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Spatial changes in the water quality of Itajaí-Açú Fluvial-Estuarine System, Santa Catarina, Brazil

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ABSTRACT

This study was carried out with the aim of evaluating the spatial variation of the water quality in the Itajaí-Açú River estuary. Seven stations along the estuary were monitored on a weekly basis, from October 2003 to December 2004, plus two stations in tributaries (Itajaí-Mirim River, the main tributary, and one reference station). This monitoring included measurements of salinity, pH, dissolved oxygen, temperature, nutrients (NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} , H_4SiO_4), Biochemical Oxygen Demand (BOD), total phosphorous and dissolved organic phosphorus (TP and DOP), particulate organic carbon (POC), suspended particulate matter (SPM) and chlorophyll-a (Chl-a). Multivariate analyses demonstrated the compartmentalization of the system based on the deterioration in water quality and marine influence. Urban development was the main factor responsible for the spatial variation of the monitored variables, resulting in increases in the indicators for organic matter and a progressive decrease in O_2 . Despite the effect of dilution by marine influence, there was an increase in ammonium, attributed to the influence of the municipal districts of Itajaí and Navegantes, close to the river mouth.

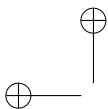
Key words: Itajaí Estuary, nutrients, organic matter, river, Santa Catarina.

INTRODUCTION

Estuaries are defined as restricted bodies of water in which the seawater is diluted, in a measurable way, by the fresh water (Pritchard 1967). These environments are generally located in places with high population densities and, as a result, they have been extensively exploited and destroyed, although they still remain one of the most resilient environments on Earth (Elliot and

well as the biota itself, are transported from the water to the salt water over relatively short distances.

The metabolism of an estuarine system is influenced by the entry of nutrients and organic matter to which it is submitted. The supply of the compounds to the estuaries has increased in recent decades due to changes in land use and occupation (Revilla et al. 2004) and, in particular, because estuaries act as receptors of domestic and industrial wastewater, often with



(Diaz 2001, Rowe 2001) as the result of the high O_2 consumption to oxidize the surplus of organic matter.

The coastal systems are densely populated areas in general and receive the influence directly from human activities that originate in the drainage basins (C.H.A. Ribeiro, unpublished data). The environmental impact of this influence depends on the type and amount of present substances, which are related to the type of activity of the drainage basin. Regions with high population densities are continually throwing organic matter and nutrients into their water bodies. Industrial regions throw heavy metals, hydrocarbons and organic matter on them. Agricultural activity has contributed to the entry of many compounds to the water bodies with fertilizers (rich in nutrients), pesticides and herbicides (C.H.A. Ribeiro, unpublished data).

In this context, the aim of this study is to determine how the water quality is modified along the Itajaí-Açu River estuary from its source, where there is no tidal influence, to its mouth, around 90 km downstream, associating this variation with the main activities carried out in its drainage basin.

AREA OF STUDY

The Itajaí-Açu River estuary is located in the South Brazil, 26.9°S and 48.66°W , in the State of Santa Catarina. Its hydrographic basin comprises an area of about $15,500\text{ km}^2$, which is close to 16% of the state area. The climate of the region, according to Köpen's classification, is humid subtropical without hydric deficit and with well-distributed rainfall throughout the year (Cfa). The average temperature in the region is higher than 18°C , with annual average rainfall and evapotranspiration of about 1400 mm and 1080 mm, respectively (Gaplan 1986).

The Itajaí-Açu River represents about 90% of the fluvial inflow to the estuary, with the remainder being attributed to smaller affluents such as the Luiz Alves and Itajaí Mirim Rivers. The average long-term discharge of the Itajaí-Açu River, which measured about 90 km upstream from the river mouth, is near $228\text{ m}^3\text{ s}^{-1}$, with minimum and maximum values of $17\text{ m}^3\text{ s}^{-1}$ and 5390

portion of the lower estuary is continually dredged to maintain the navigation channel and the access to the port. The port region is of great economic importance and is the main shipping route in the state. It also has the largest fishing port in the country (Schettini 2002a). Due to the occupation of its drainage basin, the main polluting agents of the river are sanitary waste, solid garbage and the throwing of industrial wastewater, particularly from the textile, metallurgy and galvanoplastic industries.

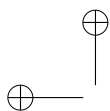
MATERIALS AND METHODS

LAND USE

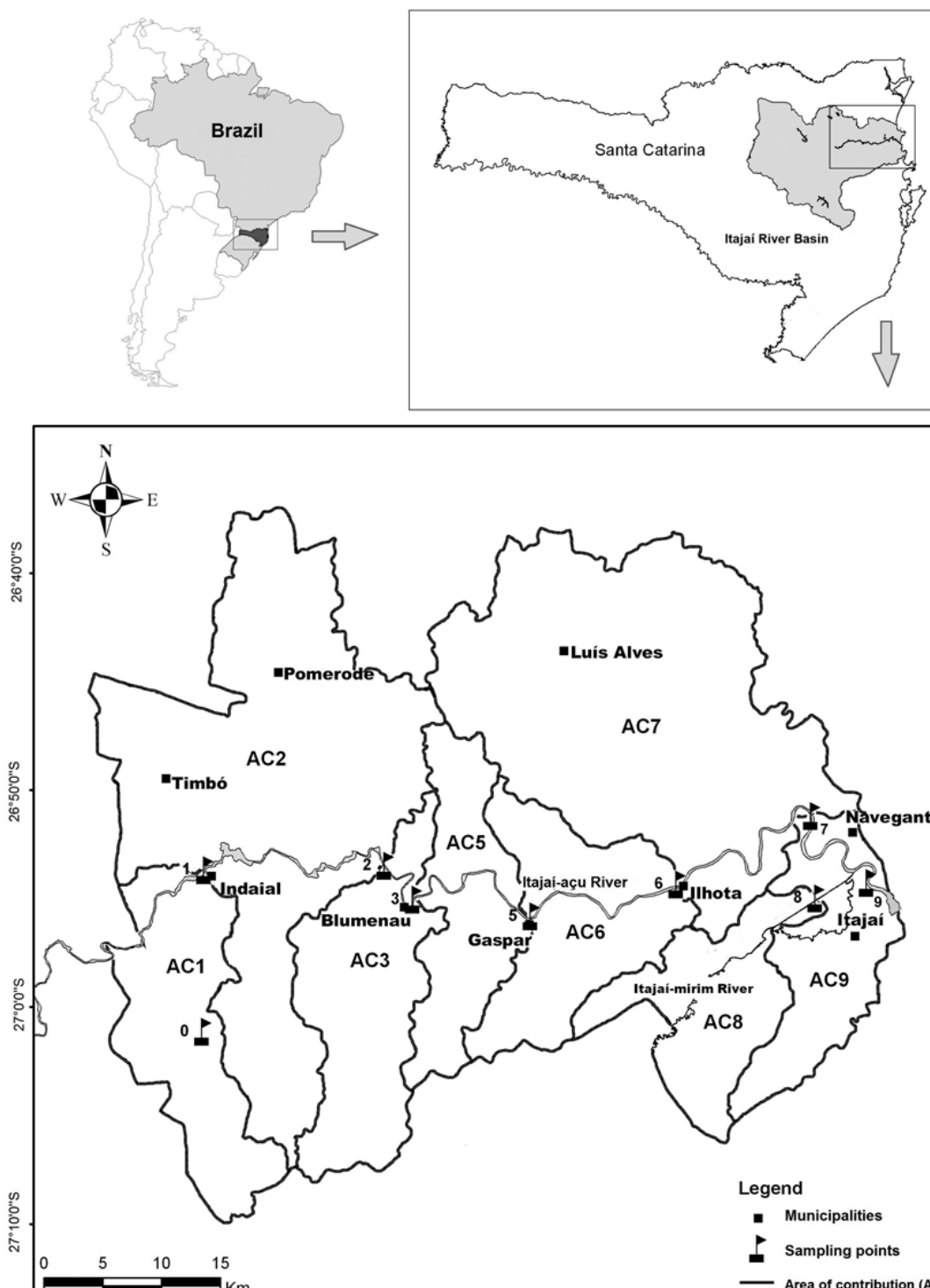
To assist in the characterization and interpretation of the results, maps of land use were used, for the final portion of the basin from the town of Indaial, which is considered by this study as the point of entry to the system. The characterization of land use was based on topographical maps of the IBGE of 2004 (scale 1:50.000) and Landsat satellite's images from 2002 in the composition RGB-453. The study area was divided into sub-units (Fig. 3), which represent areas of contribution or direct influence on the different collection stations (#1, #2, #3, #5, #6, #7, #8 and #9) and are termed the area of contribution (AC) (Rörig 2005).

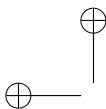
SAMPLING

The sampling campaigns were carried out on a weekly basis between October 2003 and December 2004. Nine collection stations were monitored from the town of Indaial to the river mouth, in Itajaí, with the two points being around 90 km apart (Fig. 1). The town of Indaial is the closest station to the mouth that is not influenced by the tide, and where daily measurements of fluvial discharges of the Itajaí-Açu River are taken. Among the 9 stations, 7 are situated in the main course of the Itajaí-Açu River (#1, #2, #3, #5, #6, #7, #9). In addition, two other stations were monitored: one located where there is little impact from the drainage basin (#0), and another situated in the Itajaí-Mirim River, which is the main tributary of the Itajaí River estuary, close to the



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plan also included a station 4 located in a tributary of the Itajaí-Açú River, but it was not sampled during the monitoring, which explains its absence in the sequence of sample stations.

ANALYTICAL METHODS

At the time of sampling, salinity, temperature, pH and dissolved oxygen were determined, using a Horiba U-10 multianalyzer. In the laboratory, the samples were filtered in precalcinated Whatmann GF/F fiberglass filters (approximate porosity of $0.7 \mu\text{m}$). The filtered material was separated into aliquots and frozen for subsequent determination of the nutrients through the traditional colorimetric methods. After drying in an oven (65°C), the filters were frozen for subsequent determination of the particulate organic carbon (POC). Fractions of the raw, filtered samples were digested by the potassium persulfate autoclave method to determine the total organic phosphorus (TOP) and total dissolved phosphorous (TDP), according to Grasshoff et al. (1983). Aliquots of the raw samples were incubated at 20°C to determine the BOD_5 , according to APHA-AWWA-WPCF (1998).

The dissolved nutrients (NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} and H_4SiO_4) were determined for the filtered sample using the traditional colorimetric methods, based on Strickland and Parsons (1972). The ammonium was determined using the indophenol blue method. The nitrite and nitrate were determined using the Griess reaction after reducing the nitrate to nitrite in a cadmium column prior to determination. The phosphate was determined after the addition of ammonium molybdate and ascorbic acid. The silicon was determined after the formation of a reduced silicomolybdate blue complex. All of them were read in a UV 160 A Shimadzu UV-V spectrophotometer.

To determine the SPM, aliquots of known volumes of water samples were filtered in pre-weighted filters of cellulose ester membrane with porosity of $0.45 \mu\text{m}$. After filtering, the filters were dried in an oven at 60°C for 24 hours, and weighed again. The SPM was obtained by the difference in weight before and after filtering in

The BOD_5 was determined for the raw water according to the method adapted from APHA-AWWA-WPCF (1998). The particulate organic carbon was determined for the material trapped in the filters (Whatman GF/F, porosity of $0.7 \mu\text{m}$). At the time of determination, the filters were digested with sulfuric acid and excess of potassium dichromate. After digestion, the excess of dichromate was titrated against an ammonium iron sulphate solution, according to Carmouze (1994).

The total and dissolved phosphorus was determined from aliquots of the raw and filtered sample, to obtain the total phosphorous (TP) and dissolved phosphorous (DP). The samples were digested by the potassium persulfate autoclave method at 120°C for 45 minutes. After digestion, the phosphate was determined colorimetrically as orthophosphate after reacting with ammonium molybdate according to Carmouze (1994). The dissolved organic phosphorous (DOP) was determined by the difference between the dissolved phosphorous (determined in the filtered sample after digestion) and the phosphate ions.

To determine the chlorophyll-a, aliquots of a known volume of samples were filtered in a GF/F fiberglass filter with a 25 mm diameter and the filters were extracted with 10 mL of 90% acetone (v/v) for 24 hours in darkness, inside the freezer (-15°C) (Parsons et al. 1989). The extracted samples were read in a Turner Designs® TD-700 fluorometer. For its calibration, a *Skeletonema costatum* microalgae culture was used in exponential growth.

STATISTICAL ANALYSIS

Due to the large amount of obtained data obtained, and to assist in their interpretation, the data were analyzed through 2 multivariate techniques: Cluster analysis and the technique of ordering through principal components analysis (PCA). The analyses were carried out on the standardized data matrix by the average and standard deviation according to Clarke and Warwick (2001). The analyses were initially carried out considering all the stations sampled in the 56 campaigns, including all the monitored variables (Table I).



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TABLE I
Abbreviations of the variables used in the multivariate analyses. In the spatial analysis, the overall average of each variable was used, in each station. In the temporal analysis, the overall average of each variable was used, for each sampling campaign.

Abreviation	Variable
Cla md	Chlorophyll <i>a</i>
COP md	Particulated Organic Carbon
DBO md	Biochemical Oxygen Demand
Dsc md	Average of River Discharge, including the day of sampling and the two days before it
MPS md	Particulated Suspended Material
N:P md	DIN:PO ₄ Ratio
NH ₄ md	Amonium
NO ₂ md	Nitrite
NO ₃ md	Nitrate
OD md	Dissolved Oxygen
pH md	pH
PO ₄ md	Phosphate Ions
POD md	Dissolved Organic Phosphorus
POT md	Total Organic Phosphorus
PT md	Total Phosphorus
Sal md	Salinity
Sat md	Saturation of Oxygen (%)
Si md	Silicate
Temp md	Temperature

vironmental variables are included (Clarke and Warwick 2001) for the interpretation of ecological data. The Cluster method was the Ward method, or Cluster method by minimum variance.

RESULTS

LAND USE

The estuary of the Itajaí-Açu River is situated in the final portion of the Itajaí River basin. This region includes the towns of Indaial, Blumenau, Gaspar, Ilhota, Luis Alves, Itajaí and Navegantes (Table II). The area of study was classified based on land use and occupation, considering 6 classes of land use: native forest, urban area, creeping vegetation (including cultivated areas),

is equivalent to 16% of the Itajaí River basin. The total consists of: 60,5% native forest, 7,6% urban area, 26,6% areas with creeping vegetation (mainly agriculture), 1,4% exposed soil, 2,1% areas of reforestation and 0,7% water courses. The values for the area of each class of land use considered in each area of contribution are shown in Table III.

Urban development and agriculture are two types of land use in each area of contribution that potentially exert a greater influence over the quality of water in the system. Concerning the urban development, it is worth mentioning that the area found in AC 2 and 3 which responds to the town of Blumenau, and those found in AC 7 and 9 to the towns of Itajaí and Navegantes. Regarding the agriculture, although no specific classification has been done for this use, it is within the region of ground vegetation, which is found mainly on the banks of the Itajaí River estuary. The main agricultural activity practiced in the region is irrigated rice farming (Muniz 2005), which occurs on the coastal plain of the Itajaí Basin, in the region of Gaspar, Ilhota and Itajaí, within the area of this study (Table II).

RIVER DISCHARGE

The river discharge in Indaial (station #1 of the Itajaí River estuary) presented an average of 204,2 m³/s, varying between 48,5 and 1938 m³/s in the monitored period. Despite the high variability most of the time, the discharge was low (mode = 83,4), with sporadic peaks of high discharge. This was the case of December 2003 and September and October 2004. These peaks of high discharge were interspersed by prolonged periods of low discharge.

PHYSICAL-CHEMICAL VARIABLES

Table IV shows a summary of the average results obtained at the sampling stations during the study period. The spatial variability of the salinity reflected the marine influence in the estuary. The stations that were directly subject to the marine influence (#7 and #8) presented average salinity ranging from 0 to 16, with salinity values always recorded at the bottom due to salinity



TABLE II
Socio-economic indicators for the municipal districts of the region around the Itajaí estuary.
Source: IBGE (2004), ICEPA (2005), PNUD (2003).

District	Total population (2000)	Area (km ²)	Demographic density (2000)	Rural population (2000)	Urban population (2000)	Rice culture area (ha) (2002)	Main culture (ha) (2002)
Blumenau	261,808	510.3	513.0	19,865	241,943	40	Maize (500)
Brusque	76,058	280.6	271.1	2,802	73,256	125	Manioc (250)
Gaspar	46,414	369.8	125.5	16,813	29,601	3,200	Rice (3.200)
Ilhota	10,574	245.2	43.1	4,129	6,445	2,100	Rice (2.100)
Indaial	40,194	429.9	93.5	1,812	38,382	240	Rice (240)
Itajaí	147,494	303.6	485.8	5,544	141,950	2,020	Rice (2.020)
Luiz Alves	7,974	260.8	30.6	5,850	2,124	550	Banana (3.900)
Navegantes	39,317	119.3	329.6	2,667	36,650	736	Rice (736)
Total	629,833	2519.5	—	59,482	570,351	9,011	—
Media	—	314.9	236.5	7,480	71,294	—	—
Total Santa Catarina	5,356,360	95,285	—	1,138,429	4,217,931	137,340*	—
Media Santa Catarina	—	—	56.1	3,885	14,395	—	—

*In 2004, the total area of rice culture in Santa Catarina increased to 151,800 ha.

TABLE III
Areas and classes of land use in each area of contribution (AC) in the terminal region of the Itajaí River basin.

Classes of land use		AC1	AC2	AC3	AC5	AC6	AC7	AC9	Total	
									km ²	%
Urbanized area	km ²	7.8	57.6	19.7	13.7	20.3	29.3	38.9	187.2	7.6
Water Bodies	km ²	1.5	2.7	0.7	1.9	2.3	3.3	4.2	16.5	0.7
Forests	km ²	174.3	416.0	186.2	133.4	118.1	384.1	87.9	1,500.0	60.5
Reforestation	km ²	4.6	8.2	0.7	3.0	4.1	29.6	2.5	52.8	2.1
Exposed land	km ²	0.6	6.5	7.2	1.5	4.3	11.1	4.4	35.5	1.4
Herbaceous Plants	km ²	39.8	222.8	27.6	33.0	77.1	217.6	41.7	659.6	26.6
No data	km ²	0.0	0.0	0.0	0.0	0.0	27.2	0.0	27.2	1.1
Total	km ²	228.6	713.8	242.0	186.5	226.1	702.2	360.5	2,478.8	100
	%	8.6	26.8	9.1	7.0	8.5	26.4	13.6	100	—

lower temperatures. The greatest ranges were recorded for station #0, in Indaial, due to the shallow depth of the Warnow River (Fig. 2B).

The pH throughout the estuary presented an overall average of 6,7, with minimum and maximum specific values of 4,5 and 7,9, respectively. In general, the pH was lower in stations #3 and #5. On the other hand, an

an overall average of 6,2 mg/l, ranging from 2,1 to 12,3 mg/l. In general, the concentrations tended to decrease from stations #1 up to station #9, which reflects the decrease in water quality toward the mouth of the estuary (Fig. 2D). The highest values were recorded in station #0, the reference station of the study, which is located outside the main course of the Itajaí River. On



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TABLE IV
Summary of the results obtained in the Itajaí River estuary, in samples carried out in 2003 and 2004. The averages, standard, minimum and maximum errors were calculated among the averages obtained for the sampling stations.

Variable	Mean	Standard Error	Minimum	Maximum
Salinity	3.4	1.7	0.0	15.9
Temperature (°C)	22.9	0.4	19.6	23.7
pH	6.7	0.1	6.33	7.2
O ₂ (mg/l)	6.2	0.4	4.6	8.8
DIN (μM)	63.4	5.0	30.5	77.0
NH ₄ ⁺ (μM)	22.5	2.2	6.7	33.1
NO ₂ ⁻ (μM)	1.2	0.2	0.2	2.2
NO ₃ ⁻ (μM)	45.0	5.0	22.9	56.8
PO ₄ ³⁻ (μM)	1.6	0.1	0.9	2.1
DIN/PO ₄ ³⁻ Ratio	53	5.1	29.0	84.4
H ₄ SiO ₄ (μM)	101.2	6.3	50.2	121.0
SPM (mg/l)	42.3	4.7	10.9	52.4
POC (μM)	184.8	11.5	107.1	236.0
TP (μM)	6.3	0.6	1.7	8.6
DOP (μM)	1.0	0.1	0.39	1.4
BOD (mg/l)	1.9	0.1	1.0	2.8
Chlorophyll a (μg/l)	1.7	0.2	1.1	2.9

NUTRIENTS

Dissolved Inorganic Nitrogen (DIN)

The dissolved inorganic nitrogen (DIN), which means the sum of ammoniac nitrogen (N-NH₄⁺), nitrite (N-NO₂⁻) and nitrate (N-NO₃⁻), varied from 11,0 to 175,0 μM. The main form of DIN, in general, was NO₃⁻, particularly in the stations at the fluvial extremity of the estuary. The NO₃⁻, which varied from 5,3 to 135,6 μM, showed a tendency to decrease towards the mouth of the estuary (Fig. 3A) in the stations influenced by the seawater (#7 and #9). Compared with station #0, the other stations presented much higher concentrations of NO₃⁻ (Fig. 3A).

The NO₂⁻ was the nitrogenated nutrient that presented the lowest concentrations, varying between 0,1 and 10,6 μM in the estuary. On average, the NO₂⁻ tended

The NH₄⁺ presented concentrations ranging from 1,3 to 99,8 μM in the estuary. The highest concentrations were recorded in stations #1 and #2 in a similar situation in July 2004. However, the general variation trend in NH₄⁺ was to increase spatially after the transition to Blumenau (stations #2 and #3) and close to the mouth (Fig. 3C).

Phosphate and silicate

The dissolved inorganic phosphorous, which is represented by the phosphate ions (PO₄³⁻), ranged from 0,9 to 6,2 μM. The general variation trend in PO₄³⁻ showed a decrease in the stations close to the mouth, which received a mixture of seawater, as in stations #7 and #9 (Fig. 4A).

The origin of the dissolved silicon, normally present in the form of orthosilicic acid (H₄SiO₄), is

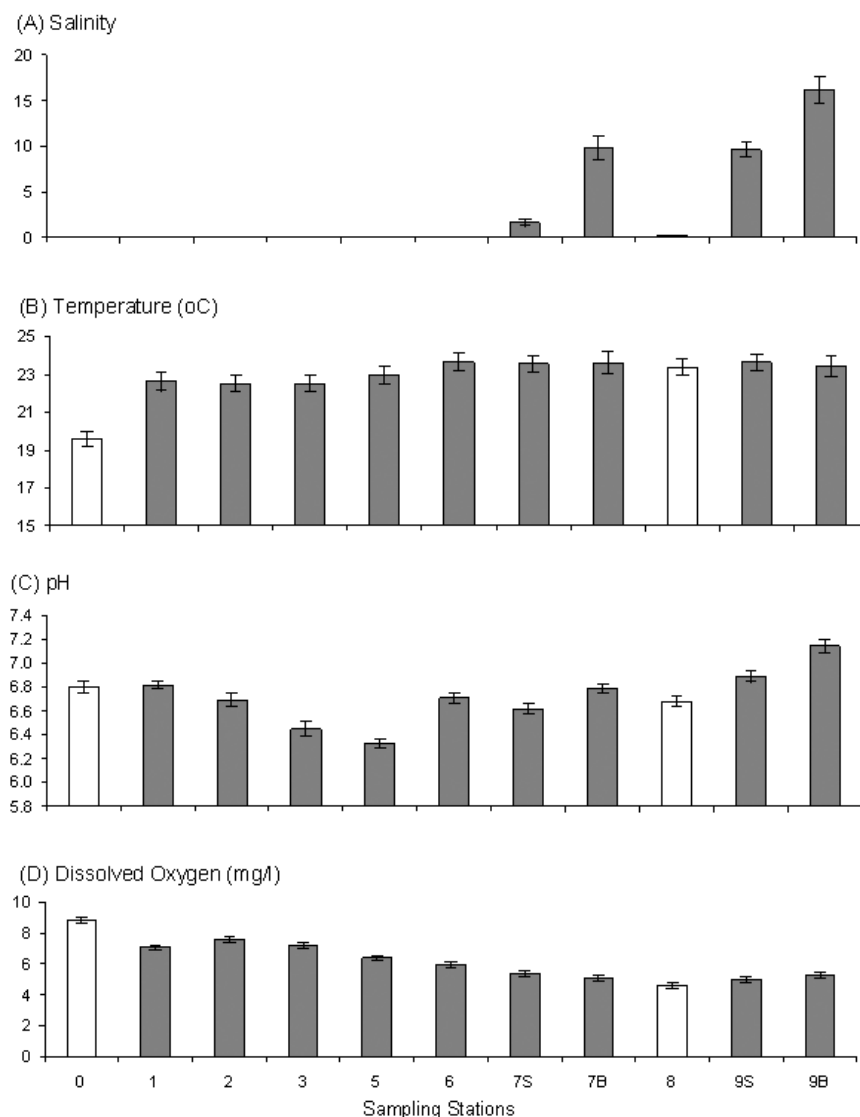


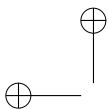
Fig. 2 – Spatial variation of (A) salinity, (B) temperature, (C) pH and (D) dissolved oxygen in the fluvial-estuarine system of the Itajaí-Açu River. Overall average and Standard Error for each sampling station, considering the entire period sampled (October 2003 to December 2004). The columns in gray represent the stations located in the estuary, and the others in the tributaries.

standard of spatial variation of Si was observed, and the average concentrations were similar among the stations (Fig. 4B). However, all the stations presented much higher Si concentrations than those of the reference station (#0) (Fig. 4B). Although the spatial variation of Si was apparently low, temporally it presented

ORGANIC MATTER AND SUSPENDED PARTICULATE MATTER (SPM)

SPM

The suspended particulate matter (SPM) presented high variability, with minimum and maximum values of 0.8



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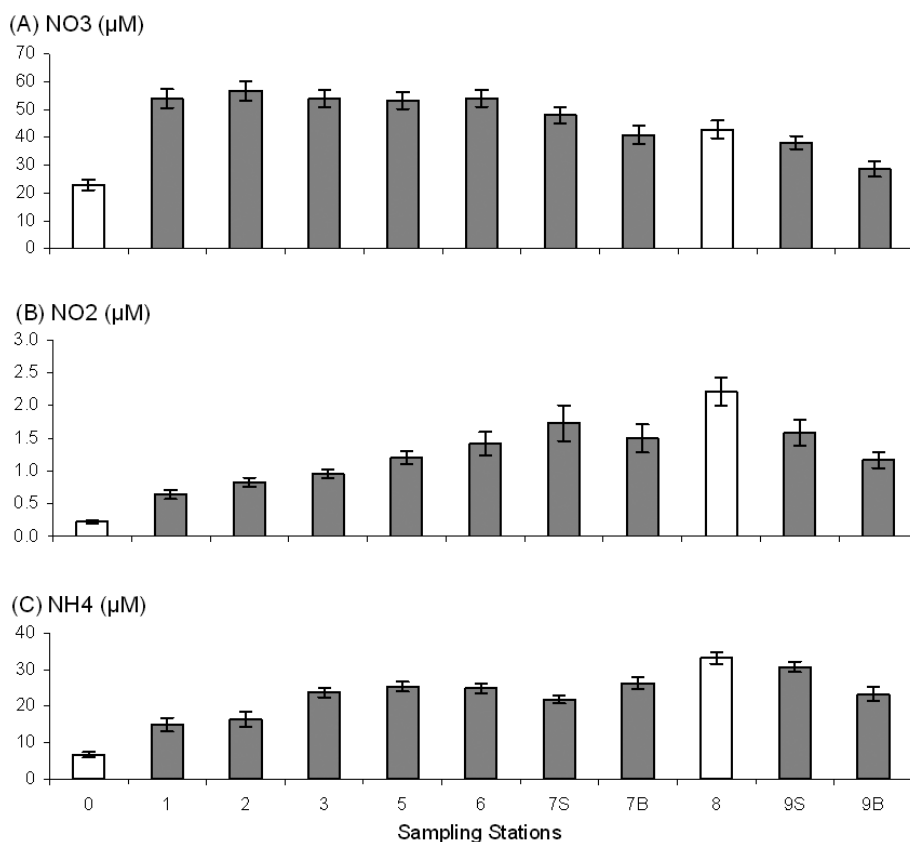


Fig. 3 – Spatial variation of (A) nitrate, (B) nitrite and (C) ammonium in the fluvial-estuarine system of the Itajaí-Açú River. Overall average and Standard Error for each sampling station, considering the entire period sampled (October 2003 to December 2004). The columns in gray represent the stations located in the estuary, and the others in tributaries.

Particulate Organic Carbon (POC)

The particulate organic carbon (POC) presented average concentrations ranging from 107 to 222 µM throughout the Itajaí estuary (Fig. 5B). No clear standard of spatial variation was observed, as demonstrated by the variation in averages for each station.

Phosphorous

The total phosphorous (TP) corresponds to all the forms of phosphorous that are present in the water, including the organic and inorganic forms, both particulate and dissolved. The TP presented an overall average of 6,2 µM, varying from 0,3 to 45,5 µM throughout the sample stations. Spatially, no major differences were

The dissolved organic phosphorous (DOP), representing up around 17% of the TP, presented an average concentration of 1,1 µM, ranging from values close to 0,3 to 8,4 µM. The standard variation in DOP was similar to the variation in TP, temporally and spatially.

Biochemical Oxygen Demand (BOD)

The biochemical oxygen demand (BOD) is a variable that indicates the concentration of organic matter in aquatic systems. In the sampled period, the BOD was monitored between April and December 2004. In this period, the BOD presented an overall average of 1,9 mg/l O₂, ranging from 0,2 to 6,5 mg/l O₂. Spatially, an increase in BOD was observed in the estuary, with higher values

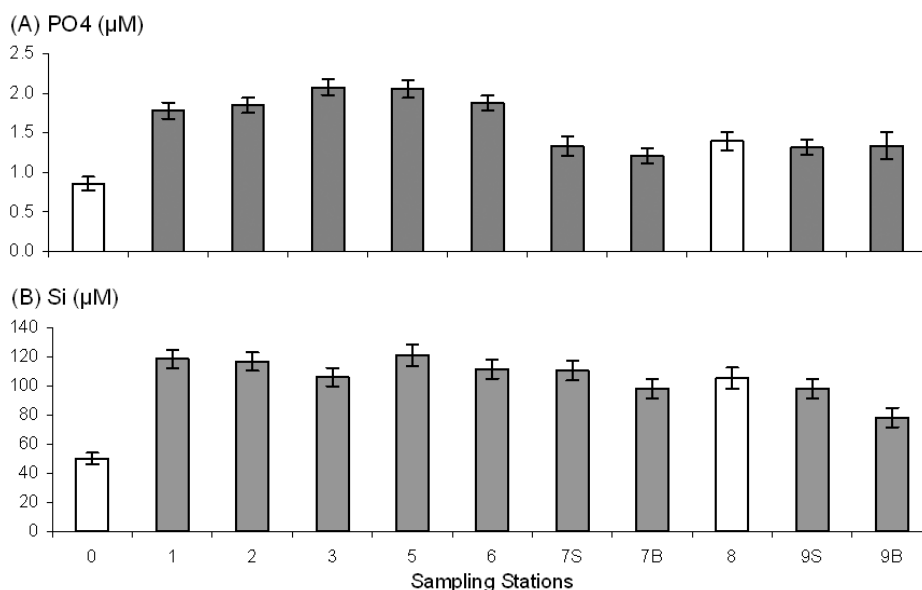
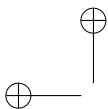


Fig. 4 – Spatial variation of (A) phosphate (PO_4^{3-}) and (B) orthosilicic acid (H_4SiO_4) in the fluvial-estuarine system of the Itajaí-Açu River. Overall average and Standard Error for each sampling station, for the entire period sampled (October 2003 to December 2004). The columns in gray represent the stations located in the estuary, and the others in tributaries.

CHLOROPHYLL-A

Chlorophyll-a presented low values throughout the estuary, for most of the study period, with measurements ranging from $< 0,1$ and $16,5 \mu\text{g/l}$ and an overage average of $1,7 \mu\text{g/l}$, but generally below $2,0 \mu\text{g/l}$ (Fig. 5E). For the stations situated close to the mouth of the estuary, the chlorophyll-a presented more significant concentrations in some stations. The highest of these occurred at the beginning of September, when the chlorophyll reached $16,5 \mu\text{g/l}$. These low concentrations are the result of the high turbidity in the estuary, which results in low light intensity throughout the water column.

DATA ANALYSIS

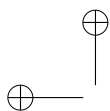
Cluster analysis

The analysis shown in the form of a dendrogram (Fig. 6) resulted in the Cluster of sampling stations, which demonstrated similar behavior for the monitored variables. These Clustered stations were, therefore, treated as a whole and denominated compartments.

identified; the first one consisted of stations #1, #2, #3, #5 and #6 and the second, stations #7, #7F, #8, #9 and #9F (Fig. 6).

The first-formed Cluster corresponded to the fluvial portion of the system and was divided into 2 subgroups, one including stations #1 and #2 and the other, stations #3, #5 and #6 (Fig. 6). The first subgroup, which included the stations further upstream from the system, corresponded to the compartment termed here as the Fluvial Extremity. The second subgroup, which included #3, #5 and #6, was called the Upper Estuary compartment.

The second major group included the stations further downstream from the system, which are influenced by the effect of salinity. Within this group, station #8 was clearly isolated from the others in that it represented the Itajaí-Mirim River, which is a tributary of the Itajaí River and was called the Itajaí-Mirim compartment. Station #9F was isolated from the others, which corresponds to bottom samples of the estuarine extremity of the system that are heavily influenced by the seawater.



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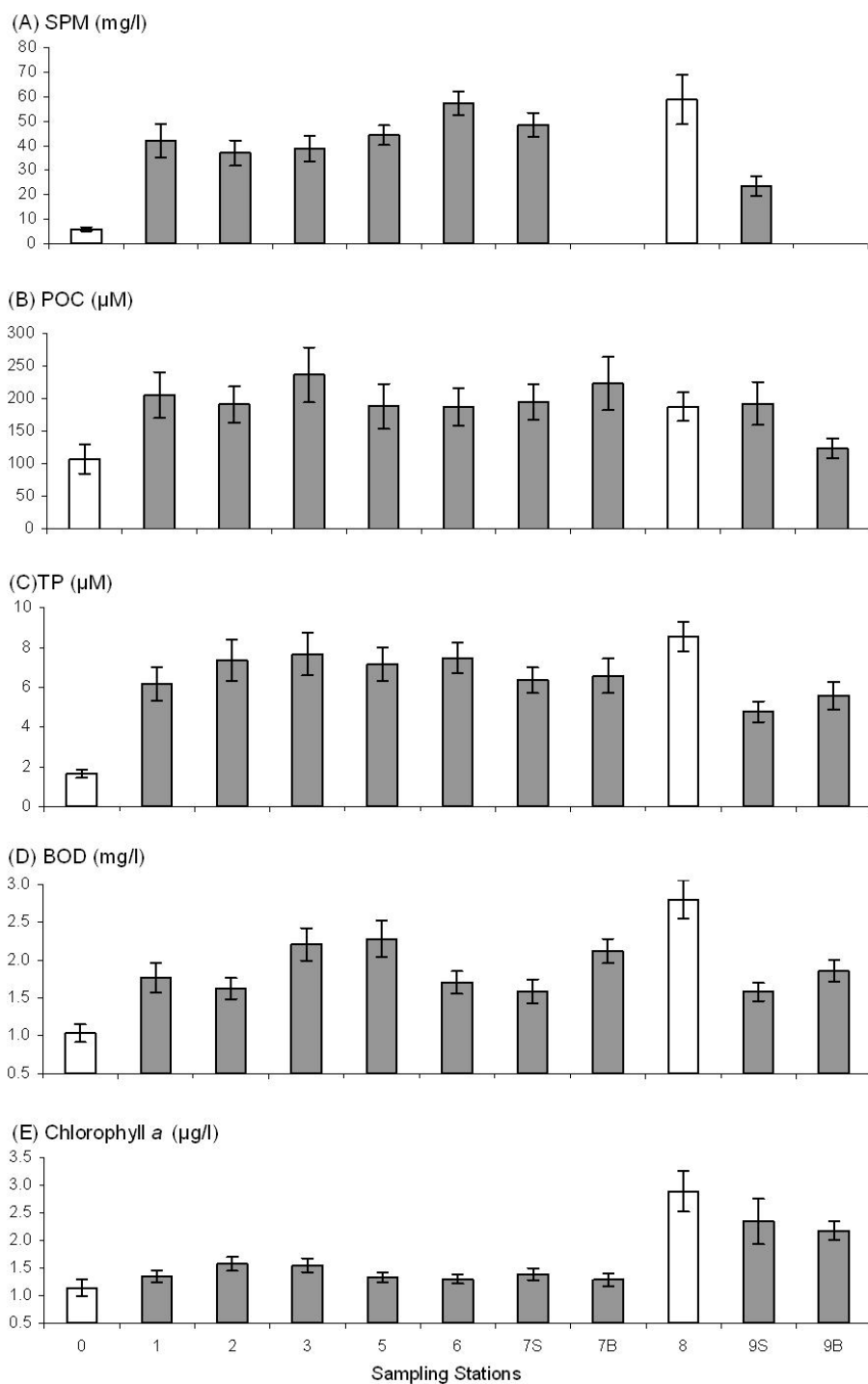
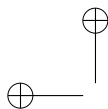


Fig. 5. Spatial variation of (A) particulate matter in suspension (SPM), (B) particulate organic carbon (POC), (C) total phosphorous



partments. Finally, the subgroup comprised of stations #7 and #7F was termed the Middle Estuary compartment. The subgroups formed by the cluster analysis are shown in Table V and Figure 6. The denominations Upper, Middle and Lower Estuary are in accordance with those proposed by Schettini (2002a) based on the distribution of salinity in the estuary. The main characteristics are shown in Table IV.

Ordering analysis

The principal components analysis (PCA) was applied to the same data matrix as that used in the cluster analysis. The factorial axes were calculated based on Pearson's r correlation matrix among the variables. The first two factorial axes of the ordering were interpreted, which explains 77% of the total variance of the data. The plane formed by factorial axes 1 and 2 showing the ordering of the variables is shown in Figure 7 (mode R). The ordering of the samples (mode Q) is shown in Figure 8.

• *Axis 1*

The first component was formed by the positive coordinates of the variables dissolved oxygen (in concentration and saturation) and pH. At the negative extremity, there are the variables TDP, TOP and TP, temperature, SPM, NH_4^+ , NO_2^+ , BOD, POC and Si.

The distribution of the samples along axis 1 corroborated the result of the cluster analysis, which discriminates station #0 at the positive extremity of the axis from the others. Stations #1, #2 and #9F were also at the positive end, but closer to the center. Station #8 was at the negative end, located in the Itajaí-Mirim River, together with stations #3, #5, #6, #7 and #7F, which were also at the negative end, close to the center.

This first axis shows the main difference in characteristics of station #0 in relation to the other collection stations of the study. It also reflects the variation in water quality throughout the estuary, with station #0 being presented by the high levels of dissolved oxygen and the lower values for organic matter (TOP, BOD, POC), particulate matter (SPM, TP) and nutrients and lower temperatures. In contrast, station #8 (Itajaí-Mirim River)

• *Axis 2*

The second axis was positively linked to salinity, pH, chlorophyll, nitrite, ammonium and N:P ratio. Dissolved oxygen, phosphate, nitrate and Si were at the negative extremity.

Concerning the collection stations, the structure seen in the cluster analysis once again repeated itself, with the stations at the fluvial extremity of the Itajaí River (#1 and #2) and Upper Estuary (#3, #5 e #6) being at the negative side of the axis. The stations of the Middle Estuary (station #7 and #7F), Itajaí-Mirim (station #8) and Lower Estuary were on the positive side. The axis is, therefore, reflected in the gradual influence of salinity the closer the stations were to the mouth of the estuary, with an increase in salinity, pH and chlorophyll-a, and a decrease in Si, nitrate and phosphate. By contrast, the ammonium and nitrate tended to increase in the Lower Estuary and Itajaí Mirim River, remaining on the positive side of the axis.

DISCUSSION

The influence of the seawater on the distribution of nutrients and organic matter in estuarine and coastal systems generally results in a decrease in the concentrations of these compounds as the salinity increases (Gago et al. 2005, Pereira Filho et al. 2001, 2002, Schettini et al. 2000, Cabeçadas et al. 1999, Morris et al. 1995). This decrease may be conservative due to the dilution (when it occurs in a form that is linearly proportional to the increase in salinity), or non-conservative (when the decrease does not linearly follow the increase in salinity). The standard of variation occurs because the origin of these compounds, whether natural or anthropogenic, is generally associated with the drainage basin. However, this standard can be modified if there is significant anthropogenic inflow throughout the salinity gradient due to activities carried out in the surroundings of the water body. The non-passive use of the land (agriculture, urbanization) in the areas near the water bodies results in increases in the entry of particulate and dissolved matter to the system and, therefore, in the decrease of quality of



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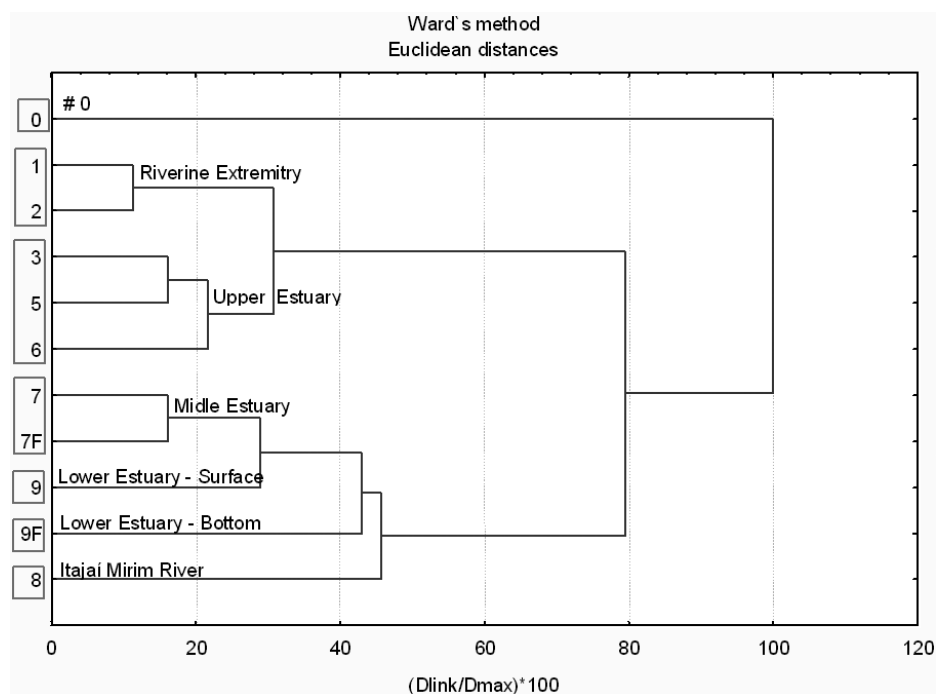


Fig. 6 – Dendrogram showing the clusters formed based on the cluster analysis carried out on the measurements of variables in each station, in the Itajaí-Açú River estuary. The clustered stations correspond to the compartments of the estuary, from its fluvial extremity (station #0, in the municipal district of Indaial (station 1), to the river mouth (station 9). The station #0 was also included.

studied area is still native forest, it is concentrated mainly in the higher regions of the basin. The main activities of anthropogenic influence and with greatest potential impact, such as urban development and agriculture, are concentrated mainly on the banks of Itajaí River and estuary. The urban areas include the regions of Blumenau and Gaspar, in the region of the Upper Estuary and Itajaí and Navegantes, at the river mouth (Fig. 1).

The standard of spatial variation for the variables, which are indicative of water quality, reflected the influence of the activities carried out in the surroundings, in particular urban development, as well as the marine influence at the estuarine extremity of the system. The Itajaí estuary is a stratified system of saline intrusion type (Schettini et al. 1996), such that seawater penetrates from the bottom and forms the saline intrusion. During the period of the study, the direct influence of seawater was observed up to station #7, about 17 km

the mouth. In the following station (station #6), 36 km from the mouth, no influence of salinity was observed, with the presence of freshwater throughout the study (Fig. 2A). Thus, an initial distinction can be made for the studied system, with stations #0, #1, #2, #3, #5 and #6 presenting only river water, and stations #7, #8 and #9 suffering from the effect of the mixture of seawater and freshwater. It is important to emphasize that the stations #1, #2, #3, #5, #6, #7 and #9 were located along the main flow of the estuary. Station #0 is a fluvial station sampled only as a reference station, which means a blank point, as it evaluates the quality of river water in a site that suffers little impact. Station #8 is located in the Itajaí Mirim River, which is the main tributary of the estuary and flows out into the main channel between stations #7 and #9 (Fig. 1). In general, the nutrient concentrations in this paper are in the range of another subtropical estuarine systems in the

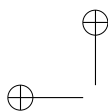
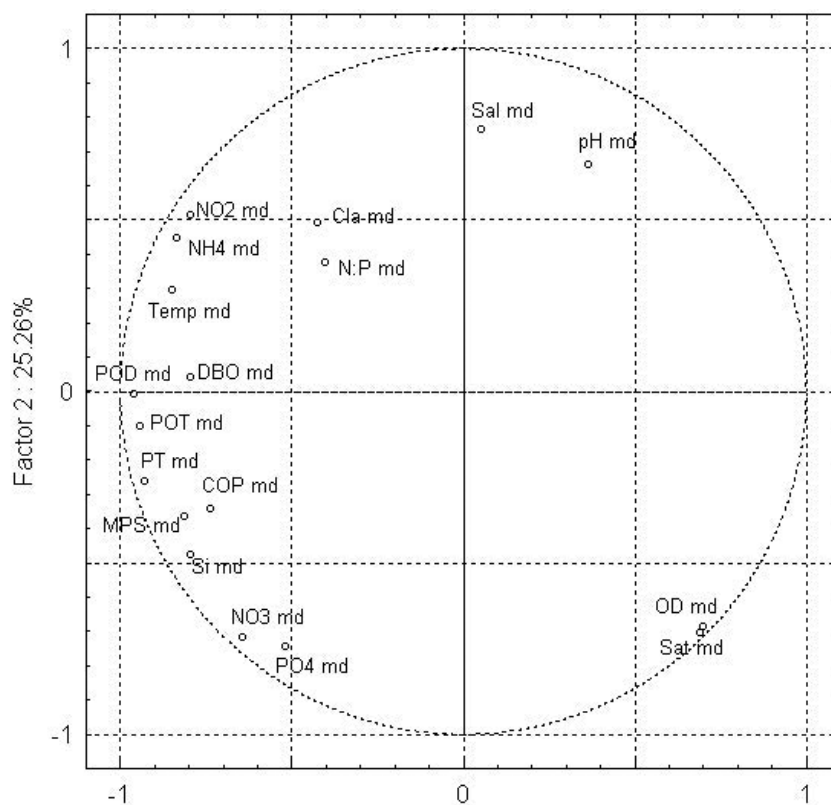


TABLE V
Main characteristics of the individual compartments by cluster analysis, and the stations included in each compartment.

Sampling stations	Names	Characteristics
Blank Point	#0	<ul style="list-style-type: none"> • High levels of dissolved oxygen. • Low concentrations of nutrients, organic matter, SPM and Chlorophyll-a
Riverine	#1 and #2	<ul style="list-style-type: none"> • Low pH and Chlorophyll-a.
Extremity		<ul style="list-style-type: none"> • High concentrations of nitrate, phosphate, silicate and SPM.
Higher Estuary	#3, #5 and #6	
Middle Estuary	#7 and #7F	<ul style="list-style-type: none"> • Influence of salinity. • High pH.
Lower Estuary – Surface	#9	<ul style="list-style-type: none"> • High concentrations of chlorophyll-a, ammonium and nitrite.
Lower Estuary – Botom	#9F	
Itajaí-Mirim River	#8	<ul style="list-style-type: none"> • Low concentrations of dissolved oxygen.





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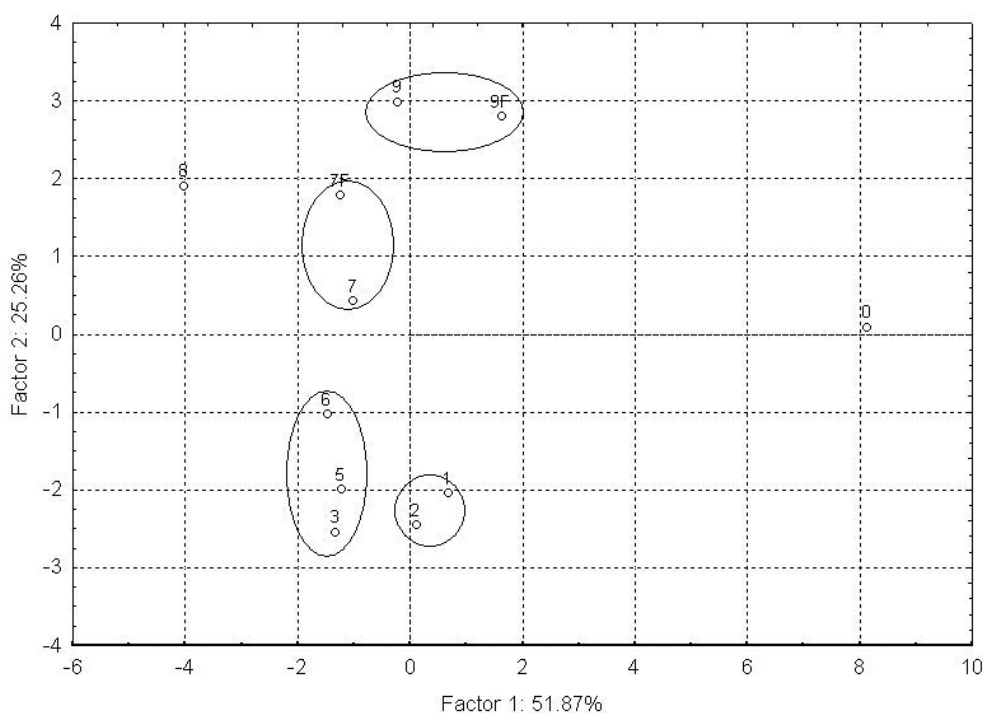


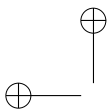
Fig. 8 – Plane formed by axes 1 and 2 of the PCA carried out on the spatial averages, showing the sampling stations (mode Q). The ellipses illustrate the associations found in the cluster analysis.

TABLE VI
Nutrient concentrations in subtropical estuarine systems.

Variable	Itajaí River Estuary	Camboriú River Estuary (Santa Catarina, Brazil)	Delta of San Francisco Bay (USA)	Tweed Estuary (UK)	Danshuei Estuary (Taiwan)	Estuary of Tantsui River (Taiwan)
	This study	Pereira Filho et al. (2001, 2002)	Smith and Hollibaugh (2006)	Uncles et al. (2003)	Wen et al. (2008)	Wu and Chou (2003)
NH_4^+ (μM)	6.7–33.1	2.4–66.2	–	–	10–1000	10–270
NO_2^- (μM)	0.2–2.2	0.2–1.8	–	0.4–2.5	–	–
NO_3^- (μM)	22.9–56.8	0.4–6.5	–	35–370	–	25–45
DIN (μM)	30.5–77.0	3.9–73.9	14–53	–	–	–
PO_4^{3-} (μM)	0.9–2.1	0.13–3.3	1.3–4.5	0.5–3.5	0.1–37	0.5–9.5
H_4SiO_4 (μM)	50.2–121	14.7–210	–	11–100	2–300	10–175

the compartmentalization of the system. The first trend shown was the separation of station #0 from all the others. This trend is reflected in the level of occupation of the region surrounding this environment by vari-

ues of dissolved oxygen (Fig. 2D) and the lower concentrations of nutrients (Figs. 3 and 4), SPM (F and organic compounds (Figs. 5B, C and D) of stations in the study.



salinity (#7, #8 and #9). The river stations were marked by high concentrations of nitrate and phosphate (Figs. 3A and 4A). Considering the river environment, stations #1 and #2, which correspond to the extremity of the system (the towns of Indaial and Blumenau), were separated from stations #3, #5 and #6 (the towns of Blumenau, Gaspar and Ilhota). The urban center of Blumenau is among these compartments, which is cut through by the Itajaí River. This separation, therefore, reflects the influence of the town of Blumenau on the chemical composition of the water. In this section of the river, increases were observed in concentrations of organic matter, which were indicated by the POC and BOD (Figs. 5B and D) and ammonium and phosphate (Figs. 3C and 4A), with all of them indicating the recent entry of wastewater.

The town of Blumenau is one of the most important and populous towns in Santa Catarina and, like almost all the state, does not have a system for collecting and treating domestic waste. This increase in the indicators for organic matter, ammonium and phosphate reflects this precarious situation. Besides the influence of wastewater, the surface flow of urban areas also shows a correlation between the deterioration of the water quality of the rivers and estuaries (Jeng et al. 2005, Crabill et al. 1999). A gradual decrease in dissolved oxygen was also observed (Fig. 2D) from station #3 up to the mouth of the estuary, which indicates an increase in its consumption to oxidize the organic matter.

The following group, which is comprised of stations #3, #5 and #6, was called the Upper Estuary and corresponds to the portion of estuary that is not directly influenced by salinity, but is subject to the variation of water level due to the tidal wave. Besides the municipal district of Blumenau, this compartment also includes the municipal districts of Gaspar and Ilhota. In both, agriculture extends over a large area, particularly over the area covered by irrigated rice farming along the banks of the estuary and to the rural part of the municipal district of Itajaí. This region is marked by the almost complete absence of shoreline fringe forest in practically the entire area (Rörig 2005), which, together with the agricul-

suffers the influence of salinity, which corresponds to the Middle and Lower Estuary of the Itajaí and Itajaí-Mirim Rivers, respectively (Fig. 6). This region was marked by the decrease in phosphate (Fig. 4A) and nitrate (Fig. 3A), and an increase in ammonium (Fig. 3C) and nitrite (Fig. 3B). This standard variation is associated with the combined effect of the increased influence of the seawater close to the mouth, and the passage of the estuary through the towns of Itajaí and Navegantes. An increase in chlorophyll-a was also observed in station #9, which corresponds to the mouth of the estuary (Fig. 5E) and is the only station that presented significant values for this variable. The increase in salinity reflects the increase in the influence of seawater on the system as a result of saline intrusion. As the seawater represents low concentrations of nutrients and organic matter compared with the fresh water, it causes the concentrations of these substances to become diluted. Thus, with the increase in salinity, a decrease in the concentrations of these substances would be expected. This fact occurred for the nitrate and phosphate. Nitrate represents the more oxidized form of dissolved inorganic nitrogen (DIN). It is formed by the oxidation of ammonium into nitrite and, finally, nitrate through nitrification (Wada and Hattori 2000). Its presence in the water is an indication of a non-recent entry to the system, and is probably associated with the continental drainage and the effect of diffuse entries through surface drainage. Its decrease at the extremity of the estuary can, therefore, be explained by the dilution by the seawater.

The origin of the phosphorus is related to the hardening of the Earth's crust, and is transported in particulate and dissolved forms by the waters of the river (Aston 1980). It may also come from the entry of domestic sewage and industrial wastewater, and from its use in agriculture. The increase in anthropogenic entries of phosphorus generally results in an increase in phosphate, which is the dissolved inorganic fraction, (Meybeck 1982). However, these increases may be hidden by the interaction of phosphate with particulate matter due to the absorption trend of the phosphate, which is a mechanism that “buffers” the phosphate concentrations



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plankton assimilation, which results in reduced concentrations of phosphate when the chlorophyll-a concentrations are high (Lebo and Sharp 1993). The decrease in phosphate in the Middle and Lower Estuary is, therefore, related to the combined effect of the dilution caused by the entry of coastal water to the estuary. The latter is associated with the effect of the phytoplankton assimilation in the Lower Estuary, which is the only region that has significant values of chlorophyll-a. Data on primary productivity of the Lower Estuary suggest that the phosphate acts as a limiting factor on the biological production in the limit region of the estuarine plume and coastal region in situations of lower river discharge (Pereira Filho et al. 2009).

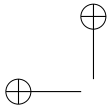
Despite the decrease in nitrate and phosphate, ammonium and nitrite present an increase in the area surrounding the mouth of the estuary, as reported in a previous study (Pereira Filho et al. 2003). This increase reflects the influence of the passage of Itajaí Mirim River, by the municipal districts of Itajaí and Navegantes on the chemical composition of the estuarine water. Together, the population of both towns is over 200.000 inhabitants. None of them has a system of collection and treatment of domestic waste, which results in high levels of ammonium in the system. The towns of Itajaí and Navegantes also have the largest fishing port in Brazil (Gep 2001). A significant amount of the fish is processed by the some plants that are spread along the banks of the estuary, which totals about 66 registered plants in the region (Gep 2001). The fish processing results in the release of wastewater that typically contains high concentrations of N, particularly in the form of ammonium (Unep 2001), as well as phosphorous and other organic compounds. Thus, the effect of the entry of seawater in the estuary, which tends to reduce the ammonium concentrations by dilution, is insufficient to reduce the concentrations of this nutrient in the system, which suggests that the levels of ammonium and/or organic matter transported into the system is very high. The increase in nitrite is constant with the increase in ammonium, which results in nitrification in the estuary. The variation in the different forms of DIN resulted in

havior. Given that its origin is related to the leaching of the Earth's crust, Si generally presents a variation related to the increase in the level of exposure to soil. However, its distribution did not demonstrate a clear relation by evaluating the averages for each station (Fig. 4B). The average concentrations of Si were relatively constant throughout the estuary, despite the increase in agriculture activity in the region surrounding stations #5, #6 and #7.

The Itajaí-Mirim River (station #8) should be highlighted. Its confluence with the estuary is very close to the river mouth (Fig. 1). This river presents the most altered chemical conditions of all the evaluated stations, as shown by the higher concentrations of nitrite, ammonium, SPM, total and organic phosphorus and BOD (Figs. 3, 4 and 5). This tributary can be considered another source of negative influence on the quality of the Itajaí River estuary. These changes in the characteristics of the Itajaí Mirim River are related to the fact that it receives all the influence from the city of Brusque, which is another important urban center of the state, and also because it receives the drainage from extensive farming areas.

This variation trend was corroborated by the principal component analysis carried out on the spatial data. The distribution of the variables along the first axis (Fig. 7) showed the association among variables that indicate the presence of organic and particulate matter (TOP, DOP, TP, POC, SPM and BOD) and were positioned at the negative extremity of the axis. The nutrients were also positioned on the negative side. In contrast, dissolved oxygen and pH were at the positive extremity of the axis. This first axis, therefore, reflected the variation in the quality of the water in the system. The second axis showed the salinity and was positioned at the positive extremity, followed by nitrite, chlorophyll-a and ammonium. The opposite extremity was characterized by dissolved oxygen, phosphate and nitrate. The second axis reflected the influence of the seawater in the estuary, in contrast to the freshwater environment.

The understanding of the distribution of the variables was clearer when the distribution of the



at the positive extremity of axis 1. By contrast, station #8 was plotted at the negative extremity. It represents the Itajaí Mirim River, which presented the worst set of values with high concentrations of nutrients and organic matter, and low values of dissolved oxygen. The other stations of the Itajaí estuary were ordered between these 2 extremes, which reflects the variation in limnological conditions due to the activities carried out in the basin. In this context, it is important to note that station #9F, which corresponds to the samples at the bottom of the Lower Estuary, was positioned on the positive side of the axis showing the improvement in the indicators as a result of the entry of the seawater. The second axis showed the separation of the sample stations based on salinity. The stations of the Lower and Middle Estuary of the Itajaí River were positioned at the positive extremity, being influenced by salinity and pH. Stations #1 and #2 were positioned at the opposite extremity, forming the Fluvial Extremity group in the cluster analysis, and stations #3, #5 and #6 correspond to the Upper Estuary.

The spatial characterization of the Itajaí-Açú River estuary showed that the estuary presents a change in the water quality indicators due to the marine influence and the influence of the urban centers. Multivariate analyses show that the system was compartmentalized in two main groups: the portion without direct influence of salinity (#1 to #6) and the stations influenced by salinity (#7 and #9). The region without the influence of salinity showed a decrease in water quality due to the influence of the town of Blumenau, which results in the compartmentalization of stations #1 and #2, located upstream from the town, and #3, #5 and #6, located downstream. In the stations influenced by salinity (#7 and #9), particularly the station closest to the mouth of the estuary (#9), the effect of dispersion/dilution resulted by the entry of the seawater at the extremity of the estuary tended to minimize.

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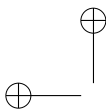
RESUMO

Esse estudo foi realizado com o intuito de avaliar a variação espacial da qualidade de água no Estuário do Rio Itajaí-Açú. Sete estações ao longo do estuário foram monitoradas semanalmente, de outubro de 2003 a dezembro de 2004, além de duas outras estações em tributários (o Rio Itajaí-Mirim, principal tributário e uma estação de referência). Esse monitoramento incluiu medidas de salinidade, pH, oxigênio dissolvido, temperatura, nutrientes (NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} , H_4SiO_4), demanda bioquímica de oxigênio (DBO), fósforo total e fósforo orgânico dissolvido (PT e POD), carbono orgânico particulado (COP), material particulado em suspensão (MPS) e clorofila-a. Análises multivariadas demonstraram a compartimentação do sistema em função da deterioração da influência marinha e da qualidade da água. A ocupação urbana foi o principal fator responsável pela variação especial das variáveis monitoradas, resultando em aumentos dos indicadores de matéria orgânica e uma progressiva diminuição no oxigênio dissolvido. Próximo à desembocadura do estuário, mesmo com o efeito de diluição provocado pela intrusão da água marinha, foi observado aumento nas concentrações de amônio, atribuído à influência de municípios de Itajaí e Navegantes.

Palavras-chave: estuário do Itajaí, nutrientes, matéria orgânica, rio, Santa Catarina.

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