

## Recent Sedimentary History of Organic Matter and Nutrient Accumulation in the Ohuira Lagoon, Northwestern Mexico

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**Abstract.** <sup>210</sup>Pb-derived sediment accumulation rates, as well as a suite of geochemical proxies (Al, Fe,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ), were used to assess the time-dependent variations of C, N, and P fluxes recorded in two sediment cores collected at Ohuira Lagoon, in the Gulf of California, Mexico, during the last 100 years. Sedimentary C, N, and P concentrations increased with time and were related to land clearing, water impoundment, and agriculture practices, such as fertilization. C:N:P ratios and  $\delta^{13}\text{C}$  suggested an estuarine system that is responsive to increased C loading from a N-limited phytoplankton community, whereas  $\delta^{15}\text{N}$  values showed the transition between an estuarine-terrestrial to an estuarine-more marine environment, as a consequence of the declining freshwater supply into the estuary due to the channeling and impoundment of El Fuerte River between 1900 and 1956. The recent increases in nutrient fluxes (2- to 9-fold the pre-anthropogenic fluxes of C and N, and 2 to 13 times for P) taking place in the mainland from the 1940s, were related to the expansion of the intensive agriculture fields and to the more recent development of shrimp farming activities.

The Mexican state of Sinaloa has 656 km of coastline and is characterized by high fishing and agriculture activity. Ohuira is a shallow and brackish coastal lagoon (average depth of 3 m, surface area of 125 km<sup>2</sup>), which supports local fishing activity including wild and cultivated shrimp for export. However, there is some concern related to the desiccation of lowlands and infilling promoted by sediment transport due to agriculture activities, as well as alteration of water quality due to waste water discharges (CONABIO 2002). Actually the lagoon receives the untreated domestic wastes from the village of Juan José Ríos (23,470 inhabitants; INEGI 2000) as well as the residual waters from 4 shrimp aquaculture facilities (350 ha; Lyle-Fritch *et al.* 2001) and El Fuerte Valley agriculture lands,

which are characterized by intensive tillage, irrigation, heavy application of fertilizers and pesticides, and monocropping.

The economic development of the region started about 1890 upon the efforts of a group of utopian socialists from the United States, who built the first irrigation system in El Fuerte Valley to develop the sugar cane industry (Gill 2003). Currently El Fuerte Valley represents approximately 15% of the irrigated lands in Mexico, and its most important crops are sorghum, corn, sugar cane, mangos, alfalfa, and chick peas, with 26, 12, 19, 2, 2, and  $1 \times 10^3$  cultivated hectares, respectively (SAGARPA 2005).

The aim of this work was to evaluate the temporal changes in sediment accumulation rates and excess nutrient fluxes reflected in the sedimentary record of C, N, and P in the Ohuira Lagoon mudflats, using <sup>210</sup>Pb chronology. C and N isotope composition was used to evaluate the relationship between the observed changes and the economic development of El Fuerte Valley.

### Materials and Methods

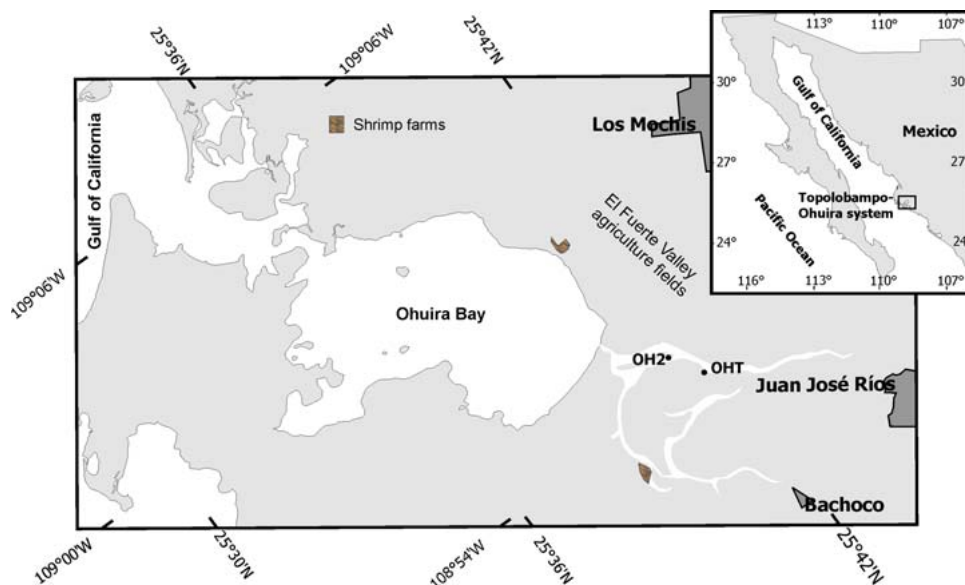
#### Sampling

Two sediment push-cores were collected with plastic tubes (7-cm inner diameter) from 2 mudflat areas of Ohuira Lagoon, in June 2004 (Figure 1). The core OHT (25°41', 108°53', 14 psu) was taken in an inner zone of the lagoon, less exposed to sea water exchange than core OH2 (25°41', 108°54', 17 psu). Core subsamples were sliced into 1-cm intervals, freeze-dried to constant weight, and stored in plastic bags until analysis.

#### Laboratory Analysis

Water content data were used to calculate the porosity and *in situ* dry sediment bulk density, to estimate the mass depth (accumulated weight per area unit, g cm<sup>-2</sup>) for each core section (Baskaran and Naidu 1995). Organic matter (OM) and carbonate (CaCO<sub>3</sub>) contents were estimated through loss on ignition (LOI) at 400°C and 750°C, respectively; OM was calculated as  $0.58 \cdot \text{LOI}_{400}$  (EPA 2006). Total phosphorus (P) was measured as molybdate reactive P by UV

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**Fig. 1.** Location of sampling sites at the tidal mudflats of Ohuira Lagoon, Sinaloa, Mexico

spectrometry, after calcination of the sediment samples (550°C, 1 h; Páez-Osuna *et al.* 1991) with an analytical precision of 4.8%. Organic carbon (OC) and total nitrogen (N) contents were measured using a FISONs NA2000 Element Analyzer after removal of the carbonate fraction in silver capsules using 1.5 M HCl. The average standard deviation of each measurement was determined by replicate analyses of the IAEA standard NBS19 (0.07 % for OC and 0.009 % for N).

Stable isotopic analyses of OM ( $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$ ) were carried out on the same samples using a Finnigan Delta Plus mass spectrometer, which was directly coupled to a Fisons NA2000 EA by means of a CONFLO interface for continuous flow measurements. Stable nitrogen and carbon isotope ratios are reported in the conventional  $\delta$ -notation with respect to atmospheric  $\text{N}_2$  (air) and PDB (Pee Dee Belemnite) carbonate standard, respectively. Uncertainties were lower than  $\pm 0.2\text{‰}$ , as determined from routine replicate measurements of the reference sample standard IAEA-NBS19 for the  $\delta^{13}\text{C}$  and standard IAEA-N-1 for the  $\delta^{15}\text{N}$ .

Sediments for Al, Fe, and  $^{210}\text{Pb}$  analyses were digested overnight in closed Savillex<sup>TM</sup> containers, on a hot plate at 200°C, in a mixture of 5:4:1  $\text{HNO}_3 + \text{HCl} + \text{HF}$  (Loring and Rantala 1992). Al and Fe were analyzed by AAS (uncertainties of 2–5%, determined from replicated analysis of the standards IAEA-356 and BCS-1). Total  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{tot}}$ ) was determined by alpha counting of  $^{210}\text{Po}$  spontaneously deposited onto silver discs (Flynn 1968) using  $^{209}\text{Po}$  as yield tracer. Uncertainty ( $\pm 4.6\%$ ) was determined through replicate measurements of standard IAEA-300.  $^{137}\text{Cs}$  and supported  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{sup}}$ , derived from the  $^{214}\text{Bi}$  photopeak) were measured on Ortec gamma detectors for a minimum of 24 h. Excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) activities were determined by subtracting  $^{210}\text{Pb}_{\text{sup}}$  from  $^{210}\text{Pb}_{\text{tot}}$  values.

## Results and Discussion

### Sedimentary Environment

Collected sediments were mostly silty clays (> 90%).  $\text{LOI}_{400}$ -derived OM and  $\text{CaCO}_3$  contents gradually decreased with depth in both cores (Figure 2A and B). These variations suggested the increasing productivity of calcareous organisms toward the most recent times, although they might also reflect the chemical carbonate dissolution driven by organic matter

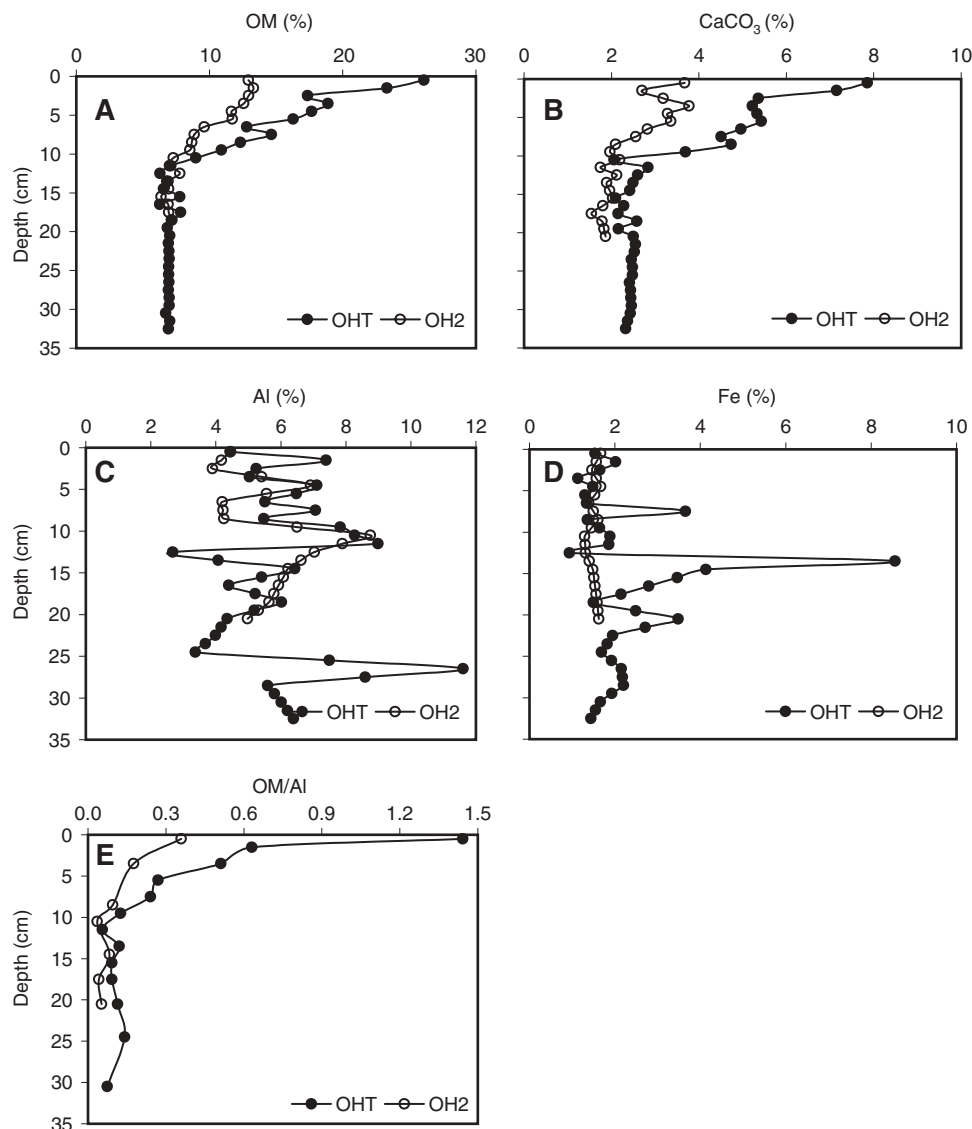
oxidation. Al profiles in both sediment cores (Figure 2C) suggested that the sediments accumulated from heterogeneous detrital sources and this variability is more evident in sediment core OHT. Fe content in both cores was low ( $\sim 2\%$ ) suggesting reducing conditions in the sediments (Figure 2D). Fe is known for being diagenetically mobile in aquatic systems depending on redox conditions. Under anoxic or suboxic conditions, ferric iron is reduced and can either precipitate as FeS or migrate to the sediment surface where it can precipitate as ferric oxides in case of oxidizing conditions (Jorgensen 1977). Therefore, the three peaks observed at intermediate depths of core OHT might be the result of ferrous sulfides precipitation.

OM/Al ratios exhibited an increasing trend from around 11 cm depth to the surface at the 2 sites (Figure 2E) suggesting an increment in the biogenic contribution over the lithogenic supply to the site, although OM diagenesis could have also influenced the OM/Al ratios decreasing with depth. Nonetheless, this trend also confirmed that these sediments are not redeposited sediments since, otherwise, the sediment profile would have exhibited uniform OM/Al ratio distribution (Emeis *et al.* 2000).

### Short-Lived Radioisotopes ( $^{137}\text{Cs}$ , $^{210}\text{Pb}$ )

$^{137}\text{Cs}$  activities in both cores were below the analytical background, as has been previously observed in other sediments from the Mexican Pacific coast (Páez-Osuna and Mandelli, 1985; Ruiz-Fernández *et al.* 2001, 2002) and explained as a consequence of poor fallout of this radionuclide over these low latitude coastal areas.

$^{210}\text{Pb}_{\text{tot}}$  activities were low (Figure 3A and B) but consistent with regional data (Ruiz-Fernández *et al.* 2001, 2002). Mixing was considered to exert a negligible effect since the nutrient profiles obtained from the same cores (see Nutrients section) showed increasing trends toward the surface with maximum values at the top of the core. If mixing were intense, these clear features would have been smoothed or



**Fig. 2.** Depth profiles of (A) LOI<sub>400</sub>-derived OM, (B) CaCO<sub>3</sub>, (C) Al, (D) Fe, and (E) OM/Al in sediment cores from the Ohuira Lagoon mudflats

blurred, and a number of organisms would have been found when sampling and subsampling. These observations supported the suitability of the sedimentary record to provide stratigraphic information. In order to verify that <sup>210</sup>Pb<sub>xs</sub> features were not caused by changes in sediment composition (mineral type, grain size distribution, OM, or CaCO<sub>3</sub> content), <sup>210</sup>Pb<sub>xs</sub> activities were normalized by OM, CaCO<sub>3</sub>, and Al concentrations, with the effect of increasing <sup>210</sup>Pb<sub>xs</sub> values without significantly modifying the features.

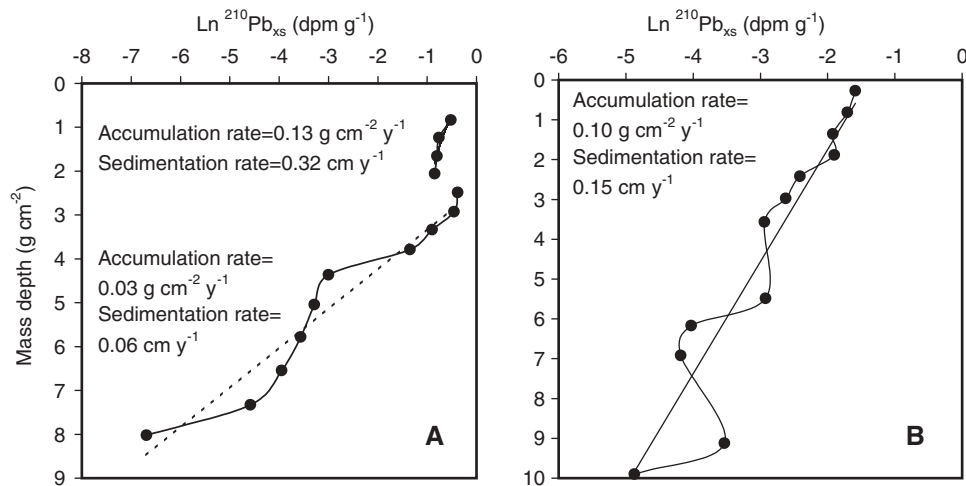
Figure 3A and B shows that both logarithmic <sup>210</sup>Pb activity depth profiles are characterized by oscillations that account for changes of accumulation rates over time. However, in the case of core OH2 an average mass accumulation rate (g cm<sup>-2</sup> y<sup>-1</sup>) could still be calculated through the Constant Flux-Constant Sedimentation model (CF-CS; Appleby and Oldfield 1992). Differently, the OHT <sup>210</sup>Pb<sub>xs</sub> profile showed two different main trends (from surface to 6 cm depth, and from 6 to 16 cm depth) suggesting a recent abrupt change of accumulation rate. In this case, the <sup>210</sup>Pb dating was calculated using the Constant Initial Concentration model (CIC; Appleby and Oldfield 1992) that allows dating

non-linear <sup>210</sup>Pb<sub>xs</sub> profiles. <sup>210</sup>Pb<sub>xs</sub> depth profiles allowed dating the sediment cores only down to 12 cm depth for core OHT and to 17 cm depth for OH2, corresponding to a time span of circa 100 years (115 ± 12 and 106 ± 11 years), the most reliable period of time for <sup>210</sup>Pb chronologies.

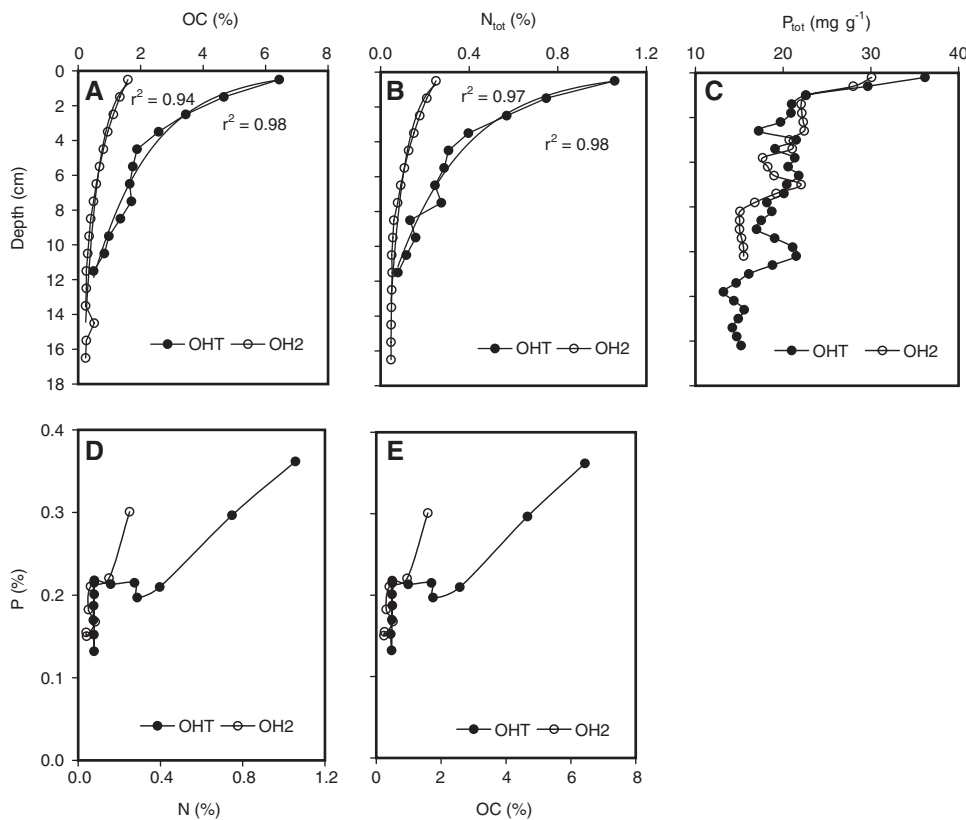
### Nutrients

Organic carbon content in both sediment cores showed the typical exponential decay with depth ( $r > 0.96$ ,  $p < 0.05$ ). Elemental analyzer-OC values were considerably lower (between 2- and 10- fold) than those estimated from LOI<sub>400</sub>-derived OM although both profiles showed similar trends.

The OC, N, and P concentrations in OHT core were consistently higher than those observed at OH2 (Figure 4A–C) but, in general, the nutrient concentrations found at Ohuira Lagoon sediments are among the typical values reported for estuarine sediments in other areas of the world (Table 1). The OC content was significantly correlated with N in both cores ( $p < 0.05$ ,  $r > 0.93$ ) and the intercepts of the best fit regression



**Fig. 3.**  $\text{Ln } ^{210}\text{Pb}_{\text{xs}}$  profile (versus mass depth) in sediment cores from Ohuira Lagoon tidal mudflats: (A) OHT, (B) OH2



**Fig. 4.** Nutrient profiles in sediment cores from Ohuira Lagoon: (A) organic carbon, (B) total nitrogen, (C) total phosphorus; and correlations between (D) P and N and (E) P and OC

lines were close to zero, suggesting that N concentrations can be considered as organic nitrogen (ON). P showed significant positive correlations with OC and N ( $p < 0.05$ ,  $r \geq 0.95$ ) but only within the topmost 10 cm (Figure 4D,E).

Sedimentation associated with tidal flooding is an important source of both N and P to tidal marshes with N usually linked mainly to organic matter and P primarily associated with the fine grained clay minerals (Morse *et al.* 2004). OC correlation with P and N likely suggests the importance of this organic-rich deposit as a nutrients reservoir. The correlation between OC and N indicates that the sources that supply OM to these sediments are present in nearly invariant proportions (Ruttenberg and Goñi

1997), while the correlations between OC and P, as well as N and P, which were found only in the superficial layers of both cores (topmost 10 cm) are either indicating a change in phosphorus main incorporation route or are simply the result of OC enrichment, since P and OC concentrations significantly correlate with each other only in high organic coastal sediments (Ingall and van Cappellen 1990).

*Organic carbon diagenesis versus nutrient enrichment.* Downcore variation in OC content is mainly attributed to changes in the supply rate and type of OM; however,

**Table 1.** Concentrations of OC, N, and P in estuarine sediments

Estuarine system	OC (%)	N (%)	P (mg g <sup>-1</sup> )	References
Ohuira Lagoon, México	0.3–6.5	0.08–1.60	13–36	This study
Culiácan River Estuary, México	0.3–3.0	0.04–0.29	443–3102	Ruiz-Fernández <i>et al.</i> (2002)
Chiricahueto Lagoon, México	0.4–4.5	0.04–0.48	160–1600	Soto-Jiménez <i>et al.</i> (2003)
Altata-Ensenada del Pabellón, México	0.1–0.5	n.a.	34–51	Páez-Osuna <i>et al.</i> (1992)
Celestín Lagoon, México	1.0–16	0.20–0.80	n.a.	Gonneea <i>et al.</i> (2004)
Chesapeake Bay Estuary, USA	1.0–4.0	0.20–0.50	0.4–0.9	Cornwell <i>et al.</i> (1996)
Winyah Bay Estuary, USA	1.0–5.0	0.10–0.40	n.a.	Goñi <i>et al.</i> (2003)
Florida Bay Estuary, USA	2.0–7.0	0.20–0.80	0.05–0.25	Orem <i>et al.</i> (1999)
Seine Estuary, France	6.0–46	0.50–3.00	0.8–1.8	Mesnager <i>et al.</i> (2002)
Shinji Lagoon, Japan	1.0–3.0	0.10–0.40	0.5–1.8	Yamamuro and Kanai (2005)
Cochin Estuary, India	0.3–3.2	0.20–0.80	0.1–20	Mathews and Chandramohanakumar (2003)
Ashtamudy Estuary, India	1.0–4.0	0.10–0.30	0.1–0.3	Babu <i>et al.</i> (1998)
Mandovi Estuary, India	0.1–3.0	0.30–3.00	0.5–6.7	Nasrolkar <i>et al.</i> (1996)
Lunawa Estuary, Sri Lanka	1.0–14	0.10–0.80	n.a.	Ratnayake <i>et al.</i> (2005)

n.a. = not available.

**Table 2.** Parameters of first-order G model for OC and ON decomposition at Ohuira Lagoon

Parameters	Sediment core	
	OHT	OH2
Organic carbon		
<i>k</i> (year <sup>-1</sup> )	0.04	0.03
Residence time (year)	23	37
OC <sub>metabolized</sub> fraction (%)	0.0015	0.11
<i>t</i> <sub>1/2</sub> (year)	16	26
Organic nitrogen		
<i>k</i> (year <sup>-1</sup> )	0.04	0.03
Residence time (year)	23	40
OC <sub>metabolized</sub> fraction (%)	0.07	0.07
<i>t</i> <sub>1/2</sub> (year)	16	27

*k* = first-order decomposition constant; *t*<sub>1/2</sub> = half-life; metabolized fraction = percent of initial concentration degraded at the sediment-water interface.

microbial consumption in the sediment has also an important role that must be taken into account when interpreting depth profiles. OC and N decomposition rates were evaluated by the first-order G model (Zimmerman and Canuel 2000):

$$G_t = G_0 e^{-kt} + G_\infty$$

where *k* is the decomposition constant at any time *t*, *G*<sub>0</sub> represents the degradable element concentration at the sediment surface, and *G*<sub>∞</sub> is the asymptotic concentration at depth, representing the refractory fraction. Parameters obtained from the model applied to OC and N vertical distributions are summarized in Table 2. OC and N decay rates at OHT were slightly higher than at OH2 and, therefore, their half-life and residence times were also shorter; however, in both cases, the amount of nutrients degraded at the sediment water interface is practically negligible (≤ 0.1%).

In order to evaluate the changes in OC and N supply to the system during the period of time comprised in the sedimentary record, the simple rate model for organic decomposition pro-

**Table 3.** Geochemical variable ranges obtained for sediment cores from Ohuira Lagoon

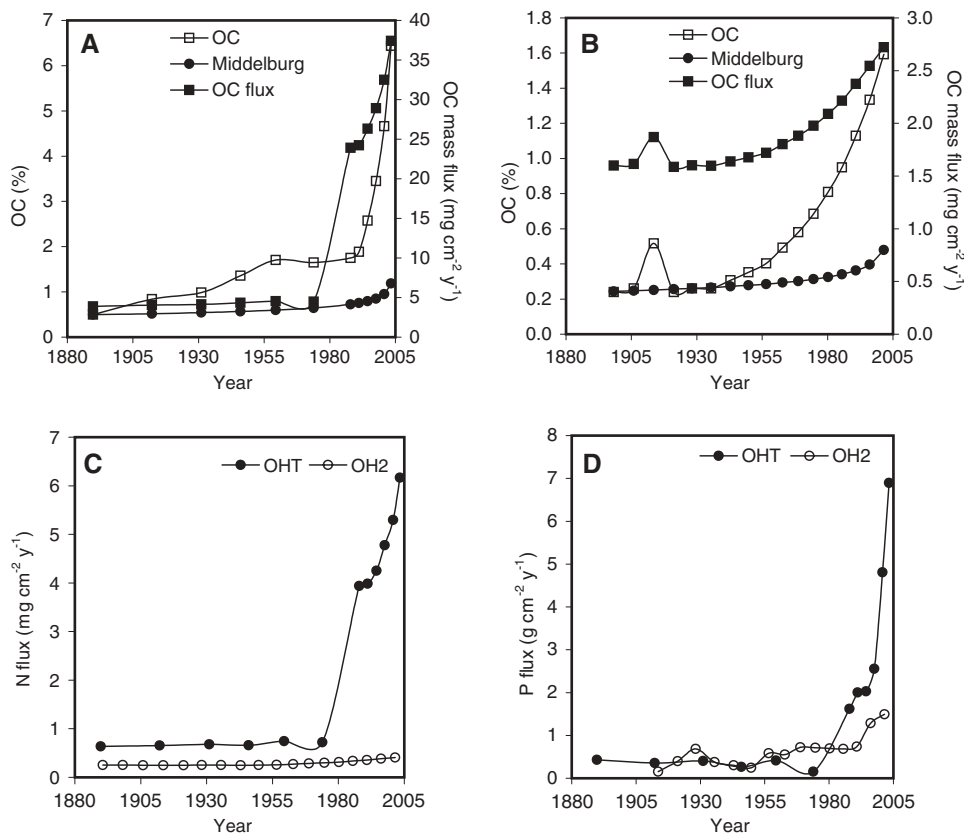
Variable	OHT	OH2
CaCO <sub>3</sub> (%)	2–8	2–4
Fe (%)	1–9	1–2
Al (%)	3–12	4–9
OC (%)	7–26	6–13
OC <sub>bck</sub> (mg g <sup>-1</sup> )	0.48 ± 0.02	0.25 ± 0.01
N (mg g <sup>-1</sup> )	0.8–11	0.4–2.5
N <sub>bck</sub> (mg g <sup>-1</sup> )	0.80 ± 0.02	0.40 ± 0.02
P (mg g <sup>-1</sup> )	13.2–36.2	15.0–30.1
P <sub>bck</sub> (mg g <sup>-1</sup> )	14.6 ± 0.6	15.2 ± 0.2
C:N	6.8–7.8	6.8–7.8
C:P	0.9–6.5	0.7–1.8
N:P	0.9–6.5	0.7–1.8
δ <sup>15</sup> N (‰)	-1 to + 10	+7 to + 12
δ <sup>13</sup> C (‰)	-14 to -18	-14 to -18
<sup>210</sup> Pb <sub>tot</sub> (dpm g <sup>-1</sup> )	0.9–1.8	0.9–1.3
Accumulation rate (g cm <sup>-2</sup> y <sup>-1</sup> )	0.03–0.13	0.10
Sedimentation rate (cm y <sup>-1</sup> )	0.06–0.32	0.15
OC fluxes (mg cm <sup>-2</sup> y <sup>-1</sup> )	4.0–37	2–3
N fluxes (mg cm <sup>-2</sup> y <sup>-1</sup> )	0.6–6.0	0.2–0.4
P fluxes (mg cm <sup>-2</sup> y <sup>-1</sup> )	0.1–7.0	0.1–1.5

posed by Middelburg (1989) was used to predict the concentration of OC and N at any time as a result of constant input and steady-state diagenesis process, according to the following equation (Cornwell *et al.* 1996):

$$G_t = G_0 e^{-(3.2t^{0.05})}$$

where *G*<sub>*t*</sub> is the metabolizable organic component of OC deposited at time *t* and *G*<sub>0</sub> represents the degradable element concentration at the sediment surface, which was chosen to provide a general correspondence between the model and the measured non-metabolizable OC concentrations (the vertical asymptote of the OC profile).

The Middelburg model underestimated most of the OC concentrations at OHT but described relatively well OC changes in core OH2 up to 11.5 cm, indicating that OC content can be accounted for by steady-state diagenesis up to that depth. The OC concentrations were higher than those predicted



**Fig. 5.** Excess fluxes temporal variations ( $\text{mg cm}^{-2} \text{y}^{-1}$ ) for OC in cores (A) OHT and (B) OH2; and for (C) N and (D) P

by the model, reflecting an increase in OC deposition starting from the early 1900s at OHT, and from the early 1940s at OH2.

Fluxes of OC and N were estimated upon OC concentrations corrected for the degradative loss occurred with time. The OC lost to degradation for any sample deposited  $t$  years ago ( $C_{\text{lost}-t}$ ) was estimated as in Zimmerman and Canuel (2002):

$$C_{\text{lost}-t} = G_{\text{O(m)}} - G_t$$

where  $G_{\text{O(m)}}$  is the OC concentration measured in the surface layer of the core and the degradation-corrected concentrations ( $C_{\text{corr}-t}$ ) for a sample of concentration  $C_{\text{mt}}$ , is then:

$$C_{\text{corr}-t} = C_{\text{mt}} + C_{\text{lost}-t}$$

The modeled fluxes of OC and N to the sediment were then calculated as the product of its modeled concentration and the  $^{210}\text{Pb}$ -derived sediment mass accumulation rates (Table 3; Figure 5A and B for OC and 5C for N).

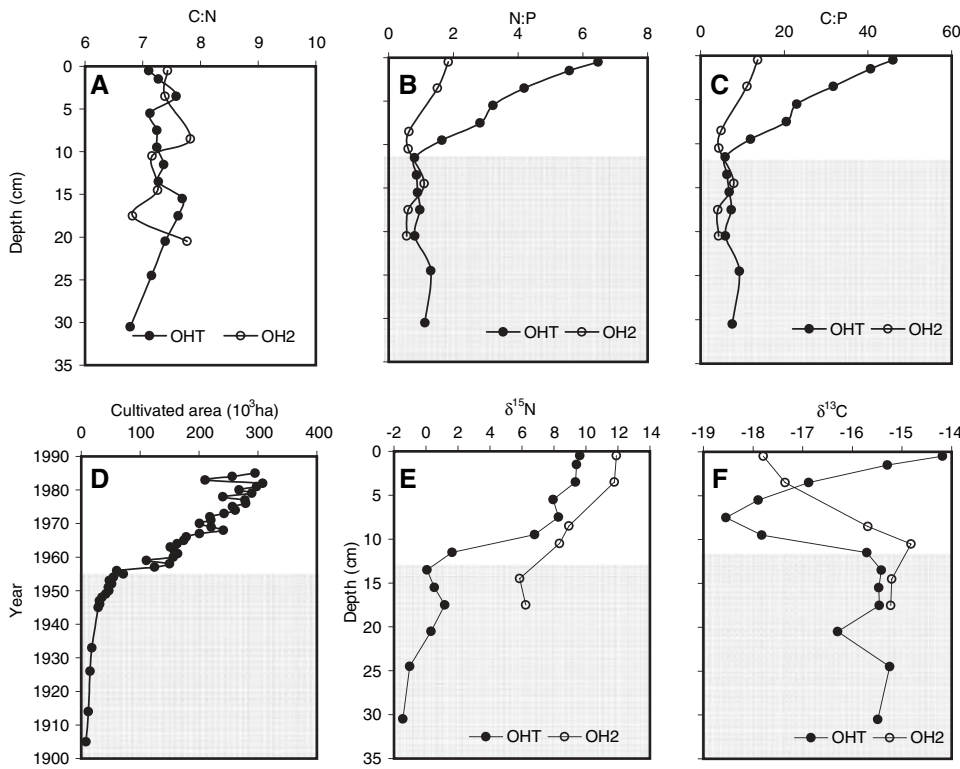
Anthropogenic P fluxes (Figure 5C) were obtained by multiplying the excess P concentrations ( $P_{\text{xs}}$ ) by the  $^{210}\text{Pb}$ -derived sediment mass accumulation rates.  $P_{\text{xs}}$  were calculated by subtracting the pre-anthropogenic P values ( $P_{\text{bck}}$ ) from the P concentrations analytically determined.  $P_{\text{bck}}$  are often obtained from the correlation between P and Fe in pristine sediments (Gerritse *et al.* 1998) under the assumption that Fe-(hydroxy)-oxides tend to adsorb the inorganic P (Shukla *et al.* 1971); however, none of the sediment cores displayed such a

relationship, likely due to their reducing conditions.  $P_{\text{bck}}$  values were, therefore, obtained from the average of the asymptotic values observed below 23 and 15 cm depth at OHT and OH2 cores, respectively (Table 3).

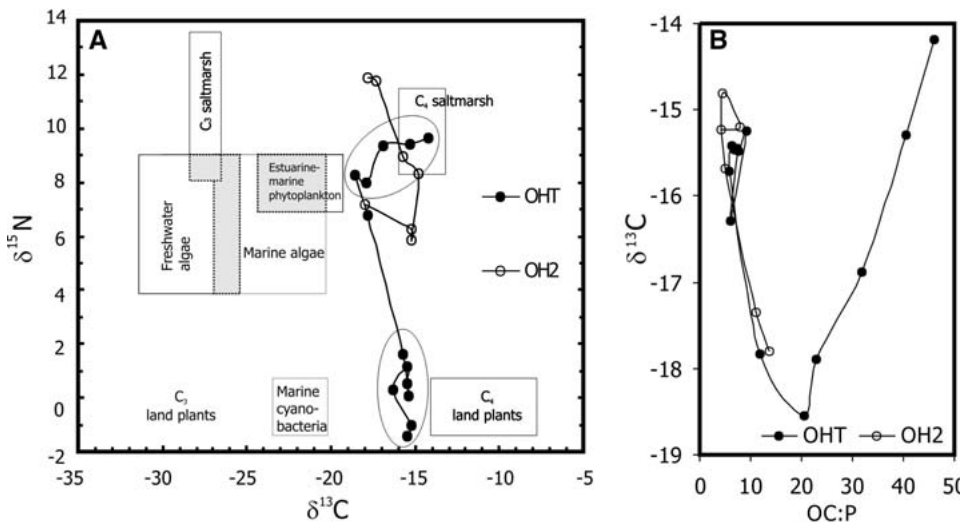
As with C and N fluxes, P fluxes were higher at OHT than at OH2. The larger nutrient enrichment observed at site OHT is most likely due to a preferential sedimentary dynamics, since site OH2 is more influenced by tides than OHT, which is currently accreting at higher sedimentation rates and receiving a higher supply of nutrients due to its proximity to the agriculture fields of El Fuerte Valley and some shrimp aquaculture facilities, established since the late 1980s. Considering that the effective sedimentary retention of the total amount of nutrients supplied to the estuaries can be as low as 40% for N and usually less than 60% for P (Tappin 2002), the N and P fluxes calculated for Ohuira cores might underrate the historical nutrient supply to the lagoon.

**Organic matter provenance.** The C:P and N:P values were rather low since the pre-anthropogenic times (pre-1900), suggesting a prevailing phosphorus clastic source in the area. Their increasing trends, based on the significant correlation found between OC and the C:P and N:P ratios ( $p < 0.05$ ,  $r^2 > 0.95$ ) were associated with the increased anthropogenic input of OM.

$\delta^{15}\text{N}$  profiles showed a similar increasing trend toward the present in both cores (Figure 6D).  $\delta^{13}\text{C}$  values above background levels showed contrasting trends (Figure 6E), with values decreasing  $\sim 3\text{‰}$  toward the surface in core OH2,



**Fig. 6.** Redfield ratios and isotopic ratios from Ohuira Lagoon: (A) C:N, (B) N:P, (C) C:P, (E) δ<sup>15</sup>N, and (F) δ<sup>13</sup>C (δ<sup>15</sup>N and δ<sup>13</sup>C are in ‰ PDB). Plot (D) shows the historical evolution of cultivated lands in El Fuerte Valley



**Fig. 7.** Information on OM sources through the relationships between (A) δ<sup>15</sup>N and δ<sup>13</sup>C (modified from Meyers 2006) and (B) δ<sup>13</sup>C and C:P ratios

whereas in core OHT after a strong decrease between 7.5 and 11.5 cm depth (1900–1959) they increased again (~4‰) in the most recent times.

Sedimentary OM found in Ohuira cores fits in the reported ranges of δ<sup>15</sup>N (–1.2 to +10.6‰; Cloern *et al.* 2002) and C:N (6 to 9; Giordani and Angiolini, 1983) for coastal and estuarine-marine organic matter, although δ<sup>13</sup>C values were higher than expected for estuarine-marine OM (–17 to –28‰; Cloern *et al.* 2002).

The decreasing δ<sup>13</sup>C values are usually related to the decrement of algal productivity with the enhancement of the isotopic discrimination against dissolved <sup>13</sup>CO<sub>2</sub> (Tenzer *et al.* 1999). However, the C:N ratios in both cores showed that the

marine algal contribution did not decrease with time and, therefore, the declining δ<sup>13</sup>C values could result from the contribution of more marine OM (–20 to –22‰; Meyers 1994).

The increasing δ<sup>13</sup>C values observed in the most superficial layers of core OHT (uppermost 8 cm; ca. 1959) could result from the input of an additional <sup>13</sup>C-enriched OM source. In both sediment cores, the δ<sup>13</sup>C and C:P plots showed the characteristic hyperbolic trend of the mixing line obtained between two end members (Figure 7B) where sediments with low C:P ratios display the heaviest δ<sup>13</sup>C values (more terrestrial-estuarine organic matter) and, at the other end of the trend, samples with high C:P ratios are characterized by lighter δ<sup>13</sup>C values (both traits of more marine-estuarine-derived organic matter; Ruttenberg and



Goñi 1997). However, in the most recent layers of core OHT, C:P and  $\delta^{13}\text{C}$  appeared directly correlated, suggesting that a new organic matter source has been introduced.  $\delta^{13}\text{C}$  values as high as  $-11\text{‰}$  have been previously observed in coastal tidal flats sediments and were related to the input of relatively coarse detritus from  $\text{C}_4$  grasses (Mook and Tan 1991). According to Van der Merwe and Vogel (1978), even a discrete terrestrial OM input, introducing a  $\text{C}_4$  plant component from cultivated fields (as corn, sorghum, or sugar cane, which are cultivated in El Fuerte Valley) could shift the  $\delta^{13}\text{C}$  values as high as  $-12.5\text{‰}$ . It is worth mentioning that the production of sorghum and sugar cane in El Fuerte Valley has significantly increased with time. Only between 1994 and 2004, sorghum and sugar cane crops passed from 9,160 to 55,807 and from 448,560 to 1,006,034 tons per year, respectively (INEGI 1994, 2005).

According to Meyers (1997), the observed  $\delta^{15}\text{N}$  profile could be the result of the reduction of freshwater supply after the partial diversion of a river. According to the plot of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  (Figure 7A), the sediment core OHT is showing the transition between two kinds of environments: (1) from the bottom of the core up to 11.5 cm depth (year 1900), a wetter environment in which estuarine OM has a more terrestrial character; and (2) from 9.5 cm depth (early 1930s) to the surface, a dryer environment in which estuarine OM has a more marine character (the values from sediment core OH2 are also located in this region of the plot).  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values increasing together can be produced by dryer conditions (runoff diminution) with bloom maxima migrating upstream (as the saline plume arrives further up in the estuarine zone) and decreased size of the bloom due to lower nutrient flux to the site (Bratton *et al.* 2003). The  $^{15}\text{N}$  increase is likely due to the decreasing input of isotopically light land-plant detritus carried by the river waters to the estuary (Meyers and Lallier-Vergés 1999) where marine algae are more abundant.

C and N isotopic changes are undoubtedly related to the development of the agroindustry in the surrounding area of Ohuira Lagoon. The period of gradual decreasing  $\delta^{13}\text{C}$  values in core OHT corresponded with the gradual increment of the cultivated area at El Fuerte Valley (Figure 6F) between 1900 and 1959, whereas in core OH2 the evidence is observed after the abrupt increase of cultivated areas between 1956 and 1957. On the other hand,  $\delta^{15}\text{N}$  increasing values are most likely the result of the reduction in fresh water supply to the site due to the creation of irrigation infrastructure of El Fuerte Valley and the consequent development of more brackish-marine conditions. Actually, the Tastes channel was built in 1892 to derive water from the El Fuerte River to the Los Mochis desert. By the mid-1940s, this channel and several other minor channels connected through 500 pumps were used to irrigate 18,000 ha. The SICAE channel was built by 1947 and the irrigated area abruptly doubled from 18,000 to 36,000 ha; and with the construction of Miguel Hidalgo dam in 1956, the irrigation capacity increased from 55,000 to 240,000 ha (Gill 2003).

## Conclusions

The combination of geochemical analysis and  $^{210}\text{Pb}$  dating was very useful to examine the past rates of sediment and nutrient sequestration in a coastal environment. C and N isotope ratios proved to be more sensible tools to trace changes in

OM provenance than C:N:P ratios. The study demonstrated that anthropogenic land use within the catchment is the main factor driving both sediment and nutrient retention in two mudflat areas of Ohuira Lagoon; although the impact is not spatially uniform and, therefore, care should be taken to avoid generalizations. The different effects of the nutrient-enriched runoff from agricultural lands observed in the two cores were related to the hydrological regime (open and partially closed subtidal areas) and the closeness to the sediment and nutrients source. Sediment accumulation in the area closer to the culture fields has increased  $\sim 5$  times with respect to the pre-anthropogenic conditions in less than 20 years, while C, N, and P fluxes increased almost 10-, 10-, and 13-fold, respectively. At the site that is more influenced by marine conditions, no changes in sediment accumulation were observed, although C, N, and P fluxes doubled during the last 60 years.

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