



Polycyclic aromatic hydrocarbons in tree barks, gaseous and particulate phase samples collected near an industrial complex in São Paulo (Brazil)



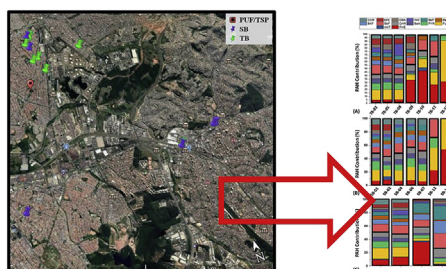
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HIGHLIGHTS

- Environmental samples were collected in an industrial impacted area in São Paulo.
- PAHs were determined in gaseous, particulate phase and tree barks samples.
- A carcinogenicity assessment for gaseous and particulate phases pointed to high risk.
- Tree barks presented an abundance of low molecular weight PAHs.
- The sample collected nearer the complex presented species from petrogenic emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

Urban trees are a new tool for pollutant monitoring since gaseous and particulate pollutants can deposit in its barks. Polycyclic aromatic hydrocarbons (PAHs) levels were determined in gaseous phase samples collected in polyurethane foam (PUF), total suspended particles (TSP) samples collected in quartz fiber filters and tree bark samples (Tipuana and Sibipiruna) collected in the surroundings of an industrial complex in the metropolitan area of São Paulo. Benzo(b)fluoranthene presented the highest average concentration in the TSP samples and phenanthrene, the highest average concentration in the PUF samples; the sum of carcinogenic equivalents for benzo(a)pyrene (BaP_{Eq}) for both phases was above 20 ng m⁻³, representing a high cancer risk. The most abundant PAH for tree barks was fluoranthene; low weight PAHs presented a higher abundance than the observed in TSP. Coronene (vehicular exhaust marker) presented good correlations with fluoranthene in the tree bark samples, suggesting an influence of vehicular emissions. A tree bark sample collected near the petrochemical area presented biomarkers of petrogenic origin (hopanoids) in the mass spectrum and an unresolved complex mixture (UCM) profile. The results suggested an influence of both vehicular and industrial sources on the air quality observed in the atmosphere and tree barks samples.

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1. Introduction

The inhabitants of the metropolitan area of São Paulo (MASP) are exposed to high levels of pollutants (Pereira et al., 2017b; Vasconcellos et al., 2011). The São Paulo metropolitan area includes industries responsible for the production of about 30% of the volume of fuels consumed, the largest consumer market in South America (PETROBRAS, 2019); it has been observed that the concentration of pollutants near this area is affecting the air quality (Caumo et al., 2018) and health problems have been observed (Zaccarelli-Marino, 2012; Zaccarelli-Marino et al., 2016).

According to the International Agency for Research on Cancer (IARC), atmospheric particulate matter (PM) is carcinogenic to humans and causes lung cancer; the agency classifies it as a carcinogenic agent of Group 1, with a strong indication of carcinogenicity (Loomis et al., 2013). The particulate matter can reach up to 100 μm of aerodynamic diameter (Da), and depending on its size can reach the respiratory tract. The most commonly studied is the inhaled PM, with $\text{Da} \leq 10 \mu\text{m}$ (PM_{10}), and the fine inhalable, with $\text{Da} \leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) (Pereira et al., 2017b).

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with two or more aromatic rings condensed in their structure. These compounds are formed through incomplete combustion or pyrolysis of organic materials, biomass burning, coal, burning of raw petroleum material and also in industrial processes; PAHs are often found in the fine fraction of particulate matter (Ravindra et al., 2008). The PAHs with 3 aromatic rings or less are more abundant in the vapor phase, while the PAHs with 4 aromatic rings are present in the vapor phase and particulate phases, depending on the atmospheric temperature (Alves, 2008).

Some studies show that air quality can be monitored by the measurement of pollutants deposited in the bark of trees. The accumulation of these pollutants by the bark occurs by physical adsorption (Hites, 2010). In the decade of 1960, the tree bark was successfully employed as an indicator of sulfur deposition in Sweden. Since then, they have been employed in several studies for the monitoring of air quality (Ameran et al., 2014; Birke et al., 2018; Pereira Netto et al., 2007; Ratola et al., 2009; Wu et al., 2019; Zhou et al., 2014). The analysis of the samples allows to provide data about the conditions to which the trees were exposed in the long term, indicating the persistent sources of pollution (Birke et al., 2018; Born and Hofmann, 1986; Cocozza et al., 2016; Orecchio et al., 2008).

Dry deposition is the main mechanism in the filtering of air pollutants by trees in non-precipitation periods and can depend on factors such as the pollutant physical and chemical properties, tree surface and microclimate (Moreira et al., 2018; Selmi et al., 2016). The partitioning between vegetation and atmosphere was found to be primarily dependant on atmospheric gas-phase PAHs concentrations and ambient temperatures, models have shown that 44% of emitted PAHs can be removed by vegetation (Orecchio et al., 2008; Simonich and Hites, 1994).

The presence of trees can lead to a reduction in the levels of gaseous and particulate pollutants in greener urban areas; it occurs due to filtering properties of the plants, passive deposition on the surface of plant body, aerodynamic dispersion properties of the tree structure and the higher wind speed and lower temperature in the open green areas (Bolund and Hunhammar, 1999; Janhäll, 2015; Jeanjean et al., 2016; Kassomenos et al., 2014; Moreira et al., 2016; Oliveira et al., 2011).

The objective of this study was to assess the PAHs concentrations in the gaseous and particulate phases, and in the tree barks collected in the surroundings of an industrial complex.

2. Methodology

The tree bark samples of the species *Tipuana* (*Tipuana tipu*), *Sibipiruna* (*Poincianella pluviosa*) were collected in the neighborhoods near an industrial complex ($n = 14$), in the cities of Santo André and Mauá in MASP, (Brazil) (Fig. 1). Approximately 80,000 people live around the industrial area (Zaccarelli-Marino et al., 2016).

The samples were collected from the trees at a height of 1.5 m around the trunk, between August and October 2016. Four sections of 8 cm $\times$ 8 cm of the tree bark were removed using titanium tools to prevent contamination. The samples were stored in plastic bags (Locosselli et al., 2019; Moreira et al., 2018).

The tree barks were cut with scissors, dried at 70 °C overnight, and then milled (PULVERISETTE 6) for 10 min at 500 rpm. Eight grams of the milled sample was weighed on an analytical balance. The extraction was carried out with a Soxhlet apparatus where cellulose cartridges and all the glassware of the equipment were pre-cleaned with dichloromethane (Merck) to avoid any contamination.

The samples were extracted for 24 h, with 200 ml of dichloromethane. The ground tree bark was inserted in the cellulose cartridge (8 g) and 4 g of sodium sulfate was added. After the extraction, the extracts were evaporated by rotary evaporator (IKA) at a temperature of ≤ 38 °C. The volume of 1 ml then was filtered and dried in a nitrogen flow. The determination of PAHs was done in a gas chromatograph coupled to a mass spectrometer (Orecchio et al., 2008).

The EPA 525 PAH Mix A (48953-U, Sigma), benzo(e)pyrene (442475, Sigma) and coronene (27830, Fluka) were used in order to obtain calibration curves, with the correlation coefficients (R^2) were greater than 0.99. The methodology determined fourteen PAHs: phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene

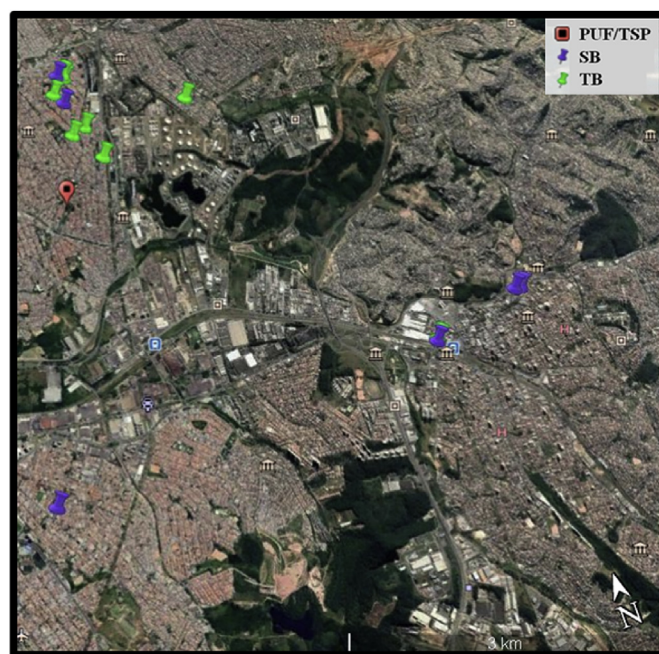


Fig. 1. Sampling sites for *Tipuana* (TB) and *Sibipiruna* (SB) trees, and PUF/TSP in the industrial complex surroundings (Google Earth).

(BeP), benzo(a)pyrene (BaP), indene(1,2,3-c,d)pyrene (IND), dibenzo(a,h)anthracene (DBA) and benzo(g,h,i)pyrene (BPE) and coronene (COR).

Techniques for PAHs determination in tree barks have been tested and the one that presented the best recoveries was adopted. Tree barks were homogenized and half of this material was spiked, and both parts were submitted to the entire extraction methodology. After the analysis, the difference between the concentrations was calculated. The recoveries for PAHs in tree barks were equal or above 50% for PHE, ANT, FLT, BaA, CHR, BbF, BkF, BeP, BaP and BPE; the recoveries were below 50% for PYR, InP, DBA and COR.

Total suspended particles (TSP) and gaseous phase samples were collected at a sampling station of the Environmental Agency of the São Paulo State (CETESB) (23° 38' 44.44" S and 46° 29' 35.71" W). A high-volume sampler (Thermo Fisher Scientific) (flow rate of 280 L min⁻¹) was used to collect simultaneously the particulate and gaseous samples. For TSP, quartz fiber filters were employed ($\phi = 110$ mm). Filters were previously heated in an oven at 600 °C for 6 h and weighed. The gaseous phase samples were collected in a polyurethane foam (PUF) that was pre-cleaned in an ultrasonic bath with acetone, adapted from Boonyatumanond et al. (2007).

Twenty-four-hour samples were collected in July 2016 (n = 30). After sampling, the TSP samples were weighed, wrapped in aluminum foil, and stored at 4 °C in the refrigerator. The PUF samples were kept in a dark box to minimize losses, and then the extraction was conducted on the same day. The samples were extracted in an ultrasonic bath for 20 min for three times with 80 mL of dichloromethane for TSP samples and 80 mL of acetone for PUF samples, previously described by Caumo et al. (2018). The extracts were then concentrated by rotary evaporation and nitrogen flux. Each concentrated sample was fractionated in a glass column with silica and alumina to separate the organic chemical classes. The fraction comprising PAHs and their derivatives was obtained by eluting a mixture of hexane and dichloromethane (1:1) described by (Pereira et al. (2017a)). Then, qualitative and quantitative analyses of PAHs were conducted in a GC/FID from Shimadzu (model 2010 Plus) with a column SH-Rtx-5(30 m × 0.32 mm × 0.25 μ m) in splitless mode and helium as the carrier gas. The temperature program was the following: 80 °C for 4 min; increasing until 200 °C (20 °C min⁻¹); from 200 °C to 270 °C (4 °C min⁻¹) and until 280 °C (5 °C min⁻¹) (de Oliveira Alves et al., 2015). Flame ionization gases were hydrogen (40 mL min⁻¹) and synthetic air (400 mL min⁻¹). The percentage of recovery testes varied between 88% and 124%, and the detection and quantification limit were of 0.002 and 0.06 ng m⁻³. The determined PAHs were the same as for tree barks, together with fluorene (FLU).

3. Results and discussion

3.1. PAHs in PUF and TSP

PAHs concentrations were determined for TSP and PUF samples collected simultaneously during the winter season in 2016 (Fig. 2 and Table S1, in the supplementary information). BbF (8 ng m⁻³), BaP (7 ng m⁻³) and BkF (6 ng m⁻³) were the most concentrated in particulate phase; PHE (20 ng m⁻³), BaP (7 ng m⁻³) and BbF (5 ng m⁻³) were dominant in gaseous phase; BaP is known to be carcinogenic to humans (IARC, 2010), and PHE is emitted by industries (Abdel-Shafy and Mansour, 2016). The sum of PAHs concentrations was of 35 and 52 ng m⁻³ for TSP and PUF, respectively. These values are higher than the sum of PAHs concentrations for samples collected in a previous study conducted in an urban area of São Paulo, highly impacted by vehicles (26 ng m⁻³) (Vasconcellos et al., 2008).

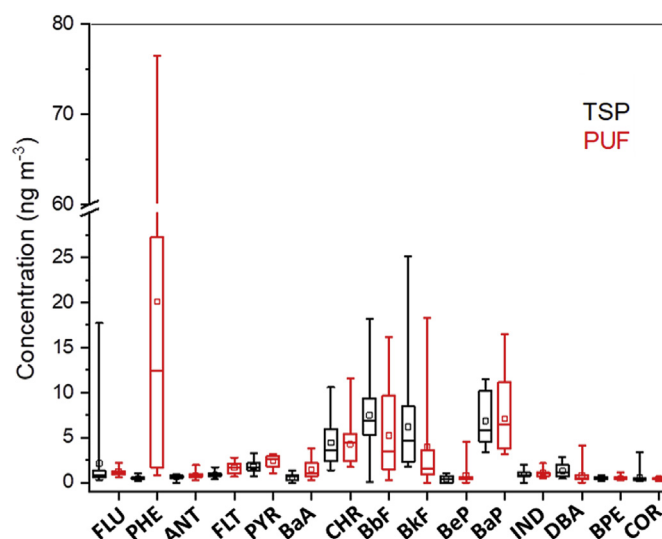


Fig. 2. PAHs concentrations for TSP and PUF.

DBA, a marker for industrial emissions (Ravindra et al., 2008), was determined in both phases and it had been predominant in TSP, and CHR, also found in all samples, is emitted mainly from the combustion of gasohol (a mixture of gasoline and ethanol) and diesel (Vasconcellos et al., 2003). BbF and BkF concentrations are similar to the observed in a previous study in the same area, where these both compounds were dominant for TSP and PUF (Caumo et al., 2018), which suggest a high contribution of fossil fuels combustion (Wang et al., 2006).

The concentrations of BaP for both gaseous and particulate phases were above the recommended standard adopted by the European Commission for Environment (1 ng m⁻³) (AQS, 2011). The carcinogenic equivalent to PAH (BaPE_q) was calculated according to the formula proposed by Nisbet and Lagoy (1992). BaPE_q value combining TSP and PUF was over 23 ng m⁻³; according to previous studies a limit value of 1 ng m⁻³ is considered for BaP equivalent indexes (Chen et al., 2017; Sánchez-Soberón et al., 2016; Silva et al., 2010) and values above this standard represent a high cancer risk to humans. BaPE_q was 2.1 for TSP samples collected at the same location during the spring season in 2015 (Caumo et al., 2018); that value is over ten times lower than the observed in this study. The lower dispersion conditions during winter may have affected the PAHs concentrations in this campaign, increasing the exposure risks (Pereira et al., 2017b).

3.2. PAHs in tree barks

The total PAHs concentrations in tree barks ranged between 21 and 491 μ g kg⁻¹ (Table 1), and were within the range observed in other studies; higher concentrations in *Pinus* barks were observed in urban and industrial sites in Palermo metropolitan area (Italy) (between 33 and 1015 μ g kg⁻¹) and in a study with *Terminalia catappa* barks done in urban Rio de Janeiro (Brazil) (from 242 to 1640 μ g kg⁻¹) (Orecchio et al., 2008; Pereira Netto et al., 2007). Compared to these studies the heavy molecular weight (HMW) PAHs concentrations were relatively higher in the present study; higher contributions of HMW-PAHs are often attributed to gasoline exhausts and, low molecular weight (LMW) PAHs (PYR, BaA, and CHR) to diesel combustion (Perrone et al., 2014). Similar values were observed in *Pinus* barks throughout urban, seaside, mountain and rural areas in Portugal and Spain (22–196 μ g kg⁻¹) (Ratola et al., 2009).

Table 1
Concentrations of PAHs in previous and in the present studies.

Site	Reference	PAHs concentrations sum (ng g ⁻¹ = µg kg ⁻¹)	Number of PAHs
Rio de Janeiro (Brazil)	Pereira Netto et al. (2007)	242–1640	21
Portugal and Spain	Ratola et al. (2009)	22–196	16
Palermo (Italy)	Orecchio et al. (2008)	33–1015	19
Mainland of China	Zhao et al. (2008)	5.1–1770	18
Jiangsu (China)	Zhou et al. (2014)	6.18–1560	15
Middle-Lower Yangtze Plain (China)	Wu et al. (2019)	27–1300	15
MASP (Brazil)	Present study	21–491	14

The different tree species (*Tipuana* and *Sibipiruna*) did not seem to show a clear difference concerning the profiles of PAHs average abundance (Fig. 3), although there was a slightly higher average concentration of PAHs for the barks of *Tipuana* than *Sibipiruna* trees (223 µg kg⁻¹ and 207 µg kg⁻¹, respectively) (Table S2); previous studies have shown that the *Tipuana tipu* tree has a deeply furrowed bark, which may favor the accumulation of particulate matter (Moreira et al., 2018).

Wu et al. (2019) found that the concentrations of PAHs in the tree barks from the same species had lower variation than from different species. However, it seems that changing from bio-monitoring tree barks to pine needles can lead to a higher detection of PAHs (2–17 times higher) (Ratola et al., 2009); the waxy surface of pine needles, composed of polyesters, paraffin, fatty acids, and secondary alcohols may be more effective in trap these compounds.

The most abundant PAHs in tree barks were fluoranthene, phenanthrene and benzo(b)fluoranthene (carcinogenic PAH). The percentage of the PAHs in the samples presented a considerable variation; the samples were collected in different trees, located in different streets, but all close to the refinery. The trees also presented different ages, this variability can influence the adsorption of the PAHs (Pereira Netto et al., 2007; Wu et al., 2019).

BbF was the most abundant PAH found in the TSP samples in 2016, and PHE in the PUF samples (Fig. 3); the similarity of PAH profile between PUF samples and tree bark (LMW-PAHs) was also observed by Wu et al. (2019), with high abundances of PHE and FLT. Tree bark and PUF PAH concentrations had responded well to gas-phase PAHs concentration monitoring in a previous study (Zhou et al., 2014). The exchanges of PAHs between air and tree bark depend on varied factors as its lipid content, surface area, roughness, so as exposure time (Wu et al., 2019). The lipids composition in the tree bark can influence its PAH accumulation since these species are highly lipid-soluble (Abdel-Shafy and Mansour, 2016). The LMW-PAHs, more present in the gaseous phase, are observed to be more related to interactions with lipids rather than HMW-PAHs (more abundant in the particulate phase); the high molecular weight species are more related to dry and wet deposition (impaction) (Kuang et al., 2015; Niu et al., 2019; Yang et al., 2008).

Phenanthrene and fluoranthene are typically found in higher abundance in tree barks and other plant materials (Pereira Netto et al., 2007; Wu et al., 2019; Zhou et al., 2014). The PAHs with 3 or 4 rings, fluorene, phenanthrene, anthracene, and pyrene, are compounds mostly found in the gaseous phase, rather than in the particulate and are found in tree barks (dry and humid deposition) (Orecchio et al., 2008).

Coronene had good correlations with the sum of PAHs concentrations, FLT and BbF ($R > 0.8$), which can be related to the vehicular emissions of particulate matter (Brito et al., 2013; Pereira et al., 2017b). PHE had weak correlations with COR ($R < 0.5$), suggesting other sources than vehicular exhaust for that species, the species can be linked to power plants that use the combustion of fossil fuel (Ravindra et al., 2008).

The IND/(IND + BPE) ratios were of 0.2 and 0.5, for *Sibipiruna*

and *Tipuana* tree barks, respectively, and equal to 0.6 and 0.7 for TSP and PUF, respectively; values between 0.35 and 0.70 indicate emission from diesel (Ravindra et al., 2008). The diagnostic ratio FLT/(FLT + PYR) was around 0.6 for *Tipuana* and *Sibipiruna* tree barks, 0.4 for TSP and 0.3 for PUF. There was a great difference between the these ratios for tree barks and the ones observed for PUF and TSP (Fig. 4), suggesting an influence of biomass burning for most of the tree barks, while the ones for PUF and TSP suggested both petrogenic and fossil fuel combustion contributions (de La Torre-Roche et al., 2009; Tobiszewski and Namieśnik, 2012). Diagnostic ratios should be used with caution depending on the type of matrix since the interaction of these compounds with the tree bark components and their volatilization can influence these ratios.

The PAHs ΣLMW/ΣHMW ratios were near 1 for the tree bark samples (*Tipuana* and *Sibipiruna*), equal to or above 1 for PUF and lower than 1 for TSP samples (Fig. 4); as already described the higher molecular weight PAHs are more likely to be found in the particulate phase and the lower molecular PAHs, in the gas phase (Agudelo-Castañeda and Teixeira, 2014; Duan et al., 2007). PAHs ΣLMW/ΣHMW ratios above 1 can also be associated to petrogenic sources (Tobiszewski and Namieśnik, 2012; Zhang et al., 2008).

A total index was calculated similarly as in Orecchio (2010):

$$\text{Total index} = \frac{FLT}{(FLT + PYR) \times 0.4} + \frac{ANT}{(ANT + PHE) \times 0.1} + \frac{BaA}{(BaA + CHR) \times 0.2} + \frac{IND}{(IND + BPE) \times 0.2} \quad (1)$$

Values above 4 represent that PAHs were prevalently originated from higher temperature processes (combustion) and values below 4, from lower temperature sources (petroleum products) (Orecchio et al., 2010). The average values were of 5, 7 and 10 for tree barks, PUF and TSP, respectively; the values suggested an influence of high-temperature processes, but it was considerably higher for TSP samples.

3.3. Species identified in the mass spectra

Some tree bark samples (01, 02, 03 and 13) were submitted to screening in the scan mode (GC/MS) (Fig. 5A, 5B, 5C, and 5D). Over 30 compounds were identified in the mass spectra, the most abundant were the plant-derived compounds (vanillin, lupeol, lupenone, fatty acids and stigmat-4-en-3-one) (Puebla et al., 2010; Seca and Silva, 2008). Anthropogenic species, such as the petroleum-related hopanes and the phthalate plasticizers (isobutyl *trans*-hex-3-enyl phthalate, bis-(2-ethylhexyl)phthalate and diisobutyl phthalate) were also observed (Alves et al., 2016; EPA, 2019). In sample 2 some non-determined PAHs were observed: 1,3-dimethylpyrene and tribenzo(b,n,pqr)perylene.

The tree bark sample (TB-13), collected near the industrial complex, presented hopanes (28-Nor-17β(H)-hopane and 28-Nor-17α(H)-hopane) and a sterane (stigmastane); some hopanoids can be considered as biomarkers of petrogenic origin (Alves et al.,

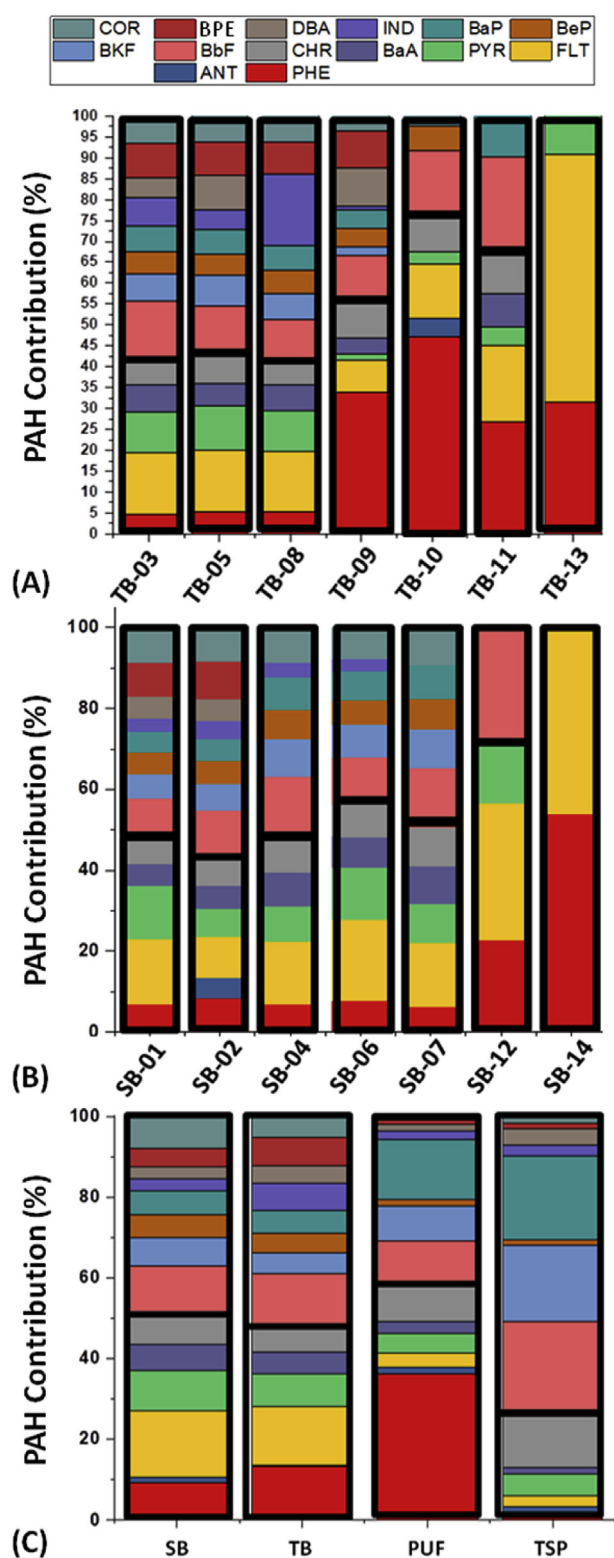


Fig. 3. PAHs contributions for *Tipuana* tree barks (TB) (A), *Sibipiruna* tree barks (SB) (B) and the average percentage for the tree barks, PUF and TSP (C).

2016), and a profile of petroleum-related contamination (Fig. 5D) was observed.

The unresolved complex mixture (UCM) occurs in a chromatogram when organic compounds from petroleum origin cannot be separated by gas chromatography (Andreou and Rapsomanikis,

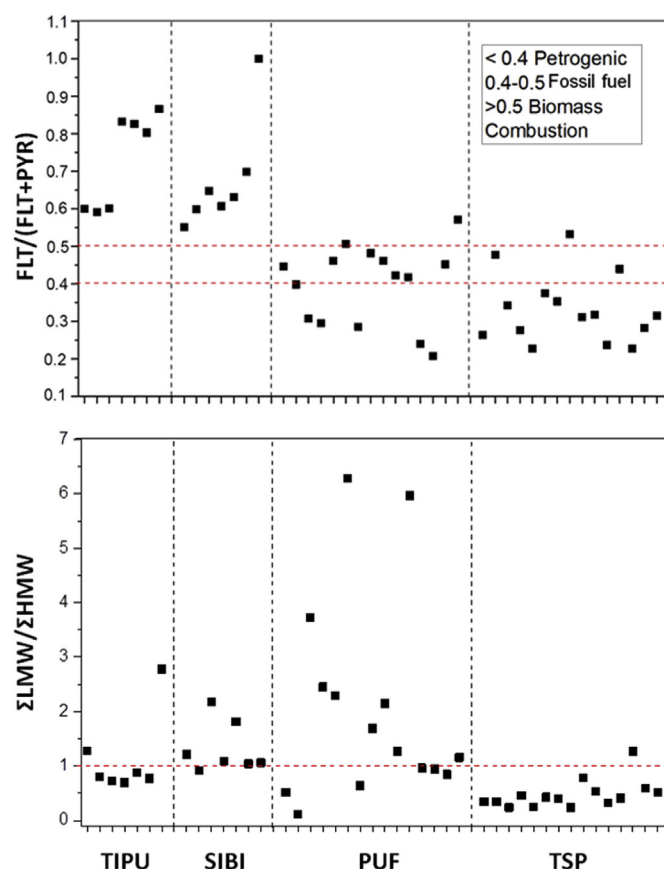


Fig. 4. $FLT/(FLT + PYR)$ and PAHs $\Sigma LMW/\Sigma HMW$ ratios for *Tipuana* and *Sibipiruna* barks, PUF and TSP.

2009; Farrington and Quinn, 2015; Matti Maricq, 2007). The ratio UCM/R (unresolved complex mixture divided by resolved compounds), which is typically applied to particulate matter samples, was found to be much higher than 1 (12.6), it suggests a strong influence from aerosols related to petroleum products emissions (Caumo et al., 2018).

4. Conclusions

The study provided the determination of airborne PAHs for gas and particulate phase, and also for tree barks in the surroundings of an industrial complex in the metropolitan area of São Paulo. High concentrations of PAHs were observed in the gas and particulate phases, the most abundant PAHs in TSP were the heavier weight BbF, BaP, and BkF and in PUF, the low weight PHE was the most abundant. These PAHs have both vehicular (diesel and gasoline) and industrial sources and calculations of carcinogenic equivalents for benzo(a)pyrene showed a value more than ten times higher compared to the standard value recommended by WHO.

The total concentrations of PAHs in tree barks were within the range observed in previous studies, but heavier molecular weight PAHs presented higher concentrations in this study. The different tree species (*Tipuana* and *Sibipiruna*) did not presented a clear difference in the profiles of PAHs average abundances. The most abundant PAHs were FLT, PHE, and BbF.

Calculations of unresolved complex mixture suggested a strong contribution from petroleum products, such as the hopanoids, that can indicate a petrogenic origin.

Further samplings could be done to observe seasonality on the

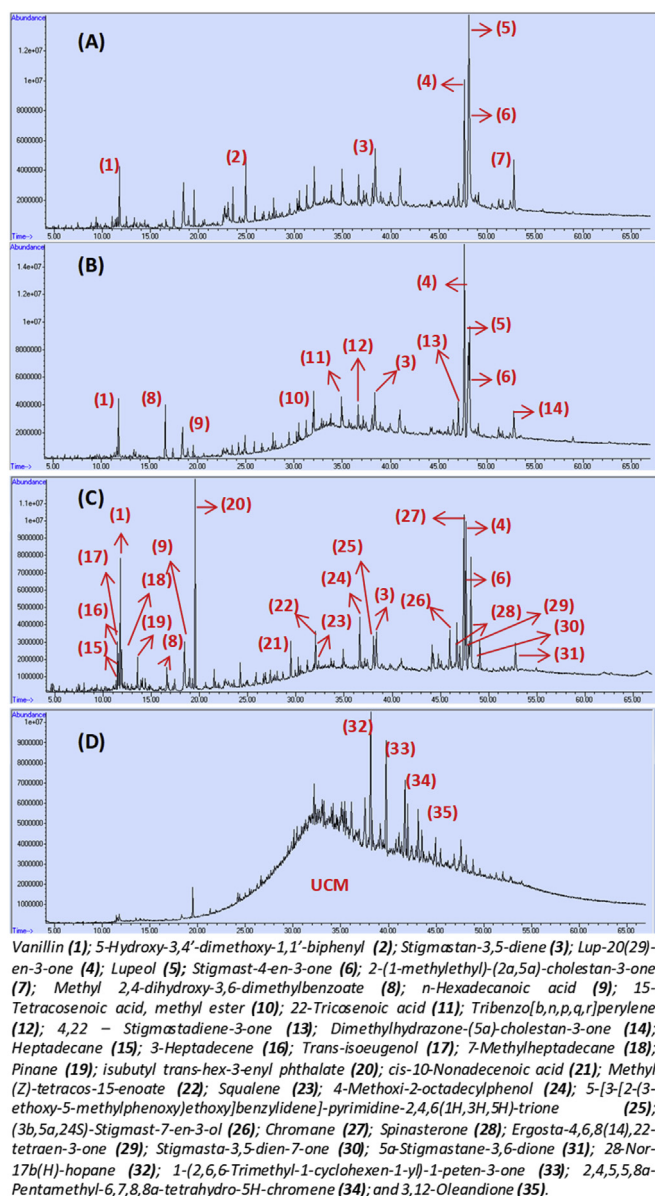


Fig. 5. Chromatogram for the samples 01 (A), 02 (B), 03 (C) and 13 (D) indicating the compounds with highest signals.

pollutant adsorption in this kind of matrix.

Conflicts of interest

The authors declare that they do not have a conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124499>.

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