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The determination of PAH by UV-Fluorescence Spectroscopy in Water of Guanabara Bay, Rio de Janeiro, Brazil

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Introduction

The city of Rio de Janeiro, second major industrial and population center of Brazil, is located around Guanabara Bay. The environmental conditions of this tropical estuarine system has raised great concern; nevertheless a systematic survey about polynuclear aromatic hydrocarbons (PAH) has never been carried out.

Presently a study is being developed involving the investigation of hydrocarbons in waters, sediments and biota. This work presents the first results related to polynuclear aromatic hydrocarbons found dissolved and dispersed in the waters of the bay.

One of the major problems of the Guanabara Bay is the discharge of untreated domestic effluents, about 19m^3 s^{-1}, produced by a population of nearly 8,000,000 inhabitants, enter this ecosystem daily. About 6,000 industries are established in this area. Also the natural resources of the bay are exploited intensively, by both fishing and recreation activities.

Guanabara Bay is an estuarine system where high sedimentation rates are observed, of the order of 1 to 2 cm year^{-1} (Godoy *et al.*, 1991). The bay is also a very productive coastal ecosystem with rates of primary production of 460 mgC m^{-3} day^{-1} (Ponciano, 1985).

Guanabara Bay can be subdivided in sections: the northeastern part is the most intact area, of lower population density, drained by relatively non polluted rivers and where remaining mangroves are preserved; in the central part lies the navigation channel, a frequently dredged area, with good water circulation; the most impacted area is the northwestern section where refinery plants from the oil industry are located and activities of oil storage and transfer are occurring. The two sections at the entrance of the Guanabara Bay are polluted mainly by harbor installations and shipyards.

Ferreira (1995) concluded that the input of petroleum hydrocarbons to the bay amounts to 173 kg day^{-1} from maritime transport, 902 kg day^{-1} from atmospheric input, and 17,005 kg day^{-1} from urban and industrial discharge. This last source accounts for 84% of the hydrocarbon pollution discharge.

The locations of the sampling stations are shown in Figure 1 with site descriptions. These stations were chosen as representative for the major anthropogenic hydrocarbon input areas to the bay.

Material and methods

Sample collection and preparation. The water samples were collected from a depth of one meter below the surface, using one-liter teflon sampler. The collector was filled several times until the total volume of ten liters was gathered for each sample. A separate sample of one liter was also collected for the determination of suspended matter. The samples were stored in two five-liter amber glass jars and kept in dark containers, at temperatures below 5° C. The storage time was always shorter then 24 hours.

All glassware and cells used in this work were carefully washed with detergent and rinsed successively with distilled water, acetone, ethanol and *n*-hexane, chromatographic grade. The filters were heat decontaminated in a furnace at 450°C.

The solvent selected for sample extractions and standard solutions was *n*-hexane. All blanks run during the analyses presented no absorbances.

Extraction. The extraction procedure was carried on according to the Manual n°.13 from IOC (1984). In the laboratory, a two-liter aliquot of each sample was filtered, under vacuum, through fiberglass filters (Whatman GF/F) of 0.7 μm nominal pore size, and twice extracted in a separation funnel with 50mL of n-hexane, chromatographic grade. The 100mL extracts were dried over sodium sulphate and their volumes were reduced to 5mL in a rotary evaporator.

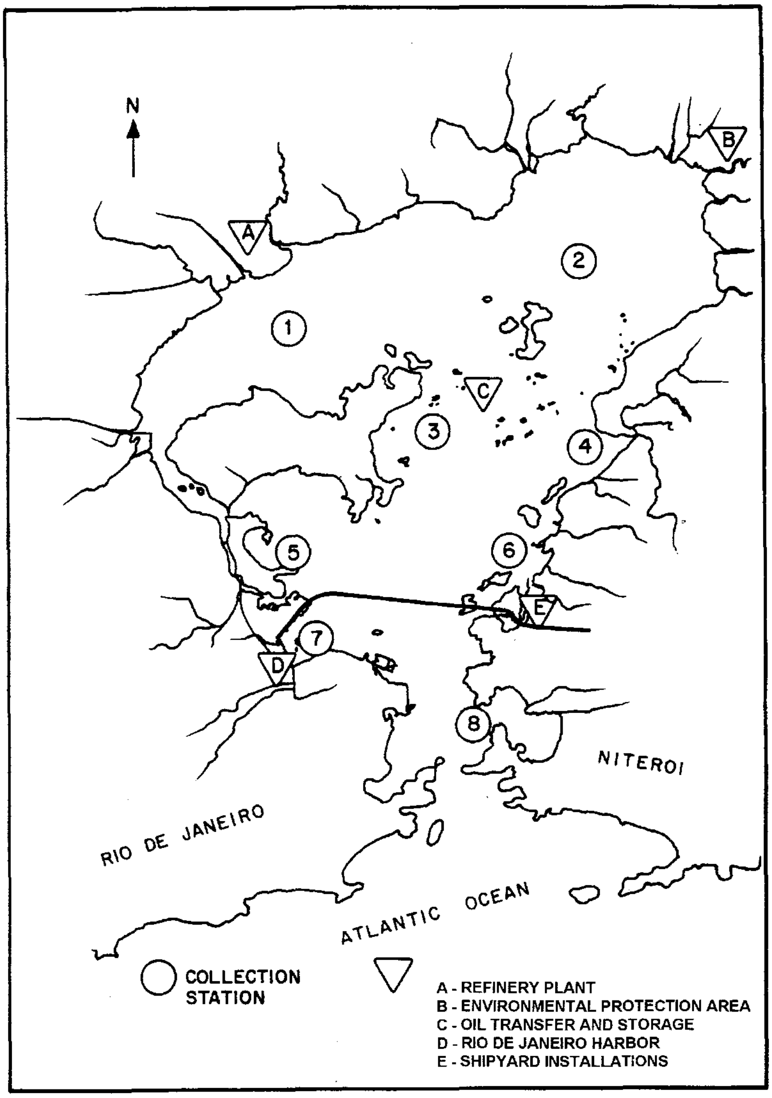

Fig. 1. Guanabara Bay and sampling stations

These final extracts were sealed in pre-weighed 10-mL flasks and analyzed by UV-fluorescence spectroscopy in order to determine the concentrations of the dissolved PAH.

The same procedure was applied to another 2-liter aliquot, except for the filtration step, in order to provide the contents of the dispersed plus dissolved PAH.

UV-fluorescence analysis. The extracts were analyzed by UV-fluorescence spectrometry (Perkin Elmer LS 30 UV-Spectrometer Model) at 310nm excitation wavelength. The fluorescence intensities were measured at 360nm, using chrysene solution as quantitative standard.

Determination of suspended matter. The one-liter sample of each collection was filtered through pre-weighed filters, identical to those used for the sample extractions.

The filters were dried in an oven at 65°C until constant weight.

Results and discussion

Table 1 shows the PAH concentration found for the extracts of the filtered (dissolved PAH) and non-filtered (total PAH) samples, and the calculated percentage of the dissolved PAH. This percentage was determined considering the non-filtered PAH as 100%.

Table 1. PAH concentrations for the extracts of filtered and non-filtered samples, percentages of dissolved PAH and suspended matter content.

Collection Station	PAH content ($\mu g\ L^{-1}$)		Dissolved PAH %	Suspended Matter ($mg\ L^{-1}$)
	Dissolved	Total		
1	0.43	1.25	34.4	95.00
2	0.21	0.93	22.6	71.33
3	0.54	1.13	47.8	111.4
4	0.22	1.14	19.2	42.63
5	1.00	1.01	99.0	63.29
6	1.40	1.66	84.3	105.2
7	1.12	2.97	37.7	43.00
8	0.70	1.32	53.0	44.60

Among the dissolved PAH results, those of stations 5 to 7 proved to be significantly higher than the remaining ones. Those three stations are surrounded by densely populated areas; station 5 is near a zone of dense and low-income population with unsufficient sewage treatment; stations 6 and 7 lie in front of a shipyard and the city harbor installations, respectively. Smaller contaminations were found for stations 2 and 4, which are closer to the northeastern area, where lower contamination was already expected. Total PAH concentration in station 7 is significantly higher than in the other sites. Station 7, facing the city harbor, showed a concentration value more than twice the average value found for the others areas.

The percentage of dissolved PAH exhibited scattered distribution. However, at stations 5 and 6 the great majority of PAH is dissolved, probably indicating relatively more recent contamination, for adsorption on the particulate matter is a slower process than dispersion and dissolution.

The high concentrations of suspended matter, shown in Table 1, were already expected since high primary productivity and sedimentation rates have already been reported for Guanabara Bay (Ponciano, 1985; Wilken *et al.*, 1986; Godoy *et al.*, 1991). No correlation was observed between the total PAH contents and suspended matter concentrations. Similar behavior was already verified in Changjiang River studies (Saliot *et al.*, 1990).

Table 2 compares the results obtained for Guanabara Bay with other similar areas. Except Augusta Bay (Domenico *et al.*, 1994), those coastal environments are exposed to tropical climate and to intensive activities of oil transportation and refining.

Conclusions

According to FAO classification (Abdullah *et al.*, 1994) coastal areas with hydrocarbon concentration below 2,5 $\mu g\ L^{-1}$ are considered unpolluted. Therefore, only the water sampled in front of the city harbor (station 7) can be classified as contaminated.

The present results are of the same order of magnitude as those found for regions 2, 5, 6, 9 and 10 (El Samra *et al.*, 1986; Badawy *et al.*,1993; Corbin,1993; Balci, 1993 and Weber & Bícego, 1991), in many of them natural sources of petroleum contamination from seabed are occurring. Areas such as 1, 3 and 4 (Emara,1990 and Badawy & Al-Harthy, 1991) revealed considerably higher concentrations, whereas 7 and 8 (Domenico *et al.*,1994 and Knap *et al.*, 1986) prove the compensating results of an adequate environmental policy.

This work can be considered as a first approach for evaluating the PAH contamination in Guanabara Bay waters. It is recommended to continue this investigation with a larger number of samples, collected in different weather conditions, tides and seasons, in order to gain a thorough picture of this environment.

Table 2. The total PAH concentration, as chrysene equivalents, range for Guanabara Bay and other similar areas.

Area	PAH concentration range ($\mu g\ L^{-1}$)	Reference
1. Southern Arabian Gulf	6.96 - 38.18	Emara (1990)
2. Northern Arabian Gulf	1.7 - 7.8	El Samra *et al.* (1986)
3. Gulf of Oman	6.67 - 95.45	Emara (1990)
4. Gulf of Oman	8.64 - 14.44	Badawy & Al-Harthy (1991)
5. Gulf of Oman	0.28 - 2.24	Badawy *et al.* (1992)
6. St. Lucia, Caribbean region	0.1 - 3.4	Corbin (1993)
7. Augusta Bay, Sicily	0.06 - 0.37	Domenico *et al.* (1994)
8. Bermudas	0.023 - 0.091	Knap *et al.* (1986)
9. Turkey Coast	0.09 - 1.92	Balci (1993)
10.S. Sebastião Channel, Brazil	0.19 - 8.52	Weber & Bicego (1991)*
11. Guanabara Bay, Brazil	0.93 - 2.97	Present work

* results expressed in artificially degraded Carmópolis Oil equivalents.

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