POLYCYCLIC AROMATIC HYDROCARBONS assesment in sediment of national parks in Southeast Brazil – PRELIMINARY RESULTS

Rodrigo Meire[1], João Paulo M Torres[1], Antônio Azevedo[1], Marcia S Pereira[1], Claudio Azevedo[1], Olaf Malm[1]

[1]Ufrj

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants formed by two or more fused benzene rings in linear, angular or cluster arrangements[1]. They are potentially carcinogenic and mutagenic promoters in biologic systems[2]. PAH are contaminants resulting from incomplete burning of organicmatter, thus primary sources for these compounds to the environment are, among others, the emissions stemming from incomplete combustion of organic matter, forest prairies and fossil fuels burning[3,4,5]. The anthropogenic activities increased dramatically the levels these contaminants in the environment. Some PAHs can be produced by plants as biogenic precursors. However, source of petrogenic origin are introduced in the environment by coal, crude oil, and refinary processes[6]. PAHs are transported mainly through fine particule in the atmosphere or aquatic environment and can reach long distances to remote areas[7,8]. Air pollution is an important exogenous factors that contribute to the input of PAHs and another contaminants in remote ecossystems like mountains and uplands. Their transport from emission sources are controlled by climate and geographical parameters like mountain winds, precipitation rates and low temperatures[8,9]. Sediments are a great tool for investigation of the trace contaminants like PAH in aquatic systems due to their high affinity to particulate and organic matter, and their relatively long persistency in the environment[10,11]. The present work makes a first screen on PAH concentration levels in surface sediments from three National parks situated along the boundaries of the states of of Rio de Janeiro and São Paulo southeast, Brazil, during 2002 and 2004 and discussed their possibles sources of contamination as well.

Material and Methods

Study area – The three national parks studied comprise rainforests, altitude fields and restinga environments. National park of Bocaina (PNSB) and Orgãos (PNSO) are situated in Serra do mar, (sierra mountain) that crosses Rio de Janeiro and São Paulo states. National park of restinga de Jurubatiba (PNJUB) is situated at the lowlands northen of Rio de Janeiro state and comprises a complex ecossystem composed of many coastal lagoons close to Macaé city.

Sample preparation:Sediment samples were colleted between 2002 and 2004 in 03 campaigns at August until September. The sediment stored in freezer. In the laboratory the samples were dried at 30°C and the fine particles (<0,074 mm) were obtained.

PAHs extraction: 6g of dry sediment were extracted consecutively with 12 mL of acetone/n-hexane mixture (4/1; 1/1 and 1/4; v/v) added with 1 mL of isooctane using hot (T=100°C) ultrasonic bath during 20 min.

The extracts were mixed and cleaned up on a colunm with Al2O3/Na2SO3deactivated with11% of water. The collumn was eluted with 20 mL of n-hexane in order to remove humic material and others interferents. The cleaned extracts were fractioned with 35 mL of n-hexane/ethyl ether (3:1) mixture on an open chromatography column with silica gel 60 (70-230 mesh ASTM). The eluates were concentrated by vacuum rotary evaporator until dry and diluted in 0.5 mL of acetonitrile.

Chromatographic method: An aliquot of 20mL was analyzed by means high performance liquid chromatography device (Shimadzu LC-10AS) equipped with a fluorescence detector (Shimadzu Model RF-10 AxL). The separation was performed in a Shimadzu CLC-ODS column (180.0 x 4.1mm i.d.), with 5mm of particle size and pore of 120Å. The isocratic run was developed with mobile phase composed by water:acetonitrile mixture (20:80; v:v). The detector was programmed with nine Ex/Em wavelenght steps: 255/325; 253/350; 333/390; 237/462; 280/430;

294/404 300/500 and 300/421. The following PAH were analyzed: Naphtalene, Fluorene, Acenafthylene, Phenantrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]Anthracene, Benzo[b]Fluoranthene, Benzo[k]Fluoranthene, Benzo[a]Pyrene, Dibenze[ah]Anthracene, Indene[123cd]Pyrene and Benz[ghi]Perilene.

Results and Discussion

The table 1 presents concentration levels of 14 PAHs analyzed in the three National parks: Serra of Orgãos, Serra of Bocaina, and Restinga of Jurubatiba. Total PAHs cocentration levels in the three Parks ranged from 47.4 to 64.1 ng/g where the PNSO is the most impacted site, PNSB and PNJUB are in the same level of impact.

Tabela 1- shows levels of PAHs (median in ng/g dry weight) in the National Parks of Serra

dosOrgãos (PNSO), Serra da bocaina (PNSB) and Restinga de Jurubatiba (PNJUB).

	PNSO	PNSB	PNJUB
	(ng/g dw)	**(ng/g dw)**	**(ng/g dw)**
Naftalene	5.22	8.01	2.22
Phenanthrene	27.85	9.29	3.30
Fluorene	1.58	2.55	11.90
Acenafthylene	*ND*	*ND*	*ND*
Anthracene	0.81	4.02	0.99
Fluorantene	6.58	0.76	15.48
Pyrene	7.17	4.02	8.30
B[a]Anthracene	0.9	0.31	1.50
B[k]Fluorantene	3.50	0.73	2.50
B[b]Fluorantene	1.22	0.32	5.71
B[a]Pyrene	1.45	0.20	*ND*
DB[ah]Anthracene	0.33	*ND*	1.16
IND[123cd]Pyrene	4.64	*ND*	*ND*
B[ghi]Perilene	*ND*	0.11	2.11
Total	**64.14**	**48.49**	**47.42**

ND- No detectable; Total – sum of 14 PAHs

Concentration levels found in the three parks are 2-fold lower than concentrations found by Torres and co-workers (2002) in industrial areas situated close to Paraíba do sul river (PSR). Figure 1 presents the PAHs profile in the 3 national parks. Phenanthrene (49%), Pyrene (13%) and (12%) Fluoranthene predominate in the profile found in PNSO.

Naphtalene and Phenantrene were the most compounds reported for PNSB (39%). Fluoranthene (35%) and B[k] Fluoranthene (17%) for PNJUB.

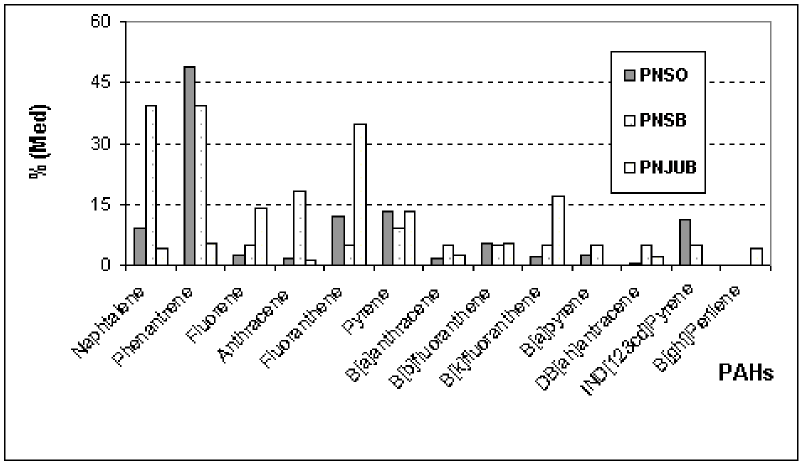

Figure 1 - PAHs profile in the sediment of Orgãos (PNSO), Bocaina (PNSB) and Jurubatiba (PNJUB) over median data.

The PAHs with pyrolytic origin are the major component in all three profiles. Main geografical effect observed is the predominance of the more volatile PAH (Phenantrene and Naphtalene) in the parks situated in the uplands (PNSO and PNSB). In order to provide a good estimate of PAHs sources[4,6], we are plotting Phenanthrene/Anthracene (Phen./Anth.) against Fluorantene/Pyrene (Fluor./Pyr.) ratios for the tree parks (figure 2).

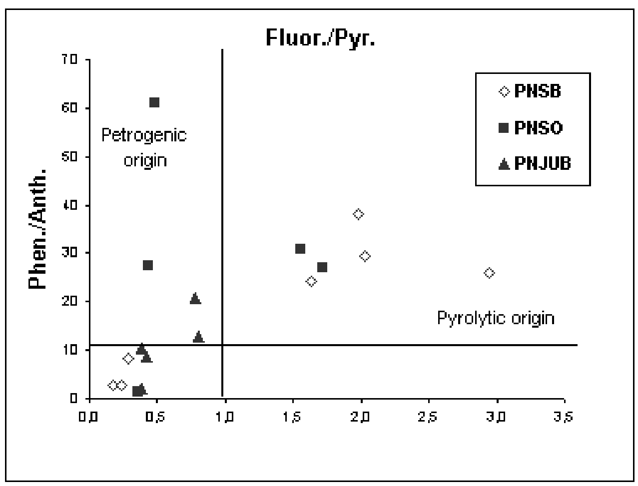

Figure 2 – Cross plot of the values of Phen./Anth. ratio against the values of the Fluor./Pyr. ratio for sediments in the three National Parks: Bocaina (PNSB), Orgãos (PNSO) and Jurubatiba (PNJUB)

Observing to the cross plot in figure 2, PNJUB exhibited rations for petrogenic origin (Fluor/Pyr <1; Phen/Anth >10). Either, PNSB and PNSO exhibited a mixed profile with PAH from both oringins (Petrogenic and pyrolytic), indicative the contribution of both sources to the whole profile in these natural parks.

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