Science of the Total Environment 624 (2018) 935–944

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Sources and distribution of aromatic hydrocarbons in a tropical marine protected area estuary under influence of sugarcane cultivation

Roxanny Helen de Arruda-Santos, Carlos Augusto França Schettini, Gilvan Takeshi Yogui, Daniele Claudino Maciel [1], Eliete Zanardi-Lamardo *

Department of Oceanography, Federal University of Pernambuco, Av. Arquitetura s/n, Recife, PE CEP: 50740-550, Brazil

HIGHLIGHTS

- Goiana estuary is slightly contaminated by PAHs.
- SPM may be a good proxy for inferring local aromatic hydrocarbons distribution.
- PAHs in sediments were mainly from sugarcane burning and engine combustion.
- PAHs in sediments are associated with organic matter and fine particles.
- PAHs concentrations probably do not cause effects to the local biota.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 19 September 2017
Received in revised form 15 December 2017
Accepted 15 December 2017
Available online xxxx

Editor: Kevin V. Thomas

Keywords:
Contamination
Estuarine turbidity maximum
PAH
Pyrolytic input

ABSTRACT

Goiana estuary is a well preserved marine protected area (MPA) located on the northeastern coast of Brazil. Despite its current state, human activities in the watershed represent a potential threat to long term local preservation. Dissolved/dispersed aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) were investigated in water and sediments across the estuarine salt gradient. Concentration of aromatic hydrocarbons was low in all samples. According to results, aromatic hydrocarbons are associated to suspended particulate matter (SPM) carried to the estuary by river waters. An estuarine turbidity maximum (ETM) was identified in the upper estuary, indicating that both sediments and contaminants are trapped prior to an occasional export to the adjacent sea. PAHs distribution in sediments were associated with organic matter and mud content. Diagnostic ratios indicated pyrolytic processes as the main local source of PAHs that are probably associated with sugarcane burning and combustion engines. Low PAH concentrations probably do not cause adverse biological effects to the local biota although their presence indicate anthropogenic contamination and pressure on the Goiana estuary MPA.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds in environmental compartments such as air, water, soil, sediment and biota (Countway et al., 2003; Chen et al., 2004; Cheollee et al., 2005; Curtosi et al., 2009; Wang et al., 2010; Chizhova et al., 2013). Sources of PAHs to the environment include industrial and urban wastewaters, fossil fuels, combustion processes and port

---

* Corresponding author.
E-mail addresses: gilvan.yogui@ufpe.br (G.T. Yogui), eliete.zanardi@ufpe.br (E. Zanardi-Lamardo).

[1] Present address: Federal Institute of Education, Science and Technology of Alagoas (IFAL), Av. Sergipe 1477, Piranhas, AL CEP: 57460-000, Brazil.

https://doi.org/10.1016/j.scitotenv.2017.12.174

activities (Zanardi et al., 1999a, 1999b; NRC, 2003; Lemos et al., 2014; Maciel et al., 2015b). Magmatic activity, biochemical synthesis, natural biomass combustion, organic matter diagenesis and erosion of the Earth's crust all constitute natural sources that used to be relevant for the PAH budget. Nonetheless, such sources have been currently considered only a small fraction of the budget when compared to anthropogenic sources (UNEP, 1992; Volkman et al., 1992; Witt, 1995). The environmental fate of PAHs is of great concern because some of them present carcinogenic and/or mutagenic potential for several organisms (Kamal et al., 2014). In addition, they are accumulated in some benthic organisms such as mollusks and crustaceans, and may pose a health threat for humans that consume shellfish (Neff, 1984; Khairy et al., 2014).

PAHs cover a wide range of environmentally relevant properties, including semi- to low volatility and intermediate to low water solubility. In addition, they are lipophilic chemicals that are resistant to degradation in biological organisms. In the water, they tend to adsorb onto suspended particulate matter (SPM) with subsequent deposition in sediments (Cullen et al., 1994; Tolosa et al., 2004) where slow chemical and biochemical transformations may occur (Paez-Osuna et al., 2002). Therefore, sediments are a suitable compartment for investigating PAHs since they integrate local contamination over time. Sediments are also considered a secondary source of contamination because either natural or anthropogenic processes may release contaminants back to the water column (Lazorchak and Josephs, 2003; Kim et al., 2014).

Coastal areas including estuaries are among the most susceptible environments regarding anthropogenic activities and have been frequently reported as contaminated by PAHs (Chouksey et al., 2004; Bícego et al., 2006; Araghi et al., 2014; Lemos et al., 2014; Maciel et al., 2015b). The watershed of Goiana River spread over an area of 2900 km^2, housing approximately 500,000 inhabitants. Land use includes various crops, sugarcane agribusiness, livestock, urban settlements, few industries and Atlantic forest patches (CPRH, 2003). Activities such as shrimp farming and fishing also take place in the estuarine portion of Goiana River. In addition, substantial investments have been made for the construction of an airport, a port and manufacturing plants (Brazil, 2014). Studies carried out in the estuary reported microplastics (Lima et al., 2014) and mercury contamination (Barletta et al., 2012). Despite anthropogenic pressure in the watersheds, the Goiana River estuary is a marine protected area (MPA) that has one the largest mangrove areas along the coast of Pernambuco (northeastern Brazil), playing a key role in ecosystem productivity and serving as a natural nursery for countless species of aquatic invertebrates (CPRH, 2003).

The Goiana river watershed is a portrait of many other small streams draining the eastern shore of northeastern Brazil where sugar cane is a major commodity. The backlands have semi-arid climate, limiting agriculture to coastal areas (about 100 km from the shoreline) originally covered by the Atlantic maritime forest. Sugar cane accounts for 32% of the total cultivated area in the State of Pernambuco (IBGE, 2017). Negative environmental impacts of the sugar cane cultivation include burning of leaves prior to harvesting, and soil erosion after harvesting. Furthermore, there is virtually no riparian vegetation near cultivated areas.

Sugar cane burning practices release hydrocarbons to the atmosphere. These chemicals are dispersed by winds, being eventually deposited on land, drained into streams, and finally transported toward the ocean. In this study we investigated the distribution of PAHs along the Goiana river estuary (from fresh to salt water). Aromatic hydrocarbons were determined in both water and sediment samples. Water column results provide an overview on the distribution of contaminants as well as the influence of tides and mixing processes. Sediment results integrate long term contamination. Relationship of aromatic hydrocarbons dissolved in water and adsorbed onto particulate matter is discussed as well possible mechanisms that trap contaminants in the estuary.

2. Materials and methods

2.1. Study area

Goiana estuary (7° 32′ S, 34° 51′ W) is located on the northeastern coast of Brazil and its main stem serves as a boundary between the states of Pernambuco and Paraíba. It is formed by the confluence of Capibaribe Mirim and Tracunhaém streams. The estuary is nearly 30 km long with widths ranging from 30 m at the upper estuary to 450 m at its encounter with the Atlantic Ocean. River depths range from 3 to 10 m. Mangrove forests occupy an area of about 4.7 km^2 (Barletta and Costa, 2009).

Climate is tropical with mean annual temperature of 27 ± 2 °C (Barletta and Costa, 2009). Rainfall is greatest over June and July (winter). Average discharges of the Tracunhaém (Brazilian Water Agency, gauge #39080000) and Capibaribe Mirim streams (gauge #39084000) are 11.0 and 8.8 m^3 s^{-1}, respectively. These two gauges account for nearly 90% of the catchment area. River flow has high seasonal and interannual variability. Monthly mean flow can be as low as 3.5 m^3 s^{-1} in the dry season (November–February) and as high as and 60 m^3 s^{-1} in the wet season (May–August). Similarly to other streams along the northeastern coast of Brazil, the river flow is influenced by large scale phenomena such as El Niño Southern Oscillation (ENSO) and Atlantic Tropical Dipole (Schettini et al., 2016a). Local tides are semi-diurnal with amplitudes ranging between 0.8 and 2.6 m during neap and spring tides, respectively (unpublished data).

Goiana estuary was declared an MPA (Resex Acaú-Goiana) in September 2007, covers about 0.67 km^2, and has been managed for sustainable use of natural resources (Brasil, 2007). The estuary encompasses a few small fishermen villages, and the local economy is based mainly on traditional fishing of mollusks, crustaceans and finfish. Outside MPA limits, agribusiness (planting, milling, and sugar and ethanol production) and mining (sand and limestone) contribute to the local economy (Ferreira et al., 2016; Barletta and Costa, 2009).

2.2. Water sampling and properties

A field trip for sampling surface water and recording water column parameters was carried out in December 14, 2015 under spring tide conditions at the peak of the dry season. This period was chosen for maximizing deterministic marine processes (tides) over probabilistic fluvial ones (river discharge). In the dry period, river outflow is smaller and steadier while tides rule over the transport of chemical substances. The main goal was to obtain water samples across the fresh to salt water gradient. An initial survey was carried out along the estuary for identifying the upper limit of salt intrusion. At the same day, a subsequent survey was carried out for sampling water for chemical analyses.

The first survey (5:30–7:00 a.m.) was carried out around high water. Vertical profiles (0.1 m resolution) of salinity, temperature, turbidity and chlorophyll were recorded every 1-km with a conductivity-temperature-depth (CTD) probe (JFE Advantech, model Rinko-Profiler with 10 Hz acquisition rate). Temperature and conductivity resolution were 0.001 °C and 0.001 mS cm^{-1}, respectively. Salinity was calculated from conductivity and temperature using PSS-78 (Practical Salinity Scale, UNESCO, 1981). Chlorophyll was recorded by a fluorometer with resolution of 0.01 ppb (uranine reference) while turbidity was recorded by a optical backscatter sensor with resolution of 0.01 FTU. The survey was 30 km long, and the upper limit of salt water intrusion was found to be at 27 km from the river mouth. Based on this knowledge, the second survey (11:00 a.m.–1:00 p.m.) was carried out around low water for recording CTD profiles every 1-km and collecting water samples every 3-km (Fig. 1), summing up 10 samples. Water samples (1 m deep) were taken in triplicate with 4 L pre-cleaned amber glass bottles attached to a stainless steel device. Water samples were collected at the bow just prior to boat stopping in order to avoid potential contamination from the boat engine oil.