

Evaluation of metals availability in sediments of the Bertioga Channel (Santos Estuarine Complex - SP - Brazil): A tool for chemical pollution monitoring*

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ABSTRACT

The Bertioga Channel (SE Brazilian coast) is part of the Santos Estuarine Complex, situated at the Baixada Santista. The Baixada Santista is a very important economic region of Brazil which, due to its intensive economic development, has been experiencing several interventions on its coastal environment. Both the largest harbor, located on the city of Santos, and the Cubatão industrial complex, which presents large chemical, petrochemical and steel industries, are found near the Bertioga Channel. As a consequence, this socially and environmentally relevant channel is exposed to various sources of pollution that can increase the content of contaminating metals in sediments. For these reasons, the main objective of this study was to analyze the availability of potentially toxic elements (Cd, Cr, Cu, Ni, Pb and Zn) in sediment cores sampled along the Bertioga Channel. In this study, the term availability refers to the possibility of metal remobilization in sediments. By applying the chemical procedure of sequential extraction of metals, it was determined the contents of the elements of interest associated with the sediments' main components, enabling the assessment of the mobile fraction and the behavior of the elements regarding their remobilization. Therefore, this study can serve as a management tool for monitoring chemical pollution in the region. In order to evaluate the chemical contamination in sediments, the elements' available levels (excepting Ni) were compared to Canadian quality guidelines (ISQG and PEL). Due to the absence of comparative values of Ni for this guide, this element was compared to values described on the CONAMA 454/2012 resolution for dredging material from the Brazilian Ministry of Environment. For the environment risk assessment, the Risk Assessment Code - RAC - was employed toward a better understanding of the risk concerning the elements' remobilization. The maximum available levels, estimated from the sum of all mobile fraction, were 22.06 mg kg⁻¹ for Cr, 5.57 mg kg⁻¹ for Cu, 11.53 mg kg⁻¹ for Ni, 36.43 mg kg⁻¹ for Pb and 57.53 mg kg⁻¹

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for Zn. Cd presented levels below its quantification limit for all samples. It was observed that, excepting Cd, there is potential for the remobilization of all those elements, even though they exist in very low concentration and are not associated, mainly, to the acid-soluble fraction (considered the most environmentally relevant one due to its mobility level). Changes on local conditions can induce the remobilization of those metals and, thus, allow them to become available to the environment. However, even when released possibly they should not be hazardous to the biota as a result of their low contents in the sediments. Despite the low concentrations of Cr, Cu, Ni, Pb and Zn and considering that the observations made in this study were based on their available contents, the results highlight an anthropic contribution of those metals for the region, the potential for their accumulation and showing the importance of such monitoring for the future protection of the local communities.

Keywords: SE Brazilian coast, potentially toxic elements, sequential extraction, Risk Assessment Code (RAC).

RESUMO

Avaliação da disponibilidade de metais em sedimentos do Canal de Bertioga (Complexo Estuarino Santista – SP - Brasil): uma ferramenta para o monitoramento da poluição química

O Canal de Bertioga é um dos canais que constitui o complexo estuarino de Santos, localizado na costa sudeste brasileira. A Baixada Santista é uma região economicamente importante do Brasil que, em razão do seu intenso desenvolvimento econômico, tem sofrido intervenções no seu ambiente costeiro. Nas imediações do Canal de Bertioga encontra-se o maior porto do país, localizado na cidade de Santos, e o complexo industrial de Cubatão que comporta indústrias de grande porte dos segmentos químico, petroquímico e siderúrgico. Como consequência, esse Canal de importância social e econômica, está exposto a diversas fontes de poluição com potencial para aumentar o teor de contaminantes metálicos nos sedimentos. Diante desse cenário, o principal objetivo desse trabalho foi analisar a disponibilidade de elementos potencialmente tóxicos em sedimentos de testemunhos coletados ao longo do Canal de Bertioga. O termo disponibilidade aqui empregado refere-se à possibilidade de remobilização dos metais presentes nos sedimentos. Aplicando-se procedimento químico de extração sequencial de metais, determinou-se o teor de Cd, Cr, Cu, Ni, Pb e Zn associado aos principais componentes dos sedimentos. Esses dados possibilitaram estimar o teor disponível e o comportamento destes elementos quanto à remobilização, tornando esse estudo uma ferramenta gerencial em termos de monitoramento da poluição química da região. O teor máximo disponível, estimado a partir da soma das frações móveis, foi 22,06 mg kg⁻¹ para Cr; 5,57 mg kg⁻¹ para Cu; 11,53 mg kg⁻¹ para Ni; 36,43 mg kg⁻¹ para Pb e 57,53 mg kg⁻¹ para Zn. O Cd apresentou teor inferior ao seu limite de quantificação em todas as amostras. Com exceção do Cd, verificou-se que há potencial para remobilização desses elementos, ainda que estejam em baixa concentração nos sedimentos. Alterações das condições ambientais poderão causar a remobilização desses metais e, conseqüentemente, deixá-los disponíveis. Entretanto, se remobilizados, em razão do baixo teor, estima-se que não representariam perigo à biota. Contudo, considerando-se que esse estudo baseou-se no teor disponível, ainda que as concentrações de Cr, Cu, Ni, Pb e Zn sejam baixas, pode-se inferir que esses resultados são indicativos de uma contribuição antrópica desses elementos na região e do potencial para acumulação de metais, mostrando a importância do monitoramento de elementos potencialmente tóxicos para proteção futura das comunidades bióticas.

Palavras-chave: costa sudeste brasileira, elementos potencialmente tóxicos, extração sequencial, Risk Assessment Code (RAC)

1. Introduction

Environmental pollution by chemical contaminants is a current and persistent issue, usually associated with the industrial and economic growth of a region. In recent decades, environmental studies focusing on metals availability have become an effective tool in the difficult challenge of integrated coastal management, assisting both in environmental impact diagnosis as in action plan that favors environmental preservation.

In aquatic environments, sediments are an important compartment, in which potentially toxic metals occupy a prominent position when contamination is considered. Although the accumulation of heavy metals in sediments provide temporary improvement in the quality of overlying water, polluted sediments can be seen as “time bombs” (Kelderman & Osman, 2007), since the contaminants are not necessarily fixed permanently in them (Förstner 1979; Calmano *et al.*, 1996; Zoumis *et al.*, 2001). A change in physicochemical conditions can result in their remobilization, which would make it

available to biotic communities. In this scenario, sediments are considered both a reservoir of chemical species and an active aquatic compartment, which plays an important role in the redistribution of these species (Cotta *et al.*, 2006; Cuong & Obbard, 2006).

The mobility, transport and fractionation of heavy metals are a function of the element chemical form, which in turn is controlled by the physicochemical and biological characteristics of the system (Sakan *et al.*, 2009).

In the mobilization of heavy metals from sediments the redox potential and pH are considered the main variables (Calmano *et al.*, 1993). Among the factors that could cause these redox changes are: (1) the increase in nutrients (Förstner, 1979), (2) the oxidation-reduction cycle that varies seasonally, especially in summer, when the concentration of oxygen in the water-sediment interface tends to decrease (El-Azim & El-Moselhy, 2005) and (3) the daily tidal currents that cause periodic changes in the redox potential of coastal

and estuarine sediments (Calmano *et al.*, 1993). Oxygen deficiency in the sediments leads to an initial dissolution of hydrated manganese oxide, followed by that of iron compounds, leading to partial remobilization of any co-precipitated with metallic coatings (Förstner, 1979). In turn, reduction of pH leads to carbonates and hydroxides dissolution, as well as increase in metallic cations desorption due to competition with H⁺ ions (Förstner, 1981). Several investigations have shown that pH decreases during sediment oxidation, being significant at metal remobilization (Förstner, 2004).

A procedure commonly used for a detailed investigation into the behavior of metals in soils and sediments is sequential extraction. The method developed and optimized by the European Community Bureau of Reference (BCR), currently Standards, Measurements and Testing (SM&T), is considered one of the most popular (Abollino *et al.*, 2011), and establishes three distinct stages in which the elements are sequentially extracted: (1) exchangeable metals and those associated with carbonates, (2) metals associated with Fe and Mn oxides, (3) metals associated with organic matter and sulfides. Considering that in unpolluted soils and sediments the metals are associated mainly to silicates and primary minerals, which forms species relatively immobile (Rauret, 1998), it can be inferred that the metal content extracted from these fractions represents an indicative of anthropogenic influence and thus demonstrates environmental pollution.

In this context, the aim of this study was to analyze the availability of Cd, Cr, Cu, Ni, Pb and Zn in sediment cores collected along the Bertioga Channel, inserted

into the Santista estuarine complex and located between latitudes 23° 51' S and 23° 57' S and longitudes 46° 08' W and 46°19'W (Figure 1).

The Bertioga Channel presents economic and social importance, including recreational and fishing activities (Silva *et al.*, 2011). The length of the Canal is of approximately 25 km, with depths up to 15 m in the region of Barra de Bertioga and some depressions to the Largo do Candinho, which observed the greatest widths; the water inflow is carried by rivers with relatively small discharges, with only the river Itapanhaú presenting a higher importance (Bernardes & Miranda, 2001).

The Baixada Santista is an economically important region of Brazil, which, because of its significance, has undergone several alterations on its coastal environment. In the vicinity of the Bertioga Channel, in the City of Santos, is located the largest port in the country, as well as the industrial complex of Cubatão, which includes large petrochemicals, chemical and steel segment industries.

As a result, this Channel is exposed to various sources of pollution that may increase the potential metal accumulation in sediments. Given this concern, several studies related to metals have been developed in the region (*e.g.*, Siqueira *et al.*, 2005; Oliveira *et al.*, 2007; Silva *et al.*, 2011; Gonçalves *et al.*, 2013.). However, available information are generally based on results from total or partial metals, making important an evaluation on the availability of potentially toxic elements in the region in order to estimate the risk of remobilization. The relevance of this kind of information is clear, both in combination with studies on the biota, as constituting an

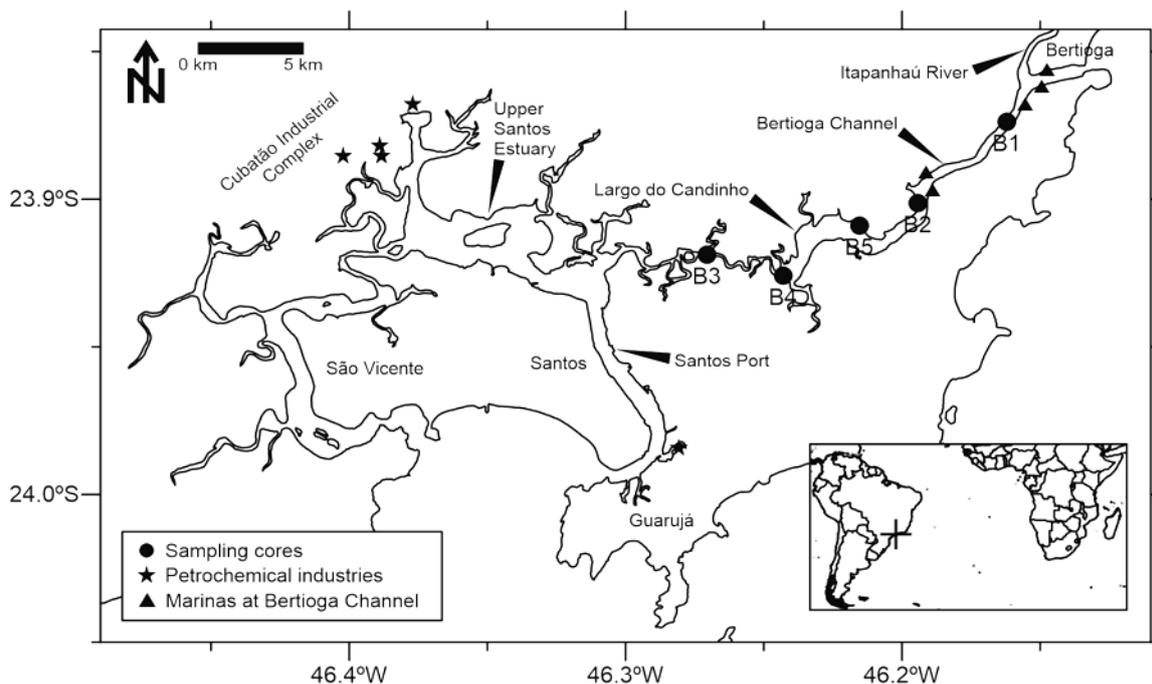


Figure 1 - Location of the sampled cores (B1, B2, B3, B4 e B5) along the Bertioga Channel.

Figura 1 - Localização dos testemunhos (B1, B2, B3, B4 e B5) coletados ao longo do Canal de Bertioga.

important coastal management tool for the monitoring of chemical pollution in the region. It is appropriate to clarify that the term “availability” used here is related to the possibility of remobilization of metals in the environment and does not reflect their bioavailability.

2. Materials and methods

2.1 Sampling and sample preparation

In February 2010 five sediment cores (B1, B2, B3, B4 and B5) were collected along the Bertioga Channel (Figure 1) using a Rossfelder VT-1 vibracorer. These sediment cores were fractionated into 2 cm thick slices and freeze-dried, after what five samples of each core (depth ranging between 0 and 10 cm) were selected, totaling 25 sediment samples that were subjected to sequential extraction. The selection of the first 10 cm layer was due to the greater biological activity and sediment-water interaction in this fraction.

2.2 Sequential extraction of metals

To determine the availability of Cd, Cr, Cu, Ni, Pb and Zn in Bertioga Channel the sequential extraction procedure was used. This method is based on the protocol developed and optimized by the European Community Bureau of Reference (BCR), currently Standards, Measurements and Testing (SM&T), described in Pueyo *et al.* (2001). The method provides three separate stages in which the metals are sequentially extracted by the chemical action of specific reagents for each of these steps. Details are included in Supporting Information.

The quantitative analysis of selected elements was performed through ICP-OES (inductively coupled plasma-optical emission spectrometry) technique (Varian analyzer, model MPX 710-ES). The quantification limits (QL) were 0.64 mg kg⁻¹ for Cd; 1.00 mg kg⁻¹ for Cr;

0.72 mg kg⁻¹ for Cu; 0.53 mg kg⁻¹ for Ni; 1.35 mg kg⁻¹ for Pb and 1.56 mg kg⁻¹ for Zn.

2.3 Environmental Chemical Analysis

The available content of Cd, Cr, Cu, Ni, Pb and Zn in the analyzed sediments was estimated from the sum of the concentration of these elements in the three fractions operationally defined by the BCR (F1 + F2 + F3). It is assumed that the metal associated with these fractions can be released if changes in environmental conditions occur (Calmano *et al.*, 1993; Marin *et al.*, 1997). For the composition of these sums only values higher than QL determined for each element were considered. The available content of Cr, Cu, Pb and Zn was compared with the quality standards established by the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life for marine sediment (CCME, 2001). Based on the effects of the elements on the biota are set two limits, the lowest limit, ISQG (Interim Sediment Quality Guideline) and the higher limit, PEL (Probable Effect Level). Due to the lack of reference values for Ni in this guide, results for this element were compared with the predicted values for dredging material in the Brazilian Ministry of Environment Resolution N^o. 454, of 2012 (CONAMA, 2012), in which quality criteria are established from N1 levels (threshold below which there is less likelihood of adverse effects to biota) to N2 (threshold above which there is a greater likelihood of adverse effects to biota). Reference values set out in those documents are shown in Table 1.

For the analysis of environmental risk were applied the Risk Assessment Code (RAC) methodology, used in several studies as a tool for better understanding of the environmental risk in relation to remobilization of metals (eg. Jain, 2004; Singh *et al.*, 2005; Ghrefat & Yusuf, 2006; Passos *et al.*, 2010). This risk assessment criteria

Table 1 - Reference values (ISQG, PEL, N1 e N2) and range of metal available content (F1 + F2 + F3), in mg kg⁻¹, in each of the sediment core.

Tabela 1 - Valores de referência (ISQG, PEL, N1 e N2) e variação do teor disponível de metais (F1 + F2 + F3), em mg kg⁻¹, em cada testemunho.

Metal	Canadian values (CCME, 2001) ^a		Resolution n ^o 454/2012 (CONAMA, 2012) ^b		B1	B2	B3	B4	B5
	ISQG	PEL	N1	N2					
Ni	-	-	20.9	51.6	6.64 – 9.30	1.77 – 3.69	8.89 – 11.53	7.57 – 10.66	9,82 – 11,09
Cd	0.7	4.2			< QL				
Cr	52.3	160			17.1 – 22.06	2.7 – 6.50	14.96 – 19.01	15.58 – 18.83	16.61 – 19.42
Cu	18.7	108			4.48 – 5.57	0.84 – 1.72	2.93 – 4.76	2.04 – 2.86	3.56 – 5.02
Pb	30.2	112			16.39 – 36.43	1.93 – 13.16	11.45 – 16.57	12.49 – 20.96	16.11 – 23.77
Zn	124	271			25.26 – 42.31	11.35 – 19.66	24.23 – 39.48	30.73 – 35.60	40.42 – 57.53

^amarine sediments; ^bsalt/brackish water; QL-quantification limit

is based on the content of exchangeable metals and those associated with carbonates, as this fraction elements are weakly bound to the sediments and therefore at greater risk of remobilization in the aquatic system (Passos *et al.*, 2010). In this work, the RAC criterion was applied based on the percentage of the element in the acid-soluble fraction (F1). As presented by previous works, when the metal percentage in this fraction is less than 1%, according to the RAC, there is no risk to the water system; between 1 and 10% a low risk is presented; between 11 and 30% there is medium risk; between 31 and 50% a high risk is predicted and, if greater than 50%, there is highest risk (Jain, 2004; Passos *et al.*, 2010; Zakir & Shikazono, 2011).

2.4 Statistical analysis

For the statistical analysis, sediment cores were considered as replicates and concentration as the variable of interest, while depth, chemical element and fraction corresponded to the three evaluated factors. Considering this type of design, multifactorial analysis of variance (three-way ANOVA), followed by Tukey HSD test, was the procedure used to identify differences between the average concentration values among different levels of the factors (i.e., sampling depth: 0, 2, 4, 6 and 8 cm; chemical element: Cr, Cu, Ni, Pb, Zn; fraction: F1, F2, F3), also testing the interaction between these (Zar, 2010). As the original data did not meet assumptions of normality and homoscedasticity, prior to testing these were log transformed (natural logarithm (value + 1)). In summary, the purpose of this statistical analysis was to assess whether the concentration in a given location was influenced by the depth of the sediment, chemical element or the fraction considered, which is the direct indication of their availability. Only data related to Cd were not included in the analysis since its concentration presented values below QL for all samples.

3. Results and discussion

The maximum available content (F1+ F2 + F3) for Cr (22.06 mg kg⁻¹), Cu (5.57 mg kg⁻¹) and Zn (57.53 mg kg⁻¹) was below their respective ISQG. As for Pb, the maximum level (36.43 mg kg⁻¹) estimated for the depth 0-2 cm of the sediment core B1, slightly exceeded its ISQG, but this was due to a single sample, featuring a specific situation. In the other B1 samples and the other analyzed sediment cores, Pb available content was less than its ISQG. The maximum Ni content (11.53 mg kg⁻¹) was smaller than those indicated in N1. Cd content was lower than its QL on the three fractions of all samples from sediment cores. These results suggest that if there is remobilization, these elements probably do not represent a danger to biota, because of their low content. Gonçalves *et al.* (2013) also determined the levels of Cr, Cu, Ni, Pb and Zn in the sedimentary column of the same sediment cores and the results indicated that the

sediments collected along the Bertioga Channel are non-toxic and not harmful for marine biota. Salaroli (2013) analyzed the levels of these elements in surface sediment samples collected along this Channel and Itapanháú river, and compared to the reference values established by the Canadian Agency, verifying that all levels were below the PEL and, in most samples, also below TEL (Threshold Effect Level).

Considering the sediment cores, it was observed that B2 presented the set of samples with lower content of available metals and this may be due to their remote location in relation to the main sources of pollution in the region. In the other sediment cores (B1, B3, B4 and B5) the evaluated elements, in general, showed relatively similar behavior in their potential for accumulation in the sediments. These sediment cores are located near potential sources of pollution and/or in regions where oceanographic conditions favor the accumulation of metals (Figure 1). B1 is closer to the city of Bertioga and marina area, B3 is near the Santista estuary, while B4 and B5 are near the region of Largo do Candinho. In this region, there is a predominance of fine sediments (Salaroli, 2013), in which occurs the enrichment of the most active components present on the sediment surface (Förstner, 2004). The Largo do Candinho is the central region of the channel in which two tidal streams meet (Rodrigues *et al.*, 2003), favoring the deposition of fine sediments. Table 1 presents the variation of available contents for Cr, Cu, Ni, Pb and Zn in sediment cores, as well as the reference values for these elements.

Observed concentration values were not influenced by sampling depth, but were by the chemical element considered (Cu < Ni < Cr = Pb < Zn - p < 0.03 for all comparisons) and the analyzed fraction (F1 < F2 < F3 - p < 0.0001 for all comparisons), with these two factors having a significant interaction (Table 2). This result can be attributed to the particular differences between the concentrations of specific elements and their association with each of the fractions. Overall, considering the first fraction, all elements showed similar levels except Zn, which presented a higher concentration (p < 0.0001 for all comparisons - Figure 2). In the second fraction the only similarity in terms of concentration was observed between Pb and Cr (p < 0.05 for the other comparisons). In the third fraction Cr, Pb and Zn showed similar levels that, in general, were higher than those of the other elements. However, a similarity in terms of concentration was observed between Pb and Ni, which due to its intermediate concentration between Pb and Cu did not differ from these two elements.

As for the available metal content and their association with each of the fractions, it was found that Cr was associated with F2 and F3 (F1 x F2 and F1 x F3 - p < 0.001). In F2 the metal is bonded to Fe and Mn oxides, and in F3 to organic matter and sulfides. In general, the bind-

Table 2 - Effect of the fraction (F1, F2, F3), element (Cr, Cu, Ni, Pb, Zn) and sediment depth in the core (0, 2, 4, 6, 8 cm) on the observed concentrations. Significant results for HSD Tukey test are presented in the text.

Tabela 2 - Efeito da fração (F1, F2, F3), elemento químico (Cr, Cu, Ni, Pb, Zn) e profundidade de amostragem (0, 2, 4, 6 e 8 cm) sobre a concentração observada.

	DF	MS	F	P
Intercept	1	603.03	2005.39	< 0.0001
Metal	4	26.40	87.80	< 0.0001
Fraction	2	88.94	295.78	< 0.0001
Depth	4	0.25	0.82	0.51
Metal X Fraction	8	5.08	16.91	< 0.0001
Metal X Depth	16	0.11	0.36	0.99
Fraction X Depth	8	0.24	0.79	0.62
Metal X Fraction X Depth	32	0.11	0.35	0.99
Error	300	0.30		

DF=degrees of freedom; MS=mean square; F=observed value relating to F distribution; p=probability associated to the F value considering DF.

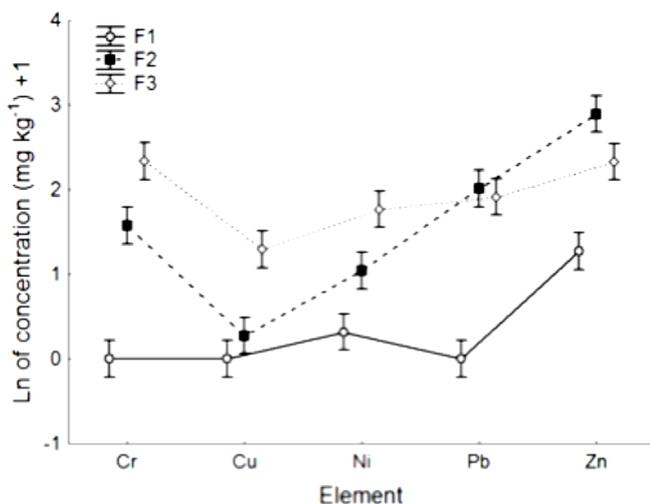


Figure 2 - Effect of the element and fraction on the observed concentration. Significant results for HSD Tukey test are presented in the text.

Figura 2 - Efeito do elemento químico e da fração sobre a concentração observada.

ing of Cr to F3 was predominant in the samples (F2 x F3 - $p < 0.001$), especially in sediment cores B1, B2 and B4.

Cu was mainly associated to F3 ($p < 0.0001$ for all comparisons), in which it is bounded to organic matter and sulfides. Only in samples of B3 and B5 sediment cores, this element was associated to F2. As reported by Morillo *et al.* (2004), it is known that Cu can easily form complexes with organic matter, because of the high stability constant of organic Cu compounds.

Ni was associated to the three phases, but especially to F3 (F1 x F3 and F2 x F3 - $p < 0.001$). The association to F1, in which the metal may be adsorbed on the surface of the sediment and, associated with carbonates, was less representative (F1 x F2 - $p < 0.001$), occurring in just a few samples of B1, B3 and B5 sediment cores. Pb presented associations with only F2 and F3 fractions (F1 x F2 and F1 x F3 - $p < 0.0001$). In sediment cores B1, B2 and B5 the association of this metal to F2 was predominant, while in B3 and B4 cores, Pb was associated mainly with F3.

Zn presented itself associated with all three fractions in all sediment cores, despite their bond with F2 being predominant (F1 x F2 and F2 x F3 - $p < 0.03$). However, comparatively to the other studied elements, Zn showed higher incidence of association to F1, even in low concentrations ($p < 0.0001$ for all comparisons - Figure 2).

Considering these results, it can be inferred that Cr, Cu and Ni are mainly associated to the organic matter and sulfides (F3), while Zn is to Fe and Mn oxides (F2), and Pb to all these components (F2 and F3). Changes in local environmental conditions may favor the release of these elements. When these are associated with F1 they may be released by changes in the ionic composition or pH reduction; if associated to F2, by changes in redox potential, and when associated with F3, they may be released under oxidizing conditions (Marin *et al.*, 1997).

Figure 3 shows the content of available elements (F1 + F2 + F3), as well as the content associated with each of the fractions. The absence of the content by one or more fractions, means that the concentration was below the QL of the element.

For a better understanding of a metal remobilization risk, it was applied the Risk Assessment Code (RAC), based on the element contents in the F1 fraction (%). Considering that Cd, Cr, Cu and Pb in all samples showed lower content in this fraction in relation to their QL, the methodology could be applied only to Ni and Zn. As a reference of total content were used the results of pseudo-total contents of Ni and Zn in these sediment cores, already published in Gonçalves *et al.* (2013).

According to the RAC criterion, Ni, in general, showed low risk (RAC < 10%) to the environment in sediment cores B1, B3 and B5. In other cores (B2 and B4), Ni content in F1 was below its QL in all samples. Generally, Zn presented low environmental risk (RAC < 10%) in the sediment cores B1, B3, B4 and B5. However, in core B2, RAC criteria indicated medium risk remobilization (RAC < 30%) in all samples. However, remembering that this methodology considers F1 concentration in relation to the total content, and reaffirming that Zn content associated with this fraction was less than its ISQG limit, if the remobilization of this element oc-

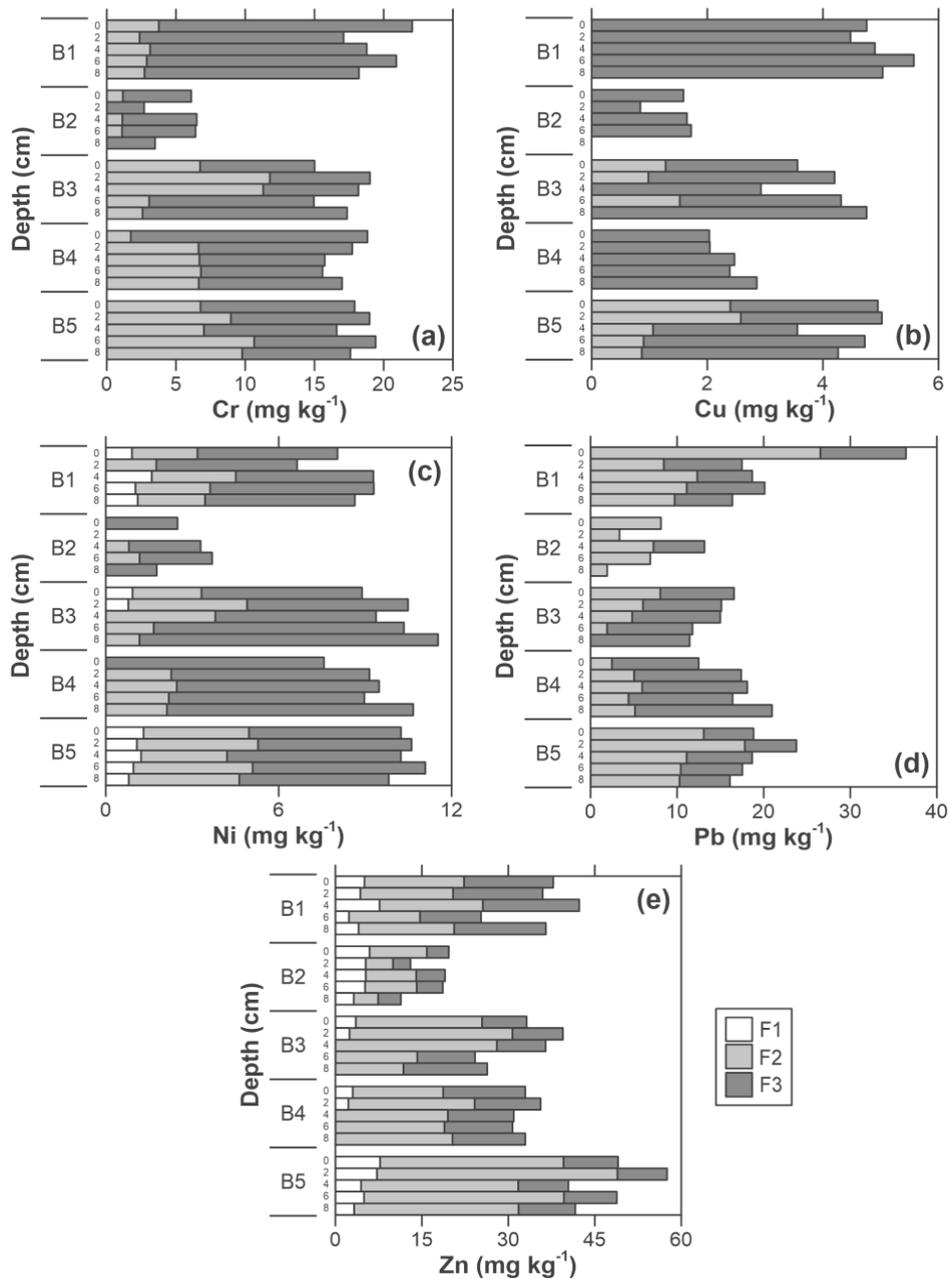


Figure 3 - Available contents of Cr (a), Cu (b), Ni (c), Pb (d) and Zn (e) (in mg kg⁻¹) and association to the mobile fractions in sediment cores of the Bertioga Channel.

Figura 3 - Teor disponível de Cr (a), Cu (b), Ni (c), Pb (d) and Zn (e) (em mg kg⁻¹) e em associação às frações móveis em sedimento de testemunhos do Canal de Bertioga.

curred, probably, it would not represent danger to the biotic communities.

In this study, the RAC criterion proved to be a complementary tool in assessing the remobilization of metals, allowing the quantification of the environmental risk. However, as reported by Ishikawa *et al.* (2009), the numerical scale RAC alone is insufficient to assess this risk, also being necessary to consider reference values of the evaluated elements, to adopt it as an efficient and reliable indicator.

Figure 4 shows the results for Ni and Zn RAC in the sediment cores. The absence of the RAC in some sam-

ples are due to their content associated with F1 being lower than the QL for the element.

4. Conclusions

The results showed that there is potential for remobilization of Cr, Cu, Ni, Pb and Zn in Bertioga Channel sediments, even though these elements were not mainly associated to the acid-soluble fraction, environmentally considered the most important due to their higher mobility. Cr, Cu and Ni were associated mainly to the organic matter and sulfides, Zn to Fe and Mn oxides and, Pb, to these four components. Changes in local envi-

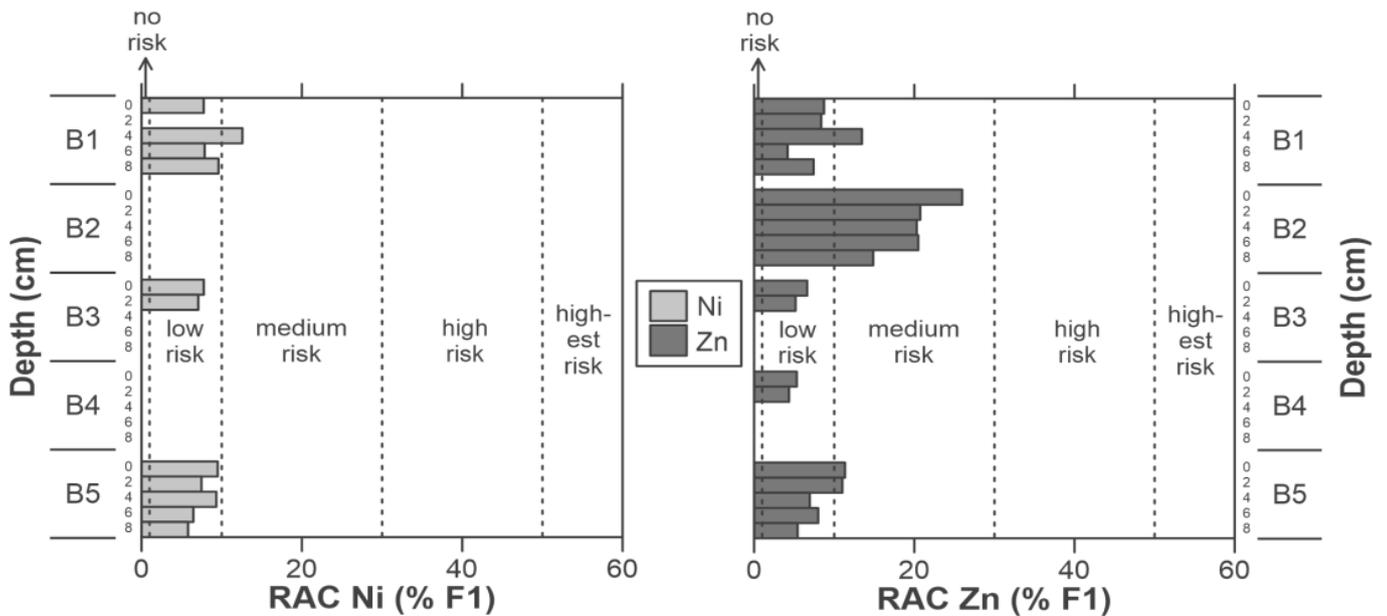


Figure 4 - Risk Assessment Code (RAC) for Ni and Zn in the cores from Bertioga Channel.

Figura 4 - Risk Assessment Code (RAC) para Ni e Zn nos testemunhos do Canal de Bertioga.

ronmental conditions, specifically in redox potential or those that lead to oxidizing conditions, may cause the remobilization of the evaluated metals and, consequently, leave them available in the environment. However, even if released, due to their low content in the sediments, it is estimated that they would not represent a danger to the biota.

RAC criterion, based on the metal content associated with the acid-soluble fraction (F1) was applied to Ni and Zn and generally indicated low risk of remobilization of these metals in the environment. Even in samples with medium risk, the content of these elements was lower than their reference values.

However, even though Cr, Cu, Ni, Pb and Zn concentrations in the sediments are low, suggesting the preservation of the region with respect to chemical contamination, considering that this study was based on the mobile fractions, it can be inferred that these results are an indicative of the possible anthropogenic contribution of these elements in the region, as well as of their potential for accumulation in sediment, showing the importance of the monitoring of potentially toxic elements for future protection of biotic communities. Continuous monitoring of chemical pollution in the region will allow the dimensioning of the possible impacts, thus contributing to the action plan in the scope of integrated coastal management.

The results presented in this study provide information about the behavior and mobility of Cr, Cu, Ni, Pb and Zn in Bertioga Channel sediments, representing a database that could assist in coastal and environmental management processes in the region.

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Appendix

Supporting Information associated with this article is available online at http://www.aprh.pt/rgci/pdf/rgci-670_Tramonte_Supporting-Information.pdf

References

- Abollino, O.; Malandrino, M.; Giacomino, A.; Mentasti, E. (2011) - The role of chemometrics in single and sequential extraction assays: A review Part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition. *Analytica Chimica Acta*, 688:104-121. DOI: 10.1016/j.aca.2010.12.020
- Bernardes, M.E.C.; Miranda, L.B. (2001) - Circulação estacionária e estratificação de sal em canais estuarinos: simulação com modelos analíticos. *Revista Brasileira de Oceanografia*, 49(1/2):115-132. DOI: 10.1590/S1413-77392001000100010
- Calmano, W.; Hong, J.; Förstner, U. (1993) - Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Water Science & Technology* (ISSN: 0273-1223), 28(8-9): 223-235.
- Calmano, W.; Ahlf, W.; Förstner, U. (1996) - Sediment quality assessment: chemical and biological approaches. In: Calmano, W.; Förstner, U. (eds.), *Sediments and toxic substances*, pp. 1-35, Springer-Verlag Berlin Heidelberg. ISBN: 978-3-642-79892-4.
- CCME (2001) - Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Updated. In: *Canadian Environmental Quality Guidelines*, 1999, Canadian Council of Ministers of the Environment (CCME), Winnipeg, MB, Canada.

- ISBN: 1896997341. Available on-line at https://www.elaw.org/system/files/sediment_summary_table.pdf
- CONAMA (2012) - *Resolução CONAMA n° 454 de 01 de novembro de 2012. Estabelece as diretrizes gerais e os procedimentos referenciais para o gerenciamento do material a ser dragado em águas sob jurisdição nacional*. Conselho Nacional do Meio Ambiente (CONAMA). DOU (Diário Oficial da República Federativa do Brasil): publicação: 08/11/2012, 1:66, Brasília, DF, Brazil. Available on-line at <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=693>
- Cotta, J.A.O.; Rezende, M.O.O.; Piovani, M.R. (2006) - Avaliação do teor de metais em sedimento do Rio Betari no parque estadual turístico do Alto Ribeira - Petar, São Paulo, Brasil. *Química Nova*, 29(1):40-45. DOI: 10.1590/S0100-40422006000100009
- Cuong, D.T.; Obbard, J.P. (2006) - Metal speciation in coastal marine sediments from Singapore using a modified BCR - sequential extraction procedure. *Applied Geochemistry*, 21:1335-1346. DOI: 10.1016/j.apgeochem.2006.05.001
- El-Azim, H.A.; El-Moselhy, Kh.M. (2005) - Determination and partitioning of metals in sediments along the Suez Canal by sequential extraction. *Journal of Marine Systems*, 56:363-374. DOI: 10.1016/j.jmarsys.2004.12.001
- Förstner, U. (1979) - Sources and sediment associations of heavy metals in polluted coastal regions. In: L.H. Ahrens & G. Protas (eds.), *Origin and distribution of the elements. Physics and Chemistry of the Earth*, 11, pp.849-866, Pergamon Press, Oxford, U.K. ISBN: 0080229476.
- Förstner, U. (1981) - Metal transfer between solid and aqueous phases. In: U. Förstner & G.T.W. Wittmann (eds.), *Metal Pollution in the Aquatic Environment*, pp.197-270, Springer - Verlag, Berlin / Heidelberg, Germany. ISBN: 978-3540128564.
- Förstner, U. (2004) - Traceability of sediment analysis. *Trends in Analytical Chemistry*, 23(3):217-236. DOI: 10.1016/S0165-9936(04)00312-7
- Ghrefat, H.; Yusuf, N. (2006) - Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*, 65:2114-2121. DOI: 10.1016/j.chemosphere.2006.06.043
- Gonçalves, C.; Figueira, R.C.L.; Sartoretto, J.R.; Salaroli, A.B.; Ribeiro, A.P.; Ferreira, P.A.L.; Mahiques, M.M. (2013) - Reconstruction of historical trends in potentially toxic elements from sediment cores collected in Bertioga Channel, southeastern Brazil. *Brazilian Journal of Oceanography*, 61(2):149-160. DOI: 10.1590/S1679-87592013000200007.
- Ishikawa, D.N.; Noale, R.Z.; Ohe, T.H.K.; Souza, E.B.R.; Scarmínio, I.S.; Barreto, W.J.; Barreto, S.R.G. (2009) - Avaliação do risco ambiental em sedimento dos lagos do Riacho Cambé, em Londrina, pela distribuição de metais. *Química Nova*, 32(7):1744-1749. DOI: 10.1590/S0100-40422009000700012.
- Jain, C.K. (2004) - Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*, 38:569-578. DOI: 10.1016/j.watres.2003.10.042.
- Kelderman, P.; Osman, A.A. (2007) - Effect of redox potential on heavy metal binding forms in polluted canal sediments in Delft (The Netherlands). *Water Research*, 41:4251-4261. DOI: 10.1016/j.watres.2007.05.058.
- Marin, B.; Valladon, M.; Polve, M.; Monaco, A. (1997) - Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta*, 342:91-112. DOI: 10.1016/S0003-2670(96)00580-6.
- Morillo, J.; Usero, J.; Gracia, I. (2004) - Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, 55:431-442. DOI: 10.1016/j.chemosphere.2003.10.047.
- Oliveira, M.L.J.; Vidal-Torrado, P.; Otero, X.L.; Ferreira, J.R. (2007) - Mercúrio total em solos de manguezais da baixada Santista e ilha do Cardoso, Estado de São Paulo. *Química Nova*, 30(3):519-524. DOI: 10.1590/S0100-40422007000300003.
- Passos, E.A.; Alves, J.C.; Santos, I.S.; Alves, J.P.H.; Garcia, C.A.B.; Costa, A.C.S. (2010) - Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal*, 96:50-57. DOI: 10.1016/j.microc.2010.01.018.
- Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, Ph., López-Sánchez, J.F. (2001) - Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *Journal of Environmental Monitoring*, 3(2):243-250. DOI: 10.1039/b010235k.
- Rauret, G. (1998) - Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta*, 46:449-455. DOI: 10.1016/S0039-9140(97)00406-2.
- Rodrigues, A.R.; Eichler, P.P.B.; Eichler, B.B. (2003) - Utilização de foraminíferos no monitoramento do Canal de Bertioga (SP, Brasil). *Atlântica* (ISSN: 2236-7586), 25(1):35-51, Rio Grande, RS, Brazil.
- Sakan, S.M., Dordevic, D.S., Manojlovic, D.D., Predrag, P.S. (2009) - Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *Journal of Environmental Management*, 90:3382-3390. DOI: 10.1016/j.jenvman.2009.05.013.
- Salaroli, A.B. (2013) - *Distribuição de elementos metálicos e As em sedimentos superficiais ao longo do Canal de Bertioga (SP)*. 105p., Dissertação de Mestrado, Instituto Oceanográfico da Universidade de São Paulo, São Paulo, SP, Brazil. Available on-line at <http://www.teses.usp.br/teses/disponiveis/21/21137/tde-29012015-113936/pt-br.php>
- Silva, P.S.C.; Damatto, S.R.; Maldonado, C.; Fávaro, D.I.T.; Mazzilli, B.P. (2011) - Metal distribution in sediment cores from São Paulo State Coast, Brazil. *Marine Pollution Bulletin*, 62:1130-1139. DOI: 10.1016/j.marpolbul.2011.02.046.
- Singh, K.P.; Mohan, D.; Singh, V.K.; Malik, A. (2005) - Studies on distribution and fractionation of heavy metals in Gomti river sediments - A tributary of the Ganges, India. *Journal of Hydrology*, 312:14-27. DOI: 10.1016/j.jhydrol.2005.01.021.
- Siqueira, G.W.; Braga, E.S.; Pereira, S.F.P.; Silva, E. (2005) - Distribuição do mercúrio em sedimentos de fundo do Estuário de Santos-SP/Brasil. *Revista Escola de Minas*, 58(4):309-316, DOI: 10.1590/S0370-44672005000400004.
- Zakir, H.M.; Shikazono, N. (2011) - Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river. *Journal of Environmental Chemistry and Ecotoxicology*, (ISSN-2141-226X), 3(5):116-126. Available on-line at http://www.academicjournals.org/article/article138006213_Zakir and Shikazono.pdf
- Zar, J.H. (2010) - *Biostatistical Analysis*. 5th ed., 944p, Pearson Prentice Hall. ISBN: 978-0321656865.
- Zoumis, T., Schmidt, A., Grigorova, L., Calmano, W. (2001) - Contaminants in sediments: remobilisation and demobilisation. *Science of the Total Environment*, 266:195-202. DOI: 10.1016/S0048-9697(00)00740-3