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Influence of urban activities on polycyclic aromatic hydrocarbons in precipitation: Distribution, sources and depositional flux in a developing metropolis, Fortaleza, Brazil

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ABSTRACT

We measured polycyclic aromatic hydrocarbons (PAHs) in bulk precipitation in the Fortaleza metropolitan area, Ceará, Brazil, for the first time. Because little information is available concerning PAHs in tropical climatic regions, we assessed their spatial distribution and possible sources and the influence of urban activities on the depositional fluxes of PAHs in bulk precipitation. The concentrations of individual and total PAHs (Σ_{PAHs}) in bulk precipitation ranged from undetectable to 133.9 ng.L⁻¹ and from 202.6 to 674.8 ng.L⁻¹, respectively. The plume of highest concentrations was most intense in a zone with heavy automobile traffic and favorable topography for the concentration of emitted pollutants. The depositional fluxes of PAHs in bulk precipitation calculated in this study (undetectable to $0.87 \,\mu\text{g.m}^{-2}$.month⁻¹) are 4 to 27 times smaller than those reported from tourist sites and industrial and urban areas in the Northern Hemisphere. Diagnostic ratio analyses of PAH samples showed that the major source of emissions is gasoline exhaust, with a small percentage originating from diesel fuel. Contributions from coal and wood combustion were also found. Major economic activities appear to contribute to pollutant emissions.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are distributed throughout the environment by atmospheric dispersion. Thus, they have been found in remote areas far from their sources (Macdonald et al., 2005). These molecules are produced in the atmosphere as byproducts of the incomplete combustion of fossil fuels or pyrolysis of organic material (Macdonald et al., 2005). Once PAHs are released into the atmosphere, they are redistributed between the gaseous and particulate phases. Low-molecular-weight (LMW) PAHs tend to be more concentrated in the vapor phase, while those with higher molecular weights (HMW) are often associated with particulates (Bidleman, 1988; Harner and Bidlemam, 1998; Pankow, 1998). Dry and wet deposition and volatilization from the water and soil are the main processes that contribute to air/water and air/soil exchange of PAHs (Godish, 1991). These molecules are predominantly found in the environment

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surrounding urban zones with high vehicular density and industrialized areas (Godish, 1991; Macdonald et al., 2005).

Studies performed in recent decades have shown that PAHs from different combustion sources vary significantly in composition and that their molecular "fingerprints" can be used to identify their sources (Li and Kamens, 1993; Khalili et al., 1995; Simcik et al., 1999; Tsapakis et al., 2002). Thus, PAH diagnostic ratios have been used to evaluate the relative contributions of coke furnaces, coal combustion, wood combustion, incineration and diesel and gasoline engine emissions in industrial and urban zones (Caricchia et al., 1999; De Martinis et al., 2002).

The complex morphology of an urban area creates highly disturbed airflows up to several meters above the height of the buildings (Louka et al., 1998). According to Godish (1991), the urban topography significantly reduces wind speeds and consequently pollutant dispersion, because pollutant sources (e.g., vehicles) are situated within "street canyons". The term "street canyons" refers to relatively large and narrow streets (also called "avenue canyons") with buildings continuously lining both sides (Nicholson, 1975). Vardoulakis et al. (2003) have comprehensively reviewed the impact of urban topography on air quality in cities.

The city of Fortaleza is the fourth most economically important city in Brazil. The city exhibits heavy traffic (520,000 vehicles) and a population of over 2.5 million people distributed across 313 km². In addition to vehicle exhaust, anthropogenic emissions arise from the local harbor, industrial facilities and petroleum extraction and refining.

The first studies of organic atmospheric pollutants in Fortaleza have reported high levels of carbonyls (Cavalcante et al., 2006; Sousa et al., 2011). High levels of organic contaminants originating from urban activities have been verified in the sediments and water of the local rivers and along the adjacent oceanic coast (Cavalcante et al., 2008; Cavalcante et al., 2009; Viana et al., 2009; Cavalcante et al., 2010).

No previous study has evaluated the distribution of PAHs in the Fortaleza region. Due to the rapid industrialization (petrochemical and steel) and growth of the vehicular fleet (4.5%.year⁻¹) in this area, this information is urgently needed. The few studies performed in major Brazilian cities [Porto Alegre (Dallarosa et al., 2008); Rio de Janeiro (Quiterio et al., 2007); Campo Grande (Ré-Poppi and Santiago-Silva, 2005); Niteroi (Pereira Netto et al., 2002); Salvador (De Andrade et al., 2002); São Paulo (De Martinis et al., 2002)] have reported high PAH levels from vehicular and industrial emissions.

Thus, the primary goal of this study was to evaluate the spatial distribution and possible sources of PAHs in bulk precipitation in the Fortaleza metropolitan area and to examine the influence of urban activities on these depositional fluxes. This study was prompted by the scarcity of data concerning PAHs in tropical climatic regions, and our results will provide a useful baseline for future assessments of air quality in Fortaleza.

2. Materials and methods

2.1. Sampling site

The city of Fortaleza is located along the Atlantic coast of northeastern Brazil (Fig. 1). It is a tropical city with temperatures between 25 and 32 $^{\circ}$ C (mean 26 $^{\circ}$ C) and a climate characterized by rainy and dry seasons. The rainy period occurs from February through July; a total of 1200 to 1400 mm of rain falls during this period, with an average of around 200 mm.month⁻¹. The dry period extends from August through December, and very little rain falls during this time (Gusev et al., 2004). There are approximately 520,000 vehicles, from which; 370,000 are light-duty vehicles, 52,000 are heavy-duty diesel vehicles (buses and trucks) and 94,000 are motorcycles. Approximately 74.9% of these vehicles use a mixture of gasoline and ethanol (gasohol), 10.5% are fueled with hydrated ethanol and 4.5% are diesel-powered (Ministry of Cities, 2011). The flexible-fuel vehicles represents about 5.3% of the total fleet, and is rapidly growing (Abrantes et al., 2009; Ministry of Cities, 2011). An average flow of 1500 vehicles.hour⁻¹ is observed in the major intersections of the city. It is estimated that 80% of the vehicle fleet cross the city of Fortaleza on weekdays (PMF, 2011).

We sampled the rainwater in the urban and suburban Fortaleza metropolitan area (Fig. 1). Bulk precipitation samples were collected at seven sites from February to July 2005. Samples were collected monthly in 1.5–2 L dark glass bottles using a 0.0283-m² (area of the mouth of the funnel) following the methods of Manoli et al. (2000) and Ollivon et al. (2002). The sampled rainwater ranged from 0.5 to 1.2 L in each of the rain events and was stored in a refrigerator at 2 °C until analysis. When the volume reached 2 L, the bottles were immediately transported to the laboratory. After that, samples were filtered with pre-cleaned (heated at 450 °C for 24 h) Whatman GF/F filters (0.7 µm, 47 mm i.d.).

The sampling sites BP1, BP3, BP4 and BP6 are placed on residential/commercial zones of the city while site BP2 is located in the coastal area. These sites present intense traffic of light and heavy vehicles. The sampling sites BP5 and BP7 are located in the city's outskirts, which are mostly residential areas and that now present a slight traffic of light and heavy vehicles. The main sources of all above sites are vehicular emissions, but depending on the weather condition site BP2 can also receive input from the port and refinery zone.



Fig. 1. Locations of bulk precipitation sampling sites.

2.2. Extraction and analysis

Spe-edTM C₁₈ (500 mg, Applied Separations) cartridges were used in solid-phase extraction (SPE) for purification and concentration according to the second optimized method of Cavalcante et al. (2007). Firstly, the sorbent cartridges were conditioned with 5 ml of Milli-Q water (Millipore) and 5 ml of 30% acetone in Milli-Q water. A volume of 2 L of sampled rainwater was passed through the cartridge at a flow of 20 mL.min⁻¹. The cartridge was centrifuged and then eluted with 1 mL of acetone:tetrahydrofuran (THF) (1:1 v/v).

Bulk precipitation extract was evaporated to 100 µL, and then 2 µL was injected into a gas chromatograph with a flame ionization detector (GC-FID). For quantification, we used internal standards obtained from Supelco and Merck. The studied PAHs were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flr), 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 (IncdP), dibenzo[a,h]anthracene (DahA) and benzo[ghi]perylene (BghiP). A surrogate standard (acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂) purchased from Supelco/Aldrich was added to each sample before extraction. The concentrations of PAHs were determined using a Shimadzu CG 17A instrument. The separation was performed on a J&W Scientific DB-5 column (30 m, 0.25 mm internal diameter, film thickness 0.25 µm). The initial oven temperature was 60 °C (10 min), increasing to 120 °C at 5 °C min⁻¹ and then to 300 °C at 3 °C.min⁻¹. The injector and detector temperatures were 280 °C and 300 °C, respectively. A calibration solution was prepared from the 16 PAHs standards (0.5 to $100 \,\mu g.m L^{-1}$), deuterated PAH solution $(d_{10}$ -acenaphthene, d_{10} -phenanthrene, d_{12} -chrysene and d_{12} -perylene) and the internal standard (2-fluoro-biphenyl). The chromatographic conditions used in the GCMS-QP5050, such as column, flow, amount of sample injected and injector temperature, are similar to the GC-FID.

The correlation coefficient (R) varied from 0.9899 to 0.9989. The limits of detection (LOD) were set at a value three times the background noise obtained for blank samples, and the limits of quantification (LOQ) were set at a value ten times the background noise. The LODs and LOOs ranged from 20.0 to 50.0 ng.mL $^{-1}$ and from 63.4 to 157.3 ng.mL $^{-1}$, respectively. The repeatability of the GC method was determined by analyzing a standard solution at 0.5 μ g.mL⁻¹, within-day and between-day. It is important to assess the repeatability of at least two parameters in the gas chromatographic method: the retention time (confirming the identity of the analyte of interest) and the peak area or height (quantifying the analyte of interest). The repeatability of the method ranged from 1.5 to 4.8% of the peak area (quantitative analysis) and from 0.02 to 0.19% of the retention time (qualitative analysis), showing satisfactory precision. Between-day repeatability, expressed as RSD, was also evaluated during two consecutive weeks and no significant alteration was observed. Therefore, the repeatability achieved with the chromatographic method under the study conditions was satisfactory (Fernandes et al., 2009).

2.3. Quality control

All data were subjected to strict quality control procedures. Each sample was analyzed in duplicate and their RSD did not exceed 5%. Confirmation of PAH identities was performed using a CG 17A gas chromatograph coupled to a mass spectrometry detector (Shimadzu model GCMS-QP5050) and the Wiley/NBS Registry of Mass Spectral Data. The two samples presenting lower concentrations (BP2 and BP7) were qualitatively determined and the PAH identities confirmed. Deuterated surrogates were used throughout the analytical procedure to compensate for losses and contamination during sample extraction and instrumental analysis. Spiked recoveries from extracts ranged from 56.4 to 91.2% for all targeted analytes (Table 1). Analysis

of a reagent blank demonstrated that the analytical system and glassware were free of contamination.

3. Results and discussion

3.1. PAH concentrations and fluxes in bulk deposition

Individual PAH concentrations in bulk precipitation ranged from undetectable to 133.9 ng.L⁻¹ (Flr), while the total PAH concentrations (Σ_{PAHs}) ranged from 202.6 to 674.8 ng.L⁻¹ (Table 1). The average Σ_{PAH} value for bulk precipitation in Fortaleza (582.3 ng.L⁻¹) is substantially higher than reported values for rural areas, such as Chesapeake Bay in the United States (12.17 ng.L⁻¹; Dickhut and Gustafson, 1995). However, it is lower than the value reported for Paris, France (995.0 ng.L⁻¹; Ollivon et al., 2002), and is similar to the level reported for Tihany, Hungary (571.2 ng.L⁻¹; Kiss et al., 2001). The most frequently detected PAHs were Phen, Flr, Pyr and Chry. This result is consistent with previous results reported for Germany (De Rossi et al., 2003), Italy (Olivella, 2006), Hungary (Kiss et al., 2001), Poland (Polkowska et al., 2000) and Scandinavia (Fernandez et al., 2003).

Wet deposition flux F_{wet} (µg.m⁻² rainy.period⁻¹) was calculated by multiplying the concentration *C* (ng.L⁻¹) of each PAH compound in rainwater (bulk precipitation) by the precipitation flux *P* (mm) for the sampling event (*i*) using an equation similar to that of Pekey et al. (2007):

$$F_{wet} = \sum_{i=1}^{i=n} C^i \times P^i.$$

The mean fluxes of individual PAHs (F_{PAHs}) ranged from undetectable to 0.87 µg.m⁻².month⁻¹ (Σ_{PAHs} = 5.6 µg.m⁻².month⁻¹) (Table 2). Because we have not found any comparable data (PAH levels in precipitation) for other Brazilian cities or tropical regions, we compared our results to previous reports from areas with different climates (Table 2).

The mean flux of the total PAH concentration ($F_{\Sigma PAHs}$) in the city of Fortaleza was approximately half the value reported by Kiss et al. (2001) and 4 to 27 times smaller than the values reported for other tourist sites and urban and industrial areas (Table 2). Variation in PAH fluxes between tropical and temperate areas can be attributed to several factors (Kiss et al., 2001). Meteorological conditions during the winter in cold-climate regions result in thermal inversions and low solar intensities. Consequently, concentrations of OH radicals are low, and the efficiency of photochemical decomposition is decreased, favoring the accumulation of pollutants in the atmosphere (Hoyau et al., 1996). High PAH deposition levels in snow can be explained by the larger surface areas of snowflakes compared to raindrops (Hoff et al., 1998). Snowstorms can remove particles from 0.2 to 2.0 µm in size, and the resulting atmospheric cleansing is 5 to 10 times more efficient than that produced by rain events (Franz and Eisenreich, 1998).

3.2. Spatial distribution

The spatial distribution of PAH concentrations, based on a kriging model, was calculated with the program Surfer 7 (Golden Software) (Fig. 2). Based on the surface plot of total PAH concentrations in bulk precipitation, the levels increase from the outskirts toward the center of the city. Our analysis of the spatial distribution of PAHs showed that the plume of highest concentrations was most intense in the same zone (Fig. 2). In addition to the considerable vehicular emissions in this zone, Fortaleza is surrounded by two industrial areas, a refinery to the northeast and other industries to the southwest (Maracanaú city) (see Fig. 1). Nevertheless, we did not observe any correlation between the plume of highest concentrations and the frequency of winds from the industrial areas. In fact, winds blew from

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Concentrations of individual PAHs (ng.L	¹), total PAH concentration	(Σ_{PAHs}) in bul	lk precipitation and	l spiked recoveries ((%).
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# of rings	Classification	РАН	BP1	BP2	BP3	BP4	BP5	BP6	BP7	Spiked recoveries ^a
2 rings	LMW-PAH	Nap	Nd	Nd	Nd	Nd	Nd	Nd	Nd	56.4 ± 7.4
		Acy + Ace	Nd	Nd	Nd	Nd	Nd	Nd	Nd	69.2 ± 2.5
3 rings		Fl	35.7 ± 5.2	Nd	45.4 ± 5.9	40.5 ± 6.9	31.2 ± 6.3	39.0 ± 5.1	Nd	88.8 ± 9.7
		Phen	60.3 ± 8.2	98.3 ± 4.2	52.0 ± 4.9	82.9 ± 7.8	74.2 ± 6.1	89.9 ± 6.7	38.0 ± 4.5	91.2 ± 8.3
		Ant	Nd	Nd	Nd	Nd	Nd	Nd	Nd	72.1 ± 9.5
4 rings	HMW-PAH	Flr	76.4 ± 6.5	133.9 ± 5.9	56.7 ± 6.3	114.9 ± 8.8	66.2 ± 7.3	102.7 ± 9.3	75.2 ± 5.4	86.0 ± 8.1
		Pyr	63.2 ± 7.2	73.8 ± 6.2	76.4 ± 6.2	98.3 ± 7.9	53.9 ± 5.3	96.1 ± 8.3	34.5 ± 4.6	77.9 ± 10.6
		BaA	Nd	Nd	Nd	Nd	Nd	Nd	Nd	72.7 ± 18.1
		Chry	55.5 ± 5.3	69.4 ± 7.2	58.1 ± 5.4	92.6 ± 9.4	56.2 ± 6.5	97.5 ± 7.1	54.9 ± 5.1	75.0 ± 22.4
5 rings		BbF	51.5 ± 6.2	Nd	62.3 ± 7.9	47.2 ± 6.5	33.2 ± 7.2	43.2 ± 5.3	Nd	71.1 ± 22.7
		BkF	34.7 ± 6.7	Nd	65.6 ± 6.5	43.2 ± 5.9	35.1 ± 6.1	40.6 ± 5.5	Nd	81.0 ± 16.3
		BaP	Nd	Nd	42.5 ± 7.9	Nd	31.3 ± 6.5	49.6 ± 5.4	Nd	77.3 ± 16.6
		DahA	Nd	Nd	Nd	Nd	Nd	Nd	Nd	70.1 ± 13.5
6 rings		IncdP	51.0 ± 7.3	Nd	89.1 ± 9.3	67.8 ± 6.7	30.5 ± 4.9	61.6 ± 6.3	Nd	76.5 ± 7.1
		BghiP	40.9 ± 5.6	35.4 ± 5.1	84.5 ± 7.9	58.6 ± 5.9	30.6 ± 4.6	54.6 ± 5.7	Nd	74.4 ± 10.3
		Σ_{PAHs}	469.2	410.8	632.6	646.0	442.4	674.8	202.6	

LMW-PAH = low molecular weight PAH.

HMW-PAH = high molecular weight PAH.

Nd = not detected.

^a Average.

the southeast throughout the year (see the wind rose in Fig. 2). Therefore, our data suggest that the spatial distribution of PAHs in Fortaleza originates locally and is not transported from elsewhere in the region.

The existence of urban street canyons with heavy automobile traffic is the main cause of the urban heat island (UHI) effect in Fortaleza (Malveira, 2003; Filho, 2011) and other cities (Sarrat et al., 2006; Solecki et al., 2006). The UHI effect is common in many urban centers (Sarrat et al., 2006). This phenomenon is primarily due to the replacement of vegetation with urbanized areas and is aggravated by pollutant emissions (generally vehicular) and heavier use of air conditioning in often poorly ventilated cities (Crutzen, 2004).

Even air movements such as sea breezes in coastal areas and anticyclonic episodes are not sufficient to disperse pollutants or to decrease the UHI effect in urban centers with complex topography (Kambezidis et al., 1995; Sarrat et al., 2006). Highly disturbed airflows up to several meters above the height of the buildings do not remove the gaseous and particulate pollutants emitted and trapped within the street canyons (Louka et al., 1998).

Although the PAH plume with the highest concentrations found in this study is located within the UHI zone reported by Malveira (2003)

Table 2

PAH fluxes in Fortaleza and other areas ($\mu g.m^{-2}.month^{-1}$).

РАН	Massachusetts, United States ¹	Bursa, Turkey ²	Tihany, Hungary ³	Mount Taishan, China ^{4a}	Fortaleza, Brazil ⁵
Nap	-	-	-		Nd
Acy + Ace	0.29	7.65	-		Nd
Fl	0.16	3.30	0.76		0.37
Phen	0.13	30.00	3.33		0.69
Ant	0.37	2.34	0.10		Nd
Flr	0.10	33.00	1.90		0.87
Pyr	1.46	19.80	2.20		0.69
BaA	1.19	2.85	0.13		Nd
Chry	2.25	18.00	0.36		0.67
BbF	2.34	3.00	0.56		0.46
BkF	8.92	2.94	0.20		0.43
BaP	0.05	2.55	0.30		0.40
IncdP	5.45	3.00	-		0.58
DahA	1.62	1.65	0.16		Nd
BghiP	-	8.40	0.40		0.49
$F_{\Sigma PAHs}$	24.3	138.5	10.4	8.17	5.6

Sources: ¹Golomb et al. (1997); ²Esen et al. (2007); ³Kiss et al. (2001); ⁴Wang et al. (2010); and ⁵this study.

^a Only recorded the total.

and Filho (2011), complex studies involving physical and chemical models are necessary to determine whether the urban topography is responsible for inhibiting the dispersion of pollutants emitted on city streets (Vardoulakis et al., 2003). Although no study has evaluated the effect of urban street canyons on pollutant dispersion in Fortaleza, our data suggest that the plume is concentrated in the city center (Fig. 2) due to the heavy traffic and favorable topography for the concentration of pollutants emitted in this zone.

3.3. Evaluation of PAH sources in Fortaleza

Table 3 shows some of the PAH ratios that are commonly used to determine the sources of pollutants in the atmosphere and the corresponding ratios found in the bulk deposition samples studied here and in China (Wang et al., 2010).

The diagnostic ratios of Flr/(Flr + Pyr) (0.56) and BaP/(BaP + Chry) (0.37) found in this study indicate the significant contributions of gasoline, diesel exhaust and catalyst equipped cars (Tsapakis et al., 2002; Manoli et al., 2004; Sienra et al., 2005; Quiterio et al., 2007) (Table 3), although the diagnostic ratio of Flr/(Flr + Pyr) can also indicate the contribution of coal combustion (Stroher et al., 2007).

The diagnostic ratios of BghiP/IncdP (0.90), BaP/BghiP (0.81) and IncdP/(IncdP + BghiP) (0.53) can be attributed to emissions from wood, diesel oil, gasoline and coal combustion (Li and Kamens, 1993; Simcik et al., 1999; De Martinis et al., 2002; Stroher et al., 2007).

The profile of pollutants emitted from light-duty vehicles can be considered unique, since Brazil is the only place where a mixture of gasoline and ethanol (gasohol), pure ethanol and vehicular natural gas are used (Abrantes et al., 2009). Our results indicate that vehicular emissions are the main sources of atmospheric PAHs in Fortaleza, especially when compared to studies about other metropolitan areas of Brazil (De Martinis et al., 2002; Quiterio et al., 2007; Stroher et al., 2007). PAH ratios corresponding to coal and wood combustion were also found. This pattern has two possible causes: the atmospheric transport of pollutants originating from burning in rural areas (less probable) or the use of coal and wood as energy sources in commercial activities, especially bakeries and restaurants. It has been estimated that 40 bags of coal are used in a single week by restaurants (in traditional barbecue preparation) in the city of Fortaleza. The contributions of these economic activities to pollutant emissions are verified by the diagnostic ratios of PAHs found in sediments from the two major rivers in the region (Cavalcante et al., 2008; Cavalcante et al., 2009). Although the relative contribution of atmospheric deposition to surface waters in



Fig. 2. a) Distribution of Σ_{PAHs} in Fortaleza and b) wind rose observed during the sampling period.

urban areas is poorly understood (Motelay-Massei et al., 2006), aquatic environments around urban centers are influenced by urban activities, and streets supply major deposits of PAHs (Motelay-Massei et al., 2006).

4. Conclusion

The PAH levels in Fortaleza are similar to those reported for other developing cities, but they are substantially lower than those found in

Table 3

Diagnostic ratios of PAHs attributed to specific sources.

	BghiP/IncdP	BaP/BghiP	Flr/(Flr + PYR)	IncdP/(IncdP+BghiP)	BaP/(BaP+Chry)
Gasoline exhaust	3.5–3.8 ^{1;a;b} 0.90 ^{7;b}		0.37 ^{8;b} 0.40–0.60 ^{6;b}	0.50 ^{5;a;b}	0.36 ^{8;b}
Diesel exhaust	1.1-1.2 ^{1;a;b}	0.46-0.81 ^{5a;b}	0.43 ^{3;b}		0.35 ^{6;b}
Wood combustion	0.80 ^{1;a;b}		0.67 ^{2;b}	0.69 ^{2;b}	0.48 ^{2;b}
Coal combustion		0.9-6.6 ^{2;b}	0.58 ^{2;b}	0.53-0.56 ^{2;b}	
Catalyst equipped cars			0.37 ^{8;b}		0.36 ^{8;b}
			0.47 ^{4;b}		
Mount Taishan, China ⁹			0.56 ^{9;c}		0.31 ^{9;c}
Fortaleza, Brazil ¹⁰	0.90 ± 0.08	0.81 ± 0.27	0.56 ± 0.09	0.53 ± 0.02	0.37 ± 0.04

Sources: ¹Li and Kamens (1993); ²Stroher et al. (2007); ³Manoli et al. (2004); ⁴Sienra et al. (2005); ⁵Simcik et al. (1999); ⁶Tsapakis et al. (2002); ⁷De Martinis et al. (2002); ⁸Quiterio et al. (2007); ⁹Wang et al. (2010); and ¹⁰this study.

Type: ^agaseous PAHs; ^bparticle PAHs and ^cdeposition PAHs.

large metropolises such as Paris. Urban activities, such as vehicular emissions and wood and coal burning (in bakeries and restaurants, for example), combined with the complex topography of areas and dense clusters of buildings are responsible for the highest PAH concentrations in the central portion of the city of Fortaleza.

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