Baseline

Aliphatic and polycyclic aromatic hydrocarbons in surface sediments collected from mangroves with different levels of urbanization in southern Brazil

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ABSTRACT

Three mangroves located in southern Brazil, Carijós (CA), Rio Tavares (RT) and Itacorubi (ITA), with distinct anthropogenic influences, were assessed with regard to the presence of aliphatic and polycyclic aromatic hydrocarbons (PAH). In this study, the *n*-alkane concentrations ranged from $1.9 \, \mu g \, g^{-1}$ (CA) to $55.6 \, \mu g \, g^{-1}$ (ITA) (dry weight). The carbon preference index (CPI) ranged from 2.1 to 7.9 and values for the terrestrial/aquatic ratio (TAR) were > 1. Thus, both indexes indicated the predominance of sediment of terrestrial origin, mainly comprised of higher plants. Concentrations of total PAH ranged from $6.8 \, ng \, g^{-1}$ (RT) to $437.3 \, ng \, g^{-1}$ (ITA). The PAH isomeric ratios indicated that these compounds originated mainly from pyrogenic sources. Nevertheless, levels of *n*-alkanes in the three mangroves were relatively low and they are considered typical of uncontaminated surface sediments, while the level of contamination with PAH was classified as low to moderate.

Mangroves are important areas of the world's coastal zones. In general, they are highly productive and provide spawning and nursery grounds for migratory species, besides playing a significant role in the global carbon cycle. Furthermore, they play a fundamental role in the sustainability of fishing communities, with high primary productivity, and they provide protection to the coastal zone, preventing erosion (Bianchi, 2007; Menezes et al., 2008; Trujillo and Thurman, 2011; Querino et al., 2013).

Brazil has one of the largest geographical zones in which mangroves are found in the world, stretching from the far north to the far south of the country. Santa Catarina Island in Florianópolis, lies within this area and it hosts important ecosystems, while social, ecological and economic factors, along with tourism, influence its numerous urban districts. In this context, the mangrove systems on the island have been subjected to the input of wastes and deforestation due to urbanization.

Santa Catarina Island hosts two of the largest mangrove and saltmarsh areas in the region. These lie within the preserved areas of the Carijós Ecological Station (CA), whose main rivers are the Ratones and Veríssimo, and the Pirajubaé Sustainable Marine Reserve, which is formed by the Tavares river (RT). A third mangrove area lies along the river Itacorubi (ITA), and this suffers the direct effects of urbanization (Pagliosa et al., 2005).

The Carijós Ecological Station is located in the northwest region of Santa Catarina Island. This is a federal Conservation Unit (CU) with a total area of 718 ha. The aim of this CU is to conserve the Ratones and Saco Grande mangroves, protecting them from the urbanization processes. Its Management Plan, approved in 2003, promotes a set of actions involving protection, research, monitoring and environmental education (Cordeiro, 2010). The Carijós mangrove lies in a preserved area, where commercial activities or the building of homes is not permitted, and visits are restricted to visitors for educational and research purposes. However, it has been reported that this Conservation Unit receives wastewater effluent from the surrounding urban areas.

The Rio Tavares basin, formed by the Tavares and Ribeirão da Fazenda rivers, lies in the south of Florianópolis (Souza-Mozimann and Roos-Oliveira, 1998). It is located within the Pirajubaé Extractive Marine Reserve, which is a federal CU designated for sustainable use. The Rio Tavares mangrove is widely used for fishing and mariculture.

The Itacorubi mangrove ecosystem is located around the southern limit of the area of mangrove distribution along the Brazilian coast and occupies a surface area of 2844.6 ha. This mangrove, supplied by the Itacorubi and Sertão rivers, is clearly the most urbanized region. The mangrove area has been subjected to numerous reclamation projects for the building and expansion of roads and residences. Reports of inputs of domestic sewage have been published by Sovernigo (2009).

Pollution from anthropogenic sources has a high potential impact

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on marine life and fisheries. It is therefore important to determine the extent of contamination and how it can affect marine life (Mostafa et al., 2009). Surface sediments provide an ideal natural archive of regional marine pollution, integrating inputs over the past few years as a result of the combined processes of deposition, runoff, water mixing, and sedimentation (Mandalakis et al., 2014). Thus, it is important to evaluate the surface sediments of coastal ecosystems to obtain information regarding their origin and composition in mangrove areas.

In this regard, chemical markers can be useful (Schulz and Zabel, 2006; Harji et al., 2008; Killops and Killops, 2005). Aliphatic hydrocarbons (AH) and polycyclic aromatic hydrocarbons (PAH) have been widely used to characterize organic matter, to distinguish between sources of contaminants and evaluate their degree of ecological impact, and to assess the conservation status of environments (Yunker et al., 2011; Hu et al., 2012; Gonul and Kucuksegin, 2012; Lima et al., 2012; Barbosa et al., 2016; Frena et al., 2016). Due to their hydrophobic nature AH and PAH are readily adsorbed onto particulate matter which will eventually settle (Maioli et al., 2011; Chen et al., 2013; Lima et al., 2012; Simoneit, 2004; Tarozo et al., 2010).

PAH are a typical group of compounds containing two or more aromatic rings, which are ubiquitous in the environment. Because of their persistence, carcinogenicity, toxicity and mutagenicity, PAH are regulated by the United States Environmental Protection Agency (USEPA) (Zedeck, 1980; He et al., 2014). One important source of PAH inputs to marine environments is pyrogenic material resulting from the combustion of organic matter associated with anthropogenic activities, including industrial processes and natural fires. PAH can also originate from petrogenic sources, such as petroleum transportation, offshore exploitation, oil spills or natural oil seeps (Mostafa et al., 2009). In general, anthropogenic sources of PAH can be classified using individual ratios based on the PAH composition and distribution as a function of the emission source (He et al., 2014; Mille et al., 2007; Yunker et al., 2002).

Despite the importance of coastal areas, few studies on the sediments of Santa Catarina Island, in particular those found in mangrove areas (Mater et al., 2004; Sovernigo, 2009), have been carried out. To the best of our knowledge, no previous studies using polycyclic aromatic hydrocarbons to investigate the influence of anthropogenic activity on the mangroves of Santa Catarina Island have been conducted. The aim of this study was to evaluate the distribution and sources of organic matter in sediments of mangroves with different levels of urbanization in southern Brazil and to provide baseline information that will be valuable for future environmental monitoring programs. The levels and sources of n-alkanes and PAH were determined in sediment samples collected from three mangroves on Santa Catarina Island: Itacorubi, Rio Tavares (Pirajubaé Extractive Marine Reserve) and Carijós (Ecological Station Carijós).

Nine surface sediment samples (0–10 cm) were collected from each mangrove using a stainless steel grab sampler. The sampling was performed in November 2013, resulting in twenty-seven samples. Sample locations are shown in Fig. 1. Sediments were freeze-dried and sieved in order to isolate the fine fraction (< 250 μm). All samples were placed in glass bottles and kept in a freezer at − 20 °C for further analysis.

A standard stock solution containing C_7-C_{40} n-alkanes was obtained from Supelco (Bellefonte, PA, USA). Perdeuterated hexadecane (Sigma Aldrich, St. Louis, USA) was employed as a recovery standard and perdeuterated triacontane (Sigma Aldrich, St. Louis, MO, USA) was used as the internal standard for n-alkanes. Working solutions were prepared by diluting the stock solution with hexane 95% (Tedia, Rio de Janeiro, RJ, Brazil).

A standard mixture of PAH containing acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g, h, i) perylene, benzo(k)fluoranthene, chrysene, dibenzo(a, h)anthracene, fluoranthene, fluorene, indene(1,2,3cd) pyrene, naphthalene, phenanthrene and pyrene was obtained from

AccuStandard (New Haven, CT, USA).

An internal standard mix of PAH containing the perdeuterated compounds acenaphthene-d_{10}, chrysene-d_{12}, naphthalene-d_8, perylene-d_{12} and phenanthrene-d_{10} was obtained from AccuStandard (New Haven, CT, USA). Working solutions were prepared by diluting the stock solution with dichloromethane 99.9% (Tedia, Rio de Janeiro, RJ, Brazil).

The extraction of analytes was performed according to an adapted version of the EPA Method 3550C (USEPA, 2007) and the procedure is described in Frena et al. (2016). The concentrated extract of n-alkanes was analyzed by gas chromatography with flame ionization detection (GC/FID) using a Shimadzu gas chromatograph model GC-2014 (Japan), with a Restek RTX-5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). An aliquot (1.0 μL) of the sample extract was injected into the GC/FID applying the splitless mode (for 1 min). The oven program was a temperature of 50 °C held for 5 min increasing to 300 °C at 6 °C min^{-1} which was held for 10 min. Hydrogen was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. The injector temperature was maintained at 280 °C and the detector temperature at 300 °C. The identification of individual n-alkanes was based on the calibration curves obtained for standard solutions prior to the analysis. The calibration curves were constructed in the range of 1–15 μg mL^{-1} with three replicates, using standard solutions containing C_7 to C_{40}. Quantification was based on response factors of authentic standards relative to perdeuterated hexadecane-d_{16} at 100 μg mL^{-1}.

The PAH extract was analyzed by gas chromatography coupled to mass spectrometry (GC–MS) - using a Thermo Finnigan model Trace GC Ultra GC interfaced to a Thermo Finnigan Polaris Q (ion trap mass analyzer) - with a Restek RTX-5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). An aliquot (1.0 μL) of the sample extract was injected into the GC–MS instrument applying the splitless mode with an initial time of 1 min (the split ratio was fixed at 1:50). The oven program was a temperature at 50 °C held for 5 min, increasing to 230 °C at 5 °C min^{-1} and then to 250 °C at 2 °C min^{-1}, and finally from 250 °C to 300 °C, which was held for 8 min. Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. The injector temperature was maintained at 250 °C. An electron impact ion source with an electron energy of 70 eV was used for the MS, and a mass range of 50 to 500 amu was scanned.

Compound identification was based on comparing individual mass spectra and GC retention times to authentic standards analyzed under the same conditions as the samples. In order to check the performance of the chromatographic method and quantify the PAH compounds, calibration curves were constructed in the range of 10–750 ng mL^{-1}, with three replicates, using standard solutions containing the 16 PAH (EPA priority pollutants, shown in Table 3). A fortified sample with the addition of the perdeuterated mixture at 100 ng mL^{-1} was used to aid the quantification of the compounds.

Samples were spiked with recovery standards (p-terphenyl-d_{14} for PAH and perdeuterated hexadecane-d_{16} for n-alkanes) prior to extraction. For both the AH and PAH fractions, surrogate standard recoveries were higher than 70% for all samples.

Quality assurance procedures included obtaining calibration curves for the quantification of n-alkanes and PAH in the sediment samples. n-alkanes and PAH were quantified using the internal calibration method based on six and seven-point calibration curves, respectively, for individual compounds. Calibration was conducted daily; the first injection after instrument tuning was a calibration standard, followed by a blank. Sample analysis was performed only after a correct instrument response was obtained. In order to evaluate the precision, three replicate analyses of one sediment sample from each mangrove were performed and the relative standard deviations were lower than 15%.

The detection limit was estimated as 3 s/S, where s is the standard deviation of the linear coefficient calculated from the calibration curve and S is the slope of the curve. The quantification limit was established