# Preliminary assessment of Miramar Petrochemical Harbor as PAH source to Guajará bay (Belém-PA-Brazil) surface sediments

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## Abstract

A preliminary study on a petrochemical harbor as a potential source of polycyclic aromatic hydrocarbons (PAH) to surface sediments of Guajará bay, located in Belém City, Pará State, Brazil, over the last 10 years is presented here. The 16 priority USEPA PAH were identified and quantified. Surface sediment samples, collected at 5 sites in the bay, near Miramar Petrochemical Harbor (TEMIR), were extracted and analyzed by high performance liquid chromatography with a diode array detector. Total PAH concentration ranged from 533.0 to 3123.3 ng $g^{-1}$ dry weight with a mean concentration of 1091.9 ng $g^{-1}$. The most contaminated places were those where muddy sediments were found with highest concentrations of organic matter. The priority PAH with low molecular weight represented 54.4% of the total abundance and indicate that the main source of contamination of the sediments was petrogenic, indicative of the relevant contribution of the petrochemical harbor activity to the input of PAH to Guajará bay. However, pyrolytic PAH coming from fuel combustion, household waste combustion and untreated sewage discharge are also potential contamination sources to this environment.

**Keywords:** polycyclic aromatic hydrocarbons; sediment; petrochemical harbor; Amazon estuary.

## 1. Introduction

Due to their toxic, carcinogenic, and mutagenic characteristics, sixteen polycyclic aromatic hydrocarbons (PAH) have been identified as priority pollutants by the United States Environmental Protection Agency (KAYAL; CONNELL, 1995). Though PAH occur naturally, generated by forest fires, volcanic eruptions and biosynthesis by organisms, the largest amount of PAH is released into the environment by human activities (WILCKE *et al.*, 2000). Therefore, PAH are not only environmental pollutants, but also useful geochemical markers of anthropogenic impacts, the temporal trends of PAH concentrations in sediments and its depositional fluxes and are correlated with historical energy consumption (LIU *et al.*, 2012). Sediments are often contaminated with complex mixtures of toxicants and represent sinks and potential sources for moderately to strongly lipophilic chemicals such as PAH (BRACK, 2003; BRACK *et al.*, 2005).

The flood plains and rivers of the Amazon region are very sensitive to environmental pollution, especially in the basins near the coastal zone whose sinuous channels are associated with a large sedimentary material load carried by the flood pulse and contribute to the residual accumulation process in this area (MATOS *et al*., 2011). Guajará bay is an integral part of the Amazon Estuary system, and functions as the main receiver of urban and industrial wastes from the city of Belém, capital city of Pará State (Northern Brazil). Miramar Petrochemical Harbor (TEMIR) is located in the Guajará bay's eastern bank, 5 km from the Belém Port.

TEMIR was built to receive, store and convey liquid and gaseous fuel products. Import of these products by cabotage predominates over waterway export. The annual cargo movement average (import + export) is over 2500 t (SANTOS, 2014). Also in this area, there is a lot of vessel traffic, as well as fuel transportation and sale in floating docks. Small spills and oil discharges in the water can characterize a punctual polluting source and insert PAHs and trace elements to the environment (JACQUES *et al*., 2007).

Research focus on PAH in Guajará bay sediments is still incipient and, for the most part, only available in the theses and dissertations of Lima (2009), Sodré (2014) and Santos (2014). The aim of this work was to evaluate, on a preliminary basis, the TEMIR as a relevant source of the priority 16 PAHs for Guajará bay surface sediments over the last 10 years.

## 2. Material and method

### Sediment sampling and characterization

Samples were collected during 2011/2012/2013, using a handheld VanVeengrab, over 5 fixed sampling sites near the Miramar Petrochemical Harbor (TEMIR) located on the eastern bank of the Guajará bay (Belém-PA-Brazil) (Figure 1). The top layer (10 cm) of each grab sample was collected using a stainless steel coop and immediately transferred to n-hexane rinsed 400 mL metal containers. Samples were kept in ice before the freezer storage prior to analysis. Samples were considered as triplicates and the sampling aimed to represent about 10 years of sediment and pollutant accumulation in the Guajará bay bottom, Santos *et al.* (2012) and Neves *et al.* (2013) determined a mean sedimentation rate of 0.8 cm/year in this estuary. The lyophilized samples were used to determine granulometry by the pipetting dispersion method. The content of organic carbon (OC) was determined by organic matter oxidation such as the method proposed by Walkley-Black (DONAGEMA *et al*., 2011). To determine organic matter (OM), OC concentration was multiplied by 1.724. The results are presented in percentage.

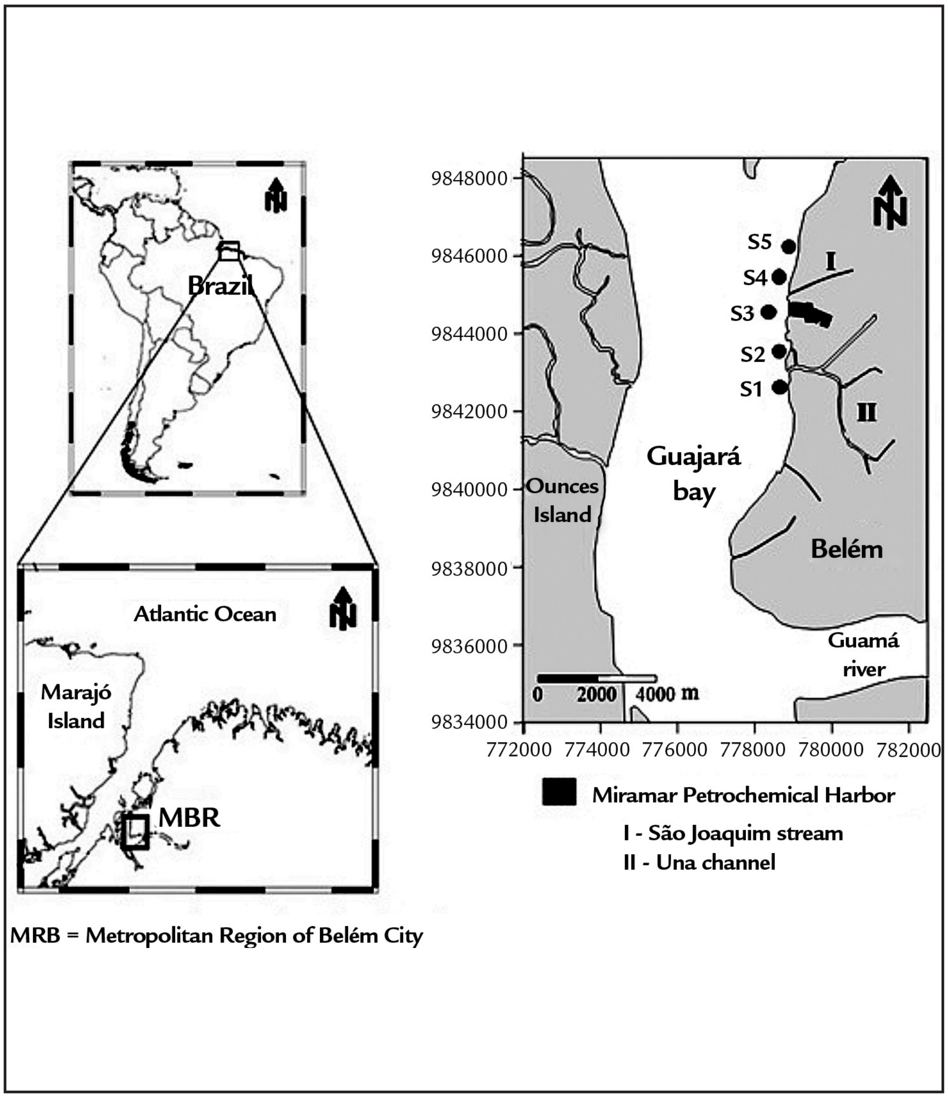

Figure 1
Sediment sampling locations.

## PAH analysis

The list of the 16 EPA priority PAH was used, which is often taken as representative for the measurement of this substance class in environmental samples (OTTE *et al.*, 2013). They are: naphthalene (*Na*), acenaphthylene (*Acy*), acenaphthene (*Ace*), fluorene (*Fl*), phenanthrene (*Phe*), anthracene (*An*), fluoranthene (*Flt*), pyrene (*Py*), chrysene (*Chr*),benzo[a]anthracene (*BaA*), benzo[*b*] fluoranthene (*BbF*), benzo[*k*]fluoranthene (*BkF*), benzo[a]pyrene (*BaP*), dibenzo[*a,h*] anthracene (*DahA*), indene[1,2,3-*cd*]pyrene (*IcdP*) and benzo[*g,h,i*]perylene (*BghiP*).

Amounts of 30 g of lyophilized sediment were spiked with10 µL of an analytical surrogate consisting of a suite of deuterated PAHs (500 ng g$^{-1}$ naphthalene-d$_{8}$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$, chrysene-d$_{12}$ and perylene-d$_{12}$ solution in *n*-hexane).

The extraction procedure and the purification and separation methods used were based on the United Nations Environmental Program with adaptations for studying environmental contaminants (MEDEIROS; BÍCEGO, 2004). PAH were extracted in ultrasonic bath during 30 min using 6 mL of dichloromethane as solvent. Empty extraction thimbles were subjected to the same extraction procedures and served as process controls. The extraction method recovery was calculated through values obtained for the internal standard.

After extraction, the solvent was concentrated in a rotary evaporator to a volume of 1 mL. The extract was fractionated by adsorption in an alumina column with silica gel when the aliphatic hydrocarbons were separated with 10 mL of n-hexane (fraction 1, not used in this work) and the PAH (fraction 2) with 15 mL of dichloromethane/n-hexane 3:7 (v/v). Fraction 2 was concentrated to a volume of 1 mL.

The analyses were performed using a HPLC equipment Dionex/Thermofisher Ultimate 3000 with a diode array detector under the following operating conditions: C16 column (250 mm x 4.5 mm x 5 µm) from Acclaim; column temperature at 30°C; pump pressure between 2870-2980 psi; automatic injection of 20 µL; flow rate of 2 mL min$^{-1}$; elution system starting with 55% acetonitrile (ACN) and 45% Milli-Q water for 5 min, increasing to 85% ACN in 30 min, system stabilization in 85% ACN for 10 min, decreasing to 55% ACN and system stabilization in 55% ACN over 5 min. Readings were taken at wavelengths of 214, 254 and 263 nm. External standard calibration curves were used to quantify the extracts. Limit of detection (LoD) and limit of quantification (LoQ) were calculated based on the International Union of Pureand Applied Chemistry (IUPAC) definition (LONG, 1983), concentrations in the range 0.05 to 2.00 µg mL$^{-1}$ were performed.

## PAH origin interpretation

In recent studies, the following indices were used by other authors to assess and determine with accuracy the origin of the PAH from various environments (SICRE *et al.*, 1987; BENLAHCEN *et al.*, 1997; BUDZINSKI *et al.*, 1997; BAUMARD *et al.*, 1998). Four significant PAH ratios were calculated for the studied samples: *Phe/An, Flt/Py, Chry/BaA* and *LMW/HMW* (LMW = *Na+Acy+Ace+Flo+Phe+Na*; HMW = *Fl+Py+BaA+Chr+BbF+BkF+BaP+DahA+BghiP+IcdP*).

The *Phe/An* index reflect was extensively used to infer nature of PAH pollution in sediments (GSCHWEND; HITES, 1981; BUDZINSKI *et al.*, 1997) An supports petrogenesis for PAH in sediments. The Similarly, *Flt* is less thermodynamically stable than *Py* and they are often associated with each other in natural matrices and a predominance of *Flt* over *Py* is characteristic of a pyrolytic process, while in petroleum-derived PAH, *Py* is more abundant than *Flt*. Generally, a *Phe/An*< 10 and *Flt/Py*>1 indicates that the contamination by PAH from a pyrolitic origin, whilst the PAH from petrogenic is characterized by *Phe/An* >10 and *Flt/Py* <1 (BAUMARD *et al.*, 1998; VAVALANIDIS *et al.*, 2008). The ratio LMW/HMW has been used to distinguish pyrogenic (< 1) and petrogenic (> 1) sources and *Chry/BaA* ratio > 1 indicates petrogenic processes (LIU *et al.*, 2007).

## 3. Results

The data concerning the sediment characterization of the samples taken from the Guajará bay, the mean concentration of the individual PAH, mean concentration of total PAH (ΣPAH), mean LMW concentration, mean HMW concentration, LoD and LoQ are shown in Table 1. A general result was that the sediment samples were essentially muddy (59.3 to 72.0%). Most of the sampling station showed low levels of OM (3.9 to 4.7%), the highest OM values were observed in sites near tributary channels.

The total concentration of USEPA priority PAH varied between 608.7 (Site 5) and 2812.6 ng g$^{-1}$ (Site 3) of dry weight. The highest concentrations of ΣPAH were observed in sites closest to the TEMIR. Among the 16 priority PAH as defined by the USEPA, the most abundant were *Phe* (16.2%), *Na* (14.8%), *Ace* (8.3%) and *Acy* (7.8%), typical of petrogenic contributions, since the Na and Phe are classified as petrogenic (PAGE *et al.*, 1999). Low molecular weight PAH represent 54.4% of the total PAH found in this work. Making use of the ratio LMW/HMW, it was possible to observe that all the studied sites receive a larger contribution of petrogenic contamination. Considering the individual values of the *Phe/An* and *Flt/Py* ratios, most of the sites were characterized by *Phe/An* values > 10 and *Flt/Py* values ≤ 1, which is characteristic of a petrogenic + pyrolytic contamination. Petrogenic sources as the most important source of contamination to Guajará bay are confirmed by the *Chry/BaA* ratio values higher than 1. Only samples of Site 1 presented *Phe/An* values < 10 and LMW/HMW values < 1, and can be called as a mixing or transition zone where it is possible to observe both pyrolytic and petrogenic contribution.

Recoveries for each individual PAH studied in sediment samples were in the range of 70% (naphthalene-d$_{8}$) to 82% (perylene-d$_{12}$). According to the US Environmental Protection Agency (EPA) method guidelines, acceptable recovery values should be in the range from 70 up to 130% (RIBANI *et al.*, 2004). The calibration curves constructed were linear over the range of interest and correlation coefficients for the majority of compounds were greater than 0.99, indicating good performance of the chromatographic method. Great results were also observed for LoD in the range 0.01 (*Na* and *An*) to 0.50 µg mL$^{-1}$(*BaA*) and for LoQ 0.05 (*Na*) to 1.67 µg mL$^{-1}$ (*BaA*).

Table 1

Total PAH (ΣPAH) concentration (ng $g^{-1}$ of dry weight), individual 16 priority PAH concentration (ng $g^{-1}$), low molecular weight PAH (LMW) concentration (ng $g^{-1}$) and high molecular weight PAH (HMW) concentration (ng $g^{-1}$) in superficial sediments of the 5 studied sites in Guajará bay, sediment characterization of the samples and the values (μg $mL^{-1}$) obtained to limits of detection (LoD) and quantification (LoQ).

| PAH | Sampling Sites | | | | | LoD | LoQ |
|---|---|---|---|---|---|---|---|
| | S1 | S2 | S3 | S4 | S5 | | |
| Na | 170.9±48.7 | 287.0±17.8 | 377.1±70.1 | 192.1±56.6 | 82.2±36.0 | 0.01 | 0.05 |
| Acy | 16.9±9.5 | 133.7±±89.4 | 349.7±270.2 | 61.6±41.0 | ND | 0.06 | 0.18 |
| Ace | 56.1±31.4 | 152.5±77.9 | 145.0±56.6 | 60.3±40.2 | 204.9±7.1 | 0.03 | 0.08 |
| Flo | 66.7±49.8 | 63.7±36.3 | 197.2±30.5 | 97.3±68.8 | 6.5±0.7 | 0.03 | 0.10 |
| Phe | 54.6±31.6 | 210.0±101.9 | 606.0±128.1 | 325.1±216.8 | 21.1±1.9 | 0.03 | 0.10 |
| An | 36.7±21.2 | 38.6±15.8 | 36.2±24.1 | 31.9±21.3 | ND | 0.01 | 0.35 |
| Flt | 90.4±35.4 | 54.5±36.3 | 97.0±67.1 | 71.9±18.6 | 40.5±8.6 | 0.03 | 0.08 |
| Py | 63.5±22.5 | 87.5±45.0 | 191.6±96.8 | 109.0±44.0 | 43.4±1.9 | 0.05 | 1.06 |
| BaA | 63.7±47.8 | 44.3±29.9 | 187.1±72.1 | 91.1±67.0 | 17.7±2.0 | 0.50 | 1.67 |
| Chr | 90.0±60.4 | 44.1±29.4 | 200.7±79.8 | 137.7±66.5 | 37.8±6.1 | 0.05 | 1.50 |
| BbF | 95.2±19.8 | 47.5±28.9 | 98.9±22.4 | 39.5±26.3 | 39.1±6.6 | 0.05 | 0.14 |
| BkF | 17.7±10.4 | 21.4±15.7 | 75.8±30.9 | ND | 28.4±5.2 | 0.04 | 0.13 |
| BaP | 84.5±54.8 | 43.8±29.2 | 61.0±0.9 | 42.2±28.1 | 28.5±2.0 | 0.06 | 0.19 |
| IcdP | 59.1±22.9 | 66.6±40.7 | 39.2±26.1 | 47.3±31.5 | ND | 0.04 | 0.13 |
| DahA | 81.9±44.4 | 57.2±32.2 | 50.6±33.7 | 48.2±31.1 | ND | 0.03 | 0.10 |
| BghiP | 97.4±48.9 | 112.2±57.9 | 99.5±66.3 | 112.5±43.7 | 58.7±37.8 | 0.05 | 0.14 |
| LMW | 401.8±230.2 | 885.5±408.7 | 1711.3±579.6 | 768.3±440.7 | 314.7±45.7 | | |
| HMW | 743.3±470.0 | 579.1±345.1 | 1101.3±496.0 | 699.4±357.8 | 294.1±101.5 | | |
| ∑PAH | 1145.1±700.1 | 1464.6±898.6 | 2812.6±1075.6 | 1467.7±798.6 | 608.7±156.3 | | |
| Sand % | 35.5 | 29.3 | 28.0 | 28.4 | 40.7 | | |
| Mud % | 64.5 | 70.8 | 72.0 | 71.6 | 59.3 | | |
| OM % | 4.7 | 4.6 | 4.3 | 4.4 | 3.9 | | |

## 4. Discussion

Based on a general view of the ΣPAH concentrations and sediment characterization of the study area, it can be observed that the highest PAH concentrations were in the sediment sites composed mainly by mud, showing that granulometry is the most important factor influencing the PAH concentration in environmental samples. Several studies confirmed the hypothesis that the PAH concentration tends to be higher in soil and sediments and with the predominance of mud, presented relatively higher concentrations of PAH (BÍCEGO *et al*., 2006; LU *et al*., 2012). The organic matter amount in the sediment showed no such importance as the grain size and may be associated with the entrance of organic matter (macro- and micronutrients) from several anthropic activities in this urbanized region, such as sewage. Since most of the channels at the Guajará bay, as São Joaquim stream and Una chanel located at studied area, do not exhibit sewage treatment systems. Small spatial variations were observed (mean value and standard deviation = 4.4% ± 0.3) in the amount of OM in the 5 studied sites due to the proximity of the sampling sites to these channels.

The ΣPAH concentrations found in the sediments of the Guajará bay near the TEMIR, which is under a heavy influence of urban and port activities, can be compared with those reported in other studies performed in fluvial systems by Guo *et al.* (2009), Meire *et al.* (2009), Leite *et al.* (2011) and Kanzari *et al.* (2012). The degree of sediment contamination may be evaluated based on the concentration of the 16 priority PAH, as determined by USEPA. Environments may be classified as "highly contaminated" when their concentration of Σ16 PAH is above 500 ng $g^{-1}$, "moderately contaminated" when that concentration is between 250 and 500 ng $g^{-1}$, and "weakly contaminated" when that observed concentration is below 250 ng $g^{-1}$ (SOCLO *et al*., 2000). Among the samples evaluated in this study, only Site 5 showed during the first sampling period a ΣPAH concentration < 500 ng $g^{-1}$. Considering the mean values of ΣPAH concentration and the 10 years period focused in this study, all the studied sites are classified as highly contaminated, presenting a ΣPAH mean concentration between 608.7 and 2812.6 ng $g^{-1}$ of dry weight.

Among the 16 priority PAH studied, the most abundant were the ones typical of petrogenic contributions. One difficulty in identifying PAH origins, is the possible coexistence of many contamination sources, and the transformation processes that PAH could have undergone before deposition in the analyzed sediments. Indices used to determine the origin of the PAH in the sampling sediments indicate a primary contribution of petrogenic contamination but it also demonstrates a pyrolytic contribution. Only the samples of Site 1 presented a predominance of rates that lead to a pyrolytic main contamination. Fuel combustion, household waste combustion and untreated sewage discharge are potential pyrolytic sources for the region as suggested by Lima (2009) and Sodré (2014). Considering this data, it is possible to indentify a gradient in petrogenic PAH contribution. In the locations nearest to TEMIR this contribution is higher and tends to decrease with the distance from the harbor increase. It shows a relevant contribution of the petrochemical harbor activity to the input of HPA to Guajará bay that can even change the existing pyrolytic pattern along of the bay, but further studies are necessary to confirm this final proposition.

## 5. Conclusions

The presence of PAH in superficial sediments of the Guajará bay can be attributed to sites that showed the influence of mud predominance. The studied area receives PAH input mainly from petrogenic sources related to the Miramar Petrochemical Harbor activities coming from oil derivative input represented by Phe and Na high concentrations and the predominance of LMW, but pyrolytic PAH input by fuel combustion, household waste combustion and untreated sewage discharge are also potential contamination sources to be in the rest of Guajará bay extension.

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