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SPATIAL PATTERNS AND ENVIRONMENTAL RISK ASSOCIATED TO TRACE METALS IN SEDIMENTS FROM SEPETIBA BAY, RIO DE JANEIRO, BRAZIL

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Tese de Doutorado apresentada ao Programa de Pós-Graduação em Engenharia Oceânica, COPPE, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Doutor em Engenharia Oceânica.

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PADRÕES ESPACIAIS E RISCO AMBIENTAL ASSOCIADO A METAIS TRAÇOS EM SEDIMENTOS DA BAÍA DE SEPETIBA, RIO DE JANEIRO, BRASIL

Sarah Karoline Rodrigues

Fevereiro/2018

Orientadores: Susana Beatriz Vinzon
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Programa: Engenharia Oceânica

A qualidade dos sedimentos da Baía de Sepetiba é afetada pela introdução de metais traço através de diversas atividades antrópicas. O índice (SQGQs) demonstrou um risco contínuo na região interna da baía devido a poluição por metais traço e que áreas mais afastadas também estão sob pressão. Cd e Zn são metais que merecem atenção especial no gerenciamento de sedimentos na região, porém o cobre aparece enriquecido em regiões próximas a restinga da Marambaia. A baía da Marambaia apresentou aumento nas taxas de sedimentação concomitante ao início do sistema de transposição de bacias dos rios Paraíba do Sul- Guandú. Altas concentrações de Cd e Zn estão presentes nas camadas correspondentes à instalação da Metalúrgica Ingá Cia. Os óxidos hidróxidos de Mn são uma importante fase trocável para os metais traço na baía. A variedade de fontes de poluição que contribuem para o enriquecimento de metais traço na baía requer um programa de monitoramento sistemático e recorrente. Altas concentrações de Zn e Cd atribuídos a Ingá, podem mascarar outros potenciais poluidores. Portanto, outros metais, como o Cu, Pb e Cr devem ser monitorados. Principalmente pelo aumento crescente das atividades industrias e portuárias na região.

Abstract of Thesis presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Doctor of Science (D.Sc.)

SPATIAL PATTERNS AND ENVIRONMENTAL RISK ASSOCIATED TO TRACE METALS IN SEDIMENTS FROM SEPETIBA BAY, RIO DE JANEIRO, BRAZIL

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The sediment quality of Sepetiba bay is affected by trace metals from input of many human activities. The environmental risk index showed high values due to trace metals pollution in the inner part of the bay, but also along Marambaia sandbar area. Cd and Zn are of critical concern for Sepetiba bay sediments management, due to their high concentrations and potential toxicity to aquatic organisms. However, copper stands out in hot spots. Marambaia bay sedimentation rates enhancement was concurrently with the introduction of Paraíba do Sul-Guandu rivers diversion system. Higher amounts of Cd and Zn were found in the inner part of the bay since 1960's, concurrently with the Ingá metallurgical Cia. establishment. Mn oxy-hydroxides compose the main phase in the sediments fractionation, which is considered an important scavenger for trace metal in the region. A systematic and recurrently monitoring program has to be implemented, since Zn and Cd high concentrations from Ingá wastes can be masking other potential sources. Therefore, other contaminants must be monitored, such as Cu, Pb and Cr. Especially due to the growth of industrial and harbor activities in Sepetiba bay basin, other point and non-point pollution sources for the system are expected.

Summary

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Chapter 1

Introduction

Coastal environments are rich natural resources, providing crucial habitats and corridors for environment conservation, recreation, cultural and economic growth. An estuary is a complex ecological system receiving and carrying plenty of continental and marine material in dissolved and particulate forms from natural and anthropogenic sources (Bellos et al., 2004).

The water quality in estuarine systems may vary depending on the geological morphology, vegetation and watershed land use. Industries, agriculture and urban settlements produce nutrients and toxic substances, such as organic and inorganic pollutants, including trace metals (Khan et al., 2014; Das et al., 2009). The enrichment of these substances degrades the water quality of the estuary and its natural function is altered (Khatri and Tyagi, 2015).

Environmental problems related to trace metals have a long history in coastal areas. Many aquatic systems have been contaminated with these elements, as a result of industrialization process (Ferreira, 2015; Singh et al., 2011). Entrance of trace metals into coastal environments can occur naturally from leaching of mineral rocks and through anthropogenic sources (atmospheric deposition, domestic and industrial effluents, wash-off from urban and agricultural areas, industrial districts, landfills, among others) (Khatri and Tyagi, 2015). These sources usually present high concentrations of metals particularly Cd, Cu, Ni, Pb and Zn (Kennish, 2001; Barcellos, 1995; Lacerda and Molisani, 2006; Lacerda et al., 2004).

Coastal cities are conducive to industrial development, since the proximity to the ocean facilitates the flow of production. Consequently, port activities are promoted and the use of navigation channels, are those of constant maintenance and deepening. In addition to the natural disturbances caused by bioturbation, currents and high energy events, the bed of estuarine regions is subject to remobilization through trawls, trawls of fishing nets and transit of vessels.

Sediments act as sinks for several contaminants that reach water bodies, and this characterizes them as good indicators of the ecosystem health (Abessa et al., 2008; Rodrigues et al., 2017, Kupryianchyk et al., 2015, Chapman et al., 2013). However, due to remobilization or changes on water column physical chemical conditions, sediments also can act as a secondary source of contaminants, if the sediments are enriched with high levels of pollutants (Soliman et al., 2015; Nasr et al., 2015; SEDNET, 2004)

Contaminated sediments management is generally thought only when an engineering project requires studies to compile a mandatory licensing report. They are developed without long-term planning and without the idealization of a sustainable strategy to reduce costs, benefit the environment and collaborate with all system users (Travers and Wenning, 2012). Bottom sediments monitoring can provide information over regions under risk of environmental impact as well as degraded areas in the environment (Abessa et al., 2006).

The object of this study, Sepetiba bay at Rio de Janeiro state, is in plain industrial and harboring development, however it can be considered one of the most contaminated site by trace metals, mostly Cd and Zn, as can be seen in the works of Rodrigues et al. (2017), Monte et al. (2015), Ribeiro et al. (2013), Gomes et al. (2009), Barcellos and Lacerda (1994) and Lacerda et al. (1987). In addition, surrounding areas considered as conservation unities as Marambaia Sandbank and Ilha Grande bay could be exposed to contamination produced on Sepetiba bay watershed, as a result of the activities developed in farthest areas, throughout resuspension of contaminated sediments and the consequent transport through the currents.

1.1. General Background and Problem statement

Brazilian coastline stretches over 10,800 km and has an area of approximately 514,000 km², along 17 states . This abundance of coastal territory and proximity to the ocean encourages the development of port activities. According to the Special Secretariat of Ports (SEP, 2017), Brazil has 15 organized maritime ports managed by SEP and 19 ports operated by state dock companies. In relation to private terminals, more than 47 are authorized by SEP.

However, harbors activities demand structural interventions. One of the costliest and concerning of them is the sediment management, mainly through dredging and disposal issues. Several tools have been created to improve sediment management practices and strategies, especially for coastal areas under strong human intervention.

Although, coastal engineering, environmental legislation and public policies involving environmental problems are issues on constant discussion. National Environmental Policy in Brazil was established in 1981 (Lei n° 6.938/81), and the National Coastal Management Plan constituted in 1988 (Lei n° 7.661/88). Despite coastal environments are legally supported, they perish due to the lack of information and proper monitoring and management.

The southeastern region of Brazil concentrates the highest population density and a variety of industrial districts. The state of Rio de Janeiro has most of its territory bathed by the Atlantic Ocean and this topographic configuration approximates the urban development to water bodies. Rio de Janeiro state has two main estuarine systems, Guanabara bay and the complex of Sepetiba and Ilha Grande bays.

Sepetiba Bay is marked by environmental conflicts: 1) industrial wastes leaching from an old electroplating plant (enriched with trace metals); 2) large industrial district in Santa Cruz, west zone of Rio de Janeiro city; 3) watershed interventions: river transposition, dam and reservoirs constructions; 4) river basin user's conflicts; 5) disordered land settlement, lack of sanitation and treatment of industrial and domestic sewage.

In the northeast part of the bay, straightened river channels bring the continental waters to the bay, forming a deltaic complex environment, most of the channels are supplied by Guandú river, the major fluvial source for Sepetiba bay (Jordão, 2017).

Guandú River has been suffering human alterations in response to water supply demand since 1700's (Jordão, 2017). According to Jordão (2017), Guandu watershed area expanded over 16,500 km^2, due to the diversion system between Paraíba do Sul – Piraí – Guandú rivers, which leads to erosion, declivity decrease and deepening of Guandú river. According to the Management Plan for Environmental Sanitation of Sepetiba Bay Basin (SEMA, 1998), approximately 70% of the fluvial waters flowing into the bay are related to the transposition, which increased 3 times the total flux of the rivers. Therefore, the amount of sediments reaching Sepetiba bay was also altered in the same proportion (Jordão 2017).

Sepetiba bay also hosts the Itaguaí harbor and the terminals of VALLE SA (Guaíba Island) and ThyssenKrupp CSA (currently purchased by the conglomerate Ternium). Dredging activities authorization necessary for ports maintenance have to deal with several socio-environmental challenges due to the environmental liabilities of Ingá Metallurgical Cia. (ECOLOGUS, 2005).

Since early 1960's, Ingá Metallurgical Company used to produce zinc of high purity from Calamine ore processing (Barcellos et al., 1997) in Sepetiba bay. The industrial processes generate residues, which were stored into a pile on the Madeira Island, Itaguaí municipality. During rainy seasons and high pluviosity events, wastes were leaching into the bay through Saco do Engenho creek, a small tidal channel within Madeira Island. Only in 1980, a containment dam was constructed around the waste pile (Marques Jr. et al., 2006), but overflows events were reported constantly. In 1996, the dam broke due to a heavy rainfall and high amounts of trace metals were dumped into Sepetiba bay waters. In 1998, the company declares bankruptcy and the environmental liability was becoming a public problem. In 2008 the Ingá territories were placed for auction by the Rio de Janeiro government and USIMINAS, a steel and mill company from Minas Gerais, purchased the place and started to dismantle the waste through remediation actions (Lindolfo, 2015).

High amounts of trace metals are found stored in the bottom sediments of the bay. Most of the published literature is focused on the concentration of these trace metals and their characterization in the inner part of bay (Fonseca et al., 2013, Lacerda et al., 1987; Barcellos et al, 1997. Barcellos et al., 1991; Barcellos and Lacerda 1994; Wasserman et al, 2001; Maddock et al., 2007; Machado et al., 2008).

However, since Santa Cruz industrial district’s opening (1960’s) several metallurgical and other industries attracting people with job offers, lead to unplanned urban settlements, landscape alteration and sewage release into waterways. The industries have been operated with little or no state supervision, which increased the number of diffuse sources of contaminants to the bay and due to the high amount of trace elements found relate to Ingá wastes, the identification of other point sources has been obstructed. Once, Santa Cruz district hosts a variety of industrial branches (metallurgy, chemistry, plastic products, textile, beverage, among others (Araújo et al., 2017)), metal release into industrial effluents from these facilities is expected. For these reason, trace metals monitoring is essential to identify sources and mitigate future environmental problems.

Marine areas, like Marambaia sandbank are not widely known, and despite the distance from anthropogenic sources of pollution, information about these areas are needed for environment management. Therefore, information need to be translate in a comprehensive and integrative way and suggestions should be given for the monitoring and management of the bay, aiming the improvement of the system and Sepetiba bay ecological services. Proper use of coastal water resources requires the development of environmental quality monitoring policies consistent with the physical and biogeochemical processes that determine the availability of contaminants, for transport and bioloxgical incorporation.

There are gaps on knowledge based on trace metals geochemistry into the bay. Spatial distribution and environmental risk assessments was approached by authors like Ribeiro et al. (2013), Fiori et al. (2013) and Lacerda et al. (1987). However, previous studies did not employ the risk associated to the trace metals concentrations in the solid phase of sediments related to aquatic life protection based on guidelines in a wider extent into the system.

Sedimentation accumulation rates (SAR), fluxes and inventories were studied by Gomes et al. (2009) and Barcellos (1995) in the inner part of bay. Here SAR, metals fluxes and inventories were applied to observe the influence of trace metals in the inner and outer regions from the main sources of pollutants to the bay. It is relevant to understand how trace metals behave in different featured regions with different environments of deposition, due to the sediments and hydrodynamic patterns heterogeneity.

Moreover, trace metals present in the sediments can be found in the exchangeable form, associated with carbonates, bound to Fe and Mn oxides, attached with organic compounds and being part of crystalline matrix (Salomons, 1995; John and Leventhal, 1995). However, only works from Fizman et al. (1984) and Souza et al. (1986) approached more than two fractions in the study of metal partitioning on Sepetiba bay. While Lacerda et al. (1987), Monte et al. (2015) and Rodrigues et al. (2017) observed two metals association phases, weakly bound and residual fraction. Sequential extraction scheme with six steps were used to obtain a higher resolution and a wider comprehension about the main scavenging phases for trace metals into the sediments and understand the mobility and availability through time in two different featured areas, while recognizing the practical applicability and limitation of this method to the environment.

The importance of updating and collecting further data on Sepetiba bay sediments is due to different sources of contamination and the variety of human interventions that the bay has gone through to the last 60 years. This works aims to contribute with new data about trace metals in sediments from Sepetiba bay using different approaches and suggests improvements for sediment quality assessment.

1.2. Research Objectives

The objective of the present work is to evaluate the main geochemical processes that govern trace metals behavior in the sediments to identify potential risk associated with these pollutants availability and mobility in a human disturbed area, Sepetiba bay, Rio de Janeiro, Brazil.

1.2.1. Specific objectives

- Estimation of a contamination index based on secondary data. A data survey of the literature available from Sepetiba bay sediments containing spatial information and metals concentration (Al, Fe, Cd, Cu, Ni, Pb and Zn) in pseudo-total and total extractions from surficial sediments were used to generate indexes based on Sediment Quality Guidelines available;

- Estimation of sediment and mass accumulation rates in the northeast and marine areas of the bay from collected cores, with the aim of identifying connections between the amount of trace metals and the changes in the sedimentation patterns among different featured areas within the bay;

- Identify the main sediment phases for trace metal fractionation in marine and estuarine areas of Sepetiba bay, through the sequential extraction method. Cores from Marambaia bay and São Francisco Channel delta were submitted to six extractions based on the following criteria: 1) exchangeable; 2) easily reducible oxides; 3) poorly crystalline oxides; 4) organic matter; 5) silicates; 6) sulfides.

1.3. Thesis outline

a. Chapter 1: gives a brief introduction, the problem statement, and research objectives;

b. Chapter 2: Sediment quality guidelines quotients estimation with secondary data: literary review, surveying articles, thesis and reports. The SQGQs offer an insight into trace metals distribution in surficial sediments from Sepetiba bay;

c. Chapter 3: Describe sedimentary conditions of trace metals in a historical based trajectory, with sedimentation rates estimation, metals concentration, fluxes, inventories and enrichment factors;

d. Chapter 4: Describe trace metals behavior with geochemistry fractionation within two different regions of Sepetiba bay, through sequential extraction methodology;

e. Chapter 5: Summarize the major findings of the thesis and offers recommendations for future studies in sediments from Sepetiba bay.

Chapter 2

Spatial patterns and environmental risk associated to metal enrichment in surficial sediments from Sepetiba bay, Rio de Janeiro, Brazil.

2.1. Introduction

Trace metals input in aquatic systems occurs through point and non-point sources, both natural and anthropogenic ones. Metals from natural sources are derived from rocks weathering, soils drainage and fluvial input. Anthropogenic contributions to this compartment are result of industrial processes and urban drainage (i.e. domestic sewage and landfill leaching) and it has led to metals enrichment in aquatic environments. Metals concentrations in contaminated sediments can be found several orders of magnitude higher than background references (natural levels) (USEPA, 2007; Kennish, 2001). Iron (Fe) and Aluminum (Al) have naturally high concentrations in sediments. On the other hand, trace metals as lead (Pb), zinc (Zn), cadmium (Cd), copper (Cu) and nickel (Ni) belong to a wider group of metals that are found at low concentration on Earth's crust. (Callender, 2003). These metals are extensively analyzed in environmental studies due to their potential toxicity, occurrence and use in industrial processes.

The southeast coast of Brazil is a heavily-populated industrial zone, which shelters 80.364.410 people in four states – Rio de Janeiro, São Paulo, Minas Gerais and Espírito Santo (IBGE, 2010). The majority of Rio de Janeiro state territory is flanked by the Atlantic Ocean and this setting brings urban and industrial development close to coastal waters. The state has two harboring areas, Guanabara bay with Rio de Janeiro port and Sepetiba bay with Itaguaí Harbor.

Environmental condition of Sepetiba bay is influenced by anthropogenic inputs of industrial wastes from an old bankrupted industry (Barcellos et al., 1997) and the industrial district in Santa Cruz area (west zone of Rio de Janeiro City). Zinc and Cd are found in extremely high concentrations, mostly in sediments in the northeast part of the bay (Rodrigues et al., 2017; Monte et al., 2015; Ribeiro et al., 2013), due the proximity of Madeira Island, where Ingá Cia wastes pile was located and the majority of fluvial input from Sepetiba watershed.

Industrialization began in Sepetiba bay basin in the middle of 1960's and the studies about trace metals concentrations of sediments started in the early of 1980's (Lacerda, 1983, Fizman et al., 1984; Souza et al. 1986; Aragon et al., 1986; Azcue et al., 1987; Lacerda et al., 1987). From 30 years ago, Lacerda et al. (1983;1987) already notice high concentrations of trace metals in the region. Lacerda et al. (1983) and Azcue et al., (1987) estimated that suspended particulate material was the main vector of contaminant's transport from the watershed to the bay. Lacerda et al. (1983) analyzed trace metals concentrations in different matrices, the pathways of these metals and human groups under environmental risk in the region. As a result, the authors found Cd and Zn with high levels in seafood (oysters and crustaceans).

In the 90's Barcellos published a variety of works about geochemical behavior of Cd and Zn (Barcellos et al., 1991; Barcellos and Lacerda, 1994; Barcellos et al., 1994, Barcellos, 1995). According these works, total input of Cd to Sepetiba bay was 2 tons y^{-1} (0.2 by atmosphere and 1.8 by fluvial sources) and for Zn was 200 tons y^{-1} (56 by atmospheric deposition and 144 by fluvial input) (Lacerda et al., 2004).

In 1998, the environmental agency of Rio de Janeiro performed a project and a report with Cd and Zn distribution was elaborate by FEEMA/GTZ (1998). The objective was to evaluate the water quality of Sepetiba bay basin (October, 1995 – June, 1998), where geochemical analyses from bottom sediments were performed. Cd and Zn concentrations, as expected, due previous findings, were high in the northeast part of the bay. According, to the report conclusions, dredging operation on bottom sediments from de bay were responsible for the fine sediments redistribution and, consequently, trace metals spread to farthest areas of the system.

Pellegatti et al. (2001) results showed Zn enrichment with respect to mean shale values, with high concentrations near to the northeast coast. According to the authors, the grain size distribution was the major controlling factor for metals distribution, where the accumulation occurred mainly in areas with fine grained sediments dominance.

Gomes et al. (2009) estimated metal fluxes and inventories from sediment cores of Sepetiba bay. The authors found sedimentation rates enhancement of 0.42 cm yr^{1} in the last 60 years, they attributed this increment to Paraíba do Sul – Guandú diversion system (see chapter 1, section 1.2.). The authors also noticed the enhancement of Cd and Zn in sediment profiles after Industrial Ingá Cia. started to work in the late 1950's at Madeira Island – Itaguaí, processing calamine ore to zinc production. Cadmium and zinc concentrations were 3 and 4 orders of magnitude higher than the thresholds suggested by CONAMA 454/2012, respectively.

A work group from Universidade Estadual do Rio de Janeiro performed extensive campaigns for sediment sampling inside Sepetiba bay and two main author's works from this group were explored in this chapter, Morales (2012) and Rocha et al., (2012;2010;2011). Rocha studied samples collected in 2008 from 91 sites on Sepetiba Bay, with the aim of understanding the geochemical distribution of metals and relate to local geological formation. Rocha (2011) pointed out that the fluvial discharge by São Francisco Channel (Estuarine section of Guandú River) is the main controlling factor of metals distribution on bottom sediments, as well as atmospheric deposition. The author also observed high concentration of trace metals, as Cu, Pb, Cr, Ni, Zn and Cd in exchangeable forms, however the grain size and the estuarine gradient can act as a dilution factor for the concentration of trace metals in the marine influenced area (Rocha, 2011; Lacerda et al., 2004). Morales (2012) used isotopic tracers of lead and metals concentration to characterize these elements in the western part of the bay (marine influenced area), near the ocean connection. The author observed trace metals enrichment in the eastern part of the bay, on the other hand disposal areas of dredged material (see Figure 2.4.2, section 2.4) inside the bay can be affecting surrounding areas of Guaíba, Itacurucá and Jaguanum Islands and also Marambaia bay, due to trace metals redistribution by currents through dispersion of fine sediments enriched with Cd, Zn, Pb, Ni and Cu.

As mentioned above for the majority of literature, areas close to northeast part of the bay, at Saco do Engenho creek (Figure 2.2.1) showed extremely high trace metals concentrations and the amount of organic carbon and sulfides binding phases were not able to make these metals unavailable to biota uptake (Rodrigues et al., 2017). Rodrigues et al 2017 observed toxicity even when there were biding agents available to association and metal retention in solid phases, which reflects the uptake of solids by biota and metals release inside their system, consequently, the authors observed chronic effects in toxicity tests and benthic community structure damage, mostly due the presence of opportunistic and dominant species.

Here, metals distribution in superficial sediments from Sepetiba bay will be reported. This chapter aims to compile secondary data information about trace metals and identify enrichment areas, due to anthropogenic input. The sediment quality guidelines quotient indexes will help to translate this data into an informative risk of impact warning for stakeholders and the target audience.

2.2. Methods

For a better understanding of metals distribution in bottom sediments from Sepetiba bay, data available of Cd, Cu, Ni, Pb, Zn, Al and Fe with geographical coordinates information were compiled. Previous published works selected were Barcellos (1995), Barcellos et al. (1997), FEEMA/GTZ (1998), Pellegatti et al. (2001), Rocha (2011), Rocha et al. (2012), Morales (2012), Rodrigues (2013) and Rodrigues et al. (2017) (Table 2.2.1).

Table 2.2.1. Information about the literature used on the assessment of trace metal distribution.

Author	Method	N° of sites*	Elements	Grain Size
Rodrigues et al. (2017)	3051A (USEPA, 1999)	5	Al, Fe, Cd, Cu, Ni, Pb and Zn	>70% Fine sediments
Rocha (2011); Rocha et al. (2012	$HF+HNO_3+H_2O_2$ (Total)	85	Al, Fe, Cd, Cu, Ni, Pb and Zn	<0.072 mm
Morales (2012)	$HF+HNO_3+H_2O_2$ (Total)	42	Al, Fe, Cd, Cu, Ni, Pb and Zn	<0.072 mm
FEEMA (1998)	Aqua regia (HNO_3 + HCl)	35	Cd and Zn	<63µm
Pellegatti et al. (2001)	Neutron Activation Analysis (INAA)	28	Fe and Zn	<63µm
Barcellos et al. (1997); Barcellos (1995)	$HF:HCl:HNO_3$	18	Al, Fe, Cd and Zn	<63µm

*Number of sampling sites used in this work.

A total of 213 sites with metals in sediments were retrieved and compiled in a spreadsheet with their coordinates and elements concentrations. From this database, spatial distribution and sediment quality guidelines quotients were estimated. Data interpolation and charts were designed with ArcGis 10.5. The study area is illustrated in figure 2.2.1, as can be seen the references are listed with their respective sites.

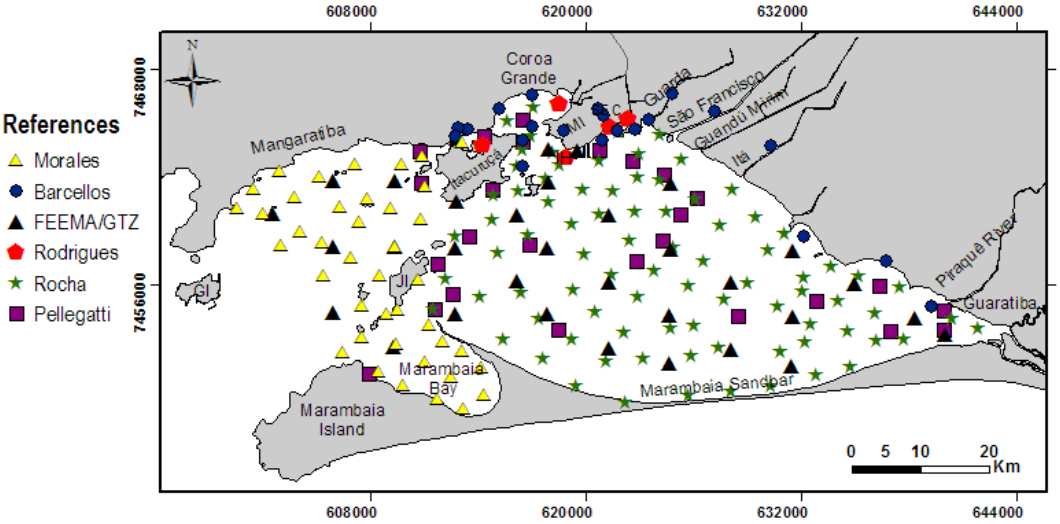

Figure 2.2.1. Sites location with available information about metals concentration in pseudo total fraction. Sources: Barcellos et al. (1997), Barcellos (1995), FEEMA/GTZ (1998), Pellegatti et al. (2001), Morales (2012), Rocha et al. (2011) and Rodrigues et al. (2017). Abbreviations on the map: Madeira Island (MI), Saco do Engenho Creek (SEC), Itaguaí Harbor (IH), Guaíba Island (GI), Jaguanum Island (JI).

The criteria for sites selection was the mean grain size (Figure 2.2.2), samples located at the medium and coarse sand areas (red and orange – 0.062 – 0.5mm) were disregarded in order to have consistency with sites and methodologies comparisons, once the majority of authors used only the fine fraction (<0.072mm) in sediment's metal extraction. Grain size distribution is shown in figure 2.2.2, where the data from Ponçano (1976) and Pereira et al. (2003) were interpolated.

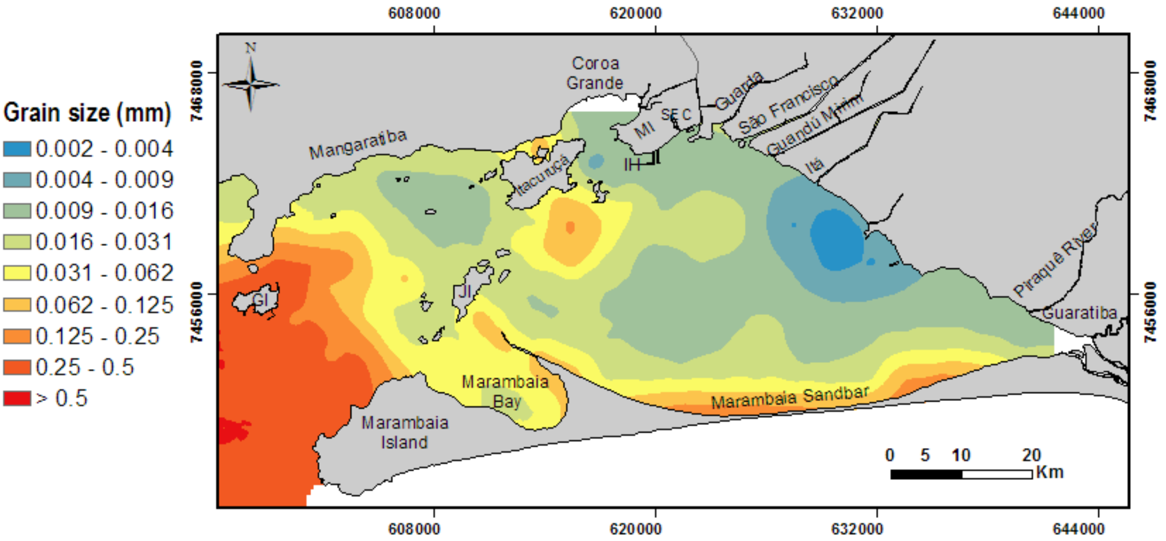

Figure 2.2.2. Mean grain size distribution according to data from Ponçano (1976) and Pereira et al. (2003).

Sepetiba bay is dominated by fine sediments in the inner part, mostly near the main channel, at the northeast region. Sandy sediments are located at the mouth of the bay and along Marambaia Sandbank. Clays are mostly found near to Saco do Engenho Creek, Guarda, São Francisco, Guandú-Mirim and Itá channels, due continental sediments input (Figure 2.2.2).

Metals spatial distribution were interpolated with Empirical Baysian Kriging method, after log transformation. Kriging assumes that the distance or direction between sample points reflects a spatial correlation that can be used to explain variation in the surface (ESRI, 2017).

Sediment Quality Guidelines Quotients were calculated based on Fairey et al. (2001) and thresholds suggested by CONAMA 454/2012 (SQGQs), where a classification index is generated for risk of environmental impact according to equation 1.

$$SQGQs = \sum_{n=1}^{5} \left(\frac{[Cd]}{L2_{Cd}} + \frac{[Cu]}{L2_{Cu}} + \frac{[Ni]}{L2_{Ni}} + \frac{[Pb]}{L2_{Pb}} + \frac{[Zn]}{L2_{Zn}} \right) /5 \qquad \text{Eq. 1.}$$

Where L2 corresponds to level 2 on CONAMA 454/2012 guidelines for each trace metal. L2 represents the concentration where the highest probability of adverse effect to biota is expected. The classification criteria were adapted from Fairey et al. (2001), Abessa et al. (2008) and Rodrigues et al. (2017). Potential scenarios of environmental risk are described according to five conditions:

1. No risk (0 to 0.1)
2. Potential risk (0.1 to 0.25)
3. Environment under risk of impact (0.25 to 0.5)
4. Under moderate risk of impact (0.5 to 1).
5. High risk of impact (> 1).

Individuals $SQGQ_{me}$ were calculated according to the following formula:

$$SQGQ_{me} = \frac{[me_{sample}]}{L2_{me}} \qquad \text{Eq. 2.}$$

Where $[me_{sample}]$ is the metal concentration in the sample and $L2_{me}$ is the threshold of the respective metal in the CONAMA 454/2012.

2.3. Aluminum and Iron

Aluminum is a major constituent of fine-grained aluminum-silicate material with which trace metals can be associated (Wang and Qin., 2007). In the study area, Al concentration distribution is probably not significantly affected by human activities. According to Barcellos et al. (1997), Al is considered tracer of continental material, from riverine influence. Al interpolation results are demonstrated in figure 2.3.1 and follow fine sediments pattern (Figure 2.3.1), with higher values near to areas with silt and clay presence and the lowest concentrations were associated with sandy areas, as can be seen in figure 2.3.1. However, Al from anthropogenic sources could be found due to sludge discharge from water treatment plant, which uses aluminum sulfate as flocculating agent and alumina ore could be lost during ship loading and unloading at Itaguaí Harbor (Figure 2.3.1).

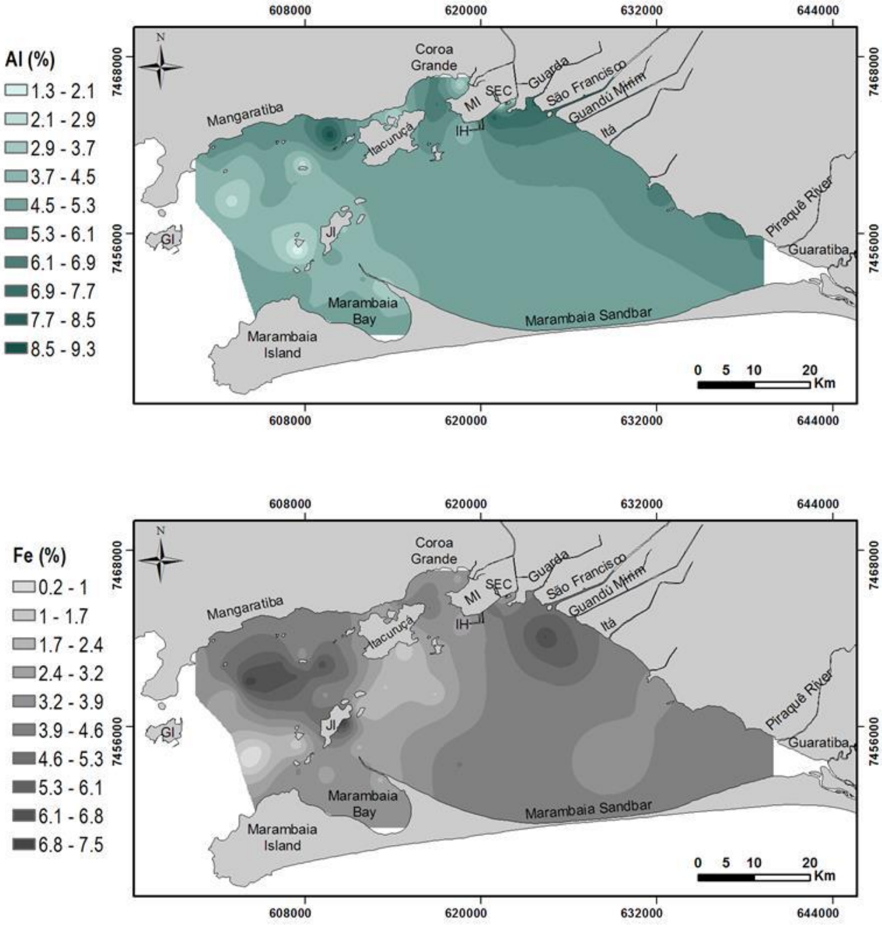

Figure 2.3.1. Percentages of aluminum (above) and iron (below) in superficial sediments from Sepetiba Bay. Soucers: Al (Barcellos et al. (1997), Morales (2012), Rodrigues (2013)) and Fe (Barcellos et al. (1997), Pellegatti et al. (2001), Morales (2012), Rodrigues et al. (2017)).

Al concentrations observed by Rodrigues (2013) were between 1.3 to 3.8% near to Madeira Island, meanwhile Barcellos et al (1997) found higher values from 5.2 to 8.4%. Gomes et al. (2009) observed Al between 2.8 and 9.3% from samples obtained at São Francisco channel mouth. For Marine areas Morales (2012) observed Al content from 1.17 to 9.5%, with higher concentrations near Mangaratiba, following fine sediments pattern.

Fe has been used also as a reference element, but its geochemistry is similar to many other traces elements in oxic and anoxic environments (Barbieri, 2016). Values compiled for iron are presented in shades of grey in the figure 2.3.1. Data interpolation showed higher concentrations at the northeast part of the bay, near the main fluvial sources, Coroa Grande, Guaratiba and Itacuruçá region.

Gomes et al. (2009) observed Fe concentrations around 4.6% in sediments near to Guandu Mirim canal, Barcellos et al. (1997) found values between 3.1 and 7.3% near to Madeira Island (MI) and Rodrigues et al. (2017) obtained Fe concentrations also near to MI around 2 and 3.3%. Marine sediments measured by Morales (2012) showed iron concentration with a wider range between 1 and 7.9%, with higher values related to finer sediments and sheltered areas, as can be seen in figure 2.3.1 Darkest colors representing higher concentrations are observed at Marambaia bay and Mangaratiba region. Pellegatti (2001) also observed high values of Fe near to northeast area and Guaratiba, from 0.2 (marine region) to 7% (near to São Francisco channel's mouth).

Anthropogenic sources of Fe are expected, mostly from metallurgical industry wastes and due to losses of iron ore during ship loading and unloading at Itaguaí Harbor. Iron ore is the main handled product in Sepetiba bay ports (Itaguaí and Guaíba Terminal), corresponding 87% of total in 2012 (LABTRANS, 2014).

2.4. Copper (Cu)

Cu can be found in a variety of minerals, for instance malachite, chalcopyrite, calcopyrite, chalcocite (WebMineral, 2017) and it has been used in manufacturing of the following products: electrical wire, metal alloys, industry machinery, antifouling and antimicrobial coatings and metal smelting activities (Zagatto and Bertoletti, 2006). Copper is an essential element to all living organisms, although only small concentrations of the metal are needed for well-being (Osredkar and Sustar, 2011). After iron and zinc, copper is the third most abundant metal in human body (Osredkar and Sustar, 2011). However, higher amounts of Cu can be toxic and with potential to bioaccumulation.

Total amount of copper in sediments from Sepetiba bay are presented in figure 2.4.1. Hotspots areas are found near to main navigation channel. The concentrations observed by the data compile for Cu were between 5 and 1160 mg Kg^{-1}. Highest value was observed in the middle of Marambaia sandbar coast line (Figure 2.4.1).

Rodrigues et al. (2017) found around Madeira Island Cu concentrations between 8.5 and 33.3 mg Kg^{-1}. Overall, Rocha et al (2010) found Cu concentrations around 4 and 310 mg Kg^{-1}, besides these values the authors observed two hotspots of 849 and 1160 mg Kg^{-1}. These sites are located adjacent to Marambaia Sandbank, near to Guaratiba region.

Morales (2012) also found high values of Cu at the bay's mouth with Cu content between 9 and 223 mg Kg^{-1}, with a hotspot outside the study area outlined here by the grain size. The author observed

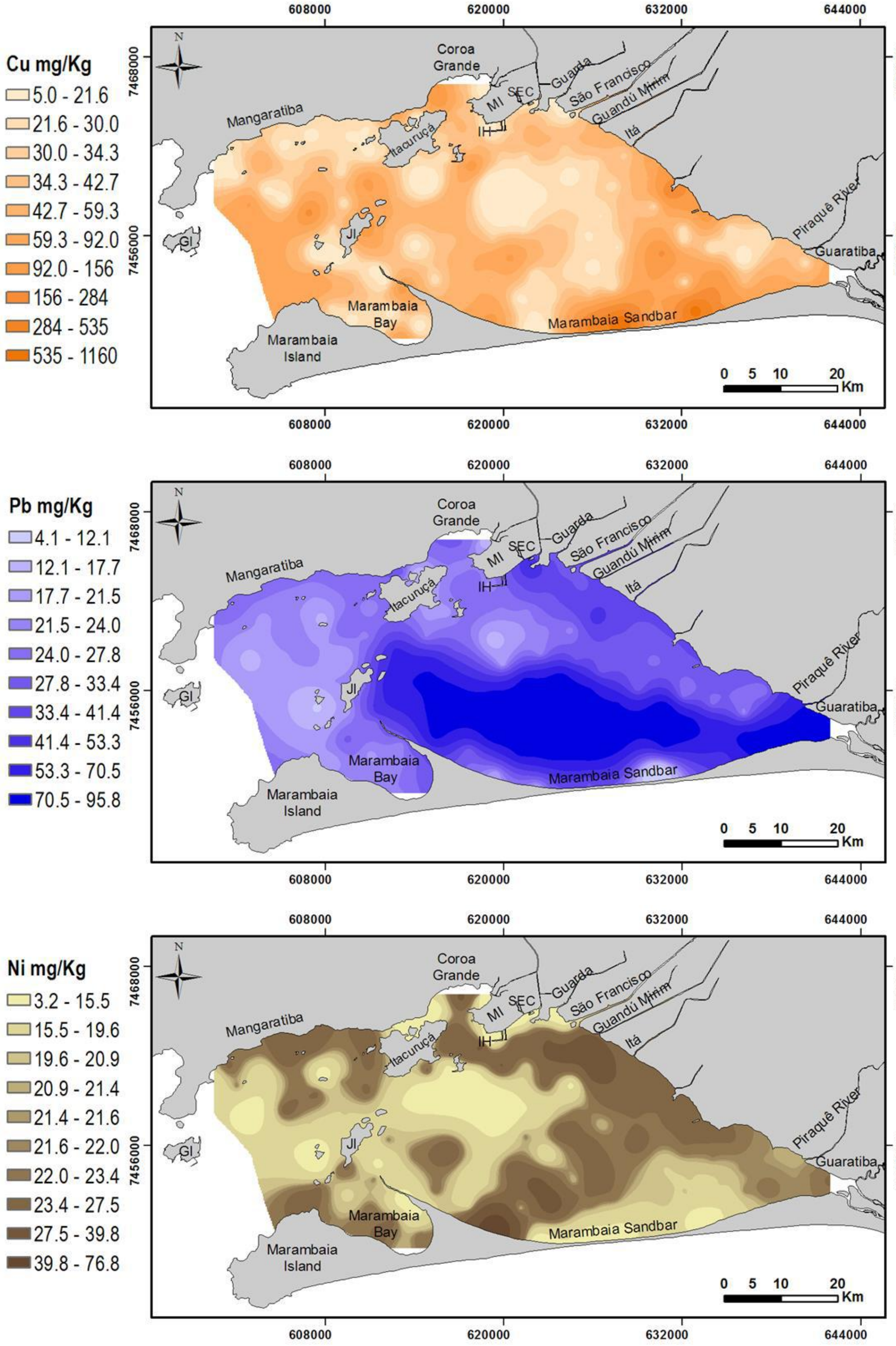

Figure 2.4.1. Strongly associated concentrations of trace metals. For Cu (Rocha (2011), Morales (2012), Rodrigues et al. (2017), Pb (Rocha (2011), Morales (2012), Rodrigues et al. (2017)) and Ni (Rocha (2011), Morales (2012), Rodrigues et al. (2017).

Besides the well-known anthropogenic sources at northeast part of the bay, areas at west and south part of the bay could be also affected by hull's ship stripping and cleaning, with in situ residues disposal of enriched material with copper oxide. In semi-enclosed waters, Cu is readily leached from the hulls of resident and visiting ships and, after oxidation, Cu^{2+} ions are able to adsorb to suspended particles which may settle on bottom sediment (Turner, 2010). Paint fragments and dusts generated during boat maintenance can be also a direct source of particulate residual contamination in such settling (Turner, 2010). Besides that, adjacent areas of Marambaia sandbank and Sepetiba bay main entrance were used as disposal sites to dredged sediment (Morales, 2012) (Figure 2.4.2).

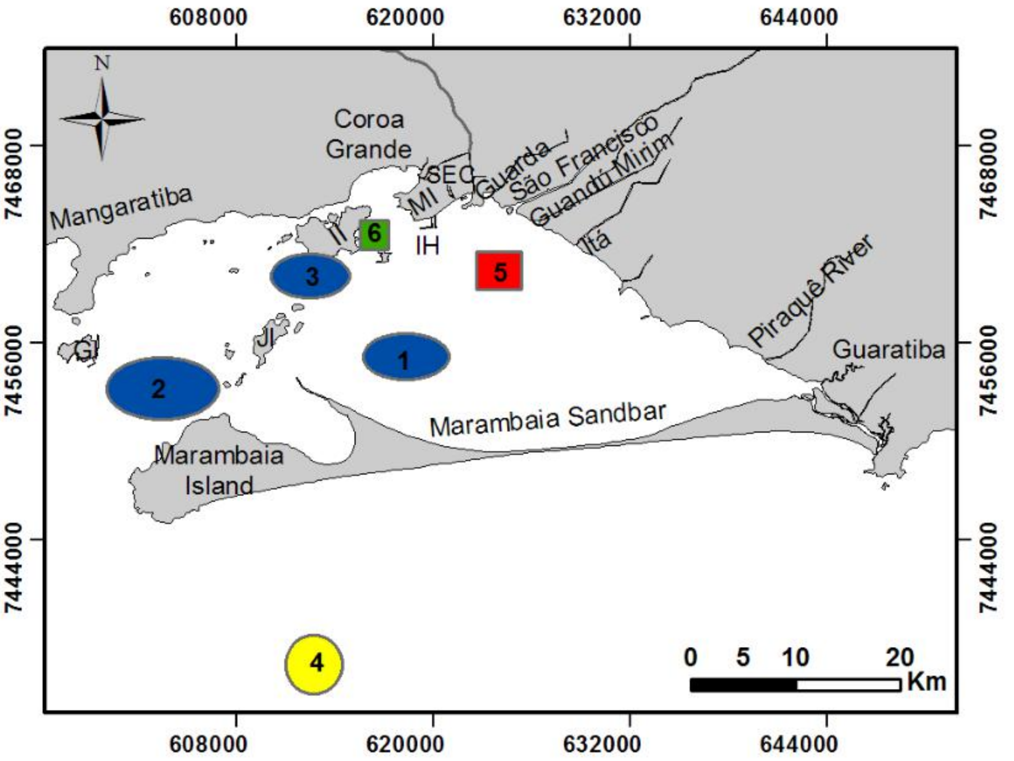

Figure 2.4.2. Disposal areas for dredging material in Sepetiba bay. Blue elipses 1, 2 and 3 are area used by CDRJ, yellow circle 4 is the external disposal area, red square 5 (Ecologus, 2005; HUSKYDUCK, 2007) is the CDF (Confined disposal facility) used by Thyssenkrupp CSA and green square 6 is the CDF used by Porto Sudeste (Ecology Brasil, 2008; Wasserman, 2009).

According to CONAMA 454/2012, Cu concentrations below 34 mg Kg^{-1}, threshold level 1 represents lower probability of adverse effects to biota. Although, concentrations above 270 mg Kg^{-1} have higher probability of biota damage (level 2). In 72 data, Cu levels were above level 1 and only 4 samples above level 2, 1 sample from

Morales (2012) and 3 samples from Rocha (2011), these samples were considered hotspots near to bay's mouth and Marambaia sandbank region.

These high amounts of Cu in farthest areas of the bay, for instance protected areas as Marambaia Sandbank, have to be better investigate. Despite of fewer occurrences of contaminated sites by Cu, this is an essential trace metal to living organisms and its enrichment can be a potential risk to Sepetiba bay biota and, consequently, to human health.

2.5. Lead (Pb)

Lead is more commonly found and mined as the lead sulfide mineral galena. Its major use today is in lead acid batteries and for radiation shields. It is also a constituent of low-melting alloys (Skerfving; Bergdahl, 2007; Buratini and Brandelli, 2006). The natural input of Pb to aquatic systems is by weathering of catchment soils and bedrocks or transported more directly within mineral matter eroded from the catchment. The airborne lead is another source from human activities, it has been transported atmospherically and deposited on aquatic systems (Callender, 2003).

Lead is a trace metal non-essential to biological functions and can bioconcentrates in the skin, bones, kidneys, and liver of fish rather than in muscle, with lower potential to biomagnification (Solomon, 2008). However, populations that consumes the whole fish or seafood, can be potentially exposed to high concentrations of lead (Wright and Welbourn, 2002). In algae, excess of Pb can inhibit photosynthesis processes, which will lead to a primary production decrease and as a consequence, an impact into the local food chain. In fishes, the bioaccumulation of Pb can affect gills function, fertility and consequently the spawning production, which can decrease the population. Pb is more toxic at lower pH and in freshwater (Wright and Welbourn, 2002).

Concentrations of Pb on Sepetiba bay sediments are represented in blue shades, after kriging interpolation (Figure 2.4.2). The values were between 4 and 96 mg Kg^{-1}. Morales (2012) observed Pb concentrations between 8 and 35 mg Kg^{-1}, Rocha (2011) 16 to 96 mg Kg^{-1} and Rodrigues et al. (2017) found Pb values from 9.7 to 63.5 mg Kg^{-1}. CONAMA 454/2012 has the following thresholds for lead: level 1 – 46.9 and level 2 – 218 mg Kg^{-1}. According to the concentrations observed Sepetiba bay, only level 1 was exceeded in the inner part of the bay, from samples analyzed by Rocha (2011).

Higher concentrations are located at northeast part of the bay, surrounded by fluvial and industrial sources and in shallow areas, along Marambaia sandbank nearshore, where the hydrodynamic conditions have lower velocities. The gradient of Pb can be associated to estuarine gradient, which is characterize by salinity, grain size, organic matter content and pH distribution. According to Ribeiro et al. (2013), higher concentrations of total organic carbon and acid volatile sulfides are found in the inner part of the bay, where it is possible to find higher amounts of trace metals, including Pb. Chakraborty et al. (2012) studying Cd and Pb speciation in estuarine sediments observed that organic matter plays a key role in controlling Pb speciation in the sediments under oxic condition. Which is the case of Sepetiba bay, with very oxygenate waters and sediments are passing through frequently resuspension events (Lacerda et al., 2004; Barcellos et al. 1997, Barcellos, 1995).

2.6. Nickel (Ni)

According to Klein and Costa (2007), Ni is a component of Earth's crust and occurs in soil, water and air. Nickel is used on metal alloys, batteries, electroplating, electronic components, factory equipment's production, among other applications (Klein and Costa, 2007). Ni enters the aquatic environment by removal from the atmosphere, surface run-off, discharge of industrial and domestic sewage and also following natural erosion of soils and rocks. In rivers, nickel is mainly transported in the form of a precipitated coating on particles and in association with organic matter (Klein and Costa, 2007).

Ni concentration in superficial sediments from Sepetiba bay were between 3.2 and 77 mg Kg^{-1}, as can be seen in figure 2.4.2. Rocha (2011) found Ni concentrations from 14 to 77 mg Kg^{-1} and Morales (2012) observed Ni values between 7 and 26 mg Kg^{-1} at the Marine influenced area. Although, Rodrigues et al. (2017) around Madeira Island found lower concentrations with values from 2.4 to 6.3 mg Kg^{-1}. Ni total concentration is correlated with aluminum concentration as can be seen in figure 2.6.1. The correlation of Al and Ni is high (r^2=0.79), suggesting that nickel probably derived from parent material, associated with fine sediments. CONAMA 454/2012 has the following thresholds for Ni: level 1 – 20.9 and level 2 – 51.6 mg Kg^{-1}. According to the concentrations observed Sepetiba bay has been enriched by Ni, mostly near to Enseada das Garças.

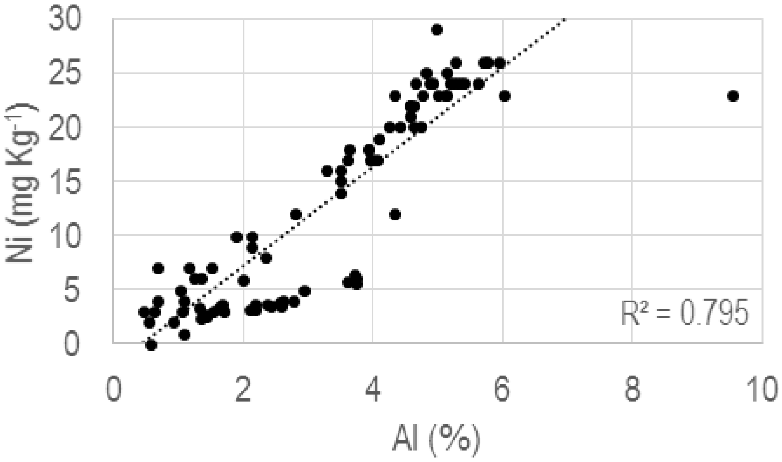

Figure 2.6.1. Scatter plots of aluminum versus nickel. The correlation between the variables is r² = 0.8.

2.7. Cadmium

Cadmium (Cd) is a trace metal ranked by the Environmental Protection Agency of United States and the Agency for Toxic Substances and Disease Registry (ATSDR, 2012) as one of the most commonly found substances at hazardous wastes and poses a potential threat to living organisms and, consequently, to human health (Nordberg et al., 2007; Klaassen et al., 2009).

Human activities have markedly increased the distribution of Cd in the global environment. Cadmium is applied in battery manufacturing, pigments, enamels, photography, semiconductors, sterilizers for plasters, plating other metals, wastes from mining activities, cigarettes, among others sources (Nordberg et al., 2007).

Concentrations of Cd on Sepetiba bay sediments are presented in figure 2.7 (chart above) and they were between 0.4 and 152 mg Kg^{-1}. Rocha (2011) found Cd concentrations from 0.4 to 23 mg Kg^{-1} and Morales (2012) observed Cd values between 0.3 to 2.7 mg Kg^{-1} at the Marine influenced area. In a sampling campaign from 1991, Barcellos (1995) found Cd concentrations between 0.4 and 152 mg Kg-1, with highest concentration at the mouth of Saco do Engenho creek. While in 2011, Rodrigues et al. (2017) found Cd concentrations with values from 0.5 to 23 mg Kg^{-1} around Madeira

Island. Cd total concentration distribution in Sepetiba bay sediments is following fine sediments pattern (Figure 2.7.1), as well as Zinc concentrations (Figure 2.7.1).

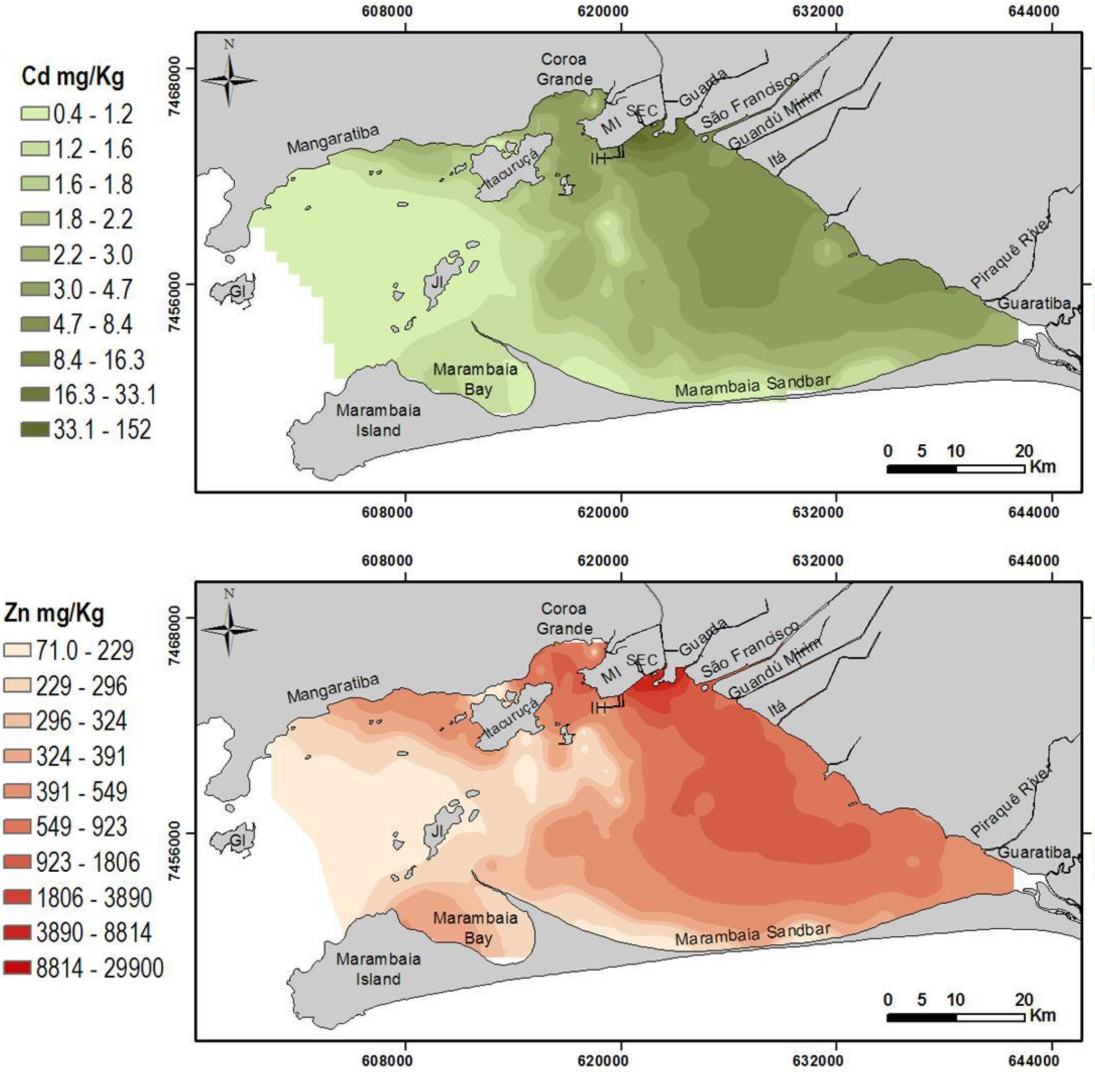

Figure 2.7.1. Strongly associated concentrations of trace metals. For Cd (Barcellos (1995), FEEMA/GTZ (1998), Rocha (2011), Morales (2012), Rodrigues et al. (2017)) and Zn (Barcellos (1995), FEEMA/GTZ (1998), Pellegatti et al. (2001), Rocha (2011), Morales (2012), Rodrigues et al. (2017)).

Metals fate in salt water is affected by several factors including pH, redox potential, ionic strength, type and concentration of organic and inorganic ligands, and the presence of solid surfaces for adsorption. Absorption and desorption processes can release trace metals from sediments (USEPA, 2007) and their toxicity in aquatic organisms varies considerably according to the organism’s species and abiotic factors (Paquin et al., 2005).

According to Gomes et al. (2009), Molisani et al. (2004) and Marques Jr. et al. (2006), the increase of Cd and Zn concentrations in the sediments coincides with the beginning of production of high purity Zn by Ingá Cia. in the early 1960’s. Around

Madeira Island, cadmium levels were 13 times higher than CONAMA 454/2012 level 1 and 1.5 times higher than level 2 (1.2 and 7.2 mg Kg^{-1}, respectively) (Rodrigues et al., 2017). Marques Jr. et al. (2006) estimated pre-industrial values for Cd below 0.2 mg Kg^{-1}, which indicates an enrichment of Cd in sediments around the Saco do Engenho mouth in 760 times than the background.

Lacerda et al. (1987) found Cd concentrations in the strongly associated fraction between 0.5 and 8.7 mg Kg^{-}1. Barcellos and Lacerda (1994) reported Cd concentrations of 2.1 mg Kg^{-1}, with an increase of 1.6 tons $year^{-1}$. According to the authors, this increase is related to the industrial development in the region, to hydrodynamic behavior and its dispersion capacity into the bay, which receives this amount of Cd per year into 447 km², while other systems can receive higher amounts, but with higher dilution capacity (Barcellos and Lacerda,1994).

Kennish (2001) estimated an input around 7000 tons $year^{-1}$ of Cd to the oceans and around 2600 tons $year^{-1}$ of this amount is accumulating in bottom sediments, with the majority of it rapidly being deposited on coastal areas near to highly industrialized and urbanized regions (KENISH, 2001).

According to Nordberg et al. (2007), Cd behaves similar to Zn, occurring naturally associated with zinc and lead in sulfide minerals. Cd has been replaced by other metals in products manufacturing, which earlier used cadmium in their composition, due to its toxicity, besides Cd application nowadays is limited in European Union countries, United States and Canada.

2.8. Zinc (Zn)

Zinc is commonly found as sphalerite and zinc oxide minerals and composes approximately 0.02% of the Earth Crust, with a mean concentration of 78 mg Kg^{-1} (Sandstead and Au, 2007). This metal is used as plating for other metals, paintings, construction industry, anticorrosion alloys and tan production. Besides that, it is commonly found in automotive equipment's, battery cells, pharmaceutical and dentistry industry, antifouling paintings, antibiotics and lubricants (Sandstead and Au, 2007).

According to Sandstead and Au (2007), metallurgic industry, ore mining activities and waste mining disposal collaborate to zinc input in coastal systems with approximately

1 to 3 million of tons of Zn per year. Therefore, fertilizers and atmospheric emissions release particles with zinc and contribute with 289-2054 x 10^3 tons year^{-1} of Zn to aquatic systems, while farming and sewage sludge add 640-1914 x 10^3 tons per year of Zn into oceans.

Zinc is an essential trace element that can be toxic to aquatic life at high levels. Zinc input into coastal ecosystems can occurs through atmospheric deposition, industrial and domestic sewage, soil and urban surface runoff, among others sources. The affinity of zinc for particulate material, especially iron and manganese oxides, and organic matter results in its sinking, and consequently deposition on bottom sediments (Campbell and Tessier 1996; CCME, 1999).

Zinc distribution is shown in figure 2.7.1. The concentrations were from 71 to 29,990 mg Kg^{-1}, with high values in the inner part of the bay, mostly on Saco do Engenho's mouth. As the compilation of data showed, concentrations of Zn in surficial sediments located close to the point sources of contamination frequently exceed background concentrations (CCME, 1999) and furthest areas are less affected by zinc contamination. According to CONAMA 454/2012, both thresholds were exceeded (Level 1: 150 and level 2: 410 mg Kg^{-1}).

In the 90's, Barcellos (1995) observed Zn content from 172 to 29,900 mg Kg^{-1}, with highest values near to Saco do Engenho creek (SEC) and between Madeira Island (MI) and Itacuruçá Island. In the FEEMA/GTZ (1998) report, zinc concentrations on superficial sediments were from 0.4 to 1980 mg Kg^{-1}. Pellegatti et al. (2001) found zinc content between 37 and 2894 mg Kg^{-1}. Morales (2012) observed Zn concentrations in the marine area between 66 and 478 mg Kg^{-1}, with higher values at Marambaia bay and near to the west side of Itacuruçá Island, at Mangaratiba nearshore. Rocha (2011) found Zn content from 82 to 3440 mg Kg^{-1} in the inner part of the bay, the author observed the highest concentrations in the mouth of Saco do Engenho Creek and Itá Channel (Figure 2.7).

Rodrigues et al. (2017) found zinc concentration between 126 and 4566 mg Kg^{-1} around Madeira Island region. Gomes et al. (2009) estimated Zn background of 54 mg Kg^{-1} next to fluvial sources and Marques et al. (2006) found pre - industrial zinc values from 69 to 103 mg Kg^{-1} at Coroa Grande. According to these values, zinc concentration at Saco do Engenho mouth (dark green colored) can be 550 times higher than the background values and 73 times higher than level 2 of CONAMA 454/2012.

The positive correlation between Cd and Zn (r^2=0.94) reinforce the contamination by these metals and their common source: the industrial input from Ingá Cia. waste pile leaching (Figure 2.8.1).

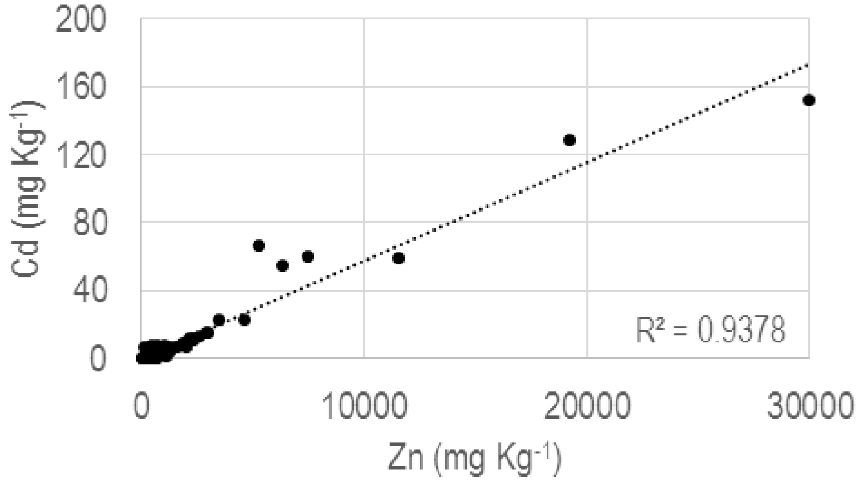

Figure 2.8.1. Scatter plots of cadmium versus zinc.

2.9. Sediments quality guidelines quotients (SQGQs)

With the aim of identify metal enrichment in superficial sediments from Sepetiba bay, the ratio between CONAMA 454/2012 level 2 thresholds and each one of the five trace metals were calculated from the compiled data, the value obtained was called $SQGQ_{me}$.

The spatial distribution of Cd, Cu, Ni, Pb and Zn are represented in figure 2.9.1. and 2.9.2. $SQGQ_{Pb}$ showed lower values, indicating no risk in the marine influenced area. Potential risk was observed, mostly, in the inner part of the bay and values were between 0.25 and 0.5 in the middle area. For $SQGQ_{Ni}$, the majority of the bay was classified under risk and the area near to Enseada das Garças were under moderate environment risk, a hotspot was observed adjacent to Marambaia bay. $SQGQ_{Cu}$ showed some hot spots, one in the main entrance of the bay and nearby to Guaratiba region, with values between 0.5 and 1 and two areas classified as high risk of impact in the Marambaia Sandbar coastline.

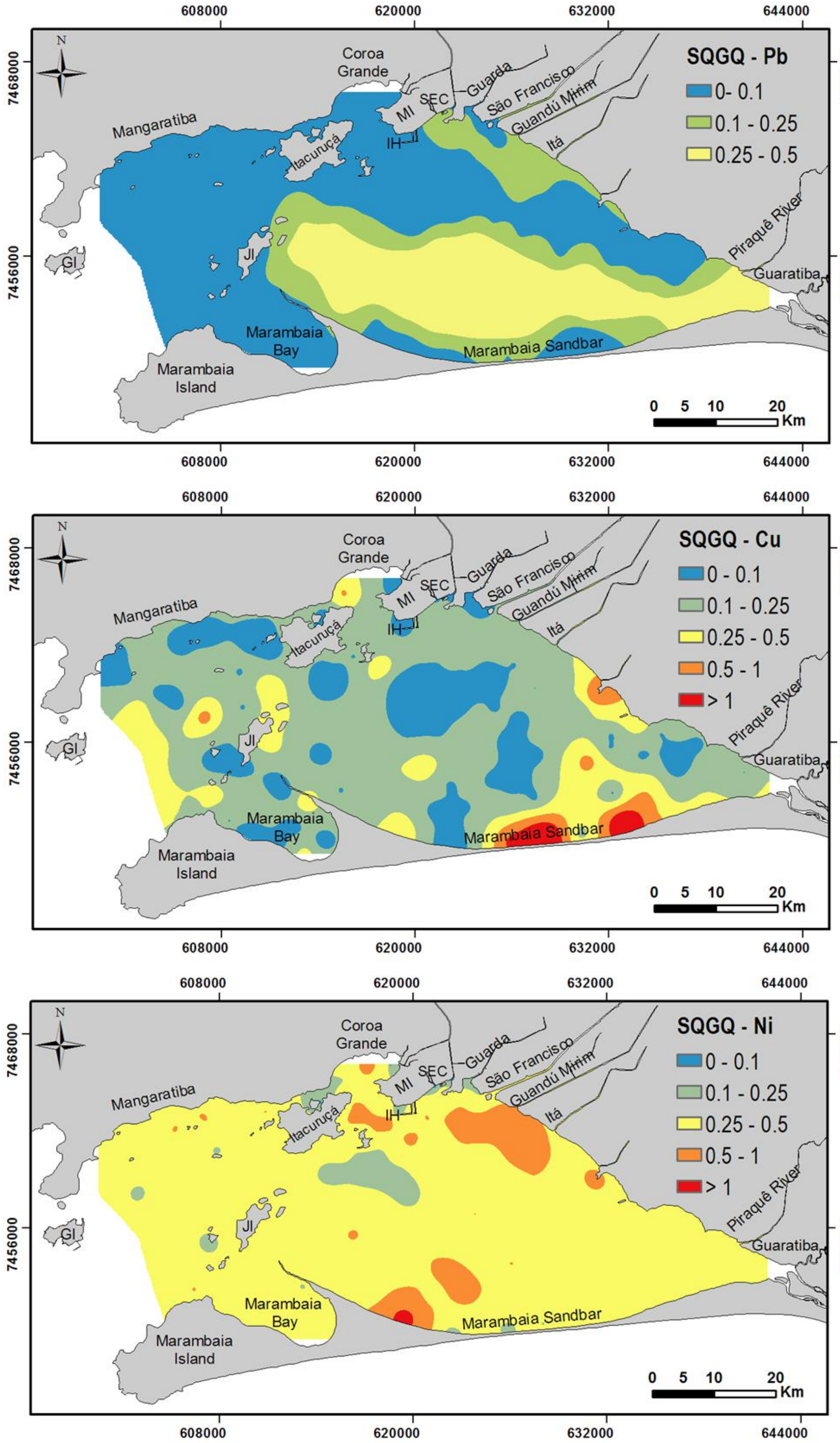

Figure 2.9.1. Ratio between metal concentration and threshold level 2 for Cu, Pb and Ni. The classification is based on sediment quality guideline quotients. Blue area does not show risk, green colored area is about potential risk, yellow represents area under risk, orange is area of moderate risk and red area is of high risk of impact.

Copper showed high $SQGQ_{Cu}$ along Marambaia sanbank coastilne, as discussed previously, probably due to residues from maintenance procedures, with scraping antifouling painting from the hulls, from disposal sites with contaminated sediments and from industrial wastes from point and non-point sources. According to NORMAN 23/DCP (Marinha do Brasil, 2007), the dumping of waste generated by anti-fouling systems at sea is prohibited. These residues (barnacles and paint residues) has to be collected at ports and shipyards. The collection, transportation, storage and final disposal of waste has to be done by specialized company liability provider, licensed by the competent environmental agency (Marinha do Brasil, 2007). However, fishermen report that ships anchoring inside the bay are performing the maintenance and disposing hull's waste and ballast water inside Sepetiba bay, away from shipyards (ALERJ, 2009). The Marambaia sandbank also is a Brazilian Army and Navy training area, with shooting practice, maintenance and use of arms and related material of all types.

Cd and Zn have similar patterns (Figure 2.7.1), due their geochemical behavior and both share the main anthropogenic source. The $SQGQ_{Cd}$ was lower than $SQGQ_{Zn}$ in the inner part of the bay. Zn spreading is higher than Cd as can be seen in figure 2.9.2, reaching Marambaia Sandbank, Mangaratiba and vicinities.

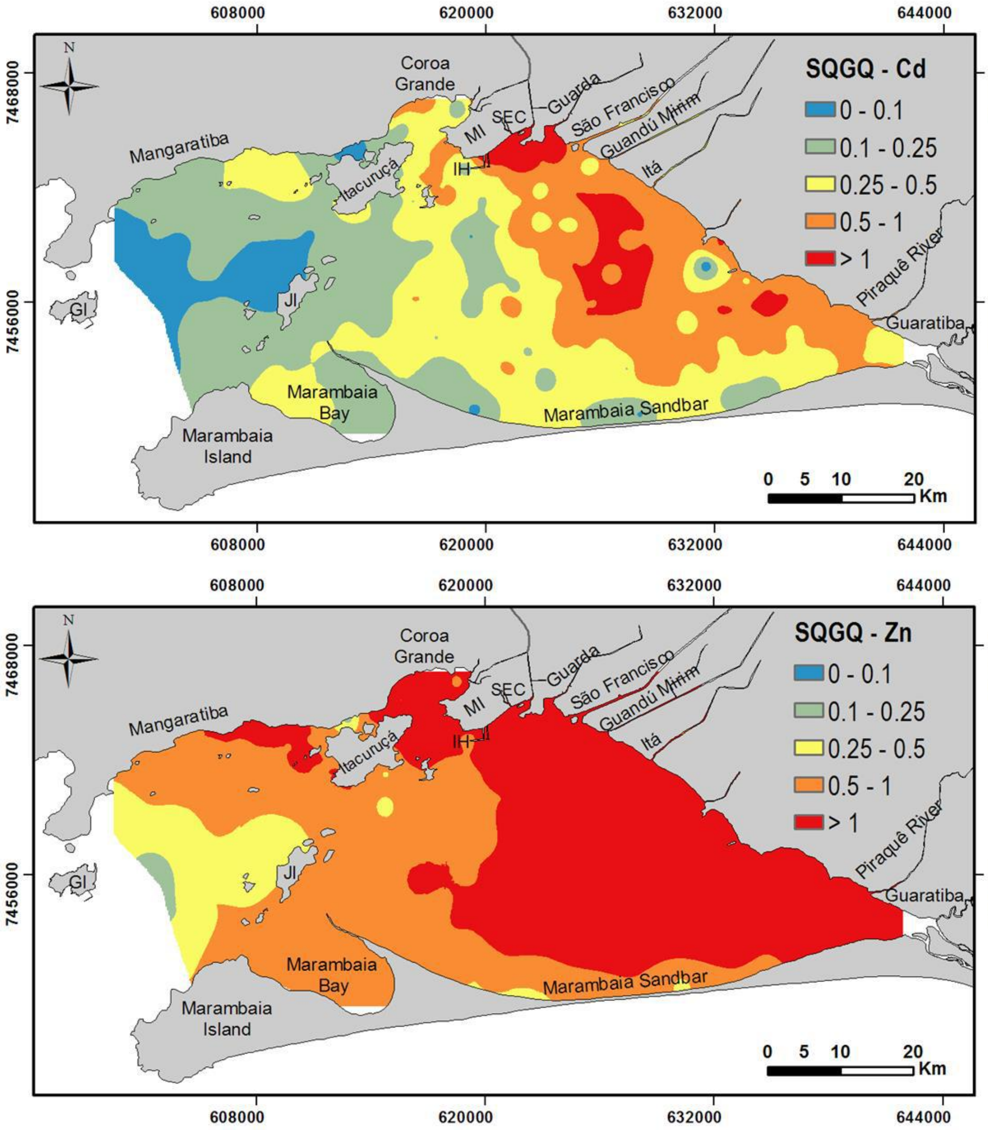

Figure 2.9.2 Ratio between metal concentration and threshold level 2 for Cd and Zn. The classification is based on sediment quality guideline quotients. Blue area does not show risk, green area is about potential risk, yellow represents areas under risk, orange is representing areas of moderate risk and red area is of high risk of impact.

The main goal of thresholds existence is providing protection to biota living in or near sediments from the potential effects associated with sediment-bound contaminants, classify sediments under risk to raise awareness of contaminated areas or pollutants of concern and evaluate spatial patterns of sediment contamination (McReady et al., 2006; Long and MacDonald, 1998). Sediment quality guidelines quotients distribution for the sum of all five trace metals studied are represented in figure 2.9.3.

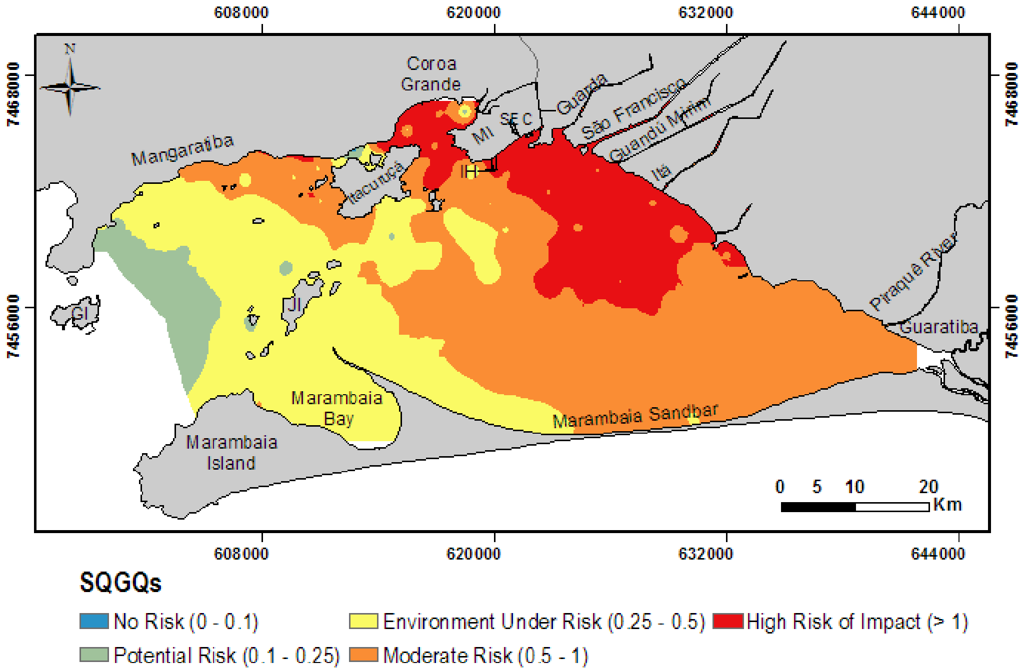

Figure 2.9.3. SQGQs spatial distribution calculated from data compile of metals concentrations in surficial sediments of Sepetiba bay.

The values of total SQGQs follow Cd and Zn pattern as can be seen in figure 2.7.1 and 2.8.1, besides that individuals $SQGQ_{me}$ for both trace metals (Figure 2.9.2) are compatible with the patterns observed in SQGQs distribution. SQGQs values showed a gradient from Saco do Engenho Creek towards the mouth of the bay (Figure 2.9.3). The sediments found near to Madeira Island area were classified as being of high risk of environmental impact, due to industrial wastes from Ingá Cia and fluvial input from main waterways at northeast side of the bay.

Table 2.9.1 presents some studies for comparison between another estuaries and bays from Brazil and worldwide. Sepetiba bay highlight the values of Cd and Zn among others systems. While Ni and Pb are not elements of immediate concern. However, Cu concentrations in some spots raise awareness, due to a potential source that has not been considered in previous studies.

Table 2.9.1 Concentrations of metals (mg kg^{-1}) in sediments from different coastal zones in Brazil and of the world (iron and aluminum concentrations are expressed in %).

	Al	**Fe**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Reference**
Patos Lagoon (RS)	1.3 - 14.6	0.7 - 7.4	0.13 - 2.4	3.3 - 97.7	-	4.2 - 45.02	12.9 - 153.6	Niencheski et al. (2002)
Guaratuba bay (PR)	-	-	0.19 - 2.77	3.23 - 22.8	-	4.3 - 7.09	3.01 - 32.66	Rodrigues et al. (2013)
Paranaguá bay (PR)	-	-	0.06 - 0.87	0.7 -23	0.1 - 38.35	1.84 - 12.95	0.4 - 310.8	Sá et al. (2004)
Santos bay (SP)	2.66	2.4	-	16.18	14.17	12.34	787.2	Buruaem et al. (2012)
Sepetiba bay (RJ)	1.3 - 9.3	0.2 - 7.5	0.4 – 152	5 - 1032	3.2 – 76.8	4.1 – 95.8	71 – 29,990	This Study*
Guanabara bay (RJ)	1.8 - 2.1	1.2 - 2.7	0.98 - 1.15	-	5.45 - 11.71	38.1 - 49.4	204 - 234	Abreu et al. (2016)
Espírito Santo bay (ES)	-	0.22 - 7.1	0.39 - 3.3	2.02 - 94.7	ND	12.4 - 132.3	3.5 - 9.7	Kumar et al. (2015)
Jundiaí-Potengi Estuary (RN)	-	0.005 - 0.65	<0.001 - 0.47	0.29 - 17.9	0.86 - 4.14	0.25 - 6.51	1.19 - 30.17	Souza et al. (2016)
Pecém (CE)	2.9	2.09	0.94	13.12	18.8	-	463.9	Buruaem et al. (2012)
Brazil North Coast	-	1.3 - 5.06	-	11 e 75	30 – 79	-	40 - 153	Lima et al. (2006)
Marajó bay (AM)	0.7 - 1.6	2.5 - 3.0	2.8 - 3.9	10- 13.5	15.9- 20.9	-	-	Lima et al. (2017)
Liaodong bay (China)	-	-	0.025 - 1.03	4.6 - 36.1	-	13.7 - 33.9	17.4 - 159	Wang et al. (2017)
Mediterranean Sea (Italy)	4.1 - 4.5	2.9 - 3.2	-	19 - 30	42 – 64	13 - 18	77 - 108	Lopes-Rocha et al. (2017)
Sydney Estuary (Australia)	-	-	ND - 52	ND- 1060	ND – 118	ND - 1932	ND - 11,300	Birch et al. (2017)
Dakar coast (Senegal)	16.8 -47.1	1.04 - 4.56	0.18 - 0.59	12.9 - 52.6	2.24 - 7.8	2.83 - 43.1	7.14 - 28.8	Diop et al. (2015)
Saint Louis Estuary (Senegal)	32.5 - 77.9	2.54 - 17.8	0.34 - 1.63	21.8 - 121	2.62 - 27.6	26 - 1308	8.98 - 88.5	Diop et al. (2015)
Cheasapeak bay (USA)	1.15 - 3.54	0.06 - 0.2	2.7 - 47.2	4.6 - 86.6	-	6.3 - 32.1	12.4 - 90.2	Coxon et al. (2016)

*Data compilation from: Barcellos (1995), Barcellos et al. (1997), FEEMA/GTZ (1998), Pellegatti et al. (2001), Rocha (2011), Rocha et al. (2012), Morales (2012), Rodrigues (2013) and Rodrigues et al. (2017).

2.10. Conclusions

Cadmium and zinc are still of critical concern for sediments management in Sepetiba bay, due to their high concentrations and potential toxicity to aquatic living organisms. However, copper showed a special concern, with spread hot spots. The arbitrary activities, as the indiscriminate disposal of hull’s painting stripping, and wastes of military equipment’s could be rising trace metals concentrations in conservation areas, as Marambaia sandbank and surroundings.

Biological effects cannot be precisely predicted only from concentration data. However, the majority of Cd, Cu and Pb concentrations ranges between level 1 and level 2, and for Zn the data are mostly above level 2 threshold. The adverse biological effects response to metal exposure at a particular location depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (for instance, pH, redox potential, particle size, organic matter and metal oxide and sulfide contents) and biological (e.g., feeding behavior and uptake rates) factors that affect metals bioavailability (CCME, 1999; Rodrigues et al., 2017).

On the other hand, the high amounts of trace metals found into the bay are concerning. Due to a variety of sources that contribute to trace metals for Sepetiba bay, a systematic and recurrently monitoring program has to be implemented. Mostly in sensitive regions as Marambaia Sandbank. Zn and Cd high concentrations from Ingá wastes can be masking other potential sources from the Santa Cruz industrial area in the Sepetiba bay watershed.

Chapter 3

Historical Trends of trace metals in Sepetiba Bay Sediments: Fluxes, Inventories and Sedimentation Rates.

3.1. *Introduction*

Human interventions in both quantity and quality of sediments cause impacts in aquatic ecosystems (Koiter et al. 2013). Regarding sediment quality, the human disturbances drive to changes in sediment physical and biogeochemical structure, besides they can be considering as a vector of substances like nutrients, pesticides, hydrocarbons, metals and pathogens (virus, bacteria, fungi) (Gellis and Wallis, 2011; Koiter, 2011).

The geochemical composition in sedimentary basin is one of the most important records of biogeochemical processes occurring across the watershed system (López et al., 2006). Bottom sediments are recognized as final storage of contaminants in aquatic ecosystems, therefore coastal environments behave as a natural barrier to the suspended material loaded by rivers.

Composition and structure of sediment`s vertical profiles offer information about processes and temporal variability, so its chemical characteristic, mineralogy and grain size structure reflects the system dynamics over a wider period than water column properties do (López et al., 2006). There are many techniques to historical reconstruction of sediment profiles. One of them is the use of natural and anthropogenic radioisotopes to estimate sediment layers age.

A method frequently used to estimate the sedimentation rate on a time scale of 100–150 years is ^{210}Pb estimation, a naturally occurring radioisotope with a half-life of 22.3 years (Lu and Matsumoto, 2005). ^{210}Pb has been widely used to sedimentation rates estimates for coastal sediments and also has been used to interpret recent geochemical changes that have resulted from the last one hundred years of industrial growth and which are preserved in areas of sediment accumulation.

This study deals with the distribution of major elements (Al, Fe and Mn) and trace metals (Cd, Cu, Ni, Pb and Zn) in six sediment cores from Sepetiba bay, which has a long history of trace metal pollution. Sepetiba bay is a coastal environment in Brazil, recognized by its economic and ecological importance, but also for its industrial waste's legacy and the environmental problems associated (Rodrigues et al., 2017; Gomes et al., 2009; Lacerda et al., 2004; Lacerda and Molisani, 2003; Barcellos et al., 1991; Lacerda et al., 1987). Nowadays high amounts of trace metals, mostly Cd and Zn, can be found in sediments in the inner part of the bay (Rodrigues et al., 2017; Monte et al., 2015, Ribeiro et al, 2013; Nascimento et al., 2016) (see chapter 2).

This chapter aims to outline through spatial and temporal scales the trace metals concentrations (Cd, Cu, Ni, Pb and Zn) in different areas of Sepetiba bay. The results obtained will provide information about environmental changes and processes that occurs in this region over recent years.

3.2. Study area

Sepetiba bay is located in the southeast part of Brazil at Rio de Janeiro State (Figure 3.2.1). The bay is dominated by tidal currents, has shallow waters, with calm and protected areas. In the northeast part of the bay remains the most important sources of trace metals to the system: 1) fluvial water from São Francisco, Guarda, Guandu-Mirim and Itá Channels, which carry out to the bay continental material and effluents from industrial and domestic origin; 2) Santa Cruz industrial district with facilities from metallurgical and chemical industries, a Municipal Water Treatment Plant and Santa Cruz Thermoelectric Power Plant; 3) Port activities, with Itaguaí Port, Porto Sudeste, Brazilian Navy submarines shipyard, Valles S/A and Thyssen Krupp mooring benches; and 4) Ingá Cia. environmental liability at Madeira Island.

Madeira Island (at the northeast: 1, figure 3.9.1) hosted the industrial wastes from the Ingá Metallurgical Cia., which produced metallic alloy of Zn from Calamine ore (Barcellos et al., 1997), the company closed in 1998. During the industry operations (started at 1960s), there were overflows of the dam that contained the industrial wastes enriched with trace metals through Saco do Engenho Creek (SEC). The pollution loadings did not stop after Inga CIA activities finished, but it was a continuum until remediation measures were taken in 2010 (Lindolfo, 2015). However, soil leaching from the area can still happen. This point source resulted in extremely elevated inputs of Cd and Zn, which are mainly dispersed in the northern and northeastern regions of this system and it can be observed in dated sediment cores (Marques Jr., 2006; Gomes et al., 2009).

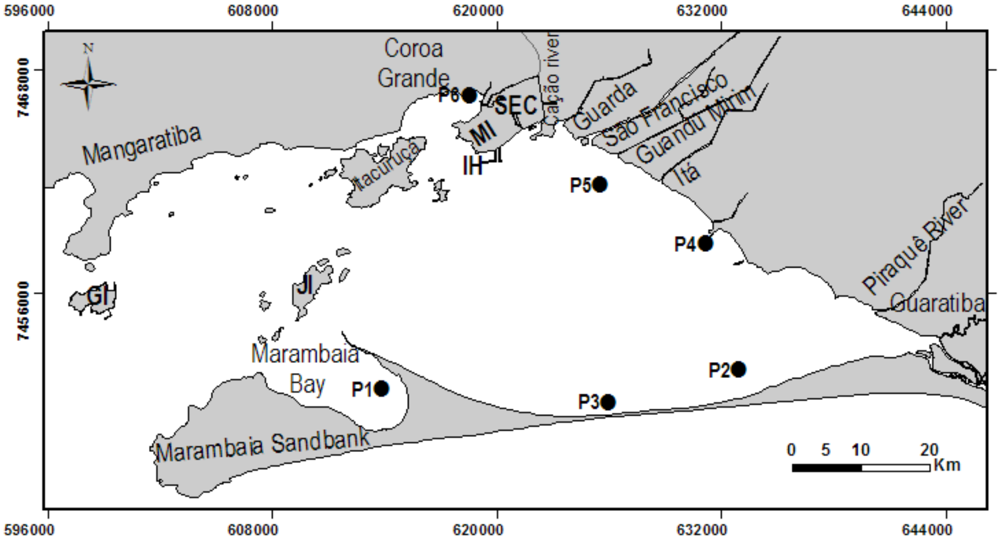

Figure 3.2.1. Sampling sites distribution in Sepetiba bay. P01 (Marambaia bay), P02 (Guaratiba), P03 (Restinga), P04 (Enseada das Garças), P05 (SFC Delta), P06 (Coroa Grande). Abreviations: MI - Madeira Island; SEC - Saco do Engenho Creek; IH - Itaguaí Harbor benches; GI - Guaíba Island; JI - Jaguanum Island.

Although, Patchineelam et al. (2010) observations indicate that trace metals contamination has been spread to furthest areas. The authors found high levels of Cd and Zn (~ 0.3 and 1700 mg Kg^{-1}, respectively) in the upper layers of sediment cores at the Marambaia bay. In the last years, Sepetiba bay has been experiencing large expansion of harboring activities, therefore, water and sediment quality can be decreasing due to dredging activities and shipping traffic.

Environments surrounding Sepetiba bay, as the marine reserves of Ilha Grande and Marambaia sandbank may be exposed to the contaminants dumped and indentified inside the bay and its watershed, through contaminated sediments resuspension events and consequently they are transported by the currents to adjacent areas.

3.3. Methods

Six sediment cores from Sepetiba bay were collected in august 2015 (Figure 3.2.1). The cores were split and sub-sampled in 3-cm intervals for P01 and P05 (designed to ^{210}Pb dating) and 5-cm intervals for P02, P03, P04 and P06. Sediments were taken with a gravity piston core in PVC tubes.

Grain size was determined with the sample disperser Hydro 2000MU coupled to particle measurer Mastersizer 2000. The dispersed samples were pumped to the cell compartment inside the equipment, where the particles were measured by laser diffraction. Ultrasonic energy was used to sample's disaggregation. The results were analyzed on the software Sysgran (Camargo, 2006) based on the equations proposed by Folk and Ward (1957).

The samples for estimations of ^{210}Pb activity were sieved and only the <63 µm fraction was used. The activity of ^{210}Pb was measured indirectly via its granddaughter ^{210}Po with a half-life of 138.4 days. The analyses were performed with 0.5g of dried and grounded sediment spiked with 1ml of ^{209}Po and digested with 10ml concentrated HCl (P.A., 12M) in a hot bath (85°C) for 6h (leaching step). After, 45ml of MiliQ water was added to the samples and subsequently 5ml of ascorbic acid (20%), then silver plates are added and the mixture is heated at 75°C for 16h, where the Po-isotopes are deposited. The activity of ^{210}Pb was measured via α-spectrometry with Canberra Passivized Implanted Planar Silicon (PIPS) detector, taking a counting time of 72h.

For some chosen depth intervals, the ^{226}Ra activity was analyzed using gamma spectrometry. This method was done to confirm if ^{210}Pb profiles reached the supported value (van den Bergh et al., 2003; Boer et al., 2006). One to five grams of freeze-dried sediment were analyzed in a GCW2522 well detector at the 295-, 351- and 609-keV emission peaks, using an external standard for calibration. The sediment accumulation rate (SAR) was obtained according to the model proposed by Appleby and Oldfield (1992), the Constant Initial Concentration (CIC) method. The excess ^{210}Pb ($^{210}Pb_{ex}$) alpha activity was estimate by subtracting total ^{210}Pb activity from the^{210}Pb activity predicted in the bottom layers (^{210}Pb supported). Gamma $^{210}Pb_{ex}$ was obtained by subtracting ^{226}Ra from the total ^{210}Pb activity.

The sediment accumulation rate (SAR) is given by the equation SAR= -λ/b, where b is the slope of the logarithm value of the excess ^{210}Pb activity versus sediment depth (Table 3.4.1) and λ is the constant decay of ^{210}Pb (0.0311 yr^{-1}). Mass accumulation rate (MAR) is given by the equation MAR=SAR * ρ, where bulk sediment density is ρ. Samples containing reworked or coarse-grained sediment will have a low initial activity and were eliminated from the accumulation rate calculation (Nittrouer et al., 1979). Layers consisting entirely of coarse grained sediment were not analyzed.

Organic matter, major and trace elements analyses were carried out on sediment samples from all six cores, without sieving. Homogenized bulk sediments powdered on an agate mortar were used for the following analyses. Organic matter content was determined through ignition during 2 hours in 450°C.

Total metals content was obtained with 500 mg of the powdered sediments. The samples were submitted to the six steps of sequential extractions (see chapter 4) for Marambaia Bay (P01) and SFC Delta (P05) cores, the sum of six steps is present here as total concentration. For Guaratiba (P02), Marambaia Sandbar (P03), Enseada das Garças (P04) and Coroa Grande (P06), 500 mg sediments were digested according to 3050b EPA method (USEPA, 1996).

The extracts were then measured in an inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine Al, Fe and Mn concentrations (SPECTRO Analytical Instruments GmbH – Germany) and the mass spectrometry (ICP-MS) was used to estimate trace metals content (Cd, Cu, Zn, Pb and Ni).

Metal inventory (M) was estimated by the formula $M_{ex} = \sum_i (C_i - C_{back}) * \rho_i * X_i$. Where C_i is the Me concentration, ρ_i is the density at depth i and X_i is the depth increment. The Metal Flux (M_{flux}) was calculated according to the formula $M_{flux_i} = (C_i - C_{back}) * MAR_i$. Where C_i is the Me concentration in the sample, C_{back} is the Me concentration on bottom layers of the core and MAR_i is mass accumulation rate at depth i.

Enrichment Factor (EF) is an index used to assess the anthropogenic contaminant deposition on sediments and soils (Barbieri, 2016). The potential contamination is calculated by normalization of one metal concentration in the top layer of soil or sediment respect to the concentration of a reference metal, such as Fe or Al, the later acts as a proxy for clay content (Abrahin and Parker, 2007; Barbieri, 2016). The reference metal content in samples originates almost exclusively from the Earth's Crust (Uduma and Jimoh, 2014).

Element concentrations measured in a deeper sediment layer can be considered a "local background" for the upper layers (Barbieri, 2016). Sediment layers from the bottom of the cores (considered the oldest ones) were used as local background reference, as comparison Gomes et al (2009) values were also considered.

The EFs were determined according equation 1.

$$EF = \frac{(C_i/Ci_{ref})_{sample}}{(C_i/Ci_{ref})_{background}} \qquad \text{Eq. 1.}$$

Where C_i is element of interest and C_{ref} is the concentration of chosen normalizer, aluminium. Enrichment factors were estimated for Cd, Cu, Ni, Pb and Zn. The EFs are classified in 5 degrees of contamination (Lopes-Rocha et al., 2017):

1. $EF<2$ non-existent or very low enrichment;
2. $2 \leq EF< 5$ moderate enrichment;
3. $5 \leq EF<20$ significantly enrichment;
4. $20 \leq EF<40$ high enrichment;
5. $EF >40$ extremely high enrichment.

Adopted QA/QC procedures included the use of replicates and repeatability tests as well as the use of blanks and standards analyses were taken. For metals, blanks and standard certified sediment (BSCC – 1 marine sediments) were treated like samples during the extractions. The respective detection limits are available in appendix section (Table 0.1).

3.4. Results and Discussion

3.4.1. Grain Size and Organic Matter

It is established that grain size distribution has a marked effect on the concentration of pollutants in sediments, due to the larger surface area to mass ratio of fine grained sediments (Parizanganeh, 2008). Significant variations in particle size distribution with depth in the sediments could therefore lead to changes in the concentration profile that do not represent real changes in trace metal levels.

Grain size and organic matter means, standard deviation, maximum and minimum are presented in Table 0.2, appendix section. Marambaia bay (P01) core was classified as sandy silt sediments, with mean organic matter of 4% (Figure 3.4.1), without a clear tendency along the core. Guaratiba site (P02) showed sandy composition, with finer content below 40 cm and OM content followed fine sediments pattern, as can be seen in figure 3.4.1, the mean OM concentration was 2.2 %. In P03 (Marambaia Sandbar) there is a dominance of silt above 45 cm, before it sand was the predominant grain size. The mean concentration of OM in P03 was 6.5% with higher values above 45 cm (Figure

3.4.1). Enseada das Garças (P04) was dominate with fine sediments dominated, with absence of sand above 50 cm depth, mean of organic matter content was 14.9%, with highest value of 26.3%. Near to the channels mouth (SFC Delta-P05), the silt content was the main grain size fraction in the whole core, the OM content was higher when compared to the cores next to Marambaia sandbank (P01, P02 and P03), showing a mean of 14.1% and highest value of 22.1%. Coroa Grande (P06) profile was dominated by silt fraction from the superficial layer to 85 cm, below this depth sand has similar concentration of silt (~40%). Mean OM content was 8%, with highest value of 14.1% (Figure 3.4.1).

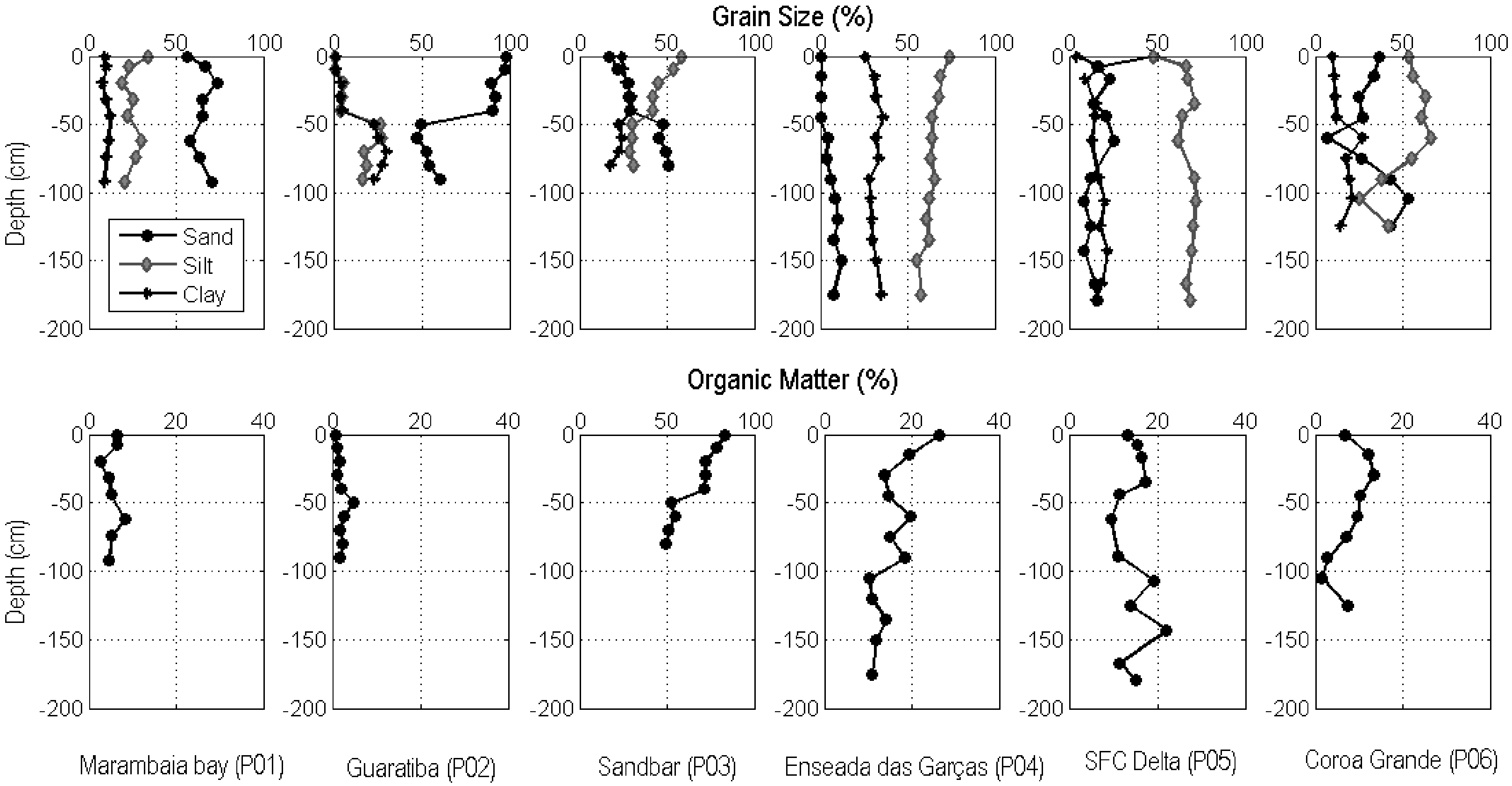

Figure 3.4.1. Organic matter content (%) is represented in black dots (panel above). Sand, silt and clay percentages are representing in the sequence of figures below, the grey dot represents silt, the black continuous line with squares is sand and dark grey asterisks is representing clay content.

OM content varied considerably across all six cores, with the Sandbar (P03) profile recording the highest values, while that from the Guaratiba (P02) had the least. Organic matter concentrations are often inversely related to grain size, therefore, the differences in OM concentrations are a reflection of textural differences. The relationship between OM and grain size is important because, a high silt content together with high OM may result in, a lower permeation of oxygen, an increased microbial oxygen uptake/demand and a subsequent buildup of products such as sulfides and consequently metals retention in sedimentary compartment (Me sulfides formation).

The alteration in the sediment profile of P02 and P03 can be associated to hydrodynamic patterns in the region. The Guaratiba region (P02) in near to a small connection with the ocean, as can be seen in figure 3.2.1, the differences of pressure during tidal cycles (barotropic gradient) between the water mass inside the bay and the open sea can enhance the flux velocities towards the channel (Cortez, 2012; Guerra, 1999). Cortez (2014) found average intensity of the currents inside Guaratiba channel of 0.7 m s^{-1}, with peaks during each high tide of 1.18 m s^{-1} and 1.4 m s^{-1}, and inside Sepetiba bay an average of 0.15 $m \cdot s^{-1}$, with peaks of 0.27 $m \cdot s^{-1}$ and 0.32 $m \cdot s^{-1}$ at the beginning of the high tide. According to Cortez (2014), the channel has been silting, consequently the carrying competence and capacity of sediment transport of the flux has change (Gilbert, 1914). If a stream narrows, the velocity increases.

Stream load is directly proportional to stream velocity and stream gradient and it is related to the amount of material transported. The greater the velocity, the greater the sum of the mass that can be transported by a stream (stream load). Components of stream load contributing to stream mass include the suspended load, dissolved load, and bed load. Wide and slow-moving streams are highly depositional while high velocity streams can move large particles (high stream competence) (Gilbert, 1914).

3.4.2. ^{210}Pb geochronology, Sedimentation Accumulation Rate (SAR) and Mass Accumulation Rate (MAR).

The ^{210}Pb within the sediment consists of ^{226}Ra supported, ^{210}Pb and atmospherically derived excess 210Pb. ^{210}Pb excess profiles from Marambaia bay (P01) and São Francisco Channel Delta (P01) are shown in figure 3.4.2.

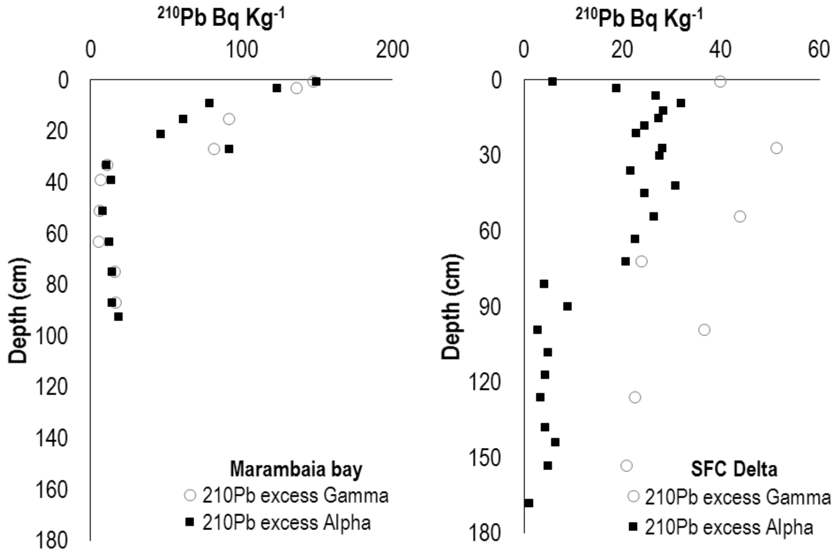

Figure 3.4.2. Excess of ^{210}Pb in sediment cores from Marambaia bay and SFC Delta. Grey line indicates results from Gamma emission method and black line indicates results from Alpha counting method.

SFC Delta (P05) total ^{210}Pb activity keeps decreasing all the way down to the base of the core, which indicates excess activity at 180 cm and that the supported (background) ^{210}Pb activity has not been reached. By fitting an exponential curve, to the measured data points for alpha counting results, it is possible estimate the supported ^{210}Pb activity of 30 Bq Kg^{-1}, which corresponds to ^{226}Ra concentrations measured in gamma counting between 29 and 32 Bq Kg^{-1} (Appendix, Table S0.3). After applying CIC model for each sediment package (upper: 2 - 74 cm and bottom: 74 – 182 cm, see Table 3.4.1), the average sedimentation rate is 4.3 cm y^{-1}, in the upper layers and 3 cm y^{-1} in the older package of sediments, which is quite high but not unrealistic for a fluvial mouth setting. Mass accumulation rates were also high in the recent layer (Figure 3.4.3)

As for Marambaia bay (P01), a rapid decrease in ^{210}Pb$_{excess}$ is observed and it is no longer present at 30 cm depth, leaving only supported ^{210}Pb activity at greater depth down core. The sedimentation rate at Marambaia bay is an order of magnitude lower than the sedimentation rate in SFC Delta (P05), mostly due to its location farthest from fluvial sources (3.4.4).

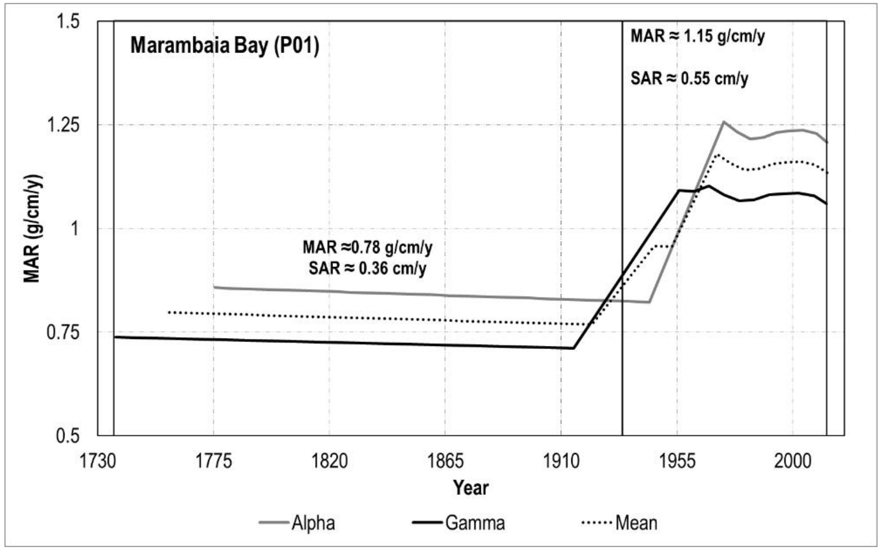

Figure 3.4.3. Mass Accumulation Rates (MAR) and Sediment Accumulation Rates (SAR) through time estimated from CIC and CRS models from Marambaia bay (P01).

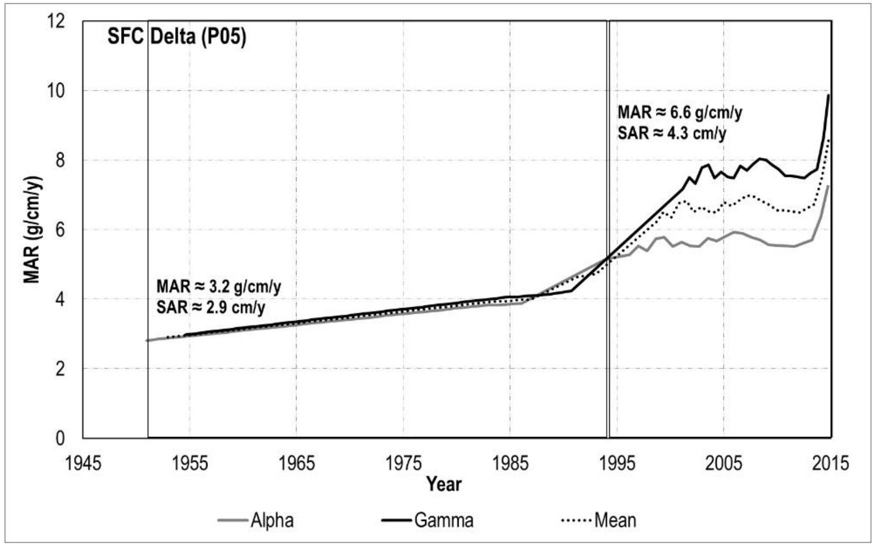

Figure 3.4.4. Mass Accumulation Rates (MAR) and Sediment Accumulation Rates (SAR) through time estimated from CIC and CRS models from São Francisco Channel Delta (SFC Delta - P05).

Table 3.4.1 shows the linear coefficients for both methods employed. Metal fluxes and mean values of Mass Accumulation Rates (MAR) and Sediment Accumulation Rates (SAR) were used from the mean of alpha and gamma results. The use of two different methods for ^{210}Pb estimation has the intention to confirm through gamma counting if the results from alpha reached the supported ^{210}Pb value (Boers et al., 2006; van den Bergh et al., 2003), which did not occur with P05 results. More information about the means, maximum, minimum and standard deviation of density (g cm^3), mass accumulation rates, ^{210}Pb, ^{226}Ra and SAR are available at appendix section (Table 0.3).

Table 3.4.1. Linear coefficients (b) at each sediment package (upper and bottom part) for alpha and gamma results.

		Alpha		Gamma	
	Depth (cm)	*b*	*r²*	*b*	*r²*
Marambaia bay (P01)	02 - 23cm	-0.053	0.98	-0.064	0.94
	23-94	-0.08	0.6	-0.093	0.6
SFC Delta (P05)	02 - 74 cm	-0.008	0.4	-0.0062	0.4
	74-182	-0.0108	0.8	-0.0104	0.8

As can be seen in figure 3.4.4, MAR values increased two times in the past 50 years for SFC Delta area (P05), rising from 3.2g cm y^{-1} to 6.6 g cm y^{-1} and at Marambaia bay from 0.8 to 1.15 g cm y^{-1} in the past 100 years (Figure 3.4.3). Despite the increase of sedimentation rates in both regions, the rate of increase is not the same, which indicates retention of continental sediments in the northeast part of the bay.

Table 3.4.2 shows the MAR and SAR values obtained for P01 and P05, and values from previous works in areas near to Guaratiba (P02), Sandbar (P03), Enseada das Garças (P04) and Coroa Grande (P06). Patchineelam et al. (2010) working on sediment core from Marambaia bay estimate sedimentation rate of 0.5 cm y^{-1}, which is the same value presented here. Gomes et al. (2009) results for a core collected in the mangrove area of São Francisco Channel Mouth, near to P05, were almost 5 times lower than the SAR observed for the mud bank in P05 (SFC Delta), which could be the reflect of a biased estimation for the upper part (0-74cm) of SFC Delta core, due to reworked material, but also Gomes et al. (2009) collected their core closest to the shore than the P05 location.

Table 3.4.2. Mass accumulation rates (MAR) and sediment accumulation rates (SAR) estimated for P01 (Marambaia bay) and P05 (SFC Delta). MAR and SAR values found in the literature for area closely to Sandbank (P03), Guaratiba (P02), Enseada das Garças (P04) and Coroa Grande (P06) are listed below, the SAR values were used for estimation of metal fluxes and inventories trends in these sites.

	Depth (cm)	MAR (g cm^{-2} y^{-1})	SAR (cm y^{-1})	References	Estimated years
Marambaia bay	0-26	1.15	0.55	This study	1960 - Nowadays
	26-94	0.8	0.4		<1960
Marambaia bay	0 - 25	-	0.5	Patchineelam et al. (2010)	-
Sandbank - Guaratiba	0 - 30	-	0.1	Borges et al. (2016)	1970 - 1997
	-	-	0.4		< 1970
Enseada das Garças	0-60	-	1.2	Borges et al. (2016)	1970 - 1997
	60-175	-	0.49		< 1970
SFC Delta	0-5	8.03	4.35	This study	Nowadays
	70 - 05	6.64	4.35		1997 - 2013
	70-125	3.95	3		1970 - 2000
	125-182	3.21	2.9		1950 - 1970
SFC mouth	0 - 40	-	2	Borges et al. (2016)	1970 - 1997
	>40	-	0.6		< 1970
SFC mouth	-	-	0.75	Gomes et al. (2009)	1960 - 2005
	-	-	0.3		<1960
Coroa Grande	0 - 16.5	-	0.8	Marques Jr. et al. (2006)	1980 - 1995
	>16.5	-	1.03		<1980

Marques Jr. et al. (2006) also applied ^{210}Pb to geochronology estimations in Coroa Grande area (P06). According to the authors, the sedimentation rates in this sector was 0.8 cm y^{-1} after 1980, before, their estimations was 1.03 cm y^{-1}.

Borges and Nittrouer (2016) used ^{210}Pb and Radiocarbon to estimate sedimentation rates in sediment cores obtained in 1996-1997. The authors found values of 2 cm y^{-1} (10-40 cm) and 0.6 cm y^{-1} (40-55cm) for SFC Delta area, 1.2 cm y^{-1} (10-50cm) and 0.4 cm y^{-1} (50-70 cm) near to Enseada das Garças (P04) and 0.4 cm y^{-1} near Guaratiba region (near to P02 and P03). According to Borges and Nittrouer (2016), these findings revealed that Sepetiba Bay sediment loads behavior may have changed in the mid-late 1970's.

Alterations due water diversion from Paraíba do Sul to Guandú river, consequently to São Francisco channel (estuarine part of Guandú river) and Sepetiba bay, have increased suspended particulate matter loads to the bay since 1950's (Lacerda et al., 2007; Molisani et al., 2006; Jordão, 2017). According to Lacerda et al. (2007), the watershed diversion led to a 8 times increase of sedimentation since urbanization process started. The changes in the sedimentation rate's patterns since 1960's observed by Borges and Nittrouer (2016), Gomes et al. (2009) and Patchineelam et al. (2010) are consistent with P01 results, which reinforces the diversion system (Paraíba do sul-Guandú), as the main changing factor for sedimentation behavior within Sepetiba bay basin.

Lacerda et al. (2007) highlighted other human interventions, which collaborate to sediment load rise as Itaguaí harbor activities (dredging and expansion) (at 1997), channels constructions and flattening (from 1910's) (Lacerda et al., 2007), Rio-Santos Highway construction (at 1990's) and growing population density.

Itaguaí Harbor construction started in 1976 (Figure 3.4.5), the main navigation channel construction and deepening occurred in the following year. According to Lacerda et al. (2004) and FEEMA/GTZ (1998), dredging and deepening of the main navigation channel were the main factors for sediments resuspension, mobilization and redistribution from the northeast part of the bay to surrounding areas. At this time, the sediments were already enriched with trace metals from the point source Ingá Cia., from diffuse sources of industries located in Rio de Janeiro metropolitan region and from soil leaching from vicinities.

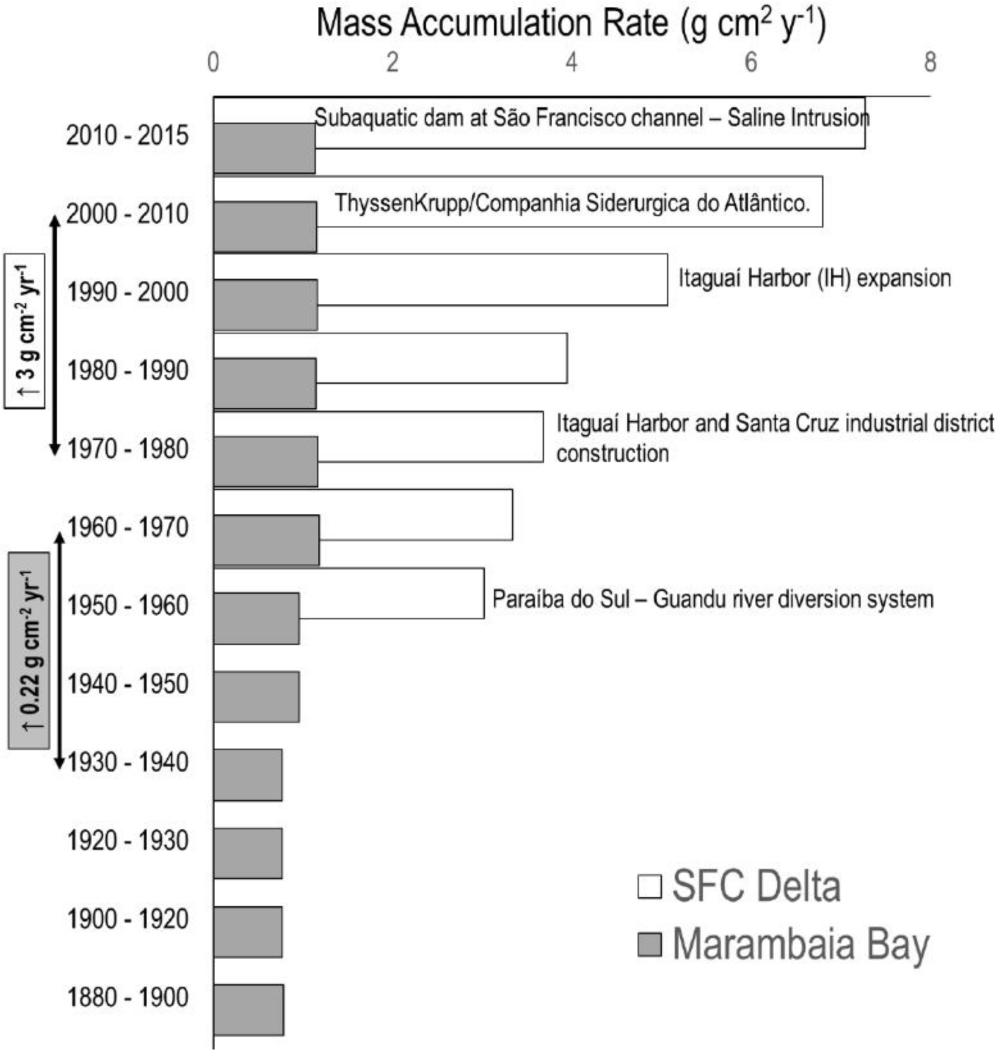

Figure 3.4.5. Chorological events versus Mas Accumulation Rate for Marambaia bay area and SFC Delta region. Events were compiled from Boskalis (2012), Jordão (2017), AEDIN (2015), Costa et al. (2015) and Weyrauch (2013).

P05 core has a biased profile, although its sedimentation rates and MAR estimations can be related to events occurred in the nearby area, as can be seen in figure 3.4.5. In 2000’s, ThyssenKrupp/CSA (Companhia Siderurgica do Atlántico) was installed nearshore alongside of São Francisco (SFC) and Guandú-Mirim channels (Figure 3.4.5), the company build a terminal port to transport its production and a system to catch waters from SFC, which is used to cool down systems through water conservancy. Afterwards, these waters are released in Guandú-Mirim channel. Between 2004 and 2010, Thyssen Krupp/CSA dredged 11 million m^3 of sedimentary material to construct the harbor basin (14.5 meters deep), with an access channel (Boskalis, 2012). To build the steel plant, 200 hectares of mangrove area were suppressed, requiring 3 million m^3 of sand, which were taken from the dredged material and the remaining 8 million m^3 of material containing clay and silt were deposited onshore in submarine confined disposal facilities (CDFs) sites nearshore. The P05 core has a reworked package of almost 1m, which can be related to the alterations performed in this period (2004-2010).

More recently, in 2015 a subaquatic dam was constructed in SFC channel, with the aim of constrain the fluvial flux and decrease the saline intrusion (AEDIN, 2015). By this period, the southeast region of Brazil was suffering a drough and the low pluviosity was influencing the overflow of Paraíba do Sul river, and consequently, the diversion system, including the São Francisco channel (Jordão, 2017). The saline intrusion was affecting the conductivity of water used by industries along the São Francisco channel, then the subaquatic dam was the urgent solution to mitigate this problem. However, small scale fishermen were affected by the alteration of hydrodynamic patterns in the channel, as a consequence, boats were damage (Marinha do Brasil, PROCESSO Nº 31.012/16). As can be seen in figure 3.4.1, the local hydrodynamic could be altered by this construction and the sediment load and settlement in the delta may have been affected, which can be related to the presence of a recent sandy layer in the SFC Delta core (P05). Nowadays, a legal injunction determined that the subaquatic dam has to be dismantled until 2018 (INEA, 2017).

3.4.3. Metal Concentrations

In general, for all elements, the concentrations were high in SFC Delta (P05), followed by Enseada das Garças (P04) and Coroa Grande (P06), mostly due to the affinity of metals to fine grained size composition and the proximity to the northeast part of the bay, region that hosts Ingá. Although, it is possible to observe high metal levels in recent layers of sediment cores from Marambaia bay (P01), Sandbar (P03) and Guaratiba (P02), when compare with older layers of the cores (Figure 3.4.6). The statistical results (means, standard deviation, maximum and minimum) are available in table 0.2 of appendix section.

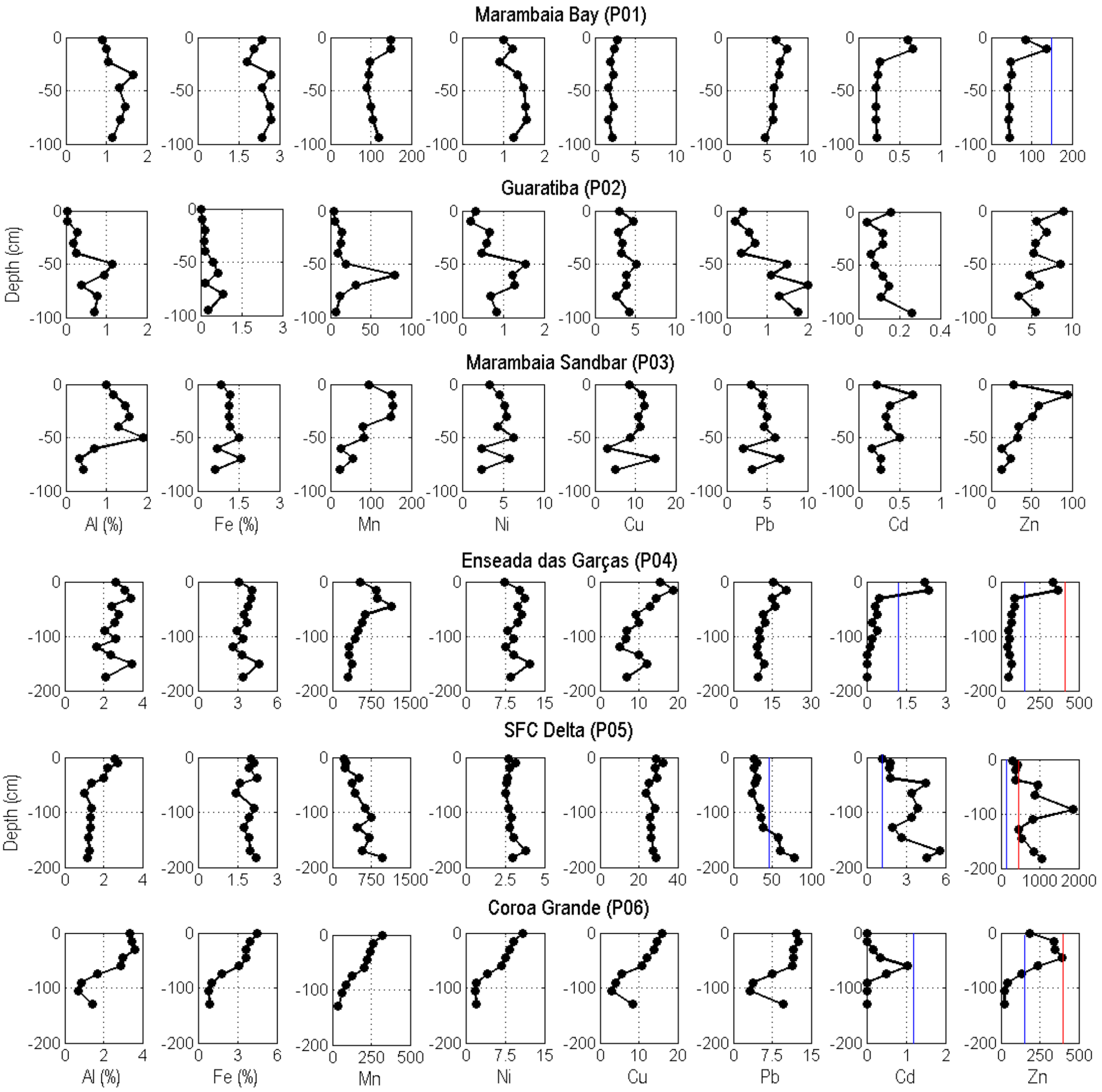

Figure 3.4.6. Metals concentration (Al, Fe, Mn, Ni, Cu, Pb, Cd and Zn) at Marambaia bay, Guaratiba, Marambaia Sandbar, Enseada das Garças, São Francisco Channel (SFC) Delta and Coroa Grande. The blue line indicates level 1 and the red line represents level 2 thresholds from CONAMA 454/2012.

Aluminum and Fe are commonly associated with clay minerals and both metals showed slight variations with depth in Marambaia bay (P01) (0.18-0.33% and 0.18 – 0.27%, respectively) (Figure 3.4.6). In the core from Guaratiba (P02), Al and Fe (0.01-0.5% and 0.02-0.8%) showed moderate variation with depth, following the fine-grained profile of the site, with lower values above 40cm. At Sandbar (P03) (Al: 0.33 – 1.9% and Fe:0.6-1.6%) also followed the fine sediments profile, however an inverse behavior is observed when compare with Guaratiba (P02), the higher Al and Fe values were found in recent layers, above 50cm.

For the inner part of the bay, Al and Fe concentrations were higher at Enseada das Garças (P04) (Al:1.6 – 3.4% and Fe: 2.6 – 4.6%), followed by Coroa Grande (P06)

(Al:0.6-3.6% and Fe:0.7-4.4%) and SFC Delta (P05) (Al: 0.5-1.3% and Fe:1.4-2.2%). The differences between these three sites can be related to diagenetic processes like organic matter degradation, sulfide oxidation and decalcification (Zwolsman et al., 1993). due to oxidation. In SFC Delta core (P05), metals mobilization could be caused by sediment remobilization events during TKCSA mooring benches construction (see section 3.4.2).

Manganese values at Marambaia Sandbank area (P03) were lower (P01 – 91-150mg Kg^{-1}, P02 - 4.7-80mg Kg^{-1} and P03– 23.7-154 mg Kg^{-1}). At the inner part of the bay, Mn concentrations were almost an order of magnitude higher, Enseada das Garças (P04) with values between 298 and 1140 mg Kg^{-1}, SFC Delta (P05): 219-964 mg Kg^{-1} and Coroa Grande (P06) with 38-322 mg Kg^{1}. Fe and Mn are redox-sensitive metals, which in oxygen rich areas they are accumulated as oxides, while in sediment depleted in oxygen the reduction and solubilization of these oxides can release them to pore water (Alvarez-Iglesias et al. 2003; Laing et al. 2009).

With the exception of Ni, all trace elements were higher at SFC Delta core (P05). Nickel presented lower concentrations and correlation with Al (r^2=0.87) (Figure 3.4.7). At Marambaia bay (P01), Ni values were from 0.92 to 1.6 mg Kg^{-1}, at Guaratiba region (P02) between 0.2 and 1.5 mg Kg^{-1} and at Sandbar (P03) from 2.32 to 6.25 mg Kg^{-1}. Ni concentrations were higher in the inner part of the bay, at Enseada das Garças (P04) with values between 7.4 and 12.2 mg Kg^{-1}, SFC Delta (P05): 2.5 and 3.8 mg Kg^{-1} and Coroa Grande (P06) with 1.8 – 10.8 mg Kg^{-1}.

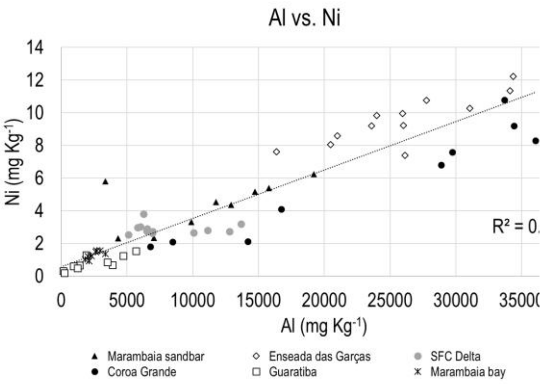

Figure 3.4.7. Nickel versus aluminum scatter plot with all results and the correlation value.

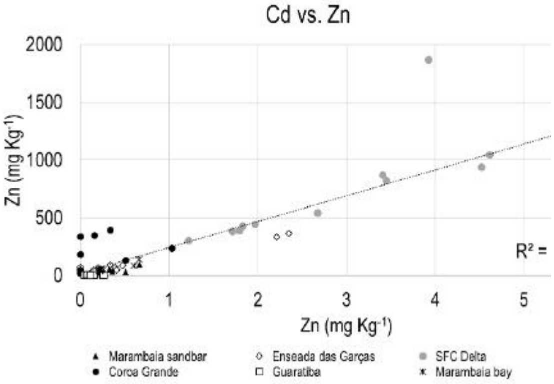

Figure 3.4.8. Zn versus Cd scatter plot with all results and the correlation value.

Copper showed higher concentration in recent layers from Sandbar (P03) (3.1 – 14.8 mg Kg^{-1}), Enseada das Garças (P04) (5.1 – 18.8 mg Kg^{-1}) and Coroa Grande (P06) (2.9 - mg Kg^{-1}). Although, the higher values were found at SFC delta (P05) (23.8 – 32.5 mg Kg^{-1}), with slightly variation along the core. Lower Cu concentrations were found at Marambaia bay (P01) (1.7 – 2.7 mg Kg^{-1}) and Guaratiba (P02) (2.6 – 5.2 mg Kg^{-1}). Copper major sources for Sepetiba bay are industrial wastes, Ingá Cia. industrial wastes and residues of hull’s ship cleaning enriched with copper oxide (see chapter 2).

Lead values at Marambaia bay (P01) were from 4.7 to 7.4 mg Kg^{-1}, at Guaratiba region (P02) between 0.2 and 2 mg Kg^{-1} and at Sandbar (P03) from 2.1 to 6.6 mg Kg^{-1}. At the inner part of the bay, Pb concentrations were higher, Enseada das Garças (P04) with values between 9.2 and 20.4 mg Kg^{-1}, Coroa Grande (P06) with 3.2 – 12.6 mg Kg^{-1} and SFC Delta (P05): 23.47 and 78.4 mg Kg^{-1}. The highest values of lead were found at the bottom of the SFC Delta core (P05), exceeding level 1 from Brazilian Sediment Quality Guideline threshold (47.6 mg Kg^{-1}, blue line at Figure 3.4.6), the region is near to the main fluvial sources and Saco do Engenho creek, a tidal channel directly affected by Ingá Cia. industrial wastes from 1960’s until 2010’s.

Cadmium and zinc are recognized as the main pollutants of Sepetiba bay sediments (Rodrigues et al., 2017; Monte et al., 2016; Ribeiro et al., 2013; Gomes et al., 2009; Lacerda et al., 2004; Barcellos and Lacerda, 1994; Lacerda et al., 1987). Cd concentrations at Marambaia sandbank area were lower: Marambaia bay (P01) were from 0.2 to 0.6 mg Kg^{-1}, Guaratiba region (P02) between 0.04 and 0.2 mg Kg^{-1} and at Sandbar (P03) from 0.1 to 0.7 mg Kg^{-1}. In the inner part of the bay, the values were higher. Coroa Grande (P06) showed values from non-detected to 1 mg Kg^{-1}, Enseada das Garças (P04) with values between non - detected and 2.3 mg Kg^{-1}, SFC Delta (P05) from 1.2 to 5.6 mg Kg^{-1}. The superficial layer from Enseada das Garças (P04) and all samples from SFC Delta core (P05) were above threshold level 1 (1.2 mg Kg^{-1}) of CONAMA 424/2012, limit below which there is lower probability of adverse effects on biota. For Zn, the same pattern was observed, at Marambaia bay (P01) concentration were from 41.7 to 137.6 mg Kg^{-1}, Guaratiba region (P02) between 3.35 and 8.92 mg Kg^{-1} and at Sandbar (P03) from 12.6 to 95 mg Kg^{-1}. Although, in the inner part of the bay, Enseada das Garças (P04) presented values between 43.7 and 364.7 mg Kg^{-1}, Coroa Grande (P06) from 21 to 393 mg Kg^{-1} and SFC Delta (P05) between 301.5 to 1868 mg Kg^{-1}. At Enseada das Garças (P04) the recent layers were above level 1 (150 mg Kg^{-1}). The majority of samples from Coroa Grande (P06) were above level 1, the start of Zn accumulation on sediments from Coroa Grande (P06) corresponds with Ingá Mercantil Cia. beginning of high purity Zn production (Marques Jr et al., 2006). And at SFC (P05) Zn concentration were above level 1 and also level 2, which are the threshold above which there is a high probability of adverse effects on biota.

Marques Jr. et al. (2006) estimated pre-industrial values for Cd below 0.2 mg Kg^{-1}, which indicates an enrichment of Cd in sediments from SFC Delta (P05) more than 25 times higher than the background reference. Gomes et al. (2009) estimated Zn background of 54 mg Kg^{-1} next to fluvial sources and Marques et al. (2006) found pre-industrial zinc values from 69 to 103 mg Kg^{-1} at Coroa Grande. According to these values, zinc concentration at SFC Delta (P05) can be more than 30 times higher than the background values and 4 times higher than level 2 of CONAMA 454/2012.

3.4.4. Principal Component Analysis

Factor 1 and Factor 2 explained 88.9% of the data variability (Figure 3.4.9). Principal Component Analysis (PCA) was elaborated with metals concentrations (Cd, Cu, Ni, Pb, Zn, Al, Fe and Mn), grain size (sand, silt and clay) and organic matter content. The eigen values and correlation can be seen in table 3.4.3.

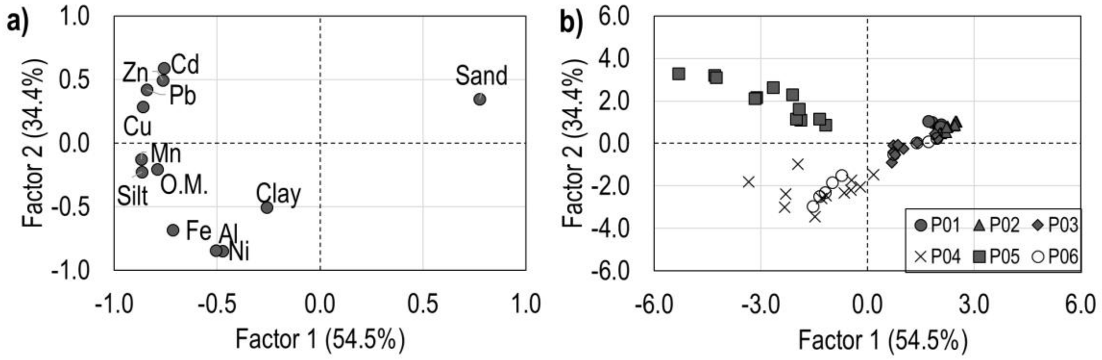

Figure 3.4.9. Principal component analysis for Marambaia bay (P01), Guaratiba(P02), Marambaia sandbar (P03), Enseada das Garças (P04), SFC Delta (P05) and Coroa Grande (P06) sites. The chart a is on mode R and chart b is on mode Q.

Table 3.4.3. Principal Component Analyses results regarding sediment chemical analyses in samples from the Sepetiba Bay cores. Values in bold were statistical significant in Pearson's correlation (r^2>0.5).

	Factor 1	Factor 2	Factor 3
Eigenvalue	4.36	2.75	0.36
% Total	54.46	34.41	4.50
Al	-0.47	**-0.85**	0.17
Fe	**-0.72**	**-0.68**	0.07
Mn	**-0.87**	-0.13	-0.45
Cd	**-0.76**	**0.59**	0.01
Cu	**-0.86**	0.28	0.24
Ni	-0.51	**-0.84**	-0.02
Pb	**-0.84**	**0.42**	-0.14
Zn	**-0.76**	0.49	0.22
OM	**-0.79**	-0.20	-0.12
Sand	0.77	0.35	0.04
Silt	**-0.87**	-0.22	0.06
Clay	-0.26	**-0.50**	-0.25

In the figure 3.4.9 (a), the first factor is mainly represented by trace metals (Cu, Cd, Pb and Zn), Fe, Mn and organic matter, which can indicate the association of trace elements to Fe-Mn oxihydroxides and to organic matter phases. Also, these trace metals can share the same sources of pollution. The majority of Cd and Zn input into Sepetiba bay are from wastes of Ingá Cia. Cu and Pb are also found in the wastes, but to a lesser extent. The remobilization and post deposition of dredged material containing high amounts of trace metals can be spreading sediments enriched with these elements to regions at south of the bay. Disposal areas for dredged material are found next to Marambaia bay, as can be seen in Chapter 2 (Figure 2.4.5).

The second factor is represented by elements of natural occurrence, where Al, Ni, Clay and Fe were negatively correlated. Ni is still present in sediments from Sepetiba bay in natural levels (Figure 3.4.9a), with lower concentrations as observed by Rodrigues et al. (2017). Concurrently, Cd and Zn are positive correlated, which reinforces these two elements as contaminants of the region (Figure 3.4.8).

In the chart b (Figure 3.4.9), it is possible to observe the relation between the sites, where SFC Delta core (P05) stands out (grey squares), mostly due to its distinct diagenetic characteristics, once the highest values of trace metals were found there and has been submitted to successive remobilization events, due to recent human interventions (TKCSA construction). While Coroa Grande (P06) and Enseada das Garças (P04) are grouped in a similar position, due to grain size characteristics, trace metals content and they also can be representative samples of the inner estuary. Lastly, samples from Marambaia sandbank area (P01, P02 and P03) are combined, due to the grain size similarities and lower concentrations of trace metals.

3.4.5. Metal fluxes and Inventories

Cd, Cu, Ni, Pb and Zn fluxes and inventories were estimate from MAR and SAR listed in table 3.4.3. MAR and SAR for samples from Marambaia bay (P01) and SFC Delta (P05) were estimated by means of ^{210}Pb Radioisotope decay calculation (section 3.4.1). For all other four sites (P02, P03, P04 and P06) the SARs were obtained from the literature (Table 3.4.2, see appendix Table 0.4), with the aim of observing trends in the profiles. These elemental fluxes and inventories help to understand the accumulation and/or depletion of the elements over time, which allows to observe effects of human interventions and elements behavior on sediments profiles.

A mean annual flux of trace metals in recent years (last 10 years) was calculated and compared with the bottom flux (Table 3.4.4). In Sepetiba bay, the fluxes of Cd, Cu, Ni, Pb and Zn had a general tendency to increase from the 1950s until 2010 (Figure 3.4.10 and 3.4.11). The difference between the flux tendencies of the sediment cores may result from the sedimentary processes occurring at each site. In Marambaia bay (P01), the increase of fluxes begins after industrialization process and the Ingá Metallurgical Cia. started to operate in the early 1960's. However, the Itaguaí Harbor facilities, navigation channel and mooring benches were constructed in the late 1970's (1976-1977), when high amounts of sediments from in and around Madeira Island were mobilized. At this time, high amounts of trace metal were being released through soils leaching from Madeira Island and throughout Saco do Engenho Creek and, consequently, to Sepetiba bay sediments.

Table 3.4.4. Baseline and actual fluxes for Cd, Cu, Ni, Pb and Zn from six different areas in Sepetiba bay. The values are in g m^{-1} yr^{-1}.

		Cd	Cu	Ni	Pb	Zn
Marambaia bay (P01)	Recent	0.07	0.31	0.12	0.69	9.55
	Bottom	0.02	0.17	0.10	0.38	3.61
Guaratiba (P02)	Recent	0.01	0.16	0.02	0.02	0.48
	Bottom	0.01	0.21	0.04	0.09	0.27
Sandbar (P03)	Recent	0.02	0.61	0.24	0.22	1.96
	Bottom	0.02	0.28	0.13	0.17	0.70
Enseada das Garças (P04)	Recent	0.40	2.84	1.35	2.83	60.87
	Bottom	0.00	0.58	0.71	0.79	4.02
SFC Delta (P05)	Recent	89.20	1505	144.4	1457.4	20049
	Bottom	133.6	837.4	86.21	2272	30273
Coroa Grande (P06)	Recent	0.00	1.92	1.29	1.45	22.13
	Bottom	0.00	0.01	0.00	0.01	0.02

On the other hand, at Sandbar (Istmus area) (P03) the process of trace metals accumulation could be started early at 1920's, mostly for copper (Figure 3.4.11). Copper oxide has been used as antifouling sheeting since 1860's (Laidlaw, 1952). At Guaratiba core (P02) the trace metals fluxes were very low (Figure 3.4.10 and 3.4.11) and the differences between old layers and recent ones are not clearly notice (Table 3.4.4). The differences between these three-nearby sites could be attributed to the location of each sediment core, Marambaia bay (P01) and Sandbank (P03) reflect sedimentation processes during calmer conditions compared to Guaratiba, where the hydrodynamic energy do not allow the sedimentation of finer particles (see section 3.4.1).

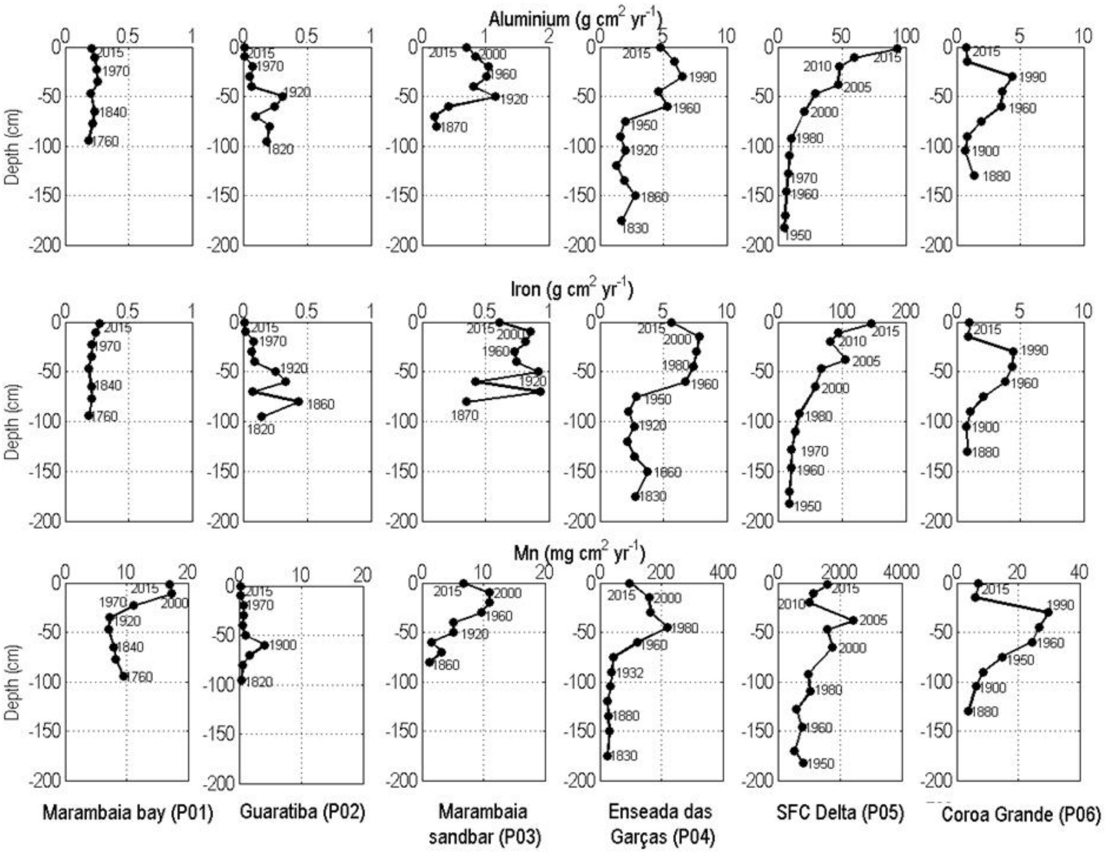

Figure 3.4.10. Al, Fe and Mn annual flux estimated for each layer in the sediment core profiles.

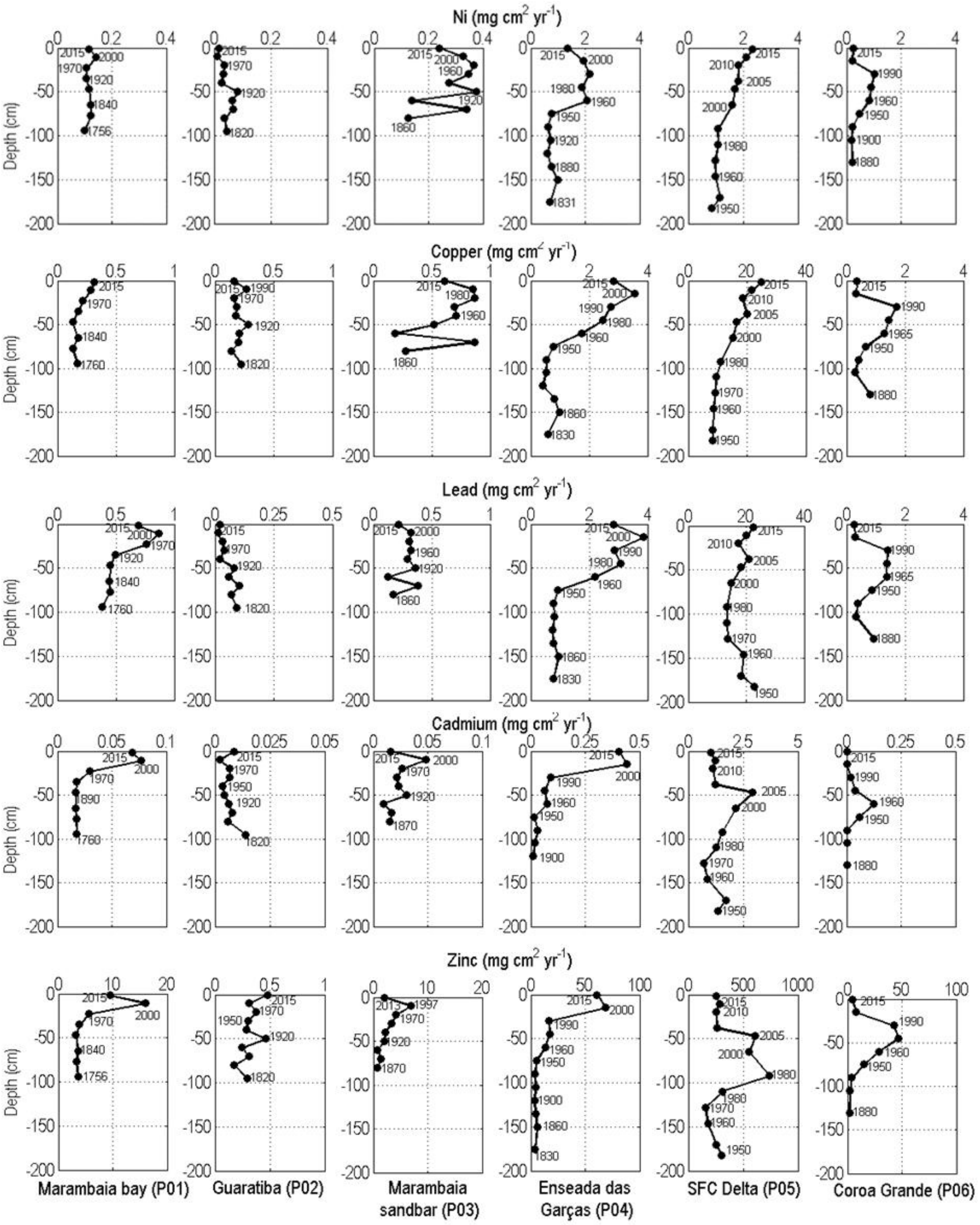

Figure 3.4.11. Trace metals annual flux estimated for each layer in the sediment core profiles.

A decrease on metal fluxes at SFC Delta (P05) was noted, when data from 1950-1960’s (bottom layers) is compared with actual fluxes (Cd: 1.3 to 0.89 g m^{-2} yr^{-1}; Pb: 22.7 to 1.4 g m^{2} yr^{-1} and Zn: 30.3 to 20 g m^{2} yr^{-1}). The lowering on Cd, Pb and Zn concentrations can be attributed to sediments recent remobilization, due to TKCSA construction and dredging activities nearby and also to remediation actions taken into Madeira Island wastes from Ingá Cia (Lindolfo, 2015). Although, Cu and Ni showed enrichment over time (Cu: 0.83 to 1.50 g m^{-2} yr^{-1}; Ni 0.086 to 0.14 g m^{-2} yr^{-1}), which can be related to a different source of contamination for these two metals.

Enseada das Garças (P04) showed enhancement for all five trace metals (Cu: 5.6 to 28.4 g m-2 yr-1; Ni: 7 to 13.5 g m-2 yr-1; and Pb: 7.9 to 28.3 g m-2 yr-1), but mostly for Cd (8 x 10^{-4} to 4.3 g m^{-2} yr^{-1}) and Zn (40.2 to 609 g m-2 yr^{-1}). In the Coroa Grande area (P06) the increase of Cu, Pb, Ni and Zn were higher, than in Enseada das Garças (P04) (Table 3.4.4).

Cadmium and zinc fluxes enhancement was higher at Enseada das Garças (P04), followed by Sandbar (P03) and Marambaia bay (P01) (Figure 4.5.11). The proximity of Coroa Grande (P06) to Madeira Island and its sheltered position could explain the accumulation of trace metals in this site from 1950's to 1990's, however there are lowering patterns towards the surface for all elements since 1990's, especially for Cd, which can be related to sediments resuspension and mobilization to other regions of the bay and to exchangeable forms (mobile phases). Monte et al. (2015) observed Cd and Zn mobilization towards weakly bound fractions after resuspension experiments with sediments from Saco do Engenho creek's mouth. However, ICP-MS problems with decetion during measurements could not be disregarded, especially for Cd with non-detectable concentrations in the upper layers, once this metal can be found in higher amounts in sediments from these regions. Rodrigues et al. (2017) found Cd concentrations in surficial sediments from Coroa Grande between 0.48 and 0.61 mg Kg^{-1} and Marques Jr. et al. found Cd content between 0 and 33cm (sediments depth) from 0.5 to 1.5 mg Kg^{-1}.

Gomes et al. (2009) estimated an enhancement of Cd mean annual flux from 1.6 x 10^{-3} to 2.2 x 10^{-2} g m^{-2} y^{-1} and for Zn from 0.26 to 4.27 g m^{-2} in the past 60 years, for sediment cores collected near to SFC Delta. The results presented here for the same area showed a decrease on these fluxes, mostly due to remobilization events during TKCSA construction.

Figure 3.4.12 shows the excess of metal inventory. Sepetiba bay is a transition system, where a degree of salinity and grain size between Marambaia bay (P01) towards P04, P05 and P06 is noticed, from a marine area to an estuarine setting. The degree is also observed in the metal retention, which naturally follows the grain size, but also reflects the proximity to the main sources of anthropogenic metals to the bay in the northeast. The core from SFC Delta (P05) presented the highest values for Ni, Cu, Pb, Cd and Zn inventories, followed by Enseada das Garças (P04) and Coroa Grande (P06). Despite the low values observed in the southern part of the Bay, the sandbar area (P03) is showing a tendency of trace metals accumulation higher than at Marambaia bay (P01) and Guaratiba (P02), which can be noticed, mostly, for Ni, Cu and Cd. The proximity of the area to the disposal sites (Figure 2.4.5) and also reflects the hydrodynamic patterns in the area, which may contribute to deposition at Sandbar (P03).

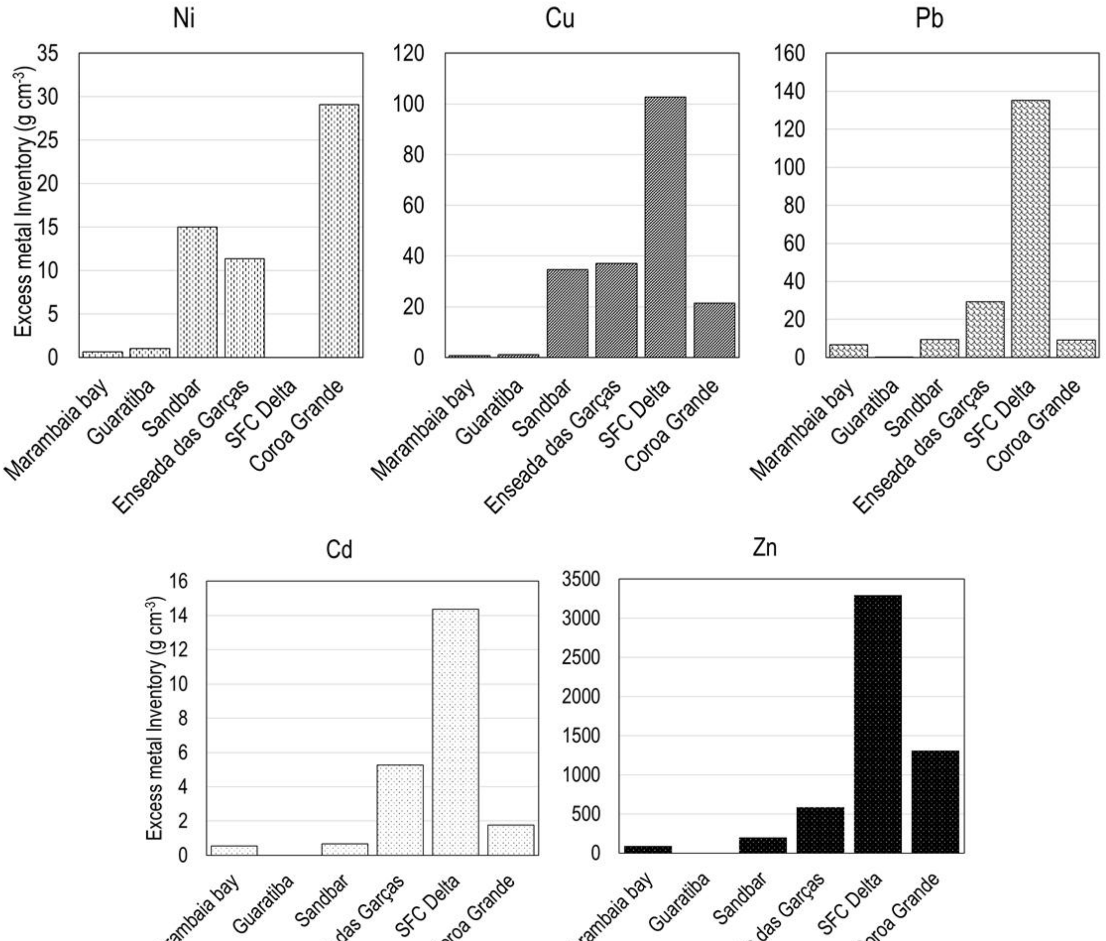

Figure 3.4.12. Excess metal inventories for Cd, Cu, Ni, Pb and Zn from six different areas in Sepetiba bay. Marambaia bay (P01) and Sandbar (P03) are near to the main entrance of the system; Guaratiba (P02) is close to the Barra de Guaratiba channel and the other three sites are located in the inner part of the bay (Enseada das Garças (P04), SFC Delta (P05) and Coroa Grande (P06).

Overall, according to Gomes et al. (2009), Molisani et al. (2004), Marques Jr. et al. (2006) and the results presented here, the increase of Cd and Zn concentrations coincides with the benefiting of high purity Zn by Ingá Cia. in the beginning of 1960's. Barcellos and Lacerda (1994) reported Cd concentrations of 2.1 mg Kg^{-1}, with an increase of 1.6 tons yr^{-1}. The authors attribute the increase to the industrial development in the region, to hydrodynamic behavior and its dispersion capacity into the bay, which receives this amount of Cd per year into 447 km^2, while other systems can receive higher amounts with higher dilution capacity (Barcellos and Lacerda,1994).

3.4.6. Enrichment Factors (EFs)

The EFs calculated for each trace metals are displayed in figure 3.4.13. The colored areas (Blue, yellow, orange and red) indicate the level of contamination proposed based on the EFs classification:

- Without color - $EF<2$ non-existent or very low enrichment;
- Blue - $2 \leq EF< 5$ moderate enrichment;
- Yellow - $5 \leq EF<20$ significantly enrichment;
- Orange - $20 \leq EF<40$ high enrichment;
- Red - $EF >40$ extremely high enrichment.

Table 3.4.5 presented the baseline values for each core analyzed and for the local literatures. The values found in the SFC Delta (P05) baseline were extremely high reflecting the trace metals contaminations due to Ingá Cia. wastes leaching. For this reason, values found by Gomes et al. (2009) were applied instead of SFC Delta bottom concentrations (Table 3.4.5).

Table 3.4.5. Baseline values found in the cores. For Cd, Cu, Ni, Pb and Zn the values are in mg Kg^{-1} and for Al and Fe the values are in percentages (%).

	Cd	Cu	Ni	Pb	Zn	Al (%)	Fe (%)	Reference
Marambaia bay	0.22	2.11	1.25	4.76	45.3	0.23	0.23	This study
Marambaia sandbar	0.28	5.1	2.32	3.2	12.9	0.4	0.6	This study
Guaratiba	0.26	4.53	0.85	1.76	5.5	0.35	0.27	This study
Enseada das Garças	ND	7	8.6	9.5	48.77	2.1	3.4	This study
SFC Delta	**4.6**	**28.9**	**2.97**	**78.44**	**1045.37**	**0.5**	**2.2**	**This study**
Coroa Grande	ND	8.4	2.11	9.64	20.9	1.4	0.9	This study
Coroa Grande	<0.2	-	-	-	69-103	-	-	Marques Jr. et al. (2006)
SFC Delta	0.34	8.09	8.32	20	54	2.78	1.59	Gomes et al. (2009)
Marambaia bay	ND	2	-	-	<500	-	-	Pachineelam e al. (2010)

In general, Cd and Zn were the elements that presented enrichment in most of the sediment samples, reaching the maximum contamination level (“extremely severe”) at São Francisco channel’ delta (P05) (Figure 3.4.13). The enrichment of Cd, Cu, Zn and Pb is a result of the Ingá wastes and other anthropogenic activities that take place near the northeast coast mainly involving the dumping of urban-industrial sewage from west zone of Rio de Janeiro city and cities from metropolitan region (Queimados, Nova Iguaçu, Seropédica).

Araújo et al. (2017), also observed higher enrichment factors in the inner part of the bay, near to SFC Delta and, mostly, at the Saco do Engenho creek mouth. Lower values were observed by the authors at Marambaia bay. As well as observed here Ni presented lower EFs for all sites (Araújo et al., 2017).

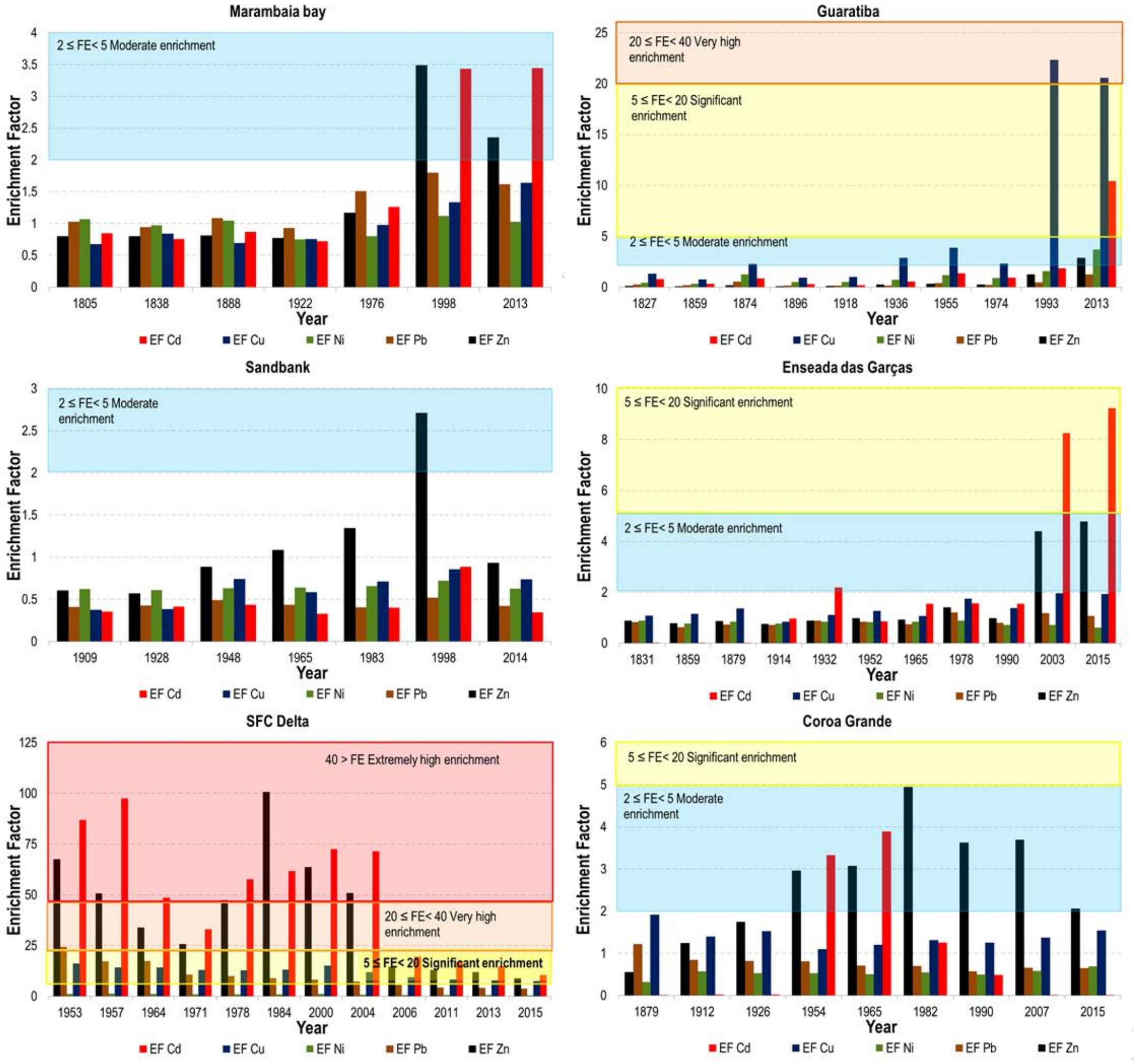

Figure 3.4.13. Enrichment Factor for Cd, Cu, Ni, Pb and Zn for six cores sampled in the Sepetiba bay. Red area: EF > 40; Orange: 20 ≤ EF < 40; Yellow: 5 ≤ EF < 20; Blue: 2 ≤ EF < 5;

Despite the low concentrations of Cu in Guaratiba (P02), its enrichment is a concern and needs to be highlighted. Besides the well-known anthropogenic sources at northeast part of the bay, residues of hull's ship cleaning enriched with copper oxide can collaborate as a diffuse source to sediments. In semi-enclosed waters, Cu can be easily mobilized from the hulls of resident and visiting boats and, after oxidation, copper can adsorb to fine particles in suspension, which may settle on bottom sediment (Turner, 2010). Besides that, Sepetiba bay waters have been used as disposal sites to dredged sediment (See chapter 2, figure 2.4.2). High amounts of Cu were found by Rocha et al (2012) near to Marambaia sandbank nearshore (from 4 to 1160 mg Kg^{-1}). Despite of fewer occurrences of contaminated sites by Cu, this is an essential trace metal to living organisms and its enrichment can be a potential risk to Sepetiba bay biota and, consequently, to human health.

3.5. *Conclusion*

Marambaia bay area is a suitable place to chronology reconstruction, due to the sedimentary profile preservation with little reworking and the core reflected the processes occurring in Sepetiba bay watershed, as can be seen in the sedimentation rates enhancement concurrently with Paraíba do Sul-Guandu rivers diversion in the 1960's-1970's. Although, chronology in a disturbed area, such as São Francisco channel's delta is challenging. Nevertheless, the core could provide information about events in the inner part of the bay, which has been occurring for the last 60 years, for instance the TKCSA establishment. The historical reconstruction of SFC Delta (P05) core recovered only 60 years, due to the high sedimentation rate on a river mouth setting. Since trace metals contamination in Sepetiba bay northeast area started in the 1960's, a baseline layer for comparison was not available in the core.

Higher amounts of Cd and Zn can be found in the inner part of the bay, however, due to a large amount of sediments remobilization events signs of trace metals enhancement and changes in the grain size patterns can be found in the Marambaia sandbank coastline (P01, P02 and P03). Cu concentration appear as an emerging contaminant, despite its presence on Ingá Cia. residues, other point and non-point sources, as antifouling paintings containing copper oxides, might be collaborating with Cu enrichment in bottom sediments.

Chapter 4

Geochemical fractionation of trace metals in sediment profiles from Sepetiba bay, Rio de Janeiro, Brazil.

4.1. Introduction

Pollution from metals began with the industrial revolution at the end of the 19th century resulting in the alteration on many metal fluxes from continental (terrestrial, fluvial and atmospheric) sources to the oceans, increasing their concentration on sediments, water and biota. The pollution by trace metals is concerning and require attention at global and local levels.

Metal input in aquatic systems is given by point and non-point sources discharge, both from natural and anthropic origin. However, the toxicity of a specific metal will depend on its chemical form and concentration in the environment. Trace metals from incoming tidal water and fresh water sources are rapidly removed from the water body and are deposited onto the sediments (Guzman and Garcia, 2002). Metals are present in sediments in a variety chemical forms and exhibit different physical and chemical behaviors (mobility, bioavailability and toxicity). Metals in estuarine sediments can be bound to different forms; adsorbed on clay surfaces or iron and manganese oxyhydroxides; present in secondary minerals lattice (carbonates, sulfides, oxides); occluded in amorphous materials such as iron and manganese oxyhydroxide; complexed with organic matter; and present in primary minerals lattice, like silicates (Pickering, 1986; Smith and Huyck, 1999).

The fractionation is a useful tool to quantify the potential effect of metals enrichment in sediments. Due to the necessity to better understand the dynamic of trace metals in sediments, different methodologies were developed to determine the metal forms and the partitioning among the chemical phases of trace metals in sediments. The sequential extractions are analytical processes where one single sample is submitted to successive leaching with growing strength extractors. The analysis of each one of these extractions provides information about metals geochemical partitioning in different sediment binding phases. The reagents in the extraction steps are assumed to remove individual phases of the material selectively, while causing relatively insignificant dissolution of other phases (Griffioen and Boers, 1993; Pickering, 1986).

The first sequential extraction methodology developed was published by Tessier (1979) and it combined 5 extractions steps. Afterwards, several methodologies were formulated (Tessier, 1979; Silveira et al., 2006; Poulton and Canfield, 2005; Claff et al., 2010; Massoud et al., 2010). Nowadays, the number of steps and the chemical extractors applied will reflect the aim of a sequential extraction. Extraction methods can be used to identify and quantify specific mineral phases, reactive fractions between interface sediment-water and pore water, characterize the distribution of metals over the reactive phases present in a sediment, which can be used to identify the availability and/or toxicity for living species (USEPA, 2007). In addition, it is possible to apply this kind of technique to discuss a differentiation between natural and anthropogenic metal enrichments in environmental studies (USEPA, 2007).

There is a vast literature on the identification of sites contaminated by trace metals, but data about fractionation of these elements in the environment, indicating their mobile phases are scarce (Claff, 2011). The majority of published studies deals with the contamination of sediments by metals using the total metal content as predictor to assess their potential effects as contaminants. Measurement of the total concentration of metals does not provide information to assess the availability, mobility and reactivity in sediments. This type of study must be explored because the distribution and behavior of the metals in the aquatic systems are strongly controlled by their partitioning in the solid phase, which consequently will have a fundamental role in the mobility, bioavailability and toxicity of these metals (Smith and Huyck, 1999; Calmano et al., 1993).

Sedimentary profiles provide temporal information on the local aquatic processes and it is possible to build a historical reconstruction of anthropogenic impacts (López et al., 2006). The analytical method to achieve these data can be done through the estimation of sediment cores age. The determination of some target pollutants and the specific activity of a natural radionuclide in the bottom sediments allows the reconstruction of the history and the identification of pollution sources. The excess of the ^{210}Pb activity in each sediment layer decreases with its age, according to the radioactive decay law. Thus, this law can be used to calculate the age of the sediment based on the initial excess of ^{210}Pb (See chapter 3).

Trace metals even at very low concentrations in the aqueous phase can have a significant impact on the ecosystem (Claff, 2011). Therefore, understanding the mobility and geochemistry of these elements should be extremely important for the management of regions where metals are introduced as a result of human activities.

Information about geochemical phases of trace metals in Sepetiba bay are scarce. There are two work with a sequential extraction scheme with more than two steps performed in the 1980's by Fizman et al. (1984) and Souza et al. (1986). The following studies were performed in two fractions, weakly bound and residual fractions (Lacerda et al., 1987; Monte et al., 2015; Rodrigues et al., 2017). In this study, sequential extraction technique, organic matter, grain size, total, inorganic and organic carbon, total sulfur and mass accumulation rates was used to interpret the metals forms and mobility through a historical point of view in sediment cores from Marambaia bay and near to São Francisco channel's mouth, two different areas within Sepetiba Bay.

4.2. Study Area

Sepetiba bay (BS) is located at southwest of Rio de Janeiro (Figure 4.2.1). The bay is surrounded by municipalities such as Mangaratiba, Itaguaí and the west zone of Rio de Janeiro city. All municipalities are exploring tourist activities in the region. However, Sepetiba bay is considered one of the most impacted coastal Brazilian environments by trace metals, due to the activities developed throughout the watershed. In addition, adjacent environments such as conservation units (Marambaia sandbank and Ilha Grande Bay) may be exposed to contaminants disposed within the Sepetiba drainage basin, due to sediments resuspension events (dredging, storms, boats traffic) particles enriched with trace metals can be transported through currents to protected areas. The bay has a well-documented history of contamination by metals (Rodrigues et al., 2017; Gomes et al., 2009; Lacerda et al., 2004; Lacerda and Molisani, 2006; Barcellos et al., 1991; Lacerda et al., 1987).

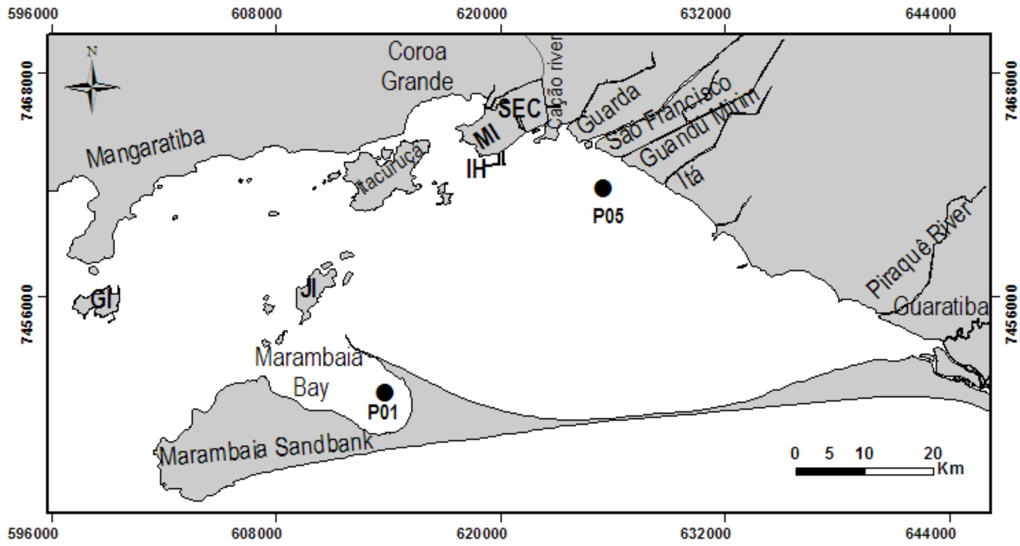

Figure 4.2.1. Sampling sites distribution and Sepetiba bay location at South America. P01 (Marambaia bay) and P05 (SFC Delta). Abbreviations: MI - Madeira Island; SEC - Saco do Engenho Creek; IH - Itaguaí Harbor benches; GI - Guaíba Island; JI - Jaguanum Island.

Several human activities are developed within the SB, such as port terminals, shipyards, fishing and a variety of industrial branches. There is an industrial district (Santa Cruz District) with large metallurgical companies, petrochemicals, beverage, rubber, chemistry, textile, mechanics, plastic products and leather tanning (Leal Neto et al., 2006; Araújo et al., 2017). In addition, energy generation and water treatment plant for population and industries supply are important factors within the management context in the region.

The main fluvial course of Sepetiba bay (Guandú River) is part of Paraíba do Sul-Guandu river diversion system, which supplies cities from Rio de Janeiro metropolitan region and the remaining water, together with the sludges are discharged into Sepetiba bay (Molisani et al., 2006). According to SEMA (1998), it is estimated that a flux of 145 m^3s^{-1} reaches Sepetiba bay and approximately 70% of the waters that flow into the bay are related with the diversion system, which was responsible for the increased by 3 times of the total inflow of the bay since 1950’s.

The presence of Itaguaí port, Porto Sudeste, Brazilian Navy shipyard, VALLE S.A and TKCSA (Companhia Siderúrgica do Atlântico - Thyssen Krupp CSA) terminals demands dredging operations that are carried out for the maintenance of navigation channels. However, actions that destabilize the reducing conditions of the sediments in the region (Fiori, 2008; Lopes-Rosa, 2011), as dredging activities, may cause resuspension and consequently metals mobilization from the bottom of the bay. According to Amado Filho et al. (1999) and FEEMAR/GTZ (1998), the Itaguaí Port expansion in 1997 was one of the main factor for the environmental quality decrease of Sepetiba bay. In addition, the construction of the TKCSA in 2000's remobilized high amounts of bottom sediments from the channel's mouth into the inner part of the bay (See chapter 3). Sediments from the northeast part of the bay are impacted by trace metals, mainly Cd and Zn since 1960 – 1970's (Lacerda et al., 1983; Aragon et al., 1987; Souza et al., 1986; Lacerda et al., 1987), due to industrial wastes from Ingá Metallurgical Cia., a former company which used to produce high purity Zn from Calamine ore (Barcellos et al., 1997).

4.3. Methods

In August 2015 two sediment cores were taken with a piston corer at Marambaia bay (P01) (94cm) and São Francisco Channel Delta (P05) (182cm) (Figure 4.2.1). The cores sections were split and sub-sampled in 3-cm intervals by taking fixed volume sub-samples in the laboratory. Sub samples designed to sequential extractions analyses were lyophilized.

Grain size were determined through the sample disperser Hydro 2000MU coupled to particle measurer Mastersizer 2000 (See chapter 3, section 3.3). Total content of sulfur and carbon were measured in approx. 0.3g of sediments at the LECO SC-632 Carbon and Sulphur analyzer. All the samples were analyzed in duplicates.

Sequential multiple extraction techniques were used to fractionate metals into different chemical phases of the sampled material. Different chemical extractors types were applied sequentially to the sediment samples, each successive treatment being more drastic in chemical action, of a different nature than the previous one. The historical trace metal pollution in Sepetiba bay requested a modified procedure for sequential extractions, due to the majority of Cd and Zn have to be found in the reactive forms (Lacerda et al., 1987; Souza et al., 1986; Monte et al., 2015; Rodrigues et al., 2017), as well as the contribution of organic pollution to the bay in minor extent. Also, the majority of SE in the literature has been performing extraction of organic matter and sulfides in the same step, which is possible, however this procedure can mask the recovery of the crystalline sulfides (FeS_2). The design was made based on several works as can be seen in table 4.3.1.

Table 4.3.1. The sequential extraction scheme planned for this work is given.

	Extractant	Target phase	References	Operational definition
S1	1M Na - Acetate	Exchangeable	Tessier et al. (1979); Griffioen and Boers (1993); Poulton and Candfield (2005); Masoud et al. (2010)	Metals adsorbed to sediments and associated to carbonate minerals
S2	1 M NH2OH. HCl in 25% (v/v) CH3COOH	Easily Reducible Oxides	Chester and Hughes (1967); Poulton and Candfield (2005).	Metal associated to Mn oxides and amorphous Fe-oxide
S3	0.2 M NH_4-oxalate + 0.2 M oxalic acid	Poorly crystalline oxides	van Oorschot and Dekkers, (2001); Poulton and Candfield, (2005); Silveira et al. (2006)	Metals associated to amorphous and poorly crystalline oxides of Al and Fe
S4	0.1M Na-Pyrophosphate	Organics	Griffioen and Boers (1993); Pickering (1986)	Metals bound to organic matter (mainly humic and fulvic acids)
S5	HF/H_3BO_3	Silicates	Griffioen and Boers, (1993)	Aluminosilicates
S6	HNO_3 65%	Crystalline Sulfides (Pyrite)	Huerta-Diaz and Morse (1990)	Crystalline sulfides and residuals of crystalline oxides and silicates

Table 4.3.1 shows that the sequential extractions scheme consists of six steps targeting: S1 - Exchangeable metals; S2 – easily reducible oxyhydroxides; S3 – amorphous and poorly crystalline oxides; S4 - bound to organic matter; S5 – silicates; and S6 – crystalline sulfides. Extractions were performed with 0.5 g of sample and 20mL of each extractant at the corresponding step. After each one of the first four extraction steps, a readsorption step with 0.1N $SrCl_2$ was performed in order to avoid transfer of species liberated from one step to next ones (Griffioen and Boers, 1993).

Exchangeable metals (S1) were extracted with 20 ml solution of 1M sodium acetate at room temperature with 5 hours of shaking, the pH 4 was achieve with acetic acid (HOAc) adjusting. In this step metals ions weakly adsorbed and carbonate minerals such as siderite and ankerite can be released (Poulton and Candfield, 2005).

Oxyhydroxides were divided into two extractions, the first one (S2) aims release easily reducible oxides (i.e. trace metals oxides, Mn oxyhydroxides as well as a small amount of amorphous Fe oxides) with the use of 20 ml solution of 1M Hydroxilamine hydrochloride dissolved in a solution of 1M of acetic acid (Chester and Hughes, 1967) at room temperature during 4 hours. The third step (S3) corresponds to oxyhydroxides second phase, where amorphous and poorly crystalline oxyhydroxides forms can be release with the employment of a mixture of 20 ml with 0.2 M Ammonium oxalate and 0.2M Oxalic acid (pH 3), the samples were shaked for 2 hours at light. According to van Oorscht and Dekkers (2001), the light exposure enhances the dissolution of Fe oxides, due to the oxalate photocatalytic reaction. The authors suggested that the fine-grained oxide minerals, such as magnetite, goethite and hematite can be released (van Oorscht and Dekkers, 2001).

The fourth step (S4) was performed to obtain the content of major and trace elements attached to organic matter. Sodium pyrophosphate has been shown a good extractant in basic pH (10), especially because of the chelating properties with metals, due to deprotonation of organic matter (Slavek et al., 1986; Griffioen and Broers, 1993). For the extraction procedure 20 ml of 0.1M $Na_4P_2O_7 \bullet 10H_2O$ (pH 10) was added to the residues from step 3 and shaken overnight. The extraction of O.M. before oxides is not suitable, due to the release of the easily reducible oxy-hydroxides by the majority of solvents applied to organic matter dissolution (Pickering, 1986).

Silicates (S5) were removed after the organic matter step through 20 ml HF (48%) solution attack, in the residues from the fourth step, during 8 hours. When the procedure was finished, 5 g of H_3B0_3 were added to the mixture with the aim of complex insoluble fluorides, forming soluble fluoroborates. These later procedure is recommended to make the resulting solution safer to handle and reducing the risk of damage to analytical instrumentation (Huerta-Diaz and Morse, 1990). The final residues were submitted to a 6th step (S6), where the sulfides and crystalline elements were released with concentrated HNO_3 (65%) attack and agitation during 2 hours inside Teflon tubes.

The extracts were then measured in an inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine Fe and Mn concentrations (SPECTRO Analytical Instruments GmbH – Germany) and the mass spectrometry (ICP-MS) was used to estimate trace metals content (Cr, Cd, Cu, Zn, Pb and Ni).

Detailed method for ^{210}Pb analysis and MAR calculations can be found in chapter 3 (Section 3.3) and the statistical results are presented in table 0.3 in the appendix section. Adopted QA/QC procedures included the use of replicates and repeatability tests as well as the use of blanks and standards analyses. For metals, blanks and standard certified sediment (BSCC – 1 marine sediments) were treated like samples during the extractions. The respective recoveries and detection limits are in table 0.1, at appendix.

In the present study, the data were classified using factor analysis (FA). The factor analysis was applied for five main fractions: Exchangeables (S1), oxides (S2+S3), organic matter (S4). Silicates(S5) and sulfides (S6). FA technique starts with the establishment of a correlation coefficient matrix from the data variables, after the eigenvector matrix that represents the magnitudes and directions of variables in space is calculated, and the eigenvalues which represent their corresponding variances. The final step includes the rotation of the principal factor (varimax rotation technique), to achieve a simple structure leading to the rotated factor matrix. Varimax is an orthogonal rotation, resulting in orthogonal rotated factors, and the most stable results can be obtained using Varimax method (Reimann et al., 2008).

4.4. *Results and Discussion*

Grain size (%), Organic Matter (%), Carbon (Total, organic and inorganic), sulfur (S), Density and mass accumulation rates (MAR) profiles are presented in figure

4.4.1. Means, standard deviation, maximum and minimum values are presented in the table 0.5 of the appendix section.

Marambaia bay (P01) density's profile has small variability along the core (from 2.06 to 2.21g cm^{-3}), with higher values close to the bottom. On the other hand, the density of the sediments from SFC Delta core (P05) varied from 1 to 1.97 g cm^{-3}, with recent layers showing higher density towards the surface. Mass accumulation rates (MAR), as expected, were higher near the channel's mouth (SFC Delta), the values were between 2.9 and 8.55 g cm^{-2} yr^{-1}, with two average sedimentation rates: 4.3 cm y^{-1} in the upper layers (2-74cm) and 3 cm y^{-1} in the older package of sediments (74-182cm), these values are high, but possible for a delta region (see chapter 3). MAR results in the Marambaia bay (P01) were from 0.8 to 1.15 g cm^{-2} yr^{-1} in the past 150 years, with two average values of sedimentation rates: 0.36 cm^{-2} yr^{-1} (2-23cm) and 0.55 cm^{-2} yr^{-1} (23-74cm) (see chapter 3).

Sepetiba bay has a predominance of fine sediments in the inner part, close to the main tributaries, and coarser particles are found near to Marambaia sandbank towards the main entrance of the bay (figure 4.2.1). Marambaia bay core (P01) was classified as sandy silt profile, with mean organic matter of 4% (Figure 4.4.1). Near to the channel's mouth (SFC Delta - P05), the silt content was the main grain size fraction in the whole core, OM content was higher when compared to P01, showing a mean of 14.1% and the highest value of 22.1%, as can be seen in figure 4.4.1. An anomaly of sand grain size was observed at the 0-2cm layer of P05 (47%), which can be associated with changes in the local hydrodynamic, which can be related to a high energetic environment. Recent alterations in the São Francisco channel course, due to a subaquatic dam construction in 2015, cause the channel narrowing, which can enhance the stream velocities and its competence of carrying larger grain sizes (see chapter 3). Besides that, the expansion of sand extraction near to SFC and Guarda channels in the last 30 years (Araújo et al., 2017) can contribute to erosion of soils and enhancement of coarse size particles discharge.

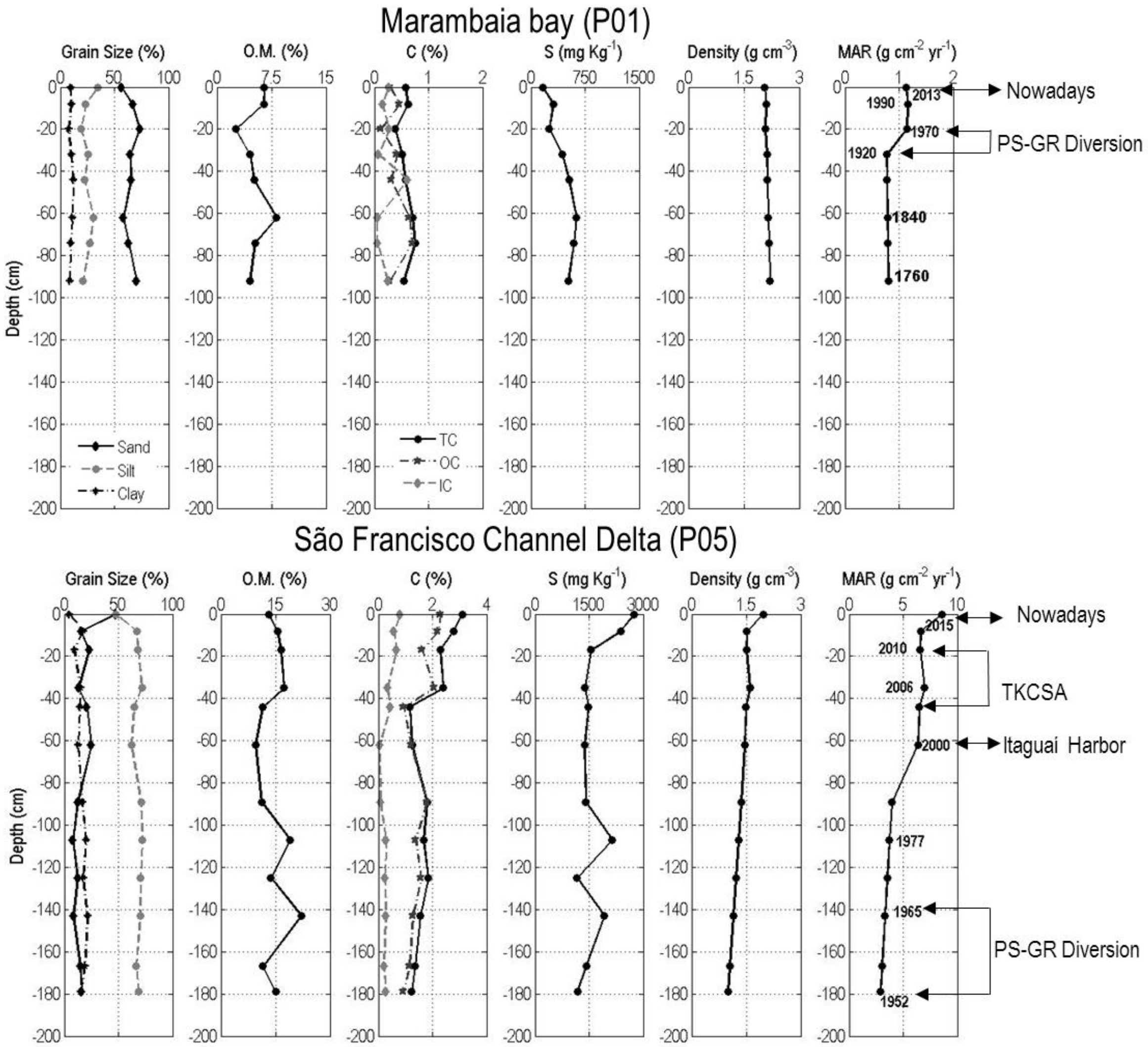

Figure 4.4.1. Organic matter content (%), S, density and MAR are represented in black dots. For grain size: the black dashed line with diamond markers represents clay content, the black continuous line with small diamonds is representing sand and grey dashed line with circles represents silt portion in percentage. The third chart represents: total carbon (TC) with black dots, organic (OC) with dark grey with dashed line and stars markers, and inorganic carbon (IC) with light grey circles markers and dashed line. The years were estimated according to MAR and SAR information obtained in chapter 3. Abbreviations: TKCSA: Thyssenkrupp/Companhia Siderurgica do Atlãntico establishment; PS-GR: Paraíba do Sul river - Guandú river system diversion started.

Total carbon at Marambaia bay (P0) varied from 0.4 to 0.7% and in the SFC Delta (P05) from 1.2 to 3.1%. P05 profile showed enrichment of C in the surface layers, these high concentrations, however, decreased with depth. The observed tendency may simply reflect changes in the amount of organic matter produced in nearby waters. Although, other factors should be considered; for instance, remobilization and changes in the sedimentation rate, which can be seen in the MAR values enhancement from 2000's, due to TKCSA navigation channel, mooring benches and mainland's facilities constructions, which leads to bottom sediments mobilization and suppression of mangrove areas

(Boskalis, 2012). Another factor that can alter carbon burial is changes in the physical-chemical conditions (temperature, pH, and Eh), which may affect decomposition and diagenesis of the organic matter (Bianchi, 2007).

Marambaia bay (P01) inorganic carbon (IC) values were from 0.05 to 0.3% and at SFC Delta (P05) between 0.04 and 0.8%. The highest values of IC in the bay are found in the inner part, these results indicate that IC of these sediments can also be related to materials from weathering minerals carried by the rivers or from precipitation under dry environments (Pinto, 2016). Inorganic carbon variations through time can be relate to variations in the carbonates supply from detrital and biogenic sources (Tripathy et al., 2014). Organic Carbon concentrations were higher than inorganic carbon, at P01 OC was from 0.1 to 0.7% and near to SFC mouth (P05) between 0.9 and 2.3%. The organic carbon patterns of both cores follow the profile of O.M. and total sulfur content.

Total sulfur content varies from 164 to 630 mg Kg^{-1} at Marambaia bay (P01) and from 1160 to 2740 mg Kg^{-1} near to SFC mouth (P05) (Figure 4.4.1). The total sulfur includes organic-S, which may include significant quantities of reduced sulfur (Rickard, 2012). Sulfur is an important redox element in estuarine environments, due to its relation with biogeochemical processes such as SO_4^{2-} reduction, pyrite (FeS_2) formation, metals cycling, ecosystem energy and atmospheric S emissions (Bianchi, 2007). Both cores are presenting S values consistent with the carbon patterns, SFC delta (P05) with higher values, mostly in the recent layers, and at P01 higher values found towards the bottom. Marambaia bay (P01) low values of C and S can indicate weathering loss and low availability of OM in the region, on the other hand, at SFC Delta the C and S availability is higher, due to continental sources proximity (Sagemans and Lyons, 2004). According to Morse and Berner (1995), C/S ratio in marine sediments is 2.8, the results for Marambaia bay (P01) and SFC Delta (P05) are below the expected ratio (Figure 4.4.2).

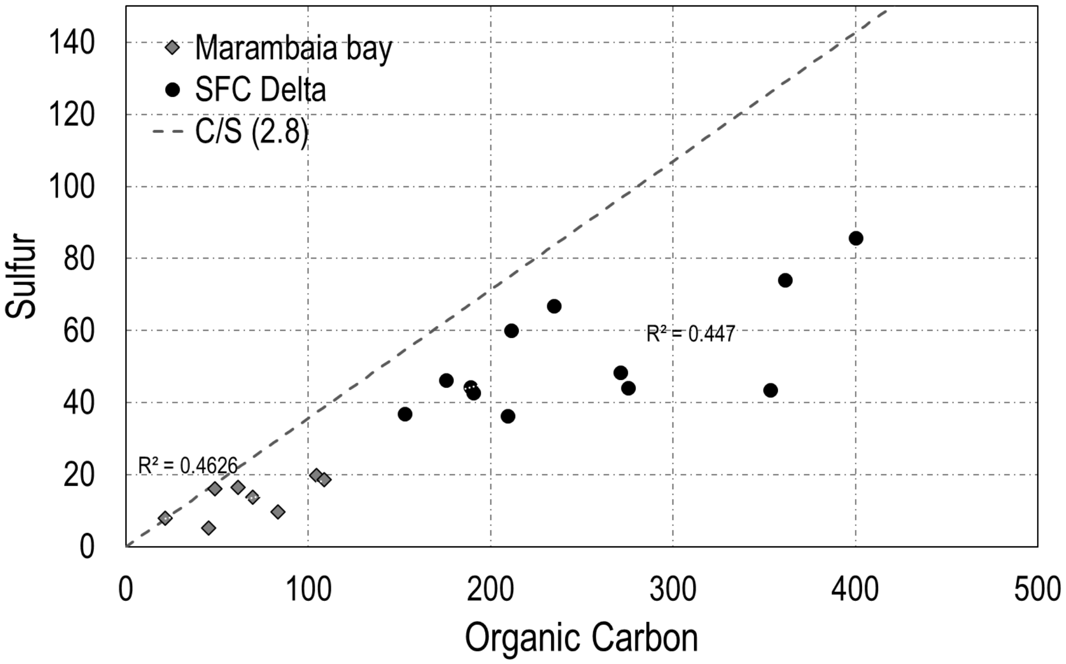

Figure 4.4.2. The chart shows S (%) versus Organic Carbon (%). Diamond markers are representing Marambaia bay (P01) and black dots are representing SFC delta (P05) mean values for each layer analyzed. The dashed grey line indicates the C:S stoichiometry ratio (Morse and Brener, 1995) for sediments.

The deviation below marine ratio is clearer for SFC Delta (P05), which presents more fine sediments and proximity to the main tributaries, enriched with sewage and organic matter from continental source, which can be conducive for an area with reducible conditions.

According to Berner (1981) geochemical classification, the two sediment cores sampled in Sepetiba bay presented different diagenetic environments. SFC Delta (P05) showed an euxinic condition (Eh: -128 to -228; S±1677), which can favor the presence of reducible metals forms, while Marambaia bay (P01) presented post-oxic conditions (Eh:-20 to -80; S±428).

The statistical results of sequential extraction are summarized in Tables 0.6 (P01) and 0.7 (P05), maximum, minimum, mean and standard deviation values for different fractions as well as the sum of all extractions (total concentration) are presented in these table at appendix section. Figure 4.4.3 (Fe, Mn, Ni, Cr) and Figure 4.4.4 (Cu, Pb, Cd and Zn) show the metals distribution along the cores P01 and P05 in different geochemical fractions (See Figures 0.1 and 0.2 for the concentrations in mg Kg^{-1} at appendix section). Estimation of the years was made based on MAR and sedimentation rates results (See chapter 3).

Fe concentrations at Marambaia bay (P01) were between 0.2 and 0.26%, while SFC Delta (P05) results were from 1.4 and 2.26%. Manganese total concentration were high in the recent layers (from 1970's) on P01 core (91 to 150 mg Kg^{-1}) and at P05 the opposite pattern is observed (219 and 964 mg Kg^{-1}), where higher content is found in the older layers (1950's). Fe and Mn total concentrations were lower at Marambaia bay region, mostly due to grain size dilution (Lacerda et al., 2004), once the analyses were performed in the bulk samples, higher amount of fine fraction are more likely to have more Fe and Mn. Fe content has the majority of the concentration observed in the oxyhydroxides fractions (S2 and S3), as can be seen in figure 4.4.3.

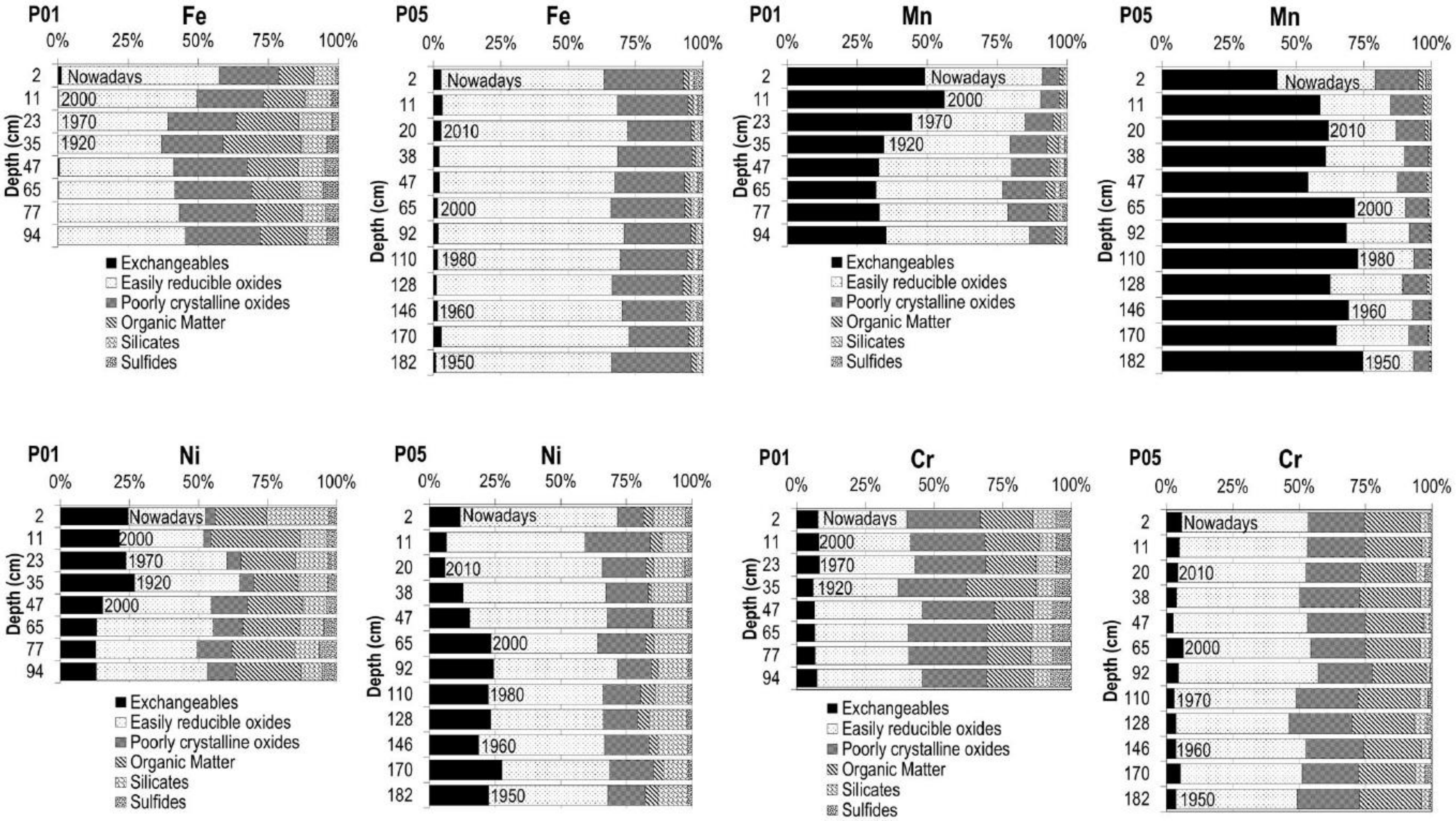

Figure 4.4.3. Sequential extractions results for Fe, Mn, Cr and Ni in sediment cores from Marambaia bay (P01) and São Francisco Channel's delta (P05). The percentages of each extraction step are given: exchangeables, easily reducible oxides, poorly crystalline oxides, organic matter, silicates and sulfides.

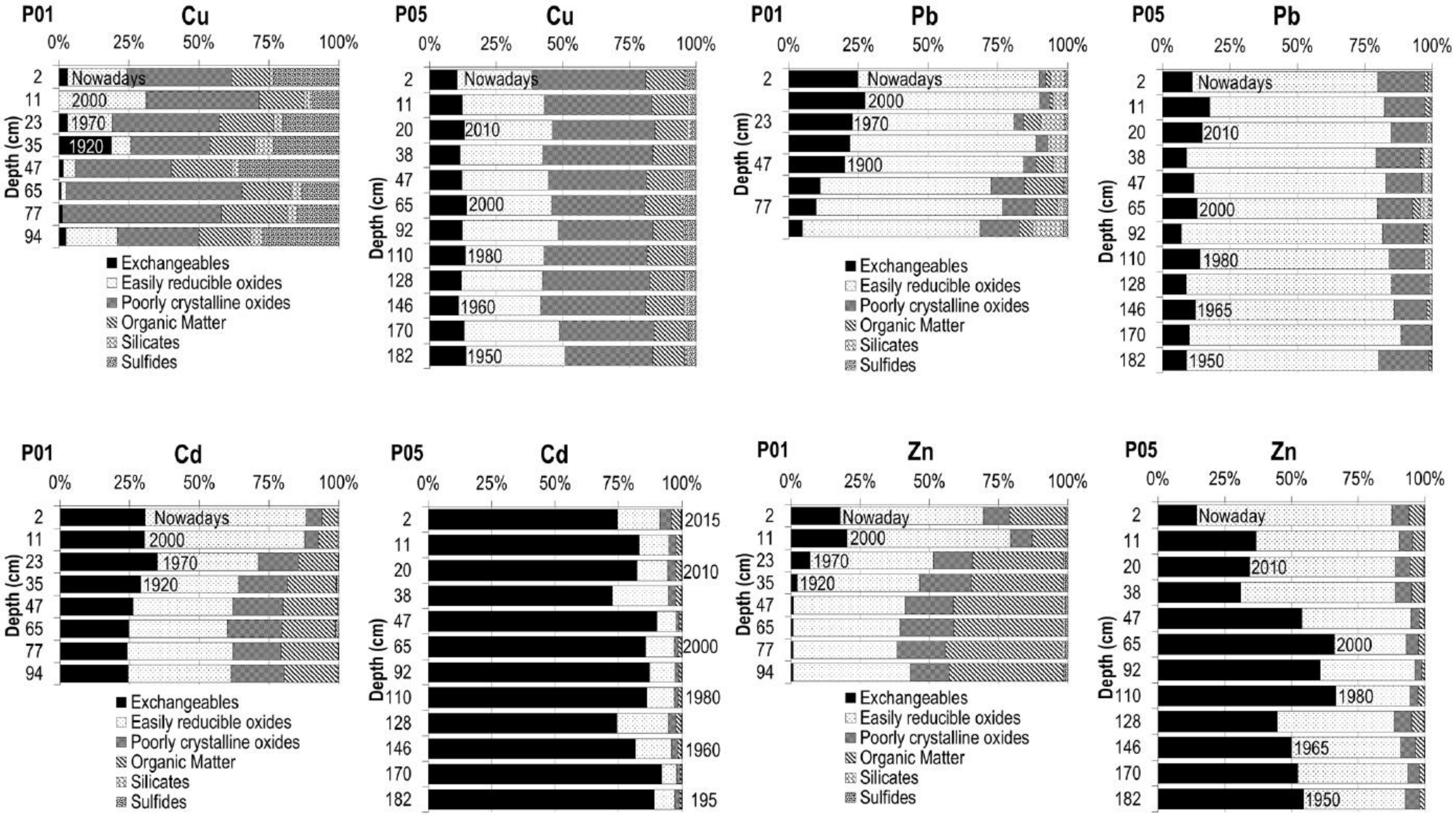

Figure 4.4.4. Sequential extractions results for Cu, Pb, Cd and Zn in sediment cores from Marambaia bay (P01) and São Francisco Channel's delta (P05). The percentages of each extraction step are given: exchangeables, easily reducible oxides, poorly crystalline oxides, organic matter, silicates and sulfides.

Iron mineralogy is a key determining the factor that influences trace metal mobility in the sediments (Huerta-Diaz and Morse, 1992; Claff, 2011). Under reducing conditions Fe minerals (predominantly pyrite (FeS_2)) strongly influence trace metal mobility (Huerta-Diaz and Morse, 1990). In both sites, iron presented higher concentrations in the oxides fractions (Reducible oxides+amorphous oxides), with 1633 mg Kg^{-1} at SFC delta (P05) and 1156 mg Kg^{-1} at Marambaia bay (P05), Iron and Mn minerals are sensitive to redox and pH changes (Burton et al., 2009; Nordmyr et al., 2008). By understanding the fate of Fe under changing redox conditions, it is possible to examine the potential fate of trace metals also released and bound during redox cycling (Koretsky et al., 2008). Therefore, both sediment core can present metals as crystalline sulfide forms. As can be seen in figure 4.4.5, the total amount of sulfur is probably deposit as inorganic sulfur, which can indicate the presence of sulfide minerals, for instance FeS_2 (pyrite).

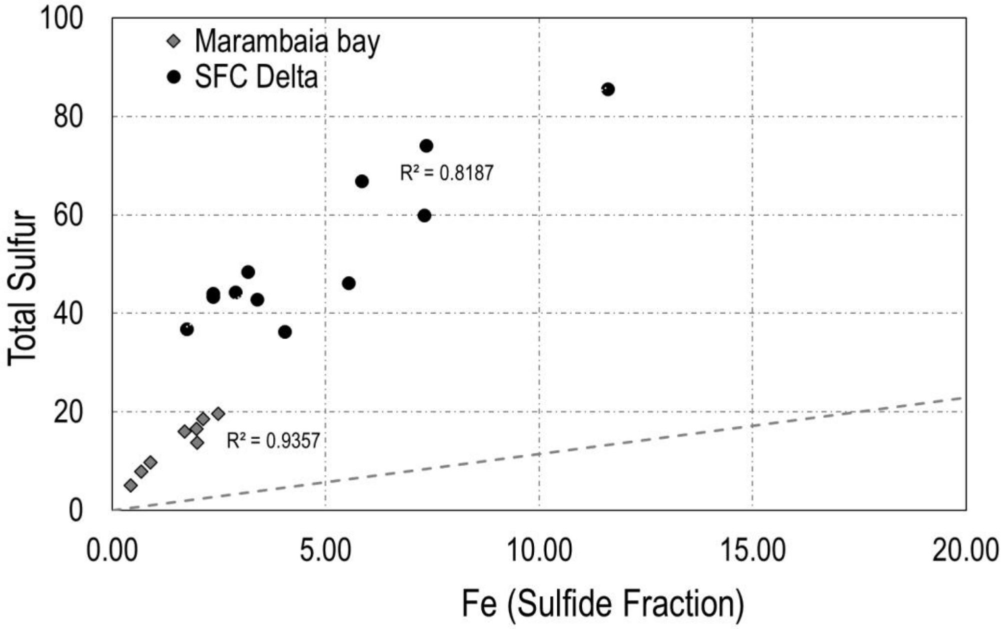

Figure 4.4.5. Portion of iron recovery in the sulfide fraction (mmol Kg^{-1}) versus total sulfur content (mmol Kg^{-1}). The dashed grey line indicates the Fe:S stoichiometry ratio of FeS_2 mineral. Diamond markers are representing Marambaia bay and black dots are representing SFC delta mean values for each layer analyzed.

On the other hand, Mn shows more availability and the highest recovery of the element was in the exchangeable fraction (S1), mostly in P05, while in P01 Mn concentrations were recovered mainly in the S2 fraction, which was the fraction where the highest recovery of Mn was expected (1M Hydroxilamine hydrochloride + 1M acetic acid). Once the environment presents reducible condition, Mn mobility to exchangeable fractions and pore water instability increases (Young and Harvey, 1992). According to Young and Harvey (1992), metals bound to Mn-oxides are more available when compared to metals associated with either Fe oxides or organics. As can be seen in table 4.4.1, the factor analysis results showed correlation between Mn and trace elements in de exchangeable (Factor 1: 59%) and oxides fractions (Factor 1:72.2%). These correlations explained the majority of the data variation for these fractions.

Lacerda et al. (1987) employed a weakly extraction (1M HCl extraction) in bottom sediments and suspended particulate matter to identify exchangeable metals in different regions from Sepetiba bay. The authors did not observed correlations between Mn and trace metals (Cr, Cd, Cu, Ni, Pb and Zn). In contrast to the results presented here, these differences can be related to the extractant employed in the method and also, due to the different grain fractions employed. Once Lacerda et al. (1987) used only the fine fraction, this work performed the extraction in the whole sample, without sieving.

Nickel is not a metal of concern in Sepetiba bay and it is highly related to fine grained sizes, silt and clay (see chapter 3), for this reason low concentrations were observed. At Marambaia bay (P01), Ni concentrations were between 0.9 and 1.5 mg Kg^{-1}, while at SFC Delta (P05) the values were from 2.5 and 3.8 mg Kg^{-1}. In both cores, Ni is found mainly in the oxyhydroxides fraction (S2+S3). Chromium total concentration at P01 were from 4.3 to 6.1 mg Kg^{-1} and at P05 between 18.3 and 51.8 mg Kg^{-1}. The majority of Cr content was in the Oxides fractions (S2+S3). Despite the lower results, chromium is a metal of concern due its toxicity. Sepetiba bay basin is under high urban and industrial development, for this reason a variety of trace metals has been reaching the bay through diffuse and point sources, so trace metal concentrations, as Cr, should be monitored, once it is employed in variety of industrial processes, such as graphics industry, artistic paints, anticorrosion paints, electroplating, steel alloys, stainless steel, welding, among other uses (Langard and Costa, 2007).

Concentration of Copper were from 1.7 and 2.7 mg Kg^{-1} at Marambaia bay (P01). On the other hand, at SFC Delta (P05), Cu concentrations were higher, with values between 23.8 and 32.5 mg Kg^{-1}. Copper was mainly in the exchangeable (S2) and poorly crystalline oxides phase (S3) (S2 - P01: 28-37% and P05: 1-31%; S3 - P01: 28-62% and P05: 33-43%). Cu total content do not exceed neither of the two thresholds of the Brazilian Sediment Quality Guidelines (SQGs) CONAMA 454/2012 (Cu – level 1:34 and level 2: 270 mg Kg^{-1};) However, copper is among different sources of pollution to the bay, such as industrial sewage, industrial wastes leaching, fluvial and from antifouling painting residues, with copper oxide in the formula, since Sepetiba bay is a leading industrial and harbor hub area, ships maintenance procedures, with scraping antifouling painting from the hulls can release paintings residues in the water (See chapter 3). According fishermen, ships anchoring inside the bay are performing the maintenance and disposal of these kind of wastes inside the bay, without control (ALERJ, 2009).

Lead total content at Marambaia bay (P01) was from 4.7 to 7.4 mg Kg^{-1} and at SFC Delta (P05) between 23.5 to 78.4 mg Kg^{-1}. The majority of Pb content was in available forms, mostly in easily reducible oxides (P01: 58 to 67%; P05: 65 to 78%). Pb exceed level 1 of CONAMA 454/2012 (46.7 mg Kg^{-1}) on the 3 oldest layers of the SFC core (P05). These layers correspond to the years from 1950's to 1970's, when the Ingá Cia. started the electroplating activities (Lacerda et al., 1987) and the wastes were disposed in the open air, without a containment barrier on Madeira Island. The wastes have been leaching to the Sepetiba bay waters through Saco do Engenho creek, a small tidal channel, which connects Madeira island midland to the inner part of the bay. According Zborowski (2008) and Marques Jr et al. (2006), only in 1980's a containment barrier around the waste pile was constructed. Due to the proximity of Saco do Engenho Creek to the wastes, high amounts of material containing trace metals were discharge into Sepetiba bay. However, events of barrier overflow were frequent during Ingá operation until its closure. Only in 2010's these wastes were remediate (Lindolfo, 2015). Factor analysis showed Pb relation with Cd, Zn and Mn in the exchangeable and oxides forms (Table 4.4.1)

Table 4.4.1. Results of the factor analysis for five fractions: Exchangeables (S1), Oxides (S2+S3), Organic Matter (S4), Silicates (S5), Sulfides (S6) and the total amount of metals (S1+S2+S3+S4+S5+S6) and sediments characteristics parameters (grain size (san, silt and clay), carbon, sulfur, organic matter content), with a significant positive loading (r larger than 0.7) as well as the variables with a significant negative loading (r lower than -0.7).

	Factor	% explained variance	Significative loadings	
Exchangeables	1	59.0%	r > 7	Mn, Ni, Pb, Cd, Zn, Silt, Clay
			r > -7	Sand
	2	18.2%	r > 7	Fe, OM, S, CT, CI, CO
			r > -7	
	3	6.7%	r > 7	Cr
			r > -7	
Oxides	1	72.2%	r > 7	Fe, Mn, Pb, Cr, Cd, Zn, Silt, Clay
			r > -7	Sand
	2	13.8%	r > 7	Ni, Cu, S, CT, CI, CO
			r > -7	Mn, Cd, Pb, Zn
Organic Matter	1	51.5%	r > 7	Cu, S, CT, CI, CO
			r > -7	
	2	14.6%	r > 7	Cr, Silt, Clay
			r > -7	Sand
	3	10.4%	r > 7	Cd
			r > -7	
	4	8.4%	r > 7	Fe and Mn
			r > -7	
Silicates	1	68.2%	r > 7	Fe, Mn, Ni, Cr, Cd, Zn
			r > -7	
	2	14.9%	r > 7	OM, S, CT, CI, CO
			r > -7	
	3	6.4%	r > 7	Pb and Clay
			r > -7	
Sulfides	1	45.5%	r > 7	Pb, Silt, Clay, OM
			r > -7	
	2	41.2%	r > 7	Fe, Mn, S, CT, CI, CO
			r > -7	
	3	11.2%	r > 7	Ni, Cr
			r > -7	
	4	8.4%	r > 7	
			r > -7	Cd
Total	1	70.0%	r > 7	Mn, Pb, Cr, Cd, Zn, Silt, Clay
			r > -7	Sand
	2	2.6%	r > 7	Fe, Cu, S, CT, CI, CO
			r > -7	

Cd total concentrations varied between 0.2 and 0.6 mg Kg^{-1} and zinc concentrations were from 41 to 137 mg Kg^{-1} at Marambaia bay (P01). While in the SFC Delta (P05), Cd content were from 1.2 and 5.5 mg Kg^{-1} and zinc from 301 to 1869 mg Kg^{-1}. At Marambaia bay, Cd and Zn enhancements stands out with an increase of 3-fold for both metals since 1970's and the strong relationship of these two metals on factor analysis results reinforces the Ingá metals wastes as a main source of these contaminants the northeast part of the bay and to distant areas, away from Saco do Engenho creek surroundings. The influence of Ingá wastes becomes clearer when exchangeable and easily reducible oxides fractions are observed in the recent layers of Marambaia bay core. The sum of these two extractions (S1+S2) totalize 87% of the total sequential extraction for Cd and 79% for Zn.

At SFC Delta (P05), Cd concentrations were mainly in the exchangeable fraction (from 73 to 92%), as can be seen in figure 4.4.4, while zinc content were concentrated mostly in S1 (14-67%) and S2 (27-73%), however from 2000's to nowadays the amount of zinc in the oxi hydroxides fraction (S2+S3) enhanced from 44 to 65%, this behavior can be related to the remobilization and consequently the oxidation of a recent package of sediments in the area. Between 2004 and 2010, Thyssen Krupp/CSA dredged 11 million m^3 of sedimentary material to construct its facilities: a harbor basin with an access channel. A mangrove area was suppressed (200 hectares) to build the steel plant requiring 3 million m^3 of sand, which were taking off from the dredged material, and the remaining 8 million m^3 of clay and silt were deposited onshore and in CDFs sites nearshore (Boskalis, 2012).

At SFC delta (P05), cadmium concentrations were above level 1 (1.2 mg Kg^{-1}) of CONAMA 454/2012 threshold. Zn concentration are all above level 1 (150 mg Kg^{-1}) and all layers before 2000's presented concentration higher than level 2 (410 mg Kg^{-1}). Since SFC Delta location is nearby Saco do Engenho creek, a peak of Zn can be seen in 1980's, with a concentration of 1868 mg Kg^{-1}, when high amounts of Cd and Zn would be expected at this time in the nearby area, once the containment barrier was constructed after 1980's.

Other studies applied sequential extractions schemes in sediments from Sepetiba bay, as can be seen in table 4.4.2, where results representative of the exchangeable fractions is presented. The results from Monte et al (2015) and Rodrigues et al. (2017) are comparable with the extraction held to recovery the exchangeable and easily reducible oxides from samples of SFC Delta core. While, Fizman et al. (1984) and Lacerda et al.

(1987) performed the SE in samples from different regions inside Sepetiba bay, but the authors considered only the fine fraction. Whereas Monte et al (2015) and Rodrigues et al., (2017) studied sediments from the region surrounding Madeira Island without sieving.

Table 4.4.2. Trace metals results in exchangeable phase from this study and from previous works performed in sediments from Sepetiba bay. The results are in mg Kg^{-1}.

	This study[a]	Fizman et al. (1984)[b]	Lacerda et al. (1987)[c]	Monte et al. (2015)[d]	Rodrigues et al. (2017)[e]
Fe	717 -15691	13200	-	7600 - 13600	4294 – 12598
Mn	68.6 - 901	-	64 - 613	104 - 285	45 – 316
Cd	0.12 - 5.5	1.9	0.5 - 7.4	0.78 - 17.8	0.15 – 21
Cr	1.75 - 34.2	38	1.2 - 29.5		-
Cu	0.06 -14.7	25.6	0.6 - 166		2.0 – 20
Ni	0.45 - 273	-	-		0.18 - 2.6
Pb	3.27 - 63	8.8	0.5 - 32.8		4.4 – 55
Zn	16.2 - 1794	96.5	8 - 635	124 - 3854	51.6 – 3878
Fraction	Total	<63um	<63um	Total	Total

[a] The values presented in the table are referent to the sum of extractions S1 and S2;

[b] Fizman et al. (1984) performed different weak extractions. The results presented here are referent to HCl 0.1M (16h at room temperature);

[c] Lacerda et al. (1987) applied the weak acid extraction with 0.1M HCl (24h at room temperature) in samples from different regions of Sepetiba bay;

[d] Monte et al. (2015) applied the extraction with 0.1M HCl (16h of agitation) in samples from nearby to Saco do Engenho Creek;

[e] Rodrigues et al. (2016) used the AVS/SEM extractions to recover trace metals in 6M HNO$_3$ (2h of agitation in room temperature).

Souza et al (1986) also observed trace metals distribution and associated phases in bottom sediments with sequential extractions method. The authors identified a mobility gradient of Cd towards the sea, which indicates, as observed in Marambaia bay (P01) recent layers, the presence of Cd in available forms in regions with higher salinity and pH. Copper and, mostly, Pb are also elements that can associated with the wastes from Ingá Cia (Barcellos, 1991), although the amount of these metals in available forms are lower than Cd and Zn (Figure 4.4.4).

Sulfides can be a relevant form of association in sub-oxic and/or anoxic regions of the system, as the northeast part of the bay, where mangrove areas, mud banks and low hydrodynamic regions can be found (Lacerda et al., 2004). As can be seen in figure 4.4.5, FeS$_2$ could be present in the bottom sediments. On the other hand, trace metals concentrations were very low in the sulfide crystalline fraction (S2). According to Huerta Diaz and Morse (1990) under anoxic conditions, Cd and Zn are immobilized, as sulfides, by cation exchange with Fe (II) or the surfaces of ferrous monosulfide substrates. Although the authors do not observed relation between the reactive fraction of Cd and Zn and the pyrite fraction.

The majority of trace metals is found in the exchangeable and oxihydroxides phases, associated to Mn (Figure 4.4.4 and table 4.4.1). Metals bound to easily reducible oxides can exchange with chemicals in the water column, while metals in poorly crystalline and crystalline oxides may be released to the pore water during early diagenesis and, subsequently, into the overlying water column (Turner, 2000).

Organic Matter phase does not seem relevant for the majority of samples and elements analysed. For copper the factorial analyses showed significant relation between this metal, carbon and sulfur. While for Zn, the OM fraction has been part of >30% of the samples in layers below 20cm at Marambaia bay (P01), mostly due to the alteration of Zn sources, once a natural element and after 1970, Zn becomes a contaminant. Zn is one of the most ubiquitous and mobile of trace metals and is transported in natural waters in both dissolved forms and adsorbed to suspended particles (Mance and Yates 1984). In an estuary, near the fluvial sources, zinc can be mobilized from particles by microbial degradation of organic matter, while in marine influenced regions, much of the zinc is found associated to inorganic and organic complexes (Mance and Yates 1984).

4.5. Conclusion

Total organic carbon and sulfur ratio results showed characteristics of a common marine environment for Marambaia bay, while São Francisco mouth presented lower ratio, indicating higher enrichment of organic material and euxinic characteristics. Sulfur are present in the sedimentary compartment mainly in inorganic form and showed a good correlation with Fe in the sulfide fraction, probably due to the presence of pyrite.

Trace metals contamination dilution was expected towards the mouth of the bay, with lower values at Marambaia bay. Mn oxy-hydroxides compose the mainly phase in the sequential extraction, which is considered an important scavenging for trace metal in the region. Factor analysis showed a good relation between Mn, Cd, Pb and Zn in the exchangeable and oxides fraction, which can be related to the same pollution source. On the other hand, Cu can be more related to organic matter phase. Cr and Ni presented good correlation with fine fraction (clay and silt), which can be associated with natural levels of these elements into bay's sediments.

The changes observed in the fractionation patterns near to SFC Delta can be related to remobilization of a deep package of sediments, leading to oxidation and exchanges between exchangeable reducing phases to the predominance of oxi-hydroxides forms for trace metals.

Once Ingá Cia. wastes has Cd and mostly Zn as marked tracers, which enables the pollution source identification, other trace metals such as Cr, Cu, Ni and Pb must be also monitored, due to the growth of industrial and harbor activities in Sepetiba bay basin, other point and non-point pollution sources for the system are expected.

Chapter 6

Final considerations

- In the data survey, the majority of Cd, Cu and Pb concentrations ranges between CONAMA Level 1 and Level 2, while Zn concentrations were frequently above Level 2 threshold. The high amounts of trace metals found into the bay are concerning. SQGQs indicate high environmental risk due to Cd, Cu and Zn levels. It was confirmed that Cd and Zn still are the metal contamination of major concern for sediments management in Sepetiba bay, due to their high concentrations and potential toxicity to aquatic living organisms. Copper showed hot spots arise, suggesting the impact of antifouling paints even in conservation areas, as Marambaia sandbank and surroundings.
- Marambaia bay area is a suitable place for chronology reconstruction, due to the sedimentary profile preservation with little reworking and the core reflects the processes occurring in Sepetiba bay watershed, as can be seen in the sedimentation rates enhancement concurrently with Paraíba do Sul-Guandu rivers diversion in the 1960's-1970's. Although, chronology in a disturbed area, such as São Francisco Channel delta is challenging. Nevertheless, the P05 core could provide information about events in the inner part of the bay, which has been occurring for the last 60 years, for instance the TKCSA establishment.
- The historical reconstruction of P05 core recovered only 60 years, due to the high sedimentation rate on a river mouth setting. Since trace metals contamination in Sepetiba bay northeast area started in the 1960's, a baseline layer for comparison was not available in the core.
- Signs of trace metals enhancement and changes in the grain size patterns can be found in the Marambaia sandbank coastline (P01, P02 and P03). Cu concentration appears as an emerging contaminant, despite its presence on Ingá Cia. residues (Ferreira, 2010; Barcellos, 1991), other point and non-point sources, as industrial residues from Santa Cruz Industrial district

and antifouling paintings containing copper oxides, might be collaborating with Cu enrichment in bottom sediments.

- Trace metals contamination dilution was expected towards the mouth of the bay, with lower values at Marambaia bay.
- Oxi-hydroxides compose the main phase in the sequential extraction, which is considered an important scavenging for trace metal in the region. However, sulfur showed a good correlation with Fe in the sulfide fraction, probably due to a predominant accumulation of pyrite that may be a secondary sink for trace metals.
- Once Ingá Cia. wastes have Cd and mostly Zn as markedly tracers, which enables the pollution source identification, other trace metals such as Cr, Cu and Pb must be monitored, due to the growth of industrial and harbor activities in Sepetiba bay basin, other point and non-point pollution sources for the system are expected to be important.
- A systematic and recurrent monitoring program has to be implemented. Mostly in sensitive regions as Marambaia Sandbank. Zn and Cd high concentrations from Ingá wastes can be masking other potential sources from the Santa Cruz industrial area in the Sepetiba bay watershed.
- Exchangeable fractions (as proxies for bioavailability) and environmental risk indexes should be considered as preferable tools to identify trace metals contamination implications on the bay environmental quality and to identify sensitive regions on monitoring programs and management plans environmental quality improvement.

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Appendix

Table 0.1. Detection limits, certified material concentrations, recovering for metals measurements in ICP-OES/MS in the sequential extractions.

	HF+HCl +HNO3	HNO3 + H2O2	BCSS - 1	Recovery SE	Recovery 3050B
Al	0.24	0.01	62610.00	4.85	23.48
Fe	0.01	0.01	32873.21	14.15	83.47
Mn	0.002	0.01	229.00	18.25	74.86
Cr	0.01	NQ	123.00	6.42	NQ
Cd	0.002*	0.001	0.25	160.00	ND
Cu	0.017*	0.01	18.50	40.00	93.51
Ni	0.021*	0.01	55.30	6.87	71.52
Pb	0.005*	0.01	27.70	76.61	56.68
Zn	0.051*	0.01	119.00	57.11	82.72

Table 0.2. Means, minimum, maximum and standard deviation for major and trace elements, organic matter, grain size. The bold values are above the CONAMA 454/2012 threshold.

	Marambaia bay (P01)				Guaratiba (P02)				Sandbank (P03)			
	Mean	*Min*	*Max*	*SD*	*Mean*	*Min*	*Max*	*SD*	*Mean*	*Min*	*Max*	*SD*
OM	5.38	2.58	8.21	1.68	2.86	0.66	8.23	2.36	6.71	2.38	11.8	3.25
Sand	64.7	56.2	73.3	5.71	73.6	47.4	97.7	21.4	35.3	17	50.9	13.1
Silt	25.4	19.1	34.4	5.14	12.9	1.07	27.3	10.6	40.2	28.6	58.9	11.1
Clay	9.82	7.54	12.2	1.40	13.8	1.09	26.7	11.4	24.5	17.6	29.7	3.80
Al	2489	1826	3352	515	2368	159	5697	1949	11000	3346	19194	5339
Fe	2371	1822	2695	309	2849	267	8165	2677	11091	6415	16020	3302
Cd	0.33	0.21	0.66	0.19	0.12	0.04	0.26	0.06	0.35	0.16	0.67	0.15
Cu	2.14	1.67	2.74	0.38	3.72	2.63	5.16	0.83	9.59	3.08	14.8	3.68
Ni	1.30	0.92	1.57	0.24	0.79	0.20	1.54	0.44	4.39	2.32	6.25	1.45
Pb	6.08	4.76	7.45	0.79	0.99	0.22	2.00	0.63	4.37	2.09	6.59	1.43
Zn	62.0	41.7	137	33.5	6.03	3.35	8.92	1.69	38.7	12.6	94.9	26.1

	Enseada das Garças (P04)				SFC Delta (P05)				Coroa Grande (P06)			
	Mean	*Min*	*Max*	*SD*	*Mean*	*Min*	*Max*	*SD*	*Mean*	*Min*	*Max*	*SD*
OM	15.5	10.8	26.3	4.64	14.7	9.53	22.1	3.68	7.89	1.43	13.3	3.99
Sand	4.91	0.00	12	4.28	18.1	8.03	47.9	10.8	34.4	6.76	77.4	19.0
Silt	64.1	55.8	74.4	4.96	66.7	47.7	72	6.69	50.2	16	66.3	16.0
Clay	31.1	25.6	35.9	2.90	15.2	4.39	21.5	4.71	15.4	6.52	29.1	7.81
Al	25900	16366	34364	5416	8145	5126	13669	2949	23217	6775	36064	11655
Fe	35715	26893	46675	5501	19472	14500	22577	2450	26091	7873	44943	14663
Mn	569	298	1140	263	515	219	964	227	174	38.4	322	99.3
Cd	0.56	ND	2.35	0.82	**3.06**	**1.22**	**5.59**	1.40	0.23	ND	**1.03**	0.35
Cu	10.7	5.07	18.8	4.14	27.5	23.8	32.5	2.32	9.81	2.93	16.0	4.81
Ni	9.54	7.40	12.2	1.49	2.90	2.53	3.80	0.34	5.87	1.81	10.8	3.41
Pb	12.6	9.17	20.4	3.47	39.2	23.5	78.4	17.2	9.26	3.19	12.6	3.59
Zn	110	43.8	**364**	112	**740**	**301**	**1868**	437	**191**	20.9	**393**	147

Table 0.3. Mass accumulation rates, sediment accumulation rates, 210Pb (Total and excess), 226 Ra values.

		MAR	Density	SAR (Alpha)	SAR (Gamma)	MAR (Alpha)	MAR (Gamma)	$^{210}Pb_{ex}$	$^{210}Pb_{tot\ gamma}$	^{226}Ra	$^{210}Pb_{tot\ alpha}$	$^{210}Pb_{Sup\ alpha}$
P01	Mean	0.90	2.14	0.44	0.40	0.95	0.85	52.49	103.22	50.73	73.62	21.13
	SD	0.17	0.04	0.09	0.09	0.18	0.17	57.19	59.85	8.09	57.91	9.16
	Max	1.18	2.21	0.59	0.51	1.26	1.10	148.55	216.13	67.57	181.00	32.45
	Min	0.77	2.06	0.39	0.33	0.82	0.71	6.01	45.56	38.30	28.56	0.00
P05	Mean	4.82	1.35	3.20	3.79	4.38	5.26	32.66	65.21	32.56	50.89	18.23
	SD	1.64	0.20	0.44	1.00	1.21	2.10	11.89	11.89	11.93	10.18	7.94
	Max	8.55	1.97	3.69	5.01	7.25	9.85	51.43	83.99	57.57	67.40	28.59
	Min	2.90	1.00	2.82	2.99	2.81	2.98	20.94	53.49	21.82	39.13	5.16

Table 0.4. Mass accumulation rates estimation for Guaratiba (P02), Sandbar (P03), Enseada das Garças (P04) and Coroa Grande (P06) from sedimentation rates from Borges et al. (2016) and Marques Jr et al. (2006). Density values are available in g cm^{-3}.

		MAR	Density
P02	Mean	0.53	1.33
	SD	0.02	0.05
	Max	0.56	1.39
	Min	0.49	1.23
P03	Mean	0.64	1.59
	SD	0.06	0.16
	Max	0.72	1.80
	Min	0.54	1.36
P04	Mean	1.29	1.59
	SD	0.56	0.05
	Max	1.93	1.68
	Min	0.77	1.52
P06	Mean	1.13	1.85
	SD	0.11	0.21
	Max	1.23	2.15
	Min	0.96	1.63

Table 0.5. Mean, standard deviation (SD), maximum and minimum values for geochemical variables (grain size, organic matter, total, inorganic and organic carbon, sulfur, density, mass accumulation rate (MAR)analyzed in sediment cores from Sepetiba bay.

	Marambaia Bay (P01)				**SFC Delta (P05)**			
	Mean	*SD*	*Max*	*Min*	*Mean*	*SD*	*Max*	*Min*
Sand (%)	64.75	5.71	73.33	56.18	18.13	10.77	47.89	8.03
Silt (%)	25.43	5.14	34.44	19.12	66.66	6.69	72.00	47.72
Clay (%)	9.82	1.40	12.19	7.54	15.21	4.71	21.51	4.39
O.M. (%)	5.38	1.68	8.21	2.58	14.69	3.68	22.08	9.53
Sulfur (%)	0.22	0.09	0.33	0.09	0.83	0.24	1.31	0.58
Sulfur (mg Kg^{-1})	428	169	630	164	1677	501	2740	1160
Density (g cm^{-3})	2.13	0.05	2.21	2.06	1.38	0.27	1.97	1.00
MAR (g cm^{-2} yr^{-1})	0.92	0.19	1.16	0.77	5.17	1.94	8.55	2.90
Total carbon (%)	0.58	0.10	0.70	0.39	1.84	0.64	3.10	1.20
Inorganic carbon (%)	0.21	0.19	0.61	0.00	0.47	0.45	1.64	0.00
Organic carbon (%)	0.41	0.20	0.70	0.12	1.38	0.61	2.40	0.08

Table 0.6. Mean, standard deviation (SD), maximum and minimum values for the sequential extraction fractions of Fe, Mn, Ni and Cr in the sediment cores from Marambaia bay (P01) and São Francisco Channel Delta (P05). The values are in mg Kg^{-1}.

		Exchangeables		**Easily reducible oxides**		**Poorly crystalline oxides**		**Organic Matter**		**Silicates**		**Sulfides**		**Total**	
		P01	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*
Fe	*Mean*	8.15	401.5	1041	12932	591.6	5057	432.1	363.2	212.6	449.4	85.8	268.6	2371	19472
	SD	8.64	156.3	165.9	1696	98.4	823.5	129.4	58.7	26.2	39.1	39.7	154.2	289.5	2346
	Max	29.2	706.9	1331	14984	735.1	6609	741	493.1	251.4	541.4	139.1	649.9	2695	22577
	Min	2.56	219.2	714.3	9339	442.4	3956	293.2	241.3	167.5	391.4	24.2	97.7	1822	14500
Mn	*Mean*	46.4	342	49.2	125.2	12	41.1	2.71	3.08	2.12	2.89	1.03	1.1	113.3	515.3
	SD	19.4	176.6	8.13	40.2	2.32	7.55	0.61	0.38	0.21	0.45	0.73	1.33	22.5	217.7
	Max	84	721.2	63.1	179.7	15.7	56.6	3.75	3.64	2.4	3.51	2.33	4.88	150.2	964.8
	Min	29.6	94	39	59.8	9.18	25.9	1.91	2.38	1.68	2.13	0.02	0.35	91.1	219.7
Ni	*Mean*	0.24	0.52	0.48	1.41	0.11	0.46	0.28	0.1	0.14	0.34	0.05	0.05	1.3	2.9
	SD	0.06	0.24	0.12	0.19	0.07	0.13	0.07	0.05	0.04	0.02	0.02	0.01	0.23	0.33
	Max	0.37	1.05	0.66	1.68	0.2	0.79	0.39	0.16	0.23	0.39	0.1	0.08	1.57	3.8
	Min	0.16	0.16	0.29	1.03	0.03	0.27	0.18	0.01	0.09	0.31	0.03	0.03	0.92	2.53
Cr	*Mean*	0.37	1.35	1.8	15.02	1.38	6.77	0.95	2.15	0.37	0.87	0.33	0.43	5.21	26.59
	SD	0.013	0.53	0.26	5.52	0.2	1.87	0.24	0.69	0.06	0.07	0.06	0.13	0.64	8.4
	Max	0.39	2.78	2.2	31.44	1.65	12.17	1.56	4.18	0.45	1.02	0.39	0.77	6.15	51.82
	Min	0.34	0.74	1.41	9.12	1.13	5.08	0.78	1.28	0.27	0.77	0.24	0.35	4.35	18.26

Table 0.7. Mean, standard deviation (SD), maximum and minimum values for the sequential extraction fractions of Fe, Mn, Ni and Cr in the sediment cores from Marambaia bay (P01) and São Francisco Channel Delta (P05). The values are in mg Kg^{-1}. Numbers in bold are above level 1 and italic represent concentrations above level 2, thresholds of CONAMA 452/2012.

		Exchangeables		**Easily reducible oxides**		**Poorly crystalline oxides**		**Organic Matter**		**Silicates**		**Sulfides**		**Total**	
		P01	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*	*P01*	*P05*
Cu	*Mean*	0.1	3.4	0.33	8.87	0.87	10.5	0.38	3.61	0.07	0.23	0.44	0.92	2.14	27.6
	SD	0.14	0.35	0.25	1.04	0.27	1.34	0.01	0.37	0.04	0.08	0.15	0.2	0.36	2.22
	Max	0.44	4	0.77	10.7	1.43	13.2	0.4	4.4	0.16	0.39	0.64	1.19	2.74	32.5
	Min	0.02	2.85	0.04	7.59	0.57	8.35	0.36	3.19	0.04	0.11	0.25	0.55	1.67	23.8
Pb	*Mean*	1.14	4.35	3.85	28.3	0.4	5.7	0.35	0.32	0.32	0.48	0.07	0.14	6.08	39.2
	SD	0.56	1.62	0.46	12.6	0.22	2.93	0.22	0.25	0.17	0.29	0.01	0.03	0.73	16.4
	Max	2.04	7.09	4.66	55.9	0.68	14.6	0.79	0.72	0.55	0.93	0.09	0.19	7.45	**78.4**
	Min	0.24	2.41	3.03	15.7	0.14	3.03	0.09	0.02	0.03	0.09	0.04	0.1	4.76	23.5
Cd	*Mean*	0.09	2.62	0.15	0.33	0.04	0.06	0.04	0.04	ND	ND	0.001	0.001	0.33	**3.06**
	SD	0.06	1.3	0.12	0.07	0.003	0.01	0.003	0.003	-	-	0.001	7 X 10-4	0.17	1.34
	Max	0.2	5.15	0.38	0.4	0.04	0.09	0.04	0.05	ND	ND	0.003	0.002	0.66	**5.59**
	Min	0.05	0.91	0.07	0.2	0.03	0.05	0.03	0.04	ND	ND	ND	ND	0.21	**1.22**
Zn	*Mean*	6.13	391.9	29.8	296	8.12	32.2	17.2	18.3	0.42	1.47	0.37	0.71	62	*740.6*
	SD	9.5	292.5	21.1	129.2	1.38	12	0.9	1.56	0.07	0.26	0.01	0.39	31.3	419.2
	Max	28	1134.6	81.2	659.9	10.7	59	18.7	20.7	0.5	2	0.39	1.75	137.6	*1868.5*
	Min	0.37	44.1	15.8	195.3	6.36	19.1	15.9	15	0.3	1.08	0.34	0.36	41.7	**301.5**

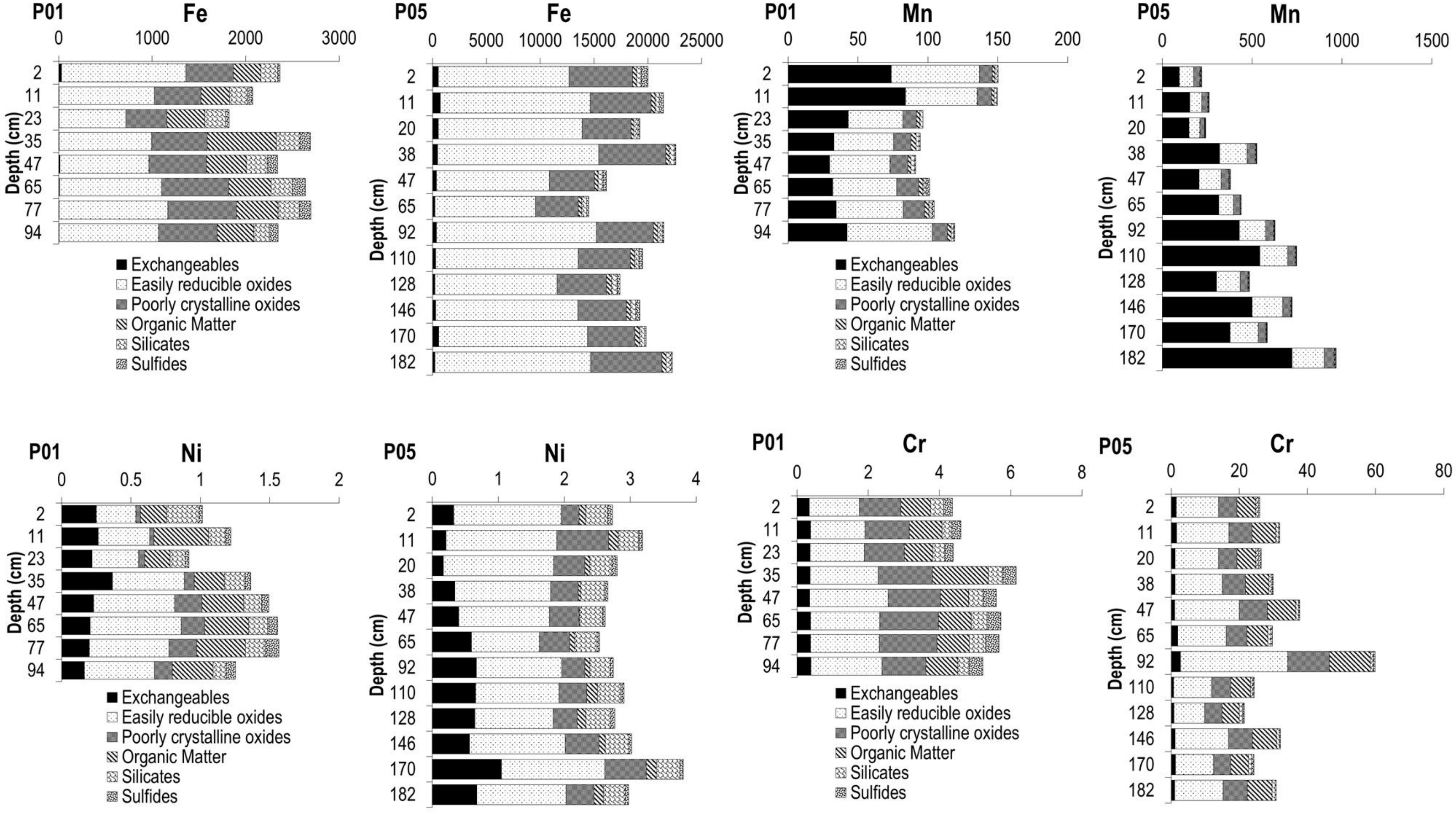

Figure 0.1. Concentrations in mg Kg-1 of Fe, Mn, Cr and Ni in the sequential extraction performed on Marambaia bay (P01) and SFC Delta (P05).

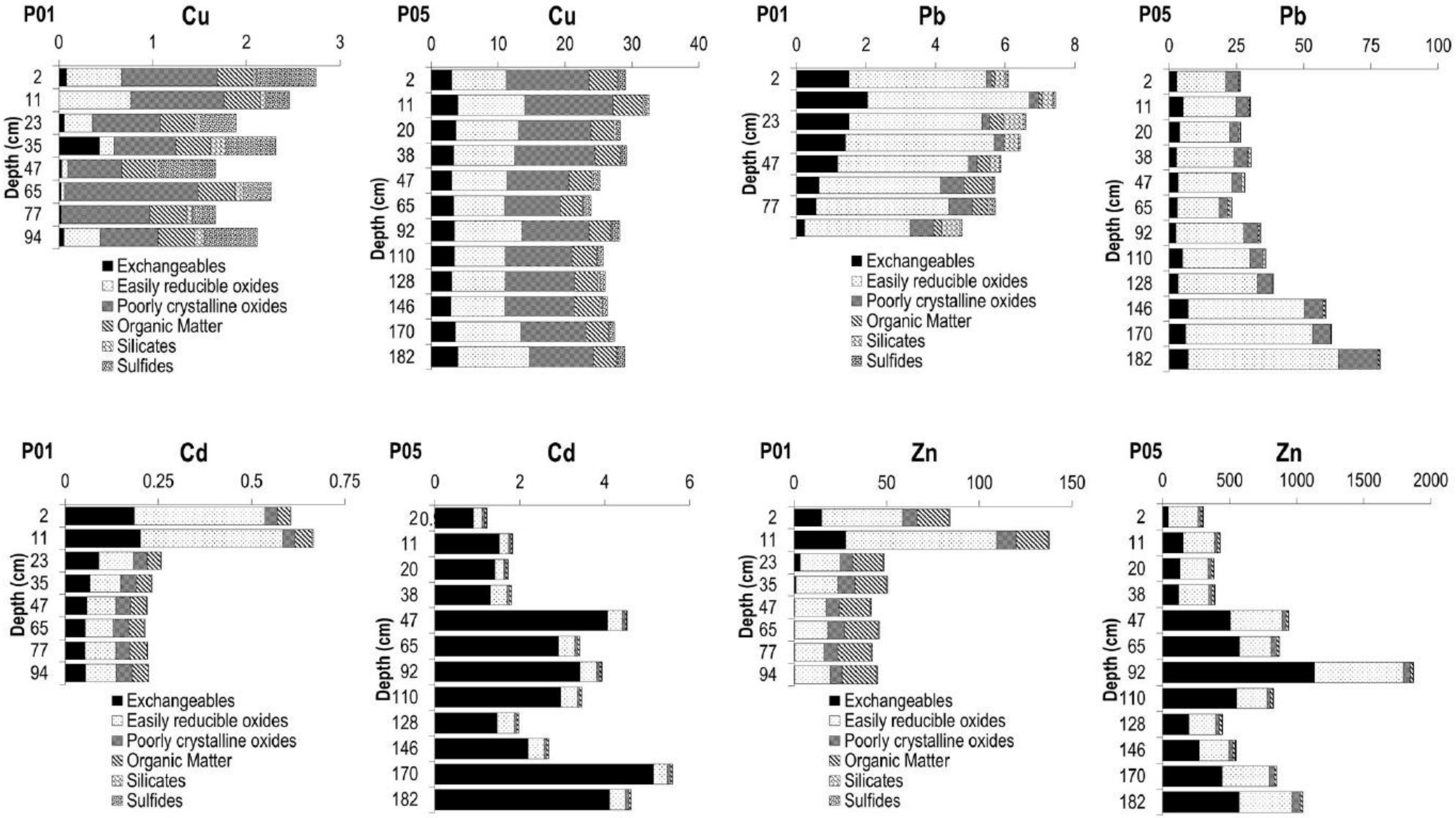

Figure 0.2. Concentrations in mg Kg-1 of Cu, Pb, Cd and Zn in the sequential extraction performed on Marambaia bay (P01) and SFC Delta (P05).