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Hydrochemical Characteristics of the Caravelas River Estuary And Surrounding Seazone, Brazil

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ABSTRACT

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Caravelas river estuary is located in an untouched zone of the Brazilian coast (south of Bahia). This zone has an important ecological role, due to its mangroves and its location, next to Abrolhos coral reef, the most important one in the Southern Atlantic Ocean. Concerning this study, some traditional parameters (temperature, conductivity, salinity) were used to understand the physical properties, as well as some different ones like: dissolved oxygen, turbidity, suspended solids and nutrients (ammonia, nitrate, nitrite and phosphorus), in order to understand the hydrochemical dynamics of this estuary. Two surveys were done (Winter/2000 and Summer/2001) during different tide conditions (falling and rising). The chemical patterns analyzed *in situ*, allowed us to classify such water as "typically coastal" (tropical water from Brazil's stream), influenced by some freshwater. Caravelas estuary behaves like a typical tide channel, influenced by coastal water. The "shallow" coastal water of the Brazilian eastern shelf is typically lack of nutrients (due to the influence of the Brazilian Current) and it receives organic material from small rivers/mangroves systems like Caravelas estuary. During the two surveys, the nutrients' level remained in the same range and with a similar spatial spread. Higher levels were reported on the inner estuary, in both seasons, showing the influence of the mangrove system, and decreased to seaward. The levels reported on the area are typical, and in Caravelas zone the material turbidity has a major role on the fertilization of the surrounding areas.

ADDITIONAL INDEX WORDS: *Estuary; coastal zone; physical characteristics; nutrients.*

INTRODUCTION

Caravelas estuary is located in an untouched zone of the Brazilian coast (south of Bahia). This zone has an important ecological role due to its mangroves and its location, next to Abrolhos coral reef, the most important one in the Southern Atlantic Ocean. The anthropogenic influence is minimum in this region. Rarely human occupation is verified (only a small town Caravelas and Ponta de Areia villa are installed in the drainage basin) and industrial activities are absent. The adjacent coastal zone is characterized by high sedimentation and productivity, and the regional economy is strongly based in shrimp fishery.

Tidal currents drive the estuarine circulation and the mixing of the water is intense because of a tidal range and little fresh water influx. In the studied area, there wasn't any significant continental water input, and according to LEIPE *et al.* (1999), Caravelas estuary behaves like a typical tide channel or as a mangrove creek that is characterized by the lack of major river source but has well-defined tidal drainage system through material exchange between inner waters and coastal zone (KJERFVE *et al.*, 1979 *apud* DAY *et al.,* 1989). According to LESSA (2001), the dynamic pattern of the estuary tends to be well mixed (no vertical gradient of temperature or salinity). The main flux was observed through Barra do Tomba (see Figure 1) and high velocities were measured near the ebb and flood. The ebb currents are the most intensive, mainly during the spring tides. This estuary is characterized by a middle tidal range (max. 3,2m) and asymmetric tide (ebb is more fast than flood because mangroves inundation).

The hydrochemical processes, mainly the nutrients behavior, in estuaries and coastal zones are usually controlled by hydrodynamics, biological and degradational factors. The ecological aspects of these bodies of water are conditioned to a certain extent by the exchange between the continental shelf and the inner waters (SMITH, 1986; VALLE-LEVINSON, 1985 *apud* SIERRA *et al.*, 2002). The effects of human activities usually are felt through various mechanisms and some times it involves increased transfer of nutrients from one environment to another, and unbalance within environments (VALIELA and BOWEN, 2002). The studies carried out usually to investigate the contaminated conditions of the estuaries. In despite of Caravelas estuary being an almost pristine area and the very few Brazilian studies about estuary environments and their hydrochemical properties and water exchange process, this study was developed to provide a background to this region.

This fieldwork was based in some traditional parameters (temperature and salinity) to characterize the physical process, as well as some different ones like: pH, dissolved oxygen, turbidity, suspended solids and nutrients (ammonia, nitrate, nitrite and total nitrogen and phosphorus), in order to understand the physicochemical properties and the exchange between the estuary and the coastal zone. The behavior of these parameters were studied according different seasons and tide situations.

METHODS

Two cruises were done one in August 2000, during the wet season (Winter) and the other in February 2001, during dry season (Summer). A Station grid of 7 sites was covered (Figure 1). Three of them were located on Caravelas estuarine zone, one in "Barra do Tomba" (Caravelas river mouth, where occurs the main water changes on the estuary) and the other three ones were set on the surrounding sea zone (toward the plume dilution). The sampling Stations positions were selected based upon previous knowledge of estuary's hydrography (DHI, 2000 and LESSA, 2001).

Sampling was done in spring tides and in two flow situations (flood and ebb), and in only one profundity (1m of the surface) due to the absence of vertical density gradients (tidal mixing is intense).

The parameters temperature, salinity, conductivity, pH and dissolved oxygen were determined *in situ* through one multiparametric probe (*Hydrolab Surveyor 3*). The Hydrolab is a probe, which can measure temperatures between 5°C and 50°C (accuracy of ±0.10°C), salinity between 0 and 70 psu (accuracy of 1%), pH between 0 and 14 (accuracy of ±0.2) and dissolved

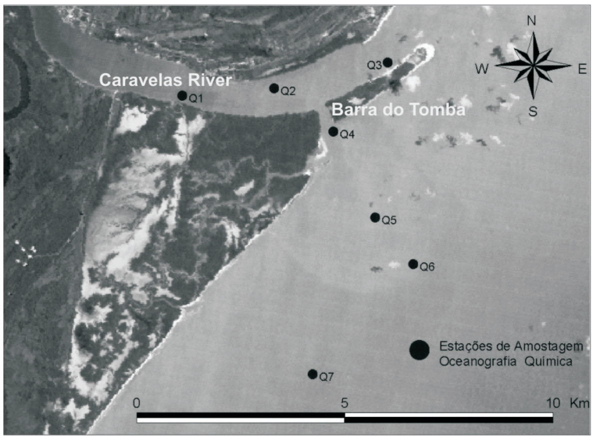

Figure 1. Location of the Caravelas Estuarine System. Alpha-numerals (Qn) indicate the sampling position (source: LANDIM, 2001). Through "Barra do Tomba" (bar oppened in the 60`s) occurs the main material exchange between inner estuary and costal zone.

oxygen between 0 and 50 mg/L (accuracy ±0.2 mg/L). Water samples for laboratorial analysis were collected with an oceanographic bottle (*Niskin*). The samples were packed in previously treated polyethylene flasks and frozen. After collection, the water samples were filtered immediately (0.45µm pore size cellulose filters).

Nutrients (NO_3, NO_2, NH_4 and Total Dissolved Nitrogen TDN and Phosphorous-TDP) were determined in the laboratory according to the methods described in GRASSHOFF *et al.* (1983) and AMINOT and CHAUSSEPIED (1983). The analytic procedure for Total Solids Suspenses-TSS follow the methods recommended by AMINOT and CHAUSSEPIED (1983).

To determine the temporal and spatial differences in nutrient concentrations and physical properties of waters was used paired *Student's t* test.

RESULTS

Physical Characteristics

Values of temperature and salinity measured along the Caravelas estuary and adjacent coastal are shown in Table 1.

During the winter the temperatures were lower, ranging from 22.83 °C to 23.68 °C, against 29.25 °C to 30.78 °C measured during the summer. Spatially none important differences were observed. The low ranges verified result from solar heating conditions range along the day.

Salinity ranged between 29.0 psu and 34.5 psu during the winter and from 36.8 psu to 38.0 psu during the summer. Once more time the seasonality was well defined.

Salinity values at the internal estuary evidence a relatively low freshwater influence. Only during the winter (wet season) and during the ebb flow salinity increases from about 29.0 psu in the internal estuary to about 34.5 psu at the coastal zone.

Total Suspended Solids, pH and Dissolved Oxigen

High values of TSS were observed during the winter associated to rainy season and wind stress more effective, that are favorable to influx of suspended solids through the rivers and to resuspension of the sediments by waves, respectively. The TSS ranged from 38.1 $mg.L^{-1}$ to 48.0 $mg.L^{-1}$ (Table 2). During the summer, the values of the TSS ranged from 2,7 $mg.L^{-1}$ to 15.7 $mg.L^{-1}$ (Table 2).

None spatial distribution pattern was observed during the winter, but during the summer the TSS increases towards the inner coast and estuary. The lower values were observed towards the oceanic region (i.e. Stations Q6 and Q7).

The pH values were typical of seawater. Nevertheless, pH

Table 1. *Temperature and Salinity in surface water during Winter (August, 2000) and Summer (February, 2001).*

	WINTER			
	Temperature (°C)		Salinity (psu)	
	Ebb	Flood	Ebb	Flood
Q1	23.00	23.38	29.0	32.8
Q2	23.10	23.50	31.0	33.0
Q3	22.99	23.64	33.6	33.6
Q4	23.07	23.68	32.8	33.6
Q5	23.05	22.83	33.2	34.2
Q6	22.95	23.08	34.0	34.5
Q7	23.13	22.98	34.0	34.3
Mean	**23.04**	**23.30**	**32.5**	**33.7**
S.D.	**0.06**	**0.34**	**1.86**	**0.65**
	SUMMER			
	Temperature (°C)		Salinity (psu)	
	Ebb	Flood	Ebb	Flood
Q1	29.34	30.78	37.5	36.8
Q2	29.34	30.62	37.5	37.4
Q3	29.30	30.50	37.5	37.7
Q4	29.51	29.85	37.2	38.0
Q5	29.51	30.01	37.6	37.8
Q6	29.33	29.25	37.8	38.0
Q7	29.67	29.59	37.7	38.0
Mean	**29.43**	**30.09**	**37.5**	**37.7**
S.D.	**0.14**	**0.57**	**0.19**	**0.44**

decreased from coast to internal estuary, showing a lack of freshwater influence. The pH values ranged from about 8.13 (i.e. Station Q7) to 7.50 (i.e. Station Q1) (Table 2).

The similar spatial distribution was observed to Dissolved Oxygen - DO, with the lowest values at the internal estuary. In general, the whole waters were well oxygenated. The mean values were 6.5 $mg.L^{-1}$ (± 0.5) to estuary and , 7.2 $mg.L^{-1}$ (± 0.4) to coastal zone. O_2 saturation levels ranged from around 99.4% (± 8.8) at the estuary to 109,7% (± 7.8) along the coast. The lowest values were measured at Station Q1 during ebb flow (Table 2).

Both pH and DO showed seasonal tendency, with the highest values of pH had been observed during the summer against the dissolved oxygen that had highest values during the winter.

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Nutrients

The ranges for our whole nutrient data set were: 1.3-6.8 µM for TDP; 52.1-97.1 µM for TDN; 3.3-8.1 µM for N-NH_4; 0.7-2.9 µM for N-NO_2 and 2.6-32.1 for N-NO_3 (Table 2).

In general, nutrient concentrations presented higher values towards the internal estuary (Stations Q1, Q2 and Q3), which decreased towards the coastal zone (Stations Q5, Q6 and Q7). The mean values along these different systems ranged from 3.9 µM to 2.3 µM to TDP; from 81.01 µM to 61.85 µM to TDN and from 20.6 µM to 10.4 µM to Total Inorganic Dissolved Nitrogen - TIDN (NH_4 + NO_2 + NO_3), respectively.

There was no clear seasonal pattern of nutrient concentrations.

DISCUSSION

The Caravelas estuary is just governed by oceanic waters with lack of freshwater contribution, as suggested by temperature and salinity data. As observed by LEIPE *et al.* (1999), the tropical waters of the Brazil Current dominated the entire region. At the sea zone, according LESSA and CIRANO (2003) a frequency distribution of the residual current directions shows a strong bimodal distribution. Southwestward flows (220°-260°) occurred during more than 73% of the time (mean velocity of 16 $cm.s^{-1}$), while northeastward flows occurred during 19% of the time (mean velocity of 18 $cm.s^{-1}$). The remaining 8% part of the time was attributed to transitory stages of the flow.

Table 2. *Values of the parameters measured in the Caravelas River estuary and adjacent coastal zone during Winter (August, 2000) and Summer (February, 2001).*

WINTER 2000	Ebb							Flood						
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q1	Q2	Q3	Q4	Q5	Q6	Q7
pH	7.50	7.61	7.94	7.95	7.96	8.01	8.02	7.83	7.87	7.89	7.93	8.00	8.05	8.06
Dissolved Oxygen (mg.L^{-1})	5.56	6.31	7.26	7.37	7.06	7.61	7.87	7.25	6.95	7.11	7.23	7.07	7.36	7.37
Oxygen Saturation (%)	76.8	88.1	103.3	104.2	99.9	108.3	111.9	103.6	99.0	102.6	104.3	100.6	104.8	104.8
Suspended Solids (mg.L^{-1})	40.3	46.1	44.8	42.1	45.3	42.0	41.0	42.4	38.2	41.7	48.0	41.0	38.1	44.3
Total Phosphorus (μM)	3.9	3.5	5.5	4.8	3.5	3.5	2.3	1.9	2.6	6.8	6.1	2.6	2.6	1.9
Total Nitrogen (ìM)	97.1	87.9	61.4	82.1	90.7	70.0	68.6	74.3	79.3	87.1	70.0	69.3	62.9	55.7
Nitrate (ìM)	19.3	10.7	2.6	8.6	3.6	5.7	4.3	32.1	13.6	4.3	6.4	4.3	6.4	5.7
Nitrite (ìM)	2.1	2.9	2.9	2.1	1.4	1.4	1.4	1.4	2.1	1.4	1.4	1.4	1.4	0.7
Ammonium (ìM)	6.0	4.9	6.0	4.6	5.6	4.6	3.9	5.1	4.6	5.1	4.1	4.3	3.7	3.3

SUMMER 2001	Ebb							Flood						
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q1	Q2	Q3	Q4	Q5	Q6	Q7
pH	7.93	7.96	8.00	7.98	8.00	8.06	8.07	7.88	8.01	8.06	8.10	8.12	8.11	8.13
Dissolved Oxygen (mg.L^{-1})	6.21	6.06	6.27	6.01	6.31	6.76	6.74	6.07	6.31	6.61	7.05	7.23	7.46	7.38
Oxygen Saturation (%)	101.6	99.0	102.3	98.6	102.7	109.9	110.6	101.2	105.2	110.2	116.3	119.3	122.1	121.5
Suspended Solids (mg.L^{-1})	7.4	15.7	7.2	6.8	5.6	3.3	2.9	6.8	12.2	6.4	5.7	4.4	2.8	2.7
Total Phosphorus (ìM)	3.5	5.2	4.2	2.9	2.9	1.9	1.6	2.6	3.9	2.9	2.3	1.9	1.6	1.3
Total Nitrogen (ìM)	70.0	94.3	83.6	59.3	56.4	55.0	52.9	68.6	87.1	81.4	57.9	55.0	53.6	52.1
Nitrate (ìM)	11.4	18.6	8.6	7.1	5.7	6.4	5.7	10.0	15.7	7.9	5.7	5.0	5.7	5.0
Nitrite (ìM)	2.1	2.9	2.1	1.4	1.4	0.7	0.7	1.4	2.1	1.4	0.7	0.7	0.7	0.7
Ammonium (ìM)	5.6	8.1	5.4	5.5	4.7	3.6	3.4	4.6	6.7	5.1	5.2	4.6	3.4	3.3

High values of TSS were observed during the winter when the meteo-oceanographic conditions are more intense.

The influx of fluvial sediments is insignificant, due the lack of continental water bodies in the region. The satellite imagery (Figure 2) shows the importance of resuspension of bottom sediments on the coastal zone. According LANDIM (in CEPEMAR, 2001) the imagery shows that the main source of suspended solids presents on the coastal zone of this region is associated to: (i) influx from estuaries and mangroves, (ii) fine sediments from coastal line erosion, mainly between Ponta do catoeiro and Barra do Tomba, (iii) fine sediments Resuspended by waves action on the shallow waters, and (iv) fine sediments resuspended by currents. So the measures obtained in this study show what can be observed in the satellite imagery, that coastal waters, main during the winter, can have high autochthonous suspended solids.

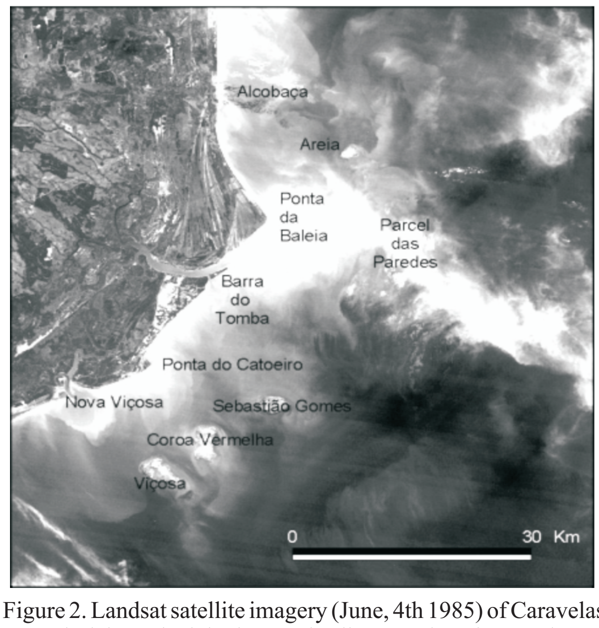

Figure 2. Landsat satellite imagery (June, 4th 1985) of Caravelas coastal plain and of the inner Abrolhos coral reefs complex. A great quantity of material in suspension can be observed in this region. The dispersion of material in suspension plume southward (S-SW) can be observed too. (Source: modified from LANDIM in CEPEMAR, 2001).

Regarding pluvial data, the year of 2000 was considered atypical in Brazil, with a reduction in the rainfalls regime that could affect the estuarine systems, and during the dry season (summer) the river flux is naturally minor. It was determinant to no observed nutrients values differences.

Except for ebb flow water during the winter at Stations Q1 and Q2 (in the estuary), in general the whole of the area studied was saturated with respect to dissolved oxygen. The average of O2 saturation percentage is about 100%, what is linked to what MEDEIROS *et al.* (1999) and OVALLE *et al.* (1999) have said during studies carried in similar areas and conditions. By the high oxygen saturation index in the stations Q5, Q6 and Q7 (± 120%), it is possible to infer that these locations are highly dominated by the phytoplankton activity (CRUZADO, 2002), which together to the salinity data indicate a process of nutrients removal along the researched sample period. In the Figures 3 and 4 it is possible to notice the tendency of all nutrients concentration flowing off to the seashore zone.

The "shallow" coastal waters, of the Brazilian eastern shelf are typically lacks nutrients (due to the Brazil Current influence) and receive organic material from small rivers/mangroves systems like Caravelas' estuary. This influence from the mangroves is noticed normally in shallow zones (<10m) (OVALLE *et al.*, 1999).

Along the Caravelas river there is a large mangrove area, which supply the adjacent waters of the estuary and coastal zone with N and P. According OVALLE *et al.* (1999) were observed high values of DOP and DON in the Caravelas mangrove systems.

The variations of total dissolved phosphorus concentrations seem to be related by the effect of the salt-water dilution, followed by the process of biological assimilation. In the Table 2 it is perceived that in the stations Q5, Q6 and Q7, the values had been lower than the ones at inner estuarine zone, indicating the intense phosphorus consumed by the phytoplankton. The operating processes in the entry of phosphorus in the system

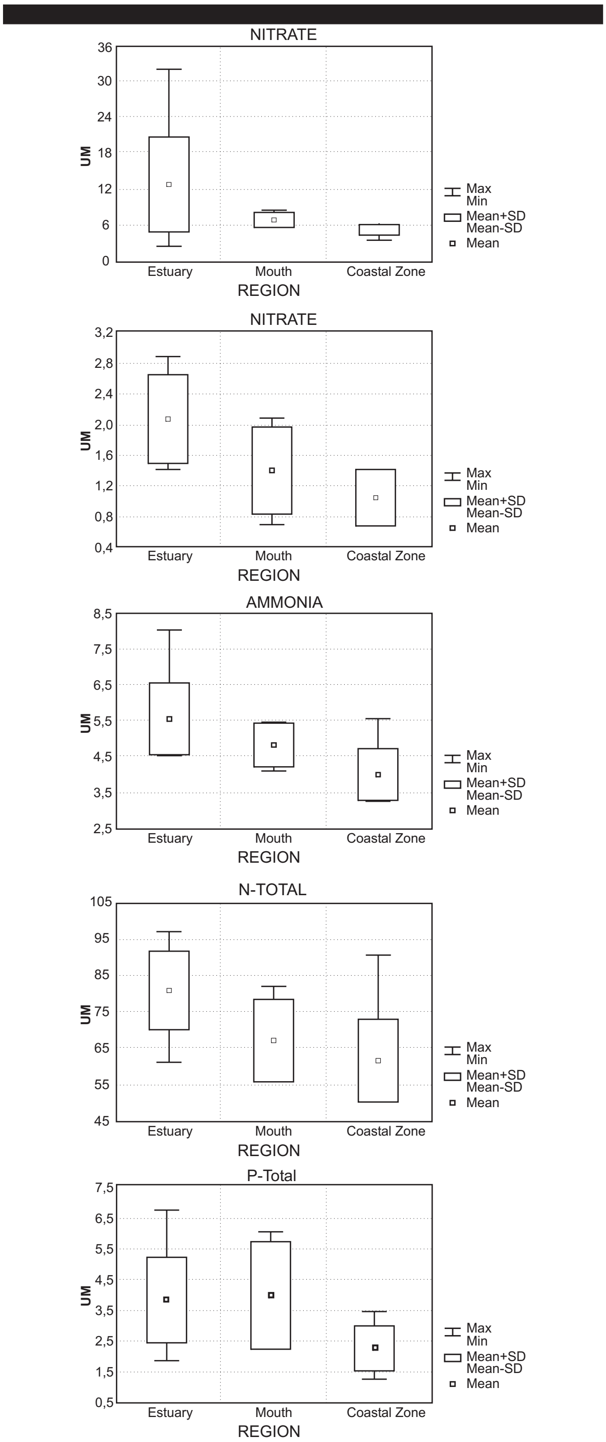

Figure 3. Spatial distribution of the NO_3, NO_2, NH_4, TDN and TDP between Caravelas estuary and adjacent coastal zone, during August, 2000 and February, 2001. Box plots with mean, standard deviation and minimum and maximum values.

would be the adsorption/desorption of the matter in suspension with the oxidation of the organic substance and the resuspension of the sediment due to the tides and winds, as verified in several estuaries of the world, like the estuary of the Amazons River, of the Sepik River, in New Guinea, of the Moresby River, in Australia and of the Paraíba do Sul River (BERNER and RAO, 1994; FOX, 1990; EYRE, 1994; KRÜGER, 2003). The phosphorous values measured in the present study are lower of other studies developed in tropical estuarine systems of Brazil like the Vitória Bay (ES), 10 21µM (STERZA, 2002), Camburiú River estuary (SC) 12 149µM (PEREIRA-FILHO *et al.*, 2001) with relative antropogenic influence (domestic sewage and fertilizers, but higher than Paraiba do Sul River estuary, 0,19 - 4,14µM probably suggesting the strong

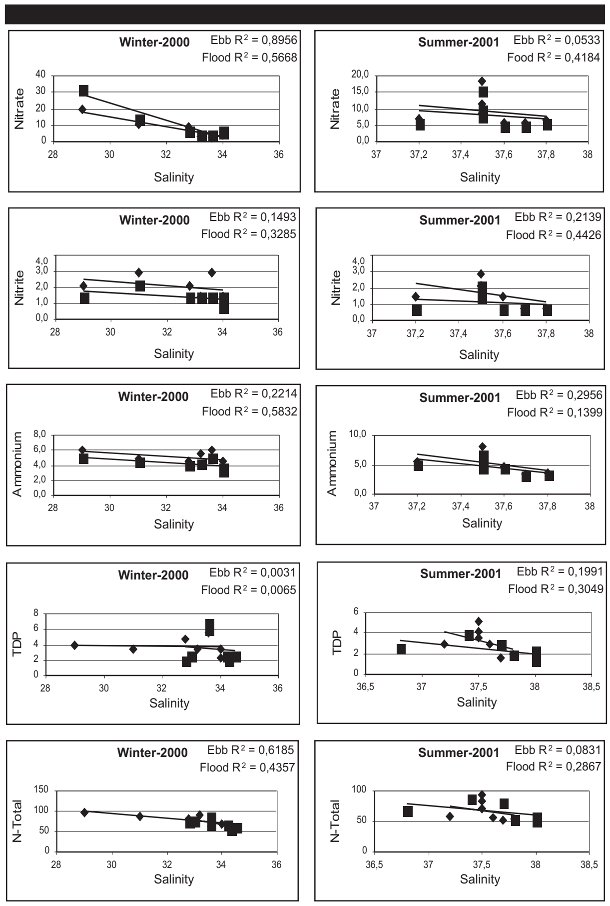

Figure 4. Plots of NO_3, NO_2, NH_4, TDN and TDP against salinity in August 2000 and February 2001 at surface. Filled diamonds denote ebb flow and filled square denote flood flow.

local productivity.

The values of the nitrogenous series had followed the same pattern values had diminished when salinity increased (Figure 3 and 4). Despite it is a well oxygenated area, the levels of ammonia can be associate to the processes of nitrate-reduction and ammonification in the superficial layers of the sediments of the stations Q1 and Q2, where the decay of OD is useful as an indicative of the organic matter oxidation in the estuary (CARNEIRO, 1998). Different of other systems, which nitrogen is directly associate to the fluvial level, in the estuary of Caravelas the physical parameters of the resuspension of the sediments and the advection of the denser waters to the surface have being shown as the main responsible for the dynamic of the nitrogen, together with the biological activity. Many authors have been suggested that dissolved P and N transport from mangrove systems to adjacent coastal waters to occur largely in organic form (OVALLE *et al.*, 1999). The TDN and TDIN obtained here confirm this tendency, and probably the coastal waters have been supported with nutrients and organic matter through the Caravelas river system. The TDN behavior, as well as the concentration range follows other studies previously developed in others estuaries, 80,2 µM in the Paraiba do Sul River estuary (KRÜGER, 2003; CARNEIRO, 1998) and 97,2 µM in Vitória Bay (STERZA, 2002).

Considering the concentration of the nutrients, the results indicate that the region has more ammonia; nitrate and nitrite than in other estuaries that are considered not polluted and even of some with certain degree of pollution, like Piraquê-Açú estuary and Barra do Riacho and Cabrália Coastal zone and Espírito Santo Bay (CEPEMAR, 1993; CEPEMAR, 1999; OVALLE *et al.*, 1999; CEPEMAR, 1995) and some others more polluted, like Camboriú and Paraíba do Sul estuary and Vitória Bay (PEREIRA-FILHO *et al.*, 2001; KRÜGER, 2003; STERZA, 2002). LEIPE *et al*. (1999) also found higher levels on the inner area of Caravelas' channel mangrove, which decreased while flowing to the sea. The levels reported on the area are typical, and in Caravelas' zone the material turbidity has a major role on the fertilization of the surrounding areas.

CONCLUSIONS

Nutrients from Caravelas estuary and adjacent coastal zone have been described in this study. As in other tropical estuaries, the water temperature is not seasonally dependent and the mixing processes are driven by changes in rainfall that may change the riverine discharge. However, the riverine discharge to the Caravelas estuary is much smaller than in the others rivers and the own physiography provide an area for phytoplancton production and sinking of organic matter. Although the wet season (summer) tends to show elevated nutrients concentrations in tropical estuaries, in this study there were no significative differences between concentrations in samples from summer and winter. The highest levels were reported on the inner estuary, showing the influence of the mangrove systems. The relationship between the nutrients and the salinity show a linear dilution of dissolved nutrients with low nitrogen and phosphorus seawater, and the other processes contributions, like biological removal, adsorpition/desorption reaction of the suspended matter and ressuspention can play important roles in controlling the geochemistry of nutrients in the Caravelas estuarine systems.

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