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# Effects of harbor activities on sediment quality in a semi-arid region in Brazil

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ABSTRACT

Tropical marine environments are rich in biodiversity and the presence of harbor activities in these areas can harm the coastal ecosystems. In this study, we assessed sediment quality of two harbors from a tropical region in Brazil by applying multiple lines-of-evidence approach. This approach included the integration of results on: (1) grain size, organic matter, organic carbon, nitrogen, phosphorus, trace metals, polycyclic aromatic hydrocarbons, linear alkylbenzenes, and tributyltin; (2) acute toxicity of whole sediments and chronic toxicity of liquid phases; and (3) benthic community descriptors. Our results revealed that the main contaminants detected in sediments from Mucuripe and Pecém Harbors were chromium, copper, nitrogen, zinc, and tributyltin. These toxicants arise from typical harbor activities. However, the changes in benthic composition and structure appear to depend on a combination of physical impacts, such as the deposition of fine sediments and the toxic potential of contaminants, especially in Mucuripe. Thus, apart from toxicants physical processes are important in describing risks. This information may assist in management and conservation of marine coastal areas.


## 1. Introduction

Both the development and operation of harbors have been associated with negative impacts on the surrounding coastal zone. Development and operation activities include the construction of jetties, changes in sediment transport, and pollution due to contaminant inputs from several diffuse sources, such as sewage, wastewater, petroleum and its derivatives, and compounds used in anti-fouling coatings (NRC, 1997). These sources are often associated with the input and spread of contaminants throughout the different environmental compartments, including waters, sediments, and biota.

Sediments require special attention because they present higher concentrations of contaminants than the water column. They act not only as a sink, but also as a secondary source of contaminants for the biota, a situation which may lead to ecological risks to benthic communities (Burton and Johnston, 2010). In port zones, dredging operations have been frequently required to increase or maintain operational depth. This process generates ecological impacts in the dredged areas through sediment removal and resuspension and also affects disposal sites, which receive the dredged material (Torres et al., 2009).

In order to understand the effects of different stressors on biota, the use of different lines of evidence has been recommended in sediment quality assessment. These lines of evidence include chemical analyses combined with ecotoxicological and ecological approaches (Chapman and Hollert, 2006; McPherson et al., 2008; Arfaeinia et al., 2016). Among these methods, the sediment quality triad, or SQT (Chapman, 1990; Long and Chapman, 1985), integrates evaluations of benthic2017 community structures with sediment toxicity and chemistry in order to provide a better assessment of pollution-induced degradation than the use of these line of evidence (LOE) alone (McPherson et al., 2008).

Tropical regions in equatorial zones such as northeastern Brazil are very biodiverse environments (Stuart-Smith et al., 2013). In

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these coastal areas, the low productivity associated with sandy sediments rich in biogenic carbonates is often found (Ekau and Knoppers, 1999; Lacerda and Marins, 2006). Therefore, anthropic impacts such as contamination may pose risks to the structure and functioning of these ecosystems.

Few studies have been performed on the quality of sediments from tropical areas, especially in equatorial and semi-arid regions. Therefore, studies focused on the associations between contamination levels and biological effects are necessary to assist in the management of the environmental effects that accumulate in dredged material. Brazil has recently expanded its industrial and harbor activities in underdeveloped regions, including the Northeast. The government considered these actions to be strategic, but they have also increased of anthropogenic pressures on coastal zones.

Economically, Ceará is one of the most important states in the Brazilian Northeast. The capital city of Fortaleza has more than 2.3 million inhabitants distributed over an area of 313 $km^2$. The city's main anthropogenic impacts involve harbor activities, factories, and a petroleum refinery (Cavalcante et al., 2009; Buruaem et al., 2012). Mucuripe and Pecém are the state's two harbors. They ship most of the goods produced and traded in the region, a factor which makes these areas vulnerable to contaminants inputs from the port activities.

In light of these factors, the main goal of this study was to investigate the sediment quality of Mucuripe Harbor and Pecém Harbor, both of which are located in the Brazilian state of Ceará. The SQT approach was applied in order to achieve this goal. Three lines of evidence (chemical analyses, sediment toxicity, and benthic community descriptors) were combined in order to produce an diagnosis of sediment quality in this tropical region of the Brazilian coast, which was chosen because of its high ecological significance and because of the recent intensification of industrial and port-related activities.

## 2. Material and methods

### 2.1. Study area

The climate of the northeastern region of the Brazilian coast is largely influenced by the Intertropical Convergence Zone (ITCZ). However, it also depends of other phenomena, such as the El Niño-Southern Oscillation (ENSO). During El Niño periods, the weather becomes drier, while during La Niña periods, rainfall volumes often go above multi-annual averages for the region. In addition, the climate is marked by semi-arid conditions with limited ranges in temperature, with averages of 24 °C to 30 °C (Paula et al., 2013). There is a predominance of trade winds coming from the E-SE at an average speed of 4 m/s, a factor which determines sediment transport in this direction (Maia et al., 1998; Jimenez et al., 1999).

Sediments from the Ceará coast exhibit organogenic and terrigenous facies. The organogenic substrates are derived from *Lithothamnium* (Rodophyta) and *Halimeda* (Clorophyta) species of calcareous algae. Their presence contributes approximately 75–95% of calcium carbonate deposition, with organic matter ranging from 23% to 46%. Sediments from terrigenous facies are characterized by siliciclastic material, including quartz sand, feldspar, heavy minerals (smectite, kaolinite and illite), and clay (Lacerda and Marins, 2006; Marques et al., 2008). The texture of sediments in the outer shelf (40 m isobath) is marked by gravel, while the sediments from the inner shelf (below the 20 m isobath) are composed of sand with biodetritic gravels and low amounts of mud — mud levels have been found to be less than 2.5% (Freire et al., 2004).

Mucuripe Harbor is located within the Mucuripe Bay in the Brazilian city of Fortaleza. Its infrastructure includes an access channel, anchorage areas, evolution basins, and a long jetty (1900 m long). Pecém Harbor is located in a port industrial complex approximately 60 km west from the capital. Pecém is an offshore terminal, which is considered to be technological advancement. It was constructed 2000 m away from the shoreline and connected to land by a bridge. Thus, the coastal currents are not completely affected by port facilities, since sediment transport occurs between the pillars of the port.

### 2.2. Sediment sampling and handling

In Mucuripe Harbor, sediment sampling was performed in August 2007 at 10 stations (Ms) from different areas. M1 and M2 were located in front of commercial docks, where the docking of ships and effluent discharges from a major oil refinery occur. M3, M4 and M5 were situated at fishing and tanker piers, where oil from the refinery is unloaded. M6 and M7 were placed at the access channel, and M8, M9, and M10 were established in unsheltered areas. In Pecém Harbor, sediments were collected from 5 stations (Ps) in January 2008. P1 and P2 were situated close to the docking piers, where steel products, bulk liquids, liquefied gases, and general cargo are shipped and docked. P3 was established at the access channel. P4 and P5 corresponded to unsheltered areas; P4 was located in a diffraction zone of waves and currents, while P5 was under the influence of the sediment transport that occurs between the pillars the port bridge (Fig. 1).

The sediments collected for toxicity tests were placed in refrigerated coolers and transported to the laboratory, where they were stored at 4 °C in dark conditions. For the benthic community analysis, three replicates were collected from each station using a Van Veen grab sampler (0.026 $m^2$). Sediment samples were carefully washed and sieved through a 0.5-mm mesh. Next, the retained material was fixed using 4% buffered formalin. It was washed and then preserved in 70% ethanol. In the laboratory, biological material was sorted, identified, and quantified under a stereoscopic microscope Zeiss® model Stemi DV4 Stereo. For the chemical analyses, two aliquots were separated. The first aliquot was dried at room temperature by using a desiccator cabinet and packed in plastic containers for subsequent metal analyses. For the analysis of the physical and chemical parameters and the assessment of organic contaminants, the sediment samples were placed into pre-cleaned aluminum foil and stored at $-20$ °C.

### 2.3. Sediment analyses

Particle size distribution was measured using the wet sieving method to separate fine sediments (silt + clay), followed by dry sieving to separate gravel and sand fractions (McCave and Syvitski, 1991). Calcium carbonate contents ($CaCO_3$) were estimated using digestion in HCl and gravimetry (Gross, 1971). After $CaCO_3$ removal, total organic carbon (TOC) levels were determined using a Shimadzu TOC-V TOC analyzer coupled with a SSM-5000A solid sample combustion unit. Organic matter content (OM) was determined using the method of ignition and gravimetry (Luczak et al., 1997). Nutrients, total nitrogen (N), and phosphorus (P) were estimated using extraction and spectrophotometry (Grasshoff et al., 1999).

The major metals (Al and Fe) and trace metals (Hg, Cd, Cr, Cu, Ni, Pb and Zn) were analyzed after extraction with an acid solution (9 ml of $HNO_3$+3 ml of HCl) according to the EPA 3051A protocol (USEPA, 1996). A high pressure microwave system was used (CEM Corporation, model MDS—2000). Lead, nitrogen, and mercury concentrations were measured using the flame mode of a Varian Spectr-AAS-220-FS fast-sequential atomic absorption spectroscope. Mercury concentrations were measured via cold vapor