

## Evidence of Systemic Changes in Trace Metal Concentrations in Subtropical Estuarine Sediments as a Result of Urbanization

P. R. Pagliosa†; A. Fonseca‡ and F. A. Barbosa†§

† Programa de Pós-graduação em Ecologia e Recursos Naturais, Universidade Federal de São Carlos, São Carlos, 13565-905, Brasil, ppagliosa@yahoo.com.br

‡ Instituto Oceanográfico, Universidade de São Paulo, São Paulo, 05508-900, Brasil, alefonse@usp.br

§ Laboratório de Limnologia, Departamento de Biologia Geral, Universidade Federal de Minas Gerais, Belo Horizonte, 30161-970, Brasil, barbosa@icb.ufmg.br



### ABSTRACT

PAGLIOSA, P. R.; FONSECA, A. and BARBOSA, F. A., 2006. Evidence of systemic changes in trace metal concentrations in subtropical estuarine sediments as a result of urbanization. *Journal of Coastal Research*, SI 39 (Proceedings of the 8th International Coastal Symposium), 1078 - 1083. Itajaí, SC, Brazil, ISSN 0749-0208.

The concentrations of Cu, Pb, Zn and Cd were analyzed in surface sediments along six estuaries in the Santa Catarina Island Bay, on the southern coast of Brazil. Estuaries located within protected areas were considered control areas of urban pollution. Estuaries in urbanized environments were considered as possibly presenting higher levels of metals within the surface sediments. Systemic changes within the environment were assessed by comparisons in spatial variations within the same estuary, within a group of estuaries and between groups of urban and non-urban estuaries. The results reveal different behaviors among metals and among the areas studied. The concentrations of Pb, Zn and Cu in the surface sediments (<0.063 mm) were higher and had greater variations in urban estuaries than in non-urban ones. Cadmium was always below detection limits, irrespective of the area analyzed. Minimum and maximum concentrations in the non-urban estuaries ranged from 11.47-26.85 mg/kg for Cu, 17.76-28.48 mg/kg for Pb and 73.37-104.80 mg/kg for Zn; and in the urban estuaries, they ranged from 13.51-37.76 mg/kg for Cu, 27.86-47.81 mg/kg for Pb and 83.84-144.27 mg/kg for Zn. The distributions of the Zn and Cu concentrations differed between points within the same estuary, indicating possible pollution sources. The Pb values in the sediments were constant throughout the urban estuaries, indicating general dispersion in these areas. The low contamination level in the local sediments was checked by comparing the heavy metals concentrations in urban estuaries of other regions in Brazil. Likewise, the reported concentrations in the non-urban estuaries were similar and often lower than those in areas considered "reference locations" for biogeochemical and ecotoxicological studies. Even with the low level of reported contamination, the systemic changes in the trace metal concentrations between urban and non-urban estuaries prove the importance of protected areas as protectors of the integrity of coastal ecosystems.

**ADDITIONAL INDEX WORDS:** *Lead, zinc, copper.*

### INTRODUCTION

The industrial expansion launched in Brazil in the mid-1950s promoted rapid urban growth, principally in coastal areas. The population in the cities increased 7.5 times during the 1970s. Today, it is estimated that 85 million people, around half of its population, live within 200 km from the sea. The growing urbanization has caused changes in the physical, chemical and biological characteristics of the estuarine systems (RIDGWAY and SHIMMIELD, 2002). The most visible and recorded impacts are restricted above all to the large industrial centers of the country, such as the São Paulo and Rio de Janeiro states, on the southeastern coast, the Bahia State, on the northeastern coast, and the Rio Grande do Sul State, on the southern coast (TOMMASI, 1987; SEELIGER *et al.*, 1988; DIEGUES, 1999). In areas where the industrialization is less intense or more controlled, there are practically no published records. In these areas, the direct and combined effects of urbanization are more difficult to quantify. The sources of pollution are varied and spread throughout the environment, complicating cause-and-effect relations.

Because they are transition areas between distinct environments, estuaries are great swallows of aquatic, terrestrial and atmospheric pollution. Among the various commonly dispersed contaminants in estuaries, heavy metals are important because of their role in biogeochemical cycles (NEUBECKER and ALLEN, 1983), sediment-persistence (FÖRSTNER, 1987), and ecological effects (MATTHIESSEN and LAW, 2002). In the estuaries, metals originate from geological intemperance, industrial processing, the direct use of metals or metal components and seepage of human and animal deposits and excreta (FÖRSTNER, and WITTMANN, 1981). The manner in which these affect the aquatic environment depend more in the chemical behavior in specific circumstances than in the levels of overall concentration. Chemical speciation and the

distribution of contaminants in the estuaries are mainly influenced by the level of salinity, suspended solids, pH, redox potential, sediment grain size and the degree of water mixture. Free dissolved ions are considered to be the most bioavailable and responsible for bioaccumulation, biotransfer and biomagnification in the trophic chain (FISHER *et al.*, 1996; BARWICK and MAHER, 2003).

The detection of metals in water samples offer only a momentary record of environmental quality, which is not always synchronized with the events that caused them. However, the study of spatial variations in the chemical composition and concentration of surface sediments is useful as a guide to indicate possible pollution sources. The hierarchical approach in environmental studies, comparing different levels of magnitude of impacts, allows the detection of isolated and systemic alterations in the concentration of pollutants.

The aim of this study is to detect the effects of urbanization on the concentration of heavy metals in the estuaries flowing into the Santa Catarina Island Bay. The concentrations of Cu, Pb, Zn and Cd were studied in the sediments of three urban and three non-urban estuaries. The non-urban areas, located within protected areas, were considered non-polluted areas and control of urban ones, which were similar to those but are surrounded by urban centers. Systemic changes were evaluated by comparing the spatial variations within the same estuary, within a group of estuaries and between groups of urban and non-urban estuaries.

### METHODS

Local rivers originate in the Pre-Cambrian granite-gneiss structures that form the Serra do Mar mountain range. They flow along a short plain of quaternary fluvial-marine sediments and out into small estuaries. The rocky formation of Santa Catarina Island is an extension of the nearby continent,

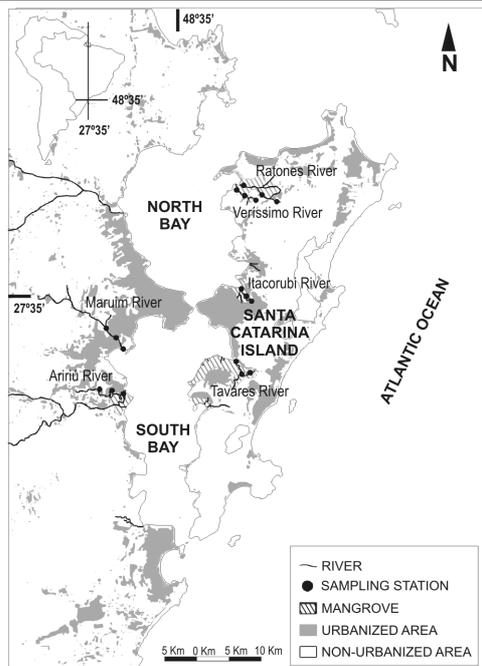


Figure 1. The Santa Catarina Island Bay, southern Brazil, showing the sampled estuaries. Mangrove areas are shadowed.

possessing the same characteristics. Six estuaries that drain off from the continent and the island to the Santa Catarina Island Bay were selected as study areas (Fig. 1). The Ratonés (RA) and Veríssimo (VE) estuaries and a considerable portion of their basins are in the Carijós Ecological Station. Meanwhile, the Tavares Estuary (TA) encompasses the mangrove swamp and salt marsh of the Pirajubaé Extractive Marine Reserve. These areas were considered as potentially non-polluted and served as control of the urbanized ones.

The population living in the Santa Catarina Island Bay watershed, which grew around 60 % in the last two decades, includes nine municipal conurbations. Along with this growth, the number of industries grew by 300 % in the last decade alone. Up until now, no study has dimensioned the changes caused by these impacts, except for the ones suffered by deforestation (CARUSO, 1990). The subaquatic estuary environment has been intensely altered by the removal of vegetation, and the beach-line has been replaced by solid-impermeable surfaces, altering the natural water-flow. In aqueous environments, in addition to fishing and maricultural activities, dredging and landfilling activities might be altering local sediment dynamics. The Itacorubi (IT), Aririú (AR) e Maruim (MA) estuaries are located in urban regions and were chosen as potentially polluted sites for the heavy metal concentration analysis in the sediments (Fig. 1).

To assess the systemic changes in the concentrations of Cu, Pb, Zn and Cd in the sediments, a hierarchical analysis was used, which compared spatial variation in sites (within the same estuary), locals (within the same group of estuaries), and areas (between urban and non-urban groups of estuaries). Three points were established in each estuary: close to the mouth, at the limit of the tidal influence and an intermediate region between these two. Through free dives, and using a core of 11 cm in diameter and 2 cm deep, three sediment samples were taken to analyze the metal content and another three to analyze the sediment properties. The level of organic matter in the sediments and the granulometric analysis were carried out according to CARVER (1970). In addition, the salinity concentration and concentration of dissolved oxygen in the bottom water were measured (STRICKLAND and PARSON, 1972).

The sediments were sieved through a mesh of 0.063 mm, and the concentrations of Cu, Pb, Zn and Cd were analyzed with flame atomic absorption spectrometry. Using 0.50 g of

sediment conditioned in a Teflon pump, metals were extracted with nitric, hydrofluoric and hydrochloric acids in standard analytical concentration. To check the analytical accuracy, a certified reference material PACS-2 (National Research Council of Canada) was used.

The concentration of each metal along the saline gradient was analyzed in urban and non-urban estuaries separately. To check the standard distribution of the data, a multidimensional scaling ordination (n-MDS) analysis was performed, using indexes of Euclidean distance as descriptors. The significant differences between urban and non-urban areas were assessed through a similarity analysis (ANOSIM), a permutation test (CLARKE and WARWICK, 1994). The nested analysis of variance was used to test for differences in the concentrations of each metal between areas, locals (nested within the respective area) and sites (nested within the respective local and area). When significant, the differences were assessed through multiple comparisons test. The homogeneity of the variances was pre-checked by the Cochran test and when necessary, a logarithmic transformation was used.

## RESULTS

The salinity concentration was typical of estuaries, with lower values in the innermost points and highest at the mouths. The salinity of the bottom water varied from 0.1 to 35.6, with lower amplitudes registered in the Maruim and Ratonés rivers and higher ones in the Aririú and Itacorubi estuaries (Tab. 1). The lowest salinity values and amplitudes, as well as the highest dissolved oxygen content found in the Maruim and Ratonés estuaries, reflect the great importance of freshwater input and a faster water flow in these systems.

As with the salinity, a tendency of decreasing sediment grain size was observed from the innermost areas to the mouth of the estuaries. The sediment mean grain size varied from fine sand with low quantities of clay-silt (< 0.063 mm) in the Veríssimo

Table 1. Salinity (S) and dissolved oxygen (DO) of bottom water, and organic matter (OM), fine (< 0.063 mm), mean grain size and metal concentration (Cu, Pb, and Zn) in estuarine sediments of Santa Catarina Island Bay, southern Brazil.

Estuary	Water			Sediment				
	S	DO ml/L	OM %	Fine %	Size phy	Cu mg/kg	Pb mg/kg	Zn mg/kg
ARIRIÚ (n = 9)								
Average	15.3	1.60	16.3	67.9	4.65	18.76	33.52	122.05
Std	11.3	0.95	5.2	24.2	1.25	1.38	4.48	12.35
Min	2.4	0.29	6.7	13.5	2.25	16.93	28.78	101.20
Max	29.5	3.00	25.4	92.3	5.99	20.56	43.86	144.27
ITACORUBI (n = 9)								
Average	24.8	0.82	10.9	64.5	4.22	26.96	32.02	96.64
Std	12.3	0.89	6.3	42.3	2.78	5.33	3.94	12.22
Min	4.9	0.00	2.2	7.4	0.15	21.49	27.86	83.84
Max	35.6	2.22	16.1	98.6	6.23	37.76	39.37	122.75
MARUIM (n = 9)								
Average	1.2	4.42	12.0	60.3	4.23	17.24	37.68	124.56
Std	1.1	0.52	7.6	39.7	2.28	1.67	5.61	12.30
Min	0.1	3.89	2.0	7.5	1.09	13.51	29.59	108.20
Max	2.7	5.21	21.1	98.4	6.42	19.47	47.81	144.27
RATONES (n = 9)								
Average	1.3	3.12	9.1	29.3	3.14	14.26	25.99	92.89
Std	0.4	0.11	6.1	14.5	1.17	2.14	1.90	9.14
Min	1.0	2.85	4.1	7.5	0.47	11.47	22.84	73.84
Max	2.0	3.20	22.0	56.8	4.38	18.59	28.48	104.8
TAVARES (n = 9)								
Average	9.9	1.58	16.8	96.0	6.16	19.30	23.57	80.79
Std	7.2	0.42	1.9	3.2	0.12	4.10	3.40	7.37
Min	2.3	1.02	14.4	88.8	5.94	12.93	17.76	73.37
Max	20.6	2.13	20.7	99.0	6.30	26.85	28.05	97.30
VERÍSSIMO (n = 9)								
Average	7.9	1.90	2.9	14.4	2.69	14.74	21.51	86.45
Std	5.3	0.61	2.1	12.1	0.70	1.07	2.06	3.01
Min	3.0	1.36	0.7	4.5	1.93	13.44	18.79	82.11
Max	16.7	2.84	6.1	34.2	3.84	16.39	23.87	91.59

Estuary ( $14.4\% \pm 12.1$ ), to fine silt with a high quantity of clay-silt in the Tavares Estuary ( $96.0\% \pm 3.2$ ). However, there were sediments with coarse and medium sand sizes in the innermost points in the Itacorubi and Maruim estuaries. The organic matter content in the sediments varied from 0.74 % in the Veríssimo Estuary, to 25.37 % in the Aririú Estuary.

Cu concentrations in the sediments varied from 11.47 mg/kg in the Ratonas Estuary, to 37.76 mg/kg in the Itacorubi Estuary, with the lower amplitudes in the Veríssimo Estuary and the higher ones in the Itacorubi Estuary. Pb concentrations were lowest in the Tavares Estuary, (17.76 mg/kg), and highest in the Maruim Estuary (47.81 mg/kg). Zn concentrations varied between 73.37 mg/kg, in the Tavares Estuary, and 144.27 mg/kg, in the Aririú and Maruim estuaries (Tab. 1). Cd concentrations in the sediments were always below the detection limit, irrespective of the site analyzed.

The n-MDS analysis showed the differences in the metal concentrations between the urban and non-urban estuaries (Fig. 2). The metal data from the Ratonas, Tavares and Veríssimo estuaries presented a patchy distribution within the same estuary and between them. This result revealed a minor variation in the metal concentrations in the non-urban estuaries. The data from the Aririú, Itacorubi and Maruim estuaries was dispersed, reflecting a greater variation in the urban estuaries (Fig. 2). The analysis of similarities detected significant differences between urban and non-urban areas (ANOSIM,  $R = 0.643$ ,  $P = 0.001$ ). The hierarchical analysis of variance detected different behavior patterns for each metal throughout both types of areas, locals and sample sites (Tab. 2). Pb concentrations were significantly greater in urban areas than in non-urban ones and did not vary within the same estuary. Zn concentration differed significantly between areas, estuaries and sample sites. The greatest concentrations were found in the innermost points of the Aririú and Maruim estuaries (Multiple Comparisons,  $P < 0.05$ , AR IT MA > RA TA VE). Cu concentrations did not show a significant difference between urban and non-urban areas. However, the greatest concentrations of it were found in the innermost site of the Itacorubi Estuary (Multiple Comparisons,  $P < 0.05$ , IT > TA > AR MA > RAVE).

The Pearson correlation analyses carried out between the physicochemical and sedimentological variables revealed different trends for each of the analyzed metals and between urban and non-urban areas for the same metal (Tab. 3). Although the samples were carried out along the saline gradient, only the Pb concentrations in the urban areas and of Zn in the

Table 2. Summary of nested analysis of variance of metal concentrations in estuarine sediments of Santa Catarina Island Bay, southern Brazil. d.f. = degree of freedom, MS = mean squares, F = F-ratio test,  $n = 3$ , ns denotes no significant differences. \* denotes significance at  $P < 0.05$  and \*\* at  $P < 0.005$ .

Source of variation	d.f.	Cu		Pb		Zn	
		MS	F	MS	F	MS	F
Area	1	0.169	2.55 <sup>ns</sup>	1550.219	25.28 <sup>*</sup>	0.186	8.74 <sup>*</sup>
Local	4	0.066	6.39 <sup>**</sup>	61.319	3.70 <sup>*</sup>	0.021	6.86 <sup>**</sup>
Site	12	0.010	6.30 <sup>**</sup>	16.555	1.2 <sup>ns</sup>	0.003	2.54 <sup>*</sup>
Error	36	0.002		13.696		0.001	

non-urban areas were inversely correlated with the salinity values (Tab. 3). The analyzed metals showed a correlation to the level of dissolved oxygen of the bottom water. However, while the Pb and Zn concentrations were positively correlated, the Cu content was inversely correlated to it. Pb concentrations were not correlated to any sedimentological variable, neither in the urban nor in the non-urban areas. Whereas the Zn concentrations in the non-urban areas showed an inverse correlation to organic matter content and a positive correlation to the sediment mean grain size, did not showed any correlation to any of these variables in the urban areas. Cu concentrations, on the other hand, exhibited significant opposite correlations to the same parameters between urban and non-urban areas. That is, while in non-urban areas, it was positively correlated to the sediment grain size (Phy) and organic matter and fine particle contents, in urban areas it was negatively correlated to the same variables.

## DISCUSSIONS

When heavily polluted areas were contrasted with non-polluted areas, great differences were expected to be found. However, in areas where heavy pollution is not evident, this argument is poorly supported because of the potential sources of variations in the data set. The use of a hierarchical sampling design, contrasting site variations within the same estuary, within a group of estuaries and between urbanized and non-urbanized areas, permitted the identification of the adverse effects of urbanization in the metal concentrations of estuarine sediments in regions with low contamination levels. The concentrations of Pb, Zn and Cu in the analyzed surface sediments were higher and had greater variations in urban estuaries than in non-urban ones. In addition, the distribution of the Zn and Cu content differed between sites within the same estuary, indicating possible pollution sources.

High concentrations of metals in surface sediment are commonly reported as having a strong correlation with organic matter content and small sediment grain size (GIBBS, 1994; CHE *et al.*, 2003). Through the deposition and resuspension processes, sediment particles are distributed in the environment in relation to their size. As metals are strongly adsorbed into the surface of fine clay particles, they generally follow this same pattern. Normalization procedures, using reference elements, such as Al and Fe, are used to discriminate the sediment size effects from that of metal concentrations. However, by mapping the sediment grain size in estuaries, the distribution of metal concentrations can also be observed and even predicted. In this study, conversely, the metal concentrations were either not related to the characteristics of the sediments or did not follow the expected pattern. This could be due to the fact that samples were extracted preferentially from areas of fine sediment deposition. The great homogeneity in particle size seems to have reduced the sediment importance in the data analysis.

The only metal which matched the distribution of organic matter and fine particles content was Cu in the non-urban areas, where the concentrations were the lowest. The high Cu concentrations in the urban estuaries, contrary to expectations, were related to the lower organic matter content and to the coarse sediments. Other studies, which analyzed Cu concentrations along non-polluted estuarine systems, have revealed the affinity of this element to organic particles

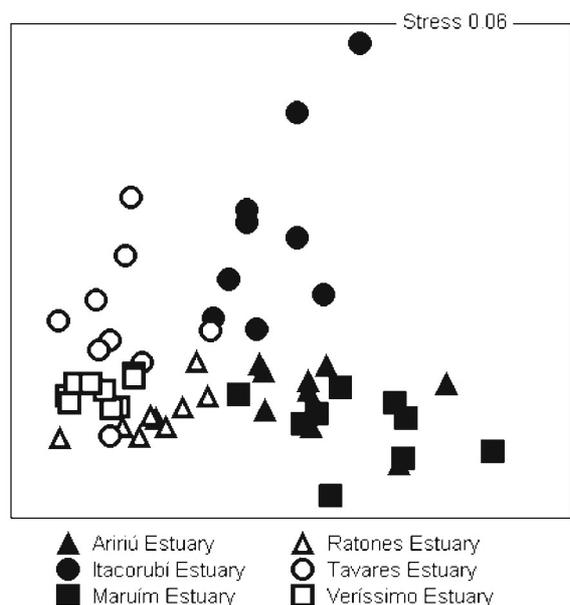


Figure 2. n-MDS of metal concentration Cu, Pb, and Zn in sediments of non-urban (empty symbols) and urban (filled symbols) estuaries of Santa Catarina Island Bay, southern

Table 3. Correlation matrix (Pearson-product) for salinity (S) and dissolved oxygen (DO) in bottom water; and organic matter (OM), fines (< 0.063 mm), mean grain size (Phy) and metal concentration (Cu, Pb, and Zn) in estuarine sediments of Santa Catarina Island Bay, southern Brazil. \* denotes  $P < 0.05$ .

Variable	S	DO	OM	Fine	Size	Pb	Cu	Zn
URBAN ESTUARIES (n=27)								
S	-							
DO	-0.56*	-						
OM	0.39*	-0.08	-					
Fine	0.51*	-0.12	0.90*	-				
Size	0.48*	-0.09	0.89*	0.98*	-			
Pb	-0.56*	0.40*	-0.18	-0.17	-0.17	-		
Cu	0.24	-0.54*	-0.50*	-0.39*	-0.45*	-0.09	-	
Zn	-0.34	0.44*	0.13	0.08	0.12	0.33	-0.69*	-
NON-URBAN ESTUARIES (n=27)								
S	-							
DO	-0.13	-						
OM	0.15	-0.14	-					
Fine	0.39*	-0.37	0.75*	-				
Size	0.41*	-0.36	0.61*	0.96*	-			
Pb	-0.05	0.51*	0.21	0.08	0.05	-		
Cu	0.16	-0.42*	0.63*	0.59*	0.50*	-0.14	-	
Zn	-0.40*	0.51*	-0.04	-0.45*	-0.51*	0.45*	-0.14	-

(LACERDA *et al.*, 1989; DE PAULA and MOZETO, 2001). In polluted areas, metal concentrations appear not to correspond directly or only to the organic matter quantity in the environment (LACERDA *et al.*, 1987; BATISTA NETO *et al.*, 2000). In general, the more polluted the environment, the more diversified the metal forms that are present (SEELIGER *et al.*, 1988). The principal cause responsible for metal deposition seems to be the reductive phase. However, studies looking at the geochemical speciation of the elements have indicated that in polluted areas an increase in the oxidative form of Cu occurs. This is due to the synergy occurring between the organic pollution and the metals, causing a remobilization from the reductive form to the oxidative form (SOUZA *et al.*, 1986).

Although Cu concentrations in the Itacorubi Estuary were high at all sites, the highest concentration was found in the innermost region. The natural course of this estuary was completely changed by the construction of various lateral channels, large landfills, and highways, as well as being used as deposits for domestic waste during the 80s and 90s (~ 250 tons/day). The fact that Cu concentrations were inversely related to those of oxygen and that there is almost no water circulation in this estuary (SORIANO-SIERRA *et al.*, 1986), are an indication that sediment remobilization caused by the straightening and widening of the banks are the main reasons for the high metal concentrations in this environment.

Zn concentrations in non-urban areas followed a typical pattern of distribution in the estuaries, decreasing with increasing salinity. This pattern, however, is also related to the coarsest sediment grain size. The decreasing Zn concentrations found from innermost sites to mouth of the estuaries is probably related to desorption and dilution processes with seawater (FÖRSTNER and WITTMANN, 1981). The greatest granulometric variations were found to occur in the non-urban areas of the Ratones, Tavares and Verissimo estuaries. The relation between Zn concentration and coarse sediment, however, was more associated to the differences between the above estuaries than between sites within the same estuary. In the urban estuaries, this situation was not the case, with Zn concentrations around 32 % greater than in the non-urban ones. Zn concentrations in the Aririú, Itacorubi and Maruim estuaries were neither related to any of the sedimentological variables nor to the bottom waters. Variations between sites were only found in the sediments of the Itacorubi Estuary.

In the mainland, just opposite to the island, urbanization growth in the southern outskirts reaches its natural boundary, the left bank of the Aririú Estuary.

The population living in the area which drains into this

estuary does not have basic sanitation and its sewerage fall directly into the water body from its beginning. Similarly, at least up to the point of tidal influence, this is the case for both banks of Maruim Estuary. This estuary is also affected by the presence of some small local industries. The high Zn concentration in the sediments of these two estuaries appears to be related to the general organic contamination throughout the system. In the Itacorubi Estuary, where garbage collection and treatment of solid residues is already in practice, high zinc levels were only present at the mouth of the estuary. This seems to be directly related to the effects of waste deposited in the last two decades still present in the area (even though it is not visible).

The Maruim, Aririú and Itacorubi estuaries exhibited high Pb concentrations. Its distribution was not related to either sediment properties nor water ones, and the values showed no change along the same estuary. This result suggests a general contamination of Pb in the sediments of the urban estuaries. Pb is typically associated with atmospheric pollution and combustion engines (REBELLO *et al.*, 1986; SEELIGER *et al.*, 1988). Although since 1989 Brazilian legislation has prohibited the use of Pb as a gasoline additive, traces of this metal have repeatedly been found in the hair of people who work along highways, and in soil and plants close to highways (DUARTE and PASQUAL, 2000).

Table 4 shows the metal concentrations in the sediments of several urbanized and non-urbanized estuaries and coastal regions of Brazil. The reference values of threshold effect level (TEL) and probable effect level (PEL) were used to compare (LAWS, 1999). When the data obtained in this study is compared with data collected in the last decade (DA SILVA *et al.*, 1996), it is found that the greatest Cu and Pb concentrations in the Itacorubi Estuary (urbanized) and in the Ratones and Tavares estuaries (non-urbanized) have practically not changed. The Zn concentrations, conversely, have experienced a clear increase (36 % on average) in these three estuaries. This result indicates a possible increase in the Zn concentration throughout the Santa Catarina Island Bay. A recent study of the tissue of locally farmed bivalve mollusks (*Crassostrea gigas* and *Perna perna*) showed that Zn levels are very close to the tolerance-limits recommended by international regulatory agencies (CURTIUS *et al.*, 2003). In order to guarantee the quality of cultivated marine resources and the local coastal ecosystems, a more detailed and preventive study about possible sources of Zn in the estuarine system as a whole is necessary.

In this study, the non-urbanized estuaries presented similar or slightly lower values than those reported in other areas of the Brazilian coast (Tab. 4). All recorded concentrations were lower than the probable effect level. The Cu, Pb and Zn concentrations in non urbanized areas were lower and in urbanized areas were close to the threshold effect level, indicating no biological community adverse effect (LAWS, 1999). Hence, the metal concentrations found can be used to differentiate between natural level and anthropogenic pollution. They may serve as reference locations for biogeochemical and ecotoxicological studies in the Brazilian coast. As in non-urbanized areas, the metal concentrations in urbanized ones were lower than those recorded in other Brazilian regions. The most important factor contributing to the current low contamination levels seems to be the absence of a point-source of pollution and/or the low industrial activity.

In spite of this, the systemic changes in the metal concentration between urbanized and non-urbanized estuaries shows the importance of protected areas for the maintenance and integrity of local estuarine ecosystems.

## LITERATURE CITED

- BAISCH, P.R.N.; NIENCHENSKI, L.F.H. and LACERDA, L.D., 1988. Trace metal distribution in sediments of the Patos Lagoon Estuary, Brazil. In: SEELIGER, U.; LACERDA, L.C. and PATCHINEELAM, S.R. (eds.). *Metal in coastal environments of Latin America. Germany: Springer-Verlag*, pp.59-64.

Table 4. Metal concentration (mg/kg) in urban and non-urban estuarine and coastal sediments from Brazil. Referenced data are given as range data; nd = not determined.

Location in Brazilian Coast	Cu	Pb	Zn
URBAN ESTUARIES			
Aririú River (S) <sup>1</sup>	17-21	29-44	101-144
Marum River (S) <sup>1</sup>	13-19	30-48	108-144
Itacorubi River (S) <sup>1</sup>	21-38	28-39	84-123
Itacorubi River (S) <sup>2</sup>	28-46	48-56	89-97
Babitonga Bay (S) <sup>3</sup>	3-73	2-83	6-1156
Patos Lagoon (S) <sup>4</sup>	1-20	8-267	20-214
Paranaguá Bay (S) <sup>5</sup>	0.5-23	2-25	0.5-311
Santos Bay (SE) <sup>3</sup>	nd	0-48	0-185
Santos Bay (SE) <sup>6</sup>	0.2-114	nd	2-90
Santos Bay (SE) <sup>7</sup>	nd	9-242	9-624
Guanabara Bay (SE) <sup>8</sup>	0-478	5-460	10-1660
Iguaçu River (SE) <sup>9</sup>	22-196	22-36	nd
Estrela River (SE) <sup>10</sup>	74-731	37-63	nd
Guarda River (SE) <sup>10</sup>	19-45	103-237	nd
São Francisco Channel (SE) <sup>9</sup>	22-28	4-86	nd
Sepetiba Bay (SE) <sup>11</sup>	2-166	6-83	18-795
Jurujuba Bay (SE) <sup>12</sup>	40-213	45-123	162-337
Acari River (SE) <sup>13</sup>	500-2700	110-440	700-1400
Todos os Santos Bay (NE) <sup>14</sup>	5-55	10-960	5-2400
Jauá Lake (NE) <sup>15</sup>	16-531	24-282	417-1511
NON-URBAN ESTUARIES			
Verissimo River (S) <sup>1</sup>	13-16	19-24	82-92
Ratones River (S) <sup>1</sup>	11-19	23-28	74-105
Ratones River (S) <sup>2</sup>	1-21	2-28	6-79
Tavares River (S) <sup>1</sup>	13-27	18-28	73-97
Tavares River (S) <sup>2</sup>	17-25	14-26	31-65
Capivari River (SE) <sup>16</sup>	4-29	13-53	24-142
Caranguejo River (SE) <sup>10</sup>	20-27	40-81	nd
Ingaíba River (SE) <sup>9</sup>	26-31	33-40	nd
Frade River (SE) <sup>17</sup>	16-31	27-47	47-106
Ribeira Bay (SE) <sup>18</sup>	14-60	9-27	4-14
Ribeira Bay (SE) <sup>19</sup>	3-32	nd	29-189

This study<sup>1</sup>

DASILVA et al. (1996)<sup>2</sup> LACERDA et al. (1987)<sup>11</sup>

TOMMASI (1987)<sup>3</sup> BAPTISTA NETO et al. (2000)<sup>12</sup>

BAISCH et al. (1988)<sup>4</sup> REGO et al. (1993)<sup>13</sup>

Sá (2003)<sup>5</sup> SEELIGER et al. (1988)<sup>14</sup>

SOUZA et al. (1998)<sup>6</sup> DASILVA et al. (2000)<sup>15</sup>

SIQUEIRA et al. (2001)<sup>7</sup> DE PAULA and MOZETO (2001)<sup>16</sup>

PERIN et al. (1997)<sup>8</sup> LACERDA et al. (1989)<sup>17</sup>

SOUZA et al. (1986)<sup>9</sup> LACERDA et al. (1982)<sup>18</sup>

LACERDA et al. (1988)<sup>10</sup> CARDOSO et al. (2001)<sup>19</sup>

BARWICK, M. and MAHER, W., 2003. Biotransference and biomagnification of selenium copper, cadmium, zinc, arsenic and lead in a temperate seagrass ecosystem from Lake Macquarie Estuary, NSW, Australia. *Marine Environmental Research*, 56, 471-502.

BATISTA NETO, J.A.; SMITH, B.J. and MCALLISTER, J.J., 2000. Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Environmental Pollution*, 109, 1-9.

CARDOSO, G.A.; BOAVENTURA, G.R.; SILVA FILHO; E.V. and BROD, J.A., 2001. Metal distribution in sediments from the Ribeira Bay, Rio de Janeiro - Brazil. *Journal of Brazilian Chemical Society*, 12(6), 767-774.

CARUSO, M.M.L., 1990. *O desmatamento da Ilha de Santa Catarina de 1500 aos dias atuais*. Florianópolis: Editora da UFSC. 158p.

CARVER, R.E., 1970. *Procedures in sedimentary petrology*. NY: John Wiley and Sons. 650p.

CHE, Y.; HE, Q. and LIN, W.Q., 2003. The distribution of particulate heavy metals and its indication to the transfer of sediments in the Changjiang Estuary and Hangzhou Bay, China. *Marine Pollution Bulletin*, 46, 123-131.

CLARKE, K.R. and WARWICK, R.M., 1994. Changes in marine communities: an approach to statistical analysis and interpretation. UK: *Natural Environment Research Council*. 144p.

CURTIUS, A.J.; SEIBERT, E.L. and FIEDLER, H.D., 2003. Avaliando a contaminação por elementos traço em atividades de maricultura. Resultados parciais de um estudo de caso realizado na Ilha de Santa Catarina, Brasil. *Química Nova*, 26(1), 44-52.

DA SILVA, M.R.; LAMOTTE, M.; DONARD, O.F.X.; SORIANO-SIERRA, E.J. and ROBERT, M., 1996. Metal contamination in surface sediments of mangroves, lagoons and Southern Bay in Florianópolis Island. *Environmental Technology*, 17, 1035-1046.

DA SILVA, E.M.; NAVARRO, M.F.T.; BARROS, A.F.; MOTA, V.F.V. and CHASTINET, C.B.A., 2000. Metal in the sediments of Jauá Lake (Camaçari, Bahia, Brazil) following an episode of industrial contamination. *Aquatic Ecosystem Health and Management*, 3, 509-514.

DE PAULA, F.C.F. and MOZETO, A.A., 2001. Biogeochemical evolution of trace elements in a pristine watershed in the Brazilian southeastern coastal region. *Applied Geochemistry*, 16, 1139-1151.

DIEGUES, A.C., 1999. Human populations and coastal wetlands: conservation and management in Brazil. *Ocean and Coastal Management*, 42, 187-210.

DUARTE, R.P.S. and PASQUAL, A., 2000. Avaliação do cádmio (Cd), chumbo (Pb), níquel (Ni) e zinco (Zn) em solos, plantas e cabelos humanos. *Energia na Agricultura*, 15(1), 46-58.

FISHER, N.S.; TEYSSIE, J.L.; FOWLER, S.W. and WANG, W.X., 1996. Accumulation and retention of metals in mussels from food and water: a comparison under field and laboratory conditions. *Environment, Science and Technology*, 30, 3232-3242.

FÖRSTNER, U., 1987. Sediment-associated contaminants - an overview of scientific bases for developing remedial options. *Hydrobiologia*, 149, 221-246.

FÖRSTNER, U. and WITTMANN, G.T.W., 1981. *Metal pollution in the aquatic environment*. Second edition. Germany: Springer-Verlag Press. 486p.

GIBBS, R.J., 1994. Metal in the sediments along the Hudson River Estuary. *Environment International*, 20(4), 507-516.

LACERDA, L.D.; PFEIFFER, W.C. and FISZMAN, M., 1982. Níveis naturais de metais pesados em sedimentos marinhos da Baía da Ribeira, Angra dos Reis. *Ciência e Cultura*, 34(7), 921-924.

LACERDA, L.D.; PFEIFFER, W.C. and FISZMAN, M., 1987. Heavy metal distribution, availability and fate in Sepetiba Bay, S.E. Brazil. *The Science of the Total Environment*, 65, 163-173.

LACERDA, L.D.; SOUZA, C.M.M. and PESTANA, M.H.D., 1988. Geochemical distribution of Cd, Cu, Cr and Pb in sediments of estuarine areas along the southern Brazilian coast. In: SEELIGER, U.; LACERDA, L.C. and PATCHINEELAM, S.R. (eds.), *Metal in coastal environments of Latin America*. Germany: Springer-Verlag. pp.86-99.

LACERDA, L.D.; SOUZA, C.M.M. and PESTANA, M.H.D., 1989. Trace metals geochemical associations in sediments of a non-contaminated estuary. *Ciência e Cultura*, 41(3), 301-304.

MATTHIESSEN, P. and LAW, R.J., 2002. Contaminants and their effects on estuarine and coastal organisms in the United Kingdom in the late twentieth century. *Environmental Pollution*, 120, 739-757.

NEUBECKER, T.A. and ALLEN, H.E., 1983. The measurement of complexation capacity and conditional stability constants for ligands in natural waters. *Water Research*, 17, 1-14.

PERIN, G.; FABRIS, R.; MANENTE, S.; REBELLO WAGENER, A.; HAMACHER, C. and SCOTTO, S. 1997. A five-year study on the heavy-metal pollution of Guanabara Bay sediments (Rio de Janeiro, Brazil) and evaluation of the metal bioavailability by means of geochemical speciation. *Water Research*, 31(12), 3017-3028.

REGO, V.S.; PFEIFFER, W.C.; BARCELLOS, C.C.; REZENDE, C.E.; MALM, O. and SOUZA, C.M.M., 1993. Heavy metal transport in the Acari-São João de Meriti river system,

- Brazil. *Environmental Technology*, 14, 167-174. Heavy metal transport in the Acari-São João de Meriti river system, Brazil. *Environmental Technology*, 14, 167-174.
- RIDGWAY, J. and SHIMMIELD, G., 2002. Estuaries as repositories of historical contamination and their impact on shelf seas. *Estuarine, Coastal and Shelf Science*, 55, 903-928.
- SA, F., 2003. Distribuição e fracionamento de contaminantes nos sedimentos superficiais e atividades de dragagem no Complexo Estuarino da Baía de Paranaguá (PR). Curitiba, Brazil: Universidade Federal do Paraná, Master's thesis.
- SEELIGER, U.; LACERDA, L.C. and PATCHINEELAM, S.R., 1988. *Metal in coastal environments of Latin America*. Germany: Springer-Verlag. 297p.
- SIQUEIRA, G.W.; BRAGA, E.S.; MENDES, A.S. and APRILE, F.M. 2001. Contaminação metálica nos sedimentos provenientes do sistema estuarino de Santos-SP/Brasil. *Anais da XIV Semana Nacional de Oceanografia* (Rio Grande, Brasil). CD-room.
- SORIANO-SIERRA, E.J.; SILVA, J.R.B.M; DERNER, R.B. and BRANCO, J.O., 1986. Aspectos ecológicos do manguezal do Rio Itacorubi, Santa Catarina, Brasil. Florianópolis: NEMAR, *Série Contribuições Científicas*, n°16, 32p.
- SOUZA, C.M.M.; PESTANA, M.H.D. and LACERDA, L.D., 1986. Geochemical partitioning of heavy metals in sediments of three estuaries along the coast of Rio de Janeiro (Brazil). *The Science of the Total Environment*, 58, 63-72.
- SOUZA, E.C.P.M.; TOMMASI, L.R. and DAVID, C.J., 1998. Microphytobenthic primary production, biomass, nutrients and pollutants of Santos Estuary (24oS, 45o20'W). São Paulo, Brazil. *Brazilian Archives of Biology and Technology*, 41(1), 27-36.
- STRICKLAND, J.D.H and PARSON, T., 1972. *A practical handbook of seawater analysis*. 2 (Bulletin, 122) Ottawa: Fisheries Research, Board of Can. 172p.
- TOMMASI, L.R., 1987. Poluição marinha no Brasil: síntese do conhecimento. *Publicação Especial do Instituto Oceanográfico de São Paulo*, 5, 1-30.