Nitrogen and phosphorus in water and sediments at Ria Lagartos coastal lagoon, Yucatan, Gulf of Mexico

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Ria Lagartos, a hypersaline coastal lagoon in the Gulf of Mexico on the Yucatan peninsula was sampled three times in a year at 30 locations, in order to quantify the nitrogen and phosphorus available in the water column and sediments. Undisturbed samples of sediment were analyzed and incubated in the laboratory to estimate ammonium and phosphate fluxes between water and sediment together with nitrification and denitrification rates. The results indicated higher ammonium liberation (250±149 µmol m⁻² h⁻¹) and nitrification (151±132 µmol m⁻² h⁻¹), than denitrification (47±33 µmol m⁻² h⁻¹). In contrast phosphate liberation from sediments was found to be low (0.67±1.31 µmol m⁻² h⁻¹). The high concentrations of organic matter (3.73±1.65 %), total nitrogen (99.14±62.73 µmol g⁻¹), and phosphorus (4.42±1.82 µmol g⁻¹) in the sediments of the lagoon, indicate that can be a sink for these elements.

[Key words: Sediment, Ria Lagartos Mexico, nitrogen, phosphorus, nitrification, denitrification]

Introduction

Marine plants require certain trace elements for growth, these nutrients are used until they become limiting and further growth is inhibited, the most important micronutrients are nitrogen and phosphorus¹. In the coastal zone these nutrients are buried in the sediments and recycled to the water increasing their availability and producing blooms of phytoplankton and others plants²-⁴. The Ria Lagartos coastal lagoon, on the northern coast of the Yucatan peninsula in the Gulf of Mexico (Fig. 1), is under pressure from human activities. When combined with the climate (low precipitation, high evaporation) and the geology (karstic) of the region⁵, this makes the lagoon prone to eutrophication, an increase in the nitrogen and phosphorus availability for primary producers that could bring negative effects like anoxic conditions in the water column⁶. The objective of this study was to determine the nitrogen and phosphorus budgets in both water and sediment, and the fluxes between these two phases through physical and biogeochemical processes.

Materials and Methods

The lagoon is very shallow (0.5-1.0 m), 80 km long, and has 94 km² of surface, and the tide is diurnal with a range of 0.6 m in the open sea. Water circulation (lagoon-ocean) is through a natural mouth at the western end of the lagoon. There are also two other artificial inlets in the western region of the lagoon. The mean annual precipitation ranges between 500 to 700 mm from the western to eastern end of the lagoon, and annual evaporation is 2,000 mm. The weather and the fact that freshwater input from springs is low, causes the lagoon to be mainly hypersaline. There are four fishing villages on the shore of the lagoon: San Felipe, Rio Lagartos, El Cuyo, and Las Coloradas, the last of which contains a salt mining industry that uses the lagoon’s water.

Surface water and recent sediments were sampled from 30 stations (Fig. 1) three times, to determine environmental changes between the winter season (north winds), the dry season and the rainy season (November 1994, March 1995 and August 1995). Water temperatures were measured with an YSI-33 meter. Surface seawater samples were taken with a Van Dorn bottle and stored in HDPE bottles at 4 °C for the transportation to the laboratory (dissolved oxygen samples were fixed in the field in BOD bottles). Analysis were made in our laboratory in Merida about a 100 km from the sampling site within the next 24 hours, pH was measured with a Beckman Phi-32 pH meter (NBS standards), suspended solids

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were estimated by filtration of 1 liter of sample through a filter Whatman GF/C\(^7\), dissolved oxygen using the Winkler method\(^8\), and oxygen saturation calculated with the equations of Garcia & Gordon\(^9\). Biochemical oxygen demand (BOD) was estimated by conducting incubations and measuring the decrease of dissolved oxygen\(^1\). Filtered water was analyzed for salinity using a salinometer (Kahlsico RS-9); ammonium, nitrite, nitrate, phosphate, silicate, and particulate nitrogen were quantified using the colorimetric techniques\(^8\), with a Shimadzu 1200 UV/VIS spectrophotometer. A hand corer (45 mm i.d., 500 mm length, Wild Co. CA USA) was used to collect sediments (3 cores of each station), and stored in acrylic tubes. The pH and the redox potential of the sediment were measured by inserting the electrodes to a depth of 3 cm (following the recommendations of Brassard\(^10\)). The top 5 cm of the cores was sliced (two 2.5 cm sections) under nitrogen atmosphere and used to analyze the following parameters of the sediments: grain size, porosity, organic matter, nutrients in the interstitial water, total nitrogen and total phosphorus. Law et al.\(^11\) reported that most of the transformation processes occur in the top 5 cm of the sediment, for this reason we take this layer as the most representative for the water-sediment interactions. The porosity ($\Phi$) of the sediments was determined by drying at 90 °C for 24 hours, the loss of weight divided by the wet weight was taken\(^12\) as $\Phi N$ the organic matter content was determined by the wet oxidation technique with an excess of dichromate and back titration with iron (II)\(^13\); the amount of sand, silt and clay (granulometry) was estimated suspending the sediment and measuring the density with a hydrometer\(^13\); the nutrient concentrations in the interstitial water (2.5-5 cm) were assessed by extraction with water of the same station under nitrogen atmosphere\(^14\). The ammonium and phosphate flux (F) was estimated using Fick's first law corrected by porosity (M), and tortuosity\(^15\): 

$$F = -\Phi D \frac{dC}{dz};$$

where $dC/dz$ is the vertical gradient (the difference of concentration between the water column and the 2.5-5 cm interstitial water) and D the diffusion coefficient. The diffusion coefficients with tortuosity correction ($D^\circ$), that were used in the calculations, were taken from Li & Gregory\(^16\): $NH_4^+ = 19.8 \times 10^{-6}$, and $PO_4^{3-} = 7.25 \times 10^{-6}$ cm²/s. Total nitrogen and total phosphorus were determined by wet oxidation of the dried sediments (always the top 5 cm) with potassium persulfate in basic and acidic conditions, respectively\(^17\). The second core was used for the assessment of denitrification rates following the methods described by Andersen\(^18\), measuring the rate of decrease in the nitrate concentration in an anaerobic incubation. The third core was preincubated and then incubated in oxygenated conditions to estimate the nitrification rates following the method of Sloth et al.\(^19\). This involves the measurement of $NH_4^+$ flux before and after the addition of a nitrification blocker. This method has the advantage of stable and controlled $O_2$ conditions in a closed microcosm, brief incubation times, calculation of rates
in individual cores, and the use of an inhibitor (acetylene) that is known to be effective in very small concentrations.

**Results**

The Ria Lagartos water showed a wide range in most of the water parameters measured (Table 1). All data were analyzed with statistical/software to identify correlations. The correlation was considered significant at a level of $p<0.05$.

Salinity reached 147.52 psu in the inner zone of Ria Lagartos and had an average of 69.48 psu in the dry season. pH values changed from one season to another, they were higher in the November sampling ($9.00 \pm 0.29$) than in March ($8.28 \pm 0.21$) and August ($8.31 \pm 0.23$). Dissolved oxygen levels ranged from less than 1 ml/l (in the inner zone) to more than 7 ml/l in the central zone. Oxygen saturation ranged from 8.6 to 168 %.

For the dissolved inorganic nitrogen in water, the total ammonium presented concentrations above 2 micromolar ($\mu$M) all the sampling periods in the lagoon. Nitrite + nitrate were in low concentrations ($<1 \mu$M) except in the zone between stations 10 to 15 ($>2 \mu$M) where there are some ground water springs, with high levels of nitrate (we measured 7-70 $\mu$M in the spring water). Particulate nitrogen concentrations presented a positive gradient from the sea to the inner zone, where the levels increased to more than 200 $\mu$M (correlation with salinity was 0.93). The inorganic phosphorus in the water was at very low concentrations, (average of 0.09 $\mu$M). High concentrations of silicate were found because the ground water springs also contribute with these ions (levels of 43-145 $\mu$M in the springs) and also presented a high ($r=0.81$) correlation with salinity (Fig. 2). Suspended solids in the Ria Lagartos lagoon ranged from low levels in the mouth to very high in the inner zone; they reach 375 mg/l in one of the samples. BOD had a wide range, with the higher values in the eastern zone, where the suspended solids were also high.

Surface sediments of the lagoon presented high porosity (above 0.6). The pH range in the sediment was from 7 to 9, except station 14 at pH 9.5. The redox potential was between -100 and -200 mV in most of the samples, meaning that the conditions were reducing. The organic matter in the sediments in most of the stations was between 3 and 4 %, although the general tendency was an increase of these levels from the area of the connection with the sea toward the inner zone of the lagoon (Fig. 5). Total nitrogen in the sediments showed lower concentrations in the zone near the sea, and higher concentrations in the inner zone. Exceptions were stations 2, 4 and 5 that presented high concentrations (Fig. 4), even though they are located near the inlet. Total phosphorus in sediments was higher in the inlet than in the inner zone (Fig. 5), showing an inverse behavior to the organic matter and nitrogen. Ammonium and phosphate concentrations in the sediment interstitial water (Table 2) were variable but higher than the respective water column concentrations (Table 1). Ammonification of organic nitrogen was high, and at stations 4 and 22, values reached to 400 $\mu$mol m$^{-2}$ h$^{-1}$ and the general trend was that the lowest ammonium fluxes were in the higher salinity zone (Fig. 6). Phosphate fluxes showed the same gradient, with the highest values (3.6 $\mu$mol m$^{-2}$ h$^{-1}$) at the stations in front of the towns of San Felipe and Rio Lagartos.

<table>
<thead>
<tr>
<th>Salinity (psu)</th>
<th>Ammonium ($\mu$M)</th>
<th>Nitrite ($\mu$M)</th>
<th>Nitrate ($\mu$M)</th>
<th>Phosphate ($\mu$M)</th>
<th>Particulate Nitrogen ($\mu$M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>60.05</td>
<td>3.24</td>
<td>0.12</td>
<td>0.69</td>
<td>0.09</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>33.90</td>
<td>1.31</td>
<td>0.12</td>
<td>0.93</td>
<td>0.27</td>
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<tr>
<td>Minimum</td>
<td>28.39</td>
<td>1.49</td>
<td>N.D.</td>
<td>0.06</td>
<td>N.D.</td>
</tr>
<tr>
<td>Maximum</td>
<td>147.52</td>
<td>8.16</td>
<td>0.50</td>
<td>3.78</td>
<td>1.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dissolved Oxygen (ml l$^{-1}$)</th>
<th>Oxygen Saturation (%)</th>
<th>BOD (ml l$^{-1}$)</th>
<th>Total suspended solids (mg l$^{-1}$)</th>
<th>Organic suspended solids (mg l$^{-1}$)</th>
<th>Inorganic suspended solids (mg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>3.39</td>
<td>83.23</td>
<td>1.36</td>
<td>44.5</td>
<td>22.3</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>1.45</td>
<td>29.70</td>
<td>0.59</td>
<td>66.9</td>
<td>45.2</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.39</td>
<td>8.57</td>
<td>N.D.</td>
<td>3.7</td>
<td>N.D.</td>
</tr>
<tr>
<td>Maximum</td>
<td>7.50</td>
<td>168.09</td>
<td>3.05</td>
<td>375.0</td>
<td>270</td>
</tr>
</tbody>
</table>
Fig. 2—Relationship silicate-salinity in the water samples of Ria Lagartos showing the increase of silicate concentration in the range of salinity 35 to 60 PSU, a decrease in the range 60 to 90 PSU and a second increase in the range 90-120 PSU.

Fig. 3—Organic matter in the sediments of Ria Lagartos. Average concentrations of the three seasons with standard deviation.

Fig. 4—Total nitrogen in the sediments of Ria Lagartos. Average concentrations of the three seasons with standard deviation.
In 5 of the 30 points studied, the nitrification rate estimated in the laboratory incubations, was not detected, but in the other 25 the rates were high with an average value over 150 µmol m⁻² h⁻¹, and the highest ones in the intermediate zone of the lagoon (160-500 µmol m⁻² h⁻¹), where the conditions are more pristine (Fig. 6). For denitrification, the 30 samples presented detectable values, around

Table 2—Average values of the most important sediment variables in Ria Lagartos during the three seasons sampled. Analysis was done in the top 5 cm section, ammonium and phosphate concentrations are from pore waters (2.5-5 cm). Redox potential was measured at 3 cm depth. [N.D.: Not detectable].

<table>
<thead>
<tr>
<th></th>
<th>Organic matter (%)</th>
<th>Nitrogen (µmol g⁻¹)</th>
<th>Phosphorus (µmol g⁻¹)</th>
<th>Ammonium (µM)</th>
<th>Phosphate (µM)</th>
<th>Redox potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>3.73</td>
<td>99.14</td>
<td>4.42</td>
<td>490.5</td>
<td>3.72</td>
<td>-166.9</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>1.65</td>
<td>62.73</td>
<td>1.82</td>
<td>283.6</td>
<td>7.03</td>
<td>46.4</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.40</td>
<td>16.36</td>
<td>1.07</td>
<td>13.3</td>
<td>N.D.</td>
<td>-258.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>7.85</td>
<td>281.20</td>
<td>12.32</td>
<td>1226</td>
<td>44.43</td>
<td>106.0</td>
</tr>
</tbody>
</table>

Fig. 5—Total phosphorus in the sediments of Ria Lagartos. Average concentrations of the three seasons with standard deviation.

Fig. 6—The nitrogen transformation processes: ammonium flux, nitrification and denitrification in the sediments of Ria Lagartos. Average of the three seasons.
50 µmol m\(^{-2}\) h\(^{-1}\), with only two stations above 100 µmol m\(^{-2}\) h\(^{-1}\) (one of these with nitrification rate not detectable, Fig. 6).

**Discussion**

Evaporation is one of the most important processes in this lagoon, causing the increase of the concentration of some substances, but a decrease in others. Salinity was about 4 and 5 times more than Gulf of Mexico seawater. pH values showed a significative increment with salinity, a normal behavior in the hypersaline environments because of the increase of the concentrations of carbonate and sulphate\(^{21}\). Dissolved oxygen levels were higher in the zones with more aquatic vegetation (central one). Salinity plays an important role in the concentrations of this gas since the correlation between these parameters was high and significant (r= -0.74). Oxygen saturation varied widely, the minimum saturation levels were values found in the first hours of the day, meaning that oxygen falls during the night. For the dissolved inorganic nitrogen in the water column, the ammonium was found to be the most abundant compound, but compared with other coastal lagoons \(^{22, 23}\) concentrations were low (by 5 to 10 times). Ammonium showed a positive correlation with salinity and negative correlation with dissolved oxygen. Ground water inputs, high in nitrite and nitrate, elevated the concentrations of these ions in the zone between stations 10 and 15. In all the stations both ions showed a negative correlation with salinity and positive correlation between them. Very high particulate nitrogen concentrations in the inner zone, relative to the seaward region, indicate that the nitrogen transformation processes (like ammonification, nitrification and denitrification) in the lagoon sediments were low. The inorganic phosphorus in the water was at very low concentrations, as usually found in karstic regions where the calcium carbonate traps the phosphates \(^{24, 14, 15}\) and inverse to the behavior in zones of igneous terrigenous materials \(^{25}\). We also observed a negative correlation of the phosphate concentrations with the water pH, which is in agreement with the process just mentioned, because at higher pH, higher is the carbonate concentration and then occurs more calcium carbonate precipitation together with phosphate. High concentrations of silicate were found in the water because of the ground water springs that are a source of these ions, which keep in solution long time \(^{26}\); in this way, the silicate presented a high correlation (r=0.81) with salinity that suggests a concentration rise caused by evaporation or other inputs and a decrease between salinities 60-100 psu (stations 19-25; Fig. 2) caused perhaps by precipitation. Suspended solid levels were very high (the average concentration was 44.5 ± 66.9 mg l\(^{-1}\) ) but in the inner zone of the Ria Lagartos lagoon this level raised to more than 300 mg l\(^{-1}\); the inorganic-organic proportion of these solids was near 1:1, meaning that both are important. BOD had a wide range, from low levels (< 1 ml l\(^{-1}\)) in stations near the sea, to high values (> 3 ml l\(^{-1}\)) in the eastern zone, where the suspended solids were also high, because of the isolation of the waters.

Surface sediments of the lagoon were highly porous; since the principal components were very fine sand, silt and clay (correlation of porosity with clay was 0.63). The redox potential values indicated that denitrification and sulphate reduction were occurring in these sediments \(^{27, 28}\). For this region the organic matter in the sediments is reported \(^{14}\) to be approximately 5%, in almost all the stations of Ria Lagartos this was the concentration, although the general tendency was an increase of these levels from the area of the connection with the sea toward the inner zone of the lagoon, suggesting that there are processes leading to accumulation of organic matter in these sediments. Statistical analysis showed that where the pH of water was high, the organic matter in sediment was also high. Total nitrogen in the sediments showed similar behavior to organic matter (correlation between the two parameters was high, 0.86), lower concentrations in the zone near the sea, and higher concentrations in the inner zone. Exceptions were stations near the connections with the sea, which presented high concentrations; this could be due to the proximity of the two fishing towns that are on the lagoon, San Felipe and Rio Lagartos.

Statistical analysis showed a significant inverse correlation between total phosphorus in the sediments with salinity, organic matter and total nitrogen. The decrease of phosphorus with increasing salinity is in agreement with the relation found by Millero et al \(^{24}\) because of the variations in the concentrations of bicarbonate ions, which changes the adsorption-desorption of phosphate (Millero et al. \(^{24}\) found that at low salinity the adsorption of phosphate by calcite is higher than at high salinity, relevant in Yucatan because of its karstic origin). The ratio N:P and the ratio C:P, had a positive correlation (r = 0.93) and also separated the stations in three groups (Fig. 7). The first
The correlation and the separation of stations with the total nitrogen-total phosphorus ratio versus carbon-total phosphorus ratio in the sediments of Ria Lagartos. Values are averages of the three seasons.

**Table 3**—Average fluxes and transformation rates in the sediments of Ria Lagartos, during the three seasons sampled. [N.D.: Not detectable]

<table>
<thead>
<tr>
<th>Fluxes and Rates</th>
<th>Average</th>
<th>Std. Dev.</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium flux (µmol m⁻² h⁻¹)</td>
<td>250.0</td>
<td>149.4</td>
<td>5.4</td>
<td>661.2</td>
</tr>
<tr>
<td>Phosphate flux (µmol m⁻² h⁻¹)</td>
<td>0.67</td>
<td>1.31</td>
<td>N.D.</td>
<td>8.86</td>
</tr>
<tr>
<td>Nitrification (µmol m⁻² h⁻¹)</td>
<td>150.5</td>
<td>131.8</td>
<td>10.2</td>
<td>529.7</td>
</tr>
<tr>
<td>Denitrification (µmol m⁻² h⁻¹)</td>
<td>47.4</td>
<td>33.0</td>
<td>4.8</td>
<td>153.8</td>
</tr>
</tbody>
</table>

The group had low nitrogen and high phosphorus, and comprised by the stations of the inlet zone and near to the villages (1, 7, 3, 6, 9, 2 and 5). The second one was formed by the stations with intermediate values of nitrogen and phosphorus (most of the stations). And the third group was formed by stations with high N:P (above 30) and C:P ratios above 140. In this last group were the stations of the inner zone of Ria Lagartos (22, 23, 24, 25, 28, 29 and 30). These results indicate that a phosphorus source exists, that could be the Gulf of Mexico water, or the sewage of the fishing villages. Most of this phosphorus is trapped in the sediments of the seaward zone.

The estimated flux of ammonium and phosphate ions was from sediment to the water column. The general trend was that the lowest fluxes for both ions were in the higher salinity zone because their interstitial water concentrations were lower. As expected, the phosphate flux had a direct correlation with the total phosphorus concentration in the sediment. The inverse correlation found, between this flux and the sediment pH, is explained by the increase of the adsorption of phosphate at the pH range 7.4 - 8.6 in calcareous sediments reported by Miller et al.²⁴ Nitrification rate in the water-sediment interface was high but variable. Ammonium flux and nitrification were correlated (r = 0.42), meaning that in sediments with more available ammonium, the nitrification rates were higher²⁹. Dissolved oxygen and nitrification also presented a positive correlation (r = 0.53) and the statistical analysis separated the stations of the east (inner zone) that have low oxygen levels and low nitrification rates, from the rest of the stations.

The estimated denitrification rates were lower than nitrification rates by a factor of 3, and the average ammonium liberation was almost two times the average nitrification (Table 3). The large differences between the three processes: ammonium production, nitrification and denitrification, indicated that the recycling of nitrogen is very large and the output is small. This explains the large amount of nitrogen that was found in the water and sediments of the lagoon. Even though phosphorus was present in the sediments...
in reasonable concentrations, the phosphate liberation was so low, meaning that most of this element is trapped by the sediments; the lagoon is a sink for phosphorus.

Even though Ria Lagartos lagoon has very few effects of industries and other human activities, the small water exchange with the Gulf of Mexico and the poor input of freshwater, makes the lagoon prone to eutrophication. The high concentrations of nitrogen and phosphorus in the sediment, together with the low denitrification rates found in this study, are important indicators that this lagoon must be protected and conserved.

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