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Distribution, sources and toxicity potential of hydrocarbons in harbor sediments: A regional assessment in SE Brazil

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ABSTRACT

Aliphatic and polycyclic aromatic hydrocarbons (PAHs) were quantified in harbors sediments from SE Brazil. The aims were to (i) compare harbors with distinct sizes and under the influence of different environmental pressures with respect to the sources and level of hydrocarbon contamination and (ii) evaluate the potential of adverse biological effects of sediment contamination by PAHs, based on sediment quality guidelines and toxicity equivalence quotient. The concentrations of total aliphatics (39.9 μg g^{-1}; 22.9–113 μg g^{-1}) and total PAHs (727 ng g^{-1}; 366–1760 ng g^{-1}) varied according to the size of and urban development around each harbor. Mixed contamination by petrogenic and pyrolytic hydrocarbons, and input of biogenic compounds, indicated the influence of both harbor activities and a myriad of urban, industrial and atmospheric inputs. The quality of sediment poses a risk to benthic biological communities, and, if dredged, this material may cause environmental damage in the waste disposal area.

1. Introduction

Human well-being has benefited from services provided by ecosystems. However, at the same time, human activities have been the responsible for significant alterations and degradation of those ecosystems (Ruddiman, 2013). Transformations in functioning ecosystems are occurring in an unprecedented manner in the last 50 years, and are more pronounced in the coastal zone, where over 75% of the world's population is concentrated (Vitousek et al., 1997). Soil use change, water management practices, urban and industrial developments and the delivery of organic and inorganic contaminants and nutrients to water bodies are among the human interventions that can pose a threat to the health of coastal ecosystems (Crossland et al., 2005; Ramesh et al., 2015).

Several classes of inorganic and organic contaminants are direct or indirect by-products of human activities. Among them, anthropogenic hydrocarbons derived from the production, transport and consumption of oil and derivatives have been responsible for the chronic or acute contamination of air, biota, water and soil/sediment worldwide (Bigus et al., 2014; Ruddiman, 2013; Tobiszewski and Namieśnik, 2012; Wang et al., 2013; Wolska et al., 2011). Of particular interest are polycyclic aromatic hydrocarbons (PAHs), whose ubiquity, persistency and biological effects (carcinogenicity, mutagenicity and/or endocrine disrupting action) have rendered them priority pollutants of environmental concern (e.g., Bigus et al., 2014; Lohmann et al., 2013; Neff, 2002; UNEP, 2003; Wang et al., 2013; Yunker et al., 2002). Non-aromatic hydrocarbons provide complementary information to that provided by PAHs, namely the characterization of petrogenic inputs and the effects of weathering and/or biodegradation on oil composition (Bajt, 2012; Bouloubassi and Saliot, 1993; Figueiredo et al., 2008; Lipiatou and Saliot, 1991; Readman et al., 2002; Tolosa et al., 2004; Wakeham, 1996). On the other hand, little attention has been given to the toxicity of the aliphatic fraction of hydrocarbons, although literature data show that light (and soluble) compounds and fractions of the 'unresolved complex mixture' (UCM) have toxic (sub-lethal) effects and may bioaccumulate in benthic invertebrates (Du et al., 2012; Frysinger et al., 2003; Gough and Rowland, 1990; Rial et al., 2013; Thomas et al., 1995).

The discrimination of hydrocarbon sources (pyrolytic, petrogenic, diagenetic or even biogenic) and their toxicity potential is necessary to evaluate the environmental effects of PAHs. On one hand, diagnostic ratios based on properties such as the number of aromatic rings,

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presence of alkyl ramifications and relative resistance to thermal decomposition of individual compounds are largely considered as source assignments of PAHs (e.g., Tobiszewski and Namieśnik, 2012; Wang et al., 1999a; Yunker et al., 2002). However, this approach may be challenging, as observed, for example, in sediments from tropical and chronically contaminated regions (e.g. Massone et al., 2013; Wagener et al., 2012). Despite the origin of the hydrocarbon, sediment quality guidelines (SQGs) based on toxicity thresholds can be used to rank the toxicity of a sediment and, consequently, the potential adverse biological effects based on PAH chemical data (Bay et al., 2012; Buchman, 2008). Another approach to evaluate sediment quality are toxicity equivalent quotients (TEQ), calculated by summing up the normalized concentration of individual PAHs to that of benzo(*a*)pyrene, which exhibits the highest adverse biological effects among commonly quantified PAHs (Dong et al., 2014; Lee and Yi, 1999; Peters et al., 1999; WHO, 1998).

In the hydrocarbon contamination and ecosystem health scenario, harbors or port complexes deserve special attention, since they may be affected by direct and indirect anthropogenic hydrocarbon sources. Ship operations (loading/unloading, illegal bilge oil discharges) and/or oil spills from tanker and non-tanker accidents are the main direct sources of contamination by hydrocarbons, whereas indirect sources include urban runoff, oil inputs from sewage-impacted urban rivers and local/regional atmospheric fallout of products originated from fossil fuel combustion by ships/vehicles and other combustion-related industrial processes. Indirect sources of contamination are particularly relevant when the port is located in an urbanized region (Dong et al., 2014; Martínez-Lladó et al., 2007; Medeiros and Bícego, 2004; Oliveira and Madureira, 2011; Smith et al., 2009).

In the present study, the sources and distribution of aliphatic and polycyclic aromatic hydrocarbons (PAHs), as well as the potential toxicity of PAHs, were assessed in eight major port complexes or harbors located on the Southeastern coast of Brazil, the most industrialized region of the country (Fig. 1). The major goals herein were to reveal the major pressures, both internal and external, responsible for compromising local environmental health in the considered harbor areas and to evaluate the effectiveness of common guidelines for sediment quality, in order to contribute to a better management of the harbor activities. A total of 90 surface sediment samples was collected during two sampling campaigns conducted in 2009 and 2010. The harbors were selected based on their sizes, type and amount of cargo and level of economic activity in their surroundings. For some of the harbors, previous information regarding sediment contamination is available, such as Santos, São Sebastião and Rio de Janeiro, whereas for others virtually none is available.

2. Materials and methods

2.1. Studied regions

Eight harbor regions were considered in the present study (Fig. 1). The description and general characteristics of each studied area is listed below, alongside their location from south to north in the SE coastal region of Brazil. Detailed information on the sampling locations of each area is provided as Supplementary material (Figs. S1–S8, Supplementary material).

The Santos port complex (Sa) is located on the southern coast of the state of São Paulo. It is the largest in the country and moves cargo from different sectors, such as metallurgy, chemical and mechanical industries and primary commodities, among others. The harbor is adjacent to a relatively large urban area. In addition, the petrochemical complex of Cubatão is located nearby, where other large terminals are in operation. Consequently, contamination by hydrocarbon and domestic and industrial wastes in the port complex and in the Santos-São Vicente estuarine region and adjacent bay is relatively well documented (Bícego et al., 2006; Bordon et al., 2011; Buruaem et al., 2013; Martins et al., 2011; Martins et al., 2008b; Medeiros and Bícego, 2004; Nishigima et al., 2001).

The São Sebastião (SS) harbor is located in a 25-km wide channel on the northern coast of São Paulo, where intense tourist, aquaculture, docking and fisheries activities occur (Pereira et al., 2007). This harbor encompasses the second largest commercial port of the state of São Paulo (mainly minerals) and the largest oil terminal (TEBAR) in the country. In the last years, accidents and harbor activities were the main causes of local anthropogenic contamination (Silva and Bícego, 2010; Zanardi et al., 1998; Zanardi-Lamardo et al., 2013).

Regarding the southern region of the state of Rio de Janeiro, two harbors were chosen. The Angra dos Reis harbor (An) is able to receive up to 29,000 deadweight tonnage (DWT) vessels, mainly serving activities from the steel industry. The Sepetiba Harbor (Sp), located in a bay with the same name, is a mid-sized port (13th place in the national rank) whose activities are focused on five business segments:

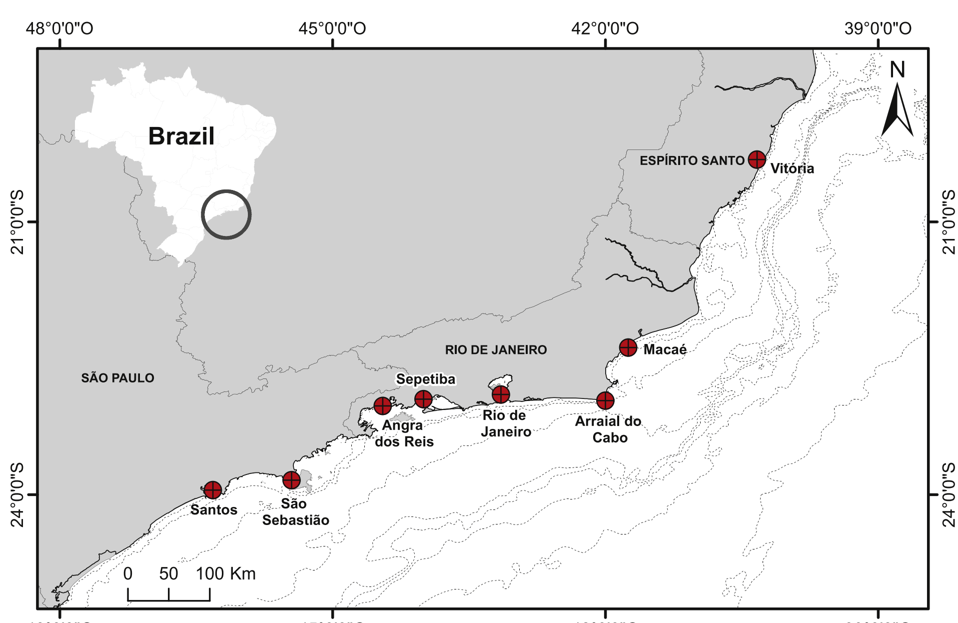

Fig. 1. Location of the eight harbor regions in SE Brazil. Detailed position of the sampling stations can be found in the supplementary information.