

## CONCENTRATION OF NUTRIENTS AND C:N:P RATIOS IN SURFACE SEDIMENTS OF A TROPICAL COASTAL LAGOON COMPLEX AFFECTED BY AGRICULTURAL RUNOFF

### Concentración de nutrientes y proporción C:N:P en sedimentos superficiales de un complejo lagunar costero tropical afectado por escurrimientos agrícolas

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**ABSTRACT.** The content of nutrients and the C:N:P ratios were analysed in the sediment of a tropical coastal lagoon system in northwestern Mexico, that receives heavy agricultural runoff since 1950. The relationship between the C:N:P ratios and the sediment type was evaluated in the coastal lagoon system of Bahía de Altata-Ensenada del Pabellón in order to identify the possible origins of the organic matter, from phytoplankton, mangroves, river inflow or agricultural wastewaters. In general, the results of the nutrient content analyses fell into two groups based on the particle size of the sediment: 1) sandy sediments in Bahía de Altata where the concentration of carbon varied from 662 to 974  $\mu\text{mol g}^{-1}$ , that of nitrogen from 11 to 75  $\mu\text{mol g}^{-1}$  and that of phosphorus from 11 to 27  $\mu\text{mol g}^{-1}$ , with a molar ratio of 34-66:1-5:1, and 2) silty clay sediments in Laguna Ensenada del Pabellón with high contents of carbon (2324 to 4080  $\mu\text{mol g}^{-1}$ ), nitrogen (121 to 635  $\mu\text{mol g}^{-1}$ ) and phosphorus (18 to 40  $\mu\text{mol g}^{-1}$ ), and a high C:N:P ratio (102-202:6-16:1). This distribution is associated with agricultural runoff and discharges from a sugar cane processing factory.

**Key words:** Nutrients in sediments, tropical coastal lagoon, agricultural runoff.

**RESUMEN.** Se analizaron los contenidos de nutrientes y sus proporciones C:N:P en sedimentos de un complejo lagunar costero tropical al noroeste de México, entre las 15 más contaminadas del país que recibe fuertes escurrimientos agrícolas desde 1950. Se evaluó la relación entre las proporciones C:N:P y el tipo de sedimento en el complejo lagunar costero de Bahía de Altata-Ensenada del Pabellón para discriminar los posibles orígenes de la materia orgánica, fitoplancton, manglar, y descargas fluviales y agrícolas. En general, los resultados de los análisis del contenido de nutrientes estuvieron dentro de dos grupos basados en el tamaño del grano del sedimento: 1) sedimentos arenosos en la Bahía de Altata donde la concentración de carbono varió de 662 a 974  $\mu\text{mol g}^{-1}$ , la de nitrógeno de 11 a 75  $\mu\text{mol g}^{-1}$  y la de fósforo de 11 a 27  $\mu\text{mol g}^{-1}$ , con una proporción molar de 34-66:1-5:1, y 2) sedimentos limo arcillosos en la Laguna Ensenada del Pabellón con altos contenidos de carbono de 2324 a 4080  $\mu\text{mol g}^{-1}$ , de nitrógeno de 121 a 635  $\mu\text{mol g}^{-1}$ , y de fósforo de 18 a 40  $\mu\text{mol g}^{-1}$ , y una proporción C:N:P alta (102-202:6-16:1). Dicha distribución se asocia con el escurrimiento agrícola y con las descargas de una industria azucarera.

**Palabras clave:** Nutrientes en sedimentos, laguna costera tropical, escurrimiento agrícola.

## INTRODUCTION

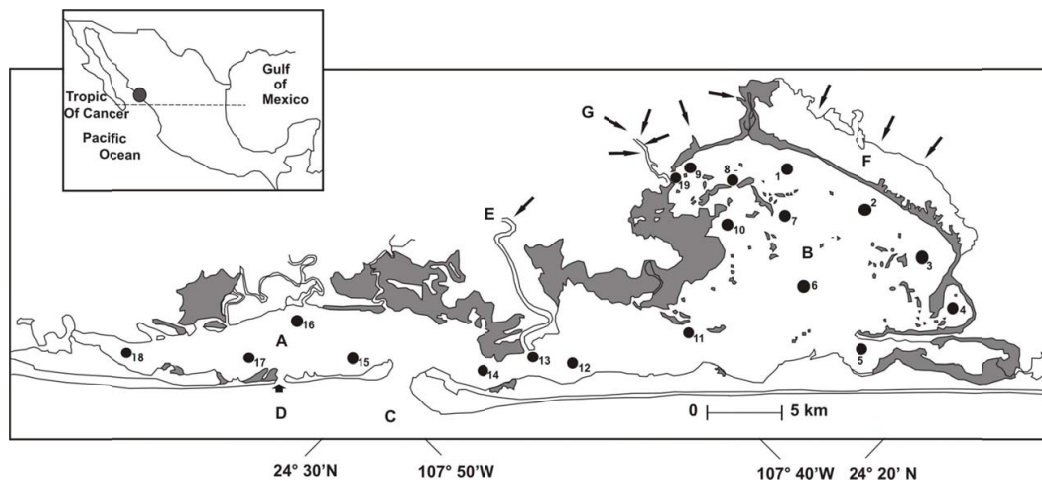
Organic matter (OM) origins in coastal waters are highly diverse. They can come from autochthonous sources such as phytoplankton, micro algae and aquatic macrophytes and also from allochthonous sources such as terrestrial vegetation, freshwater marshes and organic pollution from the upper parts of the hydrological basin. Beside, OM can exist as dissolved organic matter or as particulate organic matter (POM) detritus. Because of its nature, the OM has a great affinity to be adsorbed or absorbed by suspended clays and finally to be deposited in sediment where is partially mineralized, becoming part of the sediment or to make new compounds such as humic substances. Knowledge of the sources, chemical activity, and the final destiny of the OM and the mixture of the dynamics of estuaries are critical to the understanding of global biochemical cycles and OM diversity (Bianchi & Canuel, 2001). Bianchi (2007) considers that the concentration and molar ratios of C with other elements can provide relatively good information related to the OM cycle, considering that the Total Organic Carbon (TOC) corresponds to approximately the 50 % of the OM. Even so the TOC/TN ratio, like the Carbon isotopic ratio, can be modified during diagenesis, and C ratios with N and P can be comparable only on samples with similar sediment grain size (OzCoast, 2009).

OM mineralization begins in the water column and ends in the sediments or the soil. The sediment grain size has to be considered; for example, the degradation rate of the OM is higher in sand sediments than in silt and clay sediments (Rasheed *et al.* 2003). Generally, the OM content is higher in silt and clay sediments because of their higher specific surface. Magni *et al.* (2008) considers that the hydrodynamics and the geomorphology play an important role in the distribution and transportation of fine sediments and OM in the lagoon of Las Cabras (Sardinia, Italy). These authors find that the total Carbon distribution is a function of the increase of the fine sediments below 8  $\mu\text{m}$  in grain size. OM has a preference for fine sediments with small grain size because of the thixotropic properties of the silt

and clays to absorb water and also TOC and TN. In tidal regions such as deltas, coastal lagoons and estuaries are sediment traps mainly because of the silt and clay frequently associated with mangroves in tropical regions (OzCoast, 2009).

The sedimentary phase plays an important role in the decomposition processes of organic matter due to the size of sediment grains and interstitial spaces, as well as processes of re-suspension, reworking and redistribution to which sedimentary particles are subjected, with the wind and the tidal currents being the primary forces. Nöges *et al.* (1998) pointed out that these processes mask the nutrient cycles in the sediment, and, together with the input of external organic and inorganic matter, may prevent the C:N:P molar ratios from being constant. Other important external inputs, such as those from agricultural activities associated with the geochemical transformations, can modify C:N:P ratios and biomarker C/N, masking the identification of the origin of organic matter, as happens in the coastal lagoon complex in the California Gulf of Northwest Mexico (Altata Bay and Ensenada del Pabellón lagoon), where approximately 6 279 tons of nitrogen and 7 316 tons of phosphorus are used annually as fertilizers on sugar cane fields. This lagoon complex is surrounded by 130 000 ha of intensively irrigated agriculture lands whose wastes drain towards the lagoon complex via several drainage channels and surface runoff. In addition, Ensenada del Pabellón lagoon also receives the effluent of shrimp aquaculture and the sewage of surrounding villages. For this reason, it is classified as one of the 15 most polluted basins of the country (Campos-Villegas, 1997; Páez-Osuna, 2001; Ruíz-Fernández *et al.* 2003). The Culiacan River also receives untreated sewage from the city of Culiacan, 40 km inland, as well as from other small towns along its course (Ruíz-Fernández *et al.* 2002).

Taking these findings into account, this paper analyzed the distribution pattern of carbon, nitrogen and phosphorus concentrations in the sediments of a tropical coastal lagoon complex, and describes the relation between two grain sediment sizes and their C, N, P concentrations and their C:N:P, C:N and C:P molar ratios to discriminate the possible origins



**Figura 1.** Location of sampling sites in the tropical coastal lagoon system of Bahía de Altata (A)-Ensenada del Pabellón (B), (C) main ocean inlet (Boca de la Tonina), (D) secondary inlet (Boca del Gavilán), (E) Culiacán river, (F) Chiricahueto seasonal floodplain with *Typha* marshes and (G) sugar cane wastewater channel. The shadowed areas correspond to mangroves and the arrows to the agricultural wastewater channels.

**Figure 1.** Localización de los sitios de muestreo en el complejo lagunar costero tropical de Bahía de Altata (A)-Ensenada del Pabellón (B); (C) boca marina principal (Boca de la Tonina); (D) comunicación secundaria (Boca del Gavilán); (E) Río Culiacán; (F) planicie estacional de *Typha* de Chiricahueto y (G) canal de descarga de la industria azucarera. Las áreas sombreadas corresponden a manglar y las flechas a canales de descarga agrícola.

of organic matter from phytoplankton, mangroves, river inflow and agricultural wastewaters.

## MATERIALS AND METHODS

### Study Area

The Altata Bay-Ensenada del Pabellón coastal lagoon complex (Figure 1), is located between 24°20'-24°40' North 107°30'-107°58' West and covers a total surface area of 335 km<sup>2</sup> of which 278 km<sup>2</sup> comprises the Ensenada del Pabellón wetlands. The wetland has two sandy barrier islands that separate the lagoons from the Gulf of California. The longer one is the Peninsula de Lucenilla, measuring 38 km long by 2 km wide, which ends with an inlet known as the Boca de la Tonina that has a maximum depth of 20 m. The Culiacán River, with an annual freshwater discharge of 3 276 Mm<sup>3</sup> flows year-round into the lagoon with a variable volume of water and is located a few kilometers away from this inlet. The river flow feeds several irrigation channels before reaching the coastal lagoon complex by means of various agricultural drainage channels. The other barrier is the Peninsula de Quevedo, which is

28 km long and 1 km wide and is connected to the sea via the Boca del Gavilán, which is 5 to 10 m deep (Figure 1 D). The surrounding vegetation consists of a 100 km<sup>2</sup> fringe, and areas of dwarf mangrove swamps dominated by black mangrove *Avicennia germinans* and red mangrove *Rhizophora mangle* along the inner margins of the bay and tidal channels (Figure 1: shadowed area). Seasonal floodplains sustaining patches of halophyte vegetation of *Salicornia* sp. and *Batis maritima* are found among the mangroves (Flores-Verdugo *et al.* 1991). A large expanse of man-made *Typha* sp. marsh (23 km<sup>2</sup>), created by the drainage flow from surrounding agricultural land into a seasonal floodplain (100 km<sup>2</sup>), is located in the marine area of the coastal lagoon complex (Figure 1-F). This marsh serves as a winter residence for several hundred thousand northern pintail ducks (*Anas acuta*).

The deepest point is 5 m, at the center of the lagoon. The shallowest parts are less than 0.5 m deep and are located on the SE, where the greatest number of mangrove islands are found and where there is increased runoff originating from both agriculture and a sugar refinery (Irrigation district No.

10 > 2 730 km<sup>2</sup>).

Although the grain size of the sediment varies, Peraza-Vizcarra (1973) found mostly medium sand in Boca de la Tonina and adjacent areas. Altata Bay contains fine sand behind the Peninsula de Lucenilla, while silt and clay preponderates in the central sections of Ensenada del Pabellón lagoon and the tidal channels of the Culiacan River delta. Temperature varies between 20 °C (January-February) and 32 °C (July-August), with a mean annual rainfall of 699 mm and a potential evaporation rate of 2 130 mm. Salinity varies markedly in space and time, with the highest levels being found in the inlets and Altata Bay (35 psu), and the lowest, during the rainy season (July-October), around the edges and center of the Ensenada del Pabellón wetland (4 and 7 psu, respectively, Flores-Verdugo *et al.* 1991). The currents inside the system are caused mainly by the tides and are different for each water body, with velocities reaching 100 cm/s in channels in the wetland, and 18 cm s<sup>-1</sup> in Altata Bay.

## Methods

The 19 sampling sites were distributed in such a way as to obtain the most information regarding the relations between the C:N:P of the primary producers (phytoplankton and terrestrial vegetation), the sediment types, and the allochthonous inputs to the wetland in November, 2001 (Figure 1).

Surface sediment, to a depth of 10 cm, was collected by inserting a 5 cm Diameter core. Total organic matter was estimated by semi-quantitative methods by loss on ignition (LOI) at 550 °C (Dean 1974; Magni *et al.* 2008), and divided by 1.85 to obtain an estimate of organic carbon (Hartmann *et al.* 1973). Samples and blanks for total phosphorus were quantified by an oxidation with H<sub>2</sub>S<sub>04</sub>:HNO<sub>3</sub> (250 ml + 200 ml to one liter of water), at 150 °C and under 1 kg cm<sup>-2</sup> pressure, for two hours, according to Carlberg (1972). The phosphate was then determined with ammonium molybdate to form molybdenum blue, using ascorbic acid as a reductant (Strickland & Parsons 1972). Results are expressed as total phosphorous (% dry weight).

Total nitrogen in the sediment was estimated according to the Kjeldahl method (APHA-AWWA-

WPCF 1995), and the resulting NH<sub>4</sub> was measured following Koroleff's spectrophotometric technique for indophenol blue (Carlberg 1972). All results are expressed as total C, N or P in μmol g<sup>-1</sup> dry weight sediment in order to calculate individual C:N:P molar ratios, and to determine their relationships with sediment grain size.

## Statistical Analysis

Two replicates were collected at each site, and the cores were divided in two: one half for grain size analysis and the other half for chemical analyses, and the results were presented as an average. A 0.0625 mm mesh was used to separate the sand fraction from the silt and clay fractions (Folk 1980).

Spatial statistical analyses for C, N and P total concentrations with their C:N:P molar ratios were made, in order to classify results, this was through grouping of sampling sites as sand or silt/clay in an ANOVA analysis, for comparison with C, N, P concentrations and C:N:P molar ratios, in order to compare sand against silt/clay sediments. Statistical analyses were also required to evaluate the high variability in the method used for determining organic carbon (Mook & Hoskin 1982).

## RESULTS

Two broad, but distinct, sediment groupings within the coastal lagoon complex studied were clearly defined (Table 1). The first comprises Altata Bay (0.6 mm of sand), corresponding to stations 5, 6, 11, 12 and 14 to 18, and the wetland of Ensenada del Pabellón (< 0.001 - 0.06 mm of clay and silt). The second grouping are stations 1, 2, 3, 4, 7, 8, 9, 10, 13 and 19, which includes wetland sites near the agricultural fields (stations 1, 7, 8, 9, 10 and 19), and one site at the mouth of the river (site 13).

The distribution of OC is related to the type of sediment, as may be observed in table 1. In sandy sediments, low OC is related to lower input of organic matter and to the tidal currents influences, in comparison to silt/clay sediments with a high organic matter content, which have a tendency to be deposited in low wave/current energy sites with low oxygen contents, and which favor a high C content,

**Tabla 1.** Particle size, mean Nutrient concentration ( $\mu\text{mol g}^{-1}$ ), C:N:P, C:N, C:P and N:P molar ratios for sampling sites grouped by sediment type (sand or silty clay) (see Figure 1 for sampling sites).

**Table 1.** Tamaño de partícula, concentración media de nutrientes ( $\mu\text{mol g}^{-1}$ ), proporciones molares C:N:P, C:P y N:P para los sitios muestreados agrupados por tipo de sedimento (arena o limo-arcilla) (ver Figura 1 para los sitios de muestreo)).

Site name	Site	Millimeters	Carbon	Nitrogen	Phosphorus	C:N:P	C:N	C:P	N:P
SAND									
Las Arenitas	5	0.13	2440	75	17	143:04:01	33	143	4.4
Castillitos	6	0.21	925	32	27	34:02:01	29	34	1.2
Las Iguanas	11	0.25	1443	74	23	63:04:01	20	63	3.2
Capultita	12	0.25	1124	60	17	66:03:01	19	66	3.5
Huichoral	14	0.6	702	11	11	64:01:01	64	64	1.0
Boca Tonina	15	0.6	693	10	10	63:01:01	69	69	1.0
Oporito	16	0.6	974	53	17	57:03:01	18	57	3.0
Las Palomas	17	0.6	662	33	13	50:03:01	20	50	2.5
Isleta	18	0.6	693	61	12	58:05:01	11	58	5.1
SILT/CLAY									
Los Gueros	1	0.001-0.06	2353	121	18	131:07:01	19	131	6.7
Mogote	2	0.001-0.06	3448	286	18	192:16:01	12	192	15.9
Los Mayitos	3	0.001-0.06	3271	175	23	142:08:01	19	142	7.6
La Brasileira	4	0.13-0.25	3633	189	18	202:11:01	19	202	10.5
Las Animas	7	0.13-0.25	3714	218	31	120:07:01	17	120	7.0
Mapachero	8	0.001-0.06	2804	295	21	134:14:01	10	134	14.0
Los Patos	9	0.13-0.25	2324	134	17	137:08:01	17	137	7.9
Los Cuates	10	0.13-0.25	2800	135	21	133:06:01	21	133	6.4
Rio Culiacan	13	0.13-0.25	3070	257	18	171:14:01	12	171	14.3
Bataoto	19	0.13-0.25	4080	635	40	102:16:01	6	102	15.9

This process appears to account for the low OC content in the sandy sites, with values of  $662 \mu\text{mol g}^{-1}$  in site 17 (Las Palomas), and  $1124 \mu\text{mol g}^{-1}$  in site 12 (Capultita), both at Altata Bay, compared to silt/clay dominated sites, with  $2324 \mu\text{mol g}^{-1}$  in site 9 (Los Patos), and  $3448 \mu\text{mol g}^{-1}$  in site 2 (El Mogote), in Ensenada del Pabellón (Table 1).

Similar patterns may be observed for nitrogen (N) and phosphorus (P), with higher values in the silt/clay sites ( $121$  to  $635 \mu\text{mol g}^{-1}$  of nitrogen, and  $17$  to  $40 \mu\text{mol g}^{-1}$  of phosphorus) compared to the sandy sites ( $11$  to  $75 \mu\text{mol g}^{-1}$  of nitrogen, and  $10$  to  $27 \mu\text{mol g}^{-1}$  of phosphorus) (Table 1).

Total phosphorus varied widely, the highest content being found mainly in the silt/clay sediments of the Ensenada del Pabellón lagoon, with values as high as  $31 \mu\text{mol g}^{-1}$  in site 7 (Las Animas), and  $40 \mu\text{mol g}^{-1}$  in site 19 (Bataoto), and the lowest in the sand sediments of Boca de la Tonina, with  $10 \mu\text{mol g}^{-1}$  in site 15, and  $27 \mu\text{mol g}^{-1}$  in site 6 (Table 1).

The ANOVA analysis show significant differences between Carbon, N and P concentrations in sandy vs. silt/clay sediments as shown in table 2. They also show significant differences between C:N:P ratios in sandy vs. silt/clay sediments, except for the N:P ratio (Table 2).

## DISCUSSION

OC varied from  $662$  to  $2440 \mu\text{mol g}^{-1}$  ( $29.1 \text{ mg g}^{-1}$ ), in the sandy sampling sites, compared with  $2253$  to  $4080 \mu\text{mol g}^{-1}$ , in the silt/clay sampling sites, as Magni *et al.* (2008) found in coastal lagoons.

Comparable differences were also found by Ruttenberg & Goñi (1997) in OC content in three different marine deltaic areas, where they found a wide latitudinal range varying from  $1.97\%$  OC wet weight in clay sediments to  $0.43\%$  OC wet weight in fine sand and mud. The comparison took into account a moisture content of  $30\%$ .

**Tabla 2.** Results of the ANOVA analysis for nutrient concentrations and C:N:P molar ratios comparing the sandy vs silty clay sediments.

**Table 2.** Resultados del análisis para las concentraciones de nutrientes y proporciones molares comparando los sedimentos de arena vs limo-arcilla.

	NUTRIENT CONCENTRATION ( $\mu\text{mol g}^{-1}$ )			C:N:P MOLAR RATIOS		
	C	N	P	C/N	C/P	N/P
Sand vs Silt & Clay	**	**	*	**	**	NS*

\*\* = VERY SIGNIFICANT  $P < 0.0005$

\* = SIGNIFICANT  $0.025 < P < 0.05$

NS\* = NOT SIGNIFICANT FOR  $0.01 > P > 0.05$

Similar patterns may be observed for nitrogen (N), with significant differences between sand and silt/clay sites (Table 2). For silt/clay sediments, the amount of total nitrogen ranged from  $121 \mu\text{mol g}^{-1}$  to  $635 \mu\text{mol g}^{-1}$ ; similar association were reported by Ruttenberg & Goñi (1997), whose nitrogen concentration in clay sediments were more high compared with in sand sediments.

In general the TP concentrations showed low differences between the silt-clay and sandy sediments but significant. The most important feature in this nutrient element has been the great increment over the past 10 years. In 1990, was registered 11 to  $40 \mu\text{mol g}^{-1}$  (present study) and in the year 2000 to  $84 \mu\text{mol g}^{-1}$  (Ruíz-Fernández *et al.* 2003) as a result of an increase in agriculture and urban development. Páez-Osuna *et al.* (1992) found, in the Ensenada del Pabellón lagoon, a high content of phosphorus in silt/clay sediments, which could influence the C, N, P molar ratios used to determine the OM origin.

The highest values of C, N and P in silt-clay sediments in the present study were also observed in the sites in the Ensenada del Pabellón. However, sites 7, 10, and 19 had the highest levels of this nutrient and are close to the discharges from anthropogenic, agriculture and sugar-cane industry sewage (point G in Figure 1), as Páez-Osuna *et al.* (1998) and Ruíz-Fernández *et al.* (2003) also observed in this coastal lagoon complex.

The C:N:P molar ratios fall into two zones:

1) Sandy sites: Predominated by Altata Bay, with 34-66:1-5:1 different from phytoplankton source. In some cases, there is a predominance of sand in localities far from any marine influence, near the sandy

barrier, and with scant higher plant vegetation (Table 1). Even so, it must be taken into consideration that the physical influence of the sandy substrate accelerates the decomposition of the organic matter, thus liberating nutrients, in particular phosphorus and nitrogen, as stated by Hartmann *et al.* (1973). Bickford (1996) calculated CNP ratios in sorted sands with < 15% mud sediment of 74:7:1 which is approximately similar to those calculated in Altata bay.

2) Silt/Clay sites: Ensenada del Pabellón lagoon, producing C:N:P molar ratios between 102-202:6-16:1. This lagoon can be subdivided into two sections: the area near the terrestrial zone that receives agricultural drainage at a ratio of 202:11:1 and the center of the Ensenada del Pabellón lagoon, with a C:N:P molar ratio of 120:7:1 (site 7); in both cases the C:N:P is different from the phytoplankton sources.

This value coincides with the findings of other authors, such as Ertel & Hedges (1985), who recorded ranges between 30 and 40. In the case of the site 5 it is possible explain the large values by the presence of refractory OM from the mangrove forest, as referred by OzCoast (2009), despite the presence of sandy sediments. Regarding this, Hedges *et al.* (1986) pointed out that sandy sediment may contain remains of preserved leaves that are not integrated into the sediment, and that finer sediment may contain older, degraded organic matter, rich in immobilized nitrogen provided mainly by soils. Sites 11 and 12 it possibly show the influence of agricultural and anthropogenic discharges (the sites are in front of the Culiacan River). In this respect, Green-Ruiz & Paez-Osuna (2001) found sig-



nificant heavy metal concentration in sediments in Ensenada del Pabellón lagoon, which is considered moderately contaminated with the copper and zinc used in pesticides and from agricultural and urban runoff.

The loss on ignition procedure used to make measurements of OC can give a high variability in silts and clay, according to Mook & Hoskin (1982). Even so, the ANOVA analysis (Table 2) for C, N, P contents, and their C:N:P molar ratios indicate significant differences between the sampling sites that relate to the type of sediment (between silt/clays vs. sand).

The results also show a gradient from sandy areas, under marine influence, that are poor in carbon and nitrogen, to heterogeneous areas, under terrestrial influence (although the land is hemmed by mangrove vegetation), to the predominantly muddy central area, which is richer in carbon and nitrogen.

According to the data gleaned from this study, it is the grain size of the sediment, confirmed by ANOVA analysis, and the early decomposition of the organic matter that influence in the molar ratio, as also concluded by different authors (Hartmann *et al.* 1973; Ebise & Inoue 1991; Meyers 1994; Andrews *et al.* 1998; Datta *et al.* 1999; Chandrasekar *et al.* 2003).

Meyers (2003) point out that TOC concentrations commonly increase as sediment grain size decreases and in the Ensenada del Pabellón lagoon with silt-clay sediments, the content of TOC, TN, and TP were larger than Altata Bay with sandy sediments. However, in both cases it was difficult to pinpoint the origin of the OM by C:N:P ratios, because the diverse sources of OM such as phytoplankton, macroalgae, mangrove forest, land vegetation, urban sewage, agricultural and sugar cane activity runoff, even though in each case had different grain sizes. In this diversity, the OM sources are different, and selective degradations of the OM components also occur in the water column and during sinking and sedimentation.

The biomarker C:N ratio has been used more than the C:P ratio because of the latter's enhanced sensitivity to consumption and storage of phosphorus by algae and bacteria ( Gächter & Meyer, 1993),

not to mention the high consumption during eutrophication and the enhanced phosphorus solubility in anaerobic marine sediments (Emeis *et al.* 2000). However, the selective degradation of OM components during early diagenesis has the potential to modify C/N ratios in sediments (Meyers, 1994).

The use of this biomarker ratio in sandy sediments (C:N) divides the area under the effect of the sea in Altata Bay including the Ensenada del Pabellón lagoon into two distinct sections (Table 1): a more landward section of the bay, with values ranging from 11-20 (sites 16,17 and 18), and another, near the inlet and along the inner margins of the barrier, with values of 29-69 (sites 6, 14 and 15), indicating the enrichment of carbon over nitrogen. Site 14 is located in front of the river discharge, thus containing a low concentration of N. Ruttenberg & Goñi (1997) pointed out that changes in the C:N and C:P molar ratios are the result of changes in carbon content, rather than in the content of nitrogen and phosphorus. This factor may be especially the case in sandy substrates. Site 5 is close to mangrove vegetation, and it has high carbon and nitrogen contents with a C/N of 33.

Significantly, site 19 had the highest C, N, P concentrations in the sediments, and it is affected by the urban, agricultural and sugar cane industry drainage and is in this sense the most impacted area. It also has a curious C:N molar ratio of 6, similar to phytoplankton, but differing from the halophytic vegetation (mangrove) that grows locally with high biomass, or other sources.

Ruiz-Fernández *et al.* (2002, 2003) measured C/N ratios between 8 and 17 with very high concentrations of OM and nutrients near the Culiacan river inlet in this lagoon complex, suggesting an impact from the adjacent agricultural district. Also the C and N isotopes they found are related to wastewater discharges from agriculture as well as urban discharges. The rest of the sites had C:N values between 10 to 21, corresponding to those proposed by De la Lanza-Espino & Arenas-Fuentes (1986) to mangrove of 18 (C500:N28). However, Ertel & Hedges (1985) proposed a C:N of between 30 and 40 for higher plant remains in the sediment. Emeis *et al.* (2000) found a C:N between 10 and 15, and infe-

red that it was related to a decrease in macrophyte abundance and a high proportion of land derived organic matter; Meyers (2003) referred C:N > 20 to vascular plants. The C:N levels recorded here, 10 and 21, may be associated with an enrichment in organic material, in varying states of decomposition, arriving as agricultural and sugar industry waste discharges and distributed by currents. However, there is another possibility suggested by Matson & Brinson (1990) that involves terrestrial plant material. The shallow and muddy locality of Mapachero (site 8) is visited by birds that provide organic matter rich in urea and, consequently, has a C:N molar ratio of 10. An elevated C:N molar ratio, like that in site 10 with 21, can be explained by the increased input of organic matter from the mangrove and its high sedimentation rate with low hydrodynamic conditions. Chandrasekar *et al.* (2003) working with sediments from an estuary before and after a monsoon period found high concentrations of N between 46  $\mu\text{mol g}^{-1}$  and 856  $\mu\text{mol g}^{-1}$  that they assume was related to the predominance of fine grain sediments associated with terrestrial OM with discharges from human economic activities with C/N ratios between 7.32 to 21.9, including also mangrove detritus in the range reported in this study.

Meyers (1994) reports C/N ranges for marine sapropels between 11 and 17, from 22 to 28 for freshwater sapropels, and from 22 to 46 for peat; these results suggest that the organic matter is a mixture of detritus from vascular plants, algae and bacteria that changes according to the three sediment types under anoxic conditions. The geochemical conditions of the surface sediments of this coastal lagoon can be considered as a sapropel within recent sediments under hydrodynamic forces that define its transport and sedimentation (OzCoast, 2009), and under several OM sources such as micro and macrophytes as well as anthropogenic impacts so recent that is difficult to be considered as a marine C/N sapropel even it has a similar C/N range described by Meyers (1994). In this study the grain size defines the C, N, P distribution but it is still uncertain to know the OM origin. Magni *et al.* (2008) suggest that the OM distribution can be explained as a function of the non linear increase of the fine

sediment quantities, confirming the importance of the grain size in polluted coastal lagoons with high organic carbon discharges associated with the fine grain sediment fraction.

The TP concentration was always lower in the sandy sediments compared to the silt/clay sediments. This nutrient is probably associated with agriculture runoff as observed also in the basin of the Ganges-Brahmaputra-Meghna river of India reported by Datta *et al.* (1999). Notwithstanding the fact that, because phosphorus levels vary greatly, C:P is not considered a trustworthy indicator of organic matter (Gächter & Meyer, 1993), it will be discussed here as a general molar ratio because of its association with geochemical and sedimentary substrates.

Although a lower net phosphorus content was recorded in the sandy substrates of Altata Bay, the carbon content was found to be much lower also, compared with silt/clay sediments (Table 2), and this resulted in low C:P values of between 34 (Castillitos site 6) and 51 (Las Palomas site 17), with the single exception of site 5, located in the inner barrier of the wetland with mangrove influence, which produced a C:P of 143. This range was similar to that found by Ruttenberg & Goñi (1997) in the Amazon delta (48 to 103). They found it difficult to define the nature of organic phosphorus and total nitrogen present in the sediment, but they stated that it might be related to the nature of proteins and phospholipids. On the other hand, a high C:P molar ratio may be explained by the loss of phosphorus in anoxic sediments, as was found to be the case in silt/clay sediments, such as those in the Culiacan River (site 13) producing a ratio of 170. In the case of Altata Bay, where carbon content was low and there are no sources of organic matter arriving directly into the bay, it is possibly associated with a sandy substrate, particularly when subjected to the effect of tidal circulation that permits an enhanced OM re-mineralization.

The inner and central areas of the Ensenada del Pabellón wetland produced high C:P molar ratios, of between 102 and 202, obviously as a result of a higher carbon content, given that phosphorus was barely more abundant there than in the sedi-



ment from Altata Bay. This range is similar to that recorded by Ruttenberg & Goñi (1997) for the Gulf of Mexico (temperate area), and for the mouth of the Mackenzie River (119 to 208), where clay is predominant. Emeis *et al.* (2000) found a considerable variation in the C:P molar ratios, which they attributed to the high proportion of land-delivered organic matter with high sedimentation rates. They also found C:P molar ratios of between 50 and > 100. On the other hand Yamamuro (2000) referred a range of C:P values > 300 to correspond to terrestrial plants and those between 39-191 to be closer to the ratios of marine phytoplankton, in which case in Altata Bay-Ensenada del Pabellón values correspond to these sources. However, the anthropogenic sources in the present coastal complex must be taken into consideration.

In summary, although the grain size distribution of sediment may be heterogeneous in a tropical coastal complex due to the effects of the bathymetry, the morphology, the climate and the tides, the generalized tendency for organic matter distribution depends on sediment type, at least for sandy sediments. The areas affected by the sea in Altata Bay and behind the barrier of the Ensenada del Pabellón wetland are sandy and allow for a greater loss of OC

content (as plant sources are scarce). In addition, they tend to have little carbon and nitrogen, exhibiting a dominance of phosphorus, according to the molar ratios. The inner part of the lagoon and the mouth of the river, where there was more silt/clay with urban and agriculture activities, are characterized by a higher content of carbon and nitrogen. In both cases (sandy and silt/clay), the molar ratios lie within the wide range previously recorded by other authors for a different type of vegetation.

The C:N:P molar ratios were found to be acceptable indicators for distinguishing the sandy sediments of Altata Bay from the silt/clay of the Ensenada del Pabellón lagoon, the former having low ratios and the latter high ratios associated with agriculture runoff and urban settlements.

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## REFERENCES

- Andrews, JE, Greenaway AM, Dennis PF (1998) Combine carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary: Hunts Bay, Kingston Harbour, Jamaica. *Estuarine Coastal and Shelf Science* 46: 743-756.
- APHA, AWWA, WPCF. American Public Health Association, American Water Works Association, Water Pollution Control Federation (1995) *Standard Methods for the Examination of Water and Wastewater* 19th Edition, Washington
- Bianchi TS (2007) *Biogeochemistry of Estuaries* (Ed). Oxford University Press Inc, New York.
- Bianchi TS, Camuel EA (2001) Organic geochemical tracers in estuaries. *Organic Geochemistry* 32(4): 451-621.
- Bickford GP (1996) The effect of sewage organic matter on biogeochemical processes within mid-shelf sediment offshore Sydney, Australia. *Marine Pollution Bulletin* 33(7-12): 168-181.
- Campos-Villegas LE (1997) *Dinámica hidrológica y flujo de nutrientes (NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>) en la interfase sedimento-agua de Ensenada-Pabellón, una laguna costera del Golfo de California*. Tesis de grado, Facultad de Ciencias, Universidad Nacional Autónoma de México, México.
- Carlberg SR (1972) *New Baltic Manual: Cooperative Research Report, Series A. No. 29*. International Council for the Exploration of the Sea. Charlotte Lund Denmark.

- Chandrasekar N, Kmaresan S, Vetha-Roy D (2003) Distribution of phosphorus and nitrogen in the sediments of Tambraparani estuary, South East of India. En: Kumar A (ed) Aquatic Ecosystems. Efficient Offset Printers, New Delhi: 275-281.
- Datta DK, Gupta LP Subramanian V (1999) Distribution of C, N and P in the sediments of Ganges-Brahmaputra-Meghna river system in the Bengala basin. *Organic Geochemistry* 30: 75-82.
- Dean WE (1974) Determination of carbonate and organic matter in calcareous sediments rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Petrology* 44(1): 242-248.
- De la Lanza-Espino G, Arenas-Fuentes V (1986) Disponibilidad de nutrientes a partir de materia orgánica en un sistema lagunar. *Ciencia* 37: 249-254.
- Ebise S, Inoue T (1991) Change in C:N:P ratios during passage of water areas from rivers to a lake. *Water Resources* 25(1): 95-100.
- Emeis K, Struck CU, Leipe T, Polkhne F, Kunzendorf H, Christiansen C (2000) Changes in C:N:P burial rates in some Baltic Sea sediments over the last 150 years-relevance to P regeneration rates and the phosphorus cycle. *Marine Geology* 167: 43-59.
- Ertel JR Hedges JI (1985) Sources of sedimentary humic substances: vascular plant debris. *Geochimica Cosmochimica Acta* 49: 2097-2107.
- Flores-Verdugo F, Agraz-Hernández CM, Núñez-Pasten A (1991) Distribución, estructura y defoliación de los manglares en el ecosistema lagunar-estuarino de Bahía de Altata Ensenada del Pabellón. *Ecología de los manglares, productividad acuática y perfil de comunidades en ecosistemas lagunares-estuarinos de la costa noroccidental de México DGAP: Universidad Nacional Autónoma de México, Informe (202389).*
- Folk RL (1980) *Petrology of Sedimentary Rocks*: Hemphill Publishing Co. Austin, Texas.
- Gächter R, Meyer J (1993) The role of microorganisms in mobilization and fixation of phosphorus in sediments. *Hydrobiologia* 253: 103-121.
- Green-Ruiz C, Páez Osuna F (2001) Heavy metals anomalies in lagoon sediments related to intensive agriculture in Altata-Ensenada del Pabellón coastal system (SE Gulf of California). *Environment International* 26: 265-273.
- Hartmann M, Müller P, Suess E, vander-Weijden CH (1973) Oxidation of organic matter in recent marine sediments. "Meteor" Forschungsergebnisse Reihe. *Geological Geophysical*, 12: 74-86.
- Hedges J, Clark W, Quay PD, Rickey JE, Devol AH, Santos UM (1986) Compositions and fluxes of particulate organic material in Amazon River. *Limnology and Oceanography* 31(4): 717-738.
- Magni P, De Falco G, Como S, Casu D, Floris A, Petrov AN, Castelli A, Perilla A (2008) Distribution and ecological relevance of fine sediments in organic- enriched lagoons: the case study of the Cabras lagoon (Sardinia, Italy). *Marine Pollution Bulletin*, 56(3): 549-564.
- Matson EA, Brinson MM (1990) Stable isotopes and the C:N ratios in the estuaries of the Palmico and Nause Rivers, North Carolina. *Limnology and Oceanography* 35(6): 1290-1300.
- Meyers PA (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27: 213-250.
- Meyers PA (2003) Applications of organic geochemistry to paleolimnological reconstructions: A summary of examples from the Laurentian Great Lakes. *Organic Geochemistry* 34: 261-289.
- Mook DH, Hoskin CM (1982) Organic determinations by ignition: caution advised. *Estuarine Coastal and Shelf Science* 15: 679-699.

- Nöges P, Järvet A, Tuvikene L, Nöges T (1998) The budgets of nitrogen and phosphorus in shallow eutrophic lake Vortsjärv (Estonia). *Hydrobiologia* 363: 219-227.
- OzCoast (2009) Sediment, Organic Matter and Nutrients. Australian Online [http://www.ozcoasts.org.au/indicators/sediment\\_org\\_matter.jsp](http://www.ozcoasts.org.au/indicators/sediment_org_matter.jsp)
- Páez-Osuna F, Bojórquez Leyva H, González Farías F (1992) Carbon and phosphorus in sediments of a lagoon system associated to an agricultural drainage basin. *Anales del Instituto de Ciencias del Mar y Limnología Universidad Nacional Autónoma de México* 19(1): 1-11.
- Páez-Osuna F, Bojórquez-Leyva H, Green-Ruiz C (1998) Total carbohydrates:organic carbon in lagoon sediments as an indicator of organic effluents from agriculture and sugar-cane industry. *Environmental Pollution* 102: 321-326.
- Páez-Osuna F (2001) *Camaronicultura y Medio Ambiente: Instituto de Ciencias del Mar y Limnología, Estación-Mazatlán. Universidad Nacional Autónoma de México, México.*
- Peraza-Viscarra R (1973). *Características hidrográficas y distribución de los sedimentos en el sistema estuarino Bahía de Altata Ensenada del Pabellón, Sinaloa. Tesis Licenciatura Universidad Autónoma de Baja California, México*
- Rasheed M, Badran M, Huettel M (2003) Influenced of the sediment permeability and mineral composition on organic matter degradation in three sediments from the Gulf of Aqaba, Red Sea. *Estuarine Coastal and Shelf Science* 57(1-2): 369-384.
- Ruíz-Fernández AC, Hillaire-Marcel C, Ghaleb B, Soto-Jiménez M, Páez-Osuna F (2002) Recent sedimentary history of anthropogenic impacts on the Culiacan River Estuary, Northwestern Mexico: geochemical evidence from organic matter and nutrients. *Environmental Pollution*: 118: 365-377
- Ruíz-Fernández AC, Páez-Osuna F, Soto-Jiménez M, Hillaire-Marcel C, Ghaleb B (2003) The loading history of trace metals and nutrients in Altata-Ensenada del Pabellón lagoon complex, northwestern México. *Journal Environmental Radioactivity* 69: 120-143.
- Ruttenberg KC, Goñi MA (1997) Phosphorus distribution, C:N:P ratios, and  $\delta^{13}\text{C}$  in arctic, temperate, and tropical coastal sediments: tools for characterizing bulk sedimentary organic matter. *Marine Geology* 139: 23-145.
- Strickland JDH, Parsons TR (1972) *A Practical Handbook of Seawater Analysis. Fishery Research Board of Canada Ottawa, Canada.*
- Yamamuro M (2000) Chemical tracers of sediment organic matter origins in two coastal lagoons. *Journal Marine Systems* 26: 127-134.