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SCIENCE DIRECT

Environment International 31 (2005) 77–87

ENVIRONMENT INTERNATIONAL

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Natural and anthropogenic hydrocarbon inputs to sediments of Patos Lagoon Estuary, Brazil

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Received 2 May 2004; accepted 6 July 2004
Available online 15 September 2004

Abstract

The Patos Lagoon Estuary, southern Brazil, is an area of environmental interest not only because of tourism, but also because of the presence of the second major port of Brazil, with the related industrial and shipping activities. Thus, potential hydrocarbon pollution was examined in this study. Sediment samples were collected at 10 sites in the estuary, extracted, and analyzed by GC-FID and GC-MS for composition and concentration of the following organic geochemical markers: normal and isoprenoid alkanes, petroleum biomarkers, linear alkylbenzenes (LABs), and polycyclic aromatic hydrocarbons (PAHs). The total concentrations varied from 1.1 to 129.6 μg g^{-1} for aliphatic hydrocarbons, from 17.8 to 4510.6 ng g^{-1} for petroleum biomarkers, from 3.2 to 1601.9 ng g^{-1} for LABs, and from 37.7 to 11,779.9 ng g^{-1} for PAHs. Natural hydrocarbons were mainly derived from planktonic inputs due to a usual development of blooms in the estuary. Terrestrial plant wax compounds prevailed at sites located far from Rio Grande City and subject to stronger currents. Anthropogenic hydrocarbons are related to combustion/pyrolysis processes of fossil fuel, release of unburned oil products and domestic/industrial waste outfalls. Anthropogenic hydrocarbon inputs were more apparent at sites associated with industrial discharges (petroleum distributor and refinery), shipping activities (dry docking), and sewage outfalls (sewage). The overall concentrations of anthropogenic hydrocarbons revealed moderate to high hydrocarbon pollution in the study area.

Keywords: Hydrocarbons; Sediment; Anthropogenic; Biogenic; Patos Lagoon Estuary; Brazil

1. Introduction

Estuarine areas serve as final receptors of natural and anthropogenic organic matter derived from land and carried by river and atmosphere (Gagosian and Peltzer, 1986; Bouloubassi and Saliot, 1993). Hydrocarbons are important components of land-derived organic inputs towards coastal areas. Studies on hydrocarbons in the aquatic environment can be based on the analysis of the water column, organisms and sediments. However, sedimentary hydrocarbons have received special attention because these compounds are readily adsorbed onto particulate matter, and bottom sediments ultimately act as a reservoir of hydrophobic contaminants (Meyers, 1976; Volkman et al., 1992). A large fraction of these compounds derives from terrestrial and marine biological sources, such as vascular plants, animals, bacteria, macro- and microalgae (Saliot, 1981). Certain hydrocarbons are produced from bacterial and chemical degradation of naturally occurring lipids. However, petroleum-related sources also contribute to significant, and sometimes major, hydrocarbon inputs. As major constituents of petroleum (Tissot and Welte, 1978; Philp, 1985), hydrocarbons may enter the marine environment through

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0160-4120/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envint.2004.07.001

riverine discharges, shipping activities, sewage disposal, offshore oil production and transport, oil spills, as well as from pyrolysis/combustion of fossil fuel such as in vehicles, power plants, industrial processes, and refuse burning (Yunker et al., 1993; Gogou et al., 1996; Wakeham, 1996; Azevedo et al., 2002). Hydrocarbons are commonly found in the environment as complex mixtures deriving from multiple sources. Therefore, the confident discrimination between biogenic and anthropogenic origin, as well as the further recognition of inputs from petrogenic, pyrogenic and domestic waste sources, requires the use of geochemical or molecular markers. Geochemical or molecular markers are organic compounds that maintain the "signature" of their origins and structural modifications which occurred during transport. The use of these compounds is also needed because various hydrocarbon classes show differences in their residence time, stability, transport mechanisms and fate, depending on their physical–chemical properties and sources (Simoneit, 1978; Bouloubassi and Saliot, 1993).

The Patos Lagoon is the largest lagoon in South America (10,360 km^2). An estuary is formed in the outlet of the lagoon to the Atlantic Ocean, which occupies approximately 10% of its total area. Fig. 1 shows the estuarine region, which is shallow (generally less than 2 m), except in the entrance channel, where water depths can reach 12–14 m. The estuarine circulation is forced mostly by winds and river discharge (Moller et al., 2001). Current velocities in the entrance channel are strong at 1.5 m s^{-1} during periods of high river discharge (Fernandes et al., 2002) and predominantly southward (Moller et al., 2001). Currents are generally much weaker over the shallow regions.

The estuary is exposed to significant anthropogenic effects from the Rio Grande Superport (the second major port of Brazil, Mirlean et al., 2003a,b) and both industrial (oil refinery and terminal, fertilizer-producing plants, fishery industries) and urban areas of Rio Grande City (Mirlean et al., 2003a). The major sewage effluent of Rio Grande City (185,000 inhabitants) is disposed untreated in the estuary (Baumgarten et al., 1998). Several other smaller effluents (domestic, fluvial and industrial) are also disposed in shallow marginal bays along the area (Baumgarten et al., 2001).

The majority of the studies to date in Patos Lagoon focused on water quality and composition, organic matter and nutrient enrichment (Baumgarten et al., 2001). There are few studies on the chemical composition of the sediments in the estuary and they focused primarily on inorganic components (Baisch et al., 1989; Nienscheski et

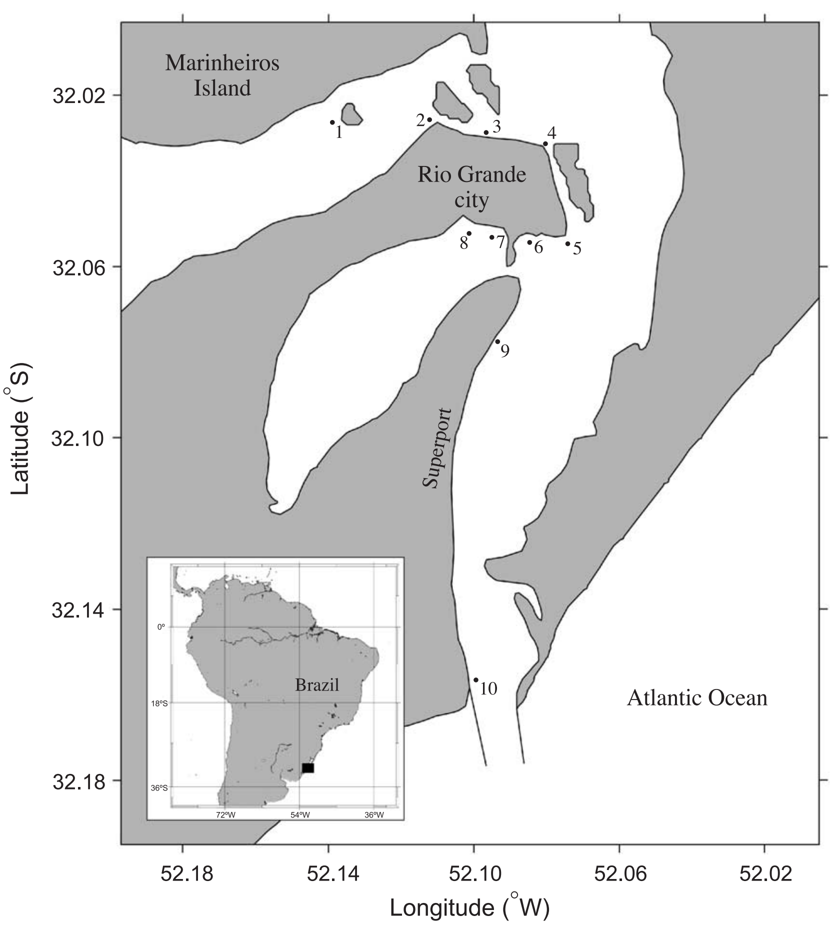

Fig. 1. Map of Patos Lagoon Estuary showing the sediment sampling sites. #1—Pombas Island; #2—marina; #3—market; #4—dry docking; #5—fertilizer industry; #6—sewage; #7—petroleum distributor; #8—petroleum refinery; #9—oil terminal; #10—lagoon mouth.