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Research article

Ecological risk assessment of sedimentary hydrocarbons in a subtropical estuary as tools to select priority areas for environmental management

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ABSTRACT

The concentration, distribution, and ecological risk of hydrocarbons, as well as bulk parameters, were determined in surface sediments of the Babitonga Bay, a subtropical human-impacted estuary in South Atlantic. Total aliphatic and polycyclic aromatic hydrocarbons (PAHs) ranged between 0.8 and 201.2 μg g^{-1} and from 8.7 to 5489 ng g^{-1}, respectively. Saguaçú Lagoon, the region near the ferry boat and the vicinity of São Francisco harbour (SFH), presented high hydrocarbon concentrations. Despite the low accumulation trend in this region, the SFH and city may act as a punctual hydrocarbon source. The inner portion of the estuary had the finest sediment grains and the highest concentrations of carbon, nitrogen, and sulphur, indicating its importance as a depositional and cumulative area. The occurrence of unresolved complex mixture suggested chronic oil contamination. Petrogenic (based on the high percentage of alkylated PAHs) and pyrolytic (according to the diagnostic ratios of PAH isomer pairs) sources were confirmed. Ecological risk assessment was evaluated by the risk quotient (RQ). All samples had at least one priority PAH present at above the negligible concentration, including naphthalene, which was observed in all samples. Only the sites near the ferry boat and at the Saguaçú Lagoon contained compounds with concentrations above their maximum permissible concentrations, while all other sampling sites are classified as "Low-risk." The spatial distribution of RQs coincides with PAHs distribution, indicating that the regions near SFH, ferry-boat, and the Saguaçú Lagoon should be considered to be priority areas when making environmental monitoring policies.

1. Introduction

Estuaries are characterized by receiving large amounts of organic matter and minerals from the drainage basin. The material flux and energy transfer make these ecosystems to be among the most important environments in terms of biological activity in the biosphere. These environments are affected by a wide range of pollutants, including trace metals, persistent organic pollutants, nutrients, oils, radionuclides, litters, and debris and have acted as a destination of industrial and municipal wastes, sewage sludge, and dredged material (Kennish, 1994; Gattuso et al., 1998; Islam and Tanaka, 2004).

Particularly, hydrocarbons derived from the production, transport, and consumption of oil and its by-products have been responsible for the chronic or acute contamination of sediments worldwide (Pinheiro et al., 2017). The primary sources of hydrocarbons in the coastal marine environments are from human activities, such as harbour operations, leakage from transport vessels and sewage. Harbour expansion is another environmental stress factor because dredging of navigational channels can lead to the transport of resuspended contaminants from sediments into the water column and to the surrounding areas (Burton and Johnston, 2010; Roberts, 2012).

Babitonga Bay is an important human-impacted South Atlantic estuary, holding approximately 160 km^2 of surface water as part of a large hydrographic complex with an area of 1400 km^2. This bay is one of the main estuarine formation in the southern coast of Brazil, and the mangrove systems surrounding the region have been assigned "high priority status" for conservation (MMA, 2007). Despite this ecological relevance, it has a historical record of marine pollution due to untreated sewage discharge, industrial disposals and harbour activities (Martins et al., 2014; Rizzi et al., 2017).

Environmental contamination has been evaluated by organic markers. These molecules are characterized by relatively high chemical

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stability to degradation processes, stable molecular structure, and direct association with biogenic (marine and terrestrial) and/or anthropic (oil and by-products) organic matter (Colombo et al., 2005; Volkman, 2006). Due to their hydrophobic behaviour, these molecules tend to adsorb on the particulate material and settle onto the seabed, which acts as a sink of these materials (Law and Biscaya, 1994).

Aliphatic hydrocarbons (AHs), such as *n*-alkanes, and polycyclic aromatic hydrocarbons (PAHs) are examined in studies related to the input of biogenic organic matter, petroleum/oil and by-products, and combustion residues (Liu et al., 2014; Martins et al., 2015; Dudhagara et al., 2016). The *n*-alkanes are synthesized by terrestrial organisms, higher plants, bacteria, and marine organisms, as phytoplankton and zooplankton (Cripps, 1989; Wang et al., 2009), and can also be related to petroleum and fossil fuels (Volkman et al., 1992). PAHs are contaminants associated mainly with anthropogenic sources, such as incomplete combustion of fossil fuels, coal, and biomass and crude petroleum/oil and its refined by-products (Guitart et al., 2007; Liu et al., 2009). Because of PAHs' mutagenic and carcinogenic properties, the United States Environment Protection Agency (USEPA) classified sixteen of them as priority pollutants (Wang et al., 2008) and defined their concentration limits termed Threshold Effect Level (TEL) and Probable Effect Level (PEL) based on the probability of deleterious effects on the biota (Long et al., 1995; Buchman, 1999).

Due to the multiple anthropogenic impacts on this large subtropical estuary in the South Atlantic, the aims of this study were to determine the concentrations of hydrocarbons, particularly *n*-alkanes and PAHs, in surface sediments of the Babitonga Bay to assess the sources of organic matter, to provide new information regarding the contamination status of this harbour area and to evaluate the ecological risk caused by anthropogenic input of hydrocarbons.

2. Study area

The Babitonga Bay (26°16′S, 48°41′W; Fig. 1) represents an important habitation for food, reproduction, and shelter to a large diversity of species and has a high level of ecological and economic importance due to its high productivity and diversity. This estuary provides shelter for mangrove vegetation distributed up to 6200 ha, representing approximately 75% of the existing mangrove systems in the coastal area of Santa Catarina State in the SW Atlantic (Cremer, 2006; MMA, 2007).

Babitonga Bay has an average depth of 6 m and a maximum depth of 28 m in the main channel that provides access to Joinville city, where the one of the major industrial complex areas of South Brazil, and the Itapoá and São Francisco do Sul harbours are located.

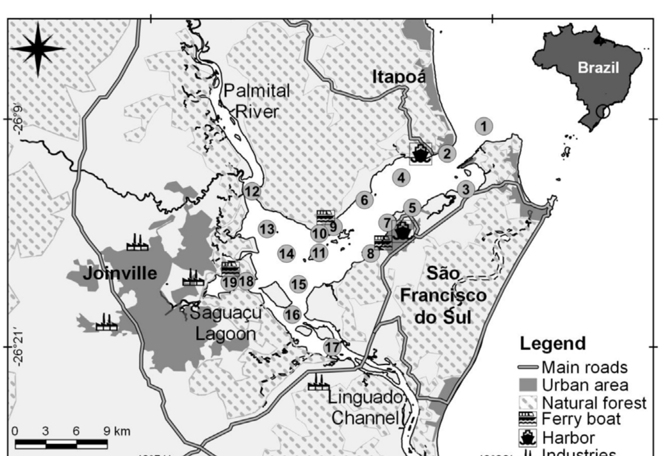

Fig. 1. Map of the study area showing the Babitonga Bay, South Atlantic, and the sampling sites.

Despite the ecological importance, Babitonga Bay has already shown signs of environmental impact due to the high anthropic pressure, specifically from the Joinville city that has a population of more than 550,000 inhabitants. Joinville city is an industrial (mainly metallurgical and textile) and urban centre, and does not have adequate waste treatment (Martins et al., 2014). São Francisco do Sul city hosts an oil terminal, and the bay surrounding the cities has large agricultural areas. Fishing, aquaculture, and harbour activities in the cities of Itapoá and São Francisco do Sul represent the economic activities in the bay (Vieira et al., 2008), which demands environmental monitoring in the region.

The estuary has two axes: the north-southward axis (N-S; which extends from the Palmital River to the Linguado Channel) and the east-westward axis (E-W; main channel, from the Atlantic Ocean to the continent). The E-W axis represents the main connection between the estuary and the open sea, while the N-S axis is the main receiver of terrestrial material from the drainage basin. The south portion of the N-S axis, the Linguado Channel, historically was the second connection to the ocean. However, a highway built on 1937 provides access to the São Francisco do Sul Island and resulted in the closure of the channel, which have changed the circulation pattern and promoted an intense siltation process in the area (Barbosa and Mazzer, 2003). The Saguaçú Lagoon, a region with poorly sorted, fine sediment and with high organic matter content (Vieira et al., 2008), is located in the inner portion. The estuary has a salt-wedge circulation system, and the input of organic matter is highly substantial and more prevalent in the rainy season due to the flooding of the major rivers (Grace et al., 2008).

3. Materials and methods

3.1. Sediment sampling

Surficial sediments from 19 sites were collected in March 2012 (Fig. 1) using a stainless-steel grab sampler (surface area: 0.04 m^2) based on procedure fully described in UNEP (2008). The top 2 cm of undisturbed surface sediment was wrapped in pre-cleaned aluminium foil (450 °C, 4 h) and stored at −20 °C. The sediments were freeze-dried, carefully homogenized with a mortar, and stored in clean glass bottles at room temperature before organic marker analysis.

3.2. Bulk parameters

Grain-size analysis was performed for all samples with a Microtrac Bluewave S3500 by laser granulometer in the range from 0.02 to 3000 μm. The results were grouped into three different classes based on grain size: sands (2000–62 μm), silts (62–4 μm), and clay (< 4 μm) using R package software according to Gilbert et al. (2012).

Elemental analyses (TOC, TN and TS) were conducted on 1.00 g of homogenized surface sediments. These samples were pre-treated with hydrochloric acid to remove inorganic carbon, washed twice with deionized water to remove chloride, and dried at 80 °C overnight. The total organic carbon (TOC) and total nitrogen (TN) were determined using a Carlo Erba 1100 CHN Analyser with a precision of < ± 8% and < ± 10%, respectively. Total sulphur (TS) was determined on a Carlo-Erba NC 2500 Elemental Analyser. All elemental analyses were performed in duplicate.

3.3. Hydrocarbons: extraction, fractionation, and instrumental analyses

The analytical method of hydrocarbons was described in detail by Wisnieski et al. (2016). Approximately 20 g of sediments were Soxhlet extracted over 8 h with 80 mL of mixed dichloromethane (DCM) and hexanes (95% *n*-hexane) (1:1). The surrogate standards, including 1-hexadecene and 1-eicosene (Supelco Analytical) and naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (AccuStandard Z-014J), were added before each blank and sample