Spatio-temporal variability in benthic exchanges at the sediment-water interface of a shallow tropical coastal lagoon (south coast of Gulf of Mexico)

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Christian Grenz[a,*], Montserrat Origel Moreno[a], Karline Soetaert[b], Lionel Denis[c], Pascal Douillet[a], Renaud Fichez[a]

[a] *Aix-Marseille Université, Université Toulon, CNRS/INSU, IRD, Mediterranean Institute of Oceanography MIO UM 110, Marseille, France*
[b] *Royal Netherlands Institute of Sea Research (NIOZ-Yerseke), and Utrecht University, the Netherlands*
[c] *Université Lille 1: Sciences et Technologies, UMR CNRS 8187 LOG, Wimereux, France*

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ABSTRACT

The sediment in Laguna de Términos, the largest and shallowest system in the Southwest portion of the Gulf of Mexico features a broad range of ecological and hydrobiological characteristics driven by annual weather cycles (dry and wet seasons), causing large salinity gradients during the wet season due to large river discharges. Four sampling campaigns were carried out during the wet and the dry seasons in 2009 and 2010 on a selection of 13 out of 35 stations. Measurements of Sediment Oxygen Demand (SOD) and nutrient fluxes at the sediment-water interface were performed using lab incubations with 15 cm diameter sediment cores. SOD fluctuated between 1327 ± 161 and $2248 \pm 359 \, \mu mol \, m^{-2} \, h^{-1}$ for dry and wet seasons respectively. Silicate effluxes were also significantly higher during the wet seasons ($89.4 \pm 15.9 \, \mu mol \, m^{-2} \, h^{-1}$) than during the dry season ($46.5 \pm 11.4 \, \mu mol \, m^{-2} \, h^{-1}$). PO_4 fluxes were low all over the study period without seasonal trend. No significant difference was measured for DIN fluxes but there was a tendency for DIN uptake during the wet season ($-2.9 \pm 18.8 \, \mu mol \, m^{-2} \, h^{-1}$) and conversely an efflux during the dry season ($24.3 \pm 7.3 \, \mu mol \, m^{-2} \, h^{-1}$). SOD correlated to organic matter and chloropigment content of the sediments while silicate fluxes responded to enhanced chloropigments in the sediments. During both seasons, total benthic nutrient fluxes overwhelmed largely riverine inputs and benthic carbon mineralization rates approximated a significant proportion of the pelagic organic carbon production. We conclude that benthic processes in Laguna de Términos are largely driven by weather variability and that they contribute substantially to carbon and nutrient budgets in this shallow subtropical system.

1. Introduction

Due to human activities, large concentrations of contaminants and nutrients have accumulated in sediments of natural water bodies, changing environmental conditions (Li and Cai, 2015; Birch, 2017). The processes that govern the fate of these substances in the sediment result from the complex interactions with the biogeochemical cycles of major redox and biogenic elements such as C, N, O, P and Si (Middelburg and Soetaert, 2004). In shallow systems, the pelagic biogeochemical cycles are strongly linked to the sediment compartments where organic matter mineralization preferentially occurs, resulting in enhanced nutrient fluxes and oxygen uptake rates at the water-sediment interface (Archer and Devol, 1992; Cowan and Boynton, 1996; Grenz et al., 2003). Denitrification, the dissimilatory reduction of NO_3^- to produce nitrous oxide (N_2O) and dinitrogen (N_2), depends on anoxic conditions (Rivera-

Monroy et al., 1995) and occurs nearly exclusively in sediments. The transformation of biologically available forms of N into inert gas, together with different external sources such as river inputs, surface runoff and atmospheric precipitation, controls the variation of pelagic nutrient concentrations over inter-annual time scales (Soetaert and Middelburg, 2009). On shorter time scales, the soluble nitrogenous compounds released from the sediments during the decomposition of organic matter can supply 30–100% of dissolved N utilized by phytoplankton in overlying water (Grenz et al., 2010).

The sediment oxygen demand (SOD) is a component of the dissolved oxygen balance of natural water bodies such as rivers, lakes or coastal zones. SOD is the oxygen transfer from the water column into the sediment and results from microbial and chemical consumption inside the sediment, including oxidation of organic matter and inorganic and metal species produced via suboxic and anoxic organic carbon

degradation (Rasmussen and Jorgensen, 1992; Cai and Sayles, 1996; Bolałek and Graca, 1996). As oxygen in sediments is utilized both directly for organic matter respiration (aerobic mineralization) and for reoxidation of reduced substances formed by anoxic mineralization, SOD is a good measure for total system mineralization.

Laguna de Términos is a shallow estuarine system on the South coast of the Gulf of Mexico, influenced by different physical forcing including wind, tides and river inputs, as well as heavy nutrient discharges, high turbidity and turbulence levels. This lagoon has been selected as a pilot site of the Global Environment Facility (GEF) Gulf of Mexico Large Marine Ecosystem Program (GoM-LME). Dissolved and particulate exchanges between sediments and the water column have been poorly documented in this system. Studies of sediment-water exchanges in Laguna de Términos have exclusively been conducted in mangrove forests (Rivera-Monroy et al., 1995; Day et al., 1996) or *Thalassia testudinum* seagrass beds (Yáñez-Arancibia and Day, 2004).

It is expected that sediment metabolism in temperate and tropical systems strongly differ. Tropical areas often are constrained by large fluctuations in precipitations which gives rise to pronounced wet and dry seasons. Furthermore, in contrast to high latitudes, seasonal changes due to temperature and light are less pronounced in the tropical zone. As those oligotrophic systems are under increased anthropogenic influence (Grenz et al., 2003), information about their metabolic state is strongly needed. In this paper, we describe exchange rates measured at the sediment-water interface in a tropical lagoon, to assess the importance of sediments in total system metabolism and to investigate how much of the variability can be ascribed to the alternations of rainy and dry seasons.

2. Materials and methods

2.1. Study site

Laguna de Términos is located at 18˚38'36"N and 91˚49'51"W, in the state of Campeche, Gulf of Mexico (Fig. 1). It is a large shallow lagoon stretching over a surface of 1936 km² with an average depth of only 2.4 m, corresponding to a total water volume of 4.65 km³ (Contreras Ruiz Esparza et al., 2014). When including adjacent marshes and fluvial-lagoon systems, the surface extends to approximately 2500 km² and together with the surrounding wetlands it forms the largest RAMSAR site (International treaty for the conservation and sustainable use of wetlands) in Mexico stretching over a total area of 7050 km² (Mitsch and Hernandez, 2013). The regional weather is humid tropical with annual precipitation ranging from 1650 to 1850 mm y^{-1}. There are two different seasons, the dry season from March through May followed but the rainy season extending from June to February, a period marked by intermittent storms (Yáñez-Arancibia and Day, 2004; Bach et al., 2005).

Laguna de Terminos is characterized by a microtidal regime (range of 0.3 m, David and Kjerfve, 1998). The lagoon receives large volumes of seasonally-varying flows of freshwater from a 49,700 km² watershed that drains portions of the Yucatan Peninsula, the lowlands of Tabasco, and the highlands of Chiapas and Guatemala. Laguna de Términos is part of the larger Usumacinta/Grijalva delta system, second in size to the Mississippi delta in the Gulf of Mexico region, and yielding similar suites of anthropogenic impacts and resource management challenges (Bach et al., 2005). The Usumacinta River flooding from Guatemala to Mexico is the largest river in Mesoamerica and one of the most significant shared water resources in the Western Hemisphere (Yañez-Arancibia and Day, 2005).

A selection of 13 stations (Table 1) was sampled for the determination of oxygen and nutrient fluxes at the sediment-water interface during the dry and rainy seasons (March 2009–2010 and October 2009–November 2010, respectively). These stations represented a sub-sample from the 35-station network visited in the frame of the multidisciplinary JEST (Joint Environmental Study of Laguna de Términos)

project, during a 2-year hydrological survey (Fig. 1, Fichez et al., 2017) and the related modelling study of hydrodynamic processes (Contreras Ruiz Esparza et al., 2014).

2.2. Core sampling procedure and benthic incubations

Due to shallowness, sediment samples were taken with a custom-built sediment core sampler equipped with 15 cm (internal diameter) x 45 cm long acrylic core liners. An anti-return valve located at the head of the corer allowed to pull the core out of the sediment bed with very limited perturbation. A 5 m long metal pipe used to sink the corer in the sediment and pull it out from the boat side, permitted to sample even the deepest stations in the middle of the lagoon. At each station, four cores were retrieved and bottom water was sampled (ca 20 l) from a Niskin bottle. Water samples were transferred in an inflatable reserve tank excluding bubbles, and were used both as bottom water control and as replacement water during the core incubations. While water samples were preconditioned on board, a CTD profile was recorded by means of a SEABIRD 19 + equipped with a fluorimeter.

Cores and reserve tanks were transported to the lab in a black container within a couple of hours after core collection. Upon return to the laboratory, cores and reserve tank were placed in a temperature controlled bath which was maintained near in situ temperatures (between 24.9 and 30.3 °C) and incubated in the dark. The reserve tank was gently stirred during the incubation period using a platform shaker. The cores were sealed with tops equipped with magnetic stirrers and gas-tight sampling ports. The sediment inside the core tube were around 25 cm height, leaving about 20 cm or a total overlying water volume of 3.5 l. Water sub-samples (120 ml) were withdrawn with a syringe through sampling port at each time, and then filtered through pre-rinsed (two times) GFF filters for nutrient analysis. Samples for the fluorometric determination of ammonia (Kérouel and Aminot, 1997) were transferred in pre-rinsed 50 ml Pyrex bottles and analyzed after recommended reaction time. Other nutrient samples were distributed in pre-rinsed acid washed polyethylene bottles (2 * 20 ml) and deep frozen for later analysis in the laboratory by a Technicon Auto-Analyser II according to Tréguer and Le Corre (1975). Blanks of filtered ultra-clean water performed for silicate analysis were always low and close to detection limits. Based on results from Kremling and Wenk (1986) and Macdonald et al. (1986), we assumed that freezing the samples did not change the silicate concentrations. The oxygen concentrations were measured continuously by microelectrodes Clark-type sensor (Unisense Microsensor Multimeter) within each core. The sensors were calibrated by Winkler titration.

As detailed in Grenz et al. (2003), nutrient flux rates were measured by monitoring the changes in concentration of overlying water at 2 h time intervals over a period of 8 h whereas oxygen fluxes were calculated over the 8 h record at 1 min time intervals. Oxygen content never fell below 55% of the initial O_2 concentrations at the end of the incubation and remained oxic (minimum O_2 content of 110 μM), a value far above the hypoxia level. Rates of concentration changes against time were calculated using linear regression (SigmaPlot 12.0 - Systat Sofware Inc). We consider the regression as significant ($p < 0.05$) when $R > 0.8054$ for a degree of freedom of 3 ($=5$-2) for nutrient fluxes and $R > 0.2301$ for oxygen fluxes (degree of freedom > 100). Outliers due to contaminations (> 500% deviation from regression line) or not significant regressions were discarded.

Sediment-water fluxes were calculated by multiplying the rates of concentration change with the water height in each core tube. In spite of the low sampling volume with respect to overlying water volume, the correction for water replacement (with bottom water from the reserve tank) was systematically applied (Denis and Grenz, 2003).

2.3. Sediment analysis

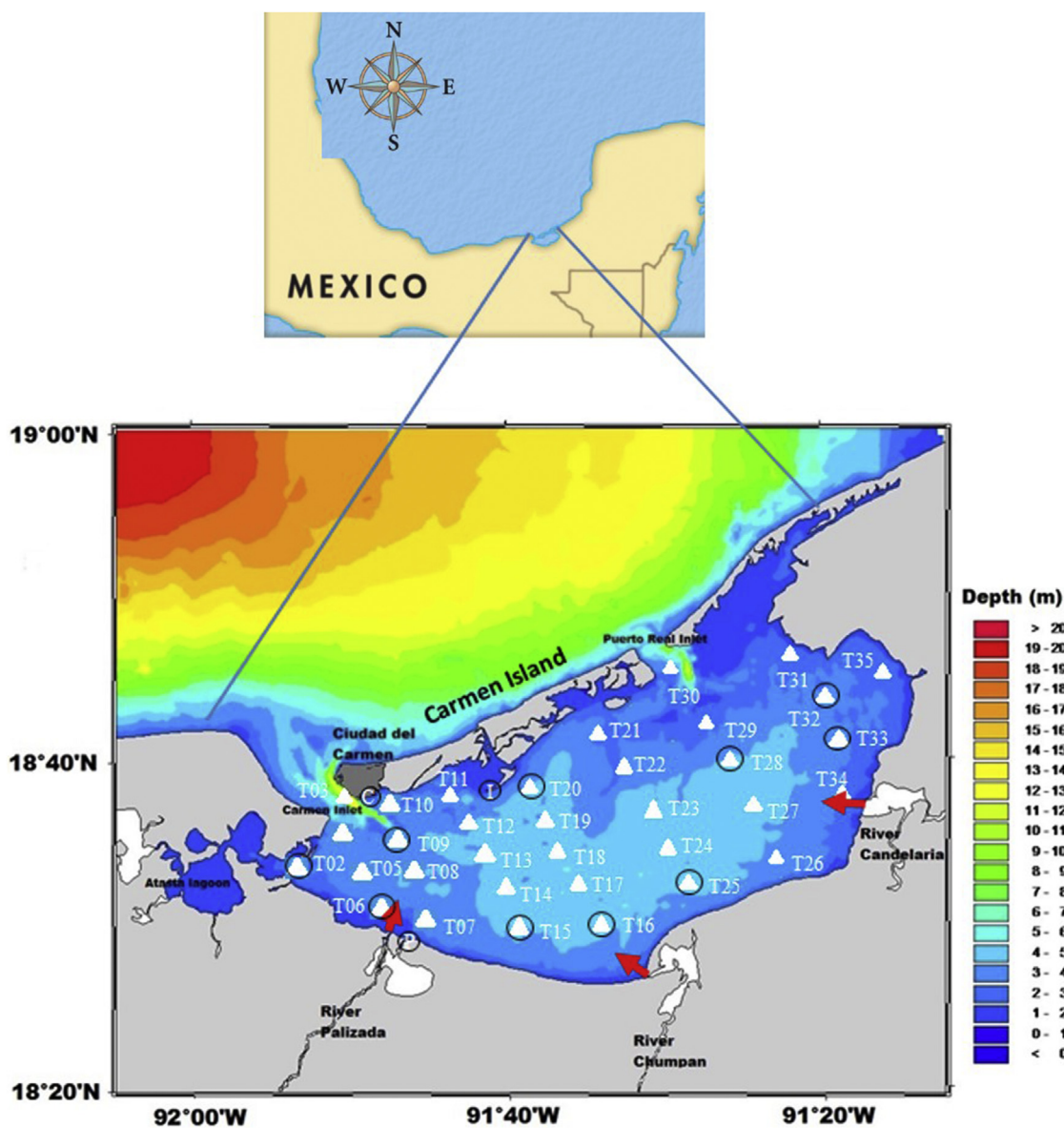At the end of the benthic flux rate experiments, the cores were

Fig. 1. Depth distribution in Laguna de Términos and location of the sampling stations visited during four field trips in 2009 and 2010. Triangles correspond to water column samplings, circles to sediment corings and red arrows to main river outflows. The main town (Ciudad del Carmen) is located at the western tip of Carmen Island (dark grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Location of the sampling sites in latitude and longitude and their sediment characteristics according to Yáñez-Arancibia (in Bach et al., 2005).

Station	North	West	Depth (m)	Sediment type
C	18°38′26.90	91°47′51.76	1.1	Coarse sand
I	18°38′09.88	91°41′52.03	1.2	Coarse sand
P	18°29′34.99	91°47′24.37	1.1	Muddy clay
2	18°33′42.00	91°53′15.00	2.7	Muddy clay
6	18°33′20.00	91°49′40.00	2.4	Muddy clay
9	18°35′28.00	91°47′15.00	2.4	Muddy clay
15	18°29′30.00	91°40′17.00	4.3	Muddy clay
16	18°29′23.00	91°33′30.00	4.3	Coarse sand
20	18°38′52.00	91°38′56.00	4.9	Muddy clay
25	18°32′03.00	91°28′39.00	4.5	Coarse sand
28	18°40′13.00	91°26′34.00	3.8	Muddy clay
32	18°43′30.00	91°21′30.00	2.6	Clay
33	18°40′00.00	91°19′34.00	3.3	Clay

subsampled in 10 successive 0.4 cm thick slices (2.6 cm diameter) down to 4 cm depth. A first set was wet and dry weighted to determine porosity calculated from water content and assuming a bulk density of 2.65 g cm^{-3} (Berner, 1980). The remainder was used for determination of particulate organic carbon and nitrogen using a Carlo Erba elemental analyser coupled to a Sercon Integra CN mass spectrometer for stable isotope ratio measurements (according to Kristensen and Andersen, 1987). A second set of sub-samples was used for chloropigments, extracted with 10 ml of acetone, centrifuged at 3000 rpm for 10 min and analyzed on a Shimadzu UV-1700 Pharmaspec spectrophotometer before and after addition of two drops of 1.2 M HCl (Strickland and Parsons, 1972; Plante-Cuny et al., 1993).

2.4. Data analyses

The environmental factors and sediment water fluxes were analyzed using two-way factorial analyses of variance (ANOVA) to test for differences as a function of sampling site and seasons (SigmaPlot 12.0, Systat Software Inc.). Pearson product moment correlation matrix was
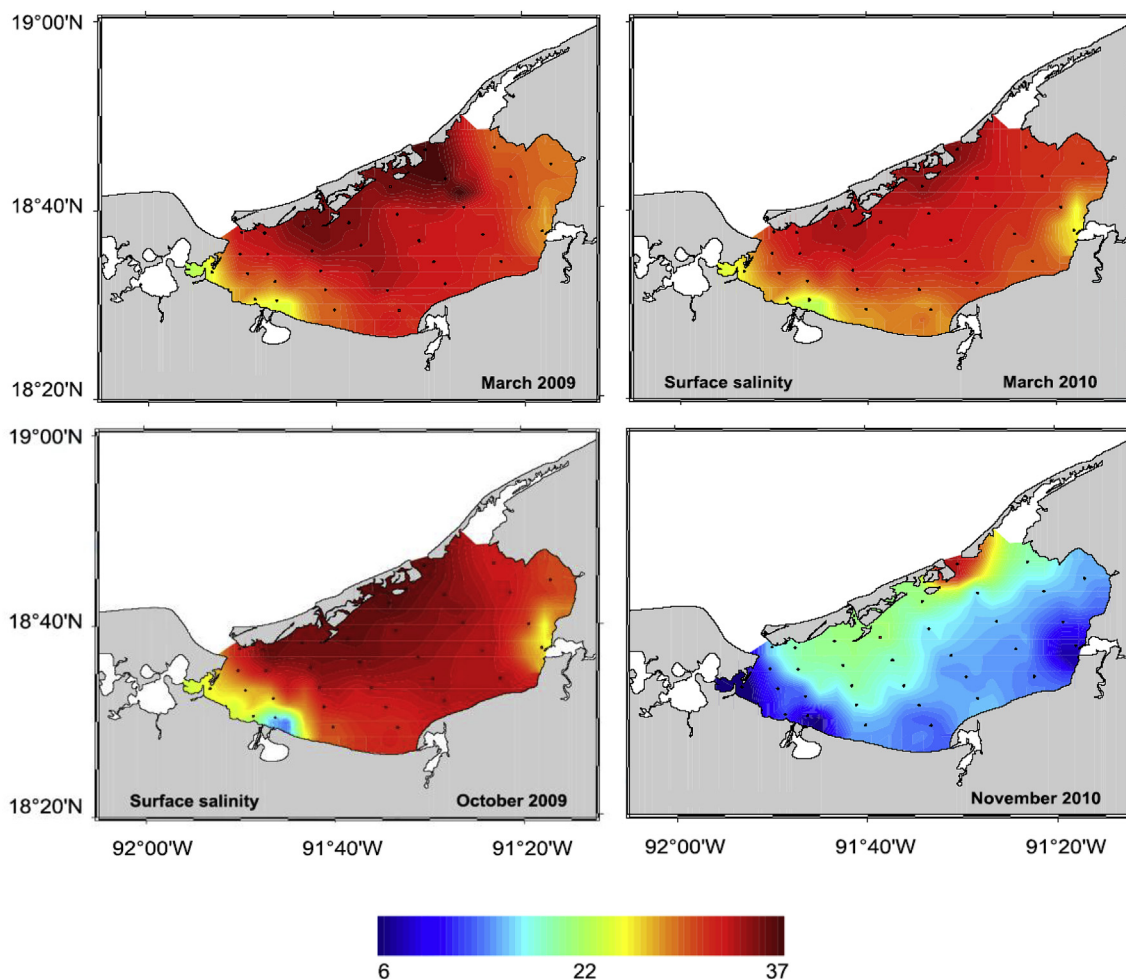
Fig. 2. Spatial distribution of salinity during dry (March) and wet (October–November) seasons of years 2009 and 2010.
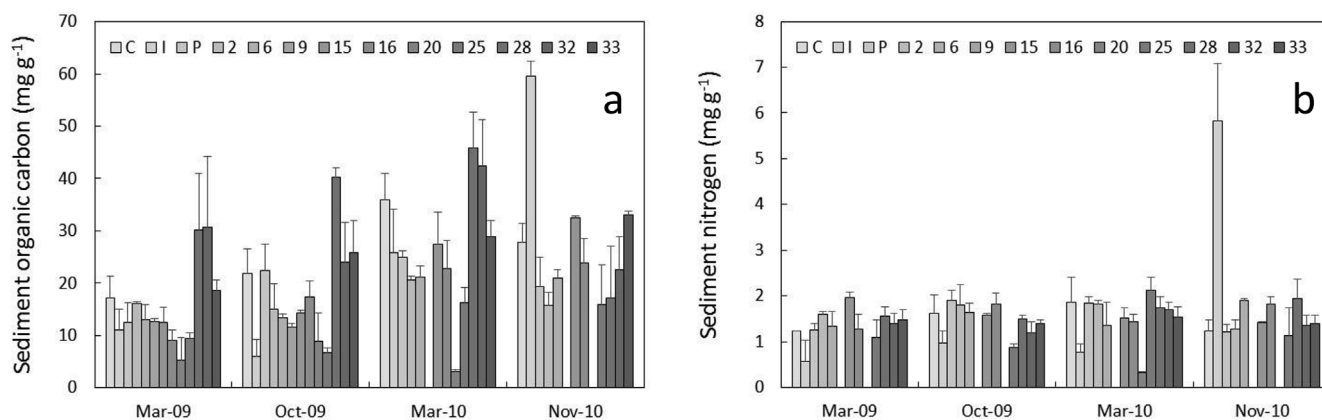

Fig. 3. Sediment organic matter content for the 13 stations sampled during the dry (March) and wet (October–November) seasons of years 2009 and 2010 (a: Organic carbon, b: Nitrogen, bars indicate sd for triplicates).

performed to determine relationships between variables. A significance level of $p < 0.05$ was used unless otherwise indicated. Kruskal-Wallis and Mann-Whitney Rank Sum tests for unpaired t-Tests, were carried out each time normality assumption of the variables with homogeneous variance was not satisfied (Shapiro-Wilk test).

3. Results

3.1. Water and sediment characteristics

Due to freshwater inputs mainly originating from the Palizada River located in the south west part of Laguna de Términos, a spatial gradient in salinity ranging from 6 to 37 in surface waters was measured during the dry (March) and wet (October and November) seasons (Fig. 2). Lowest mean salinities calculated over the whole lagoon were measured

during the wet season (less than 22). Inversely during the dry season, mean salinities were higher (around 30) and the lowest salinities were found only near the River mouths (March). A salinity distribution close to the one observed during the dry season was observed in October 2009, a period of strong positive salinity anomaly related to an El Niño Modoki driven drought episode (Fichez et al., 2017). Surface water temperatures were less variable, ranging from 25.5 to 30 °C (mean 27.7 °C). Sediment porosity varied from 0.5 to 0.8 according to stations.

Deepest stations and sites close to river mouths were characterized by muddy sediments whereas shallow stations along Isla del Carmen were characterized by coarse sands with high calcium carbonate contents (> 50%, Magallanes-Ordóñez et al., 2015). Sediment Organic carbon and Nitrogen fluctuated around a mean value of 21.0 and 1.5 mg g^{-1} for respectively but with a high spatial and temporal variability (Fig. 3a and b). Molar ratio of C versus N varied between 5 and 35, even as high as 55 at station I in March 2010. The mean value of C:N was 25.7 but with a high degree of variability (sd > 50% for n = 49).

The distribution of carbon and nitrogen stable isotopes opposed station I (−5 to −13‰ δ ^{13}C and 2.2 and 3.7‰ δ ^{15}N) on one side to station P (−23 to −29‰ δ ^{13}C and 3.8–5.3‰ δ ^{15}N) respectively corresponding to seagrass and terrestrial end members (Fig. 4). Values between −20 and −30‰ δ^{13}C and 3.5–6.5‰ δ^{15}N mostly characterized a group of western stations, namely stations P and 2 at all times, station 6 at all times except for March 2010, station 15 in March and October 2009 and station 16 in March 2009. Most other samplings were distributed within the −5 to −20‰ range for δ^{13}C and within a larger range of 1.5–7.5‰ for δ^{15}N, station C generally showing δ^{15}N values in the highest range. Station 25 strongly departed from all other groups in October 2009 and March 2010 with values close to −23‰ δ^{13}C and 1.5‰ δ^{15}N. No clear seasonal trend could be established as most differences between sampling times were too close to analytical errors.

Figs. 5 and 6 shows the spatial distribution of sediments profiles during March and October 2009, and November 2010. Unfortunately, samples from March 2010 were defrosted inadvertently and the whole series had to be discarded. The interannual variation of pigment concentrations in the first 4 cm was huge with lowest concentrations in pigments in March 2009. Taking all levels and stations together, the mean concentrations in March 2009 was 0.7 ± 0.1 and 19.8 ± 1.7 µg g^{-1} for Chl a and Phaeopigments, respectively. In October 2009 the pigments contents were higher (2.3 ± 0.6 and 30.4 ± 2.1 µg g^{-1} for Chl a and Phaeopigments) and increased in November up to 9.3 ± 4.0 µg g^{-1} for Chl a and 35.1 ± 7.7 µg g^{-1} for

Phaeopigments. This is especially true for stations I where highest values (178.3 µg g^{-1} Chl a and 211.8 µg g^{-1} for Phaeopigments) were measured in the first layer. The vertical distribution of pigments in the sediments were also highly variable, showing in some cases an exponentially decrease with depth like in station I in November (2010) and in other cases a subsurface (1.6–2 cm depth) chlorophyll peak as in stations I and 2 in October 2009.

The ratio of Chl a contents over the sum of pigments (Chl a + Phaeo) given Fig. 7, fluctuated similarly with highest values during the wet season in November 2010 (0.19 ± 0.03). During the dry season in March 2009, sediment Chl a represented less than 4% of the total pigments (0.04 ± 0.01) and October 2009 was in between (0.06 ± 0.01). Like for Chl a concentrations, the depth distribution is variable with exponential decreases in November (Stations C, P, 25), and sub-surface picks at stations I and 2 in October 2009 and stations 6, 15, 16, 32 and 33 in November 2010.

The results of the ANOVA tests showed that salinity and sediment organic carbon were the environmental factors that differed significantly among sampling sites and seasons (Table 2). In contrast, porosity, bottom water NH$_4$ and NO$_3$ significantly differed among sampling sites only, whereas temperature, sediment Chl a and bottom water Si(OH)$_4$ significantly differed among seasons. Finally, sediment nitrogen and related C/N, bottom water O$_2$ and PO$_4$ were not significantly different in space nor time (p > 0.05).

3.2. Sediment oxygen demand and nutrient fluxes

Sediment Oxygen Demand (SOD) showed high variation (Fig. 8) with minimum respiration rates measured at most stations in March 2009 (mean SOD 840 µmol m-2 h-1, sd 440, n = 51, all replicates and stations combined). Conversely, highest fluxes were recorded in October 2009 during the wet season (mean 2750 µmol m^{-2} h^{-1}, sd 1720, n = 52), whereas measurements in March 2010 and November 2010 showed intermediate SOD. The Kruskal-Wallis test confirmed a significant difference among sampling seasons but not sites (H$_{3.48}$ = 12.81, p = 0.005). The maximum SOD were measured at station I in October 2009 (7400 µmol m^{-2} h^{-1}, sd 1600, n = 4) and November 2010 (6400 µmol m^{-2} h^{-1}, sd 840, n = 3). These values were 4 times (and significantly) higher than the mean SOD measured over the whole period (1700 ± 395 µmol m^{-2} h^{-1} sd 1375, n = 49). The results of the Kruskal-Wallis ANOVA test for NO$_3$ and Si(OH)$_4$ fluxes showed significant differences among seasons only (Table 2). This was due to nitrate fluxes in October 2009 (−5.0 ± 5.5 µmol m^{-2} h^{-1}) which were significantly lower (t = 6.072, df 175, p < 0.001) and directed into the sediment, compared to the other periods when nitrate mainly flushed out the sediment (8.6 ± 2.6 µmol m^{-2} h^{-1}). Similarly, for Si(OH)$_4$, the March 2009 efflux (19.5 ± 3.5 µmol m^{-2} h^{-1}) were significantly different (Mann-Whitney U = 34.00, p < 0.001) compared to the other periods (86.0 ± 12.9 µmol m^{-2} h^{-1}). According to Kruskal-Wallis tests, ammonium and phosphate fluxes did not show significant differences in space or time (Table 2) mainly due to the large variability encountered.

The correlation matrix in Table 3 shows the relationships between the 17 main variables measured. No correlation was found between temperature and the 16 remaining variables. River inputs accounting for 95% of freshwater inputs to Laguna de Términos (Fichez et al., 2017), each significant correlation with salinity could be used as an indicator of river influence. Salinity was negatively correlated with porosity and bottom water nitrate and Si(OH)$_4$ and positively correlated with the C:N ratio of the organic matter.

Beside salinity, positive correlation between environmental descriptors of the sediments was evidenced as for porosity, organic carbon, nitrogen and chloropigments. Considering nutrients in the water column, NH$_4$ correlated with NO$_3$, and NO$_3$ with Si(OH)$_4$. Significant negative correlations were revealed between organic carbon and PO$_4$, and between NH$_4$ and O$_2$. Considering fluxes, SOD correlated
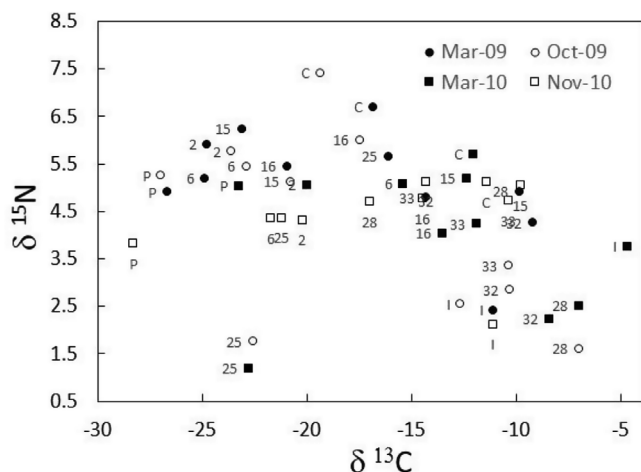

Fig. 4. Plot of stable isotopes in surface sediments (0–0.4 cm layer) of the 13 stations sampled during the dry (March) and wet (October–November) seasons of years 2009 and 2010 (Wet season in hollow symbols, dry season in plain symbols). Station positions can be found in Table 1.
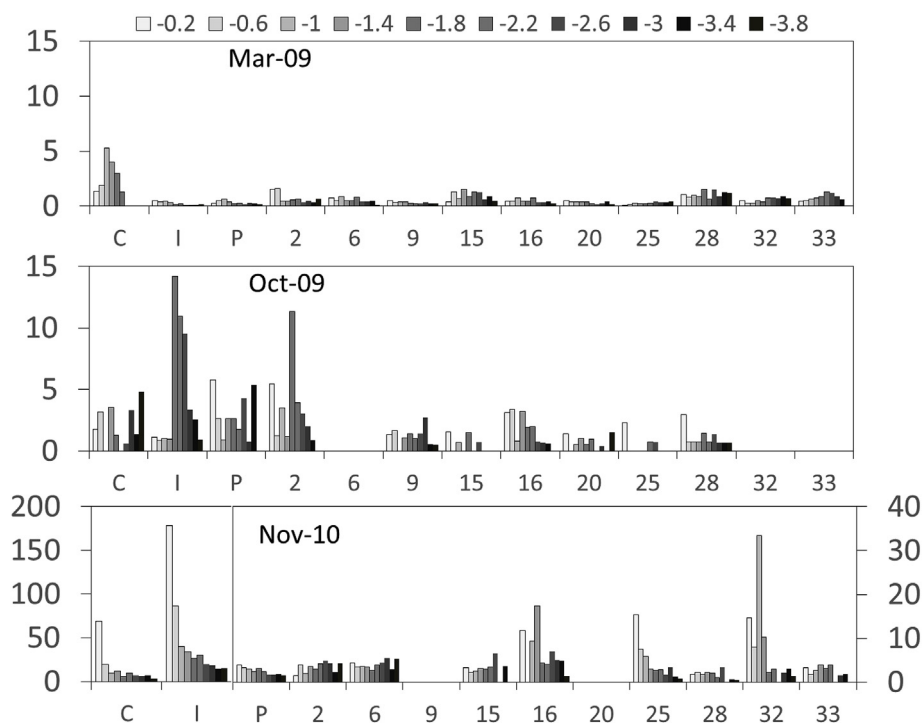
Fig. 5. Spatial distribution of sediment chlorophyll profiles during dry (March 2009) and wet (October 2009–November 2010) seasons (each layer is 0.4 cm thick, data in μg g^{-1} dry weight). Station positions can be found in Table 1.

positively with sediment descriptors (N, chloropigments) but also with PO$_4$ in the water column and silicate flux.

DIN fluxes representing the addition of NH$_4$ and NO$_3$ fluxes, obviously these fluxes were positively correlated. NO$_3$ flux correlated negatively with water column NH$_4$ and NO$_3$ and positively with NH$_4$

fluxes. PO$_4$ flux was only correlated positively to NO$_3$. Finally Si(OH)$_4$ flux was not correlated to the any other flux unless to SOD and Si(OH)$_4$ in the water column.
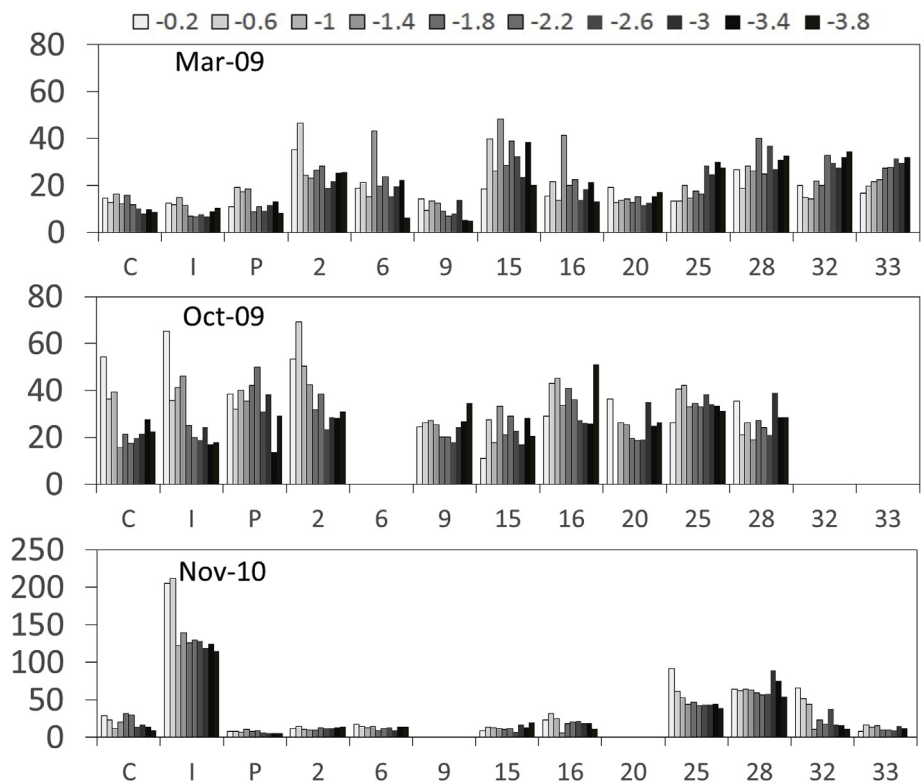

Fig. 6. Spatial distribution of sediment phaeopigments profiles during dry (March 2009) and wet (October 2009–November 2010) seasons (each layer is 0.4 cm thick, data in μg g^{-1}dry weight). Station positions can be found in Table 1.
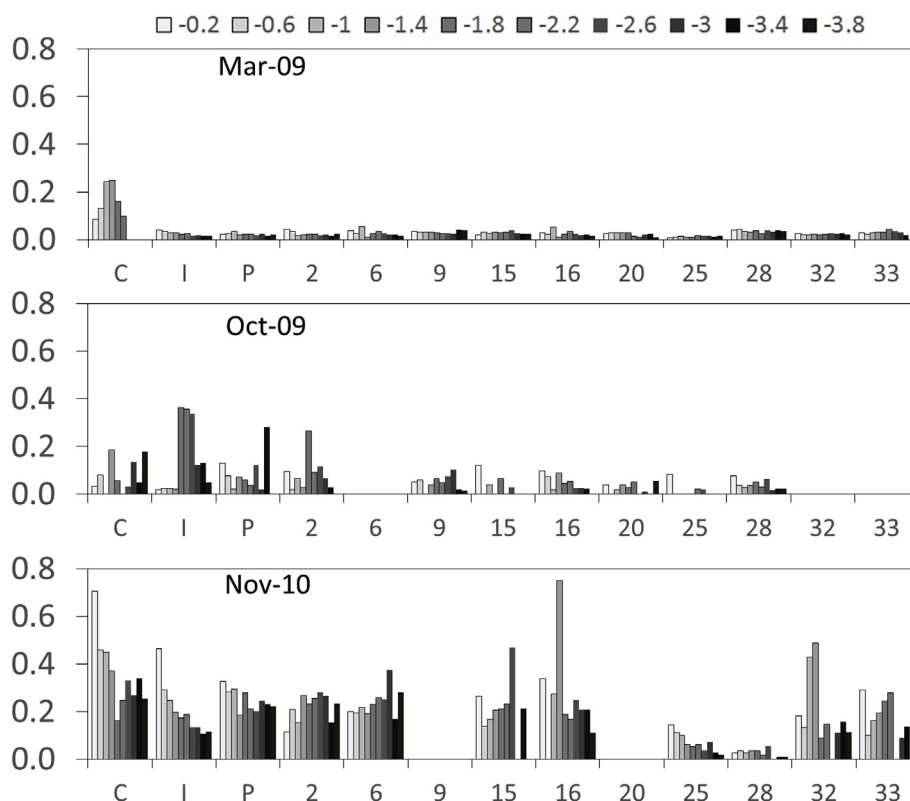
Fig. 7. Spatial distribution of profiles of the Chl a/Chl a + Phaeo ratio during dry (March 2009) and wet (October 2009–November 2010) seasons (each layer is 0.4 cm thick). Station positions can be found in Table 1.

Table 2

Two-way ANOVAs (F) and Kruskal-Wallis (H) tests to examine the differences in environmental conditions and benthic fluxes as a function of sampling site and season (*p < 0.05).

	Season	p	Site	p
Environmental conditions				
Salinity	$H_{3,48} = 16.73*$	< 0.001	$H_{12,48} = 25.25*$	0.014
Temperature (°C)	$F_{3,48} = 5.12*$	0.005	$F_{12,48} = 1.08$	0.405
Porosity	$F_{3,48} = 0.21$	0.886	$F_{12,48} = 4.26*$	< 0.001
Sediment				
organic Carbon (μg g^{-1})	$H_{3,48} = 12.23*$	0.007	$H_{12,48} = 25.44*$	0.013
Nitrogen (μg g^{-1})	$H_{3,48} = 7.32$	0.062	$H_{12,48} = 16.01$	0.191
C/N (molar)	$H_{3,48} = 5.10$	0.165	$H_{12,48} = 19.71$	0.073
Chlorophyll (μg g^{-1})	$H_{2,31} = 19.84*$	< 0.001	$H_{12,31} = 7.78$	0.802
BW-O$_2$	$F_{3,48} = 0.56$	0.648	$F_{12,48} = 1.00$	0.469
BW-NH$_4$	$H_{3,48} = 1.56$	0.669	$H_{12,48} = 28.95*$	0.004
BW-NO$_3$	$H_{3,48} = 3.80$	0.284	$H_{12,48} = 25.75*$	0.012
BW-PO$_4$	$H_{3,48} = 3.01$	0.391	$H_{12,48} = 13.65$	0.324
BW-Si(OH)$_4$	$H_{3,48} = 19.22*$	< 0.001	$H_{12,48} = 10.51$	0.572
Sediment water fluxes (μmol m^{-2} h^{-1})				
O$_2$	$H_{3,48} = 12.81*$	0.005	$H_{12,48} = 14.77$	0.254
NH$_4$	$H_{3,48} = 1.98$	0.576	$H_{12,48} = 20.78$	0.054
NO$_3$	$H_{3,48} = 8.15*$	0.043	$H_{12,48} = 11.43$	0.492
PO$_4$	$H_{3,48} = 6.60$	0.086	$H_{12,48} = 14.33$	0.280
Si(OH)$_4$	$H_{3,48} = 21.83*$	< 0.001	$H_{12,48} = 3.63$	0.989

Bottom water concentrations (BW) in μmol l^{-1}.

4. Discussion

Even if Laguna de Términos is the most thoroughly studied lagoon in Mexico, to our knowledge, no published data are available regarding nutrient fluxes or SOD measurements at the sediment-water interface. Compared to other (sub) tropical and more temperate aquatic systems, our SOD values fall in the upper range of available measurements (Table 4). Compared to our measurements, similar SOD values in temperate systems were only reported for specific sediments containing large amounts of organic matter like in catfish aquaculture ponds (Berthelson et al., 1996), in Danish and Cypriote fish farms (Heilskov et al., 2006) and underneath shellfish cultures in Ria de Vigo (Forja et al., 2004) and Thau Lagoon (Thouzeau et al., 2007).

Temperature combined with organic matter influx to the sediments control benthic mineralization logically driving coastal tropical lagoons in the upper range of SOD values, as demonstrated by the maximum values reported from shallow rivers in Hong Kong and Malaysia (Chen et al., 2000; Ling et al., 2009), and from coastal lagoons near Cancun (Valdes-Lozano et al., 2006). SOD reflects oxic microbial respiration and re-oxidation of reduced compounds (Hammond et al., 1985; Kaspar et al., 1985; Hopkinson, 1987), but physically and biologically mediated disturbances including the impact of macro- and meiofauna also affect the exchange rates between sediment and water column (Aller, 1980; Andersen and Kristensen, 1988; Kristensen et al., 1992). Quality and quantity of sediment organic matter also control nutrient fluxes and benthic respiration rates (Jahnke et al., 2005, Burdige, 2006; Alongi et al., 2011; Pastor et al., 2011).

The main picture that emerges from our data set from Laguna de Términos is the large spatial and temporal heterogeneity of sediment-water fluxes. SOD in Laguna de Términos is highly variable in space and time with a minimum of 305 ± 180 μmol m^{-2} h^{-1} at station 2 in March 2009, and a maximum of 7400 ± 1590 μmol m^{-2} h^{-1} at station I in October 2009. Like all large estuarine ecosystems, the lagoon hosts highly diverse habitats such as mangrove swamps, seagrass beds, muddy or sandy sediments. Moreover the area is characterized by a tropical wet-dry climate with high freshwater outflows in summer. The inputs from Palizada River (9.08 10^9 m^3 y^{-1}) play an important role as this inflow represents between 75% and 80% of the fresh water inputs within Términos (Smith et al., 1999; Fichez et al., 2017), producing
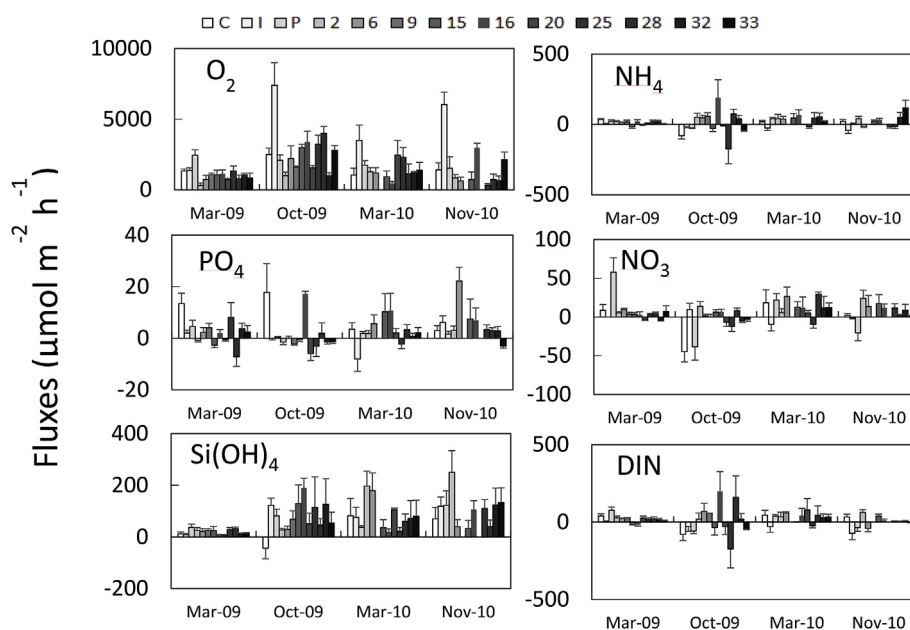
Fig. 8. Seasonal variation of SOD and nutrient fluxes during the dry (March 2009) and wet (October 2009 and November 2010) seasons.

turbid, nutrient-rich and low-salinity waters (Bach et al., 2005). On the seaside, both inlets exchange seawater from the Campeche shelf acting as a buffer maintaining high salinities and water transparency. David and Kjerfve (1998) showed that the lagoon behaves as a single hydrological unit with a net east-to-west flow-through, especially during the rainy season. The consequence is a South West to North East gradient in most of the hydro-biological variables.

As the rates of biogeochemical processes are likely to be limited by either the availability of organic matter or of terminal electron acceptors (Jorgensen, 2000), microbial active zones are often limited to the top layer of sediments. We observed that organic matter distribution in the 4 cm top layer of sediment is variable in both time and space (Two-way ANOVA), sediments containing 0.5–3% of organic carbon and 0.1–0.2% of nitrogen with C:N molar ratios above 10, indicating preferential degradation of the nitrogen-rich component. The $\delta^{13}C_{org}$ values confirm a terrestrially dominated origin of carbon in the sediments from the western part (from −27 to −20‰) shifting to a more marine influence (from −20 to −7‰) toward the north-eastern part of the lagoon. This distinction of two end-members related to a mixing trend between terrestrial and marine/seagrass sources of OM has already been shown for estuarine systems (Thornton and McManus, 1994; Ogrinc et al., 2003). The least negative values of $\delta^{13}C$ were correlated with lowest nitrogen stable isotopes in the north eastern stations including station I on the lagoon side of the barrier island Isla de Carmen. For instance Pereira et al. (2010) found similar ranges in sediments from Mãe-Bá Lagoon in Brasil. Possible explanations include the presence of seagrass detritus mixture in the bulk sediments. Marguillier et al. (1997) showed a mean range of −10.02 to −19.8‰ for $\delta^{13}C$ and +1.11 and 1.51‰ for $\delta^{15}N$ seagrass leaves in a tidal creek in Kenya. The very unique values in $\delta^{13}C$ and $\delta^{15}N$ recorded at station 25 in October 2009 and March 2010 could be linked to the stable isotope signatures of some mangrove tree species such as *Rhizophora mangle*, *Avicenia germinans* and *Laguncularia racemosa* (Kuramoto and Minagawa, 2001; Fogel et al., 2008). These species have been reported as the main mangrove tree species in the area (Day et al., 1987) but the short temporality of those two occurrences is not consistent with the permanence of fringing mangrove forest. Of much more relevance is the stable isotope signature from microbial mat reported from the mangrove system of Twin Cays in Belize (Fogel et al., 2008) that if it varied in a wide range (−13 to 25‰) for $\delta^{13}C$ was much more definite (3 to −4‰) for $\delta^{15}N$. Therefore, the values of circa −23‰ $\delta^{13}C$ and 1.5‰

$\delta^{15}N$ observed at station 25 in October 2009 and March 2010 reasonably support the hypothesis of a microbial mat temporarily forming under sustained conditions of low river inputs consecutive to the 2009 drought period (Fig. 9) and disappearing on the return of estuarine conditions in November 2010.

The small scale variability in the pigment profiles we observed between 0 and 3.6 cm was probably the consequence of bioturbation processes (transfer to deeper sediment layers), freshly deposited detritus containing high quantities of pigments (exponential decrease), blooms of microphytobenthic algae and/or resuspension processes which redistribute the organic matter. Nevertheless mean chlorophyll pigments in sediments showed a seasonal trend (Kruskal-Wallis H = 19.84, p < 0.001) mostly because of the high values measured in the sub-surface layers during the rainy season, especially in November 2010 (t = 3.004, df = 189, p < 0.003). The contribution of Chlorophyll *a* to total pigments fluctuated between 3 and 20% showing that degraded pigments dominated. Pigment content was significantly higher in October 2009 than in March 2009 (t = 6.170, df = 207, p < 0.001) but lower than in November 2010. The rain deficit in 2009 most certainly accounted for such a discrepancy. Sediments support productive microalgal communities (Sundbäck et al., 2000; McGlathery et al., 2001) in shallow and transparent waters like in the Northern and Eastern part of Laguna de Términos. SOD were positively correlated to organic matter and chloropigments in the sediments (N and Sed Chla, p < 0.05 in Table 3) as already shown in temperate and tropical systems (Lansard et al., 2008; Grenz et al., 2000, 2003, 2010). The highest SOD were observed at station I which is dominated by sediments composed of 50–75% calcium carbonate (Magallanes-Ordóñez et al., 2015). These rates are comparable to the one measured by Alongi (1996) in a sheltered lagoon containing mixed terrigenous-carbonate sediments where sulfate reduction accounted for a significant fraction of total organic carbon oxidation. We did not measure specifically sulfate reduction but the rotten-egg smell together with the appearance of a reddish layer on the sediment surface at station I could be due to the production of sulfide derived from the decomposition of seagrass material and organic matter trapped in the seagrass canopy, and DOM excreted from plant roots (Blackburn et al., 1994; Marbà et al., 2006).

The dominance in NH_4 effluxes observed during the dry season indicated degradation of sedimentary organic N (Belias et al., 2007) while the uptake by sediments measured in October 2009 could be the consequence of intense benthic primary production. The significant

Table 3
Pearson Product Moment Correlation matrix.

Variables	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Salinity (1)	–																
Temperature (2)	0.171																
Porosity (3)	**-0.324**	0.156															
Sed OrgC (4)	-0.059	0.164	**0.294**														
Sed N (5)	-0.237	0.098	**0.639**	**0.661**													
Sed Chla (6)	-0.117	0.102	**0.374**	**0.670**	**0.845**												
C:N (7)	**0.301**	0.032	-0.146	**0.295**	-0.122	-0.081											
O$_2$ (8)	-0.138	-0.154	0.062	0.140	**0.254**	**0.483**	-0.101										
NH$_4$ (9)	0.014	0.158	0.058	0.060	0.035	-0.026	-0.108	**-0.269**									
NO$_3$ (10)	**-0.561**	-0.058	0.061	0.027	0.036	-0.056	-0.137	0.035	**0.397**								
PO$_4$ (11)	0.242	0.152	-0.157	**-0.320**	-0.164	-0.153	-0.166	0.080	-0.004	-0.059							
Si(OH)$_4$ (12)	**-0.407**	0.013	0.148	0.082	0.026	0.016	0.030	-0.023	0.004	**0.470**	-0.015						
Flux O$_2$ (13)	0.188	0.052	0.086	0.125	**0.257**	**0.458**	0.158	0.154	0.024	-0.091	**0.269**	-0.081					
Flux NH$_4$ (14)	0.052	0.050	0.106	0.197	0.030	-0.111	0.067	-0.162	-0.230	-0.186	0.016	0.072	-0.192				
Flux NO$_3$ (15)	-0.224	-0.129	0.163	0.089	0.009	-0.036	-0.089	0.110	**-0.356**	**-0.257**	0.070	0.106	-0.150	**0.405**			
Flux DIN (16)	0.060	-0.042	-0.036	0.064	-0.140	-0.200	0.166	-0.159	-0.182	-0.233	0.015	0.026	-0.154	**0.829**	**0.513**		
Flux PO$_4$ (17)	-0.194	0.111	0.194	0.091	0.205	0.119	-0.190	0.018	**0.324**	**0.329**	0.121	-0.012	-0.066	0.183	0.106	0.189	
Flux Si(OH)$_4$ (18)	-0.140	0.063	0.161	0.085	0.146	0.259	0.055	-0.026	-0.224	0.078	0.257	**0.616**	0.250	0.221	0.165	0.144	-0.073

All data were compiled from the 4 surveys except for Sediment chlorophyll. Values shown are the correlation coefficients between variables. Bold coefficient values were statistically significant (p < 0.05). Positive or negative coefficients indicate positive or negative correlations with 1 or -1 being the strongest positive or negative relationship.

correlation of Si fluxes with sediment chlorophyll possibly results from mineralization of benthic diatoms or dissolution of freshly deposited frustules (Kamatani, 1982; Yamada and d'Elia, 1984; Loucaides et al., 2012). Silica release from the sediments is often considered as a diffusion flux controlled by the concentration gradient at the sediments water interface (Willey, 1978). We found on one occasion a significant influx of silicate to the sediment (Station C in October 2009) which corresponded to a period when silicate concentrations in the bottom water were higher than in interstitial pore waters (data not shown). These unusual Si influxes related to high water column silicate were also recorded by Niencheski and Jahnke (2002) in Patos lagoon (Brazil). For all other observations Si fluxes were directed towards the water column. The high positive correlation between Si fluxes and Si (OH)$_4$ in bottom waters in general (r = 0.616) showed a potential resupply of this nutrient in favor of the nutrient pool in the water column.

Although sediments are generally considered to be a significant internal source of nutrients in shallow coastal ecosystems, several studies have shown that they may be a net sink of dissolved nitrogen at least during certain times of the year (Sundbäck et al., 2000; Tyler et al., 2003). In our case and due to the high variability encountered we could not conclude whether the sediments behaved as a sink or a source of nitrogen for the lagoon.

To compare our flux data to riverine inputs, we considered the monthly freshwater inflows at the given dates (88.5, 189.9, 75.5 and 307.8 m^3 s^{-1}, for March 09, October 09, March 10 and November 2010, respectively; data from CONAGUA). River nutrient concentrations were inferred from a nutrient–salinity mixing diagram (data from P. Salles UNAM Sisal, pers. comm., from Vera-Herrera and Rojas-Galaviz, 1983, from Medina-Gomez et al., 2015, and from our data at Palizada station). We plotted nutrient data from the river mouth area against salinity (range 0–3) and used the zero salinity intercept on the regression line to calculated river concentrations of nutrients, assuming dilution as the main process involved.

Based on our data, we calculated both minimum (Mean − CI) and maximum (Mean + CI) sediment-water fluxes for the total lagoon (2000 km^2). Finally, we divided these lagoon-wide sediment-water fluxes by the river inputs for each nutrient and season (Table 5) to compare the magnitude of sediment-water exchanges with the river inputs for the entire lagoon.

During the wet season benthic efflux accounted for 1 to 4 times the Si(OH)$_4$ river inputs and 4 to 18 times the PO$_4$ river inputs. For nitrogen, benthic fluxes were 3 times lower to 12 times higher than the river inputs of ammonium given the high variability in our flux estimates, and 1 to 4 times higher for nitrate. We ended up with an equivalent sink or source of 2 times the river input for DIN considering the minimum or maximum benthic flux estimate. During the dry season, the nutrient concentrations in rivers were almost equivalent or reduced compared to the wet season. Due to lower river outflows, the benthic fluxes compared to the rivers inputs were always higher for most of the nutrient considered, from 3 to 4 times for silicates, 7 to 16 times for DIN and up to 50–160 times for phosphates. This predictable relation results from the vast area of the lagoon compared to the proportional low river discharges. When adding the high residence times of the water masses inside the lagoon (between 9 and 159 days, David and Kjerfve (1998); David (1999)), the contribution of benthic fluxes to biogeochemical cycling of nutrients becomes prominent.

A similar calculation was performed to compare pelagic primary production to benthic carbon mineralization rates. We used data from Day et al. (1987) and Gomez-Reyes et al. (1997) to calculate a mean primary production rate of 200 g C m^{-2} yr^{-1}. Considering a community respiration quotient (CRQ) of 1.1 (Denis, Univ. Lille, personal communication) and mean SOD of 1327 ± 161 and 2248 ± 359 µmol m^{-2} h^{-1} for dry and wet seasons respectively, we found that the sediments mineralized between 67 and 86% of the organic carbon produced in the water column during the dry season and between 109 and 151% during the wet season. These ranges are slightly

Table 4

Example of benthic oxygen consumptions (min max) measured in shallow aquatic systems.

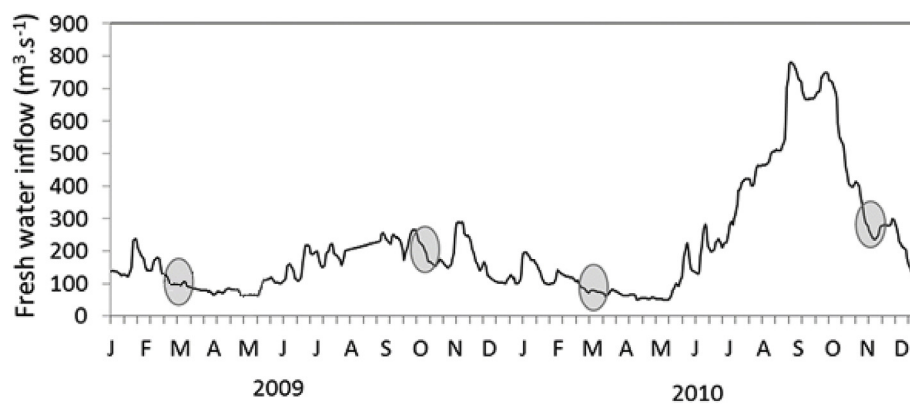| Site	Latitude	O2 (μmol m^{-2} h^{-1})		Author
Temperate systems				
Upper Waterway, Illinois	42°52N	723	4598	Butts (1974)
Eastern Michigan River	44°15N	129	3552	Bowie et al. (1985)
Chesapeake bay	37°35N	2067	4068	Boynton & Kemp (1985)
Lake Ton-Ton (Uruguay)	34°51N	1163	2286	Sommaruga (1991)
Hiroshima bay	34°20N	129	904	Seiki et al. (1994)
Tualatin River basin	45°19N	517	3358	Rounds and Doyle, 1997
NW Mississipi aquaculture pond	45°34N	3390	8728	Berthelson et al. (1996)
Upper Klamath Oregon	42°23N	1421	4779	Wood (2001)
Neuse Estuary	35°13N	2822	3616	Borsuk et al. (2001)
Golfe de Fos, France	43°22N	625	1958	Rabouille et al. (2003)
Anacostia River, USA	38°50N	1291	4650	Machelor Bailey et al., 2003
Chester River, USA	39°4N	2067	4069	Boynton et al. (2003)
Beach Haven Ridge, NW Atlantic	39°34 N	239	2819	Laursen & Seitzinger (2002)
Helsingør, Denmark	56°2N	2200	3800	Wenzhofer & Glud (2004)
Ria of Vigo, Spain	42°12N	667	8292	Forja et al. (2004)
Thau lagoon, France	43°23N	3140	10980	Thouzeau et al. (2007)
Tacan Bay, Korea	36°4N	317	1321	Kim & Kim, 2007
Hauraki Gulf, New Zeland	36°25S	128	1222	Giles et al. (2007)
Georgia Coastal plain, USA	31°14N	129	5813	Utley et al. (2008)
Keelung River, Taiwan	25°6N	310	1330	Liu (2009)
Coombabah lake, Australia	27°54S	279	4736	Dunn et al. (2012)
Derwent estuary	42°51S	532	1153	Banks et al. (2013)
Oregon Shelf, USA	44°2 N	180	520	Fuchsman et al., 2015
Gulf of Valencia, W Med	39°26N	611	2306	Sospedra et al. (2015)
(Sub)tropical systems				
Shing-Mun River, Hong Kong	22°23N	1188	18988	Chen et al. (2000)
Tolo Habor	22°25N	607	1653	Chau (2002)
New Caledonia	22°22N	550	1570	Grenz et al. (2003)
Nichupte, Mexico	21°7N	250	12875	Valdes-Lozano et al. (2006)
Goa, W Coast India	15°27′N	1460	4120	Pratihary et al. (2009)
Pompey Reef, Australia	21°0 S	821	3400	Alongi et al. (2011)
Cochin Backwater System	9°49N	995	2267	Abhilash et al. (2012)
Semariang Batu River, Malaysia	1°37N	982	14803	Ling et al. (2009)
Terminos lagoon	**18°40N**	**305**	**7400**	**This study**

Fig. 9. Daily freshwater inflows from Palizada River (m^3 s^{-1}) from January 2009 to December 2010; filled circles depict the sampling periods (data from CONAGUA, http://www.conagua.gob.mx).

Table 5

Ratio between benthic fluxes and River inputs of nutrients during the dry and wet seasons (Fluxes $\pm$ C.I. in μmol m^{-2} h^{-1}, River Concentration in μmol l^{-1}, Términos Lagoon area 2 10^9 m^2).

Season		NH$_4$	NO$_3$	DIN	PO$_4$	Si(OH)$_4$
Dry	Benthic Fluxes	20.3 $\pm$ 5.5	9.5 $\pm$ 3.2	24.3 $\pm$ 7.3	2.4 $\pm$ 1.1	46.5 $\pm$ 11.4
	River Concentration	4.7	9.8	14.5	0.2	70.0
	F/R[a]	20–40	4–10	7–16	50–160	3–4
Wet	Benthic Fluxes	10.0 $\pm$ 16.3	0.2 $\pm$ 3.7	2.9 $\pm$ 18.8	3.2 $\pm$ 1.5	89.4 $\pm$ 15.9
	River Concentration	4.1	23.8	27.9	0.8	120.2
	F/R[a]	(-3) - 12	(-1) – 4	(-2) - 2	4–18	1–4

[a] F: Benthic fuxes (min - max) x lagoon area, R: River Concentration x Flow x 10^3 (both units in μM h^{-1}).

higher to proportions calculated for sub-tropical lagoons in New Caledonia and Brazil (Grenz et al., 2010; Machado and Knoppers, 1988). Even if the study of benthic primary production was outside the scope of our study, it is noteworthy that microphytobenthos often accounts for more than 50% of the primary production in shallow ecosystems (Underwood and Kromkamp, 1999). This is particularly true in microtidal systems in the tropical areas where irradiance availability and reduced turbidity, compared to temperate macrotidal systems, enhance the period of benthic primary production over the entire diurnal time scale.

Considering C mineralization rates as calculated previously (1206 and 2011 $\mu mol\,C\,m^{-2}\,h^{-1}$) and the organic matter N/C ratio estimate, N mineralization corresponds to 47 and 80 $\mu mol\,N\,m^{-2}\,h^{-1}$ (dry and wet season, respectively). Our DIN efflux measurements were 23 and 3 $\mu mol\,N\,m^{-2}\,h^{-1}$ (dry and wet season, respectively), indicating that a substantial part of nitrogen (between 50 and more than 95% depending on the calculation) is removed by the sediments. This 'missing' DIN release appears also through the mean DIP/DIN flux ratio over all periods (1/5) which is well above Redfield (1/16) indicating that N is more efficiently removed than P. Besides, it is well known that the selective degradation of organic matter components during early diagenesis has the potential to modify the elemental stoichiometry in sediments (Boudreau, 1997). In shallow-water coastal sediments, DIN can be removed or retained mainly in 3 ways: denitrification, burial into sediments, and incorporation by primary producers (Sørensen, 1978; Seitzinger, 1988; Kelso et al., 1999). A study in the Baltic Sea showed that N assimilation by microphytobenthos far exceeded measured rates of denitrification (Sundbäck et al., 2006) underlining that these processes should be accounted for when establishing nutrient budgets in the future.

Finally, our results showed that during the wet season, benthic mineralization inferred through SOD measurements was higher than during the dry season. The reason is probably related to the river inputs which promote pelagic and benthic primary production and subsequent organic matter accumulation at the sediment surface. Related processes like bioturbation and bacterial activities accelerate the recycling of organic matter and enhance the related fluxes at the sediment-water interface. Nevertheless the impact of precipitation has to be weighted because of the ENSO event in 2009 we experienced, event which affected the magnitude of SOD with an increase in oxygen consumption by almost 50%. These higher rates may influence the oxygen balance in Laguna de Términos and lead to potential hypoxic events, moreover in the context of global climate change and the foreseen increase in dryness under these latitudes (Mendoza et al., 1997; Brito et al., 2012).

5. Conclusions

Despite the fairly large variability associated with some of the sediment oxygen and nutrient flux estimates, probably related to the high degree of small scale heterogeneity, several important conclusions can be drawn from the results. The seasonal variability exceeded the spatial variability, with peaks of mineralization rates during the wet seasons significantly related to organic matter content in the sediments. In contrast, a strong SW-NE spatial gradient was found in the isotopic signatures of the sedimentary OM and this was constant over the studied period. The low $\delta^{15}N$ combined to heavier $\delta^{13}C$ in the easternmost stations and along the inshore of the barrier island was probably due to a higher fraction of seagrass debris in the sediments. High C/N ratio emphasized the refractory nature of the sediment mixture.

Except for ammonium, benthic in- or effluxes of nutrients were always equal or higher than the river inputs, while benthic carbon mineralization rates, as inferred from SOD measurements, were equivalent to a significant proportion of the pelagic primary production. This emphasizes the predominant role played by benthic processes in the biogeochemical cycles in this tropical estuarine system regularly subjected to high freshwater inflows.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecss.2019.01.012.

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