Marine Pollution Bulletin 95 (2015) 183–194

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Sedimentary hydrocarbons and sterols in a South Atlantic estuarine/shallow continental shelf transitional environment under oil terminal and grain port influences

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ARTICLE INFO

Article history:
Received 23 January 2015
Revised 5 April 2015
Accepted 11 April 2015
Available online 29 April 2015

Keywords:
Hydrocarbons
Sterols
Sediments
Paranaguá Bay
South Atlantic

ABSTRACT

Sterols and hydrocarbons were determined in the surface sediments from the transitional environment between Paranaguá Bay and the shallow continental shelf in the South Atlantic to assess the sources of organic matter (OM) and the contamination status of an area exposed to multiple anthropogenic inputs. Total aliphatic hydrocarbon concentrations were less than 10 μg g^{-1}, which is typical of unpolluted sediments, and related to recent inputs from higher terrestrial plants. Total polycyclic aromatic hydrocarbon ranged from <DL to 14.41 ng g^{-1} (dry weight), which was predominantly derived from combustion with non-detectable levels occurring in 65% of the samples. Sterols typically related to marine sources predominated in the analysed sediments. Hence, the study area was protected from human activity. The relative absence of anthropogenic input and OM preservation clearly indicate that the organic markers analysed can be used to investigate the biogenic input of sedimentary OM in the study area.

1. Introduction

The environmental conditions of coastal areas are a cause for great concern worldwide due to the exponential increase of human activities related to industrial and urban development, trade, dredging, tourism, and agriculture over the last century. These activities have produced large amounts of anthropogenic wastes including sewage, trace elements, and organic contaminants (Clark, 2001; Islam and Tanaka, 2004).

Organic markers such as hydrocarbons and sterols have been used to determine the origin of organic matter (OM) in estuarine systems and as tracers for human activities along the coastal areas of industrial and urban centres among several geographic regions (e.g., Muniz et al., 2006; Amorri et al., 2011; Albano et al., 2013). Marine organisms or terrestrial plants can synthesise these molecules; alternatively, they can be produced by human activities and reach the oceans through routes such as rivers, continental runoffs, and atmospheric deposition as well as sewage and petroleum inputs. Once in the ocean, these organic markers can be transported by currents and deposited in sediments where they are often preserved (Yunker et al., 1995).

Sterols are organic compounds typically used to distinguish aquatic and terrestrial OM contributions from "biogenic" sources (Volkman, 2005) and indicate faecal material present in sewage inputs to coastal areas (Leeming et al., 1998; Readman et al., 2005). Several species of zooplankton, phytoplankton (e.g., microalgae, bacteria, dinoflagellates, and diatoms), and higher plants are the primary sources of "biogenic" sterols (Villinski et al., 2008). Conversely, mammals (especially humans) are the primary source of "faecal" sterols in estuary sediments (Grimalt et al., 1990; Venkatesan and Kaplan, 1990).

Aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs) have been used to assess petroleum and petroleum by-product contamination in estuarine environments (Silva and Bícego, 2010) as well as to distinguish the input of aquatic and terrestrial biogenic OM in coastal sediments (Aboul-Kassim and Simoneit, 1996; Wang et al., 2001). The anthropogenic sources of hydrocarbons in estuarine environments include the combustion of fossil fuels, sewage input, and vehicular emissions as well as petroleum and related by-product spills (Volkman et al., 1992; Yunker et al., 2002). Biosynthesis processes in aquatic organisms, higher plants, and diagenetic processes are responsible for the input of biogenic AHs (UNEP, 1992; Clark, 2001). In particular, PAHs represent the most widely studied hydrocarbons due to their mutagenic and carcinogenic effects to biota as well as their environmental classification as persistent organic pollutants (Yang et al., 2008).

Recent studies of the South Atlantic, particularly the Paranaguá Estuarine System (PES), have revealed the influence of human

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http://dx.doi.org/10.1016/j.marpolbul.2015.04.024
0025-326X/

settlements (i.e., 180,000 people according to IBGE, 2009) and industrial activities related to the presence of oil terminals and grain ports as well as the progressive dumping of domestic and industrial sewage (Martins et al., 2010a, 2011a), petroleum products (Abreu-Mota et al., 2014), and organic pollutants such as polychlorinated biphenyls (Combi et al., 2013).

The transitional environment between Paranaguá Bay and the shallow continental shelf (depth < 30 m) is economically important because it corresponds to the connection between the estuary (where the ports of Paranaguá and Antonina are located) and the ocean. The two major entrances are located to the north and the south of Mel Island, the third most popular tourist destination in Paraná state, with more than 140,000 tourists per year (Angulo et al., 2006; Fuzetti and Corrêa, 2009). Both entrances have been used as navigation channels to the port of Paranaguá since the 16th century; however, this navigation channel, particularly the inner continental shelf and the outer portion of Paranaguá Bay (Fig. 1), contains critical shoaling regions and is dredged annually to a mean depth of 15 m (Lamour et al., 2007).

Due to the size of the PES (water volume of approximately 2×10^9 m^3, covering an area of 612 km^2), we were unable to collect data in several regions, including our selected study area, with regard to sedimentary geochemical markers and organic contaminants. Nevertheless, this study analysed the concentrations of sterols and hydrocarbons in the surface sediments to assess the sources of OM and the contamination status at selected sites in a large South American estuarine environment with multiple anthropogenic inputs.

2. Study area

The PES is located along the north central coast of Paraná, South Brazil between 25°16′S and 48°17′W (Fig. 1). This estuary is bounded by two major axes: the 56-km-long Paranaguá Bay along the east–west axis and the 30-km-long Laranjeiras Bay along the north–south axis. The tidal regime in the region is semi-diurnal; the tide reaches up to 2 m in the spring (Lana et al., 2001). Mangroves, marshes, and extensive tidal plains border the region. Unvegetated tidal flats are the most common feature of this estuarine system (Egres et al., 2012).

The Serra do Mar Mountains and the Atlantic Forest surround the PES, which is connected to the ocean by three channels: (i) the Galheta Channel; (ii) the Barra Norte Channel between Mel and Peças Islands; and (iii) the Superagüi Channel between Peças and Superagüi Islands (Lana et al., 2001). The Galheta Channel is the most important link between the estuary and the continental shelf and periodically dredged to allow ships to enter Paranaguá harbour.

Human settlement of this area occurred relatively rapidly and in a disorderly manner. Cities such as Antonina, Guaraqueçaba, Morretes, Paranaguá, and Pontal do Paraná are located along the margins of the PES, with a total population of approximately 191,700 inhabitants, 133,600 of whom live in Paranaguá city (IBGE, 2009). The population intensified after the construction of the port of Paranaguá, which is currently the largest grain exportation site in Latin America, with shiploads totalling more than 25 million tons (Santos et al., 2009; Martins et al., 2010a,b). Several marinas are also located along the estuary, which are frequented

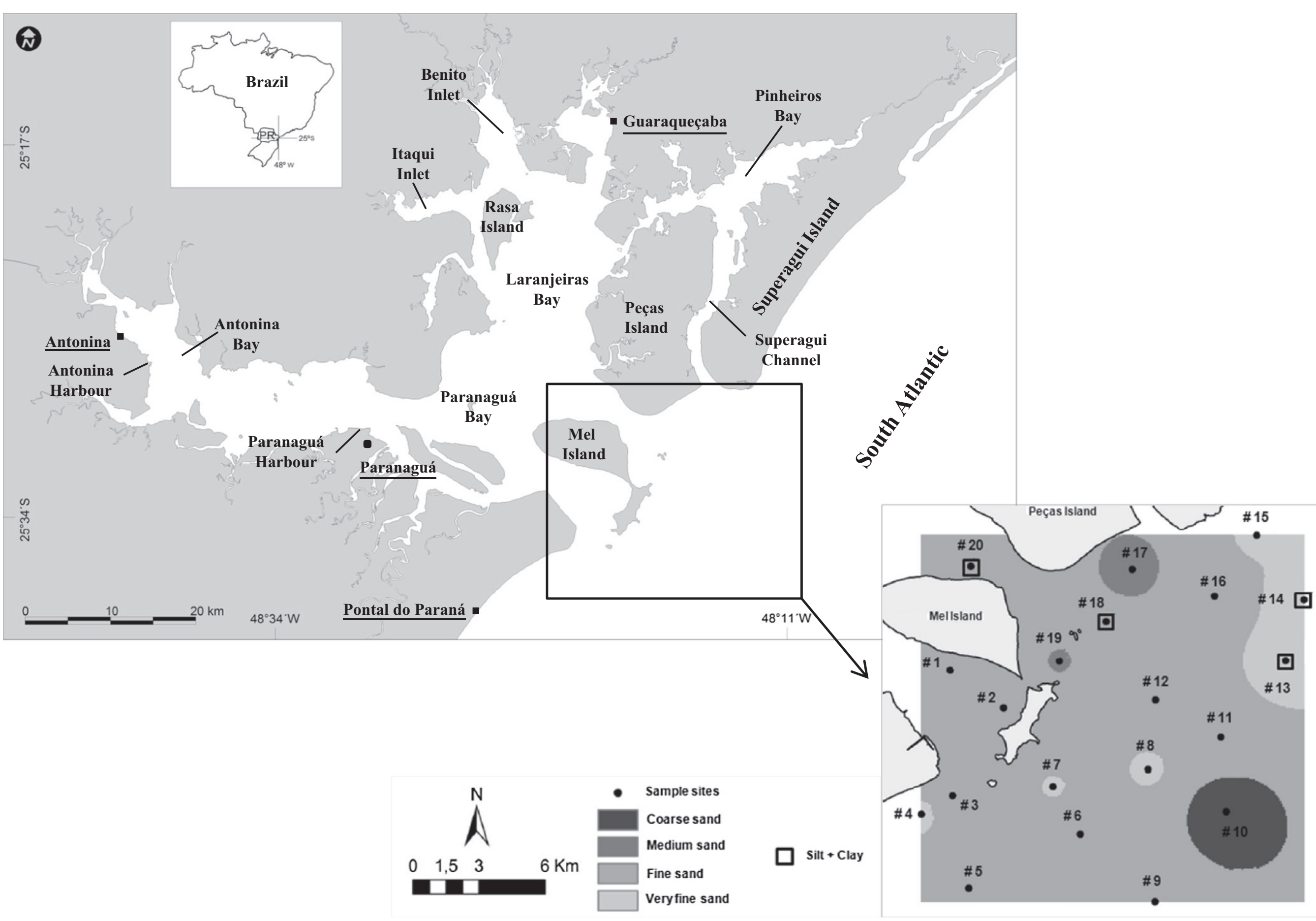

Fig. 1. Map of the study area showing grain size and the sediment sampling sites in the transitional environment between Paranaguá Bay and the shallow continental shelf in the South Atlantic, Brazil.