Polycyclic Aromatic Hydrocarbons (PAHs) Associated with PM$_{2.5}$ in Guadalajara, Mexico: Environmental Levels, Health Risks and Possible Sources

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Abstract: PM$_{2.5}$ samples were collected from January 2009 to January 2010 at two sampling sites located in the downtown (Centro) and toward the southwest (Miravalle) in the city of Guadalajara, Mexico. The environmental concentrations of 14 selected polycyclic aromatic hydrocarbons (PAHs) in PM$_{2.5}$ were identified and quantified. The most abundant PAHs in PM$_{2.5}$ samples were benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, benzo[*b*]fluoranthene, benzo[*a*]pyrene and benzo[*k*]fluoranthene, accounting for approximately 75% of the total PAHs. The total PAH concentrations at the two sampling sites ranged from 0.65 to 19.62 ng·m^{-3}. Spatial variations were found during the dry-warm season, which were attributed mainly to differing intensities of local traffic and less dispersion of air pollutants in Miravalle. Seasonal variations were associated with increases in rainfall (June-September) and differences in temperature (January–May and October–January). The benzo(a)pyrene-equivalent (BaPE) and BaP results suggest that exposure to PM$_{2.5}$-containing carcinogenic PAHs (C-PAHs) in Miravalle during the warm-dry and cold-dry seasons can be seen as representing a serious risk to human health. The contributions from potential sources to PAHs in PM$_{2.5}$ were evaluated by the diagnostic ratios between PAHs and principal component analysis (PCA). In the whole sampling period, vehicular emission activity, probably related to light and heavy traffic, was found to be the predominant contributor to PM$_{2.5}$-bound PAHs.

Keywords: PM$_{2.5}$; PAHs; source emission; health risks; BaPE

1. Introduction

Airborne particulate matter is an atmospheric contaminant that constitutes a potential hazard to citizens in polluted urban areas. Several epidemiological studies [1,2] have enlightened knowledge on this topic. Exposure to the breathable fraction of particulate matter is the most concerning because it has been found that it is the most detrimental to human health [3]. Thus far, particles with a size smaller than 2.5 μm (PM$_{2.5}$) have shown the most significant association with increases in mortality by lung cancer and cardio-respiratory diseases by long-term exposure [4]. Although there is still disagreement on the main mechanisms responsible for the health effects [5], it is well known that various harmful organic components, elements and inorganic chemical substances, which are all part of particulates, can be a human health risk [6,7].

In the organic fraction of $PM_{2.5}$, the polycyclic aromatic hydrocarbons (PAHs) are one of the most widely studied groups of organic compounds, since 16 PAHs have been listed as priority pollutants by the U.S. Environmental Protection Agency [8] because they are considered as possible or probable human carcinogens [9,10]. They are also mutagenic and can undergo atmospheric photochemical reaction in the gas phase and on particle surfaces [11,12] and can be photo-chemically transformed into highly toxic compounds such as nitrated (nitro-PAHs) and oxygenated PAHs (oxy-PAHs). They can be emitted from the incomplete combustion of carbon-containing materials and are mostly from anthropogenic sources in urban environments such as coal combustion and vehicular emissions [13]. Furthermore, they are predominantly associated with particles of smaller sizes [14]. Therefore, in order to better understand the air quality and provide more reliable support, it is essential to investigate PAHs associated with breathable particles and their emissions sources in urban zones, which would be used by local government and environmental policymakers to protect human health and improve the well-being of the population.

The Metropolitan Zone of Guadalajara is the second most densely populated area in Mexico. Deterioration of air quality, mainly in dry seasons, may be a consequence of the rapid industrial growth and high vehicular traffic in this area; it was also suggested that atmospheric conditions might favour photochemical oxidants and the blockage of pollutants [15]. Although there is an atmospheric monitoring network and studies on trace metals and inorganic ions in $PM_{2.5}$ [15,16], it is still necessary to undertake organic chemical characterization of breathable particulate matter to identify sources and to provide support to local government in the design of viable strategies with benefits to the population. A recent study found that naphthalene, phenanthrene, anthracene and chrysene likely undergo photochemical transformation to their quinones compounds, which were found in $PM_{2.5}$ at three urban locations within the Metropolitan Zone of Guadalajara during the dry and rainy season in 2012 [17]. However, there are no published data on PAHs associated with $PM_{2.5}$ before 2012. Therefore, this is the first report that focuses on analysis of PAHs in $PM_{2.5}$ in Guadalajara.

Hence, the aims of this work were to determine the PAH concentrations in $PM_{2.5}$, evaluate the potential cancer risk and identify the possible sources at two sites and during three seasons in Guadalajara city, México.

2. Materials and Methods

2.1. Material and Reagents

Standards of PAHs were obtained as a mixture, containing naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Acn), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), and benzo[*ghi*]perylene (BghiP) and dibenz[*ah*]anthracene (DBahA). Internal standards were also obtained as mixtures consisting of five deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, Phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}). Both sets of standards were supplied by Restek (Bellefonte, PA, USA). Solvents, HPLC grade, such as methylene chloride, acetone and *n*-hexane, were purchased from Burdick and Jackson-Honeywell (Muskegon, MI, USA).

2.2. Sampling of $PM_{2.5}$ and Meteorological Conditions

The study was performed on the flat roofs of two local health facilities at Guadalajara, Jalisco, Mexico. Centro (CEN), situated in the downtown, is an urban site with commercial and service activities and is surrounded by heavily travelled and paved curbed surface streets with light duty vehicles and heavy-duty diesel buses. Miravalle (MIR), located to the southwest in the city of Guadalajara, is 100 m from a major arterial street with fast vehicular traffic and a rapid transport system for passengers and is surrounded by dense residential areas and some industrial facilities (Figure 1). Those places were selected because they have atmospheric monitoring stations run by the Jalisco State

Government and have validated historical registers of $PM_{2.5}$ and meteorological measurements, which were kindly supplied for this study.

The samples of $PM_{2.5}$ were collected with a Partisol 2300 sampler (Rupprecht & Patashnick Co., Albany, NY, USA) at flow rate of 16.7 L·min^{-1} on quartz fiber filters (47 mm; Whatman) that were baked (600 °C, 8 h) before the collection to diminish organic compounds adsorbed during their transport and handling. The samples were collected approximately every third day for 24 h from January 2009 to January 2010, transported in a sealed Petri dish and stored until analysis at 4 °C. In order to obtain a sufficient amount of sample to reach the detection threshold of the chemical analysis, a pair of samples was simultaneously collected each day within 24 h, and then both filters were extracted together.

The samples were collected under three different meteorological conditions (Tables S1 and S2): The warm-dry season (WDS), from January through May 2009, was characterized by thermal inversions and the highest temperature (24 ± 2 °C); the rainy season (RS) from June through September 2009 was characterized by higher rainfall and the highest relative humidity (67 ± 17%); and the cold-dry season (CDS), from October (2009) to through January (2010), was characterized by the lowest temperature (20 ± 2°C).
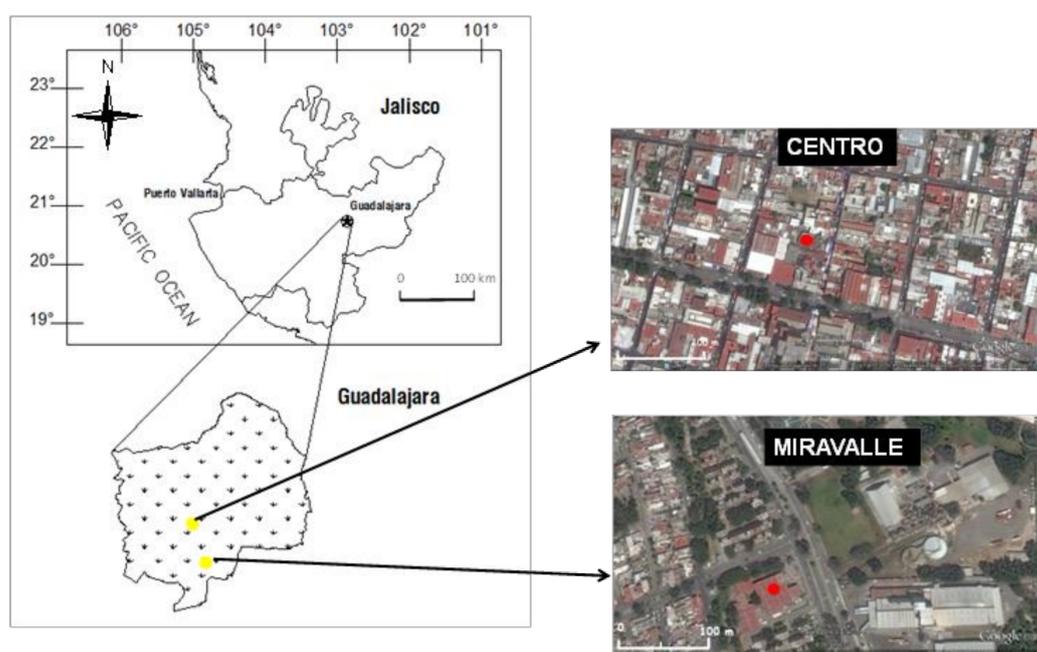
Figure 1. Location of the sampling sites in Guadalajara, Jalisco (Mexico).

2.3. Determination of PAHs: Analysis and Quality Controls

The HAPs were extracted from $PM_{2.5}$ twice with 30 mL of methylene chloride at 40 °C by ultrasonic bath (Bransonic) for 30 min. The extraction was carried out in a flask that was fitted to a condenser to avoid volatilization of compounds [18]. The organic extract was concentrated almost to dryness in a rotary evaporator RV10 (IKA), then passed through a Teflon filter (0.44 μm) and adjusted to 0.2 mL. The concentrated extract was then analyzed by gas chromatography (GC) 6890N (Agilent Technologies, Santa Clara, CA, USA) and mass spectrometry (MS) 5975 (Agilent Technologies). The standards of calibration and sample solutions were injected (2 μl) automatically at 280 °C and separated with a capillary column (HP5MS 30 m × 25 mm) with a film thickness of 25 μm (Agilent Technologies) with ultra-high purity (INFRA) helium as the carrier gas at a flow rate of 1 ml·min^{-1} and by a temperature program that was started at 40 °C, elevated at 20 °C·min^{-1} to 110 °C, then at 20 °C·min^{-1} to 300 °C and finally increased at 20 °C·min^{-1} to 310 °C (maintained for 10 min). The mass spectra were obtained by electronic impact (70 EV) and a quadrupole mass analyzer. The SCAN mode

was used to obtain the retention time and to select the *m/z* that was characteristic of each compound. The quantitation was carried out in SIM mode by calibration curves prepared by dilution of standards, ranging from 1.0–1000 ng/mL, with correlation coefficients (r^2) greater than 0.99 and detection limits between 0.83 and 23.50 ng/mL. The environmental concentrations in samples were corrected with blanks and recoveries (58–60%) with CV < 30%; the latter obtained by a previous optimized extraction procedure based on spiked real samples of $PM_{2.5}$ [19].

2.4. Statistical Analysis

The Mann-Whitney Utest was use to compared medians between sites and seasons. Spearman's rank test was used to obtain associations among particles, PAHs and meteorological parameters. These tests were applied only when at least three records were obtained and validated. Principal component analysis (PCA) was applied to evaluate emission sources for the whole period for each site.

3. Results and Discussion

3.1. PAHs Concentrations

The average atmospheric concentration ± standard deviation of the sum of 14 PAHs determined in $PM_{2.5}$ at Guadalajara was 5.65 ± 4.60 ng·m^{-3} and ranged from 4.55 ± 3.29 ng·m^{-3} to 10.2 ± ng·m^{-3} (Tables S1 and S2). The most abundant PAHs were those with higher molecular weight (HMW-PAHs: BghiP, IcdP, BbF, BaP and BkF), accounting for 74.7%, followed by middle molecular weight PAHs (MMW-PAHs: Chry, BaA, Pyr and Flt), accounting for 19.7%, and lower molecular weight PAHs (LMW-PAHs: Phe, Flu, Acy, Acn and Ant), accounting for 5.6% (Figure 2). Because HMW-PAHs have the lowest vapor pressure, that group of compounds tends to be more strongly associated with the particle phase than MMW- and LMW-PAH$_S$ [20].
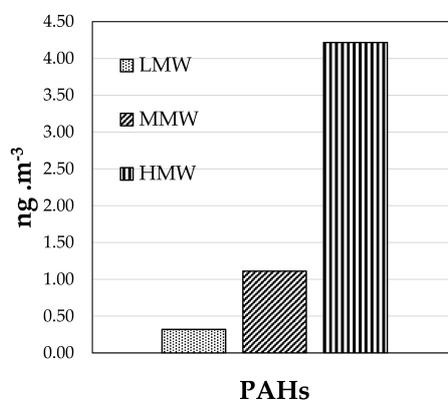

Figure 2. Abundance of the polycyclic aromatic hydrocarbons (PAHs) by molecular weight. LMW: lower molecular weight, MMW: middle molecular weight, HMW: higher molecular weight.

Individual average environmental levels of PAHs in $PM_{2.5}$ determined in this study ranged from 0.03 ng·m^{-3} (Acn) to 1.45 ng·m^{-3} (BghiP), which are the same order of magnitude as those recently reported [17], who found environmental levels of PAHs in $PM_{2.5}$ ranging from 0.01 ng·m^{-3} (Flu) to 1.25 ng·m^{-3} (BghiP) at three urban sites located in Guadalajara, México in 2012. In comparison with Mexico City, the highest city in Mexico, the concentrations found here are of the same order of magnitude as those levels reported by [21] and [22] for five local urban sites, which were found to range from 0.02 ng·m^{-3} (Flu) to 1.45 ng·m^{-3} (BghiP) but were approximately one order of magnitude lower than those recently reported, from 0.81 ng·m^{-3} (Acn) to 2.14 ng·m^{-3} (BghiP), at an urban and a semi-urban site in Cuernavaca, Mexico [23]. Guadalajara showed similar levels to Latin-American urban areas such as those found in São Paulo, Brazil [24] but much lower levels than those measured in two of Chile's urban areas, Santiago and Temuco [25]. In USA's urban sites, the compounds measured

were less abundant in cities like Atlanta [26] and those in southern California [27]. Regarding European cities, PAH levels were very similar to suburban and urban areas in Zaragoza, Spain [28], Rome, Italy [29] and in Porto, Portugal [30]. Comparable ambient levels were also reported in Nanjing [31], but the most developed and industrialized Chinese cities presented significantly higher concentrations of those compounds [32–34].

3.2. Spatial and Seasonal Patterns

Overall, average atmospheric concentrations of total PAHs were similar between both sites but showed seasonal variation, with the highest environmental levels during the dry seasons and the lowest in the rainy season (Figure 3), similar to a report from Mexico City [22]. Increases in PAH atmospheric concentrations during the cold-dry season may be attributed to lower environmental temperatures, resulting in a stronger tendency of PAH to bond to particles. Also, lower photochemical activity can lead to fewer atmospheric chemical reactions and higher ambient PAH levels, whereas a decrease in the concentrations of these compounds over the rainy season may be mainly attributed to wet deposition. Seasonal trends in Centro are consistent with those atmospheric parameters; the highest levels were found during the coldest season and the lowest were in accordance with rainfall increases and the highest temperatures. Unlike Centro, the median during the dry-warm season for Miravalle was found to be significantly higher ($p < 0.05$) than that in the cold-dry season (Figure 3b). It was observed that concentrations of HMW PAHs in Miravalle during the dry-warm period were about two times those found in Centro (Figure 3a). Since meteorological conditions such as temperature and relative humidity are similar (Figure 3) at both sites ($p > 0.05$), the different patterns in Miravalle could be mainly attributed to a substantial contribution of vehicular activity to $PM_{2.5}$ by local traffic due to the major PAHs in HMW such as IcdP and BghiP, which are indicators of fossil fuel combustion. In comparison with Centro (3.38 m/s), the lower wind speed (2.57 m/s) recorded for Miravalle could favor less dispersion of air pollutants in the warm-dry season.
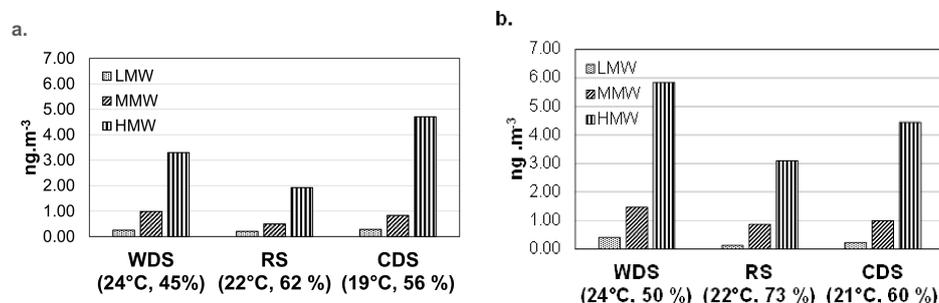
Figure 3. PAH molecular weight distribution over the three seasons in (**a**) Centro and (**b**) Miravalle. WDS: warm-dry season, RS: rainy season, CDS: cold-dry season.

3.3. Health Risks

In order to assess the carcinogenic potency for humans, the benzo(a)pyrene-equivalent (BaPE) carcinogenicity was calculated by multiplying the concentrations of each PAH species with their corresponding toxic equivalent factors (TEF); thus, atmospheric concentration of Acn, Phe, Pyr, Flt were each multiplied by 0.001, while Ant, Chry and BghiP by 0.01, BaA, BbF, BkF and IcdP by 0.1 and BaP by 1 [13,35]. The mean of the summed BaPE for the whole sampling period was 0.79 ± 0.72 ng·m^{-3} and ranged between 0.01 ng·m^{-3} and 2.52 ng·m^{-3}. The values found in Guadalajara were approximately one order of magnitude lower than those recently reported (4.05 ng·m^{-3}) in Cuernavaca, Mexico [23]. Similar levels were found in Florence, Italy (0.34–0.79 ng·m^{-3}) [36], Hamilton, Canada (0.84 ng·m^{-3}) [37] and Nanjing, China (0.42–1.35 ng·m^{-3}) [31], while higher levels were obtained in Xi'an (2–64 ng·m^{-3}) and Guangzhou (0.96–22.46 ng·m^{-3}), China [38,39]. Among those 14 HAPs, five carcinogenic compounds (C-HAPs), including BaA, BbF, BkF, BaP, and IcdP, accounted for more than 50%. In accordance with

IARC [9,10] and EPA [8], exposure to C-PAHs can be a considerable risk factor for human health. Although BaP was not the most abundant carcinogenic compound [40], it had the highest relative contribution to total potential carcinogenicity, accounting for 75%. In addition, both BaPE and BaP displayed strong seasonal variation, with their values being higher in the warm and cold seasons than in the rainy season, while they had light spatial variation with higher values in Miravalle than those found in Centro. Therefore, exposure to $PM_{2.5}$ containing C-PAHs in Miravalle during warm-dry and cold-dry seasons might present a serious risk to human health.

3.4. Sources of PAHs

3.4.1. Overall Identification

It has been shown by several ambient studies of urban districts, suburban sites and rural sites around the world that profile and individual PAHs can be used as tracers to distinguish among their diverse sources [13,24,27,29,41–43]. They have been associated with several kinds of sources like biomass burning [26], coal combustion [44], coal processing industries [45] and vehicle emissions [27,46]. In this work, the ratio of LMW, MMW and HMW was approximately 1.0:3.1:12.5 in Centro and 1.0:4.0:14 in Miravalle, indicating the dominance of HMW. It has been reported that higher high molecular weight PAH concentrations mean more typical pyrogenic products derived mainly from fossil fuel combustion [31,47], while light molecular weight-PAHs are related to non-combusted petroleum products [48]. In the urban atmosphere, those HMW-PAHs like BghiP, IcdP and BkF can be considered as tracers for vehicular emissions. In fact, BghiP is regarded as a marker of gasoline vehicles [49], while BghiP, IcdP and BbF are often the most abundant in urban areas where vehicular emission is the main source of PAH [50]. In addition, it has been observed that BghiP, IcdP, BbF, BaA and Chry are linked with both gasoline and diesel emissions [46,51,52]. Therefore, the highest environmental levels of PAHs related to fuel combustion and the influence of intense vehicular traffic in both sites suggested that PAHs in Centro and Miravalle sites may be essentially attributed to traffic exhaust.

3.4.2. Evaluation of Diagnostic Ratios

PAH isomer pair ratios are frequently used to identify the possible sources for PAHs in ambient air. The IcdP/(IcdP + BghiP), BaA/(BaA + Chry), Flt/(Flt + Pyr) and Ant/(Ant + Phe) ratios were used due to their relative stability (Figure 4). In this study, the calculated ratio values suggested a substantial contribution from vehicular traffic emissions to $PM_{2.5}$ within the Centro and Miravalle sampling areas. The ratios of IcdP/(IcdP + BghiP) varied between 0.30 and 0.52 (0.40 ± 0.05) for Centro and between 0.22 and 0.53 (0.42 ± 0.09) for Miravalle. Those values were in accordance with the range 0.20 to 0.50, where in previous studies it was shown that, for these values, the PAHs originate from petroleum sources such as liquid fossil fuel, vehicle and oil combustion [53], and those between 0.35 and 0.70 imply diesel emissions [54]. The BaA/(BaA + Chry) ratios obtained, 0.40–0.52 (0.47 ± 0.04) for Centro and 0.35–0.56 (0.44 ± 0.05) for Miravalle, were similar to 0.38–0.64 and 0.22–0.55, which have been associated with diesel and gasoline emissions, respectively [55,56]. The values of Flt/(Flt + Pyr) were 0.22–0.50 (0.45 ± 0.07) for Centro and 0.16–0.56 (0.45 ± 0.08) for Miravalle. These values are close to 0.4-0.5, which were attributed to the contribution of liquid fossil fuel combustion [57,58], specifically from gasoline combustion emissions [59]. The ratios of Ant/(Ant + Phe) were 0.02-0.20 (0.14 ± 0.05) for Centro and 0.05–0.51 (0.18 ± 0.10) for Miravalle, with most of the values >0.1, suggesting association with combustion sources [60].

3.4.3. Principal Component Analysis (PCA)

In addition to diagnostic ratios, PCA was conducted on each data set and site showing that the main contributors to PAHs were vehicular emissions activity, probably related to light and heavy traffic. However, other sources were also found, such as biomass burning and wood combustion and to a lesser extent coal combustion. For Centro (Table 1), PC1 was highly loaded with high (BbF,

IcdP, BghiP) and middle (BaA, Chry) molecular weight PAHs. IcdP is one of the tracers for gasoline vehicles [61]. BbF is used as one of the indicators for heavy-duty diesel vehicles emissions [62]. BghiP, BbF, BaA and Chry are markers of gasoline and diesel vehicles [46,50,63]. This finding is similar to those sources suggested by diagnostic ratio analysis, which also showed that fossil fuel combustion contributed to PM$_{2.5}$ in Centro. This is consistent with characteristics of vehicular traffic in Centro; this site is heavily traveled by light-duty vehicles and heavy-duty diesel buses. PC2 was predominately loaded with light molecular weight PAHs (Acn, Flu), showing an association with biomass burning or coal combustion [64]. PC3 included Phe (3-rings) and Pyr (4-rings) which are frequently associated with either wood [24] or coal combustion [65]. For Miravalle (Table 2), PC1 was highly loaded with Flt, BaA, Chry, BbF, BkF, BaP, IcdP and BghiP, which are primarily associated with gasoline and diesel vehicles [52,66]. The diagnostic ratio analysis in Miravalle was similar to PC1, i.e., PAHs in PM$_{2.5}$ are a result of mainly diesel and gasoline emissions, which are consistent with fast vehicular traffic and a rapid transport system for passengers on streets near this site. PC2 was loaded with Flu, Phe and Pyr, which are linked to wood combustion [67]. PC3 was loaded with Acn, Flu, and Ant, and PC4 with only Ant, which indicated contributions from biomass burning [68] and coal combustion [50,69], respectively.
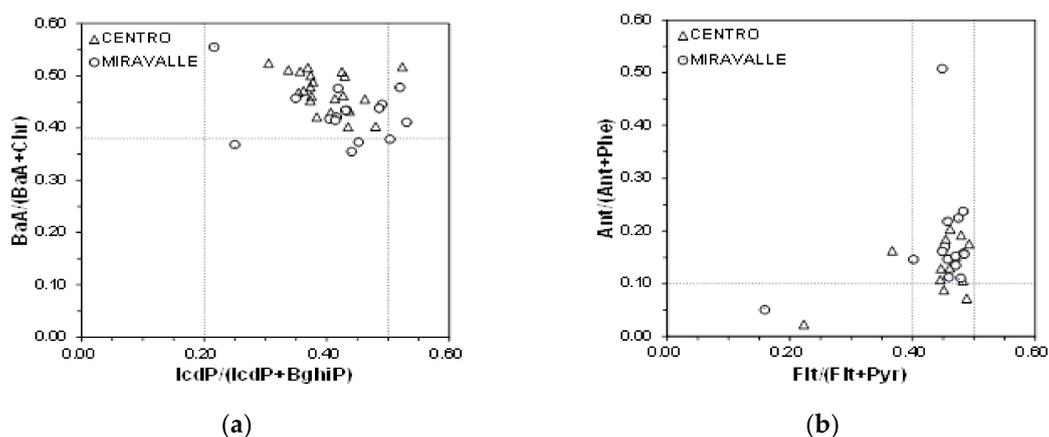
Figure 4. PAH cross plots for the ratios of (**a**) BaA/(BaA + Chry) vs IcdP/(IcdP + BghiP) and (**b**) Ant/(Ant + Phe) vs Flt/(Flt + Pyr) in Centro and Miravalle.

Table 1. Results of principal component analysis applied to concentrations of 14 Polycyclic Aromatic Hydrocarbons (PAHs) in PM$_{2.5}$ in Centro.

PAHs	PC1	PC2	PC3
Acy	0.47	−0.63	0.41
Acn	−0.19	**1.08**	−0.12
Flu	0.28	**0.87**	0.24
Phe	0.25	−0.03	**0.95**
Ant	0.86	−0.34	0.23
Flt	0.89	0.03	0.33
Pyr	0.68	0.00	**0.69**
BaA	**0.96**	−0.05	0.24
Chry	**0.94**	−0.07	0.27
BbF	**0.95**	−0.07	0.22
BkF	**0.90**	0.05	0.18
BaP	**0.96**	−0.13	0.11
IcdP	**0.96**	−0.01	0.26
BghiP	0.89	0.05	0.43
Eigenvalue	9.88	2.39	1.01
Variance cumulative (%)	67.87	84.23	91.15

PC: principal component, meaningful components were shown in bold.

Table 2. Results of principal component analysis applied to concentrations of 14 Polycyclic Aromatic Hydrocarbons (PAHs) in $PM_{2.5}$ in Miravalle.

PAHs	PC1	PC2	PC3	PC4
Acy	0.29	**0.79**	−0.24	−0.04
Ace	0.02	−0.13	−0.09	**0.99**
Flu	0.08	**0.46**	**0.98**	0.20
Phe	−0.13	**0.86**	0.41	−0.11
Ant	0.05	−0.06	**0.88**	−0.24
Flt	**0.86**	0.39	0.23	−0.11
Pyr	0.47	**0.77**	0.39	−0.09
BaA	**0.96**	0.21	0.03	0.05
Chry	**0.93**	0.27	0.11	−0.08
BbF	**0.99**	0.07	0.01	−0.00
BkF	**0.97**	0.02	0.00	0.07
BaP	**0.93**	0.13	0.02	0.14
IcdP	**0.93**	0.03	−0.07	−0.19
BghiP	**0.94**	0.00	0.06	0.07
Eigenvalue	7.92	2.90	1.28	1.13
Variance cumulative (%)	54.03	73.80	82.56	90.26

PC: principal component, meaningful components were shown in bold.

4. Conclusions

Fourteen PAHs associated with $PM_{2.5}$ were identified and quantified at a downtown location (Centro) and an urban sector (Miravalle) located in the Metropolitan Zone of Guadalajara in Mexico. The most abundant PAHs were HMW (BghiP, IcdP, BbF, BaP and BkF) followed by MMW (Chry, BaA, Pyr and Flt) and LMW (Phe, Flu, Acy, Ace and Ant). The atmospheric concentrations of PAHs showed seasonal variation, with high environmental levels during the driest seasons and lowest levels in the rainy season, due mainly to temperature and wet deposition. Spatial variation was only observed during the warm-dry season. The median of total PAHs in Miravalle was found to be the highest significantly ($p < 0.05$), which was attributed to a substantial contribution by vehicular activity to $PM_{2.5}$ from local traffic. Benzo[a]pyrene-equivalent (BaPE) carcinogenicity and contribution by BaP showed that exposure to $PM_{2.5}$ in Miravalle during the warm and cold seasons could represent a serious risk to human health. The PCA and diagnostic ratio showed that contribution from vehicular traffic emissions to $PM_{2.5}$ was probably the main source of PAHs in $PM_{2.5}$ collected in Centro and Miravalle.

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