

Variation of nitrification rates in Chelem lagoon, Yucatan, Mexico

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Sedimentary nitrification rates were measured by incubation of cores collected from Chelem lagoon (located in the Yucatan peninsula on the coast of the Gulf of Mexico). Analyses of pH and total sulfide in the pore water and total nitrogen and total phosphorous in the sediments were also carried out. Effects of human interference were discernible in the zone of the lagoon more used by man. Peak values of total nitrogen and total phosphorous with the latter exhibiting significant correlation with the sediment pH, were observed in this zone. Very low pH values were measured in Chelem sediments probably due to the high ambient hydrogen sulfide levels. The high sulphide concentrations resulted in the absence of nitrification at 5 of the 14 stations sampled; however, on the western side of the lagoon high nitrification rates ($30.2 \pm 36.9 \mu\text{mol/m}^2/\text{h}$) were measured. These rates presented significant correlation with total phosphorous content of the sediment and with the reported phosphate flux between sediment and water. The reported ammonium release from the sediments, was four times the nitrification rate, indicating that just a fraction of the ammonium produced in Chelem sediments is converted to nitrate.

In most coastal environments the vast majority of N released through diffusion from sediments to overlying water where it can be assimilated by plants, is in the form of ammonium (NH_4^+), which is generated by the decomposition and deamination of organic matter. In the presence of oxygen (O_2), a portion of the NH_4^+ generated from benthic decomposition of organic matter is oxidized to nitrate (NO_3^- /nitrification) before it can escape from the sediments. This NO_3^- may, in turn, be used as a terminal electron acceptor by denitrifying bacteria producing gaseous forms of nitrogen [nitrous oxide (N_2O) and dinitrogen (N_2)] which cannot be utilized by most plants. Thus, the coupled process of nitrification-denitrification represents a sink that excludes N away from recycling pathways, and it is quantitatively important in the N budgets of coastal systems where N losses via denitrification may account for half of the terrestrial inputs¹.

Nitrification and denitrification have received considerable attention, not only with regard to their roles in controlling NH_4^+ and NO_3^- levels but also as sources of N_2O , a green house gas which also contributes to stratospheric ozone consumption. The surface sediments in estuaries are important sites for both nitrification and denitrification, which are facilitated by the ambient conditions of low O_2 , fresh organic input and ammonium and nitrate supply².

Chelem is a coastal lagoon located on the northern coast of the Yucatan peninsula in the Gulf of Mexico. It is very shallow (0.5-1.5 m), and does not receive any inputs from rivers. This water body hosts a wide variety of environments. The western side is almost pristine, hypersaline and oligotrophic, while the eastern side is surrounded by industries, housings, roads and pipelines. It is used like a harbor (Yukalpeten) and its waters and sediments present there leads to eutrophication. Previous studies indicated that the amount of NH_4^+ released by sediments of this last zone is high and that the denitrification rates are low³⁻⁵. We present here the results of the estimation of nitrification rate in Chelem lagoon in relation to other sedimentary characteristics (pH, sulphide, total nitrogen and phosphorous).

Materials and Methods

Surface water and sediment samplings were made at 14 points in the Chelem lagoon (Fig. 1). A hand corer (45 mm i.d., 500 mm length, Wild Co. CA USA), was used to collect sediments while water samples were taken with a Van-Dorn bottle. The cores in acrylic tubes were brought to the laboratory in Merida 30 km about from the sampling site, and preincubated and then incubated in the dark at 25 °C for the estimation of the nitrification rates following

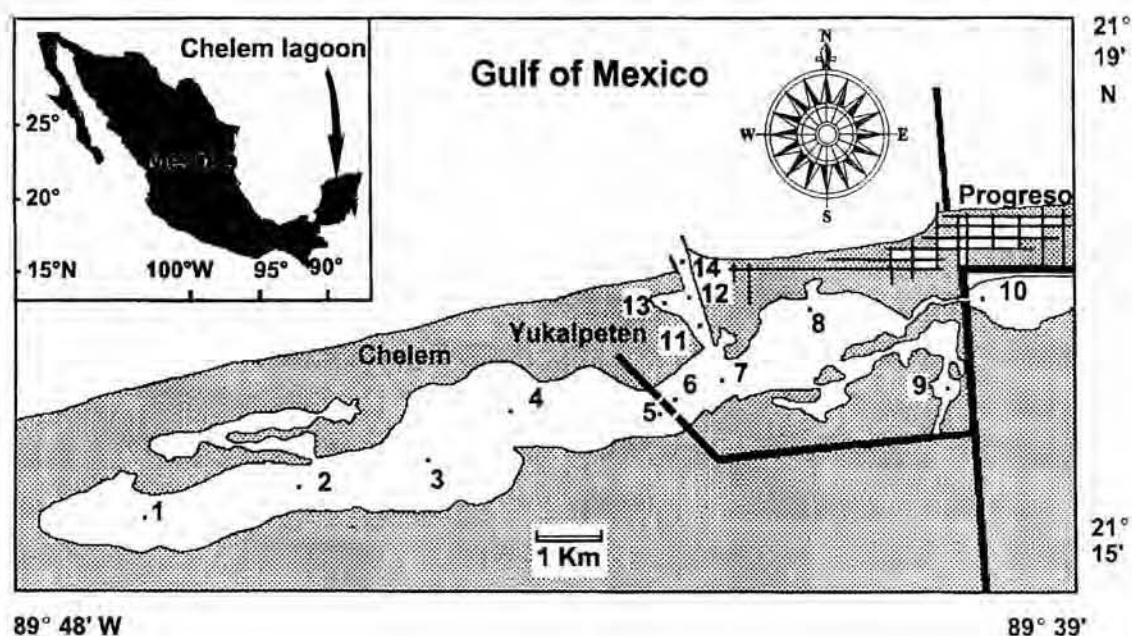


Fig. 1—Chelem lagoon, location of sampling stations, (lines are roads and docks constructed in the zone).

the method of Sloth *et al.*⁶, involving 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 use of an inhibitor (acetylene) that is known to be effective in very small concentrations.

Law *et al.*⁷ reported that most of the transformation processes occur in the top 5 cm of the sediment, for this reason we take this layer as homogeneous, but surely the chemical properties of the sediment should vary to different depths. Replicates of the cores were used to analyze the top 5 cm of sediment. The pH of the sediment was measured introducing the electrode of a pH-meter to a depth of 5 cm in each core. Total nitrogen and total phosphorous were determined by means of wet oxidation of the dried sediments with potassium persulfate in basic and acidic conditions, respectively^{8,9}. For the sulfide analysis the pore water was separated by centrifugation under N_2 atmosphere and back-titrated with iodine/thiosulfate¹⁰.

Results

Total nitrogen in sediments fluctuated between 17.2 and 338.7 $\mu\text{mol/g}$ (Table 1). The lowest concentration was found at st. 9, that is in a mangrove zone, and st. 8 located near Progreso city was characterized by the highest nitrogen content of

sediment. In the western region of the lagoon total phosphorous in sediment was minimal (2.4 - 2.7 $\mu\text{mol/g}$), while the highest values (7.1 $\mu\text{mol/g}$), occurred in the man-made opening of the lagoon, i. e., the entrance to Yukalpeten fishing harbor. The pH values of the sediments were very low in general, ranging from 3.9 at st. 12 to 6.7 at st. 10. All pH values below 5.2 corresponded to the samples of Yukalpeten harbor and the values increased both to the east and west of this area. All the sediment samples were anoxic and the pore water sulfide content ranged from 0.37 to 3.67 mM., toward the west, sts 1 and 2 had moderate values and in the center the sts 6, 7 and 11 exceeded 3 mM.

Nitrification rates were not measurable at sts 7, 8, 10, 11 and 12, but in the rest of stations this process could be detected. The measured rates ranged from 0.5 to 96.5 $\mu\text{mol/m}^2/\text{h}$, with a mean of 30.2 ± 36.8 $\mu\text{mol/m}^2/\text{h}$ which, when applied over the total area of the lagoon, yielded an overall rate of 17162 mol/d.

Discussion

The sedimentary conditions in Chelem are determined by both, natural and anthropogenic processes that occur in the different regions of the lagoon. Around Yukalpeten harbor high concentration of organic matter and elevated NH_4^+ flux from the bottom have been reported³, indicating deterioration of the sediments by the human activities, specially at

Table 1—Sampling stations and results on sediments of Chelem Lagoon

St. no.	Latitude (North)	Longitude (West)	Total nitrogen ($\mu\text{mol/g}$)	Total phosphorous ($\mu\text{mol/g}$)	pH	Total sulphide (mM)	Nitrification ($\mu\text{mol/m}^2/\text{h}$)	Nitrification (mol/day)
1	21°14' 50"	89°47' 00"	256.7	2.4	5.6	2.36	87.81	4415.4
2	21°15' 00"	89°46' 00"	173.3	2.4	6.5	2.66	85.39	3650.0
3	21°15' 10"	89°44' 30"	132.5	2.7	6.1	1.25	96.53	5927.8
4	21°15' 40"	89°43' 30"	125.2	3.5	6.3	1.03	21.19	1197.3
5	21°15' 40"	89°42' 40"	191.8	4.5	5.1	0.37	7.25	201.1
6	21°15' 40"	89°42' 30"	87.0	4.3	4.7	3.35	72.39	683.5
7	21°15' 50"	89°42' 00"	220.9	5.0	4.7	3.59	0.00	0.0
8	21°16' 30"	89°41' 00"	338.7	5.6	4.8	1.03	0.00	0.0
9	21°15' 30"	89°40' 30"	17.2	4.8	4.7	2.43	39.34	1065.4
10	21°16' 40"	89°40' 00"	80.9	4.0	6.7	0.98	0.00	0.0
11	21°16' 20"	89°42' 20"	202.4	5.9	4.4	3.67	0.00	0.0
12	21°16' 30"	89°42' 30"	198.1	6.7	3.9	0.61	0.00	0.0
13	21°16' 30"	89°42' 45"	227.9	6.2	5.2	0.47	0.53	20.9
14	21°16' 45"	89°42' 35"	73.9	7.1	4.6	2.13	11.91	0.3
Average			166.2 $\pm$ 82.3	4.6 $\pm$ 1.5	5.2 $\pm$ 0.8	1.9 $\pm$ 1.1	30.2 $\pm$ 36.8	Total=17161.8

Table 2—Nitrification rates reported for various areas

Reference No.	Area	Nitrification rate ($\mu\text{mol} / \text{m}^2 / \text{h}$)
1	Chesapeake Bay, USA	70
6	Kysing Fjord, Denmark	25
15	Chesapeake Bay, USA	77-89
16	Colne Point saltmarsh, UK	6.2-12.4
17	Narragansett Bay, USA	0.55-13.0 $\mu\text{mol} / \text{l} / \text{d}$
18	Narragansett Bay, USA	11 $\mu\text{mol} / \text{l} / \text{d}$
19	Narragansett Bay, USA	water: 0.02-11.2 $\mu\text{mol} / \text{l} / \text{d}$
20	Sluice Dock, Belgium.	90 - 1800
21	Coral reefs, Puerto Rico	267
22	Puerto Rico coral reef sponges	C.Nucula=4000, A. Varians=20
23	Great Sippewissett marsh, New England, USA	Integrated 10 cm = 2142
24	Louisiana continental shelf, USA	8.8-24.0
25	Joyuda Lagoon, Puerto Rico	0.61-7.23
26	La Parguera, Puerto Rico	0.44-10.0
27	Tama estuary, Japan	27-73
27	Odawa Bay, Japan	99.7
28	Terminos Lagoon, Mexico	2.4-28.9
29	Coral colonies, India	9.4 nmol/ mg coral hour
30	Coral reef Atol. Enewetak Marshall Isl	4.93-15.8
31	Galveston Bay, Texas, USA	1-87
Present study	Chelem Lagoon, Yucatan, Mexico	0.5-96.5

st. 8 where the organic matter content was as high as 9.2 %; NH_4^+ release was $519 \mu\text{mol}/\text{m}^2/\text{h}$.

In this work also the harbor stations clearly experienced the effects of man made alterations, since they were characterized by the highest values of total nitrogen and total phosphorus. Station 1 in the western region also had high nitrogen content, but this was probably due to natural productivity and isolation. Total phosphorus concentrations were similar to those reported for the Ganges estuary¹¹, but lower than those found by Sundby *et al.*¹² in the Gulf of St. Lawrence. The total phosphorus content showed a significant correlation ($r = -0.77$, $p \leq 0.05$) with pH, indicating that precipitation and dissolution of phosphorus is pH regulated^{13, 14}. The very low pH values measured in Chelem sediments (average 5.2 ± 0.8) were probably due to the high concentrations of hydrogen sulfide.

An evaluation of the nitrification rates of sediment indicates that the process was not detectable at sts 7, 8, 10, 11 and 12 since these stations were located within the zone that is most affected by human activities, it would appear that the natural pathways of nitrogen cycling (ammonification, nitrification, and denitrification⁶) have been greatly altered here. Probably the high concentration of sulfide in those stations is the principal cause of the absence of nitrification (sts 7 and 11 had the highest sulfide concentrations in pore waters). Kemp *et al.*¹ and Jenkins & Kemp¹⁵, reported that anoxic conditions and H_2S reduce the activity of nitrifying bacteria. Sample 12 although had a low sulphide concentration showed the lowest pH (3.9), factor that also could inhibit nitrification. Station 8 is in the Chelem zone with the highest organic matter content in the sediment³, factor that may limit nitrification, but this zone has the highest denitrification rate³.

The observed differences between the western zone and the rest of Chelem (perturbed zone), in phosphorus, nitrogen, pH and sulphide are presumably related to those in nitrification since the west side of the lagoon showed the highest rates. A comparison of the rates observed in the present study with the published estimates from some other areas (Table 2), indicates that the rates estimated for Chelem are low but in the normal range ($5 - 2142 \mu\text{mol}/\text{m}^2/\text{h}$). In addition the amount of NH_4^+ released by sediments³ ($72420 \text{ mol}/\text{d}$), is four times the total nitrification rate ($17162 \text{ mol}/\text{d}$), meaning that only a

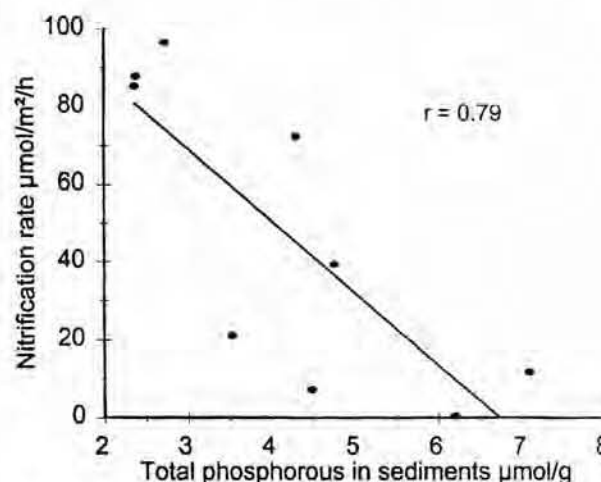


Fig. 2—Relation between nitrification and phosphorous in sediment.

fraction of the NH_4^+ produced in Chelem sediments is converted to nitrate.

Nitrification rates in Chelem showed significant ($p \leq 0.05$) correlation with total phosphorus content of the sediment ($r = -0.79$, Fig. 2) and with the phosphate flux between sediment and water ($r = 0.85$)³, indicating that the stations with high phosphate release and low total phosphorus in the sediments, are characterized by high nitrification rates. However, we point out that data on vertical distribution of the sediment properties are not available. Since the vertical gradient of properties are expected to be large in the upper few millimeters, the interpretation of our results is constrained by the absence of such vertical profiles.

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References

- 1 Kemp W M, Sampou P, Caffrey J, Mayer M, Henriksen K. & Boynton W R, *Limnol Oceanogr.* 35(1990) 1545.
- 2 Law C S, Rees A P & Owens N J P, *Limnol Oceanogr.* 38 (1993) 435.
- 3 Valdes D S & Real E, *Cienc Mar*, 20(1994) 65.
- 4 Valdes D S, *Procesos que regulan el nitrogeno inorganico y variaciones estacionales de la hidrologia en la Laguna Chelem, Yucatan* Ph D thesis, Universidad Nacional Autonoma de Mexico, Mexico, 1995.
- 5 Valdes D S & Real E, *Indian J Mar Sci.* 27 (1998) 149.
- 6 Sloth N P, Nielsen L P & Blackburn T H, *Limnol Oceanogr.* 37(1992) 1108.

- 7 Law C S, Rees A P & Owens N J P, *Estuar Coast Shelf Sci*, 33 (1991) 37.
- 8 Parsons T R, Maita Y & Lalli C M, *A manual of chemical and biological methods for seawater analysis*, (Pergamon Press London) 1984, pp 173.
- 9 Stirling, H P, *Chemical and biological methods of water analysis for aquaculturalists* (Institute of Aquaculture University of Stirling, Scotland) 1985, pp 119.
- 10 APHA/AWWA/WEF, *Standard methods for the examination of water and wastewater*, 19th edition, (American Public Health Association, Washington, USA) 1995, pp 1108.
- 11 Vaithiyanathan P, Jha P K & Subramanian Y V, *Estuar Coast Shelf Sci*, 37 (1993) 603.
- 12 Sundby B, Gobeil C, Silverberg N & Mucci A, *Limnol Oceanogr*, 37(1992) 1129.
- 13 Zimmermann C F, Montgomery J R & Carlson P R, *Estuaries*, 8(1985) 228.
- 14 Seitzinger S P, *Estuar Coast Shelf Sci*, 33 (1991) 409.
- 15 Jenkins M C & Kemp W M, *Limnol Oceanogr*, 29 (1984) 609.
- 16 Abd Aziz S A & Nedwell D B, *Estuar Coast Shelf Sci*, 22 (1986) 689.
- 17 Berounsky V M & Nixon S W, *Estuar Coast Shelf Sci*, 20 (1985) 773.
- 18 Berounsky V M & Nixon S W, *Limnol Oceanogr*, 35(1990) 1610.
- 19 Berounsky V M & Nixon S W, *Estuaries*, 16(1993) 718.
- 20 Billen G & Vanderborght J P, in: *Biochemistry of estuarine sediments-Proceedings of a UNESCO/SCOR workshop held in Melreux, Belgium* (1976) 154.
- 21 Corredor J E & Capone D G, *Proceedings of the V International Coral Reef Congress*, Tahiti, 3 (1985) 395.
- 22 Corredor J E, Wilkinson C R, Vicente V P, Morell J M & Otero E, *Limnol Oceanogr*, 33(1988) 114.
- 23 Kaplan W, Valiela I & Teal J M, *Limnol Oceanogr*, 24(1979) 726.
- 24 Miller-Way T, Boland G S, Rowe G T, & Twilley R R, *Estuaries*, 17(1994) 809.
- 25 Morell J M & Corredor J E, *Estuar Coast Shelf Sci*, 37 (1993) 203.
- 26 Mosquera A I, Corredor J E & Morell J M, *Chem Ecol*, (1999 in press).
- 27 Nishio T, Koike I & Hattori A, *Appl Env Microbiol*, 45(1983) 444.
- 28 Rivera-Monroy V H & Twilley R R, *Limnol Oceanogr*, 41 (1996) 284.
- 29 Wafar M, Wafar S & David J J, *Limnol Oceanogr*, 35 (1990) 725.
- 30 Webb K L & Wiebe W J, *Can J Microbiol*, 21 (1975) 1427.
- 31 Zimmerman A R & Benner R, *Mar Ecol Prog Ser*, 114 (1994) 275.