A critical and comparative appraisal of polycyclic aromatic hydrocarbons in sediments and suspended particulate material from a large South American subtropical estuary[☆]

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ABSTRACT

The Paranaguá Estuarine Complex (PEC) is an important socioeconomic estuary of the Brazilian coast that is influenced by the input of pollutants like polycyclic aromatic hydrocarbons (PAHs). Because of the apparent lack of comparative studies involving PAHs in different estuarine compartments, the aim of this study was to determine and compare PAH concentrations in surface sediment and suspended particulate material (SPM) in the PEC to evaluate their behaviour, compositions, sources and spatial distributions. The total PAH concentrations in the sediment ranged from 0.6 to 63.8 ng g^{-1} (dry weight), whereas in the SPM these concentrations ranged from 391 to 4164 ng g^{-1}. Diagnostic ratios suggest distinct sources of PAHs to sediments (i.e., pyrolytic sources) and SPM (i.e., petrogenic sources such as vessel traffic). Thus, the recent introduction of PAHs is more clearly indicated in the SPM since oil related-compounds (e.g., alkyl-PAHs) remain present in similar concentrations. Further, this matrix may better reflect the current state of the environment at the time of sampling because of the absence of significant degradation.

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1. Introduction

Estuarine systems are a natural environment of biological richness that are key regions in the dynamics of continental and oceanic sediments because of the large amount of organic matter and suspended particles present from drainage basins close to human activity. Therefore, estuaries act as transition areas between the watershed and the continental shelf, where pollutants can be accumulated, deposited and exported to the open ocean (Luo et al., 2006; Wang et al., 2013; Liu et al., 2014).

The Paranaguá Estuarine Complex (PEC) is a subtropical environment located on the southwest Atlantic coast of Brazil and is considered as an important estuary of this country because of its economic and social relevance, including its ties to industry, urban and harbour activities. It has also been the location of some environmental disasters involving oil tankers, especially *M/T Vicuña* in 2004, which spilt more than 4000 tonnes of fuel in the region (ITOPF, 2014).

Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants of worldwide distribution and are monitored extensively because some of which show mutagenic and/or carcinogenic potential. In this respect, the US Environmental Protection Agency (USEPA) has listed 16 of these compounds as priority control pollutants (Manoli et al., 2000). They reach the marine environment from the direct input of petroleum and its by-products, and as residues of the incomplete combustion of organic matter (i.e., coal, oil and biomass) (Guo et al., 2007; Maioli et al., 2011). These hydrocarbons are also associated with natural sources such as oil seeps, erosion of old sediments containing these compounds, spontaneous forest fires and diagenetic changes from pre-existing hydrocarbons (Saha et al., 2009).

Because some PAHs possess relative resistance to degradation processes, they convey valuable information concerning their origin, fate, forms of transport and their transformation in the environment. For this reason, they are classified as organic geochemical markers (Takada and Eganhouse, 1998; Chizhova et al., 2013). PAHs are components in fossil organic matter as products of various post-depositional geochemical reactions, such as the transformation of steroids, and can be found in crude oils because

of their stable molecular structure, which can resist the variable conditions of diagenetic processes over geological time (Takada and Eganhouse, 1998).

Because of their hydrophobicity, PAHs tend to associate with both suspended particulate material (SPM) at the water column as well as bottom sediment (Readman et al., 1984; Landrum and Robbins, 1990; Montuori and Triassi, 2012), which is recognized as the destination where some contaminants will be deposited and remain for long periods of time (Hostettler et al., 1999). Recently, SPMs have been analyzed worldwide because they reflect the current state of the environment at the time of sampling, which can be subject to momentary changes in the physical, chemical and geological forcings as a result of rainfall, tides, river discharge, weathering, erosion, etc. (Guo et al., 2007; Chizhova et al., 2013; Yang et al., 2013). Previous studies have shown that high PAH concentrations, mostly from human activities, have been detected in Brazilian estuarine environments (e.g., Medeiros and Bícego, 2004; Martins et al., 2011, 2015). However, a critical evaluation of the distribution and behaviour of PAHs in multiple compartments of subtropical estuarine systems that is associated with an integrative interpretation of PAH composition and the physico-chemical properties of the water column is lacking, which obstructs our current understanding of these pollutants.

Therefore, the aim of this study was to determine the PAH concentrations in surface sediment and SPM samples from a large subtropical estuary (Paranaguá Estuarine Complex) and to evaluate the sources of these compounds and their distribution in both matrices. It was hypothesized that if the harbour activity is the predominant anthropogenic process acting in the PEC, then high levels of low molecular weight PAHs, which are commonly associated with the direct introduction of oil and by-products, will be found in both the sediments and SPM with similar distributions of the individual compounds. The results of the PAH concentrations in SPM and sediment samples, in particular, may be compared with environmental quality guidelines, which should be helpful in establishing more efficient environmental policies in estuarine environments along coastlines worldwide.

2. Study area

The Paranaguá Estuarine Complex − PEC (25°30′S; 48°25′W, Fig. 1) is a humid subtropical environment located in the north-central sector of the Paraná state coast, Southern Brazil. The PEC has approximately 612 km^2 of total area and it can be divided into two main water bodies: (i) the bays of Paranaguá and Antonina, where this study was performed, and (ii) the bays of Laranjeiras, Guaraqueçaba and Pinheiros, which are located in the northern section and considered to be a more preserved area (Lana et al., 2001; Combi et al., 2013). Approximately 200,000 people occupy the estuarine shorelines, with the largest human settlement concentrated in the cities of Pontal do Paraná, Antonina and Paranaguá (IBGE, 2013). Coexisting in the study area are urban activities (e.g., disordered human occupation, disposal of domestic wastewater without treatment, incorrect disposed of solid waste), port, fishing, industrial activities (e.g., production of fertilizers, storage of chemical products and grains), agriculture and dredging. According to data provided by the Administration of Paranaguá and Antonina Harbors (APPA, 2015), the port activity in the PEC is responsible for mooring 2456 large ships per year, resulting in an average of 205 ships moored per month in the ports of Paranaguá and Antonina. This includes containers, bulk cargo and petroleum products. Collectively, this use of the PEC may already suggest a strong anthropogenic impact that may affect the environmental quality of this estuarine system.

The movement of tides and the fluvial input are the dominant

processes affecting the water currents and circulation in the estuary (Knoppers et al., 1987). The inner region of the PEC includes sediments ranging from clay to silt, with the exception of the mouths of the rivers, where a predominance of sands is present. In areas where there is a strong marine influence, the sediments vary from moderately to well-sorted fine to medium sands, whereas the central estuary portion includes fine to very fine sand and fine silts (Lamour and Soares, 2007).

3. Material and methods

3.1. Sampling

The sampling grid was defined along a previously verified salinity gradient (Lana et al., 2001). Geographically, the sampling sites cover the bays of Paranaguá and Antonina, with sampling sites close to the anthropogenic sources and in the navigation channel between the ports and the shallow continental shelf.

In February 2012, 15 sites in the PEC were sampled during an ebb spring tide (Fig. 1). Subsurface water samples were collected (0−1 m) to obtain the SPM. Amber glasses, previously cleaned and decontaminated, were used to obtain the water samples. For each site, 3.5 L were filtered with GF/F Whatman® ($\varnothing = 0.45$ μm) glass-fiber filters, previously calcinated at 450 °C for 12 h, then cooled in a desiccator and weighed individually. The SPM retained on the membrane were stored frozen and freeze-dried for the determination of PAHs. The SPM concentration was determined using a gravimetric method. Water samples were also collected to determine the dissolved oxygen (DO) and pH levels.

Additionally, the surface layer (0−2 cm) from the bottom sediment was collected at each site using a stainless steel bottom sampler type *Petite Ponar* with a 0.04 m^2 sampling area. After collection, the sediments were freeze-dried, macerated and placed in previously cleaned glass vials for further analysis.

3.2. Analytical procedure

3.2.1. Water column parameters

The temperature, salinity and depth were obtained *in situ* with CTD profiles (CastAway P/N 400313 SonTek). The dissolved oxygen (DO) analysis followed the titration method described by Grasshoff et al. (1999) using an automatic titrator (Metrohm 702 SM Titrino). The pH values were obtained using a pH meter (Denver UP-25).

3.2.2. Sample extraction and instrumental analysis of PAHs

In this study, the 16 PAHs classified by the USEPA as a priority for environmental monitoring were analyzed (2−3 rings: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; 4−6 rings: fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene), additional parental PAHs (dibenzotiophene, benzo[c]phenanthrene, benzo[j]fluoranthene, benzo[e]pyrene and benzo[b]chrysene), alkylated homologs (C$_1$-, C$_2$- and C$_3$-naphthalenes, C$_1$- and C$_2$-fluorene, C$_1$ and C$_2$-dibenzotiophene, C$_1$- and C$_2$-phenanthrenes, C$_1$-fluoranthene, C$_1$-pyrene, C$_1$ and C$_2$-chrysene), and two biogenic/diagenetic PAHs (perylene and retene).

The analytical procedure used for the PAHs in the marine sediments and SPM analysis was based on the United Nations Environment Programme method (UNEP, 1992). Bulk sediment samples and filters containing the SPM were individually extracted in a Soxhlet apparatus for 8 h with 80 mL of a 50% mixture of *n*-hexane and dichloromethane (DCM). In each extraction flask, surrogate standards (naphthalene-d$_8$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$, chrysene-d$_{12}$ and perylene-d$_{12}$; AccuStandard Z-014J Internal