Analysis of sediment quality in the Port of Rio de Janeiro channel: considerations about sampling methods indicated by Brazilian resolutions

Análise da qualidade do sedimento no canal do Porto do Rio de Janeiro: considerações sobre os métodos de coleta indicados pelas resoluções brasileiras

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Abstract

The environmental impacts caused by dredging and disposal of the removed sediment may cause direct and indirect effects on ecosystems and organisms. Therefore, dredging activities in Brazilian ports must follow the requirements of the regulations established by the national environmental council (with the Portuguese acronym CONAMA) in order to standardize the characterization of the sedimentary package of the area to be dredged. According to CONAMA Resolution 454/2012, two different sampling methods can be used: simple sampling or composite sampling. This study aims to analyze the results of both sediment sampling methods in the same area, through the analysis of the concentration of contaminants in the samples, to contribute to the discussion of the methodological choice of environmental quality monitoring that best suits the Brazilian context. For this purpose, two sediment sampling campaigns were carried out in the navigation channel of the Port of Rio de Janeiro, in Guanabara Bay (RJ). In the first and second campaigns, the simple and composite methods were employed respectively. The concentration of contaminants was analyzed considering firstly the different individualized variables and then correlation of the variables, using the principal component analysis (PCA). The simple sampling showed concentrations, in general, higher than the composite sampling. The principal component analysis indicates a correlation between metals, aromatic polycyclic hydrocarbons and total organic carbon, for both sampling methods, however, it exhibits the highest concentrations in the sample collected using the simple method. The concentrations of total nitrogen and total phosphorus showed a correlation with sedimentation related to the greater presence of fine sediments. It was found that the simple method better preserves the characteristics of the samples, thus being more compatible with the represented environment.

Keywords: Dredging; Guanabara Bay; contamination; heavy metals; PAHs.

Resumo

Os impactos ambientais causados por obras de dragagem e disposição do sedimento removido podem ocasionar efeitos diretos e indiretos em ecossistemas e organismos. Dessa forma, as atividades de dragagem nos portos brasileiros devem seguir os requisitos das regulamentações estabelecidas pelo Conselho Nacional do Meio Ambiente (CONAMA), com o intuito de normatização a caracterização do pacote sedimentar da área a ser dragada. De acordo com a resolução CONAMA 454/2012 podem ser realizados dois métodos distintos de coleta, sendo a coleta simples ou a coleta composta. Este estudo tem por objetivo analisar os resultados de ambos os métodos de coleta de sedimentos em uma mesma área, através da concentração de contaminantes das amostras, a fim de contribuir na discussão da escolha metodológica de monitoramento ambiental que mais se adeque ao contexto brasileiro. Para tal, foram realizadas duas campanhas de coletas de sedimentos no canal de navegação do Porto do Rio de Janeiro, na Baía de Guanabara (RJ). A primeira coleta utilizou o método simples e a segunda coleta, o método de amostragem composta. Os dados de concentração de contaminantes foram analisados primeiro através das diferentes variáveis individualizadas e depois através da inter-relação das variáveis, utilizando a análise de componentes principais (PCA). A coleta simples apresentou concentrações, em geral, mais elevadas do que a coleta composta. A análise de componentes principais aponta uma correlação entre metais, hidrocarbonetos policíclicos aromáticos e carbono orgânico total, para ambos os métodos de coleta, entretanto, aponta as maiores concentrações para a coleta simples. As concentrações de nitrogênio total e fósforo total apresentaram inter-relação com sedimentação relacionada à maior presença de finos. Verificou-se que o método simples conserva melhor as características das amostras, sendo então, mais compatível com o ambiente representado.

Palavras-chave: Dragagem; Baía de Guanabara; contaminação; metais pesados, HPAs.

1. Introduction

Dredging works are common and necessary in port areas (IADC 2010), due to the accumulation of sediments in coastal water bodies, especially in estuaries and bays. In these environments, the natural deposition of sediments occurs since they are generally confined environments and have low hydrodynamic energy (Figueiredo et al. 2014).

The disposal of dredged material is one of the most common problems in terms of coastal management. Environmental impacts caused by the dredging process and the disposal of the removed sediment have direct effects on ecosystems and organisms, or indirect effects relative to changes in water quality (Kennish 1994; IADC 2010; Filho 2004). Examples of direct impacts include the destruction of benthic habitats, resulting in the mortality of these organisms through injuries caused by mechanical action during dredging or burial in the dump area (Angonesi et al. 2006). Regarding the indirect effect, the remobilization of the bottom sediment and the release of contaminants and nutrients can deteriorate water quality and change the geochemistry of the water body (Ferreira et al. 2013), both in the dredged area and in the disposal area of the dredged material.

According to Alloway and Ayres (1997), studies on sediments deposited on seabed play an important role in the assessment of contaminants. This kind of study can infer both the current and historical quality of the aquatic system (if samples are analyzed in depth). In addition, such studies can indicate the presence of contaminants and the period the contamination occurred, also taking into consideration the historical, environmental and social contexts. The high concentration of heavy metals, pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, among other chemical compounds, can be potential sources of contamination (IMO 1972). When these contaminated sediments are remobilized during dredging interventions, the contaminants can be made available again in the water column, through variations in geochemical processes such as changes in pH, redox potential, or the presence of organic chelators (Lemes et al., 2003).

As a result, there was a need to establish guidelines and procedures for the proper management of dredging, including national reference values for the classification of dredged materials (Frohlich et al., 2015).

In 2004, the Brazilian Environment Council (with the Portuguese acronym CONAMA) approved the first standard for the analysis of dredged material: the CONAMA Resolution nº 344/2004 (BRASIL 2004). This resolution prompted a review of the national guidelines established for the classification of dredged material. This review resulted in the publication of the CONAMA Resolution nº 454/2012 (BRASIL 2012) where a second sampling method was proposed, in addition to the former method already presented in the previous resolution. Currently in Brazil, CONAMA Resolution 454/2012 also establishes the criteria for the evaluation of dredging tailings and their disposal in water bodies (Frohlich et al. 2015). Thus, the present study was elaborated to evaluate the simple and composite sampling methods of dredged material.

In the present work, we will discuss the sediment sampling methods carried out on the sea access route to the Port of Rio de Janeiro, an area that requires periodic dredging to maintain the navigable channel.

This study aims to analyze the contaminants in sediment samples obtained through the two sample methods established in the CONAMA Resolution 454/2012, in order to contribute to the discussion of the best methodological choice for the monitoring of environmental quality.

2. Study Area

The study area consists of the access channel to the container terminal of Port of Rio de Janeiro, located in the municipality of Rio de Janeiro (Brazil), on the west bank of Guanabara Bay (Figure 1). Between 2016 and 2017, a dredging for deepening the channel was performed in a stretch of the access channel to Port of Rio de Janeiro with the removal of a total volume of approximately 2.900.000 m³. To license this activity, the state environmental inspection agency required a preliminary study on the conditions of the sedimentary package to be dredged and to define its disposal site. The sediment material of this area was characterized by Godoy et al. (2012) as fine sandy and silty-clay sediments.

The Guanabara Bay - located in the state of Rio de Janeiro (Brazil) – has a drainage basin of approximately 11,000 km², with several tributaries contributing to its flow, which reaches 150 m³/s with an exchange rate of about 10% with the ocean (Perin et al. 1997). The Guanabara Bay connects to the Atlantic Ocean and has a semicircular shape, extending 30 and 28 km in the N-S and E-W axes respectively.

This bay has been impacted over the years by anthropogenic activities, such as the installation of industries and the discharge of industrial effluents; the disordered occupation of its surrounding area and the discharge of domestic effluents, dumping of solid waste or its carrying by rain; port activities; among other factors (Ternes 2019; Silveira et al. 2017). As a result, large amounts of pollutants are discharged directly into the bay and its tributaries increasing the contamination and toxicity in sediments. According to Godoy et al. (2012) and Soares-Gomes et al. (2016), the sedimentation rate has steadily increased since 1922 (0.14 cm/year), doubling in the last 5 years, from 0.60 cm to approximately 1.25 cm/year.

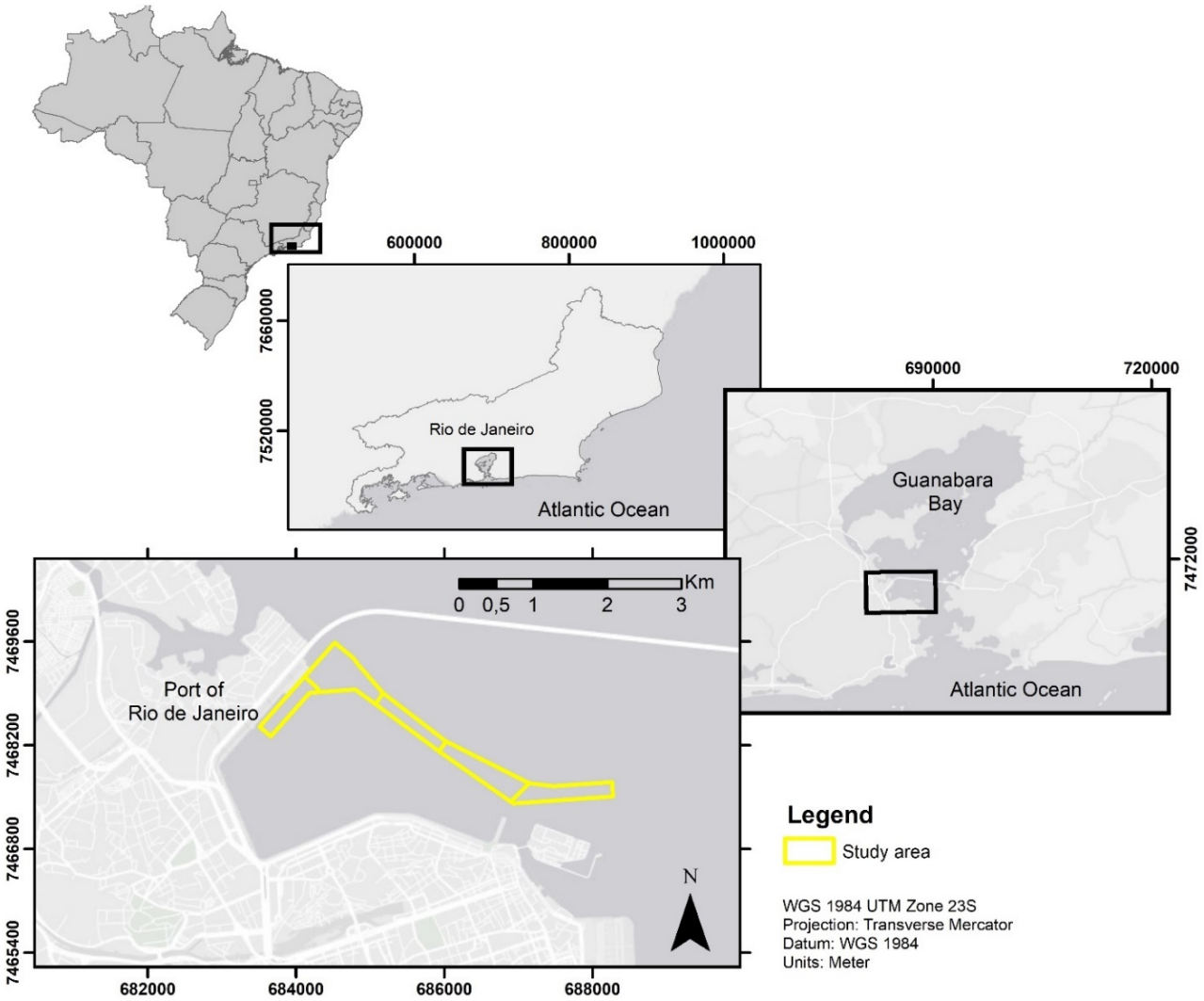

Figura 1. The study area (yellow) corresponds to the access channel to the container terminal of the Port of Rio de Janeiro, located in Guanabara Bay - Brazil.

3. Methodology

3.1 Sediment sampling

Two sediment sampling campaigns were carried out to characterize the area to be dredged in Guanabara Bay. In each campaign, only one sampling method was employed following the guidelines in CONAMA Resolution 454/2012.

The following acronyms were used to refer to the campaigns and their respective sampling method: “S” refers to the simple sampling points; “C” refers to the areas of composite sampling. It is important to note that the distribution of sampling mesh points was different in each campaign but distributed in the same area of this section of the access channel to the container terminal.

The first campaign was carried out in September 2015 using the simple sampling, which consists of a punctual sediment sampling. The distribution of points can be seen in Figure 2a.

During the simple sampling, the sediment was collected using a stainless steel Van Veen dredge and poured into a container. Each sample was stored in a properly labeled plastic bag. After obtaining the samples, they were packed in isothermal boxes at 4º C.

The second campaign was carried out in February 2016 and used the composite sampling, which consists of collecting sediment samples in a composite manner, where a small area represents a sampling point, and three sub-samples are collected there. (Figure 2b).

In the composite sampling, two types of depth samplers were used, the gravity corer and the sword corer. This sword corer was used by a diver in case the gravity corer could not penetrate a hard and compact substrate. Thus, with both tools, samples were collected representing the surface and subsurface layers of the bottom of the area to be dredged. To obtain the final

sample at each point, from the three sub-samples collected, an amount was collected from each sampled horizon. These sub-samples were poured into a stainless-steel container, mixed, and finally a portion was collected after homogenization. The plastic pastry used in the campaigns was properly prepared and labeled beforehand. In both campaigns, the sediment samples were properly stored in thermal containers and kept refrigerated to maintain their characteristics.

In both campaigns, the samples were sent to laboratories certified by the Brazilian Metrology, Quality and Technology Institute (with the Portuguese acronym INMETRO), to analyze the substances and parameters described in CONAMA Resolution 454/2012. The equipment cleaning during the sediment sampling and the conditioning and preservation of the samples followed the specifications of the Standard Methods for the Examination of Water and Wastewater, (APHA 2005), Methods for Collection, Storage and Manipulation of Sediments (U.S. EPA (2001) and the National Guide for Sample Collection and Preservation (ANA 2011).

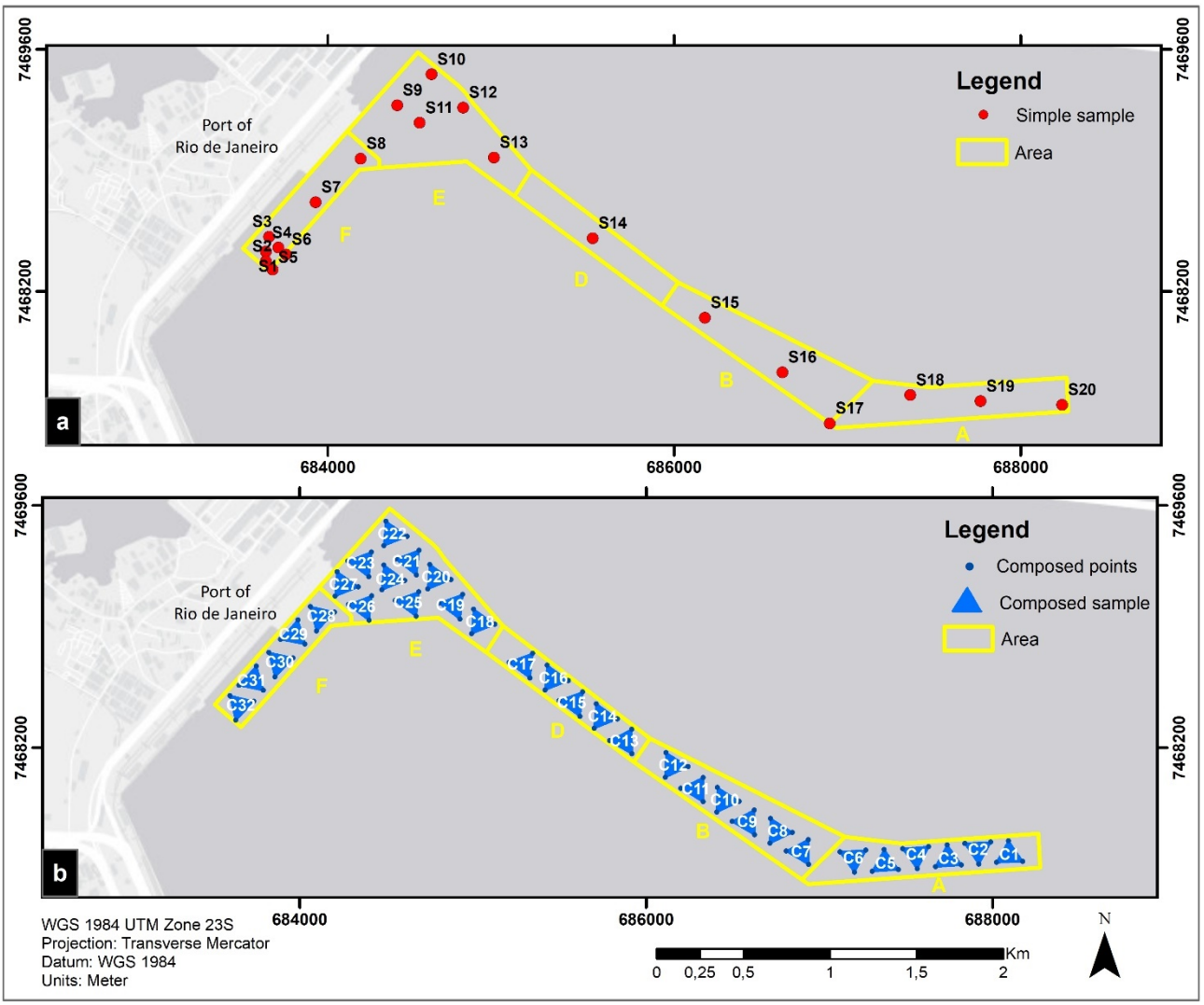

Figura 2. Characterization points of the sedimentary package to be dredged. a) Simple sampling points (S); b) Composite sampling points (C).

3.2 Laboratory sediment analysis

For both campaigns, the substances and parameters analyzed in the laboratory in the marine sediment samples were those listed in CONAMA Resolution 454/2012: Polychlorinated Biphenyls (PCBs); Organochlorine Pesticides; Tributyltin (TBT); Heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb e Zn); Polycyclic Aromatic Hydrocarbons (PAHs); Total Organic Carbon (TOC); Nutrients like Total Phosphorus (P_{Tot}) and Total Kjeldahl Nitrogen (N_{Tot}) and sediment granulometry. This resolution also establishes alert and borderline reference values for each substance, in order to guide the analysis in relation to the toxicity to the marine aquatic biota and avoid its contamination. Level 1 refers to the threshold below which there is a low probability of adverse effects to biota, and level 2 refers to the threshold above which there is a high probability of adverse effects to biota.

Table 1 shows only the analytes used in this study, besides the unit of measurement of results; the limit of detection and quantification of the method; the certified concentration of the standard; the concentration obtained with their respective recovery percentages. All

data within the recovery range were considered as satisfactory. Table 1 also briefly presents the analytical methodology used.

Table 1. Analytical quality and laboratory methodology.

Analyte	Units	Detection limit	Quantification limit	Certified	Obtained	% recovered	Methodology
N_{Tot}	mg/Kg	1.00	2.00	5.00	4.91	98.3	N-NH_3+ N-Organic Micro-kjeldahl/Colorimetry
Ar	mg/Kg	1.00	2.00	20.14	19.66	97.6	Determination of total metals by ICP-OES (Inductively coupled plasma - Optical Emission Spectrometry)
Cd	mg/Kg	0.10	0.20	19.73	19.73	100.0	
Pb	mg/Kg	0.40	1.00	35.57	35.57	100.0	
Cu	mg/Kg	0.10	0.20	27.90	27.90	100.0	
Cr	mg/Kg	0.10	0.30	41.61	41.84	100.6	
Hg	mg/Kg	0.02	0.05	9.77	9.68	99.1	
Ni	mg/Kg	0.40	1.00	28.39	29.40	103.5	
Zn	mg/Kg	0.40	1.00	41.46	41.46	100.0	
P_{Tot}	mg/Kg	1.00	6.00	19.00	22.00	115.8	Digestion 4500-P (E)
TOC	%	0.10	0.20	_	_	_	Catalytic Combustion Oxidation
PAHs	µg/Kg	1.70	5.00	_	_	_	GC-MS (gas chromatography/ mass spectrometry)
PCBs	µg/Kg	1.70	5.00	_	_	_	GC-MS (gas chromatography/ mass spectrometry)/Ultrasonic extraction
Organochlorine pesticides	µg/Kg	0.10	0.30	_	_	_	GC-MS (gas chromatography/ mass spectrometry)
TBT	µg/Kg	1.34	1.34	_	_	_	Standard Methods 6710

3.3 Statistical methodology

The normality of the data obtained was tested using the Kolmogorov-Smirnov /QQ-plot, while the homoscedasticity was tested using the Brown-Forsythe test (Zar, 2010). The assumptions for using parametric analysis were satisfied after the exclusion of outliers (±3* standard deviation) and logarithmic transformation of values (log10). The equality hypothesis (H0) between the mean values of the sediment samples was tested using the unpaired t-Student (independent samples) for samples of different sizes at a level of significance $\alpha = 0.05$.

Additionally, a statistical technique was applied through the ordering in factor axes for the main variables to assess the most relevant correlations. This multivariate test is referred to as Principal Component Analysis (PCA), allowing the visualization of the interrelationships of the variables (Sabino et al., 2014). Only the components that presented eigenvalue > 1 were considered as recommended by Reid et al. (2009), to avoid the influence of outliers. Pearson's correlation matrix was the most adequate basis for the analysis of the main components (Senez-Mello et al., 2020).

All steps described in the statistical methodology were performed using the software Statistica v.13 TIBCO Software Inc. (2018).

4. Results and discussion

The database with absolute values used in this study are shown in Table 2.

In most cases, detectable/quantifiable concentrations of PCBs, organochlorine pesticides and TBT were not found in the samples in both campaigns. Among the few samples with some concentration of these substances, all had values much lower than level 1, thus being irrelevant for this research. The same occurred with Hg and Cd concentrations.

Table 2 - Concentration of parameters and substances in the sediment samples from both campaigns.

Sample	Mud	N_{Tot}	TOC	P_{Tot}	As	Pb	Cu	Cr	Ni	Zn	∑ PAHs
CONAMA 454/12	**%**	**4800**	**10%**	**2000**	**70**	**218**	**270**	**370**	**51.6**	**410**	**4000**
S01	91.3	1950.7	4.9	669.9	16.9	118.7	141.6	102.1	37.6	325.9	7251.6
S02	59.8	428.3	5.0	481.2	16.5	247.6	179.5	112.7	41.4	570.6	13671.7
S03	35.8	1261.3	3.9	490.9	17.0	118.9	134.7	102.8	38.3	249.6	6567.6
S04	19.7	625.9	0.8	66.5	16.6	117.6	125.3	83.3	32.5	111.0	2046.0
S05	66.7	643.7	3.4	547.6	14.1	134.0	121.8	93.0	38.4	407.2	5433.2
S06	73.9	357.0	1.7	321.1	12.1	91.9	82.9	73.3	30.6	211.9	9756.0
S07	24.9	606.7	0.5	41.0	15.0	93.1	55.5	61.8	26.7	82.9	680.4
S08	66.0	344.3	1.8	277.1	16.0	91.4	317.2	104.0	42.7	237.6	2104.0
S09	41.3	218.1	1.4	187.3	14.2	73.0	74.0	87.9	35.8	106.3	769.6
S10	85.5	1427.3	3.8	526.6	15.6	86.6	99.5	92.4	33.9	219.7	1431.0
S11	39.9	468.6	1.7	178.3	14.6	78.3	78.2	88.3	35.4	291.2	1668.3
S12	81.6	588.8	2.3	308.4	12.0	63.5	61.7	69.8	27.8	218.5	1879.0
S13	42.1	572.0	2.3	353.8	13.8	73.7	74.5	75.0	27.7	275.3	3381.4
S14	55.6	1011.1	3.2	141.8	17.7	106.6	96.2	100.7	35.2	397.7	3495.3
S15	20.0	1065.4	1.7	242.9	31.5	373.1	106.4	90.9	37.7	100.1	10668.9
S16	27.9	1035.7	1.8	217.1	24.5	231.0	101.5	99.6	39.2	536.9	1553.8
S17	65.1	226.4	1.1	102.6	171.4	717.0	854.8	616.4	333.8	209.6	901.7
S18	36.4	205.1	1.0	114.6	183.1	668.1	725.9	782.9	296.2	240.8	1585.2
S19	16.6	266.0	1.3	183.7	197.0	645.4	567.0	764.7	302.5	219.0	1962.5
S20	59.0	238.0	3.7	219.0	769.7	402.9	82.0	159.3	186.6	247.3	3601.6
C01	52.9	3063.6	2.2	331.0	4.4	16.0	13.9	24.4	9.5	69.8	478.2
C02	45.6	2560.1	2.0	397.5	3.9	12.9	13.6	22.3	8.6	64.2	443.8
C03	38.0	1686.4	1.6	291.6	4.9	16.0	14.8	26.1	10.0	75.7	345.3
C04	31.2	275.9	1.6	218.3	4.5	14.1	12.5	23.8	9.1	66.7	305.0
C05	32.5	1611.6	1.5	215.0	3.4	32.0	12.5	22.1	7.7	70.7	472.5
C06	36.9	1295.7	1.4	231.6	4.8	19.2	14.4	25.5	9.2	81.0	465.6
C07	49.5	1339.9	1.2	299.2	5.1	10.8	9.0	25.4	9.5	50.1	60.5
C08	56.4	76.4	1.1	285.7	5.1	10.9	11.7	28.8	10.4	50.1	77.1
C09	34.6	1758.7	1.7	279.9	5.8	47.2	26.8	23.8	8.9	227.5	980.1
C10	33.9	1592.2	1.7	277.5	5.5	32.2	35.7	24.3	9.3	97.3	1809.7
C11	43.1	2075.9	2.7	290.1	4.4	25.5	17.2	20.0	7.5	79.0	399.8
C12	35.5	2097.0	1.6	332.8	4.1	17.3	15.6	18.5	7.2	77.5	167.9
C13	43.9	1465.2	2.4	378.2	4.2	20.8	21.5	22.8	8.2	92.9	313.2
C14	44.8	1149.7	2.3	297.7	4.1	20.9	21.5	22.7	8.3	92.8	0.0
C15	47.1	1651.3	2.1	345.1	4.7	19.4	22.3	23.8	8.8	83.3	143.3
C16	87.1	3050.9	4.3	736.8	6.3	26.9	35.2	32.8	12.2	124.7	151.0
C17	84.5	4539.2	4.2	661.0	5.8	26.2	34.1	32.2	12.0	121.8	291.7
C18	91.8	2158.5	4.0	911.5	7.4	31.7	42.6	38.6	14.0	145.1	201.1
C19	94.6	2995.5	4.1	903.9	7.0	30.6	41.6	37.6	13.7	142.2	61.2
C20	88.9	3872.1	3.9	920.3	8.0	35.0	47.8	42.5	15.4	160.8	319.7
C21	67.9	333.4	1.6	1019.1	5.0	9.1	7.4	18.5	6.9	35.7	19.9
C22	63.4	1538.9	1.1	363.8	7.5	19.2	20.0	32.9	12.6	80.9	43.9
C23	60.4	1251.7	1.0	331.0	4.2	19.3	21.9	24.7	10.6	73.4	75.4
C24	62.2	2637.1	2.3	325.7	4.6	19.9	23.4	23.7	9.5	102.4	110.3
C25	43.3	2825.1	0.3	645.2	3.2	16.3	7.8	26.0	7.7	41.8	560.6
C26	46.1	3472.1	2.6	626.0	5.4	24.2	27.3	26.7	10.6	118.1	132.5
C27	56.9	2519.8	2.2	460.6	4.4	21.2	27.4	26.3	10.7	111.8	249.8
C28	53.5	2418.4	2.2	646.0	5.4	22.2	27.1	28.3	11.4	117.3	208.4
C29	76.7	1306.2	1.7	354.5	6.1	15.9	15.8	24.9	9.6	67.1	266.3
C30	84.8	2044.6	1.7	462.6	6.1	15.8	15.9	24.5	9.5	67.8	75.4
C31	76.6	2744.0	2.5	572.3	5.3	30.8	34.3	27.1	10.6	126.8	1267.1
C32	68.9	2302.9	2.4	492.7	5.1	30.4	33.5	27.9	10.6	125.0	599.3

In most cases, detectable/quantifiable concentrations of PCBs, organochlorine pesticides and TBT were not found in the samples in both campaigns. Among the few samples with some concentration of

these substances, all had values much lower than level 1, thus being irrelevant for this research. The same occurred with Hg and Cd concentrations.

The results of the laboratory analysis of contaminants in sediments are shown in the figures below. The TOC, PTot and NTot parameters did not exceed the levels established in CONAMA Resolution, therefore, they are not shown.

The granulometry analysis of the samples is shown in Figure 3. The CONAMA considers only the sum of the percentage of silt and clay, therefore, in this study, this portion is referred to as mud.

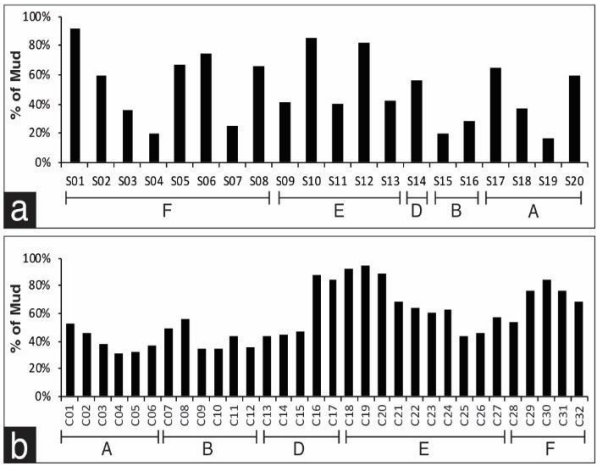

Figure 3 - Percentage of silt and clay in the stretches of the sampled area.

Figure 4 presents the sum of the PAHs values for the a) simple and b) composite samplings.

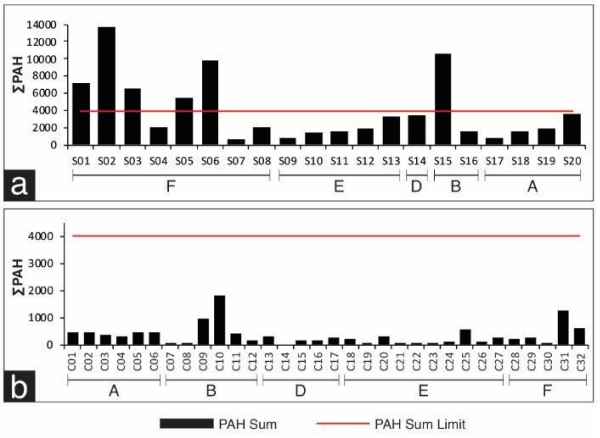

Figure 4 - PAHs concentrations in the sediment obtained in both campaigns - a) simple / b) composite samplings.

Note that in Figure 4b, referring to the composite collection, the sum of the analyzed PAHs values did not reach the maximum allowed level. In Figure 4a, however, 6 samples exhibited values above the limit established by CONAMA Resolution. It is noticed that most of simple samples with high concentrations of PAHs (S1, S02, S03, S05 e S06), were found in area F, the innermost portion of the channel, in the mooring area (Figure 2a).

It is known that the main sources of PAHs in urbanized areas are generally industrial effluents, discharge of domestic sewage and storm drainage, incineration of solid waste, oil spills, asphalt production, creosote and atmospheric deposition through the burning of fossil fuels (Kennish 1996).

According to Resende (2012), most of the PAHs found in aquatic environments are in rivers and coastal waters, remaining relatively close to their sources of contamination and decreasing with the distance from the source. Therefore, it is assumed that the high values obtained in the simple samples near Porto, come from the drainage of the Mangue Channel, a river with highly urbanized surroundings, influenced by the sources mentioned above and with visibly polluted waters (Duarte & Peixoto 2012; Rezende 2018). The Mangue Channel is the junction of Maracanã, Comprido, Joana and Trapicheiros rivers (Borges, 2013).

Christensen et al. (2010)'s study on the distribution of PAHs in Guanabara Bay showed that, among the samples collected at various points across the bay, the one collected in the port area exhibited the highest concentration of PAHs, which is in good agreement with the present study considering the samples collected using the simple sampling method.

Regarding heavy metals in sediments, Figures 5 and 6 show the metal concentration in the sediment and the lines that correspond to the levels of alertness and toxicity established by CONAMA Resolution 454/12, where level 1 (yellow) indicates the threshold below which there is a lower possibility of contamination of the biota, and level 2 (red) indicates the threshold above which there is a greater possibility of contamination of the biota.

These limits (Table 3 - Comparison of analyte values between sampling methodsTable 3) are fundamental for the characterization of the sedimentary package to be dredged, as these are reference values for the evaluation of alternatives for the disposal of dredged sediments in waters under national jurisdiction.

Figure 5 shows that, in area A (Figure 2), metal concentrations above level 2 were observed in most simple samples, mainly at S17, S18, S19, except for Zn. In this case of Zn concentrations, the highest values were distributed among the sample points of the study area.

In Figure 6, it is important to highlight that the concentrations of heavy metals in the sediments did not even reach level 2 in any sample collected using the composite sampling method.

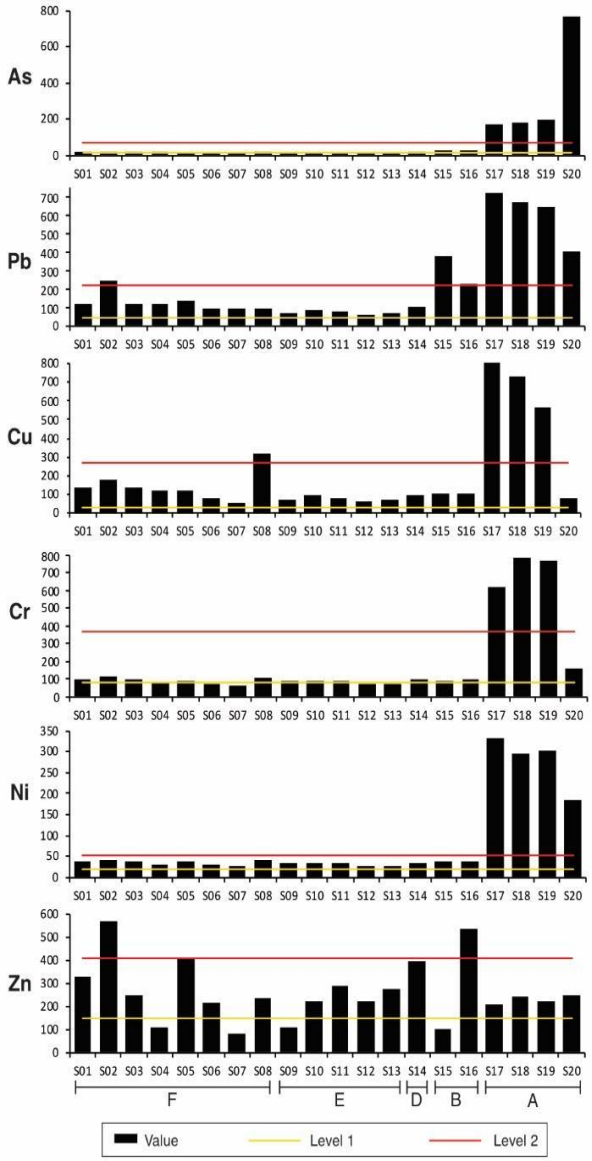

Figure 5 – Concentrations of metals in the sediment obtained by the simple sampling method.

These results indicate that the composite sampling tends to underestimate the contaminant concentration in the final sample due to the homogenization of the sub-samples. Therefore, using the composite sampling, satisfactory values are likely to be found for most of these analytes, without the need for ecotoxicity studies on biota and thus allowing the disposal of contaminated material in the predetermined marine environment (Silveira 2016).

Table 3 presents the mean concentrations and their respective standard deviations for the two sampling methods (S to Simple and C to Composite) in the sediment samples collected in the study area, as indicated in Figure 2. The t-Student test revealed that the concentrations of contaminants (metals, PAHs, PTot, TOC, and N_{Tot}) were significantly different depending on the sampling method. The TOC should be analyzed with caution as the significance of the result can be considered close to the threshold ($p = 0.048$).

For comparison purposes, reference values established by the Canadian Council for the Ministry of the Environment (CCME) in the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life where Threshold Effect Level (TEL) indicates that there is no adverse consequence to the biological community and Probable Effect Level (PEL), indicates the low contamination effect, but needs attention (Moraes et al. 2011).

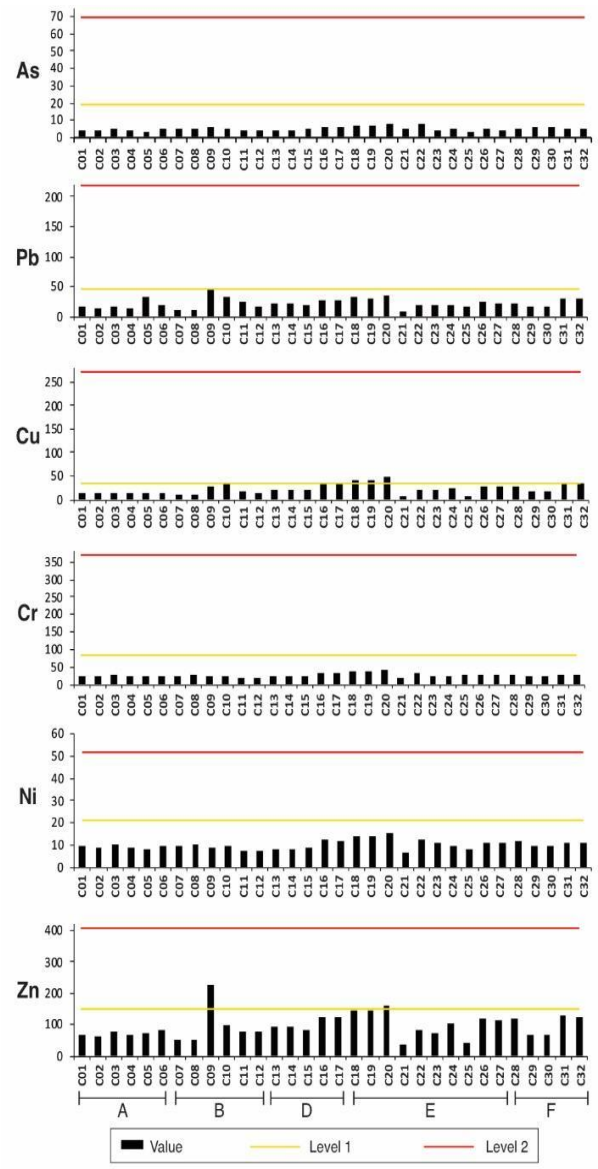

Figure 6 - Concentrations of metals in the sediment obtained by the composite sampling method.

Table 3 - Comparison of analyte values between sampling methods.

Units	Analyte	S (n=13)	C (n=28)	t-value	p	CONAMA	TEL	PEL
%	**Mud**	52.785 ± 24.535	58.700 ± 19.439	-1.239	0.222553	-	-	-
	TOC	2.977 ± 1.249	2.179 ± 1.058	2.035	0.048655	10%	1%	
mg/kg	**N_{Tot}**	828.216 ± 487.630	2308.472 ± 890.044	-6.952	0	4800	-	-
	P_{Tot}	311.554 ± 197.613	481.313 ± 237.498	-2.893	0.006209	2000	-	-
	As	15.702 ± 3.183	5.185 ± 1.218	15.435	0	70	7.24	41.6
	Pb	106.688 ± 43.131	106.688 ± 6.977	14.103	0	210	35	91.3
	Cu	95.953 ± 27.977	21.704 ± 11.006	10.299	0	270	18.7	108
	Cr	86.902 ± 13.446	26.849± 5.794	18.393	0	370	52.3	160
	Ni	33.772 ± 4.358	10.101 ± 2.117	19.625	0	51.6	-	-
	Zn	264.173 ± 130.893	89.16 ± 32.650	6.895	0	410	124	271
µg/Kg	**∑PAHs**	3015.396 ± 2159.531	251.384 ± 169.172	9.006	0	4000	766	7070.9

S: simple sampling and C: composite sampling.
t-Student test unpaired - for sampling different sizes (degree of freedom = 39).
Weighted average ± Standard Deviation (real values) and t-critic and p value (log-normalized).
(-) There are no established values.

Principal Component Analysis (PCA) confirmed the results of the t-Student test through its first main component (PC1) and also revealed important issues regarding the spatial distribution of pollutants in the region of Port of Rio. The first two factors of PCA could explain the correlations found in this study. Together, they accounted for 79.8% in explaining the total variances. The third axis (factor 3) was not represented graphically because it presented eigenvalues below 1. The red dotted line represents the cutoff value used to determine the representativeness of the factors.

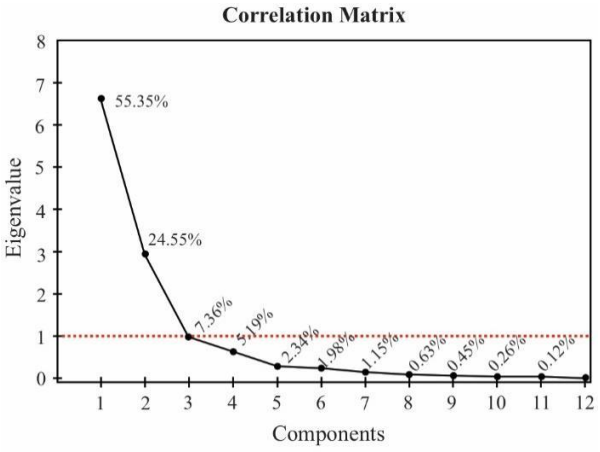

Figure 7 - Eigenvalues of the correlation matrix and percentage of explanation of the total variance achieved by each factor.

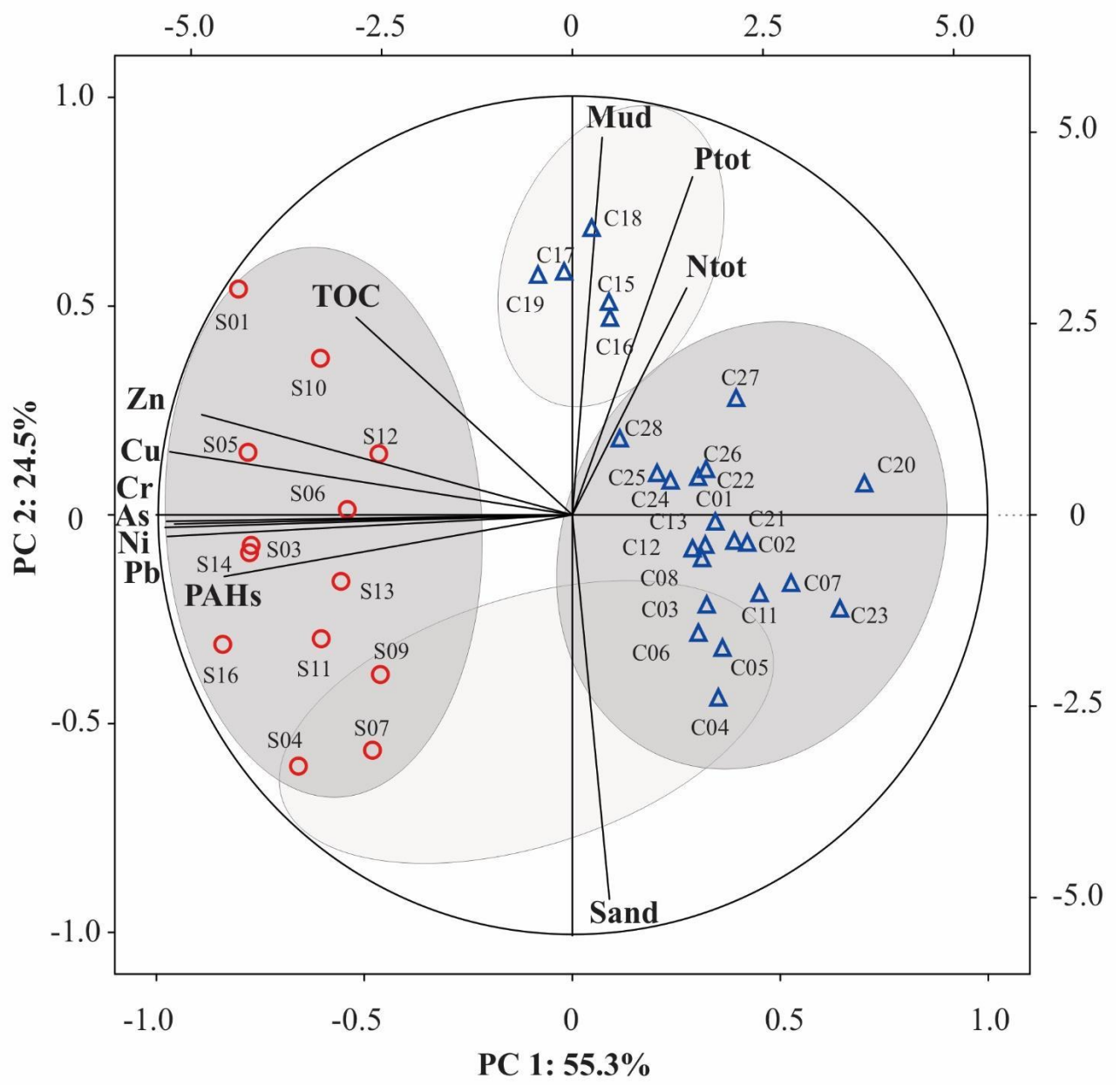

Figure 8 – Perceptual Map of the Principal Component Analysis. PC1: principal component 1; PC2: principal component 2; Vectors: principals variables (factors); Dots: sediment samples collected through simple sampling method. Triangles: sediment samples collected using the composite sampling method.

Figure 8 shows the perceptual map of scores, where points and triangles represent, respectively, the simple and composite samples, and the arrows represent the weight of the main components. Thus, the more parallel to the main component axis the weight vector is, the greater the importance of the corresponding variable.

The principal component 1 (PC1) explained about 55.34% of the data variance. In this component, the variables with the highest loading were Ni> Cr > Pb >Cu > As > Zn > PAHs > TOC, showing through the distribution of the cases a direct correlation with the samples collected using the simple method. On the other side, inversely correlated to these variables, the samples obtained using the composite method were plotted. Thus, PC1 corroborates the Student-t test, pointing once again to the distinctions inherent to each sampling method, pointing to a division of the samples into two well-defined groups, represented by the darker ellipses (Figure 8).

With a lower but still significant loading, the TOC illustrates the direct correlation of these pollutants with the organic matrix present in the sediment. A possible explanation for the TOC behavior is the influence of the sampling method in relation to the stability of the molecular bond between the predominant chemical form and the characteristics of the sediment (e.g., granulometry and quality of the organic matrix).

It is important to consider that, in the last 50 years, the flow of organic matter into the sediments has increased 10 times as a result of the intense eutrophication process in Guanabara Bay (Carreira et al. 2002).

The principal component 2 (PC2) was responsible for 24.54% of the variance of the explained data. The variable that determined this component was granulometry (percentage of silt to clay, represented in Figure 8 as mud) and secondly, its correlation with organic pollutants, as was the case with phosphate elements, nitrogen compounds and total organic carbon. Differently for PC1, which divided the cases according to the concentration of metals and PAHs, PC2 distributed the cases according to the particle size, that is, a distribution directly dependent on the region's hydrodynamics.

The positive side of this axis represents geographically the samples that are close to Porto in the areas D and E indicated in Figure 2, which corresponds to the stretch of the access channel to the container terminal. In this place, the deposition of fines and organic matter and adsorbed nutrients is favored by the decrease in energy from the currents (Catanzaro et al., 2004) and also due to the proximity to the river drainage points, such as the Mangue and Cunha Channels – that include rivers with high discharge of untreated sewage and supply of contaminants (Costa et al., 2018) – that was carried by rain drainage and runoff too (Smith et al., 2005). On the negative side of this same axis (PC2) are the samples that have a greater amount of sand, which tends to adsorb less contaminants.

The fines grains are the most important in retaining metals and other chemical compounds, as they have a large contact surface and high cation exchange capacity (between moderate to high, this, due to its negative surface charge. The high cation exchange capacity and surface charge are due to isomorphic ion substitutions in the crystalline network and the disruption of bonds in their chemical structures (Salomons & Forstner, 1984). It is important to note that fine sediments also absorb high concentrations of organic matter.

Geographically, areas A and B (Figure 2) are the closest to the deepest part of the main channel, according to bathymetry studies carried out by Catanzaro et al. (2004) and, therefore, exhibit greater flow and energy compared to areas F, E and D (Figure 2).

It is important to mention that, in these studies, even in situations where sediments have high concentrations of contaminants, biota will not always be affected, due to metal speciation. (Cesar et al. 2015). Therefore, depending on the purpose of the study, this is a fact that must be considered in the types of analysis and laboratory methods to be applied, in order to generate results compatible with the objective of the work.

5. Conclusions

In the present study, the evaluation of the different sediment sampling methods was performed, both in accordance with the national reference resolution, aiming to identify the potential and deficiencies of each method. In addition, this work reinforces the relevance of prior knowledge of the site to be dredged, considering the predominant criteria for environmental control in these areas.

The analysis of the substances and parameters in the sampled sediments indicated a high concentration of contaminants in some points, as was observed in the samples obtained using the simple sampling method, suggesting, in this case, that the composite sampling method is not the most suitable for peculiar environments such as Guanabara Bay, whose fine and muddy sediments - easily adsorbed and compacted - can originate a pool of contamination in the area of waste disposal.

A specific study with data from the disposal area of this dredging is being developed and will complement this study, providing new analyses.

Therefore, this study contributes to the discussion of the methodological quality used according to the environment to be licensed. The results presented contribute to the debate between social and economic development, with emphasis on the need for studies on monitoring activities toward the preservation of the environment.

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