Phosphorus dynamics in water and sediments in urbanized and non-urbanized rivers in Southern Brazil

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Abstract

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

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

The phosphorus cycle is strongly determined by biological processes combined with geochemical processes,

as adsorption–desorption and precipitation–dissolution. The preference of one of these processes depends on physical factors as input flux of nutrient, turbidity, residence time and the occurrence of stratification in water column (de Jonge et al., 2002). Several studies have registered the increase of phosphorus concentrations in rivers and estuaries in developing countries in recent decades (Machado et al., 1997; Carreira and Wagener, 1998; Braga et al., 2000), and also in countries already intensely urbanized in the last century (Nixon, 1995; de Jonge et al., 2002; Foy et al., 2003). However, the increase of phosphorus concentrations in the environment and its effects on the coastal waters does not follow a linear or direct relationship, but a complex one due to the interactions of water and sediments that change phosphorus concentrations along rivers and estuaries. The P release from sediments to maintain Redfield ratio proportions and N-limitation in coastal waters provides a useful framework of the importance of P cycle to primary production in coastal waters (Nixon, 1995).

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

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

2. Methods

2.1. Study area

The Santa Catarina Island Bay, southern Brazil (Fig. 1), is situated next to an amphidromic region, mainly formed by microtide, with a mean amplitude of 0.83 m for spring tide and 0.15 for neap tide, respectively (Cruz, 1998). The climate is subtropical and humid with precipitation well distributed along the year, however, with more intense rain in the winter and more frequent in summer. Prevailing winds blow from south/southeast quadrant. Mangroves are in the southern extent of their geographic distribution in the Atlantic coast of South America and are composed by the species *Rhizophora mangle*, *Avicennia schaueriana* and *Laguncularia racemosa*. The saltmarsh areas are formed by extensive monospecific banks of the graminea *Spartina alterniflora*. The two biggest local areas of mangrove and saltmarsh build the preserved area of Carijós Ecological Station, whose main sinks are the rivers Ratones (RA) and Veríssimo (VE), and the Pirajubae Sustainable Marine Reserve, which is formed by the Tavares river (TA).
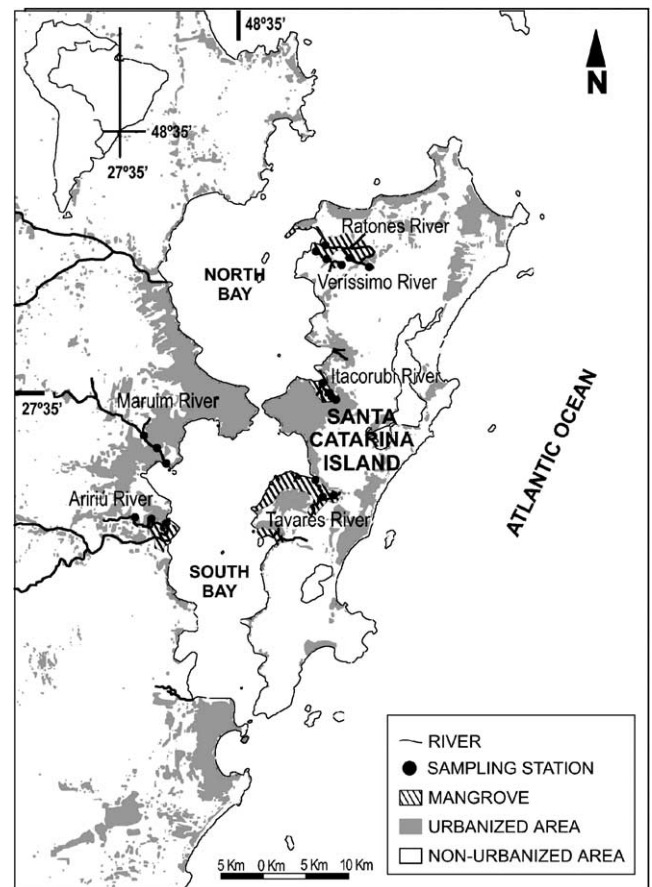

Fig. 1. The Santa Catarina Island Bay, southern Brazil, showing the sampled rivers.

These areas were considered as potentially non-polluted and were used as urbanization control.

The urbanization around the bay is intense and focused mainly on the continental portion and in the centre of the island. More than 600,000 people live on the drainage basin of the Santa Catarina Island Bay, and this number usually increases threefold with the arrival of tourists during the hot months of the year. Among the urbanized region, many streams were reordered and made impermeable, and large portions of the riverine margin were covered with land. After a recent governmental imput the region has become economically important in fisheries production, especially with the production of the exotic oyster *Crassostrea gigas* and the mussel *Perna perna* reaching 7000 ton/yr. The rivers Itacorubi (IT), Aririú (AR) and Maruim (MA), suffer directly the urbanization effects and were chosen as potentially polluted places for the analysis of P in water and sediments (Fig. 1).

2.2. Sampling design and sample treatment

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

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

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

2.3. Data analysis

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

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

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

2.4. K_d model

Phosphorus dynamics in sampled rivers were checked through adsorption equilibrium models, using the

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

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

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

3. Results

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

The hierarchical analyses of variance made for P-tot levels, separately, in water and sediments showed significant differences between urbanized and non-urbanized areas, among the rivers in each area and among each river sites (Table 1). The multiple comparison tests for P-tot in water exhibited higher values in urbanized rivers and lower values in non-urbanized ones
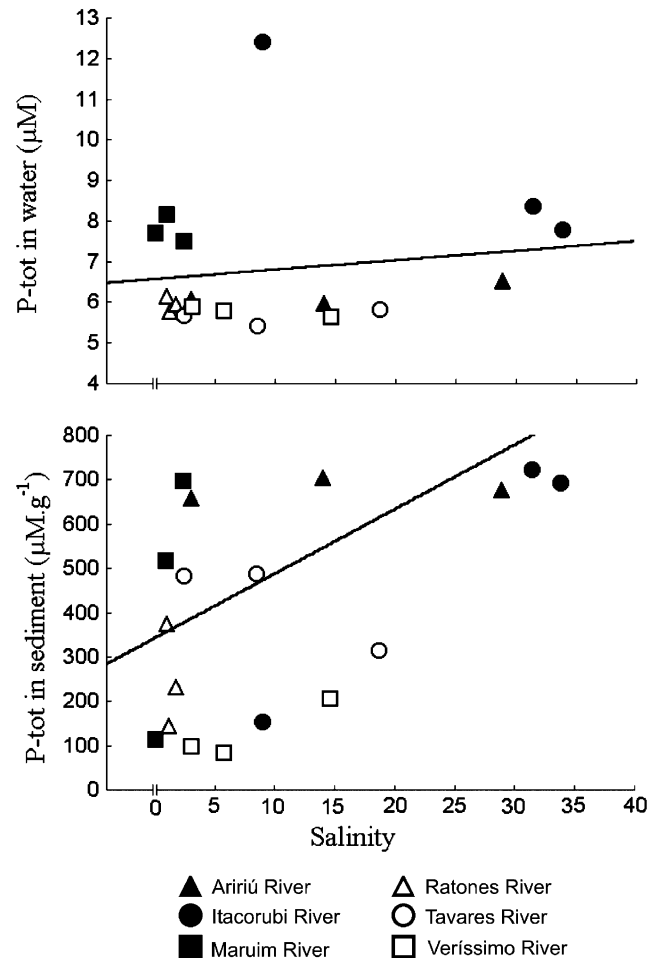

Fig. 2. Phosphorus concentration in water and sediment versus salinity in rivers of the Santa Catarina Island Bay, southern Brazil.

(Newman–Keuls test, $P < 0.05$). The test showed differences in data among urbanized rivers (Newman–Keuls test, $P < 0.05$, IT > MA > AR), but not among non-urbanized ones (Newman–Keuls test, $P > 0.05$, RA = VE = TA). The only significant differences among sites in the same river were related to higher concentrations of P-tot found in the inner site of Itacorubi river.

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

The multiple comparison test for the P-tot concentrations in the sediments showed, as in water values, higher concentrations in urbanized rivers and lower in the

Table 1
Summary of hierarchical nested analysis of variance of total P concentration in water and sediment in rivers of Santa Catarina Island Bay, southern Brazil

Source of variation	d.f.	P-tot in water		P-tot in sediment	
		MS	F	MS	F
Area	1	56.52	574.66[*]	1,052,612.00	65.45[*]
River	4	12.58	127.92[*]	167,162.00	10.39[*]
Site	12	3.35	34.03[*]	109,820.00	6.83[*]
Error	36	0.10		16,082.68	

$n = 3$, d.f. = degree of freedom, MS = mean squares, F = F-ratio.
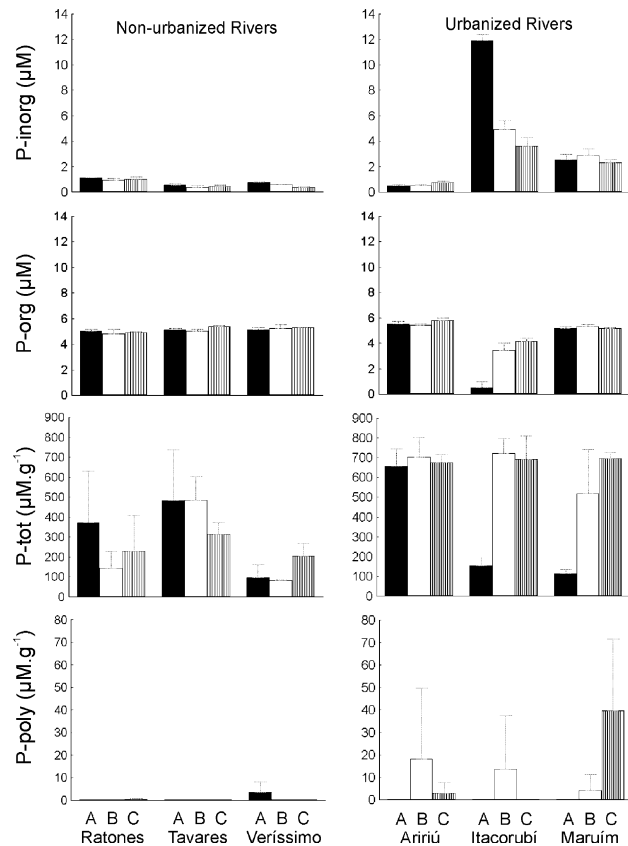   [*] $P < 0.05$.

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

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

concentrations in sediments were only analyzed graphically and showed a higher concentration in the urbanized rivers than in the non-urbanized ones, with distinct variations among sites into the same river (Fig. 3).

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

Tables 2 and 3 show respectively a summary of the physico-chemical and biological properties of the water and the sediments of the rivers sampled. In a general way there is a gradient dilution of salinity and chlorophyll *a*
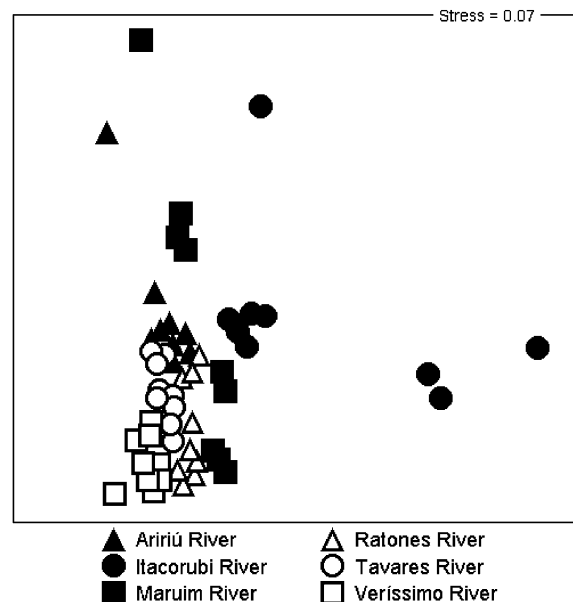

Fig. 4. *n*-MDS of inorganic and organic phosphorus in water and total phosphorus and polyphosphate in sediments of non-urban (empty symbols) and urban (filled symbols) rivers of the Santa Catarina Island Bay, southern Brazil.

Table 2
Mean concentration (±1 sd) of inorganic P (P-inorg), organic P (P-org) and physico-chemical water characteristic in rivers of Santa Catarina Island Bay, southern Brazil

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

Table 3
Mean concentration (±1 sd) of total phosphorus (P-tot), polyphosphate (P-poly) and sediment characteristics in rivers of Santa Catarina Island Bay, southern Brazil

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

from the mouth to the head of the rivers, followed by the increasing concentrations of dissolved oxygen, suspended particle matter and phaeophytin a. In the sediments, there was a general tendency of increasing the content of organic matter, fine sediments and carbonate towards the sea.

Pearson correlation analysis among inorganic and organic forms of P and physico-chemical and biological variables in water revealed different trends for each form of phosphorus in the urbanized and non-urbanized areas (Table 4). In the non-urbanized areas the P-inorg concentrations correlated positively with the levels of dissolved oxygen, suspended particle matter and phaeophytin a, and negatively with salinity and chlorophyll a biomass. On the contrary, the P-org concentrations correlated positively with the salinity and chlorophyll a biomass, negatively with suspended particle matter and phaeophytin a, and did not significantly correlated with dissolved oxygen. In the urbanized areas, the correlations among the distinct forms of P and the physico-chemical and biological variables in water did

not follow the same patterns observed in the non-urbanized areas. The P-inorg concentrations did not correlate with any variable analyzed, whereas the P-org concentrations correlated significantly with dissolved oxygen contents only.

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

The estimated variation of P, in the final result of removal (positive values) or release (negative values), for the studied rivers is presented in Fig. 5 as a P concentration function in the inner sites (P_a^W) of each river. For each river there are three values related to the calculation made of the intermediate sites, the river mouths sites and the average of these data. The results show a

Table 4
Pearson correlation matrix for organic (P-org) and inorganic (P-inorg) phosphorus versus bottom water characteristics in urbanized and in non-urbanized rivers of Santa Catarina Island Bay, southern Brazil

Water characteristic	Non-urbanized rivers ($n = 27$)		Urbanized rivers ($n = 27$)	
	P-inorg	P-org	P-inorg	P-org
Salinity	−0.71[*]	0.57[*]	0.03	−0.13
Secchi	−0.89[*]	0.50[*]	0.17	−0.25
pH	−0.74[*]	0.57[*]	0.03	−0.11
Dissolved oxygen	0.58[*]	−0.31	−0.23	0.39[*]
Suspended particulate matter	0.73[*]	−0.44[*]	−0.25	0.35
Chlorophyll *a*	−0.43[*]	0.54[*]	0.13	−0.18
Phaeophytin *a*	0.40[*]	−0.46[*]	0.15	−0.16

[*] $P < 0.05$.

Table 5
Pearson correlation matrix for total phosphorus (P-tot) and polyphosphate (P-poly) versus sediment characteristics in urbanized and in non-urbanized rivers of Santa Catarina Island Bay, southern Brazil

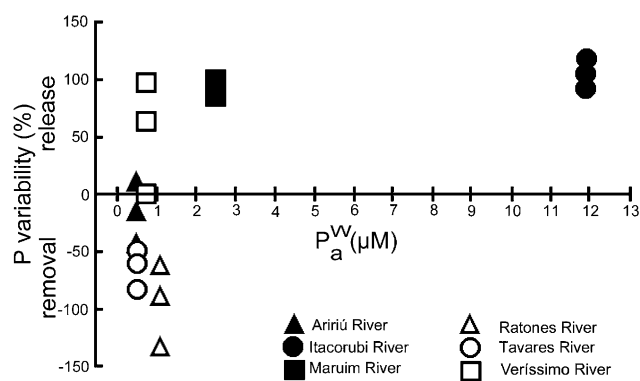| Sediment characteristic	Non-urbanized rivers ($n = 27$)		Urbanized rivers ($n = 27$)	
	P-poly	P-tot	P-poly	P-tot
Carbonate	−0.15	0.69[*]	−0.17	0.58[*]
Organic matter	−0.31	0.82[*]	0.32	0.81[*]
Sand	0.28	−0.59[*]	−0.35	−0.81[*]
Fines	−0.27	0.57[*]	0.35	0.81[*]
Chlorophyll *a*	0.05	0.11	0.47[*]	0.17
Phaeophytin *a*	−0.37	0.54[*]	0.20	0.49[*]

[*] $P < 0.05$.

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

lack of consistency between the expected removal or release behavior of dissolved P, considering the characterization of the estuary as urbanized or non-urbanized. According to the calculated values for the different sites or general mean, in Itacorubi, Maruim and Veríssimo rivers the dissolved P removal occurred, whereas in Ratones and Tavares rivers there was a dissolved P release. In Aririú river there was a release of P according to the average data in the site close to the river mouth (site *c*), whereas in the intermediate site (site *b*) the removal of P was observed.

4. Discussion

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

In strongly urbanized countries, the increase of P concentrations has been recorded as accompanying the development period. In some places this process is being reverted by the removal of submarine outfalls and implementation of sewage treatment. However, after an initial decrease period of P concentrations in the environment, the levels increased again (Zhou et al., 2000;

Foy et al., 2003). With the control of the known point source P, the unknown source begins to have a greater importance and keeps the concentrations elevated. Probably, the main agent of this increase has been the excessive utilization of P in agriculture since past times (Cloern, 2001). Oxi-reduction processes in sediments contribute to the release of P accumulated in soil, i.e., the P that was not used by plants and did not immediately become available for the water bodies next to the plantation, is released in the environment. The agriculture is one of the main factors that affects the movement of P from land to sea. Estimates show that the global flux of P to the oceans has increased threefold after the development of agriculture (Howarth et al., 1995).

In developing countries as Brazil, the restraint of punctual and diffuse P is insipient and, in the present, reveals few practical results. In urbanized region that drains towards the Santa Catarina Island Bay, the domestic effluents are discharged directly from riverine houses or through pluvial channels which collect the effluents from the houses. In most cases cesspools are built in order to collect feces and fatty matter. The official statistic of the state of Santa Catarina shows that only 13% of the residences have sewage collection system and 46% have septic cesspools (IBGE, 2002). In the rural area which drains towards the bay, the properties are small holdings under 50 ha and are based on the horticulture, especially tomatoes (Santa Catarina, 2001). Estimates reveal the use of 188 kg/year of agrotoxics per rural property mostly from the carbamates and organophosphates groups (Oliveira, 1997; Leão, 1998). Once disposed into the environment, the carbamates and organophosphates are fastly hydrolyzed resulting in nitrogen and phosphorus compounds.

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

In the present study the organic and inorganic forms of phosphorus were not quantified separately in the sediment, however, the concentrations of P-poly, a kind of

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

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

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

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

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

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

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

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