TEMPORAL AND SPATIAL DYNAMICS OF NUTRIENTS AND PARTICULATE SUSPENDED MATTER IN PARANAGUÁ BAY, PR, BRAZIL

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INTRODUCTION

A holistic knowledge of biogenic element cycling in coastal systems requires a quantit ative assessment, in temporal and spatial terms, of masses of these elements in pelagic and benthic compartments and of the fluxes between them and with the adjacent continental and oceanic systems. For these ecosystems, however, some of these key processes and fluxes are poorly known (Walsh, 1988; Wollast, 1993), particularly for the Southern Hemisphere (v. Capellen *et al.*, 1993). In estuarine regions, cyclic as well as aperiodic variations on nutrient input rates affect the magnitude and the synchronization of phytoplanktonic development, increasing or dampening natural fluctuations on primary production rates (Klump and Martens, 1983).

The high levels of primary production rates frequently registered for estuaries, are directly related to increased input of dissolved inorganic nutrients, natural or anthropogenic (Boynton *et al.*, 1982; Mallin *et al.*, 1993; Abreu *et al.*, 1995). Depending on the magnitude of nutrient loading in relation to the capacity of dilution and natural status of nutrients of the receptor water, the effects of the eutrophication may affect resources at all levels of biological organization (Gucinski *et al.*, 1990; Smetack *et al.*,

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1991). A prerequisite for understanding the eutrophication of these systems is an assessment of the factors responsible for regional and long-term variations of nutrients (Wulff *et al.*, 1990). Therefore, information about temporal and spatial dynamics of these constituents are necessary to understand the functioning of these ecosystems and, consequently, for the establishment of an environmental management for these regions.

This study constitutes the first step of a research program, which aims to understand the cycling of biogenic matter in the Paranaguá Bay. It reports on the spatial and temporal dynamics of the physical, chemical and biological structure of the pelagic compartment with emphasis on major sources and sinks of nutrients and suspended particulate matter.

AREA DESCRIPTION

The Bay of Paranaguá (Fig. 1), situated at the South Brazilian coast, Paraná State (25°03' S, 48°24' W), has an area of 456 Km^2, and is surrounded by expanses of mangroves, which constitute a main detritus source for the system (Rebello & Brandini, 1990). The bay's east-west axis constitutes the Bay of Paranaguá proper, to which its oriental portion merges to the Laranjeiras Bay (Fig. 1). The system is connected to

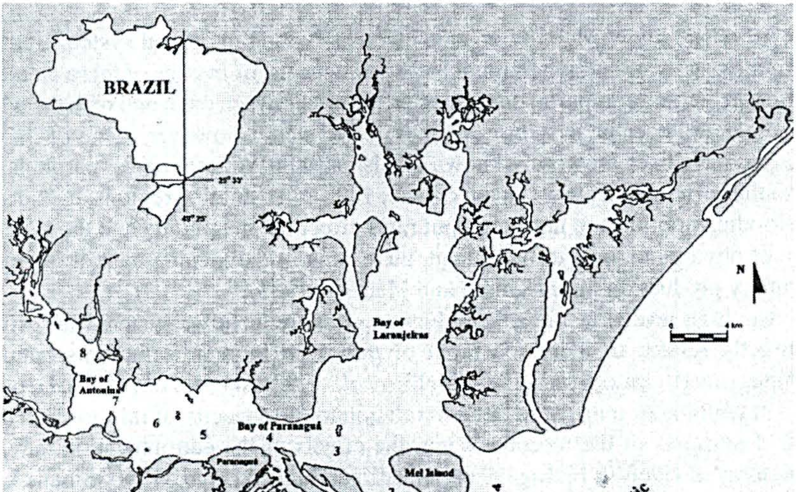

Fig. 1
Map of Paranaguá Bay: Localization of sampling stations

adjacent coastal waters by two tidal channels, Barra Norte and Galheta, separated by the Mel Island.

The tides are characterized by a semi-diurnal regime, showing variations of approximately 1.5 m (Marone, pers. comm.). The freshwater input from a few rivers is small, with a total flux attaining up to 200 m^3s^{-1}. Several mangrove tidal creeks ("gamboas") are potentially relevant as rain water catchments (Marone, pers. comm.).

Earlier studies showed that the anthropogenic influence is restricted to regions of the Paranaguá, Antonina and Guaraqueçaba cities (Knoppers *et al.*, 1987; Brandini *et al.*, 1988). The activities of the harbor of Paranaguá represent the major potential source of increasing impact for the bay's ecosystem.

MATERIAL AND METHODS

Monthly sampling cruises along the main longitudinal axis of the bay were carried out between July/1994 - June/1995 at nine stations (Fig. 1). Samples of surface and bottom waters were collected with a Van Dorn bottle. The salinity was measured with a refractometer (ATAGO, S/MILL). Water temperature and pH were measured with a pH-meter (INGOLD, WTW-pH91) equipped with a temperature sensor and transparency was determined with a Secchi disk. Samples for dissolved oxygen were fixed on board and analysed immediately after arriving at the laboratory using the Winkler method (Grasshoff *et al.*, 1983) . Water samples were filtered through GF/C filters during the cruise. Samples were kept in a cool container until the end of the cruise and henceforth stored at -18ºC for a few days prior to analyses. Nitrate, nitrite, ammonium, dissolved inorganic phosphorus (DIP) and dissolved silicate (DSi) were measured according to Grasshoff *et al.* (1983). Pigments were extracted from concentrated samples on the GF/C filters with 90 % v/v acetone over 24 h, in the dark, at 12ºC and chlorophyll *a* (Chl.-*a*) concentrations were determined fluorimetrically (Turner,10-AU) according to Strickland and Parsons (1968). Suspended particulate material retained on the filters was measured gravimetrically and particulate organic carbon (POC) was analysed by wet oxidation with dicromate (Strickland and Parsons, 1968).

RESULTS AND DISCUSSION

Knoppers *et al.* (1987) distinguished three sectors within the Bay of Paranaguá - lower, middle and upper sections, according to the pattern of stratification and physiographical characteristics. According to this classification, temporal variations of physical and chemical properties presented in the figures 2-14 and 16 are based on average values of three stations for each sector.

Physical Properties

The entire system exhibited a well-defined saline stratification only at strong ebb tides during the rainy period (summer), as in January of 1995 (Fig. 2). During the other periods, a spatial variation of the stratification pattern was observed, with waters well-mixed in the area situated at the mouth of the bay and a progressive stratification towards the inner bay, as for example in October of 1995 (Fig. 2). On the other hand, an almost homogeneous water column was observed in the whole bay in June of 1995, after strong winds. These results demonstrate that the hydrodynamic of the bay is strongly controlled by climate factors (rain regime and winds), which also affect the intensity of tides.

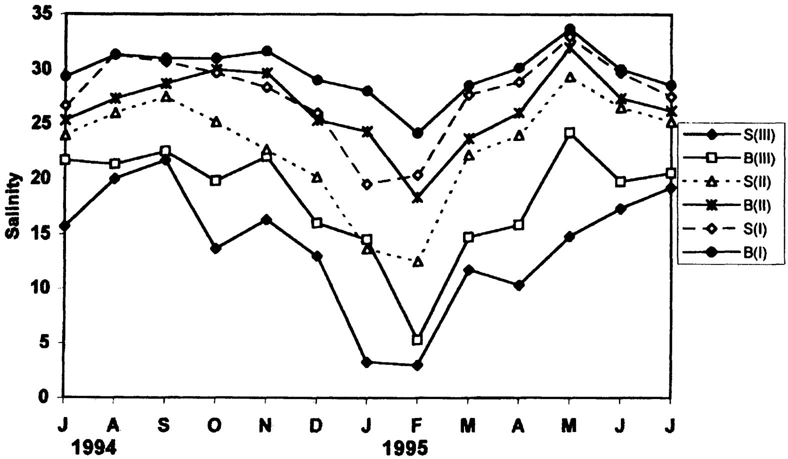

Fig. 2
Temporal variation of salinity in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water

The temperature showed a behavior similar to the salinity. Nevertheless, horizontal and vertical variations were small (Fig. 3). The transparency and pH exhibited a direct relation to the salinity, with highest values in the dry periods, at the mouth of the system (Figs. 4 and 5). The dissolved oxygen in the bottom water showed a decreasing gradient towards the inner bay (Fig. 6). No defined pattern was observed for surface waters. The lowest value (64 % saturation) was registered for bottom waters in the upper section of the bay in January of 1995. This behavior can be attributed to the spatial variability of production and respiration processes in the water column and, probably, in surface sediments (Stumm and Morgan, 1981; Carmouze, 1994; Bierman

Table 1 - Range of water column properties in some coastal ecosystems

System	Sal.	pH	T °C	O.D. (% Sat.)	Secchi (m)	dw (mg/l)	Chl.-*a* (µg/l)	POC (mg/l)	NO_3 µM	NO_2 µM	NH_4 µM	PO_4 µM	$Si(OH)_4$ µM	N:P	Reference
Paranaguá Bay	0 - 32.5	6.7 - 8.3	18.5 - 26.6	64 - 112	0.7 - 6.8	1.7 - 221	0.4 - 49	0.2 - 4	0.1 - 9	0 - 0.9	0.4 - 8	0.2 - 3	3.1 - 178	0.6 24.2	this study
Paranaguá Bay	2 - 35.5	7 - 8.25*	20 - 30	100 - 120	0.5 - 5*	2.8 - 34	0.4 - 7	0.6 - 2	0 - 13	0 - 0.3	0 - 10	0.07 - 1.4	1.5 - 140	-	Knoppers *et al.* (1987); *Rebello & Brandini (1990)
Conceição Lagoon	3 -36	8 - 8.2	15 - 30	0 - 147	R.B.	0.7 - 142	0.8 - 1604	0.1 - 2	1.9 - 13	0.02 - 0.1	0.5 - 2	0.3 - 0.7	11.7 - 275	6.3 - 29.7	Knoppers *et al.* (1984); Odebrecht & Caruso (1987)
Patos Lagoon	0 - 32.5	7.1 - 8.4	11 - 26	86 - 158	0.1 - 1.2	3.1 - 261	1 - 17	-	0 - 73	0 - 3.5	0 - 33.2	0 - 5.5	0.9 - 275	1.2 - 40	Niencheski *et al.* (1986); Baumgarten *et al.*, (1995)
Guarapina Lagoon	4 - 25.5	-	19 - 31	80 - 180	-	8.7 - 80	12.3 - 75	1.8 - 10	0.4 - 9	0.01 - 0.9	0.5 - 5	0.1 - 2.7	7.2 - 140	1.3 - 43	Machado & Knoppers (1988)
Mundaú Lagoon	0.02 - 26.1	6.4 - 8.6	25 - 30	21 - 117	0.15 - 1	-	-	-	0.3 - 33	0 - 8.5	-	0.5 - 4	20 - 417	-	Macedo *et al.* (1987)
Mundaú/ Manguaba	0.1 - 33.9	7.32 - 9.65	24 - 32	10 - 205	0.1 - 3.5	3.6 - 190	2.2 - 265	-	0.3 - 21	0 - 11	0.05 - 33	0.05 - 7	12.4 - 192	1.4 - 25.3	Machado (unpub. data)
Great Ouse Estuary (England)	0 - 35	-	3 - 21	-	0.1 - 1.5	0 - 399	0.5 - 156	-	0 - 730	0.5 - 6	0.5 - 23	2 - 48	1 - 160	10	Fichez *et al.* (1992)
Mississipi Estuary (USA)	12.5 - 30.2					0.5 - 12.6	1.1 - 14.4		0.05 - 100	-	-	0.12 - 6.1	0.2 - 28.7	-	Redalje *et al.* (1994)
Chesapeake Bay (USA)	0 - 18		3 - 27				3 - 18		0 - 100		0.5 - 7.8	0.06 - 1.2		15 - 230	Magnien *et al.* (1992)
Archipelago of Göteborg (Sweden)	0.8 - 23.5			70 - 130			<2 - 9	0.49	1.49 - 35.3		1.09 - 14.4	0.05 - 0.46		35 - 800	Selmer & Rydberg (1993)
Bay of Biscay (Spain)	26 - 34	7.5 - 8.25	20.1 - 21.8	102 - 107		0.2 - 2.7	1 - 11	0.1 - 0.5	9 - 27	0.1 - 1.9	2 - 14	0.2 - 2.2	0 - 14	18 - 60	Garcia-Soto *et al.* (1990)
Puget Sound (USA)	22 - 30		8.7 - 18.1	66 - 132					<0.1 - 1.5	<0.1 - 0.2	0.8 - 2.9	0.6 - 2.3	32 - 62	1 - 2	Thom *et al.* (1994)

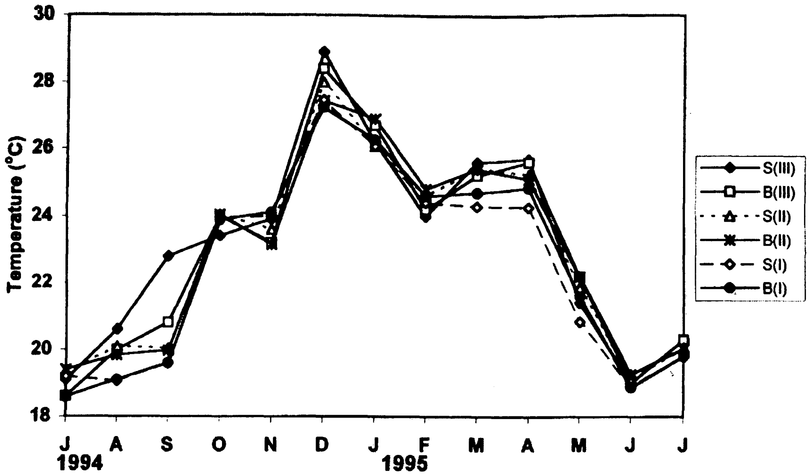

Fig. 3
Temporal variation of salinity in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surafce water; B = bottom water.

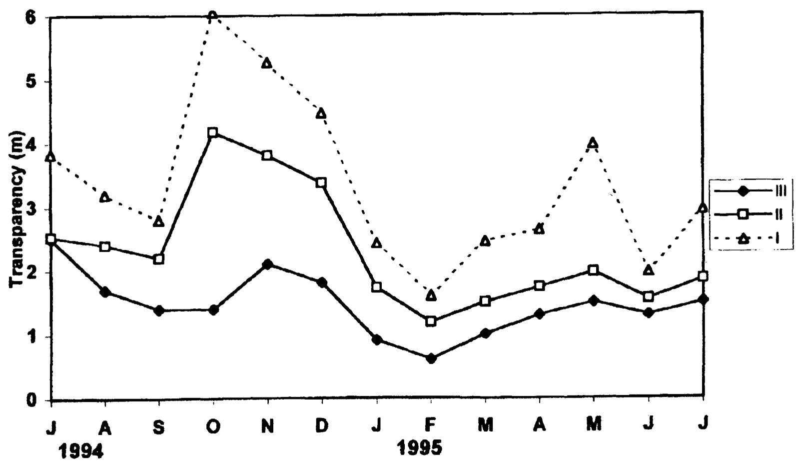

Fig. 4
Temporal variation of transparency in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay.

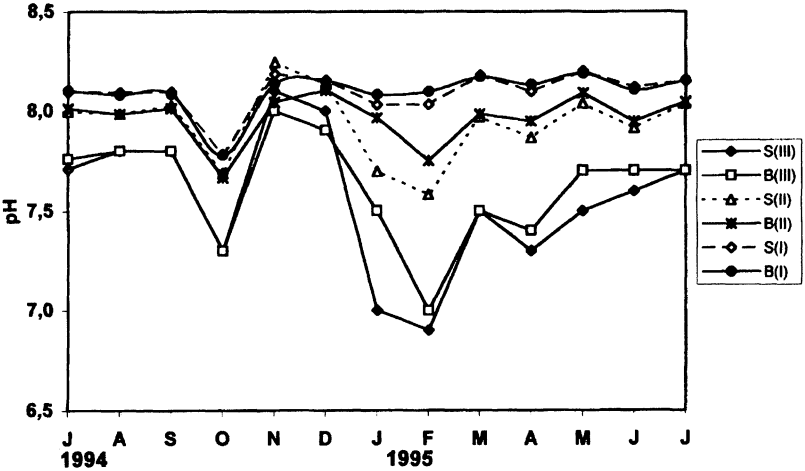

Fig. 5
Temporal variation of pH in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

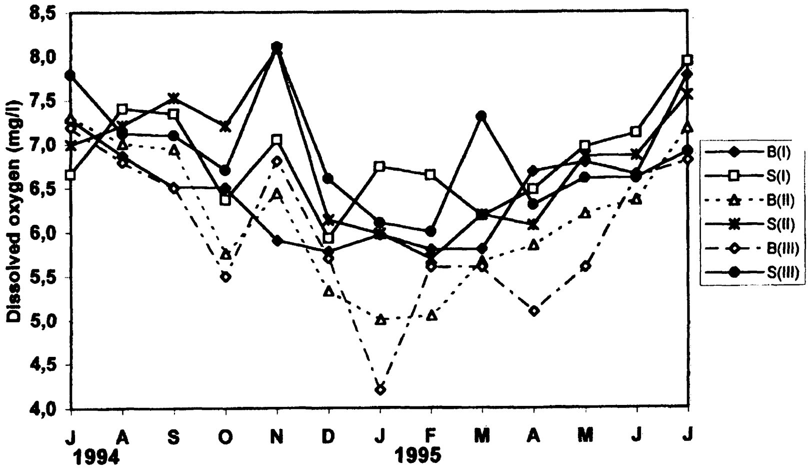

Fig. 6
Temporal variation of dissolved oxygen in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

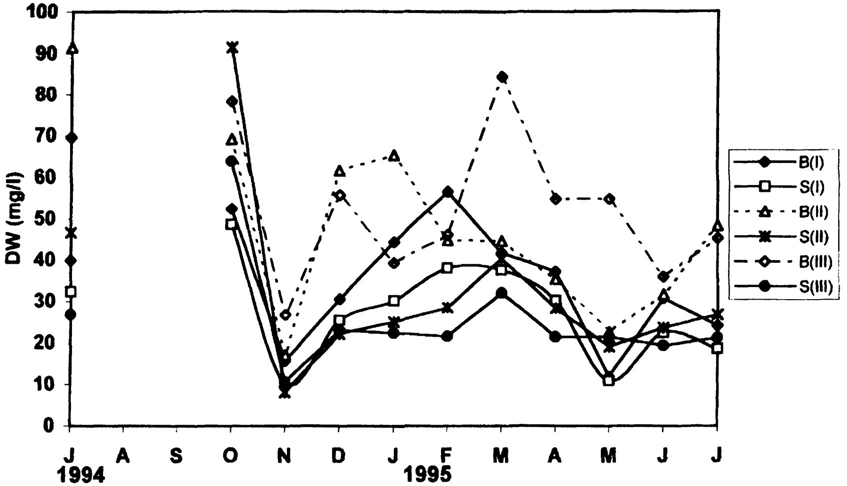

Fig. 7
Temporal variation of suspended particulate material (DW) in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

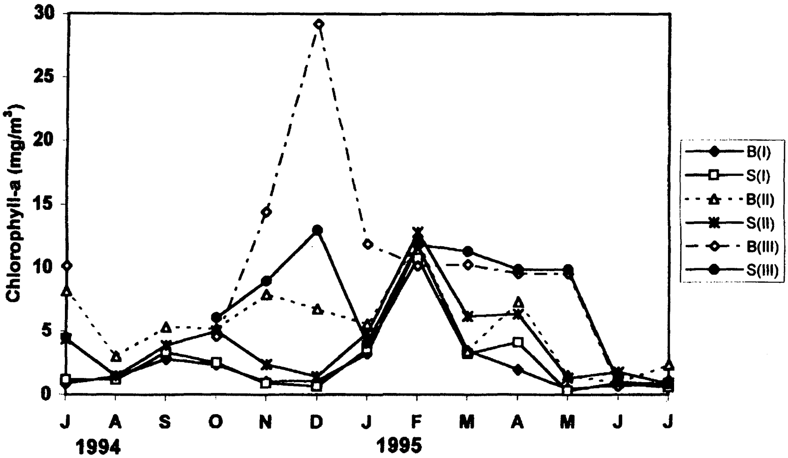

Fig. 8
Temporal variation of Chlorophyll-a in the lower (I), middle (II) and uper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

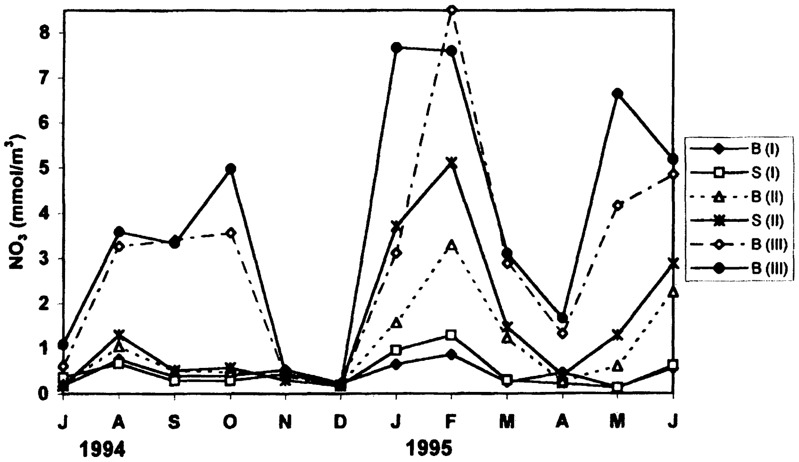

Fig. 9
Temporal variation of nitrate in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

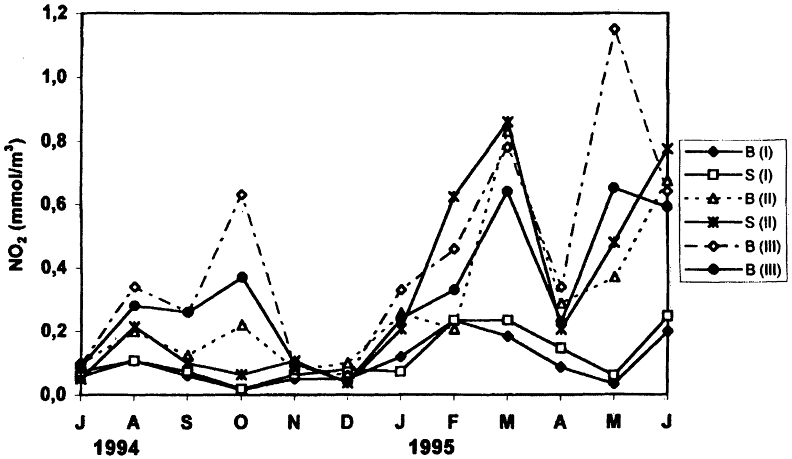

Fig. 10
Temporal variation of nitrite in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

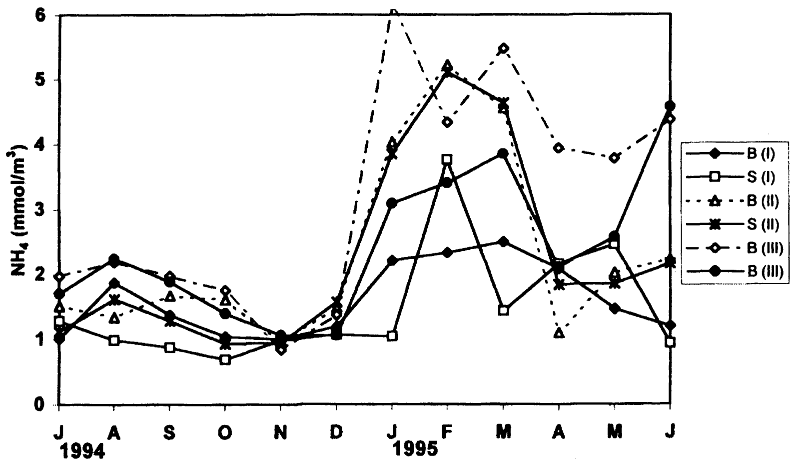

Fig. 11
Temporal variation of ammonium in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

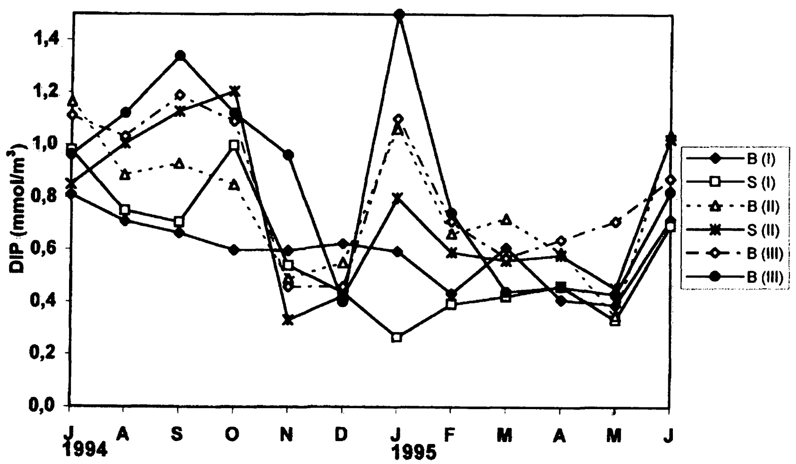

Fig. 12
Temporal variation of dissolved inorganicphosphorus (DIP) in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

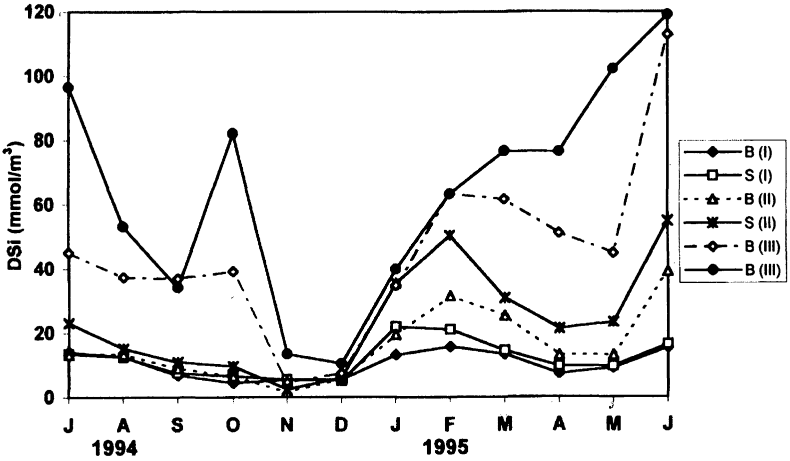

Fig. 13
Temporal variation of dissolved silicate (DSi) in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

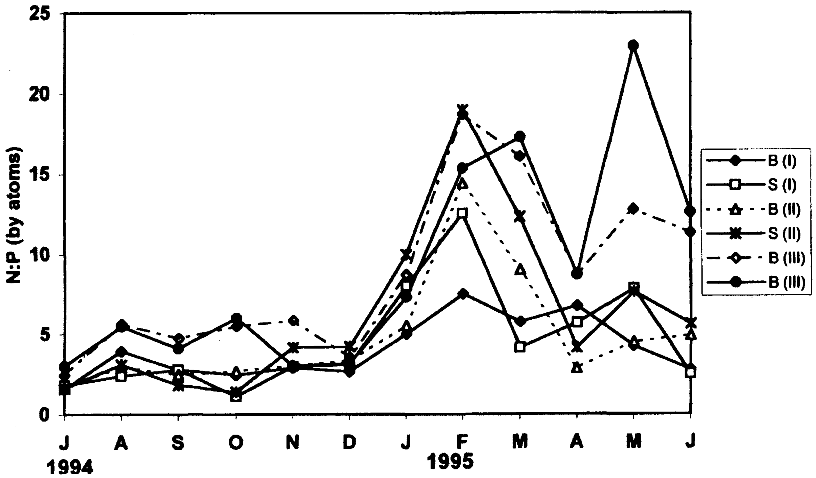

Fig. 14
Temporal variation of nitrogen: phosphorus ratios in the lower (I), middle (II) and upper (III) sections of Paranaguá Bay: S = surface water; B = bottom water.

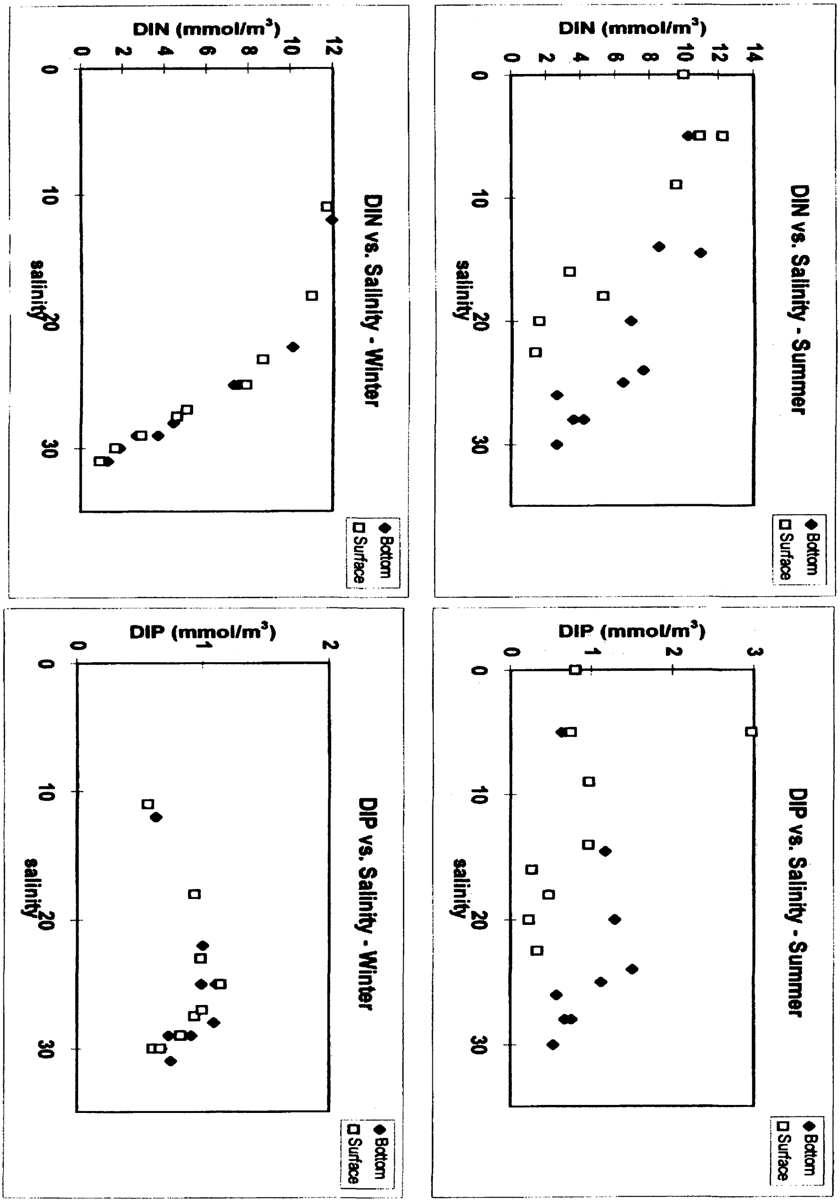

Fig. 15
Composite plot of Dissolved inorganic nitrogen and phosphorus vs. salinity.

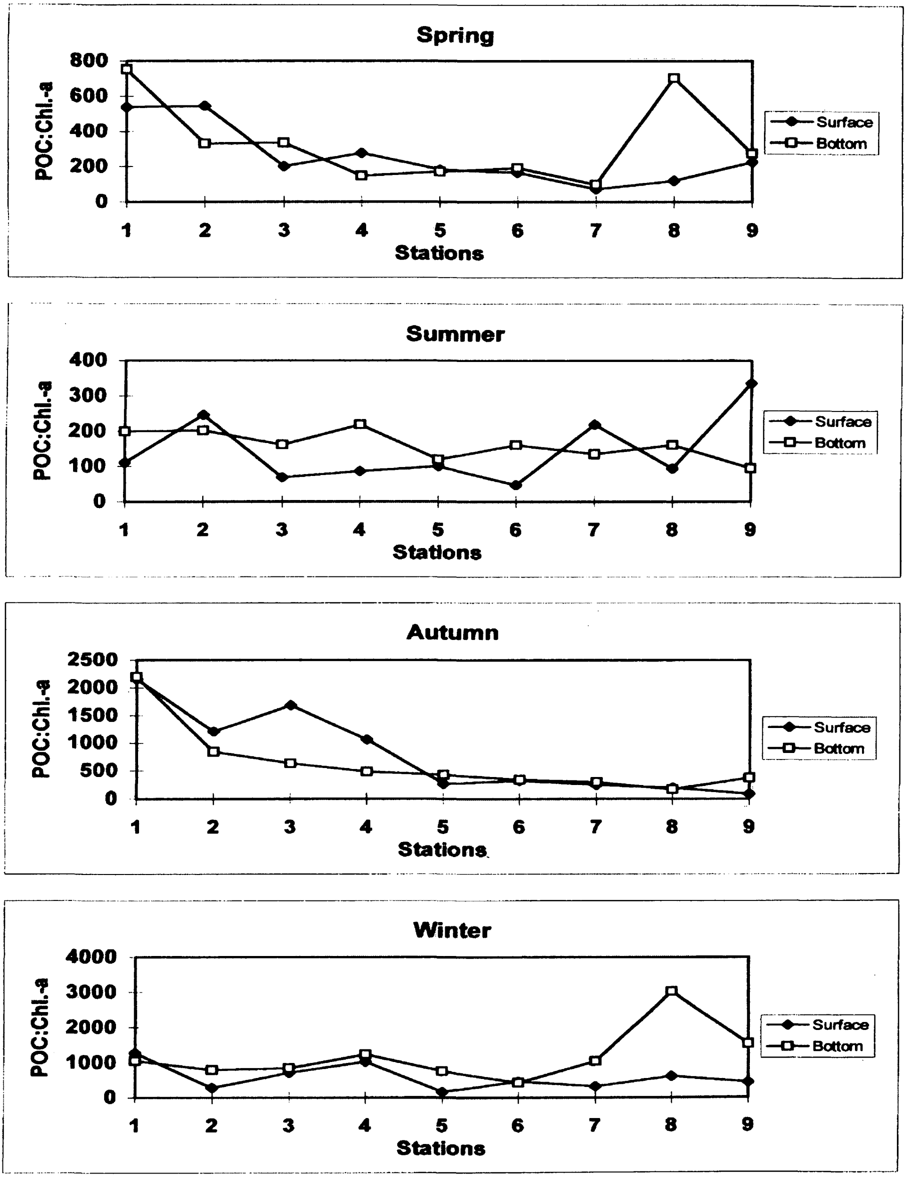

Fig. 16
Seasonal variations of POC: Chlor.-a ratios in the pelagic system of Paranaguá Bay:
S = surface; B = bottom.

et al., 1994). High variability of suspended particulate material (seston) was observed, with values ranging between 1.7 and 221 mg·dm-3. However, spatial and temporal variations did not show a well-defined pattern (Fig. 7), which is probably attributable to the complex hydrodynamics of the system and to resuspension processes of surface sediments by wind action and penetration of bottom water of higher salinity during flood tides. Although seasonal shifts in the degree of stratification are noticeable, the system largely complies to a partially mixed estuary.

Chemical Properties

In agreement with other studies on coastal and estuarine environments (Garcia-Soto *et al.*, 1990; Harrison *et al.*, 1991; Mallin, 1994; Abreu *et al*, 1995), the highest values of chlorophyll *a* and dissolved inorganic nutrients were verified in the mid and inner regions of the bay, in the rainy period (Figs. 8-13). For nitrate (Fig. 9), and mainly for dissolved silicate (Fig. 13), a more conservative behavior was observed, indicating that the continental drainage constitutes the main source of these constituents. However, a decrease of nitrate concentrations at the bottom in the mid bay, concomitantly with low values of dissolved oxygen and an increase on nitrite and ammonium concentrations (Figs. 8-10), suggests the occurrence of a sink for nitrate and a source for ammonium and nitrite in this area. This could be explained by a sequence of processes: diffusion of nitrate into anaerobic regions of the sediments where nitrate reduction occurs and subsequent nitrification of diffusing ammonium into the upper sediment layers and adjacent bottom waters. This, however, does not exclude the occurrence of the denitrification in sediments (Klump and Martens, 1983), which may be an important pathway for significant losses of combined nitrogen in coastal systems and may lead to low N:P ratios (Nixon, 1981; Nixon and Pilson, 1983; Day *et al.*, 1989). Anomalies of the Redfield ratio (N:P=16:1) are invariably found in water masses in which oxygen is depleted, and are associated with high concentrations of nitrite, the first product of dissimilatory nitrate reduction (Deuser *et al.*, 1978; Hattori, 1983). N:P ratios registered in this study showed a spatial and temporal variability, with higher values in the inner bay during the rainy season (Fig. 14). This may be mainly attributed to the increasing input derived of continental drainage during this period. Nevertheless, the relative enrichment of nitrogen compared to phosphorus registered in February could also be caused, in a certain extent, by adsorption of DIP onto particulate phases associated to low salinity and pH values (Baumgarten *et al.*, 1995; Liss, 1976). However, the predominance of N:P ratios (by atoms) lower than the classic value of Redfield demonstrates that nitrogen constitutes the potentially limiting nutrient in the bay, as in many other coastal ecosystems (Table 1).

An approach to identify removal and supply of nutrients in an estuarine system is the building of mixing diagrams or nutrient-salinity plots (Liss, 1976; Sharp, 1984; Knoppers *et al*, 1987; Brandini *et al.*, 1988; Abreu *et al.*, 1995), such as those showed in the Figure 15. Knoppers *et al.* (1987) found that the mid-bay region constitutes a source of DIP and ammonium. In this study the same pattern was observed, with the highest values of DIP and also of dissolved inorganic nitrogen, as ammonium and nitrite, in the vicinity of Paranaguá City. Although the anthropogenic input (i.e. wastewater) is a major source for these constituents in this area, the highest concentrations registered in the bottom water indicate that the benthic system must have been an important additional reservoir as also pointed out by Knoppers *et al.* (1987). The greater scattering of the values in the summer can be due to higher wastewater discharges and enhanced photosynthetic uptake occurring in this period. Moreover, these plots, as well as the spatial and temporal distribution of DIP concentrations (Fig. 11), suggest that the system may be a source of DIP for the adjacent coastal water. The supply of DIN in the bay is, on the other hand, probably compensated by removal processes, such as photosynthetic uptake and denitrification, as discussed above. Thus, the non-conservative behavior observed for DIP and DIN may be the net result of the interaction of several factors, such as: in situ biological and chemical processes, input from the continental drainage associated to the rain regime, anthropogenic input, fluxes from sediments and water movement (Garcia-Soto *et al.*, 1990; Grzetic *et al.*, 1991; Harrison *et al.*, 1991; Fischez *et al.*, 1992; Selmer and Rydberg, 1993; Mallin, 1994; Niencheski & Windom, 1994; Smith and Hithcock, 1994; Ogilvie *et al.*, 1997).

Particulate organic carbon:chlorophyll *a* ratios (POC:Chl.-*a*) showed a seasonal behavior. The highest values were registered in autumn and winter and the lowest in spring and especially in summer (Fig. 16). This pattern demonstrates a temporal variation on the source of particulate organic matter for the pelagic compartment, with relatively greater contribution of phytoplanktonic material (autochthonus production) during summer. Nevertheless, the almost high ratios indicate that the organic matter present in the Bay of Paranaguá is predominantly detritic, originating from both the phytoplankton and also the adjacent mangroves (Brandini, 1985; Knoppers & Opitz, 1984) .

Eutrophication

Nixon (1995) proposed a useful trophic classification for estuarine and coastal ocean ecosystems, based on the annual rates of organic carbon supply, either fixed by primary producers within the system of concern or introduced from outside the system. However, not all sources may be discerned in this study with respect to their contribution to the organic pool, including benthic primary producers, which also occur in shallow regions (Fonseca, in prep.). In this system, however, frequent sedimentation and resuspension induced by wind and tidal currents can transport benthic primary producers to the water column and phytoplankton to sediments (Brandini & Thamm, 1994; Moreira-Filho & Kutner, 1962), leading to complex interactions between these systems.

Unfortunately, annual estimates on primary production rates for the Paranaguá Bay, either benthic or pelagic, are not available yet. The magnitude of hourly photosynthetic rates of phytoplankton reported by Brandini & Thamm (1994), as well as rates registered in the lower section for phytoplankton (Daniel, in prep.) and for benthic producers (Fonseca, in prep.), suggest that the trophic state of the Paranaguá Bay, according to Nixon's classification, varies seasonally and spatially from almost oligotrophic in winter in the lower section to eutrophic during summer in the middle and upper sections of the bay.

Other criteria for the trophic assessment of aquatic systems take into account chlorophyll, POC and nutrient concentrations (for example: Likens, 1975; Rast & Lee, 1978). Based on these indices, the average values registered for the three studied sections lead to the same trophic pattern as that indicated by Nixon's classification.

Furthermore, there is still no data available about the total amount of allochthonus carbon entering the system. Several sources may contribute to some extent to this supply. For example, the role of mangroves in the cycling of carbon and nutrients in sub-tropical estuaries is poorly understood (Twilley *et al.*, 1996). In the Bay of Paranaguá, flux rates of organic material and dissolved nutrients from mangroves are still unknown.

The nutrient environment and the trophic status of Paranaguá Bay are the results of several external and internal biotic and abiotic processes. As mentioned above, the largest inputs of nutrients and organic material into the system are loaded from continental drainage and from the cities of Paranaguá and Antonina. Using the data of demographic growth for Paranaguá and Antonina reported by IBGE (1980; 1991), and assuming a production per capita of 2.5 g $P \cdot d^{-1}$ and 13 g $N \cdot d^{-1}$, and that 70 % of the population contributes effectively to the sewage, a rough estimation of the evolution of the antropogenic input in the last decade was built. This calculation indicates that the anthropogenic input has increased some 24% during this period. Nevertheless, as compared to earlier investigations in this area (Table I), the results of this study indicate that there was not a marked variation of the trophic state during the last 10 years. The magnitude of values of nutrients, dissolved oxygen, Chl.-*a* and particulate organic carbon (POC), suggests that the mid and inner-regions of the bay are characterized by conditions which vary from mesotrophic to eutrophic, due mainly to the anthropogenic impact of the cities of Paranaguá and Antonina. Moreover, values of these parameters were in the same range of those reported for other coastal systems and still lower than those reported for Guarapina Lagoon and the system Mundaú-Manguaba, which are characterized by either natural and cultural eutrophication, respectively (Machado & Knoppers, 1988; Machado, unpub. data).

Furthermore, lateral deposition in shallow, sheltered areas, may catch a substantial fraction of the antropogenic organic material entering the bay. Low levels of dissolved oxygen and relatively high contents of organic matter at shallow surface sediments in the middle and lower sections observed respectively by Boehs and Soares (pers. comun.) corroborate this assertion. On the other hand, increased sedimentation of organic debris could lead to higher denitrification rates in sediments, resulting in losses of nitrogen from the system as discussed above, and as such also counteracting eutrophication.

However, the short fluxing time (3.49 days, according to Marone, pers. comm.) probably constitutes the key factor dampening the eutrophication process of the system of the Bay of Paranaguá. Nevertheless, estuarine systems with rapid tidal flushing times may have a small degree of attenuation of nutrient load from the land (Ogilvie *et al.*, 1997), making the adjacent coastal area more vulnerable to anthropogenic eutrophication.

Acknowledgments

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ABSTRACT

In order to assess the seasonal and spatial variations on the trophic structure in the estuarine region of Bay of Paranaguá, 12 monthly sampling cruises were carried out between July/1994 - June/1995, at 9 selected stations along the major axis of the bay. Dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate), dissolved oxygen, pH, transparency, temperature, salinity, seston, chlorophyll-a (Chl-*a*) and particulate organic carbon (POC) in both surface and bottom waters were evaluated. The bay exhibited a striking spatial and seasonal pattern for most of the studied parameters and, except for silicate, all nutrients showed a non-conservative behavior. This is probably due to the interactions between hydrodynamic processes and different mechanisms of loss and supply of these constituents, such as biological uptake, fresh-water input associated with the rainfall regime, sediment-water interactions and sewage discharge from the city of Paranaguá. In spite of the great spatial variability observed in nutrient and chlorophyll-a levels along the salinity gradient, acute eutrophication was not detected. As expected, dissolved inorganic nitrogen:phosphate ratios demonstrate that nitrogen is potentially more limiting for the pelagic production. Marked variations of POC:Chl.-*a* indicate the occurrence of temporal changes in the source of organic detritus for the pelagic system of the Bay of Paranaguá, with a greater contribution from detritus derived from the phytoplankton in summer.

Key-words: nutrients, particulate suspended matter, trophic structure, Paranaguá Bay.

RESUMO

Investigou-se as variações sazonais e temporais na estrutura do compartimento pelágico da Baía de Paranaguá. Em 12 cruzeiros mensais de amostragem efetuados entre julho/1994 - junho/1995, cobrindo 9 estações distribuídas ao longo do eixo principal da baía, foram determinados, na água de superfície e de fundo, os seguintes parâmetros: Nutrientes inorgânicos dissolvidos (nitrato, nitrito, amônio, ortofosfato e silicato), oxigênio dissolvido, pH, transparência, temperatura, salinidade, seston, clorofila-*a* e carbono orgânico particulado. A baía exibiu padrões espacial e sazonal bem definidos para a maioria das propriedades estudadas e, com exceção do silicato, todos os nutrientes apresentaram um padrão não conservativo. Isto provavelmente representa o resultado líquido das interações entre processos hidrodinâmicos e diferentes mecanismos de transferência destes constituintes, como consumo biológico, aporte pela drenagem continental associada com o regime de chuvas, interação água-sedimento e descarga de efluentes da cidade de Paranaguá. Apesar da grande variabilidade registrada nos níveis de nutrientes, COP e Clor.-*a* ao longo do gradiente de salinidade, não foi detectado um grau elevado de eutrofização. Como já esperado, as razões nitrogênio inorgânico dissolvido:ortofosfato demonstram que o nitrogênio constitui o elemento potencialmente mais limitante para a produção pelágica. As acentuadas variações observadas nas razões COP:Clor.-*a* indicam a ocorrência de mudanças temporais na fonte de detritos orgânicos para o sistema pelágico da baía de Paranaguá, com maior contribuição de detritos derivados do fitoplâncton no período de verão.

Palavras-chave: nutrientes, material particulado em suspensão, estrutura trófica, Baía de Paranaguá.

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