Anthropogenic effects in a costal lagoon (South Portugal) related to tidal and spatial changes in nutrients

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Abstract: **-**The distribution of nitrogen compounds during tidal cycles was analyzed in Ria Formosa, a costal lagoon (South of Portugal) during the beginning of the summer season. Results indicate a significant enrichment in organic nitrogen up to 55 µmol L^{-1} in the studied areas where the anthropogenic effect was high. No significant changes were observed within tidal cycles although that may be related to low water circulation and renewal. High concentration of nitrate in pore water (up to 275 µmol L^{-1}, high amount of ammonia (~1,8 µmol L^{-1} at high tide) and high concentration of total phosphorus in sediments could be linked to sewage disposal from wastewater treatment plants associated with lower water circulation and renewal in the studied area. The samples were analyzed for Kjeldahl N, nitrate, nitrite, ammonia, phosphate, total phosphorus.

Key-Words: - nitrogen, organic nitrogen, phosphorus, lagoon, coastal, nutrients, tidal, sediments, eutrophication

1 Introduction

As transition spaces between land and sea, coastal lagoons are generally characterized not only by a high rate of dynamic changes in the natural environment and high biological productivity and diversity, but also by a high rate of human population growth and economic development, accompanied by a high rate of degradation of their natural resources [1].The Ria Formosa (Fig.1) is a barrier lagoon system

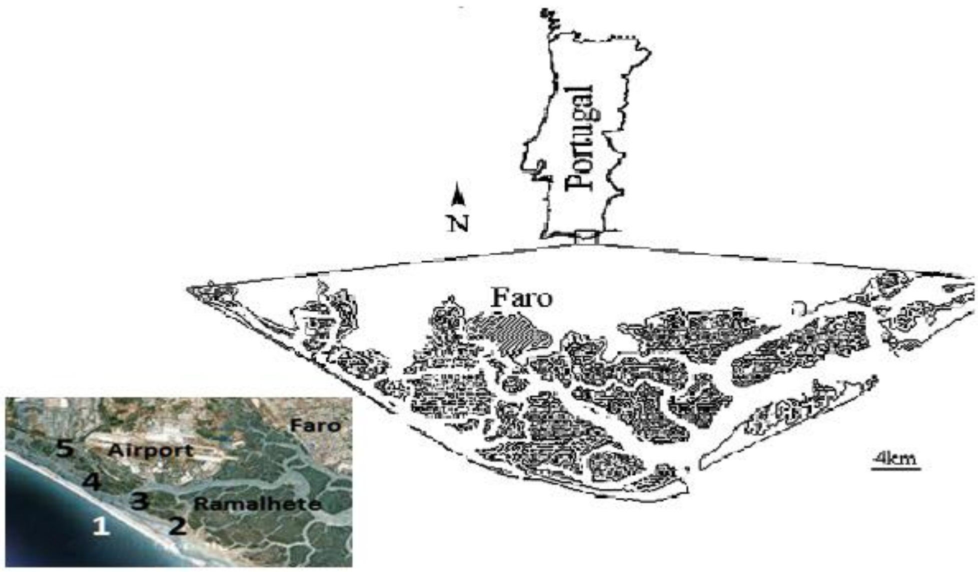

Figure 1 Studied area of the Ria Formosa, the western channel and the sampling stations

located in the Algarve coast in the southern part of Portugal, 55 km long and 6 km at its widest with a mean depth of 3 m [2]. The lagoon marsh is a complex network of tidal channels; some are navigable to the main ports like Faro, via natural or artificial inlets [3]. The lagoon is highly productive because of increased nutrient concentrations and isolation from the open sea, although and a complex tidal water exchange allows renewal inside the lagoon. Between 50 and 75% of the water in the lagoon is exchanged daily by the tides [4]. Coastal engineering and infrastructure in this part of the Ria Formosa includes an artificial inlet, an international airport on the mudflats; two large sewage treatment plants to the east and west of Faro city [5, 6, 7]. The hinterland of the lagoon is farmed intensively with the use of ammonium, nitrate, urea and phosphate fertilizers as well there are large pig and chicken farms [8]. In shallow areas of the lagoon, where a small volume of water is in contact with a large surface area of sediment, benthic fluxes are an important source of nutrients [9]. More recently, much of the sewage disposal into the western lagoon has been concentrated around the Ramalhete channel near the airport. Suffering from the impact of several touristic resorts with large areas of irrigated golf courses [10, 11] plus the urban centers [12] where population can increase 3-5 times during summer months, the western channel is highly susceptible to eutrophication problems [13]. As the dynamic of the water is strongly affected by the inlets it is difficult to predict water and nutrient circulation patterns in the lagoon [14]. However a difference in nutrient concentration with tidal conditions indicates complex processes associated with the inundation and exposure of sediments. The main nutrients causing eutrophication are nitrogen in the form of nitrate, nitrite or ammonium and phosphorus in the form of *ortho*-phosphate. In addition, supply of bio available organic phosphorus and nitrogen contribute as well to eutrophication since bacteria under oxygen consumption regenerates the organic phosphorus to phosphate and the organic nitrogen to ammonium, which is further oxidized to nitrite and nitrate. Silicate is essential for diatom growth, but it is assumed that silicate input is not significantly influenced by human activity. However, enhanced primary productivity may exhaust silicate and change the phytoplankton community from diatoms to flagellates [15]. Overloading with nitrogen and phosphorus can result in a series of undesirable effects. This may be enhanced by changes in the species composition and functioning of the pelagic food web by stimulating the growth of small flagellates rather than larger diatoms, which leads to lower grazing by copepods and increased sedimentation. The consequent increase in oxygen consumption can in areas with stratified water masses lead to oxygen depletion and changes in community structure or death of the benthic fauna. Bottom upwelling fish may either die or escape. Besides the negative biological effect there are negative economy impacts. Eutrophication can also promote the risk of harmful algal blooms that may cause discoloration of the water, foam formation, death of benthic fauna and wild or caged fish, or shellfish poisoning of humans. The Ria Formosa is a valuable regional resource to the Algarve for tourism, fisheries, aquaculture and salt extraction—all industries that rely on good water quality [16].

2 Materials and methods

Water samples were collected in pre-cleaned plastic bottles along the western channel following the artificial inlet to the dead end in May / June 2009 (Fig.1). Lagonal water samples (station 2-5) were collected in increasing distance from the Atlantic Ocean. Seawater was collected from outside the lagoon (station 1). At each sampling point, measurements of water temperature and salinity were taken in situ. Water samples were collected about 30 cm depth from the surface and kept in a cool box for transportation to the laboratory to be analyzed. Samples were analyzed for Total Kjeldahl Nitrogen (TKN), ammonia, nitrite, nitrate, total phosphorus and phosphate. Sediment cores around 25 cm lengths and 10 cm diameter were taken by means of a specific devices (Fig. 2 and 3) from the lagoon flats. The sediment samples were analyzed for humidity, organic matter, TKN and total phosphorus content.

Figure 2 Sediment core and cool box on the field

The method for TKN consists of heating the sample with sulfuric acid, which decomposes the organic substance by oxidation to liberate the reduced nitrogen as ammonium sulfate. The solution was then distilled with sodium hydroxide which converts the ammonium salt to ammonia. The amount of ammonia present was determined by back titration. The end of the condenser is dipped into a solution of boric acid. The ammonia reacted with the acid and the remainder of the acid was then titrated with a sodium carbonate solution with a pH indicator.

Nitrate / nitrite samples passed through a copper-coated cadmium reduction column. Nitrate in the sample was reduced to nitrite in a buffer solution. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-1-naphthyl – ethylene – diamine - dihydrochloride to form a color azo dye. The absorbance measured at 540 nm was linearly proportional to the concentration of nitrite + nitrate in the sample.

Nitrate concentrations were obtained by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values. Nitrite and Nitrate samples were analyzed by the auto analyzer (SAN Plus Segmented Flow Analyzer, Skalar, Breda, NL).

Ammonia in solution reacted with alkaline phenol and nitroprussid-sodium-dihydrate at 60 C° to form indophenol blue in the presence of sodium nitroferricyanide as a catalyst. The absorbance of indophenol blue at 640 nm was linearly proportional to the concentration of ammonia in the sample.

Phosphate samples reacted with ammonium-molybdate and antimony-potassium-tartrate in an acidic medium to form an antimony-phospho-molybdate complex. This complex was reduced to an intensely blue-colored complex by ascorbic acid. The absorbance measured at 880 nm was proportional to the phosphate concentration present in the sample

Figure 3 Water and sediment sampling in the studied area

The detection of total phosphorus based on the digesting with a sulfuric acid solution containing potassium sulfate and a catalyst convert all P to PO_4^-. The PO_4^- reacted with ammonium molybdate in the presence of H_2SO_4 to form a antimony-phospho-molybdate complex. Potassium antimonyl tartrate and ascorbic acid were used to reduce the complex, forming a blue color which was measured at 880 nm. This was proportional to the TP concentration. These procedures were according to the methods described by Grasshoff *et al* [17].

3 Results

3.1 Nitrogen It is noticeable the differences between the mean concentrations of nitrogen nutrients following the western channel. Coming from the open sea to the inner parts of the lagoon there was a strong increase of total nitrogen. Near the back of the barrier - station 2 inside the lagoon - the biggest difference between low and high water was found. The concentration of total nitrogen was 20 times higher at low water.

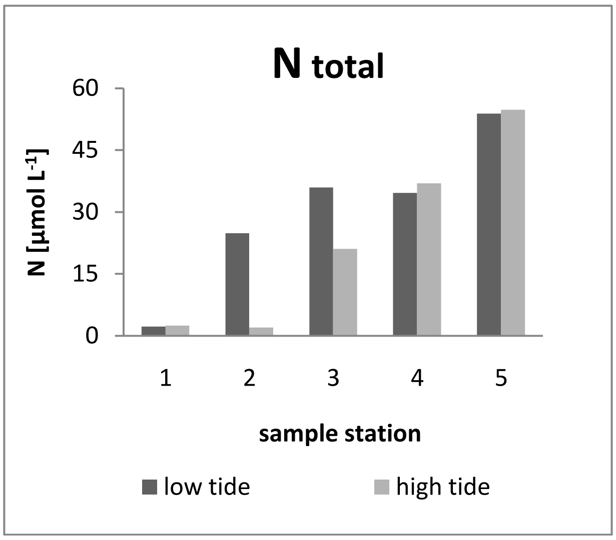

Figure 4 Distribution of total nitrogen at low and high tide

By increasing distance from the ocean this difference was equalized and stabilized at the high concentration both at low and high water over 55 µmol L^{-1} (Fig.4). There was a progressive increase in organic nitrogen (Fig. 5 and 6) from the costal station to the inner parts of the dead end of the channel. There the organic nitrogen reached more than 80% of the total nitrogen.

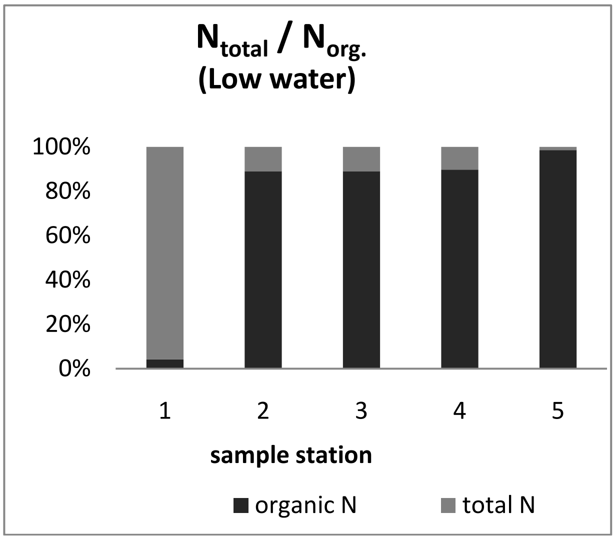

Figure 5 Percentage of organic N from the total N at low water

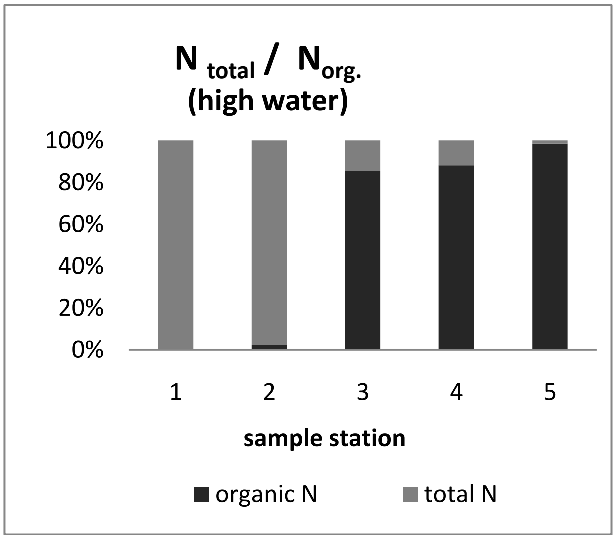

Figure 6 Percentage of organic N from the total N at high water

The concentration of organic nitrogen increased in relation to the total nitrogen at both low and high tides (Fig. 5 and 6). The highest concentrations of organic nitrogen were associated with the station 5 with 97% of organic nitrogen. Up to 55.2 µmol L^{-1} at highwater and 53.1 µmol L^{-1} at low water indicates a permanent source of nitrogen near the end of the lagoon. The costal water (station 1) showed in both tides the lowest concentrations.

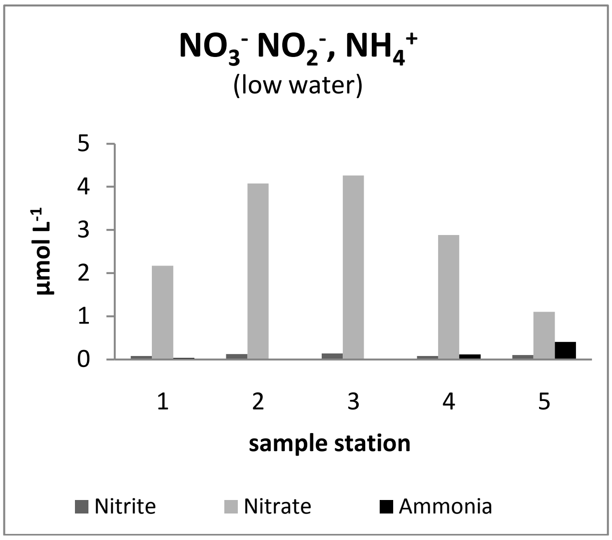

Figure 7 Inorganic nitrogen compounds at low water

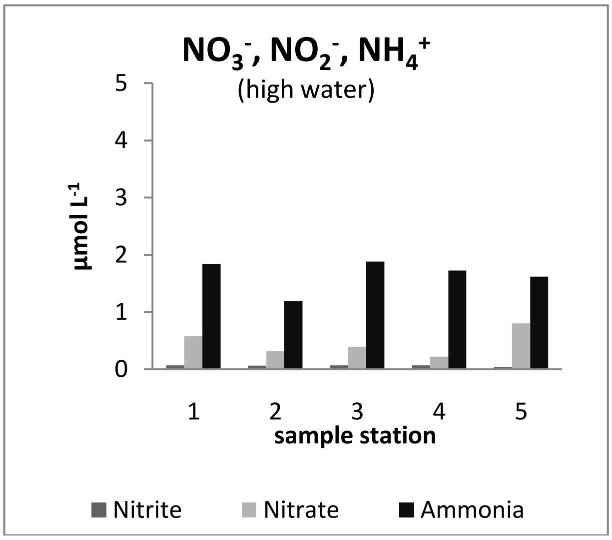

Figure 8 Inorganic compounds at high water

During the studied period the concentration of ammonia (Fig. 7 and 8) reached the highest level (~1.8 µmol L^{-1}) at high water. This was correlated with low concentration of the oxidized nitrogen forms nitrate and nitrite < 1 µmol L^{-1}. At low water there was a nearly absence of ammonia (station 1-4 with max 0.12µmol L^{-1}) and a predominance of nitrate up to 4.26 µmol L^{-1}. Only at station 5 the concentration of ammonia was with 0.8 µmol L^{-1} even at low tide high.

3.2 Phosphate

In general the phosphate concentrations were not high but there were differences between the tides and the stations.

Figure 9 shows the different concentrations of the phosphate following the western channel at low and high water. At high water, the samples from the ocean showed the smallest amount of dissolved phosphate. Towards the land there was a small increase of phosphate. At the end of the lagoon the samples showed concentrations of 2.31 µmol L^{-1} of phosphate that was the highest amount observed-

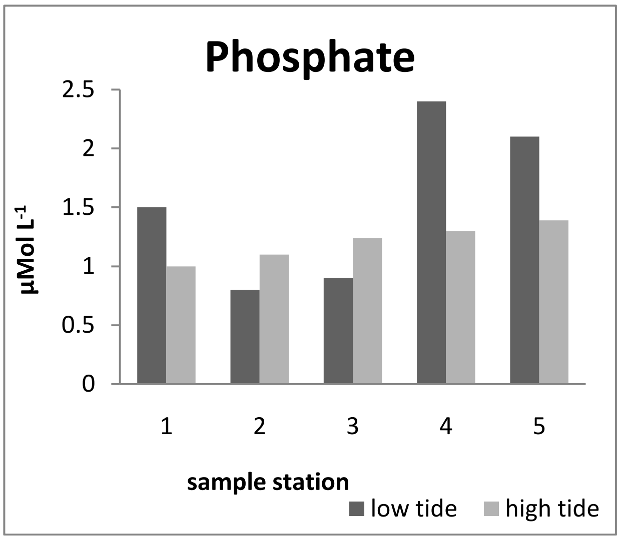

Figure 9 Distribution of phosphate during low and high tide

Based on the small amount of the increased concentration, it seems to be that phosphate at high water is quite well distributed. At low tide the highest amount of phosphate was again related to the dead end of the channel. However the smallest concentration of phosphate can be found near the inlet. The phosphate concentration in the outgoing lagoonal water is decreasing towards the ocean. Compared to the coastal water samples there is a sudden increase. The costal water contains higher amount of phosphate than the out flowing lagoonal water. Based on the nearly double of the observed concentrations of phosphate at the dead end compared to the outging lagoonal water, there must be a source of phosphate during the low tide near the transit to the land.

3.3 Sediments.

The lagoon marshes of the Ria Formosa, as transitional coastal environment located at the land / sea interface showed three main different types of sediment. Near the inlets and in the main channels of the lagoon submitted to strong currents, prevail the sandy sediments while in the inner parts of the lagoon and inter-tidal areas, mud or muddy- sand sediments predominate [18]. The sediment cores near the ocean inlet and inside the costal sediment showed pure sandy substrate. Low content of organic matter and big grain size were observed for this part of the sampling area. Following the channel to the mainland the sediments changed to muddy substrate with a high content of organic matter. This difference was also reflected in the concentration of organic N and total P inside the substrates (Fig. 10 and 11).

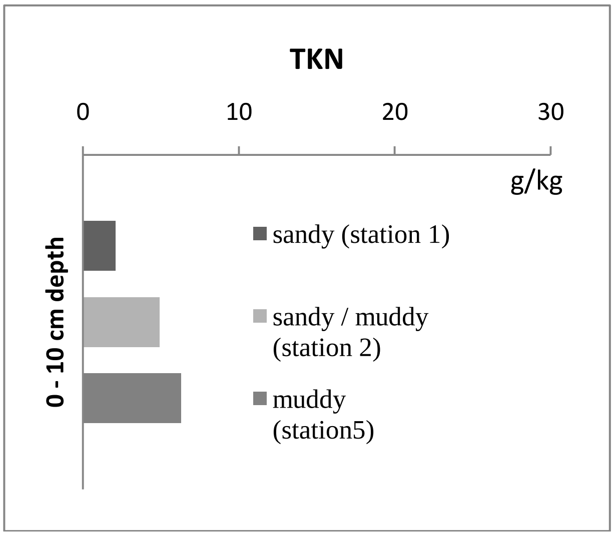

Figure 10 Total Kjeldahl nitrogen in different sediment types

The highest amount of N and P in the first 10 cm could be found in the sediments near the transition to the main land. Meanwhile the smallest concentrations were related to the costal sediments.

A strong increase in P and N towards the mainland showed the same trend as the water samples did. Nitrate inside the pore water could be found in concentrations up to max. 275 µmol L^{-1} in sediments (5- 15 cm depth) near station 5. During this sampling program none of the other samples (range from 0.2 µmol L^{-1} to 60 µmol L^{-1}) showed this high amount of nitrate inside the pore water.

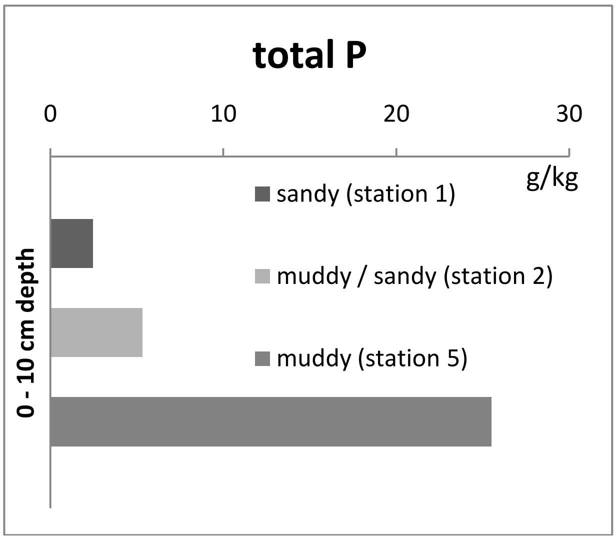

Figure 11 Total phosphorus in different sediment types

3.3 N / P ratio

The Redfield ratio (N/P) is an important tool in understanding the marine biogeochemical cycles. Indeed, the EEA emphasizes the use of nutrient ratios, especially N:P, for the assessment of eutrophication [5]. Based on the Redfield Ratio there were two different situations inside the Ria Formosa.

Table 1 and 2 show the different ratios during low and high tide.

The inflowing Atlantic water (high tide) showed low rations. Nitrogen seems to be the limiting factor for algae growth in coastal water. Due to the strong increase of organic nitrogen towards the mainland the ration rose up to more than 40. Phosphorus is limiting an algae growth with the increasing distance from the sea. In relation to the high concentration of organic N phosphorus was also at low tide the limiting factor near the dead end of the channel. As table 1 shows silicate (optimal ratio Si / P = 1) does not contribute to a nutrients limitation.

Table 1 Distribution of the N / P / Si ratio in water samples at low tide

Low tide

	Atlantic	←		Transition to the mainland		
ratio	1	2	3	4	5	6
N / P	1.5	11.3	28.3	27.7	38.2	54.4
N / P / Si	2 : 1 : 2	11 : 1 : 5	28 : 1 : 7	28 : 1 : 7	38 : 1 : 7	45 : 1 : 9

Table 2 Distribution of the N / P / Si ratio in water samples at high tide

High tide

	Atlantic	→		Transition to the mainland		
ratio	1	2	3	4	5	6
N / P	2.4	1.5	17.3	23	31.2	40
N / P / Si	2 : 1 : 4	2 : 1 :1	17 : 1 : 3	23 : 1 : 2	31 : 1 : 4	40 : 1 : 5

4 Discussion

Potential sources of nutrients to the Ria Formosa include the influx of Atlantic ocean water, benthic and water column fluxes, and human activities. In the studied area, the western channel, the contribution of the coastal water is negligible to the overall nitrogen balance in the lagoon. The amount of organic nitrogen in the costal water is low compared to the values found inside the lagoon. Total nitrogen in water inside the lagoon was 80% higher than in the surrounding coastal water. Most of the inorganic nitrogen compounds in the water samples were in the expected range and comparable to previous studies in Ria Formosa [16, 19, 20]. The highest concentrations of ammonia were in the upper level of previously found in this area at high tide. The high values for ammonia concentration were directly correlated with the sediment grain size. The sediments act as a source of nitrogen on the ebb and flood tides and appear to be a buffer of terrestrial nutrient inputs. The release was much lower in sandy sediments than for muddy sediments and brought about by bacteria, which perform various reactions of the nitrogen cycle. There were several impacts of the sediments by redox potential, due to an oxygen flux into the sediments, bacterial activity or oxygen consumption by benthic fauna [21].The availability of oxygen was responsible for the different concentrations of the oxidized nitrogen compounds at different tides and sediment layers. The overall high amount of ammonia at high water cannot be explained only by that difference observed in the sediment. At low water, when sediments were exposed the oxygen from the air can enter much more easily so aerobic metabolic processes are predominant. The nearly absence of ammonia - as the ammonification process occurs under anaerobic conditions – illustrates this. The station 5 probably with the strongest urban influence showed a higher amount of ammonia at low tide. Muddy sediments are an important nitrogen source because of the higher organic content. The result showed that the amount of organic nitrogen in the lagoon was increasing towards station 5. Phosphorus seemed to be distributed at high tide quite well in the lagoon and there was no significant enrichment in water samples. The lower concentrations of organic N and total P of sandy sediment may be attributed to the low quantity of organic matter accumulated in these areas and, possibly, due to a more efficient decomposition of organic matter. Near the urban centers the sediment is muddy with a high content of organic material. Nitrate reduction reactions are used by bacteria to oxidize these organic material and slow oxygen diffusion rates and hence these sediments are more likely to be anoxic. Phosphorus, in contrast to nitrogen, is more preserved in oxic sediments, because it is mineralized to phosphate and a substantial amount of phosphate can be retained in the sediment through adsorption to Fe oxides under oxic condition [22]. In this shallow lagoon, the influence of the bottom is of most importance on the regeneration of nutrients that enrich the water column. Ammonium and phosphates levels were higher in pore waters of muddy sediments than in sandy sediments, which means that exchanges by molecular diffusion in areas which bottom is essentially constituted by sand, are less important than in muddy sediment areas [18]. However the concentration of P and N inside the sediment samples in the present study seems not to follow this. Near the dead end in an environment with anoxic condition in relation to a high amount of organic matter the highest amount of total P was found. Nitrate as a product of N cycle is much better soluble than the P. Therefore N compounds can be washed out faster. This can explain the observed difference between the concentrations of P and N in sediments near the transition to the mainland. But it does not go along with the high amount of total P in the substrate near the sample station 5 with strongest urban influence. As the sediments are anoxic the concentration is supposed to be less than in sandy or well mixed substrates. This high amount of total P inside the sediments correlates with the high concentration of organic nitrogen in the water samples. The high amount of organic nitrogen inside the sediments and in the water column, found in this study, were related to the near presence of wastewater treatment plants. That's indicating a strong anthropogenic impact. Also the high concentration of nitrate up to 275 µmol L^{-1} inside the pore water near station 5 reflect this expected urban influence on the lagoon. The urban wastewater treatment plant may be responsible as well for the missing difference between low water and high water in observed concentrations of organic nitrogen. This suggests that the discharged wastewater was not completely distributed in this area of the lagoon. With the influence of the tourists the discharge of organic matter increases during the summer months [23] and the accumulation of nutrients may occur in inner regions where water circulation is restricted, which may lead to episodes of water quality degradation. The main inputs contributing to the nutrient balance and status of these coastal systems are the external point and diffuse sources plus the internal biogeochemical mineralization processes, including the regeneration of nutrients from organic and inorganic matter [24]. The inner parts of the lagoon under the direct influence of wastewater discharges presented higher nutrient concentration levels and consequently the water quality was degraded. As the enrichment of water by nutrients, especially compounds of nitrogen cause an accelerate growth of algae and higher forms of plant life to produce undesirable disturbance to the balance of organisms present in the ecosystem, it is necessary to carry out further studies about the influence of the wastewater discharge or the amount of NOx by the exhaust enters from the atmosphere into the lagoon system. The general streaming and currents and the exact influence of the sediment processes and the surface layers should be analyzed. Even there are no significant signs of eutrophication, high amounts of nitrogen loads can turn the whole ecosystem quite fast in such a vulnerable area.

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