Marine Pollution Bulletin xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

# Ecotoxicological assessment of sediments from an urban marine protected area (Xixová-Japuí State Park, SP, Brazil)

G.S. Araujo [a,b,*], L.B. Moreira [c], R.D. Morais [d], M.B. Davanso [a], T.F. Garcia [a], A.C.F. Cruz [a,b], D.M.S. Abessa [a]

[a] Campus Experimental do Litoral Paulista, Universidade Estadual Paulista, Praça Infante Dom Henrique, s/n, CEP 11330-900 São Vicente, SP, Brazil
[b] Instituto Oceanográfico da Universidade de São Paulo, Praça do Oceanógrafo, 191, CEP 05508-120 São Paulo, Brazil
[c] Instituto de Ciências do Mar – UFC, Universidade Federal do Ceará, Av. da Abolição, 3207 – Meireles, CEP 60165-081 Fortaleza, CE, Brazil
[d] Lecotox Análises Ambientais – Universidade Positivo, Rua Prof. Pedro Viriato Parigot de Souza, 5300 bloco marrom sala 209, Campo Comprido, CEP 81280-330 Curitiba, PR, Brazil

ARTICLE INFO

*Keywords:*
Contamination
Amphipod
Copepod
Toxicity
Marine protected area
Whole-sediment TIE

ABSTRACT

This study aimed to evaluate the environmental quality of the marine portion of Xixová-Japuí State Park (XJSP), an urban marine protected area, which is influenced by multiple contamination sources, by using ecotoxicological and geochemical analyses. Sediments were predominantly sandy, with low $CaCO_3$ and organic matter contents, and presented contamination by metals (Cd, Cu, Zn). Acute toxicity was detected in three tested samples, and copepod exposed to sediments from four stations exhibited lower fecundities, despite the absence of significant effects. Contamination and toxicity seemed to be associated, suggesting that the environment is degraded and presents risks to the biota. Whole sediment TIE indicated ammonia as a main responsible for toxicity, suggesting sewage is a main contributor to sediment degradation. As external contamination sources seem to be negatively influencing the sediment quality, the park conservation objectives are not being fully reached, demanding actions to mitigate impacts.


## 1. Introduction

A protected area (PA) may be defined as "an area of land and/or sea especially dedicated to the protection and maintenance of biological diversity, and of natural and associated cultural resources, and managed through legal or other effective means" (IUCN, 1994). The PA concept can be used for both terrestrial and aquatic environments. In this context, considering the importance of coastal ecosystems, there is a concern for the establishment of marine protected areas (MPAs). A MPA, in its turn, can be defined as "any area of intertidal or subtidal terrain, together with its overlying water and associated flora, fauna, historical and cultural features, which has been reserved by law or other effective means to protect part or all of the enclosed environment" (Kelleher et al., 1995).

However, some authors have showed that the simple establishment of a MPA is not capable to protect these areas, as there is a set of actions and policies that are required to effectively provide protection to the ecosystems (Jameson et al., 2002). Threats to the protection effectiveness of MPAs concern not only to internal factors (as fishing and overcrowding) but also to external factors, as presence of pollutant sources in the MPA vicinities (Kelleher et al., 1995). MPAs located near human activities have experienced the phenomenon of transboundary movements of chemicals (Pozo et al., 2009; Terlizzi et al., 2004) and their negative effects to biota (Davanso et al., 2013; Rodrigues et al., 2013). Thus, knowing how contamination from external sources affects the environmental quality within MPAs becomes a critical aspect that must be addressed to the proper MPA management.

In Brazil, there is a national system of protected areas (NSPA) that defines different categories of PAs, based on the degrees of desired protection, and imposes thus different restrictions to the uses of natural resources within such areas (Brasil, 2000). The NSPA also establishes guidelines and rules for managing PAs and enhancing their effectiveness; however, they are not totally followed for most of Brazilian PAs, especially the coastal PAs and MPAs. In this sense, Brazilian MPAs comprise a range of situations that may be used as examples of problems of management or lacking of protection effectiveness.

One particular case is the Xixová-Japuí State Park (XJSP), which is located on the SW of Santos Estuarine System (São Paulo State, Brazil), inserted into a region that has been severely affected by environmental impacts, particularly unplanned urban settlement, industrialization and port activities (São Paulo, 2010). Thus, the marine portion of XJSP represents an interesting example to be evaluated, in terms of how external sources may affect the environmental quality within an urban MPA and if ecological processes are effectively protected when the surroundings do not have restrictions to impacting activities.

* Corresponding author at: Campus Experimental do Litoral Paulista, Universidade Estadual Paulista, Praça Infante Dom Henrique, s/n, CEP 11330-900 São Vicente, SP, Brazil. Tel.: 55 13 3569 7119/7133.

*E-mail address:* giuliana_araujo@hotmail.com (G.S. Araujo).

0025-326X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2013.08.005

The pollution assessment in aquatic environments must recognize that, after reaching aquatic systems, pollutants are spread and transported by currents and waves, increasing the range of their distribution (Salomons and Forstner, 1984). Additionally, they tend to remain in the water column for limited periods, precipitating to the bottom and accumulating in sediments (Ingersoll, 1995), from where they can be released back to the water column or affect benthic biota. As sediments represent substrate for a wide range of species and feeding sites for many predators, sediment quality assessment constitutes a reliable strategy for evaluating environmental quality. Chemical analyses are useful to identify and quantify the contaminants, whereas ecotoxicological approaches may evaluate potential effects on aquatic biota (Costa et al., 2008). In addition, advanced techniques, as the toxicity identification evaluation (TIE) approach, have been employed to determine the chemical compounds responsible for toxicity. Sediment TIEs involve a suite of procedures that are designed to decrease, increase, or transform the bioavailable fractions of sediment contaminants to assess their contributions to sample toxicity (Burgess et al., 2000).

Considering the contamination sources that can potentially influence the marine portion of an urban MPA, this study aimed to assess the quality of sediments from XJSP marine portion and consequently to evaluate if this MPA is effectively protected from external impacts. To achieve that, geochemical analyses and ecotoxicological assays with benthic organisms were employed together with whole-sediment TIE (phase I), in order to identify the main chemical groups responsible to the toxicity.

## 2. Materials and methods

### 2.1. Study area

As previously mentioned, the XJSP is located in the metropolitan region of "Baixada Santista" (MRBS), which is highly urbanized, and comprises the Port of Santos (the largest of Brazil) and the industrial complex of Cubatão, which includes major steel and petrochemical plants. The park has 901 ha, from which 600 ha comprise its terrestrial portion and 301 ha comprise the marine zone (Fig. 1). In its turn, marine portion comprises the entire area surrounding the coastline till 200 m onshore (São Paulo, 2010); starting at the São Vicente Estuary (at Santos Bay) and reaching the beach at Praia Grande, after contouring Ponta do Itaipu (Fig. 1). Historically, MRBS occupation was marked by huge conurbation between its municipalities and high levels of air, soil and water pollution (Lamparelli et al., 2001). MRBS also has a close interface with the metropolitan region of São Paulo (MRSP), which is just 50 km away, intensifying the pressures on its natural resources, particularly those related to seasonal tourism, which may triplicate the MRBS population (São Paulo, 2010). Multiple potential sources of contaminants are present in the MRBS, according to the State Environmental Agency – CETESB (Lamparelli et al., 2001); and comprise the Port of Santos, marinas, domestic and industrial landfills, industrial effluents, sewage outfalls, urban drainage, among others. Literature showed contamination and toxicity in both waters and sediments from this region (Torres et al., 2009; Lamparelli et al., 2001), including the west portion of Santos Bay in the immediate vicinity of XJSP (Abessa et al., 2008a) and nearby areas (Abessa et al., 2005, 2008b).

### 2.2. Sediment sampling

The study area includes the marine portion of XJSP (Fig. 1), with six stations located within the park boundaries and potentially subject to the influence of contaminant sources: P1 was positioned in a low energy area and under pressure of diffuse sources; P2 and P3 were under potential influence of the sewage submarine outfall of Praia Grande; P4 and P5 were located within Santos Bay, both under possible influence of pollution sources within the São Vicente estuary and the sewage submarine outfall of Santos; and P6 was in the mouth of São Vicente estuary, which receives contributions from marinas, urban drainage, industrial and domestic landfills and sewage discharges. The geographic coordinates of the stations are shown in Fig. 1. The reference sediment was collected at Engenho d"água Beach, Ilhabela-SP (23°48′S–45°22′W), where amphipods used in the acute toxicity test were collected. The choice for using this area as reference is due to the absence of clean areas in Santos Estuarine System (Abessa et al., 2008b).

Sediment samples (2-cm surficial layer) were collected in August 8, 2011, with a 0.026 $m^2$ stainless steel "Van Veen" grab sampler, and immediately chilled. In the laboratory, the aliquots for the ecotoxicological assays were refrigerated at 4 °C, the samples for sedimentology were dried at 60 °C for three days, and those for chemical analyses were frozen.

### 2.3. Sediment properties

The sediment grain size distribution was analyzed by a two-step sieving (Mudroch and MacKnight, 1994): the first step consisted in wet sieving of more than 100 g of previously dried sediments through a fine mesh (0.062 mm) to separate fine particles (silt and clay); the difference between the initial and the final weights represented the mud fraction. The second step consisted on the dry sieving of the material retained on the 0.062 mm mesh into a set of sieves ($\Phi$ scale) in order to separate different classes of sands. The classification method was based on the scale established by Wentworth (1922). The calcium carbonate contents determination followed the protocol described by Grant-Gross (1971), which was based on the sample digestion with hydrochloric acid (HCl) 30 volumes. The analysis of organic matter (OM) content in the sediment samples followed the ignition method (Grant-Gross, 1971).

### 2.4. Chemical analyses

Metals from sediments were extracted with acqua regia ($HCl:HNO_3$ 1:3) according to USEPA 3050b protocol (USEPA, 1996). One gram aliquots of whole sediment were transferred to flasks; then 20 ml acqua regia were introduced into each flask and the mixture was heated to 90 °C for 40 min. After cooling, extracts were separated and transferred to volumetric flasks and the final volumes were adjusted to 25 mL by adding 2% HCl. The contents of Cd, Cu and Zn in the sediment samples were read by flame Atomic Absorption Spectrophotometry (model AA 6800 Shimadzu). Analysis was done in duplicate. Quantification Limits for Cd, Cu and Zn were 0.02 $\mu g\ g^{-1}$, 1.0 $\mu g\ g^{-1}$ and 1.3 $\mu g\ g^{-1}$, respectively. To verify the used methods, Estuarine Sediment BRC® 667 was evaluated, and respective recovery values were 98.14% for Cd, 119.42% for Cu and 77.68% for Zn.

### 2.5. Acute sediment toxicity tests

The acute toxicity test with sediments was performed with the amphipod *Tiburonella viscana* (Melo and Abessa, 2002; ABNT, 2008). This 10-day test used 3 replicates per sediment sample. Each test chamber (1L polyethylene vessel) was prepared with approximately 2 cm of test sediment and 750 ml seawater, and received 10 amphipods. During the test, the system was maintained at 25 ± 2 °C, with constant lighting and aeration, and the animals were not fed. The number of survivors in each chamber was counted after 10 days. Missing organisms were considered dead (Melo and Abessa, 2002). At the beginning and the end of the