



# ENVIRONMENTAL ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SURFACE SEDIMENTS OF GUANABARA BAY, RIO DE JANEIRO, BRAZIL

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## Abstract

Guanabara Bay is one of the largest coastal bays in Brazil; it measures 31 Km from South to North and has a surface area of about 400 Km<sup>2</sup> of estuarine waters. It is an eutrophic, polluted system, impacted by largely untreated domestic runoff from the 8 million human inhabitants of its basin. The immediate area surrounding the estuary is highly industrialized and includes petroleum refineries and chemical manufacturers, so the bay is subject to organic and inorganic chemicals contamination [1]. PAHs are a large group of organic compounds with two or more fused aromatic rings. They are mutagenic and carcinogenic environmental contaminants that are widely present in the air, water and aquatic systems, soils and sediments. PAHs with four- to six-ring hydrocarbons are generally of pyrogenic origin and generated by the combustion of fossil fuels and of recent organic material. PAH concentration and distribution has been examined in surface sediments samples from the Guanabara Bay; samples were collected using a Petersen grab sampler, from site designed to provide a wide geographic coverage of the bay; the dominating PAH group in the area were four- to six-ring aromatic hydrocarbons, indicating pyrolytic origin generated by the combustion of fossil fuels and of recent organic material. Values of BaA/BaP ratios in most of the samples indicated an input from gasoline combustion; all other ratios of individual PAH compounds suggested pyrolytic sources for PAHs.

## Bibliography

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Introduction



Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental contaminants which derive mainly from anthropogenic sources. The highest concentrations of PAHs are generally found around urban centres. PAHs are formed as a consequence of incomplete combustion (e.g., from fossil fuels) and are also components of crude oil and its refined products. They reach the marine environment via effluent discharges, urban run-off, atmospheric transport, and the spillage or disposal of oil and petroleum products. As they are hydrophobic, PAH tend to adsorb to particulate material and to be deposited to the underlying sediments.



Parent PAH compounds often predominate in sediments, deriving both from combustion sources and from oil [2].

The 16 PAH determined were identified on the basis of retention time matches and mass spectrum, with an external standard mixture PAH-Mix 13 (Dr. Ehrenstorfer GmbH) run on a daily basis (standard's chromatogram below); all the PAHs determined are included in the US Environmental Protection Agency (USEPA) priority pollutant list of 16 parent PAH compounds (USEPA, 1984). Samples - 20 in the Regional Area and 4 in the Test Area - were collected with a Petersen dredge, getting the first 25 cm of superficial sediment (representing, therefore, the last 30-35 years of sedimentation), carefully screened for determining the presence of animals and for checking the colour, the structure and the smell, then put in glass jars and frozen at -20° C until the analyses (GC-MS).

## PAHs Extraction

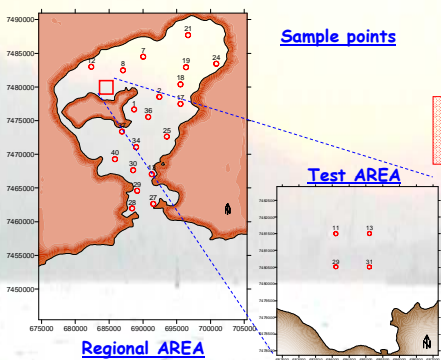
About 2 g of freeze-dried sample were weighted in a flask.

The extraction was performed with three 30 ml aliquots of a mixture of DCM/THF(9/1 v/v) using a sonication bath

the extracts were pooled and evaporated under a gentle nitrogen flux to 1-1.5 ml.

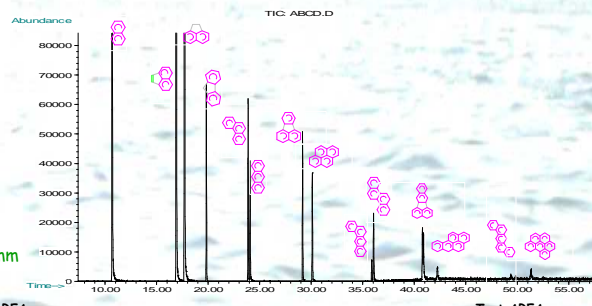
## Clean-Up Procedure

Glass chromatographic columns (1 cm internal diameter and 45 cm length with a Teflon stopcock and a 80 ml reservoir) were packed with 10 g of Florisil RS (60-100 mesh, Carlo Erba), 1 g of copper and 2 g of anhydrous sodium sulphate RPE (Carlo Erba). Analytes were eluted with 50 ml of *n*-hexane, and evaporated under a gentle nitrogen flux to 2 ml. Before the instrumental analysis, vials were let return to room temperature. All the used solvents were RS and HPLC grade, Florisil RS (60-100 mesh, Carlo Erba), anhydrous sodium sulphate RPE (Carlo Erba) were activated at 250 °C for 10 h.



## GC-MS System Components

- Gas Chromatograph : Hewlett Packhard 5890
- Detector MS : Hewlett Packhard 5970 B
- Injector : Split / Splitless, 1 uL, 300 °C
- Gas Carrier : Helium 40 Kpa
- Column : Chrompack CP-SIL 8 CB, 25 m \* 0.25 mm \* 0.25 mm
- Chem Station : Hewlett Packhard 1989-1994 ChemStation G1034 C



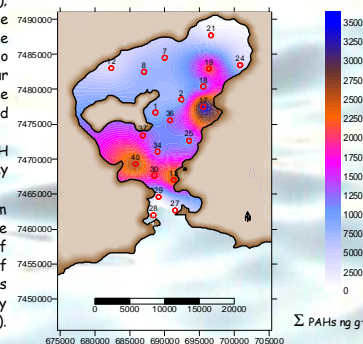
Compound ng g <sup>-1</sup>	Regional AREA														Test AREA										
	1	2	7	8	12	13	17	18	19	21	24	25	27	28	29	30	34	36	37	40	11	13	29	31	
Naphthalene	n.d.	196.1	96.2	n.d.	n.d.	84.4	95.0	n.d.	94.9	n.d.	97.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	97.2	n.d.	n.d.	n.d.	n.d.
Acenaphthylene	98.3	522.9	96.2	98.9	n.d.	168.9	285.0	98.4	284.7	n.d.	n.d.	98.0	n.d.	n.d.	n.d.	187.0	185.2	197.5	196.3	291.5	96.7	97.4	n.d.	n.d.	98.7
Acenaphthene	n.d.	32.7	n.d.	n.d.	n.d.	n.d.	95.0	n.d.	189.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	96.7	97.4	n.d.	n.d.	n.d.
Fluorene	n.d.	65.4	n.d.	n.d.	n.d.	84.4	n.d.	n.d.	94.9	n.d.	97.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Phenanthrene	294.8	163.4	192.3	98.9	98.2	928.9	190.0	196.8	379.6	98.3	391.8	96.0	n.d.	n.d.	n.d.	280.5	185.2	197.5	196.3	485.8	96.7	97.4	98.8	98.7	
Anthracene	98.3	98.0	96.2	197.9	98.2	422.2	190.0	196.8	284.7	n.d.	97.9	96.0	n.d.	n.d.	n.d.	280.5	92.6	197.5	196.3	388.7	n.d.	97.4	98.8	98.7	
Fluoranthene	589.6	424.9	384.6	296.8	196.3	2026.8	665.0	393.6	664.2	98.3	195.9	490.0	n.d.	94.5	n.d.	654.6	370.3	394.9	588.9	1263.2	193.3	194.7	197.6	197.3	
Pyrene	687.9	522.9	384.6	494.7	294.5	2195.7	950.0	590.3	948.9	98.3	293.8	588.0	n.d.	94.5	n.d.	841.6	740.6	789.8	981.5	3012.2	579.3	389.5	296.4	394.6	
Benzo [a] anthracene	491.3	457.5	480.8	494.7	98.2	2111.2	3229.9	590.3	2087.6	98.3	293.8	588.0	n.d.	94.5	n.d.	1215.6	648.1	691.1	883.3	1554.7	579.9	486.8	296.4	394.6	
Chrysene	491.3	424.9	480.8	395.7	196.3	1689.0	2660.0	492.0	1708.0	98.3	293.8	588.0	n.d.	n.d.	n.d.	1028.6	555.5	691.1	785.2	1360.3	676.6	486.8	197.6	296.0	
Benzo[b]fluoranthene	1179.2	784.3	1153.9	1582.9	883.5	2533.5	4464.9	1475.9	2941.6	629.0	489.7	1568.1	97.5	94.5	91.6	2711.8	1296.1	1579.6	1766.7	3595.2	1063.2	1168.4	691.5	887.9	
Benzo[k]fluoranthene	884.4	653.6	961.6	989.3	883.5	2871.3	5034.9	1180.7	3226.3	196.6	293.8	1078.1	97.5	94.5	274.8	2244.2	1481.3	1480.9	1963.0	2915.0	1063.2	1168.4	493.9	789.3	
Benzo[a]pyrene	1179.2	1568.7	1250.1	1484.0	196.3	4898.0	4654.9	1967.8	2941.6	98.3	391.8	1764.1	n.d.	n.d.	n.d.	2992.3	2036.8	2566.9	2846.3	5732.9	1063.2	1363.1	790.3	887.9	
Indeno[1,2,3-cd]pyrene	884.4	719.0	865.4	791.5	196.3	3124.6	4749.9	1279.1	2562.0	196.6	489.7	1078.1	n.d.	n.d.	n.d.	2618.3	1481.3	1480.9	1864.8	3109.4	483.3	1168.4	691.5	887.9	
Dibenz[a,h]anthracene	294.8	424.9	288.5	296.8	196.3	591.1	3894.9	492.0	1992.7	196.6	195.9	294.0	n.d.	n.d.	n.d.	1963.7	370.3	394.9	490.7	874.5	386.6	681.6	296.4	296.0	
Benzo[g,h,i]perylene	884.4	653.6	384.6	989.3	294.5	3124.6	4654.9	2.0	2751.8	196.6	489.7	1176.1	n.d.	n.d.	n.d.	2898.8	1666.4	1678.3	1963.0	2915.0	483.3	1265.8	691.5	986.4	
Total PAHs	8057.8	7712.7	7115.7	8211.3	3632.3	26894.7	35814.4	8956.6	32153.2	1671.5	4113.8	9604.5	195.0	472.3	366.4	19177.7	11109.6	12340.8	14722.5	27595.6	6475.9	8665.6	4840.5	6314.1	

Ratio PAHs Source	LMW/HMW	Phen/Ant	Flu/Pyr	BgP/TrP	BaA/BaP	Pyr/BaP
Pyrolytic	<1	>1	>1			
Petrogenic	>1	<1				
Vehicular exhaust		<4			15.2-6	
Fuel oil			0.6-0.9			
Gasoline exhaust				3.5	0.5	
Diesel exhaust				1.1	1.1	
Stations	Sample 7	Sample 8	Sample 13	Sample 17	Sample 19	Sample 40
LMW/HMW	0.1	0.5	0.6	0.4	0.4	0.3
Phen/Ant	2.0	0.5	0.6	1.3	0.3	0.3
Flu/Pyr	0.2	2.2	0.9	1.0	0.4	0.4
BgP/TrP	<0.1	1.0	0.7	1.0	0.7	0.2
BaA/BaP	0.1	1.3	0.4	0.9	0.3	0.5

Fig. 1: Suggested PAHs sources based on the ratio of some PAH. (Adapted from [3])

lower than 1, suggesting significant PAH inputs from pyrolytic sources. The ratios of Phen/Ant <4 pointed out the origin from combustion of vehicular fuel. Flu/Pyr ratios were less than 1, which indicated petrogenic input in the samples and it was the only ratio revealing PAH origin other than pyrolysis. BgP/TrP ratios were approximately 1.1, suggesting combustion input of diesel. Values of BaA/BaP ratios in most of the samples indicated an input from gasoline combustion. Except for some of Flu/Pyr ratio values indicating petrogenic input, all other ratios of individual PAH compounds studied by previous researchers suggested pyrolytic sources for PAHs. Heavy traffic and transportation (sample 40 is close to Rio de Janeiro's port) may have introduced large amounts of PAHs into Guanabara Bay, and should be responsible for major PAHs sum in Bay (Fig. 2). Future investigations and complete statistical analysis should be performed, in order to clarify the source.

Fig. 2: Regional Area map PAHs distribution



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Materials & Methods

Results & Discussions

Conclusions