Heavy metals in benthic organisms from Todos os Santos Bay, Brazil

Amado-Filho, GM.[a*], *Salgado, LT.*[a], *Rebelo, MF.*[b], *Rezende, CE.*[c], *Karez, CS.*[d], *and Pfeiffer, WC.*[b]

[a]Programa Zona Costeira, Instituto de Pesquisas Jardim Botânico do Rio de Janeiro, Rua Pacheco Leão, 915, CEP 22460-030, Rio de Janeiro, RJ, Brazil

[b]Laboratório de Radioisótopos, Instituto de Biofísica Carlos Chagas Filho, Universidade Federal do Rio de Janeiro, CEP 22949-900, Rio de Janeiro, RJ, Brazil

[c]Laboratório de Ciências Ambientais, Centro de Biociências e Biotecnologia, Universidade Estadual do Norte Fluminense, Av. Alberto Lamego 2000, CEP 28023-602, Campos dos Goytacazes, RJ, Brazil

[d]Programa de Ciencias Ecológicas y de la Tierra, Oficina Regional de Ciencia para América Latina y el Caribe, UNESCO, Calle Luis Piera 1992, 2°. Piso, 11000 Montevideo, Uruguay

*e-mail: gfilho@jbrj.gov.br

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(With 1 figure)

Abstract

The marine ecosystems of Todos os Santos Bay (TSB, The State of Bahia, Brazil) have been impacted by the presence on its coast of a large metropolitan area as well as of chemical and petrochemical activities. Despite its ecological importance, there is a lack of scientific information concerning metal contamination in TSB marine biota. Thus, we analyzed concentrations of metals in four species of marine benthic organisms (two seaweeds, *Padina gymnospora* and *Sargassum* sp. one seagrass, *Halodule wrightii* and one oyster, *Crassostrea rhizophorae*) in three sites from the TSB region that have been most affected by industrial activities. The concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined by Atomic Absorption Spectrophometry. The obtained data indicates that cadmium and copper in seaweeds, oysters and seagrass, as well as Ni concentrations in oysters, were in range of contaminated coastal areas. Cadmium and copper are available to organisms through suspended particles, dissolved fraction of water column and bottom sediment interstitial water. As oysters and other mollusks are used as food sources by the local population, the metal levels found in oysters in TSB may constitute a health risk for this population. Our results suggest implanting a heavy metals biomonitoring program in the TSB marine ecosystems.

Keywords: seaweed, seagrass, oyster, bioaccumulation, Todos os Santos Bay.

Metais pesados em organismos bentônicos da Baía de Todos os Santos, Brasil

Resumo

A Baía de Todos os Santos (TSB, Estado da Bahia, Brasil), vem sendo impactada pela presença, em seu entorno, de uma extensa área metropolitana e por atividades químicas e petroquímicas. Apesar de sua importância ecológica, existe pouca informação sobre a contaminação da biota marinha da TSB por metais pesados. Neste contexto, foram analisadas as concentrações de metais em quatro espécies de organismos bentônicos: duas algas, *Padina gymnospora* e *Sargassum* sp.; uma grama marinha, *Halodule wrightii*; e uma ostra, *Crassostrea rhizophorae*, em três locais das regiões da TSB mais afetadas pelas atividades industriais. As concentrações de Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn foram determinadas por espectrofotometria de absorção atômica. Os resultados obtidos indicaram que o cádmio e o cobre em algas, gramas marinhas e ostras, assim como o níquel em ostras estão, em concentrações de áreas contaminadas. Pelos resultados obtidos o cádmio e o cobre estão biodisponíveis a partir das partículas de sedimento em suspensão, fração dissolvida da coluna da água e da água intersticial do sedimento de fundo. Como ostras e outros moluscos são utilizados como fonte de alimento pelas populações locais, as concentrações de metais encontradas nas ostras da TSB podem constituir risco para as populações humanas locais. Os resultados obtidos sugerem a necessidade de implementação de um programa de monitoramento das concentrações de metais pesados em organismos dos ecossistemas marinhos da TSB.

Palavras-chave: macroalgas, gramas marinhas, ostras, bioacumulação, Baía de Todos os Santos.

1. Introduction

In contaminated environments, more important than the total load of contaminants, is the bioavailability. According to Phillips and Rainbow (1993), bioavailability can only be measured appropriately by what is found in the tissues of a target organism. Moreover, despite the importance of the chemical species of the contaminant or the abiotic conditions of the environment, bioaccumulation is a biological property and relates directly to the target organism (Beeby, 2001). Thus, it is imperative to use several organisms to evaluate environmental contamination, assessing different uptake capabilities of diverse chemical species and reservoirs.

In marine coastal zones, seagrasses and seaweeds are more exposed to the dissolved fraction of contaminants, and bivalve mollusks to the suspended particles (Rainbow, 1995). For tropical Western Atlantic coastal areas previous studies have shown three benthic organisms as good bioaccumulators of metals: the oyster *Crassostrea rhizophorae* (Guilding, 1828) exhibits high filtration rates of suspended particles and a high metal bioaccumulation capability (Lima et al., 1986; Wallner-Kersanach et al., 2000; Rebelo et al., 2003), the brown seaweeds, specially *Padina gymnospora* (Kuetzing) Sonder, 1871 exhibit high capability of accumulating metals from the dissolved fraction of water column (Amado Filho et al., 1999) and the seagrass *Halodule wrightii* Ascherson, 1868, which is an important contributor to primary production (Klumpp and Van der Valk, 1984), take up metals from both water, through leaf surfaces, and from sediment and interstitial water, by way of their roots (Pulich, 1980; Amado Filho et al., 2004).

Todos os Santos Bay – TSB (13° S and 38° W) is the largest tropical bay in Brazil with an area of about 1,000 km^2 (Figure 1) situated in the state of Bahia (BA). This bay is impacted by the presence of a large metropolitan area (the city of Salvador with 2,600,000 habitants) and industrial activity that includes chemical and petrochemical plants as well as an oil refinery and harbor activities located in the North and Northeastern area of the bay. It also receives discharges from Subae River (Figure 1), which drains an industrial area containing a lead smelter plant, a paper mill and alcohol distilleries. Water circulation is mainly controlled by tide (Lessa et al., 2001). TBS is also an important center of tourism and shell-fishing activities that take place throughout the whole bay. The most important ecosystems are the mangroves situated in the northern part of the bay. There are also reefs in several regions of the bay. Although it's considered ecologically important, there is little data available concerning metal contamination in organisms from TSB. The mollusks *Anomalocardia brasiliana* (Gmelin, 1791)*, Brachidontes exustus* (Linnaeus, 1758) and *Crassostrea rhizophorae* were analyzed for their metal content in TSB (Tavares, 1983, Wallner-Kersanach et al., 1994; 2000) and it was shown that differences between TSB area and control sites were detected only for *C. rhizophorae*.

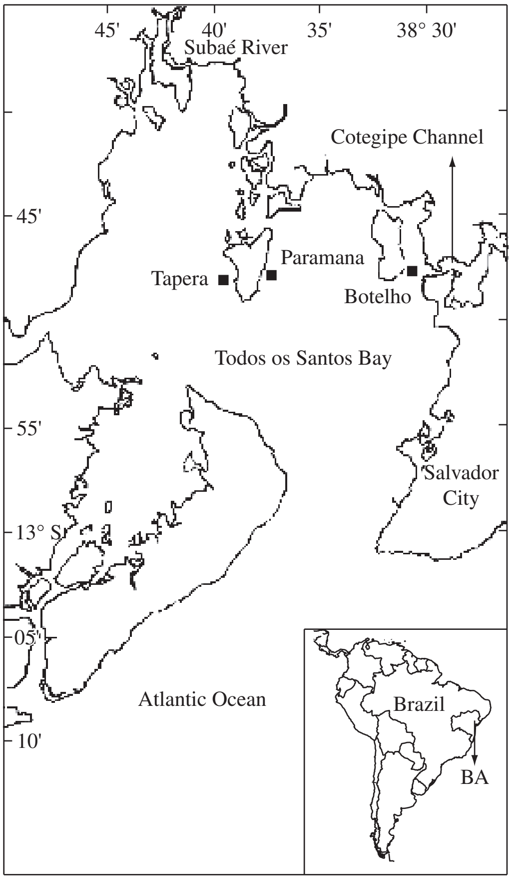

Figure 1. Location of the three collection sites studied (Tapera, Paramana and Botelho) at Todos os Santos Bay, state of Bahia (BA), Brazil. The Cotegipe Channel connects the Aratu Bay to TSB.

Our aim was to assess the heavy metals contamination in the north and northeastern areas of TSB these being the main areas affected by industrial activities. This was done by analysis of metal concentrations in marine benthic organisms: *Crassostrea rhizophorae* which is a typical sentinel organism (Lima et al., 1986; Wallner-Kersanach et al., 2000; Rebelo et al., 2003) abundant in the mangroves and reefs along the coast, the seagrass *Halodule wrightii*, which forms extensive beds on the shallow sea bottom (Amado Filho et al., 2004) and *Padina gymnospora* and *Sargassum* sp., two abundant seaweed species in Brazilian tropical areas (Karez et al., 1994a; Amado Filho et al. 1999).

2. Material and Methods

Organism samples were collected in 3 sites, Botelho, Paramana and Tapera located near industrial areas in the north and the northeastern regions of the Bay (Figure 1). Oyster samples were analyzed only for Botelho and Tapera because populations of this species were not found in Paramana. Samples were collected at the end of rainy season in August of 2000. In order to verify a seasonal effect in organism metal concentrations, samples of *C. rhizophorae* and *P. gymnospora* were re-collected in Botelho at the end of the dry season in February of 2001.

Macrophyte *Halodule wrightii* samples were collected at 2 m depth, washed and cleaned in seawater accordingly to Amado Filho et al. (2004). Roots, rhizomes and leaves were separated manually. About 3 g (wet weight) of each plant compartment were washed in seawater and in distilled water and dried at 60 °C to constant weight. The seaweeds *Padina gymnospora* and *Sargassum* sp. were cleaned of epiphytes, washed in seawater, then in distilled water, dried at 60 °C to constant weight (at least 1 g) and then homogenized in porcelain mortar. Around 20 specimens of *Crassostrea rhizophorae* with similar shell lengths (3.5 cm) and at the same tidal height (low tide) were collected at each station. Soft tissues were removed from the shells and entirely homogenized and dried at 60 °C to constant weighed and ashed (48 hours at 400 °C). The samples were digested accordingly Lacerda et al. (1987) with concentrated HNO_3 (Merck, 65%) and HCl (Merck, 37%) until complete dissolution of the organic tissues. The resulting solution was evaporated and re-dissolved in 0.1 N HCl.

The concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined by Atomic Absorption Spectrophometry (Varian AA-1475) in triplicate samples and the results expressed in $\mu g.g^{-1}$ (dry weight). Standard samples from IAEA-140 (Sea plant homogenate, *Fucus*) and NIST 296 (Mussel) were analyzed and retrieval corresponded to a minimal of 90% of the reference values.

One-Way Analysis of Variance (ANOVA) was used to compare metal concentrations between parts of *Halodule wrightii* and among sampling sites. Differences were considered significant when $p < 0.05$ (STATISCA 4.2). Comparisons between obtained data of metal concentrations of TSB organisms and previous published works were done taking in account uniformity in body size, stage of the life cycle, and season of the year.

3. Results and Discussion

Average metal concentrations in biological samples are presented in Table 1. Among the organisms sampled in TSB, *C. rhizophorae* exhibited the highest concentrations for Cu (526.1 ± 153.8 $\mu g.g^{-1}$), Cd (8.29 ± 2.43 $\mu g.g^{-1}$), Ni (1990.9 ± 91.4 $\mu g.g^{-1}$) and Zn (4733 ± 1291 $\mu g.g^{-1}$); while *H. wrightii* exhibited the highest concentrations for Cr (12.2 ± 4.9 $\mu g.g^{-1}$), Fe (5664 ± 460 $\mu g.g^{-1}$), Mn (803.5 ± 47.8 $\mu g.g^{-1}$) and Pb (13.6 ± 2.0 $\mu g.g^{-1}$); and *P. gymnospora* exhibited significantly higher values for Al (4412 ± 133 $\mu g.g^{-1}$).

The concentrations for the nine metals analyzed in *H. wrightii* population from TSB exhibited differences among plant compartments (roots, rhizomes and shoots) and sampling sites (ANOVA, $p < 0.05$). In relation to plant compartments, considerably higher concentrations were observed in the roots for eight metals (except for Mn) when compared to the rhizomes. Concentrations were also notably higher in roots for six metals (except Cd, Cu and Pb) when compared to shoots. Concentrations were significantly higher in the rhizomes compared to shoots for Cr, Fe, Mn and Pb.

The observed trend of higher metal concentrations in roots than rhizomes and shoots, suggests that *H. wrightii* roots are the main compartment for metal accumulation, reflecting the metal concentration and availability in the sediment pore waters. On the other hand, Mn which presented an elevated concentration in the shoots, has been noted in other seagrass species as a metal that tends to be accumulated in a higher degree in shoots, as was pointed out by Malea (1994), Sanchiz et al. (1999) and Prange and Dennison (2000).

In the comparison of the sample sites, it was found that samples from Botelho exhibited significantly higher concentrations than Paramana or Tapera for Al (root), Cd (root), Cu (root, rhizome and shoot), Fe (root, rhizome and shoot), Mn (rhizome and shoot) and Zn (root and shoot); Tapera presents higher concentrations than Paramana of Al (root) and Mn (shoots). No differences were detected in Cr, Ni and Pb concentrations among the three sample sites.

In relation to the metal concentrations in seaweeds, the same trend observed in the seagrass of highest metal concentrations in Botelho was seen. *P. gymnospora* presented significantly higher concentrations of Al, Cu, Fe, Mn and Zn in Botelho and Cd in Tapera. *Sargassum* spp. presented higher concentrations of Cr in Botelho, Cd in Tapera and Cu and Mn in Paramana.

In oyster samples, differences between sites were seen in the following metals, Cd, Cr, Cu, Fe, Ni, Zn. Higher concentrations of Cr, Cu, Ni and Zn were observed in Botelho and higher concentrations of Cd and Fe were observed in Tapera.

The observed trend of higher metal concentrations in samples from Botelho can be related to the localization of this site in front of Cotegipe Channel. This channel connected the Aratu Bay (Figure 1) to TSB. Most industries are situated in the northern part of the Aratu Bay. Direct anthropogenic contributions from the Cotegipe Channel originate from an ore terminal, harbor activities of naval vessels and offshore oil rig repairs, and transport of organic products (Wallner-Kersanach *et al.*, 2000).

Even though there was a general trend of higher metal concentration in both *P. gymnospora* and *C. rhizophorae* observed in the rainy season (2000) when compared to the dry season (2001) (Table 1), no significant difference ($p < 0.05$) was detected between both seasons, and the levels of all analyzed metals were maintained in the same range. The available data about salinity of TSB indicates that the main portion of the Bay is dominated by typical marine conditions (range of 33.0 and 36.7 PSU) that don't change seasonally (Wolgemuth et al., 1981; Lessa et al., 2001). In this way, the levels of metal accumulated by benthic organisms of the studied sites should be more related to the load of metals to the Bay system by the

Table 1. Mean (± standard deviation) metal concentrations ($\mu g.g^{-1}$ dry weight) in seagrass (*H. wrightii*) seaweeds (*P. gymnospora*, and *Sargassum* sp.) and bivalve mollusk (*Crassostrea rhizophorae*) from the collected sites of Todos os Santos Bay.

Species	Sites	Tissue	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Halodule wrigthii	Botelho	Root	4236 ± 153	1.56 ± 0.18	12.2 ± 4.9	32.2 ± 2.5	5664 ± 460	16.1 ± 3.0	8.2 ± 2.7	13.6 ± 2.0	23.0 ± 3.1
		Rhizome	1432 ± 28	0.70 ± 0.55	6.1 ± 0.4	15.5 ± 0.4	2800 ± 234	102.5 ± 7.4	5.3 ± 0.3	6.7 ± 1.6	30.1 ± 3.5
		Leave	1266 ± 239	0.79 ± 0.05	5.0 ± 0.8	26.3 ± 1.0	661 ± 140	803.5 ± 47.8	5.6 ± 0.1	12.8 ± 0.7	37.2 ± 1.4
	Paramana	Root	2846 ± 258	1.01 ± 0.05	10.3 ± 0.4	9.1 ± 0.3	2826 ± 84	23.9 ± 2.0	8.0 ± 1.7	13.2 ± 1.5	13.0 ± 0.1
		Rhizome	1160 ± 85	0.78 ± 0.08	2.4 ± 0.2	5.5 ± 0.6	955 ± 87	17.6 ± 0.1	4.5 ± 0.5	5.1 ± 0.8	21.1 ± 2.4
		Leave	747 ± 282	1.21 ± 0.15	1.0 ± 0.0	10.9 ± 0.2	331 ± 132	115.0 ± 4.2	4.4 ± 1.6	11.0 ± 1.5	23.2 ± 4.2
	Tapera	Root	4435 ± 458	0.90 ± 0.28	8.8 ± 0.7	9.2 ± 1.2	4160 ± 355	42.7 ± 1.5	6.8 ± 1.2	12.0 ± 3.2	16.3 ± 7.5
		Rhizome	1487 ± 280	0.80 ± 0.14	8.6 ± 1.4	7.1 ± 0.5	1737 ± 137	29.5 ± 4.5	6.2 ± 1.6	10.8 ± 1.4	26.1 ± 7.3
		Leave	933 ± 113	0.60 ± 0.10	2.2 ± 0.3	7.2 ± 0.1	447 ± 61	149.0 ± 13.9	6.3 ± 0.3	7.8 ± 0.9	17.7 ± 3.2
Padina gymnospora	Botelho	Entire	4412 ± 133	1.03 ± 0.18	5.5 ± 0.3	32.4 ± 1.3	1967 ± 15	630.4 ± 43.1	11.7 ± 0.7	9.0 ± 0.5	42.6 ± 7.4
	Paramana	Entire	2744 ± 305	1.01 ± 0.11	7.2 ± 1.9	8.8 ± 1.2	1304 ± 109	350.1 ± 24.0	7.8 ± 2.9	6.1 ± 0.7	24.4 ± 14.3
	Tapera	Entire	2774 ± 258	1.64 ± 0.19	6.0 ± 1.5	6.6 ± 0.4	1248 ± 153	584.6 ± 17.4	9.8 ± 1.5	8.7 ± 1.4	18.4 ± 1.7
Sargassum sp.	Botelho	Entire	2688 ± 601	1.29 ± 0.28	9.0 ± 0.5	6.5 ± 0.9	1234 ± 236	93.7 ± 5.9	9.1 ± 1.0	8.5 ± 1.5	13.5 ± 0.8
	Paramana	Entire	2454 ± 226	0.40 ± 0.06	7.3 ± 0.7	16.8 ± 0.5	1100 ± 115	334.9 ± 21.2	8.5 ± 0.7	11.1 ± 2.5	27.1 ± 6.7
	Tapera	Entire	2844 ± 479	1.45 ± 0.26	1.5 ± 0.3	6.0 ± 0.4	1502 ± 326	126.7 ± 8.2	9.7 ± 1.4	6.2 ± 0.7	13.7 ± 6.7
Crassostrea rhizophorae	Botelho	Entire	4.3 ± 2.9	8.29 ± 2.43	2.5 ± 0.7	276.1 ± 129.7	330 ± 48	16.4 ± 1.6	531.8 ± 92.2	6.6 ± 2.0	2099 ± 501
	Tapera	Entire	5.3 ± 1.6	2.71 ± 0.58	4.5 ± 0.6	526.1 ± 153.8	924 ± 133	17.1 ± 1.8	1990.9 ± 91.4	4.5 ± 1.3	4733 ± 1291
*Padina gymnospora**	Botelho	Entire	2744 ± 305	1.10 ± 0.13	5.9 ± 1.0	28.8 ± 1.2	1807 ± 109	709.1 ± 62.0	11.4 ± 1.2	11.4 ± 1.2	54.3 ± 5.5
*Crassostrea rhizophorae**	Botelho	Entire	3.6 ± 0.8	6.98 ± 0.75	2.2 ± 0.6	224.6 ± 44.5	260 ± 22	16.1 ± 1.2	499.2 ± 28.4	6.2 ± 1.1	1890 ± 160

*Results obtained in February 2001.

anthropogenic inputs than natural seasonal changes of abiotic parameters.

A comparison between the obtained data with other results of contaminated Brazilian coastal areas by using the same studied species shows that the metals Cd, Cu and Ni from TSB were in the similar range of concentrations (Amado Filho et al., 1999; Rebelo et al., 2003). The higher Cd concentrations of 1.56 $\mu g.g^{-1}$ in seagrass, 1.64 $\mu g.g^{-1}$ in seaweed and 8.29 $\mu g.g^{-1}$ in oyster are similar to that concentrations found in Sepetiba Bay (*H. wrightii* = 0.4-1.5 $\mu g.g^{-1}$, Amado Filho et al., 2004; *P. gymnospora* 1.0-2.7 $\mu g.g^{-1}$, Amado Filho et al., 1999; *C. rhizophorae* = 1.3-29.8 $\mu g.g^{-1}$, Rebelo et al., 2003), which have been studied due to the impact of a Cd and Zn smelting plant. Cadmium concentrations found in TSB samples are higher than that found in non contaminated Brazilian coastal areas (*H. wrightii* = 0.2-0.3 $\mu g.g^{-1}$, Amado Filho et al., 2004; *P. gymnospora* = 0.30-0.42 $\mu g.g^{-1}$, Karez et al., 1994a; *C. rhizophorae* = 0.8-2.3 $\mu g.g^{-1}$, Rebelo et al., 2003). The Cu concentrations of 32.2 $\mu g.g^{-1}$ in seagrass, 32.4 $\mu g.g^{-1}$ in seaweed and 526.1 $\mu g.g^{-1}$ in oysters were higher than those observed in Cu contaminated areas, like Guanabara Bay (*P. gymnospora* = 13.6 ± 0.9 $\mu g.g^{-1}$, Karez et al., 1994b; *C. rhizophorae* = 148 $\mu g.g^{-1}$, Carvalho and Lacerda, 1992) and the Potengi River Estuary (*C. rhizophorae* = 234 ± 55 $\mu g.g^{-1}$, Silva et al., 2001) and other less contaminated areas (*H. wrightii* = 4.0-14.1 $\mu g.g^{-1}$, Amado Filho et al., 2004). Among the three considered organisms only the oysters exhibited higher Ni concentrations. In relation to other Brazilian coastal areas, Ni concentrations in oyster found at TSB (531.8-1990.1 $\mu g.g^{-1}$) were two order of magnitude higher than previously reported values (15-20 $\mu g.g^{-1}$, Carvalho et al., 1991 and Pfeiffer et al., 1985). Wallner-Kersanach et al. (2000) who carried out transplant experiments with *C. rhizophorae* populations of TSB during the year of 1991, analyzed Cd, Cu, Pb and Zn in oysters from Cotegipe Channel (Figure 1). Comparison of data between 1991 and 2000 showed similar concentrations of Cu and Zn and an increase of Cd and Pb concentrations in 2000.

When wet weight is considered, the concentrations of Cu and Ni in oysters from TSB exceeded the limits recommended for human consumption according to the Brazilian Health Agency (Cu and Ni < 2.0 $\mu g.g^{-1}$ wet weight). As oysters and other mollusks are used as food sources by the local population, the contaminated oysters of TSB may constitute a health risk for this population.

In addition to previous results of metal concentrations in oysters (Wallner-Kersanach et al. 2000), the obtained data from TSB indicates that Cd and Cu concentrations were in range of contaminated coastal areas. This conclusion is supported by levels of Cd and Cu in seaweeds, seagrass and oysters. Cadmium and Cu are available to organisms through suspended particles, dissolved fraction in the water column and bottom sediment interstitial water. Although the observed result of Ni in oysters indicates elevated concentration, they were not supported by results in other organisms, suggesting that more evidence is needed to confirm this element as a contaminant in TSB. In summary, our results show the usefulness of analyzing different organisms that can take up metals from different ecosystem compartments and that a heavy metals biomonitoring program has to be implemented in the marine biota of TSB.

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