Nutrients in surface sediments of Mirim lagoon, Brazil-Uruguay border.

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ABSTRACT: Nutrients in surface sediments of Mirim lagoon, Brazil-Uruguay border. **Despite its ecological, economics and geopolitical importance, Mirim lagoon is still poorly known. In this paper we present the first data about organic composition and nutrient levels in lagoon sediments. Total Organic Carbon, N-total, and P-total had an average content of 1.26%, 0.163% e 0.162%, respectively. The southern part of the lagoon is characterized by higher concentrations of these elements. This is due to the proximity of the main fluvial discharges. Mirim lagoon sediments are poor in carbon and nitrogen, which is attributed to the organic input dilution, high occurrence of sediment resuspension processes, and recent deposition of lagoon substratum. The N:P ratio is low in comparison to other aquatic environments. This is likely to be associated to the intense use of phosphate fertilizers and the high frequency of sediment resuspension.**
Key-words: **nutrients, organic matter, coastal lagoon, sediments.**

RESUMO: Nutrientes nos sedimentos superficiais da lagoa Mirim, fronteira Brasil-Uruguai. **Apesar da sua importância ecológica, econômica e geopolítica, a Lagoa Mirim é ainda pouco conhecida. Neste trabalho são apresentados os primeiros dados sobre a composição orgânica e teores de nutrientes para os sedimentos da lagoa. O Carbono Orgânico Total, N-total e P-total apresentaram teores médios de 1,26%, 0,163% e 0,162%, respectivamente. A região sul da Mirim é caracterizada por maiores concentrações de C, N e P. Isto é atribuído à proximidade dos principais aportes fluviais. Os sedimentos da Mirim foram considerados pobres em C e N, o que pode ser explicado pela diluição dos aportes orgânicos, constantes trocas entre sedimento e coluna d'água e deposição recente do substrato. A razão N:P é baixa se comparada a outros ambientes aquáticos, o que provavelmente está associado ao intenso uso de fertilizantes fosfatados na bacia de drenagem e a alta freqüência do processo de ressuspensão.**
Palavras-chave: **nutrientes, matéria orgânica, lagoa costeira, sedimentos.**

Introduction

Mirim lagoon is located in the Brazil-Uruguay border (Fig. 1), which brings a high strategic interest on the knowledge of contaminant behavior and sources. At the northeast side of the lagoon is situated the Taim marsh. It is a Federal ecological protection area and UNESCO biological reserve world-known by its bird abundance and diversity. The Taim marsh is also important for regulating the water levels of the Mirim-Mangueira hydrological system and for keeping the life quality of local people.

Mirim lagoon is linked to Patos lagoon estuary through the São Gonçalo channel (Fig. 1), forming the biggest lagoon system in South America. Its water flows only to the Mirim-Patos direction, as a dam was built in 1977 for preventing the influx of brackish waters from the Patos lagoon estuary towards Mirim and avoiding rice crop salinization. Thus, in the present day Mirim is an artificially-closed coastal lagoon without any direct marine influence. Mirim lagoon has a length of 180 km, mean depth of 6 m and surface area about 3,749 km^2, being the third biggest natural lake in South America. Approximately

75% of its water body and 49% of its cachtment are located in Brazilian territory. The remainder is inside Uruguay. Water residence time is close to 205 days and the most important tributaries are Jaguarão, Cebollati and Taquari rivers, the last two being located in the Uruguayan side of the cachtment (Párraga, 1997; Beltrame & Tucci, 1998).

The hydrographic basin is scarcely urbanized, with a population of less than 1 million people. Its main cities are Pelotas (ca. 305,000) and Rio Grande (ca. 180,000), however these cities have no direct influence upon Mirim lagoon because its effluents are discharged in the São Gonçalo channel and Patos Lagoon estuary, respectively. The main economic and impacting activity in the catchment is the rice crop. It employs huge loads of fertilizers and pumps around 420 m³/s of water from Mirim lagoon (Beltrame & Tucci, 1998), an amount equivalent to 54% of the mean lagoon water output.

Despite its ecological, economical, and geopolitical importance, Mirim lagoon is still

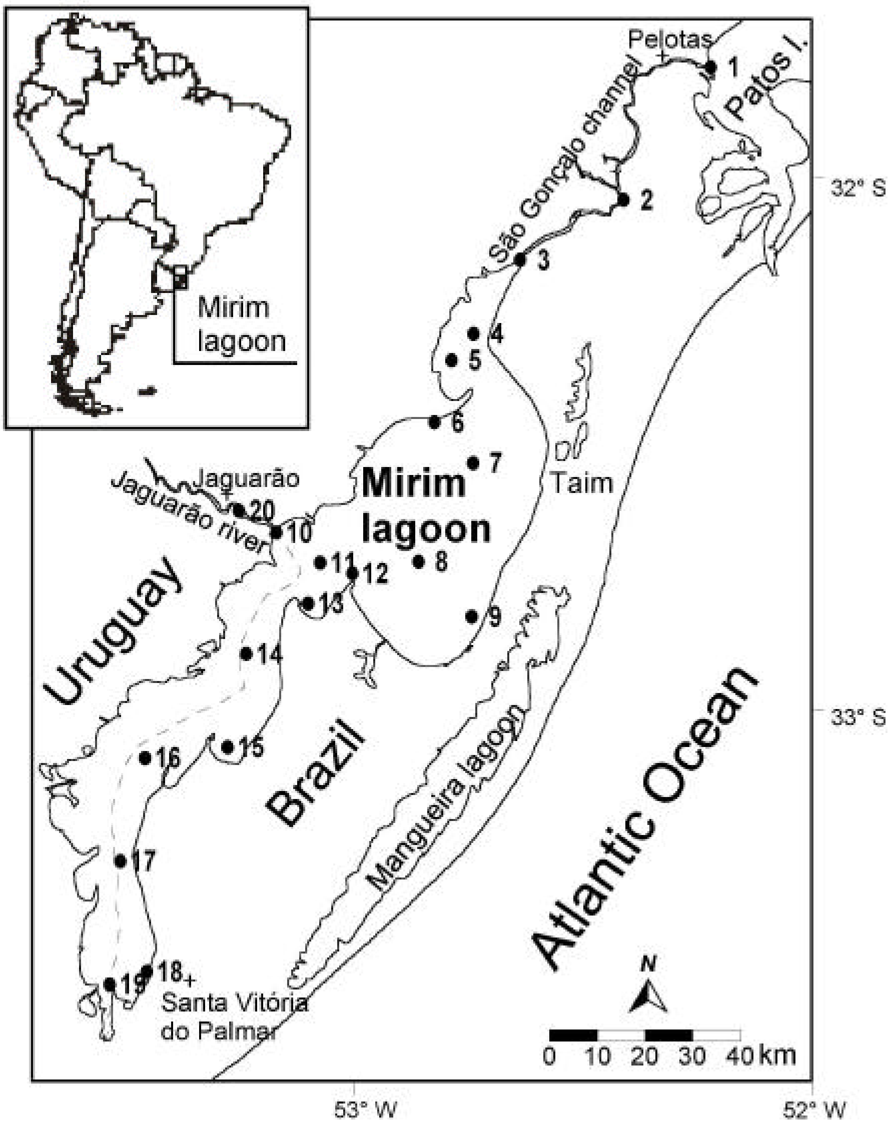

Figure 1: Study area and sampling sites

poorly known. Earlier studies are limited to geological (Vieira, 1995; Buchmann et al., 1997) and hydrological (Beltrame & Tucci, 1998) characteristics. Environmental quality related studies are also incipient (Santos, 2003; Friedrich, 2004) and there is no published research about organic composition of Mirim lagoon sediments. The aim of this paper is (i) to characterize the levels and distribution of organic carbon, nitrogen, and phosphorus in superficial sediments from Mirim lagoon and (ii) to discuss their behavior.

Material and methods

Sampling was carried out in 20 sites during September/2001 aboard the Oceanographic Ship "Larus", property of Fundação Universidade Federal do Rio Grande. Seventeen samples were collected in the main lagoon water body, two in São Gonçalo channel, and one inside Jaguarão River (Fig. 1). This strategy allows us to conduct an interpretation about C, N, and P distribution and behavior in the aquatic system. Depth of samples collection varied between 3 (at marginal sites) and 8 m (in samples 2 and 8). All the sampling procedures were conducted in the Brazilian territory of Mirim lagoon, in Rio Grande do Sul State.

A Van Veen grab was used for collecting sediment. This equipment has a good recovering level in shallow water, like coastal lagoons. Just the most superficial layer was collected, i.e., the upper 5 cm. For avoiding metallic and organic contamination, only sediment that did not have contact with the grab is collected. The samples were immediately frozen until processing in the laboratory.

Once in the laboratory, the samples were wet-sieved for separating silt and clay granulometric fraction (< 0,062 mm). Chemical analyses were performed in this granulometric range for allowing comparisons between sites with different granulometric characteristics (Salomons & Förstner, 1984). After sieving, the sediment was dried at moderate temperatures (maximum of 50°C) and pulverized.

Total Organic Carbon (TOC) concentrations were determined by organic matter oxidation method (Gaudette et al., 1974). Total Nitrogen was determined by Micro-Kjeldhal method, following Bremner (1965). For analyzing Total Phosphorus, the sediment was previously calcinated and digested with HCl diluted solution (Ruttenberg, 1992). After digestion, the colorimetric method was used for phosphorus determination (Murphy & Riley, 1962). Linear Pearson correlation analysis, classification of organic contamination of sediments (Ballinger & McKee, 1971), elemental ratios, and comparison with other ecosystems were used for data interpretation.

Results

The studied sediments had few biogenic fragments. Benthic organisms, like polychaetes and bivalves, were very scarce and vegetal fragments were virtually absent in sediment samples. Descriptive statistical of results are shown in Tab. I. In Fig. 2 to 5 are presented distribution maps of TOC, Nitrogen, Phosphorus, and N:P ratio.

Table I: Average concentrations and data range of TOC, N-total, P-total and nutrient ratios (n = 20 samples).

	TOC (%)	N-total (%)	P-total (%)	C:N (molar)	C:P (molar)	N:P (molar)
Average	1.26	0.163	0.162	8.9	20.3	2.2
St. Dev.	0.58	0.071	0.062	1.3	6.7	0.6
Maximum	2.37	0.303	0.276	11.0	32.2	3.4
Minimum	0.20	0.030	0.076	7.1	5.0	0.6

Average values of TOC were 1.26%, being the highest concentrations found in the southern part of lagoon. Total Nitrogen has a strong correlation with TOC ($r = 0.95$; $p < 0.01$), suggesting that these elements have the same sources, behavior and distribution patterns. This can be observed by comparing Fig. 2 and 3. Most elevated values of TOC and N also

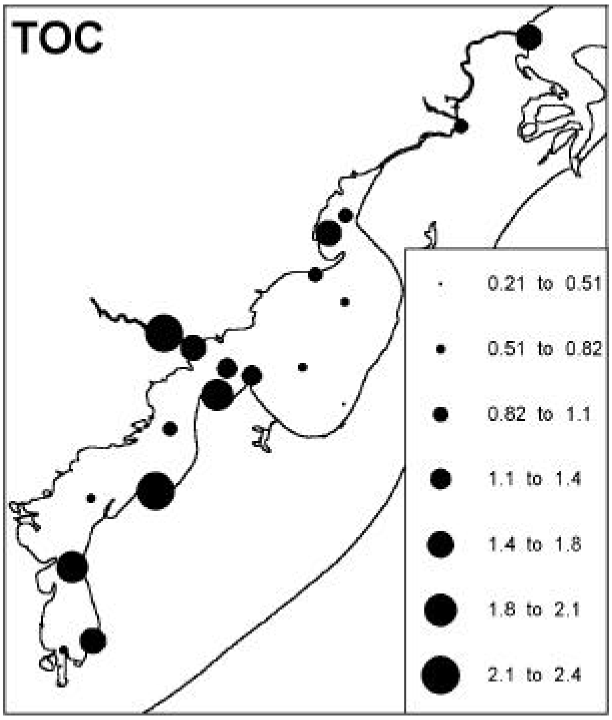

Figure 2: Distribution of TOC (values in %).

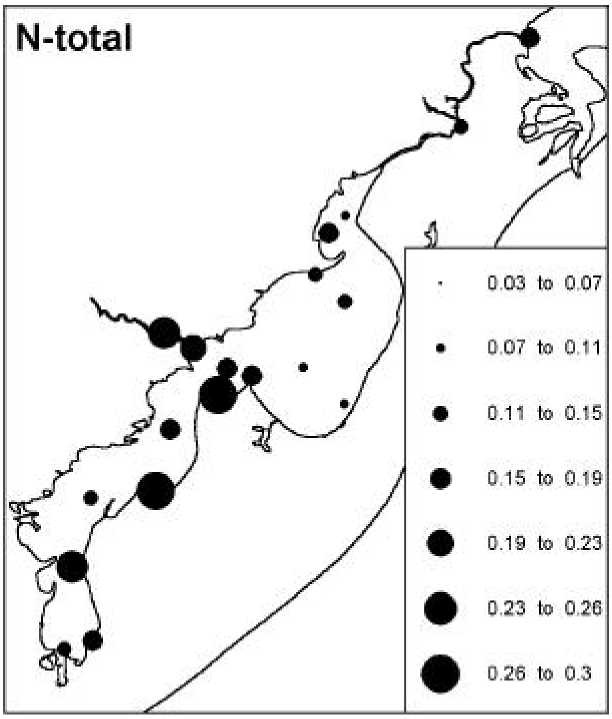

Figure 3: Distribution of N-total (values in %).

occur at sheltered and marginal sampling sites. The northern region of the lagoon is characterized by extremely low rates of carbon and nitrogen.

Phosphorus has average concentrations of 0.162%. Phosphorus also occurs in higher levels in the southern region of Mirim lagoon, being the concentrations in the northern region reduced (Fig. 4). Its distribution is also similar to that of carbon, which is demonstrated by strong correlation ($r = 0.77$; $p < 0.01$) with TOC.

The C:N molar ratio has a small standard deviation (Tab. I). C:P and N:P molar ratios showed an evident behavior, i.e., higher ratios were found in samples collected near the main fluvial inputs (Fig. 5). It indicates that rivers are probably more important sources of nitrogen than autochthonous production and/or fixation.

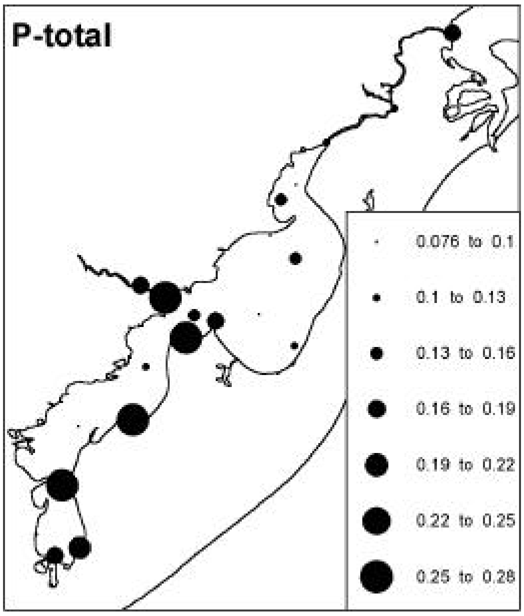

Figure 4: Distribution of P-total (values in %).

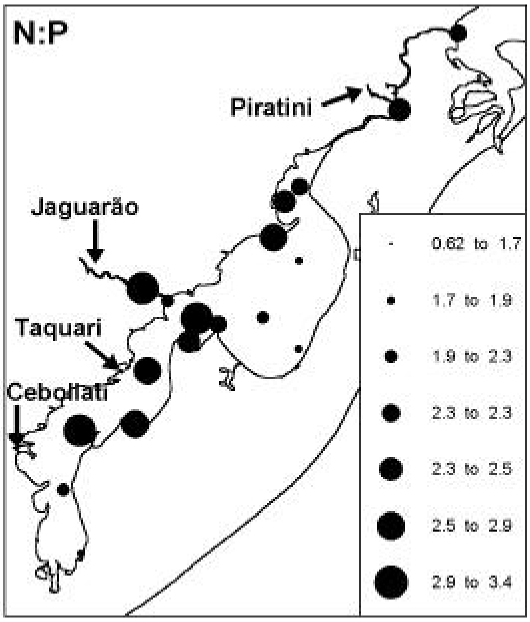

Figure 5: Distribution of N:P molar ratios and location of main rivers.

Discussion

The classification of organic contamination of Mirim lagoon sediments (Fig. 6) showed no samples fitted in Type II (high carbon contribution and slow oxygen demand) or Type IV (actively decomposing sediments, high potential of nitrogen release and oxygen demand) areas of the scatter plot. Most samples were classified as Type I, i.e., "inorganic or aged, stabilized organic deposits". Only five samples were classified as Type III, i.e., "sediments with nitrogen contribution". Nitrogen enrichment in samples classified as Type III are attributed to natural inputs, since carbon follows the same improvement pattern.

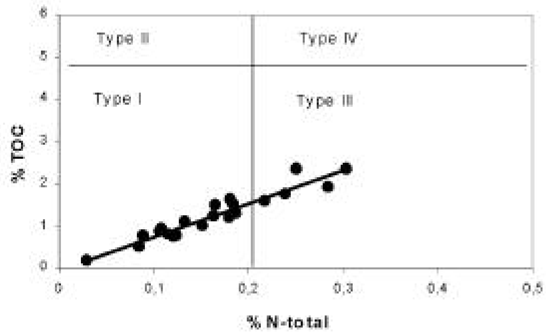

Figure 6: Classification of organic contamination in Mirim lagoon sediments (approach from Ballinger & McKee, 1971).

Mirim lagoon data are also compared to several world aquatic ecosystems (Tab. II). Carbon and nitrogen concentrations are similar to others water bodies from the Rio Grande do Sul State. However, Mirim values are usually low in comparison to sediments from other limnic and transition ecosystems all around the world, which emphasizes that Mirim lagoon sediments are poor in organic matter. This is likely to be a characteristic from the Patos-Mirim system, since this behavior has already been observed in sediments from limnic and estuarine regions in Patos lagoon (Baisch, 1994; Baisch & Wasserman, 1998). Phosphorus concentrations in Mirim lagoon are high in comparison to ecosystems listed in Tab. II.

Table II: Concentrations of TOC, N-total, and P-total in several ecosystems all around the world in comparison to Mirim lagoon. Values are equivalent to the average or range.

Local	TOC (%)	N-total (%)	P-total (%)	Reference
Mirim lagoon (RS-Brazil)	0.20-2.37	0.030-0.303	0.076-0.276	This study
Patos lagonn (RS-Brazil)	0.22-1.86	0.049-0.261	0.065-0.100	Baisch, 1994; Baisch & Wasserman, 1998
Tramandaí lagoon (RS-Brazil)	-	0.28	0.08	Silva et al., 2001
Sinos river (RS- Brazil)	1.90-3.51	0.201-0.599	0.089-0.135	Hatje, 1996
Jacuí river (RS-Brazil)	0.62-2.11	0.015-0.217	0.085-0.122	Baisch, 1994
Guaíba system (RS-Brazil)	1.36-3.61	0.210-0.476	0.102-0.175	Baisch, 1994
Rio Doce Valley lakes * (MG-Brazil)	10.7-30.0	0.5-2.3	0.08-0.34	Saijo et al., 1997
Rio de Janeiro lagoons (RJ-Brazil)	0.5-14.6	0.5-1.5	-	Knoppers et al., 1999
Baihua lake (P.R. China)	-	0.38	0.11	Wu et al., 2001
Lugu lake (P.R. China)	-	1.07	0.11	Wu et al., 2001
Erhai lake (P.R. China)	-	0.29	0.11	Wu et al., 2001
Jamsil Submerged Dam (Korea)	3.0	0.108	0.088	Kim et al., 2003
Chungpyung lake (Korea)	2.0	0.078	0.048	Kim et al., 2003
Nakaumi lake (Japan)	3.2	0.37	0.058	Yamamuro, 2000
Shinji lake (Japan)	2.3	0.28	0.072	Yamamuro, 2000
Culiacan river (Mexico)	0.3-3.0	0.04-0.29	0.044-0.310	Fernandez et al., 2002
Saguling reservoir (Indonesia)	-	0,093-0,360	0.046-0.220	Hart el al., 2002
Mejeas-Pérols lagoon (France)	2.8-6.8	0.19-0.60	0.045-0.107	Gómez et al., 1998
Taihu lake (P.R. China)	0.81-3.83	0.15-0.54	0.048-0.332	Qu et al., 2001

*Values estimated from figures

The low rates of carbon and nitrogen and the inorganic character of sediments can be considered a peculiarity of Mirim lagoon. This behavior is uncommon because coastal lagoons are usually sites of organic matter accumulation and high primary production (Nixon, 1982; Lins & Carmouze, 1993; Knoppers, 1994). Thus, three hypotheses were built for explaining the low rates of organic matter in Mirim lagoon: (1) fast organic matter remineralization; (2) the dilution of organic inputs; and, (3) the genesis and geology from the coastal plain.

The fast remineralization of organic matter is not a good hypothesis, considering that Mirim is located at a temperate climate region. On the other hand, Mirim lagoon is a shallow water body, has a very long fetch for wind-wave generation, and has low bottom declivity. These characteristics indicates that sediment resuspension processes, and consequently sediment-water interactions are very intense (Arfi et al., 1993). In this process, the sediment-accumulated organic matter is available for being quickly oxidized in the water column. This hypothesis is also supported by the incidence of most carbon and nitrogen at sheltered sites (Fig. 2 and 3), where resuspension is less probable to happen.

The organic input dilution is a possible hypothesis, considering the inexistence of important human-related inputs, and the big size of the lagoon. Furthermore, the low concentrations of carbon and nitrogen occur in the northern region, where the influence of river runoff is small. The high incidence of silt in relation to clays (Vieira, 1995; Santos, 2003) also favors dilution, since clays have a higher capacity of organic matter retention than silt sediments (Salomons & Forstner, 1984). The low rates of TOC in Patos lagoon sediments were explained by organic inputs dilution (Baisch & Wasserman, 1998).

Other aspect that probably contributes to low carbon and nitrogen rates is the geological history of Mirim lagoon. Although the origin of water body is from the Pleistocene, the current geomorphologic configuration is very recent. In the Pleistocene sea-level regression, the lagoon level decreased and its area was predominately a terrestrial ecosystem. In the Holocene (6,000 years B.P.) transgression the lagoon was submerged again (Villwock & Tomazelli, 1995). This means that Mirim lagoon is a young depositional environment, *i.e.*, there was little time for sinking and accumulating organic matter on its substratum.

Nutrients rates are very important for determining composition and growth rates of phytoplankton communities. That is why its assessment is a key factor in limnological studies (Hecky et al., 1993). Mirim lagoon sediments have an average N:P ratio of 2.2. This ratio is low in comparison to N:P of sediments from ecosystems listed in Tab. II. The low N:P ratio from Mirim lagoon sediments indicates that phosphorus is not the limiting factor for primary production, which is uncommon in limnic environments (Esteves, 1998). However, it cannot be confirmed without speciation data, since P-total data cannot be used for previewing ecological risks, like eutrophication (Kaiserli, et al., 2002). Furthermore, N:P in sediments gives an idea of sink, and not of bioavaibility.

Nutrient levels in sediments often do not accomplish water variations (Wu et al., 2001), but the comparison of both compartments can evidence certain behaviors. Unconcluded studies at Mirim lagoon water column shows that this environment is oligotrophic in relation to nitrogen nutrients (i.e., ammonium, nitrite and nitrate) and eutrophic in relation to total phosphorus (Friedrich et al., 2003). These data agree with sediments data, indicating limitation of primary productivity by nitrogen.

The high concentrations of phosphorus in comparison to other ecosystems and in relation to nitrogen can be explained by integration of anthropogenic inputs and natural processes, as follows:

(1) Use of phosphate fertilizers in the catchment is quite intense. In the Brazilian side of the catchment are applied approximately 180 $kg.ha^{-1}.year^{-1}$ of NPK fertilizers. The most used N:P:K composition is 0-5:20:20, but compositions more enriched in phosphorus are also used. The irrigated rice culture can export up to 30 $kg.ha^{-1}.year^{-1}$ of phosphorus into surrounding aquatic environments (IRGA, 2001).

(2) As described above, sediment resuspension is probably very frequent at Mirim lagoon. The process of resuspension promotes a decrease at nitrogen loads and

phosphorus enrichment at bottom sediments. In this process nitrogen is transferred to the water column, mainly as ammonium (Machado, 1989; Baumgarten et al., 1995), whereas phosphate has a high affinity for suspended matter (Esteves, 1998), being adsorbed on suspended matter during resuspension events (Gomez et al., 1998), precipitating, and accumulating in bottom sediments.

(3) Phosphorus concentrations in geological materials are quite higher than those of nitrogen (Wedepohl, 1995).

(4) Phosphorus recycling and/or regeneration at the sediment-water interface can be lower than nitrogen. Wu et al. (2001), for example, has shown that ammonium regeneration is higher than that of phosphorus in some Chinese lakes. Martens (1993) had also found lower values for phosphorus recycling efficiency in comparison to nitrogen in coastal sediments from Cape Lookout Bight, United States.

(5) High bird abundance at the region is another probable phosphorus source, throughout its dumpings.

Conclusion

In this paper we have presented the first data about carbon and nutrient content in Mirim lagoon sediments. It serves as a contribution for understanding environmental processes at Rio Grande do Sul State coastal plain and as reference for further monitoring programs.

The highest TOC, nitrogen, and phosphorus contents were verified in the southern region of lagoon, which is attributed to the proximity of the main fluvial discharges. Surprisingly, the sediments are poor in organic matter, which is attributed to the inputs dilution, high occurrence of sediment resuspension processes, and recent deposition of lagoon substratum.

Phosphorus concentrations were considerate high in relation to nitrogen and other ecosystems. This is likely to be associated to the intense use of phosphate fertilizers in the catchment and the high frequency of sediment resuspension, which tends to decrease nitrogen and increase phosphorus concentrations in bottom sediments. International management actions are necessary for decreasing fertilizers-related nutrient input and for avoiding eutrophication risks.

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