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Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

A multivariate approach and sediment quality index evaluation applied to Baixada Santista, Southeastern Brazil

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ARTICLE INFO

Keywords:

Contamination
Heavy metal
ICP-OES
Principal component analysis

ABSTRACT

Current studies use indices and chemometric approaches to assess the health quality of estuarine systems to support estuarine management. This study aims to use a multivariate approach and a set of indices to evaluate sediment health quality. Levels of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Sc, V, and Zn were quantified by ICP-OES, and nine indices were applied and evaluated individually. Most of the indices presented high values of Cu, Pb, and Zn, and the aggregative indices differed from each other in magnitude; however, the spatial distribution demonstrated the same trends. From PCA results, it was possible to differentiate lithogenic from the anthropogenic contribution, especially by Cu, Pb, and Zn. Thus, the integration of geochemical approaches and chemometric tools supported the interpretation of elemental contribution in terms of sources and pathway of heavy metals, which was similar to the results of other studies conducted in the area.

1. Introduction

Sediments are recognized worldwide as indicators of environmental status and are considered efficient tools for evaluating potential harmful elements (Ridgway and Shimmield, 2002; Rodríguez et al., 2006). Overall, sediments act as sinks of contaminants and present higher temporal stability than those in the water column, thereby resulting in higher levels, and its sampling and analytical analysis normally are easier than those of other matrices (Birch, 2017a; Hakanson, 1980). Complex processes, including adsorption, flocculation, and precipitation, lead to the deposition of particulate matter. Thus, the geochemical conditions of the sediment reflect the environmental conditions during deposition and can also act as a source of contamination, as environmental changes could release these elements into the water column (Hortellani et al., 2008; Schintu et al., 2015).

Several studies have discussed how grain size distribution influences the concentration of potential harmful elements (Buruam et al., 2012; Kim et al., 2018; Song and Choi, 2017; Unda-Calvo et al., 2019). The specific surface area of the sediment particles and the concentration of metals do not follow a linear relationship, but the larger the specific area is, the greater is the adsorption of metals (Forstner and Patchineelam, 1981; Fukue et al., 2006), showing a higher concentration of metals in muddy sediment than in sandy sediments (e.g., Rubio et al., 2000; Wang et al., 2018). Thus, normalization with a particle size

proxy becomes a common practice in this type of study, allowing the comparison between data.

The metal concentration in sediments reflects not only anthropogenic influences but also a lithogenic component derived from the weathering of rocks. These concentrations are normally referred to background values (Hernández-Crespo and Martín, 2015), and they consider chemicals that were deposited in sediments before human influence (Birch, 2017b) being a pristine material that could be obtained empirically or statistically (Birch, 2017a; Hernández-Crespo and Martín, 2015). Most of sediment quality indices include this value as a normalizer, reducing the signal of regional natural geological variations (Jiang et al., 2013), as the concentration of metals is not entirely dependent on anthropogenic factors (Grygar et al., 2013; Wang et al., 2015b). The use of global mean concentrations (crustal or shale) is increasingly being disregarded, as these background values come from soils that have different geochemical properties than those of sediments. Furthermore, this concentration does not consider the chemical composition of the rock or the processes of weathering and pedogenesis before sedimentation. Thus, the use of a sediment core is highly recommended (Birch, 2017a; Kim et al., 2017).

Thus, the determination of potential harmful elements in sediments might not be suitable when assessing the magnitude of human activity in the environment (Chen et al., 2018). To satisfactorily manage estuarine systems, the sediment quality should be fully assessed (Birch,

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<https://doi.org/10.1016/j.marpolbul.2019.04.040>

Received 2 January 2019; Received in revised form 9 April 2019; Accepted 15 April 2019

Available online 23 April 2019

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2017b). In response to environmental degradation, many ecological/chemical approaches have been used and legislation has been implemented to aid appropriate management (Birch, 2018; Schintu et al., 2015). Estuaries are strategic regions for the development of large capitals, and it is a location where contrasting interests such as those of human activities and natural systems compete with each other, thereby resulting in adverse effects to the ecological community and consequently to human health. This is the case of the Santos – São Vicente Estuarine System (SSES). This complex system is located at Baixada Santista and presents tremendous economic importance, whether in production, consumption, or housing, being responsible for 3.11% of the state gross domestic product (GDP) in 2015 (SEADE, 2018). At an ecological level, the SSES is part of the Atlantic rainforest biome and concentrates the largest mangrove forest of the São Paulo coast. The SSES is recognized as vulnerable to environmental impacts, and it is protected by conservation units (UCs) that cover > 40% of the territory (São Paulo, 2013).

The main objective of this study is (a) to use a multivariate approach to assess the trace metal contamination in Baixada Santista; (b) to select a suite of indices; and (c) to evaluate the effectiveness of their uses through their similarity and differences.

2. Materials and methods

2.1. Study area

The Santos and São Vicente Estuarine System is located in São Paulo state, Southeastern Brazil (Fig. 1). This area can be divided into three main morphological sectors: (a) the Bertioga channel; (b) Santos Bay; and (c) the upper estuary. The system is a coastal plain where high relief rivers occur near the head and meandering channels near the mouth. Thus, erosive processes prevail in the mountain region, and the dynamics of sediment deposition and marine rework prevail in the coastal plain (Almeida, 1964). The estuarine system is slightly stratified and is composed of a fluvial system and tidal flats (Rossi, 1999). The system is mainly influenced by semidiurnal tides with average amplitudes of 0.27 m at quadrature and 1.23 m at syzygy, where the principal tidal components have high amplitude gradients to the western part and toward the shallow internal regions of SSES (Harari and Camargo, 2003). The sediments found in the system are composed of a mixture from a continental source, influenced by freshwater drainage and the erosion of rocks composed of granites, migmatites, quartz, and alkaline rocks, as well as a marine source that is controlled by tidal currents and continental shelf erosion (Fukumoto et al., 2004).

2.2. Sampling design and analytical procedures

In the summer of 2013, a total of 257 sediment samples (Table S1, Supplementary data) were collected randomly, to be representative of the area, on board of a flat-bottomed boat along the SSES using a stainless steel van Veen grab. All samples were freeze-dried and homogenized for further analysis. Trace element analysis was performed following SW 846 US EPA 3050b (USEPA, 1996). This method consists of acid leaching to dissolve all environmentally available elements linked to the organic matter, carbonates, and Fe/Mn oxides and adsorbed onto fine-grained particles. The quantification of the harmful elements As, Cd, Cr, Cu, Ni, Pb, and Zn as well as particle size proxy elements such as Al, Fe, Sc, and V was performed by inductively coupled plasma optical spectrometry (ICP-OES), which provides a multi-elemental quantification based on each element's wavelength. Grain size analysis was performed only to quantify the mud fraction (clay + silt; < 0.063 mm) once it is the only fraction geochemically relevant, by subjecting the samples to wet sieving on a 0.063 mm mesh sieve.

Quality control was conducted considering the detection limits, veracity, and precision. A certified reference material (SS-2 EnviroMAT Contaminated Soil from SCP Science) was subjected to the same analytical procedure, and the results presented a relative standard deviation of < 15% and recovery between 88% and 109% for all elements. With the exception of Cd, all values were above the detection limits.

2.3. Sediment quality indices (SQI)

Among 9 indices applied in this study, a brief description of 8 indices is given in Table 1. Background values (BG) for all indices were taken from Gonçalves et al. (2013), and the chosen particle size proxy was Sc because it displayed the best correlation with mud content. Classification of all the indices is presented in Table 3.

Classification of all indices, except MPI, according to the reference level is given in Table 2. The values show a slight difference from those given in the original classification to standardize the results and have only 4 classes of contamination. The PLI does not have a comparable class; however, according to its equation, $PLI = 1$ would indicate a situation in which all observed metal concentrations are considered background values. Thus, we will treat its classification as a linear order, in which value 1 would indicate the absence of contamination and from 1, a gradual increase in the level of contamination.

Empirical sediment quality guidelines generally integrate chemical data with biological effects (Schintu et al., 2015). Normally, these

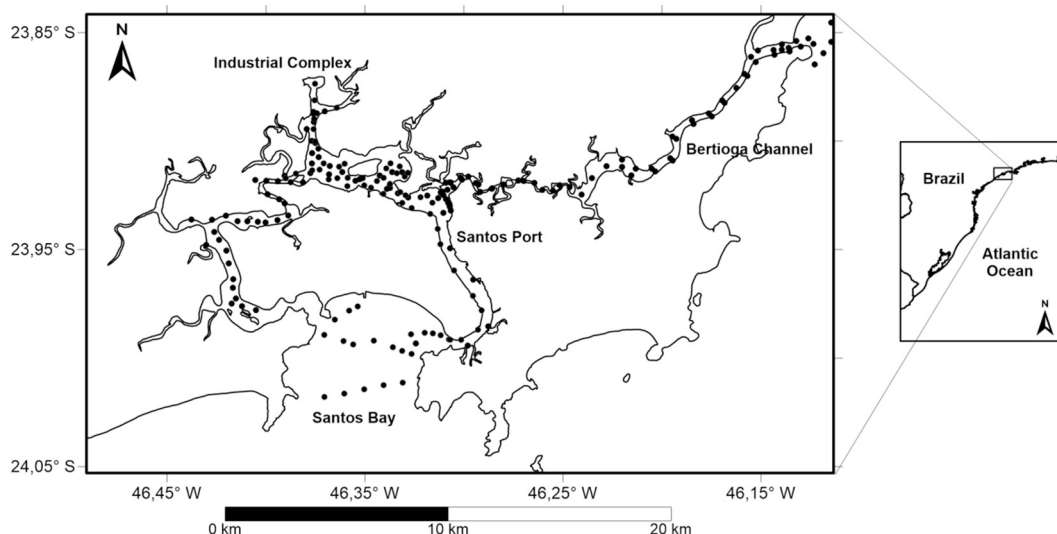


Fig. 1. Study area with all 257 sampling stations

Table 1

Description and equation of each index used in this study (C_i is the concentration of the studied element, in mg kg^{-1} ; X is the level of the normalizer element; n is the number of elements; and W the toxicity weight of the element; and %mud is the percentage of fine-grained material (< 0.063 mm)).

Index	Equation	Observations	Authors
Enrichment factor (EF)	$EF = \frac{\left(\frac{C_i}{X}\right)_{sample}}{\left(\frac{C_i}{X}\right)_{BG}}$	Quantifies the concentration of an element related to its background value	Zoller et al., 1974
Geoaccumulation index (Igeo)	$Igeo = \log_2 \left(\frac{\frac{C_i}{\%mud_{sample}}}{1.5 * \frac{BG}{\%mud_{BG}}} \right)$	The adapted equation takes into consideration the mud content to standardize the samples	Müller (1986), modified by Kim et al. (2018)
Pollution Load Index (PLI)	$PLI = \sqrt[n]{FC_1 * FC_2 * FC_3 * \dots * FC_n}$ where $FC_i = \frac{C_{i sample}}{C_{i BG}}$	Represents how many times the concentration exceeds the background value and provides a general approach to assess the toxicity of a particular sample	Tomlinson et al. (1980)
Sediment Pollution Index (SPI)	$SPI = \frac{\sum(EF_i * W)}{\sum W}$	A multielemental approach for assessing the sediment quality, taking into consideration the toxicity weight of each individual element, assigned as 1 for Cr and Zn, 2 for Ni and Cu, 5 for Pb, and 300 for Cd.	Singh et al. (2002)
Nemerow's synthetic pollution index (NI)	$NI = \sqrt{\frac{FC_{max}^2 + FC^2}{2}}$	Provides the main environmental quality domain of each individual sample	Cheng et al. (2007)
Degree of contamination	$DC = \sum_{i=1}^n FC_i$	A subindex of the ecological risk index normally used in coastal areas (e.g., Kwon and Lee, 1998)	Hakanson (1980)
Metal Pollution Index (MPI)	$MPI = \sqrt[n]{C_1 * C_2 * C_3 * \dots * C_n}$	A rarely used index to evaluate metal contamination	Usero et al. (1996)
Mean ERM quotient (mERM)	$mERM = \frac{\sum \left(\frac{C_i}{ERM_i}\right)}{n}$	Takes into consideration that the elements coexist in the environment (Zhou et al., 2014)	Long et al. (1995, 1998), Long (2000)

guidelines are based on ecotoxicology studies in which two levels are defined corresponding to (a) rarely, (b) occasionally and (c) frequently observed adverse effects (e.g., Choueri et al., 2009; Hedges and Keil, 1995; Macdonald et al., 1996). The levels of Brazilian legislation for the classification of sedimentary materials CONAMA 454/2012 (CONAMA, 2012) were used in this study and are presented in Table 1. Level 1 is the limit where no adverse effects on the biological community are observed, and level 2 is the level at which adverse effects in the biological community would most likely occur.

2.4. Statistical analysis

Many studies apply chemometric tools in environmental science focusing on sediment and soils to evaluate trace element contamination (Chandrasekaran et al., 2015; Liu et al., 2003; Ravisankar et al., 2015; Xu et al., 2014) because it is possible to identify the distribution and behavior of elements, and it might be possible to predict or estimate the variability of elements as well as their controlling factors (Qishlaqi and Moore, 2007). Thus, Pearson's correlation coefficient analysis was conducted to evaluate the strength of the relationship among elements and mud content. Principal component analysis (PCA) was performed to reduce the dimensionality of the data set.

Polar ordination was performed with the qualitative index results (1 – absence of contamination; 2 – moderate contamination; 3 – significant contamination; and 4 – strong contamination) using the Sørensen similarity index and the Beals formula, given below, to determine the similarity between indices.

Table 2

Classification of each index according to a reference level.

	EF	Igeo	PLI	SPI	NI	DC	mERM
1 – Absence of contamination	< 2	< 0	0–1	0–2	< 0.7	DC < n ^a	< 0.10
2 – Moderate	2–5	0–2	1–2	2–5	0.7–2	n < DC < 2n	0.10–0.50
3 – Significant	5–20	2–4	2–3	5–10	2–3	2n < DC < 3n	0.5–1.5
4 – Strong	20–40	4–5	> 3	10–20	> 3	DC > 3n	> 1.5
Reference	Sutherland (2000)	Müller (1986)	–	Singh et al. (2002)	Cheng et al. (2007)	Hakanson (1980)	Long (2000)

^a n is the number of contaminants.

Table 3

Threshold effect and probable effect levels from the Brazilian legislation (CONAMA 454/2012).

Element	Level 1 (mg kg^{-1})	Level 2 (mg kg^{-1})
As	19	70
Cd	1.2	7.2
Pb	46.7	218
Cu	34	270
Cr	81	370
Hg	0.3	1.0
Ni	20.9	51.6
Zn	150	410

$$x(i) = \frac{L^2 + dA(i)^2 - dB(i)^2}{2L}$$

where L is the highest distance registered in the similarity index, and dA and dB are the distances between indexes A and B, respectively, from (i) index.

This analysis presents the distances between instances in which the similarity result is represented by the gradient. All statistical analyses were performed using PAST 3.0 software.

3. Results

The mud content distribution is shown in Fig. 2. Of all samples, 74 presented 0–25% mud and were located mostly in the northern sector of Bertioiga channel and in the western part of the estuarine system, including Santos Bay. The samples with high mud content ($> 75\%$) were

Table 4
Descriptive parameters of metals and As (mg kg⁻¹) in SSES and background values from Gonçalves et al. (2013).

	Al	As	Cr	Cu	Fe	Ni	Pb	Sc	V	Zn
Mean	15,862.08	7.16	18.94	10.20	18,979.43	7.82	12.16	3.07	21.17	57.74
SD	9240.09	2.89	9.54	7.61	9049.34	4.05	8.48	1.58	9.61	69.96
Median	16,028.60	7.25	20.25	9.01	19,255.60	8.26	10.94	3.25	23.13	46.98
Max	42,819.30	14.74	44.77	48.78	43,798.20	19.28	64.02	6.07	43.42	912.56
Min	1693.82	0.30	2.50	0.50	1532.66	0.95	1.30	0.31	2.28	5.81
BG	25,052.95	13.05	37.29	8.02	12,549.90	13.28	14.45	6.38	38.65	52.12

Table 5
Pearson correlation ($\alpha = 0.05$) of all elements and mud content (%mud).

	Al	As	Cr	Cu	Fe	Ni	Pb	Sc	V	Zn
As	0.66									
Cr	0.94	0.67								
Cu	0.76	0.44	0.86							
Fe	0.94	0.73	0.95	0.79						
Ni	0.91	0.62	0.96	0.84	0.94					
Pb	0.68	0.48	0.77	0.85	0.71	0.73				
Sc	0.96	0.72	0.96	0.79	0.93	0.91	0.72			
V	0.93	0.78	0.95	0.77	0.93	0.91	0.71	0.97		
Zn	0.45	0.27	0.58	0.71	0.52	0.55	0.70	0.48	0.47	
%mud	0.80	0.59	0.83	0.71	0.78	0.76	0.63	0.87	0.82	0.40

Table 6
Number of occurrences in each class developed in this study and the descriptive parameters of each index.

	Class	Descriptive parameters						
		1	2	3	4	Max	Min	Median
EF	As	219	30	8	0	6.01	0.41	1.07
	Cr	255	2	0	0	2.33	0.70	1.07
	Cu	100	155	2	0	8.48	0.60	2.41
	Ni	246	11	0	0	3.88	0.83	1.18
	Pb	216	36	5	0	7.27	0.93	1.65
	Zn	134	120	2	1	20.78	1.04	1.97
	Sum	220	36	1	0	-	-	-
Igeo	As	184	42	21	10	5.19	-3.23	-0.59
	Cr	187	52	18	0	3.88	-2.46	-0.63
	Cu	38	191	27	1	4.24	-1.68	0.82
	Ni	170	63	22	2	4.09	-2.29	-0.42
	Pb	124	103	29	1	4.19	-1.64	0.04
	Zn	75	140	41	1	4.09	-1.40	0.47
	Sum	139	92	25	1	-	-	-
PLI		188	67	2	0	2.83	0.08	0.76
SPI		191	65	1	0	6.00	1.00	1.73
mERM		138	118	1	0	0.55	0.01	0.09
NI		90	140	22	5	12.92	0.10	0.97
DC		168	86	1	2	31.21	0.52	4.77
MPI						52.09	1.41	14.01

located at the inner part of the upper estuary.

The mean, standard deviation (SD), median, range, and the background value given by Gonçalves et al. (2013) for all analyzed elements are given in Table 4 and Table S2 of Supplementary Data. As the samples are broad spatially distributed and present distinct granulometric settings, it is normal to see variations confirmed by the high SD values, almost near the mean value for the same elements.

A Pearson correlation analysis (Table 5) revealed that all values correlated significantly ($\alpha = 0.05$) between each other. Al, Sc, and V presented strong correlation (> 0.80) with mud content (%mud). In natural circumstances, this high correlation is normal because they are like clay minerals, especially aluminosilicates. Some harmful elements such as As, Cu, Pb, and Zn demonstrated lower correlations with these elements, which may suggest some contamination signal when compared with Cr and Ni values that presented higher correlation with those elements.

Table 7
Polar ordination of the indices used.

Index	Distance
Igeo As	0
Igeo Cr	2.68
Igeo Ni	4.38
EF As	4.40
Igeo Pb	9.24
EF Ni	9.51
EF Cr	10.34
Igeo Zn	14.32
EF Pb	16.04
SPI	18.80
Igeo Cu	19.96
EF Zn	22.49
PLI	24.36
DC	25.72
mERM	28.09
EF Cu	29.31
NI	33.90

The descriptive results of each index and the number of occurrences of each class in this study are found in Table 6. To facilitate the comparison between indices, we calculated an arithmetic mean with all the results of a particular metal for EF and Igeo (Sum). All indices showed differences between classes, with some indicating strong contamination in a few samples. Nonetheless, the results showed that most of the samples indicate an absence of contamination. The EF and Igeo results are already published elsewhere (Kim et al., 2018, 2016), and these data were used in this study with a different approach.

Compared to the current SQG, all samples were below level 1, except for 6 samples that presented higher levels of Cu, Pb, and Zn (Fig. 3). Only Cu and Pb presented values above level 1, while Zn showed 2 samples above level 2. The highest concentrations of all three metals coexisting at harmful levels were observed in the inner part of the channel, next to the industrial complex. Beyond this area, Cu and Pb also coexisted in the limits of the upper estuary, next to Santos Port.

4. Discussion

In the majority of the indices, it was possible to observe a pattern of contamination in the inner part of the estuary and an absence of contamination in the rest of the area. Some indices point to a massive contamination (e.g., NI), but others demonstrated more conservative values (e.g., EF, SPI).

The SQGs provide an initial screening assessment of the potential adverse effects of chemical contaminants on benthic populations (Birch, 2018). This assessment is a fast and easy tool to apply, once it gives a qualitative result based on the relation of dose/effect. However, it is based on the bulk concentration, which does not reflect bioavailability, and, can vary depending on the element's physico-chemical proprieties. Several SQGs are available in the literature (e.g., Long et al., 1995; Macdonald et al., 1996; Persaud et al., 1993); nevertheless, most of them are developed in temperate regions that, due to the climate, present particular physico-chemical parameters and are subjected to different processes of weathering and pedogenesis compared to tropical

Table 8
Characteristics of the indices used in this study.

	Normalization by background value	Normalization by grain size	Element	Aggregative	Comparability
EF	Yes	Yes	All	–	Yes
Igeo	Yes	In laboratory	All	–	Yes
PLI	Yes	–	All	Yes	Yes
SPI	Yes	Yes	Cd, Cr, Cu, Ni, Pb, Zn	Yes	Yes
mERM	–	–	Only listed	Yes	–
SQG	–	–	Only listed	–	Yes
NI	Yes	–	All	Yes	–
DC	Yes	–	All	Yes	–
MPI	–	–	All	Yes	–

regions. Moreover, SQGs are available for a small number of chemicals and are only related only to benthic organisms (Birch, 2018). The mERM is similar to SQG, but it is developed only with ERM/ERL levels that do not take into consideration regional geological features such as SQGs (Jiang et al., 2013). Even with these disadvantages, both demonstrated high values in the upper estuary, especially in the inner part, which is next to the industrial area; these results are in agreement with those of other indices, thus demonstrating a reliable tool for assessing the expected spatial pattern.

MPI is very simple to calculate but does not compare the levels with any guideline or baseline, and there are no categories to classify if the sample is unpolluted or has strong contamination. If we calculate the MPI using background values ($MPI_{BG} = 18.42$), we would have an edge where samples below this value could indicate pristine conditions; therefore, higher values indicate contamination signals. As the index does not take into consideration the variation in metals with grain size, it is not possible to make a comparison between samples unless all data were previously divided by the mud content or by a particle-size proxy; otherwise, the spatial distribution of the magnitudes would be similar to the mud content, as we found in the area, in which higher values are found in the inner part of the estuary.

The PLI emphasizes the spatial distribution of metals but ignores some metals with low concentrations but high toxicity (Yang et al., 2009). This index allows the comparison between many estuarine systems and coastal areas, as it is widely applied (e.g., Hosseini and Sajjadi, 2018; Martins et al., 2013; Sharifinia et al., 2018; Wang et al., 2015a). Both PLI and NI use a contamination factor, which takes into account background values but not grain size; thus, depending on the

grain size of the samples, the indices may overestimate the degree of metal pollution (Zhao and Li, 2013).

The EF and Igeo are suitable only for the risk assessment of a single metal, and both indices are very similar and consider background levels as well as grain size variations. These indices are commonly used (e.g., El-Badry and El-Kammar, 2017; Gao et al., 2018; Pignotti et al., 2018; Sharifinia et al., 2018; Silva et al., 2011; Souto-Oliveira et al., 2018; Xavier et al., 2017), and a detailed description of SSES can be found in Kim et al. (2017) and Kim et al. (2018). The main purpose of both methods is to make trace element concentrations comparable between samples and elements due to standardization. For example, if the concentration of Bertioga channel is compared to that of Santos Bay, the conclusions would be that Bertioga channel presents higher values, but it must be considered that Santos Bay has higher sand content, lowering the total metal concentration.

The SPI is an aggregate index and based on the sum of EF values, including a toxicity weight in its equation. When evaluating sediment quality, this index may be the best choice because it presents a double normalization and includes an interpretation of potential deleterious effects. However, the normal weighting set is arbitrary and may be difficult to use once it does not consider variations in the geochemical background and the classification criteria (Varol, 2011). Applying SPI, differences in toxicity of metals are counterbalance, in other words, values of highly toxic elements, as Cd, are more weighted than less toxic ones like Cu and Zn, and it is a good tool to evaluate a suit of metals coexisting, but it is not a value that are going to give information about the toxicity of a particular sample. For SSES, the index presented a spatial pattern linked to EF because of your mathematical formulation,

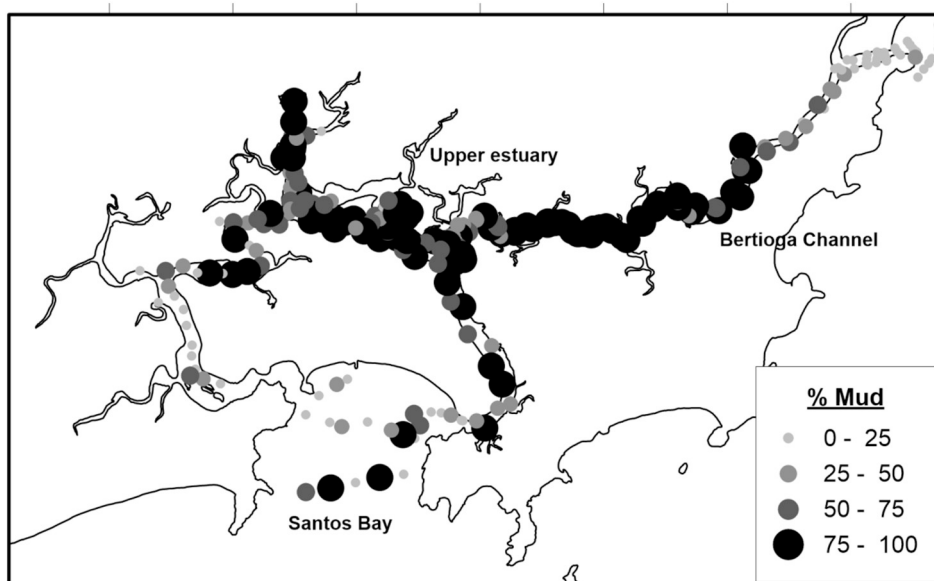


Fig. 2. Spatial distribution of mud content (%Mud) at Baixada Santista.

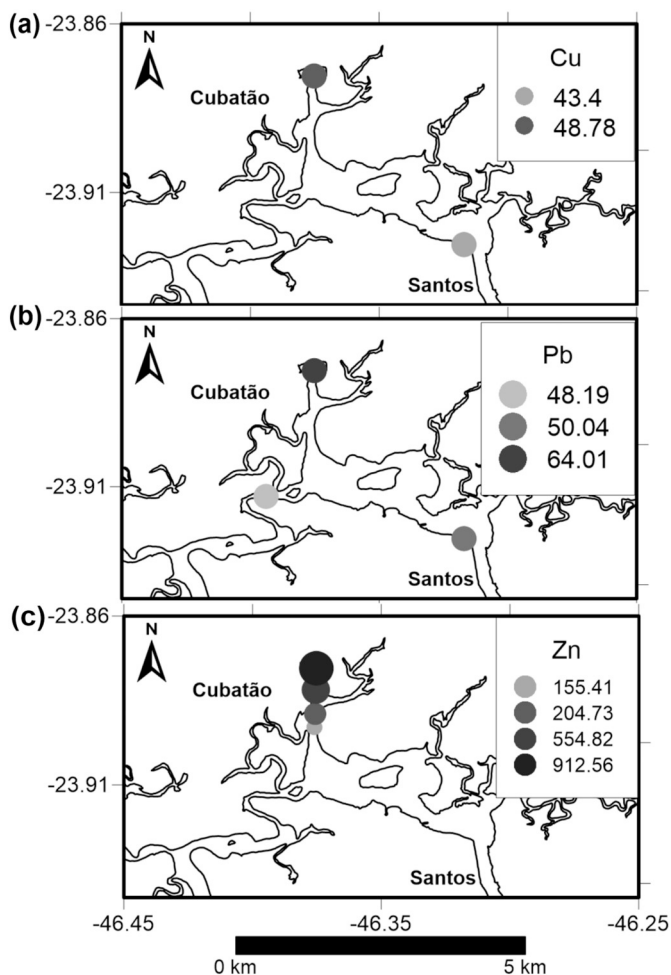


Fig. 3. Spatial distribution of the elements (mg kg^{-1}) (a) Cu, (b) Pb, and (c) Zn that exceeded the levels given by the Brazilian legislation (CONAMA 454/2012).

but as other indices, it has to consider that the values reflect a correction of elemental concentration to make those values comparable between each other and reproduce more visual data, which do not represent an absolute value.

From the polar ordination (Table 7), the Igeo As and NI were the indices with the highest dissimilarity (33.90). Some indices such as DC and PLI are very close. However, the ordination did not show the formation of groups with similar indices; nonetheless, it seems that there is a gap between EF Cr and Igeo Zn (distance = 3.98) that separated the indices in which the contamination was more remarkable than the others, even with the EF of As presenting values in class 4.

Table 8 presents a summary of all indices used in this study, and it is possible to see which index demonstrates normalization by grain size and a background value, which elements could be evaluated, which one is considered aggregative, and if the index is easily compared and largely applied (comparability).

The use of indices is strongly encouraged, as these indices can facilitate the insightful studies once the concentration data are transformed to more useful values, giving the environmental status of a particular sample; thus, it makes comprehending the interpretation easier for the nonscientific community. Some indices present more reliable results, minimizing the effects of grain size and the influence of the natural source of metals on the environment, but it must be emphasized that even though these two factors are the most important, other factors such as comparability with other studies and aggregability of metals may still hinder the study. Thus, for a wholistic understanding

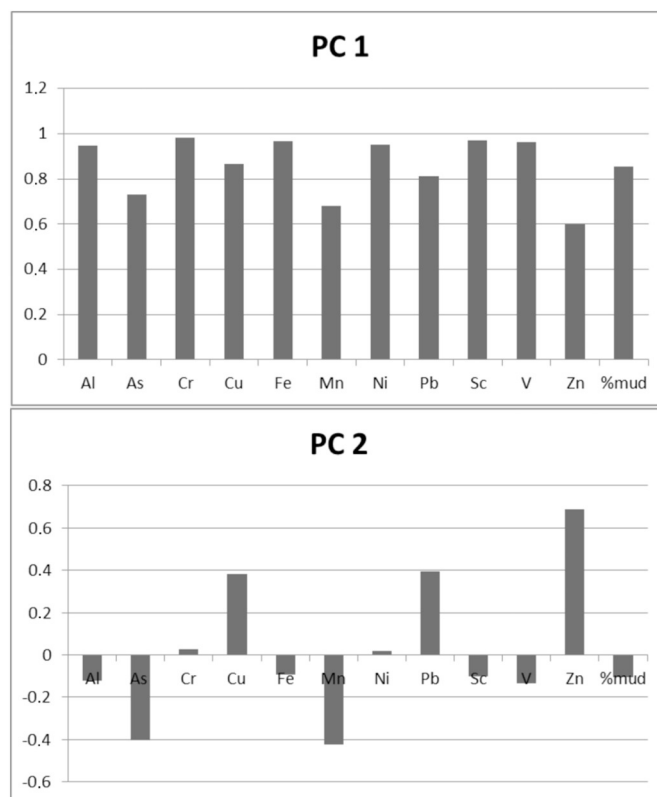


Fig. 4. Loading plots of (a) PC1 and (b) PC2 from the principal component analysis.

of sediment quality, the use of more than one index is recommended.

A principal component analysis was performed on the concentrations found, and it was possible to reduce the dimensions of all the data into two components that could explain the distribution in the study area, PC1 (78.425%) and PC2 (9.665%), which are not linearly correlated, and explained 88.09% of the variations. PC1 demonstrated higher loadings for almost all elements (Fig. 4). As many authors reported (e.g., Chandrasekaran et al., 2015; Siepak and Sojka, 2017; Zhao et al., 2016), PC1 represents the elements with natural sources derived from parental rocks linked to clay minerals, which could be observed by the high correlation between Al, Fe, and mud content. São Paulo state presents a strong weathering and desilicization environment, which results in the accumulation of Al and Fe oxy(hydroxide) (hematite, goethite, and gibbsite); thus, the specific adsorption has higher significance (Alleoni, 1995; Yu, 1997). The elements with this component represent a natural source linked to these oxides, and it can be seen that harmful elements are well correlated but not with high values.

The second component demonstrated high correlation with Cu, Pb, and Zn, the three major elements studied worldwide due to the potential toxicity, common use, and ubiquity in the environment (e.g., El-Badry and El-Kammar, 2017; Pandey et al., 2019; Sun et al., 2018). This is strong evidence that PC2 represents the anthropogenic input (Fig. 4).

When evaluating samples with the components in a scatter plot (Fig. 5), it is possible to divide, from a general view, the upper estuary from the rest of the system once the samples with positive correlation with PC2 are mostly black dots. Thus, the samples from the upper estuary are slightly different from the others, presenting little contamination signal. With the exception of 4 stations, all samples were presented as clouds of dots near the x-axis, only varying in PC1, suggesting that the study area does not show strong anthropogenic influence but only grain size variation, as the dark silver dots corresponding to the sandy stations of Santos Bay are negatively correlated to PC1.

The four samples, represented in red squares that are correlated to

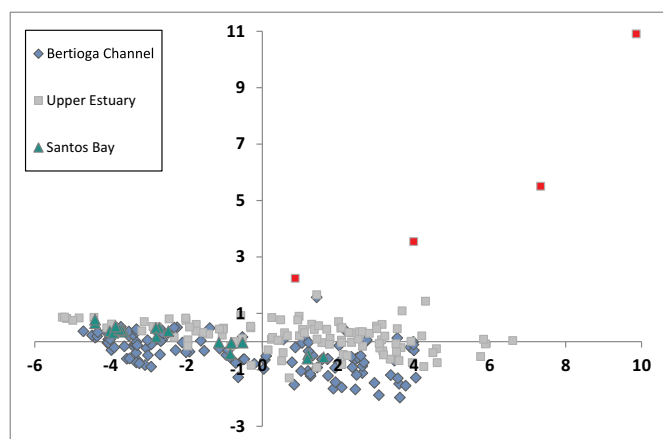


Fig. 5. Scatter plot of PC1 vs. PC2. Red squares indicate the samples well correlated with PC2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PC2 and show a strong influence of Cu, Pb, and Zn, were in agreement with all indices and correspond to the same samples that exceeded SQGs. Normally, studies conducted in port regions and next to industrial zones report that these three metals are found in high concentrations (e.g., Adamo et al., 2005; Birch et al., 2013; Chen et al., 2016; Merhaby et al., 2018).

The main source of sediments in the studied region is the erosion of alkaline rocks, which contain the studied elements, especially Al, Ni, Sc, and V. Moreover, the other associated minerals such as migmatite and chromite, which contains Fe and Cr, are very resistant to weathering and dissolution (Abreu, 1973). These factors, which were added to the several imposed measures to control contamination in 1984 (CETESB, 2001), indicate that most of the elements are lithogenic, which is in agreement with Kim et al. (2017), who used a prediction interval to establish background equations.

The concentrations found in the contaminated samples from the upper estuary, as some authors have previously reported (Cesar et al., 2007; Medeiros and Bicego, 2004), suggest that the SSES traps contaminants, which is confirmed by the low concentrations found in Bertioiga channel, an area where deposition is favored due to the confluence of waters and also the presence of mangroves in the region. Thus, even though it is located next to an anthropogenically impacted area, the channel could be considered a pristine environment, not presenting contamination by the metals presented here. Santos Bay is covered mainly by sand, which does not trap potential harmful elements, and in addition, it demonstrates a different hydrodynamic situation compared to the inner part of the estuarine system. As the area presents currents and waves with high energy, it is possible to suggest that the region may not allow the deposition of these metal contaminants to the system or the estuarine system

5. Conclusion

The use of several indices aids in the transformation of a great variety of magnitudes of concentrations to comparable data, as each index presents a particular interpretation, such as normalization by grain size/background values and adverse effect considerations. Generally, the indices could successfully report elemental concentration trends because all those studied herein present the same trends with regard to spatial distribution but do not all agree on the magnitude of contamination. Thus, for a wholistic understanding of sediment quality, the use of more than one index is recommended.

The environmental sediment assessment described in the current work identifies high-risk regions of the study area and highlights the metals of most concern, helping to focus future more comprehensive

investigations to reduce costs, effort, and time. Moreover, the integration of the geochemical approach and chemometric methods helped us to establish a simple relation among the different types of parameters measured. The results of chemometric analysis suggest the lithogenic origin of elements with natural sources derived from parental rocks linked to clay minerals and the anthropogenic origin of Cu, Pb, and Zn.

It was possible to conclude that the SSES presents levels of metals, mainly of lithogenic concentrations and some contamination signal in the inner part of the estuary, suggesting that the estuarine system acts as a geochemical barrier and that the grain size distribution is the main influence on metal levels.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001 and from FAPESP (no. 2009/01211-0; no. 2011/50581-4 and 2017/08987-0), Oceanographic Institute of University of São Paulo (IOUSP), and Laboratory of Inorganic Marine Chemistry (LaQiMar).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2019.04.040>.

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