

Geochemistry and mineralogy of recent sediments of Guanabara Bay (NE sector) and its major rivers - Rio de Janeiro State - Brazil

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ABSTRACT

Geochemical and clay mineralogical studies of bottom sediments collected along the Macacu and Caceribu rivers and Guanabara Bay were carried out in order to investigate the relationship between major source areas and recent sediments of the bay.

Clay mineralogy includes different groups with selective distribution conditioned by geomorphic features and depositional settings. Micaceous clay minerals are abundant near parent rock in the upper course, whereas kaolinite derived from varied sources is gradually concentrated towards the estuary. In the Guanabara Bay, kaolinite accumulates near river mouths, while micaceous clay minerals are converted into mixed layers in the estuary.

Analyses of heavy metal contents reveal higher levels of Zn and Cu in sediments of the bay than in river sediments. Profiles along rivers indicate a downstream decrease of heavy metals, whereas in the bay geochemical trends display greater variations. In general river mouth sediments present the lowest concentrations. At the north and east of Paquetá Island anomalous areas with the highest heavy metal contents occur.

Cu tends to concentrate in $< 2\mu\text{m}$ grain-size fraction and indicates an association with micaceous clay minerals in the upper river course. However, Cu retention seems to be further controlled by other components of bottom sediments due to changes in physical and chemical conditions of the estuarine environment. Zn shows unstable behavior along the rivers and concentrates in the bay. Pb displays small variations from river to bay sediments, and accumulates mainly in the $< 63\mu\text{m}$ grain-size fraction without any association with clay mineral.

Geoaccumulation indexes of Cu, Pb and Zn classify the study area as unpolluted in both studied rivers and in the NE sector of the bay, though the enrichment factors are higher in the bay. The study does not indicate those rivers as major sources of heavy metal pollution to the bay.

Key words: heavy metal, clay mineral, sediment, Guanabara Bay.

INTRODUCTION

Estuaries have been subject of considerable scientific interest over the last decades because of their environmental significance as material traps, and as

such they require careful and constant monitoring and management. Estuaries can be thought as filters of the river-transported chemical components, which can often emerge from the mixing zone under a considerably modified form (Schink 1980 apud Chester 1990). The measurement of pollutants

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in estuarine sediments plays an important role because of longer residence time in sediments than in the water and in suspended matter associated with discharge fluctuations. Like records of earlier pollution sediments have been increasingly recognized as carriers and possible sources of contaminants in the aquatic system (Förstner & Wittman 1981, Malle 1990).

The close association between some heavy metals and clay minerals is demonstrated by several pathway studies, but analyses on estuarine sediments are very few when compared to marine sediments (Malle 1990). Clay minerals are characterized by large surface areas per mass unit, which accounts for their capacity of enrichment in heavy metals. Thus the clay-size fraction can be a reliable indicator of environmental pollution (Förstner & Wittman 1981, Jenne 1977 apud Rybicka et al. 1995).

Guanabara Bay is an important Brazilian estuary located in the southeast coast of Brazil (Fig. 1), which has been receiving high amounts of urban effluents during last decades. Human activities (intensive urbanization and industrialization processes) promote the inflow and accumulation of polluted sediments mainly derived from the cities as Rio de Janeiro, Duque de Caxias, Nova Iguaçu, Niterói and São Gonçalo. The northeast sector of the bay was considered a "protected" area related with rural catchment areas, but Faria et al. (1995) reported a recent increase in heavy metal contents in the bottom sediments of the bay.

This study focuses on several geochemical parameters and clay mineral distribution patterns in recent sediments of inner Guanabara Bay and its major rivers.

STUDY SITE

The northeast sector of the bay is very shallow (3m in average). The tidal currents have the lowest velocities during the winter, 31 cm s⁻¹ in the upper layer (3m below sea surface) during the flood tide and 16 cm s⁻¹ in the ebb tide. In the summer, ve-

locities range from 48 cm s⁻¹ in the flood tide to 19 cm s⁻¹ during the ebb tide (JICA 1994). The lowest salinities of the bay are located in this inner sector. Large amounts of sediments and fresh water are provided by the northeastern rivers, which are strongly seasonal, reaching highest river discharges during the rainy summer (monthly averages of the Macacu River: 116 m³s⁻¹ and Caceribu River: 128 m³s⁻¹, Amador 1992). The area lies just within the tropics in southeastern Brazil, but because of its coastal location a humid sub-tropical climate with 2,500mm (high mountains) and 1,500mm (low land) of rainfall predominates between December and April. Mean annual temperature is between 20-25°C, but depends upon altitude and distance from the sea (Nimer 1989).

The study area can be subdivided into two main sectors, north and south, which include a wide variety of rock types of several ages (pre-Cambrian, Tertiary and Quaternary). The Macacu river is the main channel of the northern catchment area, draining the high mountains of Serra dos Órgãos, whereas the Caceribu river is located in the southern catchment, draining the low mountains of Serra de Maricá. Considering forty-five streams flowing into the bay, the Macacu and Caceribu rivers have the largest catchment areas representing a total area of 2,700 km². In contrast to other rivers that flow through the urban regions, both drainage networks are mostly influenced by rural activities, such as plantations (coconut, banana, orange, mandioca) and pasture along their wide floodplains. In addition, the study area also comprises a typical estuarine ecosystem covered with a mangrove forest which extends 10km landward.

METHODS

Clay mineral composition and heavy metals concentrations of Cu, Pb and Zn were determined in bottom sediment samples taken along the rivers and within the estuary.

Geochemical analyses were carried out for eight surface sediment samples from river stations

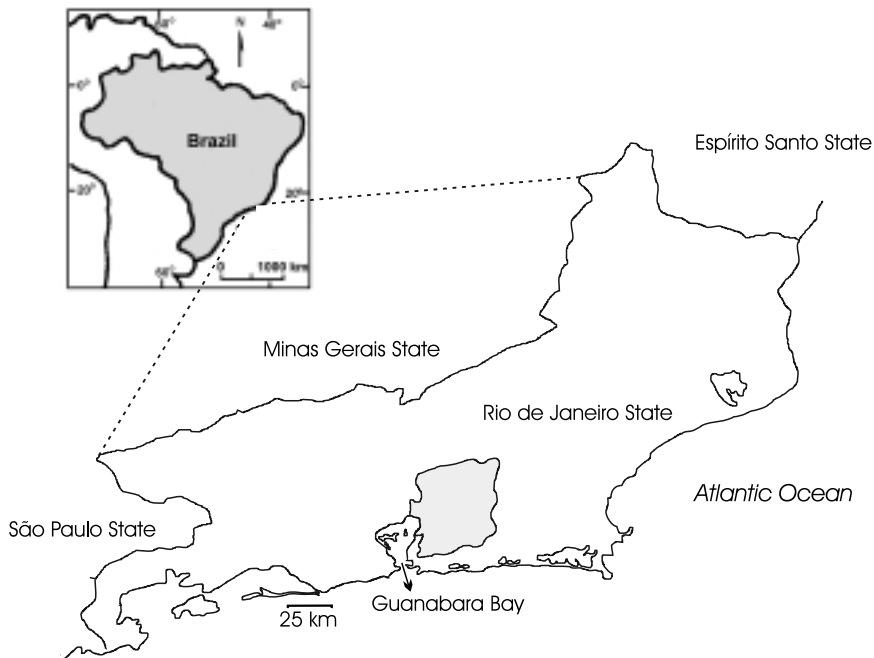


Fig. 1 – Location map of Guanabara Bay.

and eleven samples from the bay. Each sample was analyzed for two grain-size fractions: $< 63\mu\text{m}$ and $< 2\text{mm}$. The samples were digested with H_2F_2 - $(\text{HCl}-3\text{HNO}_3)$ in a teflon bomb at 110°C for 1 hour. After this procedure, Cu, Pb and Zn were analyzed in atomic absorption spectrophotometer. For quality control, USGS standards were prepared and analyzed together with the samples using the same procedures and reagents.

For mineralogical analyses, ten sediment samples were separated for identification of clay minerals. These were determined from the $< 2\mu\text{m}$ size-fraction previously freed of most interfering organic substances, salt, carbonate and iron (Jackson 1975). The samples were dispersed with ultrasonic waves and oriented on a glass slide. These clay slides were then successively run through an X-ray diffractometer Jeol - JDX 8030, under air-dried, ethylene glycol solvated and heated at 500°C in the 2θ range between $2-32$ ($\text{Cu } \alpha$ radiation). Identification of clay minerals and determination of their abundance

were based on DRX laboratory procedures according to Alves (1987). KCl saturation was performed to detect the presence of vermiculites in the bay sediments (only for station B1).

RESULTS AND DISCUSSION

MACACU RIVER

The bottom sediments upstream of M3 station are coarser, with high contents of sand, mainly derived from high mountains of Serra dos Órgãos. In upper Macacu the very low content of clay fraction mostly consists of micaceous clay minerals like illite, vermiculite, illite/vermiculite mixed layers (Fig. 2), related to high gradients of mountains (Fig. 3). These minerals represent the fine grained mica group, that concentrates near the source areas and decrease downstream to the plain regions. Along the floodplain, kaolinite concentrations increase toward the estuary, followed by mixed-layers and traces of gibbsite which also compose the clay mineral assemblages. The hot and humid climate favour chem-

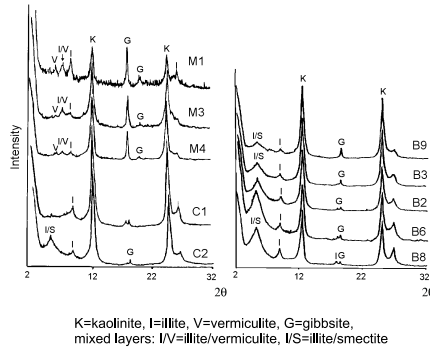


Fig. 2 – Ethylene glycol X-ray patterns in bottom sediments of Macacu and Caceribu rivers and Guanabara Bay. K = kaolinite, I = illite, V = vermiculite, G = gibbsite; mixed layers: I/V = illite/vermiculite, I/S = illite/smectite.

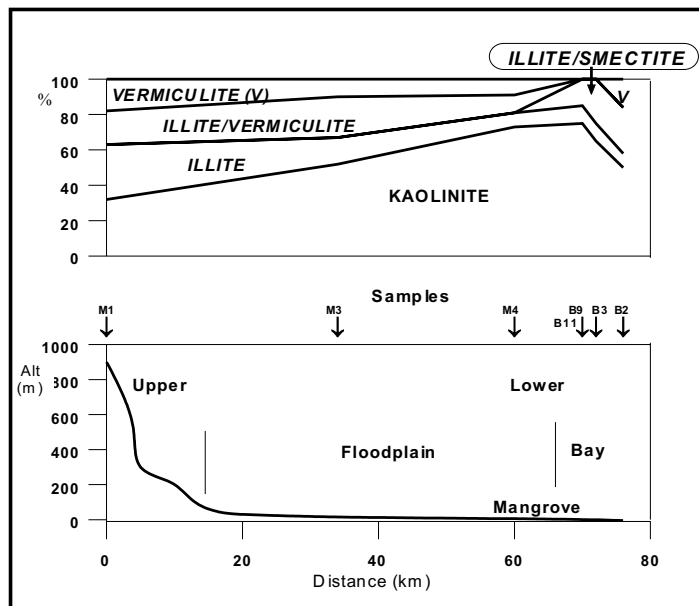


Fig. 3 – The relationship between clay mineral proportions and topographic profile of Macacu river.

ical weathering processes that together with high leaching originate this typical mineral assemblage. However, strong mechanical abrasion in the upper course makes physical weathering more efficient in formation of micaceous clay minerals (Faria 1997).

Kaolinite concentration in the lower Macacu probably records the total kaolinite derived from different weathering processes operating upstream, such as the conversion of micaceous clay minerals due to progressive leaching and also feldspar hydrolysis in

soils and rocks.

Downstream geochemical profiles (Fig. 4) show a decreasing trend of heavy metals, except Zn in 63 μ m grain-size fraction in Macacu river sediments. The results also show a tendency of Cu and Zn concentration in the 2 μ m grain-size fraction. Downstream of station M2 the river receives urban effluents from smaller cities like Cachoeiras de Macacu, Guapi-Mirim and Magé, and also crosses a fishing club at station M4. Except for the very high concentration of Zn in station M4, apparently related to motorboat-generated pollution, heavy metal concentrations tend to decrease downstream even under influence of these cities. Chester and Aston (1976) recognize that the overall chemical composition of river-transported sediments is controlled by a number of factors. These include the geological nature of the catchment area; the drainage conditions; the intensity of local weathering processes and anthropogenic contamination, which can be significant in certain regions. The Macacu River does not exhibit an increasing trend despite urban input of heavy metals because its drainage network is very efficient and the leaching is most intense in its catchment, thus dispersing the trace elements.

In the clay fraction, Cu and Zn concentrations decrease downstream more rapidly until station M3, apparently associated with micaceous clay minerals. Furthermore, organic matter and kaolinite contents are very abundant in the estuarine sediment. Pandarinath and Narayana (1992) reported desorption mechanism in estuarine environment. This may be a possible reason for poor correlation between heavy metals and clay minerals in the Macacu estuary, since kaolinite does not correlate with the studied metals. On the other hand, humic acids can exert a high influence in the speciation of some metals within river waters, especially under low pH values. Mantoura et al. (1978 apud Chester 1990) predicted that more than 90% of the Cu and Hg in river waters are complexed by humic material. Humic complexed material tends to decrease with increasing salinity, but this decrease, which is rapid

for Mg, Ca, Zn, Cd, Mn and Co, is slow for Cu and Hg (Chester 1990). Both metals, mainly Cu, could be partly retained by organic matter, very abundant in the mangrove forest zone, which may explain the lowest heavy metal concentrations detected in this region.

CACERIBU RIVER

The highest sample station C1 is located in the middle course of the river and its sediment is mostly composed of fine sand fraction (Faria 1997). Downstream, silt makes up the dominant fraction and the organic matter content increases in the sediment. Clay mineralogy is very similar to that of Macacu River (Fig. 2), only differing by the absence of vermiculite. Kaolinite is concentrated along the river toward Guanabara Bay, and illite/smectite mixed layers also appear in estuarine sediments.

The geochemical profiles (Fig. 4) in Caceribu river also show a decreasing trend toward estuary in both analyzed grain-size fractions, but heavy metals do not display tendencies to concentrate in the clay fraction. Cu levels are lower than in the Macacu river and the lowest concentration is located in the river mouth (station B11). In comparison to Macacu river, Caceribu includes in its catchment a greater number of towns like Rio Bonito, Tanguá, Porto das Caixas and Itaboraí, despite that heavy metal contents were lower than those analyzed in Macacu River sediments. The southern catchment area presents different aspects from the geomorphological and geological viewpoints. The relief does not consist of high mountains, but is dominated by the lower mountains of the Serra de Maricá, the rock composition of which is notably poor in Cu (Braz Sanchez unpubl. data). Furthermore, traces of gibbsite also occur in the clay-size fraction of river sediments. The lower gibbsite content of Caceribu samples as compared to Macacu may reflect the more intense leaching in the Macacu catchment. This can be attributed to the geomorphological properties of Serra dos Órgãos and its higher precipitation rates. In addition, the north rivers have higher contents of mafic minerals in their

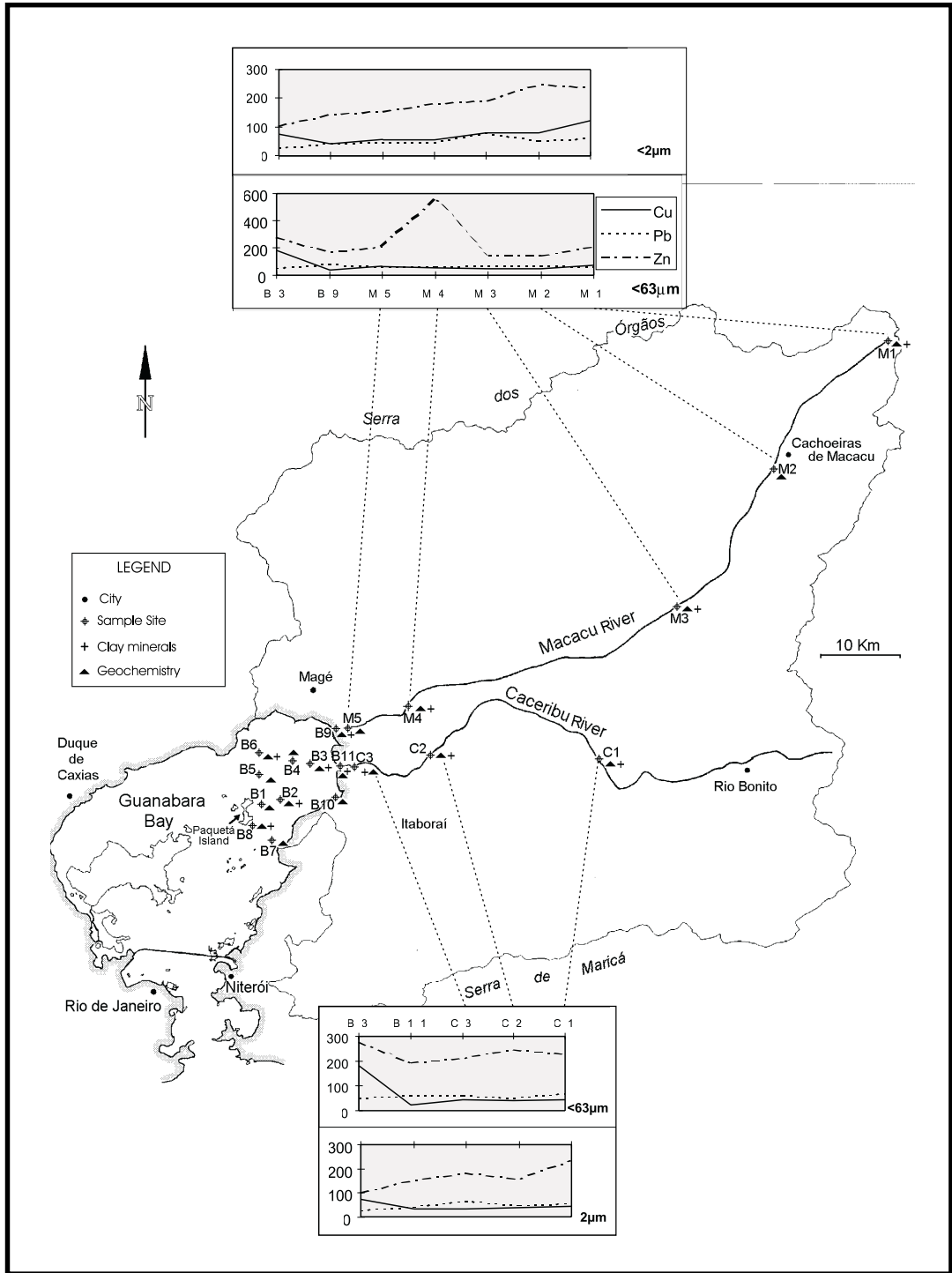


Fig. 4 – Location map of major rivers of Guanabara Bay with samples sites (M1-M5 for Macacu River, C1-C3 for Caceribu River and B1-B11 for bay stations) and heavy metals profiles (Cu, Pb and Zn in $<63\mu\text{m}</math> and $2\mu\text{m}</math> grain-size fractions).$$

bedload differing considerably from Caceribu river sediments (Faria 1997). Lithological units in the southern catchment comprise mostly rocks with acid composition, providing a natural background which superimposes the anthropogenic input of heavy metals to the sediment. The main difference between the rivers is observed in Cu profiles, with lower values in Caceribu river, whereas Zn concentrations are very similar in $2\mu\text{m}$ fraction. Pb profiles have the same pattern, and concentrations are also very similar in both rivers.

GUANABARA BAY

The bottom sediments of the inner sector of Guanabara Bay consist of mud, up to 80% of $63\mu\text{m}$ fraction (Haekel et al. 1985) with a high content of organic matter. The sediment is mostly terrigenous, and dominant clay-size fraction includes mainly kaolinite in addition to illite (mica), vermiculite, illite-vermiculite and illite/smectite mixed layers (Figs. 2 and 5). In the Bay, kaolinite tends to flocculate and concentrate near the river mouths, whereas the content in illite/smectite mixed layers increases seaward. Small amounts of illite are recorded in the sediments, and illite distribution in the bay is homogeneous.

In average, Guanabara Bay sediments have higher levels of Cu and Zn than the continental sediments (Table I). Therefore, the same comparison for Pb revealed that there is a minor variation in the Pb content among these depositional environments. In general, heavy metal distribution patterns indicate river mouths as the regions with the lowest concentrations in both analyzed fractions (Figs. 6, 7 and 8). They also indicate anomalous sectors of high concentrations on the north and east sides of the Paquetá Island, probably related to anthropogenic input from the island and other polluted areas around the bay. According to JICA (1994), the major pollution sources are the high effluent loads of the industrial complex from northwestern basins of the bay. Furthermore, the urban pollution derived from densely industrialized and residential ar-

eas, roads, railroads, airports, harbours. Artificial embankments in Rio de Janeiro and Niterói cities affect mainly the southern area of the bay, although it may reach the inner part of the bay due to tidal current action. The analysis of the heavy metal trends eliminate these major rivers as pollution sources to the bay as their heavy metal inputs are seemingly unrelated to the origin of these anomalies.

TABLE I

Heavy metals concentrations in average shale, Macacu River, Caceribu River and Guanabara Bay sediments.

	Cu	Pb	Zn
Average shale*	45	20	95
Macacu river sediments (<63mm)	58	67	255
Caceribu river sediments (<63mm)	43	62	228
Guanabara Bay sediments (<63mm)	119	69	290
Macacu river sediments (<2mm)	79	57	204
Caceribu river sediments (<2mm)	40	58	194
Guanabara Bay sediments (<2mm)	78	40	199

*Turekian and Wedepohl (1961) apud Förstner and Wittman (1981). The concentrations are in ppm.

Geochemical and mineralogical data indicate that the lowest concentrations of heavy metals are located in kaolinite-rich sediments. However, the highest heavy metal concentrations do not correlate with any clay mineral group, which may be attributed to changes in physical and chemical estuarine conditions. In addition, the role of organic matter in the formation and transformation of clay minerals, as well as in heavy metal adsorption have not been well investigated in this sector of the bay.

The finest grain-size fraction of river sediments point out to a continuous enrichment in heavy met-

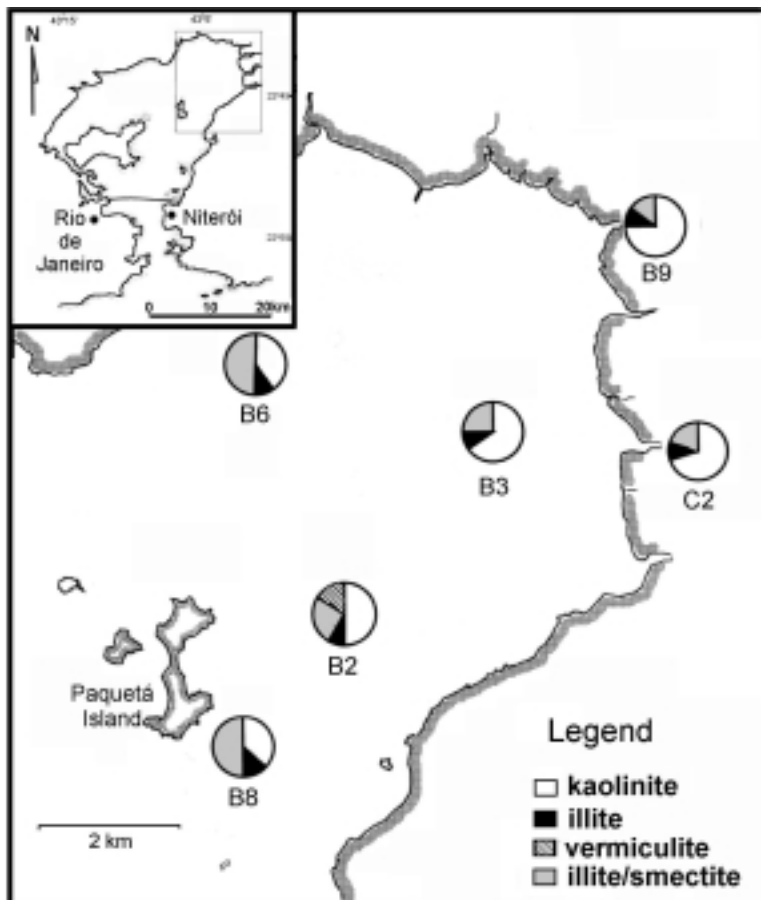


Fig. 5 – Clay mineral distribution in bottom sediments of northeastern sector of the bay (relative percent of $2\mu\text{m}$ grain-size fraction).

als due to the active surface of Fe-oxides and clay minerals (Förstner & Wittman 1981). Metal sorption reactions of metals in different competing clay minerals studied by Rybicka et al. (1995) show the highest Pb enrichment for smectite and illite. Several environmental studies use clay mineral associations in sediments to trace the sediment transport in the estuarine environment (Irion & Zöllmer 1990, Pandarinath & Narayana 1992, Wijayananda & Cronan 1994). This association could not be observed for Pb in the studied area because Pb concentrations in $< 63\mu\text{m}$ fraction are higher than in $< 2\mu\text{m}$ fraction. This is probably related to the presence of feldspar, which like quartz is a very common min-

eral in bottom sediments. The association of both Cu and Zn with clay minerals is unclear in the bay, possibly because other components or combinations of them that may have played a more significant role in mobilization processes of these heavy metals.

SEDIMENT POLLUTION

The quantification of pollution has been calculated by using an enrichment factor with respect to average shale (Turekian & Wedepohl 1961 apud Förstner & Wittman 1981). Table II shows the metal enrichment factors for Macacu and Caceribu river sediments and the Guanabara Bay sediments. The table also indicates higher factors for Pb in relation to Cu

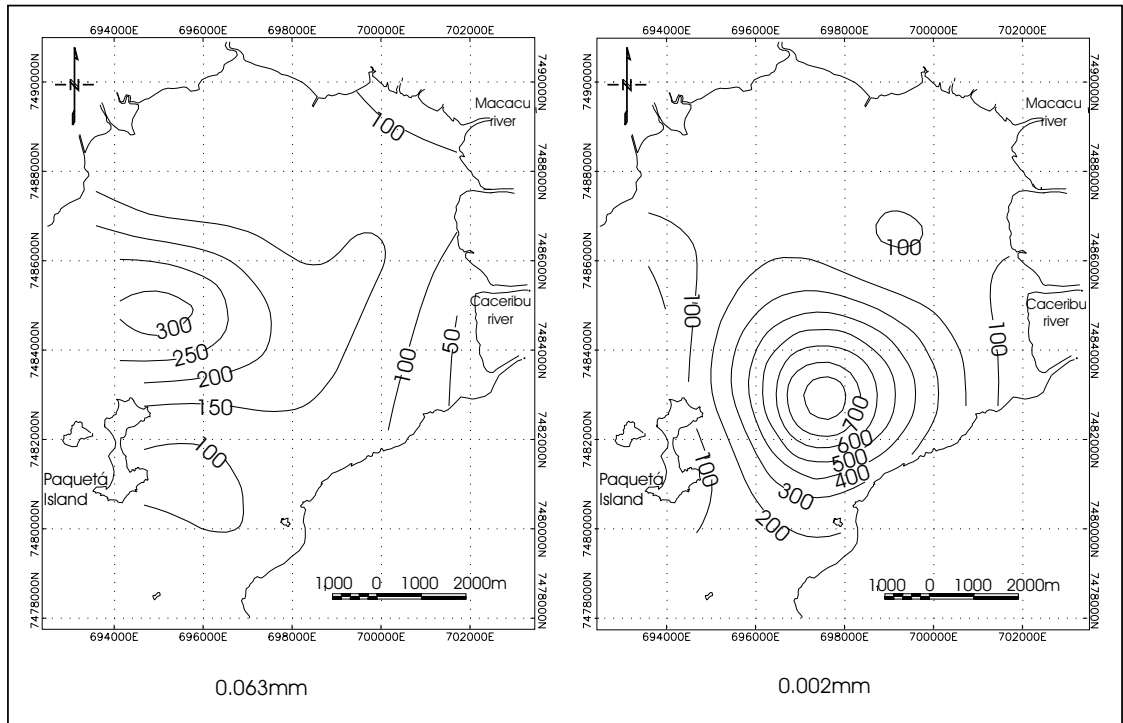


Fig. 6 – Cu distribution in bottom sediments of northeastern Guanabara Bay (contour lines are in ppm).

and Zn factors. The average was also calculated, and Figure 9 shows the input relation between the rivers and the bay. Cu average enrichment factor in the rivers remains within the natural background, characterized by lower average (1.0), whereas Zn and Pb averages reflect anthropogenic inputs in both studied environments (2.1 for Zn and 2.7 for Pb in the rivers, and 2.4 for Zn and 2.7 for Pb in the bay). Baptista Neto (1996) studied the sediments of the south of the bay, under high urban influence, and detected a wider range of enrichment factors for these metals (4.5-27 for Cu, 2-8 for Pb and 3-10 for Zn). The geoaccumulation index proposed by Müller (1979) for the pollution quantification was also calculated for sample stations, but in all of them the index remains in class 0, or unpolluted for Cu, Pb and Zn.

CONCLUSIONS

The rivers provide high contents of kaolinite to the bay, as well as minor proportions of illite (mica), ver-

miculite, illite/vermiculite and illite/smectite mixed layers. Besides climatic conditions, topography is an important factor that also controls the conversion and distribution of clay minerals along the rivers. In addition, gibbsite is relatively more abundant in Macacu sediments than Caceribu, possibly due to more efficient leaching attributed to the geomorphic features of Serra dos Órgãos. In the bay, a selective distribution of clay minerals occurs in function of fluvial discharges and hydrodynamic conditions of the bay, so that kaolinite tends to concentrate near the river mouths and illite/smectite mixed-layers concentrates seaward.

In general, heavy metals do not correlate with any specific clay mineral. However Cu tends to concentrate in $< 2\mu\text{m}$ grain-size fraction of river sediments and is apparently related to micaceous clay minerals in the upper course of rivers. Other factors, including components of the sediment with higher capacity of adsorption and complex changes

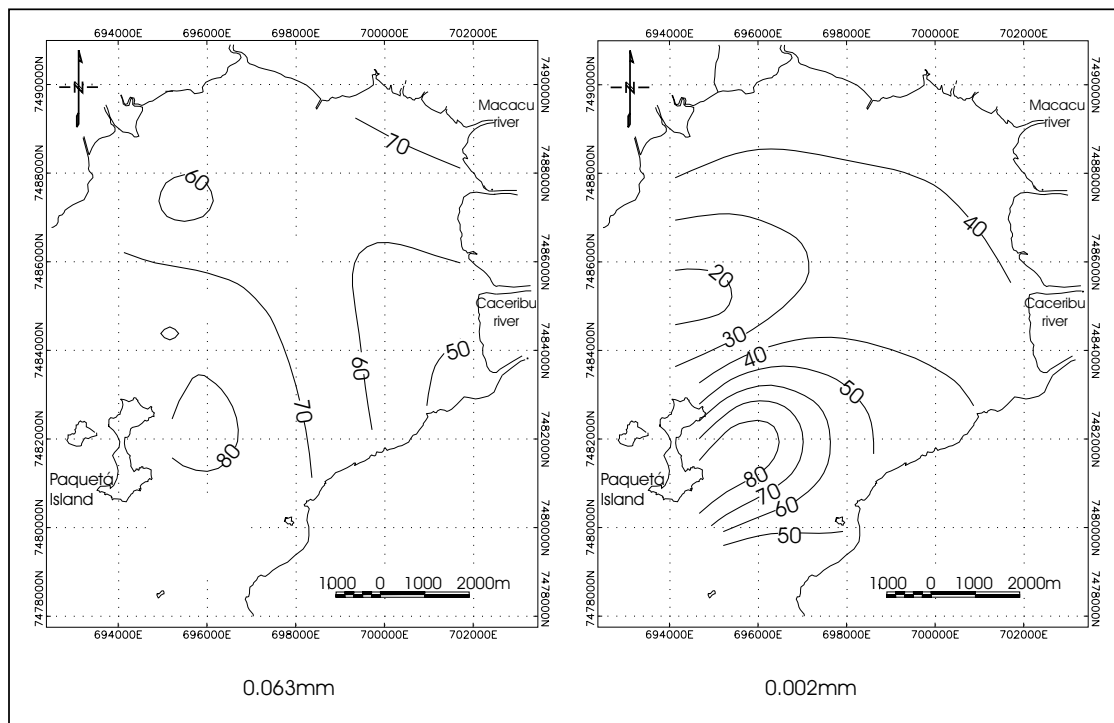


Fig. 7 – Pb distribution in bottom sediments of northeastern Guanabara Bay (contour lines are in ppm).

in physico-chemical conditions of the estuary, should be checked in future studies.

Heavy metal profiles exhibit a decreasing downstream trend along the rivers with lowest concentrations located in the river mouths. Concentration maps indicate highest concentrations to the north and east of Paqueta Island in Guanabara Bay. Heavy metal levels of river sediments reflect the geochemical properties of the source areas. The mangrove forest with its organic mud substrate seems to control the heavy metal supply to this inner sector of the bay, which still remains relatively unpolluted.

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RESUMO

A correlação dos sedimentos recentes da Baía de Guanabara com as suas principais áreas-fontes foi realizada a partir de análises geoquímicas e de argilominerais em amostras de fundo coletadas ao longo dos rios Macacu e Caceribu e na baía.

Os argilominerais indicam uma distribuição seletiva intimamente associada às características do relevo e aos ambientes deposicionais. Os argilominerais micáceos são predominantes na região do alto curso próximos à área-fonte primária, enquanto que a caulinita, proveniente da decomposição de diversos minerais, se concentra gradativamente em direção ao estuário. Na Baía de Guanabara observa-se um acúmulo de caulinita na região de foz dos rios, ao passo que os argilominerais micáceos são con-

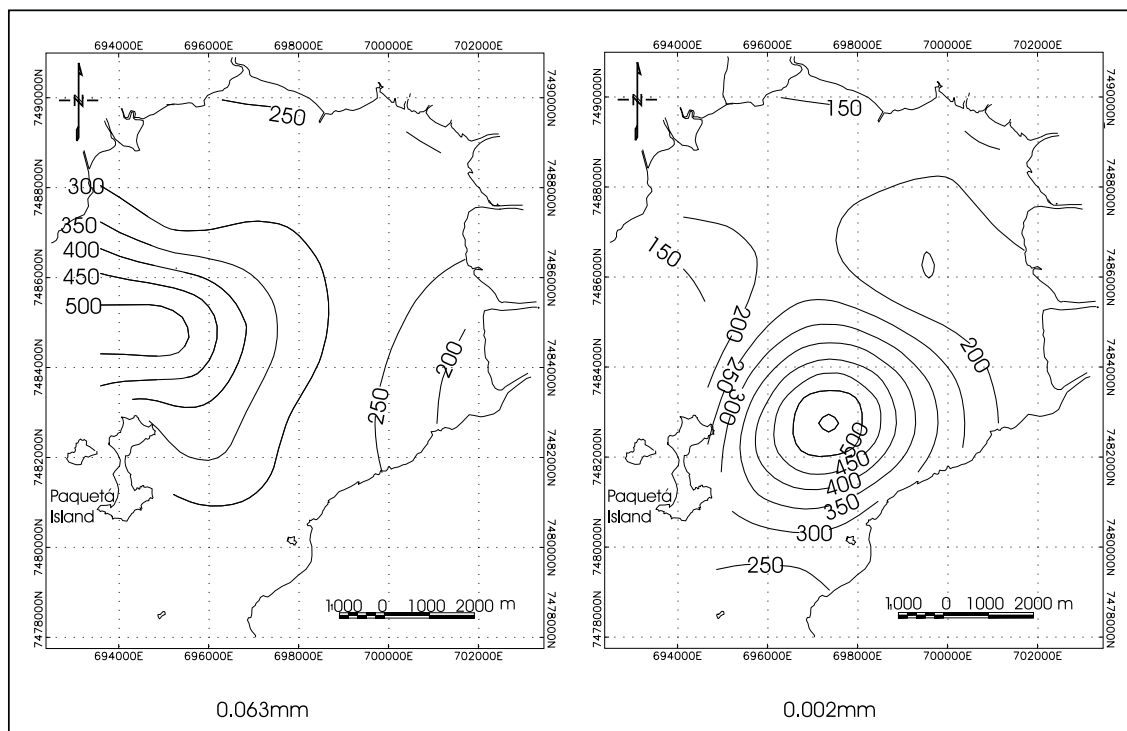


Fig. 8 – Zn distribution in bottom sediments of northeastern Guanabara Bay (contour lines are in ppm).

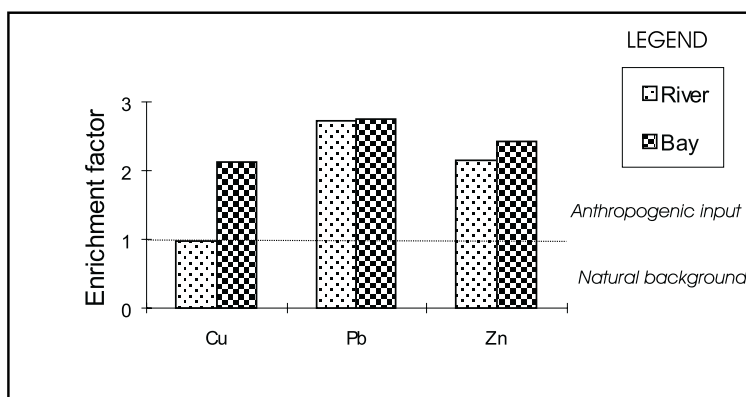


Fig. 9 – Comparison of average enrichment factors of fluvial and Guanabara Bay sediments.

vertidos em interstratificados e depositados no fundo da baía.

As análises geoquímicas dos metais pesados no sedimento da baía detectaram níveis de Zn e Cu superiores aos níveis encontrados nos sedimentos fluviais. Os perfis de con-

centração dos rios estudados exibem um decréscimo na concentração dos metais ao longo de seus cursos, ao contrário da baía que apresenta maiores variações. De modo geral, as regiões de foz dos rios destacam-se pelas concentrações mínimas dos metais, e as áreas anômalas de

TABLE II

Metal ratios with average shale in bottom sediments.

Station	Cu	Pb	Zn
M1	1,60	3,11	2,07
M2	0,84	2,66	1,16
M3	1,46	4,60	2,08
M4	1,00	2,65	4,84
M5	0,96	2,34	1,59
C1	0,95	3,32	2,30
C2	0,63	1,95	1,83
C3	0,74	2,23	1,64
B1	1,61	4,05	3,99
B2	3,18	3,25	2,65
B3	2,97	2,04	2,19
B4	1,90	2,41	2,34
B5	7,11	3,72	5,67
B6	2,06	1,93	1,95
B7	1,59	2,97	2,00
B8	1,72	2,90	2,03
B9	0,67	3,02	1,39
B10	0,44	1,32	1,08
B11	0,49	3,29	2,25

concentrações máximas situam-se ao Norte e a Leste da Ilha de Paquetá.

O Cu tende a se concentrar na fração argila podendo estar associado aos argilominerais micáceos do alto curso. Entretanto, no baixo curso, outros componentes do sedimento podem controlar a retenção do Cu em função das bruscas mudanças das condições físico-químicas no ambiente estuarino. O Zn apresenta um comportamento instável ao longo dos rios e tende a se concentrar na Baía de Guanabara. Foram detectadas pequenas variações entre as concentrações de Pb dos sedimentos fluviais e da Baía de Guanabara. Este elemento tende a se concentrar mais na fração < 63 μ m e não se associa a nenhum grupo de argilominerais.

Apesar dos fatores de enriquecimento dos metais pesados serem mais elevados na baía do que os fatores encontrados nos rios, os índices de acumulação de Cu, Pb e Zn ainda classificam a área de estudo como não poluída tanto os rios como o setor NE da baía. Este estudo não indica estes rios como as principais fontes poluidoras de metais

pesados na Baía de Guanabara.

Palavras-chave: metal pesado, argilomineral, sedimento, Baía de Guanabara .

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