

## HEAVY METAL DISTRIBUTION, AVAILABILITY AND FATE IN SEPETIBA BAY, S.E. BRAZIL

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### ABSTRACT

The total flux, distribution and fate of Cu, Cr, Cd, Zn, Mn and Pb were studied in Sepetiba Bay, Rio de Janeiro, SE Brazil. Metal contamination in the bay is of the same order of magnitude as historically contaminated areas of Europe and North America, in spite of the recent (15–20 years) contamination of the area.

The estimated metal fluxes to the bay in tons per year are: Cu, 2.7; Cr, 10.9; Cd, 0.9; Zn, 11.5; Mn, 20.4; and Pb, 4.5. For most metals, transport to the bay is mainly by suspended particulate matter; for Cd and Cr 90 and 47% of the total flux was in dissolved forms. Most metals transported by suspended particulate matter were in weakly bound forms.

Analysis of bottom sediments showed two groups of metals in relation to their distribution and source in the bay. Manganese and Cu showed higher concentration along the southern parts of the bay, showing no correlation with the other metals, and probably being derived from natural sources. The other metals were present at higher concentrations along the depositional area of fluvial sediments, at the northern part of the bay, and are derived from industrial and urban sources.

### INTRODUCTION

This work was undertaken to study the fate, distribution and bioavailability of common industrially derived metals (Cu, Cr, Cd, Zn, Mn and Pb) in Sepetiba Bay, Rio de Janeiro, SE Brazil. The peculiar characteristics of this water body: no organic pollution (Fonseca et al., 1978; Lacerda et al., 1983); well oxygenated waters and with a single point source of metallic pollutants, provides a good model for the study of metal dynamics in coastal areas. The bay is one of the most important fishery areas in the state of Rio de Janeiro and presents typical environmental conditions of most protected areas along the Brazilian coast.

#### *Study site*

Sepetiba Bay is a 519 km<sup>2</sup> semi-enclosed salt-water body located approximately 60 km south of Rio de Janeiro city. During the last 15 years an industrial

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park has been established in the area, basically metallurgical, which releases effluents into the bay containing heavy metals and gives rise to metal concentrations in the water in excess of the Brazilian Standards for the Environment; this has been of great concern to local environmental state authorities (Table 1) (Fonseca et al., 1978).

Water circulation in the bay is controlled by tides and the pattern of surface currents follows bottom topography, creating a preferential deposition area along the northern coast (Sugio et al., 1979).

Fluvial water inputs to the bay are concentrated along the NE coast, where the watersheds of five rivers are responsible for 95–99% of the total fluvial inputs to the bay. Among these, the Canal de São Francisco (CSF) and Rio Guandu (RG) constitute 75% of the watersheds' total input, corresponding to an annual flow of  $1.45 \times 10^{11}$  l (Fonseca et al., 1978).

The industrial park located between these two rivers (CSF and RG) discharges its effluents into them 3 km from the coast, thus providing a single-point effluent release (Lacerda et al., 1983). Moreover, the intensive utilization of the bay's biological resources enhances the possibilities of metal transfer to man through the marine seafood chain.

The principal geographical and hydrographical features of the Sepetiba Bay area are illustrated in Fig. 1.

## MATERIALS AND METHODS

### *River water*

Fluvial water samples were collected from the two main tributary rivers: Canal de São Francisco and Rio Guandu, in two sampling periods: July 1981 (peak of the dry season) and May 1982 (end of the rainy season). The total number of samples was 19; collection sites are shown in Fig. 2a. Samples were collected just below the water surface with 5.0 l polyethylene bottles, and immediately transported to the laboratory. Within 48 h, the samples were filtered through Millipore filters ( $0.45 \mu\text{m}$ ), evaporated to a final volume of 30 ml, acidified with 1.0 ml concentrated  $\text{HNO}_3$  and then maintained at  $4^\circ\text{C}$  until analysis, which was carried out within 2 weeks of collection. All samples were run in duplicate using a Varian Techtron AA-120 Atomic Absorption

TABLE 1

Brazilian standard maximum permissible concentrations for various elements in tap and sea water ( $\text{mg l}^{-1}$ ) (Fonseca et al., 1978).

Samples	Cu	Cr	Cd	Zn	Mn	Pb
Tap water	0.02	0.05 <sup>a</sup>	0.001	0.18	0.1	0.03
Sea water	0.05	0.05 <sup>a</sup>	0.005	0.17	0.1	0.01

<sup>a</sup> Hexavalent chromium.

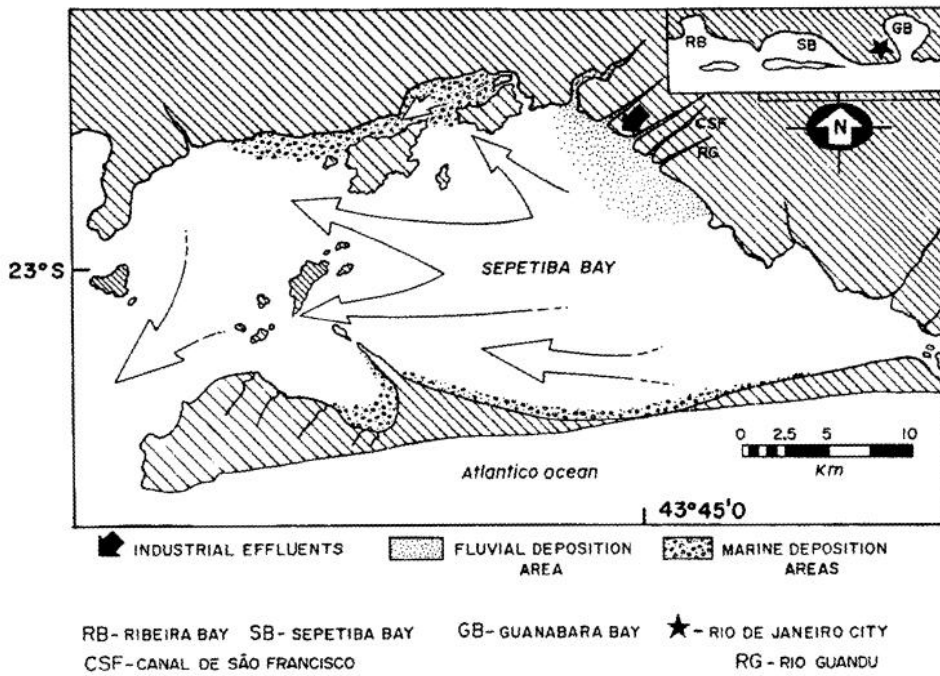


Fig. 1. Sepetiba Bay. Principal geographical and hydrographic features.

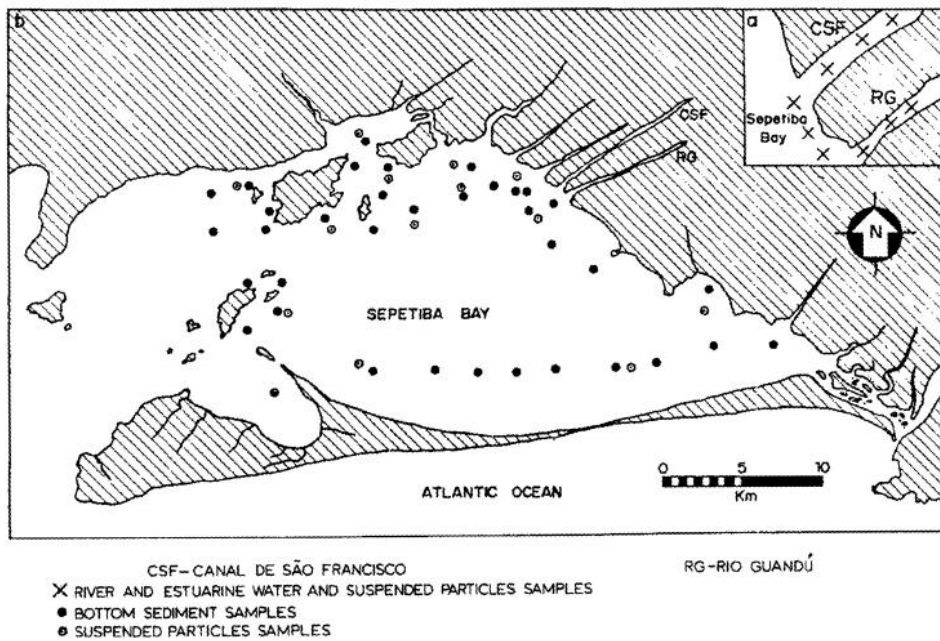


Fig. 2. Location of sampling points. (a) Fluvial inputs; (b) Sepetiba Bay.

spectrophotometer for the analyses of Cu, Cr, Cd, Zn, Mn and Pb concentrations. Regent blanks were performed for all analyses. Reproducibility ranged between 0 and 10% and quality of analyses was evaluated through intercomparison programs. Sensitivity for all metals was much below measured values.

### *Suspended particulate matter and bottom sediments*

Suspended particulate matter was considered to be the material retained in filters of 0.45  $\mu\text{m}$  pore diameter. The material sampled from the rivers was collected directly from the main stream at the sites shown in Fig. 2a and filtered in the laboratory. Samples from the bay were collected by boat using the same procedure as for riverwater at the sites shown in Fig. 2b. When the suspended particulate mass was < 0.1 g, samples were pooled. The total number of samples was 11 for the fluvial system and 14 for the bay.

Bottom sediments were collected by means of van Veen grab collectors at 37 points throughout the bay (Fig. 2b). All samples were sieved within 24 h, and 3.0–5.0 g of the silt + clay fraction (0.63  $\mu\text{m}$ ), oven-dried at 80°C for 24 h, were used for chemical analyses.

Chemical extraction of heavy metals from both suspended particles and bottom sediments followed two distinct sequential processes: samples were first treated with 0.1 N HCl (15 ml per gram dried sample) at room temperature for 24 h and then filtered through Whatman 44 filter paper. The extract was considered to include metals retained on the surface of sediment particles, at cation exchange sites, and weakly adsorbed by Fe-hydroxides and Mn-oxides, thus representing the metals bound to sediment from aqueous solution (Chester and Voutsinou, 1981); in Sepetiba Bay this fraction includes all anthropogenic metals, as shown by Fiszman et al. (1984). After filtration, the residual bottom sediment samples, plus filter, were digested at  $\pm 100^\circ\text{C}$  until dry with a mixture of HCl + HNO<sub>3</sub> + HClO<sub>4</sub> (3:3:1), redissolved in 0.1 N HCl, filtered, and diluted to a final volume of 30 ml with deionized water. This process was considered to extract the resistant metal fraction associated with Fe-hydroxide and Mn-oxides, and organic matter, plus the majority of metals contained within discrete minerals (Fiszman et al., 1985).

## RESULTS AND DISCUSSION

### *Heavy metal inputs to the bay*

In Sepetiba Bay the majority of the industrial effluents containing heavy metals enter through two main rivers, Canal de São Francisco and Rio Guandu, which account for  $\sim 75\%$  of fluvial inputs into the bay.

The results given in Table 2 show heavy metal concentrations in dissolved

TABLE 2

Heavy metal concentrations (mean and range) and fluxes in the main fluvial system to Sepetiba Bay

Element	Dissolved concentration ( $\mu\text{g l}^{-1}$ ) ( $n = 19$ )	Particulate concentration ( $\mu\text{g g}^{-1}$ ) ( $n = 11$ )	Dissolved flux ( $\text{tons year}^{-1}$ )	Particulate flux <sup>a</sup> ( $\text{tons year}^{-1}$ )	Total flux ( $\text{tons year}^{-1}$ )
Cu	6.1 (1.0–9.7)	76.4 (26.1–116.0)	0.9	1.8	2.7
Cr	36.7 (1.8–83.2)	253 (58.9–680.0)	5.3	5.6	10.9
Cd	5.8 (0.2–11.1)	4.0 (0.9–7.6)	0.8	0.1	0.9
Zn	14.0 (2.1–35.0)	412 (219–798)	2.0	9.5	11.5
Mn	27.0 (0.3–275.0)	719 (353–1036)	3.9	16.5	20.4
Pb	12.7 (1.9–26.7)	116 (51.3–320)	1.8	2.7	4.5

<sup>a</sup> Mean mass concentration of suspended matter =  $0.16 \text{ g l}^{-1}$ .

and particulate fractions, and the calculated fluxes from the two main river systems. The location of sampling points used for these calculations are shown in Fig. 2a.

The relative importance of each metal to the total flux was:  $\text{Mn} > \text{Zn} > \text{Cr} > \text{Pb} > \text{Cu} > \text{Cd}$ . For most of the metals studied suspended particles are responsible for the greater part of the total concentration and flux, but for Cd and Cr the dissolved flux accounted for 93 and 47% of the total respectively.

Gibbs (1973), studying metal transport and partitioning in the virtually unpolluted Amazon and Yukon rivers, reported that  $> 90\%$  of total metal concentration and transport was due to suspended particles. However, in rivers with a heavy anthropogenic influence the dissolved fraction can be equal to, or even surpass, the particulate loads (de Groot et al., 1976); thus the pattern of partitioning could be useful in order to identify the degree of pollution of a river system (Salomons and Forstner, 1984).

Table 3 compares heavy metal partitioning found in this study with values from several rivers with different pollution histories. It is clear that the situation in the study area is far from the natural condition, being quite similar to historically contaminated rivers of Europe such as the Rhine, in spite of the industrial development in the Sepetiba area being only 15–20 years old. The possible reason for such high contamination seems to be the concentration of industries along a small segment of the rivers very close to the coast and the dominance of metallurgical industries.

TABLE 3

Heavy metal partitioning between dissolved and particulate fractions (as percentages of the total) in the Sepetiba Bay river system (CSF + RG) and other river systems with different degrees of pollution) (D = dissolved, P = particulate)

River	Reference	Fraction	Cu	Cr	Cd	Zn	Mn	Pb
CSF + RG	This study	D	33	49	89	17	19	40
		P	67	51	11	83	81	60
Rhine (FRG)	De Groot et al., 1976	D	50	20	72	66		17
		P	50	80	28	44		83
Rhine (Netherlands)	Forstner and Muller, 1974	D	36	30	56	63		28
		P	64	70	44	37		72
Amazon (Brazil)	Gibbs, 1973	D	7	10			17	
		P	93	90			83	
Yukom (USA)	Gibbs, 1973	D	3	13			10	
		P	97	87			90	

#### *Transport of heavy metals in the bay*

As metal can exchange from suspended particles to water and vice-versa during transport, metal concentrations in particles collected from the bay were compared with those from other rivers, in order to check for conservative behaviour of metals in this compartment. The results are summarized in Table 4.

The concentration relationship between metals remained the same and although a greater variability was found, no significant differences were detected between metal concentration in the bay or riverine suspended particulate, indicating that this compartment is an important route for metal distribution throughout the bay.

TABLE 4

Heavy metal concentrations [mean ( $\bar{X}$ ) and range in  $\mu\text{g g}^{-1}$  dry wt.] in suspended particles from the rivers and the bay

	Cu	Cr	Cd	Zn	Mn	Pb
<b>Rivers</b>						
$\bar{X}$	76.4	243	4.0	412	719	116
$n$	(11)	(11)	(11)	(11)	(11)	(11)
Range	26-166	59-680	0.9-7.6	219-798	353-1036	51-320
<b>Bay</b>						
$\bar{X}$	61.6	152	3.2	390	788	139
$n$	(14)	(14)	(14)	(14)	(14)	(14)
Range	27.6-106	12-467	2.1-5.1	37-1651	139-1579	40-460

$n$  = number of samples.

### *Availability of metals in suspended particles*

The total metal concentration in the suspended particulate matter does not represent the fraction available for biological uptake, since the proportion of the total strongly held in the geological matrix of particles cannot be extracted by biological metabolism (Fowler, 1982).

In order to verify the proportion of the total metal concentration potentially available for bioaccumulation, a weak acid extraction process was used (see Materials and Methods section). The results of this extraction are presented in Table 5 as percentages of the total metal concentrations; great variability was found between elements.

Metals such as Cd, Zn and Mn in suspended particles were almost totally found in the weakly bound fraction, with percentages as high as 100% in the case of Cd. These values suggest that these particles may be the principal sources of these elements to the biota. Thus it is expected that those animals directly associated with this compartment, such as filter-feeding molluscs and fish, will contain high levels of these metals due to their greater availability in the suspended particulate matter. Pfeiffer et al. (1985) showed that filter-feeding organisms were the most contaminated animals in the bay. Lima et al. (1986) also found a high metal content in oysters of the area and showed a good spatial correlation between metals in oyster and in the suspended matter of the bay. These results confirm the role of suspended matter in transfer of metals to the local biota.

### *Heavy metal distribution in bottom sediments*

Table 6 presents the mean and range of weakly and strongly bound heavy metal fractions in the bottom sediments of Sepetiba Bay collected from the sampling points shown in Fig. 2b. The relationship among total metal concentrations was: (Mn, Zn) > Cr > Pb > Cu > Cd, similar to that found in the suspended particles, although Zn seems to concentrate in bottom sediments, increasing in concentration with respect to Mn.

When taking into account the weakly bound metal fraction only the relationship is: (Mn, Zn) > Cu > Pb > Cr > Cd, indicating that Cr while in the third highest concentration, remains in a non-available form.

When comparing concentrations of weakly bound metals in bottom sediments and suspended particles, the availability of all metals decreased in the former, indicating that in the bay, metals are most strongly bound to bottom

TABLE 5

Percent of weakly bound metal in suspended particulate matter in Sepetiba Bay

Cu	Cr	Cd	Zn	Mn	Pb
70.9	43.6	100	84.4	96.2	66.8

TABLE 6

Mean values and ranges of heavy metal concentrations in Sepetiba Bay bottom sediments ( $n = 37$ )

	Cu	Cr	Cd	Zn	Mn	Pb
Total concentration						
<i>X</i>	38.8	84.4	2.5	288	301	35.7
Range	2.1-166	23.9-121	0.5-8.7	18.1-795	123-788	6.5-85.7
Weakly bound concentration						
<i>X</i>	22.9	9.5	1.9	183	194	16.4
Range	0.6-166	1.2-29.5	0.5-7.4	8-635	64-613	6.5-32.8

sediments, this being best illustrated by Cr, the availability of which decreased from 44% in the suspended particles, to 9.5% in bottom sediments.

The metals studied could be divided into two distinct groups according to their distribution in the bottom sediments: one, including Cr, Zn, Cd and Pb, presenting higher concentration along the north coast of the bay, while the other, represented by Cu and Mn, reached their highest concentrations along the south coast (Fig. 3). The distribution of metals from the first group is coincident with the pattern of sediment deposition from rivers and surface currents (Fig. 1), indicating that these elements have their main source in the industrial park. The distribution of Cu and Mn, however, followed the distribution of marine sediments entering the bay from the adjacent ocean (IPT, 1975), therefore these metals seem to be derived from natural sources rather than from industrial activity in the bay.

Table 7 shows a correlation matrix between weakly bound metal concentra-

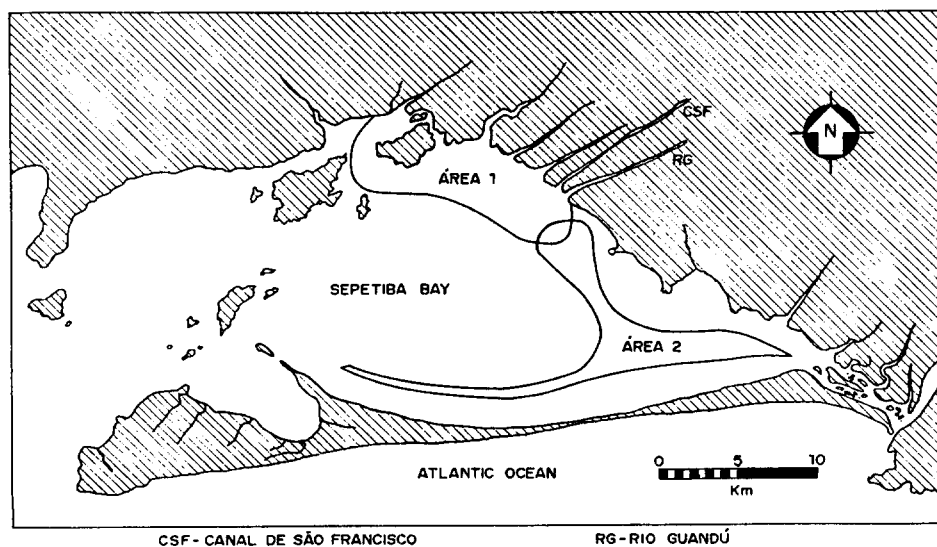


Fig. 3. Distribution pattern of heavy metals in Sepetiba Bay (refer to text).



TABLE 7

Correlation matrix between heavy metal concentration (weakly bound fraction) in bottom sediments of Sepetiba Bay

	Cu	Cr	Cd	Zn	Mn	Pb
Cu	1.000					
Cr	-0.379*	1.000				
Cd	0.373	0.079	1.000			
Zn	0.083	0.175	0.769**	1.000		
Mn	0.149	-0.217	0.312	0.060	1.000	
Pb	0.250	0.409*	0.747**	0.588**	0.028	1.000

\*  $P < 0.05$ ; \*\*  $P < 0.01$ ; DF = 66.

tions in the bottom sediments of the bay. Assuming that this fraction represents the proportion of total metal concentration derived from human activity, it demonstrates a lack of correlation between Mn and all other elements: only Cu showed a weak correlation with Cd and a negative one with Cr. On the other hand the typical anthropogenic elements (e.g. Cd, Zn and Pb) were strongly correlated with each other, confirming our previous hypothesis of different sources for the two groups of metals.

Table 8 compares the values found in Sepetiba Bay bottom sediments with those from other areas under various contamination conditions. Sepetiba Bay can be classified as a system with moderate contamination, with metal levels similar to those found in the Gulf of Venice and Long Island Sound. The difference between Sepetiba Bay and these water bodies is that the bay has only 10 to 20 years of industrial development while the others have been heavily industrialized since the beginning of this century.

## CONCLUSIONS

Sepetiba Bay with its semi-enclosed geography, the absence of sewage releases, and an almost single-point effluent release provided an opportunity to study the distribution and fate of heavy metals.

The absence of organic pollution in the fluvial system, the low mass of suspended matter and the large quantities of metals released, show that the dissolved fraction of the total metal flux can be equal to, and even surpass, that contained in particulates; the proportions found for the dissolved fluxes of Cd, Cr and Pb are possibly the highest ever reported.

The high proportion of weakly bound metals in the particulate matter (as high as 100% for Cd) shows the role of this component, not only as the most important metal transport pathway, but also as a transfer agent of metals to biota. On the other hand the decrease in metal availability in bottom sediments indicates that this latter compartment is far from being just an accumulator of metals, but that it also segregates metals from the environment by making them strongly bound to sediment particles. This role is best illustrated for Cr.

TABLE 8

Comparison between total metal concentrations in contaminated bottom sediments of Sepetiba Bay and other natural and contaminated areas  
 —Arbitrary classification of contamination: (+) natural to slight contamination; (++) moderate contamination; (+++) heavy contamination  
 ( $\mu\text{g g}^{-1}$  dry wt.)

Site	Classification	Cu	Cr	Cd	Zn	Mn	Pb
Ribeira Bay, Brazil Lacerda et al., 1982	+	7.7	30.9	0.23	83	1.23	28.5
Raie de Angraz, France Rapin, 1981	+	20	68	0.4	955		45
Gulf of Venice, Italy Donazollo, 1981	++	2.3-46	3.7-120	0.05-3.9	2-450		10-68
Long Island Sound, U.S.A. Grieg et al., 1977	++	2-269	3.3-278	0-3.8	2.3-354	12-1218	4-210
Derwent Estuary, Australia Bloon and Ayling, 1977	+++	5-10100	0.5-258	1-862	50-10400	1-8900	1-15000
Spencer Gulf, Australia Ward and Young, 1981	+++	3-122		0.5-267	11-16667	66-1227	2-5270
Sepetiba Bay, Brazil This study	++	2.1-166	23.7-121	0.05-8.7	18.1-795	123-788	6.5-83

Finally, the results demonstrate the rapid increase in metal pollution in the bay regardless of the youth of its adjacent industrial park, indicating a need for early control and monitoring of recently installed industrial activities.

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