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POLYCYCLIC AROMATIC HYDROCARBONS ASSESSMENT IN SEDIMENT OF NATIONAL PARKS IN SOUTHEAST BRAZIL

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Abstract

The aim of this work was to assess the levels of polycyclic aromatic hydrocarbons (PAHs) in the environment and their sources found in protected regions of southeastern Brazil. Samples of sediments were collected at four National Parks: Itatiaia National Park (PNIT), Serra da Bocaina National Park (PNSB), Serra dos Órgãos National Park (PNSO) and Jurubatiba National Park (PNJUB). The National Parks studied comprise rainforests, altitudinal fields and ‘restinga’ environments located in the Minas Gerais, Rio de Janeiro and São Paulo states. The sampling was conducted between 2002 and 2004 from June to September. In general, the environmental levels of PAHs found were similar to those in other remote areas around the globe. PNIT exhibited the highest median values of total PAHs in sediment ($97 \text{ ng}\cdot\text{g}^{-1}$), followed by PNJUB ($89 \text{ ng}\cdot\text{g}^{-1}$), PNSO ($57 \text{ ng}\cdot\text{g}^{-1}$) and PNSB ($27 \text{ ng}\cdot\text{g}^{-1}$). The highest levels of total PAHs (576 and $24430 \text{ ng}\cdot\text{g}^{-1}$) could be associated to a point source contamination where are characterized for human activities. At PNSB and PNIT the PAH profiles were richer in 2 and 3 ring compounds, whereas at PNSO and PNJUB, the profiles exhibited 3 and 4 ring compounds. The phenanthrene predominance in most samples could indicate the influence of biogenic synthesis. The samples with a petrogenic pattern found in this study might be associated with the vicinity of major urban areas, highway traffic and/or industrial activities close to PNSO and PNIT. At PNIT and PNJUB, forest fires and slash and burn agricultural practices may drive the results towards a pyrolytic pattern.

Keywords

polycyclic aromatic hydrocarbons; Serra da Bocaina; Serra dos Órgãos; Itatiaia; Restinga de Jurubatiba; sediment and Southeast Brazil

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a unique class of persistent organic pollutants (POPs) consisting of two or more fused benzene rings in linear, angular or cluster arrangements (Netto et al., 2000). They are considered priority organic pollutants in view of their

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carcinogenic potential and ability to act as mutagenic promoters in biologic systems (WHO, 1983; EPA, 1987). PAHs originate from incomplete burning of organic matter, thus primary sources for these compounds to the environment are, among others, the emissions stemming from forest fires and fossil fuel burning (Page et al., 1999; Yunker et al., 2002; Brito et al. 2005). Several anthropogenic activities can increase dramatically the levels of these contaminants in the environment. However, some PAHs can be produced by plants as biogenic precursors and might be an important contribution to the total PAH concentrations in remote areas (Wilcke et al., 2000; Hafner et al., 2005).

PAHs are transported mainly through fine particle in the atmosphere or aquatic environment and can reach long distances to remote areas (Wickstrom and Tolonen, 1987; Rose and Rippey, 2002). Air pollution is an important exogenous factor that contributes to the input of PAHs and others contaminants in remote ecosystems like mountains and uplands. Mountain areas have received more attention in identifying and assessing organic contaminants (Fernández et al., 1999). In a recent review, Daly and Wania (2005) state that the transport of some organic pollutants in mountain areas are controlled by climate and geographical parameters, such as diurnal mountain winds, precipitation rates and low temperatures. In particular, more volatile compounds seem to reach higher altitudes, in contrast to less volatile contaminants. In the tropics, the precipitation rates might be an important factor in mountain regions and may govern contaminant amplification. However, few studies have been done in tropical areas (Colombo et al., 2000; Torres et al., 2002; Quiroz et al., 2005). Barra and co-workers (2005) verified that the PAH levels in the Andean mountain soils were affected by local contaminating sources such as human influence. Wilcke and co-workers (2003) had identified strong evidence for PAH biogenic sources in soil and vegetal biomass at different tropical Brazilian ecosystems, such as the Amazon basin, the Atlantic rainforest and the Cerrado areas.

Sediments are a great tool for the investigation of trace contaminants such as PAH in aquatic systems due to their huge affinity for particulate and organic matter, and their relatively long persistence in the environment (Warren et al. 2003). The present work provides an initial screening of PAH concentration levels in surface sediments in the tropics from four National parks situated at mountain and coastal areas along the boundaries of the states of Rio de Janeiro, Minas Gerais and São Paulo in southeast Brazil, during 2002 and 2004.

2. Experimental

2.1 Study area

The four National Parks studied comprise rainforests, high altitude fields and restinga environments. The National Parks of Bocaina (PNSB), Orgãos (PNSO) and Itatiaia (PNIT) are located between Serra do mar and Serra da Mantiqueira (sierra mountain) that crosses Rio de Janeiro, Minas Gerais and São Paulo states (figure 1). These mountain areas can reach high altitudes of approximately 2,400 meters above sea level. The National Parks of Restinga de Jurubatiba (PNJUB) is located in northeast Rio de Janeiro state lowlands, enclosing Macaé, Quissamã and Carapebus cities and comprises a complex ecosystem including many coastal lagoons. These ecosystems (or ecozones) are considered hotspot conservation areas for high biodiversity and endemic species (Myers et al., 2000; Scarano, 2002).

2.2 Sample preparation

The sediment samples were collected between 2002 and 2004 from June until September at the four National Parks. In the field, the samples were collected in wide mouth jars previously washed with acetone. The collected sediments were identified and stored in a refrigerator (4° C). In the laboratory, sediment samples were disaggregated and then wet sieved using 74 µm

stainless sieve. The $< 74 \mu\text{m}$ fraction of dried sediments (clay) was obtained and oven dried at 30°C for future analyses.

2.3 Analytical procedures

For PAH extraction, 6g of sediment were extracted consecutively with 12 mL of an acetone/n-hexane mixture (4/1: 1/1 and 1/4; v/v) using an ultrasonic bath set at 90°C for 20 minutes. One milliliter of isooctane was added prior to each PAH extraction step. The extracts were filtered and combined in a glass flask. The combined extracts were concentrated to 1 mL by vacuum rotatory evaporator. All solvents used in these experiments were residue-analysis quality and other reagents were supplied from Tedia Co. (Ohio, USA). All glassware was rinsed three times with HPLC grade acetone prior to analysis.

In order to remove potential interferences such as humic materials and elemental sulfur, the combined extracts were passed through a chromatography column filled with 7g of $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_3$ deactivated with 11% of water (Japenga et al., 1987; Torres et al., 1999). Twenty mL of n-hexane was used to elute PAHs from the cleanup column. The cleaned extracts were concentrated to 1 mL by vacuum rotary evaporation and then eluted through another chromatography column filled with silica gel 60 (70–230 mesh ASTM) with 35 mL of n-hexane/ethyl ether (3:1; v/v). The eluents were concentrated by vacuum rotary evaporation until dry and then diluted with 0.5 mL of acetonitrile.

2.4 Chromatographic method

An aliquot of $20\mu\text{L}$ of the acetonitrile extract was analyzed using a high performance liquid chromatograph (Shimadzu LC-10AS) equipped with a fluorescence detector (Shimadzu Model RF-10 AxL). The separation was performed on a Shimadzu CLC-ODS II column ($180.0 \times 4.1\text{mm}$ i.d.), with $5\mu\text{m}$ of particle size and pores of $120\text{\AA}$. The isocratic run was completed with a mobile phase composed of water:acetonitrile mixture (20:80; v: v). The detector was programmed with eight Ex/Em wavelength steps: 255/325; 253/350; 333/390; 287/462; 280/430; 294/404 300/500 and 300/421. The following PAHs were analyzed: naphthalene (NAPH), fluorene (FLU), phenantrene (PHEN), anthracene (ANTH), fluoranthene (FLUOR), pyrene (PYR), benz[a]anthracene (B[a]A), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz[ah]anthracene (DB[ah]A), indeno [123cd]pyrene (IND) and benzo[g,h,i]perylene (B[ghi]P). The PAH detection limits in sediment extracts were calculated as being three times the standard deviation of the blank concentrations. The detection limits were between $1.31 \text{ ng}\cdot\text{g}^{-1}$ for naphthalene and $0.71 \text{ ng}\cdot\text{g}^{-1}$ for fluoranthene, and were between $0.01 \text{ ng}\cdot\text{g}^{-1}$ and $0.47 \text{ ng}\cdot\text{g}^{-1}$ for the other PAH compounds.

2.5 Standards and reference materials

The PAH standard reference material was obtained from NIST (No. 1647c). PAH recovery was evaluated using reference material of marine sediment provided by the International Atomic Energy Agency (IAEA-417) for international intercomparison exercises. The mean PAH recovery and coefficient variation values reported were 87.2 % and 3.8 %, respectively.

3. Results and discussions

3.1 Environmental levels

Table 2 shows the median values and the range of PAHs measured in sediments obtained from the four National Parks. In general, PNIT showed the highest median value of total PAH ($97 \text{ ng}\cdot\text{g}^{-1}$ d.w.), followed by PNJUB ($89 \text{ ng}\cdot\text{g}^{-1}$ d.w.), PNSO ($57 \text{ ng}\cdot\text{g}^{-1}$ d.w.) and PNJUB ($28 \text{ ng}\cdot\text{g}^{-1}$ d.w.). The highest levels of total PAHs found for PNIT ($24430 \text{ ng}\cdot\text{g}^{-1}$ d.w.) and PNJUB

(576 ng·g⁻¹ d.w.) are probably related to local contamination, where the potential point sources are located.

The PNIT collection site (LAT 22°27'16"S; LOG 44°36'25"W) is characterized by its proximity to human settlements which may be responsible for the can increase the total PAH concentration in the sediments. The settlements are located at low areas of the National Park where tourists and scientific researchers take shelter. Pereira and co-workers (2004a) identified higher levels of total PAHs in atmospheric aerosols for the lower areas located near the entrance to the Itatiaia National Park and is possibly influenced by human presence. At PNJUB, some collection sites are influenced by the Carapebus lagoon located at the border of the National park of Jurubatiba (LAT 22°19'36"S; LOG 41°35'53"W) which could be more subjected to point contamination sources. This area is influenced by human presence with agricultural activities and domestic waste products.

The total PAH concentrations in the National Parks located in southeast Brazil are found to be lower than those found in mountain areas of central and east Europe, and other remote areas around the world (Table 3). Further, sediment levels found in the National Parks are one or two orders of magnitude lower than levels found in sediments from urban and industrial areas in the United Kingdom, USA and Brazil. Torres and co-workers (2002) reported higher concentrations of total PAH (40,000 ng·g⁻¹) in sediments at Paraiba do sul drainage, a hundred kilometers away from PNIT but near a huge industrial area.

3.2 PAH Profiles

PAH fingerprints showed relatively similar profiles at the four National Parks (figure 2). Naphthalene (47%) and phenanthrene (24%) were the most predominant PAHs in PNSB. For PNIT, phenanthrene (30%) was most predominant followed by naphthalene (17%) and fluoranthene (10%). In PNSO and PNJUB, the PAH profiles for 3 and 4 rings were more common. Phenanthrene (47 and 23%), fluoranthene (14 and 25%) and pyrene (11 and 18%) were most predominance for both National Parks respectively. The presence of more volatile PAHs (i.e. NAPH and PHEN) could be explained by the high dispersion capacity of these pollutants associated with meteorological conditions, such as precipitation rates, winds and annual temperatures (Beniston, 2000;Daly and Wania, 2005). Pereira and co-workers (2004b) identified the predominance of NAPH and PHEN at PNIT in atmospheric aerosols and suggested a possible petrogenic origin. In agreement with some researchers (Hoffman et al., 1984;Douben, 2003; Britto et al., 2005), the predominance of 2 and 3 rings may indicate a petrogenic source (PNSB and PNIT), while 3 and 4 rings might result from contributions from both petrogenic and pyrolytic PAH sources (the situation in PNSO and PNJUB).

Another possibility is that PAH like naphthalene, phenantrene and perylene are a good PAH index of biological synthesis. Chen and co-workers (1998) showed that naphthalene is an important chemical mediator for communication in termites (*Coptotermes formosanus*). Daisy and co-workers (2002) verified the insecticidal properties of naphthalene synthesized by entophytic fungi species (*Muscolor vitigenus*) found in the Peruvian Amazon. The high contribution of PHEN to the total PAHs in all the National Park sediments could be possible evidence of biological origin. PHEN could be synthesized from biogenic precursors like alkyl phenanthrenes, found mainly in plant tissues. Wilcke and co-workers (2003) verified high frequency of PHEN relative to other PAH constituents in the Brazilian rainforests.

3.3 PAH Sources

Figure 3 exhibits the cross plotting of some PAH ratios to obtain a better evaluation of PAH origins in sediments for each National Park. There are a number of studies in the scientific literature that use this approach to indicate PAH origins (Budzinski et al., 1997; Readman et

al., 2002). In this work, phenanthrene/anthracene (PHEN/ANTH) values were plotted against fluoranthene/pyrene (FLUOR/PYR) values for each sediment sample for all four National Parks. To make a PAH fingerprint plot, “burning” soil from a sugar cane crop (closed Carapebus Lagoon - PNJUB), which represent a pyrolytic fingerprint, was also included in Figure 3. The analysis of the “burning” soil for PAHs followed the experimental steps outlined for the sediment samples in section 2.3. The plot in Figure 3 could not confirm a clear trend for all the stations in the National Parks, but some observations are important for PAHs fingerprints in this study.

In PNJUB, the pyrolytic fingerprints (PHEN/ANTH <15; FLUOR/PYR >1) reported at stations #27, #28 and #29 (Table 1) represent the Capapebus lagoon, which in this case, might be characterized by local point contamination. Part of the Carapebus lagoon is bordered by vast sugar cane cropping. Sugar cane burning is a part of the traditional activity in this agricultural area. Agricultural activity is an important source of PAHs near local aquatic systems (Azevedo et al., 2002; Gomes and Azevedo, 2003). In PNIT, occasional forest fires may also drive the ratios towards a pyrolytic origin (station #5). In PNSO, a petrogenic origin (PHEN/ANTH >15; FLUOR/PYR < 1) is found characterized at the stations #11 and #12 located near of National Park's headquarters. A petrogenic fingerprint could be related to the proximity of highway traffic that crosses the National Park. The same could be observed at some other stations at PNIT (stations #7, #8, #9 and #10). The PNSB did not show any clear trend for PAH fingerprints in its sediments (stations #18, #19, #20 and #21).

4. Conclusions

In conclusion, the PAH levels reported in this study are in the low range values compared to the mountain and other remote areas measured in the Northern Hemisphere. The highest PAH values reported here could be related to local contamination originating from human activities close to or at the borders of the National Parks. The relatively high phenanthrene contributions for PAHs profiles found in the four National Parks could derive from intrinsic factors, like biogenic synthesis. These PAH profiles reported for the National Parks are similar to other Brazilian ecosystems such as the Atlantic rainforest and Amazon basin. Petrogenic fingerprints found in this study could be explained by the proximity of highways and cities near to the National Parks of Orgãos and Itatiaia. Forest fires, slash burning and burning of agricultural and human waste residues are practices that may drive the PAH levels towards the pyrolytic pattern in the National Parks of Itatiaia and Jurubatiba (Carapebus lagoon).

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Figure 1. Study of area. (⊗) National Parks: 1) Itatiaia; 2) Bocaina; 3) Órgãos and 4) Jurubatiba. Source: IBGE 2006

Figure 2.
PAH profiles in sediments for each National Park.

Figure 3.

Plot of the isomeric ratios PHEN/ANTH (phenanthrene vs anthracene) against FLUOR/PYR (fluoranthene vs pyrene) for sediments from each National Park, and one burn soil matrix (burn soil) to attempt delineation of pyrolytic sources.

Table 1

Location of sampling stations

National Parks	Localization	Latitude	Longitude	Altitude (masl)	Ecozones
1	Rio Campo Belo (Marombá)	22°25'45"S	44°37'10"W	1100	Rainforest
2	Rio Campo Belo (Lago Azul)	22°27'07"S	44°36'48"W	827	Rainforest
3	Rio Tapera (Afluente C.B.)	22°27'16"S	44°36'25"W	813	field
4	Brejo da Lapa (meio)	22°21'30"S	44°44'13"W	2136	field
5	Brejo da Lapa (margem)	22°21'30"S	44°44'13"W	2136	Altitude field
6	Geladeira turfa (afluente Campo Belo)	22°22'38"S	44°41'35"W	2421	Altitude field
7	Ponte (afluente Campo Belo)	22°22'47"S	44°41'19"W	2415	Altitude field
8	Rio Campo Belo (Alagado)	22°22'52"S	44°41'10"W	2422	Altitude field
9	Rio Campo Belo (abrigo reboças-barragem)	22°23'06"S	44°40'16"W	2413	Altitude field
10	Mauá (cachoeirinha)	22°17'44"S	44°36'49"W	1800	Rainforest
11	Ponto 1 – Cachoeira 1	22°27'15"S	43°00'34"W	903	Rainforest
12	Ponto 2 – Cachoeira 2	22°27'28"S	43°01'21"W	1886	Rainforest
13	Ponto 3 - Vale das Antas	22°27'33"S	43°02'23"W	2036	Rainforest
14	Ponto 5 - Camping - Represa Montante	22°27'34"S	43°01'40"W	2062	field
15	Ponto 6 - Camping - Represa Jusante	22°27'34"S	43°01'40"W	2062	field
16	Ponto 7 - cachoeira barragem- sede (Rio Beija-flor)	22°27'06"S	43°00'02"W	1892	Rainforest
17	Ponto 8 - Sede Guapi (Rio Soberbo)	22°29'16"S	43°59'59"W	n.i	Rainforest
18	Ponto 2 - Rio Mambucaba	22°44'32"S	44°42'44"W	1532	Rainforest
19	Ponto 3 - Rio Paraitinga	22°44'12"S	44°42'44"W	1574	field
20	Ponto 4 – Alagado	22°44'39"S	44°40'57"W	1564	Rainforest
21	Ponto 5 - Rio Paraitinga Jusante de Pt. 3	22°47'46"S	44°42'31"W	1520	Rainforest
22	Lagoa Cabiúnas	22°17'59"S	41°04'24"W	Sea level	Restinga
23	Lagoa Cabiúnas	22°17'59"S	41°04'24"W	Sea level	Restinga
24	Lagoa Cabiúnas	22°17'59"S	42°04'24"W	Sea level	Restinga
25	Lagoa Comprida	n.i	n.i	Sea level	Restinga
26	Lagoa Comprida	n.i	n.i	Sea level	Restinga
27	Lagoa de Carapebus	22°19'36"S	41°35'53"W	Sea level	field
28	Lagoa de Carapebus	22°19'36"S	41°35'53"W	Sea level	Restinga
29	Lagoa de Carapebus	22°19'36"S	41°35'53"W	Sea level	Restinga

n.i: no information

masl: meters above the sea level

Table 2

Median and range of PAH concentrations ($\text{ng}\cdot\text{g}^{-1}$) in sediments samples for each National Park.

	PNIT(n=10) ¹		PNSO(n=7)		PNSB(n=4)		PNJUB(n=8)	
Naphthalene	15.9	(5.8–155.7)	4.7	(2.1–10.6)	8.0	(<DL -48)	9.1	(2.2–26.5)
Phenanthrene	28.5	(3.5–3257.8)	25.7	(1.1–35.8)	9.3	(3.5–33.8)	28.1	(8.0–111.3)
Fluorene	1.7	(0.9–48.6)	1.6	(<DL -2.0)	2.6	(<DL -4.4)	3.0	(1.2–5.9)
Anthracene	0.8	(<DL ² -172.8)	0.8	(<DL -1.3)	0.8	(<DL -13.0)	1.2	(<DL -15.5)
Fluoranthene	17.1	(1.3–5763.0)	7.3	(2.1–14.6)	1.5	(<DL -6.6)	16.4	(3.0–155.9)
Pyrene	10.2	(0.6–4501.4)	5.8	(1.1–13.6)	4.0	(<DL -5.6)	16.8	(1.3–103.9)
Benzo[a]anthracene	4.3	(0.2–2566.3)	0.9	(0.6–3.1)	<DL	<DL	1.6	(0.5–17.4)
Benzo[b]fluoranthene	10.9	(1.4–2366.0)	3.1	(1.7–6.8)	0.7	(0.2–1.7)	2.9	(0.6–27.8)
Benzo[k]fluoranthene	2.9	(0.1–1466.4)	0.9	(<DL -2.5)	0.3	(<DL -1.3)	2.9	(1.3–14.1)
Benzo[a]pyrene	0.9	(0.1–2603.0)	1.4	(<DL -5.2)	<DL	<DL	1.1	(0.1–27.7)
Dibenz[a,h]anthracene	1.4	(1.1–11.3)	0.7	(<DL -1.0)	<DL	<DL	1.2	(0.6–2.1)
Indeno[1,2,3-cd]pyrene	0.6	(0.6–9.7)	4.6	(2.7–6.6)	<DL	<DL	2.4	(0.3–21.5)
Benzo[g,h,i]perylene	2.2	(0.1–1508.4)	<DL	<DL	0.1	(<DL -0.6)	2.2	(2.1–47.6)
Sum of PAHs	97.3	(15.7–24430.4)	57.4	(11.4–103.2)	27.3	(3.7–115)	88.9	(21.1–576.4)

¹ sample number;

² **<DL** – Values below detection limits.

Table 3

Comparison of PAH levels in sediments with other areas around the world. Figure 1

Localization	PAH (ng·g ⁻¹)	References
Itatiaia National Park	16–372 (24254) ¹	<i>This study</i>
Bocaina National Park	04 – 115	<i>This study</i>
Orgãos National Park	11– 103	<i>This study</i>
Jurubatiba National Park	21– 576	<i>This study</i>
Mountains		
Central Europe	180–1100	Fernandez <i>et al.</i> , 1999
East Europe	1300–18000	Fernandez <i>et al.</i> , 1999
Arresjoen (Artic)	260	Fernandez <i>et al.</i> , 1999
Laja Lake (Chile)	46–359	Quiroz <i>et al.</i> , 2005
Remote lakes		
Adirondack Park, NY (USA)	2900–11000	Tan e Heit, 1981
Larto lake, LA (USA)	100	Catallo <i>et al.</i> , 1995
Florida, NE (USA)	300–1800	Furlong <i>et al.</i> , 1987
Urban and industrial areas		
Michigan lake (USA)	1300–3500	Simcik <i>et al.</i> , 1996
Zurich Lake (CH)	15000	Walkeman <i>et al.</i> , 1980
Washington (USA)	7000	Walkeman <i>et al.</i> , 1980
Priest pot (UK)	16000	Cranwell e Koul, 1989
Paraiba do sul river, RJ (Brazil)	40000	Torres <i>et al.</i> , 2002

¹ extreme value