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Export of Dissolved and Particulate Carbon and Nitrogen From a Mangrove-Dominated Lagoon, Yucatan Peninsula, Mexico

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ABSTRACT

Mangrove ecosystems can significantly influence adjacent coastal areas by acting as either sources or sinks of organic carbon and nutrients. In this study, the total export of carbon and nitrogen from Celestun Lagoon, located on the Yucatan Peninsula, Mexico, was measured during two different seasons. The net export of dissolved and particulate carbon and nitrogen was calculated using measured concentrations within the lagoon coupled with hydrodynamic measurements of lagoon water exchange and published water budgets. The results show that Celestun Lagoon is a source of both organic carbon and nitrogen to the adjacent coastal ocean. Dissolved organic carbon accounted for 92% of the total carbon export, while the particulate form of organic nitrogen accounted for between 65-85% of the total nitrogen export. Groundwater is the major source of dissolved inorganic nitrogen to Celestun Lagoon, but is an insignificant source of both particulate and dissolved organic carbon. The majority of dissolved inorganic nitrogen from the groundwater is recycled within the lagoon, with only a small fraction (approximately 10%) exported to the coastal ocean. Due to the significant export of carbon and nitrogen from the lagoon to the coastal ocean, changes in lagoon functioning or groundwater composition, such as from pollution, will result in changes to the carbon and nitrogen budgets of the adjacent coastal ocean."

Key Words: Outwelling, Coastal Ecosystems, Organic Carbon, Organic Nitrogen, Inorganic Nitrogen, Groundwater

INTRODUCTION

Mangrove ecosystems are generally regarded as important contributors of organic carbon and other nutrients to adjacent coastal ecosystems, yet there is increasing evidence that the total flux and direction of the net flux are highly dependent on the hydrology and physical characteristics of the specific ecosystem (Twilley 1985, Twilley 1988). Current estimates place the worldwide mangrove area between 166,000 and 180,000 km^2 (Field 1995, Spalding et al. 1997, Valiela et al. 2001) and mangrove forests cover approximately 5,200 km^2 in Mexico (Yanez-Arancibia et al. 1993). In many areas of the world mangroves occupy the important boundary between the land and the sea, and approximately 75% of tropical intertidal vegetations consists of mangroves (Twilley 1985). Previous studies have shown that mangrove ecosystems may significantly influence adjacent coastal areas through various mechanisms such as nutrient and carbon export (e.g. Dittmar and Lara 2001, Lee 1995, Odum and Heald 1975) sediment stabilization and storm protection (Alongi 2002), and nursery habitat for economically important species (Alongi 2002, Mumby et al. 2004). In order to understand the current interactions between mangrove habitats and the coastal ocean and to better predict the large-scale effects of either destruction or restoration of mangrove ecosystems, it is necessary to quantify fluxes of carbon and nitrogen from these systems to the coastal ocean in specific geographical areas. Carbon and nitrogen exist in both dissolved and particulate forms, and although many early studies focused entirely on fluxes of particulate matter (see Lee 1995), there is now strong evidence that dissolved forms may comprise a much greater percentage of the total nutrient flux than particulate forms (Davis et al. 2003, Dittmar and Lara 2001, Twilley 1985). In this study, we measured dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN) including nitrate, nitrite and ammonia, and particulate organic carbon

and nitrogen (POC and PON) in Celestun Lagoon, Mexico, and in the adjacent coastal waters. The net C and N fluxes through the lagoon and into the coastal ocean were estimated using mean concentrations of particulate and dissolved C and N coupled with hydrodynamic measurements of net water velocity over several tidal cycles and published water budgets for the lagoon.

STUDY SITE

Celestun Lagoon is located near the northwestern tip of the Yucatan Peninsula (Figure 1). The lagoon and surrounding area (590 km^2) were designated as the Ria Celestun Biosphere Reserve in 1989. The port and town of Celestun (population approximately 6,000) are located to the west of the lagoon, and currently there is no significant urban or industrial development near the shores of the lagoon. Celestun is a long and narrow lagoon that is generally very shallow (1.2 m) except for a 100 m wide, 15 km long tidal channel that runs from the mouth of the lagoon to about the middle of the northern section of the lagoon. Celestun Lagoon runs approximately parallel to the Yucatan Peninsula coast, and the lagoon is open to the Gulf of Mexico through a 410 m wide mouth at its southwest end (Herrera-Silveira 1994).

Brackish groundwater discharges into Celestun from large springs located in the northern and middle parts of the lagoon, and from many small springs throughout the lagoon (Herrera-Silveira et al. 1998). The groundwater discharge results in a year-round salinity gradient with fresher water in the northern section grading out to seawater salinities near the mouth. In order to build a bridge across the lagoon leading to the port and town of Celestun, the center part of the lagoon was partially filled in 1979, which resulted in changes in sedimentation and circulation patterns between the half of the lagoon south of the bridge and the half north of the bridge (Herrera-Silveira 1996). Long-term nutrient monitoring indicates that Celestun has not shown evidence of considerable eutrophication (Herrera-Silveira et al. 1998); however, moderate increases in groundwater nitrate and ammonia concentrations have been observed in the springs discharging into Celestun, possibly due to agricultural or sewage runoff (Herrera-Silveira et al. 2005).

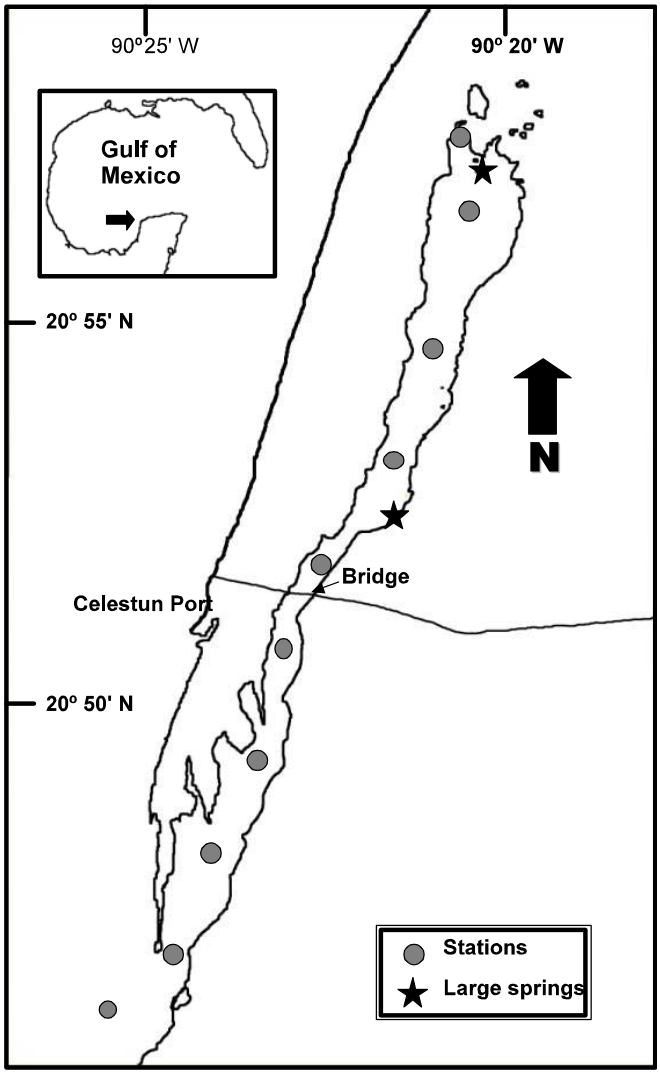

Figure 1. Yucatan map and Celestun Lagoon with transect sampling locations and locations of major ground water discharge within the lagoon

Celestun is surrounded by approximately 22.3 km^2 of well developed mangrove forest consisting of *Avecenia lagunculara*, *Rhizophora mangle*, and *Laguncularia racemosa* (Gonneea et al. 2004, Herrera-Silveira et al. 1998). Extensive algae and seagrass beds consisting predominantly of *Chara fibrosa, Batosphora oerstedi, Chaetimorpha linum, Ruppia sp.,* and *Halodule wrightii* are present throughout the lagoon, covering approximately 65% of the lagoon sediment (Herrera-Silveira et al. 1998).

The geology of the northern Yucatan Peninsula is primarily flat-lying Tertiary limestone, and the karstic nature of the region results in very few rivers and little or no surface runoff, except at the height of the rainy

season. The climate on the Yucatan Peninsula is characterized by a dry season from March through May during which rainfall is typically less than 50 mm, a rainy season from June through October during which the majority of the annual rainfall (>500 mm) occurs, and the "nortes" season from November through February characterized by moderate rainfall (20-60 mm) and intermittent high wind speeds greater than 80 km hr^{-1} (Herrera-Silveira 1994). Average mean air temperatures range from 20ºC in January to a high of 35ºC in August, with an average mean annual temperature of 26.2ºC (Herrera-Silveira 1996).

The major primary producers in Celestun Lagoon can be divided into four general groups: phytoplankton, seagrasses (primarily *Halodule wrightii*), macroalgae, and mangroves. Herrera-Silveira (1994) reported strong seasonal variations in primary productivity of phytoplankton, *Halodule wrightii*, and macroalgae, characterized by large peaks in productivity occurring in June and November. Herrera-Silveira (1994) attributed the largest productivity peak, occurring in June, to the onset of the rainy season. Total estimated annual carbon input (fixation) from these four sources to Celestun lagoon is 52216×10^6 g C y^{-1} (Table 1), with mangroves contributing just over 60% of the total carbon input to the system.

Gonneea et al. (2004) determined total carbon storage in Celestun Lagoon sediments by measuring sedimentation rates and organic carbon in sediment cores taken throughout Celestun Lagoon (Table 1). They reported that 1229×10^6 g C $y^{!1}$ were stored in lagoon sediments, which is 2.4% of total primary production in Celestun.

The primary objective of this work is to determine the inventories of dissolved and particulate carbon and nitrogen within Celestun Lagoon, and to couple this information with studies of the lagoon productivity and water dynamics in order to estimate the direction and net flux of carbon and nitrogen in both dissolved and particulate forms between Celestun lagoon and the coastal ocean during different seasons. This data will enable us to assess whether or not carbon and nitrogen from the lagoon environment could be important to the food web in the adjacent coastal area.

MATERIALS AND METHODS

Extensive surface water sampling was conducted along a lengthwise (northeast-southwest) transect of Celestun Lagoon during the middle of the dry season (March-April 2003) and analyzed for DOC, DIN, POC, and PON. Four replicate sampling transects were conducted during the 2003 March-April research trip in order to address potential short-term variability in C and N concentrations within Celestun Lagoon. Surface water sampling along the transect was conducted on March 27 and April 8, 11 days apart. On each sampling day, two full lagoon transects were sampled, one during incoming tide and the other during outgoing tide.

DOC samples were also collected along the same lagoon transect in July 2002 during the beginning of the rainy season, and samples for POC, PON, and DIN were collected in October 2001 near the end of the rainy season. Samples from the adjacent coastal waters were collected at the same periods. In March-April 2003, samples were also collected over the course of a tidal cycle from one of the largest springs located in Celestun in order to better quantify variability in the groundwater source. During all three trips additional samples were collected from two springs located in Celestun Lagoon and three wells located in the town of Celestun approximately 1.5 km from the lagoon in order to examine groundwater as a possible source of either dissolved or particulate C and N.

DOC

Samples for DOC were collected with a 60-mL plastic syringe and immediately filtered through sterile 0.25 μm syringe filters into acid-washed borosilicate glass scintillation vials with Teflon-lined screw caps. Samples were kept inside a cooler while in the field and frozen upon return to the laboratory (approximately 1-4 hours after collection). Samples were prepared for analysis by thawing the sample and acidifying an aliquot to a pH of 2-3 in a pre-ashed glass analysis tube using 1 M HCl.

Samples were analyzed at the Biogeochemistry Laboratory at Stanford University on a Shimadzu TOC-5000A Total Organic Carbon Analyzer. Five standards ranging from 1 mg $L^{!1}$ to 100 mg $L^{!1}$ were prepared using a potassium hydrogen phthalate solution. Coefficient of variation for the standards above 1 mg $L^{!1}$ was <3%. The detection limit for the chosen sensitivity range was ~1 mg $L^{!1}$. Collection and analysis of four sets of triplicate samples yielded an average standard error of 7%, which includes natural variability within a single station, variability from sampling and handling procedures, and analytical error.

Table 1. Estimated carbon inputs and carbon burial in Celestun Lagoon

	Net Primary Productivity $g\ C\ m^{-2}\ yr^{-1}$	Total Area $10^6\ m^2$	Total Carbon $10^6\ g\ C\ y^{-1}$
Phytoplankton[a]	150	28	4200
Halodule[a]	285	13	3705
Macroalgae[a]	498	23.6	11753
Mangroves[b]	1460	22.3	32558
TOTAL C INPUTS			52216
	Carbon Burial	Total Area	Total Carbon
Mangrove sediments[c]	30	22.3	669
Seagrass sediments[c]	20	28	560
TOTAL C BURIAL			1229

a) Herrera-Silveira 1994; b) Herrera-Silveira and Zaldivar, personal communication, 2002; c) Gonneea et al. 2004

POC and PON

Samples for POC and PON analysis were collected by filling 1 L opaque plastic bottles with unfiltered surface water, and storing the samples in a cool, dark environment until brought to the lab. Each sample was then vacuum-filtered under low pressure through a pre-combusted Whatman GF/C filter to collect the particulate matter, and the exact volume of water filtered was recorded. The total volume of water that was filtered varied depending on how quickly the filter became clogged with particulate matter. The samples were prepared by rinsing the filter with 5 mL of 0.1 N HCl to remove any residual $CaCO_3$, rinsing with 10 mL of Milli-Q water, and drying at 50-60°C in an oven. The samples were analyzed at the Stable Isotope Laboratory at Stanford University on a Finnigan MAT isotope ratio mass spectrometer and a Carlo Erbo NA1500 Series II elemental analyzer, which measured total organic carbon and total organic nitrogen.

DIN

During October 2001, surface water samples were collected in 1 L opaque plastic bottles and stored at 4°C. Samples were filtered and analyzed for dissolved inorganic nitrogen species at the Laboratorio de Produccion Primaria, CINVESTAV, in Merida, Mexico. NO_3^-, NO_2^-, and NH_4^+ were determined according to the methods described in Herrera-Silveira (1998). Samples taken during March-April 2003 were filtered directly into 50 mL opaque plastic bottles, frozen, and sent to Oregon State University for analysis of NO_3^- and NO_2^-. NH_4^+ was not measured on the March-April 2003 samples because freezing of the samples results in unreliable NH_4^+ values.

Hydrodynamics

In July 2002, a Vector acoustic Doppler velocimeter and an Ocean Sensors OS2000 CTD (Conductivity, Temperature, and Depth) were deployed during the sampling period from July 13th through July 17th in order to calculate water exchange in the lagoon by measuring the tidal height, water velocity, water temperature, and salinity at five minute intervals. The instruments were deployed together in the boat channel directly in front of the Ducks Unlimited Mexico (DUMAC) field station near the midpoint of the lagoon, approximately 420 m north of the Celestun bridge (Figure 1). The purpose of this deployment was to produce an accurate estimate of net water flux between the lagoon and the coastal ocean during one sampling period, and to compare this estimate to previous seasonal estimates calculated from salinity and silica budgets for Celestun Lagoon.

RESULTS AND DISCUSSION

Dissolved Organic Carbon

A clear gradient in DOC concentrations was observed, with the highest DOC concentrations occurring in the north lagoon, transitioning to much lower values at the mouth of the lagoon (Table 2).

Statistical analysis of the results from both trips was performed in order to better understand variability

in DOC concentrations over short time scales, between sections of the lagoon, and between the two sampling trips. Short- term variability in DOC concentrations at each station was determined by calculating the standard deviation in DOC concentration for each station (10 stations total) from the March-April 2003 trip for which there were four separate sampling events (ebb tide and flood tide transects on two occasions 11 days apart). Paired student t-tests were performed in order to compare the results from each station at different sampling times. Results from these analyses indicated that there were no significant differences in tphe mean concentrations of DOC during ebb and flood tide, and between the lagoon transects sampled 11 days apart. The results from the four March-April 2003 sampling transects were there-fore pooled for the determination of average DOC concentrations (Table 2) used in export flux calculations. Average DOC concentrations measured in the lagoon in July 2002 (rainy season) were about twice as high as those measured in March-April 2003, and the groundwater DOC concentrations in July 2002 were over three times higher than in March-April 2003. However, there was no significant difference between the adjacent coastal water DOC concentrations measured during the two trips.

In March-April 2003, DOC concentrations throughout Celestun lagoon showed a negative correlation with salinity (Figure 2a), indicating that the decrease in DOC concentration from north to south in the lagoon may be the result of mixing with low-DOC, high salinity coastal water, and not the result of either lower DOC input or consumption of DOC within the lagoon. The average DOC concentration at the station located in the far north of the lagoon was significantly higher when compared to salinity than DOC concen-trations from the other stations, which may indicate a change in DOC source or input strength for the far northern section of the lagoon. In July 2002, salinity and DOC values showed a pattern indicating a three end-member mixing system (Figure 2b), with unmixed lagoon water

Table 2. Dissolved organic carbon concentrations and salinity in Celestun lagoon

	March-April 2003			July 2002		
	Av DOC mg L^{-1} (range)	Salinity	stations #	Av DOC	Salinity	stations #
North lagoon	12.45 (4.02-32.08)	20.8 (14.4-30)	5	26.55 (11.37-52.42)	20.2 (17.2-22)	7
South lagoon	4.82 (2.14-9.17)	31.3 (20-39)	6	9.01 (5.67-15.02)	30.5 (25-36)	6
Adjacent coast	3.12 (2.14-4.39)	34.2 (26.5-39)	1	3.53 (2.31-5.44)	36.8 (34-39)	6
Lagoon springs	1.00 (b.d.-1.65)	25.2 (20.2-28)	2	3.24 (1.39-5.09)	16 (15-17)	2
Wells	1.36 (b.d-1.77)	3.1 (2.6-3.5)	2	2.01 (b.d-4.21)	3 (0-5)	3

b.d: below detection

Table 3. Dissolved inorganic nitrogen concentrations for Celestun Lagoon

	March-April 2003		October 2001		
	NO_3^-+ NO_2^- μg-N L^{-1} (range)	stations #	NO_3^-+ NO_2^- μg-N L^{-1} (range)	NH_4^+ μg-N L^{-1} (range)	# stations
North lagoon	89.5 (30.7-166)	5	43.6 (8.1-84.2)	76.0 (34.3-119)	4
South lagoon	150 (27.4-259)	5	73.3 (27.8-126)	48.9 (27.7-75.2)	4
Adjacent coast	101 (27.4-186)	1	31.9 (11.7-43.9)	40.2 (17.7-63.0)	6
Lagoon springs	633 (305-975)	2	1190 (864-1520)	163 (96-230)	2
Wells	1340 (648-1770)	2	0.119 (041.1-252)	108 (26.2-119)	4

(represented by the far north station), groundwater, and adjacent coastal ocean water all significantly affecting DOC concentrations and salinity throughout the lagoon. Much higher ground-water inputs occur in Celestun lagoon during the rainy season than in the dry season (Gomez and Herrera-Silveira 2002), and the majority of the springs are located in the north and middle parts of the lagoon. It appears that input of low-DOC, moderate-salinity groundwater had a much greater influence on the spatial pattern of DOC in Celestun in July 2002 than in March-April 2003. DOC concentrations in the lagoon springs and local wells were much lower than in the lagoon.

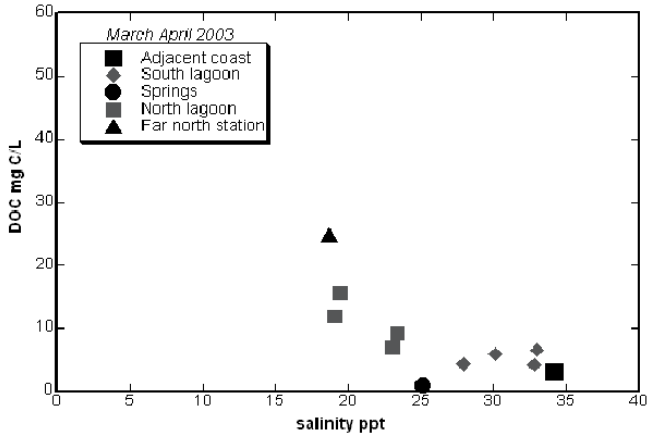

Figure 2a. Plot showing a negative correlation between average salinity and average DOC concentrations from Celestun transect stations sampled during the March-April 2003 trip.

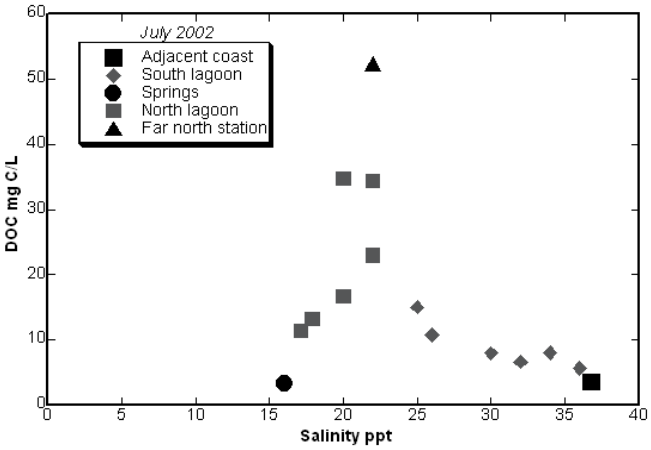

Figure 2b. Plot of salinity vs DOC for July 2002 showing three end member mixing between upper lagoon water, ground water, and seawater.

Dissolved Inorganic Nitrogen

DIN patterns in Celestun lagoon were very different from DOC patterns, and exhibiting no clear gradient along the lagoon transect or any significant relationship to lagoon salinity (Table 3). The highest measured values for all DIN species were found in the lagoon springs and local wells.

DIN concentrations were highly variable between stations throughout the lagoon during both sampling trips. The ranges of NO_3^- + NO_2^- concentrations measured in each section of the lagoon and in the adjacent coastal ocean were larger than any changes in mean concentrations over tidal cycles or between sampling weeks. NO_3^- concentrations ranged from 10-100 times higher than NO_2^- concentrations. For both tidal cycles and both weeks of the March-April 2003 trip, average NO_3^- + NO_2^- concentrations were 1.5 to 2 times higher in the south lagoon than in the north lagoon, with the difference being statistically significant at the 95% confidence interval (CI). This same pattern appears in the October 2001 lagoon transect, however the difference was not statistically significant. NO_3^- +NO_2^- concentrations were much higher in the lagoon springs than in the lagoon and coastal waters, and the ground water is a known source of both NO_3^- and NO_2^- to the lagoon (Herrera-Silveira 1996, Herrera-Silveira et al. 2004). Fairly large variations in groundwater NO_3^- + NO_2^- concentrations were observed in both the lagoon springs and town wells, particularly during the March-April 2003 trip. For the lagoon springs, which are brackish, these changes may represent tidally driven mixing with seawater, while the differences between the freshwater town wells could indicate differences in local ground water flow patterns, proximity to sources of nitrogen contamination, or a combination of both. Dissolved inorganic nitrogen dynamics in Celestun have been studied extensively over various time periods during the past 10 years (i.e. Herrera-Silveira 1996, Herrera-Silveira 1998) and the lagoon and coastal concentrations measured in this study fall within the previously reported concentration ranges. However, several of the NH_4^+ concentrations measured in October 2001 in the lagoon springs and local wells are above the previously reported range for Celestun groundwater (0.014-0.154 mg-N/L) (Herrera-Silveira 1998). Additional groundwater monitoring would be required to determine if this reflects short term and/or seasonal variability not captured in previous studies, or long term increases in NH_4^+ concentration, possibly the result of groundwater contamination from agricultural

or sewage run-off. Peaks in NH_4^+ concentrations generally occur in the middle section of Celestun during the months of February and July (Herrera-Silveira 1996), and the NH_4^+ concentrations measured in October 2001 fall in the low range of previously reported values for Celestun (Herrera-Silveira and Comin 1995, Herrera-Silveira 1996). Herrera-Silveira (1998) reported that DIN concentrations in Celestun are primarily influenced by a combination of groundwater inputs and biological activity, and that a mobile zone of high phytoplankton productivity may be responsible for much of the spatial and temporal variability observed in DIN concentrations.

Particulate Organic Carbon and Nitrogen

During both the March-April 2003 and October 2001 sampling trips, particulate organic carbon and nitrogen showed identical spatial and temporal patterns, with an average C:N atomic ratio in the POM of 7.03. For all sampling transects, greater variability in POC and PON concentrations between stations was observed in the north lagoon, and no consistent concentration gradients were apparent in relation to either salinity or location within the lagoon (Figures 3a,b and 4a,b). POC and PON concentrations measured in the lagoon springs and local wells were 1-2 orders of magnitude lower than

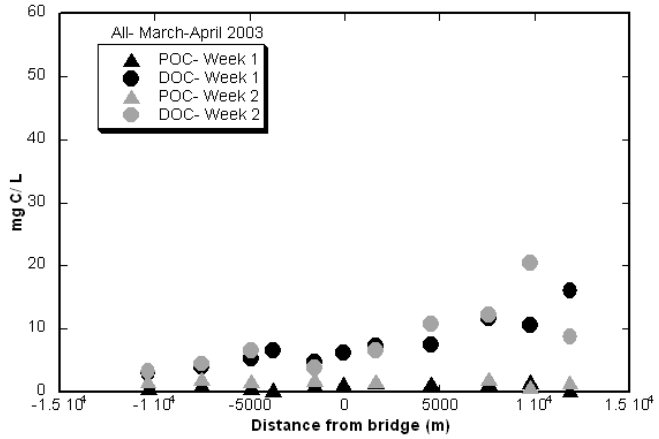

Figure 3a. Distribution of particulate and dissolved organic carbon (mg C L^{-1}) during the dry season sampling trip along the middle transect in Celestun lagoon.

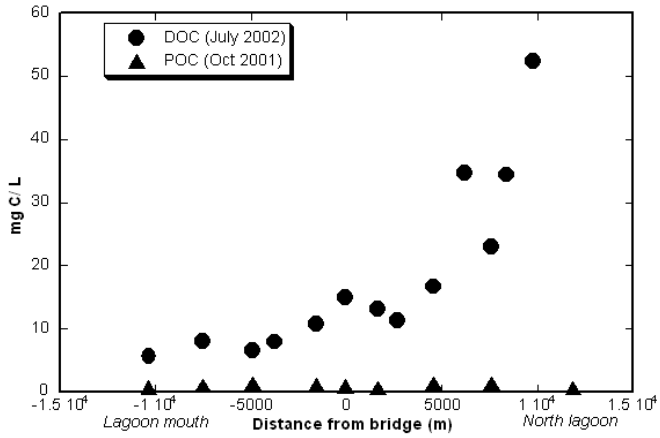

Figure 3b. Distribution of particulate and dissolved organic carbon (mg C L^{-1}) during the rainy season sampling trips along the middle transect in Celestun lagoon.

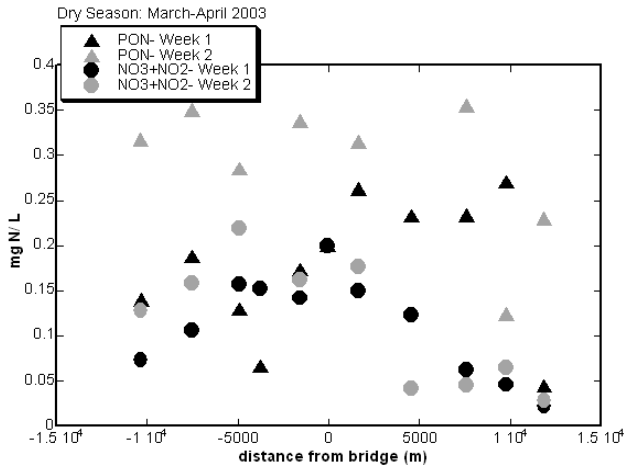

Figure 4a. Distribution of particulate and dissolved nitrogen (mg N L^{-1}) during the dry season sampling trip along the middle transect in Celestun lagoon.

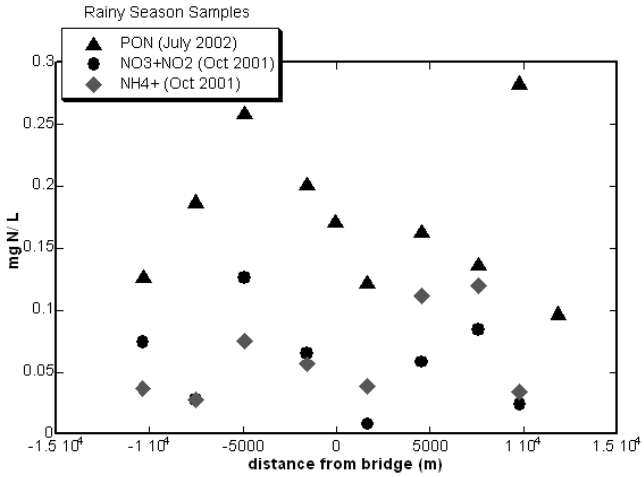

Figure 4a. Distribution of particulate and dissolved nitrogen (mg N L^{-1}) during the rainy season sampling trips along the middle transect in Celestun lagoon.

average lagoon concentrations, indicating that groundwater discharge is not a major source of POM to either the lagoon or the coastal ocean.

No significant differences were observed in POC and PON concentrations at flood and ebb tide. However, mean POC and PON concentrations throughout the lagoon and adjacent coastal ocean increased significantly (99.9% CI) between the first and second pairs of sampling transects conducted during the March-April 2003 trip Table 4a,b). Paired Student's t-tests (using matching station locations) indicate that the changes in POC and PON concentrations between the two sampling weeks in March-April 2003 was greater than the difference between the average daily concentrations at each station during the March-April 2003 trip and the concentrations at each station measured during the October 2001 trip. These data indicate that either there are no significant differences in POC and PON concentration between the rainy season and the dry season, or that much more extensive sampling is required to resolve significant seasonal differences from the short time scale (weekly) fluctuations in concentration. POC and PON concentrations did not show any significant correlations or similarities in spatial and temporal patterns with either DIN or DOC, indicating that different sources and cycling dynamics influence each of these variables.

WATER FLUX IN CELESTUN LAGOON

In order to estimate fluxes of dissolved and particulate carbon and nitrogen from Celestun lagoon to the coastal ocean, we used both published seasonal estimates of water flux out of the lagoon and a water flux estimate based on hydrodynamic measurements conducted over the July 2002 sampling period. Additionally, published estimates of seasonal groundwater flux were used to calculate the contribution of groundwater to the carbon and nitrogen concentrations in the lagoon. As discussed earlier, groundwater is a major source of DIN, but contains very low concentrations of DOC, POC, and PON. However, due to high groundwater discharge rates, particularly during the rainy season, DOC, POC, and PON from groundwater must be included in the flux calculations. Calculating total export of C and N from the lagoon depends largely on the chosen estimate of both groundwater flux and

Table 4a. Particulate organic carbon concentrations (mg L^{-1}) in Celestun Lagoon

	March-April 2003			October 2001	
	Week 1	Week 2	stations #		stations #
North lagoon	1406 (610-1899)	1777 (520-3065)	5	1010 (633-1420)	5
South lagoon	945 (635-1416)	1905 (1252-2444)	4	1098 (916-1379)	4
Adjacent coast	816 (635-996)	1780 (1252-2308)	1	759	1
Lagoon springs	76 (53-135)**		2	357	1
Wells	106 (92- 120)		2	-	-

**Average of both weeks, no significant difference between mean concentrations of week 1 and week 2.

Table 4b. Particulate organic nitrogen concentrations (mg $L^{!1}$) in Celestun Lagoon

	March-April 2003			October 2001	
	Week 1	Week 2	stations #		stations #
North lagoon	232 (88-320)	293 (86-459)	5	161 (98-284)	5
South lagoon	158 (119-214)	323 (223-412)	4	206 (172-260)	4
Adjacent coast	141 (120-162)	318 (220-412)	1	128	1
Lagoon springs	11.0 (b.d.- 26.5)**		2	68	1
Wells	14.6 (11.1-18.1)		2	-	-

**Average of both weeks, no significant difference between mean concentrations of week 1 and week 2.

Table 5. Seasonal estimates of Celestun Lagoon water fluxes (10^4 m^3 d^{-1})

	Rainy Season	Nortes Season	Dry Season
Average groundwater flux into lagoon[a]	65.1	31.0	24.6
Average water flux from lagoon to ocean[a]	64.9	26.1	20.8
Water flux (this study) July 13-17, 2002	35		

a) from Gomez and Herrera-Silveira 2002

total water flux out of the lagoon. Measurements and published estimates for these fluxes are presented in Table 5. Gomez and Herrera-Silveira (2002) calculated these fluxes using salt, silica and water volume mass balance data collected over several years. The water flux measured during the sampling period in July 2002 represents a single sampling period of 5 days, although this flux was measured directly and not calculated by mass balance models. The months of June through October are generally considered to be the rainy season on the Yucatan Peninsula when over 60% of the total annual rainfall occurs. The net water flux out of the lagoon calculated from hydrodynamic measurements made during the July 2002 sampling period is much closer to the published water flux estimate for the dry season (March-May) than for the rainy season. Herrera-Silveira (1996) reported that although the rainy season typically begins in June, lagoon water levels and groundwater flow do not reach peak values until August. It is likely that the discrepancy between the measured net water flux in July 2002 and the published estimate for the rainy season is due to annual variations in the onset or net amount of precipitation during rainy season, and the lag time between the start of heavy rains and the period of highest groundwater flow.

Seasonal C and N Flux

Although calculating seasonal carbon and nitrogen fluxes from a small number of sample sets presents many limitations, this calculation allows us to put some constraints on potential fluxes and also to determine whether or not the lagoon is likely an important source of C and N to the adjacent coastal ocean. We used measurements taken during the March-April 2003 trip (to represent the dry season values, and combined measurements from the October 2001 and July 2002 trips to produce estimates for the rainy season. In order to calculate the average amount of a given nutrient exported from Celestun Lagoon to the adjacent coastal ocean, volume-weighted average concentrations of particulate and dissolved C and N were calculated for the entire lagoon by multiplying the average concentrations in the north and south sections of the lagoon by the volume of water present in each section (18×10^4 m^3, north lagoon; 16×10^4 m^3, south lagoon) (Tables 6a,b and 7a,b). Since there were no measure-ments taken for this study during the nortes season, average values for this season were estimated using both previously published seasonal trends in lagoon dynamics and measured values from this study.

Carbon Flux

Results from the March-April 2003 trip (dry season) did not show any significant short-term variability in DOC concentrations, and DOC values measured during the rainy season in July 2002 were much higher than the dry season values. No DOC measurements exist for the nortes season (November-February), and therefore an average value was calculated from the dry season and rainy season concentrations in order to calculate an annual carbon flux. The assumption that the nortes season DOC values would fall between the high rainy season values and lower dry season values was made because the nortes season represents a mid-point for many biological and physical variables associated with the lagoon such as groundwater discharge, precipitation and temperature, average salinity, and phytoplankton primary productivity (Herrera-Silveira 1996). POC concentrations within the lagoon followed a very different pattern, and the short-term variability in concentration between the two sampling weeks of the March-April 2003 trip was much larger than the differences between the two seasons. POC also did not show any correlations with any previously studied parameters that could be used to predict a seasonal pattern. For this reason, all the POC measurements within the lagoon were averaged to produce a single value with no seasonal fluctuations. There was, however, a large seasonal difference in POC concentrations in the spring water, with the October 2001 spring water containing 5 times more POC than the average for the March-April 2003 trip, or 2.7 times more POC than the

Table 6a. Average carbon concentrations (mg C L^{-1}) used in flux calculations

	Dry Season	Rainy Season	Nortes Season
DOC- lagoon transect	8.86	18.30	13.58
DOC- lagoon springs	1.00	3.25	2.13
POC- lagoon transect	1.350	1.350	1.350
POC- lagoon springs	0.076	0.357	0.217

**All nortes season values are estimates based on field measurements taken during dry and rainy season trips and previously observed seasonal lagoon dynamics.

Table 6b. Carbon input from groundwater and export from the lagoon. All flux values reported in 10^6 g C yr^{-1}

Carbon Flux Type	Dry Season	Rainy Season	Nortes Season	Annual
DOC from groundwater	22.6	323	79.2	425
POC from groundwater	1.72	35.5	8.08	45.3
Total DOC export	169	1817	425	2411
Total POC export	25.9	134	42	202
Total C export	195	1951	468	2613

Slight discrepancies in totals are due to rounding.

Table 7a. Average nitrogen concentrations (mg N L^{-1}) used in flux calculations

	Dry Season	Rainy Season	Nortes Season**
NO_3+ NO_2^- - lagoon transect	0.199	0.0576	0.1283
NO_3+ NO_2^- - lagoon springs	0.633	1.19	0.9115
NH_4^+ - lagoon transect	*	0.0633	*
NH_4^+ - lagoon springs	*	0.163	*
PON- lagoon transect	0.230	0.230	0.230
PON- lagoon springs	0.011	0.068	0.0395

**All nortes season values are estimates based on field measurements taken during dry and rainy season trips and previously observed seasonal lagoon dynamics. * No recent data available

Table 7b. Nitrogen input from groundwater and export from lagoon. All flux values reported in 10^6 g N yr^{-1}

Nitrogen Flux Type	Dry Season	Rainy Season	Nortes Season	Annual
NO_3^-+ NO_2^- from ground water	56.8	283	103	443
PON from ground water	0.988	6.48	4.47	11.9
NH_4^+ from ground water	*	(38.8)	*	*
Total NO_3^-+ NO_2^- export	9.05	13.6	12.2	34.9
Total NH_4^+ export	*	(15.0)	*	*
Total PON export	17.5	54.5	21.9	93.9
Total N export	26.6	68.1 (83.1 w/NH_4^+)	34.1	128.8

Slight discrepancies in totals are due to rounding; *No recent data available

highest single sample measured in March-April 2003. It is likely that this higher POC concentration is not the result of changes in particulate matter within the groundwater itself, but instead is the result of higher groundwater discharge causin oncreased mixing and resuspension of particulate matter at the submarine discharge point. Since a moderate amount of rainfall occurs during the nortes season, an estimated ground water POC value for this season was calculated using an average of the rainy season and dry season measured values. Average annual carbon concentrations were calculated using the average concentration for each season weighted by the number of months per year represented by the season. Carbon export was calculated using published seasonal estimates of net water flux out of the lagoon instead of the flux measurements taken during the July 2002 trip, since the published estimates include peak groundwater flows and are therefore more likely to be representative of the entire rainy season.

Estimates of seasonal carbon fluxes indicate that the majority of total carbon flux out of the lagoon occurs in the dissolved form, with DOC accounting for approximately 92% of the total annual carbon flux out of the lagoon. Although DOC concentrations in groundwater discharging into Celestun are low, groundwater discharge rates into the lagoon are high, and DOC from groundwater accounted for approximately 16% of the total annual carbon export from the lagoon. Therefore, it is likely that natural or anthropogenic changes in ground water DOC concentration would not only affect the biological processes within the lagoon, but could have a significant impact on the adjacent coastal waters as well. POC from ground water represented a much smaller amount of the seasonal total carbon export (0.8% ! 2%), however, groundwater POC accounted for a much larger percentage of total POC in the rainy season than in the dry season (26% to 6.6%, respectively). It appears that while POC in the lagoon did not show a discernable seasonal change due to high short-term variability, a much larger seasonal change was observed in the groundwater POC concentrations than in the groundwater DOC concentrations. Extensive ground water sampling was conducted during the March-April 2003 trip, and no significant differences were found over the tidal and weekly time scales for either DOC or POC concentrations. This indicates that the controlling factors for POC concentrations are different for the ground water than they are for the lagoon. Changes in groundwater POC concentrations may be important to lagoon functioning, because of the large seasonal changes observed in the ground water contribution to total lagoon POC, however, it is unlikely that these changes will have much impact on the adjacent coastal ocean, due to the small percent of total carbon export contributed by POC.

Comparison of the estimated annual carbon export with the carbon inputs to Celestun Lagoon presented in Table 1 shows that approximately 5% of the net annual carbon input to the lagoon is exported to the adjacent coastal ocean. Mass balance calculations indicate that burial and export only account for approximately 7.4% of the net primary productivity of Celestun Lagoon, indicating that there is an extremely high rate of carbon regeneration through heterotrophic activity within the lagoon. According to the calculations presented in Table 6b, approximately 74% of the total annual carbon export occurs during the rainy season, which is a very strong seasonal signal. These estimates are only based on sampling events during two different seasons, which presents an important limitation that may be critical to understanding carbon cycling within the lagoon and coastal ocean. There are currently no available measurements of carbon distribution within the lagoon or groundwater during the nortes season. As mentioned earlier, there is a large peak in primary production during the rainy season, and also a secondary peak during the onset of the nortes season. Measurements of carbon concentrations during this secondary peak would help in the understanding of how carbon fluxes relate to biological cycling within the lagoon and help better constrain annual estimates of carbon flux.

Nitrogen Flux

Nitrogen export was calculated using the same methods described for carbon, and the estimated average concentration and fluxes of DIN species and PON are presented in Table 7a and Table 7b. Due to the limited seasonal data for NH_4^+ distribution in this study, NH_4^+ was not included in the seasonal flux calculations. Nortes season values for all ground water N concentrations and PON in the lagoon were estimated in the same way as C values described in the previous section. NO_3^-+ NO_2^- followed a different seasonal pattern than DOC, and higher NO_3^-+ NO_2^- concentrations in the lagoon were measured during the dry season than during the rainy season. This is a reversal of the pattern reported in several previous studies, where NO_3^-+ NO_2^- concentrations within the lagoon were highest in the rainy season and lowest in the dry season, with the nortes season falling in the middle

(Gomez and Herrera-Silveira 2002; Herrera-Silveira and Comin 1995). A possible explanation for this discrepancy is that primary productivity in the lagoon is much lower in the dry season than in the rainy season, and therefore the October 2001 sampling may have occurred during a period of rapid nitrogen uptake, leading to low nitrogen concentrations within the lagoon. Since the distribution of NO_3^-+ NO_2^- within the lagoon has both high spatial and temporal variability, the estimated seasonal nitrogen export represents a very rough approximation of potential fluxes to the adjacent coastal ocean.

Both NO_3^-, NO_2^-, and NH_4^+ concentrations in ground water appear to be undergoing a long-term increase, possibly due to anthropogenic influences. Herrera-Silveira (1996) reported that the average NO_3^- concentrations in Celestun ground water between 1989-1990 were 0.28, 0.84, and 0.21 mg-N L^{-1} for the dry, rainy, and nortes seasons, respectively. Quarterly ground water sampling conducted between 1999 and 2002 resulted in a range of NO_3^-concentrations between 0.84-1.96 mg-N L^{-1} (Herrera-Silveira et al. 2004), and the results from this study are closer to this range. NH_4^+ concentrations in ground water measured monthly between 1989-1990 averaged about 0.014 mg-N L^{-1}, with no detectable seasonal variations (Herrera-Silveira 1996), while the range reported for the 1999-2002 quarterly sampling study was 2.8-28 μg-N L^{-1} (Herrera-Silveira et al. 2004). During the October 2001 sampling trip, NH_4^+ concentrations in Celestun ground water ranged from 0.096 to 0.230 mg-N L^{-1}, up to 8 times higher than the previously reported high value. These large changes in nitrogen inputs from ground water may have already caused changes in nitrogen cycling within the lagoon and export to the adjacent coastal ocean. In order produce accurate estimates of N export, it will be necessary to repeat some of the previous nutrient-distribution studies in Celestun so that the data will reflect long term changes in nutrient inputs and concentrations.

Estimates of seasonal nitrogen fluxes indicate that unlike carbon, the majority of total nitrogen is exported in the particulate form. The ground water contains low concentrations of PON, and despite high ground water fluxes, only 13% of the annual total PON flux can be attributed to ground water contributions, suggesting that the majority of PON is either created within the lagoon or in the surrounding mangrove forest and brought into the lagoon through tidal action or local surface run-off. Annually, PON contributes approximately 73% of the total nitrogen export (not considering NH_4^+). Using the estimates for the rainy season and including the NH_4^+ flux, PON contributes 65% of the total nitrogen flux to the coast for the season, which is still highly significant. Results from the October 2001 sampling trip show that NH_4^+ may be an equal or slightly more important source of nitrogen from the lagoon to the adjacent coastal ocean than NO_3^- + NO_2^-. Therefore, the annual fluxes presented here, which do not include NH_4^+, represent low estimates of total nitrogen flux out of the lagoon. The majority of dissolved nitrogen that is discharged in the ground water is taken up in the lagoon and not exported to the coastal ocean. On an annual basis, these calculations suggest that less than 10% of the NO_3^- + NO_2^- that enters the lagoon through ground water is exported from the lagoon. For October 2001, about 40% of the NH_4^+ from ground water was taken up within the lagoon, and 60% was exported to the coastal ocean.

CONCLUSIONS

Measurements of dissolved and particulate forms of carbon and nitrogen in Celestun lagoon combined with net water flux calculations indicate that both carbon and nitrogen are exported from the lagoon to the adjacent coastal ocean. Dissolved organic carbon accounts for approximately 92% of the total carbon flux out of the lagoon, indicating that organic carbon in particulate form is not very important to the overall carbon export budget for the lagoon. The calculated annual carbon export from Celestun to the adjacent coastal ocean is $2{,}613\times 10^6$ g C yr^{-1}, which is approximately 0.1% of the reported DOC flux from the Mississippi and Atchafalaya Rivers to the Gulf of Mexico (Malcom and Durum 1976). Total carbon export from Celestun lagoons accounts for approximately 5% of the net primary productivity of the lagoon and surrounding mangrove forest. Although the total carbon export from the lagoon is negligible when compared to inputs from large rivers in the northern Gulf of Mexico, the Yucatan Peninsula has almost no river discharge to the coast due to the karstic topography. Therefore, export from the lagoon may be a highly significant source of organic carbon to the adjacent coastal ocean of the Yucatan Peninsula. In contrast to carbon export, the majority of nitrogen exported from the lagoon was in the particulate form, with PON accounting for 65-85% of the total nitrogen export. Due to recent increases in ground water concentrations of NO_3^- and NH_4^+, coupled with high

spatial and temporal variability in nitrogen concentrations throughout the lagoon, the errors in seasonal estimates of nitrogen export are probably much higher than those for estimates of carbon export. Up to 90% of the nitrogen entering the lagoon through ground water appears to be recycled within the lagoon, and although Celestun is a strong nitrogen sink, calculations indicate that small amount of the total nitrogen entering the lagoon is exported to the adjacent coastal ocean. The total annual nitrogen export from Celestun is approximately 0.06% of the total nitrate input of the Mississippi River to the Gulf of Mexico calculated by Antweiler et al. (1996).

Celestun lagoon and the surrounding mangrove forest export particulate and dissolved nitrogen and organic carbon to the adjacent coastal ocean, and the majority of this export occurs during the rainy season, primarily due to increased ground water flow and net water flux out of the lagoon. Due to the significant export of dissolved and particulate material out of the lagoon, changes in lagoon functioning, such as the increasing levels of various nitrogen species in the ground water detected in this and other recent studies, will most likely directly affect the supply of nutrients to the coastal ocean. Therefore, increased monitoring and protection efforts are necessary to protect Celestun and the adjacent coastal area, both of which provide important fishing areas for the coastal population, as well as significant income from the tourism industry.

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REFERENCES

Alongi, D. 2002. Present state and future of the world's mangrove forests. Environmental Conservation 29(3): 331-349.

Antweiler, R., Goolsby, D. and Taylor, H. 1996. Nutrients in the Mississippi River. Pages 73-86, In: Meade, R. (Editor) Contaminants of the Mississippi River, 1987-92. US Geological Survey Circular 1133.

Davis, S., Childers, D., Day, J., Rudnick, D. and Sklar, F. 2003. Factors affecting the concentration and flux of materials in two southern Everglades mangrove wetlands. Marine Ecology Progress Series 253: 85-96.

Dittmar, T. and Lara, R. 2001. Do mangroves rather than rivers provide nutrients to coastal enviroments south of the Amazon River? Evidence from long-term flux measurements. Marine Ecology Progress Series 213: 67-77.

Eagle, M. 2002. Tracing organic matter sources in mangrove estuaries utilizing $^{*13}C$, $^{*15}N$, and C/N ratios. Master's Thesis, Stanford University, Stanford, USA.

Field, C. 1995. Impact of expected climate change on mangroves. Hydrobiologia 295: 75-81.

Gomez, I. and Herrera-Silveira, J. 2002. Celestun Lagoon, Yucatan (a revision). LOICZ Biogeochemical Modeling Node- electronic resource (http://data.ecology.su.se/mnode/index.htm)

Gonneea, M., Paytan, A., and Herrera-Silveira, J. 2004. Tracing organic matter sources and carbon burial in mangrove sediments over the past 200 years. Estuarine, Coastal and Shelf Science 61: 211-227.

Herrera-Silveira, J. 1994. Phytoplankton productivity and submerged macrophytes biomass variations in a tropical coastal lagoon with groundwater discharge. Vie Milieu 44(3-4): 257-266.

Herrera-Silveira J. 1996. Salinity and nutrients in a tropical coastal lagoon with groundwater discharges to the Gulf of Mexico. Hydrobiologia 321: 165-176.

Herrera-Silveira J. 1998. Nutrient-phytoplankton production relationship in a groundwater influenced tropical coastal lagoon. Aquatic Ecosystem Health and Management 1(3-4): 353-372.

Herrera-Silveira, J. and Comin, F. 1995. Nutrient fluxes in a tropical coastal lagoon. Ophelia 42: 127-146.

Herrera-Silveira, J., Ramirez, J., and Zaldivar, A. 1998. Overview and characterization of the hydrology and primary producers communities of selected coastal lagoons of Yucatan, Mexico. Aquatic Ecosystem and Health Management 1(3-4): 353-372.

Herrera-Silveira, J., Young, M., Aranda, N., Troccoli, L., and Paytan, A. 2005. Spring water quality and evidence of human impacts in coastal lagoons of the Yucatan Peninsula, Mexico. in review.

Lee, S. 1995. Mangrove outwelling: a review. Hydrobiologia 295: 203-212.

Malcom, R. and Durum, W. 1976. Organic Carbon and Nitrogen Concentration and Annual Carbon Load of Six Selected Rivers in the United states. US Geological Survey Water-Supply Paper 1817F. 21 pages.

Mumby, P., Edwards, A., Arias-Gonzales, J., Lindeman, K., Blackwell, P., Gall, A., Gorczynska, M., Harborne, A., Pescod, C., Renken, H., Wabnitz, C. and Llewellyn, G.

2004. Mangroves enhance the biomass of coral reef fish communities in the Caribbean. Nature 427: 533-536.

Odum, W. and Heald, E. 1975. The detritus-based food web of an estuarine mangrove community. Pages 265-286, In: Cronin, L. (Editor) Estuarine Research. Academic Press, New York.

Spalding, M., Blasco, F. and Field, C. 1997. World Mangrove Atlas. International Society of Mangrove Ecosystems. Okinawa, Japan. 178 pages.

Twilley, R. 1985. The exchange of organic carbon in basin mangrove forests in a southwest Florida estuary. Estuarine, Coastal and Shelf Science 20: 543-557.

Twilley, R. 1988. Coupling of mangroves to the productivity of estuarine and coastal waters. Pages 155-180, In: Jansson, B. (Editor) Coastal-Offshore Ecosystem Interactions. Springer-Verlag, Berlin.

Valiela, I., Bowen, J., and York, J. 2001. Mangrove forests: one of the world's threatened major tropical environments. BioScience 51(10): 807-815.

Yanez-Arancibia, A., Lara-Domingues, A., Zapata, G. and Arriaga, E. 1993. Mangroves of Mexico. Pages 3-4, In: Lacerda, L. and Field, C. (Editors) Proceedings, Workshop on Conservation and Sustainable Utilization of Mangroves in Latin America and Africa Regions. International Society for Mangrove Ecosystems, Okinanwa,