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Metal Distribution in Sediments from the Ribeira Bay, Rio de Janeiro – Brazil

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O estudo de metais em áreas preservadas assume grande relevância devido à falta de níveis de base para comparação com estudos em áreas impactadas. Para 23 amostras de sedimento de superfície da Baía da Ribeira, RJ, foram determinadas por ICP/AES as concentrações de Ti, Ca, Mg, Fe, Al, Sr, La, V, Y, Ni, Cu, Cr, Mn e Zn. Hg foi determinado por CVAAS. Utilizando Al como referência, os metais foram classificados como associados, intermediários, inversamente associados e não associados a Al. A análise de agrupamento dos dados confirmou esta classificação, exceto para o Hg. A análise de agrupamento dos locais amostrados gerou 3 grupos, controlados por granulação, influência continental e influência marinha. Fatores climáticos e hidrodinâmicos, além das características dos solos, são importantes na distribuição dos metais. A área apresenta níveis naturais de metais, comparáveis a folhelhos médios e a outras áreas impactadas e não impactadas.

Investigation of metal distribution in preserved areas is highly relevant due to the present-day lack of reliable databases against which to assess contamination. 23 samples of surface sediments from the Ribeira Bay, Rio de Janeiro State, Brazil, were analyzed by ICP/AES for Ti, Ca, Mg, Fe, Al, Sr, La, V, Y, Ni, Cu, Cr, Mn and Zn. Hg concentrations were determined by CVAAS. With respect to Al, metals were classified as strongly correlated, correlated, inversely correlated and non-correlated. Cluster analysis of the concentration data confirmed this, except for Hg. Cluster analysis of the sampling sites produced three groups, on the basis of grainsize, continental input, and marine input. Climatic and hydrodynamic factors, as well as soil characteristics, are important controls of the metal distribution in this region. The Ribeira Bay has a natural background metal content, when compared with average shales and with other impacted and non-impacted regions.

Keywords: metal distribution, Ribeira bay, coastal regions, sediments, normalization

Introduction

In many tropical countries, foreign trade has driven industrialization to coastal areas, due to the easy establishment of port passages to exportation. Therefore, in countries like Brazil, Colombia, Mexico, among others, more than half of the population and most of the industrial production are located along the coast, resulting in high levels of contamination in these regions. It is therefore not surprising that coastal ecosystems in tropical areas are among the most threatened by environmental impact derived from human activity. The Brazilian state of Rio de Janeiro is a typical example of such a situation, with about 80% of its population and industrial activity concentrated at the coast, especially near Guanabara and Sepetiba Bays[1].

In Brazil, research on metal contamination is currently carried out in regions under high environmental threat, such as the Santos (São Paulo state), Guanabara (Rio de Janeiro state), and Todos os Santos (Bahia state) bays; in more preserved regions, however, avaliable data are still much scarce[2].

The Ribeira Bay, in the Angra dos Reis region, is an important tourist resort of Rio de Janeiro State. Considering its well preserved condition, the few available data on the metal content of its sediments[3] have been used as natural (background) reference values for comparison with metal distribution data from other, more contaminated bays of the region. Another highly relevant factor is the location of the Ribeira Bay between two major industrial centres: the

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industrial area of Rio de Janeiro (Guanabara and Sepetiba Bays) and that of Paraíba Valley[4].

Despite the awareness of the metal contamination issue in the neighboring Sepetiba Bay, relatively few studies have been carried out concerning the Ribeira Bay. Although less impacted, this site hosts industrial plants (Verolme Shipyard), the Angra dos Reis Port, and an oil terminal (TEBIG-Petrobrás), all relevant sources of metal contamination.

Metal contamination impacts the coastal environment through atmospheric precipitation, fluvial income and direct effluent disposal. Fluvial income is the main carrier of continental metals to coastal zones, especially through suspended particulate materials[5].

When the rivers reach the marine environment, the main fraction of suspended particulate material is deposited near the coast, acting as a geochemical barrier to the flow of metals into the open ocean. Nevertheless, the intense biological activity and the great diversity of environmental conditions, especially in tropical regions, still result in extensive variations in metal content, promoting seasonal removals and regeneration of biological productivity cycles, depositing and removing metals in sediments, and causing chemical exchange between dissolved and particulate phases[6].

This study aims to investigate metal distribution on coastal marine sediments of the Ribeira Bay, a region currently showing a reasonably high degree of preservation, with no significant anthropogenic metal sources. The results are potentially useful as a reference database for metal concentration under natural conditions, thus providing parameters against which environmental research data from neighbouring and/or similar regions may be compared. In order to achieve this goal, concentrations of each studied metal were normalized to Al, as the reference element[7]. On the basis of correlation coefficient[8], metals were classified as: a) strongly correlated to Al, b) correlated to Al, c) inversely correlated to Al, or d) non-correlated to Al. Finally, the data were subjected to cluster analysis.

Experimental

Site description

The Ribeira Bay is a semi-confined salt water body, located at the northern part of Ilha Grande Bay, Rio de Janeiro State (Figure 1), comprising the Bracuí, Ariró and Japuíba Coves. The Bay is about 172 km^2 in area, with medium and maximum depth of 7 and 21 m, respectively. The local weather is extremely wet, with a rainfall index between 2000 and 2600 mm and annual temperatures ranging from 18 to 23 °C [4].
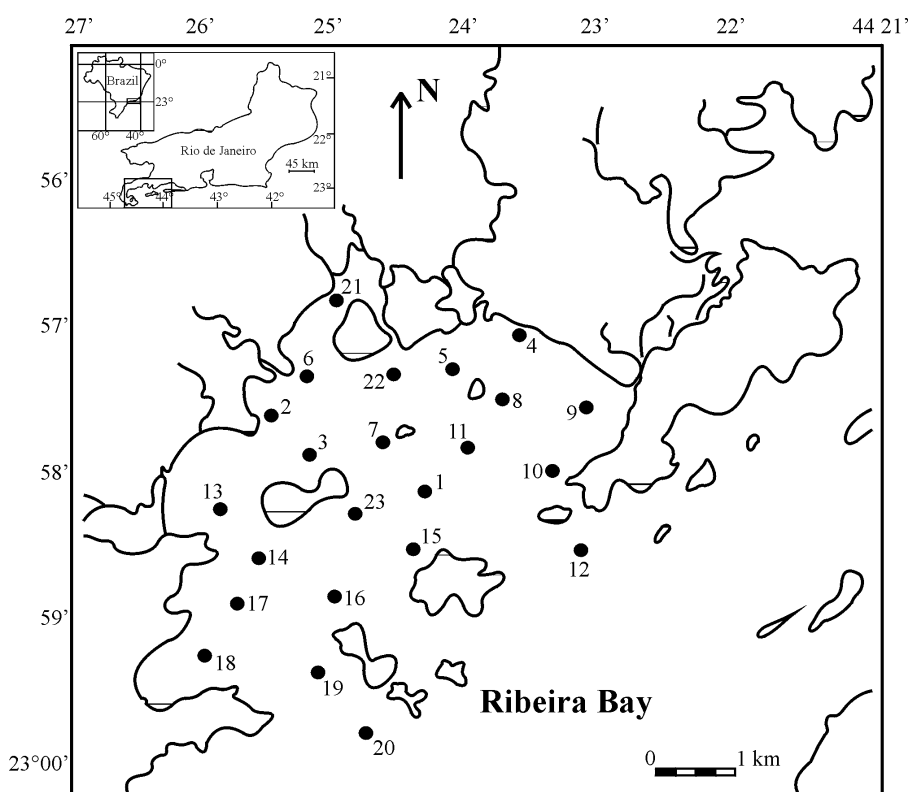

Figure 1. Location of sampling sites.

Mangroves occur near river mouths in the area. The predominant riverside vegetation forms an entangled system of roots which concurs to the accumulation of sediments, allowing the passage of fine-grained materials only, which are then deposited in the Bay[9].

The Ribeira Bay is surrounded, to the east and to the west, by homogeneous and heterogeneous migmatites with gnaissic or granulitic paleosome. To the northeast border, rocks of the charnockitic association predominate, together with intermediate to basic rocks, especially diorite, gabbro and pyroxenite. In the areas surrounding the Bracuí and Ariró Coves, marine quaternary sediments dominate[10].

Sampling and analytical techniques

A group of 23 surface sediment samples were collected at Bracuí Cove (Figure 1), along the Ribeira Bay, using a Van-Veen type stainless steel ground probe. The samples were transported to the laboratory in low-temperature (0°C) containers, and frozen immediately. Metals were extracted from a 1.000 g aliquot of dry (50 °C for 24 h) sediment, following the method proposed by Thompson and Walsh[11]. All determinations were made on the whole sample because the silt-clay fraction (< 0.063 mm) was always dominant. The weight percentage of the silt-clay fraction varied in the range 62-98%, as determined through wet sifting with standard nylon sieves. The concentration of Ti, Ca, Mg, Fe, Al, Sr, La, V, Y, Ni, Cu, Cr, Mn, and Zn, were determined by a Spectroflame FVM03 Atomic Emission Spectrometer with Inductive Coupled Plasma source (ICP/AES). Hg was determined by a Coleman Bacharach 50D cold-vapour atomic absorption spectrophotometer (CVAAS).

Analytical results were monitored with NIST (National Institute of Standards and Technology-USA) soil reference standard (San Joaquin Soil) which was analysed jointly with the samples. The results were found to be accurate (Table 1).

For the samples BR 04 and BR 21, the main minerals were determined by XRD analysis, made on non-oriented whole sample. Additionally, the clay fraction was separated in a centrifuge and analyzed according to the method of Moore and Reynolds Jr[12], for the study of clays (oriented samples air-dried and glicolated). All XRD analyses were carried out in a RIGAKU D/MAX-2A/C GEIGERFLEX diffractometer, equiped with a Cu tube, operating at 40 KV and 20 mA. The whole sample analyses consisted of a 2 to 60º scanning, at a velocity of 2º/min. In the clay fraction, the analyses consisted of a 2 to 35º scanning, at a velocity of 2º/min.

Table 1. Certified values compared with results obtained through a series of four independent digestions of the *San Joaquin Soil* Standard.

Element	Certified values (μg g^{-1})	Average results (μg g^{-1})	Results range (μg g^{-1})
Ca (%)	1.89±0.05	1.86	1.71-1.91
Mg (%)	1.51±0.05	1.33	1.29-1.38
Ti (%)	0.342±0.024	0.31	0.29-0.33
Fe (%)	3.60±0.11	3.22	3.05-3.47
Al (%)	7.50±0.06	7.00	6.93-7.49
Sr (μg g^{-1})	231±2	196	189-214
La (μg g^{-1})	23*	28	25-30
Y (μg g^{-1})	18*	14	13-16
V (μg g^{-1})	112±5	105	92-118
Ni (μg g^{-1})	88±5	98	86-102
Cu (μg g^{-1})	34.6±0.7	28	26-32
Cr (μg g^{-1})	130±4	108	102-120
Mn (μg g^{-1})	538±17	523	503-558
Zn (μg g^{-1})	106±3	99	94-101
Hg (μg g^{-1})	1.40±0.08	1.18	1.13-1.28

* recommended values. n = 4, except Hg, where n = 8.

Results and Discussion

A strong continental metal affiliation in the sediments arriving at the Ribeira Bay, was demonstrated by previous authors[9,13], who established the existence of a significant homogeneity at the bottom of the Bay, leading to the presence of clay species with high metal fixation capacity. This was confirmed by the dominance of smectites and chlorites over other clay minerals.

Table 2 shows the average concentrations and the ranges of metal content in the Ribeira Bay sediments. Note that these figures are comparable with the average shales[14], confirming that metal concentrations in the bottom sediments of Ribeira Bay are within the range of natural sediments.

Table 3 shows a comparative chart of metal concentration in various impacted and non impacted areas, confirming the existence of natural, background metal levels at the Ribeira Bay, and strengthening the relevance of this area as a reference region for comparison with environmental studies in neighbouring and/or similar regions. Hg, Zn, Cr and Cu are important contaminants, since in the States of Rio de Janeiro and São Paulo there are impacted areas which show high concentrations of these elements. For instance, in the Sepetiba Bay there is a Zn contaminations, whereas in the Guanabara Bay the main contaminants are Cr and Cu, and in the Santos Bay, the main contaminant is Hg. For all the above mentioned elements, the concentrations obtained in the present study of the Riberia Bay are well below those of the impacted nearby areas. These figures can potentially be used as reference values of a non-impacted area under the same (tropical) weather regime.

Table 2. Metal concentrations in bottom sediments from Ribeira Bay (Average, minimum, maximum, and standard deviation). Values for the average shale (Bowen, 1979) are also shown.

				Metals				
n = 23	Al (%)	Ti (%)	Ca (%)	Mg (%)	Fe (%)	Hg (ng g^{-1})	Zn (µg g^{-1})	Mn (µg g^{-1})
Average	8.89	0.48	1.82	1.46	4.08	28	113	469
Min	2.33	0.11	0.49	0.54	1.06	10	29	202
Max	10.88	0.58	9.71	1.65	4.97	53	189	981
SD	1.99	0.10	2.22	0.23	0.88	11	37	176
Shale	8.80	0.46	1.60	1.60	4.80	180	120	850

				Metals			
	Ni (µg g^{-1})	Sr (µg g^{-1})	La (µg g^{-1})	V (µg g^{-1})	Y (µg g^{-1})	Cu (µg g^{-1})	Cr (µg g^{-1})
Average	45	163	50	87	13	14	72
Min	27	85	26	20	5	3	24
Max	73	708	84	166	18	32	110
SD	13	135	15	31	3	8	23
Shale	68	300	49	130	41	39	90

Table 3. Comparative Chart of metal concentration in various impacted and non impacted areas. Expanded from Lacerda (1987), using additional data.

	Hg	Zn	Cr	Cu	Ni	Mn	Fe	Al
Todos os Santos Bay, BA[15] *	0.001-0.82	5-2400		5-55				
Sepetiba Bay, RJ[16] *		588	57	73	92	326	4.0	10.0
Guanabara Bay, RJ[17] *		78-124	111-623	91-731				
Santos Bay, SP[18] *	0.02-1.15	20-81	2-46	0.4-19				
Patos Lagoon, RS[19] *		20-214	8-337	0.8-20				
Spencer Gulf, Austrália[20] *		11-16667		3-122		66-1227		
Mangaratiba Bay, RJ[17] #		195-230	97-108	23.5-31.2		233-609	2.25-4.50	
Ribeira Bay, RJ[2] #		83	31	7.7		1.25		
Ribeira Bay, RJ # (this study)	0.010-0.053	29-189	24-110	2.5-32	27-73	202-981	1.06-4.97	2.33-10.88

Al and Fe in (%), others in (µg g^{-1}). #Non impacted regions; *Impacted regions

It is also noteworthy that the results obtained by Lacerda et al.[2], over 15 years ago, for a lesser number of metals (Zn, Cr, Cu, and Mn) in the Ribeira Bay, are within the concentration ranges obtained in the present study, except for Mn. For this element, the figures obtained during the present research are in the same order of magnitude as those of other neighbouring regions, such as the Sepetiba and Mangaratiba Bays (Table 3), whilst Lacerda *et al.*[2] reported much lower Mn values (1.25 µg g^{-1}).

Results obtained for each metal were normalized using Al as a reference element. Through a correlation coefficient study, metals were classified in four groups.

Three metals (Fe, Ti, Mg) are strongly associated with Al, showing correlation coefficients of 0.98; 0.86 and 0.85 respectively (see Figure 2 for examples). Such metals are typical constituents of ferromagnesian aluminium silicates and a strong covariance with Al is expected. Since the regional rocks are rich in micas (especially biotite), this correlation is consistent with a common source for these metals[13].

The second group of metals, comprising Zn, Y, V, Hg, Cu, and Cr still show significant positive correlation with Al (correlation coefficients between 0.76 and 0.65 – see Figure 3 for selected examples). The correlation is not as strong as in the first group (Fe, Mg, and Ti), but aluminium silicates, such as clays, are still the most important source for these metals. In a study conducted at Bracuí Cove (Angra dos Reis), Bidone and Silva-Filho[13] showed that, at least in the case of Cu, biotite is the main carrying media and the only one with enough stability to survive transportation and reach the Bay sediments.
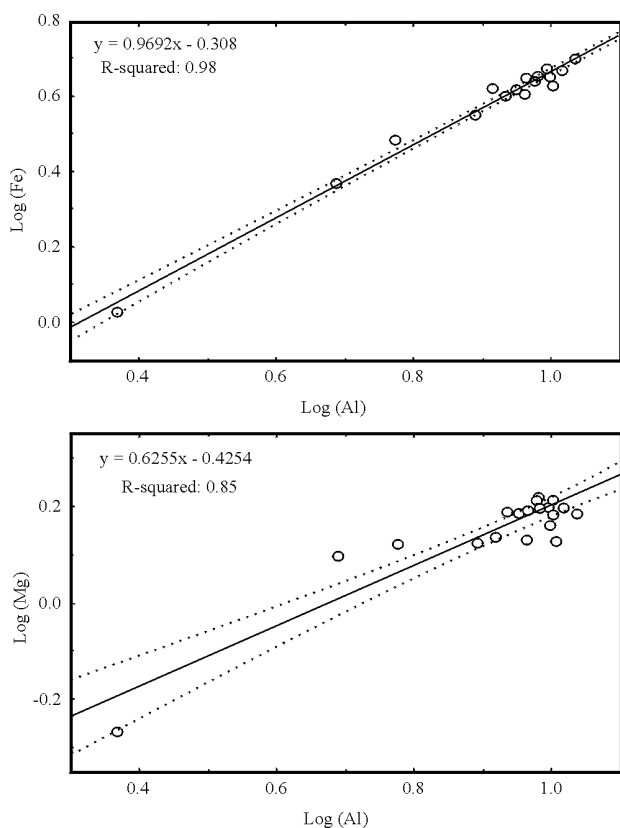
Figure 2. Correlation plot Log (Al) vs Log (Fe) and Log (Mg). Dotted lines are the 95 % confidence limits of the regression (solid line).

The third group, composed by Ca and Sr (Figure 4), has special characteristics. The negative correlation of both metals with Al, suggests that: a) they come from a source independent of aluminium silicates and b) they are not significantly adsorbed by aluminium silicates. Ca and Sr must have a marine origin, since biogenic carbonates (especially carbonate shells) constitute the most important sediment fraction for such elements in the region. Although a possible source for Ca could be the continental silicate rocks, the high correlation coefficient between Ca and Sr (0.85) stresses a common origin for both elements, and suggests that their most probable source is carbonate minerals.

Finally, the fourth group is composed by the metals Mn, La (Figure 5), and Ni, which lack any correlation with Al. This suggests control by one or more alternative mineral phases (oxide/hydroxide of Fe and Mn; phosphates; organic matter). Aluminium silicates and biogenic carbonates may also carry these metals, although at very low concentration. With regard to La, the occurrence of monazite in sediments of the studied area[21] is probably the best explanation for its origin. The high correlation coefficient between Ni and Mn (0.83) suggests that oxides and hydroxides are the main mineral phases controlling the distribution of these metals. Ni was demonstrated by Pendias et al.[22] to be easily mobilized, precipitating in association with Fe and Mn in oxides and hydroxides.
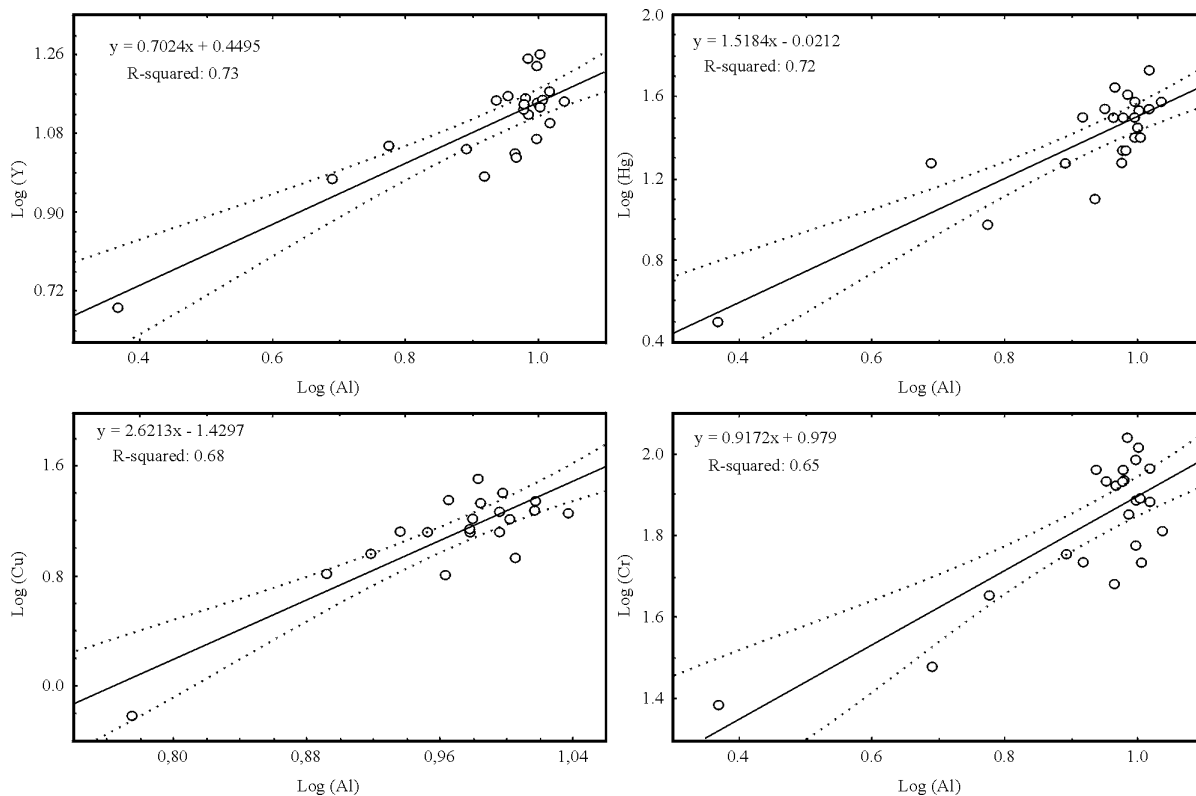

Figure 3. Correlation plot Log (Al) vs Log (Y), Log (Hg) Log (Cu), and Log (Cr). Dotted lines are the 95 % confidence limits of the regression (solid line).
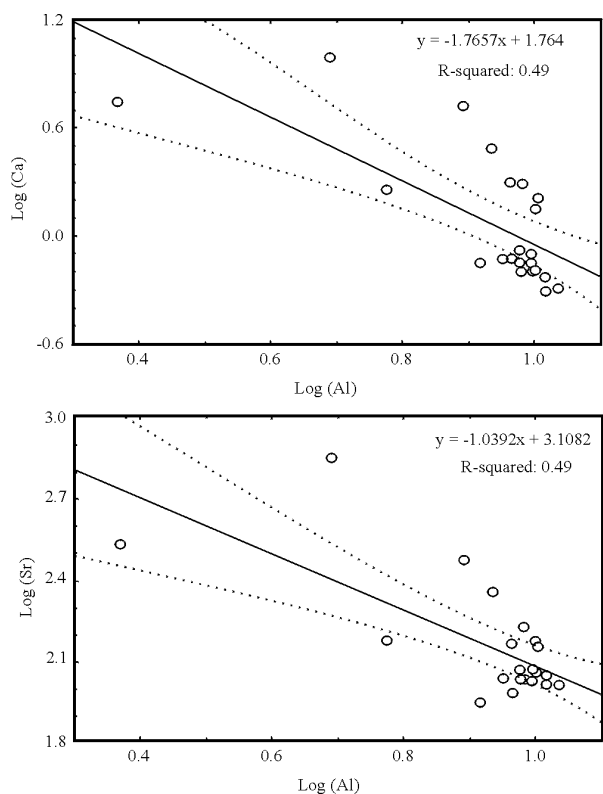
Figure 4. Correlation plot Log (Al) vs Log (Ca) and Log (Sr). Dotted lines are the 95 % confidence limits of the regression (solid line).
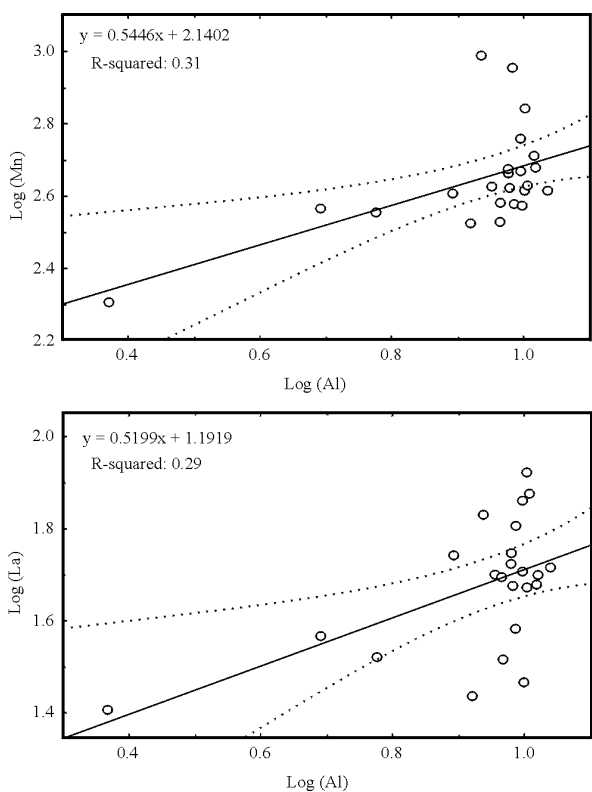

Figure 5. Correlation plot Log (Al) vs Log (Mn), Log (La), and Log (Ni). Dotted lines are the 95 % confidence limits of the regression (solid line).

The XRD results show that the sediments in the region consist mostly of the minerals smectite, gibbsite, kaolinite, quartz, chlorite, microcline, monazite and ilmenite. Additionally, the presence of fragments of carbonate shells was detected in the coarse-grained fraction.

The XRD study did not detect the presence of biotite, but showed that clay minerals are likely to be a major host of metals in sediment. Thefore, even if the metals are carried by micas, these minerals arrive at the Bay altered to smectite, kaolinite, and gibbsite, depending on the source, type of alteration and transportation conditions.

To test the results obtained with the Al normalization, a cluster analysis was performed. The percentage of fine grainsize particles and the content of organic matter were included in the dataset for this particular study. The resulting dendogramme (Figure 6) shows 3 main groups:

The characteristics of the first group (to the left of the dendogramme), formed by Ca and Sr, are completely different from the other metals studied. This is in good agreement the results obtained in normalization, confirming that Ca and Sr have a distinct (*i.e.*, marine) source, comprising biogenic carbonates, present in high concentration in sediments with coarser grain size.
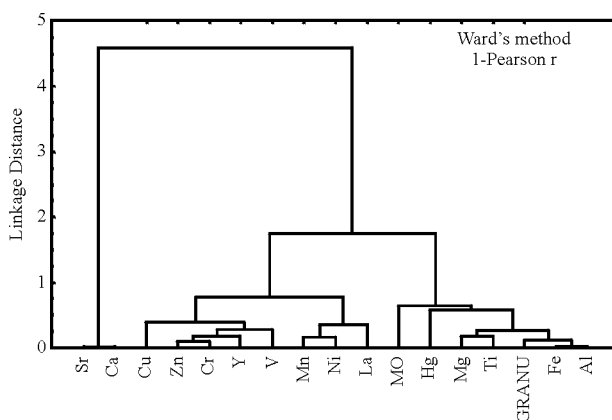

Figure 6. Dendogramme grouping of the metal concentration database (GRANU = percentage of fine-grained material; MO = organic matter).

The second group, to the right of the dendogramme is formed by the variables Fe, Ti, Al, Mg, percentage of fine grainsize particles (GRANU), organic matter content (MO) and by Hg. These parameters show strong correlation with each other. In the case of the major elements, as deduced from the normalization study, the geology of area (biotite – rich granites and gneisses) explains their origin, the ferromagnesian aluminium silicates being the main carriers. Hg is closely associated with the organic matter, which occurs dominantly in same grainsize fraction (fine-grained particles) as the Al rich phases (clays).

The central group is clearly subdivided in two subgroups. The first subgroup is formed by Ni, Mn and La, in good agreement with the normalization results. Mn and Ni are more closely associated, both elements being hosted by hydroxides and oxides of Mn. La, which appears as an isolated branch, has its source in phosphates (monazite), which is consistent with the mineralogy of the region and explains the lack of correlation with any other metal. The other subgroup comprises Cu, Y, V, Cr and Zn, *i.e.*, the remainder of the studied trace elements. According to normalization, these metals are associated with Al, but the dendogramme shows that they form a separate group.

Figure 7 shows the results of a cluster analysis of the sampling sites. In order to investigate the main characteristics of the sample sites, it is previously necessary to understand some factors concerning local hydrodynamics, in a region with little tide width, where the difference between the maximum and the minimum is small, and the annual tide distribution is homogeneous, regardless of the season. As a consequence, streams related to wind activity are the main causes of internal circulation in the local coves. Due to the small depth (scarcely over 15 m) such streams also cause the re-suspending of settled material and, probably, the transfer of material outside the coves. Such wind-related streams are more active during the winter, due to the occurrence of frequent cold fronts in that region[13].
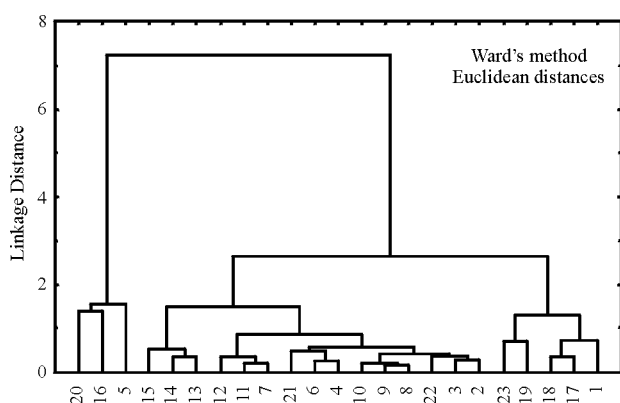

Figure 7. Dendogramme grouping of 23 sample sites, based on metal distribution.

In the coves, the circulation is precisely defined by the wind regime. It is anticlockwise when the weather is calm and clockwise during pre and post frontal winds. Post frontal winds, typically with a strong southern component, induce streams whose speed can be increased by up to 5 times or more[13].

Considering the importance of the hydrodynamic factors, the cluster analysis was applied to the study of sample sites[23]. This resulted in three main groups (Figure 7).

In the first group (to the left of the dendogramme), points 16 and 20 are under strong marine influence, presenting very high concentrations of Ca and Sr (9.61 and 5.60% Ca; 708 and 335 μg g^{-1} Sr), low concentrations of Al and Fe (4.89 and 2.33% Al; 2.33 and 1.06% Fe), and coarser grainsize (62% of fine-grained material, in both sites). Point 5 is also characterized by coarser sediment (65% of fine-grained), but is distinguished from the other points of this group by relatively lower concentrations of Ca and Sr (1.80% Ca and 145 μg g^{-1} Sr).

The second group (to the right of the dendogramme), composed by sites 1, 17, 18, 19, and 23, is characterized by normal concentrations of Al and Fe for all samples (Al ranging from 7.79 to 10.11% and Fe from 3.53 to 4.24%), but is distinguished from the central group by slightly high concentrations of Ca in points 17 (1.99%), 18 (1.62%), 19 (5.22%) and 23 (3.08%), as well as by fewer coarse particles in point 1 (75% of fine-grained material). This group is the most susceptible to the climate variations and to changes associated with hydrodynamic factors, because of its combined marine and continental character; the marine influence depends on climatic and hydrodynamic factors. In favourable conditions (arrival of cold fronts), such points will be subjected to a stronger marine influence, as a consequence of the higher intensity of the marine streams in the area.

The third group (in the center of the dendogramme), comprises the largest number of points, characterised by homogeneity regarding grainsize (> than 80% of fine-grained material), normal concentrations of Ca (0.49 to 1.96%), Sr (93 to 145 μg g^{-1}), and Fe (4.14 to 4.97%), but high concentrations of Al (8.96% to 10.88). Therefore, this group is interpreted as dominated by continental influence. The erosion susceptibility of the soils in the region, together with the development of tourism, are important factors controlling this dominantly continental contribution.

Conclusions

The similarity of the metal concentration in the Ribeira Bay with average shales, and the comparison between Ribeira Bay and other impacted and non-impacted regions, confirm that the metal content in the studied area can be explained by natural conditions.

Normalization of metal concentration data clearly indicated that Ca and Sr biogenic carbonates and ferromagnesian aluminium silicates are responsible for the existence of two separate groups (marine- and continental-derived) of metals in the Bay.

The mineralogical study of the two points nearest to the continent, confirmed the importance of the continental

metal input into the region. At these sites, the sediments are composed mostly by clay minerals, especially kaolinite, gibbsite, smectite, ilite and chlorite, which are major hosts of metals in sediment.

The cluster analyses performed for metal content, grain size and organic matter, confirmed most of the results obtained in normalization, but showed the association of Hg with the organic matter, which was not previously evidenced. The organic matter has affinity with fine particles, coexisting in same grainsize fraction of the sediments.

The sampling sites were classified into three main groups where grain size (% of fine-grained material), the Fe and Al concentration (continental influence) and the Ca and Sr concentration (marine influence) were the determinant factors for the discrimination. This technique highlighted some characteristics of each group. The group to the left of the dendogramme, is dominated by marine influence. The central group is mostly influenced by continental sources. The third group, to the right, shows an intermediate behaviour, combining both a marine and a continental character.

In spite of results confirming that Ribeira Bay remains a non impacted area, it is important, in future studies, to pay special attention to climatic and hydrodynamic factors, which directly influence the metal distribution in the region.

Acknowledgements

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