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# Enrichment diagram (ED)

## A graphic approach for assessing inorganic enrichment and contamination in marine sediments of Sepetiba Bay (SE Brazil)

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**Abstract**

**Purpose** – The purpose of this paper is to validate and apply enrichment diagrams (EDs) to determine metal and as enrichment and contamination in the sediments of Sepetiba Bay.

**Design/methodology/approach** – Through inducted coupled plasma – optical emission spectrophotometry, total element (As, Cd, Cu, Ni, Pb and Zn) concentrations were assessed for the construction of EDs and comparison with enrichment factors (EFs) in 65 samples collected in Sepetiba Bay.

**Findings** – Based on the EDs, it was observed that the sediments around the urban area of Sepetiba and ItaguaíHarbor were contaminated with Cd, Cu, Ni, Pb and Zn. These contaminants were expected due to the urban and industrial discharges into the bay and the activities at ItaguaíHarbor.

**Originality/value** – The ED was successful regarding its ability to evaluate inorganic contamination in Sepetiba Bay. In addition, this method was able to define a proper background sample for calculating EFs.

**Keywords** Enrichment, Metals, As, sediment, Sepetiba

**Paper type** Research paper

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## 1. Introduction

Currently, the impacts of releasing wastes into the environment are a major ecological concern. Inorganic pollutants contribute to between 70 and 80 percent of marine contamination (Crossland *et al.*, 2005) that reach the coastal zones from riverine discharges, atmospheric transport and soil lixiviation processes (Health, 1987). These contaminants deteriorate the water and sediment quality, which can create problems regarding toxicity, persistence and bioaccumulation in the trophic webs (Marins *et al.*, 2004).

Sediments have been widely used as indicators of environmental quality due to their high capacity for incorporating contaminant substances at concentrations that are several orders of magnitude greater than in adjacent waters (Furness and Rainbow, 1990; Hortellani *et al.*, 2008). Therefore, sediments can be used to detect the presence of contaminants that remain insoluble after their release into the water column (Lemes, 2001).

Approximately two-thirds of the world population resides in coastal zones (Small and Nicholls, 2003). Consequently, the surrounding ecosystems are pressured by this occupation. Several studies have verified the impacts of humans on aquatic systems due to their constant addition of pollutants to these systems (Guerra *et al.*, 2010; Kehrig *et al.*, 2007; Machado *et al.*, 2004; Molisani *et al.*, 2004; Rule, 1986; Wang *et al.*, 2008).

To evaluate inorganic contamination in aquatic sediments, a number of indexes and normalization factors were created. One such index is the enrichment factor (EF), which is used to separate the signals of natural and anthropogenic contributions and to assess anthropogenic influences (Yongming *et al.*, 2006). The EF normalizes an element of interest against one that is conserved in the system, such as Al, Fe, Mn or Sc (Sutherland, 2000; Ribeiro *et al.*, 2010). In addition, the EF can be used to determine the similarity of a sample to its regional background (Sutherland, 2000).

Sepetiba Bay (Figure 1) is located 60 km from the Rio de Janeiro metropolitan region (SE Brazil) in an area that has suffered considerable urban and industrial development in recent decades. Its drainage basin has approximately 400 industries many of which are metallurgic and the wastes from these industries, which are rich in metals and other potentially toxic substances, are directly released into the bay and its waters (Paraquetti *et al.*, 2004; Cunha *et al.*, 2009; Gomes *et al.*, 2009). For example, the currently deactivated Companhia Mercantil Industrial Ingá generated large amounts of residues from processing calamine to obtain Zn (Pinto, 2005).

Itaguaí Harbor, located in Sepetiba Bay, has an area of ten million $m^2$ that can effectively accommodate large vessels (Pellegatti *et al.*, 2001). This port brought intense economic development to the region and negative environmental consequences from direct water contamination from the atmosphere (Pedlowsky *et al.*, 1991; Wasserman *et al.*, 2000).

This study used a graphical enrichment diagram (ED) approach for evaluating the enrichment and contamination of As, Cd, Cu, Ni, Pb and Zn in the bottom sediments of Sepetiba Bay. These EDs will enable the detection of enriched samples in a simple plot. For validation, this method was compared with the widely used and accepted EF results.

## 2. Materials and methods

### *2.1 Sampling*

Sediment samples were collected in 2003 with a stainless steel Van Veen bottom grab sampler at 65 different sites that were distributed throughout Sepetiba Bay (Figure 1). These samples were frozen, lyophilized, weighted and transferred to plastic containers for subsequent analyses.

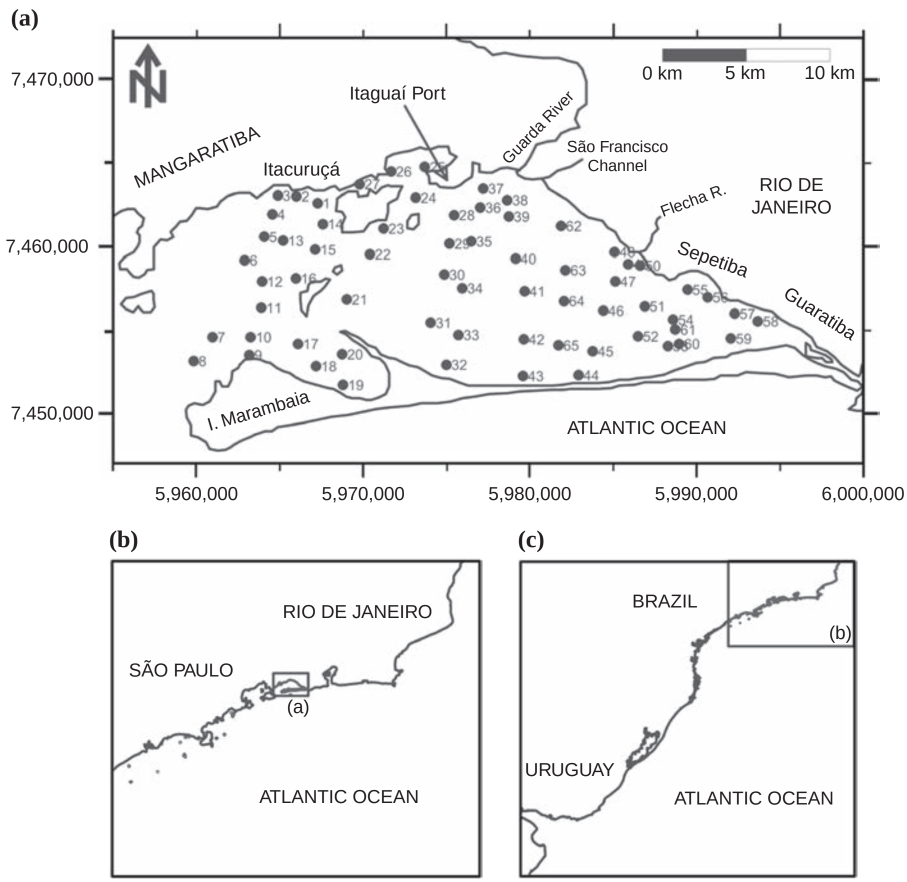



**Figure 1.**
Sepetiba Bay (a) located in Rio de Janeiro state coast (b) Southeast Brazil (c)

*2.2 Total element concentrations*

The total element concentrations were determined using sediment total digestion with hydrofluoric (HF) and nitric ($HNO_3$) acids in a microwave oven, as recommended by the United States Environmental Protection Agency (2003). As, Cd, Cu, Ni, Pb and Zn concentrations were determined by inducted coupled plasma – optical emission spectrophotometry (Spectro, model Spectro Flame M120E).

As, Cd, Cu, Ni, Pb and Zn certified reference materials of NIST-SRM 2704 (National Institute of Standards and Technology, riverine sediment), MESS2 (National Research Council of Canada, estuarine sediment) and IAEA-Soil-7 (International Atomic Energy Agency, soil) were used to determine the accuracy of the method. The precision and accuracy were checked by using the relative standard deviation (RSD) and the relative error (RE), respectively, of the measured data. The experimental data errors were smaller than 10 percent.

*2.3 EF*

The EF is a mathematical tool for assessing the presence of metals in a system. The EF considers the geological composition of the sedimentary matrix and is a way to quantify anthropogenic contributions (Sutherland, 2000; Ribeiro *et al.*, 2010). The EF was calculated with Equation (1), in which $M$ is the trace element of interest, $X$ is an eligible normalizer (reference metal) and $(M/X)_{\text{sample}}$ and $(M/X)_{\text{background}}$ are the ratios between the trace element and the normalizer in the sediment and background samples, respectively (Förstner and Salomons, 1980):

$$\text{EF} = (M/X)_{\text{sample}}/(M/X)_{\text{background}} \tag{1}$$

Elements like Al, Fe, Sc and Mn, which are not anthropogenic contaminants, are considered normalizing elements (Ribeiro *et al.*, 2010). For this study, Fe was used as the normalizer element, and the background sample was provided by the data from Barcellos (1995), which also studied the basal element concentrations in Sepetiba Bay.

The following five-category ranking was used to evaluate the degree of enrichment that resulted from anthropogenic contamination: EF values lower than 2 indicate minimum contamination; EF values between 2 and 5 indicate moderate contamination; EF values between 5 and 20 indicate significant contamination; EF values between 20 and 40 indicate very high contamination; and the EF values greater than 40 indicate extremely high contamination (Sutherland, 2000).

### *2.4 ED*

Normally, the background samples chosen for the EFs may be the earth's crustal shale (Turekian and Wedepohl, 1961), or the vertical bottom sediment profiles in the studied region. There are advantages for the use of both. For example, it is difficult to use mean crust values, because they do not truly represent the background of the studied region. On the other hand, vertical sediment profiles to establish background mean values are not always available.

Regarding the enrichment analysis of the superficial bottom sediment samples, the ED can be used to determine the anthropogenic inorganic enrichment without a background value by only using the total element concentration of interest and of a normalizer element. The proposed EDs construction method is provided below. Excel (Microsoft, version 2010) was used to perform all of the necessary calculations for each step:

(1) The total $M$ (trace element of interest) and $X$ (normalizer element unaffected by anthropic activities in the system) concentrations were used to create a plot of $X$ vs $M$ for all samples. If the sample size is large, the relationship between $M$ and $X$ tends to reach the natural proportion between these elements in the studied system. This observation is important because the natural proportion represents the regional metal background.

(2) On this plot, if the sample size is sufficiently high (the term "high" will be explained below), the outlying samples should be removed from the plot. For this purpose, a sample can be considered as outlying (differently from outlier) if it is visually separate from the main $M$ vs $X$ relationship.

(3) After removing the outlying samples, the roughly linear regression model was used to create an equation for the element's behavior in the sediment.

(4) The linear regression curve and its lower and upper 95 percent confidence intervals are plotted for all samples. Samples above the upper confidence limit are considered enriched in the study area.

A large number of samples are recommended for this method in an area as large as Sepetiba Bay. With a large number of samples, the linear regression represents the behavior of the elements in the sediment. For 95 percent confidence and 95 percent reliability, the minimum proposed sample size is 58 for a spatial area equivalent to Sepetiba Bay, based on the application of the Clopper-Pearson method for confidence intervals (Clopper and Pearson, 1934).

## 3. Results and discussion

### *3.1 Quality control*

The quality of the As, Cd, Cu, Ni, Pb and Zn measurements was verified with selected certified reference materials. The mean values and standard deviations that were obtained for replicate analyses of the certified reference materials are presented in Table I.

The results presented in Table I indicated highly accurate analyses with RSDs of between 2.5 percent for Zn and 9.0 percent for Pb. The results for all analyzed elements agreed with the certified values with REs smaller than 10 percent.

### *3.2 Total element concentrations*

Figure 2 presents the spatial distribution of the total element concentrations in the Sepetiba Bay sediments. The greatest As and metal concentrations were observed in the NE portion of the bay near the mouths of the São Francisco Channel and the Guarda River. Most of the industrial wastes are dumped into the bay at this location.

Table II presents the descriptive statistics for the As and other elements. The Pb concentrations were slightly above the Interim Sediment Quality Guidelines (ISQG) limit of 30.2 mg kg$^{-1}$ (Canadian Council of Ministers of the Environment (CCME), 2006) and the average shale concentration of 12.5 mg kg$^{-1}$ (Taylor and McLennan, 1995). Several studies have investigated the distribution of As and metals in Sepetiba Bay (Barcellos and Lacerda, 1993; Ferreira *et al.*, 2010; Lacerda *et al.*, 1987; Perin *et al.*, 1997; Souza *et al.*, 2012), however, these results could not be compared with the ones presented in this study because the analytical methods were different (this study employs total sediment digestion, and the others used partial sediment digestion).

As, Cd, Ni and Zn are considered as pollutants in Sepetiba Bay. The As, Cd and Ni concentrations were greater than the ISQG limit and the Zn concentrations were

| Element | Reference material | Certified concentration (mg kg$^{-1}$)[a] | Measured concentration (mg kg$^{-1}$)[b] | Precision (RSD) (%) | Accuracy (RE) (%) |
|---|---|---|---|---|---|
| As | NIST-SRM 2704 | 23.2 ± 0.8 | 22.3 ± 0.6 ($n$ = 14) | 2.7 | 3.9 |
| Cd | NIST-SRM 2704 | 3.45 ± 0.22 | 3.60 ± 0.26 ($n$ = 14) | 7.2 | 4.3 |
| | IAEA-Soil-7 | 104[c] | 100 | [d] | 3.8 |
| Cu | MESS2 | 39.2 ± 2.0 | 35.5 ± 2.9 ($n$ = 7) | 8.2 | 9.4 |
| Ni | MESS2 | 49.3 ± 1.8 | 45.6 ± 4.0 ($n$ = 7) | 8.8 | 7.5 |
| Pb | MESS2 | 21.9 ± 1.2 | 19.9 ± 1.8 ($n$ = 7) | 9.0 | 9.1 |
| Zn | NIST-SRM 2704 | 438 ± 12 | 475 ± 12 ($n$ = 14) | 2.5 | 8.4 |

**Notes:** Quality control through the evaluation of precision and accuracy of the methodology. [a]Concentration values represented in the form (median ± confidence interval); [b]concentration values represented in the form (mean ± standard deviation); [c]value of information; [d]value not determined

**Table I.** Concentrations of As, Cd, Cu, Ni, Pb and Zn (in mg kg$^{-1}$) in standard reference materials

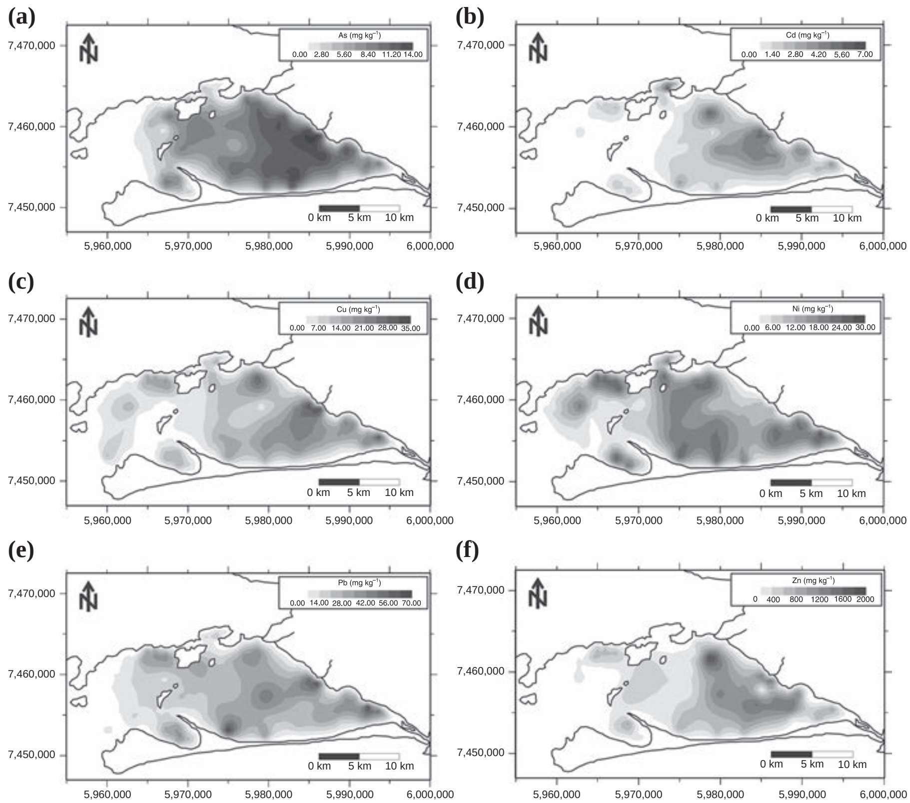



**Figure 2.**
Spatial distribution of the total concentration of elements (in mg $kg^{-1}$) in sediments of Sepetiba Bay (SE Brazil)

**Notes:** (a) As, (b) Cd, (c) Cu, (d) Ni, (e) Pb, (f) Zn

**Table II.**
Descriptive statistics of the metals and As concentration (in mg $kg^{-1}$) in sediments of Sepetiba Bay (SE Brazil)

| | Concentration (mg $kg^{-1}$) | | | | |
|---|---|---|---|---|---|
| | This study | | | Canadian environmental quality guideline | |
| Element | Mean | Median | Range | ISQG | PEL |
| As | 7.66 | 9.00 | 1.00-14.00 | 7.24 | 41.60 |
| Cd | 2.01 | 1.58 | 0.02-7.40 | 0.70 | 4.20 |
| Cu | 14.37 | 14.46 | 1.61-33.04 | 18.70 | 108.00 |
| Ni | 15.22 | 19.00 | 1.77-27.00 | 18.00 | 36.00 |
| Pb | 29.28 | 29.40 | 2.90-69.50 | 30.20 | 112.00 |
| Zn | 600.32 | 500.00 | 23.70-1,941.00 | 124.00 | 271.00 |

**Note:** Comparison with the Canadian Environmental Quality Guideline (CCME, 2006)

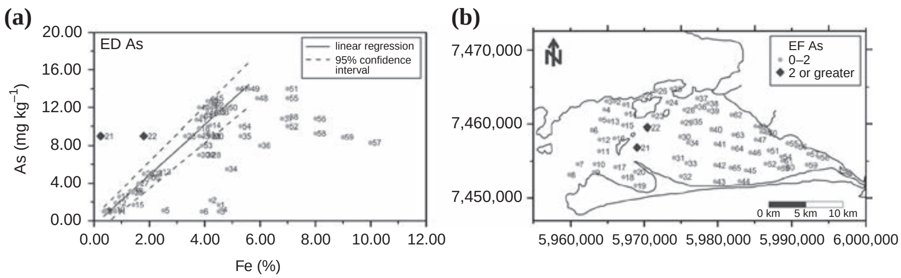
greater than the probable effect level value (CCME, 2006). This contamination resulted from repeated environmental accidents that spilled large amounts of zinc ore waste into the bay. However, in 2005, Federal authorities began an environmental recovery program of the wastes (Pinto, 2005).

### *3.3 EFs and EDs*

To validate the potential of the ED for assessing inorganic enrichment and contamination, Figures 3 through 8 provide a visual comparison between the EDs and the samples in which the EF values were greater than two (indicating contamination).

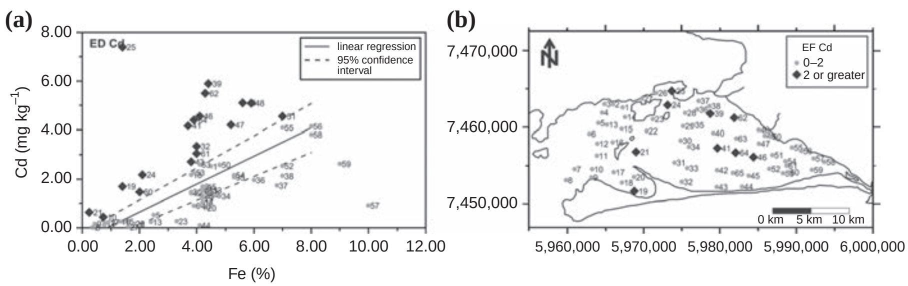
The group of samples that was enriched in EDs was similar to the group that was enriched based on the EFs (Figures 3 through 8). The samples that were enriched are summarized in Table III with their respective elements.

The EFs results were all reproduced in the EDs, because all of the samples that were enriched after the EF calculations were also shown as enriched in the EDs. The EDs



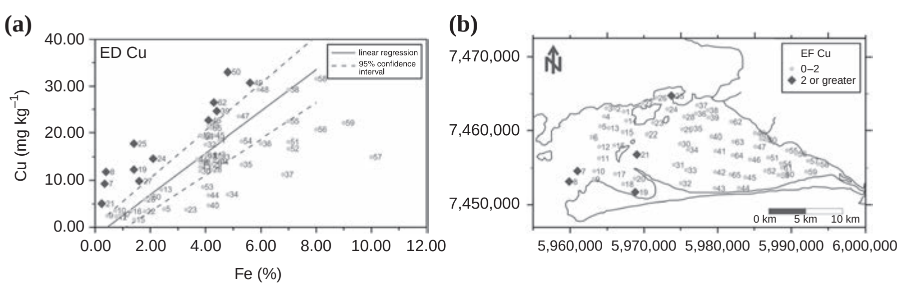

**Notes:** (a) ED, enrichment diagram; (b) EF, enrichment factor. Black rhombuses indicate enriched samples

**Figure 3.** Comparison between ED and EF for the total concentration of As (in $mg\,kg^{-1}$)




**Notes:** (a) ED, enrichment diagram; (b) EF, enrichment factor. Black rhombuses indicate enriched samples

**Figure 4.** Comparison between ED and EF for the total concentration of Cd (in $mg\,kg^{-1}$)




**Notes:** (a) ED, enrichment diagram; (b) EF, enrichment factor. Black rhombuses indicate enriched samples

**Figure 5.** Comparison between ED and EF for the total concentration of Cu (in $mg\,kg^{-1}$)

presented a greater number of enriched elements than the EFs, because the diagram includes samples that have lower enrichment values (EF > 1.7, instead of random value > 2.0). Therefore, it can be stated that the ED consistently defines a limit for polluted samples (based on the 95 percent confidence interval), while EF limit is rather random. It is concluded that the ED was more powerful regarding its capacity for detecting enriched samples.

By examining the enriched sample positions, it was observed that the enriched samples occurred in and near the Itaguaí Harbor (Cd, Cu, Ni and Pb), in the NE region of the bay, near the Sepetiba urban area (Cd and Zn) and in the NW area around

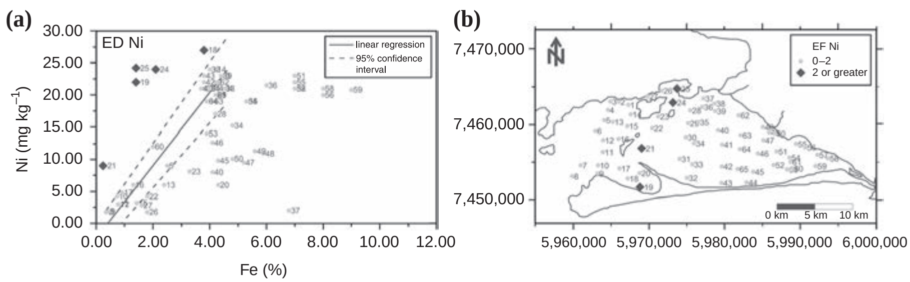



**Figure 6.**
Comparison between ED and EF for the total concentration of Ni (in $mg\,kg^{-1}$)

**Notes:** (a) ED, enrichment diagram; (b) EF, enrichment factor. Black rhombuses indicate enriched samples

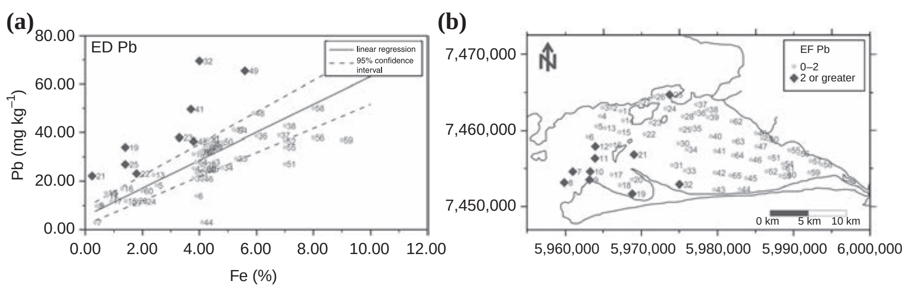



**Figure 7.**
Comparison between ED and EF for the total concentration of Pb (in $mg\,kg^{-1}$)

**Notes:** (a) ED, enrichment diagram; (b) EF, enrichment factor. Black rhombuses indicate enriched samples

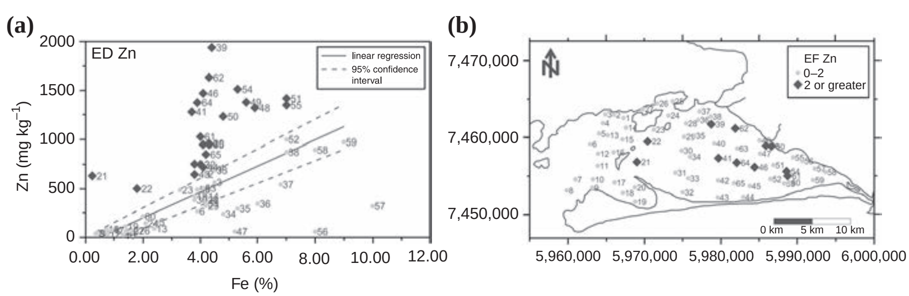



**Figure 8.**
Comparison between ED and EF for the total concentration of Zn (in $mg\,kg^{-1}$)

**Notes:** ED, enrichment diagram; (b) EF, enrichment factor. Black rhombuses indicate enriched sample

| Sample | Enriched element DEs results | FEs results |
|---|---|---|
| 7 | Cu, Pb | Cu, Pb |
| 8 | Cu, Pb | Cu, Pb |
| 9 | Pb | Pb |
| 10 | Pb | Pb |
| 11 | Pb | Pb |
| 12 | Pb | Pb |
| 18 | Ni | No element |
| 19 | Cd, Cu, Ni, Pb | Cd, Cu, Ni, Pb |
| 20 | Zn | No element |
| 21 | As, Cd, Cu, Ni, Pb, Zn | As, Cd, Cu, Ni, Pb, Zn |
| 22 | As, Zn | As, Zn |
| 24 | Cd, Cu, Ni | Cd, Ni |
| 25 | Cd, Cu, Ni, Pb | Cd, Cu, Ni, Pb |
| 27 | Cu | No element |
| 32 | Cd, Pb | Pb |
| 39 | Cd, Zn | Cd, Zn |
| 41 | Cd, Pb, Zn | Cd, Zn |
| 46 | Cd, Zn | Cd, Zn |
| 47 | Cd | No element |
| 48 | Cd, Zn | No element |
| 49 | Cd, Pb, Zn | Zn |
| 50 | Cu, Zn | Zn |
| 51 | Zn | No element |
| 54 | Zn | Zn |
| 55 | Zn | No element |
| 60 | Cd | No element |
| 61 | Cd, Zn | Zn |
| 62 | Cd, Cu, Zn | Cd, Zn |
| 64 | Cd, Zn | Cd, Zn |
| 65 | Zn | No element |

**Table III.** Samples with enriched elements for EDs and EFs

Marambaia Island (Cd, Cu, Ni and Pb). These findings were expected because they have inorganic contaminant sources due to the harbor activities and the input of urban wastes (especially through Flecha River). The most commonly enriched element was Zn, which indicated contamination from historical activities of the Companhia Mercantil Industrial Ingá (a Zn processing industry) (Pinto, 2005).

If the results from Figure 2 were analyzed, the conclusions regarding heavy metal and As contamination in Sepetiba Bay would differ because the high-metal concentrations do not necessarily indicate contamination considering that the natural contributions cannot be evaluated by assessing these levels. Enrichment analysis, such as the ED, is a simple and efficient method for evaluating the anthropogenic input of metals and semimetals (such as As) in environmental matrices (such as sediments).

## 4. Conclusions

The ED proved to be a useful method for assessing the presence of enriched metals and As in the studied marine sediments when compared with the EFs results. This method was able to verify which samples in a given area were enriched relative to a normalizer element with conservative behavior (such as Fe, which was used in this study). The data required to use this method includes the concentrations of the elements of interest and the normalizer element. This data requirement is an advantage of ED due to the difficulties in choosing a proper background sample.

By applying EDs for metals and As in Sepetiba Bay, it was observed that the sediments around the urban area of Sepetiba and Itaguaí Harbor are contaminated with Cd, Cu, Ni, Pb and Zn. This contamination was expected due to the discharge of urban and industrial wastes into the bay and the port activities of Itaguaí Harbor.

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## Further reading

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