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Integrated sediment quality assessment in *Paranaguá* Estuarine System, Southern Brazil

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ABSTRACT

Sediment quality from *Paranaguá* Estuarine System (PES), a highly important port and ecological zone, was evaluated by assessing three lines of evidence: (1) sediment physical–chemical characteristics; (2) sediment toxicity (elutriates, sediment–water interface, and whole sediment); and (3) benthic community structure. Results revealed a gradient of increasing degradation of sediments (i.e. higher concentrations of trace metals, higher toxicity, and impoverishment of benthic community structure) towards inner PES. Data integration by principal component analysis (PCA) showed positive correlation between some contaminants (mainly As, Cr, Ni, and Pb) and toxicity in samples collected from stations located in upper estuary and one station placed away from contamination sources. Benthic community structure seems to be affected by both pollution and natural fine characteristics of the sediments, which reinforces the importance of a weight-of-evidence approach to evaluate sediments of PES.

1. Introduction

Many port managers deal with the continuous effort of dredging waterways in order to keep the necessary water depth to allow safe navigation. Dredging activities can cause severe environmental impacts, especially when the sediments to be removed are contaminated. Among such effects, the resuspension of the bottom during such operations may turn the settled contaminants soluble again (DelValls et al., 2004); moreover, high concentrations of chemicals in the dredged material may be toxic to the biota at the disposal area (Stronkhorst et al., 2003; Sousa et al., 2007). Since sediment contamination inflicts severely the management of dredged material (Salomons and Brils, 2004), proper assessment of sediment quality is essential in areas where dredging operations are executed.

Many specialists have endorsed the idea of using different lines of evidence (LOE) in sediment quality assessments, such as toxicity tests and benthic community structure surveys rather than using only the traditional chemical analyses. Whilst the aim of chemical analyses is only to quantify the contaminants present in the sediments, sediment toxicity tests are used to determine whether contaminated sediments are potentially harmful to the biota, including measurements of the interactive toxic effects of complex chemical mixtures in sediment (MacDonald and Ingersoll, 2003). *In situ* benthic community surveys are, in turn, useful to indicate impacts of in-place pollutants in aquatic environments, reflecting sources of stress over time, and taking into account the effects of contaminants over a number of different benthic species that occupy different niches and have different tolerances to chemical contamination. Therefore, in order to obtain a realistic estimation of the sediment quality, and to reduce uncertainties, specialists recommend the integration of different LOE in sediment quality assessments (Cesar et al., 2007; DelValls et al, 2004; Mozeto et al., 2004; Chapman et al., 2002).

The integration of environmental data can be performed through different univariate and multivariate techniques; multivariate analyses permit the integration of data of different natures (e.g. chemical concentrations on sediments, toxicity endpoints, benthic community descriptors), resulting in a wider analysis that allows a deeper and more robust interpretation of the data. Principal component analysis (PCA) is one of the most common techniques of combining environmental data by multivariate analysis (Landis and Yu, 1999) and it has been successfully utilized in integrating sediment data for sediment quality assessments

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(Cesar et al., 2007; Riba et al., 2004a, b; DelValls and Chapman, 1998; Carr et al., 1996).

However, environmental quality assessments, and especially the WOE approach, have been traditionally applied in highly degraded sites as a consequence of both chronic (industrial, mining, port activities) and acute impacts (contaminant spills; Morales-Caselles et al., 2008, 2007; Martín-Díaz et al., 2005). There is little information of the biological responses (toxicity and benthic community alterations) in mildly contaminated environments, which is the situation found in most of the coastal areas around the world, including some legally protected areas. Therefore, the WOE approach is potentially a useful tool to assess sediments in such areas, but its applicability was rarely tested.

In this study we assessed the sediment quality of *Paranaguá* Estuarine System (PES) (*Paraná* State, Brazil) by using three LOE: (1) sediment physical–chemical analyses; (2) toxicity tests; and (3) benthic community structure. These data were integrated by PCA.

The PES may be considered as slightly impacted when compared to other areas in Southern–Southeastern Brazilian coast. It is part of the Cananéia–Iguape–Peruíbe (CIP) estuarine-lagoon complex (also named Lagamar), which is considered a Federal Environmental Protected Area. The PES is a relevant site not only due to the importance of its mangroves, islands, inlets, and bays but also because it constitutes an important port zone in South America. Potentially harmful products such as petroleum derivatives, fertilizers, and minerals, as well as grains are handled in the ports of *Paranaguá* and *Antonina*. Previous studies have detected sediment contamination in some areas of the PES (Sá and Machado, 2007), reaching moderate levels; however the ecosystem response to such contamination has not been studied yet. This study aimed to evaluate the quality of PES sediments, including the chemistry, the analysis of the biological responses, and the integration of both approaches. Also, it allowed us to appraise the usefulness of this integrative approach to assess sediments from low-to-moderated impacted zones. In addition, the ecologically reliable information provided for this area is intended to support the management of dredged material from the navigational channel of the Port of *Paranaguá*.

2. Materials and methods

2.1. Study area

Paranaguá Estuarine System (25°16′–25°34′S; 48°17′–48°42′W), located on the coast of the *Paraná* State, Southern Brazil (Fig. 1), is one of the biggest estuarine systems in America. It is formed by two main bays: the *Paranaguá* Bay, with W–E orientation, and the *Laranjeiras* Bay, with N–S orientation. The estuarine system is bordered by the Atlantic Ridge and its coastal zone is divided into five environmental units: mangrove plain, coastal plain with forest, coastal plain with agriculture and urban facilities, fluvial plain with forests, and fluvial plain with agriculture (MMA, 1996). Approximately 19% of the Atlantic rainforest remnants of Brazil are situated in this area and this was the first part of the Atlantic rainforest to be considered as a 'biosphere reserve' by UNESCO in 1995. Because of its extraordinary ecological importance, 16 conservation unities of environmental protection are established in the area of the PES. Furthermore, since the year 2000 the inclusion of the PES in the Ramsar's list of wetlands of international importance has been discussed, as part of the 'Iguape–Cananéia–Peruíbe estuarine-lagoon complex' (IBAMA, 2008).

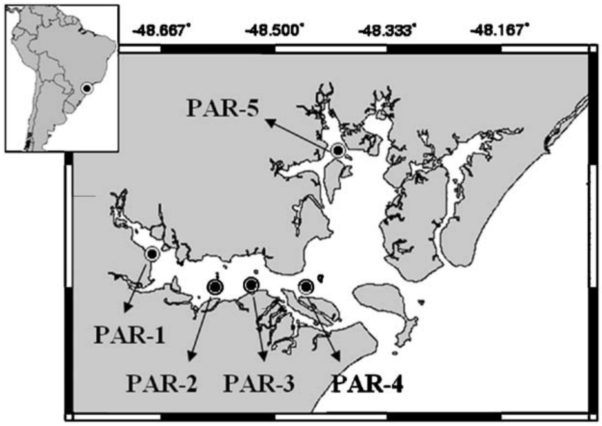

Fig. 1. Localization of the sampling stations in the Paranaguá Estuarine System (PES).

The major Southern Brazilian port, the port of *Paranaguá*, is placed in the *Paranaguá* Bay. This is the biggest port for grain export in South America (Marone et al., 2000) but also other products such as fertilizers, minerals, and petroleum derivatives are handled in the port of *Paranaguá*. Additional environmental pressures in the area of the PES include the *Ponta do Félix* Port Terminal, an uncontrolled urban landfill in *Paranaguá*, which receives 130 tons of residues per day without any treatment, non-planned urban development bordering the estuary (and the consequent discharges of nontreated sewage), as well as agriculture (with wide use of agrichemicals).

2.2. Approach

2.2.1. Sediment collection

Four sampling stations were set along the navigational channel of port of *Paranguá* and *Ponta do Félix* Terminal, in the *Paranaguá* Bay, in order to identify the gradient of contamination along the channel; one additional station was situated in the *Benito* Bay, away from the contamination sources (Fig. 1). Sediment samples were collected synoptically for physical–chemical, toxicity, and macrobenthic community structure analyses. Three replicates of sediments were collected in each station by using a 0.02 m^2 Petit-Ponar grab sampler. For physical–chemical analysis and toxicity tests, the sediments were kept in coolers with ice until their transportations to laboratory, where they were stocked at 4 °C in the dark. For benthic community structure analysis, samples were sieved through a 500 μm mesh bag. Macroinvertebrates retained on the screen were fixed with 4% buffered formalin, subsequently washed, and then transferred to 70% isopropyl alcohol prior to sorting and identification. Each sieved sample had individual taxa identified and enumerated by using stereoscope microscopy, in order to assess species richness and abundance. All organisms were sorted and identified to family level and their abundance was calculated.

2.2.2. Physical–chemical analyses

Grain size analysis was performed by the wet sieving process according to Mudroch and Macknight (1994). This technique consists of a series of sieves for sandy sediments and a flocculation and pipette determination for silts and clays.

Total organic carbon (TOC) was analyzed by combustion at 900 °C for total carbon (TC) and phosphoric acid addition for inorganic carbon (IC), which are transformed to CO_2 and determined by an infra-red (IR) detector on a Shimadzu TOC 5000 attached to a solid sample module SSM 5000A (Standard Methods, 2000).

Metals (Ag, Cd, Cu, Cr, Ni, Pb, and Zn) and metalloids (As and Se) were extracted from sediment samples according to Method 3050B (USEPA, 1996a) in which an aliquot of 2 g of sediment is weighed ($\pm$0.0001 g) and subjected to an acid extraction with concentrated HNO_3 and 30% H_2O_2 and heated to about 90 °C. Concentrations were determined by flame atomic absorption spectrophotometry (F-AAS) for Cu, Cr, Ni, Pb, and Zn, graphite furnace (GF-AAS) for Ag and Cd, and hydrate generation (HG-AAS) for As and Se. Mercury was extracted by a combination of Methods 245.5 and 245.6 from USEPA (1991a), which employs concentrated HNO_3 and H_2SO_4, with $KMnO_4$ 7.5%, $K_2S_2O_8$ 8%, and $NH_2OH \cdot HCl$ 15% heated on a water bath to 95 °C. Mercury concentration determination was done by cold vapor spectrophotometry (CV-AAS). Detection limits varied from 0.02 to 5 $mg\,kg^{-1}$ depending on the metal and equipment used on the analysis.

Organic compounds analyses were conducted as follows: 10 g ($\pm$0.0001 g) of sediments was ultrasound extracted on a 50 mL mixture of n-hexane/acetone 1:1 twice. The extract was concentrated on a rotary evaporator to a volume of 2 mL and on a nitrogen flux to 1 mL (an USEPA Method 3550B; USEPA, 1996b). After that, it was passed through a clean-up column with silica gel, eluted with 50 mL of dichloromethane/hexane 2:3 mixture, and concentrated to 1 mL on rotary evaporator and nitrogen flux (an USEPA Method # 3630C; USEPA, 1996c).

Extracts were analyzed on a GC–MS Shimadzu model QP 2010 with methods prepared for each compound class that was being evaluated. Polycyclic aromatic hydrocarbons (PAHs) were analyzed according to Method 8270C (USEPA, 1996d). Following this method, the compounds analyzed were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, p-terphenyl-d14, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene. Standard solution from Supelco was obtained at a concentration of 2000 $mg\,L^{-1}$. The method was created in the selected ions monitoring (SIM) mode, with an