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Baseline

Polycyclic aromatic hydrocarbons (PAH) in superficial water from a tropical estuarine system: Distribution, seasonal variations, sources and ecological risk assessment

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ABSTRACT

This study aimed to evaluate the PAH distribution, sources, seasonal variations and ecological risk assessment in superficial water from the Japaratuba River, Brazil. PAH concentrations ranged from 4 to 119 ng L^{-1}. It was observed that the PAH total concentrations and profiles showed significant differences when comparing the dry season (summer) with the rainy season (winter). Furthermore, most of the PAH originated from pyrogenic sources in the winter, whereas a mixture of sources was observed in the summer. PAH concentration levels found in this study were considered lower than those obtained in other estuarine systems. Ecological risk assessment was determined for individual PAH, based on the risk quotient (RQ) to evaluate the risk of aquatic biota's exposure to PAH. Results suggested that the Japaratuba River has achieved a moderate degree of ecological risk for high molecular weight, showing the importance of identifying these carcinogenic and mutagenic compounds in aquatic systems.

Polycyclic aromatic hydrocarbons (PAH) are compounds that consist of two or more condensed rings and might be scattered into the particulate matter, sediments and water columns through natural and anthropogenic combustion (Li et al., 2014; Lin et al., 2015; Abdel-Shafy and Mansour, 2016). Due to their carcinogenic, mutagenic and teratogenic effects, these compounds have been considered harmful to humans (Ravindra et al., 2008). Therefore, 16 PAH were classified as priority pollutants according to the United States Environmental Protection Agency (USEPA) (Manoli et al., 2000),which continue to be reported in different studies worldwide (Ravindra et al., 2008; Wolska et al., 2012; Lewis and Russel, 2015; Celino et al., 2012; Patrolecco et al., 2010; Sarria-Villa et al., 2015; Malik et al., 2011; Zhao et al., 2014; Yan et al., 2016; Santana et al., 2015). Although the majority of the PAH might be introduced in the environment through anthropogenic inputs, they can also originate from natural sources (Wolska et al., 2012). Their introduction in aquatic environments, such as rivers, lakes, reservoirs and estuaries might affect the aquatic biota, as well as the wildlife and humans via the food chain (Fernandes et al., 1997).

Estuaries are commonly defined as semi-enclosed coastal water bodies that have a free connection with the open sea, extending from the rivers to the limits of the tidal zones, in which salt water is significantly diluted with fresh water derived from land drainage (Pritchard, 1967). They are also vital for the majority of marine fauna, showing a global importance due to their food sources and biodiversity, not to mention their historical and cultural impact on humanity over the centuries (Zhang et al., 2016). Therefore, evaluating the PAH presence in estuarine systems has proven to be very important, considering their ecological risk to the environment. Based on that, the risk quotient (RQ) has been widely used. It is based on the concentration of a certain PAH or their sum (ΣPAH) and the toxic equivalent factors (Cao et al., 2010; Yan et al., 2016).

Japaratuba River Basin plays an essential role in the development of Sergipe State, Northeast Brazil. Mineral and chemical industries, agriculture, manufacture and harbor areas are some of the activities that are directly benefitted by the existence of this estuarine system, not to mention the largest onshore oilfield in Brazil, located in Carmópolis City, which has an extension of > 150 km^2 and approximately 1200 exploration oilers. Therefore, an ecological risk associated with the presence of anthropogenic activities near the Japaratuba River has been observed. Domestic and industrial effluents, as well as by-products associated with petroleum exploration, have been introduced into the Atlantic Ocean through the Japaratuba estuarine system. These inputs

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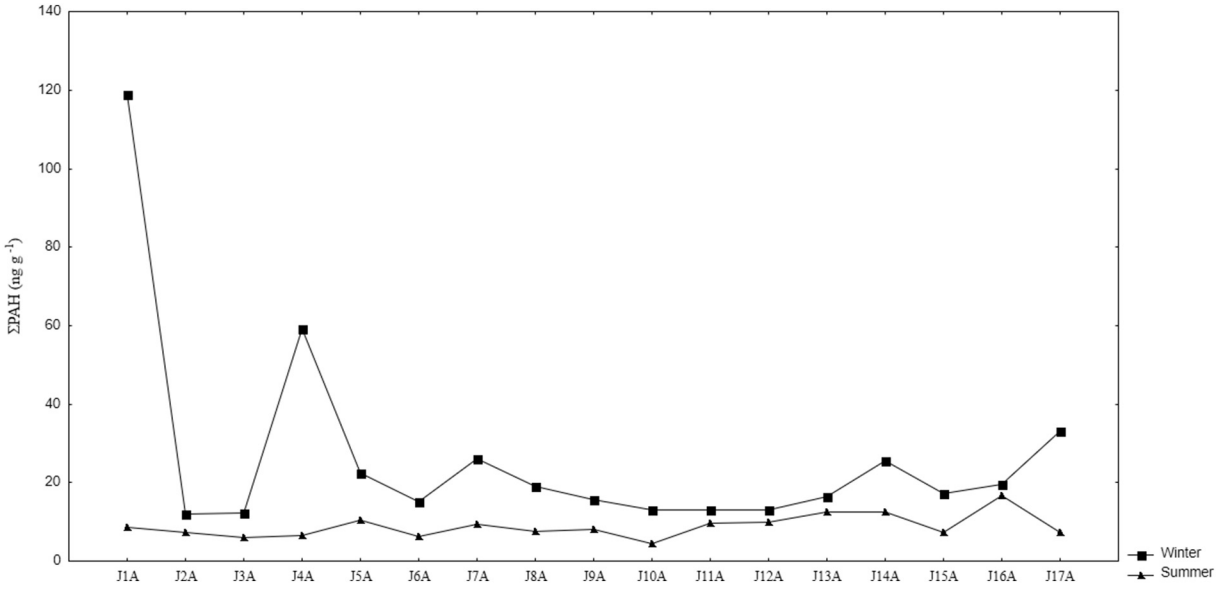

Fig. 1. ΣPAH concentrations in water samples from the Japaratuba River Basin.

have been modifying the environmental quality of the region due to the introduction of inorganic and organic pollutants (Pantaleão et al., 2007; Secretária de Estado do Meio Ambiente e dos Recursos Hídricos, 2016). In addition, studies related to PAH contamination in the Japaratuba River Basin have never been reported in the literature, even though the presence of anthropogenic processes related to the economic activities of the region has increased over the years.

The objectives of this study are to: (i) investigate the PAH distribution, composition profiles and seasonal variations in superficial waters from the Japaratuba River Basin; (ii) determine the PAH sources using principal component analysis (PCA), ratios and indexes; and (iii) evaluate the ecological risk assessment through a risk quotient (RQ) that is based on toxic equivalence factors (TEF), which might associate the ecological risk to the individual PAH and ΣPAH. Also, the results of this study will provide valuable information for regulatory actions aiming to improve the quality of water in the Japaratuba River Basin.

Forty-six superficial water samples were collected in the Japaratuba River Basin in the winter of 2016 and the summer of 2017. Among the water quality parameters, salinity, pH, turbidity and temperature values ranged from 0.23 to 22.28‰, 6.0 to 7.3, 45 to 150 cm and 13.5 to 28.0 °C in the winter, whereas in the summer these values ranged from 0.08 to 9.81‰, 6.1 to 7.7, 44 to 72 cm and 11.0 to 34.0 °C, respectively. These are typical values considering the climate in this area, with two outstanding seasons, one rainy (winter) and another dry (summer). Sampling was performed using clean amber glass bottles. Once in the laboratory, the samples were stored and kept at 4 °C. Each sample (4 L) was filtered using glass filters (Macherey-Nagel, 47 mm Ø, GF-1, Germany) under vacuum. Prior to extraction, samples were spiked with a known amount of surrogate standards (naphthalene-*d*8, acenaphthene-*d*10, phenanthrene-*d*10, chrysene-*d*12 and perylene-*d*12 — AccuStandard, USA). Liquid-liquid extractions were performed with 150 mL (3 × 50 mL) of *n*-hexane (HPLC grade — MACRON, USA). The extracts were then combined and concentrated until reaching a final volume of 1.0 mL, when internal standard (*p*-terfenil-d14 — Supelco, USA) was added for GC–MS/MS analysis.

Polycyclic aromatic hydrocarbons were analyzed using a gas chromatograph (Shimadzu GC–MS TQ8040 — Kyoto, Japan), equipped with an AOC5000Plus autosampler and a split/splitless injector. A SBL 05-MS capillary column (30 m × 0.25 mm i.d., 0.25 μm of film thickness — Supelco, USA) was used under the following conditions: 40 °C for 1 min up to 150 °C at 20 °C min^{-1}, increasing to 220 °C at 10 °C min^{-1} and up to 300 °C at 10 °C min^{-1}, being finally held at the final temperature for 7 min. The GC–MS interface was kept at 300 °C. Helium (99.999% purity) was used as carrier gas at a flow rate of 1.2 mL min^{-1}. PAH were quantified using a multiple reaction monitoring (MRM) mode with argon (99.998% purity) as collision gas. The ion source was operated at 280 °C with an electron ionization source of 70 eV.

Surrogates, internal standard and blank samples were used to validate the analytical method employed in this study. Accuracy and reliability were determined by using blank samples containing 16 priority PAH and surrogate standards. Individual PAH recovery ranged from 65% (Naf) to 84% (Pyr), with a standard deviation of < 10%. Limits of detection ranged from 0.05 ng L^{-1} up to 0.25 ng L^{-1}, whereas the limits of quantification ranged from 0.15 ng L^{-1} to 0.50 ng L^{-1}. Spiked samples were analyzed, showing PAH recoveries ranging from 83% to 101% in the winter and from 61% to 107% in the summer. These data were considered accurate and reliable, as they did no show interference of external contaminants in the GC–MS analysis. Statistical analyses were performed using Statistica Software 7.0. Furthermore, a Shapiro-Wilk test was performed to evaluate the normal distribution of the data, whereas the difference between statistical groups was evaluated through the Wilcoxon signed rank test. Ecological risk assessment was determined by using toxic equivalent factors for each PAH as described by Liu et al. (2012).

ΣPAH concentrations ranged from 12 to 119 ng L^{-1} and 4 to 17 ng L^{-1}, with a mean value of 17 and 9 ng L^{-1} in the winter and in the summer, respectively (Fig. 1). The highest concentration values were found in the winter (J1A), in the areas located next to the river mouth whereas the lowest concentration values were found up river, in the summer (J10A).

A significant difference involving the 16 PAH was also observed when considering the 17 sampling areas ($p < 0.05$), in which the total PAH concentration in the summer was lower (152 ng L^{-1}) than in the winter (462 ng L^{-1}). This finding suggests that local drought, which increased the temperature, as well as the biodegradation and photodegradation processes by planktonic communities, and the increasing deposition of particulate matter in the aquatic system through the tidal phenomenon, might be some of the factors that reduced the PAH concentration in the dry season (Yamada et al., 2003; Rügner et al., 2014; Jalón-Rojas et al., 2015).

As shown in Table 1, the PAH total concentrations were relatively low in this study, but they were considered higher than those found in Todos os Santos and Tampa Bay, regions of great economic importance