Ecotoxicology and Environmental Safety 106 (2014) 195–203

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Integrated assessment of metal contamination in sediments from two tropical estuaries

Marcos Krull [a],*, Denis M.S. Abessa [b], Vanessa Hatje [c], Francisco Barros [a]

[a] Laboratório de Ecologia Bentônica, PPGEcoBio, Instituto de Biologia, Rua Barão de Geremoabo s/n., Campus Ondina, Universidade Federal da Bahia, CEP 40170-115 Salvador, BA, Brazil
[b] Núcleo de Estudos sobre Poluição e Ecotoxicologia Aquática, UNESP, Campus Experimental do Litoral Paulista, São Vicente, SP, Brazil
[c] Laboratório de Oceanografia Química, Instituto de Química, Universidade Federal da Bahia, INCT de Ambientes Marinhos Tropicais, Salvador, BA, Brazil

ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form
22 April 2014
Accepted 23 April 2014
Available online 20 May 2014

Keywords:
Sediment quality triad
Jaguaripe
Subaé
Nitokra
Reference sites

ABSTRACT

In order to evaluate if sediment metal contamination is responsible for benthic degradation and identify possible reference sites in Todos os Santos Bay (TSB), comparisons between a highly impacted (Subaé) and less impacted (Jaguaripe) estuarine systems were made based on (i) field assessment of macrobenthic assemblage, (ii) sediment metal concentrations and (iii) chronic toxicity test with the tropical copepod *Nitokra* sp. Data were integrated by multivariate analysis (BIOENV and PCA) and the ratio-to-mean (RTMe) approach. Estuaries were divided into four different salinity zones to avoid misclassification of benthic conditions. Salinity was the main variable correlated to the benthic distribution in both estuaries, indicating that categories based on salinity features seem to be suitable in TSB. Correspondence among lines of evidence differed in low and high metal contaminated systems. Chronic toxicity was found along both the entire systems, being considerably higher in Jaguaripe. However, there was no clear evidence of metal contamination and benthic alteration in most stations of Jaguaripe. Although the concentrations of Sr and Cu were correlated to the benthic assemblage in Jaguaripe, it is unlikely that toxicity has been caused by these elements. The benthic assemblage distribution of Jaguaripe seems to be rather related to natural stressful conditions of transitional waters. Even though the Jaguaripe estuary might not be pristine, it can be used as a reference estuary for benthic assessment in TSB. Regarding the Subaé estuary, toxicity and Zn were also correlated to the benthic assemblage and most stations showed signs of benthic alteration and metal contamination. All lines of evidence were in agreement providing evidences that metal contamination might be responsible for benthic degradation in Subaé.

1. Introduction

Estuaries are recognized as some of the most productive environments on the planet, supporting many different ecosystem goods and services (Costanza et al., 1997; Savage et al., 2012). However, estuaries have been extensively degraded by increased pressure caused by population growth and development of anthropogenic activities, making these systems particularly susceptible to metal contamination (Mathews and Fisher, 2008). Similar to other contaminants, metals accumulate in estuarine sediments and may affect the structure and function of these ecosystems (Zonta et al., 2007). This is a worldwide issue which many emerging countries are now facing due to the rapid increase of anthropogenic impacts on their coastal zones and lack of proper government regulatory controls (Kennish, 2002).

Although estuarine degradation is a global issue, evaluating the possible effects of pollution on estuarine systems is still not an easy task (Chapman and Wang, 2001; Elliott and Quintino, 2007; Zonta et al., 2007). Estuaries are unique ecosystems which are subject to strong physical–chemical gradients, such as salinity, temperature, dissolved oxygen, and grain size (Sanz-Lázaro and Marín, 2009). Thus, identifying pollution effects in estuaries becomes complicated due to the interactions among several variables, making the interpretation of the responses complex and confusing (Dauvin, 2008). The recognition of such complexity has led to increasing support for the use of multiple lines of evidence (LOEs) in sediment quality assessment in estuaries (e.g. Anderson et al., 1997; Borja et al., 2008a, 2012; Riba et al., 2004).

For instance, a meaningful assessment involves multiples lines of evidence, typically from sediment chemistry, ecotoxicology and benthic ecology (Batley et al., 2002). Integrative assessments

---

* Corresponding author.
E-mail addresses: marcoskpl@gmail.com (M. Krull), dmabessa@clp.unesp.br (D.M.S. Abessa), vanessahatje@gmail.com (V. Hatje), franciscobarros.ufba@gmail.com (F. Barros).

http://dx.doi.org/10.1016/j.ecoenv.2014.04.038
0147-6513/© 2014 Elsevier Inc. All rights reserved.

of these three LOEs, known as the sediment quality triad (SQT), have been used for almost 30 years now (e.g. Chapman et al., 1987; Long and Chapman, 1985) and still is considered as one of the most appropriate approach for evaluating pollution-induced degradation (Batley et al., 2002; Gray and Elliott, 2009). The rationality of this approach is that each SQT component complements the information provided by each other, and no sole component could predict the effects of the others (Carr et al., 1996). There are other LOEs which could also be used in integrated assessments (e.g. biomarkers and manipulative experiments); however, the number and which lines of evidence are evaluated will depend on what question is intended to answer and the availability of funds and facilities (Chapman, 1990; Chapman and Hollert, 2006). Regardless of integrated assessment of contaminated sediment, it has been used for decades worldwide; the number of published studies of this kind is surprisingly limited in Brazil (e.g. Abessa et al., 2008; Buruaem et al., 2013; Paixão et al., 2011).

In order to avoid misclassification of benthic condition when studying effects of pollution and the establishment of reference sites, it is necessary to account for different habitat-specific within an estuary (Vincent et al., 2002). Because salinity is recognized as the main factor influencing species distribution in estuaries, many authors suggested that the assessment of benthic conditions in transitional waters should be based according to salinity zones (e.g. Bald et al., 2005; Borja et al., 2008b; Muxika et al., 2007). Furthermore, salinity is also an important controlling factor for the partitioning of contaminants between sediments and estuarine waters (Chapman and Wang, 2001). Thus, it is important to consider specific salinity zones when assessing pollution induced degradation in estuarine systems.

Todos os Santos Bay (TSB) stands out as the second largest bay in Brazil, with an area of approximately 1200 km^2 (Cirano and Lessa, 2007), and also for its ecological, historical and socio-economic importance. Because of increased pressure in this area over the past 60 years, the environmental quality of TSB has been influenced by several anthropogenic activities such as industrial and untreated domestic effluents, solid wastes, ports and agriculture (Hatje and Barros, 2012). There are many estuarine contributors to TSB, and among the most important are the Jaguaripe (2200 km^2) and Subaé (600 km^2) rivers (Fig. 1). The upper Subaé estuary is recognized as one of the most contaminated regions of TSB, mostly due to a large waste reservoir of a lead smelter which operated between 1960 and 1993 in Santo Amaro municipality (Hatje et al., 2006, 2009). A large amount of metal enriched wastes was improperly stored nearby the river, and still represents an important source of trace metals for the system (Hatje et al., 2006). On the opposite, the Jaguaripe estuary is thought to be relatively low impacted, considering (i) a general lower anthropogenic influence on this system, (ii) much lower metal concentrations in sediments when compared to the other estuarine systems of TSB and (iii) presents a well-conserved mangrove on most of the estuarine shore (Hatje and Barros, 2012).

Although there is an increased concern about the possible effects of contamination on TSB, until date, there was no comprehensive sediment toxicity assessment or evaluation of possible reference sites in estuarine systems of this bay. The importance of establishing and using reference sites for reliable detections of environmental disturbance is a consensus in literature (e.g. Green, 1979; Hurlbert, 1984; Underwood, 1994) and have been required by the European Water Framework Directive (WFD, 2000). This is a critical issue in estuarine systems because nearly all estuaries are influenced in some way by anthropogenic activities (Kennish, 2002), making truly undisturbed sites practically unavailable (Krantzberg et al., 2000). In this sense, reference areas are not expected only to be pristine, but will comprise areas for which any ecosystem alteration is within acceptable bounds (Chapman, 2007).

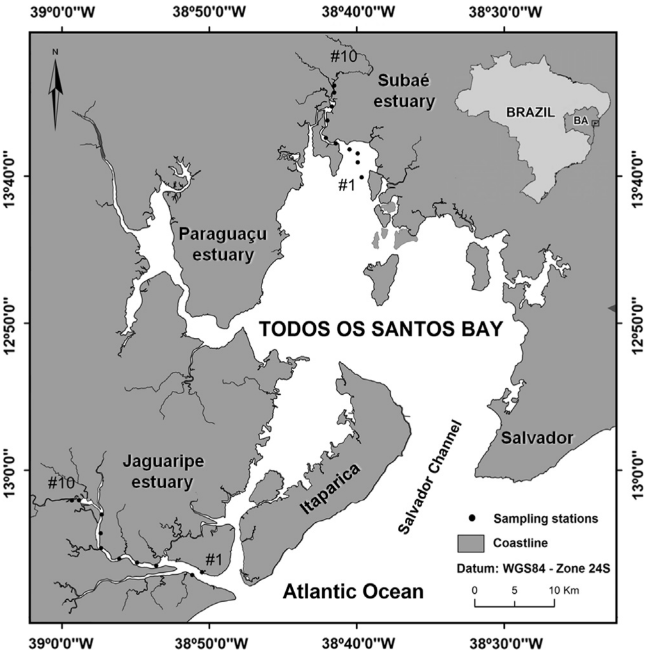

Fig. 1. Sampling stations of the Subaé and Jaguaripe estuaries, Todos os Santos Bay, BA, Brazil.

Therefore, the aims of this study were to (i) compare the sediment quality in two estuarine systems from TSB subject to different metal sources, and determine if metals are responsible for ecosystem degradation; and (ii) determine if the Jaguaripe estuary may be used as a reference area in TSB. To achieve these goals, three lines of evidence were evaluated: trace metal concentrations in sediments, chronic toxicity to the tropical copepod *Nitokra* sp., and field assessment of the macrobenthic assemblage.

2. Methods

2.1. Sample collection and processing

Sediment samples were collected over 10 stations along the salinity gradient of the Jaguaripe and Subaé estuaries (Fig. 1). Stations were numbered J1–J10 in Jaguaripe and S1–S10 in Subaé from the lower estuary to the upper estuary. All stations had depth ranging from 2 m to 4 m in flood tide. Sediment samples at all stations were haphazardly collected and analyzed for trace metal contamination, toxicity testing, particle-size distribution and macrofaunal benthic assemblage structure. For trace metals, all glass and plastic materials used during collection and analysis were previously decontaminated. All labware were immersed for at least 24 h in a detergent solution (5 percent) and for a further 48 h in 10 percent HNO_3 solution. They were then rinsed with ultra-pure water, dried on a clean covered bench and stored in zip-lock bags before use. Surficial sediments (top 3 cm) were collected with a stainless steel van Veen grab for chemical and toxicity analyses. Between replicates, the grab was washed with ambient water. All samples were maintained on ice, in the dark, during transport to the laboratory. Sediment samples for chemical analysis were stored frozen and samples for whole sediment toxicity testing were immediately sealed and stored at 4 °C in the dark. Toxicity tests were performed within less than one week after sampling.

2.2. Sediment physical–chemical analysis

For chemical analyses, sediments were freeze dried, homogenized and then comminuted in a ball mill. Trace elements (Al, Ba, Cr, Co, Cu, Fe, Mg, Mn, Pb, Sr, V and Zn) were extracted with 1.0 mol L^{-1} HCl (Hatje et al., 2006; Hatje and Barros, 2012) and determined by ICP OES (VARIAN Vista-Pro, Mulgrave, Australia). Extractions with 1.0 mol L^{-1} HCl release metals associated with labile phases, which are expected to be the most bioavailable, in contrast to the resistant mineral matrix (Hinrichs et al., 2002). All samples were analyzed in triplicates. Precision and accuracy of analytical methods were assessed by analysis of certified reference materials MESS-3 and PACS-2 (National Research Council of Canada, Canada). Results indicated good analytical precision and incomplete extraction (i.e. recovery