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Influence of urbanization on air quality based on the occurrence of particle-associated polycyclic aromatic hydrocarbons in a tropical semiarid area (Fortaleza-CE, Brazil)

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Abstract This study reports the first measurements of polycyclic aromatic hydrocarbons (PAHs) in particulate matter in the metropolitan area of Fortaleza-CE, Brazil. We studied the influence of urban topography on the occurrence of PAHs and the depositional flux (F_{PAHs}) and characterized the emission sources and health risks of PAHs. Of the 16 PAHs evaluated, only 10 PAHs with more than 4 aromatic rings were found. The total PAH concentration (Σ_{PAHs}) ranged from 1.73 to 2.83 ng m^{-3}. The F_{PAHs} value ranged from 0.008 to 0.0182 μg m^{-2} day^{-1}. These fluxes are comparable to the values obtained at sites with developing urbanization or sites that use heating; however, they are smaller than the values obtained at industrial and large metropolis sites. An examination of the influence of urban topography revealed that the building density considerably increased the particulate matter concentration; however, urban vegetation had the opposite effect. Light-duty vehicles were the most important emission source of PAHs in the metropolitan area of Fortaleza. However, industrial activities (e.g., asphalt and steel production), combustion (e.g., coal and wood), and paved roads had a modest contribution. The health risk from PAHs in Fortaleza is higher at sites with a higher traffic flow, and the level of this health risk is similar to the risk level in other developing cities.

Keywords PAHs · Distribution · Source contribution · Tropical region · Dry deposition flux

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Introduction

PAHs are produced in the atmosphere as by-products of the incomplete combustion of fossil fuel or the pyrolysis of organic material containing carbon and hydrogen (Seinfeld and Pandis 1998). Therefore, they are ubiquitous in the environment and are primarily found in rural, urban zones with high vehicular density, or in industrialized areas (Simcik et al. 1999; Bari et al. 2010). PAHs are distributed in the environment through atmospheric dispersion. Thus, they have been found in remote areas far from anthropogenic sources (Seinfeld and Pandis 1998). The main processes contributing to the exchange of PAHs from air to water and from air to soil are dry deposition, wet deposition, and volatilization from water and soil.

Studies performed during the recent decades have shown that the composition of PAHs varies with the emission source (Simcik et al. 1999); these "fingerprints" can be used to identify the sources of PAHs. Studies have used the PAH mass balance as a diagnostic ratio for the contribution of PAHs from certain sources, including coke ovens, coal combustion, wood combustion, incineration, and diesel and gasoline engines in industrial and urban zones (De Martinis et al. 2002; Manoli et al. 2004; Netto et al. 2006; Ströher et al. 2007; Cecinato et al. 2014; Vicente et al. 2016).

The complex morphology of urban areas leads to a highly disturbed airflow up to several meters above the tops of buildings (Louka et al. 1998). According to Godish (1991), urban topography (e.g., buildings and trees) significantly reduces wind speed, consequently reducing the dispersion of pollutants because pollutant sources (e.g., vehicles) are situated within canyon-like streets. Simultaneously, in these street canyons, urban plants can act as a sink for particles of various sizes (Beckett et al. 1998, 2000). These factors indicate that the building and greening indices have an important influence on air quality.

The first studies of organic pollutants in the atmosphere of Fortaleza reported high levels of carbonyls (Cavalcante et al. 2006). High levels of organic contaminants originating from urban activities have been shown in the area's sediments and aquatic environment (Cavalcante et al. 2007, 2008). However, no previous study has evaluated the distribution of PAHs in particulate matter. Due to the rapid industrialization (including petrochemical, steel, and other industries) and the growth of the vehicular fleet (4.5 % $year^{-1}$) in the area, this information is urgently needed (IBGE 2010). Therefore, this study aims to evaluate air quality in a developing metropolis on the Brazilian tropical semiarid coast. Specifically, we evaluated the occurrence of PAHs and their depositional flow considering the urban topography of the metropolitan area of Fortaleza. We also estimated the contribution from various sources and the risks of the PAH levels. Our results will inform public policy on air quality management in cities in expanding urban areas, such as Fortaleza.

Materials and methods

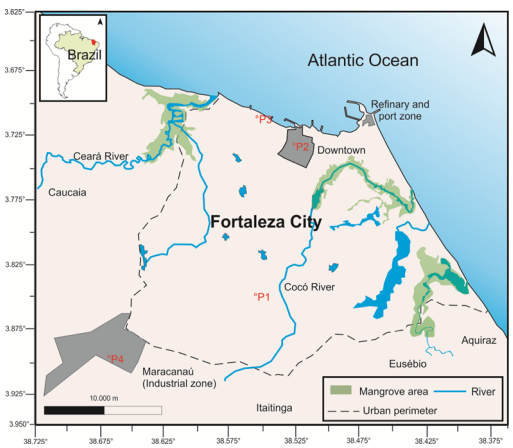
Sampling site

The city of Fortaleza is located on the Atlantic coast of northeastern Brazil (Fig. 1). The climate is tropical, with annual average minimum and maximum temperatures of 26 and 32 °C, respectively. Fortaleza is characterized by rainy and dry periods: the rainy period (1200 to 1400 mm/period) is from February to July, and the dry period is from August to December (Gusev et al. 2004). Atmospheric deposition sampling of PAHs was conducted in the urban and suburban zone of Fortaleza (Fig. 1). Particulate samples (TSP) were collected on quartz fiber filters using high volume sampling (Energética AGVPTS2) at four stations, for a total of 16 samples. Fortaleza has approximately 2.2 million inhabitants and an area of 313 km^2. There are approximately 430,000 vehicles in the city, of which 314,500 are light-duty vehicles, 35,600 are heavy-duty diesel vehicles (busses and trucks), and 64,500 are motorcycles (IBGE 2010).

Determination of PAHs

The quartz fiber filters were extracted with 3 × 100 mL hexane/acetone (1:1) for 30 min under ultrasonic agitation in a 500-mL clean glass jar. After the agitation step was completed, the extract was combined and filtered to remove any particles. The cleanup step was performed using a glass column (25 cm × 1 cm id) filled with silica gel/alumina. Next, the column was eluted with 80 mL each of a series of solvents with different polarities (hexane and hexane/ethyl acetate). The elution was concentrated using rotary evaporation and then reduced with pure nitrogen gas prior to gas chromatography analysis.

We analyzed the samples using gas chromatography for the following PAHs: 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



P1. Located on the outskirts of the city of Fortaleza, on a street with a low traffic flow, green index=8.17% and building index=34.4%.

P2. Located in the central area of the city of Fortaleza on an avenue with a high traffic flow, green index=6.15% and building index= 53.52%.

P3. Located on an avenue with access to the center of Fortaleza, with an average traffic flow, green index= 7.78% and building index= 47.74%.

P4. Located in the industrial area around the city of Fortaleza, with a low traffic flow, green index=3.54% and building index= 25.62%.

Fig. 1 Location and characteristics of the sampling stations

(BghiP). Details of the cleanup step and instrumental determination of the PAHs can be found in Cavalcante et al. (2008).

Quality control

An analysis of laboratory blanks (reagent and quartz fiber filters) demonstrated that the analytical system and glassware were free of contamination. Quantification of PAHs was performed using an internal calibration curve (with a range of 50–1000 ppb and an angular coefficient of 0.9 to 0.99). A surrogate standard (acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) purchased from Supelco/Aldrich was added to each sample before extraction. 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 55 to 90 % for all targeted analytes.

Deposition flux (F_{dry})

The value of F_{dry} was calculated by multiplying the concentration of each PAH compound in the particulate matter by its dry settling velocity as follows (Shannigrahi et al. 2005):

$$F_{dry} = \sum_{i=1}^{i=n} C^{i} \times V^{i}_{d}$$

where C (ng m^{-3}) is the particle-associated concentration of the PAHs and V_d is the mean particle deposition velocity (7.23×10^{-6} m s^{-1}) for the sampling event (i) using a model from Pekey et al. (2007).

Urban topography

Urban topography was measured using the geographical information system (GIS) from the building and greening indices of the metropolitan area of Fortaleza. The raster data consisted of georeferenced images from the Quick Bird satellite. The geographic coordinate system was SIRGAS with UTM projection on metric zone 24. We created vectors for blocks, buildings, and green areas using ArcMap 10.1 (Fig. 2). The 3D file was developed from field altimetry data using the ArcScene10.1 software (Fig. 2).

Sources

PAH levels were used to identify hydrocarbon sources related to vehicular traffic (light-duty diesel, heavy-duty diesel, catalyzed and non-catalyzed cars), industrial activities (asphalt production and steel plants), biomass combustion (wood and coal), and paved roads based on six diagnostic ratios, BaA/(BaA + BaP), Pyr/BaP, Cry/(BaP + Cry), Flr/(Flr + Pyr), BaA/(BaA + Cry), and Ind/(BghiP + Ind), found in the literature (Rogge et al. 1993; Kavouras et al. 2001;

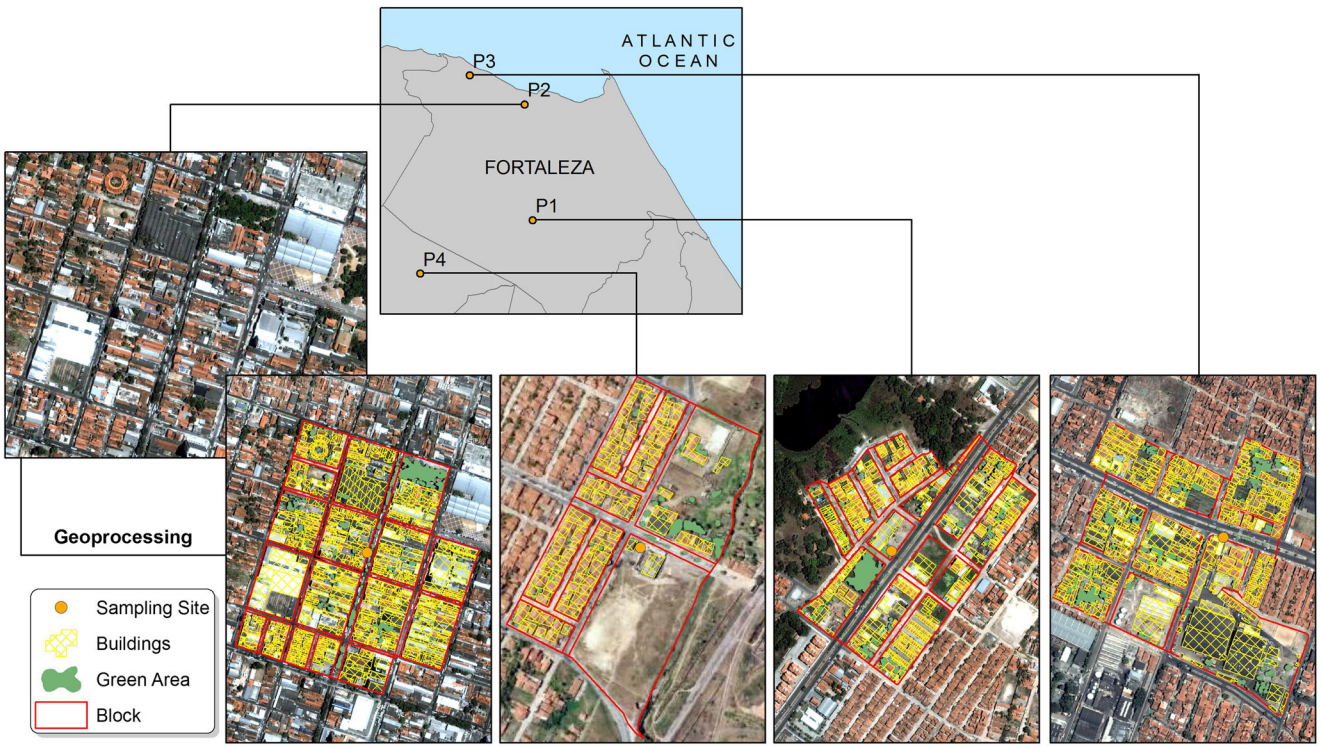


Fig. 2 Vectorization of buildings, green areas, and blocks from the Quick Bird satellite image

Manoli et al. 2004; Ravindra et al. 2006; Ströher et al. 2007; Cecinato et al. 2014).

Risk

The risk to human health from PAHs was estimated using the Incremental Lifetime Cancer Risk (ILCR) model. We quantitatively estimated the risk of PAH levels in the area based on the standard US EPA model (USEPA 1997; Wang 2007) with the variables listed in Table 1. The model was used to evaluate the ILCR in terms of inhalation as follows:

$$\mathrm{ILCR} = \frac{(\mathrm{CS} \cdot \mathrm{IR} \cdot \mathrm{ED} \cdot \mathrm{EF} \cdot \mathrm{L})}{(\mathrm{BW} \cdot \mathrm{ATL} \cdot \mathrm{NY})} \cdot \mathrm{CSF}$$

where CS is the sum of the PAH concentrations based on the toxicity of a benzo[a]pyrene (BaP)-equivalent using the toxic equivalency factors (TEF) (mg m^{-3}) elaborated by Nisbet and LaGoy (1992), IR is the inhalation rate (m^3 h^{-1}), ED is the duration of exposure (h $week^{-1}$), EF is the frequency of exposure (week $year^{-1}$), L is the exposure time during life (years), BW is the body weight (kg), ATL is the expected lifespan (years), NY is the number of days per year (day $year^{-1}$), and CSF is the carcinogenic risk factor (mg kg^{-1} day^{-1}) determined by the ability of BaP to cause cancer (Wang 2007).

Results and discussion

Occurrence and deposition fluxes of PAHs

PAHs, including 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), were identified in particulate matter from the metropolitan area of Fortaleza for the first time. We did not detect naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phen), or anthracene (Ant) in this study. The TSP and PAH concentrations and their flows are summarized in Fig. 3. The total PAH concentrations (Σ_{PAHs}) ranged from 1.73 to 2.83 ng m^{-3}. The P2 station had the highest Σ_{PAHs} with a value of 2.83 ng m^{-3}, followed by the P3 station (2.08 ng m^{-3}), the P1 station (2.0 ng m^{-3}), and the P4 station (1.73 ng m^{-3}). We found no LMW PAHs (composed of two and three rings) in the particulate phase, which is consistent with the results of other studies (Lee et al. 2008; Thang et al. 2014). According to Tasdemir and Esen (2006), two- to three-ring PAHs are more volatile, thus tending to partition into the gas phase in the atmosphere.

We then compared the calculated total dry deposition flux of particulate PAHs with other studies. For comparison, it is convenient to express dry deposition fluxes of Σ_{PAHs} loading as a daily flux. The F_{PAHs} in the metropolitan area of Fortaleza (0.11–0.18, mean 0.14 μg m^{-2} day^{-1}) has a similar magnitude to the flux in Vegoritis, Greece, (0.11 μg m^{-2} day^{-1}, Terzi and Samara 2005) and in Tihany, Hungary (0.14 μg m^{-2} day^{-1},

Table 1 Description of the variables used to estimate the risk of cancer from PAHs

Variable	Description	Value	Unit
CS	Concentration of the contaminant	–	mg m^{-3}
IR	Inhalation ratio (adult)	1.02[a]	m^3 $hour^{-1}$
ED	Duration of exposure (adult)	40[b]	hour $week^{-1}$
EF	Exposure frequency	52	week $years^{-1}$
L	Exposure time	35[c]	years
BW	Body weight	75	kg
ATL	Life expectancy	72	years
NY	Number of days in year	365	day $years^{-1}$
CSF	Risk factor carcinogen	3.85	–

[a] Air inhalation rate of a person performing normal activities (USEPA 1997)

[b] Occupational hours of one person per week

[c] Occupational years of a person over their lifetime

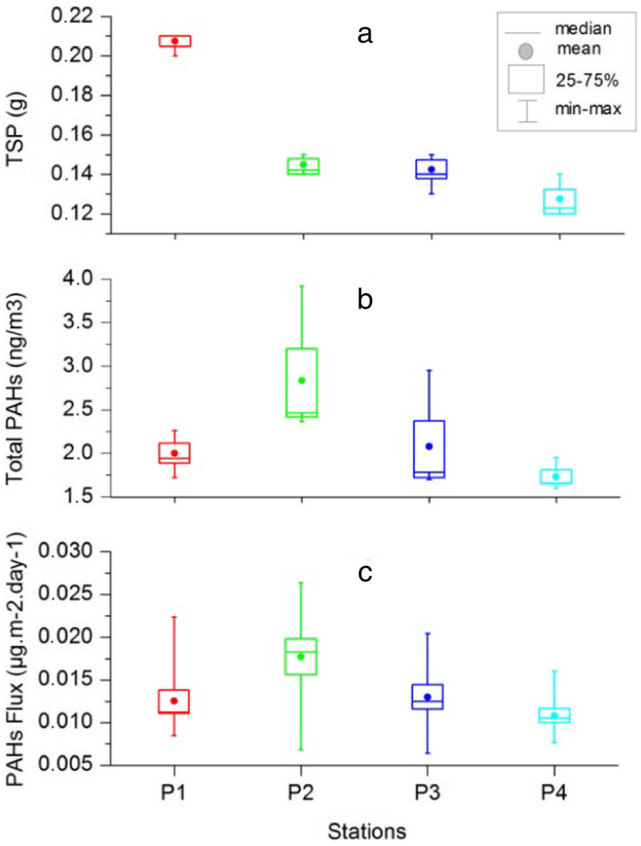


Fig. 3 **a** TSP level. **b** Σ_{PAHs}. **c** F_{PAHs}

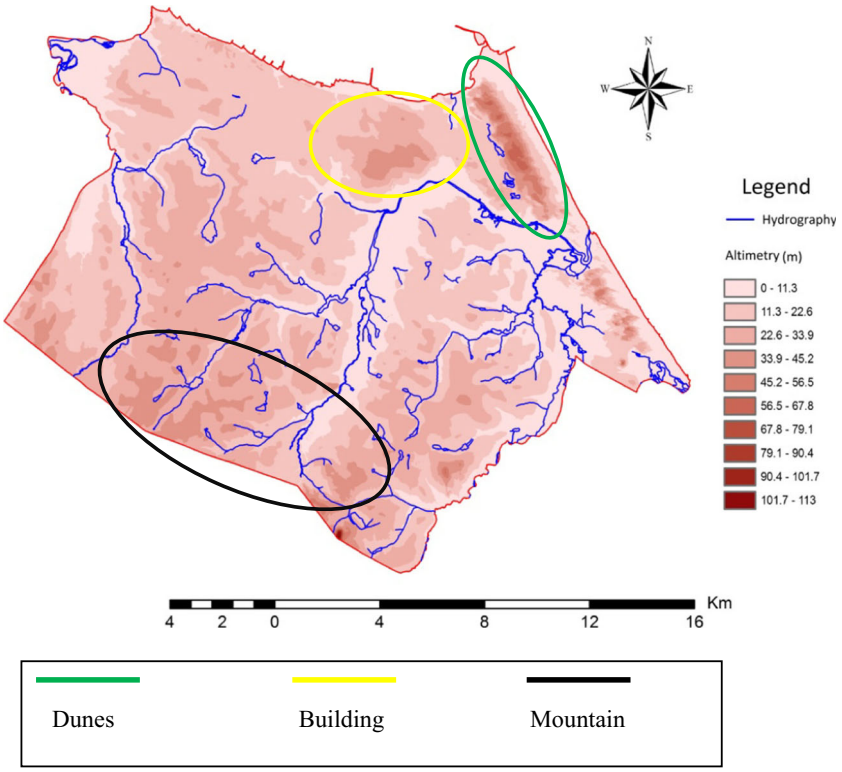


Fig. 4 Topography of the metropolitan area of Fortaleza

Kiss et. 2001); this value is lower than the F_{dry} in Paris, France (mean 0.38 μg m^{-2} day^{-1}, Ollivon et al. 2002), and in Izmit Bay, Turkey (1.3 μg m^{-2} day^{-1}, Pekey et al. 2007).

Topography along with green and building indices

The dispersion of airborne pollutants through streets and avenues in urban environments is a complex process that can be affected by various factors, including the local atmospheric chemistry, meteorology, and the characteristics of urban roads, as well as architecture and trees (Uehara et al. 2000).

The metropolitan area of Fortaleza has a north to south unevenness of approximately 65 m. The higher altitude areas (the highest area, Fig. 4) in the region are dunes along the coastline (55 m), neighborhoods with tall buildings (60 m), and mountain ranges over 100 m high to the south (Fig. 4).

Samples were collected at the geographic center of each area. Note that the P2 station has a concentration of buildings with greater verticality than the P4 station. This relationship is shown in Fig. 5. This pattern of urban topography influences the dispersion of pollutants, as detailed below.

The P2 station had the greatest building index (53.52), followed by the P3 (47.74), P1 (34.40), and P4 stations (25.62). The P2 station also had the highest building index and showed the highest PAH concentration. Based on these results, we performed a simple regression between building index and PAH concentrations (Fig. 6) that result in a coefficient of determination (R^2) of 0.6293, indicating a strong correlation between the two variables. These results suggest that approximately 62.93 % of the variation in the PAH concentration can be explained by the variation in the constructed area, which explains the results found for the P2 station. This explanation is plausible because greater topography, associated with the ambient building arrangements, significantly reduces the wind speed, consequently reducing the pollutant dispersion through the streets (Godish 1991; Xie et al. 2005).

In relation to the green areas rate, the index was highest in P1 (8.17), followed by the P3 (7.78), P2 (6.15), and P4 stations (3.54) (Fig. 6). The value of the coefficient of determination (R^2) was −0.4241, indicating that the contribution from trees is higher to decrease the concentration of PAHs, hence decreasing the particulate matter. The inverse correlation is plausible since the urban vegetation may play a role in improving the local air quality. Particulate pollutants could be dry deposited on plant surfaces through gravity sedimentation and impaction or could be simply deposited on the surface wax (Beckett et al. 2000; Nowak 2006; Jim and Chen 2008). Specifically, plant species and leaf surface roughness might determine the capability of particulate removal (Beckett et al. 1998). Even in the period of higher levels of particulate matter, continuous coverage trees have high particulate removal efficiency (Jim and Chen 2008). Large trees with large leaves retain particulate more effectively than do small trees with small leaves due to the greater surface area and adsorption capacity (Beckett et al. 2000). Urban vegetation is responsible for the removal of more than

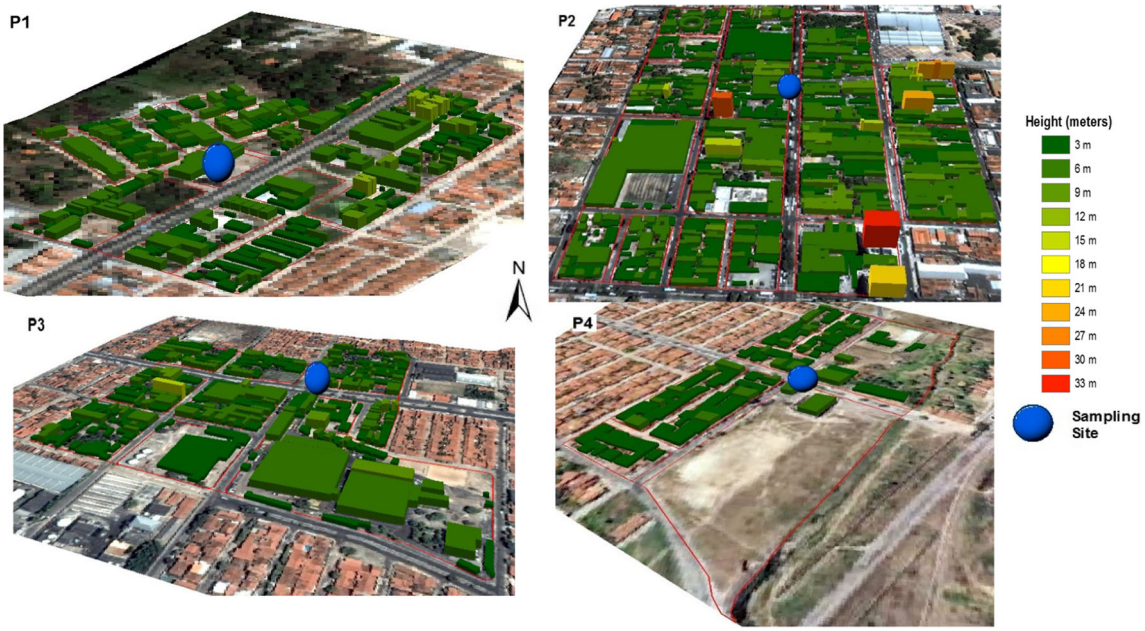


Fig. 5 3D extrusion of the constructed area

335,000 tons of particulate matter in the US, working as a natural "biotechnology" to reduce some of the adverse environmental and health effects associated with urbanization (Nowak 2006; Nowak et al. 2006). For example, the ambient particulate concentrations were lower in neighborhoods with dense vegetation than in neighborhoods without it (Freiman et al. 2006).

Unfortunately, the influence of meteorology, emission sources, vegetation, air movement, and the shapes and sizes of urban construction on air quality is not yet clear, primarily because these variables can act together and/or separately, making each urban environment unique and unmatched. However, our results confirm previous findings using computational and structural models revealing that the vegetation and building arrangements in urban cities influence the air quality (Beckett et al. 1998; Louka et al. 1998; Vardoulakis et al. 2003; Xie et al. 2005; Buccolieri et al. 2009).

Contribution of emission sources

We use diagnostic ratios of some airborne PAHs from previous studies to estimate the sources of emissions in the metropolitan area of Fortaleza (Rogge et al. 1993; Kavouras et al. 2001; Manoli et al. 2004; Ravindra et al. 2006; Ströher et al. 2007). Cross-plots of these diagnostic ratios (Fig. 7a–d) suggest that emissions from light-duty diesel and car engines were dominant in the area, followed by lesser contributions from industrial emissions (e.g., asphalt production). These results are characteristic of the emission sources in most urban areas. In the metropolitan area of Fortaleza, light-duty vehicles represent 70 % of the vehicle fleet, and there is an asphalt production plant in the urban center (Pinheiro et al. 2009). The diagnostic ratios BaA/(BaA + Cry), Flr/(Flr + Pyr), and Ind/(Ind + BghiP) can be used to differentiate between sources associated with automotive pyrolysis and industrial and biomass combustion sources (e.g., coal and wood) (Manoli et al. 2004; Ströher et al. 2007). Cross-plots of these diagnostic ratios (Fig. 7e, f) suggest that pollutant sources such as steel and paved roads are also significant in the metropolitan area of Fortaleza. However, the most prevalent emissions are from light-duty diesel and car engines; coal and wood are also important emission sources. This finding can be explained by the fact that many commercial activities, including bakeries and restaurants (particularly grills), use wood or coal as an energy source. In the southern part of the metropolitan area of Fortaleza (the peripheral zone), iron and steel production industries are installed in the large port.

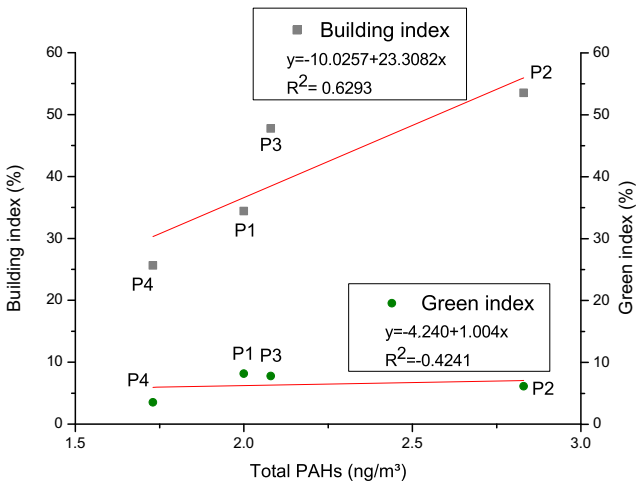


Figure 6 Correlation between green index, building index, and PAH concentration

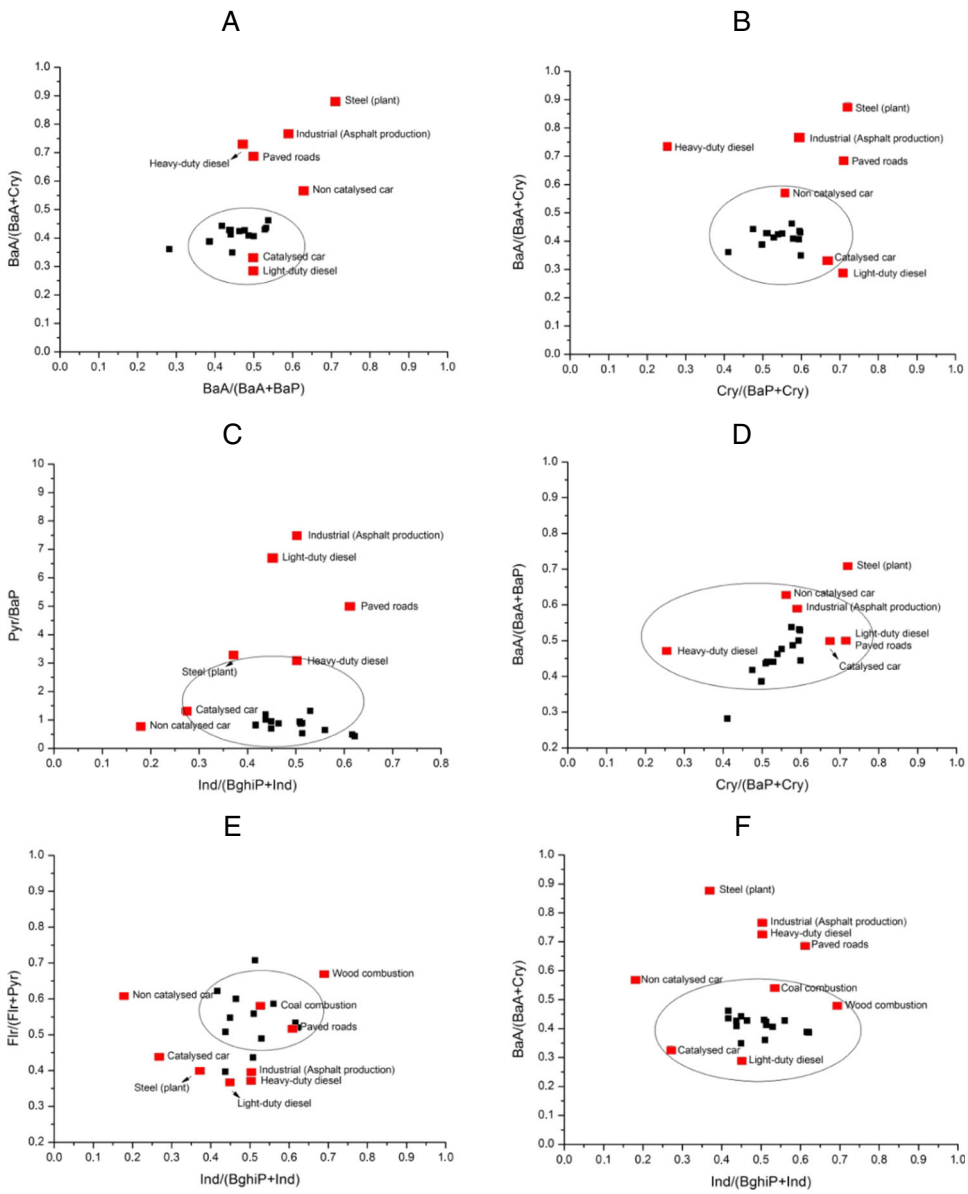


Fig. 7 Specific diagnostic ratios of PAHs used to estimate emission sources

(■) Fingerprint of emission sources based on diagnostic reasons

(■) Sources of emission estimates based on diagnostic reasons

Similar emission patterns to those found in this study occur in other southern hemisphere cities (Kavouras et al. 2001; De Martinis et al. 2002; Netto et al. 2006). The use of natural gas, pure ethanol, and the mixture of 80 % gasoline/20 % ethanol used in the Brazilian vehicular fleet should result in different PAH patterns than those found in other urban areas around the world (De Martinis et al. 2002). The metropolitan area of Fortaleza includes a mixture of vehicle types in which a variety of fuels, some of which are oxygenated, are used (gasoline blends, alcohol, diesel, biodiesel, and natural gas). In particular, ambient levels of acetaldehyde in the atmosphere over Brazilian cities are generally higher than those for other international cities (Cavalcante et al. 2005, 2006). Unfortunately, few studies have examined the PAHs emitted in motor vehicular exhaust in Brazilian urban areas. For this reason, our ability to characterize the sources of PAH emissions in airborne particles in the metropolitan area of Fortaleza is limited.

Potential cancer risk to humans from PAH levels

The International Agency for Research on Cancer (IARC) considers various PAHs to be probably (group 2A) or possibly (group 2B) carcinogenic to humans. Moreover, some mixtures containing PAHs are known to be carcinogenic to humans (group 1) (IARC 1987). In this study, we used the ILCR as a

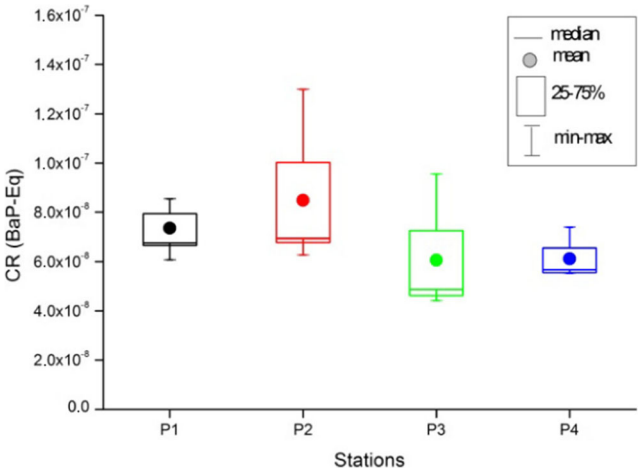


Fig. 8 Determining the risk of cancer at the four stations studied

guide to identify the potential cancer risk to humans from the environmental pollution of PAHs. Cancer risk levels ranged from 10^{-8} to 10^{-7} (Fig. 8). In terms of regulation, an ILCR of 10^{-6} or lower, as found in this study, poses no risk to human health; an ILCR greater than 10^{-4} indicates a high risk of cancer (Wang 2007).

The highest risk of cancer found in this study was at the P2 station, which had the highest concentration of PAHs in particulate matter and a large number of vehicles. Christense and Arora (2007) reported that vehicle emissions were the main anthropogenic source of PAHs in air pollution, and their levels are highest in the central, metropolitan, or commercial areas of large cities. According to Dong and Lee (2009), highly toxic levels of PAHs existed in the center of Ulsan (South Korea); they attributed this finding to the high traffic flow in the area. Moreover, there is a high potential for the suspended particulate matter that is deposited on streets to be exposed to PAHs generated from vehicle emissions, the asphalt pavement, and rubber tires (Takada et al. 1990; Murakami et al. 2005; Aryal et al. 2006).

Conclusion

This study provided data on the influence of urban topography on air quality based on the occurrence, emission sources, and health risks of PAHs in a developing city in Brazil's tropical semiarid region. PAHs with two and three rings were not observed in the study, and the highest levels were found in the center of the city where the vehicle flow is highest. The deposition flux of PAHs is similar in magnitude to that in other areas with pollution sources associated with developing urbanization and heating. An analysis of the influence of urban topography based on building and green indexes showed that building density is correlated with an increase in PAH concentrations; in contrast, urban vegetation has the opposite effect. Light-duty vehicles were the most influential emission source in the metropolitan area of Fortaleza. However, emissions from industrial sources (asphalt and steel production), combustion (coal and wood), and paved roads are also important. The health risks of PAHs in Fortaleza are similar in magnitude to those in other developing cities, and these risks are associated with increased vehicular flow.

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