

Spatial distribution of polycyclic aromatic hydrocarbons in *Terminalia catappa* L. (Combretaceae) bark from a selected heavy road traffic area of Rio de Janeiro City, Brazil

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Abstract

The levels of 21 polycyclic aromatic hydrocarbons (PAHs) with molecular weights between 128 Da (naphthalene) and 300 Da (coronene) were determined in *Terminalia catappa* L. (Combretaceae) bark. Tree bark samples were collected in the campus of Oswaldo Cruz Foundation, a green area located in a very intensive traffic area of Rio de Janeiro City, Brazil and about 10 km away from the city center. Samples were submitted to ultrasonic extraction with dichloromethane and analyzed by high-resolution gas chromatography–mass spectrometry. Individual PAH levels varied from 1.23 to 327 ng/g and phenanthrene, fluoranthene and pyrene predominated in all samples. Total PAH levels ranged from 242 to 1640 ng/g with a mean of 628 ng/g. The levels of total PAHs and of total carcinogenic PAHs showed not a clear dependence with tree location and distances to the main routes of that area. No correlation was observed also with PAH levels previously found in total suspended particulate thus indicating that in this area tree bark PAH levels cannot be used to assess their atmospheric levels.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are important organic contaminants since many of them and PAH mixtures exhibit mutagenic and/or pro-carcinogenic properties [1,2]. PAHs are ubiquitous and their formation, sources and fate have been extensively reviewed [3–5].

It is well known that organic matter combustion is an important PAH source and vehicular emission represents one of their major sources to urban atmospheres. After formation, PAHs can get distributed between the gaseous and particulate phases of the

atmosphere according to their vapor pressures [3]. PAHs can be transported over large distances and be deposited on surfaces such as soils, plants etc. Moreover there are strong indications of biological sources of certain PAHs. For example, the high levels of naphthalene, perylene and phenanthrene found in the soils of certain Brazilian forest areas were attributed to be of biological origin [29–31].

The levels of PAHs and other lipophilic semi-volatile organic compounds (L-SVOCs) in plants depend on atmospheric processes (transport and deposition) since uptake from soil is limited due to their physicochemical properties. The accumulation of L-SVOCs and PAHs in plants was reviewed [6–8]. It has at least three meanings: (a) atmospheric PAHs and L-SVOCs are deposited on plant surfaces, therefore (b) edible vegetables may represent a way of human intake of L-SVOCs and PAHs through diet and (c) plants can be used as passive samplers for atmospheric pollution studies. As a consequence, tree bark, plant

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leaves (including conifer needles), mosses and lichens have been used as biomonitors for PAHs and other substances such as organochlorine compounds in atmospheric pollution assessment studies [9–15,33].

It has been estimated that vegetation was able to remove $44 \pm 18\%$ of the total atmospheric PAHs [11,12]. A relationship between PAH levels in pine needles and population density was found in UK. The levels of all PAHs except phenanthrene were shown to decrease along south to north across UK [13].

In urban areas, PAH levels in plant leaves [14] and in tree bark [15] were larger than in rural or control sites. In both studies the observed differences were attributed to different atmospheric pollution levels. In *Laurus nobilis* leaves, good correlations between the concentrations of PAHs, Pb and Br were found indicating that vehicular emission is a source of PAHs and those two elements that are considered fossil fuel combustion markers [16]. In *L. nobilis* leaves, higher levels of benzo[ghi]perylene, that are dependent of vehicular emission, were found in the neighborhood of larger cities demonstrating the role of vehicular emission to the PAH burden in plant leaves. Total concentrations of carcinogenic PAHs in the atmosphere and in leaves were also correlated [17]. Seasonal variation of PAH levels was found in azalea leaves. Good correlation between the levels of perylene and benzo[a]pyrene in azalea leaves and in total suspended particulate (TSP) was observed but no correlation was found for the most volatile pyrene [18].

The aim of this study was to assess PAH concentrations in tree bark samples collected in FIOCRUZ Campus, Rio de Janeiro, Brazil that is located in the vicinity of the major highway system of the city. *Terminalia catappa* L. (Combretaceae) trees were chosen for this study since they are widespread in Rio de Janeiro City. The correlations between the PAH levels found in tree bark and TSP samples collected in the same area and period [19] were also evaluated.

2. Materials and methods

2.1. Reagents and solvents

Solid PAH standards from both AccuStandard (CT, USA) or Aldrich Chemical Co. (WI, USA) were employed. Dichloromethane (HPLC grade), hexane and toluene (both Omnisolv-Residue Analysis) were purchased from E M Science (NJ, USA). SPE SiO₂ cartridges (3 mL; 500 mg) from PR Cola (RJ, Brazil) and a SPE Vacuum Manifold (Waters Corporation, WI, USA) were used to cleanup sample extracts.

2.2. Sampling sites and tree bark sample collection

Tree bark samples were collected in the Campus of Oswaldo Cruz Foundation (FIOCRUZ Campus), a green area of approximately 700,000 m² located about 10 km away from Rio de Janeiro City Center, in the vicinity of the most important highway system of the city (Fig. 1). One side of the campus faces the twelve lanes Brasil Avenue, the main highway to Rio de Janeiro City (245,000 vehicles day⁻¹) while another faces the six lanes Leopoldo Bulhões Avenue, which crosses several dis-

tricts of the city. FIOCRUZ Campus is also influenced by Yellow Line (181,000 vehicles day⁻¹) and partially by Red Line (130,000 vehicles day⁻¹).

Tree bark samples were collected from *T. catappa* trees. FIOCRUZ Campus was divided into quadrates for tree selection. Fifteen quadrates were chosen by random numbers and a tree was sampled in each one. Superficial (1–5 mm thick) portions of TB (10–20 g) were cut with a pocket-knife between 1.20 and 1.50 m from the soil, around the trunk to avoid preferential wind and deposition directions. The samples were placed in dark glass jars and chilled at 8 °C.

2.3. Sample extraction and cleanup

Tree bark samples were cut with a scissors and homogenized before extraction. Sub-samples of ~1.5 g were precisely weighed and treated as previously described [19–21]. Briefly, samples were extracted in aluminum foil covered amber bech-ers with four portions of 20 mL of CH₂Cl₂ during 20 min each. A solution containing the internal standards was added to the extract after the first extraction step. Each combined extract was concentrated up to 10 mL in rotary evaporator ($T < 40$ °C) and centrifuged at ambient temperature to exclude remaining solids. Extracts were further evaporated under gentle high purity N₂ flow after addition of toluene (100 µL) as a keeper. Each concentrated extract was transferred onto a SPE-SiO₂ cartridge (3 mL, 500 mg) previously activated with CH₂Cl₂ (10 mL). The PAH rich fraction was eluted with 6 mL of hexane, evaporated under N₂ flow after addition of another toluene aliquot (100 µL) and transferred to 2 mL vial, which was kept in refrigerator until analysis by high resolution gas chromatography–mass spectrometry (HRGC–MS).

2.4. HRGC–MS determination of PAHs

Qualitative and quantitative PAH analysis were performed by HRGC–MS in a HP5890 gas chromatograph interfaced to a HP5970 mass selective detector and a DB5–ms column (30 m; 0.25 µm; 0.25 mm; J&W Scientific, CA, USA). Oven temperature was kept at 95 °C during 1 min, increased to 120 °C at 10 °C/min, hold at this temperature for 2 min and heated to 300 °C at 4 °C/min with 10 min final hold. Both injector and transfer line were kept at 280 °C. All injections were manually performed in splitless mode with hot needle technique.

Extracts were analyzed in full scan mode and by selected ion monitoring (SIM). Ionization was performed by electron impact at 70 eV. Mass spectra were recorded between 50 and 350 amu. Molecular ions [22] were used to draw reconstructed chromatograms and in SIM mode. PAHs were identified by comparison of mass spectra and retention times with previously data obtained through injection of native standards. Quantitative analysis was performed by selected ion monitoring (SIM) using PAH molecular ions [22]. Molecular ions were also used for the internal standards: 2,2'-binaphthalene (254 Da) [23], perdeuterated naphthalene (136 Da), 9-phenylanthracene (254 Da) and 9,10-diphenylanthracene (330 Da) [19–21].

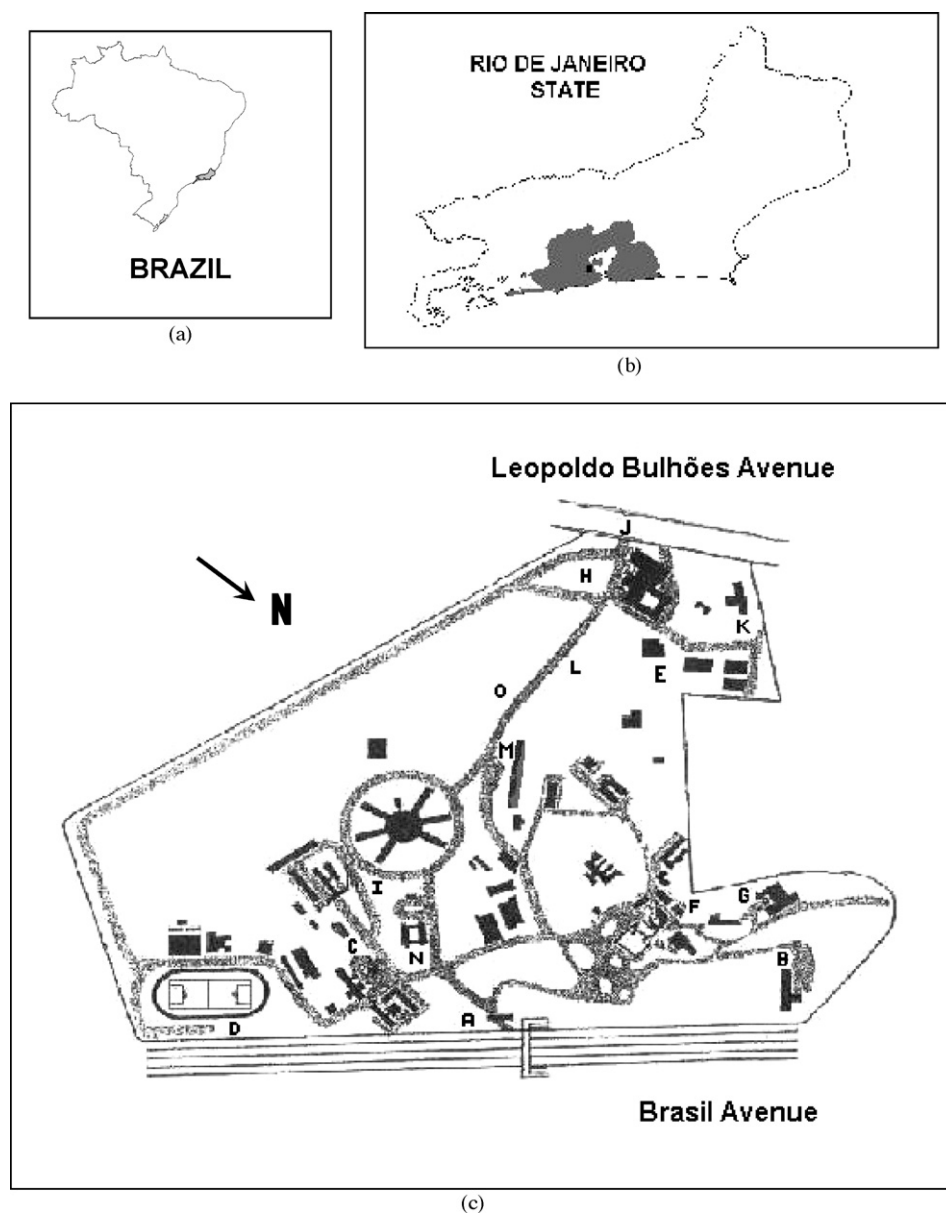


Fig. 1. (a) The gray area corresponds to Rio de Janeiro State in Brazil map. (b) The Metropolitan Area of Rio de Janeiro City (gray area) and the approximate localization of FIOCRUZ Campus are indicated in the map of Rio de Janeiro State. Approximate localization of sampled trees in FIOCRUZ Campus (c). In this map the gray areas correspond to internal routes or buildings and the capital letters indicate the sampling points.

3. Results and discussion

Quantitative results of PAH determination in tree bark samples of *T. catappa* trees are shown in Table 1. Individual PAH levels varied from 1.23 to 327 ng/g. Phenanthrene, fluoranthene and pyrene predominated in all samples. Phenanthrene accounted for 8% to 20% of total PAH concentration (\sum PAHs). Fluoranthene and pyrene represented 10–20% and 9–26% of \sum PAHs respectively while chrysene contributed with 5%–9% of \sum PAHs. The sum of the levels of those PAHs represented ~50% of \sum PAHs. Phenanthrene, fluoranthene and pyrene were also previously found to be among the predominant PAHs in pine needles in UK [13] and in leaves of *Quercus ilex* L. [14]. Those four PAHs were the most prevalent in different plant materials [33].

In the studied area, PAHs are possibly mainly derived from emission of heavy and light duty vehicles including buses, trucks and automobiles that employ diesel oil, ethanol and gashol (a mixture containing up to 24% of ethanol in gasoline) [24 and references therein]. Since it is known that diesel and gasoline vehicles emit phenanthrene, fluoranthene and pyrene as major PAHs vehicular emission would account for the predominance of those PAHs in the studied samples.

\sum PAHs ranged from 242 to 1640 ng/g with a mean of 628 ng/g. There are apparently four distinct groups of TB samples: one group with \sum PAHs greater than 1200 ng/g, a second group with \sum PAHs between 582 and 705 ng/g, a third group with ~440 ng/g and a group with the lowest \sum PAHs among all samples (~260 ng/g).

Table 1
PAH concentrations (ng/g; d.w.) in tree bark samples collected in FIOCRUZ Campus and mean diameters (cm) of trunks in sampled areas. Approximate tree localization in Fiocruz campus is shown in Fig. 1

PAHs	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	Mean	S.D.
Naphthalene	76.1	38.0	34.9	19.4	9.85	10.1	24.3	17.0	25.8	18.7	11.2	48.2	29.5	6.61	12.5	25.5	18.3
Biphenyl	12.0	9.22	5.35	2.93	1.23	3.01	2.70	2.41	6.18	2.29	1.90	8.09	4.40	2.04	2.96	4.44	3.13
Acenaphthene	31.3	14.1	3.20	5.85	4.33	5.66	4.53	1.20	5.25	1.53	3.73	8.48	4.24	1.49	3.04	6.53	7.57
Acenaphthylene	14.5	8.37	4.16	2.42	3.40	6.03	3.83	3.07	3.85	2.69	3.31	14.5	4.05	3.69	3.33	5.41	3.96
Fluorene	7.64	29.9	20.4	7.15	8.95	8.95	11.5	6.98	14.0	8.55	5.53	20.5	15.7	8.44	11.0	12.4	6.72
Phenanthrene	126	271	140	20.8	20.8	35.3	63.4	47.2	92.6	43.7	56.8	219	64.0	26.4	44.7	84.8	74.6
Anthracene	10.1	8.81	4.26	2.01	1.33	1.90	2.39	2.10	5.12	2.38	2.99	13.2	2.65	1.40	2.19	4.19	3.61
2-Methylphenanthrene	61.8	92.2	39.1	9.26	6.51	9.36	18.2	9.23	23.0	9.95	14.3	42.14	13.9	7.12	12.0	24.5	24.6
Fluoranthene	145	327	129	27.7	26.6	55.6	70.2	41.5	95.4	37.5	100	235	83.0	36.0	52.8	97.6	84.6
Pyrene	317	266	95.4	38.0	24.7	57.2	79.9	31.5	78.2	30.4	117	186	92.3	41.9	63.2	101	88.3
Benzo[a]anthracene	32.7	64.2	23.1	10.1	11.7	19.2	12.6	8.06	27.5	14.4	31.1	82.9	18.8	10.0	14.2	25.4	21.3
Chrysene ^a	77.4	151	59.8	18.6	22.9	35.2	24.2	19.7	50.6	22.0	44.5	119	36.6	17.4	24.3	48.2	39.6
Benzo[k]fluoranthene	44.2	65.6	26.2	13.0	16.7	31.4	25.2	9.89	28.2	11.2	45.5	63.2	41.0	17.1	23.0	30.8	17.7
Benzo[b]fluoranthene	22.9	42.7	17.0	7.43	8.60	20.6	13.6	6.37	19.0	7.79	30.7	40.1	25.8	11.3	14.5	19.2	11.5
Benzo[e]pyrene	44.8	41.8	16.3	6.77	12.3	18.6	15.8	7.22	19.2	7.36	26.2	40.2	26.0	11.1	14.1	20.5	12.8
Benzo[a]pyrene	34.7	55.1	19.9	11.3	15.3	29.9	19.4	7.88	24.2	10.3	38.2	54.3	30.6	15.2	18.8	25.7	14.8
Perylene	8.61	11.0	4.02	2.85	2.95	7.35	3.61	1.63	5.11	2.38	8.00	10.8	6.68	3.83	4.38	5.55	3.02
Benzo[ghi]perylene	66.4	76.1	34.5	25.6	35.4	57.0	32.4	8.90	31.0	14.9	16.4	67.8	54.5	29.4	14.9	37.7	21.5
Indene[1,2,3-cd]pyrene	13.6	10.2	4.57	2.89	4.45	5.48	3.57	1.91	4.12	2.19	58.9	9.78	7.66	3.57	76.1	13.9	22.2
Dibenzo[a,h]anthracene ^b	42.4	34.9	15.7	11.2	13.7	21.5	13.3	4.84	15.2	7.28	4.72	32.6	26.0	12.6	11.5	17.8	11.4
Coronene	47.3	22.0	7.99	13.7	10.8	16.9	7.84	3.20	8.79	4.58	53.9	21.7	17.6	5.16	3.78	16.4	15.3
∑PAHs	1237	1640	705	259	262	456	452	242	582	262	675	1337	605	272	427	628	438
Sum of carcinogenic PAH levels	291	352	160	89.7	102	174	131	60.0	160	79.5	232	366	208	93.2	174		
% of carcinogenic PAHs	23.5	21.5	22.7	34.6	38.9	38.1	29.0	24.8	27.4	30.3	34.4	27.4	34.4	34.3	40.7		
TTEFs (ng of benzo[a]pyrene/g of sample)	58.1	86.5	32.8	18.4	24.6	45.4	29.7	12.3	37.3	16.4	70.3	85.6	48.3	23.7	50.2		
Tree diameter (cm)	133	98	64	162	75	178	61	115	124	135	116	76	105	94	108		

TTEFs = total toxic equivalent factor expressed as ng of benzo[a]pyrene/g of sample.

^a coeluted with triphenylene under our analytical conditions.

^b coeluted with dibenzo[a,c]anthracene under our analytical conditions.

\sum PAHs in tree bark was not clearly related to tree localization regarding Brasil Avenue and/or Leopoldo Bulhões Avenue (Fig. 1). For example, sample B (1640 ng/g) and sample A (1237 ng/g) that showed two of the highest values of \sum PAHs came from trees located near Brasil Avenue where the larger vehicular emission occur. In contrast, sample L (1337 ng/g) was taken in a tree that is located \sim 1 m away from an internal route of the campus and sample D, which came from a tree near Brasil Avenue showed \sum PAHs of only 259 ng/g.

Our findings suggest that besides the distances to the main PAH sources – the above mentioned routes and avenues – other factors may influence the deposition of PAHs in the studied trees. Such factors would include relative altitudes of sampling points, preferential wind directions, distances to the closest buildings and possibly also other trees and vegetation. Moreover photolytic and biological degradation of certain PAHs may also affect their levels and their relative distributions [33]. Indeed our data agree well with previous results that showed a wide variation of \sum PAHs in pine needles within a relatively small sampling area [13].

Considering that the exposed tree bark surface depends on the mean tree diameter in the sampled tree, the correlation between the mean tree diameters in the sampled areas and \sum PAHs was studied. No correlation ($R = -0.195$) was found indicating that \sum PAHs is not directly dependent on the exposed tree area thus corroborating our hypothesis that other factors besides exposition affect the PAH content of the samples.

Total carcinogenic PAH levels (\sum CARC), here considered as the sum of those classified by IARC as probable human carcinogens (2A) (namely benzo[*a*]anthracene, benzo[*a*]pyrene and dibenzo[*a,h*]anthracene) and as possible human carcinogens (2B) (namely naphthalene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and indene[1,2,3-*c,d*]pyrene) [25] contributed with 21.5%–40.7% of \sum PAHs with a mean of 30.8%.

Toxic equivalent factors (TEF) that compare the individual carcinogenic potency of individual PAHs with that of benzo[*a*]pyrene [3,26] were also applied to compare tree bark samples. Individual PAH concentrations were multiplied by their TEF and the results were summed leading to total toxic equivalent factors (TTEF) of sample (Table 1). This approach was successfully applied in the study of PAHs associated with TSP [28]. TTEF values ranged between 12.3 and 86.5 ng of benzo[*a*]pyrene equivalent/g of sample.

Neither \sum CARC nor TTEF were correlated with tree diameter. Both showed no dependence on tree localization regarding Brasil Avenue and Leopoldo Bulhões Avenue.

A direct comparison of our data with previous studies through parameters such as individual PAH levels, \sum PAHs, \sum CARC or TTEFs is difficult due to differences in analytical and sampling methods and in the set of studied PAHs. As pointed before, the levels of primary atmospheric pollutants in plants also depend on sampling site location, meteorological conditions and temperature. Moreover different plant species and even their morphological parts show diverse accumulation abilities for PAHs [32] and other organic substances.

To put our data into perspective, a comparison with previous data for PAHs in plants is shown in Table 2. Emphasis, was

done in the comparison of the levels of benzo[*a*]pyrene (due to its carcinogenic properties) and of the predominant PAHs (namely phenanthrene, fluoranthene and pyrene) with previously published results (Table 2).

The levels of phenanthrene, fluoranthene and pyrene observed in this work are in the range of the values found in *Q. ilex* L. leaves collected near roads [14], in pine needles [13] and in plane tree bark from urban areas [15]. Data reported here for benzo[*a*]pyrene are comparable to the values found in *Q. ilex* L. leaves collected near roads [14] but with lower maximum values (Table 2). The levels of those four PAHs suggest that their ranges are characteristic of intensive automotive traffic areas.

No correlation was found between the mean levels of individual PAHs in tree bark from FIOCRUZ Campus and in total suspended particulate [19] collected in points A and J. Many factors may contribute to this lack of correlation. First of all is the fact that PAH levels varies widely in both total suspended particulate and in tree bark in directions that are not only dependent on PAH sources. Second, transportation of PAHs alters their levels and distributions due to photochemical degradation and reaction with nitrogen oxides of the air [33] affecting individual PAHs in different proportions.

Although the ratios of selected PAHs has to be carefully evaluated due to their reactivity and volatility, the ratio phenanthrene/anthracene of the studied samples may be illustrative of the deposition process. This ratio varied between 10.3 and 32.9 with a mean of 20.3 that is closer to the ratios (between 10 and 30) previously found in remote areas where transportation is the major responsible for PAHs [33]. This result indicates that the PAHs in the studied tree bark samples may be constituted of recently emitted PAHs together with PAHs that remained for a longer period in the atmosphere where their distribution and levels were changed.

Despite the lack of correlation between PAH levels in total suspended particulate and in tree bark the ratio fluoranthene/(pyrene + fluoranthene) showed a mean value of 0.49 ± 0.08 in good agreement with the previous value (0.43 ± 0.08) obtained for car emissions [27] denoting the importance of this source in the studied area.

A further comparison of PAH levels and their distributions in tree bark samples and in total suspended particulate may be obtained by summing the levels of PAHs containing the same number of rings (Table 3). Tetracyclic PAHs predominated in plants with lower and comparable percentages of tri- and pentacyclic PAHs according to previous data obtained for different plant parts and materials [13–17,32]. However another picture was shown in total suspended particulate were pentacyclic PAHs predominated with lower percentages of tetra- and hexacyclic PAHs [19].

Data of Table 3 indicates that the distributions of PAHs according to the number of rings are different in both media. Since vapor phase PAHs were not evaluated in the previous work [19], the estimate of atmospheric PAHs considering only the particulate phase leads to an underestimate. Here, we suggest that at least part of the gaseous phase PAHs would contribute to the higher levels of phenanthrene, pyrene, fluoranthene and chrysene found in tree bark when compared to total suspended

Table 2
Range of PAH concentrations (ng/g) in plant leaves or plant bark observed in previous studies

PAHs ^a	<i>T. catappa</i> tree bark (this work)	<i>Platanus hybrida</i> plane bark ^b (Sturaro et al. [15])		<i>Quercus ilex</i> L. plant leaves (Alfani et al. [14])			<i>Laurus nobilis</i> plant leaves (Lodovici et al. [17])	<i>Laurus nobilis</i> plant leaves (Lodovici et al. [16])	<i>Pinus sylvestris</i> pine needle (Tremolada et al. [13])
	Road	Urban area	rural area	Control	Parks	Roads	Several sites	Several sites	Several sites
Naphthalene	6.61–76.1	117–230	27.5	15.1–23.7	32.1–41.5	33.7–82.9			
Biphenyl	1.23–12	21.7–75.0	8.3						
Acenaphthene	1.20–31.3	23.3–62.5	16.7	14.8–31.4	7.57–30.46	8.38–163			
Acenaphthylene	2.42–14.5			4.79–27.0	2.67–6.20	2.93–19.6			<0.5–40
Fluorene	5.53–29.9	82.5–108	22.5	2.11–5.91	6.39–10.00	6.23–24.1			<1–343
Phenanthrene	20.8–271	197–446	59.2	12.5–23.7	76.9–118	124–405		ND–34.8	8.9–1810
Anthracene	1.33–13.2	27.5–55.0	ND	2.69–14.8	6.46–11.6	11.0–67.4			<0.3–27
2-Methylphenanthrene	6.51–92.2	153–612	20.8						
Fluoranthene	26.6–327	50.8–457	ND	7.54–13.5	58.4–98.7	112–626	6.2–155.7	10.3–82.4	<6–458
Pyrene	24.7–317	35.0–372.5	ND	7.35–8.37	67.0–160	180–1335	0–145	ND–424.0	<3–233
Benzo[<i>a</i>]anthracene	8.06–82.9			1.95–3.44	14.6–46.5	55.1–358	0.8–40.3	0.8–13.2	<1–18
Chrysene ^b	17.4–151			8.58–9.87	39.1–79.7	133–543	2.5–109.8	ND–416	2.2–135
Benzo[<i>k</i>]fluoranthene	9.89–65.6			2.40–6.76	12.5–36.7	53.6–174	0.5–93.3	3.7–42.5	1.2–21
Benzo[<i>b</i>]fluoranthene	6.37–42.7			1.53–4.84	8.40–19.8	23.5–109	0.32–13.3	0.1–1.21	0.55–8.4
Benzo[<i>e</i>]pyrene	6.77–44.8			1.84–6.69	12.8–46.9	71.5–246			
Benzo[<i>a</i>]pyrene	7.88–55.1			0.91–4.49	3.32–16.7	20.7–92.9	0.2–13.1	2.5–22.5	0.49–7.9
Perylene	1.63–11.0								
Benzo[<i>ghi</i>]perylene	8.90–76.1			0.27–1.82	1.59–6.99	0.00–53.8	0–10.9		
Indene[1,2,3- <i>cd</i>]pyrene	1.91–76.1			0.05–1.37	0.05–4.20	0.00–35.0	0–1.6	ND–7.9	<0.6–3.2
Dibenzo[<i>a,h</i>]anthracene ^a	4.72–42.4			0.00	0.00	0.00		3.2–89.8	<0.3–7.7
Coronene	3.2–53.9			19.6–22.2	18.7–58.9	40.7–428			<0.3–3.1

ND = not detected.

^a For seek of homogeneity and for comparison purposes all previously published data were rounded according to the same criteria.

^b Originally expressed as ng/cm² and converted to ng/g with author data.

Table 3

Percent contributions of PAHs containing from 2 to 6 rings in the studied tree bark samples

Number of rings	Plant bark			TSP ^a mean (%)
	Minimum (%)	Maximum (%)	Mean (%)	
2	1.9	8.6	5.2	0.0
3	12.8	29.9	21.3	5.4
4	32.8	49.3	40.9	28.4
5	14.1	28.4	20.4	39.4
6	5.8	22.2	12.3	26.8

^a TSP = mean data for total suspended particulate from the studied area. Naphthalene, acenaphthene and acenaphthylene were not determined in total suspended particulate. See Ref. [19] for further details.

particulate. Similar conclusion was reached by Nakajima et al. [18] when comparing the levels of pyrene, benzo[*a*]pyrene and perylene in total suspended particulate, vapor phase and azalea leaves [18].

4. Conclusions

The levels of 21 PAHs were determined in tree bark of *T. catappa* L. (Combretaceae) collected in an urban area submitted to the influence of high vehicular traffic. PAH individual levels varied between 1.23 and 327 ng/g while their total levels varied between 242 and 1640 ng/g. Good correlation was observed between total PAHs and total carcinogenic PAHs in tree bark indicating common sources.

PAH levels in tree bark and in total suspended particulate matter showed no correlation in the studied area possibly because different processes control their levels in both media. Thus our study indicates that tree bark cannot be directly used to assess the atmospheric distribution of PAH due to unknown controls of their concentrations in tree bark.

Although no correlation was found between the levels of PAHs in tree bark and total suspended particulate, the ratio fluoranthene/(fluoranthene + pyrene) suggests that automotive emission may play a role to the burden of PAHs in tree bark. The large ratio phenanthrene/anthracene indicates that part of the PAHs remains for a long time in the atmosphere before deposition in tree bark.

Further work is needed to clearly establish the relationships between the levels of PAHs in the atmosphere (particulate + gaseous phase) and in tree bark.

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