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THE IMPACT OF URBANIZATION ON BIOSPHERE RESERVES: A COMPARATIVE STUDY OF PROTECTED AND NON-PROTECTED COASTAL AREAS

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Summary

1. INTRODUCTION 1

2. OBJECTIVES 3

3. ACTIVITIES 3

3.1. Rivers survey (pilot sampling): 3
3.2. Sampling procedures 6
3.3. Laboratorial structure 8
3.4. Scientific production 8

4. MANUSCRIPT ELABORATED 9

4.1. WATER: Urbanization impact on subtropical estuaries: a comparative study of water properties in urban areas and in protected areas 10
Abstract 11
Introduction 12
Methods 13
Results 15
Discussion 20

4.2. SEDIMENTS: Evidence of systemic changes in trace metal concentrations in subtropical estuarine sediments as a result of urbanization 25
Abstract 26
Introduction 27
Methods 28
Results 30
Discussion 35

4.3. WATER-SEDIMENTS INTERACTIONS: Phosphorus dynamics in the water and sediments from urbanized and non-urbanized rivers in Southern Brazil 41
Abstract 42
Introduction 43
Methods 44
Results 49
Discussion 56

4.4. FAUNA-WATER-SEDIMENTS INTERACTION: Assessing the environment-benthic fauna coupling from urban areas and preserved areas of southern Brazil 62
Abstract 63
Introduction 64
Methods 66
Results 70
Discussion 83

5. LITERATURE CITED 89

1. INTRODUCTION

The urbanization processes can be understood as a demographic domain and an important recent agent in the transformation of earth (Pickett et al., 2001). Despite the fast growth in the metropolitan areas, suburban areas are growing faster than any other zone. This growth occurs on and interdigitated with natural areas and has been causing alterations in physical, chemical and biological characteristics of aquatic systems adjacent to urbanization areas (Paul & Meyer, 2001).

In general, urbanization, mainly in coastal areas, has been responsible for making elevated concentrations of nutrients available to aquatic environment. The use of large-scale of artificial fertilizers and detergents and the extensive connection of sewage to the sea has been producing a new and already common process denominated cultural eutrophication (Smith et al., 1999; de Jonge et al., 2002). In these cases, sediments and bottom water may suffer from hypoxia or anoxia as a consequence of the increase in respiration and decomposition of organic matter, which usually causes the massive death of benthic fauna. Due to its great capacity of assimilation, trough processes of transformation and retention of nutrients, great amounts of organic matter are necessary in order to create a deleterious effect on the estuarine systems. What usually occurs in aquatic systems is the stimulus of primary production and changes in communities structures.

Besides eutrophication, the entrance of non-nutrient pollutants and invasive species, the overfishing, the alterations of habitats and global climatic changes are the main agents causing the change of biodiversity in shallow coastal ecosystems (New, 1995; Levin et al., 2001). In urbanized estuaries, where most of these perturbations occur, the maintenance of the ecological properties depends on the budget between its capacity to dilute substances and the magnitude of pollutants entrance in the system, as well as the exchanges between the distinct environments (Lee, 1999; Cloern, 2002). The functioning of these transition zones depends primarily on the fluxes of energy and matter with the terrestrial environment and with the adjacent sea (Dame & Allen, 1996; Koch & Wolff, 2002).

The present challenge in coastal cities is to manage the fast urban growth and the preservation of the environment for the sustainable development. Several action strategies have been suggested and stimulated to reduce these impacts. The most common is the creation of preservation units.

The industrial expansion launched in Brazil in the mid-1950s promoted rapid urban growth, principally in coastal areas on the Atlantic Forest Biosphere Reserve. 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 aquatic systems (Ridgway & 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, 1995; 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 harder to quantify. The sources of pollution are varied and spread throughout the environment, raising difficulties to establish any cause-effect relations.

The comparison between several urbanized (non-protected) and non-urbanized areas (protected) may be an alternative to establish relations of cause-effect and consequences of ecological changes in aquatic systems with the absence of historical data. In this case, despite the intrinsic differences of each system, same sized areas, situated in the same geographic region, having similar environmental characteristics and varying basically according to the presence or absence of urbanization around them, can be contrasted.

2. OBJECTIVES

Aiming this perspective, the study tried to evaluate the effects of urbanization on aquatic environments of the Atlantic Forest Biosphere Reserve. Trough comparison of spatial variability in the quality of water, sediments, benthic fauna and interactions among these constituents the work had as specific purposes:

- WATER: Urbanization impact on subtropical estuaries: a comparative study of water properties in urban areas and in protected areas
- SEDIMENTS: Evidence of systemic changes in trace metal concentrations in subtropical estuarine sediments as a result of urbanization
- WATER-SEDIMENTS INTERACTIONS: Distribution of phosphorus in the water and sediments of urbanized and non-urbanized rivers
- FAUNA-WATER-SEDIMENTS INTERACTION: Predicting the spatial variability of benthic macrofauna in urbanized areas and protected areas trough environmental differences

Next, the carried out activities, a brief description of the study area, general proceedings and the design sample are presented. The specific purposes mentioned above will be treated separately (item 4.0) and as full texts.

3. ACTIVITIES

3.1. Rivers survey (pilot sampling):

All the principles of the study are based on the comparison among same sized areass, situated on the same geographic area, having similar environmental characteristics and varying basically as the presence or absence of urbanization around it. This phase of the work had as the main objective the previous evaluation of the environmental characteristics along eighteen rivers that drain towards the Santa Catarina Island Bay, with the purpose of:

(i-) check the adjustment of the rivers initially suggested for the study;

(ii-) define the sampling points.

The similarities in the sedimentological characteristics have guided the choice of rivers and points, once this parameter is intimately related to the hydrology and extremely influences the chemical properties and the components of the biota. This proceeding has guaranteed a minimum control on the variables that are commonly related to the changes in physical, chemical and biological properties in estuarine systems and that could confound the evaluation on the effects of urbanization.

The following rivers situated on the continental portion comprising the cities of Palhoça, São José, Florianópolis and Biguaçú were covered by land and water: Cubatão Sul river, Aririú river, Grande river, Passa Vinte river, Araújo river, Buchele river, Três Henriques river, Serraria river, Caveiras river and Biguaçú river. The rivers situated on the island portion comprising the Florianópolis city were covered by land and water: Tavares river, Fazenda river, Itacorubi river, do Sertão river, Vadik river, Pau do Barco river, Ratones river and Veríssimo river.

By the recognition of the rivers that surround the Santa Catarina Island Bay (27° 29´S - 48° 30´W), the rivers Aririú, Maruím and Itacorubi were chosen as urbanized areas potentially polluted , and the rivers Tavares, Ratones and Veríssimo were chosen as reference sites or urbanization control (Fig. 3.1-1). The permission for sampling of biological material was obtained with the Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis - IBAMA do Ministério do Meio Ambiente – MMA (license CNPT 010/2002, for sampling river Tavares and license CGEUC 068/2002, for sampling rivers Veríssimo and Ratones).

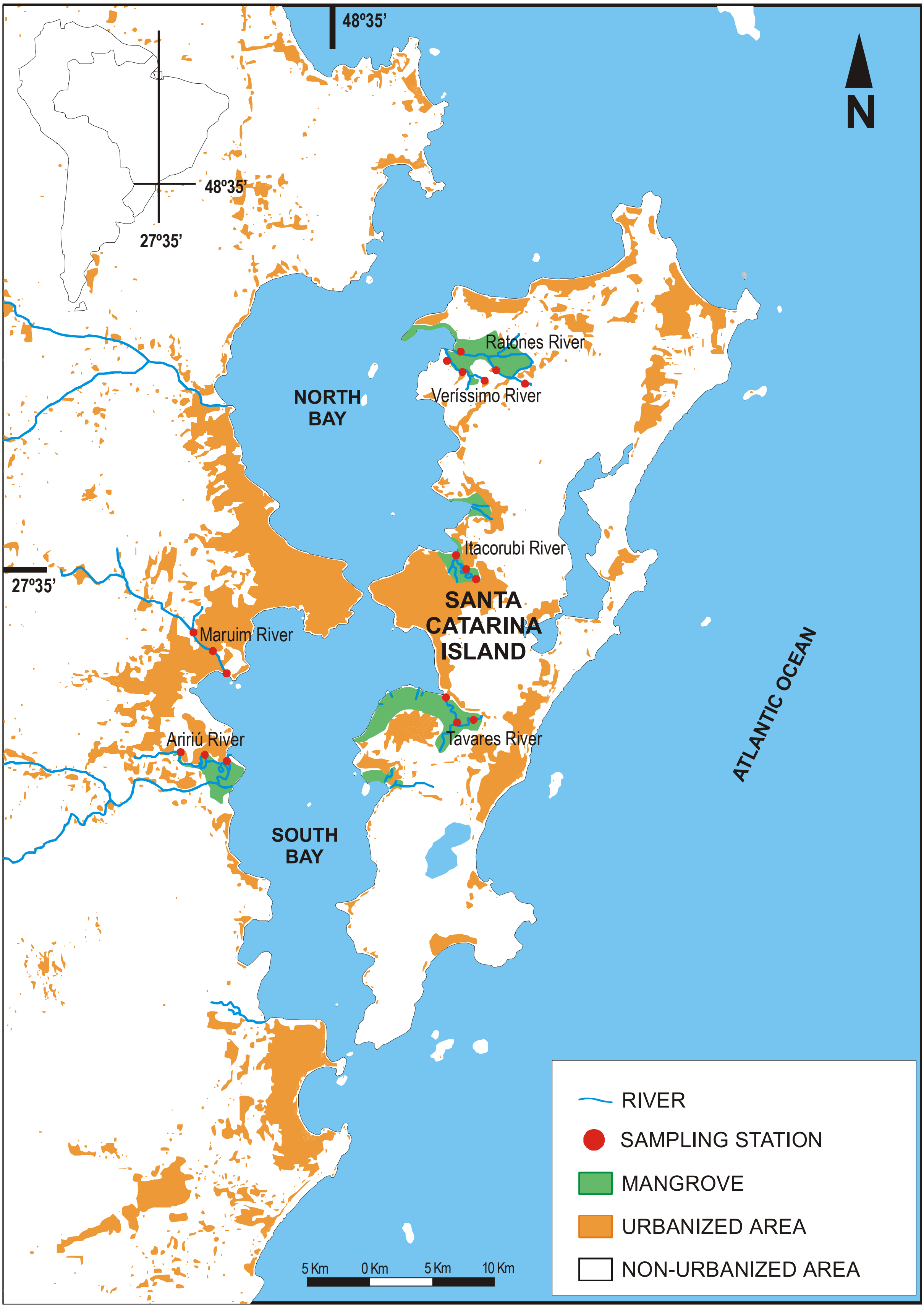

Figure 3.1-1. The Santa Catarina Island Bay, southern Brazil, showing the sampled rivers.

3.2. Sampling procedures

The local rivers form a great mosaic of urbanized areas intercalated with preservation units (Fig. 3.1-1). This situation enabled the discrimination of rivers with similar environmental characteristics in: i-) urbanized rivers and ii-) non-urbanized rivers. For the study of benthic macrofauna, and the physical and chemical characteristics of the sediments and water a hierarchical design sampling was used, comparing punctual (among sites whiting the same river), local (among rivers in the same area) and regional (among groups of rivers in urbanized and non-urbanized areas) spatial variations (Fig. 3.2-1). In each river, 3 sampling points were established: in the high salinity region, close to the river mouth, in the low salinity region, close to the tidal influence limiting zone, and in the intermediate region, between these two situations.

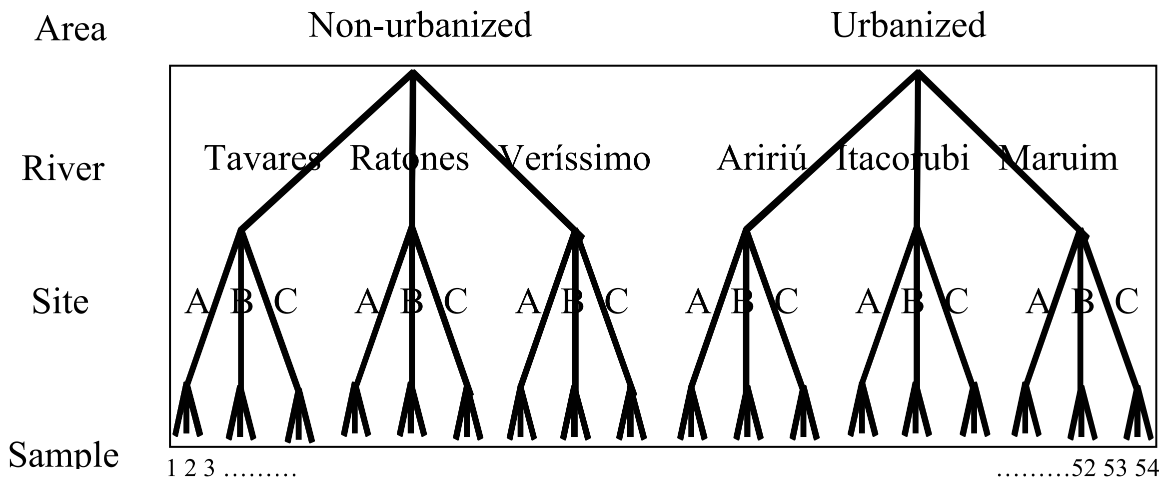

Figure 3.2-1. Schematic diagram of the hierarchical sampling design.

Through autonomous diving in each of the rivers and sampling points, surface sediments were collected for physical, chemical and biological analysis (Fig 3.2-2). In each point 21 samplings were made, being three for sedimentological analysis, three for heavy metals analysis, three for microphytobenthos and 12 for the analysis of benthic macrofauna.

Altogether, 378 samples of sediments were taken.

In the same sampling points, Van Dorn bottles were used for the sampling of bottom waters for physical, chemical and biological analysis (Fig. 3.2-2). The temperature, pH, and secchi disc were measured in triplicate and three samples were taken for the analysis of each variable: three for dissolved oxygen, three for inorganic dissolved nutrients (nitrite, nitrate, nitrogen, phosphate and silicate), chlorophyll *a*, phaeophytin *a*, suspended particulate material and salinity; and three for the analysis of N-ammoniacal. Altogether 162 samples of water were taken.

The sampling was made within eight days in April, 2002 and involved fifteen people with the accompaniment of the Environmental Police (3rd Environmental Military Police Platoon of Santa Catarina).

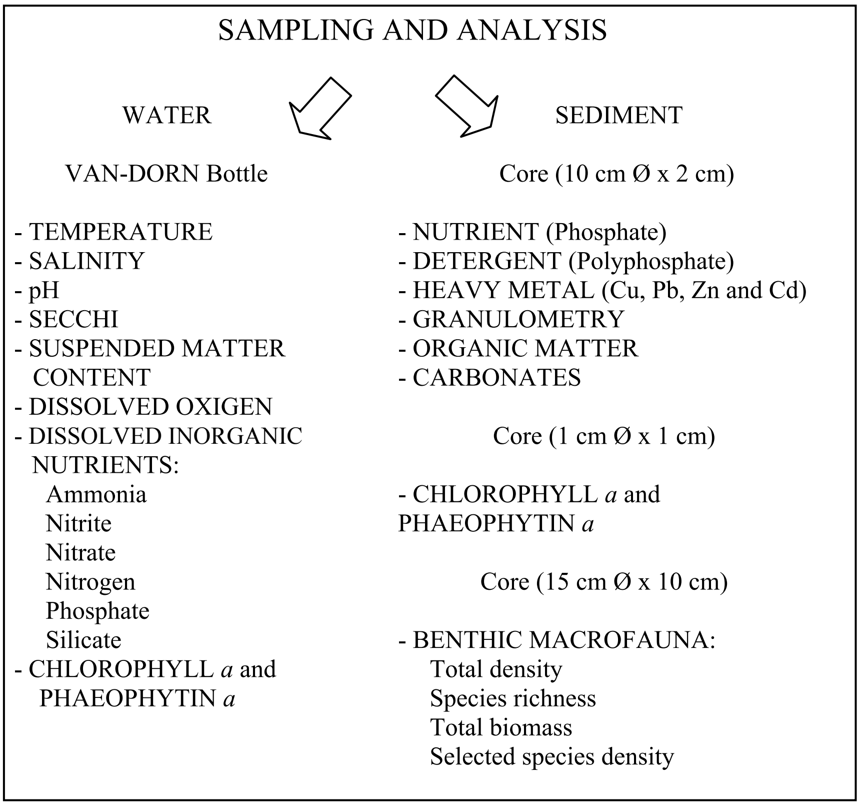

Figure 3.2-2. Schematic diagram of the water and sediments sampling and analysis.

3.3. Laboratorial structure

The analysis of benthic macrofauna were carried out in the Benthos Laboratory of the Núcleo de Estudos do Mar da Universidade Federal de Santa Catarina;

The analysis of dissolved oxygen, salinity, suspended particulate material, microphytobenthos and phytoplankton (biomass and chlorophyll *a* and phaeophytin *a*) were made in the Hydrology Laboratory of the Núcleo de Estudos do Mar da Universidade Federal de Santa Catarina;

The sedimentological analysis were made in the Sedimentology Laboratory of the Centro de Estudos do Mar da Universidade Federal do Paraná;

The analyses of heavy metals were processed in the Central Analysis of the Chemical Department of the Universidade Federal de Santa Catarina;

Nutriente analyses were processed in the Nutrient Laboratory of the Instituto Oceanográfico da Universidade de São Paulo.

The laboratory analysis involved 15 people, among researchers, technicians, graduation and post-graduation students.

3.4. Scientific production

This study was part of the author’s doctor thesis in Ecology and Natural Resources. The thesis was defended in the Universidade Federal de São Carlos with the title “Variação espacial nas características das águas, dos sedimentos e da macrofauna bêntica em áreas urbanas e em Unidades de Conservação na Baía da Ilha de Santa Catarina” and was approved with grade “A” and distinction.

Part of the study was presented in the “International Coastal Symposium”, occurred in March, 14-19, 2004, in Itajaí - Santa Catarina - Brazil. The abstract of both publications is published in the ICS2004 - Book of Summary, pages 132 and 189. The document can be found on the Symposium webpage: http://www.cttmar.univali.br/~ics2004/8th_ICS_Summary_Book.pdf. The complete papers are being published in the *Journal of Coastal Research*, as follows:

- Pagliosa, P. A.; Fonseca, A.; Barbosa, F. A. R. and Braga, E., 2004. Urbanization impact on subtropical estuaries: a comparative study of water properties in urban areas and in protected areas, *Journal of Coastal Research*, 39:00-00.

- Pagliosa, P. R.; Fonseca, A. and Barbosa, F. A. R., 2004. Evidence of systemic changes in trace metal concentrations in subtropical estuarine sediments as a result of urbanization. *Journal of Coastal Research*, 39:00-00.

4. MANUSCRIPT ELABORATED

4.1. WATER: Urbanization impact on subtropical estuaries: a comparative study of water properties in urban areas and in protected areas

Abstract

The creation of conservation units in mangrove areas has allowed retaining, at least locally, the increasing urbanization in coastal areas. The physical, chemical and biological spatial dynamics of the aquatic system draining into the Santa Catarina Island Bay, Southern Brazil, was evaluated to verify the effects of urbanization. A hierarchical design with various spatial scales of samples within urban and non-urban (control) estuaries was used. As control areas, three estuaries situated within mangrove conservation units were chosen. Three other estuaries with environmentally similar features to those of the control ones, except for being located within urban sites, were chosen as anthropogenically-impacted areas. The concentrations of dissolved nutrients, suspended particulate matter and phytoplanktonic biomass were found to be between three to six times greater in urban estuaries than in non-urban ones. The nutrients average concentrations in the non-urban estuaries were 13 ± 3.4 µM for ammonia, 0.5 ± 0.2 µM for nitrite, 6.2 ± 7.5 µM for nitrate, 0.67 ± 0.29 µM for phosphate, and 39.8 ± 19.9 µM for silicate; and in the urban estuaries, they were 72.5 ± 39 µM for ammonia, 3.2 ± 1.8 µM for nitrite, 14 ± 13.4 µM for nitrate, 3.32 ± 3.43 µM for phosphate, and 31.5 ± 21.3 µM for silicate. In urban estuaries, the dissolved inorganic nitrogen was generally three times greater than in non-urban ones, and although the differences in dissolved organic nitrogen and phosphorus concentrations were not as high between them, the variations were the greatest. Similarly, chlorophyll *a* and phaeophytin *a* presented a higher concentration in urban estuaries (31.1 and 46.4 $\mu g.L^{-1}$) than in non-urban ones (15.8 and 26.2 $\mu g.L^{-1}$), hence the average ratio Chlo*a*:Phae*a* was twice as much in non-urban estuaries. The maintenance of the current mangrove areas, as well as a more efficient control of the domestic and industrial discharges and other activities occurring around the conservation units is suggested as a necessary strategy to maintain the water quality in the Santa Catarina Island Bay.

Introduction

In the first decade of the 21^{St} century it has been estimated that half of the world's population will be living in urban areas (Barbiéri, 1999). As developed countries are already highly urbanized, urbanization growth is nowadays occurring in developing countries. In Brazil, the recent increase in the number of contamination episodes recorded all along the coastal region (almost 7500 km) has been found to be related, directly or indirectly, to the effects of urbanization (Diegues, 1999; Braga et al., 2000; Leão and Dominguez, 2002).

Urban growth in coastal cities causes evident alterations in the quality of marine environments, affecting animals and plants. The increase concentration of inorganic nutrients and dissolved organic matter to concentrations above natural levels are the most serious and common form of perturbation affecting coastal marine systems (GESAMP, 2001). Eutrophication, particularly, is a process able to lead a whole aquatic system to collapse. Some of its typical symptoms are increase turbidity, excessive growth of opportunistic plankton species, oxygen depletion and extensive mortality of benthic organisms. Typically, these events tend to occur in shallow areas, where sediments are fine and the water column stratified, such as estuaries (Gray et al., 2002; De Jonge et al., 2002).

Due to retain the organic matter and dissolved inorganic nutrients coming directly from the terrestrial environment or through sewage, estuarine systems play a fundamental role in the biogeochemical cycling. The maintenance of the ecological properties of estuaries depends on the balance between their capacity to dilute the pollutants and the type and magnitude of the discharge in the system.

Presently, the challenge for coastal cities lies in the need for simultaneous management of the rapid urban growth and the sustainable protection of the environment. In order to reduce these impacts, various strategies at regional and global levels have been suggested and encouraged. In this context, the creation of conservation units has been invocated to salvaguard the gene pool and biological variability in the ecosystems. However, in spite of the great importance of conservation units, especially for aquatic units, many questions about their implementation, such as minimum area needed, on the one hand, and cultural, social and political conflicts, on the other, remain unanswered. Hence, are conservation units, in actual fact, able to sustain the biological diversity and the essential ecological processes of aquatic environments? Is environmental quality guaranteed by the implementation of aquatic conservation units or does it depend on the human activities carried out in the surroundings?

As part of a wider study that evaluates the growing effects of urban centers in coastal environments, this study investigated the physical, chemical and biological spatial dynamics of aquatic systems of urban and non-urban estuaries in the Santa Catarina Island Bay, southern Brazil. The sampling was carried out in locations where control areas were situated within conservation units, hence potentially pollution-free, and also in similar areas, but adjacent to urban centers, thus potentially impacted.

Methods

The hydrodynamics of the Santa Catarina Island Bay is controlled by the micro-tidal force, with average amplitudes of 0.83 m for spring tides, and 0.15 m for neap tides (Cruz, 1998). Whereas the predominant winds are north/north-eastern, the south/south-eastern ones are of greater intensity. The latter ones being responsible for the formation of derive waves, causing some water turbulence in the interior of the bay. Several estuaries that occur all along the almost 80 km long coast and drain their waters into the bay are originally colonized by mangroves and salt-marshes (Fig. 3.1-1). The mangroves which are composed by *Rhizophora mangle*, *Avicennia schaueriana* and *Laguncularia racemosa* species, are at their limit of the geographic distribution in the southern Atlantic coast of South America. Salt marshes, on the other hand, are composed of large mono-specific banks of *Spartina alterniflora* species. The largest two remaining areas of mangroves and salt marshes in the region are the Carijós Ecological Station, with the Ratones and Veríssimo estuaries as their principal water receptors, and the Pirajubaé Marine Sustainable Reserve, drained by the Tavares Estuary. In this investigation, these areas were considered as pristine and were used as controls for the urbanized estuaries.

According to the local authorities, although not quantified, the principal effects of urbanization are caused by the disposal of domestic, industrial, and hospital residuals, agricultural run-off, and soil erosion (Santa Catarina, 1997). Over 600.000 people inhabit the drainage basin of the Santa Catarina Island Bay, figure which over the warm months of the year, tends to triplicate with the tourist arrival. The agricultural work in the region is based on the horticultural farming, principally tomatoes that use in average 188 kg/farm/year of agro-chemicals, usually belonging to the carbamate and organophosphate chemical groups. Thus, the Itacorubi, Aririú and Maruim estuaries are located in the middle of urban centers, and were chosen to analyze their water quality as potentially polluted estuaries (Fig. 3.1-1).

To evaluate the physical, chemical and biological variables of the aquatic compartment, a hierarchical sampling design was used. Two groups of estuaries were selected, those localized within urban areas and those within conservation units. Each of these groups was composed of three estuaries. In each estuary, three different sites along its length were sampled: at the mouth of the estuary, at the limit of the tidal influence and in the intermediate region between those two.

Using a bottle of the type "Van-Dorn", water from near the bottom of the estuaries was sampled for a period of a week in April 2002. Similarly, using a portable pH meter (Hach, mod. 50205, 0.01 precision), water temperature and pH were measured in the field. For the dissolved oxygen analysis, samples were collected and processed according to

Winkler (Grasshoff et al., 1983). Likewise, salinity was measured using the conductivity method (TDS Hach mod. 44600). To assess the amount of suspended matter and phytoplanktonic pigments present, water samples were filtered (GF-52C Schleicher and Schuell). The filtered solution was then used to analyze the dissolved inorganic nutrients. The concentration of ammonia, phosphate and silicate were measured by using spectrophotometry and the colorimetric method (Grassholff et al., 1983). Nitrite and nitrate were analyzed using the Auto-Analyzer II® system – Bran-Luebbe (Tréguer and Le Corre, 1976). The dissolved organic phosphorus (DOP) and nitrogen (DON) were determined by the photo-oxidation technique (Armstrong et al., 1966). Dissolved inorganic nitrogen (DIN) was calculated by the sum of nitrate, nitrite and ammonia concentrations. Chlorophyll *a* and phaeophytin *a* were determined by spectrophotometry.

To analyze the data distribution pattern, the multi-dimensional scaling ordination (n-MDS) was used, taking the Euclidian distance index as descriptors. The significance of the difference between urban and non-urban areas was evaluated through an analysis of similarity (ANOSIM), a permutation test.

Results

The physical, chemical and biological variables from the bottom water of urban and non-urban estuaries are summarized in Table 4.1-1. In average, pH and temperature were rather similar between sites and estuaries. Salinity values, conversely, showed greater variations in urban estuaries than in non-urban ones, varying from 0.1 to 35.6 and from 1 to 20.6, respectively. Although the dissolved oxygen showed similar averaged values, the more extreme values were found in urban estuaries, varying from 0,00 to 5,20 ml.L^{-1}, while in non-urban ones the variation was from 1,02 to 3,20 ml.L^{-1}.

Table 4.1-1: Summary of the physical, chemical and biological variables of water in urban and non-urban estuaries of the Santa Catarina Island Bay, southern Brazil. O_2 in ml.L^{-1}, Nutrients in µM, Seston in mg.L^{-1}, Chl*a* and phae*a* in µg.L^{-1}.

	Urban (*n* = 27)		Non-urban (*n* = 27)	
Variable	Average (±Sd)	Range	Average (±Sd)	Range
Salinity	13.8 (13.5)	0.1-35.6	6.4 (6.2)	1.0-20.6
Ph	7.0 (0.4)	6.5-7.7	7.0 (0.2)	6.7-7.3
T ^oC	24.1 (0.9)	22.8-26.0	24.8 (1.2)	23.3-26.7
O_2	2.28 (1.76)	0.00-5.21	2.20 (0.79)	1.02-3.20
$SI(OH)_4$	31.5 (21.3)	2.6-82.7	39.8 (19.9)	7.4-73.8
PO_4	3.32 (3.43)	0.39-12.45	0.67 (0.29)	0.22-1.20
DOP	4.5 (1.6)	0.0-5.9	5.1 (0.2)	4.4-5.6
% DOP:DTP	64 (27)	0-93	88 (5)	80-96
NH_4	72.5 (39.0)	17.0-161.3	13.0 (3.4)	8.5-23.0
NO_3	14.0 (13.4)	1.3-48.8	6.2 (7.5)	0.5-27.2
NO_2	3.2 (1.8)	0.8-7.3	0.5 (0.4)	0.1-1.8
DON	75.8 (58.8)	12.7-214.0	24.1 (9.4)	1.7-46.3
% DON:DTN	44 (21)	9.9-77	55 (14)	6.8-73.9
% DIN:DTN	89 (45)	19-180	19 (9.8)	10-43
% NH_4:DIN	82 (11)	58-94	74 (18)	36-95
% NO_3:DIN	14 (11)	2.3-37	23 (19)	4.5-63
N:P	66 (82)	8-336	30 (9)	15-52
Seston	26.8 (7.9)	13.4-46.8	31.4 (20.8)	5.7-62.8
Chl*a*	31.1 (38.3)	0.0-122.8	15.8 (19.4)	0.0-69.4
Phae*a*	46.4 (48.5)	0.0-176.2	26.2 (31.9)	0.0-108.9
Chl*a* : Pheo*a*	2.5 (4.0)	0.1-14.2	4.9 (7.3)	0.1-20.0

Silicate concentration were found to be high in both urban (2.6 to 82.7 μM) and non-urban areas (7.4 to 73.8 μM), the highest concentrations being found in the Veríssimo and Ratones estuaries (Fig. 4.1-2). Concentrations of DIP were 5 times greater in urban estuaries (0.39 a 12.45 μM) than in non-urban ones (0.22 a 1.20 μM). DOP, on the other hand, presented greater concentrations in non-urban areas (4.4 to 5.6 μM) than in urban ones (0.0 to 5.9 μM.). In relation to the total dissolved phosphorus (TDP), the percentage of DOP varied from 80 to 96 % in non-urban estuaries and from 0 to 93 % in urban ones.

Ammonia, nitrite and nitrate concentrations were 5, 2 and 6 fold in urban estuaries than in non-urban ones, respectively (Tab. 4.1-1 e Fig. 4.1-2). DON concentrations, similarly, were 3 times as great in urban estuaries (75.8 ± 58.8 μM) than in non-urban ones (24.1 ± 9.4 μM). The principal constituent of the DIN was ammonia, varying from 58 to 94 % in urban areas and from 36 to 94 % in non-urban ones. While the DON in urban areas stood for the 45 ± 21 % of the total dissolved nitrogen (TDN), in non-urban ones (the DON) represented 55 ± 14 % (of the TDN).

Moreover, while in urban estuaries the N:P ratio varied from 8 to 336, with an average of 66 ± 82, in non-urban ones they varied from 15 to 52, with an average of 30 ± 9.

Chlorophyll *a* and phaeophytin *a* concentrations were greater in urban areas than in the non-urban ones, varying from 0 to 122.8 $\mu g.L^{-1}$ and from 0 to 176.2 $\mu g.L^{-1}$ in urban ones, and from 31.1 to 46.4 $\mu g.L^{-1}$ and 15.8 to 26.2 $\mu g.L^{-1}$ in non-urban ones, respectively. Hence, the Chlorophyll *a*:Phaeophytin *a* ratio varied from 0.1 to 14.2 in urban areas, and from 0.1 to 20 in non-urban ones. The suspended matter content, conversely, varied more and showed greater concentrations in non-urban estuaries, with concentrations varying from 5.7 to 62.8 $mg.L^{-1}$, than in urban ones, varying from 13.4 to 46.8 $mg.L^{-1}$.

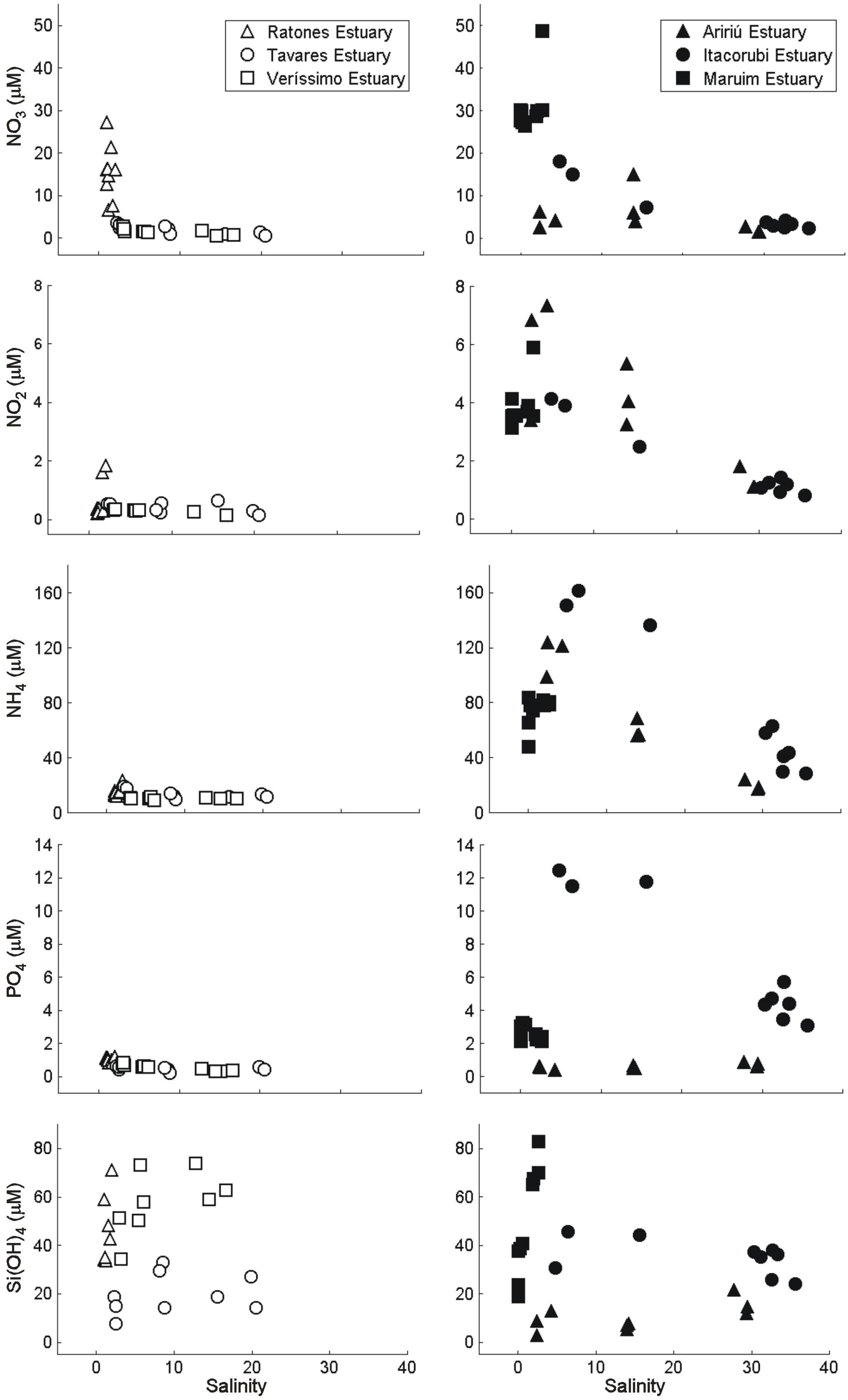

Figure 4.1-2. Nutrient concentrations versus salinity in non-urban (empty symbols) and urban (filled symbols) estuaries of the Santa Catarina Island Bay, southern Brazil.

The differences in the physical, chemical and biological variables of the bottom water of urban and non-urban estuaries were evidenced by the multivariate analysis (stress = 0.16) and the similarity analysis confirmed it (ANOSIM, R = 0.502, p = 0.001, Fig. 4.1-3). Due to the intrinsic variations of every estuary, the data in the graph was rather dispersed, independent of the sampled area.

Figure 4.1-3. n-MDS of physical, chemical and biological variables of non-urban (empty symbols) and urban (filled symbols) estuaries of the Santa Catarina Island Bay, southern Brazil.

Discussion

The impact caused by human activities and presence have brought about a decline in mangrove and salt marsh swamp areas. The land reclamation and contamination of these water bodies are conspicuous and have been recorded all over the world (Ridgway and Shimmield, 2002). This study was carried out in an area of high anthropogenic pressure and reduced industrial activity. The more evident effects are those related to the discharge of domestic sewage *in natura* directly from residences (when located at the mangrove margin) or the sewers (when coming from further up the estuary). The results showed the large overload of nitrogenous and phosphorous compounds released into the environment in urbanized estuaries. In the conservation units, on the other hand, these compounds exhibited values considered natural for pristine areas.

Values from dissolved nutrients exhibited in the water of several estuarine systems in the south and south-eastern Brazil are displayed in Table 4.1-2. In order to compare them with the data set of this study, the values between urban and non-urban areas, according to the authors' discussion, were examined and separated out. Until now, none of those studies had simultaneously evaluated the differences between urban and non-urban estuaries.

The dissolved inorganic nitrogenous and phosphorous compounds are important in the characterization and detection of problems related to eutrophication (Cloern, 2001). Silicate, nitrite, nitrate, ammonia and phosphate concentrations reported in urbanized areas in this study were similar and sometimes even greater than those described in the Santos Estuarine System, the Patos' Lagoon and the Guanabara Bay (Tab. 4.1-2). These places in Brazil are assumed to be the most polluted estuarine systems situated in high population density areas, and where harbor and industrial activities are high. Independent of the urban-ring size in the surrounding area this result evidences that sewage discharge in water bodies can cause rather high nutrient values. In addition to that, it has to be said, particularly with reference to studies carried out by Braga et al. (2000), in the Santos Estuary - São Paulo State, by Baumgarten et al. (1998), in the Patos' Lagoon - Rio Grande do Sul State, and by Kjerfve et al. (1997), in the Guanabara Bay - Rio de Janeiro State, that their values were obtained directly from sewage entry points, hence being the sites with the highest concentrations of pollutants.

Silicate concentrations in the urbanized studied estuaries, gave evidence of terrestrial origin, varying according to localized sediment removal sites, either caused by dredging, straightening and widening of the banks, as in the Itacorubi Estuary, or caused by the presence of concrete walls directly above the water bodies, as at the Maruím Estuary mouth. Dissolved phosphate, on the other hand, exhibited particularly high concentrations in the Itacorubi Estuary, reaching concentrations as high as 50 times that of the others. These values can be resulting from processes, such as the assimilation and adsorption of it by suspended organic matter, and flocculation due to changes in salinity, inducing phosphate sedimentation, with lower concentrations at the mouth of the estuary. The concentrations of dissolved phosphate at the mouth of the Itacorubi Estuary, nonetheless, were still greater than any of the other five studied estuaries.

At high concentrations, similarly, nitrogenous compounds also exhibited a dilution tendency along the estuaries. The water physical mixing processes, caused by seawater entrance in the system, remove and dilute compounds that are being discharged in the estuaries via small fluvial sewers, or directly from domestic residences. This phenomenon can be appreciated principally in Itacorubi and Aririú estuaries. Besides that, the high ammonia values can be additionally originating by the hydrolysis of urea (Braga et al., 2000), especially considering the high amounts of DON present in these estuaries.

The DIN concentrations are directly related to the primary production and decomposition processes (Gray et al., 2002). Generally, the greater the nutrient concentration, the greater the production in the system and the higher is the chlorophyll *a* concentrations.

Nonetheless, a large organic matter contribution to the system can hinder nutrient regeneration and favor denitrification processes, resulting in oxygen depletion in the water column (Nixon, 1981). In this investigation, this process was evidenced by the differences between the DIN composition found in urban areas versus conservation units. In the former, the reductive nitrogenous form (ammonia) predominated in the DIN, whereas in the latter, although with still high values of DIN, there was an increase in the oxidative nitrogenous compounds (nitrate).

For phytoplanktonic production, the N:P average ratio in both types of estuaries systems, urban and non-urban, was found to be greater than the one proposed by Redfield (16:1). In non-urban estuaries, primary production in the inner waters were limited by phosphate, with salinity concentrations lower than 5 and high suspended organic matter content. At the mouth of the estuaries, conversely, where salinity concentration is at its highest, the limitation compounds were the nitrogenous ones. The discharge and maintenance of DIN in non-urban estuaries are greater than the DIP compounds, which must be being adsorbed by suspended solids (Fonseca et al., 2002; Kocum et al., 2002). Besides that, the DIN dilution and assimilation along the estuaries can be the principal factor limiting its presence in the more saline waters. The average N:P ratio in urban areas was twice as high than in conservation units, this occurring without the variation of limiting nutrients along the salinity gradient. The phosphorus adsorption and the nitrogen diverse entry points along the estuaries continued to have a greater N:P ratio than 16, reaching extreme values of 336. These results are in accordance with the general tendency found in polluted and non-polluted coastal areas. The primary production is being limited by nitrogenous compounds in the non-impacted areas and by phosphorous compounds in the impacted ones (Cloern, 2001; De Jonge et al., 2002).

Table 4.1-2: Nutrient concentrations in urban and non-urban estuarine systems of southern and south-eastern Brazil. Referenced data are given as range data or mean; nd = not determinated.

Location	Non-urban Estuaries					Urban Estuaries				
	NO_3 µM	NO_2 µM	NH_4 µM	PO_4 µM	$SI(OH)_4$ µM	NO_3 µM	NO_2 µM	NH_4 µM	PO_4 µM	$SI(OH)_4$ µM
Santa Catarina Island Bay [1]	0.5-27	0-2	8.5-23	0.2-1	7-74	1-49	1-7	17-161	0.4-12	3-83
Conceição Lagoon [2, 3, 4, 5]	0.4-4	0-0.3	1-2	0-7	1-39	0-3	0-0.5	0.5-11	0.0-5	2-77
Camboriú River [6]	-	-	-	-	-	0-6	0-2	2.4-66	0.13-3	15 -210
Babitonga Bay [7]	1-3	0.1-0.5	3-5	0-1	11-36	2.9	2.75	62.1	1.4	33
Paranaguá Bay [8, 9]	0-3	0-1	0.4-22	0.2-1	11-99	0-13	0-1	0.6-13	0.3-4	20-362
Patos Lagoon [10,11, 12, 13]	10-79	0-1	0-14	0-2	0-400	1-101	0-3	0-924	0-44	1-256
Santos Bay [14, 15]	0-19	0-4	1-23	0.5-3	10-50	0-120	0-15	0.8-95	0.2-24	1-160
Guanabara Bay [16]	-	-	-	-	-	1-7	0-3	2-124	0.3-12	nd

This study [1]	Fonseca *et al*. (2002) [5]	Machado et al. (1997) [9]	Baumgarten *et al*. (1998)[13]
Knoppers et al. (1984) [2]	Pereira-filho *et al*. (2001) [6]	Almeida *et al*. (1984) [10]	Braga *et al*. (2000) [14]
Odebrecht and Caruso (1987)[3]	Kuroshima and Bellotto (1998)[7]	Baumgarten *et al*. (1995)[11]	Gianesella *et al*. (2000) [15]
Souza-Sierra *et al*. (1987) [4]	Brandini and thamm (1994) [8]	Santos *et al*. (1997) [12]	Kjerfve *et al*. (1997) [16]

The mangrove areas located in conservation units, however, are not totally free from the surrounding's urbanized dynamics. This was particularly evident in the Ratones and Veríssimo estuaries, both of which constitute the Carijós Ecological Station. Despite that, these estuaries exhibit high silicate values. With the purpose of draining the swamp areas, in the last decades the Ratones Estuary natural course was deviated through engineering works. Nowadays, a large and straight channel became the principal watercourse of the estuary. The change in water current caused by this man-made channel in both, the inlet and outlet, as well as the levelling of the ground in the surroundings can explain the sediment remobilization and maintenance of the silicate high concentrations. The Veríssimo Estuary, conversely, located in the same conservation unit and nearby the Ratones Estuary, has not suffered any change in its watercourse, hence is localized in the most preserved area of the unit. However, due to sand exploitation in the innermost region of it, near the Units limits could be causing the high silicate concentrations in this estuary. Besides that, the high nitrate concentrations in the Ratones Estuary was also very notorious, reaching values up to 30 times greater than the minimum one registered.

This work shows that water quality in urbanized estuaries around the Santa Catarina Island Bay contained very high nitrogenous and phosphorous compounds values. The mangrove conservation units, on the other hand, by supporting the nutrients in normal levels, guaranteed water quality in the estuarine systems, even when located closed to urban centers. The maintenance of natural features in the aquatic system will depend to a large extend on the urbanization control carried out around these areas. Hence, the aquatic system responds and reflects to any activity carried out in the catchments. Due to this, mangrove size maintenance as well as the treatment of all foreign effluents are urgent measures that have to be implemented should these impacts are going to cease.

4.2. SEDIMENTS: Evidence of systemic changes in trace metal concentrations in subtropical estuarine sediments as a result of urbanization

Abstract

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 conservation units 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 generalized contamination 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 conservation units as protectors of the integrity of coastal ecosystems.

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 swallowers 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 conservation units, 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, 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. 3.1-1). The Ratones (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. 3.1-1).

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 describers. 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 Ratones rivers and higher ones in the Aririú and Itacorubi estuaries (Tab. 4.2-1). The lowest salinity values and amplitudes, as well as the highest dissolved oxygen content found in the Maruim and Ratones 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 Estuary (14.4 % ± 12.1), to fine silt with a high quantity of clay-silt in the Tavares Estuary (96.0 % ± 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.

Table 4.2-1: 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.

	Water		Sediment					
Estuary	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

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 Estuary (14.4 % ± 12.1), to fine silt with a high quantity of clay-silt in the Tavares Estuary (96.0 % ± 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 Ratones 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. 4.2-1). 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. 4.2-2). The metal data from the Ratones, 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. 4.2-2). 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. 4.2-2). 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 > RA VE).

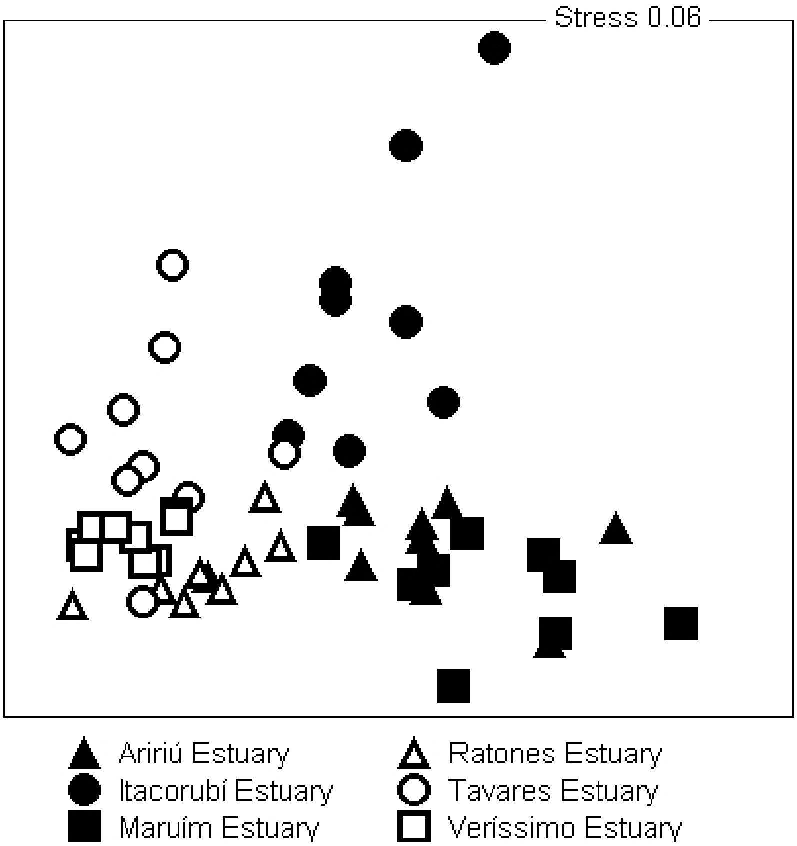

Figure 4.2-2. n-MDS of metal concentration Cu, Pb, and Zn in sediments of non-urban (empty symbols) and urban (filled symbols) estuaries of Santa Catarina Island Bay, southern Brazil.

Table 4.2-2: 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 ns	1550.219	25.28 *	0.186	8.74 *
Local	4	0.066	6.39 **	61.319	3.70 *	0.021	6.86 **
Site	12	0.010	6.30 **	16.555	1.2 ns	0.003	2.54 *
Error	36	0.002		13.696		0.001	

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. 4.2-3). Although the samples were carried out along the saline gradient, only the Pb concentrations in the urban areas and of Zn in the non-urban areas were inversely correlated with the salinity values (Tab. 4.2-3). 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.

Table 4.2-3: 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	-

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.

Discussion

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 (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 Veríssimo 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 4.2-4 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. 4.2-4). 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 conservation units for the maintenance and integrity of local estuarine ecosystems.

Table 4.2-4: Metal concentration (mg/kg) in urban and non-urban estuarine and coastal sediments from Brazil. Referenced data are given as range data; nd = not determinated.

Location in Brazilian Coast	Cu	Pb	Zn
Urban estuaries			
Aririú River (S) [1]	17-21	29-44	101-144
Maruim River (S) [1]	13-19	30-48	108-144
Itacorubi River (S) [1]	21-38	28-39	84-123
Itacorubi River (S) [2]	28-46	48-56	89-97
Babitonga Bay (S) [3]	3-73	2-83	6-1156
Patos Lagoon (S) [4]	1-20	8-267	20-214
Paranaguá Bay (S) [5]	0.5-23	2-25	0.5-311
Santos Bay (SE) [3]	nd	0-48	0-185
Santos Bay (SE) [6]	0.2-114	nd	2-90
Santos Bay (SE) [7]	nd	9-242	9-624
Guanabara Bay (SE) [8]	0-478	5-460	10-1660
Iguaçu River (SE) [9]	22-196	22-36	nd
Estrela River (SE) [10]	74-731	37-63	nd
Guarda River (SE) [10]	19-45	103-237	nd
São Francisco Channel (SE) [9]	22-28	4-86	nd
Sepetiba Bay (SE) [11]	2-166	6-83	18-795
Jurujuba Bay (SE) [12]	40-213	45-123	162-337
Acari River (SE) [13]	500-2700	110-440	700-1400
Todos os Santos Bay (NE) [14]	5-55	10-960	5-2400
Jauá Lake (NE) [15]	16-531	24-282	417-1511
Non-urban estuaries			
Veríssimo River (S) [1]	13-16	19-24	82-92
Ratones River (S) [1]	11-19	23-28	74-105
Ratones River (S) [2]	1-21	2-28	6-79
Tavares River (S) [1]	13-27	18-28	73-97
Tavares River (S) [2]	17-25	14-26	31-65
Capivari River (SE) [16]	4-29	13-53	24-142
Caranguejo River (SE) [10]	20-27	40-81	nd
Ingaíba River (SE) [9]	26-31	33-40	nd
Frade River (SE) [17]	16-31	27-47	47-106
Ribeira Bay (SE) [18]	14-60	9-27	4-14
Ribeira Bay (SE) [19]	3-32	nd	29-189
Reference Values [20]			
TEL (threshold effect level)	18.7	30.2	124
PEL (probable effect level)	108	112	271

This study [1]	Lacerda et al. (1987) [11]
Da Silva et al. (1996) [2]	Baptista Neto et al. (2000) [12]
Tommasi (1987) [3]	Rego et al. (1993) [13]
Baisch et al. (1988) [4]	Seeliger et al. (1988) [14]
Sá (2003) [5]	Da Silva *et al*. (2000) [15]
Souza *et al*.(1998) [6]	De Paula and Mozeto (2001) [16]
Siqueira et al (2001) [7]	Lacerda et al. (1989) [17]
Perin *et al*. (1997) [8]	Lacerda et al. (1982) [18]
Souza et al. (1986) [9]	Cardoso et al. (2001) [19]
Lacerda *et al*. (1988) [10]	Laws (1999) [20]

4.3. WATER-SEDIMENTS INTERACTIONS: Phosphorus dynamics in the water and sediments from urbanized and non-urbanized rivers in Southern Brazil

Abstract

Phosphorus flux models show the removal tends to be a common feature in polluted estuarine systems whereas the release of P to the adjacent coastal area occurs in pristine environments. This study analyses the distribution of P in the water and sediments along six rivers in the south coast of Brazil. Three rivers localized inside protected areas where considered non-polluted areas and used as control for the urbanization. The other three, situated among urbanized areas, where considered as having potential elevated concentrations of P. Results denoted different behavior of P in the water and sediments located in urbanized and non-urbanized areas. The concentrations of dissolved organic (P-org) and inorganic (P-inorg) phosphorus in the water, and total phosphorus (P-tot) and polyphosphate (P-poly) in sediments where higher in the urbanized rivers in respect to the non-urbanized ones. Both P of punctual origin and P of diffuse origin contributed to the maintenance of elevated concentrations and disturbed the natural fluxes along the polluted rivers. The minimum and maximum concentrations in the urbanized areas varied between 0.39-12.45 (μM) for P-org and 0.00-5.92 (μM) for P-inorg in the water, and between 89.90-808.16 ($\mu M.g^{-1}$) for P-tot and 0.00-76.51 ($\mu M.g^{-1}$) for P-poly in the sediments. In the non-urbanized areas concentrations varied between 0.22-1.20 (μM) for P-inorg and 4.43-5.56 (μM) for P-org in the water, and between, 45.91-652.26 ($\mu M.g^{-1}$) for P-tot and 0.00-8.61 ($\mu M.g^{-1}$) for P-poly in the sediments. Using an hierarchical sampling design and a simple model of variation of P (K_d model) it was possible to demonstrate that urbanized and non-urbanized estuaries may act as sinks or sources of P. The analysis of variation of P in different points along each one of the six rivers showed that release and removal areas may occur within a same river independent of its urbanization.

Introduction

Estuaries may act as sources or sinks of compounds that enter the system trough the adjacent coastal area, underground water, rivers, soil and atmosphere. Among the many compounds commonly dispersed into the rivers and estuaries, phosphorus is important due to its buffering mechanism. The buffering mechanism of P is known for maintaining its concentrations close to constant values, providing an additional reservoir for primary production (Smil, 2000), and for its involvement in the natural weathering, which interferes in the vertical distribution of P in the sediments (Froelich, 1988).

The phosphorus cycle is strongly determined by biological processes combined with geochemical processes, as adsorption-desorption and precipitation-dissolution. The preference of one of these processes depends on physical factors as input flux of nutrient, turbidity, residence time and the occurrence of stratification in the water column (de Jonge et al., 2002).

Several studies have been registering the increase of phosphorus concentrations in rivers and estuaries in the last decades in developing countries (Machado et al., 1997; Carreira and Wagener, 1998; Braga et al., 2000), and, in the last century, in countries already intensely urbanized (Nixon, 1995; de Jonge et al., 2002; Foy et al., 2003). However, the increase of phosphorus concentrations in the environment and its effects on the coastal waters does not follow a linear or direct relationship, but a complex one due to the interactions water-sediment which change phosphorus concentrations along rivers and estuaries.

Prastka et al. (1998) have used an equilibrium model in trying to predict the effects of the increasing input of P in rivers and estuaries on the functioning of coastal aquatic systems. This kind of model, also known as partition equilibrium, has been used for biogeochemical studies of environments (Morris, 1986; Turner, 1996) and also to establish criterion for the analysis of water and sediment quality (Van Der Meent et al., 1991). The model uses the concept of K_d (partition coefficient) which is the rate between the particulate and dissolved concentrations of any chemical constituent in thermodynamic equilibrium. The model is quite simple and predicts that the increase of dissolved inorganic phosphorus concentrations in rivers may improve the removal of phosphorus by the particles in the low salinity zone of estuaries. In another words, this may imply that the removal of P is a feature of polluted estuarine systems, whereas the release of phosphorus to the adjacent sea occurs in non-polluted environments.

The aim of this study is to describe the path of phosphorus in the near bottom water and in the riverine sediments situated among urbanized areas and protected areas of the Santa Catarina Island Bay, south coast of Brazil. In particular were verified the relationship of phosphorus with other variables of water and sediment and also the trend of behavior of these rivers as sinks or sources of inorganic dissolved phosphorus to the adjacent sea, using the equilibrium model of K_d. In addition, the degree of pollution related to urbanization around the estuaries was analyzed through the concentration of polyphosphate in sediments. The polyphosphates do not occur naturally in estuarine areas, serving as a potential indicator of the occurrence of recent contaminations and environmental quality.

Methods

Study Area

The Santa Catarina Island Bay is situated next to an amphidromic region, characteristically formed by microtide, with a mean amplitude of 0.83 m for spring tide and 0.15 for neap tide, respectively (Cruz, 1998). The climate is subtropical and humid with precipitation well distributed along the year, however, with more intense rain in the winter and more frequent in summer. Prevailing winds blow from south/southeast quadrant. Mangroves are in their south boarder of the geographic distribution of Atlantic coast in South America and are composed by the species *Rhizophora mangle, Avicennia schaueriana* e

Laguncularia racemosa. The saltmarsh areas are formed by extensive monospecific banks of the graminea *Spartina alterniflora*. The two bigger local areas of mangrove and saltmarsh compose the preserved area Carijós Ecological Station, whose main sinks are the rivers Ratones (RA) and Veríssimo (VE), and the Pirajuba e Sustainable Marine Reserve, which is formed by the Tavares river (TA). These areas were considered as potentially non-polluted and were used as urbanization control (Fig. 3.1-1).

The urbanization around the bay is intense and focused mainly on the continental portion and in the centre of the island. More than 600,000 people live on the drainage basin of the Santa Catarina Island Bay, and this number usually triplicates with the arrival of tourists during the hot months of the year. Among the urbanization, many streams were reordered and made impermeable, and large extents of the margin boarder were covered with land. After a crescent governmental stimulus the region are becoming economically important in fisheries production, especially with the production of the exotic oyster *Crassostrea gigas* and the mussel *Perna perna* reaching 7,000 ton/yr. The rivers Itacorubi (IT), Aririú (AR) and Maruim (MA), suffer directly the urbanization effects and were chosen as potentially polluted places for the analysis of P in water and sediments (Fig. 3.1-1).

Sampling design and sample treatment

The hierarchical analysis was used to evaluate the phosphorus dynamics in the water and sediments, comparing punctual (sites within the same river), local (rivers within the same area) and regional (rivers of urbanized and non-urbanized areas) spatial variations. Six rivers were studied, being three in urbanized areas and three in non-urbanized and preserved areas. In each river, 3 sampling sites were established: in the high salinity region, close to the river mouth, in the low salinity region, close to the tidal influence limiting zone, and in the intermediate region, between these two situations.

In April, 2002, the bottom water in each sites and river studied was sampled in triplicate using a van Dorn bottle with horizontal closing device. Samples were filtered with 0.45 μm membranes (filter GF-52C Schleicher and Schuell) for the estimates of suspended particulate matter and phytoplankton pigments, chlorophyll a and phaeophytin a (Strickland and Parson, 1972). The filtered solution was used to the analysis of dissolved inorganic phosphorus (P-inorg) and dissolved organic phosphorus (P-org). The P-inorg was determined trough the colorimetric method, according to Grasshoff et al. (1983), and measured in a digital spectrophotometer Bausch and Lomb. The P-org was determined as the difference between P-inorg and total dissolved phosphorus. The last was analyzed trough photo-oxidation according to Armstrong et al. (1966), adapted by Saraiva (2003). The samples for the analysis of dissolved oxygen were collected and processed according to Winkler method (Grasshoff et al., 1983). In laboratory, salinity was measured trough the conductivity method (TDS Hach mod. 44600).

Through autonomous diving, in each site three samples of sediments were taken for the analysis of total phosphorus (P-tot) and polyphosphate (P-poly), and three samples for the sediment analysis. Core of 11 cm diameter and 2 cm deep, pre-washed with hydrocloric acid 10 % and distilled water were used. The P-tot and the P-poly concentrations in sediment were determined trough the method proposed by Áspila (1976), utilizing 16 hs extraction and acid digestion. The content of organic matter of the sediments was determined by the percentage difference in weigh after ignition (550 °C for 1 h) and burning carbonate by acidification (HCl 10 %). The granulometric analyses were carried out by the pipette analysis and sieving according to Carver (1970). The microphytobenthic biomass was collected in triplicate with a 1 cm diameter and 1 cm high sampling device. The samples were stored in dark plastic flasks and kept at low temperature until the arrival in laboratory where they were frozen (-12 °C) for posterior analysis of pigments. The extraction of pigments, the absorbance reading of chlorophyll *a* and phaeophytin *a* and the calculation of concentrations were made according to the method described by Plante-Cuny (1978).

Data Analysis

The distribution of P-tot concentrations in water and sediments was analyzed along the salinity gradient. Hierarchical analysis of variance were used to test differences in P-tot concentrations in water and sediments among areas, rivers (nested inside the respective area) and sampling sites (nested inside the respective river and area). For significant differences, the evaluation was made trough multiple comparison tests, the Newman-Keuls test. The homogeneity of variances was previously checked by Cochran test, and logarithm transformation was used whenever needed.

The distribution pattern of concentrations of P-inorg, P-org in water and P-tot and P-poly in sediments was analyzed with the multidimensional scaling ordination (n-MDS). The normalized Euclidian distance indexes on fourth root transformed data were used. The differences on multidimensional structure between urbanized and non-urbanized areas were evaluated through analysis of similarity (ANOSIM), a permutation test (Clarke and Warwick, 1994).

Pearson correlations were made separately for the river data of urbanized and non-urbanized areas. For water samples, the analyses were performed among each one of the water physico-chemical and biological variables and the values of P-org and P-inorg. For the sediment samples, the data from sediment and biological variables were contrasted with the values of P-tot and P-poly in sediments.

K_d Model

Phosphorus dynamics in sampled rivers was checked through adsorption equilibrium models, using the partition coefficient K$_d$. The model predicts the decrease of dissolved P concentrations in the water and in riverine sediments towards the sea. In the mixing zone there is an increase of suspended particulate matter and consequently resuspended P increases. Along the estuary, reactions of adsorption-desorption occur modifying the final concentration of P in sediments, resulting in removal or release of P to the adjacent sea. In the present study, the inner sampled site in each river (site a), was used as reference for the riverine concentrations. The intermediate (site b) and river mouth (site c) sites were used separately or as means for the calculation of P variability along each estuary. The removal or release of P was given by the formula:

$$\Delta P = \frac{(P_a^W K_d M_{b,c}) - (\alpha P_a^W (M_{b,c} - M_a)) - (M_a P_a^S)}{1 + (K_d M_{b,c}(1-\alpha)) + (\alpha K_d M_a)}$$

Where P_a^W and P_a^S are the concentrations of P in the water (^{W}) and in the sediments (^{S}), respectively in the inner sites ($_a$) of the estuaries. M_a and $M_{b,c}$ are the suspended particulate matter (M) concentrations in the inner sites ($_a$) and along the estuaries (sites $_b$ or $_c$, or mean value), respectively. K$_d$ is the rate between P concentration in sediments ($P_{b,c}^S$) and water ($P_{b,c}^W$) of the estuaries. The models assumes that P in the water (P_a^W) and sediments ($P_a^S\ M_a$) that reach the estuaries, plus the resuspended fraction ($P^{res} + M^{res}$), equals P in the water ($P_{b,c}^W$) plus P in the sediments ($P_{b,c}^S + M_{b,c}$) along the estuaries, after the equilibrium reactions. α is the rate between resuspended P (P^{res}) and P in the sediments ($P_{b,c}^S$) in the estuaries. The suspended particulate matter of the estuaries ($M_{b,c}$) equals the sum of particulate material that enters the estuary (M_a) and the resuspended (M^{res}) one. The complete derivation and the detailed discussion of the model can be found in Prastka et al. (1998).

Results

The distribution of the P-tot concentrations in the water and sediments along the salinity gradient of the rivers is shown on Figure 4.3-2. P-tot concentrations in the water showed a general trend of maintaining constant values with the increase of salinity and the P-tot concentration in the sediment tended to increase with salinity. However, distinct variations in the concentrations of P-tot occurred depending on the river.

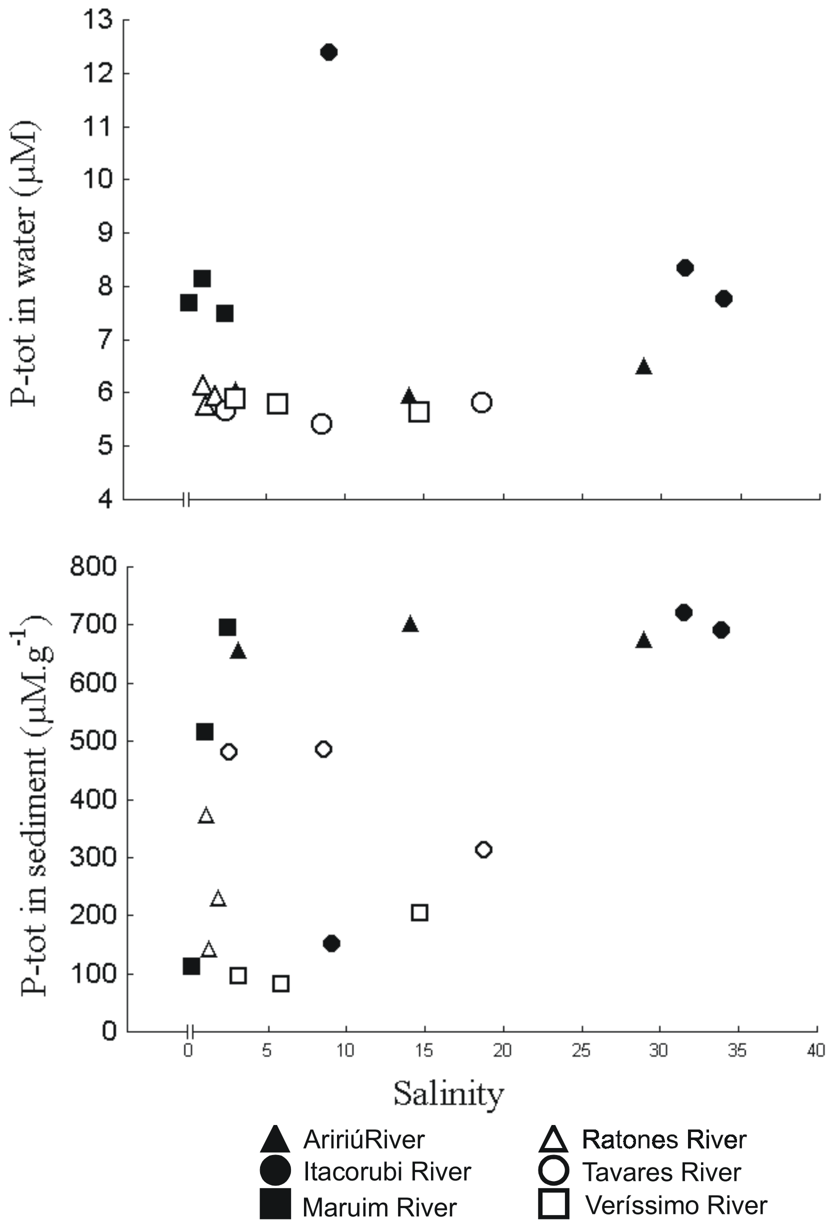

Figure 4.3-2. Phosphorus concentration in water and sediment *versus* salinity in rivers of the Santa Catarina Island Bay.

The hierarchical analysis of variance realized separately for the levels of P-tot in the water and in the sediments showed significant differences between urbanized and non-urbanized areas, among rivers within each area and among sites within each river (Table 4.3-1). The multiple comparison tests for P-tot in the water exhibited the highest values in urbanized rivers and lowest values in the non-urbanized ones (Newman-Keuls test, $P < 0.05$). The test showed differences among data from urbanized rivers (Newman-Keuls test, $P < 0.05$, IT > MA > AR), but not among data from the non-urbanized ones (Newman-Keuls test, $P > 0.05$, RA = VE = TA), and the only significant differences among sites within the same river were related to higher concentrations of P-tot found in the inner site of Itacorubi river.

Table 4.3-1: Summary of nested analysis of variance of total P concentration in water and sediment in rivers of the Bay of Santa Catarina Island, southern Brazil. n = 3, d.f. = degree of freedown, MS = mean squares, *F* = *F*-ratio, * denotes significance at $P < 0.05$.

Source of variation	d.f.	P-tot in water MS	P-tot in water *F*	P-tot in sediment MS	P-tot in sediment *F*
Area	1	56.52	574.66*	1052612.00	65.45*
River	4	12.58	127.92*	167162.00	10.39*
Site	12	3.35	34.03*	109820.00	6.83*
Error	36	0.10		16082.68	

These variations on the concentrations of P-tot in the water can be better understood if we observe separately the inorganic and organic forms. Figure 4.3-3 shows clearly the prevalence of organic form over the inorganic one. In the non-urbanized areas both concentrations of inorganic and organic forms kept constant along the same river and among rivers. On the other hand, in the urbanized areas the P-inorg concentrations were higher in the Itacorubi and Maruim rivers, and the P-org concentrations were lower in Itacorubi river. When compared to the other rivers, the values of P-inorg and P-org in the inner site of Itacorubi river presented a clear reverse trend, with higher concentrations of inorganic forms and lower concentrations of organic ones.

The multiple comparison test for the P-tot concentrations in the sediments evidenced, as the water values, higher concentrations in urbanized rivers and lower in the non-urbanized ones (Newman-Keuls test, $P < 0.05$; Fig. 4.3-3). For the urbanized rivers the P-tot concentrations in the sediments were higher in the Aririú river than in any other river (Newman-Keuls test, AR > (MA = AR)). In the non-urbanized area, the highest concentrations of P-tot were in the Tavares river (Newman-Keuls test, TA > (VE = RA)). Only in the inner sites of Itacorubi and Maruim rivers were found P-tot concentrations in the sediments significant lower than in the other sites of these rivers. Significant differences among the P-tot concentrations along the other rivers were not found.

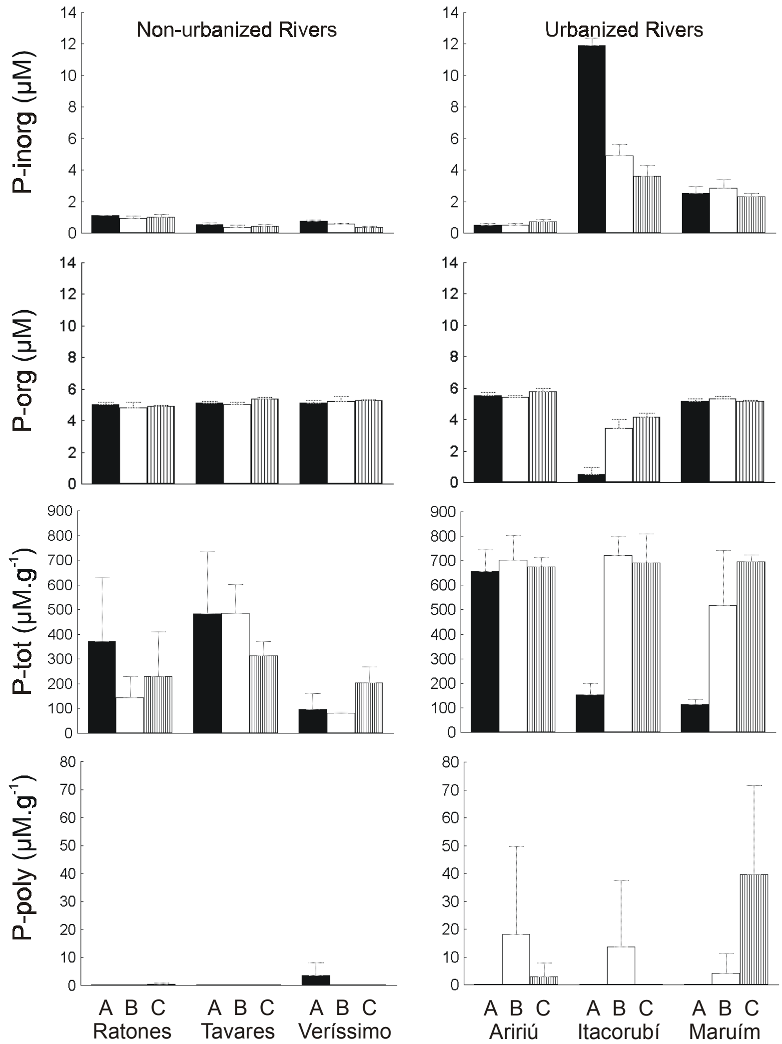

Figure 4.3-3: Concentration of inorganic P (P-inorg) and organic P (P-org) in water and total P (P-tot) and Polyphosphate (P-poly) in sediment in rivers of the Bay of Santa Catarina Island, southern Brazil. A = inner site, B = intermediate site and C = site in the mouth of the estuary.

The P-poly concentrations in the sediments were also higher in the urbanized rivers compared to the non-urbanized ones, with distinct variations among sites into the same river (Fig. 4.3-3).

The multivariate analysis (n-MDS) of the data of P-org and P-inorg in the sediments pointed differences between urbanized and non-urbanized rivers (ANOSIM, R= 0.308, P = 0.001; Fig. 4.3-4). The samples from the non-urbanized rivers occurred concentrated, showing the strong aggregation of the data. On the other hand, samples from urbanized rivers occurred dispersed in the graphic exhibiting the high variation of the distinct forms of P in the water and sediments of these environments.

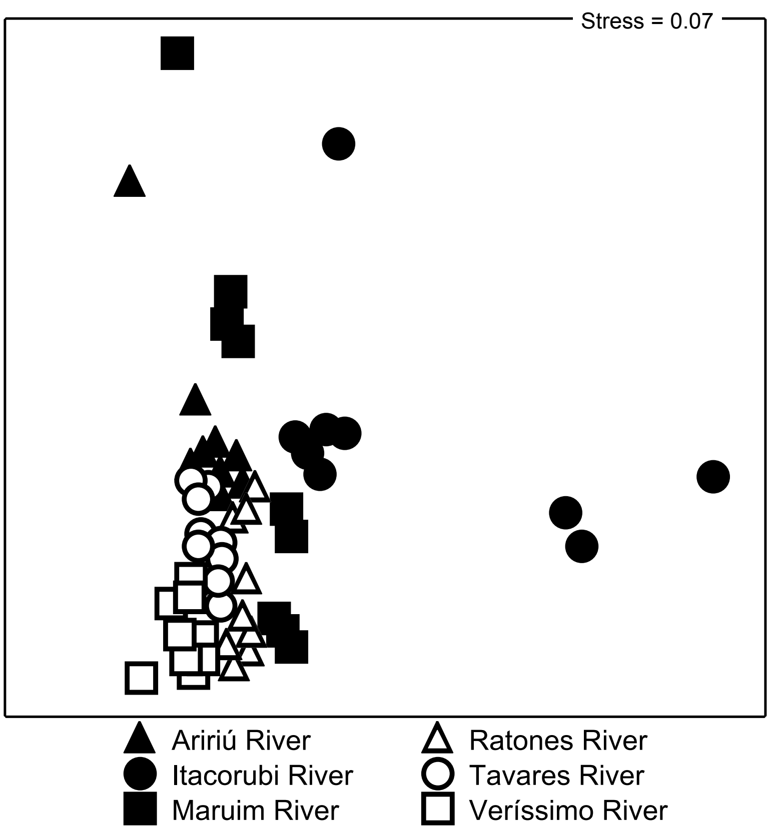

Figure 4.3-4: n-MDS of inorganic and organic P in water and total and polyphosphate P in sediments of non-urban (empty symbols) and urban (filled symbols) estuaries of the Santa Catarina Island Bay, southern Brazil.

Tables 4.3-2 and 4.3-3 show a summary of the physico-chemical and biological properties of the water and the sediments of the rivers sampled, respectively. In a general way there is a dilution gradient of salinity and chlorophyll *a* from the mouth to the head of the rivers, followed by the increase of concentrations of dissolved oxygen, suspended particulate matter and phaeophytin *a*. In the sediments, there was a general tendency of increasing content of organic matter, fine sediments and carbonate towards the sea.

Table 4.3-2: Mean and standard deviation of inorganic P (P-inorg), organic P (P-org) and physico-chemistry water characteristic in rivers of Santa Catarina Island Bay, southern Brazil.

Rivers		P-inorg µM	P-org µM	S	DO $ml.L^{-1}$	SPM $Mg.L^{-1}$	Chl-*a* $\mu g.L^{-1}$	Phae-*a* $\mu g.L^{-1}$
Aririú	Mean	0.58	5.60	15.35	1.60	24.24	13.65	57.61
	sd	0.15	0.20	11.25	0.95	6.52	20.70	37.85
Itacorubi	Mean	6.81	2.70	24.78	0.82	22.13	59.33	55.18
	sd	3.90	1.71	12.27	0.89	4.59	49.70	69.30
Maruim	Mean	2.56	5.22	1.16	4.42	34.09	20.17	26.28
	sd	0.43	0.13	1.14	0.52	6.76	22.14	26.88
Ratones	Mean	1.02	4.93	1.35	3.12	56.10	7.71	51.89
	sd	0.13	0.22	0.36	0.11	5.72	11.36	39.19
Tavares	Mean	0.44	5.18	9.91	1.58	18.59	14.83	15.13
	sd	0.13	0.19	7.23	0.42	16.46	17.87	22.76
Veríssimo	Mean	0.56	5.20	7.85	1.90	19.44	24.77	11.72
	sd	0.18	0.20	5.34	0.61	8.21	24.64	11.94

Table 4.3-3: Mean and standard deviation of total phosphorus (P-tot), polyphosphate (P-poly) and sedimentological characteristics in rivers of Santa Catarina Island Bay, southern Brazil.

Rivers		P-tot $\mu M.g^{-1}$	P-poly $\mu M.g^{-1}$	Carbonate %	OM %	Sand %	Fines %	Chl-*a* $mg.m^{-2}$	Phae-*a* $mg.m^{-2}$
Aririú	Mean	678.30	7.01	11.17	16.33	31.18	67.98	30.51	96.53
	sd	72.07	18.04	3.85	5.19	23.27	24.16	22.38	57.30
Itacorubi	Mean	522.19	4.57	10.92	10.88	32.62	64.52	28.97	61.81
	sd	286.68	13.71	5.75	6.28	38.31	42.31	9.70	17.66
Maruim	Mean	441.96	14.56	7.76	11.99	39.60	60.33	50.49	60.36
	sd	282.91	24.98	6.65	7.65	39.63	39.74	42.16	48.83
Ratones	Mean	248.77	0.11	8.16	9.15	69.95	29.31	23.31	54.81
	sd	191.71	0.32	6.31	6.09	13.37	14.49	6.51	10.78
Tavares	Mean	427.72	0.00	10.62	16.81	4.03	95.97	12.38	51.16
	sd	166.09	0.00	1.32	1.93	3.19	3.19	8.59	20.54
Verríssimo	Mean	128.26	1.17	5.09	2.93	85.58	14.42	13.39	28.15
	sd	73.12	2.86	1.66	2.15	12.06	12.06	6.88	19.16

Pearson correlation analysis among inorganic and organic forms of P and physico-chemical and biological variables in the water revealed different trends for each form of phosphorus in the urbanized and non-urbanized areas (Table 4.3-4). In the non-urbanized areas the P-inorg concentrations correlated positively with the levels of dissolved oxygen, suspended particulate matter and phaeophytin *a*, and correlated inversely with salinity and the biomass of chlorophyll *a*. On the contrary, the P-org concentrations correlated positively with the salinity and chlorophyll *a* biomass, correlated negatively with suspended particulate matter and phaeophytin *a*, and did not correlate significantly with dissolved oxygen. In the urbanized areas, the correlations among the distinct forms of P and the physico-chemical and biological variables in the water did not follow the same pattern observed in the non-urbanized areas. The P-inorg concentrations did not correlate with any variable analyzed, whereas the P-org concentrations correlated significantly with dissolved oxygen contents only.

Table 4.3-4: Correlation matrix (Pearson-product) for organic and inorganic P *versus* bottom water characteristics in urbanized and in non-urbanized rivers of Santa Catarina Island Bay, southern Brazil. * denotes significance at $P < 0.05$.

Water characteristic	Non-urbanized rivers ($n = 27$)		Urbanized rivers ($n = 27$)	
	PID	POD	PID	POD
Salinity	-0.71 *	0.57 *	0.03	-0.13
Secchi	-0.89 *	0.50 *	0.17	-0.25
pH	-0.74 *	0.57 *	0.03	-0.11
Dissolvido Oxigen	0.58 *	-0.31	-0.23	0.39 *
Suspended Prticulated Material	0.73 *	-0.44 *	-0.25	0.35
Chlorophyll *a*	-0.43 *	0.54 *	0.13	-0.18
Phaeophytin *a*	0.40 *	-0.46 *	0.15	-0.16

The P-tot concentrations in the sediment presented significant correlations with the levels of carbonate, organic matter, phaeophytin *a* and fine particles (silt-clay) from the sediment and correlated inversely with the sand percentage in both urbanized and non-urbanized areas (Table 4.3-5). The P-poly concentrations in the sediment did not correlate at all with the sediment and biological variables of the non-urbanized areas, but only with the biomass of chlorophyll *a* in the urbanized area.

Table 4.3-5: Correlation matrix (Pearson-product) for total P (P-tot) and polyphosphate (P-poly) *versus* sediment characteristics in urbanized and in non-urbanized rivers of Santa Catarina Island Bay, southern Brazil. * denotes significance at $P < 0.05$.

Sediment Characteristic	Non-urbanized rivers (n = 27)		Urbanized rivers (n = 27)	
	P-poly	P-tot	P-poly-	P-tot
Carbonate	-0.15	0.69 *	-0.17	0.58 *
Organic Matter	-0.31	0.82 *	0.32	0.81 *
Sand	0.28	-0.59 *	-0.35	-0.81 *
Fines	-0.27	0.57 *	0.35	0.81 *
Chlorophill *a*	0.05	0.11	0.47 *	0.17
Phaeophytin *a*	-0.37	0.54 *	0.20	0.49 *

The variation of P, with the final result of removal (positive values) or release (negative values), estimated for the studied rivers is presented in Figure 4.3-5 as a function P concentration in the inner sites (P_a^W) of each river. For each river there are three values, related to the calculation made from the intermediate sites data, from the river mouths sites data and from mean values of these data. The results show a lack of consistency between the expected behavior of removal or release of dissolved P considering the characterization of the estuary as urbanized or non-urbanized. According to the calculated values for the different sites or general mean, in Itacorubi, Maruim and Veríssimo rivers the removal of dissolved P occurred, whereas in Ratones and Tavares rivers there was a release of dissolved P. In Aririú river there was a release of P according to the averaged data in the site close to the river mouth (site c), whereas in the intermediate site (site b) the removal of P was observed.

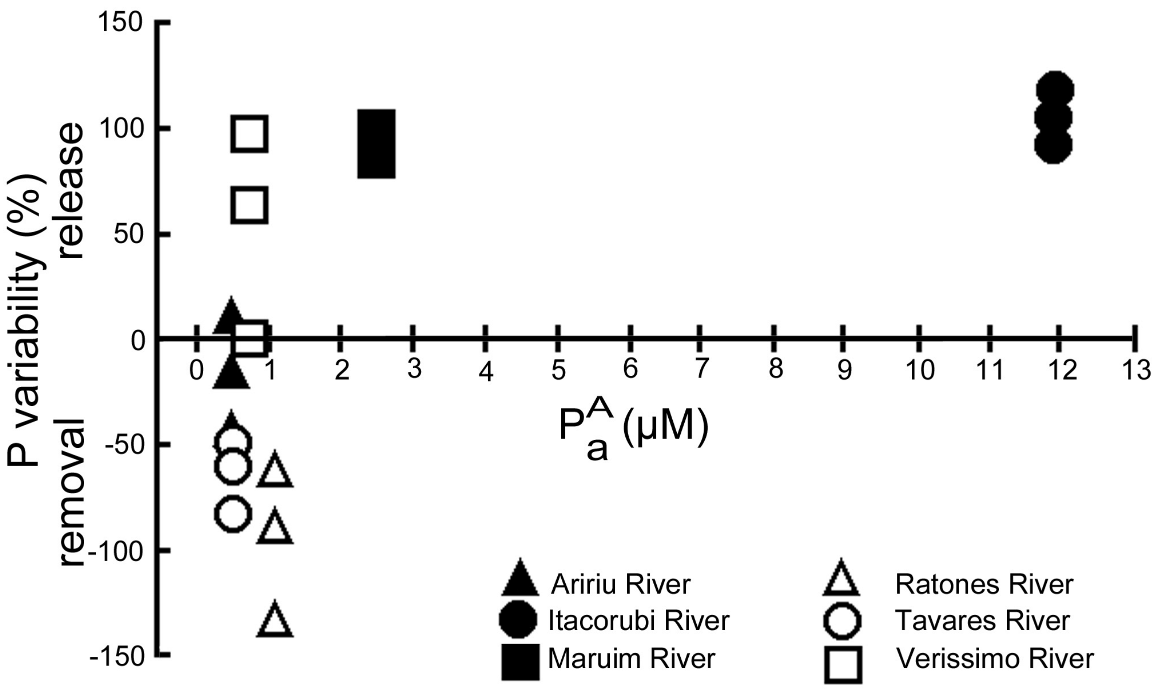

Figura 4.3-5. Predictive Model of P variability (%), considering release (+) and removal (-) of P in function of P concentration in inner sites (P_a^A) of non-urban (empty symbols) and urban (filled symbols) rivers of the Santa Catarina Island Bay, southern Brazil.

Discussion

The results of the present study revealed the great input of P from the urbanized areas. In the water, the P-inorg reached mean concentrations 5-fold higher in urbanized rivers than in non-urbanized ones, whereas the P-org presented similar concentrations in both areas. In the sediments, the concentrations of P-tot and P-poly were 2 and 20-fold higher, respectively, in the urbanized area compared to the non-urbanized one. This result was expected once the discharges of urban and rural effluents are the main agents causing the increase of P and other dissolved nutrients in the aquatic environment (Caraco, 1995). Before the beginning of the urbanization process, around year 1800, the adjacent sea may have been the main supply of P for estuarine systems (de Jonge et al., 2002). After the increasing urbanization, there was an inversion, with estuaries becoming great sources of P to the adjacent sea and, consequently, regulating of coastal primary production (Howarth et al., 1995).

In strongly urbanized countries, the increase in P concentrations has been recorded as accompanying the period of development. In some places this process is being reverted trough the removal of submarine outfalls and implementation of sewage treatment. However, after an initial period of decrease in concentrations of P in the environment, the registered levels increase again (Zhou et al., 2000; Foy et al., 2003). With the control of point source P, the no point source P begins to have more importance and keeps the concentrations elevated. Probably, the main agent of this increase in concentrations is the excessive utilization of P in agriculture, from past times to present (Cloern, 2001). Oxi-reduction processes in sediments contribute to the release of P accumulated in soil, i. e., the P that has not been used by plants and has not immediately become available for the water bodies next to the plantation, is released to the environment. The agriculture is one of the main factors affecting the movement of P from land to sea. Estimates show that the global flux of P to the oceans has increased 3-fold after the development of agriculture (Howarth et al., 1995).

In developing countries as Brazil, the restraint of punctual and diffuse P is insipient and, at present, reveals few practical results. In the urbanized region that drains towards the Santa Catarina Island Bay, the domestic effluents are discharged directly from riverine houses or trough pluvial channels which collect the effluents from the houses. In most cases cesspools are built in order to collect feces and fatty matter. The official statistic for the state of Santa Catarina shows that only 13 % of the residences have sewage collection systems and 46 % have septic cesspools (IBGE, 2002). In the rural area which drains towards the bay, the properties are small holdings under 50 ha and are based on the horticulture, especially tomatoes (Santa Catarina, 2000). Estimates reveal the use of 188 kg/year of agrotoxics per rural property mostly from the carbamates and organophosphates groups (Oliveira, 1997; Leão, 1998). Once disposed into the environment, the carbamates and organophosphates are fastly hydrolyzed resulting in nitrogen and phosphorus compounds.

The great discharge of compounds into the sea alters the natural fluxes and the relation between several kinds of substances (Jickells, 1998). In the present study this fact was evidenced comparing the behavior of different forms of P in the water and sediments along urbanized and non-urbanized rivers. The P-inorg and P-org in the water of non-urbanized rivers were closely related with the physico-chemical properties of the water and with the phytoplankton biomass in these areas. On the other hand, in the urbanized rivers the spatial trends of concentrations of different forms of P did relate neither to physico-chemical properties nor with phytoplankton biomass in the water. Besides, the analysis revealed that in urbanized areas, in contrast to non-urbanized ones, the behavior of P in the water varies among rivers and among sites into a same river. These results show consistently that punctual and diffuse P contributes to keep elevated concentrations of this element in the environment and alter natural fluxes along river-estuary system.

In the present study the organic and inorganic forms of phosphorus were not quantified separately in the sediment, however, the concentrations of P-poly, one kind of P-inorg, and P-tot were evaluated. The P-poly does not occur naturally in coastal-marine environments, being found especially in surface layers of sediments in lakes (Carman et al., 2000). Its presence in estuarine systems is commonly associated to use and discharge of domestic and industrial effluents (Grasshoff et al., 1983). In the present study, the presence of P-poly was detected in five of the six rivers evaluated. The concentrations were higher in urbanized rivers than in the non-urbanized ones, and were related to the concentration of chlorophyll a. This result indicate that P-poly may be abundant in the eutrophic waters, acting as an additional source of inorganic P. Field and laboratory tests have been showing that P-poly is used during the development of microalgae (Aidar et al., 1997) and other organisms can accumulate long chains of P-poly intracellular under aerobic conditions and in hydrolysis under anoxic conditions (Gächter et al., 1988). Nevertheless P-poly may also act as a toxic agent, depending on the concentrations, the organisms involved, the characteristics of the environment and the synergism with other pollutant compounds.

The presence of P-poly in the sediments from the urbanized estuaries was expected and is related to the urbanization around the water bodies. However, the detection of P-poly in two of the nine sites sampled in non-urbanized rivers denotes the need of a better control of urbanization around the local protected areas. The site in Ratones river where the P-poly was detected has a confluence with Papaquara river which drains a wide urbanized area on the extreme north of Santa Catarina Island. The inner portion of Veríssimo river, where P-poly was detected, is close to the border with a mangrove area and with the preserved area itself. Although the region is characteristically dominated by restinga vegetation and the properties are small rural establishments, there are activities for the extraction of sand. Probably the use of detergents for the cleaning of machinery is a potential source of P-poly to the local sediments.

The spatial variability of the concentrations of P-tot in sediments in both urbanized and non-urbanized areas were related to the contents of organic matter, carbonates and grain size. As the concentrations of P-tot in water, the concentrations of P-tot in the sediments exhibited variation among sites into the same river in the urbanized areas. In the inner sites of Maruim and Itacorubi rivers sediments were composed of coarser particles, and, consequently, lower levels of organic matter. In the same sites elevated concentrations of P-inorg were detected in the water, evidencing the small capacity of sorption of P by local sediments.

The sorption of P to sediment particles may occur according to two processes, a rapid sorption onto reactive surfaces followed by a slow dissolution for the sub-surface of the particles (Froelich, 1988). The estuaries evaluated in the present study are small ones and therefore more susceptible to infrequent fluxes, when compared to larger estuarine systems.

The environmental unpredictability may mediate sorption-desorption processes trough remobilization of sediment particles and water. In small estuaries, the kinetics of the adsorption process, i. e., the variability of the adsorbed phosphate, may be an important factor once the residence time of the water may be too short to reach the reactions equilibrium. This fact may explain the local variations of the sediment-water fluxes along the studied rivers. On the other hand, the adsorption capacity of P onto the particles is related to the composition of the sediment. As show in this study, sediments with elevated levels of sand have small surface areas and consequently have less importance in the adsorption process. In contrast, sediments with elevated levels of organic matter, and consequently Fe and Al hydroxides, have great capacity to adsorb P (Lopez et al., 1996). In estuaries with this kind of sediment, decreases in the concentrations of oxygen may promote the reduction of iron and the release of P (Carreira and Wagener, 1998), influencing locally in the direction of P flux.

The increasing occupation of intertidal zones in the studied urbanized rivers, with the embankment of mangrove and salt marsh areas, are frequent and tend to make sediments, which would serve as P sources, unavailable. The suppression of mangrove and salt marsh areas reduces the residence time of water in the system and tends to intensify the water flux during the ebb tide (Wolanski and Ridd, 1986), which also favors the export of P to the adjacent sea (Salcedo and Medeiros, 1995; Tappin, 2002). The elevated concentrations of P entering the system also induce a higher rate of export. However, modeling of P variations suggest that polluted estuaries would have a tendency to serve as sinks, whereas non-polluted estuaries would act as sources of P to adjacent coastal waters (Prastka et al., 1998). This apparent contradiction in the final balance between P removal or release by estuaries is understandable, once the flux of P follows a complex and non linear path due to the interactions water-sediment which affects the concentrations along rivers and estuaries. The use of a hierarchical sampling design, comparing different variations ranges of P among several polluted and non polluted rivers was able to detect differences among groups of rivers and differences within a same river.

In summary, the use of a dynamic equilibrium model of P (K_d) evidenced that both kinds of estuaries, urbanized and non urbanized ones, may act as sinks or sources of P. The separate analysis for different sites along each river showed that export and deposition areas may occur within the same estuary, independently of the factor that it is polluted or not.

4.4. FAUNA-WATER-SEDIMENTS INTERACTION: Assessing the environment-benthic fauna coupling from urban areas and preserved areas of southern Brazil

Abstract

The increasing urbanization may alter water, sediments and benthic communities properties in estuarine systems. In places where there are no historical data for the direct establishment between causes and effects of environmental changes, the comparison between urbanized and non-urbanized areas may be an alternative. The impacts of urbanization on the benthic macrofauna associations were investigated using a hierarchical sampling design, evaluating the spatial changes inside the same river, among rivers and between groups of urbanized and non-urbanized rivers. In addition predictive models to the fauna were constructed based on the sediment and water characteristics in urbanized and non-urbanized rivers in the Bay of Santa Catarina Island, south of Brazil. The benthic community differed in the structure and pattern of variation between urbanized and non-urbanized areas. The benthic fauna was divided into i) sensitive species assemblage, formed by polychaetas *Nephtys fluviatilis* e *Heteromastus similis* and by the crustacean *Kalliapseudes schubarti*; and ii) tolerant species assemblage, formed by the polychaeta *Laeonereis acuta* and by an unidentified oligochaetas Tubificidae. The assemblage of species more sensitive to environmental alterations presented smaller variation in the abundance among points in the urbanized areas. In contrast, the more tolerant species assemblage showed an increase in the variation among points in urbanized rivers. Changes in the characteristics of the sediments and also in the water properties were directly related to alterations in the fauna.

Introduction

The present challenge in coastal cities is to manage the fast urban growth and the preservation of the environment for the sustainable development. To this end, the implementations of protected areas have been suggested and stimulated, but it realizes conflicts between conservation priorities and human activities. In fact, many preserved areas are surrounded by dense human populations and may protection and maintenance of the biological integrity of the ecosystems be dependent of it.

To establish cause-effect relations and ecological change consequences of urbanization processes on aquatic systems is critical for conservation managers. The urbanization processes can be understood as a demographic domain and an important recent agent of land transformation (Pickett et al., 2001). This occurs on and interdigitated with natural areas and has been causing alterations in physical, chemical and biological characteristics of aquatic systems adjacent to urban areas (Paul and Meyer, 2001).

Urbanization has been responsible for making elevated concentrations of nutrients available to aquatic environment. The use of large-scale of artificial fertilizers and detergents and the extensive connection of sewage to the water bodies have been producing cultural eutrophication process (Smith et al., 1999; de Jonge et al., 2002). In these cases, sediments and bottom water may suffer from hypoxia or anoxia as a consequence of the increase in respiration and decomposition of organic matter, which usually causes the massive death of benthic fauna. Due to its great capacity of assimilation, trough processes of transformation and retention of nutrients, great amounts of organic matter are necessary in order to create a deleterious effect on aquatic systems. What usually occurs is the stimulus of primary production and changes in communities structures.

Besides eutrophication, the entrance of non-nutrient pollutants and invasive species, the over fishing, the alterations of habitats and global climatic changes are the main agents causing the change of biodiversity in shallow water ecosystems (New, 1995; Levin et al., 2001). In urbanized estuaries, where most of these perturbations occur, the maintenance of the ecological properties depends on the budget between its capacity to dilute substances and the magnitude of pollutants entrance in the system, as well as the exchanges between the distinct environments (Lee, 1999; Cloern, 2002). The functioning of these transition zones depends primarily on the fluxes of energy and matter with the terrestrial environment and with the adjacent sea (Dame and Allen, 1996; Koch and Wolff, 2002). The composition, the spatial variability and species richness of benthic macrofauna are particularly important in this exchange process, because they act as mediators of fluxes between benthic-pelagic compartments (Lohrer et al., 2004). The benthic fauna is the main link between primary producers and secondary consumers in estuaries (Foreman et al., 1995; Raffaelli, 1999).

Studies on ecology of soft bottom benthic communities in estuarine systems on the Atlantic coast of South America are recent and in most cases there is no historical data or new programs of continuous monitoring. As in other parts of the world, alterations in structure of benthic communities have been associated to environmental changes caused by increasing urbanization. However, direct relations of cause-effect have been registered just in cases of obvious impacts (Bemvenuti et al., 2003). In places where urbanization is less intense there are practically no registers published, making direct and combined effects of urbanization harder to quantify. In these places the pollution sources are variable and dispersed into the environment, raising difficulties to establish any relations of cause-effect.

The comparison between several urbanized and protected areas may be an alternative to establish cause-effect relations and ecological changes consequences in aquatic systems with the absence of historical data. In this case, despite the intrinsic differences of each system, same sized estuaries, situated in the same geographic region, having similar environmental characteristics and varying basically according to the presence or absence of urbanization around them, can be contrasted.

This study focus on natural and induced environment-benthic fauna coupling. The aims are to investigate the composition, density, biomass, species richness and spatial variability of the benthic macrofauna assemblages and discuss the predictive capability of sediments and water properties in pristine and urban rivers. Sites in the Santa Catarina Island Bay, south of Brazil, with direct human influence were selected as disturbed urban environment, whereas pristine and protected riverine environments were selected as urban controls.

Methods

Study area and sampling design

The Santa Catarina Island Bay (27° 29´S - 48° 30´W) is a large channel where discharge several rivers originated in *Serra do Mar* mountain range. In the island and in the continent the rivers flow along a short plain of quaternary fluvial-marine sediments and out into small estuaries settled with an extensive zone of mangrove and salt marshes. The mangroves are in their south boarder of the geographic distribution of Atlantic coast in South America and are composed by the species *Rhizophora mangle*, *Avicennia schaueriana* e *Laguncularia racemosa*. The salt marsh areas are formed by extensive monospecific banks of the graminea *Spartina alterniflora*.

The local tide is characteristically a microtidal with semidiurnal regime and diurnal inequalities, whose influence does not reach more than 3 km inside the rivers. Winds from the south and north quadrants are the main physical agents influencing the local hydrodynamics. The climate of the region is subtropical humid with no dry season characteristic, but a reduction in the volume of rain from April to September (Cruz, 1998).

The local rivers form a great mosaic of urbanized areas intercalated with preserved areas (Fig. 3.1-1). This situation enabled the discrimination of rivers with similar environmental characteristics in urbanized rivers and protected rivers. For the study of benthic macrofauna, and the physical and chemical characteristics of the sediments and water a hierarchical sampling design was used, comparing punctual (among sites within the same river), local (among rivers in the same area) and regional (among groups of rivers in urbanized and protected areas) spatial variations. In each river, 3 sampling sites were established: in the high salinity region, close to the river mouth; in the low salinity region, close to the tidal influence limiting zone; and in the intermediate region, between these two situations.

Sampling Procedures

The samples were undertaken through autonomous diving and in triplicates for all parameters in each site. However, averaged values of four cores of 15 cm diameter and 10 cm height constituted each one samples of benthic macrofauna. In the field the samples were separated in 0.5 mm sieves and fixed in 5 % buffered formalin. In laboratory, under microscopy, the fauna was separated and identified until the lowest taxonomic levels. The total biomass of organisms (AFDW) was determined by the loss of weight under ignition at 550 °C for 1 h, after drying at 60 °C until constant weight.

In addition, sediments samples were collected using cores of 11 cm diameter and 2 cm height for the analysis of the concentration of phosphorus, polyphosphate, heavy metals and sediment standard analysis. The total phosphorus was determined through the colorimetric method according to Armstrong et al. (1966) and Grassholff et al. (1983). Polyphosphate was evaluated using the method proposed by Áspila et al. (1976) and adapted by Strickland and Parsons (1972). The concentrations of cooper, lead, zinc and cadmium in sediments (0.063

mm fraction) were analyzed with flame atomic absorption spectrometry after extraction with nitric, hydrofluoric and hydrochloric acids in standard analytical concentration. The content of organic matter of the sediments was determined by the % difference in weigh after ignition (550 °C for 1 h) and burning with H_2O_2 and the carbonate by acidification (HCl 10 %). The granulometric analyses were carried out by the sieving and pipette analysis according to Carver (1970). The microphytobenthic biomass was collected with a core of 1 cm diameter and 1 cm height. The extraction of pigments, the absorbance reading of chlorophyll *a* and phaeophytin *a* and the calculations of concentrations were made according to the method described by Plante-Cuny (1978).

The bottom water in each site and river studied was sampled in triplicates. Samples were filtered with 0.45 µm membranes (filter GF-52C Schleicher and Schuell) for the estimates of suspended particulate matter and phytoplaktonic pigments, chlorophyll *a* and phaeophytin *a* (Strickland and Parson, 1972). The filtered solution was used to the analysis of dissolved inorganic nutrients. The total phosphorus and the silicate were determined by the colorimetric method according to Armstrong et al. (1966) and Grasshoff et al. (1983). Total nitrogen was analyzed using an autoanalyzer II® - Bran-Luebbe. The samples for the analysis of dissolved oxygen were collected and processed according to Winkler method (Grasshoff et al., 1983). In laboratory, salinity was measured trough the conductivity method (TDS Hach mod. 44600).

Data Analysis

The hierarchical nested analysis of variance was used to test for differences in total densities, total biomass, species richness and densities of selected species among areas, rivers (nested within the respective area) and sample sites (nested within the respective river and area). When significant the differences were evaluated through Newman-Keuls multiple comparison tests. The homogeneity of variances was previously checked by Cochran test and logarithm transformation was used whenever necessary.

The extent to which the overall pattern of the community change in urban areas and in preserved areas was assessed through a MDS ordination analysis. Matrices were derivate using Bray-Curtis dissimilarity on untransformed faunal data and Normalised Euclidean Distance on fourth-root transformed environmental data. The differences among areas in the multidimensional pattern for the benthic community and for the environmental variables were tested through the analysis of similarity (ANOSIM, Clarke and Green, 1988).

The Spearman rank correlation (ρ) between similarities matrices of selected species and that of all species data was used to select the group of species that better represent the pattern of the whole community. This procedure was well known to measure of agreement between MDS configurations for species data and the multivariate patterns of associated environmental variables (Clarke and Aisnworth, 1993). The subset of species selection procedure is analogous to stepwise multiple regression, in which subset selection proceeds using a “forward selection-backward elimination”. The algorithm extracts from the original matrix the subset of species with Spearman correlation value higher than 0.95. Excluding the first subset, the investigation follows to find out if the others subset of species also represents well the pattern of the community. The method was firstly developed to quantify the level of structural redundancy in studies of temporal community response to environmental change (Clarke and Warwick, 1998). Here, the same peel procedure was applied to select a group of species that better represent the spatial pattern of the whole community in all studied areas, only in preserved area and only in urbanized area.

To assess the environment-benthic fauna coupling in urban areas and preserved areas a multiple regression analysis was used. The analyses were run with all environmental variables (water + sediment) and separated for water and sediment variables. To avoid redundancy, variables with tolerance values smaller than 0.05 were excluded from the analysis. The significances of the models were tested using ANOVA.

Results

Table 4.4-1 shows the species richness, total biomass and total mean densities registered in six studied rivers. Twelve great taxon groups were identified with polychaetas and crustaceans dominating in number of species (60 %) and in individuals (80 %). The total densities varied between 0 - 784 ind.0.07 m^{-2} and richness from 0 to 12 species 0.07 m^{-2}. The polychaetas *Nephtys fluviatilis* and *Heteromastus similis*, the tanaidacea *Kalliapseudes schubarti* and an unidentified oligochaeta Tubificidae were the organisms numerically dominant and more frequent along the rivers.

Results of ANOVA for the descriptive measures of community are shown in Figure 2 and Table 4.4-2. Tests indicated that total biomass, total densities and species richness of macrofauna differed significantly between urbanized and protected areas, among rivers within each area and among sites within each river. Differences among groups of rivers from urbanized and protected areas were significant for the total densities and species richness, but not for the fauna biomass. Multiple comparison tests revealed that total densities were higher in Veríssimo river (Table 4.4-2) and in the inner site of all rivers (Fig. 4.4-2). The species richness was higher in Veríssimo river and, in contrast to densities, was higher in the mouths of urbanized rivers (site C) and did not differ along any of the protected ones. The total biomass of macrofauna was higher in the inner site of Itacorubi river than in any other ($p < 0.05$) and did not differ significantly among sites and rivers from protected areas.

Table 4.4-1: Mean (ind.0.07 m^{-2}) and standard deviation (in parentesis) of benthic macrofauna descriptive characteristics and species in rivers of Santa Catarina Island Bay, southern Brazil.

	Aririú	Itacorubi	Maruim	Ratones	Tavares	Veríssimo
Biomass (x 10^{-4} g AFDW)	79.1 (96.7)	482.0 (720.2)	60.9 (43.8)	82.8 (81.7)	179.7 (138.7)	224.2 (308.7)
Total density	49.3 (53.8)	36.7 (73.5)	75.3 (73.6)	100.7 (129.4)	93.0 (71.6)	273.7 (329.3)
Species richness	6.6 (2.9)	2.6 (1.6)	3.7 (2.4)	5.4 (1.7)	4.3 (0.5)	7.4 (1.4)
POLYCHAETA						
Heteromastus similis	23.3 (43.9)	0.9 (1.7)	0.9 (1.5)	77.1 (117.0)	12.7 (9.6)	50.8 (55.0)
Nephtys fluviatilis	8.3 (6.7)	-	-	14.9 (15.3)	47.7 (31.3)	2.7 (1.5)
Capitella sp.	0.4 (0.9)	0.1 (0.3)	3.4 (4.8)	1.1 (1.8)	-	4.1 (5.3)
Laeonereis acuta	0.1 (0.3)	5.7 (8.7)	1.1 (1.8)	-	-	0.6 (1.3)
Aricidea (*aricidea*) sp.	1.8 (4.6)	-	-	-	-	0.6 (1.1)
Scoloplos (*Leodamas*) sp.	0.2 (0.7)	0.1 (0.3)	-	0.8 (1.3)	0.7 (1.0)	0.2 (0.4)
Glycinde multidens	0.6 (1.0)	0.1 (0.3)	-	0.2 (0.4)	0.3 (1.0)	0.6 (0.9)
Polydora websteri	1.2 (3.3)	-	-	-	-	-
Isolda pulchella	-	-	-	1.0 (1.0)	-	-
Sigambra grubii	0.2 (0.7)	-	-	-	-	0.4 (1.0)
Mediomastus californiensis	0.1 (0.3)	-	-	0.2 (0.4)	-	0.1 (0.3)
Cossura sp.	0.4 (0.9)	-	-	-	-	-
Magelona papilicornis	-	-	-	0.1 (0.3)	-	-
Polychaeta sp.1	-	-	-	-	-	0.1 (0.3)
Polychaeta sp.2	0.1 (0.3)	-	-	-	-	-
MOLLUSCA						
Tellina nitens	-	-	0.2 (0.4)	0.3 (0.7)	0.2 (0.4)	2.1 (2.3)
Tagelus plebeius	0.1 (0.3)	-	-	-	-	-
Heleobia australis	-	0.1 (0.3)	-	-	-	-
Nudibranchiata	0.7 (0.9)	-	4.3 (7.7)	-	-	1.3 (3.3)
CRUSTACEA						
Kalliapseudes schubarti	1.2 (1.6)	0.1 (0.3)	0.1 (0.3)	2.8 (4.2)	26.4 (32.3)	204.7 (287.1)
Ostracoda	0.3 (0.7)	-	-	0.6 (0.7)	-	0.1 (0.3)
Anomura	-	0.3 (0.7)	0.1 (0.3)	0.1 (0.3)	-	0.1 (0.3)
Corophium sp.	0.1 (0.3)	-	-	-	-	0.2 (0.7)
Caridae	-	-	-	0.1 (0.3)	--	0.1 (0.3)
Callinectes sp.	-	-	0.2 (0.7)	-	-	-
Amphipoda	-	-	0.1 (0.3)	-	-	-
Copepoda	0.1 (0.3)	-	-	-	-	-
Cumacea	0.1 (0.3)	-	-	-	-	-
OLIGOCHAETA						
Tubificidae	4.0 (4.2)	29.0 (68.6)	64.2 (77.7)	0.9 (1.5)	4.9 (8.8)	2.8 (3.5)
HIRUDINEA	-	-	0.1 (0.3)	-	-	-
NEMATODA	4.9 (11.0)	0.1 (0.3)	-	-	-	0.9 (1.4)
SIPUNCULA	-	-	-	-	0.1 (0.3)	0.9 (2.7)
PHORONIDA	0.8 (1.7)	-	-	-	-	-
INSECTA						
Hydrophilidae	-	-	0.4 (0.7)	-	-	-
Chironomidae	-	-	-	0.1 (0.3)	-	0.2 (0.7)
Nematocera	-	0.1 (0.3)	-	-	-	-
Hemiptera	0.1 (0.3)	-	-	-	-	-
COLLEMBOLA	-	-	-	-	-	0.1 (0.3)
FORAMINIFERA	-	-	-	0.2 (0.4)	-	-
NEMERTINA	-	-	-	0.1 (0.3)	-	-

Table 4.4-2: Summary of nested analysis of variance and Newman-Keuls test (NK) of benthic macrofauna assemblage in rivers of Santa Catarina Island Bay, southern Brazil.

Sources of Variation	d.f.	MS	*F*	Teste NK
			Total density	
Area	1	3.153	52.609 **	NU>U
River	4	0.627	10.466 **	
River (NU)	2	0.443	32.422 **	VE>TA>RA
River (U)	2	0.812	7.645 *	MA AR>IT
Site	12	1.311	21.882 **	
Site (NU)	6	1.238	90.692 **	A>B>C
Site (U)	6	1.385	13.039 **	A>B>C
Error	36	0.060		
Error (NU)	18	0.014		
Error (U)	18	0.106		
			Species number	
Area	1	29.630	14.159 **	NU>U
River	4	30.370	14.513 **	
River (NU)	2	22.370	13.727 **	VE>TA>RA
River (U)	2	38.370	15.014 **	AR>MA IT
Site	12	8.130	3.885 **	
Site (NU)	6	1.852	1.136 ns	-
Site (U)	6	14.407	5.638 *	C>A>B
Error	36	2.093		
Error (NU)	18	1.630		
Error (U)	18	2.556		
			Total biomass (AFDW)	
Area	1	0.000036	1.144 ns	-
River	4	0.000452	14.566 **	
River (NU)	2	0.000082	1.623 ns	-
River (U)	2	0.001	72.165 **	IT>AR MA
Site	12	0.000628	20.233 **	
Site (NU)	6	0.000128	2.518 ns	-
Site (U)	6	0.001	99.066 **	A>C B
Error	36	0.00003		
Error (NU)	18	0.000051		
Error (U)	18	0.000011		

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 $P<0.005$, NU = non-urbanized, U = urbanized, TA = Tavares river, RA = Ratones river, VE = Veríssimo river, AR = Aririú river, IT = Itacorubi river, MA = Maruim river, A = inner site, B = intermediate site, C = mouth of river site.

The multidimensional distribution pattern of all macrofauna species exhibited differences between groups of urbanized and protected rivers (ANOSIM, global $R = 0.328$, $p = 0.001$, Fig. 4.4-3). The subset of species that better represented the general structure of community were the polychaetas *Nephtys fluviatilis*, *Heteromastus similis*, *Capitella* sp., the tanaidacea *Kalliapseudes schubarti* and the unidentified Tubificidae (ρ = 0.969, Table 4.4-3). Additionally, when verified separately for urbanized (ρ = 0.958) and protected rivers (ρ = 0.954), the analysis detected that *Laeonereis acuta* and *Aricidea (Aricidea)* sp. are important species too structuring the faunal assemblage in urbanized areas.

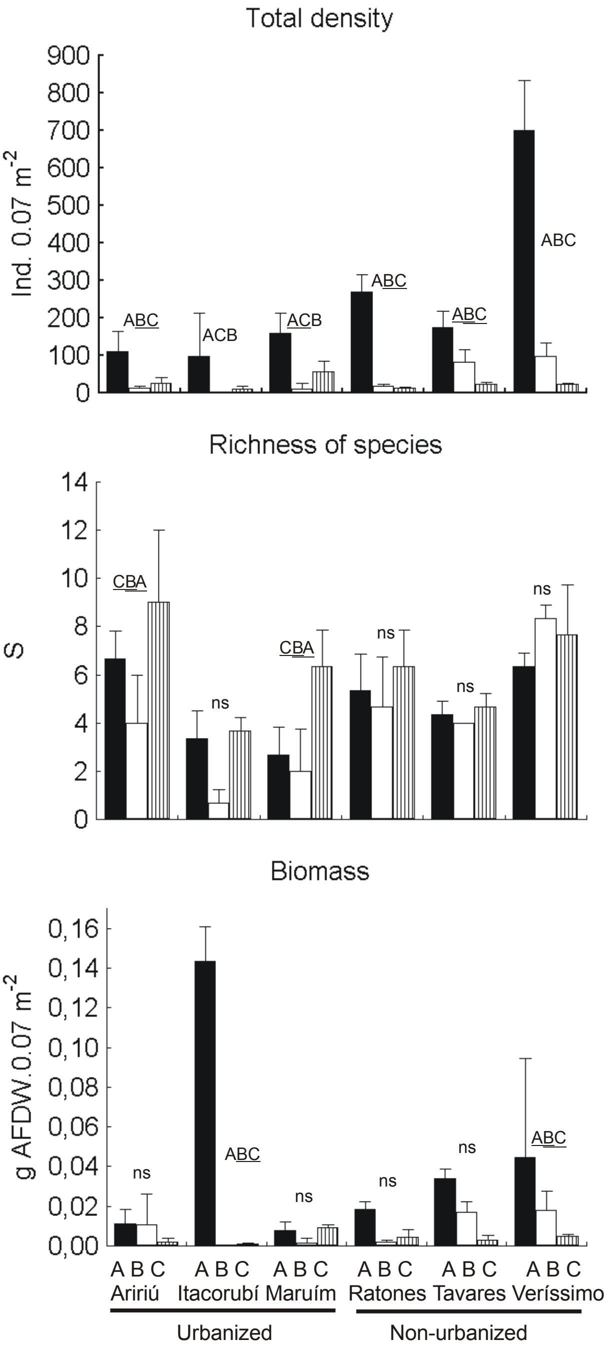

Figure 4.4-2. Mean and standard deviation of benthic macrofauna assemblage in urbanized and non-urbanized rivers of Santa Catarina Island Bay, southern Brazil. Results of Newman-Keuls test Between sites within rivers. A = inner site, B = intermediate site and C = site in the mouth of the river.

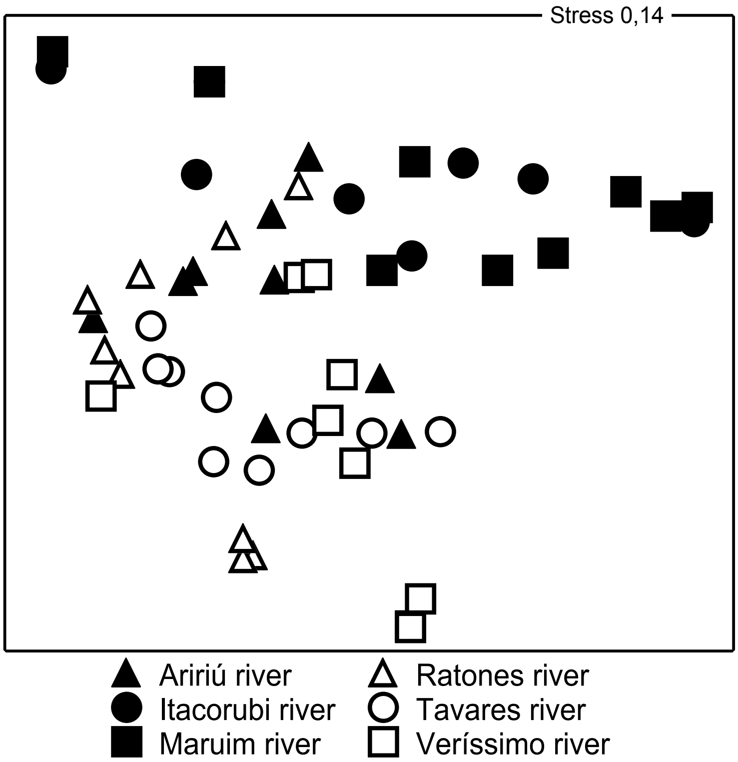

Figure 4.4-3: n-MDS of benthic macrofauna in non-urban (empty symbols) and urban (filled symbols) rivers of the Santa Catarina Island Bay, southern Brazil.

Table 4.4-3: Results of the BVSTEP procedure for the best species subsets representing the community pattern. The data are calculated separated for non-urbanized and urbanized areas.
ρ = Sperman rank correlation.

	Total	Non-urban	Urban
1st subset	ρ = 0.969 *Nephtys fluviatilis* *Capitella* sp. *Heteromastus similis* *Kalliapseudes schubarti* Tubificidae	ρ = 0.954 *Nephtys fluviatilis* *Heteromastus similis* *Kalliapseudes schubarti*	ρ = 0.958 *Nephtys fluviatilis* *Capitella* sp. *Heteromastus similis* Tubificidae *Laeonereis acuta* *Aricidea* (*Aricidea*) sp.
2nd subset	ρ = 0.439 Chironomidae Amphipoda Hemiptera Total biomass	ρ = 0.651 *Isolda pulchella* *Scoloplos* sp. *Mediomastus californiensis* *Magelona papilicornis* Caridae Collembola Ostracoda *Laeonereis acuta* *Aricidea* (*Aricidea*) sp. Polychaeta sp.1 Total biomass	ρ = 0.373 Coleoptera Hirudinea Chironomidae Amphipoda Hemiptera Foraminifera Total biomass

The results of hierarchical nested analysis of variance for selected species group revealed significant differences between urbanized and protected areas, among rivers within each area and among sites within each river (Table 4.4-4 and Fig. 4.4-4). *Aricidea (Aricidea)* sp. was not considered due to the fact that it occurred punctually, with low densities and did not fit into the assumption of homogeneity of variances. The multiple comparison tests showed that *Nephtys fluviatilis*, *Heteromastus similis* and *Kalliapseudes schubarti* were more abundant in the protected rivers, whereas the Tubificidae and *Laeonereis acuta* were more abundant in urbanized rivers. *Capitella* sp. was the only species not to show significant differences between urbanized and protected areas and to occur with higher densities in intermediate site (site B) between the river mouth and the limit of tidal influence zone. The contrast between urbanized and protected areas revealed that all analyzed species showed different patterns of distribution along the rivers. *N. fluviatilis*, *Capitela* sp. and *K. Schubarti* differed significantly among sites in protected rivers, but not in urbanized ones. Tubificidae and *L. acuta*, on the other hand, differed among sites in urbanized areas and did not differ in protected areas. *H. similis* was the only species to differ significantly among sites into urbanized and protected rivers.

The sediment characteristics along the rivers can be observed in Figure 4.4-5. The particle size and the organic matter contents decreased from the inner portion to the mouths of the rivers. The sediments varied from fine silt to fine sand poorly sorted, although punctually, coarser grains have occurred in the inner sites of Maruim and Itacorubi rivers. The heavy metals, total phosphorus, polyphosphate, chlorophyll *a* and phaeophytin *a* concentrations were higher in urbanized areas than in the protected ones. The concentrations of lead and zinc tended to decrease towards the river mouths, whereas chlorophyll *a* and polyphosphate tended to increase. The contents of phaeophytin *a* and total phosphorus did not exhibit great variation along the same river.

Table 4.4-4: Summary of nested analysis of variance and Newman-Keuls test (NK) of selected benthic macrofauna species in rivers of Santa Catarina Island Bay, southern Brazil.

Sources of Variation	d.f.	MS	*F*	Teste NK	MS	*F*	Teste NK
		Nephtys fluviatilis			*Capitella* sp.		
Area	1	4854.519	135.615 **	NU>U	2.241	0.511 ^{ns}	-
River	4	2540.741	70.978 **		35.519	8.093 **	
River (NU)	2	4873.148	81.019 **	TA>RA>VE	40.704	26.167 **	VE>RA TA
River (U)	2	208.333	18.204 **	AR>IT MA	30.333	4.200 *	MA>AR IT
Site	12	735.685	20.552 **		23.426	5.338 **	
Site (NU)	6	1446.370	24.047 **	A>B>C	36.630	23.548 **	B>C A
Site (U)	6	25.000	2.184 ^{ns}	-	10.222	1.415 ^{ns}	-
Error	36	35.796			4.389		
Error (NU)	18	60.148			1.556		
Error (U)	18	11.444			7.222		
		Heteromastus similis			Tubificidae		
Area	1	7.445	270.154 **	NU>U	4.376	36.721 **	U>NU
River	4	0.780	28.303 **		0.679	5.694 *	
River (NU)	2	0.874	35.223 **	VE>TA>RA	0.170	1.812 ^{ns}	-
River (U)	2	0.686	22.642 **	AR>IT MA	1.188	8.203 *	MA>IT AR
Site	12	1.773	64.331 **		0.927	7.775 **	
Site (NU)	6	2.442	98.467 **	A>B>C	0.449	4.794 *	-
Site (U)	6	1.104	36.405 **	A>C>B	1.404	9.701 **	A>C>B
Error	36	0.028			0.119		
Error (NU)	18	0.025			0.094		
Error (U)	18	0.030			0.145		
		Kalliapseudes schubarti			*Laeonereis acuta*		
Area	1	11.184	166.161 **	NU>U	0.446	44.045 **	U>NU
River	4	1.572	23.352 **		0.184	18.192 **	
River (NU)	2	2.990	30.203 **	VE>TA>RA	0.037	2.712 ^{ns}	-
River (U)	2	0.153	4.301 *	AR IT MA	0.332	50.197 **	IT>MA>AR
Site	12	0.943	14.013 **		0.345	34.010 **	
Site (NU)	6	1.860	18.789 **	A>B>C	0.037	2.712 *	-
Site (U)	6	0.026	0.733 ^{ns}	-	0.652	98.718 **	A>C>B
Error	36	0.067			0.010		
Error (NU)	18	0.099			0.014		
Error (U)	18	0.036			0.007		

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 $P < 0.001$, NU = non-urbanized, U = urbanized, TA = Tavares river, RA = Ratones river, VE = Veríssimo river, AR = Aririú river, IT = Itacorubi river, MA = Maruim river, A = inner site, B = intermediate site, C = mouth of river site.

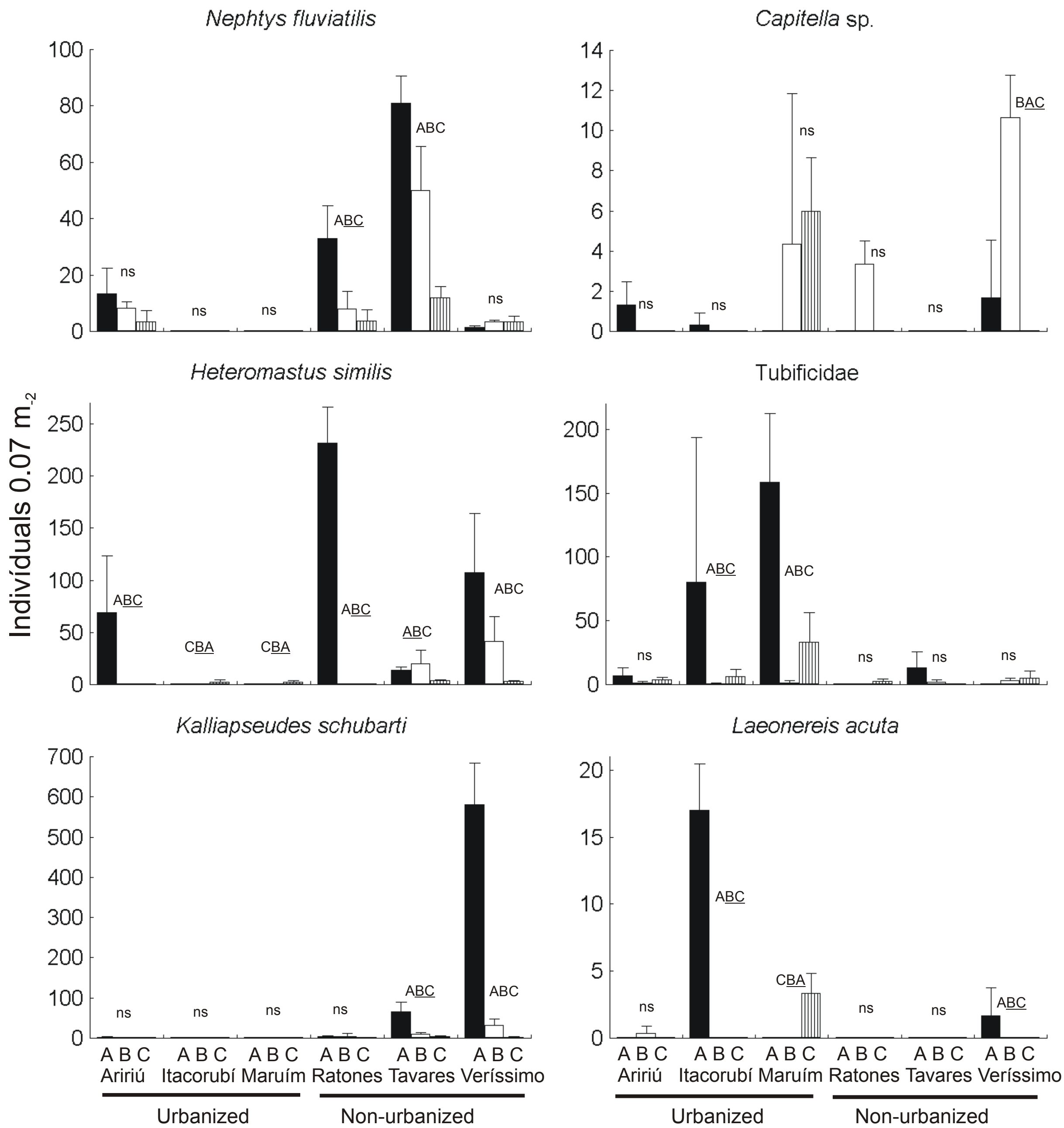

Figure 4.4-4. Mean and standard deviation of benthic macrofauna selected species in urbanized and non-urbanized rivers of Santa Catarina Island Bay, southern Brazil. A = inner site, B = intermediate site and C = site in the mouth of the river.

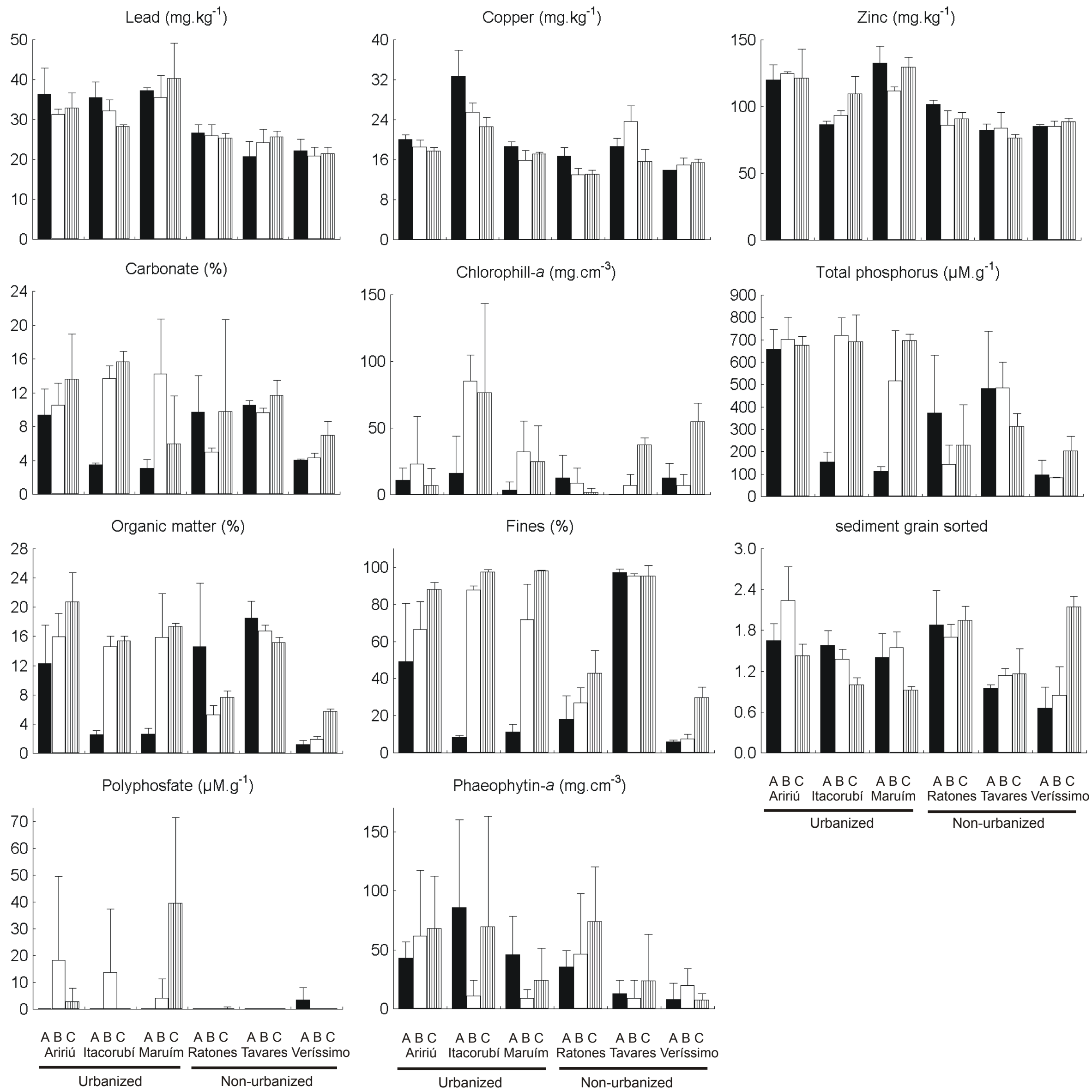

Figure 4.4-5. Mean and standard deviation of sediment properties in urbanized and non-urbanized rivers of Santa Catarina Island Bay, southern Brazil. A = inner site, B = intermediate site and C = site in the mouth of the river.

The water properties along the studied rivers can be observed in Figure 4.4-6. The salinity and pH distributions were typical of estuaries, with smaller values in the inner portions and higher in the mouth regions. In contrast, the dissolved oxygen concentrations were highest in the inner sites of the rivers. In general the concentrations of total dissolved nitrogen, total dissolved phosphorus, chlorophyll *a* and phaeophytin *a* were higher in urbanized rivers than in protected ones.

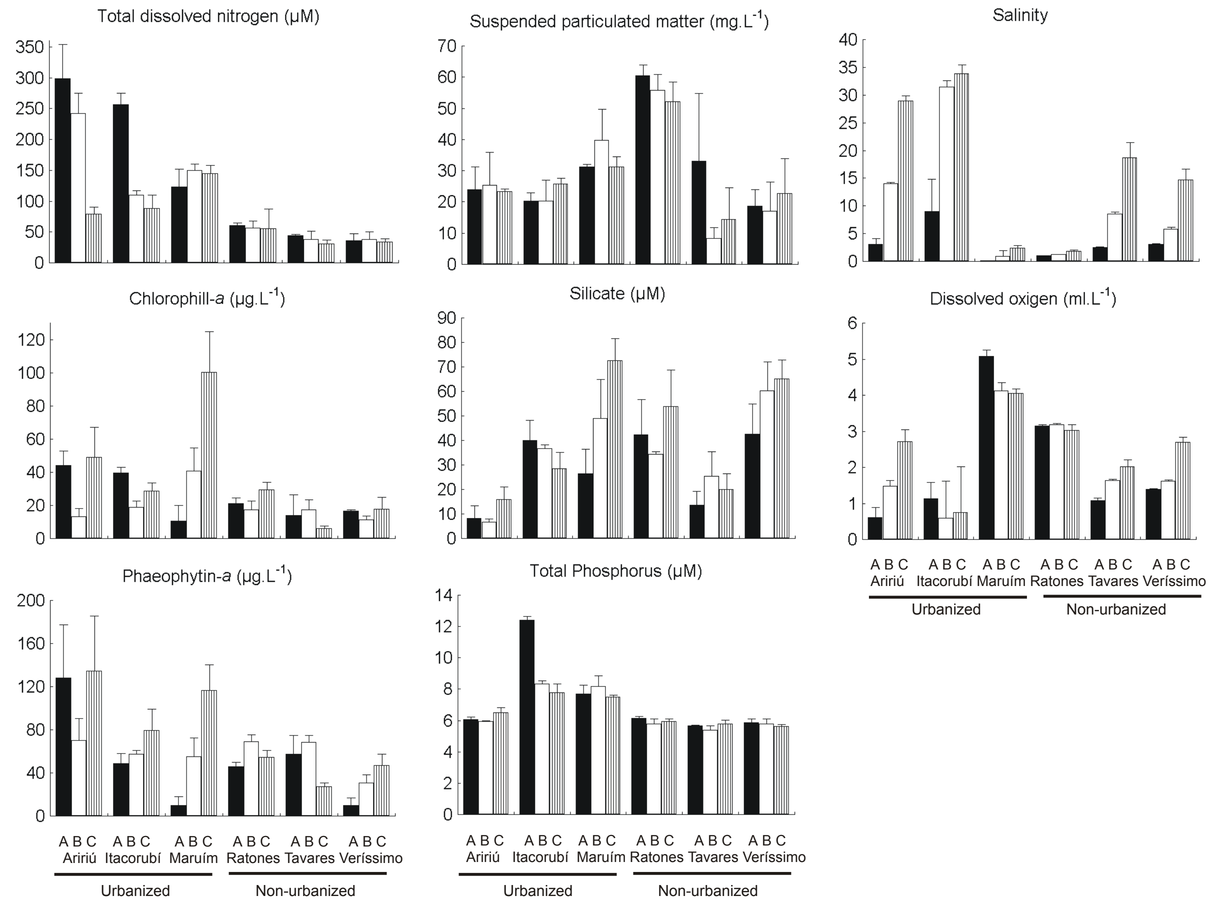

Figure 4.4-5. Mean and standard deviation of water properties in urbanized and non-urbanized rivers of Santa Catarina Island Bay, southern Brazil. A = inner site, B = intermediate site and C = site in the mouth of the river.

The multivariate pattern (MDS) of the environmental variables showed the great distinction between urbanized and protected rivers (ANOSIM, global $R = 0.435$, $p = 0.001$, Fig. 4.4-7).

The multiple regression analysis processed separately for the urbanized and protected areas made it possible to establish relationships between benthic fauna and the environment state (Tables 4.4-5 and 4.4-6). *Nephtys fluviatilis*, *Heteromastus similis*, *Capitella* sp. and the total densities presented stronger (highest R^2) general (water + sediment) relationships with environment variables in the protected areas than in the urbanized areas. Conversely, Tubificidae, *Laeonereis acuta*, species richness and total biomass presented strongest general relationships with environment data in urbanized areas. The same tendencies between areas were observed for these and those individual species and faunal indicators when considering only sediment variables. The relationships between fauna and water data were stronger in urban areas than in protected areas. *Kalliapseudes schubarti* was the only selected species with very similar R^2 between protected and urbanized areas despite of if take in account general, water or sediment variables and if high or low relationship.

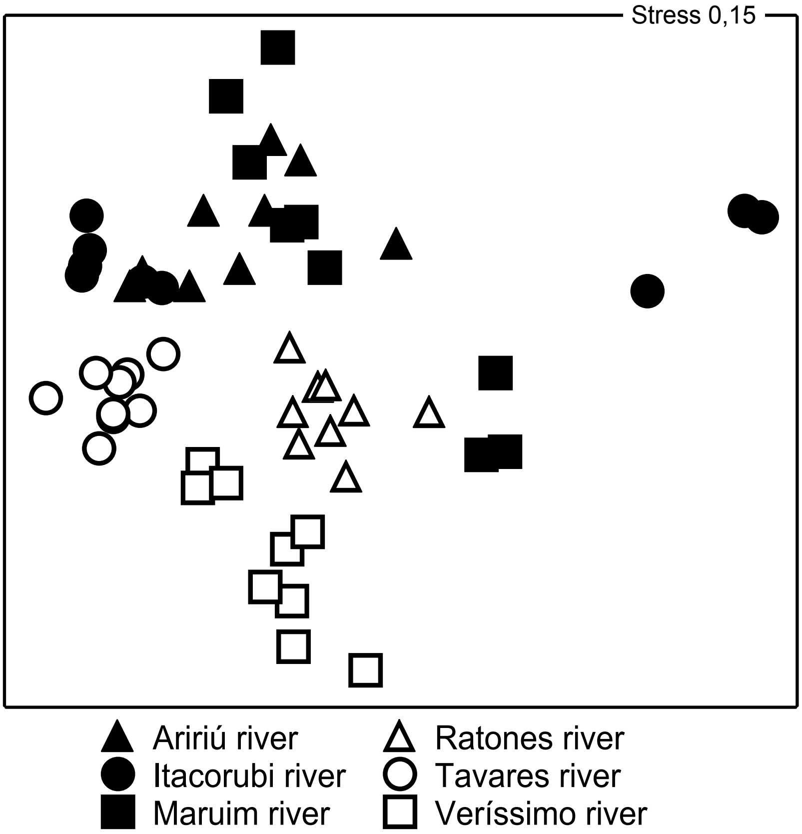

Figure 4.4-7: n-MDS Of water and sediment properties in non-urban (empty symbols) and urban (filled symbols) rivers of the Santa Catarina Island Bay, southern Brazil.

In the protected areas, the analysis showed total density and densities of *Nephtys fluviatilis*, *Heteromastus similis*, *Kalliapseudes schubarti* and *Capitella* sp. with higher relationships with the sediment variables (all $R^2 > 0.74$) than with the water variables (all $R^2 < 0.53$). *Laeonereis acuta* presented significant relationships only with sediment data, and total biomass only with water variables, but both was very low. The relationship of species richness and density of Tubificidae was very similar and low for water and sediment variables, although the former was significant and the latter not.

Table 4.4-5: Relationships between fauna and environment variables.

	General model (water + sediment)		Water model		Sediment model	
Protected areas	R^2	*P*	R^2	*P*	R^2	*P*
Total density	**0,95**	**0,000**	**0,48**	**0,005**	**0,74**	**0,000**
Species richness	**0,52**	**0,001**	**0,45**	**0,001**	**0,46**	**0,006**
Biomass	**0,66**	**0,005**	**0,56**	**0,002**	0,20	0,071
Nephthys fluviatilis	**0,94**	**0,000**	**0,53**	**0,001**	**0,82**	**0,000**
Heteromastus similis	**0,88**	**0,000**	**0,32**	**0,010**	**0,79**	**0,000**
Kalliapseudes schubarti	**0,84**	**0,000**	**0,38**	**0,025**	**0,75**	**0,000**
Capitella sp.	**0,91**	**0,000**	0,31	0,077	**0,82**	**0,000**
Tubificidae	0,15	0,149	0,09	0,124	0,08	0,141
Laeonereis acuta	0,43	0,054	0,34	0,101	**0,15**	**0,046**
Urbanized areas						
Total density	**0,81**	**0,003**	**0,59**	**0,003**	**0,51**	**0,001**
Species richness	**0,84**	**0,000**	**0,29**	**0,045**	**0,65**	**0,000**
Biomass	**0,91**	**0,000**	**0,88**	**0,000**	**0,86**	**0,000**
Nephthys fluviatilis	**0,86**	**0,000**	**0,66**	**0,000**	**0,75**	**0,000**
Heteromastus similis	**0,61**	**0,002**	**0,38**	**0,011**	**0,41**	**0,006**
Kalliapseudes schubarti	**0,86**	**0,000**	**0,39**	**0,022**	**0,74**	**0,000**
Capitella sp.	**0,56**	**0,028**	**0,39**	**0,022**	**0,49**	**0,023**
Tubificidae	**0,84**	**0,000**	**0,43**	**0,004**	**0,59**	**0,001**
Laeonereis acuta	**0,91**	**0,000**	**0,87**	**0,000**	**0,82**	**0,000**

In urbanized areas, all tested fauna and environment relationships was found to be significant and exhibited similar values for sediment and water variables, irrespective of if high or low values. Except for the number of species and *Kalliapseudes schubarti* whose multiple correlations were higher with sediment variables than with the water variables.

The predictive capability of individual environment variables on faunal models are summarized in table 4.4-6 for general (water + sediment), water and sediment models. The major of environment variables correlated with selected species and faunal indicator, except phaeophytin *a* when considering only water variables. Phaeophytin *a* and grain sorted, in sediment, and chlorophyll *a*, dissolved oxygen and phosphorus, in water, were the variables having most relationships with benthic fauna in protected areas (predictive capability above 56 %). However, chlorophyll *a*, phaeophytin *a*, lead, cooper and phosphorus, in sediments, and salinity, phosphorus, nitrogen, silicate and suspended particulate matter, in water, were the explanatory variables that appeared more frequently in the predictive models of fauna in urbanized areas.

Table 6. Relationships between fauna and environment variables: Percentage of R^2 Variability and Predictive capability of environment variables for general, water and sediment models.

	Protected areas		Urbanized areas	
General model (water + sediment)	R^2 variability	Predictive capability	R^2 variability	Predictive capability
Salinity	14	67	16	33
Phaeophytin (w)	24	67	24	44
Phaeophytin (s)	12	67	32	56
Chlorophyll (w)	8	56	24	44
Chlorophyll (s)	16	56	26	33
Nitrogen	23	56	47	44
Dissolved Oxygen	38	56	16	67
Cu	10	33	24	67
Carbonate	4	11	19	56
Phosphorus (w)	23	22	27	89
Pb	19	44	18	78
Fines	28	44	36	33
Organic matter	57	33	7	22
Polyphosphate	41	44	16	11
Phosphorus (s)	16	33	32	44
Grain order	12	44	20	22
SPM	11	33	33	44
Silicate	24	44	53	33
Zn	31	33	11	33
Water (w) model				
Dissolved Oxygen	21	67	38	33
Chlorophyll	5	56	8	44
Phosphorus	6	56	14	100
Nitrogen	11	44	15	56
Salinity	27	44	24	56
SPM	0	0	8	67
Silicate	10	33	22	56
Phaeophytin	0	0	0	0
Sediment (s) model				
Phaeophytin	10	67	29	78
Grain order	25	56	24	44
Phosphorus	21	33	34	67
Chlorophyll	10	44	28	56
Pb	15	33	24	56
Cu	31	11	18	56
Zn	29	33	36	33
Polyphosphate	22	44	22	22
Fines	19	44	44	33
Organic matter	51	33	15	22
Carbonate	17	22	21	44

When evaluating the general model (water + sediment) the fauna was found to be predicted most of times by salinity, phosphorus, nitrate and chlorophyll *a* in water, and phaeophytin *a* in water and sediment in protected areas. In urbanized areas the variables having most relationships with fauna was dissolved oxygen and phosphorus in water, and carbonate, phaeophytin *a*, cooper and lead in sediment. Other result of note was the phosphorus in water appearing practically in all models (general and water).

The averaged variability (%) in the increment of R^2 (ordered by partial correlation coefficients) showed organic matter contributing more to general and sediment models, and salinity and oxygen to water models in protected areas. Fines in sediment model, oxygen in water model and silicate and nitrate in general models were variables more responsible for the R^2 increment in urbanized areas.

Discussion

Due to the great spatial and temporal variability in the natural characteristics, the ecological effects of urbanization in rivers are hard to distinguish, being better recognized when the impacts become obvious. The comparison between impacted rivers and rivers presumably not impacted, not always shows satisfactory results because it is difficult to find control places not affected. However, the study of physical, chemical and biological characteristics following the same sampling procedures for information on the benthic fauna provided a better reliability concerning the ecological changes in the rivers from the Santa Catarina Island Bay, once there are no previous data in order to establish cause-effects relations.

Results of multi- and univariate analysis showed that assemblages of soft bottom animals in the studied urbanized rivers were different from the ones in the protected rivers. This general conclusion is consistent with the expected result, once several studies have been demonstrating general trends of change for the biota with the contamination and eutrophication of the environment (Inglis and Kross, 2000; Grall and Chauvaud, 2002; Matthiessen and Law, 2002). The increasing urbanization has been causing unequivocal alterations on mangrove forests and salt marsh areas (Soriano-Sierra et al., 1997), in water quality (Pagliosa et al., 2004b) and in sediments (Pagliosa et al., 2004a+) from the Santa Catarina Island Bay. The mangrove forests were reduced in 30 % from the original covering due to the opening of drainage channels, dredging, deposition of sediments, occupation in order to construct roads and residences. In urbanized areas, the input of dissolved nutrients, suspended particulate matter and phytoplankton biomass were distinct from the concentrations, from the inputs and from the existing relations among water properties in protected areas. In sediments, the concentrations of lead, zinc, total phosphorus, polyphosphate and microphytobenthic biomass were more elevated, and presented the highest variations in urbanized areas. In contrast, rivers localized in preserved areas exhibited heavy metals and nutrients concentrations in water and sediments considered natural for non-impacted areas, serving as reference places for environmental studies in the south coast of Brazil (Pagliosa et al., 2004a, 2004b). These results provided a consistent situation for the hypothesis test on the influence of urbanization on biomass, composition, species richness and spatial variability of the benthic macrofauna assemblages, and for the formulation of predictive models based on the characteristics of sediments and water in urbanized and protected areas.

The animal communities may answer to impacts of environmental changes with the increase in the variation of abundance of certain taxa groups, or even with changes in taxonomic composition between impacted and non-impacted sites and within samples from impacted sites (Warwick and Clarke, 1993). However, interactions between variability of organisms or of their communities and the concentrations of pollutants are complex (Luoma, 1996; Grant, 2002). In the present study the benthic community differed in species composition, species richness, total biomass and total and dominant species density between urbanized and protected areas and among sites along the rivers. The complexity in the answers of the fauna was evident but could be rationalized into two distinct patterns: i-) The species assemblage more sensitive to environmental changes presented a different pattern of sample variation among sites in urbanized areas when compared to the registered pattern in protected areas. In contrast, ii-) the more tolerant species assemblages increase the sample variation among sites in urbanized rivers. This was caused, mainly, by the remarkable reduction in densities of sensitive species and increase in densities of tolerant species in urbanized areas.

The predominance, composition and richness of registered species in the protected rivers are consistent with the reports of other studies made with sub-littoral benthic fauna in small estuaries with mangrove in the Brazilian subtropical region (Lana, 1989; Lorenzi, 1998). Densities, in general, were more elevated in the inner portions and significant differences in the species richness along the estuaries did not occur. The numerically dominant species were the polychaetas *Nephtys fluviatilis* and *Heteromastus similis*, besides the tanaidacea *Kalliapseudes schubarti*. However, as expected, differences in the general composition and in the densities among the several rivers occurred.

The population densities of *N. fluviatilis*, *H. similis* and *K. schubarti* were drastically reduced in urbanized areas. They also presented discrete abundance in Aririú river, the least impacted of the three urbanized rivers. The results indicate that these species are quite sensitive to environmental alterations, despite the fact that they have different life strategies, feeding habits and behavior. The tube-building tanaidacea *K. schubarti* has deposit selective-suspension feeder habits, living on the surface layer of sediments. The multiple regression analysis showed that this species presented strongest relationships with the characteristics of sediments and lowest relationships with water properties. Despite the remarkable differences in densities from urbanized and protected areas, the predictive variables related to this species were very similar in both areas. The generalist polychaeta *N. fluviatilis* also revealed strong relationships with the properties of sediments, both in protected and urbanized areas. However, there was an increase in the importance of the water properties in the urbanized area. *N. fluviatilis* is a quite mobile organism and seems to exert influence on the young forms of *H. Similis* trough predation (Bemvenuti, 1994). Although the deposit feeder polychaeta *H. similis* does not have great mobility, it is agile burrower which allows it to reach deeper depths in the sediment than other species. Its high tolerance to anoxic conditions is reflected on the predictive model, once it was the only one of the sensitive species not related with dissolved oxygen concentrations. This polychaeta exhibited strong relationships with the properties of sediments in protected areas and low relationships with the properties of water and sediments in urbanized areas. This may suggest that, while the densities of *H. similis* in protected areas can be controlled by infauna predators, in urbanized areas their low densities are more related to competition with other sub-surface deposit feeder species, as *Capitella* sp., *Laeonereis acuta* and oligochaetas, than to general changes in the environment.

The distribution pattern of *N. fluviatilis*, *H. similis* and *K. schubarti* along the urbanized and protected areas suggests that this species form an association of sensitive species to environment changes. They may be used as good quality indicators of local estuarine systems and, probably, of the subtropical region and hot-temperate region of South Atlantic, approximately between 23-35º S latitude. Thus these species are frequent in the great estuarine complexes with mangrove and salt marsh of the south and southeast Brazil (Tommasi, 1970; Lana, 1986) and also in restricted salt marsh zones in the South America (Mañe-Garzon, 1949; Orenzanz and Estivariz, 1971; Capitoli et al., 1978; Muniz and Venturini, 2001).

On the other hand, the polychaeta *Laeonereis acuta* and the unidentified Tubificidae were the dominant species in urbanized rivers and occurred with reduced densities in protected areas. According to the distribution pattern of *L. acuta* and Tubificidae, when dominants these organisms form a tolerant species association which may be used as indicators of unsavory environmental quality in local estuarine systems. The specimens of *L. acuta* in urbanized areas presented increased body sizes, being the main responsible for the rise in total biomass of these areas. The eutrophication registered in the local urbanized rivers has been promoting the growth of macroalgae, especially *Enteromorpha* and *Ulva*, in the inner portions of small streams at the end of winter. The polychaeta *L. acuta* is the dominant organism in biomass and number in these places (*pers. obs*.). *Laeonereis acuta* and the unidentified Tubificidae are widespread registered in the intertidal zone of estuaries in the south and southeast of Brazil, inside mangroves, salt marshes and unvegetated areas (Bemvenuti, 1997; Lana et al., 1997; Omena and Amaral, 2000; Pagliosa and Lana, 2003). Both are usually associated to bottoms with high contents of mud and organic matter, being considered as indicators of organic enrichment. This result is in accordance with one of the main effects of urbanization, which alters the sediment characteristics, causing the organic enrichment and decrease in grain size (Amaral et al., 1998; Frouin, 2000). However, in the present study *Laeonereis acuta* and the Tubificidae presented strong relationships with all environment variables (water + sediment) and showed very similar relationships when analyzed separately for water and sediment variables in urbanized areas. In contrast, in protected areas they did not relate with any environment properties, joint or separated for water and sediment. This suggests that the answers of these species are more related to general changes in environments, in water and sediments, than simply to modifications in the sediment characteristics.

The polychaeta *Capitella capitata* is the species commonly reported as indicator of organic enrichment in estuaries, lagoons and costal regions all around the world. However it is also considered as a complex of species, once it varies greatly in its taxonomic characters, raising difficulties in its regional differentiation. This great taxonomic confusion makes the conclusions on the distribution pattern of *Capitella* masked. *Capitella* sp. and oligochaetas numerically dominate the sediments of a local mangrove (Netto and Gallucci, 2003). In the present study, although in low densities, the Capitellidae occurred in all rivers, without differentiation between urbanized and protected areas. *Capitella* sp. presented strong relationships with the characteristics of the sediments from protected areas and low relationships with water and sediment variables from urbanized areas. This result suggests that *Capitella* sp. does not have a direct relation with the general effects of urbanization, at least in the studied scale. For being associated with high organic matter sediments, independent of the environmental conditions, *Capitella* sp. seems to be more related to small aggregations (patches) of organic enrichment in sediments. Due to its sedentary habit, its strategies of colonization after environmental perturbations are more related to fast recruitment and to passive transport to available areas with small possibilities of competition with other species (Netto and Lana, 1994). The results of the present study evidenced that not only the changes in the characteristics of the sediment but also in the water properties were directly related to the differences in the macrofauna community between urbanized and protected areas. When analyzing the group of variables from sediments and water that best predicted the general characteristics of community we can notice that:

i-) The characteristics of water and sediments related by the predictive model in protected areas were the ones typically discriminated as influencing the distribution of fauna along estuarine systems, as dissolved oxygen, chlorophyll *a* and dissolved nutrients in water and grain sorted and concentrations of phaeophytin *a* in sediments. Within these environments, the dominant fauna was mainly composed of tube-builders, agile burrowers of sub-surface and explorers of the deeper layers of the sediments. All these activities help in the sediments oxygenation and in the process of nutrients transference from sediments to water (Rysgaard et al., 1995; Cornwell et al., 1999; Cloern, 2001; Gray et al., 2002);

ii-) On the other hand, the properties of water and sediments related to environmental degradation became more important in the explanatory models of fauna distribution in urbanized areas. The most current properties in the predictive models were the concentrations of lead, cooper, phosphorus, chlorophyll *a* and phaeophytin *a* in sediments and elevated contents of phosphorus, nitrogen, silicate, suspended particulate matter and salinity in water. In these places there was a clear impoverishment of fauna, trophic groups and life habits. There was the predominance of discrete mobile forms and burrowers of sub-surface and exclusion of suspension feeders as crustaceans and mollusks.

The results of the present study are the first attempt to predict the effects of urbanization on local benthic communities. Only with the inclusion of temporal variations will we be able to provide consistence to the generated models. However, the study of spatial variation of fauna in urbanized and protected areas revealed that the understanding of animal-sediment-water interaction is the key to construct predictive models able to lead the strategies to restoration or mitigation of environmental impacts caused by the increasing urbanization.

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