FI/(FI+

Py) and BaPy/(BaPy/Ch) suggest lower diesel contribution in D compared to other sites. Although these ratios give similar information, they do not agree with those drawn from PAH typology and discussed above. It is relevant to stress that field samples are subjected to a mixture of several different inputs and environmental factors; therefore, the use of diagnostic ratios requires prudence.

As shown in Table 3, the thresholds for diagnostic ratios are very variable in the literature. Most diagnostic ratio thresholds cannot be considered categorically for source appraisal, due to inconsistencies in the reported values. Some authors have shown the limitations of diagnostic ratios (Lima 2006; Pereira-Netto et al. 2002; Abrantes et al. 2004). In the present study, some diagnostic ratios (see Fig. 7a, d) show a trend useful to infer the relative importance of a certain source in the sampling sites.

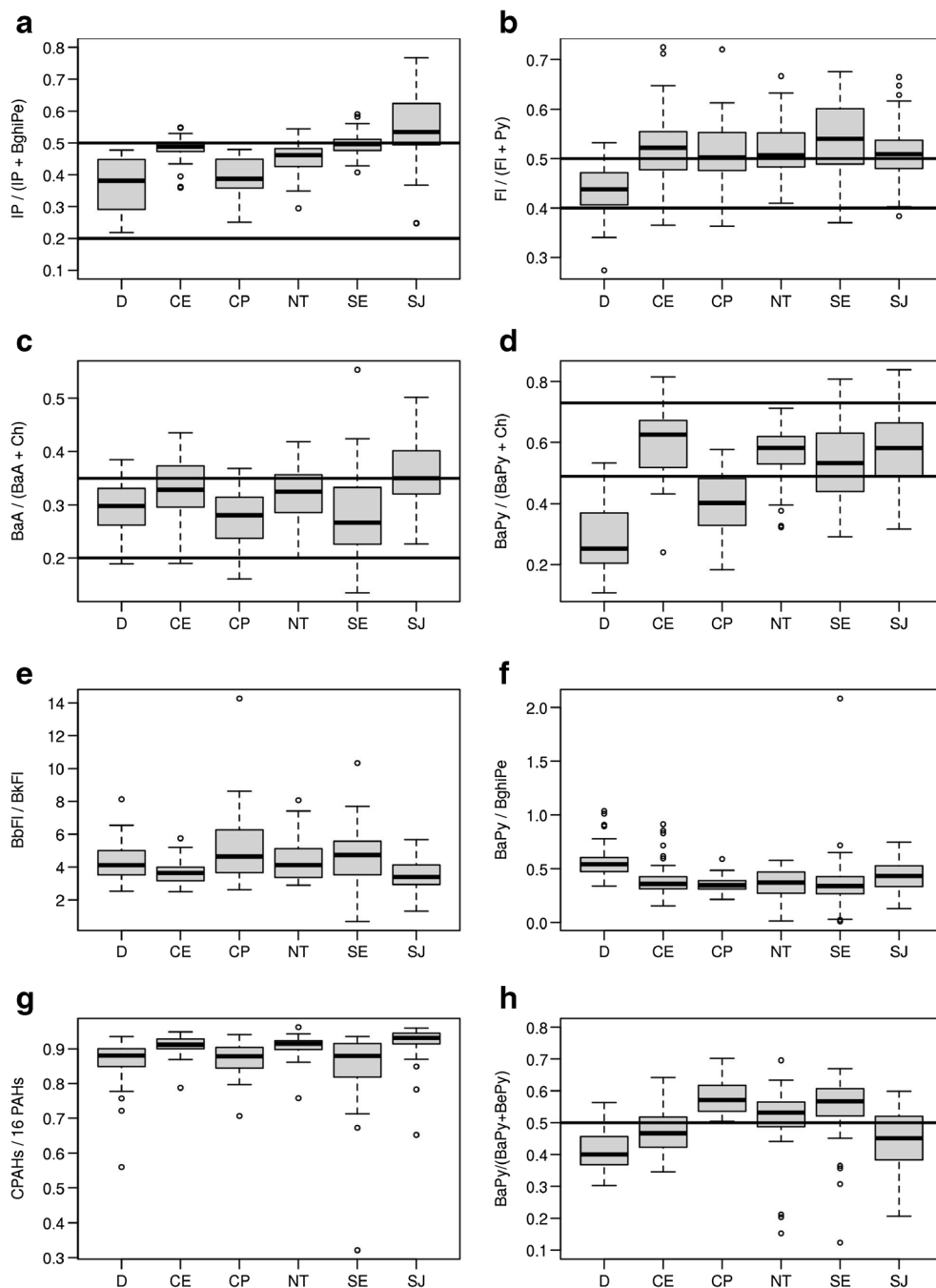
Difference in reactivity can be used to obtain information on particle aging. This is the case of the ratio between benzo(a)pyrene and benzo(e)pyrene (Table 3) which are emitted in equivalent amounts, but the former compound is less resistant to photochemical degradation (Panther et al. 1999). In the results of RJMA (Fig. 7h), there is no clear evidence of this phenomenon. The PM<sub>2.5</sub> corresponds to recent emissions, and possibly the time they have resided in the atmosphere is insufficient to lead to the low ratio values observed by other authors for larger particle sizes (Lima 2006; Tobiszewski and Namiehnik 2012).

Although diesel emissions are the principal source of atmospheric particulate matter (Souza et al. 2013; INEA 2009), in the present work, gasoline combustion appears as the main source, probably due to temperature influence on gas-phased particulate matter partitioning. Higher temperatures enrich particulate matter in the high molecular weight compounds by preferential loss of the low molecular weight compounds (Panther et al. 1999; Esen et al. 2008).

Less frequently used PAHs can provide extra information to assist source interpretation. Figure S3 (supplementary material) shows box and whiskers for these PAHs in different sampling sites. In spite of some compounds being at low concentration, often close or below quantification limits, a PAH typology showing predominance of indeno(7,1,2,3-cdef)chrysene appears in most sites. Predominance of indeno(7,1,2,3-cdef)chrysene in atmospheric samples was also reported by Bi et al. (2003) and attributed to vehicular emissions.

Yunker et al. (2011) suggests the use of the following diagnostic ratios: ICh/(ICh+BghiPe), DajA/(DahA+DajA), and Pi/(Pi+DahA), to distinguish PAHs derived from petroleum, oil combustion, and biomass combustion. The values found for these ratios in the present work indicate that most samples carry residues of petroleum combustion. This result concurs with the source

**Fig. 7** Different PAH diagnostic ratios applied to Rio de Janeiro Metropolitan Area sampling sites



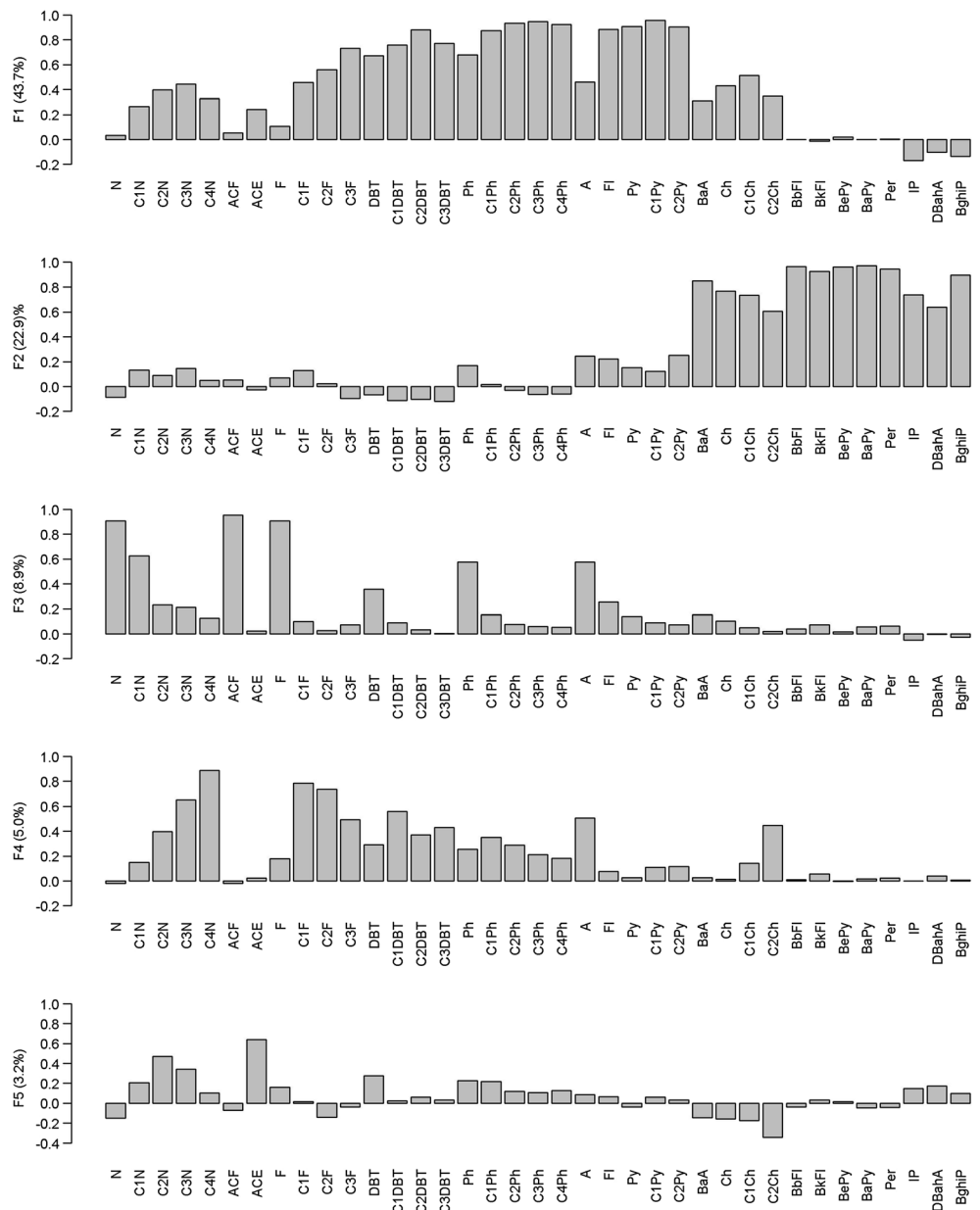
indications obtained after an overall evaluation of other diagnostic ratios, as discussed above.

Retene reported in atmospheric samples as predominantly derived from biomass burning (Simoneit 2002) was present in all D samples, while in SE, a rural area, quantification was possible in only 12 % of the samples. The geographical distribution of retene, similarly to that of other PAHs discussed above, is not compatible with biomass combustion. Although retene has been rarely associated to vehicular emissions (Khalili et al. 1995; Westerholm et al. 1996), this is its most probable source in D site.

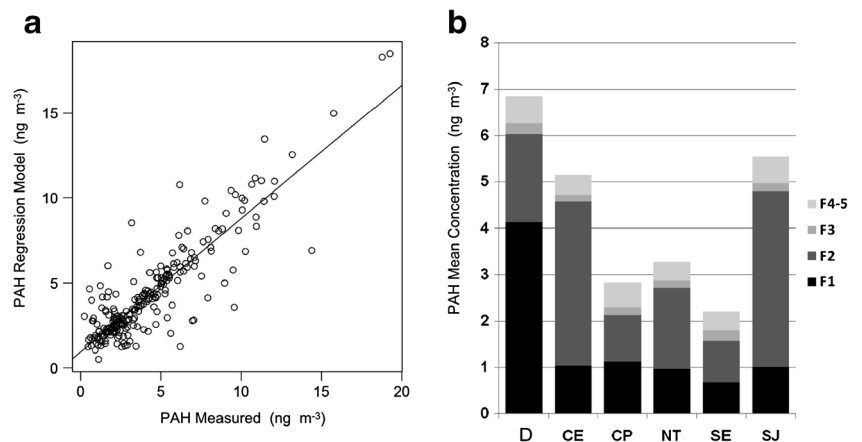
### PCA-MLR

Figures 8 and 9 present the results obtained from the PCA-MLR. Factor 1 comprises 43.7 % of total variance and includes PAHs derived from unburned fuel due to the abundance of low molecular weight compounds and the bell shape distribution in the alkylated series. In factor 2 are the high molecular weight compounds derived from fuel combustion, principally of gasoline and diesel as supported by the evidences presented under the sections “Aliphatic hydrocarbons” and “Aromatic hydrocarbons”. In factor 3 predominates light

**Fig. 8** Factor loadings from principal component analysis with varimax rotation in atmospheric particulate sample PAH results



**Fig. 9** PCA-MLR results for PAHs in atmospheric particulate samples (PM<sub>2.5</sub>) in Rio de Janeiro Metropolitan Area



compounds from combustion, in a typical distribution of alkylated compounds that decreases from  $C_0$  to  $C_n$ . The other two extracted factors did not represent a specific source pattern and, consequently, they were not defined. Factors 4 and 5 were considered as including undetermined sources.

The linear regression model produced by the five factors to predict total PAH concentration showed good adjustments ( $R^2=0.78$ ,  $F<0.05$ ), and, as shown in Fig. 9a, there is good relation between predicted and real concentration. Unburned fossil fuel (factor 1) has high contributions in CP and D (Fig. 9b), concurring with the previous discussion under the section “Aromatic hydrocarbons.” The other sampling sites are predominantly influenced by high molecular weight PAHs derived from fuel combustion (factor 2).

Higher relative deviations shown in Fig. 9a for some samples are due to the low PAH concentrations. Considering the elevated number of analyzed samples (236) and the generally low relative deviation, this model produces a reliable source appraisal for the RJMA.

The indications of the statistical model corroborate the observations (section “Diagnostic tools”) that gasoline combustion is the main source of PAHs to the atmospheric particulate matter in the studied region.

## Conclusions

The present work is the first in Brazil to report hydrocarbon data for  $PM_{2.5}$  sampled weekly over the time span of 1 year, covering a wide sampling grid. Therefore, the results are sufficiently robust to be used as reference in future evaluations and trend analysis.

In Rio de Janeiro Metropolitan Area, precipitation is the most important meteorological phenomenon affecting particulate matter and hydrocarbon concentrations. Atmospheric hydrocarbon concentration can be considered low compared to other metropolitan areas so far studied in Brazil and abroad. The most probable explanation for the actual low concentrations is the change of the fuel matrix with the use of biofuels.

The main hydrocarbon source in atmospheric particulate is vehicle emission, especially of gasoline. Diagnostic ratios are useful tools to identify combustion trends in sampling sites, but thresholds proposed in the literature are not adequate for unequivocal source appraisal. The quantitative appraisal through PCA-MLR gave results which are in closer agreement to the combustion pattern in the studied sites than the diagnostic ratios and typology analysis.

In the atmosphere, differences in compound reactivity, in particulate matter—vapor phase-water phase partition, and in meteorological conditions interfere with the process of source appraisal. However, despite the difficulties intrinsic to this system, the extensive knowledge of the study sites as well as

of the likely sources supports the adopted approaches and the conclusions derived therefrom.

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