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Original Article

Polycyclic aromatic hydrocarbons in $PM_{2.5}$ and PM_{10} atmospheric particles in the Metropolitan Area of Costa Rica: Sources, temporal and spatial variations

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) concentrations in PM_{10} and $PM_{2.5}$ particles were measured at 14 monitoring sites (12 for PM_{10} and 2 for $PM_{2.5}$), located in the Metropolitan Area of Costa Rica, from January to November 2013. High-volume air samplers with pretreated quartz filters were used to collect the particles. The analytical determination was carried out using high-performance liquid chromatography (HPLC). The most abundant PAHs were benzo[a]anthracene, indeno(1,2,3-cd)pyrene, dibenz[a,h] anthracene and acenaphthylene. Ratios obtained by correlating the concentration of some PAHs, both PM_{10} and $PM_{2.5}$, suggest that gasoline and diesel vehicles are the main sources in the area being studied. This is consistent with the results obtained when applying the positive matrix factorization (PMF) analysis, since vehicles accounted for 62–74% of total emissions in the area; burning wood fuel was the second source of emissions, contributing between 7 and 15%; and road dust was third, with almost 8%.

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1. Introduction

Both $PM_{2.5}$ and PM_{10} (particles with aerodynamic diameters equal or less than 2.5 and 10 μm, respectively) have gained attention in recent years due to their role in various atmospheric processes, their adverse effects on health, and their impact on climate change (Habre et al., 2014; Menon et al., 2002). Human exposure to these particles can aggravate chronic respiratory and cardiovascular diseases, disrupt the immune system and even damage lung tissue (Chen and Zhao, 2011).

Particles can originate from natural and anthropogenic sources, and can be emitted directly into the atmosphere (primary sources) or be formed by chemical reactions from gaseous sources (secondary sources) (Zheng et al., 2005). Particle matter size distribution and chemical characteristics can provide valuable information to better understand the sources, formation mechanisms and transportation patterns of particles (Buczynska et al., 2014). A significant part of the impact of particles can be attributed to the presence of polycyclic organic matter, mainly composed of polycyclic aromatic hydrocarbons (PAHs), and their nitrated (nitro-PAHs) and oxygenated (oxy-PAHs) derivatives (Ré-Poppi and Santiago Silva, 2005).

By definition, a polycyclic aromatic hydrocarbon (PAHs) is formed of two or more line-angle benzene rings containing only carbon and hydrogen. PAHs are originated during the incomplete combustion and pyrolysis of biomass and fossil fuels (Keyte et al., 2013). The chemistry of PAHs shows how some of these particles are stable enough to survive the pyrolysis process through combustion, entering the environment as complex mixtures of primary pollutants in high-enough quantities to cause direct damage on human health (Finlayson-Pitts and Pitts, 2000). PAHs may vary from gaseous to solid, according to their number of rings. Low molecular mass compounds tend to concentrate in their gaseous phase, while high molecular mass compounds are often associated with particles. Once PAHs enter the atmosphere, they are redistributed as gaseous particles, according to the pressure of steam, physicochemical characteristics of aerosols, and weather conditions (Lohmann and Lammel, 2004).

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PAHs in particulate matter have called special attention because of their potential carcinogenic and mutagenic effects (Villalobos-Pietrini et al., 2007). Low molecular weight PAHs of two or three rings are commonly toxic but not carcinogenic; the opposite happens with PAHs such as benzo[a]pyrene and dibenzo[a,h]anthracene. Benzo[a]pyrene (BaP) is the traditional PAHs exposure marker—present in most PAHs sources—and is used as a benchmark for their potential carcinogenic, genotoxic or mutagenic effects. Therefore, the International Agency for Research on Cancer (IARC) has classified it as Group 1 - "carcinogenic to humans" (IARC, 2010).

Costa Rica, despite being a small country of only 51 100 km^2, is not free of air pollution problems, particularly in the Metropolitan Area, which has become the country's most important urban system in recent years. Within a relatively small extension of 1 997 km^2, the Metropolitan Area houses 92% of the country's industry, 85% of its trade and services activities, 70% of its vehicle fleet and 52,7% of its population, and generates 70% of the country's gross domestic product. The concentration of those important commercial and industrial activities in such a small geographic area, is causing a relevant impact on the air quality, creating an exposure to the citizens on high concentrations of $PM_{2.5}$ ranged from 21 to 29 $\mu g/m^3$ as annual average (Herrera, 2012). While efforts have been taken by the air quality monitoring network to measure the mass concentration of particles in the Metropolitan Area, it is essential to obtain information about the chemical composition of these particles, particularly its organic fraction.

Accordingly, this study allows a preliminary diagnosis of PHAs levels in PM_{10} and $PM_{2.5}$ particles, an analysis of their temporal and spatial variability, and a greater probability of identifying possible sources through the use of receiver models.

2. Experimental

2.1. Sampling

Fourteen monitoring sites were selected for the PM_{10} and $PM_{2.5}$ sampling (Fig. 1). The sites were selected according to the most relevant land use patterns in the Metropolitan Area: commercial, industrial and residential. Detailed description for them is listed in Table 1. The sampling campaign took place from January to November 2013. Both PM_{10} and $PM_{2.5}$ samples were collected once every six days, using high-volume air samplers. Thermo Andersen mass flow controllers (MFC) were used with a flow rate of (1.13 ± 10%) $m^3 min^{-1}$. The flow calibration of each equipment was made comparing the readings of drop pressure generated by the flow passing through a calibrated critical orifice (454 TISCH VARIFLO) with the drop pressure sampler reading.

2.2. PM_{10} and $PM_{2.5}$ mass concentration

PM_{10} and $PM_{2.5}$ samples were collected over 24 h on pre-fired (at least 5 h at 900 °C), pre-conditioned quartz fiber filters (Whatman CAT No. 1851-865). PM_{10} and $PM_{2.5}$ mass concentration determinations were carried out gravimetrically. The results are reported as standard concentration in $\mu g\ m^{-3}$ for an average 24 h. The mass concentration uncertainty was ±1.2 $\mu g\ m^{-3}$. Sample

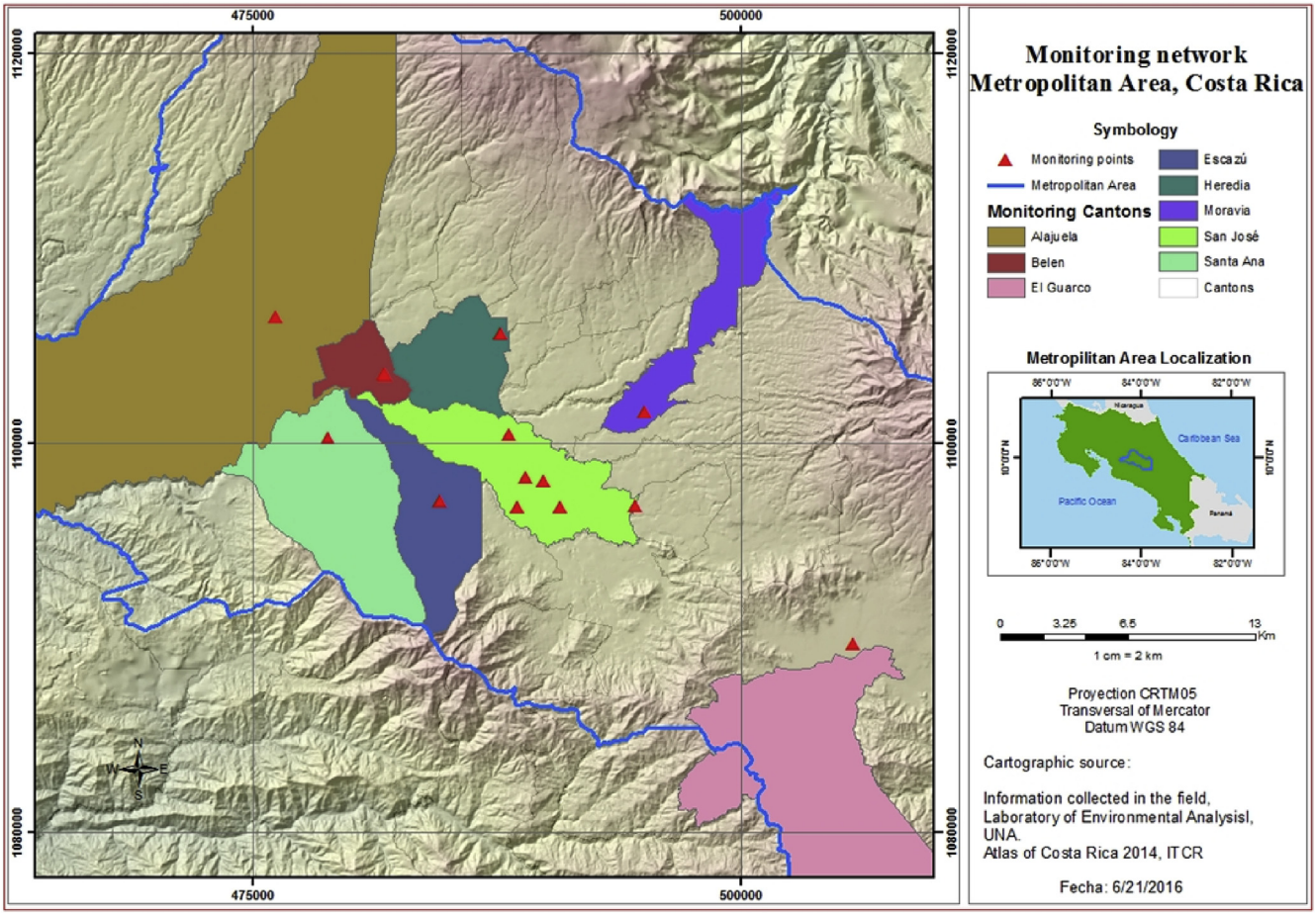


Fig. 1. Map of the sampling sites for HPAs monitoring in the Costa Rican Metropolitan Area.

Table 1
Sampling sites description for PM_{10} and $PM_{2.5}$ within the Costa Rican Metropolitan Area.

Identification code	Municipality	Localization	Measured parameters	Sampling site category
CAT-SJ	San José	San José Metropolitan Cathedral	PM_{10}	Commercial Zone
SP-SJ	San José	Park section, San José Municipality	PM_{10}	Commercial –residential zone transition
CRH-SJ	San José	Recycle Center, San José Municipality	PM_{10}	Commercial –residential zone transition
CNU-SJ	San José	National Electricity Company (CNFL), La Uruca	PM_{10}	Industrial Zone
RNZ-SJ	San José	National Property Register, Zapote	PM_{10}	Commercial Zone
PM-SJ	San José	Municipality Building, MSJ	$PM_{2.5}$	Commercial –residential zone transition
ES-SJ	Escazú	Municipality Building, Escazu	PM_{10}	Commercial Zone
BE-HE	Belén	La Ribera Belén	$PM_{2.5}/PM_{10}$	Industrial Zone
ER-HE	Central	National University, Heredia	PM_{10}	Commercial Zone
MT-SJ	Santa Ana	Matra Company, Santa Ana	PM_{10}	Commercial Zone
PI-CA	El Guarco	Industrial Park, Cartago.	PM_{10}	Industrial Zone
EA-SJ	Moravia	EATON Company, Moravia	PM_{10}	Residential Zone
UTN-AL	Central	Technical National University, Alajuela	PM_{10}	Commercial –residential zone transition

handling procedures for the filters were strictly controlled to avoid any possible contamination.

2.3. Sample extraction

For PAHs analysis, each filter was subject to a Soxhlet extraction that employed 190 ml of dichloromethane as a solvent to reach four cycles per hour during four consecutive hours. The extract was concentrated on a rotary evaporator up to an approximate volume of 10 ml. Another 10 ml of acetonitrile were added to change the solvent, evaporating approximately 0.5 ml. Finally, the extract was quantitatively decanted into 1 ml balloons using a Pasteur pipette.

The sample was transferred to an amber glass vial, by passing it through a Millipore microporous polyvinylidene fluoride (PVDF) Millex-HV teflon filter with a porosity of 0.45 μm, using a glass syringe. All glassware used underwent a cleaning process with organic matter-free soap and type-1 ultrapure water, as well as a rinsing process with HPLC grade acetone, and subsequently dried in an oven at 150 °C for 15–30 min.

2.4. Chemical analysis

PAHs concentrations were quantified using a DIONEX ICS-3000 liquid chromatography system that included an auto sampler model AS-1 with temperature control, a VWD-1 UV/visible single-channel detector, connected to a RF-2000 fluorescence detector, and an Acclaim 120 C_{18} stationary phase column of 5-μm and 120 Å. The use of two detectors in a simultaneously way allows getting better sensibility for the different compounds. A curve calibration from 0.05 mg/l to 1 mg/l was used to quantify PAH concentration for 14 compounds, and another from 0.05 to 0.7 mg/l was used for benzo[k]fluoranthene, based on a certified primary solution containing the 15 PAHs, with a concentration of 200 mg/l for all compounds (Chem Service, catalog number PNA-550RPM). The primary solution included the following compounds: naphthalene (NaP), acenaphthylene (Acy), fluorene (Fl), phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), benzo [ghi]perylene (BghiP) and indeno[1,2,3-cd]pyrene (IND). Table 2 describes the instrumental conditions used in the analysis. For quality control, sampling and reagent blanks were analyzed and subtracted from the measured values of samples. Before sample analysis, method recoveries were tested by spiking standards of 15 target PAHs in cleaned sampling filter. The recoveries were 96 ± 15%. In addition, Table 3 shows the results of the method performance parameters obtained during validation. Detection and quantification limits were calculated using the Meier and Zünd (2001) method, which is based on the confidence limits of the calibration curve to determine the minimum statistically detectable amount.

2.5. Positive Matrix Factorization (PMF)

The PMF model was used to identify PM_{10} and $PM_{2.5}$ sources and estimate source contributions. The PMF is a mathematical receptor model based on the principle that a relationship between source and receptor exists when mass conservation can be assumed (Paatero, 1997). It decomposes a matrix of speciated sample data into two matrices factor contributions (g) and factor profiles (f) in order to understand the factors or sources impacting the speciated sample data. PMF solves the general receptor modeling problem using weighted least squares (http://www.sciencedirect.com/science/article/pii/S0169809516301041Poirot et al., 2001).

3. Results and discussion

3.1. PAHs levels

Table 4 details the average and standard deviation of the mass concentrations of PM_{10}, $PM_{2.5}$ and PAHs concentrations in collected particles during the monitoring campaign. The annual mean PM_{10} levels were higher in industrial (BE–HE, CNU-SJ) and high traffic commercial (ER-HE) sites, 38, 34 and 31 $\mu g\ m^{-3}$, respectively. For all sampling sites, PM_{10} annual and 24 h average time concentrations are below the recommended Costa Rican guidelines for a PM_{10} concentration (50 and 150 μgm^{-3}, respectively). It was found that the $PM_{2.5}$ concentration in the sampling sites (BE-HE and PM-SJ) was higher than 15 μgm^{-3}, which is the annual goal of the USA National Ambient Air Quality Standard. Daily concentrations exhibited 31% and 25% exceedances respectively, of the 24 h limit of the USA $PM_{2.5}$ National Ambient Air Quality Standard (35 μgm^{-3}). The comparison was done with USA standards, as Costa Rica does not have an air quality standard for $PM_{2.5}$.

Table 2
Instrumental conditions for PAHs concentration analysis.

Mobile phase flux	1 ml/min		
Mobile phase gradient	Time (min)	Acetonitrile percentage	Deionized water percentage
	0	60	40
	20	100	0
	35	60	40
Column Temperature	20.00 °C		
Auto sampler Temperature	20.00 °C		
Injection volume	25 μl		
UV/VIS Detector	254 nm		
Fluorescence Detector	Excitation: 340 nm Emission: 425 nm Gain: 1		

Table 3
Validation parameters for the PAHs analytical method.

Compound		Detection limit (mg/l)	Quantification limit (mg/l)	Air detection limit (ng/m^3)	Air quantification limit (ng/m^3)	Repeatability variation coefficient (%)	Reproducibility variation coefficient (%)
Naphthalene	NaP	0.03	0.04	0.02	0.03	1.85	2.42
Acenaphthylene	Acy	0.02	0.04	0.01	0.03	4.33	4.21
Fluorene	Fl	0.03	0.06	0.02	0.04	1.70	10.09
Phenanthrene	Phe	0.03	0.05	0.02	0.03	2.40	2.73
Anthracene	Ant	0.03	0.05	0.02	0.03	2.46	2.88
benzo[ghi]perylene	BghiP	0.03	0.05	0.02	0.03	2.25	2.11
Chrysene	Chr	0.03	0.06	0.02	0.04	2.25	2.11
benzo[a]anthracene	BaA	0.02	0.03	0.01	0.02	3.56	3.90
Fluoranthene	Flu	0.02	0.03	0.01	0.02	2.31	3.05
Pyrene	Pyr	0.04	0.08	0.03	0.06	4.72	7.40
Benzo[b]fluoranthene	BbF	0.03	0.05	0.02	0.03	2.33	2.90
benzo[k]fluoranthene	BkF	0.05	0.08	0.03	0.06	2.27	2.36
benzo[a]pyrene	BaP	0.06	0.06	0.04	0.05	2.68	3.97
dibenzo[a.h]anthracene	DBA	0.03	0.06	0.02	0.04	1.93	2.97
indeno[1,2,3-cd]pyrene	IND	0.05	0.09	0.03	0.06	2.44	2.68

The total PAHs concentrations of PM_{10} and $PM_{2.5}$ are in the ranges of 2.94–46.90 ng m^{-3} and 7.19–40.96 ng m^{-3} respectively. PAHs can be classified by their numbers of rings as follows: 2-ring including NaP; 3-ring including Acy, Fl, Phe and Ant; 4-ring including Flu, Pyr, BaA and Chr; 5-ring including BbF, BkF and BaP; 6-ring including IND, DBA and BghiP. Results show (Fig. 2) that the most abundant compounds are made up of four and six rings, while the less abundant compounds were those containing two and three rings in both $PM_{2.5}$ and PM_{10}. The lower concentrations could be explained by their higher vapor pressure and volatility in comparison with larger PAHs. Two and three ring PAHs are primarily found in the gaseous phase, resulting in a higher fraction of four to six rings PAHs in the particle phase.

Table 5 shows the relationships between PAHs in PM_{10} and $PM_{2.5}$ particles for the sampling site, located in the municipality of Belen. This municipality was selected for analysis due to the location of equipment, which allows simultaneous measurement of both PM_{10} and $PM_{2.5}$ fractions. In BE-HE, the Fl, BghiP, Chr, Flu, DBA and Pyr compounds showed percentages above 80%, primarily in the $PM_{2.5}$ fraction. When comparing the average data of concentrations of Fl, Flu, BghiP, BaA, Pyr, BkF, BaP, DBA and IND obtained in the Metropolitan Area of San José (Table 6) with annual average data reported in urban centers of other countries (China, Korea, Chile and Italy), most cities showed lower concentrations than San Jose, except Mexico City, which reported similar concentrations (Saldarriaga, 2008).

Also, when the Kruskall-Wallis statistical test was applied to determine if there were significant differences between monitoring sites (significance level of 0.05), the study showed that BE-HE, ER-HE and CNU-SJ sites were found to be significantly different ($p > 0.05$). The concentration values of $\sum$15 PAHs in these sites were ranged to 385–680% higher than values for the samples collected in the other sites. This is due to the role of BE-HE, CNU-SJ and ER-HE as industrial and high traffic commercial areas. In BE-HE, ER-HE and CNU-SJ sites, 4-ring PAHs (72.3–71.4%) and 6-rings (17.4–19.4%) exhibit the highest mass percentages when compared with other sites. The high percentage of high molecular weight PAHs indicates the sources are high temperature processes, such as the combustion of fuels in engines (Mostert et al., 2010).

On the other hand, most of the sampling sites located in commercial and residential zones ((EA-SJ, UTN-AL, CAT-SJ, SP-SJ) showed higher mass percentages for 2 (11.9–13.5%) and 3 rings (18.0–24.5%) PAHs, compared to the same compounds reached in the industrial sites (1.3–6.9%).

Some individual PAHs (except Ant, Pyr, IND y BbF) showed seasonal trends (Table 7) with higher concentrations found in rainy season (May–November) (p-values < 0.001) than in the dry season (January–April). For example, total mean concentrations of PAHs were 38.05 and 9.82 ng/m^3 for the rainy season and 22.1 and 5.72 ng/m^3 for the dry season in the CNU-SJ and CRH-SJ sites, respectively. This may be explained by the fact that the compounds identified in this study are photosensitive, so a greater abundance is expected in the rainy season as the increase in cloud cover directly decreases the intensity of radiation in the atmosphere. However, not all compounds have the same sensitivity to radiation. As it is shown in Fig. 3, the low molecular weight PAHs mass percentage is significantly reduced within all the sampling sites during the dry season. On the other hand, high molecular weight PAHs mass percentage increased at the same period, due to their low vapor pressure that makes to be kept in the particles. Additionally, PM_{10} and $PM_{2.5}$ mass concentrations were lower during the dry season and increased gradually in the rainy season. This situation can be explained as during the dry season, the average wind speed in the Metropolitan Area increases as a result of the influence of Alisios winds movement from the Caribean Sea favoring the dispersion of pollutants.

3.2. Potential sources of emissions

Several authors have reported using diagnostic ratios as a tool to approach PAHs emission sources with greater certainty. In this study, these ratios were calculated from the mean values of PAHs ratios (Table 8). The ratio of Flu/(Flu + Pyr) is lower than 0.40 for the petroleum source, and higher than 0.50 for biomass and coal combustion (Han et al., 2011). The IND/(IND + BghiP) ratio can be used to identify traffic sources. The value in the range from 0.35 to 0.70 indicates that the PAHs were emitted from diesel engines (Ravindra et al., 2006). The BaA/(BaA + Chr) ratios in the range from 0.35 to 0.70 was also used for identifying the dominant source of PAHs at the roadside environment and in particular the origin can be associated to diesel engines, vehicle emissions and wood burning (Kaur et al., 2013). Six ring-PAH ratio (BaP/BghiP) have been used in order to identify between traffic and non-traffic sources of PAHs. Low BaP/BghiP ratios indicate that vehicular traffic is the major PAH source and higher values indicate other fuel sources (Brown and Brown, 2012).

Table 8 showed that for PM_{10} and $PM_{2.5}$, the averaged values of Flu/(Flu + Pyr) are ranged to 0.26–0.48 and 0.32–0.35, respectively. It indicates that petroleum derivated combustion are important sources for PAHs in the Metropolitan Area. For all the sampling sites, the averaged BaA/(BaA + Chr) ratio is higher than 0.35, indicated that PAHs could be originated from engine emissions.

Table 4
PAHs average concentration (ngm^{-3}) for PM_{10} and $PM_{2.5}$ sampling sites. January to November 2013.

	Sampling site													
	BE-HE $PM_{2.5}$	BE-HE PM_{10}	ER-HE PM_{10}	MT-SJ PM_{10}	PI-CA PM_{10}	EA-SJ PM_{10}	UTN-AL PM_{10}	CAT-SJ PM_{10}	SP-SJ PM_{10}	CRH-SJ PM_{10}	CNU-SJ PM_{10}	RNZ-SJ PM_{10}	PM-SJ $PM_{2.5}$	ES-SJ PM_{10}
N	44	45	42	44	44	45	45	42	42	43	44	44	42	43
PM (μgm^{-3})	29 (14)	38 (12)	31 (16)	23 (8)	26 (7)	17 (5)	27 (7)	23 (6)	27 (7)	29 (8)	34 (9)	23 (7)	22 (7)	22 (6)
∑ PAHs	40.96	46.90	39.10	4.06	4.87	4.11	7.20	2.94	3.21	8.00	29.08	6.04	7.19	5.31
NaP	0.55 (0.13)	0.80 (0.20)	1.00 (0.60)	0.90 (0.60)	0.40 (0.30)	0.49 (0.36)	1.00 (0.30)	0.41 (0.19)	0.37 (0.21)	0.29 (0.10)	0.70 (0.60)	0.52 (0.34)	0.42 (0.35)	0.67 (0.53)
Acy	1.25 (0.50)	2.00 (1.10)	1.00 (0.70)	0.50 (0.30)	2.33 (1.24)	0.34 (0.18)	0.70 (0.40)	0.34 (0.23)	0.60 (0.29)	0.46 (0.26)	1.00 (0.30)	0.47 (0.21)	0.77 (0.45)	0.49 (0.38)
Fl	0.70 (0.40)	0.80 (0.50)	0.80 (0.45)	0.10 (0.03)	0.08 (0.02)	nd	0.40 (0.10)	nd	nd	nd	0.50 (0.10)	0.18 (0.05)	0.26 (0.08)	0.14 (0.04)
Phe	0.30 (0.20)	0.40 (0.20)	0.70 (0.40)	0.20 (0.08)	0.37 (0.19)	0.35 (0.17)	0.35 (0.16)	0.15 (0.03)	0.14 (0.08)	0.22 (0.16)	0.40 (0.30)	0.23 (0.06)	0.23 (0.17)	0.17 (0.04)
Ant	0.03 (0.01)	0.04 (0.02)	0.08 (0.07)	0.03 (0.01)	0.10 (0.04)	0.05 (0.02)	0.05 (0.02)	0.04 (0.01)	0.06 (0.01)	0.05 (0.02)	0.14 (0.05)	0.04 (0.01)	0.05 (0.01)	0.04 (0.01)
BghiP	0.18 (0.10)	0.20 (0.10)	0.40 (0.30)	0.14 (0.06)	0.12 (0.05)	0.20 (0.12)	0.20 (0.10)	0.20 (0.11)	0.28 (0.06)	0.29 (0.16)	0.21 (0.07)	0.20 (0.13)	0.24 (0.12)	0.19 (0.09)
Chr	0.14 (0.08)	0.16 (0.08)	0.50 (0.20)	0.37 (0.02)	0.07 (0.03)	0.17 (0.09)	0.46 (0.17)	0.10 (0.04)	0.15 (0.02)	0.13 (0.09)	0.18 (0.01)	0.12 (0.05)	0.14 (0.05)	0.08 (0.04)
BaA	29.20 (0.20)	33.00 (11.00)	24.00 (9.00)	1.00 (0.18)	0.79 (0.53)	1.08 (0.67)	2.50 (0.50)	0.52 (0.72)	0.11 (0.03)	4.75 (1.30)	20.00 (3.00)	3.22 (1.81)	3.83 (2.32)	2.56 (1.37)
Flu	0.09 (0.05)	0.11 (0.08)	0.60 (0.30)	0.04 (0.02)	0.03 (0.01)	0.14 (0.08)	0.30 (0.20)	0.07 (0.03)	0.09 (0.01)	0.09 (0.05)	0.20 (0.08)	0.08 (0.04)	0.07 (0.03)	0.05 (0.02)
Pyr	0.17 (0.10)	0.20 (0.10)	0.80 (0.60)	0.09 (0.04)	0.07 (0.05)	0.29 (0.16)	0.32 (0.16)	0.11 (0.08)	0.14 (0.04)	0.25 (0.12)	0.27 (0.01)	0.14 (0.06)	0.15 (0.05)	0.09 (0.04)
B(b)F	0.16 (0.10)	0.20 (0.10)	1.00 (0.80)	0.13 (0.07)	0.08 (0.05)	0.22 (0.12)	0.30 (0.07)	0.19 (0.13)	0.16 (0.11)	0.39 (0.25)	0.38 (0.09)	0.18 (0.12)	0.19 (0.11)	0.17 (0.07)
BkF	0.09 (0.05)	0.13 (0.05)	0.12 (0.07)	0.07 (0.02)	0.08 (0.02)	0.11 (0.06)	0.07 (0.03)	0.08 (0.05)	0.12 (0.03)	0.14 (0.07)	0.08 (0.05)	0.08 (0.04)	0.12 (0.04)	0.07 (0.03)
BaP	0.20 (0.08)	0.26 (0.10)	0.30 (0.20)	0.15 (0.05)	0.08 (0.04)	0.20 (0.12)	0.19 (0.10)	0.21 (0.14)	0.31 (0.08)	0.25 (0.17)	0.18 (0.06)	0.17 (0.11)	0.19 (0.09)	0.14 (0.08)
DBA	7.40 (0.40)	7.80 (0.70)	7.50 (0.90)	0.05 (0.02)	0.06 (0.01)	0.06 (0.05)	0.06 (0.08)	0.10 (0.09)	0.10 (0.07)	0.05 (0.03)	4.56 (0.02)	0.07 (0.02)	0.06 (0.02)	0.06 (0.02)
IND	0.50 (0.20)	0.80 (0.20)	0.30 (0.20)	0.30 (0.10)	0.21 (0.11)	0.41 (0.24)	0.30 (0.10)	0.42 (0.15)	0.58 (0.12)	0.64 (0.35)	0.28 (0.15)	0.34 (0.21)	0.47 (0.23)	0.39 (0.19)

Value in parenthesis shows the data standard deviation.

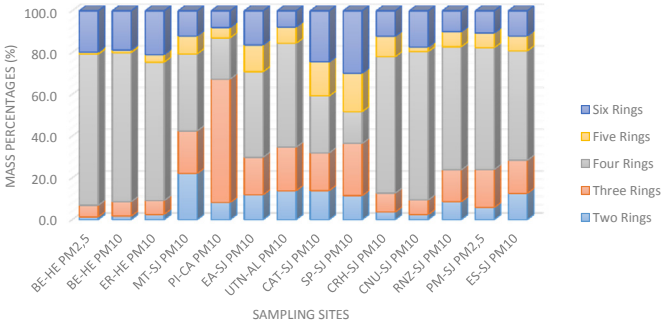


Fig. 2. PAHs distribution by the number rings at the sampling sites.

Table 5
$PM_{2.5}/PM_{10}$ PAHs concentration ratios for BE-HE sampling site. January to November 2013.

Compound	Ratio $PM_{2.5}/PM_{10}$
NaP	0.69
Acy	0.62
Fl	0.88
Phe	0.75
Ant	0.75
BghiP	0.90
Chr	0.88
BaA	0.88
Flu	0.82
Pyr	0.85
B(b)F	0.80
BkF	0.69
BaP	0.77
DBA	0.95
IND	0.62

BaP/BghiP ratios are between 0.67 and 1.11. According to these results, the existence of a common source of PAHs (i.e. industry) is noticeable. The relationship between IND and BghiP for most sites show values between 0.4 and 0.8. According to Rogge (1993), this may be produced by the contribution from diesel vehicles. In addition, Yang (1998) states that a 0.36–0.57 ratio indicates a contribution from industrial furnaces. On the other hand, IND and BghiP are gasoline vehicle combustion markers (Khalili et al., 1995; Kulkarni and Venkataraman, 2000) that show higher average concentrations in sampling sites located in San Jose (CAT-SJ, SP-SJ, CRH-SJ) and Belen (BE-HE). Fl was present in Alajuela (UTN-AL), San Jose (CAT-SJ, SP-SJ, CRH-SJ) and Heredia (ER-HE). Cry, Pyr and BbF isomers are considered products of diesel vehicle combustion, and were found in all of the analyzed sampling sites; providing proof of the contribution of mobile sources to PAHs compounds. There were not a significantly difference between averaged diagnostics ratios in dry and rainy seasons.

Table 6
PAHs concentration in PM_{10} (ng/m^3) compilation for different urban centers.

Compound	Liwan. Chine	Napoles (Italy)	Santiago (Chile)	Seoul (Korea)	México DF (México)	San José (this paper)
Fl	0.7	1.4	1.6	2.3	0.2	nd
Phe	0.8	0.9	1.9	1.5	–	0.2
BghiP	12.8	7.1	22.3	3.2	0.9	0.2
BaA	1.3	1.6	2.5	1.8	0.2	1.6
Pyr	–	–	–	–	0.2	0.2
BkF	3.0	5.7	3.2	4.9	0.7	0.4
BbF	5.6	2.2	4.0	2.6	0.3	0.2
DBA	4.3	–	2.9	–	0.1	0.1
IND	7.8	3.7	9.9	3.6	0.7	0.5

San Jose data was calculated as average concentration of all sampling sites located in this municipality. Source: Saldarriaga, 2008.

Table 7
Dry and rainy season PAHs average concentration (ngm^{-3}) in PM_{10} and $PM_{2.5}$ at San Jose sampling sites.

	Sampling sites														
	Rainy season							Dry season							
	CAT-SJ	SP-SJ	CRH-SJ	CNU-SJ	RNZ-SJ	PM-SJ	ES-SJ	CAT-SJ	SP-SJ	CRH-SJ	CNU-SJ	RNZ-SJ	PM-SJ	ES-SJ
N	27	28	29	30	29	28	29	15	14	14	14	15	14	14
PM (μg/m^3)	28 (5)	32 (6)	35 (5)	38 (9)	30 (6)	26 (7)	25 (6)	20 (4)	23 (5)	27 (6)	29 (5)	19 (5)	20 (3)	18 (6)
NaP	0.58 (0.11)	0.51 (0.23)	0.41 (0.35)	1.20 (0.27)	0.81 (0.33)	0.76 (0.29)	0.57 (0.22)	0.23 (0.17)	0.28 (0.14)	0.22 (0.09)	0.25 (0.13)	0.10 (0.06)	0.26 (0.14)	0.35 (0.16)
Acy	0.45 (0.14)	1.02 (0.45)	0.59 (0.16)	1.61 (0.09)	0.59 (0.13)	1.03 (0.35)	0.72 (0.29)	0.27 (0.12)	0.29 (0.07)	0.28 (0.13)	0.36 (0.15)	0.41 (0.17)	0.45 (0.23)	0.31 (0.16)
Fl	nd	nd	nd	0.62 (0.25)	0.27 (0.14)	0.40 (0.03)	0.10 (0.06)	nd	nd	nd	0.45 (0.23)	0.13 (0.08)	0.16 (0.12)	0.17 (0.08)
Phe	0.22 (0.09)	0.18 (0.05)	0.27 (0.09)	0.43 (0.14)	0.26 (0.05)	0.15 (0.08)	0.09 (0.03)	0.10 (0.05)	0.10 (0.07)	0.17 (0.08)	0.35 (0.15)	0.16 (0.11)	0.30 (0.15)	0.24 (0.11)
Ant	0.03 (0.01)	0.06 (0.02)	0.04 (0.02)	0.08 (0.01)	0.02 (0.02)	0.04 (0.01)	0.04 (0.02)	0.04 (0.03)	0.06 (0.03)	0.06 (0.02)	0.17 (0.03)	0.05 (0.02)	0.05 (0.01)	0.04 (0.02)
BghiP	0.21 (0.09)	0.29 (0.12)	0.33 (0.14)	0.22 (0.08)	0.23 (0.10)	0.26 (0.09)	0.21 (0.05)	0.18 (0.12)	0.26 (0.12)	0.24 (0.14)	0.21 (0.12)	0.18 (0.15)	0.21 (0.08)	0.16 (0.09)
Chr	0.11 (0.07)	0.18 (0.09)	0.15 (0.08)	0.24 (0.07)	0.16 (0.05)	0.17 (0.06)	0.10 (0.04)	0.08 (0.06)	0.12 (0.08)	0.11 (0.07)	0.11 (0.15)	0.08 (0.05)	0.10 (0.07)	0.06 (0.04)
BaA	0.95 (0.32)	0.16 (0.11)	6.41 (1.24)	27.2 (3.22)	4.48 (1.14)	5.58 (0.73)	2.86 (0.87)	0.15 (0.09)	0.06 (0.05)	2.55 (2.73)	14.6 (5.61)	2.54 (0.92)	1.35 (1.74)	2.03 (1.29)
Flu	0.07 (0.03)	0.11 (0.05)	0.12 (0.04)	0.25 (0.10)	0.09 (0.02)	0.09 (0.03)	0.06 (0.02)	0.05 (0.03)	0.07 (0.04)	0.06 (0.05)	0.17 (0.09)	0.05 (0.03)	0.04 (0.03)	0.03 (0.02)
Pyr	0.09 (0.04)	0.12 (0.08)	0.14 (0.05)	0.18 (0.11)	0.10 (0.08)	0.10 (0.07)	0.06 (0.04)	0.13 (0.07)	0.17 (0.09)	0.40 (0.15)	0.31 (0.12)	0.19 (0.09)	0.18 (0.08)	0.12 (0.05)
B(b)F	0.16 (0.05)	0.10 (0.06)	0.29 (0.16)	0.25 (0.11)	0.15 (0.06)	0.10 (0.07)	0.17 (0.09)	0.21 (0.07)	0.20 (0.08)	0.47 (0.21)	0.54 (0.18)	0.21 (0.09)	0.28 (0.13)	0.20 (0.06)
BkF	0.09 (0.04)	0.14 (0.05)	0.27 (0.06)	0.12 (0.02)	0.09 (0.04)	0.11 (0.03)	0.08 (0.04)	0.07 (0.05)	0.11 (0.05)	0.10 (0.11)	0.07 (0.05)	0.06 (0.04)	0.06 (0.07)	0.06 (0.03)
BaP	0.24 (0.09)	0.33 (0.14)	0.29 (0.08)	0.21 (0.09)	0.22 (0.05)	0.26 (0.07)	0.17 (0.04)	0.17 (0.09)	0.29 (0.13)	0.21 (0.17)	0.17 (0.09)	0.12 (0.07)	0.13 (0.11)	0.10 (0.08)
DBA	0.13 (0.03)	0.17 (0.08)	0.05 (0.02)	5.11 (1.02)	0.10 (0.02)	0.04 (0.02)	0.06 (0.03)	0.07 (0.04)	0.05 (0.02)	0.04 (0.03)	3.95 (1.45)	0.04 (0.03)	0.07 (0.03)	0.04 (0.03)
IND	0.37 (0.15)	0.57 (0.22)	0.46 (0.22)	0.17 (0.08)	0.25 (0.10)	0.32 (0.12)	0.30 (0.13)	0.47 (0.21)	0.78 (0.13)	0.81 (0.17)	0.42 (0.19)	0.39 (0.12)	0.58 (0.15)	0.47 (0.12)

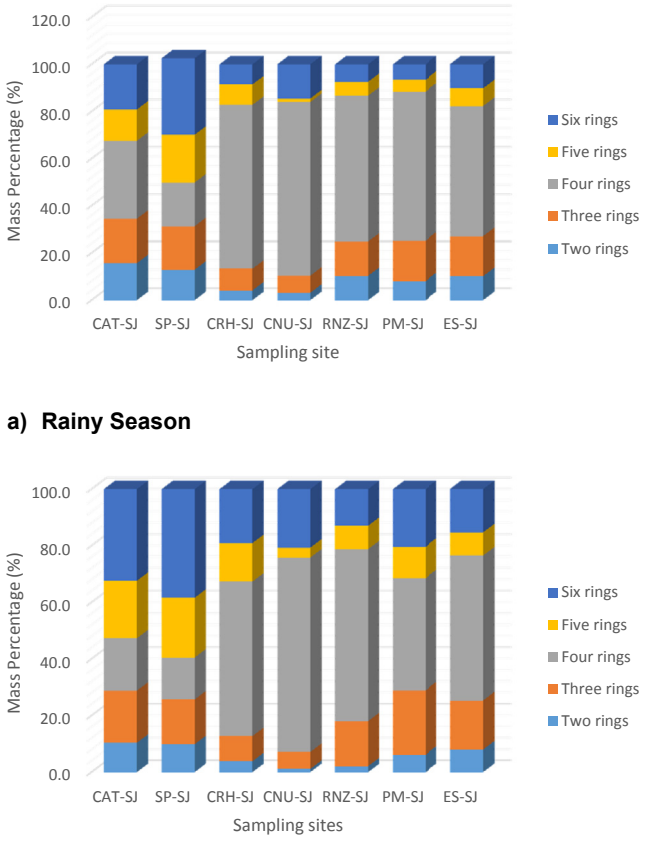


Fig. 3. Temporal PAHs distribution by the number rings at the sampling sites.

Once potential PAHs emission sources were established, it was essential to use Spearman's correlation coefficient as a means of corroborating some preliminary findings. As shown in Table 9, the most important correlations for PAHs in PM_{10} primarily occur between gasoline and diesel combustion markers. As mentioned above, IND is a gasoline vehicle combustion marker similar to BkF; the correlation coefficient between these compounds is 0.631 and their isomer is 0.590, indicating a moderate to high correlation. On

Table 8
PAHs diagnostic relations for PM_{10} samples obtained in the Costa Rican Metropolitan Area.

Site	BaP / BghiP	IND / IND + BghiP	BaA / Chr + BaA	Flu / Flu + Pyr
BE-HE $PM_{2.5}$	1.11	0.74	1.00	0.35
BE-HE PM_{10}	1.30	0.80	1.00	0.35
ER-HE	0.75	0.43	0.98	0.43
MT-SJ	1.07	0.68	0.73	0.31
PI-CA	0.67	0.64	0.92	0.30
EA-SJ	1.00	0.67	0.86	0.33
UTN-AL	0.95	0.60	0.84	0.48
CAT-SJ	1.05	0.68	0.84	0.39
SP-SJ	1.11	0.67	0.42	0.39
CRH-SJ	0.86	0.69	0.97	0.26
CNU-SJ	0.86	0.57	0.99	0.43
RNZ-SJ	0.85	0.63	0.96	0.36
PM-SJ	0.79	0.66	0.96	0.32
ES-SJ	0.74	0.67	0.97	0.36

Table 9
Spearman correlation coefficients for PAHs concentrations in PM_{10}.

	Nap	Acy	Fl	Phe	Ant	BghiP	Chr	BaA	Flu	Pyr	BbF	BkF	BaP	DBA
Nap														
Acy	0.268													
Fl	0.003	−0.096												
Phe	0.122	0.121	0.074											
Ant	0.027	0.092	0.080	0.378										
BghiP	0.157	0.117	0.199	**0.493**	**0.574**									
Chr	0.137	0.277	−0.002	**0.539**	0.433	**0.692**								
BaA	0.137	0.287	0.261	0.246	0.081	0.213	0.339							
Flu	0.104	0.154	0.149	**0.551**	**0.644**	**0.712**	**0.731**	0.417						
Pyr	0.054	0.157	−0.025	**0.527**	0.421	**0.617**	**0.815**	0.368	**0.793**					
BbF	0.102	0.128	0.163	**0.464**	**0.551**	**0.812**	**0.703**	0.341	**0.770**	**0.663**				
BkF	0.077	0.033	0.103	0.319	**0**.410	**0.714**	**0.634**	0.132	**0.610**	**0.586**	**0.620**			
BaP	0.127	0.138	0.192	0.374	**0.496**	**0.733**	**0.753**	0.253	**0.722**	**0.616**	**0.720**	**0.655**		
DBA	0.168	0.221	0.150	0.255	0.215	0.430	0.422	**0.480**	0.487	0.444	0.371	0.413	0.410	
IND	0.066	−0.018	0.130	0.192	0.392	**0.643**	0.367	−0.185	0**.469**	0.337	**0.590**	**0.631**	**0.585**	**0.975**

Bold numbers represent significant correlations at $p < 0.05$.

the other hand, BghiP (Khalili et al., 1995; Kulkarni and Venkataraman, 2000) is considered another gasoline marker with a high correlation to benzofluoranthene isomers (0.812 for [b] and 0.714 for [k]). The BkF isomer is also registered in gasoline mobile sources.

In the case of diesel vehicle emissions, there are high correlations between PAHs compounds (Khalili et al., 1995; Kulkarni and Venkataraman, 2000; and Simcik et al., 1999) such as Chr with Flu (0.731), Pyr (0.815) with BbF y BkF (0.703 and 0.634), BaP (0.733) and IND (0.643). Wood burning contributions show a moderate correlation between Fl and Flu (0.551) and Fl and Pyr (0.527). These results, compared to those obtained in mobile source markers, indicate that wood burning is a source, but not the main cause of PAH compounds emissions, since Pyr and Flu are also diesel combustion products and the relationship between them could also be from mobile sources.

Table 10 shows very high correlations between gasoline and diesel combustion markers in $PM_{2.5.}$ However, it also shows a different correlation for burning wood markers when compared to Table 9, in which the Fl–Flu relationship changes from moderate to high (0.725), indicating that biomass burning processes directly contribute to the smallest fraction.

Four factors were obtained after a PMF analysis of the PAHs concentration database—each with a profile that could have physical meaning (Fig. 4). In the PMF analysis, the Q value indicates the degree of concordance in the adjustment model (Comero et al., 2009) while the r^2 value represents the degree of correlation between measured and estimated concentrations (Wang et al., 2009). In this study, the Q value for the data series converged on a stable value of 55.1. The theoretical Q value and the average r^2 were 62.1 and 0.967, respectively.

Results indicated a significant influence of emissions from mobile sources, particularly gasoline and diesel combustion engines, which were responsible for 62%–74% of total PAHs emissions in the area. Gasoline profiles were mainly identified by the presence of BaP, Fl and BghiP, while diesel profiles were identified by a greater presence of BghiP, BbF, Chr, Flu and Pyr and reports from other studies (Ravindra et al., 2008). These results are consistent with data obtained in the diagnostic relationship analysis, which mainly characterizes diesel and gasoline emissions.

Wood combustion turned out to be the second main source of PAHs emissions, responsible for 7%–15%. Wood combustion profiles were mainly identified by the presence of Acy and BaP, as reported in other studies (Schauer et al., 2001; Kulkarni and Venkataraman, 2000).

Road dust contributed nearly 8% of fine particles, resulting from the mixture of various sources (road surfaces, exhaust pipes, oil and fuel, tires, and building materials), thus comprising a group of contributions from multiple sources (Liu et al., 2007). The dust profile was mainly identified by presence of BaP, IND, Chr and Pyr, as reported in other studies (Liu et al., 2007; Park and Kim, 2004).

Table 10
Spearman correlation coefficients for PAHs concentrations in $PM_{2.5}$.

	Nap	Acy	Fl	Phe	Ant	BghiP	Chr	BaA	Flu	Pyr	BbF	BkF	BaP	DBA
Nap														
Acy	0.538													
Fl	−0.078	0.156												
Phe	−0.380	−0.211	−0.257											
Ant	0.177	0.215	**−0.591**	**0.657**										
BghiP	0.213	0.355	0.085	**0.452**	**0.542**									
Chr	0.153	0.356	0.175	**0.479**	**0.512**	**0.911**								
BaA	−0.259	0.110	**0.816**	0.015	−0.365	0.271	0.394							
Flu	−0.097	0.008	−0.052	**0.725**	**0.623**	**0.690**	**0.739**	0.136						
Pyr	−0.048	0.259	0.111	**0.549**	**0.478**	**0.768**	**0.774**	0.246	**0.737**					
BbF	−0.042	0.146	0.415	0.322	0.173	**0.477**	**0.530**	0.411	**0.455**	**0.535**				
BkF	0.139	0.255	0.060	**0.517**	**0.579**	**0.966**	**0.942**	0.244	**0.773**	**0.772**	**0.529**			
BaP	0.201	0.342	−0.048	0.316	**0.448**	**0.737**	**0.688**	0.045	**0.590**	**0.588**	0.248	**0.776**		
DBA	0.120	0.113	−0.100	**0.571**	**0.556**	**0.688**	**0.681**	−0.009	**0.796**	**0.693**	0.393	**0.759**	**0.682**	
IND	0.122	0.291	0.097	**0.547**	**0.557**	**0.975**	**0.932**	0.281	**0.726**	**0.824**	**0.525**	**0.973**	**0.753**	**0.749**

Bold numbers represent significant correlations at $p < 0.05$.

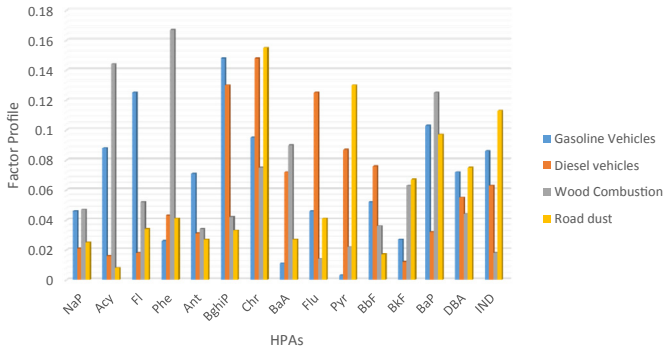


Fig. 4. Plot of profiles of each factor obtained by the PMF model.

4. Conclusions

According to the data collected in this study, the most abundant PAHs are formed by five or six rings (IND, DBA and BbF), while the less abundant PAHs are formed by two to four rings (NaP, Fl and Flu). BaA was found in all monitoring sites; however, it showed significant concentration differences in collectors located in commercial, commercial/residential and industrial areas. $PM_{2.5}/PM_{10}$ ratios reveal that Fl, Flu and Pyr compounds showed percentages of over 80%, the main contribution of which was from mobile sources, indicating a possible source of PAHs.

Data obtained when using diagnostic relationships for both PM_{10} and $PM_{2.5}$ suggest that mobile sources make the greatest contributions of PAHs to the environment; these primarily include diesel and gasoline combustion, with a smaller contribution coming from industrial furnaces. The Spearman's rank correlation coefficient showed very high correlations for diesel and gasoline combustion markers, and moderate correlations for industrial furnaces. This proves the importance of the contribution of mobile sources to average daily PAHs concentrations.

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