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Petroleum hydrocarbons in water from a Brazilian tropical estuary facing industrial and port development



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ABSTRACT

A fast paced industrial and port development has occurred at Suape Estuary, Northeast Brazil, but no information about hydrocarbon concentrations in water is available to this area. Considering that, the contamination level of Suape was determined by UV-Fluorescence in terms of dissolved and/or dispersed petroleum hydrocarbons (DDPHs), during wet and dry seasons. DDPHs ranged between 0.05 and 4.59 $\mu\text{g L}^{-1}$ Carmópolis oil equivalents and 0.01–1.39 $\mu\text{g L}^{-1}$ chrysene equivalents, indicating DDPHs close to a baseline contamination level. Some relatively high concentrations ($>1 \mu\text{g L}^{-1}$) were probably associated with shipyard operations (hull paintings and ship docking), pollutants remobilization by dredging operations, occasional industrial discharges and oil derivatives released by vessels. DDPHs concentrations were lower in the wet season suggesting that the increased dilution rates caused by rainfall dominated upon the wet deposition of atmospheric combustion-derived PAHs process. Results in this study may be used as baseline to further studies in this area.

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Suape Estuary is located 40 km South from Recife, the capital of Pernambuco State, Brazil. One hundred companies involving diverse activities such as PET (polyethylene terephthalate) production, gas transporting and fuels distribution recently started their operation at the Suape Industrial Port Complex (SIPC) within the estuary margins. SIPC is the major industrial investment in the Brazilian Northeast, and additional 35 industries are being installed, including a petroleum refinery which will start its operations at the end of 2014. SIPC also includes one of the most modern ports in Brazil, responding for a significant portion of goods imports and exports in the Northeast region. Some studies have reported environmental alterations after SIPC installation, such as: man-

grove deforestation (Braga et al., 1989), flooding of mangroves areas (Braga et al., 1989), changes in hydrodynamic patterns (Paiva and Araújo, 2010), structural changes in the zooplankton communities (Silva et al., 2004), and a decrease in biodiversity of ichthyoplankton (Bezerra Júnior et al., 2011).

Besides these impacts, SIPC activities represent a potential source of different kinds of pollutants to the estuary including oil contamination. The most common petroleum sources related to anthropogenic activities are urban runoff, untreated industrial and domestic effluents, burning of petroleum and fossil fuels, harbor activities, oil spills, and problems related to oil production and transport (UNEP, 1992; NRC, 2003). In addition, PAHs from activities developed in cities located nearby this estuary (e.g. industries, fossil fuel combustion from vehicles, etc.) could also be transported by atmosphere and deposited in the water column (Kiss et al., 2001; Gaga and Tuncel, 2002). The polycyclic aromatic hydrocarbons (PAHs) are the most soluble compounds in the water present

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in petroleum (NRC, 2003), and therefore they have been extensively studied as dissolved and/or dispersed petroleum hydrocarbons (DDPHs) in areas near ports (Zanardi et al., 1999a,b; Bicego et al., 2002), oil spills (Doval et al., 2006; González et al., 2006) and areas receiving riverine runoff with high urban effluents (Wu et al., 2011; Montuori and Triassi, 2012).

The evaluation of PAH contamination in coastal areas is an important topic, as some PAH molecules are potent carcinogenic agents to both humans and wild animals (Samiullah, 1985; Douben, 2003), while others have already been associated to cellular alterations in mussels (Francioni et al., 2007); physiological and cellular modifications in crabs (Dissanayake and Bamber, 2010); increases in mortality rates of shrimps larval stage (Bechmann et al., 2010) and damages on foraging skills of fish species (Carvalho et al., 2008). However, the approaches to investigate PAH in water are in general expensive and require a long time to be performed, but UV-Fluorescence Method is an efficient, inexpensive and simple tool that gives a fast and general idea about the system integrity pointing out “hot spots” to future investigations (Zanardi et al., 1999b; Doval et al., 2006; Bicego et al., 2009).

Although a fast industrialization process is underway within Suape Estuary, which includes the establishment of an oil refinery, to our knowledge there are no published studies focused on contamination by PAHs in waters from Suape Estuary. The principal aim of this study involves the evaluation of contamination levels by PAHs in Suape as total water DDPHs. The experimental design will address the influence of SIPC industries, river discharges, and other potential sources of oil in the estuarine area of Suape during wet and dry periods of the year, using UV-Fluorescence technique.

Suape Estuary was originally formed by four rivers discharging into Suape Bay: Massangana, Tatuoca, Merepe and Ipojuca (Fig. 1). However, after the development of SIPC and its port the waters of Merepe and Ipojuca Rivers could no longer reach Suape Bay. Nowadays, Tatuoca River is partially barred and Suape Bay receives mainly continental waters from Massangana River (Fig. 1). Suape Bay is protected by a sandstone barrier reef with two breaks, Northeast and Southeast, through which seawater gets in and out of the estuary (Fig. 1).

Suape Estuary is located in a hot and humid pseudotropical climate with prevailing Southeast winds, where the wet season occurs from March to August and the dry season from September to February (Silva et al., 2004). The hydrodynamic is characterized by semidiurnal tides with average amplitudes of 2.04 m at spring tide and of 0.91 m at neap tide (PETROBRAS, 2006). Currents inside the bay have higher velocities at surface than at the bottom (PETROBRAS, 2006). In the channel and in the plume of Massangana River the currents flow southeast in low tide and north-west in high tide. In the port area, in general currents flow south-west in low tide and Northeast in high tide (PROMAR, 2010).

Triplicate 1 m deep water samples were taken in 7 stations inside Suape Bay and Massangana River during low tide (Fig. 1). The samples were collected in 8 cruises, with 4 cruises during the end of the wet season (August/2011) and 4 at the end of the dry season (February/2012). Samples were taken with 4 L pre-cleaned amber glass bottles attached to a custom-designed metal frame device. Bottles were released ahead of the boat right before it stopped, in order to avoid oil contamination from the vessel.

The 4 L water samples were extracted with 20 mL of n-hexane pesticide grade, added directly to the sampling bottles, immediately after the samples were collected. Extracts were dried with Na₂SO₄ (previously furnace at 450 °C) and concentrated to 10 mL on a rotary evaporator. DDPHs were measured by fluorescence spectroscopy according to IOC (1984) with modifications in the extraction by Ehrhardt (1983). DDPHs fluorescence of extracts was measured using quartz cuvettes in a SpectraMax M3 Molecular Devices Spectrofluorimeter, with excitation/emission wavelengths of 310/360 nm.

In this study, the concentration of DDPHs was expressed in two different units, calculated based on two calibration curves. Chrysenes was proposed by IOC (1984) as a standard in DDPHs studies, allowing worldwide comparison of results by different authors (Atwood et al., 1987; Corbin, 1993; Kornilios et al., 1998; Nayar et al., 2004; Doval et al., 2006). Carmópolis oil was chosen because it comes from one of the largest reserves in the Northeastern Brazilian coast, and it has already been used as standard in Brazilian coastal and open water studies (Zanardi et al., 1999a,b; Bicego

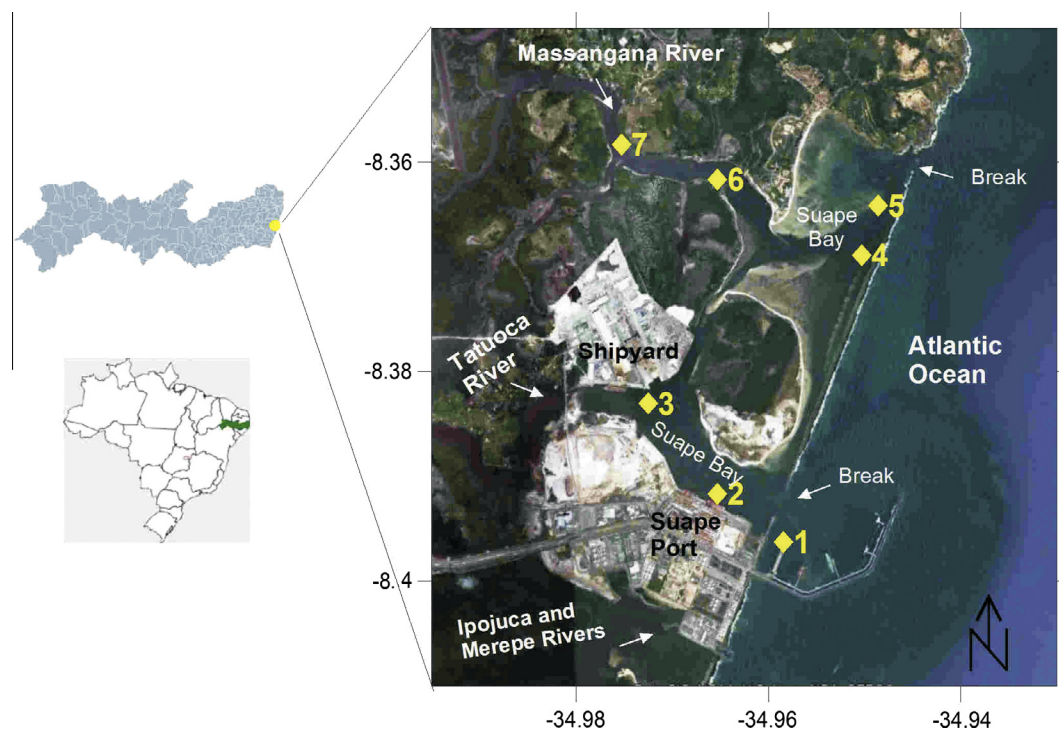


Fig. 1. Sampling stations of sub-surface water in Suape Estuary, during wet and dry season (August 2011 and February 2012, respectively).

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