

GEOCHEMICAL PARTITIONING OF HEAVY METALS IN SEDIMENTS OF THREE ESTUARIES ALONG THE COAST OF RIO DE JANEIRO (BRAZIL)

CRISTINA M.M. DE SOUZA, MARIA HELOISA D. PESTANA and LUIZ D. LACERDA*

Departamento de Geoquímica, Universidade Federal Fluminense, Niteroi, 24201 RJ (Brazil)

ABSTRACT

The geochemical partitioning of Cu, Cd, Cr and Pb was studied in sediments of three estuaries along the coast of Rio de Janeiro. The results show that, under contaminated conditions, the lithogeneous fraction of the total metal concentration decreases in importance, and mobile fractions dominate. Dilution with less contaminated marine sediments and the effect of salinity on metal behaviour could only be observed in the uncontaminated estuary. Under oxic conditions the reducible fraction is the more important sink for metals among the mobile phases. However, in the area with high organic sewage inputs, the oxidizable fraction can account for the greater fraction of total metal content. This latter result suggests a synergistic effect between organic pollution and metal contamination, since metals in oxidizable forms may be remobilized during mixture with oxic marine sediments.

INTRODUCTION

In the study of heavy metal contamination of coastal regions, estuaries are the areas of most concern. Because of the rapid changes in the physical and chemical conditions of the water mass and the complex hydrodynamic processes, metals undergo changes in their speciation and distribution patterns (So, 1978; Salomons and Förstner, 1984). These changes result in a net accumulation of metals in estuarine areas, mostly in particulate forms (Wollast and Peters, 1978; Jouanneau, 1982).

The analysis of bottom sediments coupled with sequential extraction techniques in the study of metal transformation processes, accumulation patterns and biological availability, constitute a powerful tool in metal pollution research in estuarine areas (Ahlf, 1983; Badri and Aston, 1984; Davies-Colley et al., 1984).

Sequential extraction techniques give a better view of the available fraction of the total metal concentration that may undergo changes due to alterations in the physico-chemical and biological characteristics of the environment (Salomons and Förstner, 1984). Although questions still exist regarding the degree of selectivity of these techniques, they have been used with success in comparative studies of metal contamination of coastal areas (Calmano and

*To whom correspondence should be addressed.

Förstner, 1983; Megellati, 1983; Patchineelan and Förstner, 1983; Fiszman et al., 1984).

The state of Rio de Janeiro presents the most contaminated coast of Brazil in relation to heavy metals. Its littoral area is characterized by closed bays in which industrialization has rapidly developed in recent decades. Two of these bays, Guanabara and Sepetiba, are, at present, highly contaminated by heavy metals, and contamination of seafood in these areas has been reported to be a potential threat to the local population (Lacerda, 1983; Pfeiffer et al., 1985). Despite the magnitude of the problem, few studies exist on the metal geochemistry of these areas.

This report deals with the geochemical distribution of Cu, Cr, Pb and Cd in bottom sediments of estuarine areas of Guanabara Bay and Sepetiba Bay, and at an unpolluted site similar to these two areas, through sequential extraction techniques. The work is intended to supply the local environmental authorities with background information for the development of environmental regulations.

STUDY AREAS

The study was carried out in three estuaries with similar geomorphological characteristics along the coast of Rio de Janeiro State, Brazil (lat. 23°S). One of the areas is located along the Ingaiba River at Mangaratiba Bay, with no industrial and urban development. This was the control area. Waters in this area are clean and sediments dark colored due to the high biotite content. They are sandy at the fluvial part of the estuary with an increase in the silt-clay fraction towards the sea.

Sepetiba Bay is located along the São Francisco Canal, a highly industrialized area but with no urban development. Most of the industrial activity is metallurgic and no organic sewage effluents are present. Waters are also clean and sediments are brown muddy sands, which also show an increase in the silt-clay fraction towards the sea.

Guanabara Bay is located along the Igauçu River and receives the effluents from the chemical, metallurgic and oil industries. It also receives untreated effluents, mostly organic sewage, from the Rio de Janeiro City population. Waters and sediments are very dark colored and sulfidic gas could be smelt along the entire river. The oxygen concentration in the waters has always been reported as being $< 2 \text{ mg l}^{-1}$, and the whole water column is frequently anoxic.

A complete description of anthropogenic sources of metals as well as the environmental quality of the three areas is discussed elsewhere (Lacerda, 1983, Lacerda et al., 1982, 1983).

MATERIAL AND METHODS

Samples were collected along salinity gradients in all three areas. In the control area, three stations were established: Station 1, fluvial; Station 2, estuarine; and Station 3, marine. In the contaminated areas, four stations were

TABLE 1

Location and physico-chemical parameters measured in sediments from the 11 sampling stations along the three studied areas

	Station	Temperature (°C)	Salinity (‰)	pH	Organic matter (%)	Distance from river mouth (m)
Ingiba River	1	23	1.61	6.11	3.2	-1000
	2	25	13.1	7.06	6.6	0
	3	25	13.2	7.61	2.2	+500
São Francisco Canal	1	23	0.08	6.61	6.7	-6.200
	2	31	4.99	7.33	8.1	-200
	3	30	4.99	7.16	7.5	0
	4	29.5	11.16	7.43	5.4	+1.300
Iguaçu River	1	27	3.1	7.17	15.6	-6000
	2	26	8.8	6.78	5.1	-3.500
	3	27	10.1	7.21	23.9	0
	4	28	11.3	7.44	17.7	+1000

established: Station 1, fluvial; Station 2, higher estuarine; Station 3, lower estuarine; and Station 4, marine. The location and physico-chemical characteristics of all sampling stations are presented in Table 1.

Two surface sediment samples were collected at each station. In the laboratory, pH and salinity of samples were measured with appropriate electrodes. Sub-samples were ashed (450°C/24 h) for gravimetric determination of organic matter. Samples were then wet sieved to separate the < 63 µm fraction for chemical analysis.

The extraction scheme used was that of Megellati (1983), except that the BaCl₂ of the first step was replaced by CH₃COONH₄, to avoid precipitation of BaCO₃ in the sample extract, which reduces the sensitivity of the atomic absorption method used (S.R. Patchineelan, personal communication). Previous results have shown that this modification does not affect the extraction of other phases present in these samples (Lacerda et al., 1984). The sequential extraction sequence for 1.0 g dry sediment was:

- Exchangeable metals: CH₃COONH₄ (20 ml), 2 h agitation.
- Oxidizable phase: 30% H₂O₂ + 0.02 M HNO₃ (5:3) (16 ml), 5 h agitation + 1 h at 98°C, lixiviation with 3.5 M CH₃COONH₄ (10 ml), 1 h agitation.
- Carbonatic phase: 0.6 M CH₃COOH + 1 M CH₃COONa (1:1) (35 ml), 5 h agitation.
- Reducible phase: NH₂OH, 0.1 M HCl + 25% CH₃COOH v/v (1:1) (35 ml), 4 h agitation + 1 h at 98°C, lixiviation with 3.5 M CH₃COONH₄ (10 ml), 1 h agitation.
- Residual phase: conc. HF + conc. HClO₄ (5:1) (12 ml) at 100–150°C until dryness, redissolution with conc. HClO₄ (2 ml) at 100–105°C until dryness, and redissolution with conc. HNO₃ (2 ml) at 60–80°C for 15 min.

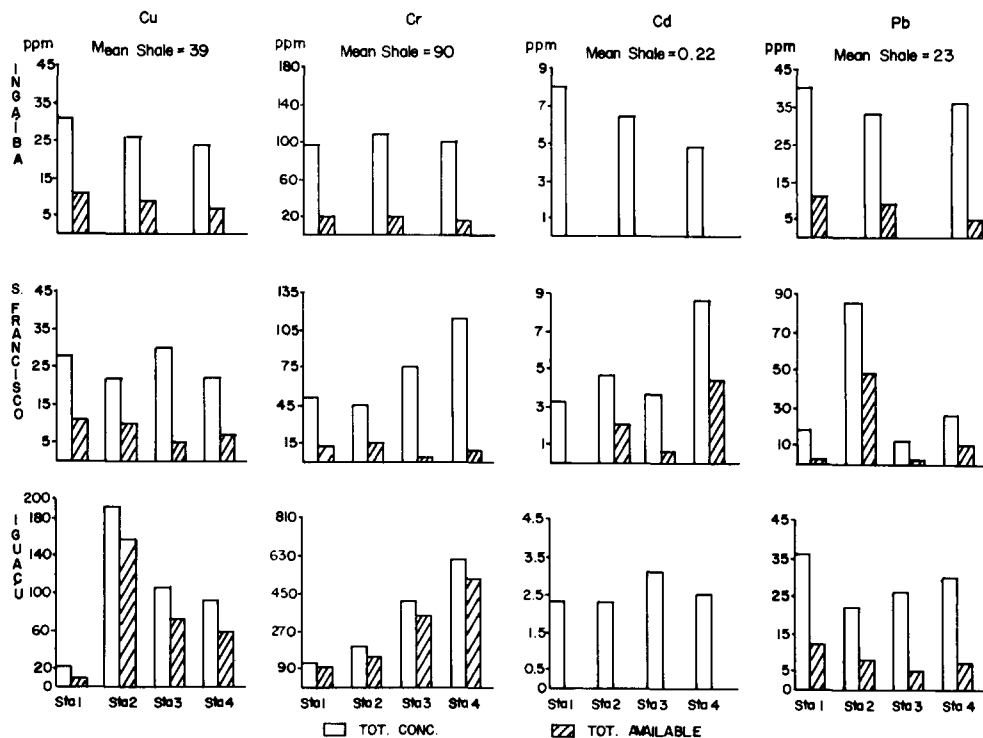


Fig. 1. Total concentrations and sum of mobile phases of heavy metals in the three estuarine systems studied. Mean shale values are from Bowen (1979).

After each step, samples were centrifuged, filtered and stored in polyethylene bottles for analysis. All metal determinations were performed using conventional atomic absorption spectrophotometry using standard techniques.

RESULTS

Total concentrations

The total concentrations and the sum of all mobile fractions for the metals studied in all three areas are presented in Fig. 1. The sum of the mobile fractions is always less than 40% of the total concentration for all metals measured in the control area. In the polluted areas however, it can reach values as high as 80% of the total, exemplified by Cu and Cr in the Iguaçú River and, to a lesser extent, Cd in the São Francisco Canal.

Total metal concentrations were quite variable. Cadmium and Pb concentrations were lowest in the Iguaçú River and highest in the São Francisco Canal, with the control area showing intermediate values. Compared with mean shale concentrations (Bowen, 1979), the values for Cd and Pb were always higher in

the areas examined in this study, particularly in the control area and the São Francisco Canal. Copper and Cr concentrations were comparable with the mean shale value at most stations except the Iguaçu River, where Cr concentrations can reach six-fold and Cu two-fold the average values, and in the São Francisco Canal, where Cr can reach values as high as 114 ppm.

The variation of total metal concentrations along the salinity gradient was also different between the control and polluted areas and among the different metals (Fig. 1). In the control area, the total concentrations of Cd and Cu decreased towards the marine station, while Pb and Cr remained constant. In the polluted areas, only Cu in the Iguaçu River and Pb in the São Francisco

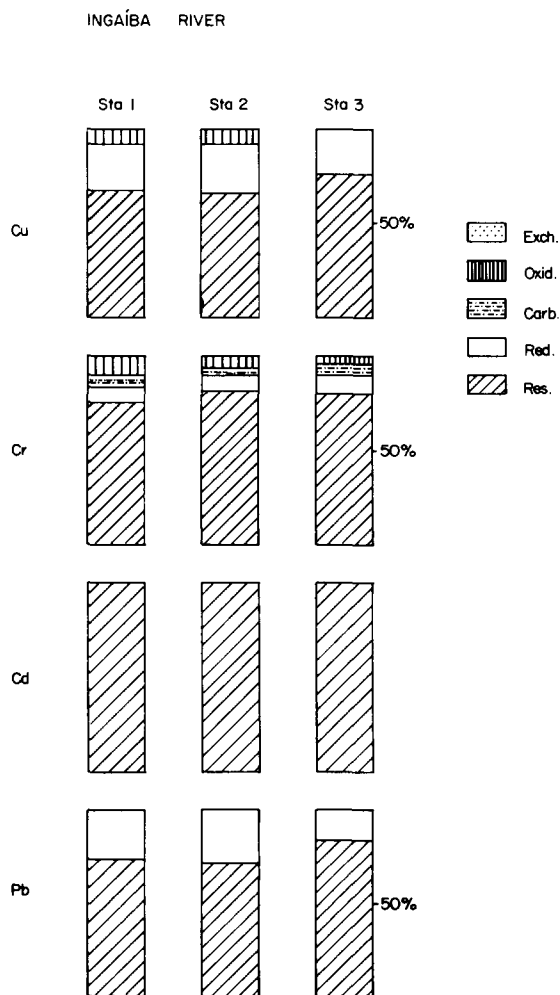


Fig. 2. Geochemical partitioning of heavy metals in the control area along the Ingaíba River, Mangaratiba Bay, Rio de Janeiro. Exch, exchangeable; Oxid, oxidizable; Carb, carbonatic; Red, reducible; Res, residual.

Canal showed a decrease towards the sea. However, as the fluvial stations of the two river systems had the lowest concentrations, this pattern may be a reflection of anthropogenic sources rather than of dilution with less contaminated marine sediments. Copper in the São Francisco Canal and Cd in the Iguaçú River were constant along the entire gradient, while Pb in the Iguaçú River and Cr in the two polluted areas increased towards the sea. The sum of mobile metal fractions followed, in general, the variations of the total concentrations, except for Cd in the Iguaçú River which was undetectable in this area.

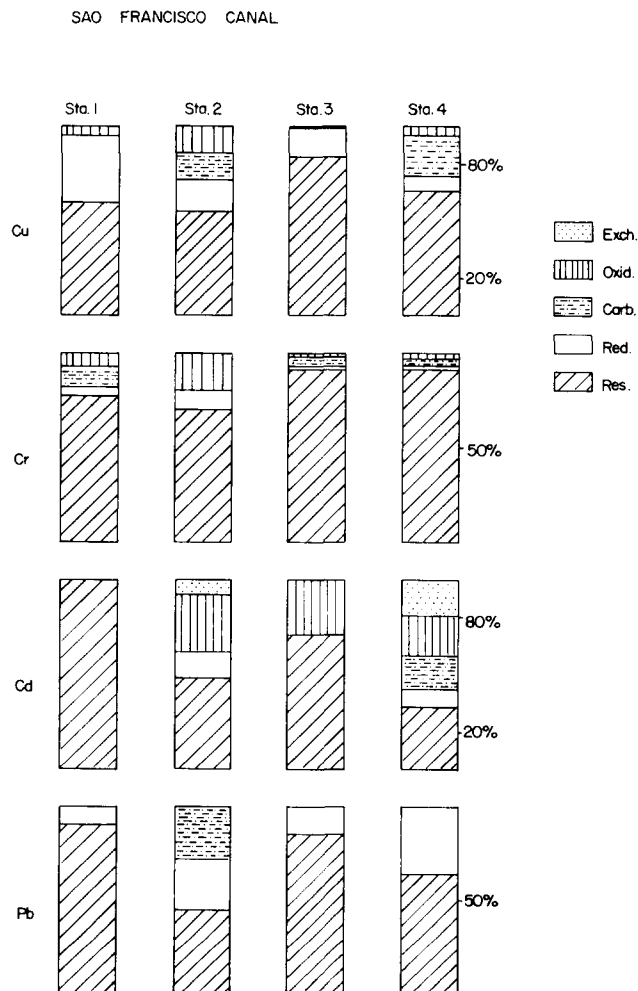


Fig. 3. Geochemical partitioning of heavy metals along the São Francisco Canal, Sepetiba Bay, Rio de Janeiro. Exch, exchangeable; Oxid, oxidizable; Carb, carbonatic; Red, reducible; Res, residual.

Geochemical partitioning

Figure 2 shows the geochemical partitioning of metals in the control area. It is characterized by a low diversity of geochemical phases containing metals. All four metals had more than 65% of their total concentrations in the residual (lithogeneous) fraction. In the case of Cd and Cr, the residual phase accounts for 100 and 80% respectively of their total concentrations. The only mobile fraction containing significant amounts of metals is the reducible phase, indicating a highly oxidizing environment.

In the polluted areas (Figs 3 and 4), a significant decrease in importance of the residual phase was observed for all metals, with the exception of Pb and Cd

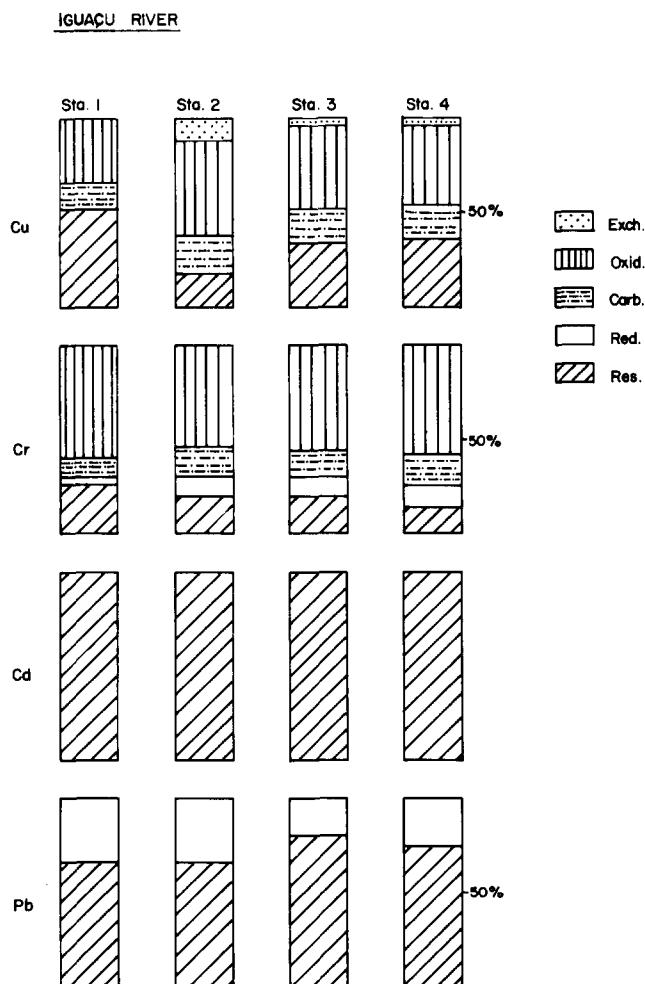


Fig. 4. Geochemical partitioning of heavy metals along the Iguaçú River, Guanabara Bay, Rio de Janeiro. Exch. exchangeable; Oxid, oxidizable; Carb, carbonatic; Red, reducible; Res, residual.

in the Iguaçú River, and of Cr in the São Francisco Canal. A significant increase in the oxidizable fraction of Cu and Cr in the Iguaçú River may be a reflection of the contamination of the area by these two metals and of the reducing conditions in the area. In the São Francisco Canal the carbonatic and, to a lesser extent, the exchangeable fractions become important for Cd and Cu, and for Pb in the higher estuarine station. However, the residual fraction maintained its dominance. In general, all metals, with the exception of Pb, increased in diversity of occurrence with increasing salinity, but the presence of anthropogenic sources along the river precludes further discussion of this aspect.

DISCUSSION

Geochemical partitioning of metals in estuarine sediments depends on the supply and form of the anthropogenic emissions. Our results show that the more contaminated the river system, the more diversified the forms of metals present. This result supports those of Salomons and Förstner (1980) and Calmano and Förstner (1983), who showed that a decrease in relative importance of the residual (lithogeneous) fraction is associated with contaminated conditions. These authors have also shown that the reducible phase is a major sink for trace metals. However, our results only confirm this view in the case of the unpolluted area and Sepetiba Bay, where organic contamination is absent. In the Iguaçú River, which receives great quantities of organic-rich sewage, the oxidizable fraction can be more important as a sink for heavy metals than the other mobile phases, especially for Cr and Cu.

The importance of the oxidizable fraction in the Iguaçú River suggests a 'synergistic' effect between organic and metal pollution, since the reducing conditions of the river will allow remobilization of metals from the reducible phase and, during mixture with marine oxic sediments, the dissociation of the reduced compounds (Patchineelan and Förstner, 1983). This process may result in an increase in the biological availability of metals.

Preference for a specific geochemical phase is observed with Pb. Regardless of river system or position along the salinity gradient, this element, apart from the residual phase, only occurred in the reducible fraction.

Metal association with the carbonatic phase only occurred under polluted situations. The high percentage of Pb in this fraction (28%) at the lower estuarine station of the São Francisco Canal illustrates this observation, since it occurs close to the most important point source of metallic effluent in the area.

The effect of salinity upon the geochemical partitioning of metals was hardly observed. Cadmium, however, was more evenly distributed in the saline station of the São Francisco Canal, the only area with a significant anthropogenic contribution of this metal. This result agrees with those of Ahlf (1983) and Moore and Ramamoorthy (1984), who have pointed out the high mobilization rates of Cd when entering saline environments.

The dilution effect resulting from the mixing of river and marine sediments (Groot et al., 1976), could only be detected in the control area, especially for Cu and Cd whose concentrations in the sediments of Mangaratiba Bay are particularly low (Lacerda et al., 1982). However, in areas of generalized contamination, this effect may be unimportant. In the sediments of Guanabara and Sepetiba Bays, the high concentrations of Cr in the first bay and of Cr and Cd in the latter bay (Pfeiffer et al., 1982; Lacerda, 1983; Fizman et al., 1984), create an inverse gradient with higher concentrations in the saline stations and progressively lower ones in the estuarine and fluvial stations.

After the analysis of 18 rivers worldwide, Salomons and Förstner (1980) concluded that Cd levels in tropical rivers are lower than in temperate ones. Our results, however, show Cd concentrations, even in the non-contaminated area, that are at least five times higher than some contaminated areas of England (Badri and Aston, 1983), two times higher than the polluted Weser estuary values (Calmano and Förstner, 1983) and similar to that of the River Rhine (Calmano and Förstner, 1983). This may be due to the proximity of natural sources of Cd, since the Ingaiba River drains granitic-gneissic rocks located ~3 km from the sea, while the examples of Salomons and Förstner (1980) were of rivers draining extensive intemperized plains (e.g. the Orinoco). Also, the great difference, almost two-fold, between Cd concentrations in the lithogeneous fractions of the control area and that of the Iguaçú River, suggests that local geological features are quite important, making generalizations at the regional level difficult.

In conclusion, the use of sequential extraction procedures can be an effective method for comparative studies between natural and contaminated areas, as well as between areas subject to different types of contamination (e.g. organic versus inorganic). Our results also show that under heavy contamination, especially in areas of restricted water circulation such as in closed bays, certain aspects of metal behavior such as dilution with less contaminated marine sediments, and salinity gradients, under estuarine conditions, cannot easily be observed. Finally, generalizations involving metal concentrations at the regional scale must place appropriate weight on the very large local variations.

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