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Using a tiered approach based on ecotoxicological techniques to assess the ecological risks of contamination in a subtropical estuarine protected area

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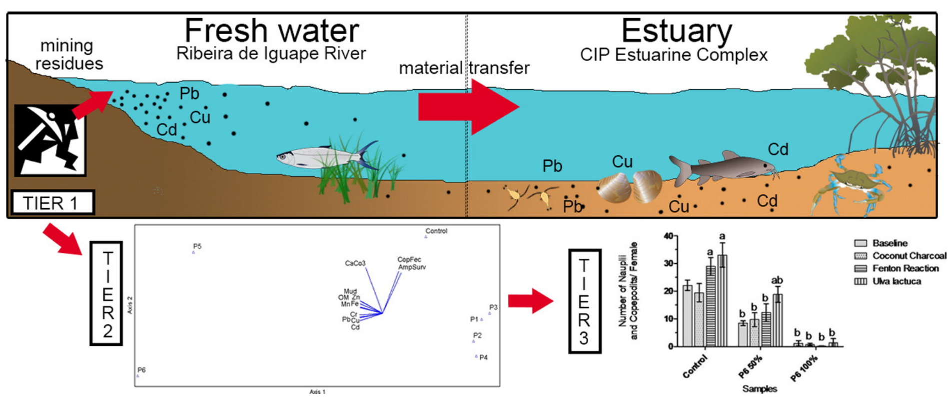
HIGHLIGHTS

- Mining residues cause sediment contamination at CIP-PA estuary
- Combination of ammonia and metals was the main cause of sediment toxicity
- The AVS/SEM approach was not effective in predicting sediment toxicity
- Depositional areas had higher toxicity, metal levels and presented ecological risk
- Using several LOEs allowed the establishment of cause-effect relationships

GRAPHICAL ABSTRACT



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ABSTRACT

This study sought to assess the ecological risks of sediments from the northern portion of an estuarine protected area (Cananéia-Iguape-Peruíbe Protected Area — CIP-PA). The CIP-PA is located on the southern coast of São Paulo State, Brazil and is influenced by former mining activities along the Ribeira de Iguape River (RIR). We used a tiered approach based on multiple lines of evidence (geochemical analyses, toxicity tests, and whole sediment toxicity identification and evaluation) in order to assess environmental quality. The sediments presented a heterogeneous composition, but the samples collected close to the RIR exhibited higher concentrations of metals (Cd, Cr, Cu, Pb) and toxicity. Multivariate analysis showed that toxicity was associated with metals, mud, organic matter, and $CaCO_3$ quantities. The whole-sediment toxicity identification evaluation approach indicated that ammonia and metals were responsible for sediment toxicity. Overall, we concluded that the sediments collected at depositional areas from the northern portion of the CIP-PA presented high levels of metals, which originated from former mining areas located in the upper RIR basin, and that this contamination had toxic effects on aquatic invertebrates. The tiered approach was useful for identifying the degradation of sediment quality and also for indicating the causes of toxicity. Because the CIP-PA is an important estuarine protected area that is ecologically at risk, large-scale measures are required to control the sources of contamination.

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1. Introduction

Ecological risk assessment (ERA) is a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (USEPA, 1992). ERA has been used to understand and predict the relationships between stressors and ecological effects in order to evaluate human-induced changes that are considered ecologically undesirable (USEPA, 1998). Thus, ERA focuses on adverse effects generated or influenced by anthropogenic activity, and often involves the assessment of chemical, physical, or biological stressors or aspects.

ERA has been frequently conducted as a tiered approach. The assessment process offers more information that contributes to legislative and scientific decisions. ERA identifies stressors, their origins, and interactions between stressors and ecological variables, and it is also used to evaluate the ecological effects of the stressors identified (USEPA, 2000). Although ERA can be employed to assess the risks of a range of environmental stressors, it has been used mainly to evaluate possible risks associated with the contamination of aquatic ecosystems (Choueri et al., 2010; Chapman and Anderson, 2005).

Because environmental risks depend on the nature of the stressors and their interactions with the specific abiotic and biotic components of the ecosystem, each ERA should be conducted following specific steps. However, two major elements must be included in any ERA: characterization of effects and characterization of exposure (USEPA, 1998). When assessing ecological risks due to contamination, chemical or geochemical methods provide information on the nature and degree of contamination, while ecotoxicological methods detect the occurrence of potential biological effects (Adams et al., 1992; Petrovic and Barcelo, 2004) and provide information about both effects of and exposure to contaminants (Castro et al., 2006; Antunes et al., 2008; Chapman and Anderson, 2005).

Due to their relative simplicity, reliability, and affordability, ecotoxicological bioassays are considered one of the best ways to evaluate the effects of single and multiple contaminants and estimate their toxic potential in the environment (USEPA, 2002; Castro et al., 2006). When toxicity tests are combined with chemical analyses, they provide much more powerful information for scientific and legislative decision-making. However, both chemical and ecotoxicological approaches have limitations. The direct quantification of contaminants does not necessarily reflect the bioavailability to biota or the biological effects, nor does it allow for the results of interactions of multiple contaminants to be evaluated (Chapman et al., 1998; Meyer, 2002). Moreover, the range of measured contaminants is often limited due to both economic and technical restraints; thus, chemical measurements have often been restricted to the most common substances (Choueri et al., 2010). Meanwhile, ecotoxicological techniques may be influenced by confounding factors, and their application may be limited to a very small number of test protocols (with few test-species). In other words, the test conditions may not fully represent the exposure conditions in the natural environment.

In order to deal with limitations inherent to each technique alone, ecological risk assessments of sediments have used multiple lines of evidence (LOE) (Chapman et al., 2002; Choueri et al., 2010), and may incorporate new techniques to provide more information for decision-making processes (Chapman and Hollert, 2006).

In recent years, more advanced techniques have been developed to identify active toxicants in contaminated sediments. Of these techniques, sediment toxicity identification and evaluation (TIE) has been the most frequently adopted (Anderson et al., 2006). The TIE approach involves a suite of procedures that are designed to decrease, increase, or transform the bioavailable fractions of contaminants in order to assess their contributions to the toxicity of the sample (Araújo et al., 2013). This approach was first developed in the United States, in the 1980s to be employed within the US Clean Water Act as part of efforts to identify and remove toxic chemicals from municipal and industrial effluents discharged into the environment. In the 1990s, researchers started to use TIE to evaluate sediment interstitial waters, and later, this technique was adapted for use with whole sediments (Ho and Burgess, 2013; USEPA, 1992; USEPA, 2007). When assessing sediment quality using TIE, the three most frequently characterized classes of toxicants are nonionic organics, cationic metals, and ammonia. Sediment TIE has the potential to become a new LOE in ERA, as it provides information on the causes of toxicity (Araújo et al., 2013).

The use of multiple LOEs, including sediment TIE, provides a sensitive approach for detecting environmental disturbances and also enables estimates of environmental risks in slightly to moderately contaminated sites (Nipper et al., 1998), including marine protected areas influenced by external sources of contamination (Araújo et al., 2013).

This study used a tiered approach based on LOEs to assess the ecological risks of sediments from the northern portion of the Cananéia-Iguape-Peruíbe Protected Area (CIP-PA), an estuarine protected area that is located on the southern coast of São Paulo State in Brazil.

2. Materials and methods

2.1. Study area

The CIP-PA comprises the Cananéia-Iguape-Peruíbe (CIP) Estuarine Complex and the cities of Iguape, Cananéia, and Ilha Comprida (Fig. 1). This region is considered to be of international importance and was included within the Atlantic Rainforest Biosphere Reserve by UNESCO. Brazilian legislation has also placed the region in a protection category that was established to achieve a sustainable balance between the anthropic uses of the area's natural resources and the protection of the natural ecosystems (Moraes, 2004).

The estuarine complex is formed mainly by barrier islands and estuarine channels, which together form a complex net of water bodies. The banks of these water bodies are occupied by a set of fragile ecosystems that require protection, especially in the case of the mangroves, mudflats, and other wetlands (Schaeffer-Novelli et al., 1990). The hydrodynamic circulation of the area is influenced by tidal waves, winds, and the contributions from several rivers (Miranda et al., 1995; Myao and Harari, 1989), the most significant of which is the Ribeira de Iguape River (RIR) located in the northern portion of the CIP-PA.

The region has experienced significant changes over the past 150 years, especially after the construction of an artificial channel (known locally as Valo Grande) that connected the river to the estuary (see Fig. 1). This channel redirected approximately 70% of the RIR water flow toward the interior of the estuarine complex, thus modifying the freshwater–saltwater balance within the estuary and discharging large amounts of suspended solids in the area. Because residues from former mining activities are deposited on the riverbanks from the upper portion of the RIR (Guimarães and Sígolo, 2008a, 2008b; Kummer et al., 2011), unknown amounts of metals were continuously introduced into the river.

Since then, the RIR has been a major contributor of both nutrients and contaminants to the CIP estuarine complex (Mahiques et al., 2009), especially in the portions influenced by RIR discharges. The RIR still possesses a secondary (former) natural mouth known as the Barra do Icapara, which opens into the Atlantic Ocean near the city of Iguape and which is located at the border between the CIP-PA and the marine protected area of the southern coast (the local acronym for which is the APAMLS). As a consequence of these RIR contributions, metals have accumulated in the sediments (Aguiar et al., 2008; Mahiques et al., 2009), and some elements have been found at concentrations comparable to those observed in polluted industrial areas (Aguiar et al., 2008; Guimarães and Sígolo, 2008a, 2008b; Mahiques et al., 2009).