Heavy metals in the Guanabara Bay biota: Why such low concentrations?

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Heavy metal concentrations in the marine biota of Guanabara Bay, Rio de Janeiro, are very low, compared to other contaminated areas along this coast. Notwithstanding this, the bay receives extremely high inputs of such contaminants. Concentrations found in benthic algae, crustaceans and molluscs are similar to those found in noncontaminated areas of the Rio de Janeiro coast. The large inputs of sewage result in partially reducing conditions of the bay's water as well as high sedimentation rates; this maintains heavy metals buried in anoxic sediments unavailable for biological uptake.

As concentrações de metais pesados na biota marinha da baía de Guanabara, Rio de Janeiro, são comparativamente muito baixas, embora a baía receba uma carga muito grande desses contaminantes. As concentrações encontradas em algas bentânicas, crustáceos e moluscos são inclusive similares àquelas encontradas nos mesmos organismos em áreas não contaminadas do litoral do Rio de Janeiro. As grandes cargas de esgotos domésticos lançados na baía de Guanabara, resultam em um ambiente parcialmente redutor e em altas taxas de sedimentação, que mantêm os metais fortemente ligados ao sedimento sob forma não-disponível para incorporação biológica.

Guanabara Bay is the most important drainage system of the Rio de Janeiro coast, located at 22° S, 43° W (Fig. 1), with an area of approximately 381 km^2, and 80% of its area with depths less than 10 meters.

The bay receives the drainage of 35 rivers and an untreated urban waste discharge of 600 ton/day from 12 municipalities with an estimated population of 9 million inhabitants. The bay's watershed also harbors the second largest industrial area of the country with approximately 6,000 industries, two harbors, two airports, oil terminals and shipyards (1); consequently most of its area is partially or totally degraded (2).

Although Guanabara Bay has been the object of diverse environmental discussions, very few studies have been done dealing with heavy metal distribution in the bay's aquatic biota (3). Therefore the objective of this work is to quantify the heavy metal (Zn, Cu, Cd, Pb, Mn and Ni) concentrations and distribution in benthic marine organisms from the Guanabara Bay.

We have analyzed organisms from three different areas inside Guanabara Bay (Fig. 1). Three specimens of each species representing the most conspicuous and abundant ones presently occurring in the bay, were collected at each point. The samples were treated for conventional atomic absorption determination of heavy metals. Details of analytical procedures are published elsewhere (4,5).

All results are presented in Table 1. Concentrations of all metals found in a given species were similar regardless of sampling site, with the exception of Pb which is particularly enriched at the Praia Vermelha beach. However, differences among species were observed reflecting the distinct physiologies (6) and alimentary habits (7) of each species. The highest concentrations of all metals occurred in filter-feeding molluscs (*P. perna* and *C. brasiliana*) and crustaceans (*Balanus* sp.), and lower in the green algae *U. fasciata*. Filter-feeding animals, among the marine biota, generally present the highest bioaccumulation factors of heavy metals, due to the ingestion of large amounts of metal-rich suspended particles (6-9).

Zinc concentrations were highest in all organisms, with values up to 2,658 µg/g and 1,308 µg/g in *C. brasiliana* and *Balanus* sp. respectively. The lowest Zn concentration (1.3 µg/g) was found in the green algae *U. fasciata*. The high Zn concentrations, particularly in molluscs and crustaceans, were probably due to the importance of this element in the metabolism of these animals, where Zn is an important constituent of about 90 different enzymes (8). Also these organisms are known to accumulate Zn in polymetallic granules, which allow extremely high Zn concentrations without affecting the animal's metabolism (8).

Copper presented the highest values in *C. brasiliana* (148 µg/g) and the lowest in *U. fasciata* (8 µg/g). Manganese presented its highest concentrations in *A. brasiliana* (153 µg/g), and the smallest in *T. haemastoma* (10 µg/g). *A. brasiliana* is a sediment dwelling bivalve, in contrast to all other organisms sampled, and is exposed to sediment porewater, where Mn concentrations are very high. Therefore it is not surprising that this species presented the highest Mn content (11). These elements, in spite of being essential, Cu for molluscs and crustaceans due to its importance in the gas exchanges in the blood of these organisms (8), and Mn which participates in the algae's Krebs cycle (10), pre-

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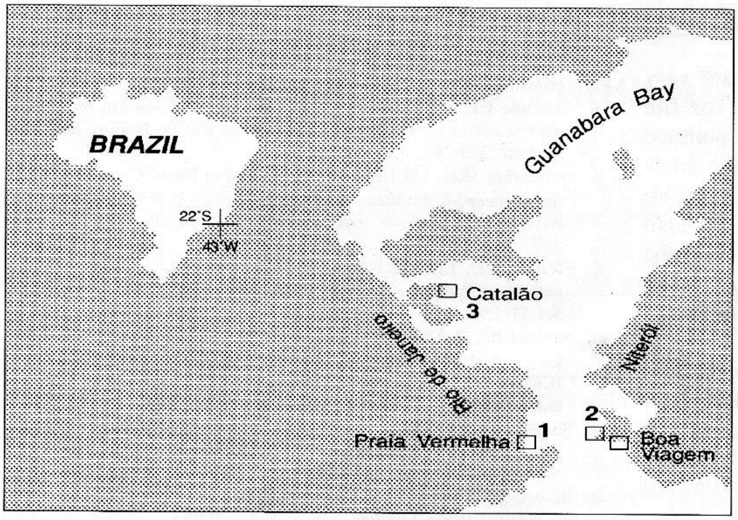

Figure 1. Location of sampling sites in Guanabara Bay, Rio de Janeiro.

Table 1 — Heavy metal concentrations in marine biota of the Guanabara Bay[a].

Organisms	*Ni*	*Cu*	*Cd*	*Mn*	*Zn*	*Pb*
Praia Vermelha Beach (Station 1)						
Fissurela sp.	nd[b]	36	0.7	14	112	4
C. brasiliana	3	148	0.4	36	1302	nd[b]
C. subrugosa	3	11	2	12	100	2
T. viridula	0.9	59	nd[b]	22	286	1
P. perna	3	11	0.1	14	132	4
Balanus sp.	22	21	12	34	1308	4
U. fasciata	0.6	8	nd[b]	10	1.3	2
T. haemastoma	0.9	62	1	10	277	0.8
B. caicarum	0.6	9	0.2	10	104	nd[b]
Boa Viagem Beach (Station 2)						
C. brasiliana	2	111	0.7	29	2658	nd[b]
T. haemastoma	2	23	0.6	11	396	nd[b]
U. fasciata	2	8	nd[b]	78	27	nd[b]
Balanus sp.	1	8	0.6	48	460	nd[b]
P. perna	8	99	0.1	20	169	1
C. subrugosa	2	8	2	14	33	1
B. caicarum	1	9	nd[b]	16	100	2
C. costatum	9	9	0.9	30	208	0.4
Catalão Beach (Station 3)						
B. caicarum	0.5	13	0.1	47	69	1
A. brasiliana	2	16	1	153	146	nd[b]

[a] Mean values in μg/g
[b] Not detectable

sented lower concentrations when compared to other contaminated sites (5,11).

Cadmium, lead and nickel presented the lowest concentrations among the studied metals. For Cd the highest concentration was in *Balanus* sp. (12 μg/g), all other animals presenting very low Cd concentrations. The highest lead concentrations were found in *P. perna*, *Balanus* sp. and *Fissurela* sp. (4 μg/g).

The highest Ni concentrations were observed in *Balanus* sp. (22 μg/g), being relatively low in all other organisms. Considering that these metals do not have any known physiological function in marine organisms (9), the concentrations found probably reflect the levels of bioavailable metals in the area (6), thus suggesting low concentrations in the bay's environment.

In general the concentrations found in the studied organisms were similar to those of areas without metal contamination, and very low when compared to other contaminated areas (Table 2).

Zinc concentrations are up to ten times lower than concentrations reported in other contaminated areas of the Rio de Janeiro coast. In Sepetiba Bay, for example, Zn concentrations of up to 5,500 μg/g, 9,500 μg/g and 2,508 μg/g have been reported for *Balanus* sp., *C. brasiliana* and *T. haemastoma* respectively (11). Also Zn concentrations were similar to those found in noncontaminated areas like Angra dos Reis and Arraial do Cabo (11).

Table 2 — Comparison of heavy metals concentrations (μg/g) in different areas of the Rio de Janeiro coast submitted to different degrees of contamination and from the Guanabara Bay (GB). Only organisms occurring in all sites are compared. Data from Sepetiba Bay (SB) are from Pfeiffer et al (5) and Carvalho et al (11); and from Angra dos Reis (AR) and Arraial do Cabo (AC) are from Carvalho et al (11).

Organisms		*Pb*	*Cd*	*Zn*	*Ni*	*Cu*	*Mn*
P. perna	GB	2	0.1	150	6	10	17
	SB	nd[a]	1	205	7	7	18
	AC	33	2	140	17	7	8
C. brasiliana	GB	129	0.6	1980	3	129	32
	SB	1	2	973	-	3	3
	SB	13	9	9500	18	25	30
T. haemastoma	GB	0.4	0.9	336	2	43	10
	SB	7	11	2508	13	49	11
	AC	37	5	392	13	51	12
	AR	4	3	987	21	153	17
U. fasciata	GB	0.9	nd[a]	20	1	8	44
	AC	50	0.6	22	23	8	54
	AR	2	nd[a]	6	17	7	18
	SB	20	0.2	19	11	3	44
Balanus sp.	GB	2	7	884	12	14	41
	SB	10	6	5500	20	6	28
	AC	47	6	405	38	4	13
T. viridula	GB	1	nd[a]	286	0.9	59	22
	AC	37	0.9	239	21	41	9
	SB	7	1	372	21	55	75
	AR	5	1	3	12	73	27
C. subrugosa	GB	2	2	67	2	9	13
	AC	52	1	39	22	7	9

[a] Not detectable

Nickel, cadmium and lead concentrations were particularly lower in Guanabara Bay organisms when compared to other contaminated sites and much lower than the concentrations reported from noncontaminated areas like Angra dos Reis and Arraial do Cabo (3, 5,11). The only exception was the Pb content in *C. brasiliana* which was higher in the Guanabara Bay. Copper, on the other hand, presented similar concentrations throughout the Rio de Janeiro coast, probably reflecting the intense metabolic control of this essential metal by marine organisms (8).

Manganese concentrations, however, were, contrary to all other metals, higher in organisms from the Guanabara Bay. The partially reducing conditions of the bay's water would increase the solubility of Mn, thus making it more available for biological uptake (3).

Heavy metals can be associated with diverse geochemical forms according to the physicochemical conditions of the environment, having a higher or lower bioavailability (12). Metals can be found adsorbed in ionic exchange sites; complexed to organic molecules; co-precipitated with oxy-hydroxides of Fe and Mn, carbonates, sulfides or in the detritic lattice of minerals (13). These chemical forms will eventually control heavy metal availability rather than their total concentrations (6,8,9,14).

High heavy metal concentrations in sediments and very high metal inputs were previously reported for the Guanabara Bay, which is considered as a highly polluted area as compared to other industrialized coastal areas (1,14). Even comparing other sites along the Rio de Janeiro coast, inputs of metals to the Guanabara Bay are also higher. Notwithstanding this, heavy metal contents in the Guanabara Bay biota are lower than in other contaminated sites along the Rio de Janeiro coast and similar to noncontaminated areas (11).

The highest concentrations of heavy metals in Guanabara Bay sediments were mainly found along the Northwestern coast of the bay (1,15), where water circulation is restricted, and the largest inputs of industrial and urban wastes occur. This area was classified as totally degraded by Teixeira et al (2) in a study on the biodiversity of algae.

Souza et al (13) and Lacerda et al (16) surveyed metal concentrations and geochemistry in sediments along the Rio de Janeiro coast. As expected, Guanabara Bay presented much higher sediment concentrations of Cr, Pb, Cu and Zn, than other contaminated sites, with the major fraction of the total concentration bound to reduced compounds, in particular sulfides. Sulfides are known to control metal solubility and bioavailability in partially reducing environments (17) therefore decreasing metal toxicity (9).

Heavy metals that enter the Guanabara Bay from its drainage system are probably bound to organic compounds, associated to oxy-hydroxides of Fe and Mn and/or absorbed in ionic exchange sites. When these pollutants reach the bay, they are submitted to intense reducing conditions and released to the water column where they immediately react with sulfide ions widely distributed in these waters, due to high organic matter remineralization and anoxia. After reacting with sulfides, the metals are precipitated, being immobilized in the anoxic sediments. Metal sulfides are in general very stable under reducing conditions, and nonavailable for biological uptake (17). The only exception of this pattern is Mn, which is more soluble under reducing conditions.

The lower concentrations of heavy metals found in the studied organisms certainly reflect the process described above, and the higher manganese concentrations strongly suggest this. Therefore, notwithstanding the high inputs of heavy metals into the Guanabara Bay, the prevailing reducing conditions keep them nonavailable for biological uptake. However, such high concentrations of metals reported for Guanabara Bay sediments suggest that the bay's environment has a very high toxic potential and if the reducing conditions change, high concentrations of metals can be made bioavailable becoming a serious threat to the local biota. ■

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