



## Coupling spectroscopic and chromatographic techniques for evaluation of the depositional history of hydrocarbons in a subtropical estuary



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### ABSTRACT

Spectroscopic and chromatographic techniques can be used together to evaluate hydrocarbon inputs to coastal environments such as the Paranaguá estuarine system (PES), located in the SW Atlantic, Brazil. Historical inputs of aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs) were analyzed using two sediment cores from the PES. The AHs were related to the presence of biogenic organic matter and degraded oil residues. The PAHs were associated with mixed sources. The highest hydrocarbon concentrations were related to oil spills, while relatively low levels could be attributed to the decrease in oil usage during the global oil crisis. The results of electron paramagnetic resonance were in agreement with the absolute AHs and PAHs concentrations measured by chromatographic techniques, while near-infrared spectroscopy results were consistent with unresolved complex mixture (UCM)/total *n*-alkanes ratios. These findings suggest that the use of a combination of techniques can increase the accuracy of assessment of contamination in sediments.

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### 1. Introduction

Petroleum hydrocarbons are commonly found as ubiquitous constituents of coastal environments, because they are accumulated in estuarine sediments and are preserved over time. As sediments act as sinks of petroleum hydrocarbons, sediment cores have been widely used to reconstruct the geochemical histories of estuarine systems (Hostettler et al., 1999).

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants

prevalent in the recent sediments of estuaries (Pereira et al., 1999), and are derived from anthropogenic sources such as the combustion of biomass and fossil fuels (pyrogenic sources) (Hites et al., 1977), as well as spillages of petroleum and its byproducts (petrogenic sources) (Gogou et al., 2000). The United States Environmental Protection Agency (USEPA) includes sixteen PAHs on the lists of priority pollutants, due to their mutagenic and carcinogenic effects (Venturini et al., 2008).

In coastal environments, aliphatic hydrocarbons (AHs) can be derived from biogenic sources, such as marine biota and higher plants, or from anthropogenic sources, such as urban runoff, atmospheric deposition, and industrial inputs (Aboul-Kassim and Simoneit, 1996). The total AHs consist of a wide spectrum of *n*-alkanes and branched compounds, as well as an unresolved complex

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mixture (UCM) that is often associated with the presence of degraded oil residues (Sutton et al., 2005).

Spectroscopic and chromatographic techniques can be used together to evaluate hydrocarbon inputs to estuarine systems (Morel et al., 1991). Recently, gas chromatography coupled to mass spectrometry (GC–MS), together with visible and near-infrared (VIS–NIR) spectroscopy, have been used in combination with various multivariate techniques to determine total PAHs in contaminated soils (e.g. Okparanma et al., 2014) and petroleum hydrocarbon concentrations (e.g. Forrester et al., 2013), but studies of contaminated estuarine sediments are rare. Near-infrared spectroscopy is a tool that can be used to identify petroleum-derived contaminants, as it is sensitive to combinations and overtones of C–H, N–H, O–H, and S–H bonds (Stallard et al., 1996).

Fe(III) ions are often used as electron acceptors in the anaerobic oxidation of organic contaminants in sediments. In polluted environments, quinone moieties in humic substances are reduced and act as mediators of electron transfer reactions between reducing microorganisms and Fe(III) oxides or Fe(III)-containing clay minerals such as ferrihydrite, lepidocrocite, goethite, and hematite, resulting in increased organic free radical (OFR) concentrations (Scott et al., 1998). The semiquinone radical, a product of quinone reduction, is active in electron paramagnetic resonance (EPR). However, the Fe(II) ions produced by reduction of Fe(III) are not active. Hence, the EPR technique is useful for detection of Fe(III) phases (such as iron oxides) that are considerably more complex than diluted Fe(III) cations in a silicate or oxide host phase. A reducible Fe phase is required as an electron acceptor after metabolic processes involving nitrate, Mn(IV), and aerobic respiration in microorganisms (Monien et al., 2014), which can be intensified by the presence of contaminants in subsurface sediments. Consequently, the levels of semiquinone may increase, while Fe(III) concentrations can be lower.

Furthermore, Mn(II), derived from the reduction of Mn(IV), is EPR active and its presence can be indicative of an environment that is more reduced (more polluted).

The aims of this work were: (i) determination of the concentrations and historical inputs of AHs and PAHs in sediments from the Paranaguá estuarine system (PES), in order to assess the temporal distributions and possible sources of these compounds related to urban and harbor development; (ii) characterization of sediment samples by spectroscopic techniques; and (iii) comparison of two different methods (spectroscopic and chromatographic) as complementary and effective tools for the evaluation of hydrocarbon inputs.

## 2. Study area

The PES, located on the southeastern Brazilian coast in the SW Atlantic (25°30'S; 48°25'W) (Fig. 1), has an area of approximately 612 km<sup>2</sup> and comprises two water bodies. The western section formed by the Paranaguá and Antonina Bays (around 260 km<sup>2</sup>) is economically the most important.

This region is a designated Environmental Protection Area and since 1995 has been considered a Biosphere Reserve by the United Nations Educational, Scientific and Cultural Organization (UNESCO), due to its ecological importance (Lana et al., 2001; Martins et al., 2012).

The population of the estuary region is concentrated in the towns of Paranaguá and Antonina, with 149,467 and 19,414 inhabitants, respectively (IBGE, 2014). The main economic activities include fishing and aquaculture, urban development and tourism, petrochemical facilities, and the harbors of Antonina (built in 1920) and Paranaguá (built in 1872). Paranaguá harbor is the main South American grain terminal and is the third most important port in terms of loading and unloading operations, with 8,540,000 tons transported in 2009 (Choueri et al., 2009; Martins et al., 2010a,

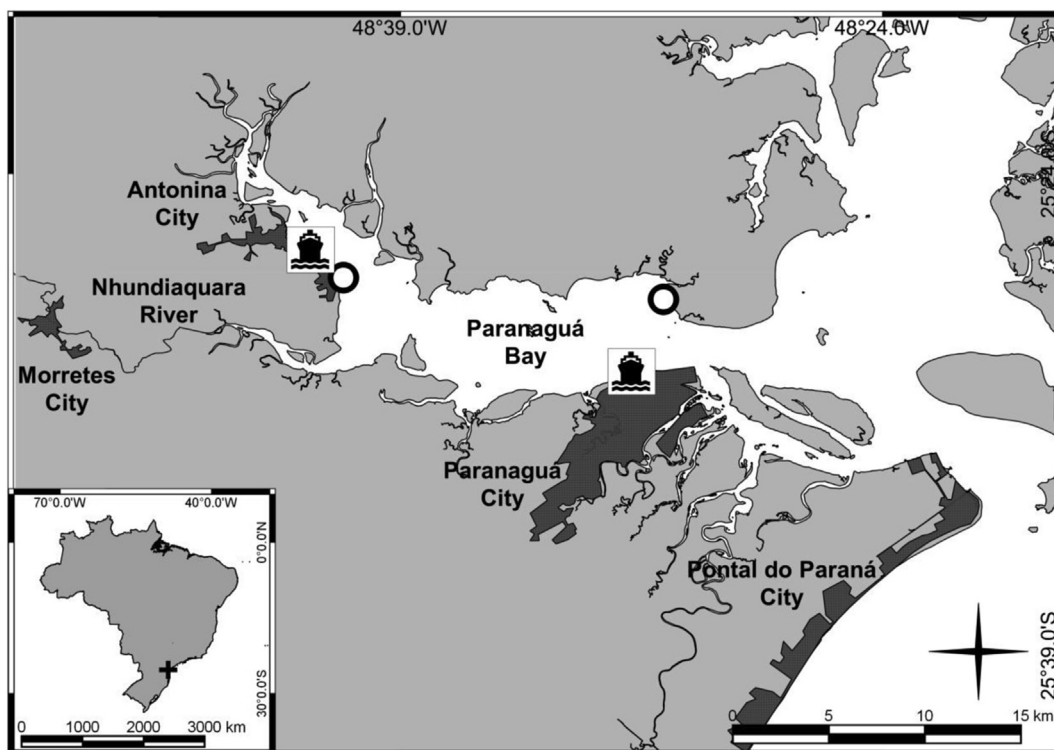


Fig. 1. Locations of the sampling sites (O) and the harbors (■) in the PES, SW Atlantic, Brazil.

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