



The impact of urbanization on tropical mangroves (Fortaleza, Brazil): Evidence from PAH distribution in sediments

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ABSTRACT

This investigation represents the first environmental diagnosis of the distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in sediments from a tropical mangrove in Fortaleza, northeastern Brazil. Sediment cores from six sampling stations in the Cocó and Ceará Rivers were retrieved in June–July 2006 to determine 17 priority PAHs. The total PAH concentrations (Σ_{PAHs}) ranged from 3.04 to 2234.76 $\mu\text{g kg}^{-1}$ (Cocó River) and from 3.34 to 1859.21 $\mu\text{g kg}^{-1}$ (Ceará River). These levels are higher than those of other cities with more industrial development. PAH concentrations did not reach probable effect levels (PELs). However, from 4.5 to 87.5% of individual PAH concentrations can occasionally cause adverse biological effects for aquatic organisms. The PAH molecular ratios indicate that the PAHs in the sediment core were derived mainly from petroleum, wood, and charcoal combustion (pyrogenic source), and that atmospheric deposition and urban runoff may serve as important pathways for PAH input to the sediment. Clearly, the Σ_{PAHs} in sediments collected in the Cocó and Ceará Rivers indicate that ongoing pollution is more severe than past pollution.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) enter aquatic environments via industrial discharge, petroleum spills, the combustion of fossil fuels, automobile exhaust, and non-point sources such as urban runoff and atmospheric deposition (Wang et al., 1999; Yunker et al., 2002; Macdonald et al., 2005). A number of PAHs are carcinogens, and due to their persistence in the environment, more information about their sources is needed (IARC, 2007).

The discharge of effluents into rivers and estuaries located in industrial and urban centers pollutes ecosystems. Most of the pollutants are adsorbed onto particulate material in the rivers, which causes efficient loading of the pollutants into the oceans (Baudo et al., 1990).

Sediments are sinks for particle-sorbed contaminants in aquatic systems and can serve as reservoirs for toxic contaminants that threaten the health of aquatic biota (Chen and White, 2004). As most of the chemical compounds have an affinity for sediment

particles, sedimentary deposits can record human influences (Baudo et al., 1990). Sediment cores have been used to assess hydrocarbon pollution history in industrialized countries such as the USA (Macdonald et al., 2005), but not in tropical South American countries. Studies using sedimentary recorders, through sediment cores, show significant correlations between PAH concentrations and changes in the energetics matrices (Macdonald et al., 2005). In the USA, a peak of PAH concentrations was verified in the sediment layer representing the 1950s, when the use of charcoal was higher than other energy sources. A reduction in the PAH trends between the 1970s and 1980s was attributed to the transition from charcoal to oil and natural gas (domestic heating) as energy sources (Macdonald et al., 2005).

Economically, Fortaleza is the fourth most important city in Brazil. The city has heavy traffic (505,000 vehicles) and about 2.3 million inhabitants distributed over an area of 313 km². In addition to vehicular emissions, other anthropogenic impacts come from the local harbor, industries, and a petroleum refinery. Studies on organic pollutants in the atmosphere of Fortaleza have attributed considerable carbonyls and PAH levels to vehicular activity and the combustion of fossil materials (Cavalcante et al., 2006; Cavalcante, 2007).

There are 172,000 km² of mangrove areas in the world; their ecological importance is due to their unique features, such as high

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productivity, abundant detritus, and high levels of organic carbon, which may make them a preferential site for the uptake and preservation of PAHs from anthropogenic inputs (Bernard et al., 1996). Few studies have been carried out to assess the distribution and accumulation of PAHs. Nowadays mangroves in China are the most studied of these ecosystems (Zheng and Richardson, 1999; Zheng et al., 2000; Tam et al., 2001; Ke et al., 2002; Zheng et al., 2002; Ke et al., 2005), followed by Brazil (Medeiros and Bicego, 2004a; Medeiros and Bicego, 2004b; Venturini and Tommasi, 2004).

The city of Fortaleza has 14.1 km² of mangrove area; 60% of this is located in urban areas. Fishing and capture of mollusks are important economic and subsistence activities for many families. As elevated concentrations of contaminants such as PAHs have been recorded in estuarine and mangrove sediments (Bernard et al., 1996; Ke et al., 2005; Liu et al., 2005; Medeiros et al., 2005), monitoring these ecosystems is a priority. Thus, the main goal of this study was investigate the spatial and vertical distribution of PAH contamination in estuarine and mangrove sediments. The study also analyzed PAH sources and possible toxicity. The present study was motivated by the scarcity of data about PAHs in tropical countries; these results may be useful to assess future sediment quality in the city of Fortaleza.

2. Materials and methods

2.1. Sample collection and preparation

The city of Fortaleza is located on the Atlantic coast of north-eastern Brazil at 3°9'S and 38°3'W (Fig. 1). It is a tropical city with temperatures between 26 and 32 °C and is characterized by rainy and dry periods. Rain occurs from February to July (1200 to 1400 mm/period and an average of around 200 mm/month), while

the dry period is from August to December, with negligible precipitation (Cavalcante, 2007).

Sediment samples from the Cocó and Ceará Rivers were taken in June–July 2006 (Fig. 1). Alumni tubes (previously cleaned with acetone and hexane) were manually driven into the sediment and extracted to recover the core material. In general, between 25 and 45 cm of sediment was recovered (see Fig. 2). Each sediment core was frozen on the day of collection in order to minimize microbial decay and evaporation. The sediments were sectioned at 5-cm intervals, lyophilized, sieved (removing stones and residual roots) and frozen before extraction and analysis.

2.2. Extraction and analysis

Sediment samples (30 g dry wt) were transferred to pre-washed 250 ml glass tubes to which a surrogate standard mixture containing four deuterated PAHs (d10-acenaphthene, d10-phenanthrene, d12-chrysene and d12-perylene) in acetone, purchased from Sigma-Aldrich, was added. Sediments were then extracted with 4 × 40 mL acetone/hexane (1:1 v/v) by sonicating for 60 min. All sample extracts were then further purified by liquid–solid chromatography on silica/alumina to remove organic polymers, aliphatic and polar compounds according to an optimized method (Cavalcante et al., 2008). The concentrations of PAHs were analyzed using a Shimadzu CG 17A gas chromatograph interfaced with a flame ionization detector (GC-FID). The separation was performed on a DB-5 column J&W Scientific (30 m, 0.25 mm i.d., film thickness 0.25 μm). The initial oven temperature was 60 °C for 10 min and was then increased to 120 °C at 5 °C min⁻¹ and 120 to 300 °C at 3 °C min⁻¹. The injector and detector temperatures were 280 °C and 300 °C, respectively. Quantification was carried out by the internal standard method using Supelco and Merck standards. The PAHs studied were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace),

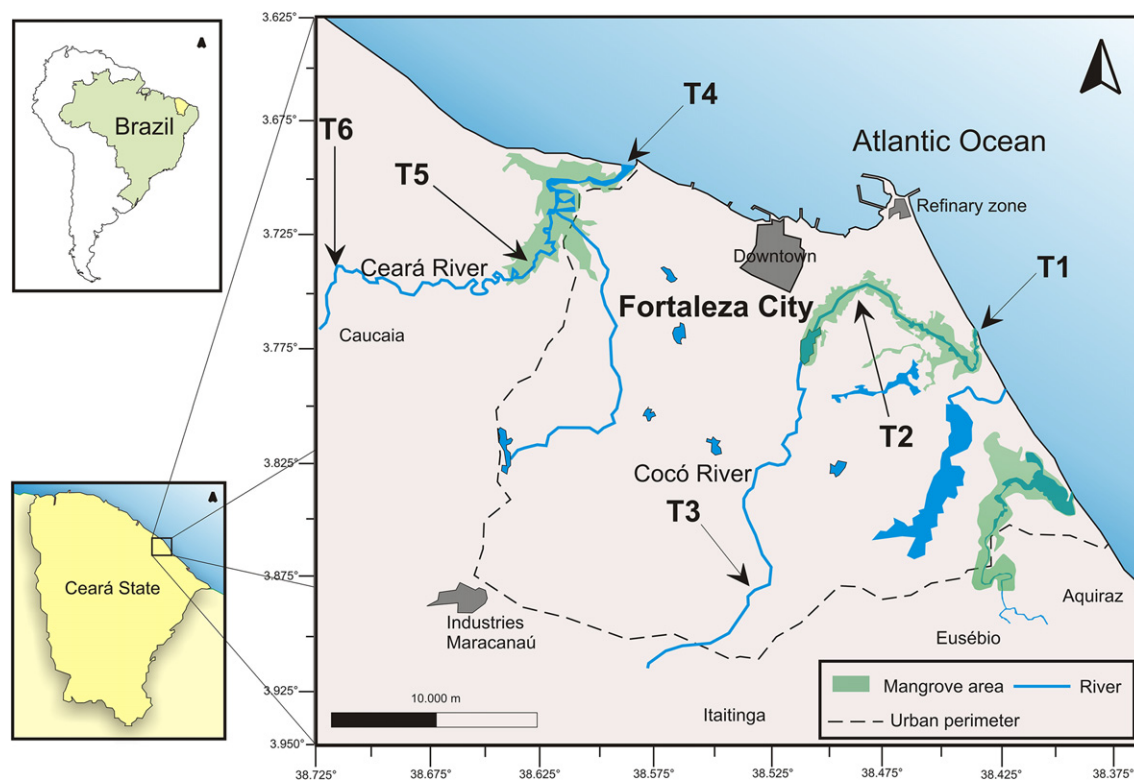


Fig. 1. Sampling sites in the Cocó and Ceará Rivers.

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), perilene (Per), indeno[1,2,3-cd]pyrene (IncdP), dibenzo[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP). Minimum detection limits for PAHs ranged from 0.2 to 0.5 $\mu\text{g mL}^{-1}$. PAH confirmation (20% samples) was done by gas chromatograph using a CG 17A coupled to a mass spectrometry detector (Shimadzu model GCMS-QP5050); the NIST library was also used.

Total organic carbon (TOC) of sediment was determined by the potassium dichromate oxidation method (Strickland and Parsons, 1972). The overall precision of the analysis, expressed as the relative standard deviations (RSD), was less than 5% ($n = 3$).

2.3. Quality control

All data were subject to strict quality control procedures. Deuterated surrogates were used throughout the analytical procedure to compensate for losses and contamination during the extraction of the samples and instrumental analysis. Spiked recoveries from sediment samples ranged from 59 to 110% for all targeted analytes. Analysis of a reagent blank demonstrated that the analytical system and glassware were free of contamination.

3. Results and discussion

3.1. Concentration, classification and toxicological significance of PAHs

Total PAH concentrations (ΣPAHs) ranged from 3.04 to 2234.76 $\mu\text{g kg}^{-1}$ (Cocó River) and from 3.34 to 1859.21 $\mu\text{g kg}^{-1}$ (Ceará River) (Fig. 2). In most cores, ΣPAHs decreased towards the deep layers, except in some cases such as perilene (Per), which increased in cores T3 and T5. In cores T1, T2, T4 and T6, Per levels decreased together with ΣPAHs (in different magnitudes). Thus, ΣPAHs in sediment collected in the Cocó and Ceará Rivers indicates that ongoing pollution is more severe than past pollution.

The major PAH concentrations were observed at both the Cocó and Ceará mouths. Murphy et al. (1988) reported that more 90% of hydrocarbons are adsorbed on particulate material in the rivers and do not cross the estuarine zone. This is due to the dramatic changes in physico-chemical conditions driven by the mixture of fresh and saline waters. The salinity also increases the adsorption of pollutants onto particles, concentrating pollutants in estuaries via flocculation (Hegemen et al., 1995; Brunk et al., 1997). Thus, the estuarine region operates as a sink of particles/pollutants transported from the rivers.

The ΣPAHs found in the Cocó and Ceará Rivers are below the levels reported in places with more industrial activity (Todos os Santos bay, Santos, Mai Po and Hong Kong) (Table 1). However, when compared with places with reduced industrial activity (Deep Bay and São Sebastião), the ΣPAHs found in the Cocó and Ceará Rivers were higher (Table 1). In addition, using the classification suggested by Benlahcen et al. (1997), 48.9% of the sedimentary layers were classified as medium, which is typical of an urban-industrial zone (Fig. 3). Thus, the data show that PAH levels in both rivers of the city of Fortaleza are above those of other cities with more industrial development.

The destruction of the margins, barrages and embankment in certain sections of the rivers along the Ceará coast is primarily responsible for changes in estuarine hydrodynamics (Vasconcelos and Freire, 1985) and can contribute to the decreased dispersion of pollutants entering the aquatic environment.

The mechanisms of biomagnification and food chain accumulation of organic chemicals are still not clear (van der Oost et al., 2003),

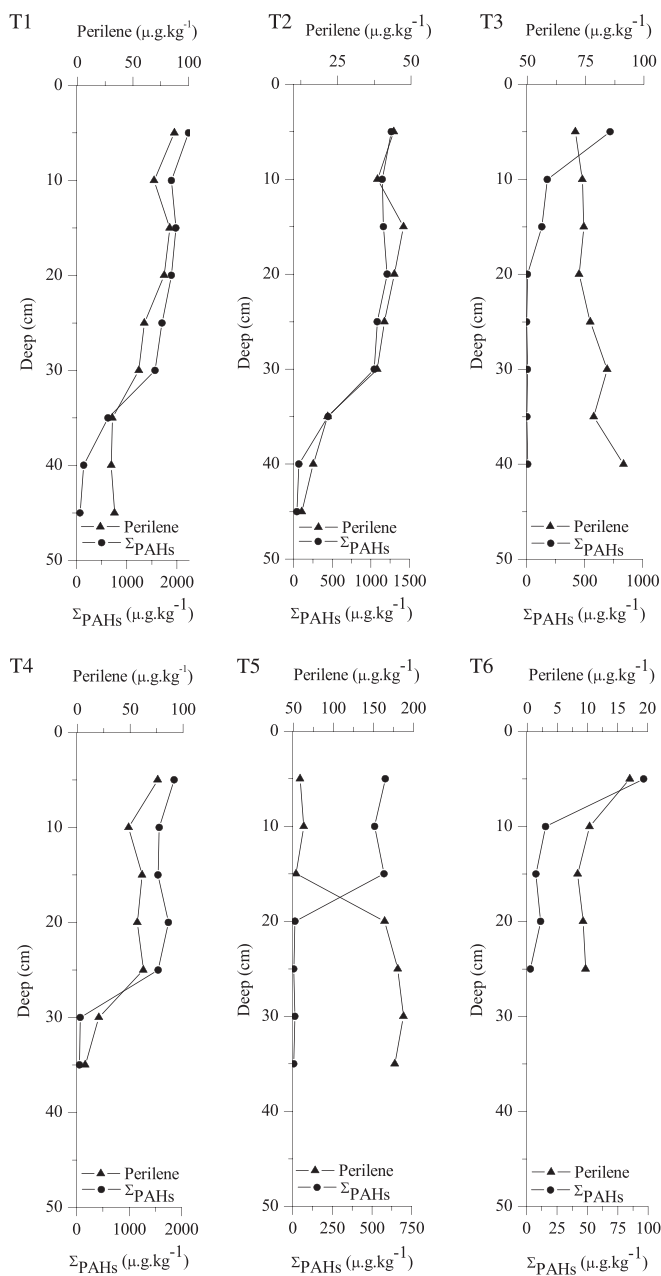


Fig. 2. ΣPAHs and perilene concentrations.

although Russell et al. (1999) provided strong evidence for biomagnification of chemicals with $\log K_{ow}$ values greater than 6.3, some evidence exists for biomagnification of chemicals with $\log K_{ow}$ values between 5.5 and 6.3, and no evidence for biomagnification of chemicals with $\log K_{ow}$ values less than 5.5. Marti-Cid et al. (2007) reported that fish and seafood consumption by children of Catalonia, Spain accounts for intakes from 5.11 to 5.21 ng PAHs/kg/day. Thus, since many families rely on fish and shellfish capture in both the Cocó and Ceará Rivers, we employed the Canadian sediment quality guidelines for protection of aquatic life (SQG) to evaluate the potential biological concerns of sedimentary PAH levels (Environment Canada, 1999). The agency establishes temporary quality standards (TQS) and probable effect levels (PEL) for organisms in sediments (Table 2). TQS and PEL are flexible tools for interpreting and assessing the toxicological significance of chemistry data for the sediment. PAH concentrations in sediments below the TQS usually

Table 1

Σ_{PAHs} surface sediments (upper 5 centimeters) and comparison with mangrove sediments from other places.

Place	Activity	Σ_{PAHs} $\mu\text{g kg}^{-1}$
Todos os Santos Bay, Salvador-Brazil ^a	Urban/petrochemistry	8.0–4163.0
São Sebastião channel, São Paulo-Brazil ^b	Urban/petrochemistry	20.4–200.3
Santos, São Paulo-Brazil ^c	Urban/arbor/petrochemistry	79.6–15389.1
Deep Bay, China ^d	Arbor/petrochemistry	237.0–726.0
Hong Kong SAR, China ^d	Urban/arbor/petrochemistry	56.0–3758.0
Mai Po, China ^e	Urban/petrochemistry	685.0–4680.0
Cocó River, Fortaleza-Brazil ^f	Urban	720.7–2234.7
Ceará River, Fortaleza-Brazil ^f	Urban	96.4–1859.2

^a Source: Venturini and Tommasi, 2004.

^b Source: Medeiros and Bicego, 2004b.

^c Source: Medeiros and Bicego, 2004a.

^d Source: Zheng and Richardson, 1999.

^e Source: Tam et al., 2001.

^f Source: This study.

cause no adverse effects for aquatic organisms, while concentrations above the PEL are frequently associated with adverse biological effects.

PAH concentrations did not reach the PEL barrier, but 4.5–87.5% of PAH levels are between the TQS and PEL zones (Table 2). Phen and Ant levels never reached the TQS barrier, while 46.9 to 87.5% of the values for Ace + Acy, BaA and BaP were between the TQS and PEL zones. PAH concentrations between the TQS and PEL can occasionally cause adverse biological effects for aquatic organisms (Environment Canada, 1999).

3.2. Correlation of PAHs with TOC

It has been demonstrated that the characteristic of the sediment influences the distribution and concentration of PAHs. Important factors included chemical composition of organic matter and the presence of clay minerals (Witt, 1995; Wang et al., 2001). In the present study, there was no relationship between TOC and Σ_{PAHs} (Fig. 4), which also has been reported by others works (Coakley et al., 1993; Wade et al., 1994; Tam et al., 2001). Some studies suggested that PAHs distributions and concentrations should be determined more by direct contribution, and not by sediment type (Raoux and Garrigues, 1991; Coakley et al., 1993; Tam et al., 2001). Besides, Simpson et al. (1996) showed that the relationship between PAHs levels and TOC was significant for highly polluted places, what is not the case for the sediments of Cocó and Ceará Rivers.

Table 2

Temporary quality standard (TQS), probable effect levels (PEL) and incidence (%) in sediment from Cocó and Ceará Rivers.

PAHs	TQS ($\mu\text{g kg}^{-1}$)	PEL ($\mu\text{g kg}^{-1}$)	% < TQS	TQS < % < PEL	% > PEL
Nap	34.6	391.0	76.9	23.1	0
Ace + Acy	12.6	1017.0	12.5	87.5	0
Fl	21.2	144.0	95.5	4.5	0
Phen	86.7	544.0	100.0	0.0	0
Ant	46.9	245.0	100.0	0.0	0
Flr	113.0	1494.0	80.0	20.0	0
Pyr	153.0	1398.0	93.7	6.3	0
BaA	74.8	693.0	53.1	46.9	0
Chry	108.0	846.0	90.9	9.1	0
BaP	88.8	763.0	46.8	53.1	0

3.3. Source determination

Perilene (Per) is a PAH with five aromatic rings and isomers of BbF, BkF and BaP ($\text{C}_{20}\text{H}_{12}$). Its origin is still controversial (Silliman et al., 1998; Jiang et al., 2000; Silliman et al., 2000; Silliman et al., 2001). Compared with other PAHs, low concentrations of Per are released into the atmosphere during the burning of fossil fuel, probably due to its thermodynamic instability or large reactivity (Silliman et al., 1998). Furthermore, Per is only found in sediments and is absent in the water (Silliman et al., 1998).

In general, PAH levels in polluted areas are highest in recently deposited sediments. However, in the case of Per, the levels increase toward the deep (old) sediments. This indicates that Per is not carried and deposited in the sediment like other PAHs, but formed after deposition from anaerobic diagenesis of organic matter (Silliman et al., 1998; Jiang et al., 2000; Silliman et al., 2000; Silliman et al., 2001). Silliman et al. (2000) reported that Per concentrations in a sediment core from Lake Ontario (Canada) increased significantly under the bioturbation zone (anoxic conditions). Anoxic conditions are thus the principal prerequisite for the formation of Per in the sedimentary column (Silliman et al., 1998; Jiang et al., 2000; Silliman et al., 2000; Silliman et al., 2001).

Although a variety of precursor materials for Per have been suggested, none have been confirmed. Silliman et al. (2000) did not find significant correlation between Per levels and the carbon/nitrogen ratio or with the organic carbon in continental sediments. However, the same author established a hypothesis in which the formation of Per is controlled by microbial activity (*in situ*), as the organic carbon source is indefinite (Silliman et al., 2001).

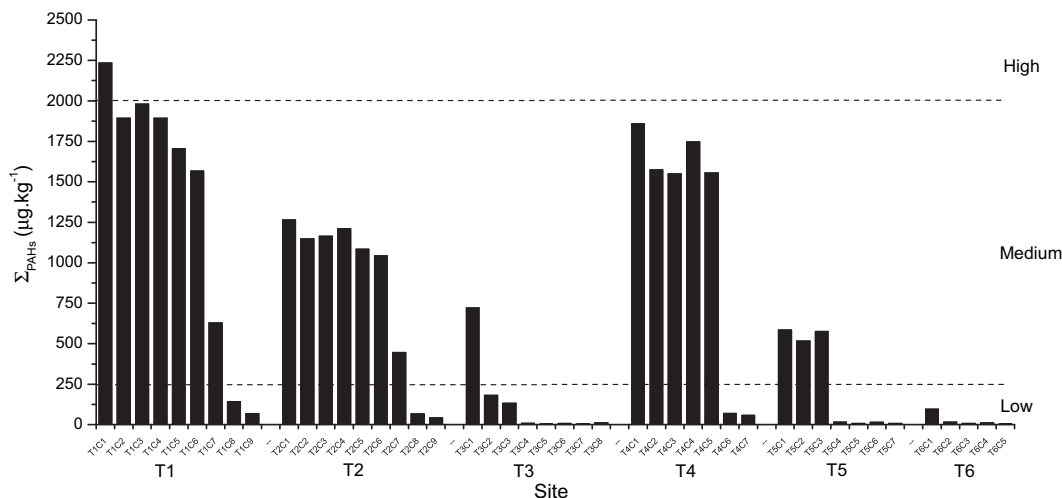


Fig. 3. Classification of Σ_{PAHs} found in sedimentary layers.

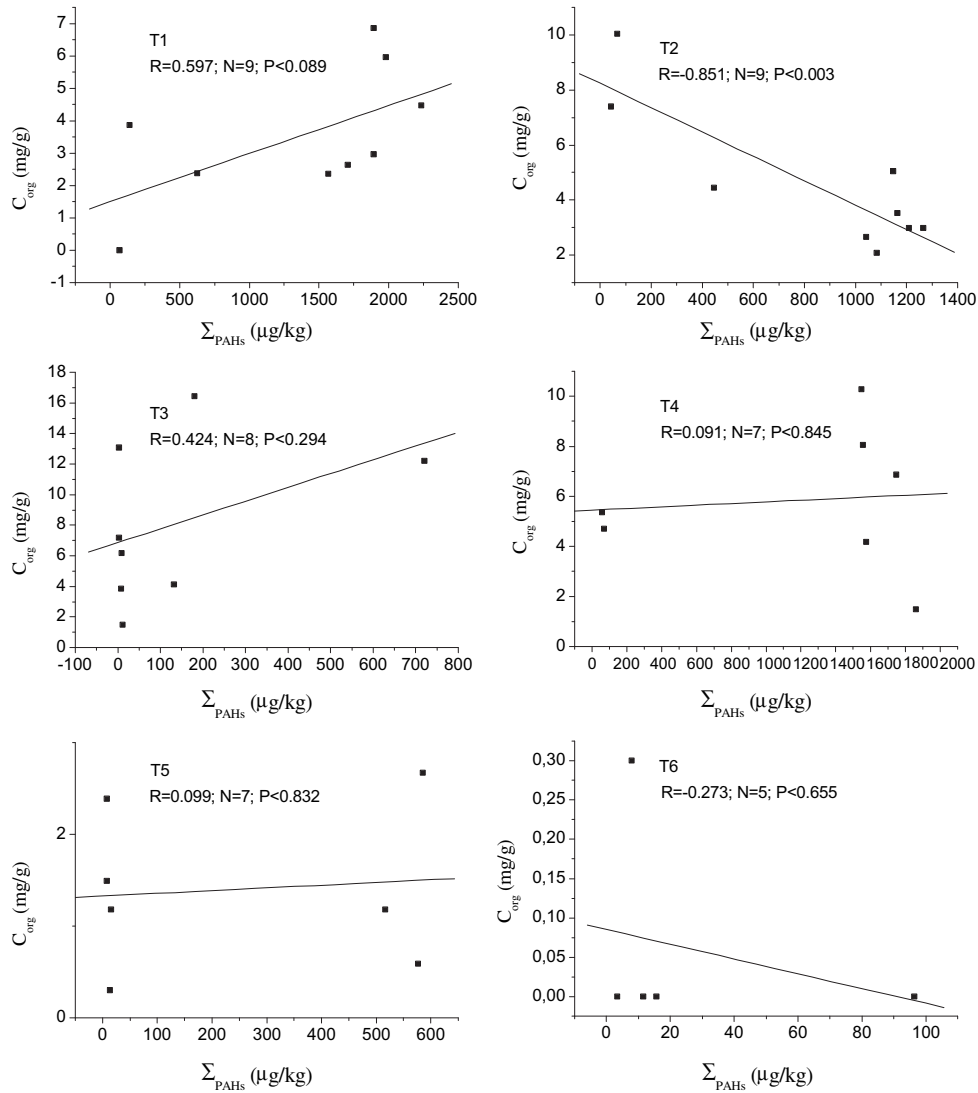


Fig. 4. Correlation plots of Σ_{PAHs} vs TOC.

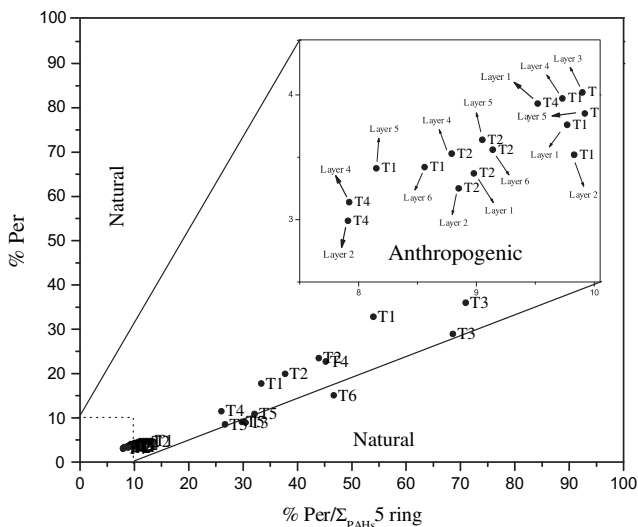


Fig. 5. %Per versus %Per/ Σ_{PAHs} 5 rings ratios for the Cocó and Ceara Rivers.

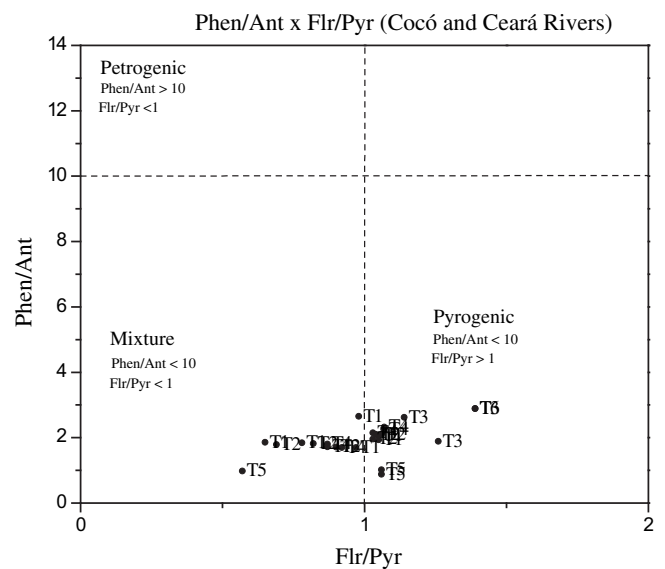


Fig. 6. Phen/Ant versus Flr/Pyr ratios from the Cocó and Ceará Rivers.

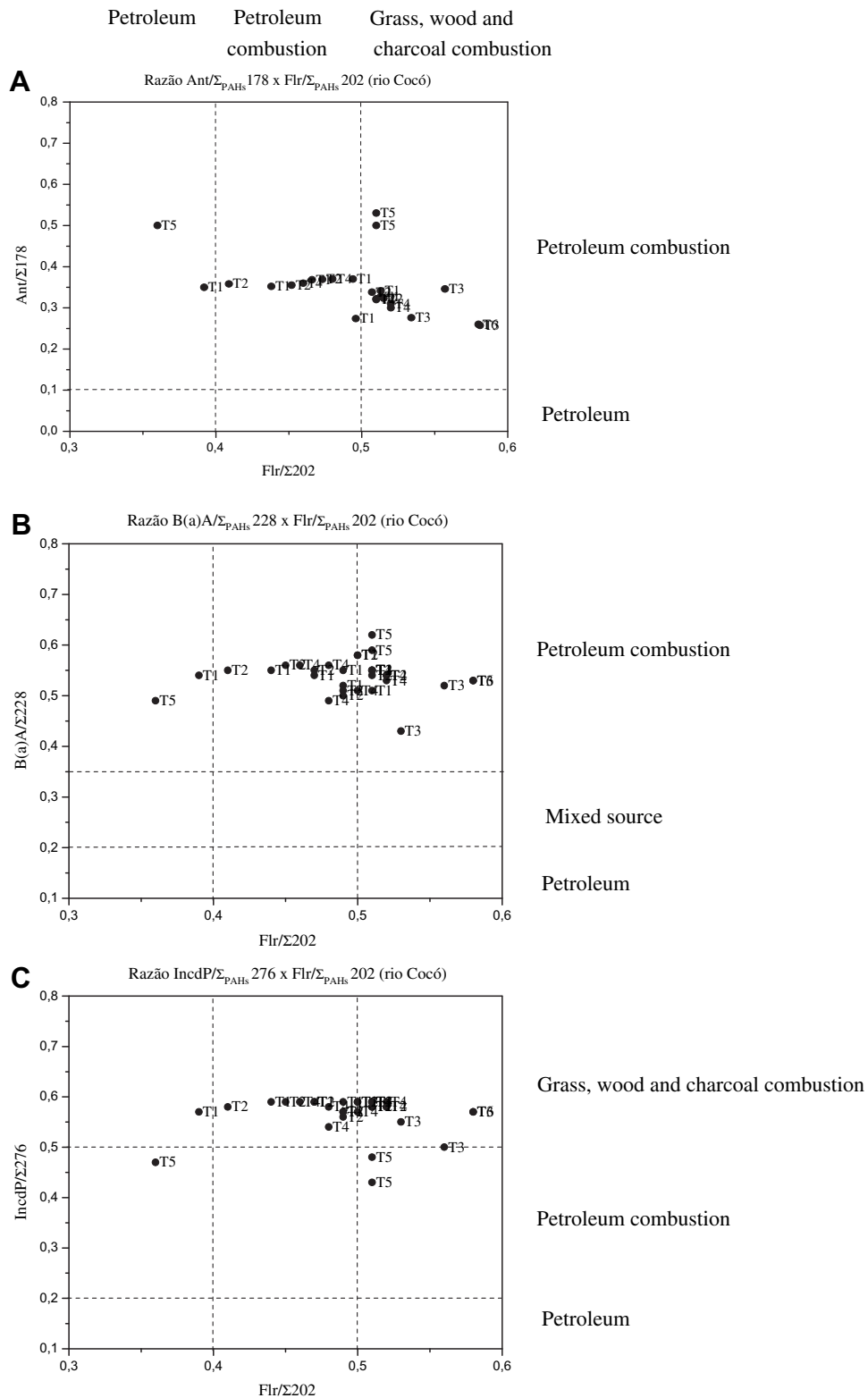


Fig. 7. PAH ratios and their sources in sediments from the Cocó and Ceará Rivers.

Alternatively, fungi are proposed to be the major precursor carriers for Per in sediments, as perylenequinone structures have been previously suggested as the natural precursors for Per; perylenequinone pigments exist in many fungal bodies, and fungi have played important roles in geological processes (Jiang et al., 2000). The low concentration of Per in recent sediments is

attributed the instability of quinone in the oxide zone (Jiang et al., 2000).

Although the origin of Per remains enigmatic, several studies have used the molecular ratio of Per and other PAHs to distinguish natural and anthropogenic sources in sediments (Baumard et al., 1998; Tolosa et al., 2004; Liu et al., 2005).

The %Per is the percentage of Per concentration relative to the total PAH concentrations. Values >10% suggest natural origins for this compound (Baumard et al., 1998), while ratios of %Per to total concentration of PAHs with five aromatic ring (%Per/ $\Sigma_{\text{PAHs 5 rings}}$) higher than 10% indicate diagenetic processes (natural). For ratios lower than 10%, an anthropogenic origin is more likely (Tolosa et al., 2004).

The %Per versus %Per/ $\Sigma_{\text{PAHs 5 rings}}$ ratio for the Cocó and Ceara Rivers are plotted in Fig. 5. At sites T1 and T2 (Cocó River), most of the layers show anthropogenic inputs, while at T3, no anthropogenic inputs were observed. In the Ceará River, only site T4 had layers that were anthropogenically influenced. PAHs levels from the Cocó River are higher than in the Ceará River as it crosses a large urban area with high vehicular traffic. In addition, the Cocó River is surrounded by avenues, so in the rainy period, water reaches the river via urban runoff (Cavalcante, unpublished data).

3.4. Petrogenic versus pyrogenic sources

Molecular ratios have been used to determine source types (petrogenic or pyrogenic). Phen/Ant and Flr/Pyr ratios, specifically, are widely used as diagnostic tools (Benlahcen et al., 1997; Baumard et al., 1998; Tam et al., 2001; Yim et al., 2005). Due to differences in the thermodynamic properties and kinetic characteristics of some PAHs, it is possible to precisely establish the source of the compounds in the sediment (Benlahcen et al., 1997; Baumard et al., 1998). Processes involving high temperatures, such as the combustion of organic material (pyrogenic process), usually liberate PAHs with Phen/Ant ratios < 10, while the slow maturation of the organic material during catagenesis (petrogenic process) leads to Phen/Ant ratios > 10 (Benlahcen et al., 1997; Baumard et al., 1998). Likewise, Flr/Pyr ratios > 1 and < 1 indicate pyrogenic and petrogenic sources, respectively (Benlahcen et al., 1997; Baumard et al., 1998).

In this study, the primary source of PAHs to sediment was from a pyrogenic process (Fig. 6). However, a considerable number of layers showed a mixture of petrogenic and pyrogenic sources (Phen/Ant < 10 and Flr/Pyr < 1). This behavior was verified in other rivers near urban centers with activities related to the transport and storage of fossil fuel (Tam et al., 2001; Liu et al., 2005; Yim et al., 2005; Colombo et al., 2006; Vane et al., 2007). Yim et al. (2005) suggested that this behavior can be related to the precedence of the energy source. According to author, the product of the combustion of charcoal from Europe and North America produces an Flr/Pyr ratio > 1, different from charcoal from Australia (Flr/Pyr ratio 0.3–0.7). In addition, their behavior can be a result of processes related to the dynamics of PAHs in the atmosphere (Liu et al., 2005). Vane et al. (2007) reported that this behavior is characteristic of regions with several sources, such as industrial sources, combustion of fossil fuel, burning of charcoal and wood, and urban runoff. Our data suggest that pyrogenic processes are the primary source of PAHs in both rivers, and urban runoff urban is responsible for transporting PAHs.

3.5. Estimation of anthropogenic source

Yunker et al. (2002) used molecular ratios of PAHs to differentiate several types of sources from industrial and urban areas. In both the Cocó and Ceara Rivers, over 90% of the sediment layers investigated had anthropogenic inputs from petroleum, wood and charcoal combustion (pyrogenic process) (Fig. 7). The city of Fortaleza possesses a considerable vehicular fleet, and several sectors still use charcoal and wood as a source of energy. According to Cavalcante (2007), the main emissions into the atmosphere are

from gasoline and oil combustion, although wood and charcoal burns are also expressive.

4. Conclusion

PAH distributions in the Cocó and Ceará Rivers showed the highest concentrations in estuarine and mangrove zones; the levels are above those of other cities with more industrial development. In estuarine and mangrove zones, the vertical distribution showed that past pollution was less than in the present day. PAH concentrations in estuarine and mangrove zones can occasionally cause adverse biological effects for aquatic organisms. Molecular ratios showed that petroleum, wood and charcoal combustion (pyrogenic process) are the primary sources of PAHs for both rivers.

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