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# Comparison of Polycyclic Aromatic Hydrocarbon (PAHs) concentrations in urban and natural forest soils in the Atlantic Forest (São Paulo State)

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#### ABSTRACT

Studies about pollution by Polycyclic Aromatic Hydrocarbons (PAHs) in tropical soils and Brazil are scarce. A study was performed to examine the PAHs composition, concentrations and sources in red-yellow Oxisols of remnant Atlantic Forest of the São Paulo State. Sampling areas were located in an urban site (PEFI) and in a natural one (CUNHA). The granulometric composition, pH, organic matter content and mineralogical composition were determined in samples of superficial soils. The sum of PAHs ( $\Sigma$ HPAs) was 4.5 times higher in the urban area than in the natural one. Acenaphthylene, acenaphthene, fluorene, phenanthrene and fluoranthene have been detected in the soils of both areas and presented similar concentrations. Acenaphthene and fluorene were the most abundant compounds. Pyrene was twice more abundant in the soils of natural area ( $15 \ \mu g.kg^{-1}$ ) than of the urban area and fluoranthene was the dominant compound ( $203 \ \mu g.kg^{-1}$ ) in urban area (6.8 times higher than in the natural area). Some compounds of higher molecular weight, which are tracers of vehicular emissions showed significant concentrations in urban soils. Pyrene represented 79% of  $\Sigma$ PAHs whereas it has not been detected in natural soils. The results showed that forest soils in urban area are characterized by the accumulation of high molecular weight compounds of industrial and vehicular origin.

Key words: Atlantic Forest, polycyclic aromatic hydrocarbons, PAHs, tropical forest, tropical soils, urban soils.

#### INTRODUCTION

The Polycyclic Aromatic Hydrocarbons (PAHs) are chemicals with carcinogenic and mutagenic potential and are mainly derived from incomplete combustion processes of stationary (industries, incineration, heating) as well as mobile sources (vehicular emissions). The contribution of natural source of PAHs is limited, be-

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ing restricted to forest burning (Gonzalesvila et al. 1991, Jenkins et al. 1996). The low molecular weight PAHs (2 and 3 aromatic rings) are found preferentially in the gas phase, while the compounds of larger molecular weight (4 to 6 aromatic rings) are adsorbed on the surface of suspended particles.

The high demand for fossil fuels and its combustion as a consequence of the high urbanization rate with the industrial development and the increase in the population and vehicular fleet during the last decades caused a rise

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in the emission of PAHs to the atmosphere. These compounds, as well as many other contaminants, are emitted directly into the atmosphere, and then submitted to wet and dry deposition. Soils are a primary sink for contaminants due to their capacity to retain hydrophobic chemicals (Wild and Jones 1995). Their accumulation in urban soils degrades the soil quality and represents a risk for humans and ecosystems.

The studies of the behavior of PAHs have begun in the seventies, but their results cannot be fully extrapolated to tropical regions because of the differences in climate. As Wilcke et al. (2003) emphasized, "in the last two decades, much research work has produced an improved understanding of the sources and fate of the hazardous PAHs in temperate environments. In contrast, little is known about the sources and fate of PAHs in tropical environments".

In Brazil, studies related with PAHs have recently been conducted to investigate their presence in the atmosphere of urban centers such as São Paulo city (Bourotte et al. 2005, Vasconcellos et al. 2003, Martinis et al. 2002) and Rio de Janeiro city (Santos et al. 2002, Fernandes et al. 2002, Azevedo et al. 1999, Miguel and Pereira 1989, Miguel and Andrade 1989, Daisey et al. 1987). Very few studies were conducted regarding PAHs in soil (Wilcke et al. 2003, 2004).

Thus, the objectives of this work were to characterize the composition and identify the distribution pattern of PAHs in two contrasting tropical soils: an urban forest soil, located in a remnant forest inside the São Paulo city (PEFI), and a natural forest soil located in the Atlantic Forest and considered as non-polluted reference (CUNHA).

#### MATERIALS AND METHODS

#### SAMPLING LOCATION

The Metropolitan Region of São Paulo (MRSP) with an approximate area of 8,000 km<sup>2</sup> is located in the southeastern part of Brazil (23°S and 46°W), has about 17 millions inhabitants distributed over an urbanized area of about 1,747 km<sup>2</sup> and is the third largest urban agglomeration in the world. The MRSP has about 2,000 industrial plants and 7.2 millions vehicles (20% of the national fleet) which are responsible for the emission of 98% of CO, 97% of hydrocarbons, 97% of NO<sub>x</sub>, 52% of particulate matter and 55% of  $SO_x$ . Diesel vehicles represent 6.5% of the total fleet and their emissions constitute 18,4% of total vehicular emissions of hydrocarbons and 77% of particulate matter emissions, corresponding to 70,600 and 19,700 tons, respectively (CETESB 2006).

The chosen areas for integrated monitoring are located in the Parque Estadual das Fontes do Ipiranga – PEFI (urban) and in the Parque Estadual da Serra do Mar – Núcleo Cunha/Indaiá – CUNHA (natural). The first one is under strong anthropic influence and the second one is not under that influence. The location of the two areas is shown in Figure 1.

# Urban Forest - PEFI

The study area is located in the Southeastern region of the São Paulo City County between parallels 23°38'08" and 23°40'18"S and meridians 46°36'48" e 46°38'00"W and 50 km from sea shore. This site is located in a remnant part of the Atlantic Forest forming a 526 ha Reserve Park named PEFI (Parque Estadual das Fontes do Ipiranga) entirely located within the urban area, in the neighborhood of the largest industrial region of South America, and thus submitted to high urban pollutants impact. This urban forest has a large portion of natural vegetation still preserved. Because of the extension of its vegetation cover, PEFI is recognized as an outstanding area of São Paulo city for its environment and social aspect (Bicudo et al. 2002). PEFI's climate is influenced by extra-tropical (e.g. frontal systems) and tropical (e.g. squall lines and convergence zones) systems. Based on climatological time series of 67 years (1933-1999) the mean annual rainfall is 1368 mm with a dry period from May until August. The mean temperature for the coldest month is 15°C (July) and for the two hottest months are 21–22°C (January–February). The chosen catchments have a drainage area of 21 ha with 0.044 m.m<sup>-1</sup> of declivity. It is on crystalline rocks with gneisses and secondarily micaschists. Over these rocks it is found clay, sand and gravels belonging to the São Paulo Formation. The topography presents undulated forms with heights between 770 m and 825 m being part of the central ridge hills of the São Paulo city. The soils are red-yellow latossol (Brazilian soil Classification) derived from phyllite, schist and granit-gnaissics rocks. Chemically these soils are poor, with low cation exchange capacity, acidic,

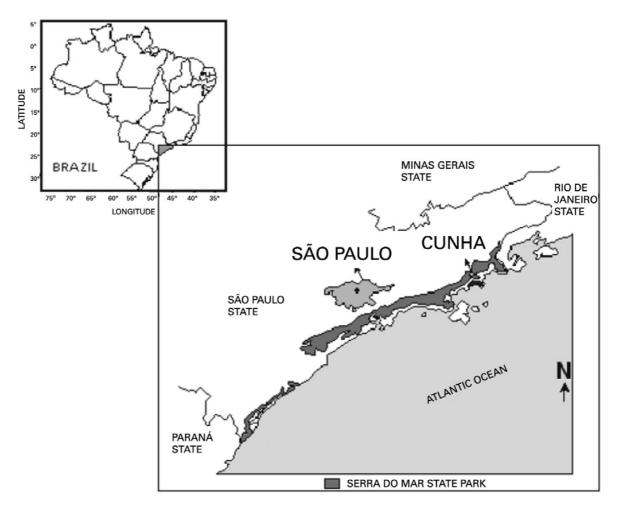


Fig. 1 – Localization map of the two study areas.

with toxic levels of aluminum and potential characteristics for phosphorus fixation (Struffaldi-De-Vuono et al. 1984).

# Natural Forest - CUNHA

The Cunha-Indaiá Núcleo is located between the parallels 23°13′28″ and 23°16′10″S and meridians 45°02′53″ e 45°05′15″W in the Northern portion of the State of São Paulo, 250 km from the Metropolitan Area of São Paulo, within the Serra do Mar State Park and hosts Eng. Agr. Walter Emmerich Forest Hydrology Laboratory of the Institute of Forestry of the State of São Paulo. It is about 15 km apart from the Atlantic Ocean at an altitude of 1050 m from sea level. It covers an area of 2,854 ha with hills and small valleys. The area is mainly covered with a primary forest named Atlantic Forest. A secondary forest is found on abandoned pasture or crops on the slopes. Pasture and bamboos cover the alluvial zones (Cicco et al. 1987). The mean maximum and minimum temperatures are 26°C and 16°C respectively. The mean annual rainfall is 1500 mm with the main rainy period being from September until April and the driest one from May until August. This region has a moist tropical climate. The geologic formation in this region belongs to the Brazilian crystalline complex of Pre-Cambrian with granites, gneisses, crystalline schists and diabase rocks from the Mesozoic age. The soils are developed on Pre-Cambrian granite, gneiss and schist; they are classified as red-yellowish Oxisols. The highlands portion have topography composed of low hills with marked declivity and rounded tops at intermediate heights and at the valleys the inclinations have low gradient around 10 to 20 degrees and the drainage density is low with undulated landscape.

#### SOIL SAMPLING AND PREPARATION

For each sampling point, three sub-samples were taken and mixed in order to obtain a bulk sample. In both sites, sampling was realized during winter of 2000 at the following depths: 0-5 cm, 5-10 cm and 10-20 cm. Samples were sieved to < 2 mm, kept in aluminum foils and plastic hermetic bags and stored in freezer until analysis. Part of the samples was sieved at 105 meshes for powder X-Ray diffraction analyses and pH determination was done on bulk, non sieved samples.

Granulometry was performed by sedimentometry. Carbon content was measured with a Shimadzu TOC-5000 equipment, and soil mineralogy was investigated by powder X-Ray diffraction.

# EXTRACTION AND PAHS ANALYSIS

PAHs concentrations were obtained by CG-MS after a soxhlet extraction of soil samples (20 g) with 250 ml of dichloromethane during 24h. After concentration of the extracts by evaporation with a rotary evaporator and a gentle flux of  $N_2$ , samples were submitted to a purification stage by using SPE cartridges (SUPELCO).

The analysis of 16 PAHs (16 US EPA priority PAHs) was carried out in a gas chromatograph (Hewlett Packard 6890) system connected to a Mass Spectrometer (5972A). The separation of the compounds was carried out through a capillary column RTX 5Sil-MS (Restek) of 30 m length, 0.25 mm of internal diameter and 0.25  $\mu$ m of film thickness using Helium as the carrier gas. The oven initial temperature (50°C) was kept during 1 minute and afterwards, with a rate of 10°C/min the temperature was raised to 280°C and kept by 5 min and finally with a rate of 8°C/min the temperature reached 310°C and maintained by 10 min. The analytical quality control was performed using blanks and calibration curves with 6 points (2.0, 1.0, 0.4, 0.2, 0.1 e 0.04 mg.L<sup>-1</sup>) as well as with certified standards from Supelco (EPA610) and Restek. The validation of this protocol was carried out through the analysis of certified reference material (Urban Dust NIST SRM 1649a). As recovery values were low for naphthalene, the obtained values were discarded. The PAHs quantified were: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene

(CRY), benzo(b,k)fluoranthene (BbkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IND), dibenz(a,h)an-thracene (DahA) and benzo(ghi)perylene (BghiP).

### **RESULTS AND DISCUSSION**

# SOIL CHARACTERISTICS

The study was limited to the upper soil horizons which interact with atmosphere. In Tables I and II, the descriptive morphology of soil profile is presented for CUNHA and PEFI, respectively. The mineralogical composition, determined by powder X-Ray Diffraction, is very similar in both CUNHA and PEFI soils and typical of tropical soils. Physico-chemical characteristics of both soil profiles are presented in Table III. The CUNHA soil shows a sandy clay texture, near to the limit with clay texture. The PEFI soil is slightly sandier. The low carbon content of the 0–5 cm of the PEFI profile is likely due to anthropic reworking. For both soil profiles, pH values are typical of acidic tropical soils.

TABLE I Morphological description of soil in Cunha sampling site.

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Depth (cm)	Description				
0–5	Homogenous dark brown, porous, crumb structure,				
	high amount of graminaceous roots.				
5-10	Heterogeneous color due to brown patches, struc-				
	ture from crumb to subangular blocky. Porosity				
	decreasing with depth. High biological activity.				
10-40	Towards depth brown patches progressively turn				
	strong brown and occupy higher volume. Brown				
	patches from filled fauna and root pipes. Decreas-				
	ing of the amount of roots.				
40–60	Strong brown, angular blocky structure with mi-				
	croaggregated sub-structure, more friable than up-				
	per horizons.				
60–100	Reddish-yellow, massive structure with microag-				
	gregated sub-structure, fragile.				

#### PAHS SOIL CONCENTRATIONS AND SOURCES

PAHs concentrations integrated in the 0–20 cm topsoil horizons for both soils different depths are presented in Table IV. The mean concentration of the total PAHs ( $\Sigma$ PAHs) for all profile was 180  $\mu$ g.kg<sup>-1</sup> in CUNHA and 818  $\mu$ g.kg<sup>-1</sup> in PEFI. The  $\Sigma$ PAHs concentration was 4,5 times higher in the urban soil than in the natural one. According to the classification of soil contamination by PAHs established by Maliszewska-Kordybach

 TABLE II

 Morphological description of soil in PEFI sampling site.

Depth (cm)	Description				
0-5	Homogenous dark brown structure, high amount				
	of graminaceous roots.				
5-10	Dark brown, clean quartz grains, some hard red				
	ferruginous nodules, porous, crumb structure, high				
	amount of graminaceous roots.				
10-30	Heterogeneous color due to brown patches, some				
	small hard red ferruginous nodules, black patches				
	due to charcoal grains from 10 to 20 cm, clean				
	quartz grains, subangular blocky structure with				
	microaggregated substructure. Decreasing of the				
	amount of roots.				
30–60	Strong brown with brownish-yellow patches, mas-				
	sive structure with microaggregated substructure,				
	more compact than the upper horizon, some soft				
	red ferruginous nodules.				
60–100	Strong brown, medium and coarse quartz gravels,				
	massive structure with microaggregated substruc-				
	ture, some soft red ferruginous nodules.				

TABLE III Physico-chemical characteristics of Cunha and PEFI soil profiles.

F							
			Fine				
Depth	Total sand	Silt	fraction	C	pН		
(cm)	(%)	(%)	$(<2 \ \mu m)$	(%)	pm		
			(%)				
	CUNHA						
00–15	45	9	46	2.86	4.15		
10-20	52	8	40	1.76	4.70		
20-30	49	9	42	1.76	4.64		
30-40	47	9	44	-	4.58		
40–60	47	7	46	1.52	4.54		
60-80	45	9	46	1.34	4.52		
80–100	45	9	46	1.27	4.43		
		PEF	I				
00–05	56	4	40	1.86	5.09		
05–10	54	4	42	2.32	4.85		
10-20	52	6	42	2.18	4.86		
20–30	49	9	42	1.95	4.87		
30-40	52	6	42	1.62	4.78		
40–60	50	4	46	1.41	4.75		

(1996) considering a total of 16 PAHs, CUNHA soil is not contaminated ( $< 200 \ \mu g.kg^{-1}$ ) whereas PEFI soil can be considered as contaminated since the obtained value for  $\Sigma$ PAHs ranged between 600 and 1000  $\mu$ g.kg<sup>-1</sup>.

The studies assessing the environmental contami-

nation by PAHs in natural or urban soils pointed out that the predominant compounds are principally associated with traffic emission sources and additionally to minor sources such as industrial processes and domestic heating. Compounds of lower molecular weight such as ACY, ACE, FLU, PHE and PYR were detected with similar concentrations in CUNHA and PEFI soils. ANT, however, was under the limit of detection in both soils. Compounds of higher molecular weight, such as BaA, CRY, B(bk)F, BaP, IND and BghiP were under the limit of detection in CUNHA but with significant concentrations in PEFI, over 45  $\mu$ g.kg<sup>-1</sup>. FLT, which has an intermediate molecular weight, was detected in CUNHA (30  $\mu$ g.kg<sup>-1</sup>) but exhibited a very higher concentration in PEFI ((203  $\mu$ g.kg<sup>-1</sup>).

In CUNHA, ACE and FLU were the most abundant compounds which accounted for 50% of the  $\Sigma$ PAHs, the remaining 50% being due to ACY, PHE, FLT and PYR. Some studies suggested that low molecular weight PAHs are likely to be naturally produced in poorly-anthropized areas in Brazil (Wilcke et al. 2003). Natural sources are thus possible to explain the low molecular weight PAHs in the CUNHA soil. In PEFI, FLT was the dominant compound and contributed to 25% of the  $\Sigma$ PAHs. The other most abundant compounds were BghiP, BbkF and BaP which are typical tracers for fossil fuel combustion and contributed on 33% of the  $\Sigma$ PAHs.

The combustion derived PAHs (FLT, PYR, CRY, BbkF, BaA, BaP, IND and BghiP) accounted for 80% and 25% of the  $\Sigma$ PAHs in the PEFI soil and the CUNHA soil, respectively. The carcinogenic group (BbkF, BaA, CRY,BaP, IND and DBahA) accounted for 42% of the  $\Sigma$ PAHs in the PEFI soil, while this group was not detected in CUNHA.

The repartition pattern of the PAHs in the PEFI soil is similar to patterns observed in other urban areas, as for example in New Orleans, notwithstanding the higher  $\Sigma$ PAHs in New Orleans (Fig. 2).

Some studies also showed that PAHs concentrations in soil correlate with PAHs levels in the atmosphere (Wilcke 2000). A recent study in the São Paulo city showed high concentrations of PAHs in the atmosphere which can promote a continuous flux of PAHs from the atmosphere to the soils as they are still emitted by primary combustion sources (Bourotte et al. 2005). Some

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# TABLE IV

Compounds		CUNHA		PEFI	
		$\mu$ g.kg <sup>-1</sup>	%	$\mu$ g.kg <sup>-1</sup>	%
Acenaphthylene	ACY	22,5	13	37,5	5
Acenaphthene	ACE	45,0	25	45,0	6
Fluorene	FLU	45,0	25	45,0	6
Phenanthrene	PHE	22,5	13	37,5	5
Anthracene	ANT	<dl< td=""><td>0</td><td><dl< td=""><td>0</td></dl<></td></dl<>	0	<dl< td=""><td>0</td></dl<>	0
Fluoranthene	FLT	30,0	17	203,0	25
Pyrene	PYR	15,0	8	7,5	1
Benzo(a)anthracene	BaA	<dl< td=""><td>0</td><td>52,5</td><td>6</td></dl<>	0	52,5	6
Chrysene	CRY	<dl< td=""><td>0</td><td>75,0</td><td>9</td></dl<>	0	75,0	9
Benzo(bk)fluoranthene	B(bk)F	<dl< td=""><td>0</td><td>90,0</td><td>11</td></dl<>	0	90,0	11
Benzo(a)pyrene	BaP	<dl< td=""><td>0</td><td>82,5</td><td>10</td></dl<>	0	82,5	10
Indeno(1,2,3-cd)pyrene	IND	<dl< td=""><td>0</td><td>45,0</td><td>6</td></dl<>	0	45,0	6
Dibenz(a,h)anthracene	D(ah)A	<dl< td=""><td>0</td><td><dl< td=""><td>0</td></dl<></td></dl<>	0	<dl< td=""><td>0</td></dl<>	0
Benzo(ghi)perylene	BghiP	<dl< td=""><td>0</td><td>97,5</td><td>12</td></dl<>	0	97,5	12
ΣPAHs	180	100	818	100	

PAHs concentration values (in  $\mu$ g.kg<sup>-1</sup>) in Cunha and PEFI soils integrated in the 0–20 cm topsoil horizons. (*<DL*: lower than detection limit).

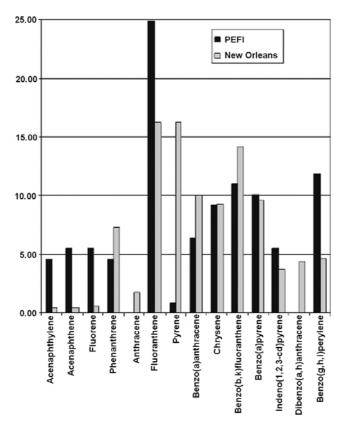


Fig. 2 – Individual contribution of PAH compounds for PEFI soil (this study) and New Orleans urban soils (Mielke et al. 2004) (values in % of the  $\Sigma$ PAHs).

Location	Area	Number of PAHs	Concentration $(\mu g.kg^{-1})$	Sampling depth	Reference	
São Paulo	Urban	1.4	818	0.20	This study	
	Natural	14	180	0–20 cm		
Bangkok	Urban	20	129.2	0–5 cm	Wilcke et al. 1999	
	Amazon (Terra Firme)		145			
	Amazon (Igapó)	- 20	38		Wilcke et al. 2003	
Brazil	Pantanal		68	0.10 am		
DIAZII	Cerrado central		17	0–10 cm		
	Mata Atlântica		115			
	Caatinga		23			
	Forest (Forest of Bretonne)		940	3–10 cm		
	Natural (Honfleur)	14	450			
France (Seine Basin)	Suburban (Harfleur)		1670		Motelay-Massei et al. 2004	
	Urban (Rouen)		2780			
	Industrial (Oissel)		3390			
	Unpolluted	16	112	0–3 cm		
Spain (Tarragona County)	Residential		736		Nadal et al. 2004	
	Industrial		1102			
	Suburban			731*	2.5	
USA (New Orleans)	Inner city	16	2927*	2.5 cm	Mielke et al. 2004	
Korea	Agricultural soils	16	158*		Nam et al. 2003	
China (Tianjin)	Industrial	16	818.2		Wang et al. 2003	
Japan (Tokushima)	Urban	13	610.6		Yang et al. 2002	
Estonia	Rural	11	233-770	0–10 cm	Trapido 1999	
	Urban (Tallinn)		2240			
	Industrial (Kohtla-Järve)		12390			
Norway	Central region	9	69	0–5 cm	Aamot et al. 1996	
	Southeastern region		527			
Poland	Silesia region	16	264 (28–2447)	0–15 cm	Maliszewska-Kordybach 1996	
Australia (Brisbane)	Suburban	16	471	0–5 cm	Pathirana et al. 1994	
Austria (Linz)	Industrial	18	1450		Weiss et al. 1994	

TABLE V Total PAHs mean concentrations in soil (in  $\mu$ g.kg<sup>-1</sup>) in other countries of the world (\*median value).

markers are indicative of combustion sources: ratio between PAHs such as PHE/ANT, FLT/PYR, BaP/BghiP, BaA/CRI or IND/BghiP, are characteristic of pyrogenic origin such as motor vehicle exhausts, heavy industrial emissions, biomass burning, etc. (Bourotte et al. 2005). The values obtained in this study indicated PAHs sources associated with gasoline vehicle emissions or fossil fuels combustion by industry.

PAHs levels reported in the literature from soils of urban and natural areas are presented in Table V. The  $\Sigma$ PAHs observed in Cunha is slightly higher than others values from poorly-anthropized areas from Brazil (Wilcke et al. 2003) or other countries (Nadal et al. 2004, Nam et al. 2003, Aamot et al. 1996). This could indicate the beginning of a contamination in the Cunha area. The values reported in Table V also support that urban environments present significantly higher PAHs concentrations in relation to natural ones. We must point out that most of these studies are related with urban soils of temperate climates of North Hemisphere and that studies performed in Tropical regions are yet scarce. Although analytical methods, number of quantified compounds and soil characteristics vary among theses different studies, tropical soils presented lower concentrations than soils of temperate climates, except for New Orleans. Total PAHs concentrations observed in PEFI soils are lower than the ones reported for industrial soils by Motelay-Massei et al. (2003) for Oissel soils (3390  $\mu$ g.kg<sup>-1</sup>), Nadal et al. (2004) for Tarragona soils (1102  $\mu$ g.kg<sup>-1</sup>), Trapido (1999) for Estonian soils (12, 390  $\mu$ g.kg<sup>-1</sup>) or Wang et al. (2003) for Tianjin soils (812.2  $\mu$ g.kg<sup>-1</sup>). Total PAHs concentrations in PEFI are also lower than other urban soils of North Hemisphere. Nadal et al. (2004) found a mean of 736  $\mu$ g.kg<sup>-1</sup> in Terragona residential soils, Motelay-Massei et al. (2004) concentration values of 2780  $\mu$ g.kg<sup>-1</sup> in Rouen urban soils and Trapido (1999) observed a mean level of 2240  $\mu$ g.kg<sup>-1</sup> in Estonian urban soils. These concentrations are, however, similar to the values reported by Yang et al. (2002) for Tokushima urban soils (610.6  $\mu$ g.kg<sup>-1</sup>) and higher than those found in Bangkok (129.2  $\mu$ g.kg<sup>-1</sup>) by Wilcke et al. (1999). For natural soils, the total PAHs concentrations in the current study are similar with those reported by Wilcke et al. (2003) for Amazon soils (145  $\mu$ g.kg<sup>-1</sup>) and Mata Atlântica soils (115  $\mu$ g.kg<sup>-1</sup>), as well as to the levels reported by Nadal et al. (2004) for Spanish unpolluted soils (112  $\mu$ g.kg<sup>-1</sup>) and by Nam et al. (2003) for agricultural soils of Korea (158  $\mu$ g.kg<sup>-1</sup>).

Lower accumulations in tropical urban soils compared to temperate urban soils can be related to lower organic matter content. Studies generally reported that PAHs accumulate in organic matter rich horizons because of their affinity with soil organic matter (Krauss et al. 2000, Wilcke 2000). Gaboriau and Saada (2001), when studying PAHs retention by kaolinite, confirmed that composition of organic matter is the primary factor in PHEN retention by the soils. Tropical soils are indeed usually poorer in organic matter when compared with temperate soils. Average organic matter content in the topsoil 20 cm of the PEFI soil was 2.1%, to be compared to values around 4.0% for most temperate soils (Brady and Weil 1999). Higher volatilization, lixiviation and degradation, contributing to lower  $\Sigma$ PAHs in soils, are also expected in tropical areas, due to higher average temperature and rainfall (Maliszewska-Kordybach 1993, Krauss et al. 2000).

### CONCLUSION

The results showed that the soil of the São Paulo urban area (PEFI) are greatly submitted to anthropogenic emissions and suffer the impact of the city. The PAHs accumulation is characterized by high molecular weight PAHs produced by gasoline and other fossil fuels combustion. Despite the high urbanization of the area, however, the  $\Sigma$ PAHs values of the urban soil are relat-

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ively low with regard to other urban areas under cold or temperate climates. This is likely due to lower retention, because of low organic matter content of the soil, and to higher sink, owing to the higher temperature and rainfall of tropical climate. With regard to natural area (CUNHA), more studies are necessary to provide a minimum knowledge about natural production and PAHs behavior (lixiviation, evaporation, biodegradation, etc.).

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#### RESUMO

Estudos sobre a poluição por Hidrocarbonetos Policíclicos Aromáticos (HPAs) são escassos em solos tropicais e no Brasil. Um estudo foi realizado para examinar a composição, as concentrações e fontes de HPAs encontrados em Latossolos vermelho-amarelo (Oxissolos), remanescentes de Mata Atlântica no Estado de São Paulo. As áreas de estudos localizaram-se em um sítio urbano (PEFI) e um natural (CUNHA). A composição granulométrica, pH, teor de matéria orgânica e composição mineralógica foram determinados em amostras de solo superficial. A soma dos HPAs analisados (ΣHPAs) foi 4,5 vezes mais elevada na área urbana do que na área natural. Acenaftileno, acenafteno, fluoreno, fenantreno e fluoranteno foram detectados, em concentrações similares, nos solos das duas áreas. Acenafteno e fluoreno foram os compostos mais abundantes. O pireno foi duas vezes mais abundante no solo da área natural (15  $\mu$ g.kg<sup>-1</sup>), e o fluoranteno foi o composto dominante (203 µg.kg<sup>-1</sup>) na área urbana (6,8 vezes mais elevado que na área natural). Alguns compostos de alto peso molecular, traçadores de emissões veiculares, foram detectados em quantidades significativas no solo da área urbana. O pireno representou 79% da EHPAs, enquanto que não foi detectado na área natural. Estes resultados evidenciaram que os solos de floresta em áreas urbanas são caracterizados pela acumulação de HPAs pesados oriundos de emissões industriais e veiculares.

**Palavras-chave:** Floresta Atlântica, hidrocarbonetos policíclicos aromáticos, HPAs, floresta tropical, solos tropicais, solos urbanos.

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