Analytical strategies for determining the sources and ecotoxicological risk of PAHs in river sediment

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ABSTRACT

In this work, analytical strategies were applied aiming at determining sources and ecological risk of PAHs in river sediments. A total of 23 PAHs (16 EPA + 7 alkylated derivatives) were determined in sediment samples. The concentration of total PAH ($\sum_{23}$PAH) span from 0.260 to 2.10 µg g^{-1} dw. The molecular ratios indicated a prevalence of pyrolytic pollution sources due to wood combustion processes and refined oil products. The ecological risk was assessed by considering the Sediment Quality Guidelines (SQGs). It was noted that all of the individual PAH concentrations are below the ERM (average variation effect). The $\sum_{23}$PAH was also below the total of ERL (low variation effect) from 4.02 µg g^{-1} dw. The synergy between individual PAHs was assessed using the indices of quality (mSQGq). Accordingly, the risk associated with the simultaneous contamination of the total PAH varied from low to moderate for the different sediments samples of river. The river is located in the state of Bahia, in a region that concentrates the first and largest integrated industrial complex of Brazil.

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1. Introduction

Sediments constitute one of the main compartments of the aquatic environment where organic matter and hydrophobic organic contaminants can be accumulated becoming both carriers and reservoirs of pollutants. Some pollutants may be associated with fine sediment particles, causing gradual or immediate deterioration of the aquatic system, being still susceptible to transportation farther from the source by advection to other ecosystems. So it has great importance in the evaluation of environmental pollution monitoring since they provide time-integrated information [1].

Among the organic pollutants, the polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds composed of two or more condensed aromatic rings. Their hydrophobicity depends on the number of the aromatic rings and tends to accumulate in sediments and in the tissue of several organisms [2]. Several works have been carried out to assess the levels of PAHs in marine sediments [3,4], river sediments [5,6] and lake sediments [7,8]. These compounds are of great environmental concern, because they belong to the group of priority pollutants, potentially toxic, carcinogenic and mutagenic. Their presence in the environment constitutes a threat to marine life and also for other ecosystems, due to their high toxicity and bioaccumulation potential.

The river flows through densely populated basin and it is used as a recreational area by the local community. It is located in the state of Bahia, northeastern Brazil, in the Camaçari city. The Camaçari Petrochemical Complex is situated in this city, which is the largest integrated industrial complex in the Southern Hemisphere. The complex has over 90 chemical companies and other activities. Despite the environmental pressure, studies to evaluate the possible contamination in the rivers and lagoons of the region of Camaçari and adjacent cities are scarce. The only work found was published in 2011, and refers to the distribution of heavy metals (Pd, Zn, Cd, Cu and Cr) in the sedimentary substratum of the Sauípe River, located about 50 km from the city of Camaçari [9]. So it is evident the need for monitoring in this region due to industrial exploitation that occurs for >35 years. Given that, it is clear that it is extremely important environmental monitoring of this ecosystem. Therefore, the present work aims to fill this gap of knowledge, aiming to evaluate the distribution, source and ecotoxicological risk of PAH in sediments collected in the Capivara River during dry seasons as a characteristic river of tropical ecosystems flowing through industrialized areas.

2. Materials and methods

2.1. Sampling methods

2.1.1. Study area description

The Capivara River (−12° 47′ 52″ S, −38° 13′ 44″ W, −12° 44′ 25″, −38° 9′ 5″ W), is located in the Camaçari City, state of Bahia, northeastern of Brazil. It comprises of approximately 43 km in length. It's river a shallow, with average water depth of 8 m. It is important for ecology since it housed within an environmental protection area — APA Capivara River created in 1993,comprising an area of 1800 ha [10]. Throughout its course, it houses habitats of high ecosystemic importance such as wetlands, floodplains fields, marshes and forest of shrubby tree dunes and mangroves. However, the Capivara River is located near large industrial and urban areas. Accordingly, it is vulnerable to receive discharges of industrial effluents and domestic sewage. In addition, in the region there is an outfall, which discards Complex's industrial effluents into the sea.

The Camaçari City (12°41′51″ S, 38°19′27″ W) is one of the most densely populated (ca. 242,970 inhabitants) and most economically developed areas in state of Bahia. It's located the Camaçari Petrochemical Complex, which is the largest integrated industrial complex in the Southern Hemisphere.

2.1.2. Samples collection and storage

Considering its territorial extension 12 sampling sites were chosen, as shown in Fig. 1. These were strategically established, due to its proximity to residential areas and chemical industries. The samples were collected in November of 2014, corresponding to the dry period of the year. From the 12 sites sampled, 9 (P1–P9) were located in different representative areas of the riverbed and 3 sites (P11–P13) in the Interlagos lagoon, which is the largest lagoon near the river, as shown Fig. 1.

The sediments samples were collected using a dredge, stored in aluminum containers and transported in refrigerated conditions to the laboratory. The samples were lyophilized for 72 h and sieved through 100

μm aluminum sieves. These were stored in aluminum containers and kept refrigerated at 0 °C until analysis.

2.2. Analytical methods

2.2.1. Chemicals and reagents

All reagents used were of the highest analytical grade (97–99%) and obtained from Merck (Darmstadt, Germany). Standard solutions of deuterated surrogates containing naphthalene (d8), anthracene (d10), pyrene (d10), benzo(a)pyrene (d12) were obtained from Cambridge Isotope Laboratories (Andover, Massachusetts, USA). Decafluorobiphenyl used as internal standard was obtained from Merck (Hohenbrunn, Germany). Standard solution supplied by Dr. Ehrenstorfer (Augsburg, Germany) contained a mixture of 16 PAH priority US EPA namely, naphthalene (N), acenaphthylene(ACY), acenaphthene (ACE), fluorene (F), phenanthrene (P), anthracene (A), fluoranthrene (Fl), pyrene (Py), benz(a)anthracene (BaA), chrysene (C), benzo(b)fluoranthene (BbFl), benzo[k]fluoranthene (BkFl), benzo(a)pyrene (BaPy), indeno(1,2,3-cd)pyrene (IPy), dibenz(a,h)anthracene (DBA), and benzo(ghi)perylene (Bper). And alkylated derivatives metyl-naphthalene (C1N), dimetyl-naphthalene (C2N), metyl (C1P) and dimetylphenanthrene (C2P), metylpyrene (C1Py), benzo(e)pyrene (BePy) and perylene (Per) supplied by Dr. Ehrenstorfer (Augsburg, Germany).

2.2.2. Instrumental analysis

Extraction was carried out on a Pressurized Solvent Extraction (Applied Separations, Allentown, PA). The total carbon analyzer LECO CR-412 Carbon Analyzer, infrared detector (IR) and autosampler rack Glazed. PAHs were determined by gas chromatography TRACE-GC (Manchester, UK) coupled to a mass spectrometer TRACE-MS (Thermo Finnigan) in the electron impact mode (70 eV ionization energy), using the selective ion monitoring acquisition mode. The ion source and transfer line temperatures were held at 250 °C and 280 °C respectively. The gas chromatograph was equipped with fused silica column TRB5-MS of 30 m × 0.25 mm ID × 0.25 μm film thickness (Teknokroma, Barcelona, Spain). Helium was used as carrier gas (99.9995%) at a constant flow
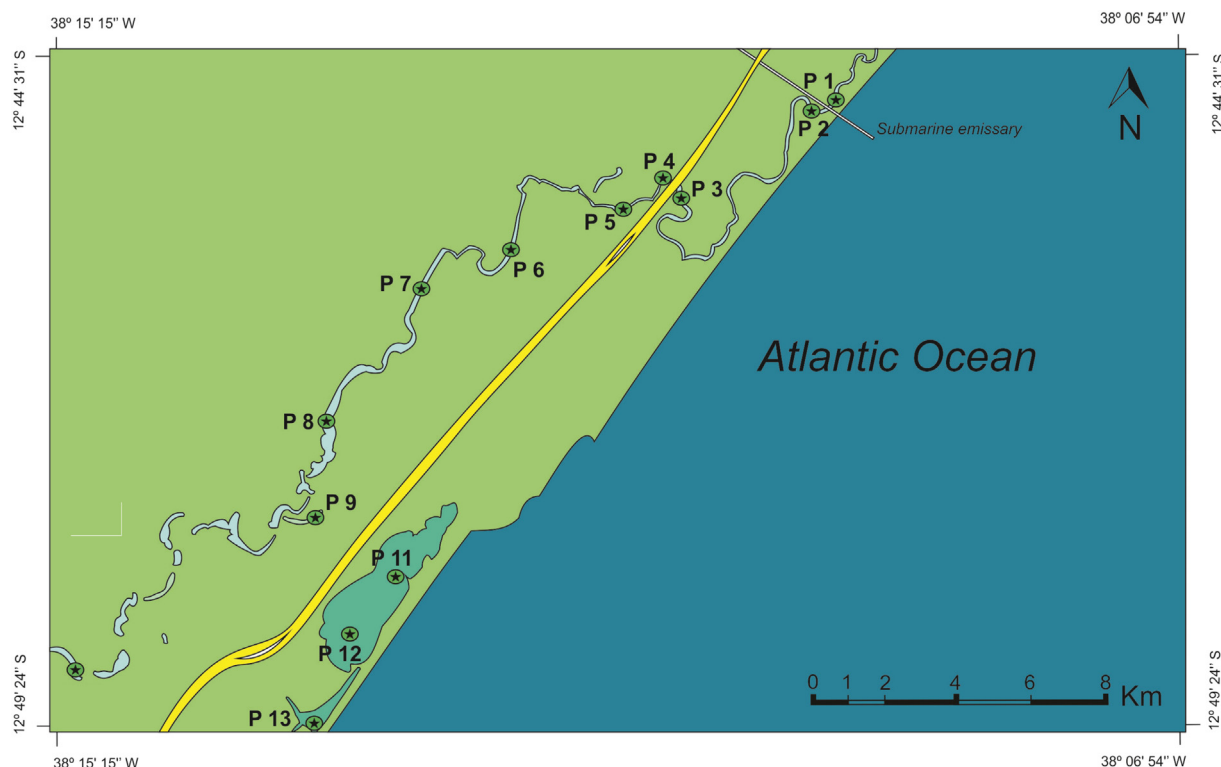

Fig. 1. Sampling sites of the sediments of the Capivara River.