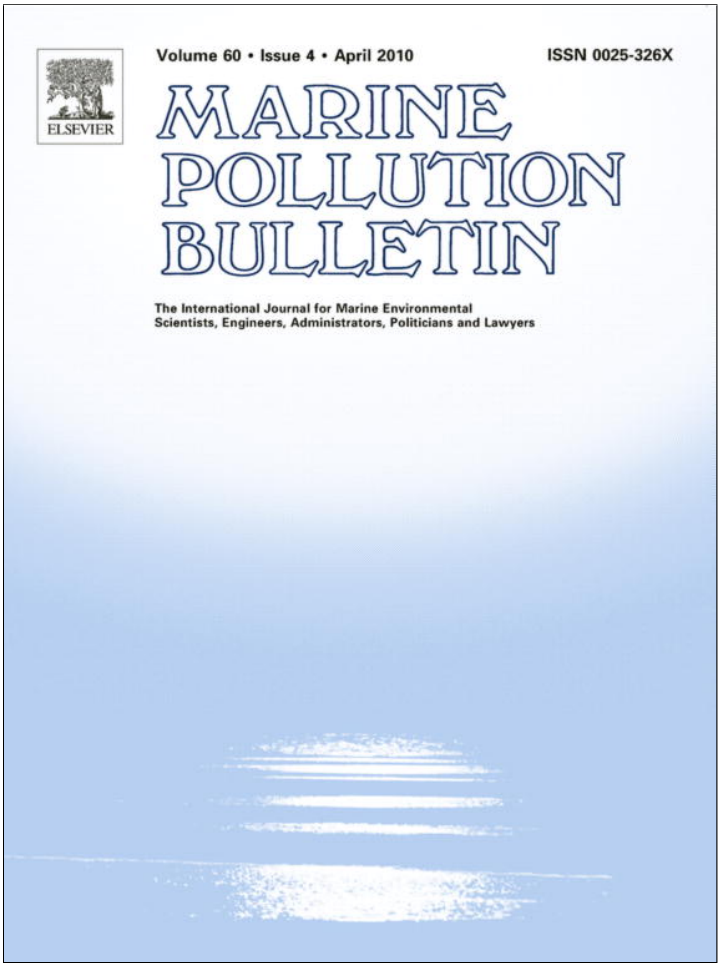
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Baseline

Spatial distribution of metals in sediments of the Ribeira Bay, Angra dos Reis, Rio de Janeiro, Brazil

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ABSTRACT

This study aims to analyze the spatial distributions of several metals in sediments from five sites in Ribeira Bay, Brazil. Ribeira Bay is a very important area to the local community, due to its artisan fishery, and it also has a biological relevance for many marine species that use mangroves as nursery and feeding sites. According to the results, the area was not considered a metal polluted area. Despite not having a significant source of metals inside the Bay nowadays, Ilha Grande Bay harbors a shipyard, an oil terminal, and a commercial port, as well as two thermonuclear power plants (Angra I e II), all of which indirectly influence the study area.

Coastal areas are characterized by high organic matter and nutrients from the continent, having a fragile coastal ecosystem dependent on terrestrial conditions (Yáñez-Aracibia and Sánchez-Gil, 1988). Industrialization of coastal areas is very common in countries characterized by exploitation and importation economics, causing serious damage to coastal ecosystems, e.g. contamination of metals (Cardoso et al., 2001). The spilling of industrial wastes promotes an imbalance of the elements that occur naturally in the environment (Carvalho, 1995). These metals connect, forming metallic compounds that join the sediments (Tommasi, 1977). Fluvial waters are a significant vector of metals to marine sediments. Besides organisms, carcasses of the hitter fall to the seafloor with decomposition and metal accumulates in marine sediments.

Metal behavior depends exclusively on sediment composition of substrate: sediments composed of clay and silt have a larger absorption capacity. Humid acids and oxides connected to the organic matter also exercise metal attraction (Connell and Miller, 1984). Studies related to metals are more frequent in regions where the environment suffers strong anthropogenic pressures, e.g. Guanabara Bay (Lacerda, 1983; Lacerda et al., 1984), Sepetiba Bay (Lima, 1987; Silva, 1988) and Rodrigo de Freitas Lagoon (Koblitz et al., 2001; Andreata et al., 1994).

There have not been many studies about heavy metals in Ribeira Bay, besides the one done by Cardoso et al. (2001). Other studies such as Patchineelam et al. (1989), Souza et al. (1986) and Assembléia Legislativa do Estado do Rio de Janeiro (1996) were carried out in areas near Ribeira Bay. Ribeira Bay is a very important area to the local community, due to its artisan fishery, and it also has a biological relevance for many marine species (e.g. *Diplectrum radiale* and *Micropogonia furnieri*), that use mangroves as nursery and feeding sites (Meurer and Andreata, 2002a,b; Freret and Andreata, 2003). Ribeira Bay has been suffering with intense urbanization since the 1970s due to the construction of the Verolme Yard, considered the biggest naval construction of Latin America. The Tamoios Environmental Protection Area has been created for this reason.

Our aim was to analyze the spatial distributions of Co, Cu, Ni, Zn, Ag, Cd, Mn, Mo, Pb, Cr, V and Fe in sediments from five sites in Ribeira Bay.

Ribeira Bay is located in the Northern region of Ilha Grande Bay, municipality of Angra dos Reis, latitude 22° 55′/23° 02′S and longitude 044° 18′/044° 26′W (Fig. 1). The city of Angra dos Reis has been growing very fast since 1970 and several ecosystems are found in its 172 km^2. We selected five sites. Site 1 is in Japuíba cove, characterized by the presence of mangroves and drained by the Palombeta River, Japuíba River, Parado River, Mãe Clemência River, Moreira and Gamboa River. It has a mean depth of 7.1 m. Site 2 is located at Ariró cove, having a mean depth of 10.25 m. Site 3 is situated at Bracuí cove where the rivers Bonequeira, Frade, Ambrósio, Grataú and Bracuí discharge. It is characterized by brackish waters and a mean depth of 5.60 m. Site 4 is in the Saco Piraquara de Fora. This area is influenced by cooling water effluent from the Angra I and II thermonuclear power plants. Its mean depth is 12 m. Site 5 is located at the entrance channel of the Bay, with a mean depth of 20 m. Its water has a greater oceanic influence. The sediments of inside bay sites (1, 2 and 3) are characterized basically by silt and clay. External areas (sites 4 and 5) are constituted by coarse sand and gravel.

Monthly sampling was carried out between January 1999 and March 2001. The sampling was done using a Van Veen bottom grab. Sediment samples were placed in plastic containers and kept

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Fig. 1. Study sites in Ribeira Bay, Angra dos Reis, Brazil.

under ice until they reached the laboratory. All analyses were carried out at CPRM – Brazilian Geological Service. A fraction of each sample was dried in an air-circulating stove, regulated to 40–50 °C. The dry sample was sifted on a 0.177 mm mesh. The material not restrained was digested with concentrated hot nitric acid (HNO_3), which was appropriated for detecting traces. The following elements were analyzed: cobalt (Co), copper (Cu), nickel (Ni), and zinc (Zn) with a minimum of 1 mg/L detected by the applied methodology; silver (Ag), cadmium (Cd), manganese (Mn), and molybdenum (Mo) with a minimum of 2 mg/L detected by the applied methodology; lead (Pb) with a minimum of 4 mg/L detected by the applied methodology; chromium (Cr) with a minimum of 5 mg/L detected; vanadium (V) with a minimum of 8–10 mg/L detected; and iron (Fe) with 0.01% detected by the applied methodology. Amounts were determined using atomic absorption spectrometry with air acetylene or nitrogen–acetylene oxide flame, according to Ward et al. (1969) and Perkin Elmer Corporation (1976). A similarity test was carried out through cluster analyses from simple Euclidian distance.

Twenty-seven monthly samples were analyzed, creating a total of one hundred and five samples. All elements were found in each sample. Sites 4 and 5 had smaller amounts of metal concentration in the sediments, while the other three sites had the highest means according to each element. Cadmium, molybdenum and silver maintained constant values throughout all sites with 0.2, 2 and 0.2 mg/L, respectively. The highest amount of manganese, lead and iron was found in site 1 with 504.2, 24.7 and 4.2 mg/L, respectively. Copper presented the highest mean in site 2 with 23.4 mg/L, as well as zinc and chromium with 77.3 and 66.3 mg/L, respectively. Site 3 showed the highest means for cobalt with 8.4 mg/L, for nickel with 20.6 mg/L and vanadium with 53.1 mg/L (Table 1).

A similarity test (Fig. 2) established that sites 2 and 3 were highly similar, as well as sites 4 and 5, which were equally similar. Site 1 presented a similarity index closer to sites 2 and 3 than to the others. This test verified that Ribeira Bay can be divided in two large areas. Sites 1, 2, and 3 represent the inner bay, and 4 and 5, the outer bay.

Despite not having a significant source of metals inside the Bay nowadays, Ilha Grande Bay harbors a shipyard, an oil terminal, and a commercial port, as well as two thermonuclear power plants (Angra I and II), all of which indirectly influence the study area. Also, there is a considerable untreated waste outfall. According to Ikeda et al. (1989), Ilha Grande Bay presents a low water circulation, which contributes to the accumulation of metals in the inner bay. The external area presents smaller values, where sediments are composed of very fine sand, which is unfavorable for the accumulation of metals. This area presents a larger water mass renovation alongside smaller river influence.

Table 1
Mean, minimum and maximum values and the total mean in mg/L referring to each element in all sampling sites (St) during January 1999 and March 2001 on Ribeira Bay, Rio de Janeiro.

Metals		St 1	St 2	St 3	St 4	St 5	Total mean
Cu	Mean	12.4	23.4	16.4	2.9	3.1	11.64
	Maximum	15	30	24	15	19	–
	Minimum	6	12	1	1	1	–
Pb	Mean	24.7	23.6	19.6	7.8	6.7	16.48
	Maximum	36	30	28	32	24	–
	Minimum	10	12	6	4	2	–
Zn	Mean	72.8	77.3	74.3	20.3	19.4	52.82
	Maximum	86	90	89	76	78	–
	Minimum	12	64	9	9	8	–
Ag	Mean	0.2	0.2	0.2	0.2	0.2	0.2
	Maximum	0.4	0.5	0.4	0.4	0.4	–
	Minimum	0.2	0.2	0.2	0.2	0.2	–
Co	Mean	7.9	8.1	8.4	2.2	2.2	5.76
	Maximum	10	10	11	8	8	–
	Minimum	1	7	1	1	1	–
Ni	Mean	17.6	20.3	20.6	3.1	3.5	13.02
	Maximum	23	25	28	21	19	–
	Minimum	1	10	2	1	1	–
Cr	Mean	60.3	66.3	65	18.3	18	45.58
	Maximum	78	78	82	64	68	–
	Minimum	8	56	12	10	10	–
Cd	Mean	0.2	0.2	0.2	0.2	0.2	0.2
	Maximum	0.2	0.2	0.2	0.2	0.2	–
	Minimum	0.2	0.2	0.2	0.2	0.2	–
Fe	Mean	4.2	3.9	0.6	2.1	1.3	2.42
	Maximum	5.18	5.2	4.9	9.2	1.34	–
	Minimum	0.72	3.36	0.6	0.52	0.46	–
Mn	Mean	504.2	346.9	330.9	126.2	108.1	283.26
	Maximum	780	415	510	365	320	–
	Minimum	120	250	60	56	50	–
Mo	Mean	2	2	2	2	2	2
	Maximum	4	2	2	2	2	–
	Minimum	1	1	1	1	1	–
V	Mean	49.4	53	53.1	15.5	14.7	37.14
	Maximum	66	64	68	52	56	–
	Minimum	16	16	4	4	4	–

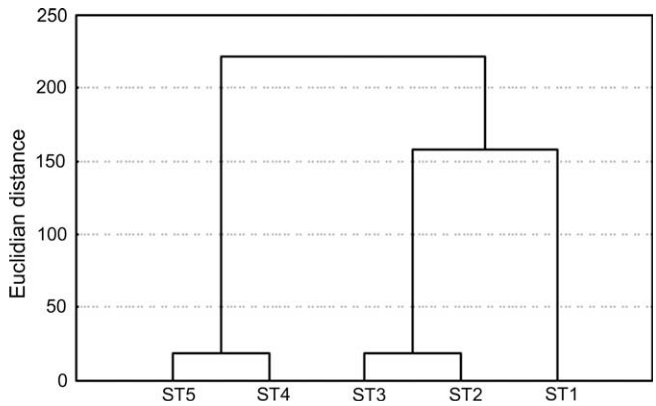

Fig. 2. Similarity among study sites in Ribeira Bay, Angra dos Reis, Brazil.

The results found for Ribeira Bay presented low values as compared to other areas such as Santos Bay, Sepetiba Bay, Mangaratiba Bay, and Guanabara Bay, which is heavily impacted. Cardoso et al. (2001) has found similar values, corroborating the statements that Ribeira Bay is not a polluted area (Table 2).

Ribeira Bay was considered a non-polluted area, according to the pollution levels determined by the international rules (Ontario Ministry of the Environment – OME and United States Environmental Protection Agency – EPA) (Table 3); however, chromium

Table 2
Total mean comparison in mg/L to results obtained by other papers like: [a]Patchineelam et al. (1989); [b]Sema (1980); [c]Souza et al. (1986); [d]Cardoso et al. (2001).

Metals	Ribeira Bay	Sepetiba Bay[a]	Santos Bay[b]	Guanabara Bay[c]	Ribeira Bay[d]	Mangaratiba Bay[c]
Cu	11.64	73	24	367	29	274
Pb	16.48	–	–	–	–	–
Zn	52.82	588	101	51	109	213
Ag	0.2	–	–	–	–	–
Co	5.76	–	–	–	–	–
Ni	13.02	92	–	–	50	–
Cr	45.58	57	24	367	67	102.5
Cd	0.2	–	–	–	–	–
Fe	2.42	4	–	–	3	337.5
Mn	283.26	326	–	–	591.5	421
Mo	2	–	–	–	–	–
V	37.14	–	–	–	–	–

Table 3
Classification of pollution level (total means) in mg/L of each element according to the American rules for sediment OME and EPA, in conformity to the lowest effect level (LEL), heavily polluted category (HPC) and severe effect level (SEL).

Metals	Total mean	LEL	HPC	SEL
Cu	11.64	16	50	110
Pb	16.48	31	60	250
Zn	52.82	–	–	–
Ag	0.2	–	–	–
Co	5.76	–	–	–
Ni	13.02	16	50	75
Cr	45.58	26	75	110
Cd	0.2	0.6	6	10
Fe	2.42	20000	25000	40000
Mn	283.26	460	500	1100
Mo	2	–	–	–
V	7.14	–	–	–

was considered low in its effects. Although this element has been considered one of the most toxic metals, it cannot be stated that it is acting in a toxic manner, because its toxicity depends on pH rendering it more or less available in the aquatic environment. High pH values favor the formation of toxic compounds such as CrO^{2-}, while the lower pH values favor the non-toxic compound Cr^{2+} (Silva, 1996).

These results indicate a non-polluted area, suggesting regular monitoring of metals in the sediments should be undertaken, due to the rapid growth of the Angra dos Reis urban area. Ribeira Bay is an area constantly used by the fishing community and is of great significance in the area of estuarine organisms biology.

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