

**FATE OF POLICYCLIC AROMATIC HYDROCARBON (HPAs) DURING EX-SITU AERATION OF A FLUID MUD FROM GUANABARA BAY, RJ, BRAZIL.**Krepesky N.<sup>1</sup>, Bispo M. G. S.<sup>4</sup>, Torres J. P.<sup>2</sup>, Malm O.<sup>2</sup>, Crapez M. A. C.<sup>3</sup>, Silva C. G.<sup>1\*</sup>

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**Abstract**

Guanabara Bay is an impacted semi-enclosed estuary, located between cities of Rio de Janeiro and Niteroi that is bordered by 12,000 industries, two major harbors, two oil refineries, two important airports, two navy bases, dozens of a shipyards and a large number of ferries, fishing boats and yachts. Large amounts of suspended solids, organic matter, heavy metals and hydrocarbons are discharged into Guanabara Bay and accumulate in the bottom sediments. One of the proposed remediation actions for the Guanabara Bay Remediation Program (PDBG) includes the use of air stimulation by tangential aeration of the bottom sediments with air pumps. However, since the contaminants are not permanently fixed to the sediments, any change in the physicochemical parameters, such as pH, may significantly influence the mobility of these contaminants into the environment. The remobilization of toxic materials to the water column is only a secondary result of concentration gradients, oxidation of anoxic sediments by bioturbation, or by resuspension caused by flooding, organic contaminant decay and transfer into a more mobile form. In this context, we created 3 independent microcosms for evaluation of aeration on the fate of polycyclic aromatic hydrocarbons (PAHs) from a liquid mud layer collected at 3.9 m depth of NW of Guanabara Bay and placed into glass boxes for 19 days. Salinity, temperature, pH and Eh, dissolved oxygen values were measured at the field during material pumping and were monitored during aeration experiments at days 3, 10 and 19. Bacterial metabolism followed Eh values and dissolved oxygen concentration on water. The PAHs Naphthalene, Fluorene, Acenaphthylene, Pyrene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[a,h]Anthracene, Indeno[1,2,3-cd]pyrene concentration were searched. Benzo[a]pyrene (68.24  $\mu\text{g.g}^{-1}$ ) and Benzo[b]fluoranthene (103.11  $\mu\text{g.g}^{-1}$ ) presented highest concentrations among the samples analyzed. Statistical least square analyzes by JMP 5 software, indicate that dissolved oxygen responds for pH indices and Eh values, as well as for Acenaphthylene, Naphthalene, Fluorene and Benzo[b]fluoranthene concentrations ( $p < 0.05$ ). Fluorene, pyrene and Benzo[b] fluoranthene may be a response of Eh and pH ( $p < 1$ ). These results may be useful as an alert to avoid undesirable consequences on marine environment.

**Introduction**

Guanabara Bay (S22°50' and W43°10') is an impacted estuary located between cities of Rio de Janeiro and Niteroi. It receives 91 tributaries and its drainage basin has a water flow of 150  $\text{m}^3.\text{s}^{-1}$  with an exchange rate of about 10% with the ocean<sup>1</sup>. It is bordered by 12,000 industries. More than 6,000 are located in the drainage basin. It also harbors two oil refineries, responsible for the processing of 17% of the national oil<sup>2</sup>. Thousands of ships dock annually in the port of Rio de Janeiro and the bay has also two navy bases, a shipyard and a large number of ferries, fishing boats and yachts<sup>2</sup>.

In spite of the pollution control plan created by a State Environmental Agency (FEEMA) in 1979, the water quality situation in Guanabara Bay stills critical. Several sewage plants have been constructed in the past 30 years, but only 15% of the enormous amount of domestic and industrial waste discharge into the bay was subjected to any form of sewage treatment in 1991. Previous studies found that 18 ton day<sup>-1</sup> of petroleum hydrocarbons enter the bay, of wich 85% has its source in urban runoff. Large amounts of suspended solids, organic matter, heavy metals and hydrocarbons are discharged into Guanabara bay and accumulate in the bottom sediments<sup>2</sup>.

Much is discussed on the best remmediation plan for this environment. However, politicians and researchers did not reach an agreement yet. One of the proposals for the Guanabara Bay Remediation Program (PDBG) is air stimulation by tangential aeration of the bottom sediments with air pumps.

It is well accepted that sediments are an efficient concentrator of persistent organic chemicals, such as PAHs and PCBs. However, since the contaminants are not permanently fixed in the sediments<sup>3</sup>, any change in the physicochemical parameters, such as pH, may significantly influence the mobility of these contaminants into the environment<sup>4</sup>. The remobilization of toxic materials to the water column is only a secondary result of concentration gradients, oxidation of anoxic sediments by bioturbation, or by resuspension caused by flooding, organic contaminant decay and transfer into a more mobile form<sup>3</sup>.

In this context, we proposed an evaluation of aeration on the fate of polycyclic aromatic hydrocarbons (PAHs) from a liquid mud layer collected from 3.9 m depth of NW of Guanabara Bay (22°45'34" S and 43°11'23" W) and placed into 3 glass boxes for 19 days.

### Material and Methods

In January 2004, 1,500 L of the mud layer with 60 g.L<sup>-1</sup> of suspended matter were pumped with a 1.5 Hp pump into closed containers, and transported into laboratory, avoiding undesirable oxidation. Salinity (American optical, model 10419), temperature, pH and Eh (pH – meter CG 837, Schott Gerate), and dissolved oxygen (O<sub>2</sub> – meter CG 867, Schott Gerate) values were measured at the field during material pumping. A mud aliquot referred as T-0 was also separated for assay control.

In the lab, the collected mud layer were distributed among three 400L capacity glass boxes – B1, B2 and B3 (dimensions: 0.5 x 0.5 x 1.60 m), covered with a black mantle, in order to guarantee 12 hours of illumination exclusively from 15 W fluorescent lamps<sup>5</sup>. Each box received 375 L of the liquid mud. An aeration system were created inside the boxes with air pumps of 1 ½ Hp connected to perforated pipes and one hose to collect aliquots for analysis. Each box was aerated independently from bottom to surface during 19 days. Room temperature was controlled at 20°C.

Aliquots from the liquid mud were collected from the boxes (B1, B2 and B3) at days 3, 10 and 19 to investigate the fate of PAHs concentration on the suspended matter.

The liquid mud collected was hot-dried at 42°C, macerated and then 3.0g of each day was weighted. PAHs and PCBs were extracted from the mud with n-hexane-acetone (1:1) using ultrasonic bath at 90°C for 40 minutes. Clean up was performed using a desulphurization mixture based on alumina, sodium-sulfite, sodium hydroxide column eluted with n-hexane. A fractionation step used silica-gel columns eluted with n-hexane (fraction 1) and n-hexane-ether (fraction 2, 9:1) were performed to separate PCBs from PAHs.

PAHs concentrations were determined by High Performance Liquid Chromatography (HPLC); coupled to a fluorescence detector, Shimadzu (RF-10 AxL) with the bombs LC-10 AT and LC-10AS; column CLC-ODS with 25 cm, 4.6 mm diameter, and a particle with 5µm and 120 Å pore. The mobile phase was composed by a mixture of acetonitrile:water (80:20 v/v) with isocratic flux of 1.5 mL.min<sup>-1</sup>. The detector was programmed for 8 steps of excitation/emission: 255/325; 253/350; 333/390; 237/462; 280/430; 249/404; 300/500 and 300/421<sup>6</sup>. The PAHs Naphthalene, Fluorene, Acenaphthylene, Pyrene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[a,h]Anthracene, Indeno[1,2,3-cd]pyrene were searched. The software Borwin 1.2 was used for chromatogram integration and pollutant concentration calculation. Reagent blanks followed all extraction, clean up and fractionation steps.

Dissolved oxygen, pH, Eh and PAHs values were statistically analyzed by least squares using JMP5 software by SAS Institute Inc, USA.

### Results and Discussion

The average values of physical and chemical characteristics of B1, B2 and B3 are presented at Table 1. During aeration, salinity increased from 29 to 32 and the temperature in the microcosmos decreased from 24 to 19°C, reaching equilibrium with room atmosphere, pH falled from 7.8 to 5.7, redox potential (Eh) increased from 20.0 mV to 177.7 mV and dissolved oxygen (Dis. O<sub>2</sub>), initially null reached 2.5 mg.L<sup>-1</sup> at day 19. Salinity increase may be related to water evaporation during experiment time. Others<sup>1</sup> also found that dissolved oxygen is close to zero at bottom of Guanabara Bay (3 -19 m).

Table 1: Average physical and chemical properties of B1, B2 and B3 during 19 days of aeration.

Time (days)	pH	Salinity (‰)	T (°C)	Eh (mV)	Dis. O <sub>2</sub> (mgL <sup>-1</sup> )*
0	7.8	29	24	20.0	0
3	6.5	31	18	58.3	3.8
5	6.2	32	19	96.5	2.9
10	5.9	31	20	181.0	2.0
19	5.7	32	19	177.7	2.5

\*T: temperature (°C); Eh: redox potential; Dis. O<sub>2</sub>: dissolved oxygen

The liquid mud presented Naphtalene, Acenaphthylene, Fluorene, Pyrene, Benzo[a]anthracene, Benzo[k]fluoranthene, Benzo[b]fluoranthene and Dibenzo[ah]anthracene. Pyrene were the main contaminant at T(0) with 30.70  $\mu\text{g.g}^{-1}$ . Benzo[b]fluoranthene and Benzo[a]pyrene presented highest concentrations (103.11  $\mu\text{g.g}^{-1}$  and 68.24  $\mu\text{g.g}^{-1}$ ) at T(3) and T(10) respectively among all samples analyzed (Fig. 1).

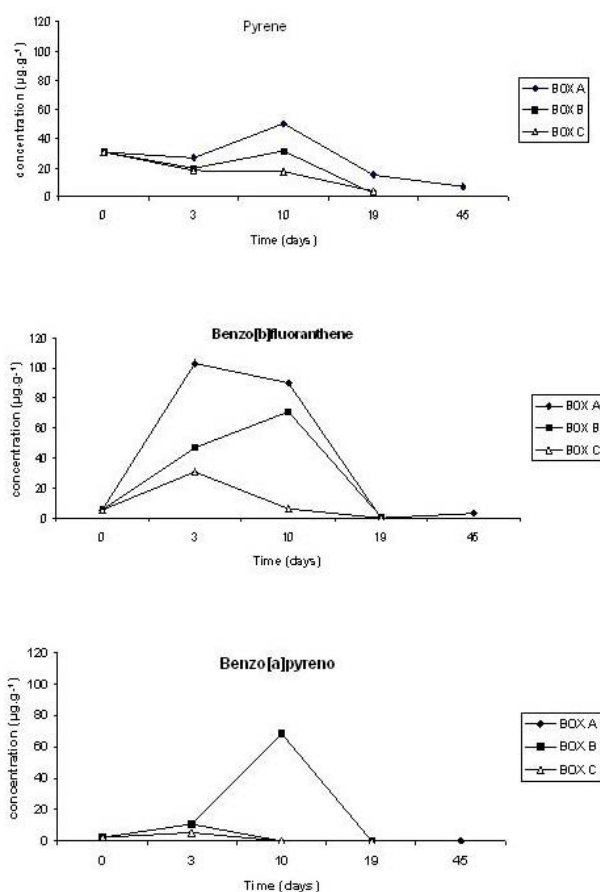


Fig. 1 – Pyrene, Benzo[b]fluoranthene and Benzo[a]pyrene concentrations ( $\mu\text{g.g}^{-1}$ ) of the 3 mesocosms (A, B and C) as a function of time (days) of aeration experiments.

Pyrene, B[b]fluoranthene and Benzo[a]pyrene have more than 3 aromatic rings. High molecular weight PAHs are hydrophobic compounds that can accumulate in sediments and organisms. PAH can be of pyrogen origin (characterized by a lesser degree of alkylation) or derived from oil spill. Emissions of PAH as combustion by-products can be an important source to atmosphere. These can be transferred to aquatic environment via wet or dry deposition. Benzo[a]pyrene are a known carcinogen<sup>7</sup> and are derived from incomplete combustion.

Statistical least square analyzes by JMP 5 software, indicates that dissolved oxygen responds for pH and Eh values. Acenaphthylene, Naphthalene, Fluorene and Benzo[b]fluoranthene concentrations ( $p < 0.05$ ) are a response of dissolved oxygen. Eh and pH responds for Fluorene, pyrene and Benzo[b] fluoranthene concentrations ( $p < 1$ ). Thus, high molecular weight PAH concentration response to physicochemical variations can cause deleterious consequences on environment. More analysis are necessary for data comprovation. However, these results may be useful as an alert to avoid undesirable consequences on marine environment.

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