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### Influence of Effluents from a Wastewater Treatment Plant on Nutrient Distribution in a Coastal Creek from Southern Brazil

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#### **ABSTRACT**

The hypothesis that effluents treated through activated sludge process cause changes in nutrient biogeochemistry of receiving water bodies was investigated in Vieira creek, southern Brazil. Dissolved oxygen, suspended matter, and pH did not vary among the sampling stations. Nutrient, biochemical oxygen demand, and conductivity values were significantly higher downstream from the Wastewater Treatment Plant (WWTP) effluents. Further downstream, nitrate concentrations were higher due to ammonium nitrification, organic matter remineralization and/or the occurrence of unidentified sources. Per capita nutrient emission factors were estimated to be 0.16 kg P.yr<sup>-1</sup> and 4.14 kg N.yr<sup>-1</sup>. Under pristine conditions, low N:P ratios were observed, which were significantly increased downstream due to the high ammonium input. The mixing zone of the nitrogen-rich waters from Vieira creek with the phosphorus-enriched waters from Patos lagoon estuary was considered under high risk of eutrophication. The results could be useful for planning and management of WWTP-effluent receiving waters in temperate regions from developing countries.

Key words: Activated sludge; nutrients; contamination; coastal zone; biogeochemistry; eutrophication

#### INTRODUCTION

The world's coastal ecosystems receive high amounts of contaminants as a result of human activities. Aquatic environments adjacent to urban centers are highly affected by the environmental pressure, since they are the usual receptors for the domestic and industrial effluents. The greater concentration of urban centers at the coastal zone makes it particularly sensitive to sewage inputs. In addition to the high organic load, domestic sewage carries a large variety of contaminants, including pathogens, pharmaceuticals, plastics, heavy metals, petroleum hydrocarbons, and nutrients.

Although nutrients are essential for primary production, high concentrations can trigger an eutrophication process. Nowadays, eutrophication is considered one of the greatest threats to the coastal ecosystems (Goldberg, 1995), leading to a reduction in aquatic biodiversity, a disordered growth of primary producers, and increasing respiration rates in response to the rapid production of organic matter (Esteves, 1998; Júnior et al., 2006; Pereira et al., 2005). Global nutrient inputs into the coastal ocean is an increasing environmental problem, as it has tripled between the 1970s and the 1990s (Smith et al., 2003).

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In southern Brazil, the anthropogenic input of nutrients and signs of eutrophication have been observed since the 1980's (Almeida et al., 1993; Kantin and Baumgarten, 1981). The main causes of such contamination are the use of fertilizers in the agricultural activities (Santos et al., 2004) and the discharge of untreated urban sewage (Baumgarten et al., 1998; Baumgarten et al., 1995; Niencheski and Windom, 1994). Therefore, the implementation of sewage treatment processes has been considered a key solution to avoid eutrophication.

Sewage discharge into aquatic bodies is one of the greatest environmental problems in Brazil, as only about 14% of the cities have some kind of sewage treatment. The activated sludge process is the most widely used biological wastewater treatment for both domestic and industrial plants in the world, and one of the most used in Brazil. Biological wastewater treatment involves the transformation of dissolved and suspended organic contaminants into biomass and evolved gases, mainly CO<sub>2</sub> (Wei et al., 2003). Although such a process considerably reduces the whole organic load and the pathogen concentration of the effluent, nutrients are not removed (Andreadakis, 1997).

In the present work, the hypothesis of changes in water quality and biogeochemistry of aquatic systems caused by the discharge of secondarily-treated urban effluents was investigated. Estimates of nutrient emission factors and the likely significance of nutrient input into a phosphorus-enriched, semi-enclosed bay are also presented. The results obtained are important due to the dearth of similar investigations in small lotic water environments from Brazil (Petrucio et al., 2005) and in temperate regions from developing countries.

#### MATERIAL AND METHODS

The hypothesis that treated urban effluents do cause changes in the water quality of aquatic ecosystems was tested in Vieira creek (~32°S, 53°W), located in the city of Rio Grande, Rio Grande do Sul state, Brazil (Fig. 1). Vieira creek is a small, lotic environment that receives treated and, at times, raw effluents from the "ETE-Parque Marinha" wastewater treatment plant (WWTP). This WWTP treats domestic sewage from nearly 4,000 households, accounting for approximately 16,000 people, through activated sludge process.

The treated wastewater is continuously dumped into Vieira creek, whereas the raw effluent is only dumped when the sewage input exceeds the WWTP's capacity or during maintenance. The average treated effluent discharge into Vieira creek is 70 L.s<sup>-1</sup>. Vieira creek flows into Mangueira bay, a choked, microtidal, and shallow bay in the estuary of Patos lagoon. Mangueira bay is a natural nursery for commercially-valuable species, and has a high ecological importance for the estuarine region (Baumgarten et al., 1995; Castello, 1985).

Eighteen water sampling campaigns were carried out between June and November 2002. The water discharge of Vieira creek ranged from 1.4 to 3.5 m<sup>3</sup>.s<sup>-1</sup> (mean 2.4 m<sup>3</sup>.s<sup>-1</sup>) during this period. The location of the WWTP and its effluent emissaries allows for sampling stations to be strategically established (Fig. 1). Station 1 was located upstream from the effluent emissaries, reflecting natural environmental conditions. Station 2 was located downstream from the raw effluent, thus making its physical and chemical parameters representative of the raw effluent's impact. At Station 3, the influence of treated effluent was examined, as the station was located immediately downstream from it. Finally, the self-depuration ability of the creek was examined at Station 4, located approximately 700 m downstream from both effluents.

Water for the chemical analysis was collected in pre-washed plastic containers. Temperature, pH, and conductivity were determined immediately after sampling. Dissolved oxygen (DO) and biochemical oxygen demand (BOD) were determined through the iodometry method (APHA, 1989). Particulate suspended matter (SM) was defined as the material retained by a 0.45-μm filter. From the filtered fraction, phosphate, silicate, nitrite, nitrate, and ammonium were determined through colorimetric (Strickland and Parsons, 1972). Concentrations found for the parameters studied at the different sampling stations were compared through analysis of variance (one-way ANOVA) with a 95% significance level. Significant differences were tested by Tukey's post-hoc multiple test.

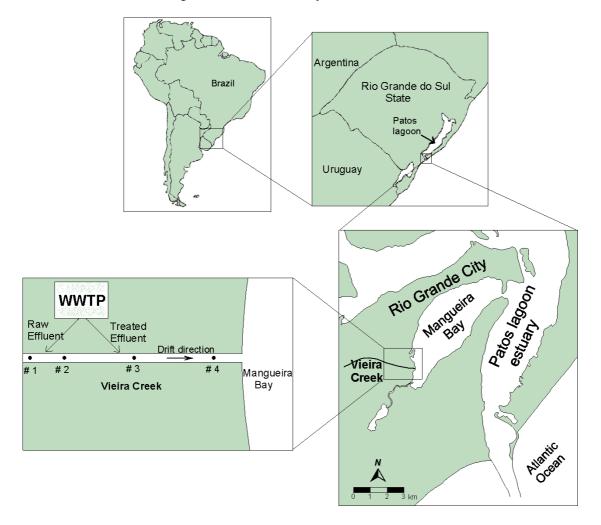
#### **RESULTS AND DISCUSSION**

## Spatial variability and biogeochemical processes

Descriptive statistics for the studied chemical variables and ANOVA results are shown in Table 1. Temperature, pH, suspended matter and oxygen values were similar among the sampling stations, but the values of conductivity, BOD, and nutrients varied significantly (p<0.05). The conductivity increase at Station 3 (Fig. 2) indicated the influence of the WWTP treated effluent on the quality of Vieira creek waters, while the increase found at Station 4 pointed out to ion inputs other than the treated effluent alone. No correlations were found between the water discharge and the measured parameters. However, this should be better assessed, considering that 2002 was a rainy

year and the discharge of Vieira creek varied within a narrow range.

BOD can be used to evaluate the success of the treatment system in removing organic matter from the effluent. The higher values in the samples downstream from the treated effluent (Table 1; Fig. 2) indicated that treatment was not removing 100% of the organic and, probably, bacterial load of the sewage. The variability in BOD determinations reflected fluctuations in the efficiency of the treatment. According to the WWTP administration, the efficiency of the treatment process usually ranges from 95 to 99%. The similarity of BOD values between Stations 1 and 2 showed that raw effluent was never released, confirming visual observations during the sampling procedures.



**Figure 1** - Schematic representation of sampling stations along Vieira creek and relative location to Patos lagoon estuary, Rio Grande do Sul state, Brazil.

Nutrient concentrations presented a marked variation among the sampling stations (Fig. 2; Table 1). The lowest nutrient concentrations occurred at Stations 1 and 2, while an increase was observed at Station 3, which is inherent to effluent-receiving waters subjected to secondary treatment. The significant increase in conductivity, nitrite and nitrate concentrations from Station 3 to Station 4 (Table 1) indicated (1) additional anthropogenic input along this section of Vieira creek (i.e., raw wastewater from local inhabitants); (2) a significant nitrification process, as expected in oxygenated and ammonium-rich environments (Silva et al., 2001); and/or (3) mineralization of the anthropogenic-derived organic matter. The increase in nutrient concentrations at Station 4 also indicated that the self depuration ability of the creek was lower than nutrient inputs, and that the anthropogenic dissolved nutrients had not been incorporated by local primary producers.

Although the WWTP was not expected to alter the silicate levels in Vieira creek, the slightly higher silicate concentration in tations 3 (Table 1) indicated a detectable influence of the effluent on the silicate content. Higher silicate concentrations in Station 4 supported the hypothesis of other natural or anthropogenic inputs between Stations 3 and 4, probably as baseflow (groundwater seepage). Phosphate behavior, in turn, was probably influenced by the suspended matter distribution. As phosphorus presents high sedimentary affinity, high concentrations of suspended matter favor the removal of the dissolved phosphorus (Gomez et al., 1998). In the waters around the city of Rio Grande, low-salinity conditions with high suspended matter loads favored the retention of phosphorus in the suspended matter (Baumgarten et al., 1995). Therefore, the low suspended matter content in Vieira creek and the sandy nature of its sediments favored most of the phosphate to be in dissolved rather than particulate form. This process appears to explain its high concentrations.

According to water quality criteria from the state's legislation, Vieira creek water is classified as Class 2 (Baumgarten and Pozza, 2001). Phosphate concentrations at Stations 3 and 4 usually surpassed the legal limits (0.025 mg.L<sup>-1</sup>) for the class, while ammonium concentrations exceeded the maximum limits (0.02 mg.L<sup>-1</sup>) a few times. The BOD limit (5 mg.L<sup>-1</sup>) was exceeded twice at Stations 3 and 4, probably due to problems in the

sewage treatment. The other variables under investigation did not reach beyond the legal limits.

#### **Outputs to Patos lagoon estuary**

A comparison between the nutrient concentrations was conducted in order to investigate whether inputs from Vieira creek increased the dissolved nutrients levels of Mangueira bay. As a result of the elevated domestic and industrial inputs, Mangueira bay is nutrient-enriched (Phosphate: 3.0  $\mu$ M; Nitrate: 12.5  $\mu$ M; Nitrite: 0.5  $\mu$ M; Ammonium:  $5.9 \mu M$ ; Silicate:  $71.8 \mu M$ ). Mangueira bay acts as a phosphate reservoir, since its levels are normally three times higher than in other areas of Patos lagoon estuary, mainly due to industries input from local fertilizer (Baumgarten et al., 1995). Nitrite and ammonium levels found in Mangueira bay were generally similar to the ones found at Stations 1 and 2, and one order of magnitude below values found at Stations 3 and 4. Silicate and phosphate levels were always lower than Mangueira bay at stations upstream from the WWTP and slightly higher at stations located downstream. Such data indicated that Vieira creek probably enriched Mangueira bay in terms of nitrite and ammonium.

Nutrient proportions are highly important in the determination of the growth and composition of the phytoplanktonic communities, making its assessment a key factor in limnologic studies (Hecky et al., 1993). Phytoplankton usually assimilates nitrogen and phosphorous at an atomic ratio near 16. Levels under 16 indicate an excess of phosphate in relation to nitrogen, whereas values over 16 indicate an excess of nitrogen over phosphate relative to the primary producers demand (Redfield, 1958). In the present study, most N:P ratios at Stations 1 and 2 were lower than 16, indicating that nitrogen was the limiting factor for primary production in Vieira creek, when in its pristine condition. At Stations 3 and 4, N:P ratios were highly over 16, demonstrating that the influx of nitrogen nutrients from the WWTP was relatively more important than the phosphorous input. Such results showed that the distribution of nutrient species was altered by the effluent input, similar to what has been found for larger rivers (Howarth et al., 1996; Martinelli et al., 1999).

Generally, the N:P ratio in Patos lagoon and its estuarine region is lower than 10 (Abreu et al.,

1994; Baumgarten et al., 1995; Bergesch, 1990) and laboratory studies demonstrated that nitrogen was the main limiting factor for the primary producers (Jesus and Odebrecht, 1999). Thus, the greater input of nitrogen nutrients relative to phosphate from Vieira creek to Mangueira bay brings eutrophication risks and could contribute to the degradation of the estuarine region. The fact Mangueira bay is a semi-enclosed environment may aggravate such a situation (Al-Muzaini et al., 1999; Laws et al., 1999). However, the influx of nutrients into Mangueira bay during water dominance brings eutrophication risk, considering that salt waters dilute the regional anthropogenic inputs (Baumgarten et al., 1998).

The nutrient load exported from Vieira creek to the Patos lagoon estuary (Mangueira bay) was estimated by multiplying the concentration of dissolved nutrients from Station 4 by the observed water discharge. Values ranged between 2.8 kg.day<sup>-1</sup> for nitrite and 177.8 kg.day<sup>-1</sup> for ammonium (Table 2). Mangueira bay has an average depth of 1.5 m and a superficial area of 27 km<sup>2</sup> (Monteiro et al., 2005). Using these figures concentration and its average nutrient (Baumgarten et al., 1995), the total average nutrient load in the bay could be calculated and compared with Vieira creek's daily input. This calculation indicated that the total amount of dissolved nutrients in Mangueira bay was as follows: P-PO<sub>4</sub> (1229 kg), N-NO<sub>3</sub> (1600 kg), N-NO<sub>2</sub> (86 kg); N-NH<sub>4</sub> (2755 kg), and S-SiO<sub>2</sub> (24780 kg). By comparing these values with the average daily inputs from Vieira creek shown in Table 2, it could be estimated that in only about 15 days Vieira Creek supplied to Mangueira Bay an amount of N-NH<sub>4</sub> equivalent to its total stock. The replacement times for P-PO<sub>4</sub> (150 days) and S-SiO<sub>2</sub> (388 days) were much longer.

This finding not only quantitatively reinforced that the WWTP effluent was an important source of nutrients (especially ammonium) to Mangueira bay, but also indicated that a significant part of this input must be quickly removed from the system (i.e., biological uptake, sediment accumulation, and/or exportation to the estuary), otherwise Mangueira bay dissolved nutrient concentrations would be much higher. In Patos lagoon estuary, nutrients supplied by the freshwater supply were rapidly removed in the oligohaline region (Niencheski et al., 1986; Niencheski and Windom, 1994; Windom et al.,

1999), which could cause localized toxic algae blooms. Therefore, the region near the outlet of Vieira creek might be at a high risk of eutrophication. Taking into account that this work quantified only the nutrient inputs from the treated effluents, other investigations should use the values presented here and compare it with other inputs (i.e, industrial and urban effluents), outputs (sedimentation and outflow), and biogeochemical transformations rates (uptake, nitrification, etc) within Mangueira bay. Such studies would be needed to establish nutrient budgets in the bay, which might help to determine regional pollution prevention strategies.

#### Per capita emission factors

An estimation of the relative contribution of anthropogenic inputs is also presented in Table 2, relative to the total nutrient content in Vieira creek. It was calculated through the difference between the concentrations at Station 4 (downstream) and Station 1 (upstream). The results showed that the baseline nutrient levels in Vieira creek were strongly altered by the effluent input from the WWTP. Nitrogen anthropogenic inputs were the most important ones, followed by phosphate. In fact, ammonium usually was the most enriched nutrient in other effluent-receiving waters (Howarth et al., 1996; Martinelli et al., 1999; Robson and Neal, 1997a; Robson and Neal, 1997b).

By dividing the anthropogenic contribution of inorganic nutrients by the number of households served by the WWTP (4,000), it was possible to estimate the emission factor, reaching 15.45 kg N-NH<sub>4</sub><sup>+</sup> per household per year (Table 2). Assuming that an average of four people lived in each household, the per capita emission factor (how much each dweller emits to the environment after his or her effluent was treated through the activated sludge process) showed an average of 0.16 kg P.yr<sup>-1</sup> and 4.14 kg N.yr<sup>-1</sup> (Table 2). Those emission factors could be representative of receiving bodies in developing countries from temperate regions, and are important for assessing the impacts of secondarily-treated wastewaters on the biogeochemical balance of nutrients, for inferring the assimilative capacities of the water environment, and for planning the correct placement of future WWTPs.

The estimations of per capita nitrogen emission factors (Table 2) were very similar to the world average, which is 4.35 kg per person per year

(Smith et al., 2003). This indicated the deficiency of the activated sludge process in the removal of nitrogen from the domestic sewage. World estimates of dissolved inorganic phosphate emissions (0.53 kg per person per year) were three times higher than the levels estimated for Vieira creek, which could be related to the fact that a larger amount of phosphate was retained in the sludge.

Fig. 3 presents a summary of processes discussed in this paper. Secondary treatment caused the input of organic matter to be small and, consequently, the oxygen levels were within the natural ranges.

However, the anthropogenic input of nutrients significantly altered baseline levels of Vieira creek waters. The distribution of nitrogen species and N:P ratios in Vieira creek were changed by the treated effluent inputs. Ammonium input was of the greatest environmental concern. In addition, Mangueira bay, which receives Vieira creek's input, has been shown to be a nitrogen-limited environment. Therefore, even small additions of dissolved nitrogen might cause significant ecological changes and be hazardous to human and ecosystem health.

**Table 1 -** Results of the studied parameters (mean; minimum and maximum) at each sampling station and results of variance analysis.

	Station 1	Station 2	Station 3	Station 4	ANOVA
Temp (°C)	16.61	16.50	16.56	16.62	1=2=3=4
	(10.5 - 22.5)	(10.7 - 22.5)	(10.8 - 22.5)	(10.8 - 22.5)	
Cond. (µS/cm)	84.89	85.37	109.21	139.64	4>3>2=1
·	(75.5 - 103.8)	(75.5 - 103.2)	(92.8 - 141.6)	(122.5-196.4)	
pН	6.09	6.11	6.17	6.24	1=2=3=4
	(5.3 - 6.91)	(5.15 - 6.87)	(5.3 - 6.92)	(5.45 - 6.93)	
SM (mg L <sup>-1</sup> )	3.16	2.76	5.97	4.68	1=2=3=4
	(0.5 - 9.2)	(0.4 - 7.6)	(0.67 - 37)	(1.2 - 13.33)	
DO (mg L <sup>-1</sup> )	6.75	6.88	6.80	6.62	1=2=3=4
	(3.33 - 9.3)	(3.24 - 9.4)	(2.93 - 9.4)	(0.88 - 9.5)	
BOD <sub>7</sub> (mg L <sup>-1</sup> )	1.10	1.05	3.30	4.35	4=3>2=1
	(0.3 - 3.8)	(0.11 - 2.7)	(0.6 - 12.2)	(0.72 - 11.2)	
Phosphate (µM)	0.63	0.60	3.61	3.93	4=3>2=1
	(0.22 - 1.58)	(0.31 - 1.25)	(0.68 - 12.12)	(1.55 - 12.95)	
Silicate (µM)	14.37	16.59	28.67	36.29	4=3>1; 1=2;
	(5.0 - 30.4)	(6.1 - 47.7)	(8.9 - 79.0)	(11.0 - 78.9)	2=3
Nitrite (µM)	0.29	0.36	0.82	3.17	4>3>2=1
	(0.00 - 0.65)	(0.06 - 0.88)	(0.15 - 2.25)	(0.48 - 11.67)	
Nitrate (µM)	2.00	2.24	5.60	16.50	4>3>2=1
-	(1.02 - 3.04)	(1.47 - 3.07)	(1.88 - 7.49)	(3.80 - 33.49)	
Ammonium					
$(\mu M)$	3.58	4.22	65.25	74.75	4=3>2=1
	(0 - 33.9)	(0 - 59.9)	(29.6 - 124.3)	(37.2 - 185.1)	

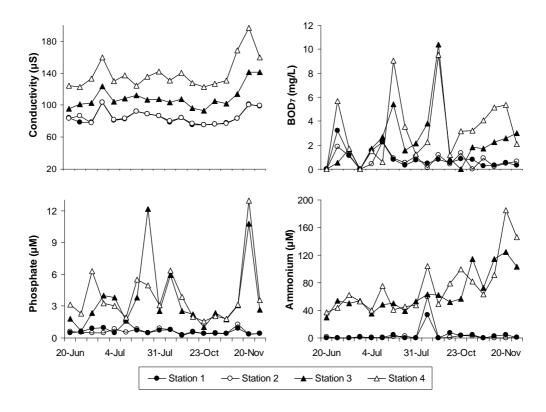
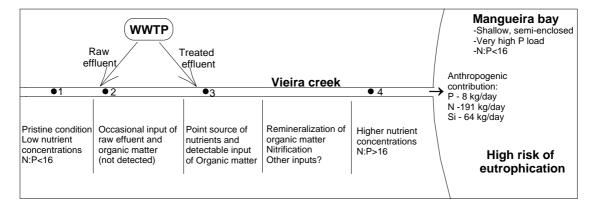


Figure 2 - Concentrations of some water quality indicators in Vieira creek at the four sampling points.

Table 2 - Nutrient input into Mangueira bay, relative anthropogenic contribution and per capita emission factors.

	Input to Mangueira bay (kg/day)	Relative anthropogenic contribution (%)	Dissolved inorganic nutrient yield (kg.household <sup>-</sup> ¹.year <sup>-1</sup> )	Dissolved inorganic nutrient yield (kg. person <sup>-1</sup> .yr <sup>-1</sup> )
P-PO <sub>4</sub>	8.2	83.9	0.63	0.16
Si-SiO <sub>2</sub>	63.8	60.4	3.52	0.88
N-NO <sub>2</sub>	2.8	90.8	0.23	0.06
$N-NO_3$	10.8	87.9	0.86	0.22
$N-NH_4$	177.8	95.2	15.45	3.86



**Figure 3** - Schematic diagram summarizing the processes associated to treated-sewage input from the WWTP into Vieira creek.

#### **CONCLUSIONS**

Fig. 3 presents a summary of processes discussed in this paper. Secondary treatment caused the input of organic matter to be small and, consequently, the oxygen levels were within the natural ranges. However, the anthropogenic input of nutrients significantly altered baseline levels of the waters of Vieira creek. The distribution of nitrogen species and N:P ratios in Vieira creek were changed by the treated effluent inputs. Ammonium input was of the greatest environmental concern. In addition, Mangueira bay, where Vieira creek drains to, has been shown to be a nitrogen-limited environment. Therefore, even small additions of dissolved nitrogen might cause significant ecological changes and be hazardous to human and ecosystem health.

Although BOD determinations indicated that the system efficiently removed most of the organic load from the sewage, the treated effluent significantly changed the water quality and the biogeochemistry of Vieira creek. This was aggravated by the fact that the WWTP was a continuous source. Considering that the secondary treatment did not prove fully satisfactory, more effective measures of environmental control would be needed, such as wastewater tertiary treatment with the aim of removing the nutrients from the effluent. Another suggestion would be the use of a different water body for effluent dilution, with a greater size and self-depuration ability.

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#### RESUMO

A hipótese de que efluentes urbanos tratados através de um sistema de lodo ativado causam alterações na qualidade de água de ambientes aquáticos foi investigada no Arroio Vieira, Rio Grande, RS. Amostras de água foram coletadas a montante e a jusante dos emissários de uma estação de tratamento de esgoto (ETE). Oxigênio, material em suspensão e pH não variaram espacialmente. Já os valores para os nutrientes e para a demanda bioquímica do oxigênio foram significativamente maiores a jusante dos efluentes. Mais a jusante, as concentrações de nitrato aumentam devido à nitrificação do nitrogênio amoniacal, remineralização da matéria orgânica ocorrência de outros aportes identificados. A emissão de nutrientes per capita após o tratamento dos efluentes domésticos (0.16 kg P ano<sup>-1</sup> e 4.14 kg N ano<sup>-1</sup>) é elevada. O aporte dos efluentes da ETE causa uma alteração acentuada das razões N:P, sendo os valores maiores a jusante da ETE devido ao aporte preferencial de nitrogênio amoniacal. Os resultados indicam que no local onde as águas do Arroio Vieira, enriquecidas em nitrogênio se misturam com as águas do estuário da Lagoa dos Patos, enriquecidas em fósforo, há grande risco de eutrofização. Os resultados são úteis para o planejamento e gerenciamento de águas receptoras de efluentes em regiões temperadas de paises em desenvolvimento.

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