

1995

## **Nitrogen Fluxes in Mangrove Sediments and Their Coupling With Aquatic Primary Productivity in Terminos Lagoon, Campeche, Mexico.**

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NITROGEN FLUXES IN MANGROVE SEDIMENTS AND THEIR COUPLING  
WITH AQUATIC PRIMARY PRODUCTIVITY IN TERMINOS LAGOON,  
CAMPECHE, MEXICO

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

in

The Department of Oceanography and Coastal Sciences

by  
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May 1995



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"..Por que poesía es el ingrediente indispensable para captar la vida y transformarla, y para mi, Ciudad del Carmen y su entorno (Laguna de Términos) son poesía que necesita rescatarse..."

Cd. Del Carmen, Campeche, Mexico  
February 1991

Dedicado a mis padres, Martha Monroy y Refugio Rivera con todo mi amor y cariño, y a mis hermanos, Oscar y Jaime, por su apoyo y constante aliciente

## ACKNOWLEDGMENTS

I would like to thank members of my committee: John Day, Robert Twilley, James Grace, Barry Moser, and Irving Mendelssohn for their guidance and support throughout my research program. I want to acknowledge my outside committee member, Kenneth Damann, for his interest in my research, and Robert Gambrell for his valuable comments and criticisms to my work. My deep gratitude to my co-major professors, Robert Twilley and John Day, for giving me the opportunity to pursue and achieve one of the most important goals in my life.

Several people contributed to different phases of my research. I received important support for logistics and facilities from personnel at the Sede "El Carmen" - Instituto de Ciencias del Mar y Limnología of the Universidad Nacional Autónoma de México and the EPOMEX program of the Universidad Autónoma de Campeche. In particular, Francisco Vera-Herrera, Jose Luis Rojas-Galaviz, Alejandro Yañez-Arancibia, and Armando Ortega provided invaluable assistance to my field program. Carlos Coronado-Molina, Hernán Alvarez-Guillén, María del Carmen Ramírez, Lol-Ha, Ronald Boustany, Juan Luis Casanova, Jose Guadalupe Aguilar-Sosa, Pedro Juan Lopez, Arturo Toledano, Jorge Reda, Andrés Reda, Alfonso Martinez, Richard Day, Megan Jones, and John Rybzick provided invaluable assistance in the laboratory and the field. A number of students from the Universidad Autónoma del Carmen and Universidad Autónoma Metropolitana-Xochimilco also assisted in the field.

Special thanks to R. L. Mulvaney for his help in analyzing the  $^{15}\text{N}$  gas samples, and my gratitude to Jim Lynch, Washington Cárdenas, Claudia Muñoz, Shawn Theriot, and Nicole Hairston from the University of Southwestern Louisiana for their skilled and untiring help in preparing samples for  $^{15}\text{N}$  analysis. I thank my friend Nicolás Orlayneta for his poetry and comments about science and literature during my stay in Cd. del Carmen. They gave me a different perspective about myself.

And I thank my family and Megan Jones, whose love and understanding help me to make a reality one of my dreams.

This study was funded by the Program in Science and Technology Cooperation Office of the Science Advisor, U. S. Agency for International Development (Grant DPE-5542-G-SS-8011-00), the U. S. Man and the Biosphere Program, and the International Union for the Conservation of Nature.

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## ABSTRACT

The significance of nitrogen transformations in mangrove sediments to the exchange of nitrogen in mangrove forests and influence on aquatic primary productivity was studied between 1990-1992 in Terminos Lagoon, Mexico. Fluxes of dissolved inorganic and organic nitrogen, particulate nitrogen (PN), and total suspended sediments (TSS) were measured in a fringe mangrove forest using the flume technique. There was a net import of  $\text{NH}_4^+$  and  $\text{NO}_2^- + \text{NO}_3^-$  from the creek and basin forest, while particulate (PN) and dissolved organic nitrogen were exported to the creek and basin forest. There was a net import of TSS to the fringe forest from both the creek and basin forests. Rates of direct and coupled denitrification were measured using  $^{15}\text{N}$  isotope techniques in intact sediment cores from fringe, basin, and riverine mangroves. The highest direct rates were measured in the riverine mangrove ( $221 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) followed by the fringe mangrove ( $9.4 \mu\text{mol m}^{-2} \text{h}^{-1}$ ); while rates in the basin mangrove ranged from 1.9 to  $4.5 \mu\text{mol m}^{-2} \text{h}^{-1}$ . Direct denitrification rates in sediment cores from the fringe mangrove enriched with  $100 \mu\text{mol } ^{15}\text{N-KNO}_3^-$  were  $<0.7$  and from 4.5 to  $7.7 \mu\text{mol m}^{-2} \text{h}^{-1}$  in cores enriched with  $200 \mu\text{mol}$ . The lack of  $^{15}\text{N}$  production in cores from the fringe, basin, and riverine mangroves amended with  $\leq 200 \mu\text{mol } ^{15}\text{NH}_4^+/\text{core}$  and the high recovery of  $^{15}\text{N}$  in the sediment indicate that coupled nitrification-denitrification was not an important nitrogen transformation. Most of the applied  $^{15}\text{N}$  was recovered as particulate nitrogen in the sediment. Primary production in a tidal creek bordered by mangrove forest and in open waters of Terminos Lagoon was stimulated more than 50% throughout the year by additions of standing surface water (1 and 5 mL) from inside a fringe mangrove forest. This study supports the evidence that 1) mangroves are efficient at recycling and retaining nitrogen throughout several processes that reduce export and 2) mangroves are nitrogen transformers importing dissolved inorganic nitrogen and exporting organic nitrogen which could increase primary productivity in adjacent coastal waters.

## CHAPTER 1

### INTRODUCTION

Mangrove forests are among the most productive coastal ecosystems of the world (Lugo et al. 1988, Clough 1992). They are located along tropical and subtropical coastlines between 29°N and 25°S (Tomlinson 1986). According to the World Resources Institute (1986) there are about 240,000 km<sup>2</sup> of mangroves forests along subtropical and tropical coasts of the world. Despite their large extension and the recognition of mangroves as valuable coastal resources, information about their ecological function is still scarce (Robertson 1992). In particular, there has been limited work on the significance of mangrove ecosystems to the productivity and nutrient cycling of estuarine and coastal waters (Twilley 1988, Lugo et al. 1990).

In tropical and subtropical estuaries, phytoplankton production rates can be higher than in temperate estuaries. These high production rates are often associated with patterns of river flow (Flores-Verdugo et al. 1987, Rojas Galaviz et al. 1993) and the presence of large extensions of mangrove forests (Ricard 1984, Robertson & Blaber 1992). For example, Prakash & Rashid (1969) found that significant input of terrigenous humic material through land drainage resulted in nutrient enrichment of coastal waters and high phytoplankton production. Thus, phytoplankton primary productivity rates in tropical coastal lagoons is enhanced by adjacent mangrove forests (Prakash 1971, Ricard 1984, Morrel & Corredor 1993). These coastal systems receive nutrients, litter, and organic matter from mangrove forests through the action of tidal inundation and river discharge, which influences phytoplankton and bacterial secondary production. Yet, it is not clear how nitrogen enriched humic substances exported from mangroves forests enhance aquatic primary productivity.

Nitrogen is generally considered a limiting nutrient in tropical and temperate wetlands (Nixon 1981). Due to the strong dependency of wetlands on hydrologic conditions (Gosselink & Turner 1978), processes such as slow oxygen diffusion combined with an oxygen demand established from a high concentration of organic matter in these systems create ideal conditions for the anaerobic pathways of the nitrogen cycle (Howard-Williams et al. 1993). Denitrification, the dissimilatory reduction of NO<sub>3</sub><sup>-</sup> to gaseous products including NO, N<sub>2</sub>O and N<sub>2</sub> (Knowles 1982), is an important nitrogen



transformation under anaerobic conditions that accounts for 15-70% of the sediment-water flux in estuarine and coastal sediments (Seitzinger 1988). In combination with nitrification, the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ , coupled nitrification-denitrification (Jenkins & Kemp 1984) can be an important nitrogen sink in the nitrogen budget of coastal sediments.

Information on the nitrogen cycle in mangrove ecosystems is very limited (Lugo 1990, Alongi & Sasekumar 1992). Although exchange studies between mangrove forest and coastal waters have shown that these forested wetlands export detritus (Twilley 1988), the effects of this exchange on nitrogen transformations inside the forest are not clear. Denitrification studies from eutrophic mangrove systems show that mangroves are efficient in removing dissolved inorganic nitrogen (i. e.  $\text{NO}_3^-$ ), but it is not clear if this denitrification capacity is a general property of mangroves in non-polluted regions. Moreover, different types of mangroves may have different denitrification capacities due to the diverse hydrological factors and geomorphological conditions that determine their specific function and structure (Cintron-Molero & Schaeffer-Novelli 1992). Thus, the role of mangroves as nitrogen sinks under eutrophic conditions and sources of detritus under natural conditions create an apparent contradiction that needs to be addressed (Tiedje 1988, Twilley 1988). Mitsch & Gosselink (1993) showed that wetlands can be a sink of inorganic nutrients and a source of organic nutrients. Apparently, this transformation is a mechanism that explains the dual role of mangroves as sinks and sources. However, there are no comprehensive studies relating the exchange of nitrogen at the mangrove-estuary boundary to denitrification inside the mangrove forest. This type of study would help to determine the temporal and spatial role of mangroves as sink, sources or transformers of nitrogen.

In this dissertation, I examined some transformations in the nitrogen cycle of mangrove forests to evaluate the role of these wetlands as sinks, sources, and transformers of nitrogen. I also examined the influence of nutrients exported from mangrove forests on the aquatic primary productivity of adjacent estuarine waters. I addressed several specific questions. First, do mangroves import dissolved inorganic nitrogen or dissolved or particulate organic nitrogen? That is, is there a net import of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ? I addressed this question by measuring nitrogen exchange at the boundary between a tidal creek and a

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fringe mangrove forest throughout a 17-month period using the flume technique (Chapter 2). Second, what is the effect of exported water overlying mangrove sediments on the aquatic primary productivity of adjacent estuarine waters? Also, is there a difference in net aquatic primary productivity between waters adjacent to mangrove forest and those far away ( $> 1$  km)? Different volumes of water collected inside a fringe mangrove forest were added to estuarine waters and net productivity measured in different seasons. Simultaneously, aquatic primary productivity was measured in two locations. One was located in the middle of a tidal creek surrounded by mangrove forests, and the other in open waters of the estuary (Chapter 3).

The final question addressed was, what is the importance of denitrification as a nitrogen sink in mangrove forests and how does it relate to nitrogen exchange at the tidal creek-mangrove boundary? Particularly, is there a difference in denitrification rates among riverine, fringe, and basin forests? What is the dominant type of denitrification, coupled nitrification-denitrification or direct denitrification? Also, what are the dominant processes and variables in the nitrogen cycle of mangrove forests? Rates of denitrification were measured using  $^{15}\text{N}$  techniques in different seasons in fringe, basin, and riverine forests (Chapter 4 and 5). Finally, based on these results a conceptual model is proposed where important variables and nitrogen transformations are related to describe nitrogen cycling in mangrove ecosystems (Chapter 6).

Chapter 2 was accepted for publication and is in its second revision in the journal *Estuarine, Coastal and Shelf Science*. Chapter 3, 4, and 5 will be submitted for publication shortly.

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## CHAPTER 2

### FLUX OF NITROGEN AND SEDIMENT IN A FRINGE MANGROVE FOREST IN TERMINOS LAGOON, MEXICO\*

#### Introduction

Nutrient exchange between mangroves and nearshore waters is poorly understood given the difficulty of measuring nutrient fluxes in coastal wetlands (e.g Boto & Robertson, 1990; Wattayakorn *et al.*, 1990). Although some studies in mangrove forests have shown a net export of detritus (Heald, 1969; Boto & Bunt, 1981a; Twilley, 1985; Flores-Verdugo *et al.*, 1987) and a negligible net exchange of nitrogen (Boto & Wellington, 1988), much work is necessary before we can determine the role of mangroves in nutrient cycling in tropical estuarine ecosystems. Furthermore, the flux of nutrients may vary among different types of mangroves such as riverine, fringe, and basin forests (Twilley, 1988). These differences among mangrove types may be related to the influence of geomorphology and hydrodynamics on the exchange of materials with estuarine and coastal waters (Thom, 1982; Lugo *et al.*, 1988; Twilley, 1988).

The role of mangroves in coastal nitrogen cycling may be conceptually similar to that of salt marsh ecosystems. Studies have indicated that salt marsh-estuarine systems act as nitrogen transformers, importing dissolved inorganic forms of nitrogen and exporting dissolved and particulate, reduced forms (Nixon, 1980; Valiela, 1983; Whiting *et al.*, 1989). However, generalizations are still limited since the exchange of nitrogen between a particular marsh and adjacent estuary is related to several factors such as geographic location, climate, geomorphology, hydrology, and age of development (Valiela, 1983). Since mangroves are forested wetlands located in the intertidal zone of the tropics, the forest structure and high annual temperatures may alter the factors which are known to influence nutrient fluxes in temperate salt marshes (Nixon, 1980). Thus, care must be taken in extrapolating ideas about nutrient fluxes obtained from temperate tidal marshes to tropical tidal forests (Boto & Wellington, 1984; Alongi, 1990).

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Results from different flux studies of intertidal wetlands may vary depending on the method used to calculate nutrient exchange. Initial studies of fluxes were often performed at the mouth of a tidal creek connecting small marsh drainage basins to estuaries (Axelrad *et al.*, 1976; Stevenson *et al.*, 1977; Daly & Mathieson, 1981; Stern *et al.*, 1986; Whiting *et al.*, 1987). This experimental approach integrates processes in both the intertidal marsh and the tidal creek, making specific conclusions about the functions of wetlands difficult (Childers & Day, 1988). Direct measurements of fluxes from specific zones of intertidal marshes have been accomplished during the last 15 years using the flume methodology (Wolaver *et al.*, 1980; Wolaver & Zieman, 1983; Wolaver *et al.*, 1983; Chalmers *et al.*, 1985; Bowden, 1986; Wolaver & Spurrier, 1988a,b ; Whiting, *et al.* 1989; Childers & Day, 1990a,b). This method measures nutrient fluxes across the marsh boundary using a flume constructed along the intertidal zone of marsh surface (Wolaver *et al.*, 1983). A modification of the flume technique was developed by Childers & Day (1988) to measure fluxes in infrequently inundated microtidal marshes. Based on these flume studies, most salt marshes appear to import dissolved inorganic nutrients and organic carbon, along with total nitrogen and total phosphorus. In most cases particulate nutrients are exported, while no discernible pattern exists for dissolved organic nitrogen.

Studies of exchange in mangrove ecosystems have focused on the outwelling of nutrients to nearshore waters that link processes in forest, tidal creek and coastal boundary systems. Most of the available information on nutrient fluxes in mangrove ecosystems has been determined using an "Eulerian" (Imberger *et al.*, 1983) analysis of flux in tidal creeks (Boto & Bunt, 1981b; Boto & Bunt, 1982; Woodroffe, 1985d; Boto & Wellington, 1988; Wattayakorn *et al.*, 1990). Results of these nutrient flux studies have been particularly confusing because of the combination of processes both within the forest and adjacent waters. Twilley (1985) and Woodroffe (1985a, d) were the first to use modified hypsometric techniques to study exchange of detritus directly at the boundary of mangrove forests and coastal waters; reducing ambiguities associated with processes in the tidal creek. But neither of these studies included nutrient exchange. Furthermore, to date no studies have used the flume methodology to specifically quantify material flux at the mangrove-

tidal creek interface. In this study we used the flume technique to estimate fluxes of organic and inorganic nitrogen and total suspended sediments in a fringe mangrove forest in Terminos Lagoon, Mexico. We assessed (1) the role of the mangrove forest as a sink or source of nitrogen, (2) the seasonality of nitrogen fluxes, and (3) the total sediment exchange. We hypothesized that the fringe mangrove in Estero Pargo transforms dissolved inorganic nitrogen into particulate and dissolved organic nitrogen that is exported into an adjacent tidal creek throughout the year.

### Study Area

Terminos Lagoon (18° 40' N, 91° 30' W) is a large (approximately 1800 km<sup>2</sup>), shallow (mean depth 3.5 m) coastal lagoon located in the southwestern section of the Yucatan Peninsula in the state of Campeche, Mexico (Fig. 2-1). It is connected to the Gulf of Mexico via two passes, one at each end of Isla del Carmen, which is a barrier island that separates the lagoon from the open gulf. Prevailing easterly winds create a net east-to-west circulation of coastal waters in the lagoon (Mancilla & Vargas, 1980; Graham *et al.*, 1981). The climate of the area is tropical with annual average air temperatures ranging from 18°C to 36°C. Tides are mixed diurnal with a mean tidal range of about 0.5 m. The Candelaria, Chumpán and Palizada rivers are major sources of freshwater discharge (Phleger and Ayala-Castañares, 1971). Average annual precipitation (1680 mm yr<sup>-1</sup>) is seasonal, with a rainy season from June to October, which is associated with frequent tropical convectional rains. The winter storm, or "Norte", season is from November to February, with strong north winds and frontal rains. The dry season is from March to June. Peak river discharge occurs in the latter months of the rainy season from September to November. The lagoon is bordered almost completely by extensive mangrove swamps. Three species are dominant: *Rhizophora mangle* L. (red mangrove), *Avicenia germinans* L. (black mangrove), and *Laguncularia racemosa* Gaertn. f. (white mangrove) (Day *et al.*, 1987). Details of the physical and biological processes in Terminos Lagoon are included in summaries by Phleger & Ayala-Castañares (1971), Yañez-Arancibia (1987), Yañez-Arancibia & Day (1982), and Yañez-Arancibia *et al.* (1988).

The flume study was conducted in a fringe mangrove forest along Estero Pargo (Fig. 2-1), a tidal creek located on the lagoon side of the barrier island

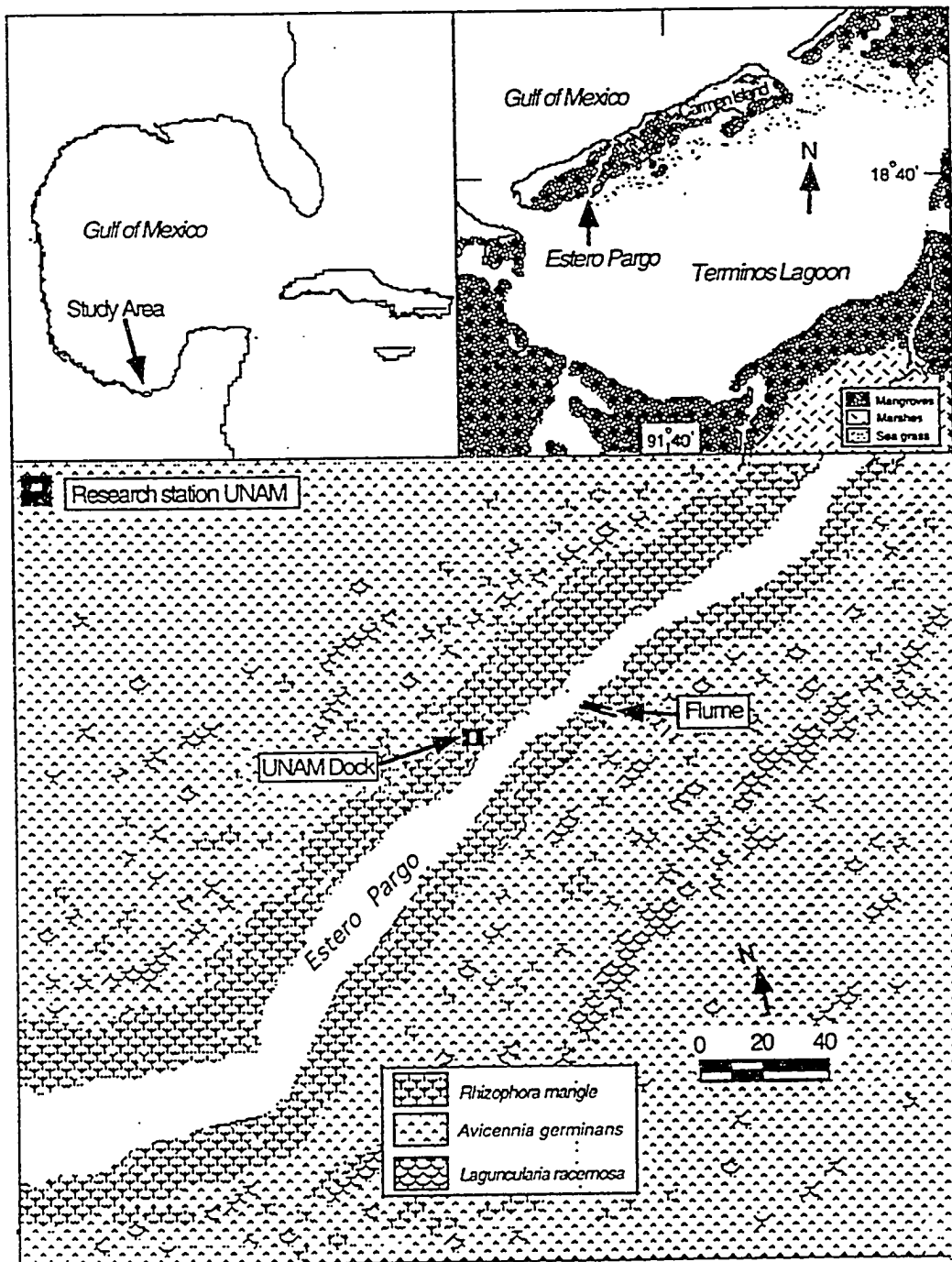


Figure 2-1. Map of Terminos Lagoon showing flume location in Estero Pargo.



Isla del Carmen. Estero Pargo is 5.9 km long with a 12.9 km perimeter. The width of the tidal channel ranges from 14 to 251 m and averages 80 m (Ley-Lou, 1985). The width of the tidal channel at the site of the flume is 14 m. The mangroves adjacent to the tidal creek are characteristic of fringe forests with regular tidal inundation, while the inland mangroves are characteristic of basin forests which are infrequently flooded (Lugo & Snedaker, 1974; Day *et al.*, 1982; Lynch *et al.*, 1989). Soil salinities in the fringe forest range from 30 to 35 ‰ and are controlled by the seasonal salinity of creek waters in Estero Pargo (Day *et al.*, 1987).

## Materials and Methods

### Field sampling

A flume similar to that of Childers & Day (1988) was constructed in a fringe mangrove forest along Estero Pargo dominated by *R. mangle* and located approximately 1.5 km from Terminos Lagoon. The flume extended 12 m into the forest from the edge of the tidal creek and was open at each end (Fig. 2-2) at the tidal creek and forest ends of the flume. The flume nearly transversed the width of the fringe forest; about 3 m beyond the forest end of the flume was a transition to a basin forest dominated by *A. germinans*. The flume walls consisted of 0.80 high x 5.0 m long sections of flexible plastic sheets forming two parallel vertical walls 2 m apart (Fig. 2-2). The flexibility of the plastic sheets facilitated installation throughout the prop roots, with minimum disturbance to prop roots while assuring parallel placement of the walls. The walls prevented lateral water movement as the flood tide inundated the forest without altering normal flow. Boardwalks on either side of the panels prevented disturbance of the forest surface during sampling. The plastic sheets were removed following each tidal analysis to prevent long term effects such as shading, edge scouring, and wrack accumulation.

Nitrogen exchange was measured during tidal inundation at the mangrove-tidal creek interface (Fig. 2-2A, B). Tidal waters in the flume were sampled during a full tidal cycle in August, September, October, November, and December 1990, and February, April, June, and July 1991. Two and three consecutive tides were sampled in August 1991 and January 1992, respectively. Duplicate water samples were taken simultaneously and temperature measured at each end of the flume (tidal creek and forest ends,

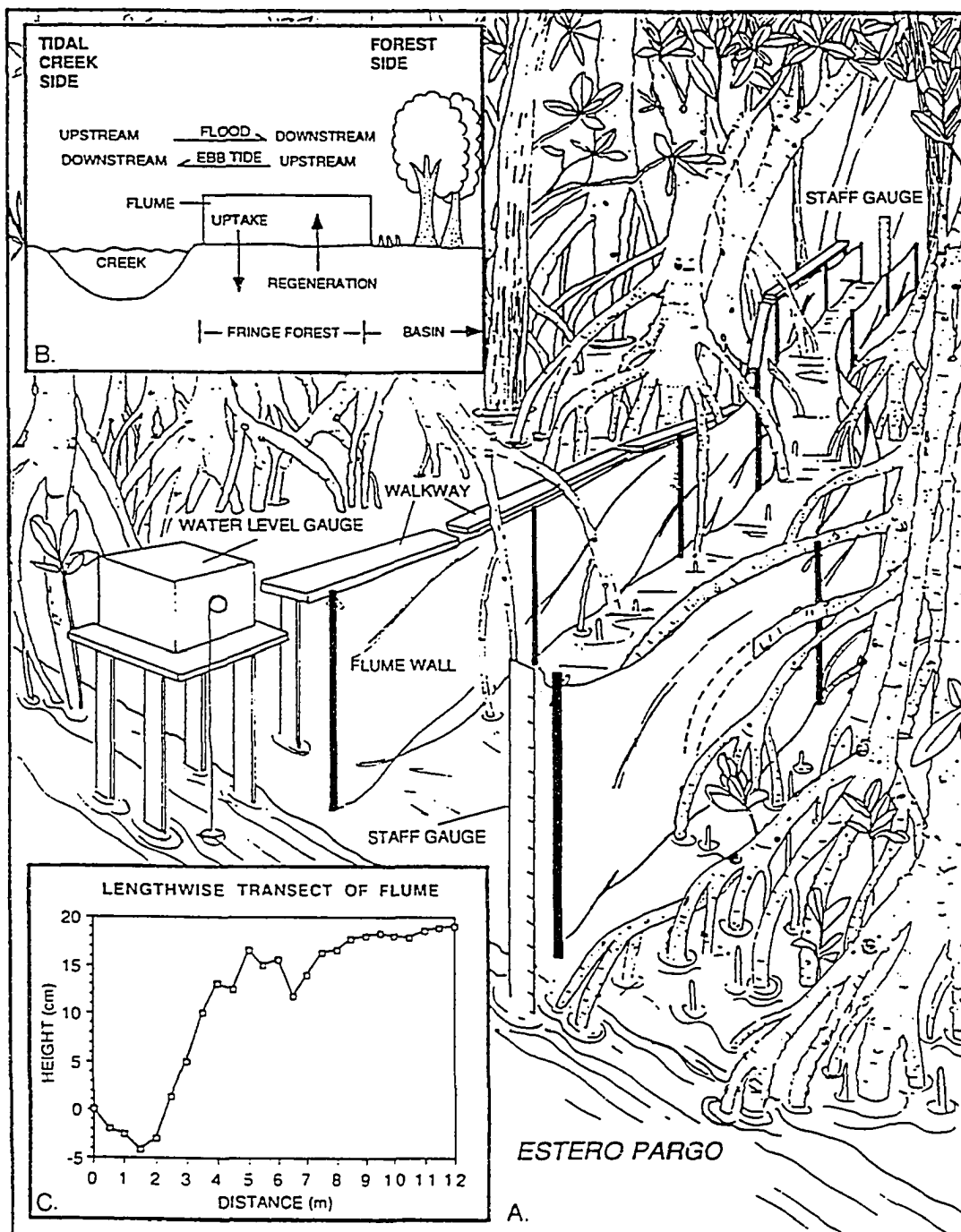


Figure 2-2. (A) Conceptual drawing of flume on mangrove surface. (B) Schematic diagram of calculation terms to determine instantaneous fluxes of materials in and out of the flume. (C) Microtopographic profile along the flume.

Fig. 2-2B ) every 2 h during a tide (ca. 6 samples each on the flood tide and ebb tide) following the approach of Childers & Day (1988) . Water was drawn from 10 cm below the surface of the tidal water column with a hand-operated PVC Nalgene® vacuum pump. Water levels were continuously monitored with a Richards-Type water level recorder (Weathertronics Inc. Model 6510) and stage heights were noted every 2 h at two staff gauges on each end of the flume. Microtopography within the flume (Fig. 2-2C) was used to calculate changes in water volume during a tide. Fluxes were calculated from estimates of changes in water volume together with measures of nutrient concentration at each end of the flume (Wolaver *et al*, 1985; Childers and Day, 1988).

**Laboratory analyses.** Samples were immediately transported back to the laboratory for processing and analysis of ammonium ( $\text{NH}_4^+$ ), nitrate + nitrite ( $\text{NO}_2^- + \text{NO}_3^-$ ), dissolved organic nitrogen (DON), particulate nitrogen (PN), and salinity. Total suspended sediment concentrations (TSS) were determined on replicate water samples filtered through pre-ashed, preweighed Whatman® GF-F glass fiber filters. Filters were dried and weighed and TSS calculated. After weighing, filters were stored in a vacuum desiccator until PN and PC analyses. PN and PC concentrations were determined with a Perkin-Elmer 240 C elemental analyzer within two months of collection. Portions of each water sample were filtered and analyzed immediately for ammonium concentrations with the phenolhypochlorite method (Solórzano, 1969). Nitrate + nitrite was determined by cadmium reduction and autoanalysis of nitrite (Strickland & Parsons, 1972). Dissolved organic nitrogen was determined by persulfate oxidation on a filtered sample, (D'Elia *et al.*, 1977; Valderrama, 1981) followed by nitrate + nitrite analysis. Salinity was determined with a hand-held refractometer (Atago® 02949-10).

**Flux calculations and statistical analyses.** We used a modification of the flume technique to calculate fluxes of nutrients and suspended sediments (Childers & Day, 1988). We modified the formula of Childers and Day (1988; p. 487) to obtain net areal flux as indicated below:

$$\text{Net areal flux (mg m}^{-2}\text{h}^{-1}\text{)} = \frac{(\text{total flux})_{\text{upstream}} - (\text{total flux})_{\text{downstream}}}{(\text{flume area} \times \text{total time})}$$

Our formula is based on a constant area of the flume that is inundated for the duration of the tide, in contrast to the time-weighted area of inundation in the formula of Childers & Day (length should be replaced by area in their formula to express the flux in  $\text{mg m}^{-2} \text{h}^{-1}$ ). They calculated fluxes when the flume was not completely inundated since the flooding regime is irregular in coastal Louisiana. They also assumed that when export occurred from the inland end of the flume during flood tide, materials were transported to the bay, since marshes in Louisiana are frequently intersected by open waters. In contrast, fringe mangroves in Estero Pargo are regularly flooded during most of the year, except during the dry season, and flood tide waters exiting the inland end of the flume may enter the basin mangroves, depending on tidal amplitude. We calculated fluxes only when there was water at both ends of the flume (90 % of the time on average for all sampling dates). Net fluxes were obtained by adding flood (import rates, positive) and ebb (export rates, negative) fluxes for each tide.

Uptake and regeneration of nutrients within the flume were assumed to control the magnitude and direction of net export and import rates. Concentration changes within the flume result from sediment-water and prop root-water interactions as well as water column processes. Nutrients released during flood tide enter the basin forest, while nutrients released during ebb tide represent nutrient export to the tidal creek. Net uptake in the flume represents nutrient import to the fringe forest from basin forest during ebb tide, or import from the tidal creek during flood tide. As shown in Figure 2B, upstream nutrient content (mg) measured at the tidal creek end of flume on the flood tide (half-tide) and the forest end on the ebb tide (half-tide) are considered "before treatment" samples. Downstream concentrations, as sample values from the other end of the flume, are "after treatment" measurements (Childers & Day, 1988). The fringe forest within the flume is considered as a "treatment" since the nutrient concentrations in the water mass entering the flume could be modified by regeneration and uptake within the flume.

To test if fluxes were significantly different from zero within each individual full-tide, nutrient content (mg) was pooled into upstream and downstream values and compared using a paired t-test (JMP® SAS Institute, 1989). In addition, a binomial test was performed to evaluate if the observed number of rejections

from the t-tests was significant. Nutrient content for ebb and flood half-tides were also tested for significance with a paired t-test since water masses flowing through a flume during each half-tide might be independent.

To evaluate if changes in nutrient content (mg) were time dependent during a tide (flood vs ebb), or if location in the flume (tidal creek end vs forest end) had an effect, we used a split-plot design. For this analysis, all the nutrient contents (mg) passing across each end of the flume for all sampling dates (360 observations) were used in a general linear model (GLM, SAS Institute, 1989). In this analysis, we included the following factors in the main plot: season ("Norte", rainy, dry), month, tide (flood and ebb) and the interaction month\*tide. In the subplot we tested flume end (tidal creek and basin forest) and its interaction with month and tide. After performing the analysis, linear contrasts were used to evaluate differences between treatments.

Annual nutrient and sediment exchanges were calculated by first multiplying the net hourly flux by tide duration within the flume (h). This flux per tide was then multiplied by the respective tide frequency for each month. Tide frequency per month was obtained from predicted tides for the lagoon (Geofisica, 1990, 1991, and 1992). Monthly flux rates were summed to estimate the net annual flux. Fluxes from the same month but different year were averaged. Both significant (48) and non-significant (3) fluxes were included to estimate annual fluxes.

To illustrate seasonal variation of nutrient concentrations and suspended sediments, we calculated means and standard deviations from the total number of samples taken for each analyte during ebb and flood tide ( $6 < n < 13$ ) for each sampling date.

## Results

**Nutrient concentrations and physical parameters.** Water temperature in the flume ranged from 22.3 °C to 31.2 °C. The lowest temperature occurred in January 1992 during the "Norte" season, and the highest in June 1991 at the beginning of the rainy season (Fig. 2-3). Salinity ranged from 21 to 42 ‰ and followed the same seasonal pattern as temperature. The lowest salinity was observed in October 1990, near the end of the rainy season, and the highest in June 1991. There was a significant decrease of salinity from September to

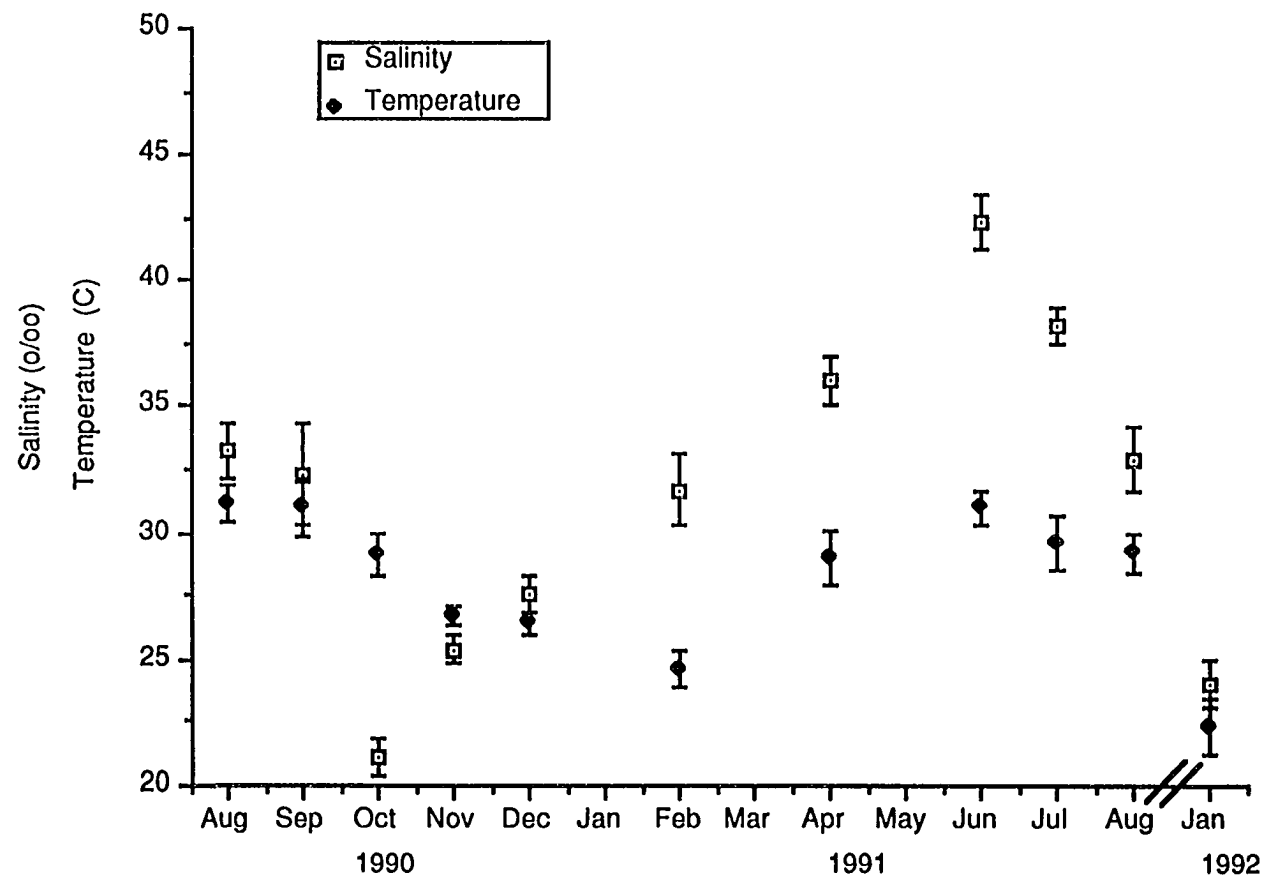


Figure 2-3. Seasonal pattern of mean salinity and temperature during tidal inundation of the flume in a fringe mangrove at Estero Pargo

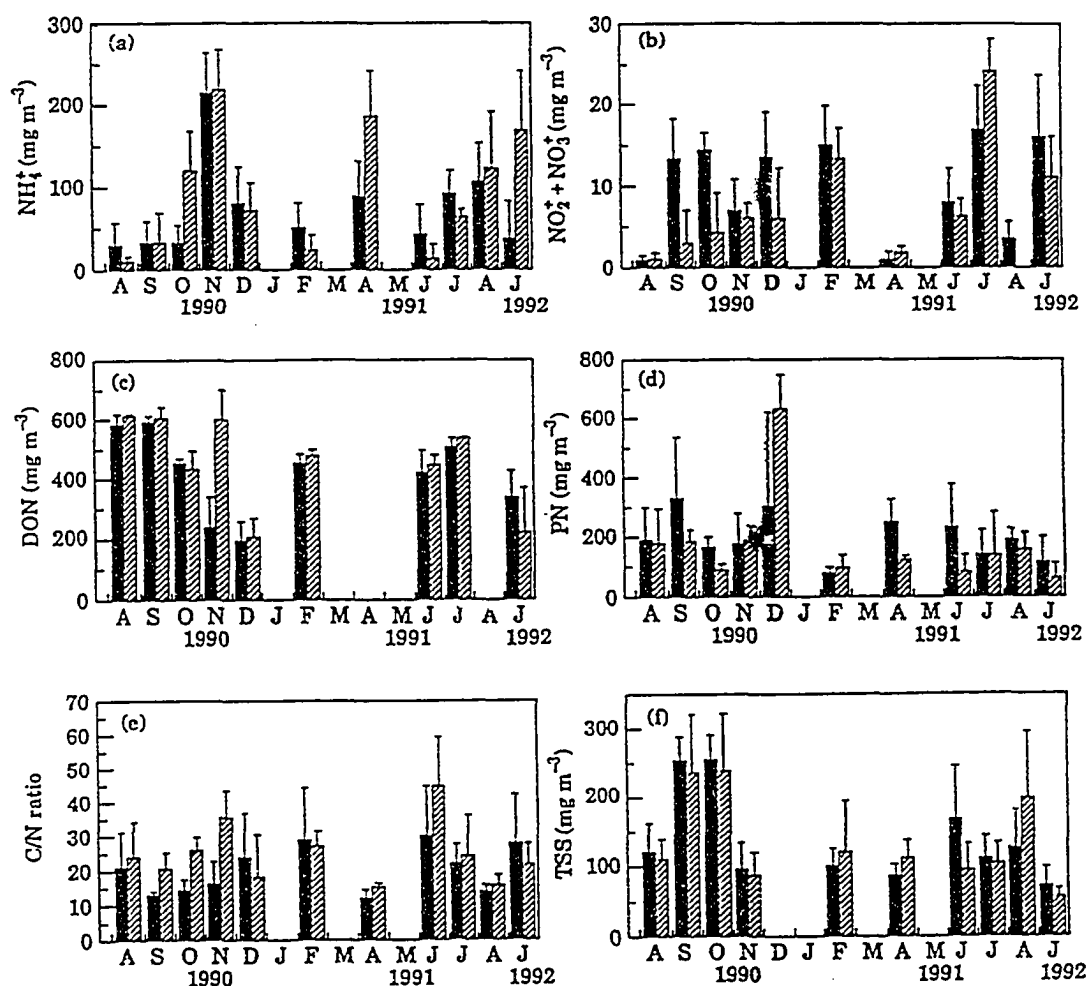




Figure 2-4. Seasonal pattern of concentration means of (a) ammonium, (b) nitrite + nitrate, (c) dissolved organic nitrogen, (d) particulate nitrogen, (e) carbon:nitrogen ratios, and (f) total suspended sediments during tidal inundation of the mangrove surface.  represents flood tide;  represents ebb tide. Concentration means with standard deviations are shown for comparison purposes and are not used to calculate net exchange (see methods).

October 1990 (11.2 ‰) indicating the influence of river discharge to the lagoon.

Ammonium concentrations ranged from 15.8 to 723.4 mg m<sup>-3</sup> during the study and were generally much higher than NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>. Concentrations of NH<sub>4</sub><sup>+</sup> were generally higher in the dry and "Norte" seasons, the latter was the period of maximum concentrations. Mean ebb and flood concentrations of NH<sub>4</sub><sup>+</sup> (Fig. 2-4A) were >200 mg m<sup>-3</sup> during November 1990, compared to < 50 mg m<sup>-3</sup> in August 1990 and June 1991. Concentrations of NH<sub>4</sub><sup>+</sup> were generally above 100 mg m<sup>-3</sup> during Norte events, corresponding to a decrease in salinity. NH<sub>4</sub><sup>+</sup> concentrations were higher during ebb tide than during flood tide when concentrations were generally > 100 mg m<sup>-3</sup>, except for November 1990 when concentrations during both half-tides were similar (Fig. 2- 4A). When average concentrations during a tide were <100 mg m<sup>-3</sup>, flood tide concentrations were higher than ebb.

Concentrations of NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> ranged from 2.6 to 68.8 mg m<sup>-3</sup>. Mean NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> concentrations of flood tide had slight seasonal variation ranging from 10 to 15 mg m<sup>-3</sup>, with the exception of August 1990, and April and August 1991 when concentrations were < 5 mg m<sup>-3</sup> (Fig. 2-4B). Mean ebb tide concentration generally increased from summer to Norte season during 1990, but the highest mean concentration was observed in July 1991 (Fig. 2-4B). Higher concentrations of NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> during ebb tides were associated with the dry period.

Mean concentrations of DON ranged from 110 to 600 mg m<sup>-3</sup> (Fig. 2-4C) and maximum concentrations occurred in August and September 1990. Mean flood and ebb concentrations were similar for all months sampled except for November 1990, when ebb concentrations were double the concentrations during flood tide (Fig. 2-4C). PN concentrations ranged from 60 to 705 mg m<sup>-3</sup>, but most of the concentrations were about 200 mg m<sup>-3</sup> (Fig. 2-4D). Maximum mean concentration of 600 mg m<sup>-3</sup> was observed in December 1990 during ebb tide. With the exception of this December sampling, PN concentrations during flood were similar or slightly higher than ebb tide concentrations. PN concentrations were usually lower than DON concentrations, and the combination of the two dominated the nitrogen pool.



The C/N ratio of particulate material was higher during ebb tides in 8 of the 11 months that tides were sampled during the study (Fig. 2-4E). C/N ratios were  $<15$  on only 5 of the 11 months, and these were only during flood tides. During the ebb tide of June 1991, mean C/N ratio was nearly 45. Concentrations of TSS ranged from 56 to 263  $\text{mg m}^{-3}$ . Maximum TSS mean values occurred in September (262.8  $\text{mg m}^{-3}$ ) and October (259.7  $\text{mg m}^{-3}$ ) 1990, and were similar for both flood and ebb tides (Fig. 2-4F). There was little seasonal difference in mean concentrations for the remaining months.

**Fluxes.** Dissolved inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_2^- + \text{NO}_3^-$ ) was imported to the fringe forest from the creek and basin forest, while particulate and dissolved organic nitrogen were exported to the creek and basin forest. Total exchanges of nitrogen were much greater between the tidal creek and the fringe forest than between the fringe and basin forests (Fig. 2-5). Ammonium import rates were much greater than export rates (Fig. 2-5A) which averaged 3.78  $\text{mg m}^{-2} \text{h}^{-1}$ . On average, 90 % of the  $\text{NH}_4^+$  imported to the fringe mangrove occurred during flood tide. The basin forest was also a source of  $\text{NH}_4^+$  to the fringe forest in November 1990, April and August 1991, and January 1992. In this latter month the forest was the only source. The highest import rate of  $\text{NH}_4^+$  (11  $\text{mg m}^{-2} \text{h}^{-1}$ ) occurred in November 1990. Ammonium export was much lower than import and averaged 0.39  $\text{mg m}^{-2} \text{h}^{-1}$ . Maximum export was in December 1990 (0.7  $\text{mg m}^{-2} \text{h}^{-1}$ ) during ebb tide.

The average  $\text{NO}_2^- + \text{NO}_3^-$  import rate (0.31  $\text{mg m}^{-2} \text{h}^{-1}$ ) was greater than export (0.1  $\text{mg m}^{-2} \text{h}^{-1}$ ) (Fig. 2-4B). The tidal creek was the source of 90 % of the imported  $\text{NO}_2^- + \text{NO}_3^-$ . Export occurred only in April 1991 at 0.09  $\text{mg m}^{-2} \text{h}^{-1}$  and was exported to the tidal creek during ebb tide. The export flux in August 1990 was not significantly different from zero ( $p > 0.05$ ).

There was net export of DON from the fringe forest to both the basin forest and the tidal creek during 6 of the 9 mo (Fig. 2-5C). On most measurements DON was exported from the flume. In August, September, and October 1990, and February 1991 DON was exported to the basin forest, whereas export to the tidal creek occurred in November 1990 and June 1991. DON was imported from the basin forest in December 1990, and from the tidal creek in July 1991 and January 1992. All the net half-tide fluxes of DON were  $< 1.5 \text{ mg m}^{-2} \text{h}^{-1}$ ,

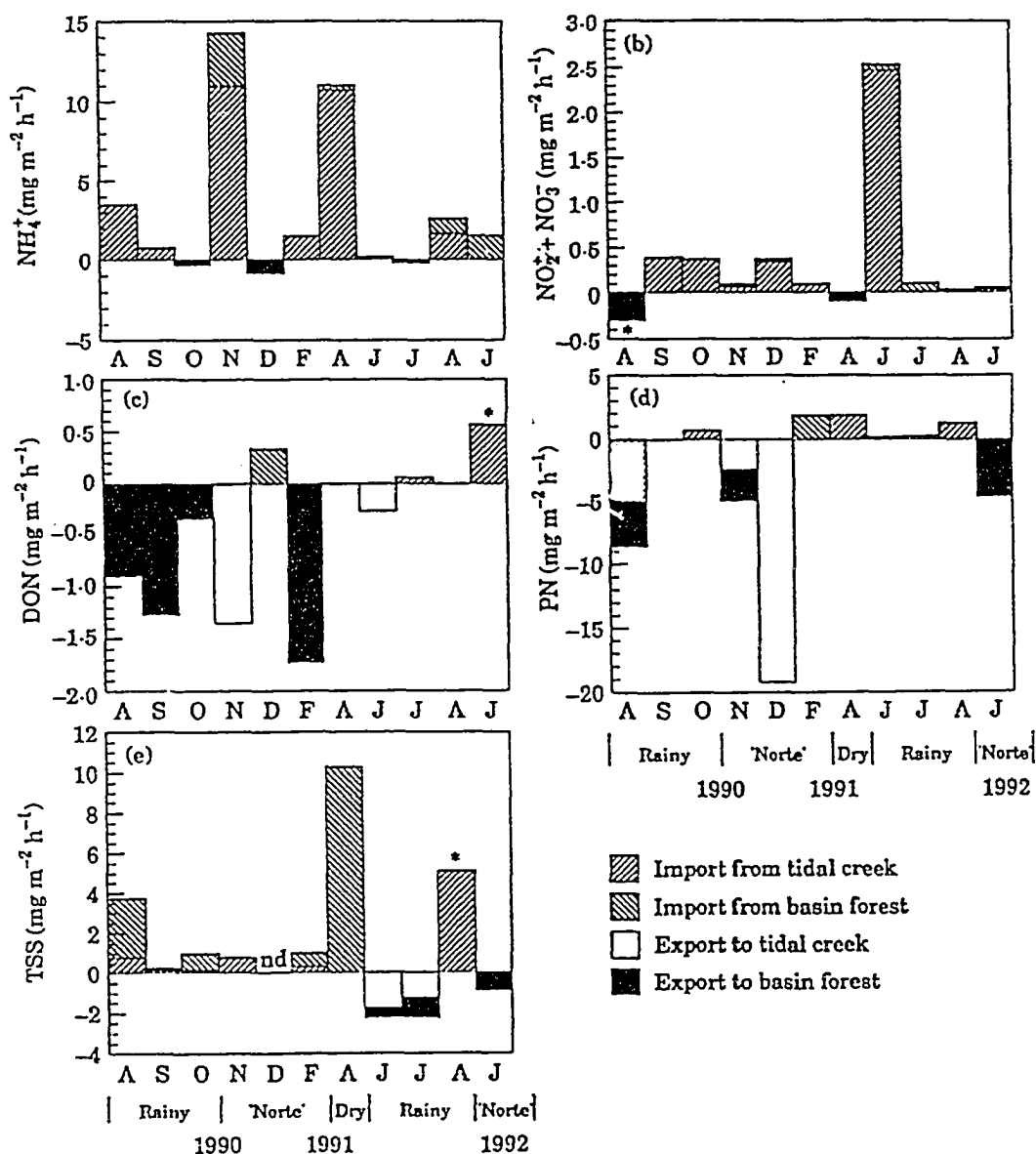


Figure 2-5. Net fluxes of whole tides for (a) ammonium, (b) nitrite + nitrate, (c) dissolved organic nitrogen (DON), (d) particulate nitrogen (PN), and (e) total suspended sediments (TSS) in the mangrove flume. Positive flux is import to the mangrove surface; negative flux is export to the inundating water. (\*) denotes flux not significantly different ( $p > 0.05$ ). nd = no data.

except for February 1991, although the concentrations were higher than the other forms of nitrogen.

There was a strong net export of PN from the fringe forest, especially to the tidal creek (Fig. 2-5D). The average PN export ( $5.3 \text{ mg m}^{-2} \text{ h}^{-1}$ ) was much higher than import ( $1.0 \text{ mg m}^{-2} \text{ h}^{-1}$ , Fig. 2-5D). PN export to the tidal creek during ebb tides was much higher ( $4.2 \text{ mg m}^{-2} \text{ h}^{-1}$ ) than to the forest during flood tides. PN export to the fringe forest was associated with rainy conditions during sampling. The tidal creek was the dominant source of PN during flood tides in September ( $0.06 \text{ mg m}^{-2} \text{ h}^{-1}$ ) and October ( $0.8 \text{ mg m}^{-2} \text{ h}^{-1}$ ) 1990, and April ( $2.15 \text{ mg m}^{-2} \text{ h}^{-1}$ ) and August ( $1.54 \text{ mg m}^{-2} \text{ h}^{-1}$ ) 1991.

Import of TSS in the fringe forest was observed during all months (Fig. 2-5E). The inland forest was the main source (80 %) of suspended sediments for the fringe forest since uptake occurred during ebb tides. The higher C/N ratios for the majority of ebbing tides suggests that the suspended material from the basin forest was deficient of nitrogen which indicates an enrichment in refractory lignocellulitic detrital material. The highest flux ( $10.3 \text{ g m}^{-2} \text{ h}^{-1}$ ) occurred in April 1991. Suspended material was exported from the fringe forest in June and July 1991, prior to the rainy season, and January 1992 during the "Norte" season. Also, on average, 80 % of the sediments were exported to Estero Pargo. Import of TSS from the tidal creek in August 1990 was not significant ( $p > 0.05$ ).

Estimates of total fluxes are calculated as products of concentration and water flux for each 2-h interval of a tide. They, therefore, are volume weighted and used to compare the relative flux of materials during half-tides. Results of linear contrast to test seasonality of nutrient content are shown in Table 2-2. All materials but PN showed a significant difference between the "Norte" and rainy season ( $p \leq 0.05$ ). Differences between the dry and "Norte" seasons were observed for  $\text{NO}_2^- + \text{NO}_3^-$  (1.8 vs 12.5 mg). TSS (79.2 vs 189.9 mg) was the only component showing differences between dry and rainy seasons. PN showed no seasonality (Table 2-2).

Ninety four and eighty one percent of the paired t-tests performed on nutrient content for the whole and half-tide cycles, respectively, were significantly different from 0 ( $p < 0.05$ ).  $\text{NO}_2^- + \text{NO}_3^-$  in August 1990, TSS in August 1991, and DON in January 1992 were the only fluxes during tides that were not

Table 2-1. Values of p from the factorial split-plot analysis of nutrient content (mg) in the flume at Estero Pargo.

	p> F				
	NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	DON	PN	TSS
Season	0.0013	0.0001	0.0049	0.5424	0.0001
Month	0.1099	0.0001	0.4233	0.0003	0.0001
Tide	0.2079	0.0042	0.0009	0.0303	0.0010
Month*Tide	0.6333	0.0001	0.4083	0.9147	0.8017
Location (Loc)	0.9348	0.2509	0.9046	0.2656	0.9503
Month*Location	0.9998	0.9655	0.9980	0.5634	0.1756
Tide*Location	0.7666	0.7181	0.8114	0.6329	0.0474
Month*Tide*Loc	0.9989	0.9960	0.9950	0.9868	0.0836

Table 2-2. Contrast for nutrients and total suspended sediments showing differences between seasons.

Material	Season		
	Dry	'Norte'	Rainy
NH <sub>4</sub> <sup>+</sup>	133.7 (82.1) <sup>a</sup>	230.8 (31.0) <sup>a</sup>	55.7 (31.0) <sup>b</sup>
NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup>	1.8 (2.7) <sup>a</sup>	12.5 (1.0) <sup>b</sup>	7.2 (1.0) <sup>a</sup>
DON	nd	381.6 (51.8) <sup>a</sup>	568.4 (56.3) <sup>b</sup>
PN	170.4 (95.8) <sup>a</sup>	234.8 (36.2) <sup>a</sup>	237.4 (35.0) <sup>a</sup>
TSS	79.3 (32.2) <sup>a</sup>	95.4 (13.1) <sup>a</sup>	189.9 (12.2) <sup>b</sup>

Means (SD) of nutrient content (mg) followed by different letters were significantly different (p<0.05).

nd, No data; DON, dissolved organic nitrogen; PN particulate organic nitrogen; TSS, total suspended sediments.

significant (Fig. 2-5). Table 2-1 shows p values from the split-plot analysis performed for the nutrient and sediment contents (mg) at both ends of the flume. There was a significant difference between seasons for all the analytes with the exception of PN ( $p = 0.54$ ). Differences among months were significant for  $\text{NO}_2^- + \text{NO}_3^-$ , PN, and TSS ( $p < 0.01$ ). Tide stage (ebb and flood tide) had an important effect on  $\text{NO}_2^- + \text{NO}_3^-$ , DON, PN and TSS content but not for  $\text{NH}_4^+$ .  $\text{NO}_2^- + \text{NO}_3^-$  showed a significant interaction between month and tide suggesting that flooding and ebbing waters had different influences on  $\text{NO}_2^- + \text{NO}_3^-$  content. Differences between opposite ends of the flume or their interaction with month were not significant for any of the analyses indicating that location within the flume or its interaction with time did not have an influence on nutrient content. TSS was the only parameter that had a significant difference ( $p = 0.04$ ) in the interaction between tide and location. There was no interaction between month, tide, and direction for all entities.

There was a net annual import of  $\text{NH}_4^+$ ,  $\text{NO}_2^- + \text{NO}_3^-$ , and TSS to the fringe mangrove forest (Fig. 2-6) from both Estero Pargo (the tidal creek) and the basin forest. In contrast, the fringe forest exported PN and DON to the creek and basin forest. Import of  $\text{NH}_4^+$  from the tidal creek to the fringe represented 84 % of annual flux in contrast to much less transport of  $\text{NH}_4^+$  from the basin forest. The tidal creek also provided most of the  $\text{NO}_2^- + \text{NO}_3^-$  import to the fringe forest. Export of PN to Estero Pargo was  $0.52 \text{ g m}^{-2} \text{ yr}^{-1}$  and represented 90 % of the total annual export. However, most of the DON exchange was with the basin forest, where nearly 75% of the DON was exported from the fringe. Both Estero Pargo and the tidal creek were sources of TSS ( $210 \text{ g m}^{-2} \text{ yr}^{-1}$ ). On an annual basis the basin forest was the principal supplier of TSS in comparison to the tidal creek ( $60 \text{ g m}^{-2} \text{ yr}^{-1}$ ). Overall, there was a slight net uptake of total nitrogen into the fringe forest of  $0.004 \text{ g m}^{-2} \text{ yr}^{-1}$ .

### Discussion

Past studies of nutrient exchange between mangroves and adjacent tidal creeks have found small or no net annual exchange in either inorganic or organic nitrogen. Our study suggests, in contrast to other mangrove systems, that the fringe mangrove forest in Estero Pargo acts as a sink of inorganic nitrogen and as a source of dissolved and particulate nitrogen, (Fig. 2-6). The tidal creek was the principal source of  $\text{NH}_4^+$  and  $\text{NO}_2^- + \text{NO}_3^-$  to the fringe

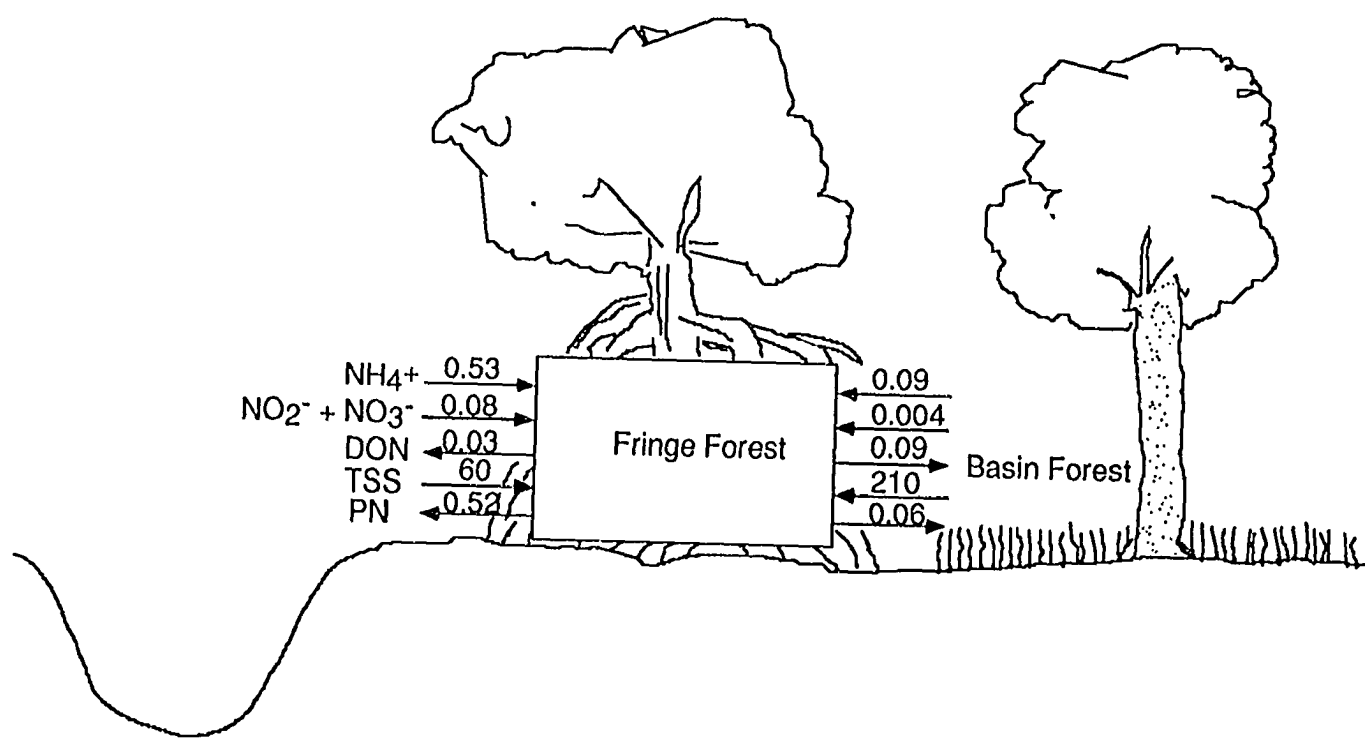


Figure 2-6. Net annual fluxes (g m<sup>-2</sup> yr<sup>-1</sup>) in fringe mangrove at Estero Pargo. Arrow into the forest is import; arrow out of the forest is export.

Table 2-3. Estimates of net annual nitrogen flux for mangrove forests. Positive values are import by the mangrove forest while negative values are export to adjacent estuarine waters. All values are in  $\text{g m}^{-2} \text{yr}^{-1}$ .

Reference	Location	Type	$\text{NH}_4^+$	$\text{NO}_2^- + \text{NO}_3^-$	DON	PN
Boto and Bunt, 1981	Coral Creek, Australia	Fringe/Basin				-2.0
Boto and Wellington, 1988	Coral Creek, Australia	Fringe/Basin	0.15	-0.03	1.3	
This study	Estero Pargo, Mexico	Fringe	0.53	0.08	-0.03	-0.52



forest, while the basin forest was the main source of TSS. The exchange of nitrogen species was much greater at the creek end of the flume as compared to forest end. The net uptake of  $\text{NH}_4^+$  ( $0.53 \text{ g m}^{-2} \text{ yr}^{-1}$ ) and the net release of PN ( $0.52 \text{ g m}^{-2} \text{ yr}^{-1}$ ) at the creek/flume interface were approximately equal, and were much greater than the other nitrogen fluxes. For example, net exchange of  $\text{NH}_4^+$  at the creek/fringe interface was higher than at the fringe/basin interface by a factor of 6,  $\text{NO}_2^- + \text{NO}_3^-$  by a factor of 20, and PN by a factor of 8.6. Only DON exchange was higher at the fringe/basin interface.

Net annual fluxes of inorganic nitrogen from the fringe mangrove in Estero Pargo are higher than those reported for mangroves in Coral Creek, Australia by Boto & Wellington (1988) (Table 2-3).  $\text{NH}_4^+$  was imported in both Estero Pargo and Coral Creek; while  $\text{NO}_2^- + \text{NO}_3^-$  was also imported in Estero Pargo, but was exported from mangroves to Coral Creek. DON and PN annual fluxes were lower in Estero Pargo than the site in Australia. The magnitude of  $\text{NH}_4^+$  and  $\text{NO}_2^- + \text{NO}_3^-$  fluxes from the mangrove system in Coral Creek is only 30 % of those measured in Estero Pargo. However, DON and PN net fluxes in Estero Pargo are only 2 % and 26 % of those reported for Coral Creek, respectively. PN flux in Coral Creek may be underestimated since it represents only the flux of nitrogen that is associated with the transport of leaf litter and not the microdetritus suspended in the water column (Boto & Bunt, 1981). In our study, we focused on suspended microdetritus and not the macrodetritus leaf flux of PN, also causing an underestimate of total PN flux. These two systems also had differences in the direction of DON flux. Coral Creek imported DON whereas this nutrient was exported from the fringe forest in Estero Pargo.

The high concentration and fluxes of organic and inorganic nitrogen in Estero Pargo compared to other studies of mangrove forests may reflect differences in methodology and hydrology. Nutrient concentrations in mangrove systems are usually reported for tidal channels (i.e. Boto, 1982; Nixon *et al.*, 1984; Boto & Wellington, 1988; Wattayakorn *et al.*, 1990; Ovalle *et al.*, 1990; Thong *et al.*, 1993), which include the effects of mudflats, creek bottom and water column on nutrients exchanged with the forest. Nutrient concentrations and fluxes are thus integrated values of the biogeochemical processes occurring in each of these habitats (Whitting *et al.*, 1989) and do not necessarily specifically isolate the effect of mangrove forests on concentrations.

In contrast to mangrove systems, several marsh studies have used flumes to measure flux of materials which can be compared to measurements in Estero Pargo. Overall, flux studies using the flume technique showed that most marshes import dissolved inorganic nitrogen and total nitrogen (Wolaver *et al.*, 1980, 1983; Bowden, 1986; Whitting *et al.*, 1989). Wolaver *et al.* (1985) found that most of the  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were removed from the tidal water while it resided in tall *Spartina alterniflora* areas. Also, Wolaver & Zieman (1983) reported constant import rates of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  during most part of the year as was the case for Estero Pargo. Direction of fluxes regarding organic nitrogen is more variable and is dependent on the geomorphology and climatic conditions of the marsh under study (Valiela, 1983; Childers, 1994). Whiting *et al.* (1989) found a net export of DON and import of PN whereas Wolaver *et al.* (1980) reported a net import of DON. Childers & Day (1990) discussed the high variations in magnitude and direction of marsh-open water exchanges depending on the successional stage of the estuary within the deltaic cycle of coastal Louisiana. In a broader scale, studies from Southeastern estuaries in the United States have shown that there is not a relationship between latitude and marsh water column fluxes. Age-dependent differences in marsh-water column flux patterns result in very small-scale spatial variability within a given marsh (Childers, 1994). In Estero Pargo weather forcing appears to be the major factor controlling the magnitude and direction of sediment and nitrogen fluxes.

The decrease in salinity during the rainy season indicates that nutrient concentrations in Estero Pargo are influenced by inputs from rainfall and river discharge to the lagoon. The steady decline in salinity during the rainy season (with a maximum reduction from 33 to 21 ‰ from September to October 1990) reflects freshwater input from rainfall and river discharge (Yáñez-Arancibia & Day, 1982). In our study, the increase of  $\text{NO}_2^- + \text{NO}_3^-$  concentrations from August 1990 to February 1991 coincided with the seasonally higher concentrations of  $\text{NO}_2^- + \text{NO}_3^-$  in the lagoon during the rainy season (Yáñez-Arancibia & Day, 1982). Mean  $\text{NO}_3^-$  concentrations were also different with values of  $21 \text{ mg m}^{-3}$  during the rainy season and  $7 \text{ mg m}^{-3}$  during the dry season. Botello & Mandelli (1975) also found seasonal effects in  $\text{NH}_4^+$  with mean concentrations of 28 and  $175 \text{ mg m}^{-3}$  in the rainy and dry seasons,

respectively. Ovalle *et al.* (1990) reported maximum  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations of 68.3 and 103.6  $\text{mg m}^{-3}$ , respectively, for a mangrove tidal creek in Brazil. In contrast, Boto & Wellington (1988) measured  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON concentrations of 8.4, 1.7, and 70  $\text{mg m}^{-3}$ , respectively, in Coral Creek, Australia. These concentrations in Coral Creek are not influenced by terrestrial inputs and represent less than 5% of maximum concentrations of these nutrients measured in Estero Pargo. Those mangrove systems linked to inputs from upland watersheds during the rainy season have higher concentration of nutrients in waters inundating the forests.

The exchange of nutrients among the tidal creek, the fringe, and the basin forest subsystems in Estero Pargo is strongly influenced by seasonal weather forcing, such as winter storms, that can influence the magnitude and direction of water flow. The effect of winds and rain are important in determining export of materials from the forest, particularly PN and DON. Although concentrations of PN were not seasonal, we observed large exports of PN to Estero Pargo in November and December 1991, and export to the basin forest in January 1992 when water levels were high (Fig. 2-5D). Weather conditions in February were typical of the "Norte" season when strong winds and heavy rain increased the flooding of mangrove forest. Physical forcings can modify the transport of materials drastically, as indicated by a high export rate of PN in December that was followed by a low PN import rate from February to August 1992.

Seasonal variation in the direction or magnitude of either inorganic or organic nitrogen fluxes has not been as clearly discerned in other mangrove ecosystems. Boto & Wellington (1988) concluded that there was no seasonal variation in the direction or magnitude of nutrient fluxes in Coral Creek in contrast to the patterns we observed in Estero Pargo. They concluded that mangrove forests were very efficient in conserving nitrogen. Coral Creek is a tidally dominated channel with minimal freshwater input occurring only during heavy monsoonal rain periods (Boto & Wellington, 1988). Salinities in this system are rarely lower than 33 ‰ (Wolanski & Gardiner, 1981). In contrast, Estero Pargo shows a well defined rainy season associated with winter storms and has a wide range of salinities (17- 40 ‰) during the year. Ovalle *et al.* (1990) did a mass balance of nine tidal cycles in a mangrove swamp in Brazil and found that the nutrient exchange was balanced. The net exchange of

nutrients between a mangrove tidal creek and an adjoining bay was negligible. Also, Wattayakorn *et al.* (1990) calculated export rates in the Klong Ngao estuary in Thailand and observed "very weak" rates of  $\text{NO}_2^- + \text{NO}_3^-$  and TN exchange. Yet, Thong *et al.* (1993) suggested that the floor of a mangrove forest is a major source of inorganic nitrogen in the west coast of Peninsular Malaysia.

In this study there was a net import of TSS to the fringe forest from both the creek and basin forests, but the net input was 3.5 times higher at the fringe/basin interface. We estimate a net annual sediment import of  $60 \text{ g m}^{-2} \text{ yr}^{-1}$  from the tidal creek to the fringe mangrove (Fig. 2-6). The net annual import from the basin forest to the fringe forest was  $210 \text{ g m}^{-2} \text{ yr}^{-1}$ . Woodroffe (1985c) reported a net export of TSS from a mangrove swamp in New Zealand. He found a high variation of TSS concentrations over a tidal cycle and the lowest concentrations at or near slack high water. These fluxes for mangroves are within the lower range reported for estuarine marshes ( $100 - 13\,900 \text{ g m}^{-2} \text{ yr}^{-1}$ ) (Stevenson *et al.*, 1988). The highly significant interaction between the direction of the tide and location inside the flume from the analysis of variance (Table 2-1) support the idea that most of the sediment imported to the fringe forest came from the basin forest (Fig. 2-5E). Fluxes of TSS depended on the timing of events (either during the ebb or flood tide) and wind direction. Stevenson *et al.* (1988) found that storm events in tidal marshes serve as much to increase sediment import as they do to promote exports. Fluxes of sediments in Estero Pargo (Fig. 2-5E) during typical storm events showed this pattern since the magnitude and direction are different during similar climatological conditions (Table 2-4). For example, there was an import of sediments in February 1991 whereas export occurred in January 1992. Both months correspond to the "Norte" season. Thus the higher accretion rates in a fringe forest compared to more inland mangrove sites in Estero Pargo as measured by Lynch *et al.* (1989) using Pb-210 could be the result of sediment redistribution following these "Norte" events.

The different sources of suspended particulate material to the fringe forest may influence the quality of transported material. Tidal export of litter and organic matter in mangrove ecosystems has been well documented (Boto & Bunt, 1981a; Boto & Bunt, 1982; Odum *et al.*, 1982; Twilley, 1985; Woodroffe,

Table 2-4. Hydrological and weather conditions during flume sampling

Sampling date	Maximum tide height (cm)	Duration of inundation (h)	Rainfall (mm) <sup>a</sup>	Weather conditions
12-13 August 1990	47.0	6	18.0	Short but hard rain between 22.0 and 24.00h; overcast
21-22 September 1990	50.2	12	0.0	Clear sky
20-21 October 1990	59.0	12	0.0	Strong rain previous to sampling; overcast
2-3 November 1990	68.0	14	0.0	Overcast
2-3 December 1990	86.0	16	0.3	Overcast; slight rain
1-2 February 1991	50.0	12	28.3	Overcast; rain
23-24 April 1991	46.5	10	0.0	Clear sky
3-4 June 1991	48.0	10	0.0	Clear sky
11-12 July 1991	43.0	12	nd	Partially cloudy
4-6 August 1991	34.0	16	nd	Partially cloudy; slight rain
14-17 January 1992	67.0	26	6.4	Strong north wind; scatter rain
nd, no data				

<sup>a</sup>Data from a meteorological station 250m from study site.

1985a; Woodroffe, 1985b; Twilley *et al.*, 1986; Flores-Verdugo *et al.*, 1987; Gong & Ong, 1990; Twilley *et al.*, 1992). Although we did not measure litter transport directly, we measured a net export of PN. We also observed large export of leaves and reproductive structures during ebb tides mainly during the rainy and "Norte" seasons. Export of PN and DON from fringe forest to the tidal creek (and DON to the basin forest) supports the outwelling concept for mangroves in coastal ecosystems. Particulate material exported from the forest during ebb tides generally had a higher C/N ratio than particulate matter imported into the forest on the flooding tide. This indicates that there was a greater nitrogen demand during ebb tide caused by the export of nitrogen deficient detritus from fringe and basin mangroves. This nitrogen deficiency may be linked to the uptake of ammonium observed in the flume throughout the study. Several studies have reported the enrichment of nitrogen in decomposing leaf litter that may influence nitrogen immobilization on the forest floor (Twilley *et al.*, 1986). The use of the flume technique within the mangrove forests could allow us to link observations of specific processes (i.e., nitrification, denitrification) to better understand the flux of nitrogen in this mangrove forest.

Patterns of nutrient and sediment exchange between the tidal creek and fringe mangroves in Estero Pargo may not be representative of other types of mangroves, such as riverine and basin mangroves, surrounding Terminos Lagoon. Differences in the frequency and duration of tidal flooding, and amount of river input, may influence nutrient exchange among riverine and basin mangroves differently in comparison to the fringe mangrove forest in this study. The differences in nutrient exchange between types of forest could be further increased by variations between consecutive tidal cycles within a particular forest. To evaluate this variation we calculated material fluxes for each cycle for the 2 and 3 consecutive tidal cycles sampled in August 1991 and January 1992, respectively. We observed from 1 to 180 percent variation with respect to the integrated net flux (Fig. 2-5) for both experiments. High percentage of variation was observed for  $\text{NH}_4^+$  in August 1991, and DON,  $\text{NH}_4^+$ , and PN in January 1992 (Fig. 2-7). Yet, flux direction remained the same for all tidal cycles. This variability is caused by changes in water volume inside the flume due to differences in the duration of tidal flooding between tides. Climatic

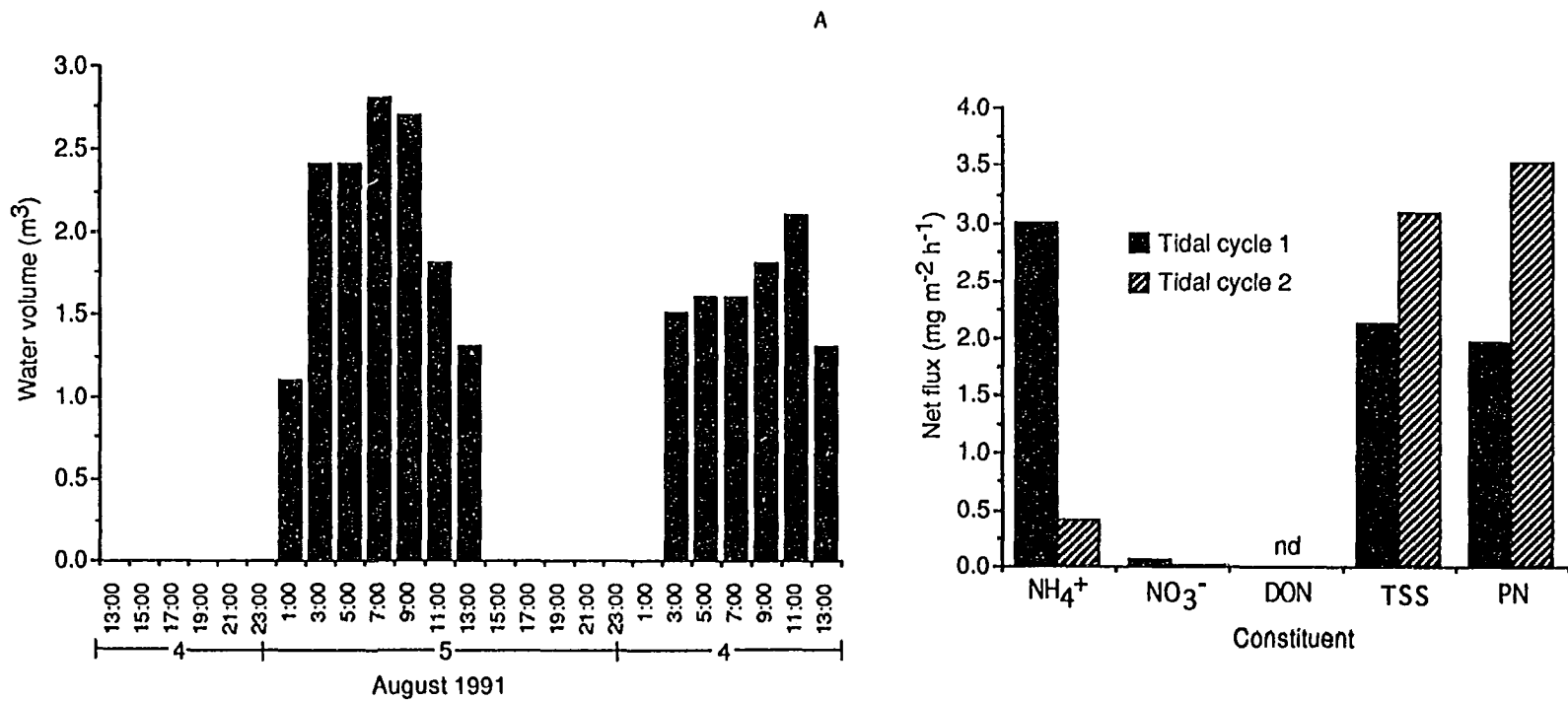


Figure 2.7. Water volume and net fluxes of constituents of two (A: August 1991) and three (B: January 1992) consecutive tidal cycles within the flume.

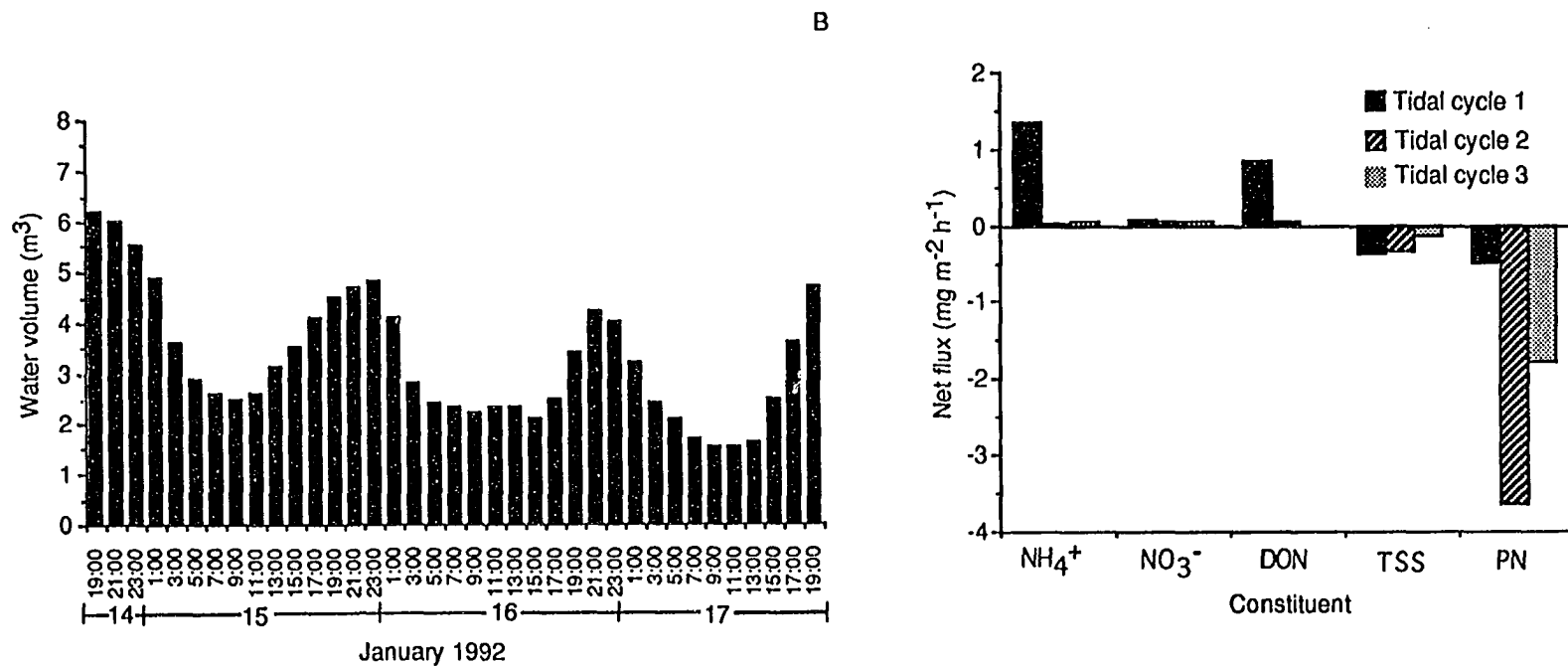


Figure 2.7. Con'd.



factors such as wind velocity and direction, and rain events affected tide duration during these particular periods (Table 2-4).

The flume technique may prove to be an important approach to evaluate nutrient fluxes in other types of forest before generalizations can be made for the entire estuary. Large aerial extrapolations are limited since our results are based on intensive measurements from 1-2 tidal cycles per month and there is no replication of mangrove sites. As Twilley (1988) found for detritus export, even though export rates per unit area for fringe mangroves may be double that of basin forests, the greater aerial extent of the more inland forest results in similar contributions of both types of mangroves to the carbon budget of a lagoon in southwestern Florida. Also, fluxes in Estero Pargo might be underestimated since residual drainage fluxes (Whiting *et al.*, 1989; Childers *et al.*, 1993) and fluxes associated with rainfall events were not evaluated. Residual water was observed mainly at the beginning of the dry season and lasted throughout the beginning of the rainy season.

Differences in the magnitude and direction of nitrogen fluxes may reflect differences in hydrology and geomorphology among mangrove ecosystems (Woodroffe, 1985a, b, c; Twilley, 1985; Twilley, 1988). The results from this study show that the fringe mangrove forest in a lagoon is an area of active nutrient transformations. For nitrogen, there was an uptake of DIN (mostly from the creek) and a export of PN (mostly to the creek). Thus, inorganic nitrogen was transformed to organic and particulate nitrogen by the fringe forest. The tidal creek seems to supply the DIN and the basin forest supplies nitrogen deficient particulate material to the fringe mangrove. Thus, this mangrove forest contributed detritus to the estuarine water column and serves as a sink of inorganic nutrients as has been shown for other coastal wetlands (Wolaver & Zieman, 1983; Wolaver *et al.*, 1983; Bowden, 1986; Whiting *et al.*, 1989; Childers & Day, 1990). Potentially, the export of organic matter from mangroves can stimulate aquatic primary productivity, sustain secondary productivity in estuarine and coastal waters (Odum & Heald, 1972), and "buffer" inputs of nutrients and other materials from terrestrial sources. This dual function of fringe mangroves in a lagoon setting is similar to concepts of nitrogen flux in coastal marshes (Odum, 1988). The nitrogen transformations and tidal hydrology are complex in intertidal wetlands, and the flume proved to

be an important tool to discern these nutrient flux patterns. Studies of other mangrove forests in different geomorphological and hydrological environments are needed to better understand the function of mangroves in the nutrient dynamics of the coastal zone.

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## **CHAPTER 3**

### **AQUATIC PRIMARY PRODUCTIVITY AND ITS COUPLING WITH THE ADJACENT MANGROVE FOREST IN TERMINOS LAGOON, MEXICO**

#### **Introduction**

Phytoplankton productivity is a major source of organic carbon for most estuarine ecosystems throughout the world (Day et al 1989). In tropical and semitropical estuaries phytoplankton production rates can be higher than in temperate estuaries and high production rates are often associated with patterns of river flow (Flores-Verdugo et al. 1987, Rojas Galaviz et al. 1993). Although there is evidence of the influence of several environmental factors on phytoplankton productivity in estuarine systems, it is poorly understood how these complex interactions control primary production (Alpine and Cloern 1992), especially in tropical systems.

There are a number of factors influencing phytoplankton production, which can affect at different levels according to whether they have an inhibitory or stimulatory effect either on the plankton as a whole, or on the physiology of particular taxonomical groups (Ricard 1984). Factors such as precipitation and river discharge exhibit broad seasonal patterns affecting available light and nutrient levels (Boynton et al. 1982, 1983) which make productivity patterns more variable in lower latitudes (Day et al. 1989). Temperature and day length seldom limit primary productivity (or metabolism), and it is the magnitude and timing of allochthonous pulses of nutrients and organic matter that control patterns of aquatic primary productivity in tropical estuaries.

Primary productivity of coastal waters is linked to the relative inputs of autochthonous and allochthonous organic matter, particularly in areas of high river discharge (Prakash 1971). Prakash & Rashid (1969) found that significant input of terrigenous humic material through land drainage resulted in nutrient enrichment of coastal waters and led to enhanced phytoplankton production. Humic substances that enter coastal and estuarine waters affect plankton communities in diverse ways (Langis et al. 1986, Prakash et al. 1973). Because of the chelating abilities of humic substances, essential trace metals are made available to the phytoplankton and toxic metals may be chelated thus avoiding toxic effects (Toledo et al. 1982). There is also

evidence that nitrogen in humic compounds is directly available to some algal taxonomic groups (Granéli et al. 1985; Carlsson & Granéli 1993).

Although there is experimental evidence of the stimulation effect of humic substances on phytoplankton production in mangrove dominated systems (Prakash et al. 1973) studies addressing seasonal changes of this stimulatory effect in specific environments are scarce. Phytoplankton primary productivity rates in tropical coastal lagoons may be enhanced by mangrove forests (Ricard 1984, Morrel & Corredor 1993). These coastal systems receive nutrients, litter and organic matter from mangrove forests through the action of tidal inundation and river discharge (Boto & Bunt 1981, Twilley et al. 1986, Flores-Verdugo et al. 1987, Robertson et al. 1988, Gong & Ong 1990, Flores-Verdugo et al. 1990, Alongi 1990, Twilley et al. 1992), which can influence phytoplankton and bacterial secondary production (Moran 1991, Selvam et al. 1992). Twilley (1985) found that nearly 75% of the total organic carbon exported from basin mangrove forests in south Florida was dissolved organic carbon and was strongly related to the cumulative tidal amplitude within the forest. Boto and Bunt (1981) reported that an Australian riverine mangrove forest exported  $10 \text{ g C ha}^{-1} \text{ d}^{-1}$  of mangrove litter, and represented the major component of organic matter exported to adjacent coastal waters. Also, Rivera-Monroy et al. (1994) found that a the fringe mangrove forest bordering Estero Pargo (the site of this study) exported particulate and dissolved organic nitrogen, and was a sink of dissolved inorganic nitrogen. Most studies have focused on how organic materials from mangrove forests support secondary production (e. g. Odum & Heald 1972, Benner & Hodson 1985, Camilleri & Ribí 1986, Moran et al. 1991), however, it is likely that carbon and nitrogen exported from mangrove forests enhance aquatic primary productivity, as it has been demonstrated in temperate coastal systems (Carlsson & Granéli 1993, Carlsson et al. 1993).

Previous work in Terminos Lagoon, a tropical coastal lagoon in the state of Campeche, Mexico, showed that there is a strong seasonality in aquatic primary production (Day et al. 1988). Chlorophyll *a* and aquatic primary productivity increased in the open waters of the lagoon during the rainy season and reached a peak during the beginning of the frontal passage season, which is dominated by strong winds. Day et al. (1988) reported that in February, addition of low and moderate volumes of mangrove water containing humic

substances significantly increased respiration and net production and they suggested that the stimulatory effect of dissolved organic matter exported from mangroves might be an important factor controlling and maintaining phytoplankton production. Before a direct relationship between dissolved organic matter exported from mangrove forests and aquatic productivity can be established, further studies are needed to evaluate the stimulating effect of mangrove drainage on the net aquatic primary production in tropical ecosystems.

In this study, we investigated 1) the seasonal aquatic primary productivity (APP) differences between a tidal creek bordered by extensive mangrove forests and a station located in open waters of Terminos Lagoon, and 2) how addition of filtered water from a fringe mangrove forest floor affected APP. We hypothesized that the addition of filtered mangrove water significantly increased the net aquatic productivity in water from Terminos Lagoon during the dry season, and that net productivity in Estero Pargo was higher than that in open waters of Terminos Lagoon due to the discharge from mangrove forests to the tidal creek.

### Study Area

Terminos Lagoon ( $18^{\circ} 40' \text{ N}$ ,  $91^{\circ} 30' \text{ W}$ ) is a large (approximately  $1800 \text{ km}^2$ ), shallow (mean depth 3.5 m) coastal lagoon located in the Southwestern section of the Yucatan Peninsula in the state of Campeche, Mexico (Fig. 3-1). It is connected to the Gulf of Mexico via two passes, one at each end of Isla del Carmen, a barrier island that separates the lagoon from the open Gulf. Prevailing easterly trade winds create a net east-to-west circulation of coastal waters in the lagoon (Graham et al. 1981, Mancilla & Vargas 1980). The climate of the area is tropical with annual average monthly air temperatures ranging from  $18^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ . Tides are mixed diurnal with a mean tidal range of about 0.3 m. The Candelaria, Chumpán and Palizada rivers are major sources of freshwater discharge (Plegher & Ayala-Castañares 1971). Average annual precipitation ( $1680 \text{ mm yr}^{-1}$ ) is seasonal, with a rainy season from June to October, which is associated with frequent tropical convectional rains. The winter storm or "Norte" season is from November to February with strong north winds and frontal rains, and the dry season is from March to late May or early June. Peak river discharge occurs in the latter months of the rainy season from

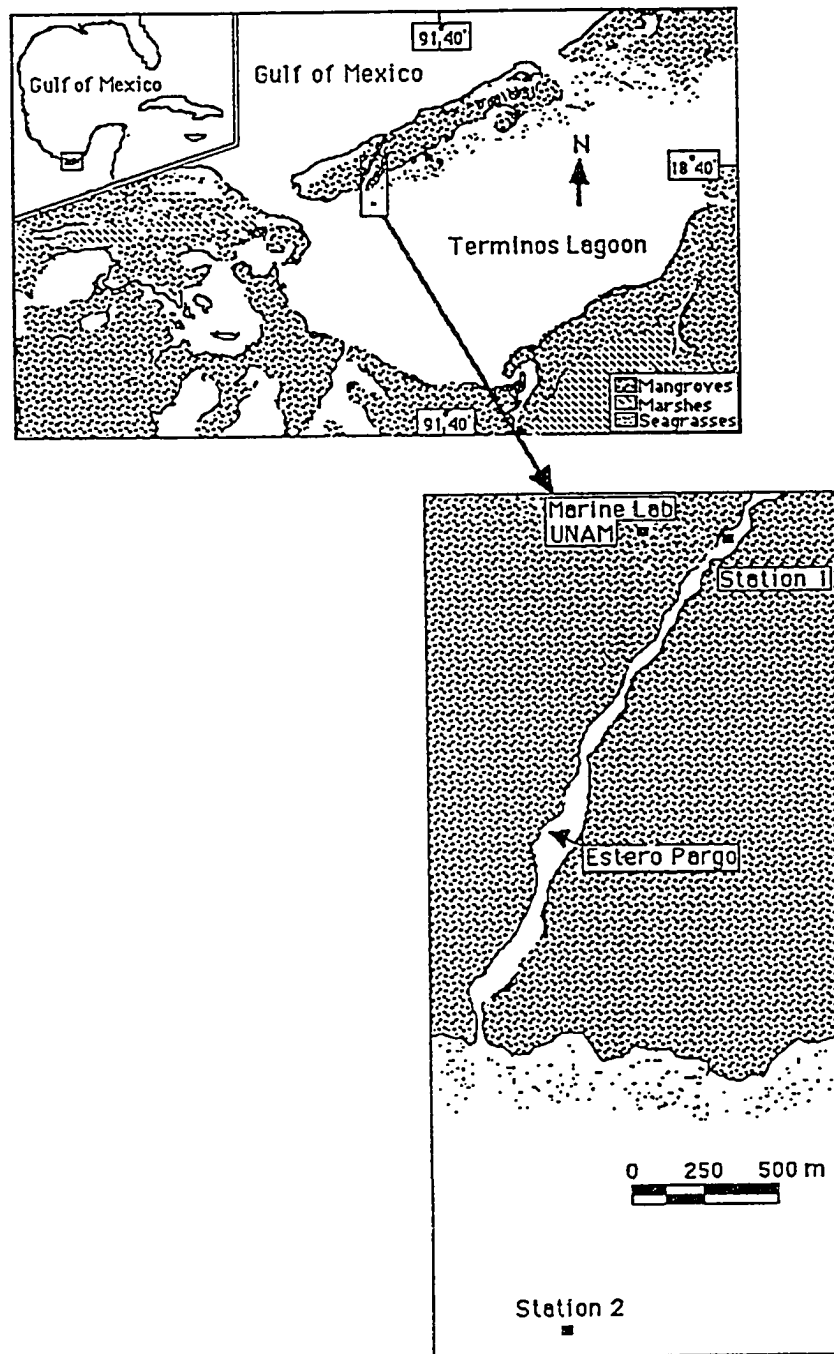


Figure 3-1. Location of sample stations in Terminos Lagoon, Campeche,

September to November. The lagoon is bordered almost completely by extensive mangrove swamps. Three species are dominant: *Rhizophora mangle* L. (red mangrove), *Avicennia germinans* L. (black mangrove), and *Laguncularia racemosa* Gaertn. f. (white mangrove) (Day et al. 1987). Details of the physical and biological processes in Terminos Lagoon are included in summaries by Phleger & Ayala-Castañares (1971) and Yañez-Arancibia & Day (1982).

The study was conducted in a tidal channel located on the lagoon side of Isla del Carmen (Estero Pargo) and a station located in the lagoon approximately 1 km from the mouth of the channel (Fig. 3-1). Estero Pargo is 5.9 km long with a 12.9 km perimeter and the width of the tidal channel ranges from 14 to 251 m and averages 80 m (Ley-Lou 1985). The mangroves adjacent to the tidal creek are characteristic of fringe forests with regular tidal inundation, while the inland mangroves are characteristic of basin forests which are infrequently flooded (Lugo & Snedaker 1974, Day et al. 1982, Lynch et al. 1989). Soil salinities in the fringe forest range from 30 to 35 ‰ and are controlled by the seasonal salinity of creek waters in Estero Pargo (Day et al., 1987).

### **Material and Methods**

#### **Sample collection and incubations.**

**Productivity experiments.** Water samples were collected from Estero Pargo (Station 1) and a station located in Terminos Lagoon (Station 2) (Fig. 3-1). Sampling was done in February, April, May, June, August, September, November 1990, and January, February, March, June, and July 1991. Vertical water column light profiles were taken at each station with a Licor® Li-1000 datalogger and a Li-192SA underwater PAR (photosynthetically active radiation) sensor. Surface water temperature and salinity were measured with a Beckman® (RS5-3) salinometer. Water was sampled from 15-25 cm depth in opaque 25 L carboys and incubated *in situ* at the Estero Pargo station. Clear and opaque 300 mL BOD bottles were filled under subdued light within 0.5 h after sampling and incubated using the light and dark bottle oxygen technique (Gaarder & Gran 1927, Hall & Moll 1975). Triplicate BOD bottles were placed in neutral density screens bags of one to four layers transmitting 75, 44, 27, and 14 % of incident light, respectively. Bottles were suspended from a floating frame in the tidal creek at 15 cm from the surface for 3 h. Initial and final

oxygen concentrations were measured with an Orbisphere® model 2607 oxygen meter ( $\pm 0.01 \text{ mg L}^{-1}$ ) with stirrer and a Clark type temperature-compensated polarographic electrode (Kanwisher 1960). Incident radiation was recorded continuously during the incubation with a Licor® 190SA deck quantum sensor.

**Addition experiments.** Standing surface water from inside the fringe mangrove forest bordering Estero Pargo was collected the same dates as in the productivity experiments. This water was carefully sampled from small ponds 10-15 cm deep with a 500 mL plastic beaker to avoid stirring of particles and transferred to 1 L acid washed (10% HCl v/v) plastic bottles. The water was transported immediately to the laboratory and vacuum-filtered through preashed GF/F glass fiber filters. Aliquots of 0, 1, 5, 10, 20, and 50 mL of filtered mangrove water were added to clear and opaque 300 mL BOD bottles and diluted to 300 mL with water collected from the lagoon (Station 2). Triplicate BOD bottles of each treatment were placed in one layer of neutral density screening transmitting approximately 75% of incident light. To calculate oxygen concentration changes, corrections were made to account for the dilution of the lagoon water samples by the added mangrove water (Day et al. 1988). Bottles were incubated using the light and dark bottle oxygen technique.

Air temperature and precipitation data were collected daily for the study period at a weather station located in Estero Pargo in very close proximity to one of the sampling locations (Station 1, Fig. 3-1). Air temperature data represent the mean monthly temperature measured daily at 10:00 AM. Data for 1988, 1989 and 1992 were obtained from the same weather station and recorded by personnel at the Marine Laboratory of the Instituto de Ciencias del Mar y Limnología-UNAM.

**Productivity calculations and statistical analysis.** Photosynthetic parameters describing photosynthesis versus light intensity (P-I curve) were derived using a two-step curve fitting procedure (Jasby & Platt 1976, Platt et al. 1980). The net oxygen production was fitted to the function given in Kirk (1983):

$$P = \frac{P_m \alpha E_d}{(P_m^2 + \alpha^2 E_d)^{1/2}};$$

where  $P_m$  is the maximum photosynthetic rate,  $E_d$  is irradiance, and  $\alpha$  is the photosynthetic efficiency (the slope of the light-limited part of the P-I curve) (Kirk 1983). Photosynthesis-irradiance (P-I) curves were not fit through the origin (Plat and Harrison 1980) but through points below the abscissa (low light levels and dark bottles) to reduce errors in calculating the initial slope of the P-I curve ( $\alpha$ ) (Lewis et al. 1984, Madden 1992).  $\beta$  (photoinhibition index parameter) was not considered to obtain a better fit to empirical data at the critical and lower light levels since significant photoinhibition was not observed in the incubations for either station. Madden (1992) discussed the effect of  $\beta$  on productivity calculations and found that the inaccuracy introduced by failing to account for inhibition at high levels was compensated by a better fit in the light limited and  $P_{max}$  region of the P-I curves. P-I curves and vertical water column light profiles for each sampling date were used to calculate *in situ* productivity values for the entire water column. Hourly net production was multiplied by the number of hours of PAR occurring per day to estimate daily net production. Oxygen metabolism values were converted to carbon values using a photosynthetic quotient of 1.2 (0.313 g C/g O<sub>2</sub>) and expressed as mg C m<sup>-2</sup> d<sup>-1</sup> (Strickland & Parsons 1972, Vollenweider 1974).

A factorial design was used to test productivity differences between the six volumes of filtered mangrove water, sampling dates, and their interaction in a general linear model (SAS-JMP® 1994). To test differences in net aquatic primary productivity between areas within each month a nested design was used for the productivity experiments. After performing the analysis, linear contrasts were used to evaluate differences among treatments.

### Results

PAR during incubations ranged from 1069 - 1675  $\mu$ Einsteins m<sup>-2</sup> s<sup>-1</sup> (Table 3-1). Incubations were performed mostly during clear, sunny conditions. Water salinity and temperature range was 25-38 ‰ and 22.9 - 33 °C, respectively. Mean monthly temperature ranged from 21-34 °C at the end of the dry season to 18-22 °C during the "Norte" season. Maximum salinity values were observed on 12 June 1990 in Terminos Lagoon at the end of the dry season. Averaged monthly irradiance range was 765 - 1133  $\mu$ Einsteins m<sup>-2</sup> sec<sup>-1</sup> (Fig. 3-2). Maximum and minimum irradiances were observed in August 1990 and June 1991, respectively.

Table 3-1. Environmental conditions, Production/Respiration ratios (P/R), and photosynthetically active radiation (PAR,  $\mu\text{Einstein m}^{-2} \text{ s}^{-1}$ ) during incubation, and water temperature and salinity during sampling collection.

Date	Mean PAR during incubation (around noon)	KD ( $\text{m}^{-1}$ ) <sup>*</sup>		PG/R†		PN/R°		Salinity (‰)		Temperature (°C)		Weather
		TL*	EP£	TL	EP	TL	EP	TL	EP	TL	EP	
1990												
February, 6	1136.4	1.90	1.20	2.6	3.8	1.6	2.8	25.0	31.0	22.9	24.7	partially cloudy
April, 5	1266.0	1.50	2.24	8.8	2.6	7.8	2.5	32.9	32.0	28.3	29.7	clear, sunny
May, 9	1260.0	2.00	2.40	6.7	16.0	5.6	15.0	36.4	35.0	28.8	29.4	clear, sunny
June, 12	1269.0	2.24	1.90	1.3	3.4	0.3	2.4	35.0	38.0	29.0	29.2	partially cloudy
August, 15	1675.2	1.22	1.04	11.2	3.1	10.2	2.1	28.0	26.0	30.0	29.0	clear, sunny
September, 11	1636.0	1.92	1.63	2.4	9.8	1.4	8.8	30.0	28.0	28.5	30.0	clear, sunny
November, 3	1069.3	1.22	1.04	8.6	5.5	7.6	4.5	26.2	25.8	29.0	29.0	partially cloudy
1991												
January, 6	1556.8	1.22	nd	1.0	nd	0.03	nd	26.8	27.2	25.2	33.0	clear, sunny
February, 19	1655.4	2.18	1.68	1.1	1.8	0.11	0.8	25.9	32.0	23.4	25.5	clear, sunny
March, 29	1561.0	1.04	1.50	1.2	1.1	0.17	0.2	33.5	34.7	27.1	27.2	clear, sunny
June, 6	1652.8	0.83	1.27	5.0	3.1	4.01	2.1	36.4	36.2	30.4	30.4	sunny
July, 18	1333.1	1.38	0.48	1.1	3.4	0.05	2.4	30.5	35.0	29.8	31.4	clear, sunny

\*Vertical attenuation coefficient

•Terminos Lagoon

£= Estero Pargo

† = Gross production/Respiration ratio

° = Net production/Respiration ratio

nd= no data



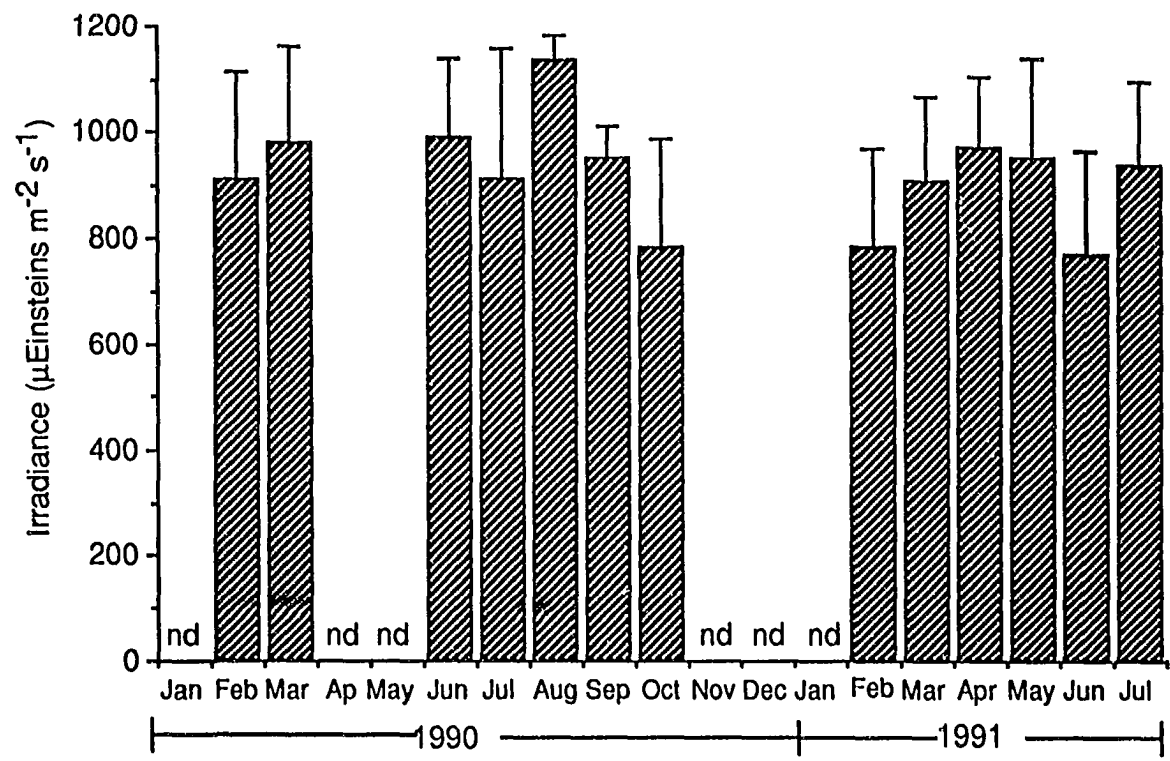


Figure 3-2. Average daily incident photosynthetically active radiation during the study period. nd= no data.

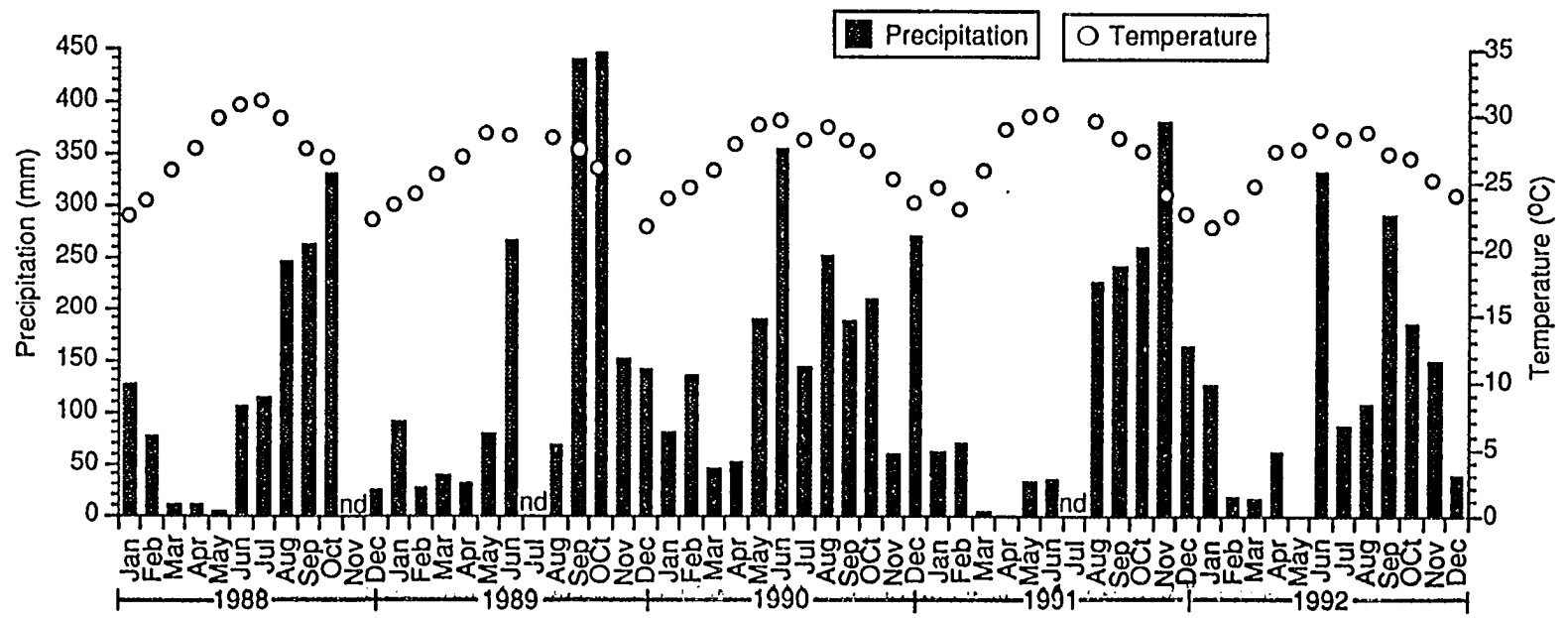


Figure 3-3. Monthly precipitation and mean air temperature in Terminos Lagoon. Climatic parameters were measured in a weather station located 200 m from the Estero Pargo station.

Significant differences in precipitation were observed between 1990 and 1991 (Fig. 3-3). Total precipitation for the period of January through June in 1990 and 1991 was 855 mm and 202 mm, respectively. 1991 was a dry year where maximum temperatures of up to 41 °C were observed in April and May. The high interannual variability between 1990-1991 is characteristic of this area as indicated by the temperature and precipitation record from 1988 to 1992. Similar high temperatures was recorded in 1988 when precipitation for the first part of the year (January-June; 330 mm) was also low indicating that 1988 and 1991 were dry years. Precipitation in June was higher in 1989, 1990, and 1992 than in 1988 and 1991. Annual precipitation for 1988, 1989, 1990, 1991, and 1992 was 1303, 1776, 1974, 1472, and 1414 mm, respectively.

**Net aquatic primary productivity (NAPP).** The model used to estimate photosynthetic parameters fitted well measured net production at different irradiance values in each experiment (Fig. 3-4). P-I curves were different between sites and months, and reflect differences in the physiological state of the phytoplankton community. For example, incubations on 5 April, 9 May, and 12 June 1990 showed a slight light saturation, while almost linear P-I curves for 15 August 1990, 7 June 1991, and 19 February 1991, suggest that phytoplankton were light-limited.

Daily NAPP between the tidal creek and the lagoon were significantly different in all months ( $p < 0.05$ ) except in August and September 1990 (Fig. 3-5). Productivity ranged from 0.03 to 6.5 and from 0.09 to 5.2 g C m<sup>-2</sup> d<sup>-1</sup> in the lagoon and tidal creek, respectively. The highest productivity occurred in June 1991 for both areas. Production rates in July 1991 were higher in Estero Pargo than in the lagoon station. Although there was no consistent pattern between water clarity and NAPP, the highest NAPP rates occurred when there were relatively clear waters. The mean value for  $K_d$  was about 1.5 for both areas.  $K_d$  ranged from 0.48 to 1.22 in August and November 1990 and June and July 1990 when NAPP was highest.

During 1990, the mean of all daily net production measurements was 1.31 g C m<sup>-2</sup> d<sup>-1</sup> for Terminos Lagoon and 0.89 g C m<sup>-2</sup> d<sup>-1</sup> for Estero Pargo. This is equivalent to an annual production rate of 478 g C m<sup>-2</sup> d<sup>-1</sup> for Terminos Lagoon and 324 for Estero Pargo. We feel that these annual values should be considered only as general estimates because there were several months when

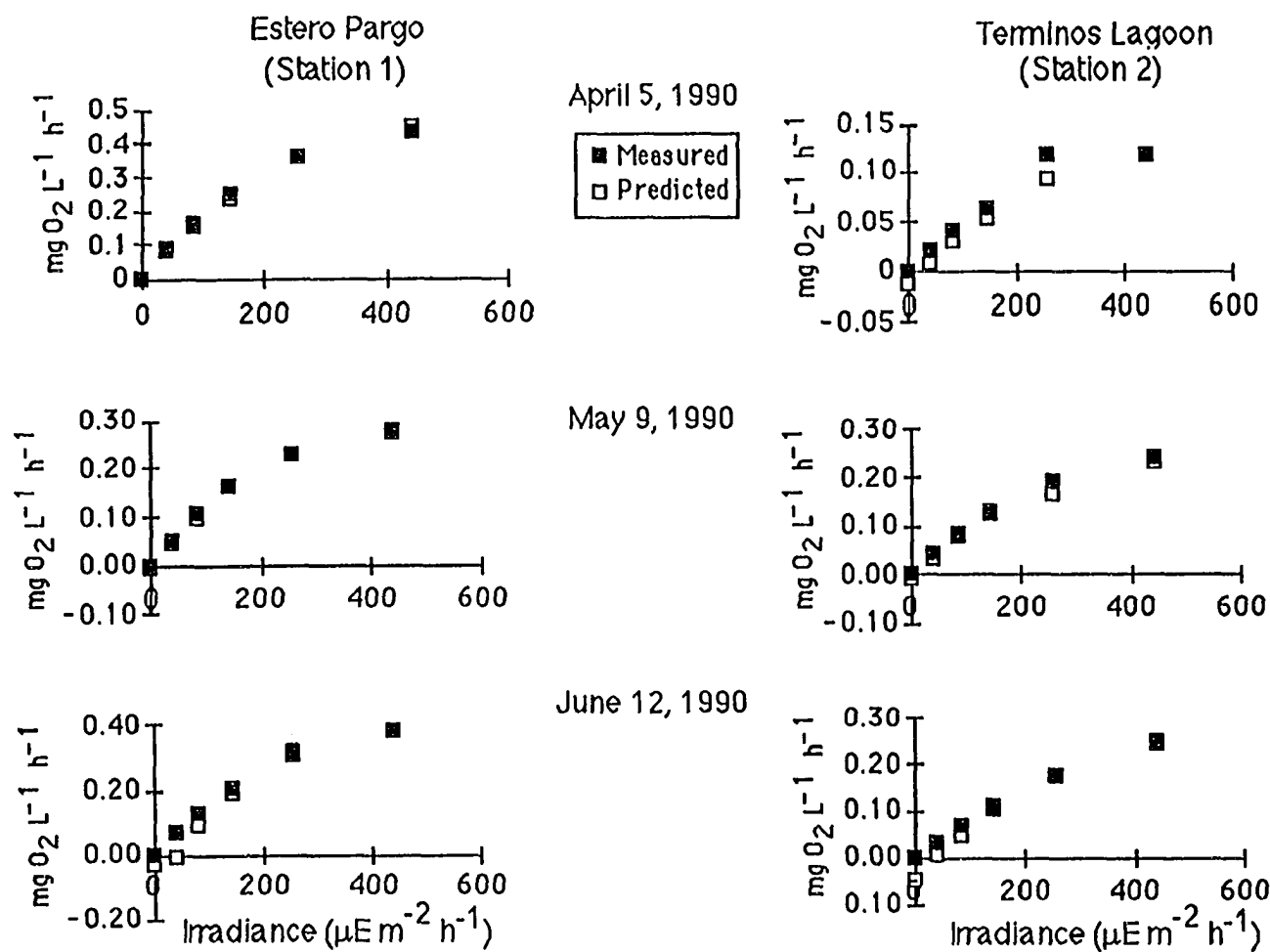


Figure 3-4. Photosynthetic-irradiance (P-I) curves for incubations of representative samples from different seasons in both stations. Samples were suspended from a floating frame in Estero Pargo. Expected values were calculated using a two-step curve fitting procedure (*See methods*)

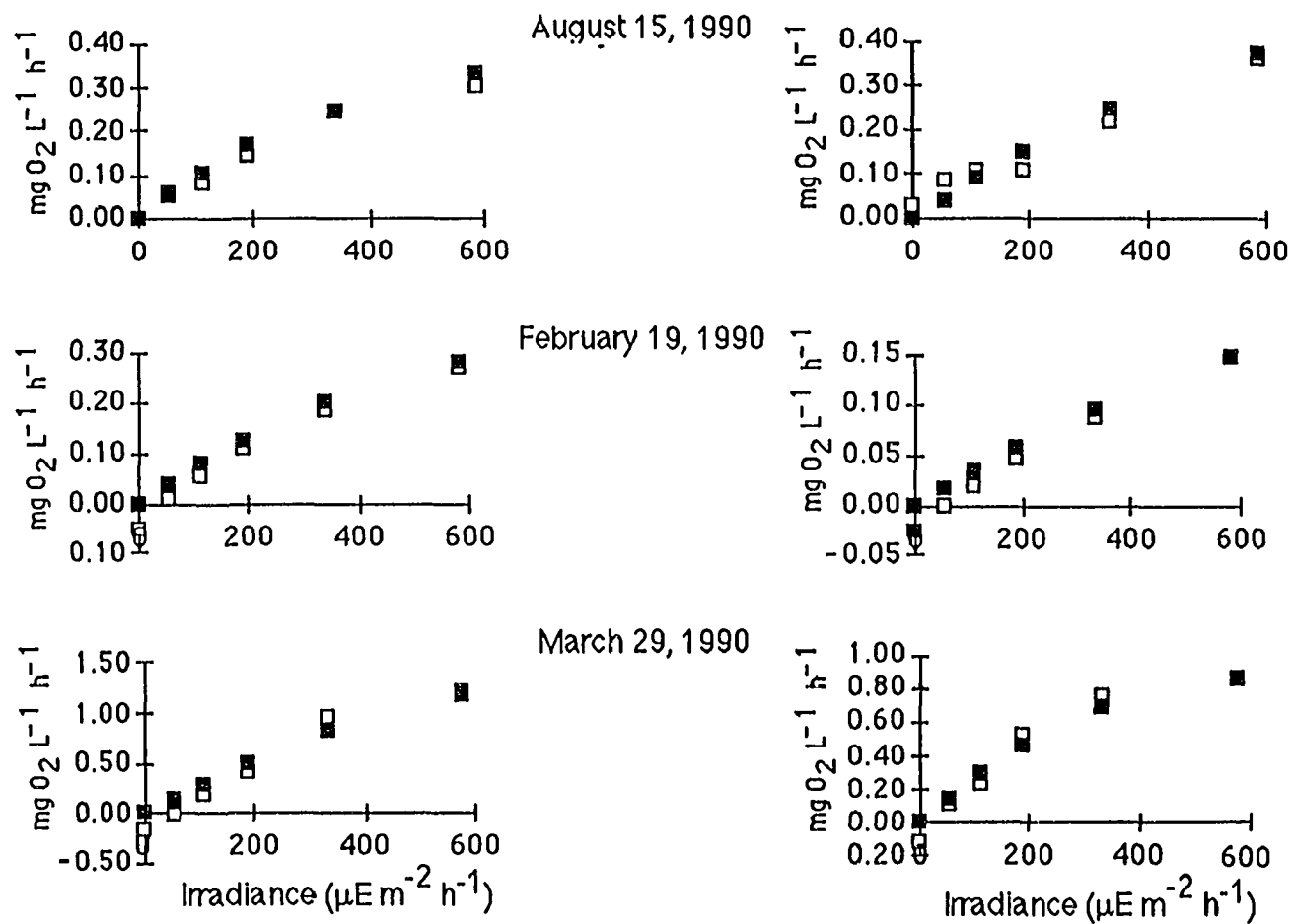


Figure 3-4. Con'd.

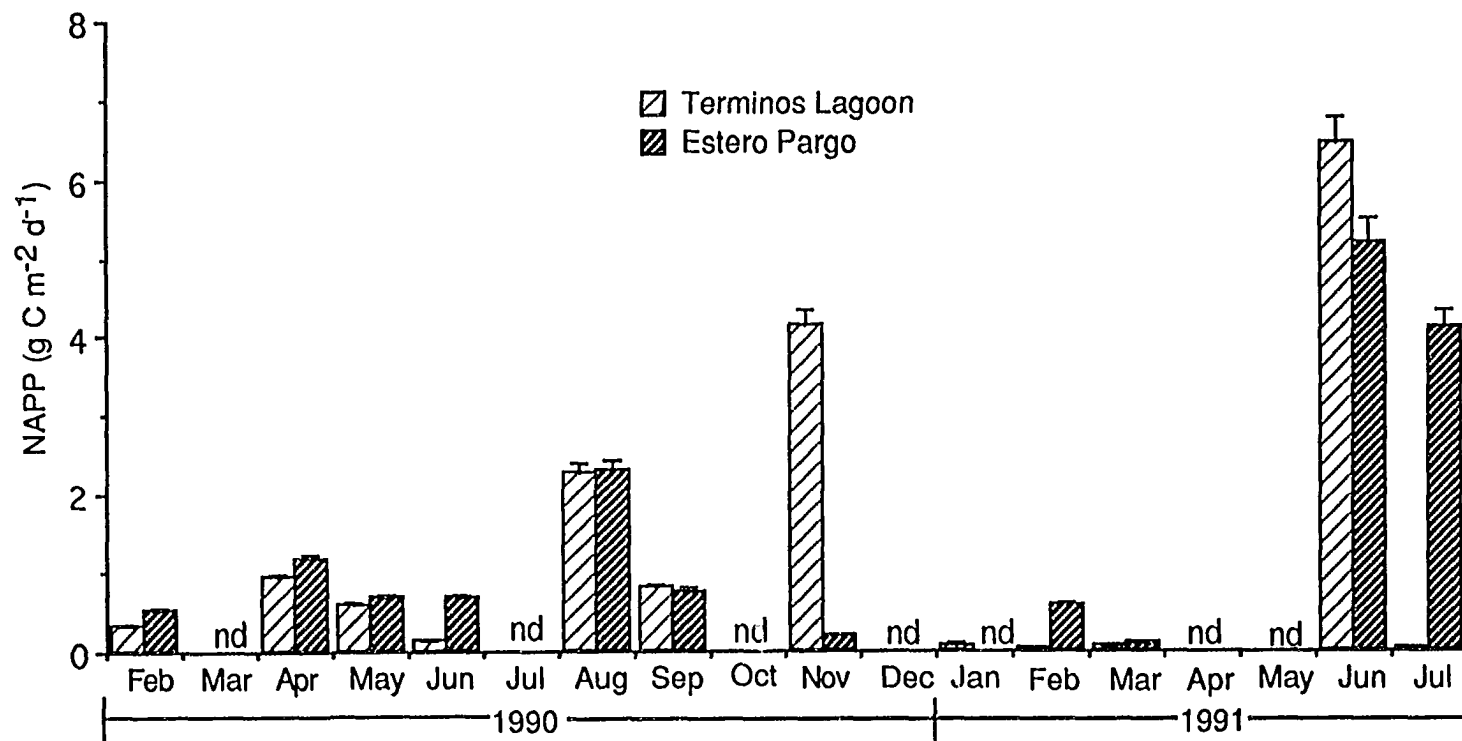


Figure 3-5. Daily net aquatic primary production for different months in Estero Pargo (Station 1) and Terminos Lagoon (Station 2). Error bars are 1 standard deviation for means of 3 replicates. nd= no data.

no measurements were taken and because of the one very high reading in November for the lagoon. The mean of all daily measurements in 1990 and 1991 was  $1.32 \text{ g C m}^{-2} \text{ d}^{-1}$  for Terminos lagoon and  $1.34$  for Estero Pargo. This is equivalent to annual rates of  $481$  and  $489 \text{ g C m}^{-2} \text{ d}^{-1}$ , respectively, for the two systems. The gross production to respiration ratio ( $P_G/R$ ) range was  $1.0 - 11.2$  and  $1.1 - 16.0$  in Terminos Lagoon and Estero Pargo, respectively; whereas net production to respiration ratio ( $P_N/R$ ) range was  $0.03 - 10.8$  for Terminos Lagoon and  $0.2 - 15$  for Estero Pargo (Table 3-1). Average  $P_G/R$  and  $P_N/R$  ratios in both stations were consistently higher in 1990 ( $4.5 - 6.4$ ) than in 1991 ( $0.87 - 2.4$ ).

**Addition experiments.** Addition of one or five ml of filtered mangrove water led to significant stimulation of NAPP in 12 of 24 measurements, no significant change in 10 of 24 measurements and a significant decrease in NAPP in 2 of 24 measurements. The percentage net stimulation of productivity ranged from 20 to 350% (Fig. 3-6) and degree of stimulation was greater in 1990 when there was greater rainfall. There were significant differences in production rates among treatments (0, 1, 5, 10, 20, 50 mL) ( $p < 0.001$ ), months ( $p < 0.001$ ) and the interaction treatment\*month ( $p < 0.001$ ). This interaction indicates that the amount of filtered mangrove water added to the bottles had a variable effect on production rates, depending on the month. NAPP rates ranged from  $0.001$  to  $0.27 \text{ mg C L}^{-1} \text{ h}^{-1}$  for all experiments. The highest rates were observed in experiments performed in June ( $0.25 - .27 \text{ mg C L}^{-1} \text{ h}^{-1}$ ) and July 1991 ( $0.16 - 0.22 \text{ mg C L}^{-1} \text{ h}^{-1}$ ) but the highest percent stimulation occurred June, September and December 1990. Figure 3-6 shows results for selected months within each season. Rates were reduced drastically (12 times) after adding 50 mL on 29 March 1991 when compared to the no addition treatment (0 mL). Significant reductions were observed in February 1991 (5 ml) and July 1991 (1 ml) (Fig. 3-7). The magnitude of the positive responses after addition of 1 and 5 mL mangrove water was not constant for all experiments. The percentage increase generally was higher at the end of the dry season and during the rainy season.

### Discussion

Our results show that Terminos Lagoon was considerably more productive in 1990-1991 than has been reported earlier. The production rates in EsterPargo,

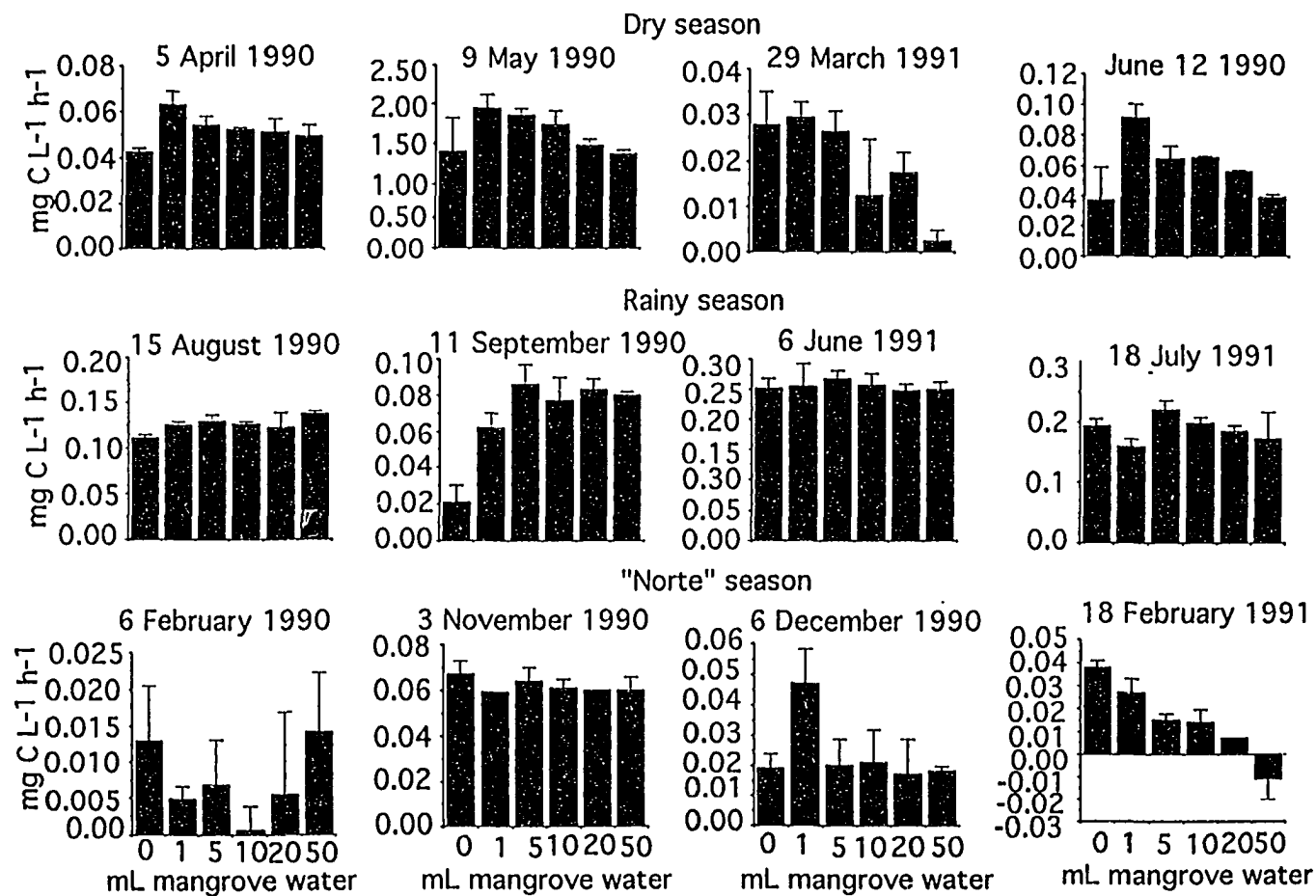


Figure 3-6. Seasonal net aquatic primary productivity of water samples from Terminos Lagoon treated with different volumes of filtered surface mangrove water. Error bars are 1 standard deviation for means of 3 replicates.



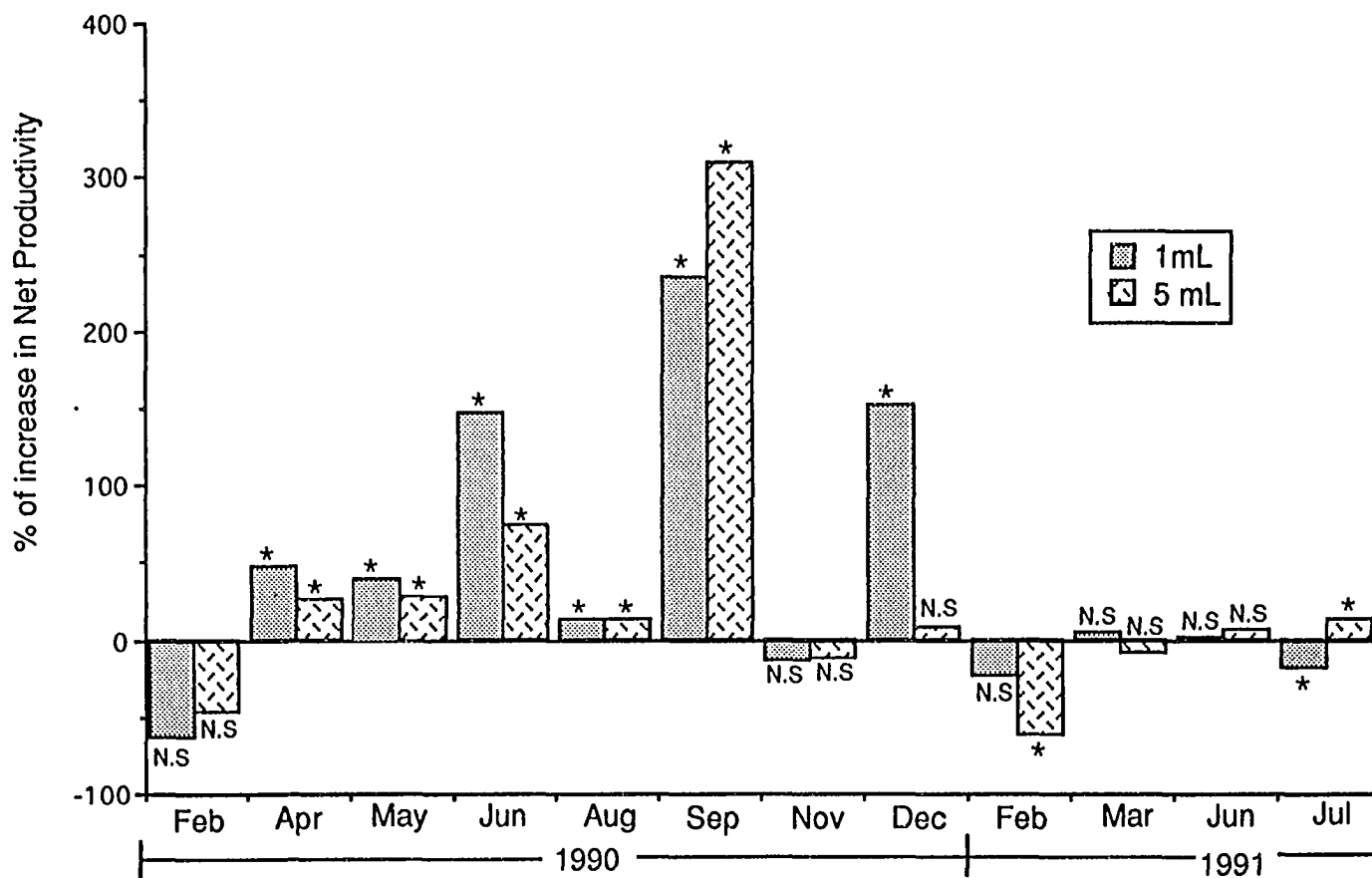


Figure 3-7. Percentage of increase in net productivity of water samples from Terminos Lagoon treated with 1 and 5 mL of mangrove water in different months. (\* = significant  $p < 0.05$ , NS = no significant).

however, were similar to earlier reports. The average Pn/R ratios in both areas show that the water column was autotrophic ( $Pn/R > 1$ ). Terminos Lagoon is strongly influenced by weather forcing (Yañez-Arancibia & Day 1982), and aquatic primary productivity rates have been shown to reflect variations in river discharge and precipitation among years (Day et al. 1982) as observed in 1990 and 1991, particularly during the rainy season. Interannual variation in precipitation is quite high and the dry year in 1991 is similar to the extended dry period in 1988 (Fig. 3-3). These annual fluctuations in precipitation influence NAPP. Water column primary production values at the stations in Estero Pargo and Terminos Lagoon reflect differences in the magnitude and frequency of nutrient inputs from river discharge and mangrove forests. Day et al. (1988) reported high productivities during the dry season (March through May) in Estero Pargo and during the rainy season (June through October) in Terminos Lagoon. They explained this difference as nutrient and light limitation in Terminos Lagoon and Estero Pargo, respectively. We observed the same pattern in the dry season but not during the rainy season. Productivity rates were very similar in both areas in August and September 1990, and June 1991 (Fig. 3-5). Apparently, there is an strong interaction between nutrient loading during high river discharge and primary productivity. High aquatic primary productivity (Day et al. 1988) and high nutrient concentrations (Botello & Manelli 1975) have been measured during the period of peak river discharge (Yañez-Arancibia et al. 1988). Rivera-Monroy et al. (1995) found significant export of particulate (PN) and dissolved organic (DON) nitrogen from the fringe forest in Estero Pargo during the rainy and "Norte" seasons. They reported PN export rates of  $3.9 \text{ mg m}^{-2} \text{ h}^{-1}$  and  $0.62 \text{ mg m}^{-2} \text{ h}^{-1}$  in August and November 1990, respectively. Also, significant export of DON was observed in November 1990 ( $1.3 \text{ mg m}^{-2} \text{ h}^{-1}$ ) and June 1991 ( $0.075 \text{ mg m}^{-2} \text{ h}^{-1}$ ). Export of nitrogen from the fringe forest coincides with high net aquatic primary production rates obtained for the same months in Estero Pargo. Day et al (1988) found that during the wet season, aquatic primary productivity in the lagoon was higher near the shore than towards the center of the lagoon. The mangrove forests in Estero Pargo thus act as a source of nutrients and other stimulating substances, as shown by the addition experiments, and therefore maintain higher production rates in comparison to nutrient depleted waters in the open

lagoon during the dry season. Yet, light limitation can occur as increasing concentrations of total suspended sediments and humic substances limit light penetration and reduce primary production throughout the water column in the rainy season.

Day et al. (1982, 1988) reported NAPP estimates for Terminos Lagoon in the late 1970's and mid 1980's of 197 and 219 g C m<sup>-2</sup> y<sup>-1</sup>, respectively. Ley-Lou (1985) measured a NAPP of 336 g C m<sup>-2</sup> h<sup>-1</sup> for Estero Pargo. He reported that Estero Pargo was heterotrophic with a low average P<sub>N</sub>/R (0.82). Our results show that the water column was autotrophic in 1991 (average P<sub>N</sub>/R= 1.4) and 1990 (average P<sub>N</sub>/R= 5.6). Ley-Lou (1975), however, used the diurnal curve method (Hall & Moll 1975), which includes benthic metabolism. This shows that the benthic community in bottom sediments and attached to mangrove prop roots are important components in controlling total system metabolism in Estero Pargo.

P<sub>N</sub>/R ratios during the first part of the year were lower in 1991 than in 1990 suggesting that metabolic processes were different. This difference might be due to low precipitation (202 mm) from January through June in 1991. Twilley (1982, 1985) has shown how precipitation influenced the hydrology and export rates of dissolved and particulate organic carbon in mangrove basin forests. Rivera-Monroy et al. (1995) measured water levels in Estero Pargo in 1990 and 1991 and observed low water levels in 1991 during the dry season in comparison to high water levels in the "Norte" season. Our results show that mangrove surface water stimulated production rates to a greater degree in 1990, thus it is possible that the export of mangrove water from the fringe forest was low during the early part of 1991.

P<sub>N</sub>/R ratios were generally higher in Estero Pargo. This suggests that the plankton community structure between the areas might be different and therefore respond differently to changing environmental factors. For example, Kannan & Vasantha (1992) reported significant differences in phytoplankton species composition and population densities between an area influenced by extensive mangrove forests and another characterized by the "rich" growth of seaweeds and seagrasses in the Vellar-Coleroon estuarine system, India. They found 67 species of diatoms, 12 species of dinoflagellates, and 3 species of bluegreen algae. This taxonomical composition compares to that reported by

Gomez-Aguirre (1974) in open waters of Terminos Lagoon where he identified 45 genera in the phytoplankton community including 34 diatoms, 4 dinoflagellates, 3 chlophytes, 2 cyanophytes, and 2 rhodophytes. Since there is no phytoplankton community structure data for Estero Pargo it is difficult to evaluate the effect of species composition on production rates in each area.

The downwelling attenuation coefficient ( $K_d$ ) is an indicator of turbidity conditions in a given water body (Kirk 1983). The highest values are found in very turbid waters ( $>2.0 \text{ m}^{-1}$ ) and the lowest in oceanic waters ( $<0.11 \text{ m}^{-1}$ ). The vertical attenuation coefficient for downward irradiance of PAR has been shown to be dependent on water colour in lake systems (Eloranta 1978, Jones & Arvola 1984), which in turn is strongly dependent on dissolved organic carbon.  $K_d$  values in Terminos Lagoon ( $0.48 - 2.4 \text{ m}^{-1}$ ) (Table 3-1) are within the range ( $0.2 - 5.6 \text{ m}^{-1}$ ) reported for coastal and estuarine waters (Madden 1992). We observed higher  $K_d$  values at the lagoon station than in Estero Pargo during the rainy season and the reverse pattern during the dry season. Figure 3-8 shows the attenuation of downward quantum irradiance for three sampling dates during the rainy and dry season. The attenuation coefficient on 11 September 1990, in the middle of the rainy season, is higher in Terminos Lagoon ( $1.92 \text{ m}^{-1}$ ) than in Estero Pargo ( $1.63 \text{ m}^{-1}$ ). The reverse pattern occurred on 29 March and 7 June 1991. Although high  $K_d$  values are related to low integrated primary production, there was not a direct correlation between these two factors. Madden (1992) found in a shallow, extremely turbid, river-dominated estuary one of the highest net primary productivities reported in estuarine systems. He explained this by analyzing the relationship between the light regime and the temporal and spatial variation of photosynthetic parameters affected by a shallow water column and a shallow mixed depth. McMahon et al. (1992) also reported similar relationships in the Shannon Estuary, Ireland. The interaction between  $K_d$  and NAPP can be observed on November 3, 1990. On this sampling day we measured the highest NAPP in Terminos Lagoon in 1990. This date had the lowest  $K_d$  value of 1990, suggesting that phytoplankton was not light limited. In addition, the  $P_N/R$  ratio was high indicating a low respiration, which also contributed to the high NAPP value. Low respiration can be the result of a stable water column where benthic organisms and organic compounds remain in the bottom. The limited number of light profiles performed

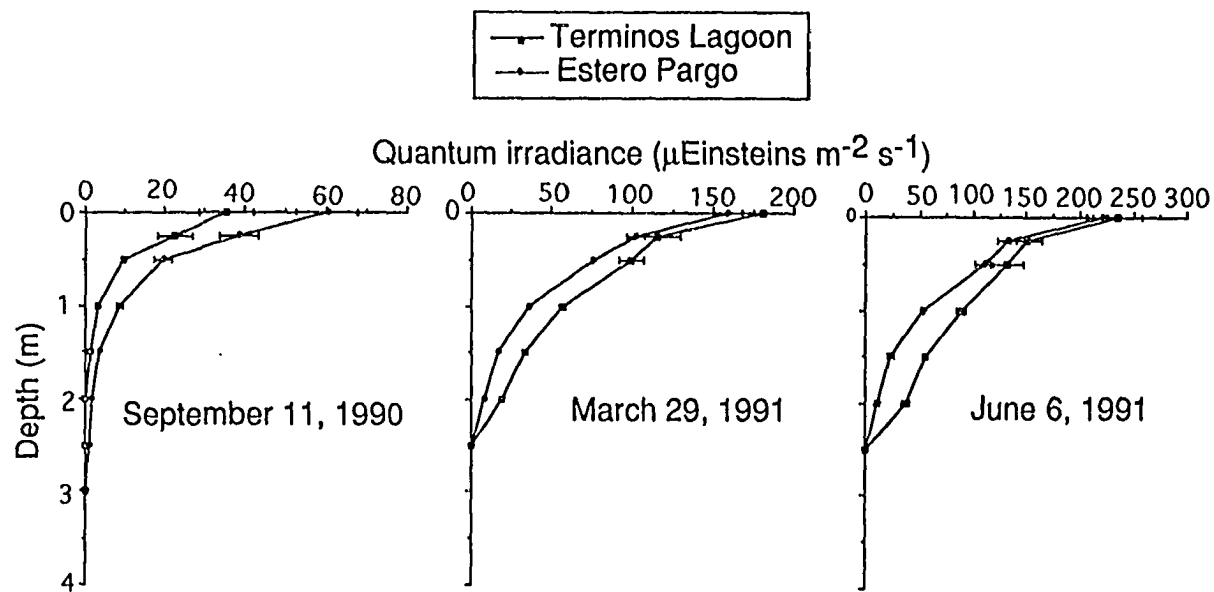


Figure 3-8. Attenuation of downward quantum irradiance of PAR with depth in Terminos Lagoon and Estero Pargo in different seasons. error bars are 1 standard deviation for means of 3 replicates.

Table 2. Net aquatic primary productivity (NAPP) in mangrove dominated tropical and semitropical coastal systems. NAPP is in  $\text{g C m}^{-2} \text{ yr}^{-1}$  (modified from Ricard 1984, and Flores-Verdugo et al. 1988)

Location	NAPP range	Reference
Venezuelan Gulf, Venezuela	35-182	Curl 1960
Cochin Estuary, India	128-310	Quasim 1973
Porto Novo Estuary, India	98-321	Sundararaj & Krishnamurthy 1973
Cananea Region, Brazil	36.5-292	Tundisi et al. 1975
Mukue Lagoon, Africa	416	Kwei 1977
Huizache-Caimanero Lagoon, Mexico	894	Edwards 1978
Chautengo Lagoon, Mexico	248	Mee 1978
Phangha Bay, Thailand	182-876	Wium-Andersen 1979
Baie du Lévrier, Mauritania	511	Sevrin-Reyssasc 1980
Rookery Bay, USA	251	Twilley 1982
Biscayne Bay, USA	13-46	Roman et al. 1983
Mandovi Estuary, India	1.5-232	Verlencar & Qasim 1985
El Verde Lagoon, Mexico	522	Flores-Verdugo et al. 1988
Barra de Navidad Lagoon, Mexico	242	Sandoval-Rojo et al. 1988
Teacapan-Agua Brava Lagoon, Mexico	309	Flores-Verdugo et al. 1990
Gulf of Tehuantepec, Mexico	25.5-522	Robles Jarero & Lara-Lara 1993
Terminos Lagoon, Mexico	219	Day et al. 1982
Terminos Lagoon, Mexico	197	Day et al. 1988
Terminos Lagoon, Mexico	478	This study
Estero Pargo, Mexico	336	Ley-Lou 1985
Estero Pargo, Mexico	324-489	This study

during our study, lack of measurements of other photosynthetic parameters (i. e., light saturated production normalized to chlorophyll concentration) and chlorophyll *a* concentrations make the interpretation of  $K_d$  values difficult in broader temporal and spatial scales. Further studies are needed to elucidate the interaction between the light regime and the phytoplankton physiological state in both areas.

Aquatic primary productivity values estimated for Estero Pargo and Terminos Lagoon compare to those reported in tropical and subtropical coastal systems (Table 3-2). Verlencar & Qasim (1985) reported an annual rate of  $232 \text{ g C m}^{-2} \text{ yr}^{-1}$  for estuarine waters on the Goa coast, India, an area strongly influenced by monsoons. Ricard (1984) reviewed net primary productivity values in different mangrove lagoon waters and reported maximum rates of 292 and  $321 \text{ g C m}^{-2} \text{ yr}^{-1}$  for the Cananea mangrove region in Brazil and the Porto-Novo mangrove area in the Eastern Indian coast, respectively. Wium-Andersen (1979) measured primary production rates of up to  $876 \text{ g C m}^{-2} \text{ yr}^{-1}$  in mangrove waters of Phangha Bay in the south-west coast of Thailand. This bay is very productive and surrounded by extensive mangrove forest areas as is the case in Estero Pargo. Flores-Verdugo et al. (1988) calculated a net aquatic primary production of  $522 \text{ g C m}^{-2} \text{ yr}^{-1}$  in a coastal lagoon with an ephemeral inlet on the Pacific coast of Mexico. They observed a strong seasonal pattern related to rainfall and riverflow with the highest values occurring during the wet season. Sandoval-Rojo et al. (1988) found that in Barra de Navidad, a small coastal lagoon also on the Pacific Coast of Mexico, the highest net productivity value was measured during the rainy season. Net annual productivity was  $241 \text{ g C m}^{-2} \text{ yr}^{-1}$  and decreased during the time of highest river flow due to extreme turbidity. Robles-Jarero & Lara-Lara (1993) observed a maximum and an average net productivity rate of 522 and  $255 \text{ g C m}^{-2} \text{ yr}^{-1}$ , respectively, in the Gulf of Tehuantepec. This coastal area is productive and regulated by intermittent intensive winds ("Nortes") between November and February as in the case of Terminos Lagoon. Flores-Verdugo et al. (1990) concluded that despite high net aquatic productivity ( $309 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), the Teacapán-Agua Brava system was heterotrophic most of the year due to the influence of high organic matter from rivers and surrounding mangroves. This shallow coastal lagoon is strongly influenced by riverflow and rainfall.

Rojas-Galaviz et al. (1992) suggested that high year-round production in Terminos Lagoon is controlled by sequential "pulses" of different primary producers. By analyzing the seasonal productivity of mangrove forests, seagrasses, submersed freshwater aquatic vegetation, epiphytes and microphytobenthos, and aquatic primary productivity, they proposed that primary production follows a "seasonal programming" where primary producers shift throughout the year to maintain high production levels in Terminos Lagoon. Results from our study show that there is also an interannual variability of aquatic primary production which changes this "programming" from year to year. Bartell et al. (1988) proposed that temporal shifts can occur in the relative importance of biotic and abiotic mechanisms regulating primary production. Following this principle, Alpine and Cloern (1992) showed that temporal shifts toward "top-down control" that occur against a background of abiotic "bottom-up control" play an important role in regulating distribution, biomass and primary production of phytoplankton. High fluctuations in river discharge and rainfall (Fig. 3-3) can cause these temporal shifts in Terminos Lagoon since the effect of physical forcing on phytoplankton biology is dynamic and reflects a wide spectrum of timescales (e.g., Alpine and Cloern 1992, Prézelin 1992). The "seasonal programming" proposed for Terminos Lagoon to explain high year-round production should also be analyzed by taking into consideration the effect of larger time scales on the productivity of this estuary.

Day et al. (1988) found that small additions of filtered mangrove water from Estero pargo had a stimulatory effect on oxygen production in light bottles containing water from Terminos Lagoon. Yet, these studies were carried out only at the beginning of the dry season. Our results show that this stimulation occurs during all seasons where addition of low volumes (1 and 5 mL) of surface water stimulated productivity of more than 50% in most of the experiments. High percentages of increase in net productivity were observed during high and low river discharge conditions, indicating that surface mangrove water can stimulate aquatic primary productivity throughout the year. Overall, the magnitude of the stimulation in aquatic productivity by addition of mangrove water was not the same for 1990 and 1991 suggesting an interannual variability. Stimulation was higher in 1990, a period of higher rainfall and high



water levels which would have led to more flooding of the mangroves (Rivera-Monroy 1995).

Although identification of humic substances responsible for the stimulation was not performed in this study, others studies have shown that these substances can lead to increasing APP. Studies in temperate systems and results from laboratory experiments have shown that phytoplankton biomass formation can be stimulated by the addition of humic substances (Prakash and Rashid, 1968; Prakash et al 1973; Gediorowska and Plinski 1986, Carlsson and Graneli 1993; Carlsson et al. 1993). Humic substances in coastal waters influenced by catchment areas dominated by wetlands (Anderson et al. 1989, Moran 1991) can stimulate the growth of several groups in plankton communities (Prakash 1971, Prakash, et al. 1973, Granéli, et al. 1985, Gedziorowska & Plinski 1986, Moran 1991, Carlsson and Granéli 1993). Humic substances are quantitatively important in many aquatic systems, ranging from 25% to as much as 90% of the dissolved organic carbon in marshes and swamps (Moran & Hodson 1990). These compounds constitute the largest fraction of dissolved organic matter in most natural waters (Thurman 1985). However, there are few *in situ* estimates of the effect of drainage water from mangrove forest on aquatic primary productivity in tropical systems.

Evidence from mangrove systems indicate that approximately 30 to 50% (Camilleri & Ribí 1986) of the organic matter in mangrove leaves are leachable water-soluble compounds such as tannins and sugars (Cundell et al. 1979). Cooksey & Cooksey (1978) reported that soluble organic carbon materials present in extracts of sediments are capable of promoting growth in benthic diatoms. This response was observed at the time of red mangrove leaf fall adjacent to Little Card Sound, Florida. Moran (1991) found high concentrations of lignin phenol in waters overlying a mangrove swamp and the formation of significant amounts of dissolved organic matter, humic substances and dissolved lignin phenols during decomposition of red mangrove leaves. Twilley (1982) measured significant amounts of dissolved organic carbon (DOC) leaching from mangrove leaves; thus providing a source of DOC to the surface waters of basin mangrove forests in southwest, Florida. Rivera-Monroy et al. (1995) observed a large export of dissolved organic nitrogen during ebb tides mainly during the "Norte" and rainy seasons in a fringe mangrove forest in

Estero Pargo. Water overlying this mangrove forest was used to perform the addition experiments. The impact of mangrove-derived dissolved organic matter on both the microbial food web of adjacent planktonic environments and the magnitude of phytoplankton nitrogen uptake rates depend on the quality and quantity of exported material (Moran et al. 1991; Carlsson et al. 1993). Granéli et al. (1986) and Toledo et al. (1980) suggested that land drainage enriched with organic matter had stimulating effects on marine phytoplankton due to trace metal chelation. Other workers have suggested that humic substances may act as binders or inactivators of trace metals which could be essential or toxic to many phytoplankton species (Mackey 1984, Toledo, et al. 1982). Complexation of trace metals by humic substances has been widely reported, but the ecological implications are not well-understood (Jones 1992). Studies in mangrove dominated systems have shown that lignocellulose derived humic substances were also assimilated into microbial biomass (Benner & Hodson 1985, Moran 1991).

In several cases we observed inhibition of NAPP with high additions. Prakash & Rashid (1969) and Prakash & Rashid (1968) pointed out that growth inhibition can occur at high concentration of humic substances due to the selective absorption of light by the increased amount of yellow color, thus limiting photosynthesis. Also, Jones (1992) discussed how dissolved organic compounds, particularly humic substances, have a very important effect on light attenuation and suggested that humic substances can "compete" with phytoplankton for available quanta and therefore potentially restrict photosynthesis production. Guildford et al. (1987) reported that addition of moss-peat material decreased primary productivity due to the binding of iron. However, they also reported that reduction of light penetration by addition of suspended sediment depressed primary productivity. Cooksey and Cooksey (1978) noted an increasing inhibition of diatom growth by sediment extracts before the beginning of the rainy season. They observed that sediment extracts were brown in color indicating the presence of tannins, that could be toxic to some microalgae (Craigie & McLachlan 1974). Ricard (1984) pointed out that tannins released by mangrove trees inhibit the growth of phytoplankton by "direct action" or by lowering of pH. Prakash et al. (1973) concluded that growth inhibition caused by high concentrations of humic substances is due

mainly to excessive metal binding. Jackson & Hecky (1980) also reported an inverse relationship between dissolved organic carbon and primary productivity and suggested that humic substances reduced iron availability to phytoplankton through the formation of humic-iron-phosphate complexes.

This is the first annual study where the coupling between aquatic primary productivity and mangrove surface water has been evaluated for an annual cycle in a tropical system. Stimulation of aquatic primary production occurred in water from Terminos Lagoon forest during all seasons after addition of surface water overlying a fringe mangrove. This indicates that drainage from mangrove forests can enhance water column primary productivity in adjacent estuarine waters throughout the year. In addition to export of dissolved organic matter, river discharge and precipitation also can regulate aquatic primary productivity in Estero Pargo and Terminos Lagoon. River flow controls phytoplankton production by changing inputs of nutrients from the watershed to the estuary and modifying light availability through stratification, gravitational circulation, and relocation of the turbidity maximum (Day et al. 1989). Also, environmental conditions such as time of day, quantum scalar irradiance, photoperiod, temperature, availability of nutrients, and phytoplankton community structure can affect photosynthesis and thus primary production (Coté & Platt 1983, Vincent 1992, Frenette et al. 1993). It is the combined effect of river discharge, drainage from mangrove forests, and constant temperature and solar irradiance throughout the year that make Terminos Lagoon one of the most productive Mexican coastal lagoons.

Mangrove forests surrounding Terminos Lagoon have been removed in some areas as a result of human activities such as urban development, oil exploration and road construction (Yañez-Arancibia & Day 1988b). Furthermore, since there is a period of seven years between our studies and those by Day et al. (1982,1988), it is plausible that nutrient enrichment is occurring due to increasing usage of fertilizers for extensive agriculture in the upper watershed. It is not known if the nutrient load into the lagoon has increased during the last years and how it will affect aquatic primary productivity in the long term. Further nutrient sampling is needed during high river discharge conditions before a relationship can be established. Since results from this study indicate that mangrove forests can influence primary

productivity in adjacent estuarine waters in Terminos Lagoon, it is important to evaluate the combined effect of excessive nutrient loading and carbon and nutrient export from mangrove forests.

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## CHAPTER 4

### DIRECT DENITRIFICATION IN MANGROVE SEDIMENTS IN TERMINOS LAGOON, MEXICO

#### Introduction

Mangroves are a dominant feature of diverse coastal landscapes in the tropics (Por 1984) including river deltas, lagoons, estuaries, and carbonate platforms (Twilley et al. 1995). These forested wetlands are important to the productivity of tropical estuaries (Boto et al. 1985, Lugo et al. 1990, Twilley et al. 1992), yet there is limited information about nutrient cycling in these intertidal macrophytes. Although nitrogen is an essential element to a variety of biological processes in mangrove forests (Alongi et al. 1992), there are few ecological studies of nitrogen transformations within mangrove ecosystems (Twilley 1988, Alongi et al. 1992). In particular, it is not clear how coupled nitrogen transformations within the forest influence the exchange of nitrogen at the boundary of mangroves with coastal waters.

A few studies of nitrogen flux between mangroves and coastal waters concluded that mangroves may be a significant sink of dissolved inorganic nitrogen in tidal waters. For example, Walsh (1967) observed that  $\text{NO}_3^-$  concentrations entering a mangrove tidal creek in Hawaii decreased with distance inland, but no nitrogen fluxes were directly measured. Nedwell (1975) reported that about 90 % of  $\text{NO}_3^-$  in a polluted station receiving sewage effluent was removed in a mangrove bordered tidal river in Fiji. Rivera-Monroy et al. (1995) measured nitrogen fluxes between Estero Pargo, an unpolluted tidal creek, and a fringe mangrove forest in Terminos Lagoon, Mexico. They reported that mangrove sediments were a sink of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  throughout the year. The fluxes of inorganic nitrogen were also measured between the fringe and adjacent basin mangroves; the latter mangrove exported some  $\text{NO}_3^-$  and  $\text{NH}_4^+$  to the fringe mangrove. Denitrification, the dissimilatory reduction of  $\text{NO}_3^-$  to produce  $\text{N}_2\text{O}$  and  $\text{N}_2$ , was considered the process that contributed to  $\text{NO}_3^-$  loss in these mangrove studies. Yet, there are few direct measurements of denitrification and estimates of how these rates influence the exchange of nitrogen in mangrove forests (e. g. Alongi et al. 1992). Denitrification may be

an important process that regulates nitrogen flux at the mangrove-estuary boundary (Twilley 1988).

Denitrification is primarily dependent upon anoxic conditions, the presence of an energy source, and availability of  $\text{NO}_3^-$  substrate (Mosier & Schimel 1993). Depending on the  $\text{NO}_3^-$  source, there are two types of denitrification. Direct denitrification is fueled by  $\text{NO}_3^-$  that diffuses into sediments, while coupled denitrification is supported by  $\text{NO}_3^-$  produced by nitrification in sediments (Jenkins & Kemp 1984, Henriksen & Kemp 1988). Most of the denitrification studies in mangroves have focused on direct denitrification to understand the potential use of mangroves as a natural tertiary treatment of wastewater (Nedwell 1975, Corredor & Morell 1994). However, there is practically no information on direct denitrification in mangroves under natural conditions (i.e. Iizumi 1986), nor how these rates may differ among riverine, fringe, or basin mangroves (Lugo & Snedaker 1974, Twilley 1988).

Corredor and Morrel (1994) measured high denitrification rates in a fringe mangrove in Puerto Rico receiving secondarily treated sewage effluent. They concluded that mangrove sediments were capable of denitrifying up to 15 times the normal  $\text{NO}_3^-$  concentrations (200 - 1000  $\mu\text{M}$ ) dissolved in the effluent. However, Boto and Wellington (1988) reported that  $\text{NO}_3^-$  was actually exported from an unpolluted mangrove tidal channel in Australia. Denitrification rates in intertidal sediments from that system were low (Iizumi 1986) and represented minor losses of nitrogen from the ecosystem (Alongi et al. 1992). There are conflicting results on the denitrifying capacity of mangrove sediments leading to the confusion on the role of mangroves as a  $\text{NO}_3^-$  sink (Corredor and Morrel 1994).

In our study, we assumed that denitrification could account for the uptake of  $\text{NO}_3^-$  observed in flux studies of mangroves by Rivera-Monroy et al. (1995), demonstrating the importance of this transformation to the fate of nitrogen in fringe and basin mangroves. We expected higher denitrification rates in the fringe mangroves than in the basin mangroves due to differences in nitrate availability. To test this hypothesis, we measured the effect of different  $\text{NO}_3^-$  concentrations on rates of denitrification in intact sediments cores from fringe and basin forests in Estero Pargo during different seasons using  $^{15}\text{N}$  isotope techniques.

## Material and Methods

**Study area.** This study was carried out in Terminos Lagoon ( $18^{\circ} 40' \text{ N}$ ,  $91^{\circ} 30' \text{ W}$ ), a large ( $\sim 1800 \text{ km}^2$ ), shallow coastal lagoon located in the southwestern section of the Yucatan Peninsula in the state of Campeche, Mexico (Fig. 4-1). The climate of the area is tropical with annual average air temperatures ranging from  $18$  to  $36^{\circ}\text{C}$ . Tides are mixed diurnal with a mean tidal range of about  $0.5 \text{ m}$ . Average annual precipitation ( $1680 \text{ mm yr}^{-1}$ ) is seasonal, with a rainy season from June to October, which is associated with frequent tropical convective rains. The winter storm, or "Norte", season is from November to February, with strong north winds and frontal rains. The dry season is from March to June. Peak river discharge occurs in the latter months of the rainy season from September to November.

The lagoon is bordered almost completely by extensive mangrove forests that are dominated by three species including *Rhizophora mangle* L. (red mangrove), *Avicennia germinans* L. (black mangrove), and *Laguncularia racemosa* Gaertn. f. (white mangrove) (Day et al. 1987). Estero Pargo is a tidal creek located on the lagoon side of the barrier island Isla del Carmen. The forests adjacent to the tidal creek are characteristic of fringe mangroves with regular tidal inundation, while the inland forests are characteristic of basin mangroves which are infrequently flooded (Lugo & Snedaker 1974, Day et al. 1982). The bulk of the soil material in both mangroves consists of organic matter with many inclusions of fibrous mangrove roots and of coarser woody material. Bulk density in the fringe and riverine mangroves is  $0.28$  and  $0.31 \text{ gdw cm}^{-3}$ , respectively (Lynch et al. 1989b). Total nitrogen concentration in sediments reported for the fringe mangrove is  $5.7 \text{ mg gdw}^{-1}$  and for the basin mangrove is  $9 \text{ mg gdw}^{-1}$  (Lynch 1989a). Terminos Lagoon and Estero Pargo have been described in detail elsewhere (Phlegher & Ayala-Castañares 1971, Ley-Lou 1985, Yañez-Arancibia & Day 1988).

**Experimental design.** Two experiments were performed to evaluate direct denitrification in mangrove sediments. The first experiment was to investigate spatial variation in denitrification rates by comparing results from the fringe and basin mangroves in the rainy season (July 1991). The second experiment was to determine the effect of different concentrations of  $\text{NO}_3^-$  on denitrification rates and was performed in the fringe mangrove during the "Norte" season

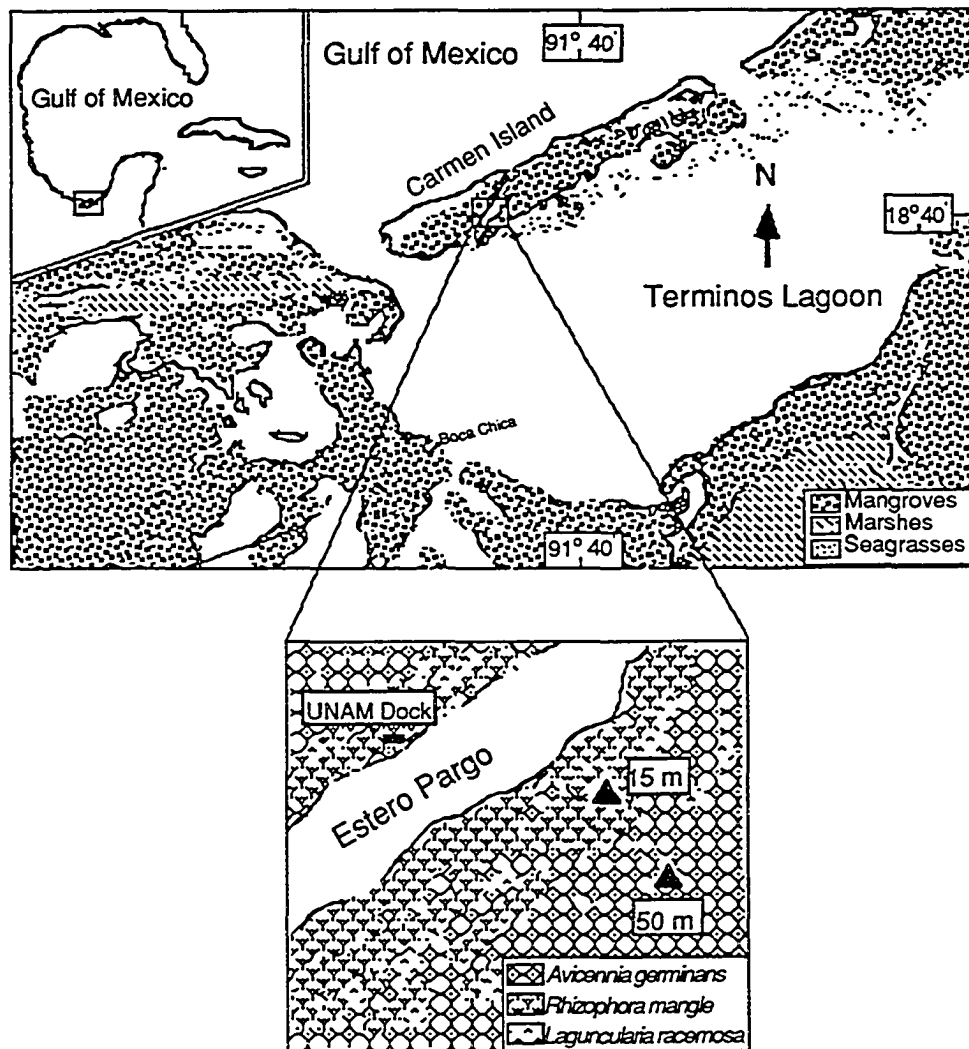


Figure 4-1. Location map for sediment cores collected in the fringe and basin mangrove forests in Estero Pargo, Mexico.

(January 1992). There were similar concentrations of  $\text{NO}_3^-$  used in the rainy and "Norte" seasons in the fringe mangrove to also allow a temporal comparison of rates. Experiments were conducted in intact sediment cores collected about 15 m (fringe) and 50 m (basin) inland from the tidal creek in Estero Pargo (Fig. 4-1) .

Four cores were collected from each of the two mangroves for the site comparison study while six cores were used in the fringe mangrove for the concentration study. Plexiglass cylinders (30 cm long and 15 cm i.d.) were carefully placed on the sediment surface and forced approximately 25 cm into the sediment. The cores were sampled in close proximity to each other to minimize spatial variability and were considered as replicates. Pneumatophores were present in all cores and precautions were taken to assure that the aerial portions of pneumatophores were not damaged during core sampling. Pneumatophore density was similar in both forests ( $428 \pm 100 \text{ m}^{-2}$ ) despite the dominance of *Rhizophora mangle* trees in the fringe mangrove. After collecting the core, a rubber cap was placed on the core base and secured with two aluminum bands. The cores were carefully transported in the dark back to the laboratory. Sediment temperature was measured during core sampling. Floodwater in each site was collected with previously acid-washed (10% HCl v/v) 1 L plastic containers.

Nitrogen-15 enrichment to the cores was  $200 \mu\text{mol/core } ^{15}\text{N-KNO}_3$  (99 atom %  $^{15}\text{N}$ ) for the site comparison experiment in July 1991 ( $0.16 \text{ g m}^{-2}$ ). Cores collected in the fringe mangrove in January 1992 were randomly assigned to concentrations of either 25, 100, or  $200 \mu\text{mol/core } ^{15}\text{N-KNO}_3$  (2 cores per treatment). These enrichments represent <2% of the amount added in similar studies of wetland sediments (e. g.  $19 \text{ g m}^{-2}$ , Reddy et al. 1989;  $10 \text{ g m}^{-2}$ , Lindau & Delaune 1991). Concentrations used in our study were selected to assure that  $^{15}\text{N}$  emission reflected denitrification rates under natural conditions, yet providing a measurable  $^{15}\text{N}$  signal in the cores. Caffrey and Kemp (1992) also used similar  $^{15}\text{N}$  enrichment of  $0.15 \text{ g m}^{-2}$  to study direct denitrification in subtidal sediments. The isotope solutions were made with filtered (GF/F) floodwater collected in the field at the same time as the cores. Solutions were injected into each core at the surface, and at 2 and 9 cm depth to distribute the isotope throughout the core. A water depth of 1-2 cm was maintained over the



sediment surface within the cores throughout the experiments with ambient floodwater. After isotope enrichment, the cores were incubated outdoors in the dark using a covered plastic chamber under ambient temperature (mean ambient temperature was 28 °C).

In the site comparison experiment, one core was removed from the chamber at 1, 3, 5, and 8 days following  $^{15}\text{N}$ -enrichment. At that time pneumatophores were cut about 1 cm from the top of the core and covered with silicone grease (Corning®) to minimize altering the normal exchange of gases through these root structures (Scholander 1955, Curan 1985, Nickerson & Thibodeau 1985, McKee et al. 1988). Production of  $\text{N}_2$  was trapped in the headspace of each core by placing a plexiglas lid with gasket on the core top that was secured with 6 screws distributed evenly around the lid to form a gas-tight connection. The depth of each headspace was recorded, and zero-time gas samples were collected immediately after the headspace was sealed. Gas samples were taken from the headspace using a gas-tight syringe and hypodermic needle through a rubber septum sealed in the lid. Aliquots of 5 mL were withdrawn at 1 and 10 h, transferred to glass rubber-stoppered Vacutainers® (75 mm long by 10 mm i. d.), and stored until assay by  $^{15}\text{N}$  mass spectrometry. Vacutainers® were stored immersed in water to prevent contamination of atmospheric gases. After each headspace sampling, an equivalent volume (5 mL) of air was replaced to maintain pressure inside the core, and the core was returned to the incubation chamber. Changes in oxygen concentration in the headspace throughout the 10 h incubation were determined on a second 5 mL aliquot sampled at the same time  $^{15}\text{N}_2$  gas samples were taken. Oxygen and  $\text{N}_2$  concentrations were measured with a gas chromatograph (SRI Instruments Model 8610) equipped with a TCD detector and a CTR dual-phase column (Alltech®) using helium as carrier gas. Oxygen concentrations changed <14 % in all experiments and  $\text{N}_2$  concentrations were constant over time (data not shown).

At the end of the 10 h time series, 50 mL of overlying water was sampled and each core sectioned at approximately 4 cm intervals to obtain 5 sediment samples per core. Replicate sediment subsamples (50 g per sample) were used for extraction of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (Sumi & Koike 1990) with 2 N KCl (150 mL of KCl per 50 g of sediment) for 1 h. Another two subsamples ( $\approx 35$  g) were

also taken from each sample for analysis of percent water (dried at 60 °C for 48 h) and bulk density. Dry sediments were ground with mortar and pestle, and assayed for total carbon and nitrogen and  $^{15}\text{N}$  content in four subsamples per sample.

Sampling of headspace and sediment during the  $\text{NO}_3^-$  concentration study followed a similar procedure as the site comparison study. Headspace samples were collected at 1 and 10 h periods following  $^{15}\text{N}$  application and after sealing the headspace in each core. Headspace sampling was repeated in each core at 1, 3, and 5 days. At the end of the 5 d incubation the six cores were then sectioned and processed for nutrient and  $^{15}\text{N}$  analyses as described above.

**Sample analysis.** Total carbon and particulate nitrogen were analyzed with a LECO® CHN elemental analyzer. Overlying water and KCl extracts were analyzed for  $\text{NH}_4^+$  (Solórzano 1969) and  $\text{NO}_3^-$  (Grasshoff et al. 1983) concentrations. Nitrogen concentrations and sediment densities were used to calculate total  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and PN per core. Headspace samples were assayed for nitrogen isotopic masses of 28, 29, and 30 by injecting directly into a nuclide Model 3-60-RMS double collector instrument (Measurement and Analysis Systems, Bellefonte, PA). Air samples obtained at the beginning of the 10 h time series sampling were analyzed as a reference gas on the IRMS inlet using the sample inlet (Mulvaney & Kurtz 1982).

$^{15}\text{N}$  enrichment in overlying water, KCl extracts and sediment were measured with a JASCO  $^{15}\text{N}$  emission spectrometer.  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  in the overlying water and KCl extracts were isolated by sequential steam distillations using MgO to raise the pH above 9.0 (Keeney & Nelson 1982) following reduction of  $\text{NO}_3^- + \text{NO}_2^-$  to  $\text{NH}_4^+$  by Devarda's alloy (Bremer 1965). Carryover between samples was minimized by a distillation of ethanol between each sample (Fiedler & Proksch 1975). Fifty mL of the condensate were collected directly onto approximately 0.035 g of ion sieve (Union Carbide #W-85). The ion sieve trapped 95% of the  $\text{NH}_4^+$  based on preliminary experiments with 50 mL of distillate. The ion sieve was collected on a 25 mm A/E filter, dried (60 °C), placed in petri dishes, and stored in a vacuum desiccator until assay for  $^{15}\text{N}$  content. Recovery of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  following this distillation procedure averaged 99% and 75%, respectively. Samples were prepared by first converting organic and inorganic nitrogen to nitrogen gas with a dry

microDumas combustion technique (Fielder & Proksch 1975). Sediment and ion sieve samples were placed in previously degassed (550 °C, 12h) discharge tubes (Pyrex glass 6.0 mm O.D) containing CaO and Cuprox. The tubes were evacuated to 1 mTorr, and filled with argon to 1 Torr, and preheated to remove residual water vapor. Tubes were again evacuated to 1 mTorr and argon added to obtain vacuum of 1 Torr. The tubes were sealed and later combusted at 550 °C for 12 h and cooled to room temperature for another 12 h. The atom%  $^{15}\text{N}$  for samples was then determined with a JASCO  $^{15}\text{N}$  analyzer (Model N-150). Three scans of the light emission spectra of the 28 and 29 mass were performed on each sample. The instrument was calibrated with commercial standards prepared from samples analyzed by mass spectrometry (Japan Spectroscopic Co. Instruction Manual model N, 1986). The formula used to calculate atom% was:

$$^{15}\text{N}(\text{atom}\%) = \frac{100}{2R + 1}$$

$$\text{where } R = \frac{^{14}\text{N}_2}{^{14}\text{N}^{15}\text{N}} \text{ (Fielder \& Proksch 1975).}$$

Denitrification rates were calculated using a mass spectrometric procedure developed for determination of  $^{15}\text{N}$ - $\text{N}_2$  evolved from sediments treated with  $^{15}\text{N}$ -labeled substrates (Mulvaney & Kurtz 1982, Mulvaney & Kurtz 1984, Mulvaney & Boast 1986). Significant differences between rates of  $^{15}\text{N}$ - $\text{N}_2$  production between treatments in the  $\text{NO}_3^-$  concentration experiment were determined with a one-way ANOVA with a level of significance of 0.05 (SAS, 1993). A two-way analysis of variance was used to test differences in sediment  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations between areas in the site comparison experiment.

## Results and Discussion

**Nutrient concentrations and atom %  $^{15}\text{N}$  enrichment.** Mean  $\text{NH}_4^+$  concentrations were significantly higher ( $p < 0.05$ ) in the fringe than in the basin mangroves in July 1991 (Table 4-1, Fig. 4-2). Concentrations ranged from 22 to 44  $\mu\text{g gdw}^{-1}$  in the fringe mangrove and from 6 to 18  $\mu\text{g gdw}^{-1}$  in the basin mangrove. There was a decline from 18  $\mu\text{g gdw}^{-1}$  at 0-6 cm to 7  $\mu\text{g gdw}^{-1}$  at 18-23 cm in the basin mangrove (Fig. 4-2).  $\text{NH}_4^+$  concentrations did not show any pattern with depth in the fringe mangrove. Although  $\text{NO}_3^-$  concentrations

Table 4-1. Bulk density (BD g cm<sup>-3</sup>), carbon to nitrogen ratios (C:N), and extractable-N (µg gdw<sup>-1</sup>) averaged with depth (0-23 cm) in cores from fringe and basin forests incubated at different days in July 1991; mean values (± 1 SD).

Forest type	Parameter	Incubation time			
		1	3	5	8
Fringe	BD	0.20(0.01)	0.26(0.01)	0.20(0.01)	0.20(0.01)
	C:N	25.1(5.1)	22.1(1.7)	19.0(0.61)	21.3(1.5)
	NH <sub>4</sub> <sup>+</sup>	35.3(12.2)	28.0(15.5)	37.2(8.11)	37.1(14.5)
	NO <sub>3</sub> <sup>-</sup>	6.7(1.4)	4.5(2.9)	7.0(3.01)	11.4(6.0)
Basin	BD	0.22(0.01)	0.4(0.01)	0.22 (0.01)	0.60 (0.02)
	C:N	22.3(1.2)	23.6(1.7)	22.8(1.2)	39.2(16.0)
	NH <sub>4</sub> <sup>+</sup>	14.7(5.9)	11.9(10.0)	8.3(6.8)	9.1(1.9)
	NO <sub>3</sub> <sup>-</sup>	3.7(0.8)	4.1(0.9)	2.4(1.7)	3.2( 1.5)

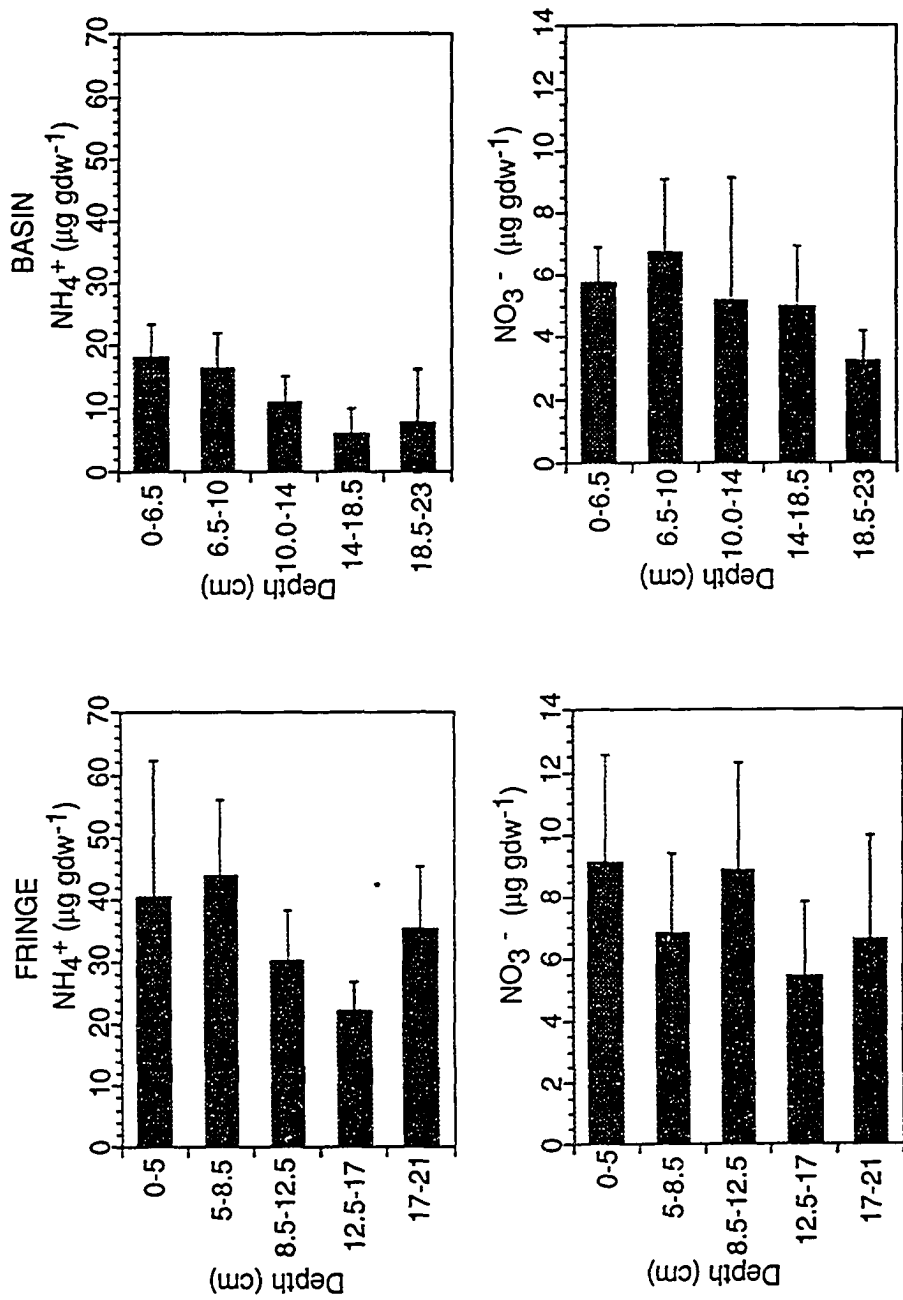


Figure 4-2.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations with depth in cores from the fringe and basin forest in July 1991.

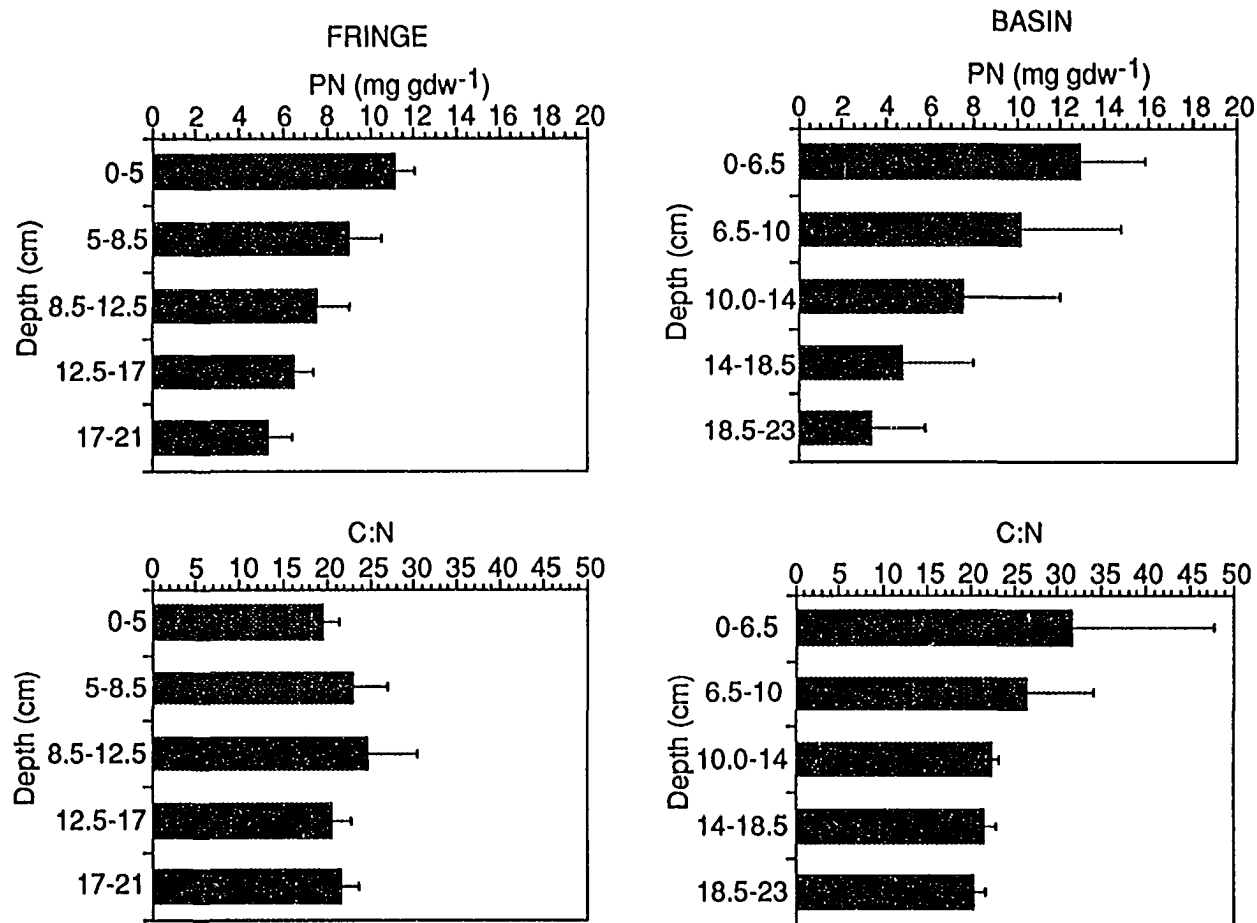


Figure 4-3. Particulate nitrogen (PN) and carbon to nitrogen ratios (C:N) with depth in cores from the fringe and basin forest in July 1991.

were higher in the fringe than in the basin mangrove, this difference was not significant ( $p > 0.05$ ). Mean  $\text{NO}_3^-$  concentrations ranged from 5.5 to 9.0  $\mu\text{g gdw}^{-1}$  in the fringe mangrove and from 3.5 to 6.5  $\mu\text{g gdw}^{-1}$  in the basin mangrove. There were no differences in  $\text{NO}_3^-$  concentrations with depth in either area. Particulate nitrogen (PN) concentrations decline with depth in both mangroves (Fig. 4-3). PN decreased from 11  $\text{mg gdw}^{-1}$  at 0-5 cm to 5.5  $\text{mg gdw}^{-1}$  at 17-21 cm in the fringe mangrove. In the basin mangrove there was a large variation associated with the mean at each depth, and concentrations declined from 12.5  $\text{mg gdw}^{-1}$  to 3  $\text{mg gdw}^{-1}$ . PN concentrations were higher in the top 10 cm in the basin mangrove than in the fringe mangrove. C:N ratios were not significantly different with depth in either mangrove, although a slightly higher ratio was measured in the basin mangrove in the top 10 cm. Ratios ranged from 19 to 25 in the fringe mangrove and from 21 to 32 in the basin mangrove.

Mean  $\text{NH}_4^+$  concentrations were significantly lower ( $p < 0.05$ ) in duplicate cores treated with 25  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$  than in cores treated with 100 and 200  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$ . Mean  $\text{NO}_3^-$  concentrations were higher in cores amended with 200  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$ , but this difference was not significant (Table 4-2). There were no differences in mean C:N ratios and bulk densities in all treatments (Table 4-2). Mean  $\text{NO}_3^-$  concentrations with depth were higher in cores enriched with 200  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$  with values of 7.5-9  $\mu\text{g gdw}^{-1}$  at 12-19 cm, compared to 2-3  $\mu\text{g gdw}^{-1}$  for the other two treatments (Fig. 4-4). Mean atom %  $^{15}\text{NO}_3^-$  and  $^{15}\text{NH}_4^+$  enrichment with depth for all treatments ranged from 0.1-0.31 and 0.1-0.39, respectively (Table 4-2).

**$^{15}\text{N}_2$  production.** Denitrification rates were different in the fringe and basin mangroves in July 1991, although sediments from both areas were treated with the same  $^{15}\text{N-KNO}_3^-$  concentration (200  $\mu\text{mol/core}$ ) (Fig. 4-5). The highest denitrification rate (9.4  $\mu\text{mol m}^{-2} \text{h}^{-1}$ ) was observed in the fringe mangrove after 3 d of incubation. This was the only flux of labeled  $\text{N}_2$  observed in this mangrove during the 8 d incubation period. In contrast,  $^{15}\text{N}_2$  fluxes in the basin mangrove declined from 4.5  $\mu\text{mol m}^{-2} \text{h}^{-1}$  after 1 d to 1.9  $\mu\text{mol m}^{-2} \text{h}^{-1}$  at day 8. No fluxes were observed at this site on day 3 and 5. C:N ratios and bulk density of the core sampled on day 8 were different than the other cores in this experiment (Table 4-1). Mean bulk density in the 8 d core was 0.60  $\text{gdw cm}^{-3}$

Table 4-2. Bulk density (BD g cm<sup>-3</sup>), carbon to nitrogen ratios (C:N), extractable-N (μg gdw<sup>-1</sup>) averaged with depth (0-20 cm), and atom% enrichment in duplicated cores from a fringe forest enriched with different <sup>15</sup>NO<sub>3</sub><sup>-</sup> concentrations in January 1992; mean values (± 1 SD).

Parameter	<sup>15</sup> NO <sub>3</sub> <sup>-</sup> treatment concentration		
	25	100	200
BD	0.22(0.01)	0.26(0.06)	0.21(0.01)
C:N	16.8(0.6)	18.6(2.0)	17.4(0.2)
NH <sub>4</sub> <sup>+</sup>	12.9(7.8)	24.5(4.0)	22.9(8.7)
NO <sub>3</sub> <sup>-</sup>	2.7(1.6)	2.9(1.8)	6.2(3.2)
atom % <sup>15</sup> NO <sub>3</sub> <sup>-</sup>	0.1(0.2)	0.3(0.1)	0.2(0.1)
atom % <sup>15</sup> NH <sub>4</sub> <sup>+</sup>	0.1(0.1)	0.4(0.4)	0.2(0.2)



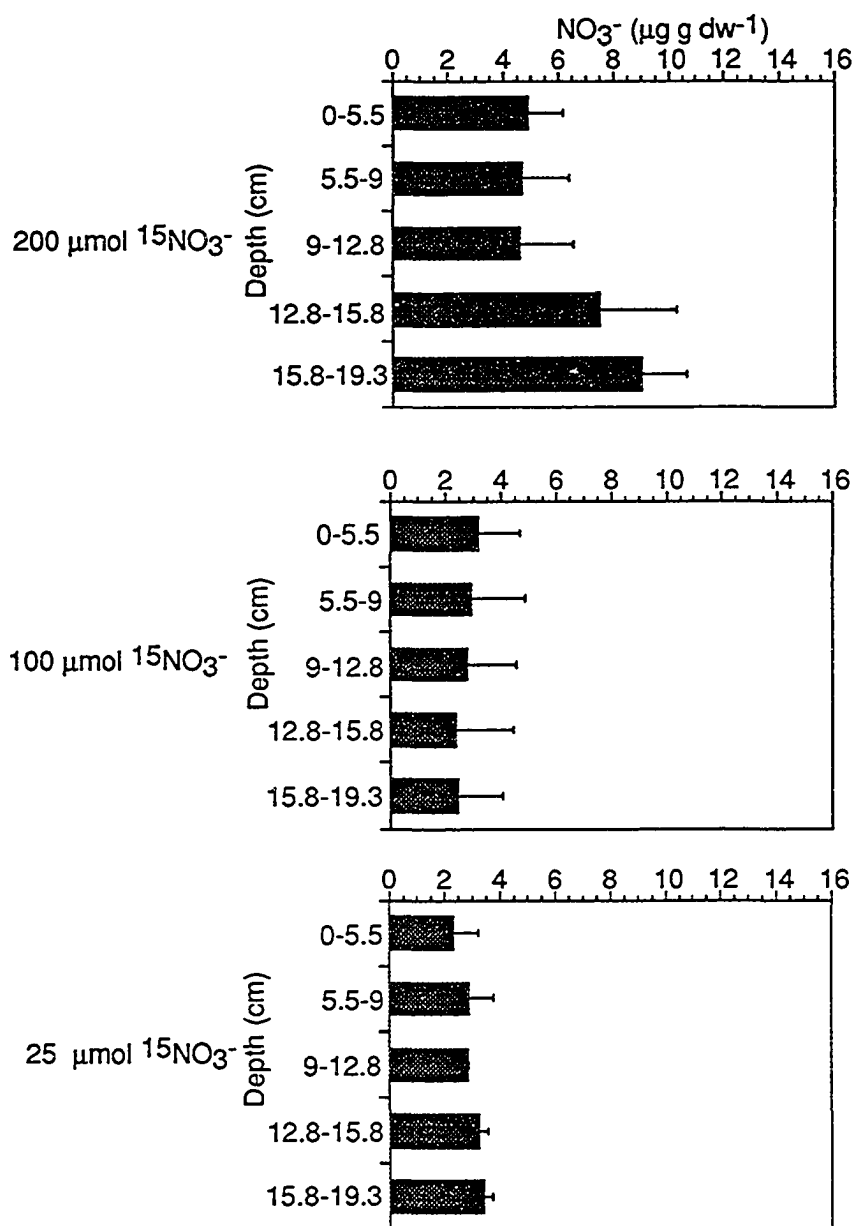


Figure 4-4.  $\text{NO}_3^-$  concentrations with depth in cores from the fringe forest enriched with different  $^{15}\text{N-KNO}_3^-$  concentrations in January 1992.

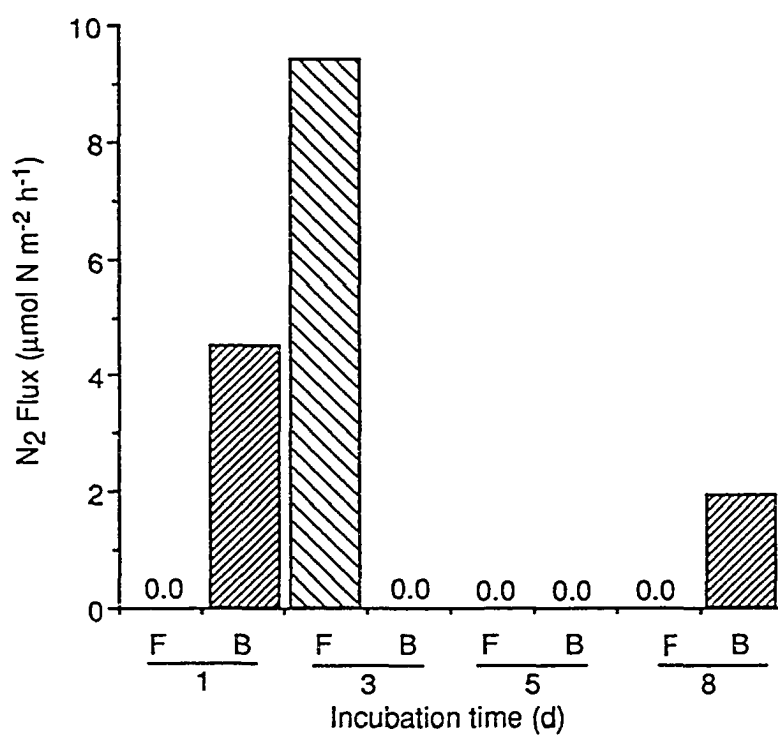


Figure 4-5. Denitrification rates at different incubation times in sediment cores from the fringe (F) and basin (B) mangrove forests in Estero Pargo, Mexico in July 1991.

in contrast to 0.22 (1 d), 0.36 (3 d) and 0.22 (5 d)  $\text{gdw cm}^{-3}$ ; mean C:N ratios with depth were also higher (39 vs 22) at 11-23 cm.

Similar concentrations of extractable nitrogen were observed in all cores from the basin mangrove (Table 4-1), yet the different physical properties of sediments in these experiments may have influenced the timing of  $^{15}\text{N}_2$  fluxes. Nielsen et al. (1990) pointed out that even when there are high densities of denitrifiers in sediment, diffusion processes influenced by bulk density (Rosenfeld 1979, Mackin and Aller 1984) can control the supply of electron donors or acceptors, even when such nutrients are present at high concentrations. Nielsen (1992) also observed some variability among cores and mentioned that the differences probably reflected variation in biological activity. Lindau & Delaune (1991) and Risgaard-Petersen et al. (1994) found high variation in  $\text{N}_2$  fluxes among replicates and attributed it to the non-homogeneity of cores used in their experiments. Kessel et al. (1993) stated that the major problem in estimating N losses by denitrification was the high degree of spatial and temporal variability of this process. We also observed some inconsistent patterns in the presence of  $^{15}\text{N}_2$ ; yet similar rates in replicated cores, particularly in the enrichment experiment in January 1992, indicate that most of the experimental cores represented homogenous sediment conditions in both mangroves.

Gas "entrapment" has also been reported as an important process contributing to spatial variability in nitrogen flux in flooded sediment systems. Lindau et al. (1988) found that 28% of the applied  $^{15}\text{N}$ -urea and 40% of the  $^{15}\text{N}$ - $\text{KNO}_3^-$  was "trapped" as  $\text{N}_2$  and in unvegetated sediment chambers 33 d after nitrogen application. Katyal et al. (1989) reported that after 16 days, 41% of the applied  $^{15}\text{NO}_3^-$  ( $10 \text{ g m}^{-2}$ ) was still "entrapped" as  $\text{N}_2$ . Also, Lindau & Delaune (1991) calculated that 23% of the added  $^{15}\text{NO}_3^-$  remained in sediment cores collected from a *Spartina alterniflora* marsh. Although we did not measure the amount of  $^{15}\text{N}_2$  dissolved in the pore and overlying water directly, estimates using Bunsen solubility coefficients (Weiss 1970) (Table 4-2 and 4-3) show that  $\text{N}_2$  concentrations were very low in cores where  $^{15}\text{N}_2$  in the headspace was detected. This suggests that gas "entrapment" as defined by Lindau et al. (1988) was not significant in either experiment.

Pneumatophores have been considered as organs responsible for gas exchange between the atmosphere and the internal tissue of mangroves (Andersen & Kristensen 1988). Reddy et al. (1989) showed that aerenchyma tissue in aquatic plants can function as conduits for  $N_2$  and  $N_2O$  from anaerobic sediments to the atmosphere. Lindau & Delaune (1991) also concluded that the accumulation of these gases in flooded sediments could have been "greatly" reduced if live *Spartina alterniflora* had been included in their experiments. Further work is needed to evaluate if "entrapment" of  $N_2$  occurs in mangrove sediments in other type of mangroves (e.g. riverine, dwarf), as well as the role of pneumatophores in controlling  $N_2$  fluxes to the atmosphere.

**Mass Balance.** The recovery of  $^{15}N$  was <55% in the site comparison experiment between fringe and basin mangroves after 8 d of incubation (Table 4-3). These estimates of  $^{15}N$  recovery do not include  $^{15}N$  in larger roots and pneumatophores since these nitrogen pools were not measured. The largest  $^{15}N$  fraction was measured in the sediments with recovery ranging from 35 to 54 % in the fringe mangrove, and from 44 to 56 % in the basin mangrove. The second largest  $^{15}N$  fraction was measured in the extractable  $NH_4^+$  pool.  $^{15}NH_4^+$  represented <3% of the total  $^{15}N$  recovered in the fringe mangrove and <5% in basin mangrove.  $^{15}NO_3^-$  concentrations were <1 % in both mangroves (Table 4-3). Similarly, the amount of  $^{15}NO_3^-$  and  $^{15}NH_4^+$  in the overlying water was almost zero and represented a very small fraction of the total  $^{15}N$  added in cores. Caffrey & Kemp (1992) also found a small fraction (<1%) of  $^{15}N$  in the overlying water of vegetated cores.  $^{15}N_2$  in the headspace was detected after 3 d in the fringe mangrove (92  $\mu g$ ) and after 1 d in the basin mangrove (29  $\mu g$ ). This flux of nitrogen represented <3 % of the recovered  $^{15}N$ .  $^{15}N_2$  dissolved in the pore and overlying water in both mangroves was also a small portion of the recovered  $^{15}N$  (<1%) (Table 4-3).

Mass balance in the fringe and basin mangroves suggests that there are other  $^{15}NO_3^-$  sinks. Since we used intact cores, it is possible that some  $^{15}NO_3^-$  was absorbed by the root system. Christensen et. al. (1990) pointed out that the presence of plants and their root can make  $NO_3^-$  unavailable to denitrifying bacteria through uptake and assimilation. Boto et al. (1985) reported that in laboratory experiments  $NO_3^-$  uptake was critical for fine root development of *Avicennia marina* seedlings. Also,  $NO_3^-$  uptake by algae attached to

Table 4-3. Distribution of applied  $^{15}\text{N}$  (ug/core) among various forms of nitrogen including nitrogen gas ( $\text{N}_2$ ), extractable N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ), sediment nitrogen and total  $^{15}\text{N}$  recovered at different times following enrichment as an average with depth ( $\approx 0\text{-}20$  cm) in cores from fringe and basin mangroves in the rainy season. Mean ( $\pm 1$  SD).

Date	Forest Type	Time (d)	Applied N (ug/core)	$\text{N}_2^{\text{¶}}$	Extractable $^{\text{£}}$ N		Overlying water			$\text{N}_2^{\text{¶,†}}$ Pore water	Sediment	Total
					$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{N}_2$			
4 July 1991	Fringe	1	2970	0	38 (8)	0.9 (0.5)	-	-	0	0	999 (261)	1040
		3	2970	92	61 (19)	2.0 (0.3)	0	0	2	0.1 (0)	1022 (346)	1179
		5	2970	123	96 (9)	1.0 (0.8)	-	-	0	0	1174 (433)	1394
		8	2970	123	82 (22)	1.0 (0.3)	0	0	0	0	1403 (530)	1609
7 July 1991	Basin	1	2970	29	142 (40)	1.0 (0.4)	0	0	0	0	1160 (210)	1332
		3	2970	44	81 (19)	0.3 (0.2)	0	0	-	0	1459 (639)	1584
		5	2970	44	110 (37)	3.0 (0.8)	-	-	-	0	1504 (515)	1661
		8	2970	69	43 (10)	0.2 (0.1)	-	-	1	0.1 (0)	1430 (242)	1543

$^{\text{¶}}$  = Calculated using Bunsen solubility coefficients (Weiss 1970)

$^{\text{£}}$  = Includes all 5 sections per core

$^{\text{¶,†}}$  = Includes only first 2 top sections ( $\sim 0\text{-}10$  cm) of core

(-) no data

Table 4-4. Mass balance of  $^{15}\text{N}$  for enrichment experiment performed in duplicate cores from the fringe forest in January 1992. Units are  $\mu\text{g } ^{15}\text{N excess } (\pm 1 \text{ SD})$ .

Core Partition	Amendments ( $\mu\text{mol}$ )					
	2970		1485		371	
	1	2	1	2	1	2
$\text{N}_2$ Headspace <sup>¶</sup>	56	84	0.0	7	0.0	0.0
$\text{N}_2$ <sup>¶</sup> Overlying water	1	2	0.0	0.2	0.0	0.0
$\text{N}_2$ Pore water <sup>¶,†</sup>	0	0.1	0.0	0.0	0.0	0.0
Extractable-N <sup>£</sup>						
$\text{NH}_4^+$	2 (0.2)	22 (0.0)	207 (21.4)	16 (1.3)	2 (0.3)	9 (0.1)
$\text{NO}_3^-$	7 (0.1)	6 (0.0)	53 (7.6)	31 (4.1)	0.1 (0.0)	0.1 (0.1)
Overlying water <sup>£</sup>						
$\text{NH}_4^+$	-	-	-	-	-	-
$\text{NO}_3^-$	-	-	-	-	-	-
Sediment <sup>£</sup>	2035 (861.5)	2818 (682.9)	1299 (629.0)	1419 (598.6)	155 (219.5)	286 (194.7)
Total recovered	2101	2932	1559	1473	157	295

<sup>¶</sup>= Calculated using Bunsen solubility coefficients (Weiss 1970)

<sup>£</sup>= Includes all 5 sections per core; some values for extractable-N are missing in both cores at 2970 and 1485  $\mu\text{mol}$  treatments

<sup>†</sup>=Includes only first 2 top sections (~0-10cm) of core

(-) no data

pneumatophores (Dor 1984, Rodriguez & Stoner 1990) and in the sediments could be another  $\text{NO}_3^-$  sink inside the cores. Apparently, "competition" for  $\text{NO}_3^-$  between denitrifiers and uptake by these nitrogen pools might be important in the fringe and basin mangroves during the rainy season.

As in the site comparison study, sediments in the substrate concentration study had the largest accumulation of  $^{15}\text{N}$  (Table 4-4). The recoveries of excess  $^{15}\text{N}$  for both cores enriched with  $200\ \mu\text{mol/core}\ ^{15}\text{N-KNO}_3^-$  were 70 and 98%, higher than values in the site comparison study. For the replicated cores enriched with  $100\ \mu\text{mol/core}\ ^{15}\text{N-KNO}_3^-$  the recoveries were 99 and 105 %, and for the cores in the  $25\ \mu\text{mol/core}\ ^{15}\text{N-KNO}_3^-$  treatment the recoveries were lower at 42 and 80 % (Table 4-4). The second largest fraction of  $^{15}\text{N}$  recovered in this experiment was the exchangeable nitrogen pool. The highest recovery (14%) of extractable  $^{15}\text{NH}_4^+$  was measured in one of the cores enriched with  $100\ \mu\text{mol/core}\ ^{15}\text{N-KNO}_3^-$ ; but overall the recovery of  $^{15}\text{N}$  in this pool was < 10%.  $^{15}\text{NO}_3^-$  recoveries in the KCl-extracts for all cores were < 4%.  $^{15}\text{N}_2$  in the headspace, and pore and overlying waters represented < 2% of the recovered  $^{15}\text{N}$ .  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  in the overlying water were not determined in this experiment due to analytical problems. The recovery of extractable nitrogen pool in the  $1485\ \mu\text{g}\ ^{15}\text{N-KNO}_3^-$  and  $2970\ \mu\text{g}\ ^{15}\text{N-KNO}_3^-$  enrichments may be underestimated due to missing values at some depths. However, this underestimate does not change the overall amount of recovery since low  $^{15}\text{N}$  concentrations were generally found in the extractable nitrogen pool.

Recovery of  $^{15}\text{N}$  in the  $\text{NO}_3^-$  enrichment experiment in January 1992 was >80%, higher than the site comparison study in July 1991. In both experiments most of the recovered  $^{15}\text{N}$  in all cores was measured in the sediment. The low recovery of  $^{15}\text{N}$  in the extractable pool (which includes pore water  $^{15}\text{N}$  and exchangeable  $^{15}\text{N}$ , Mackin and Aller 1984) indicates that adsorption of  $^{15}\text{N}$  was low. This suggest that a large amount of inorganic nitrogen was probably absorbed by sedimentary bacteria. Davidson et al. (1992) concluded that microbial assimilation of  $\text{NO}_3^-$  may be an important pathway for  $\text{NO}_3^-$  retention in forest ecosystems. This might be the case in Estero Pargo given the low  $\text{NO}_3^-$  concentrations observed in both mangroves (Table 4-1). When the C:N ratio of substrate is low (<15:1) decomposers are not N limited (Morris 1991),

and a net release of inorganic nitrogen to the sediment solution occurs (i.e. mineralization). The high C:N ratios measured in sediments in the fringe (19 - 25.1) and basin (22.3 - 39.2) mangroves in Estero Pargo (Table 4-1) indicate that nitrogen assimilation by bacterial populations in the sediments was probably favored over mineralization.

Seasonal changes in bacterial activity can account for the different responses observed in cores from the fringe mangrove in July 1991 and January 1992. Although levels of isotope enrichment were the same in both experiments ( $200 \mu\text{mol/core } ^{15}\text{NO}_3^-$ ),  $\text{N}_2$  production was measured after 1 d of incubation in January 1992, but not until 3 d of incubation in July 1991. Robertson et. al. (1992) found that tidal flooding had a significant effect on bacterial productivity and growth in mangrove sediments. Hydrology may also be important in Estero Pargo due to seasonal differences in tidal flooding. Rivera-Monroy et al. (1995) found that the frequency of inundation in the fringe mangrove was higher in the "Norte" season than in the rainy season. They also pointed out that frequency of flooding was higher in the fringe than basin mangroves particularly in the dry season. Further work is needed to determine the seasonal densities and productivity of microbial communities in Estero Pargo to evaluate the influence of hydrology and litter quality on nitrogen transformations during decomposition.

We observed  $^{15}\text{NH}_4^+$  in KCl extracts (Tables 4-3 and 4-4) from sediment in both experiments indicating that  $\text{NO}_3^-$  "ammonification", the reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  (Koike & Sorensen 1988), occurred in all the incubations. In contrast to denitrification, which represents a net loss of nitrogen from an ecosystem,  $\text{NO}_3^-$  "ammonification" recycles nitrogen within the ecosystem as  $\text{NH}_4^+$ . In general, denitrifiers dominate environments in which the C:N ratio is low ( $<15$ ), whereas  $\text{NO}_3^-$  is primarily reduced to  $\text{NH}_4^+$  in carbon rich environments ( $\text{C:N} > 20$ ) (Cole & Brown 1980). Denitrification and  $\text{NO}_3^-$  ammonification can occur simultaneously in sediments; the dominance of one process over the other depends on  $\text{NO}_3^-$  concentrations and C:N ratios of the sediments (King & Nedwell 1987, Rehr & Klemme 1989). Smith et al. (1982) found in marsh sediments that  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  decline from 52% to 4% of the total when  $\text{NO}_3^-$  availability increased.



$\text{NO}_3^-$  ammonification may be an important nitrogen transformation in mangrove ecosystems due to their generally low  $\text{NO}_3^-$  sediment concentrations (pore waters = 0-21  $\mu\text{M}$ , Alongi et al. 1992, Boto 1992) and high C:N ratios (>20) (Boto & Wellington 1984, Twilley et al. 1986, Steyer 1988, Lynch 1989a,b, Lugo 1990). Certainly,  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  in temperate coastal sediments is equally or sometimes more important than denitrification (Sørensen 1978, Nishio et al. 1982, Koike & Sorensen 1988). Koike and Sorensen (1988) pointed out that the reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  in the deeper layers of marine sediment demonstrated that the organisms involved in this reaction were probably fermenters (e.g. *E. Coli* and *Achromobacter*, Herbert and Nedwell 1990) or sulfate reducers which possess a constitutive enzyme system for  $\text{NO}_3^-$  reduction. Despite the potential key role of  $\text{NO}_3^-$  ammonification might have in the nitrogen cycle in mangrove ecosystems, there are no published references on this process.

**Denitrification and  $\text{NO}_3^-$  exchange**  $^{15}\text{N}_2$  fluxes from sediment cores in the fringe mangrove treated with different concentrations of  $\text{NO}_3^-$  were distinct (Fig. 4-6). After one day of incubation, denitrification rates ranged from 4.5 to 7.7  $\mu\text{mol m}^{-2} \text{h}^{-1}$  in the 200  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$  treatment, but  $^{15}\text{N}_2$  production was not observed at 25 and 100  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$  during initial 24 h of incubation. Rates declined by approximately 80 % in both cores enriched with 200  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$  after 3 d of incubation. The only observed production of  $^{15}\text{N}_2$  in the other two treatments was measured in one core at 100  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$ , while no  $\text{N}_2$  flux was observed during the five day experiment in either of the two cores amended with 25  $\mu\text{mol/core}$   $^{15}\text{NO}_3^-$ . Thus, rates were significantly higher ( $p < 0.05$ ) in cores enriched with 200  $\mu\text{mol/core}$   $^{15}\text{N-KNO}_3$ , while there was no significant difference in the 25 and 100  $\mu\text{mol/core}$   $^{15}\text{N-KNO}_3$  amendments. However, by day 5 denitrification rates were 0.08  $\mu\text{mol m}^{-2} \text{h}^{-1}$  in one core at 200  $\mu\text{mol/core}$ , and 0.11  $\mu\text{mol m}^{-2} \text{h}^{-1}$  in the 100  $\mu\text{mol/core}$  enrichment.

The spatial and seasonal variation of denitrification in marine sediments has been associated with both the kinetic nature of denitrification capacity and differences in  $\text{NO}_3^-$  concentration (Twilley & Kemp 1986). The kinetic response of denitrification in mangrove sediments to  $\text{NO}_3^-$  concentration has been investigated indirectly using  $\text{NO}_3^-$  uptake (reduction) from overlying water

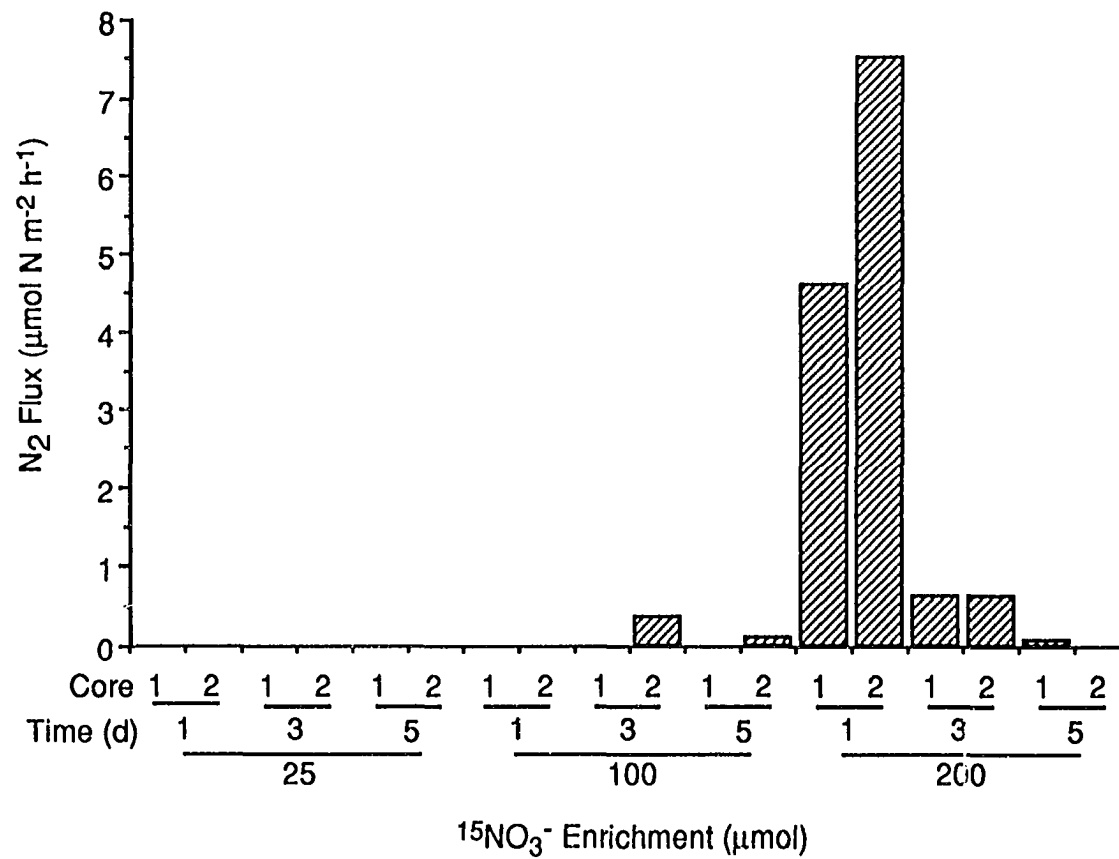


Figure 4-6. Denitrification rates at different  $\text{NO}_3^-$  enrichments and incubation time in sediment cores collected in the fringe forest in January 1992 in Estero Pargo, Mexico.

(Nedwell 1975, Iizumi 1986, Shaiful 1987). The kinetic nature of  $\text{NO}_3^-$  uptake (potential denitrification) is described with  $K_m$  values that represent  $\text{NO}_3^-$  concentrations at one-half the saturated uptake (reduction) rates.  $K_m$  values ( $\mu\text{M}$ ) for mangrove sediments vary from a low of 10-69  $\mu\text{M}$  for mangroves in Hinchinbrook Island, Australia (Iizumi 1986), to higher values of 167-189  $\mu\text{M}$  for mangroves in Selangor (Shaiful 1987), and 180-600  $\mu\text{M}$  in mangroves impacted by sewage enrichment in Fiji (Nedwell 1975). Mean denitrification rate at Hinchinbrook Island was 0.18  $\text{mg N m}^{-2} \text{d}^{-1}$  (Iizumi 1986) compared to range of 26.2-87.6  $\text{mg N m}^{-2} \text{d}^{-1}$  in the polluted site in Fiji (Nedwell 1975). Maximum  $\text{NO}_3^-$  reduction rates ( $V_{\max}$  using a kinetic approach) in mangrove sediments using a flow through core design was 443.5-510.7  $\text{mg N m}^{-2} \text{d}^{-1}$  in two mangrove sites in Selangor (Shaiful 1987). The extreme variation in the kinetic nature of potential denitrification ( $\text{NO}_3^-$  uptake) in mangrove sediments follows the pattern of lower affinity (higher  $K_m$ ) and higher capacity (higher  $V_{\max}$ ) in areas of higher carbon and nitrogen supply (Twilley & Kemp 1986).

The highest rates of  $\text{NO}_3^-$  uptake by mangrove sediments in Estero Pargo was about 60  $\text{mg N m}^{-2} \text{d}^{-1}$  (179  $\mu\text{mol m}^{-2} \text{h}^{-1}$ , Rivera-Monroy et al. 1995), similar to the medium range of rates measured in mangrove sediments described above by Nedwell (1975). Maximum rates of  $\text{NO}_3^-$  reduction in mangrove sediments, using the flume technique, occurred in June 1991 at the beginning of the rainy season and was associated with elevated  $\text{NO}_3^-$  concentrations in the river (Rivera-Monroy et al. 1995). They assumed that  $\text{NO}_3^-$  reduction in waters flooding the fringe mangrove was lost through denitrification, and concluded that this fringe mangrove was a sink of nitrogen. However, as shown by our  $^{15}\text{N}$  experiments, denitrification accounted for a minor portion of the applied  $^{15}\text{NO}_3^-$ ; suggesting that this mangrove acts as a transformer of nitrogen (Nixon & Lee 1986) rather than a nitrogen sink.

This is the first work where  $^{15}\text{N}$  techniques have been used to evaluate denitrification rates in mangrove sediments. Addition of inorganic  $^{15}\text{NO}_3^-$  to sediment cores from fringe and basin mangroves in Estero Pargo had minor effect on rates of denitrification. Mass balances in both mangroves showed that a large percentage of the added  $^{15}\text{NO}_3^-$  was transformed into particulate nitrogen in the sediment, while a small fraction was reduced to  $\text{NH}_4^+$ . The dominance of these nitrogen transformations can probably be associated with

the low availability of  $\text{NO}_3^-$  and the high (>20) C:N ratios of these mangrove sediments. Yet, additional work is needed to evaluate the importance of root and algae uptake in competing with denitrifiers for  $\text{NO}_3^-$ . Results from this study indicate that the capacity for denitrification in oligotrophic mangrove sediments is low. The reduction of  $\text{NO}_3^-$  in tidal waters in mangroves, particularly at low concentrations, may not necessarily be associated with loss due to denitrification. Thus, studies of nitrogen cycling based on changes in  $\text{NO}_3^-$  concentration in tidal waters, such as the studies referred to above, may not accurately describe the function of mangroves as a nitrogen sink.

Studies in coastal marine sediments in temperate regions have shown that nitrification is a major source of nitrate for denitrification (Henriksen & Kemp 1988, Seitzinger 1988, 1990), but it is not clear if this is the case for tropical and subtropical coastal ecosystems (Alongi et al. 1992). Nitrifying bacteria have been measured in mangrove sediments, but rates are generally low at  $<0.22 \mu\text{mol g}^{-1} \text{d}^{-1}$  (Iizumi 1986, Shaiful et al. 1986, Alongi et al. 1992). Shaiful (1987) estimated that nitrate reduction (denitrification) has the capacity to consume 89-90% of the  $\text{NO}_3^-$  derived from nitrification. However, direct estimates of coupled nitrification-denitrification in mangroves are needed to evaluate the contribution of this source of  $\text{NO}_3^-$  to nitrogen loss in mangrove ecosystems. Spatial and temporal patterns of total denitrification in mangrove sediments of Estero Pargo will depend on determinations of coupled nitrification-denitrification rates to complement the low rates of direct denitrification described in this study.

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## CHAPTER 5

### DENITRIFICATION IN MANGROVE SEDIMENTS IN TERMINOS LAGOON, MEXICO: A COMPARISON AMONG FRINGE, BASIN, AND RIVERINE MANGROVES

#### Introduction

Nitrification serves as a potentially important source of  $\text{NO}_3^-$  for denitrification in marine sediments (Henriksen and Kemp 1988; Tiedje 1988). The two most important factors regulating nitrification are usually the availability of oxygen and the supply of  $\text{NH}_4^+$  by mineralization (Jensen et al. 1994). Thus, benthic mineralization and nitrification play important roles in regulating denitrification in aquatic sediments (Roy et al. 1994). The denitrification supported by  $\text{NO}_3^-$  diffusing from overlying water into sediments is referred to as direct denitrification, whereas denitrification supplied with  $\text{NO}_3^-$  from nitrification within the sediment is often referred to as coupled nitrification-denitrification (Nishio et al. 1983, Jenkins and Kemp 1984, King and Nedwell 1987, Jensen et al. 1994). In general, denitrification appears to be limited by  $\text{NO}_3^-$  availability in estuarine and coastal marine sediments (Twilley and Kemp 1986), and therefore sediment nitrification, in effect, regulates denitrification in many sediments (Sørensen 1978, Jenkins and Kemp 1984, Seitzinger and Nixon 1985, Henriksen and Kemp 1988, Jørgensen and Tiedje 1993). Rivera-Monroy et al. (in review) also demonstrated that denitrification rates in mangrove sediments responded to increased concentrations of  $\text{NO}_3^-$ , as has been shown in studies of mangrove sediments using  $\text{NO}_3^-$  uptake as index of denitrification rates (Nedwell 1975, Iizumi 1986, Shaiful 1987).

Flume studies in a fringe mangrove showed that sediments removed  $\text{NO}_3^-$  and  $\text{NH}_4^+$  from tidal waters throughout the year (Rivera-Monroy et al. 1995), suggesting that these sources of inorganic nitrogen may support both direct and coupled denitrification. However, most of the  $^{15}\text{NO}_3^-$  applied to mangrove sediments was immobilized in the particulate nitrogen pool and not reduced to nitrogen gas (Rivera-Monroy et al. in review). Other reports describe high direct denitrification rates in nutrient enriched mangroves (Nedwell 1975, Corredor and Morrel 1994) compared to more oligotrophic forests (Iizumi 1984). Apparently, these differences are related to the amount of nitrate that is

immobilized by decomposers and therefore not available for denitrifiers in mangrove sediments (Alongi 1988a,b, Kristensen et al. 1988, Kristensen et al. 1992, Rivera-Monroy et al. in review). The few denitrification studies in mangrove sediments have addressed only direct denitrification (Nedwell 1975, Iizumi 1986, Corredor and Morell 1994, Rivera-Monroy et al. in review) with little information on the role of coupled nitrification- denitrification in the nitrogen cycle of different ecological types of mangroves (Lugo and Snedaker 1974, Twilley 1988).

The coupling of nitrification and denitrification in intertidal wetland sediments is influenced by redox conditions that are maintained by frequency of tidal inundation (Smith and Patrick 1983; Armstrong et al. 1986). The hydrology of wetlands, including frequency and duration of tides, determines oxygen availability in wetland soils and is particularly important to nitrification. Alternating aerobic and anaerobic conditions result in greater total loss of nitrogen from the soil than from continuous anaerobic conditions (Wiljer and Delwiche 1954). Under laboratory conditions, Reddy and Patrick (1975) have shown that alternating wet and dry conditions of marsh sediments at 2 day intervals result in a tremendous potential in nitrogen loss by maximizing the coupling among mineralization-nitrification-denitrification processes. The different hydroperiods of riverine, fringe, and basin mangroves may influence the coupling of nitrification-denitrification in these different types of forests (Twilley 1988).

In this study, we measured coupled nitrification-denitrification in fringe, basin, and riverine mangroves in different seasons in Terminos Lagoon, Mexico using  $^{15}\text{N}$  techniques. The objectives of this study were 1) to compare coupled denitrification rates in fringe, basin and riverine mangroves; 2) to evaluate the differences between direct denitrification and coupled denitrification in a riverine mangrove which is subjected to elevated concentrations of  $\text{NO}_3^-$  during high river discharge; and 3) summarize these results of coupled denitrification with previous studies of direct denitrification (Rivera-Monroy et. al. submitted) to describe patterns of denitrification in mangrove sediments at Terminos Lagoon. Our hypotheses were that a) coupled denitrification rates are higher in the fringe mangrove than either the basin or riverine mangroves, and b) direct denitrification is higher than coupled denitrification in mangrove sediments.

Studies of nitrogen flux in a fringe forest in Terminos Lagoon (Rivera-Monroy et al. 1995) also will allow us to determine the importance of denitrification (direct and coupled nitrification-denitrification) to the exchange of nitrogen at the mangrove-estuary boundary.

### Material and Methods

**Study area.** This study was carried out in Terminos Lagoon (18° 40' N, 91° 30' W), a large (~1800 km<sup>2</sup>), shallow coastal lagoon located in the southwestern section of the Yucatan Peninsula in the state of Campeche, Mexico (Fig. 5-1). The climate of the area is tropical with annual average air temperatures ranging from 18°C to 36°C. Tides are mixed diurnal with a mean tidal range of about 0.5 m. Average annual precipitation (1680 mm yr<sup>-1</sup>) is seasonal, with a rainy season from June to October, which is associated with frequent tropical convectional rains. The winter storm, or "Norte" season, is from November to February, with strong north winds and frontal rains. The dry season is from March to June. Peak river discharge occurs in the latter months of the rainy season from September to November. The lagoon is bordered almost completely by extensive mangrove forests that are dominated by three species including *Rhizophora mangle* L. (red mangrove), *Avicenia germinans* L. (black mangrove), and *Laguncularia racemosa* Gaertn. f. (white mangrove) (Day et al. 1987). Estero Pargo is a tidal creek located on the lagoon side of the barrier island Isla del Carmen. The mangroves adjacent to the tidal creek are characteristic of fringe mangroves with regular tidal inundation, while the inland mangroves are characteristic of basin mangroves which are infrequently flooded (Lugo and Snedaker 1974, Day, et al. 1987). The bulk of the soil material in both mangroves is made of clay with many inclusions of roots and of coarser woody material. Bulk density in the fringe and riverine mangrove is 0.28 and 0.31 g cm<sup>-3</sup>, respectively (Lynch et al. 1989). Total nitrogen concentration in sediments reported for the fringe mangrove is 5.7 mg gdw<sup>-1</sup> and for the basin mangrove 9 mg gdw<sup>-1</sup> (Lynch et al. 1989). Terminos Lagoon and Estero Pargo have been described in detail elsewhere (Plegher and Ayala-Castañares 1971, Ley-Lou 1985, Yañez-Arancibia and Day 1988).

**Experimental design.** Four experiments using intact sediment cores were performed to evaluate differences in denitrification rates during the rainy (June 1990), "Norte" (November 1990), and dry (March and May 1991) seasons in the

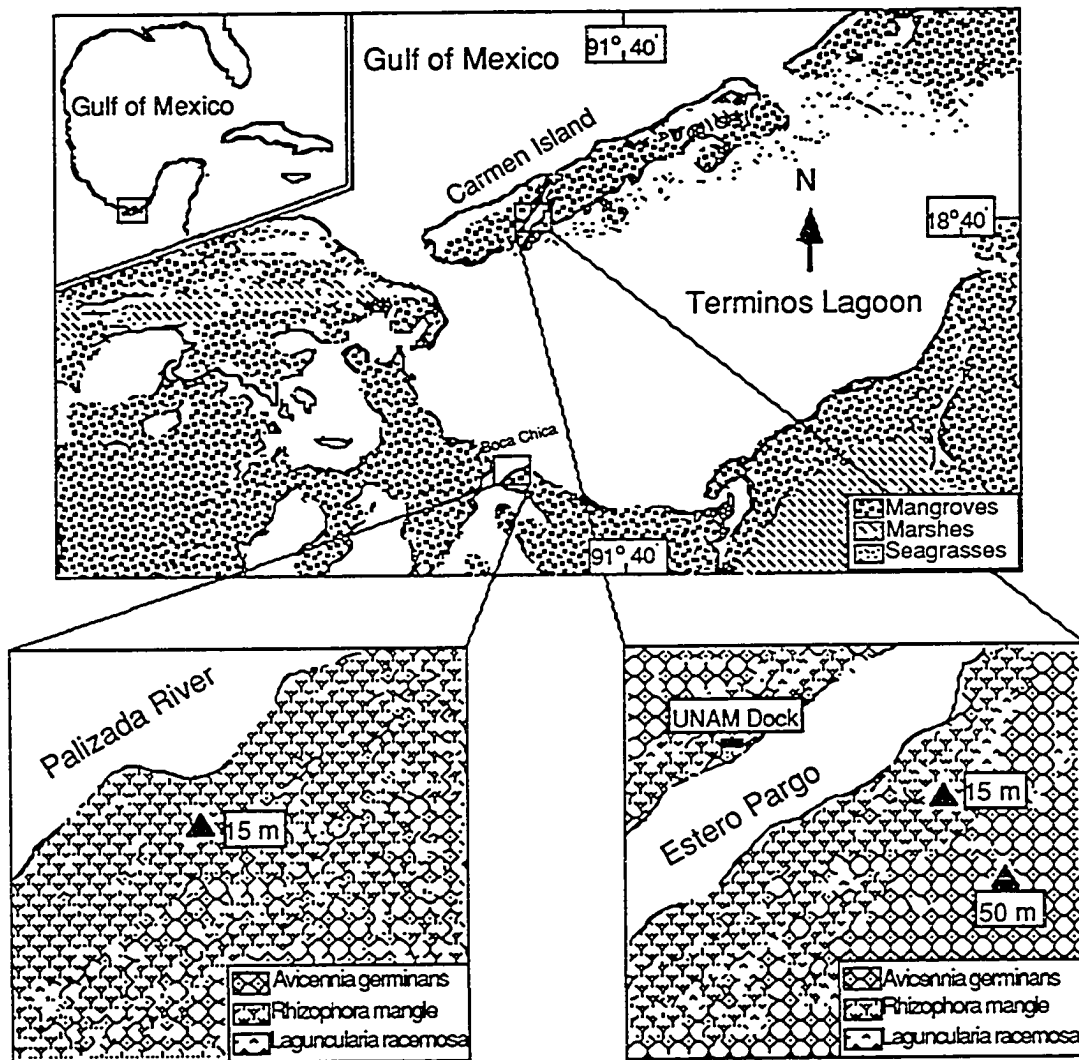


Figure 5-1. Map of Terminos Lagoon showing sampling sites in Estero Pargo and Boca Chica.

fringe mangrove in Estero Pargo. To compare denitrification rates between the fringe and riverine mangrove in Boca Chica, cores were also collected in the riverine mangrove in November 1990 and March 1991. In addition, seasonal changes in coupled denitrification rates were evaluated in the basin mangrove by sampling cores in May 1991 (dry season) and August 1991 (rainy season). Another experiment was to compare differences between direct and coupled denitrification rates in cores collected in the riverine mangrove in July 1992. All cores were sampled about 15 m (fringe) and 50 m (basin) inland from the tidal creek in Estero Pargo (Fig. 5-1). Cores in the riverine mangrove were collected 15 m inland from the Palizada river (Fig. 5-1).

Four cores were sampled in June 1990 and May 1991 in the fringe mangrove while two cores were collected in the riverine and fringe mangrove in November 1990 and March 1991. Four cores were also obtained in the basin mangrove in May 1991 and August 1991. For the comparison between direct and coupled denitrification in the riverine mangrove eight cores were collected. The sediment cores were obtained with plexiglass cylinders (30 cm long and 15 cm i.d.), which were carefully placed on the sediment surface and forced to a depth of approximately 25 cm. Cores were sampled in close proximity to each other to minimize spatial variability and were considered as replicates.

Pneumatophores were present in all cores and precautions were taken to assure that they were not damaged during core sampling. Pneumatophore density was  $428 \pm 100 \text{ m}^{-2}$  in both the fringe and basin mangrove, and  $329 \pm 88 \text{ m}^{-2}$  in the riverine mangrove. After collecting the core, a rubber cap was placed on the core base and secured with two aluminum bands. The cores were carefully transported in the dark back to the laboratory. Soil temperatures were measured during core sampling. Floodwater in each site was collected with previously acid-washed (10% HCl v/v) 1 L plastic containers.

Cores were enriched with  $^{15}\text{N}$  isotopes at concentrations of  $200 \mu\text{mol/core}$   $(^{15}\text{NH}_4)_2\text{SO}_4$  (99 atom %  $^{15}\text{N}$ ) for the experiments in June and November 1990, and March, May. An application of  $100 \mu\text{mol/core}$   $(^{15}\text{NH}_4)_2\text{SO}_4$  (99 atom %  $^{15}\text{N}$ ) was used at the basin mangrove in August 1991. In the experiment to compare direct and coupled nitrification-denitrification in the riverine mangrove in July 1992,  $450 \mu\text{mol/core}$  of  $(^{15}\text{NH}_4)_2\text{SO}_4$  (99 atom %  $^{15}\text{N}$ ) were added to four cores and  $450 \mu\text{mol/core}$  of  $^{15}\text{N-KNO}_3^-$  (99 atom %



$^{15}\text{N}$ ) applied to another set of four cores. All isotope solutions were made with filtered (GF/F) floodwater obtained in the field when cores were collected. Solutions were injected into each core at the surface and at 2 and 9 cm depth to distribute the isotope throughout the core. A water depth of 1-2 cm was maintained over the sediment surface within the cores throughout the experiments in August 1991 (basin mangrove) and July 1992 (riverine mangrove) with ambient floodwater. The rest of the cores were incubated with floodwater at the sediment surface. After isotope enrichment, the cores were incubated outdoors in the dark using a covered plastic chamber under ambient temperature (mean temperature was 28 °C).

In June 1990, May and August 1991, and July 1992, one core was sequentially removed from the incubation chamber at 1, 3, 5, and 8 days after  $^{15}\text{N}$  enrichment. The pneumatophores were cut about 1 cm from the top of the core and covered with silicone grease (Corning) to minimize exchange of gases through these root structures (Scholander 1955, McKee et al. 1988). Production of  $\text{N}_2$  was trapped in the headspace of each core by placing a gasketed plexiglass lid on the core top and secured with 6 screws distributed evenly around the lid to form a gas-tight connection. The depth of each headspace was recorded, and zero-time gas samples were collected immediately after the headspace was sealed. Gas samples were taken using a gas-tight syringe and hypodermic needle from the headspace through a rubber septum sealed in the lid. Aliquots of 5 mL were withdrawn at 1 and 10 h, transferred to glass rubber-stoppered Vacutainers® (75 mm long by 10 mm i. d.), and stored until assay  $^{15}\text{N}$  using mass spectrometry. Vacutainers® were stored immersed in water to prevent contamination from atmospheric gases leaking into the Vacutainers®. After each headspace sampling, headspace was replaced with sample volume (5 mL) of air to maintain the same pressure inside the core, and the core was returned to the incubation chamber. Changes in oxygen concentration in the headspace throughout the 10 h incubation were determined on a second 5 mL aliquot sampled at the same time  $^{15}\text{N}_2$  gas samples were taken. Oxygen and  $\text{N}_2$  concentrations were measured with a gas chromatograph (SRI Instruments Model 8610) equipped with a TCD detector and a CTR dual-phase column (Alltech®) using helium as carrier gas. Oxygen concentrations changed <14 %

in all experiments and  $N_2$  concentration was constant over time (data not shown).

At the end of the 10 h incubation 50 mL of overlying water was sampled in those cores where floodwater was present. Each core then was sectioned at approximately 4 cm intervals to obtain 5 soil samples per core. Replicate soil subsamples (50 g) per sample were used for extraction of  $NH_4^+$  and  $NO_3^-$  (Sumi and Koike 1990) for 1 hour with 2 N KCl (150 mL of KCl per 50 g of sediment). Another two subsamples ( $\approx 35$  g) were also taken from each sample for analysis of percent of water (60 °C drying) and bulk density. Dry sediments were ground with mortar and pestle and assessed for total carbon and nitrogen and  $^{15}N$  content in four subsamples per layer.

Sampling of headspace and sediment in cores collected in the riverine and fringe mangroves in November 1990 and March 1991 followed a similar procedure as described above. However, since only two cores were collected per site, gas samples were obtained only at 1 and 10 days after  $^{15}N$  application. After headspace sampling the cores were then sectioned and processed for nutrient and  $^{15}N$  analyses as previously described.

*Sample analysis.*- Total organic carbon and nitrogen were analyzed with a Perkin Elmer CHN elemental analyzer. Overlying water and KCl extracts were analyzed for  $NH_4^+$  (Solórzano 1969) and  $NO_3^- + NO_2^-$  (Grasshoff et al. 1983) concentrations. The nitrogen isotopic masses of 28, 29, and 30 were measured in headspace samples by injecting directly into a nuclide Model 3-60-RMS double collector instrument (Measurement and Analysis Systems, Bellefonte, PA). Air samples obtained at time 0 during the 10 h time series sampling were analyzed as reference gas on the IRMS inlet using the sample inlet (Mulvaney and Kurtz 1982).

$^{15}N$  enrichment in overlying water, KCl extracts and sediment were measured with a JASCO  $^{15}N$  emission spectrometer.  $^{15}NH_4^+$  and  $^{15}NO_3^-$  in the overlying water and KCl extracts were isolated by sequential steam distillations using MgO to raise the pH above 9.0 (Keeney and Nelson 1982) following reduction of  $NO_3^- + NO_2^-$  to  $NH_4^+$  by Devarda's alloy (Bremner 1965). Carryover between samples was minimized by a distillation of ethanol between each sample (Fiedler and Proksch 1975). Fifty mL of the condensate were collected directly onto approximately 0.035 g of ion sieve (Union Carbide

#W-85). The ion sieve trapped 95% of the  $\text{NH}_4^+$  based on preliminary experiments with 50 mL of distillate. The ion sieve was collected on a 25 mm A/E filter, dried (60 °C), placed in petri dishes, and stored in a vacuum desiccator until assay for  $^{15}\text{N}$  content. Recovery of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  following this distillation procedure averaged 99% and 75%, respectively. Samples were prepared by first converting organic and inorganic nitrogen to nitrogen gas with a dry microDumas combustion technique (Fielder and Proksch 1975). Sediment and ion sieve samples were placed in previously degassed (550 °C, 12h) discharge tubes (Pyrex glass 6.0 mm O.D) containing CaO and Cuprox. The tubes were evacuated to 1m Torr, and preheated with argon to remove residual water vapor. Tubes were again evacuated to 1m Torr and filled with argon to 1 Torr, and preheated to remove residual water vapor. The tubes were sealed and later combusted at 550 °C for 12 h and slowly cooled to room temperature for another 12 h.

The atom%  $^{15}\text{N}$  for these samples was determined with a JASCO  $^{15}\text{N}$  analyzer (Model N-150). Three scans of the light emission spectra of the 28 and 29 mass were performed on each sample. The instrument was calibrated with commercial standards prepared from samples analyzed by mass spectrometry (Japan Spectroscopic Co. Instruction Manual model N, 1986). The formula used to calculate atom% was:

$$^{15}\text{N}(\text{atom}\%) = \frac{100}{2R + 1}$$

$$\text{where } R = \frac{^{14}\text{N}_2}{^{14}\text{N}^{15}\text{N}} \text{ (Fielder \& Proksch 1975).}$$

Denitrification rates were calculated using a mass spectrometric procedure developed for determination of  $^{15}\text{N}\text{-N}_2$  evolved from soils treated with  $^{15}\text{N}$ -labeled compounds (Mulvaney and Kurtz 1982, Mulvaney and Kurtz 1984, Mulvaney and Boast 1986). Bunsen solubility coefficients (Weiss 1970) were used to calculate the dissolved  $\text{N}_2$  concentration in the pore and overlying water from the concentration in the gas phase. Significant differences between nutrient concentrations were determined with a one and two-way ANOVA with a level of significance of 0.05 (SAS-JMP 1993)

Table 5-1. Concentrations of extractable inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ,  $\mu\text{g gdw}^{-1}$ ) and particulate nitrogen (PN,  $\text{mg gdw}^{-1}$ ) concentrations along with carbon to nitrogen ratios (C:N), and bulk density (BD,  $\text{g cm}^{-3}$ ) averaged with depth (~0-2- cm) in cores from fringe, basin, and riverine forests incubated for different days in 1990, 1991, and 1992. Mean values ( $\pm 1$  SD).

Date	Season	Isotope	Incubation (d)	Nitrogen Concentrations			C:N	Bulk Density
				NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	PN		
Fringe Mangrove								
25 June, 1990	Rainy	15NH <sub>4</sub> <sup>+</sup> (200 μmol/core)	1	46.3 (18.0)	4.8 ( 3.2)	11.9 ( 3.8)	21.2 ( 1.7)	0.20 (0.03)
			3	51.1 (12.0)	4.0 ( 4.8)	10.1 ( 3.9)	19.4 ( 2.3)	0.19 (0.03)
			5	61.2 (13.5)	3.1 ( 1.0)	10.2 ( 4.7)	20.3 ( 1.4)	0.24 (0.07)
			8	60.5 (16.6)	0.1 ( 0.1)	10.9 ( 4.4)	18.8 ( 2.0)	0.22 (0.06)
29 November, 1990	Norte	15NH <sub>4</sub> <sup>+</sup> (200 μmol/core)	1	27.6 ( 7.7)	8.1 ( 1.3)	8.6 ( 2.4)	20.1 ( 1.9)	0.22 (0.04)
			10	31.9 (18.8)	4.2 ( 1.2)	8.8 ( 3.2)	17.8 ( 1.4)	0.24 (0.03)
9 March, 1991	Dry	15NH <sub>4</sub> <sup>+</sup> (200 μmol/core)	1	21.8 (15.0)	1.8 ( 0.5)	7.6 ( 2.5)	16.9 ( 0.9)	0.28 (0.04)
			10	23.2 (12.2)	1.5 ( 0.6)	7.0 ( 2.8)	16.3 ( 0.8)	0.34 (0.10)
21 May 1991	Dry	15NH <sub>4</sub> <sup>+</sup> (200 μmol/core)	1	23.3 (10.1)	0.7 ( 0.2)	9.6 ( 4.0)	22.5 ( 1.9)	0.22 (0.01)
			3	23.8 ( 4.9)	0.3 ( 0.2)	9.1 ( 3.2)	24.6 ( 5.1)	0.26 (0.05)
			5	17.3 (15.0)	0.3 ( 0.2)	6.2 ( 4.4)	24.0 ( 0.5)	0.36 (0.20)
			8	31.5 (11.4)	0.6 ( 0.1)	8.8 ( 4.0)	22.9 ( 2.4)	0.24 (0.10)
Basin Mangrove								
21 May 1991	Dry	15NH <sub>4</sub> <sup>+</sup> (200 μmol/core)	1	15.2 ( 5.4)	0.5 ( 0.2)	8.6 ( 3.0)	20.2 ( 1.5)	0.30 (0.05)
			3	19.2 (10.5)	0.7 ( 0.2)	7.0 ( 3.5)	21.2 ( 2.1)	0.30 (0.15)
			5	27.9 (10.1)	0.9 ( 0.1)	8.6 ( 2.3)	22.7 ( 0.6)	0.30 (0.09)
			8	10.7 ( 3.3)	0.2 ( 0.1)	7.5 ( 4.2)	23.6 ( 1.8)	0.26 (0.05)
2 August 1991	Rainy	15NH <sub>4</sub> <sup>+</sup> (100 μmol/core)	1	28.4 ( 9.0)	12.3 ( 3.3)	7.3 ( 2.6)	24.2 ( 1.9)	0.24 (0.05)
			3	17.6 ( 7.2)	15.6 ( 6.5)	9.2 ( 2.4)	22.0 ( 1.8)	0.20 (0.07)
			5	20.4 ( 4.0)	9.2 ( 1.3)	8.9 ( 2.5)	21.6 ( 1.6)	0.22 (0.04)
			8	50.6 (17.9)	10.0 ( 0.9)	9.3 ( 2.3)	21.4 ( 2.1)	0.24 (0.05)
Riverine Mangrove								
29 November 1990	Norte	15NH <sub>4</sub> <sup>+</sup> (200 μmol/core)	1	14.2 ( 4.4)	2.3 ( 0.4)	1.3 ( 0.6)	33.2 (17.8)	0.46 (0.10)
			10	9.4 ( 4.1)	2.0 ( 0.3)	1.0 ( 0.8)	33.1 (11.7)	0.40 (0.10)
9 March 1991	Dry	(200 μmol/core)	1	6.2 ( 2.8)	0.7 ( 0.3)	1.5 ( 0.6)	29.5 ( 2.7)	0.96 (0.09)
24 July 1992	Rainy	15NH <sub>4</sub> <sup>+</sup> (450 μmol/core)	1	29.4 (30.3)	5.4 ( 1.7)	2.8 ( 0.7)	19.5 ( 1.5)	0.30 ( 0.1)
			3	26.4 (19.6)	6.3 ( 1.0)	3.1 ( 0.9)	22.2 ( 1.4)	0.36 ( 0.1)
			5	28.8 (20.0)	6.3 ( 1.6)	3.0 ( 0.6)	22.4 ( 1.2)	0.30 ( 0.1)
			8	29.4 (12.2)	7.8 ( 2.0)	3.5 ( 0.5)	16.4 ( 4.5)	0.32 ( 0.0)
30 July 1992	Rainy	15NO <sub>3</sub> <sup>-</sup> (450 μmol/core)	1	29.7 (22.0)	7.3 ( 3.8)	4.8 ( 0.6)	12.9 ( 0.9)	0.34 (0.05)
			3	29.4 (12.0)	5.9 ( 0.9)	5.6 ( 0.1)	11.8 ( 0.5)	0.38 (0.08)
			5	60.6 (21.0)	5.3 ( 1.2)	4.4 ( 1.0)	15.6 ( 1.6)	0.28 (0.04)
			8	22.9 (12.9)	5.3 ( 1.5)	3.7 ( 1.1)	17.9 ( 2.4)	0.36 (0.09)

## Results

**Nitrogen concentrations.** Mean  $\text{NH}_4^+$  concentrations in cores from the fringe mangrove were higher in the rainy season ( $46\text{--}60\ \mu\text{g gdw}^{-1}$ ) than in the 'Norte' ( $27\text{--}31\ \mu\text{g gdw}^{-1}$ ) and dry seasons ( $17.3\text{--}31.5\ \mu\text{g gdw}^{-1}$ ) ( $p < 0.05$ ) (Table 5-1). This pattern was also significant in the riverine mangrove where  $\text{NH}_4^+$  values ranged from  $22$  to  $60\ \mu\text{g gdw}^{-1}$  in the rainy season, and from  $6$  to  $14\ \mu\text{g gdw}^{-1}$  in 'Norte' and dry seasons ( $p < 0.05$ ).  $\text{NH}_4^+$  concentrations in the basin mangrove in the dry season ( $10\text{--}27\ \mu\text{g gdw}^{-1}$ ) were lower than in the rainy season, although these differences were not significant.  $\text{NO}_3^-$  concentrations were generally higher in the rainy season in all mangroves, probably as a result  $\text{NO}_3^-$  concentrations in floodwaters in Estero Pargo and Boca Chica associated with higher river discharge to Terminos Lagoon (Rivera-Monroy et al. 1995). The highest  $\text{NO}_3^-$  concentrations ( $9.2\text{--}15.6\ \mu\text{g gdw}^{-1}$ ) were observed in August 1991 in the basin mangrove.  $\text{NO}_3^-$  concentrations were similar among enriched and non-enriched cores from the riverine mangrove in July 1990.

Particulate nitrogen (PN) values were significantly lower ( $p < 0.05$ ) in the riverine mangrove ( $1.0\text{--}5.6\ \mu\text{g gdw}^{-1}$ ) than in the fringe ( $6.2\text{--}11.9\ \mu\text{g gdw}^{-1}$ ) and basin ( $7.0\text{--}9.3\ \mu\text{g gdw}^{-1}$ ) mangroves. Although PN values were higher during the rainy season in the fringe and riverine mangroves, values were similar for both seasons in the basin mangrove. Bulk density was significantly higher in the riverine mangrove (mean =  $0.39\ \text{g cm}^{-3}$ ,  $p < 0.01$ ) than in the fringe (mean =  $0.25\ \text{g cm}^{-3}$ ) and basin (mean =  $0.26\ \text{g cm}^{-3}$ ) mangrove. There were no significant differences in bulk density among seasons from any of the mangroves. In general, we observed lower PN values associated with higher bulk density.

C:N ratios were significantly different among seasons in the fringe and riverine mangroves. C:N values in the fringe mangrove were  $16.3\text{--}16.9$  in March 1991 compared to ratios of  $18.8\text{--}21.2$  in June 1990,  $17.8\text{--}21.1$  in November 1990, and  $22.9\text{--}24.0$  in May 1991. C:N ratios in the riverine mangrove were higher in November 1990 ( $33.1\text{--}33.2$ ) than on 24 July 1991 ( $16.4\text{--}22.4$ ) and 30 July 30 1991 ( $11.8\text{--}17.9$ ). These seasonal differences in C:N ratios can be the result of seasonal flooding of the forest with riverine sediment during the rainy and Norte seasons (Rivera-Monroy et al. 1995). Figure 5-2 shows mean  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations with depth of cores

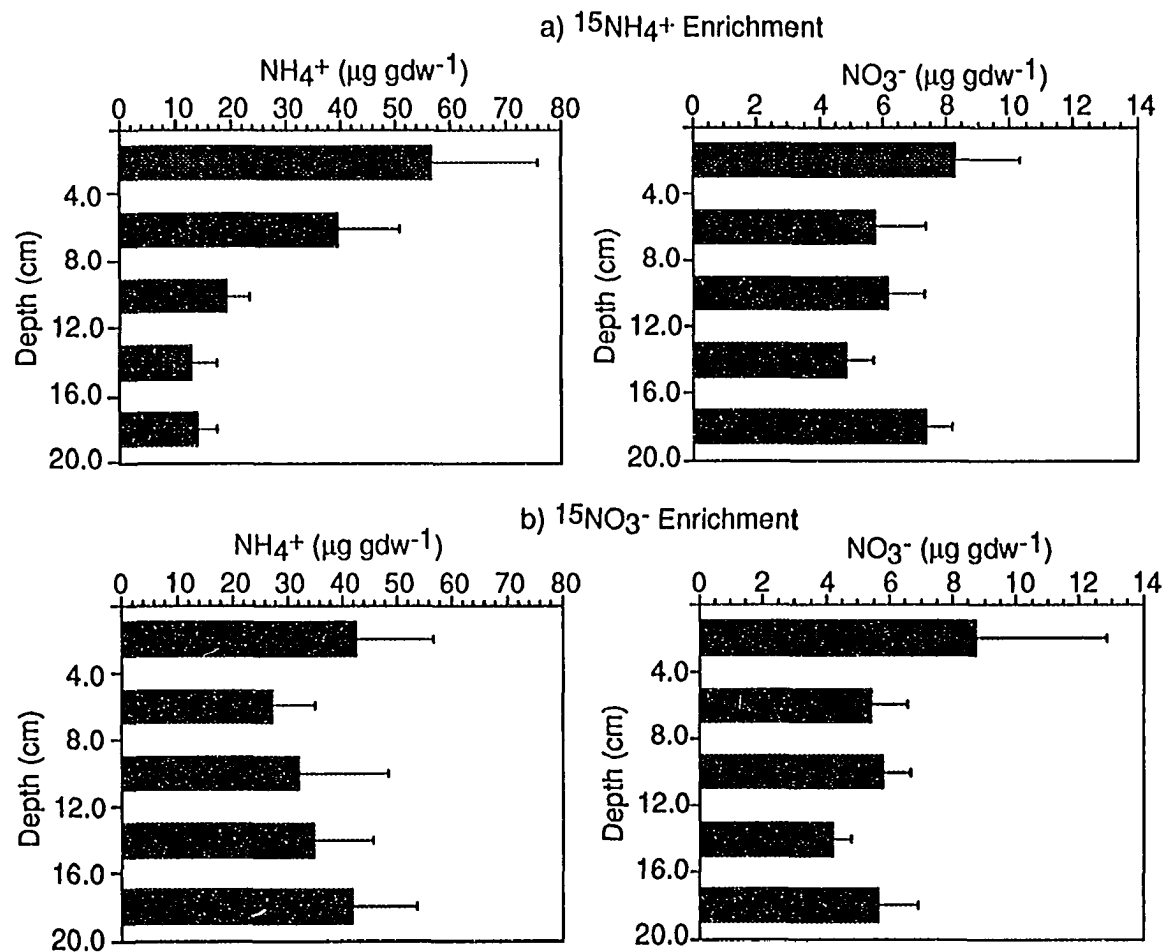


Figure 5-2. Mean  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations ( $\mu\text{g gdw}^{-1}$ ) with depth in sediments from the riverine mangrove forest enriched with  $^{15}\text{NH}_4^+$  (24 July 1991) and  $^{15}\text{NO}_3^-$  (30 July 1991).

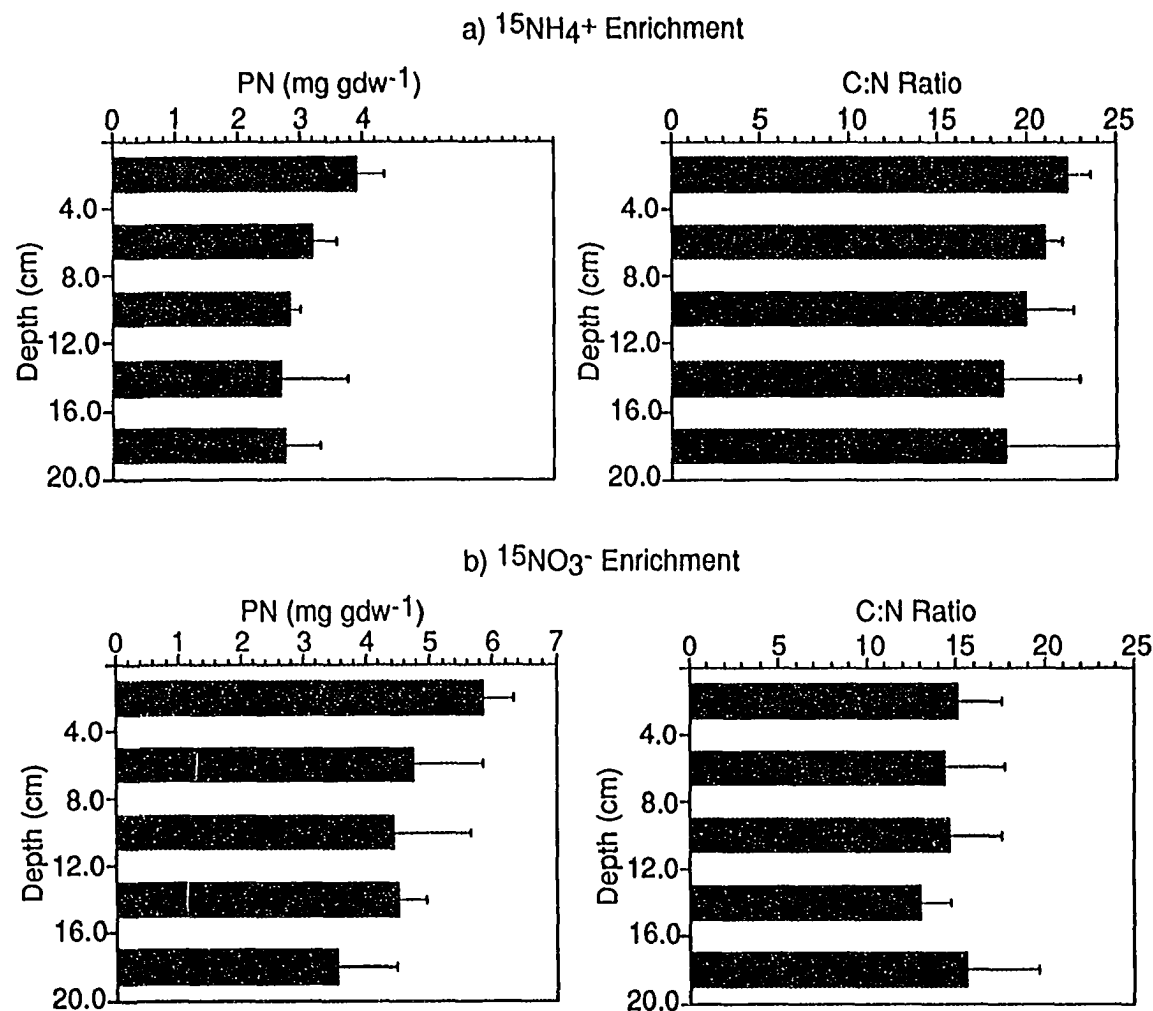


Figure 5-3. Mean PN (mg gdw<sup>-1</sup>) and C:N ratio with depth in sediments from the riverine mangrove forest enriched with  $^{15}\text{NH}_4^+$  (24 July 1991) and  $^{15}\text{NO}_3^-$  (30 July 1991).

collected in the riverine mangrove and enriched with either  $^{15}\text{NH}_4^+$  (24 July 1991) or  $^{15}\text{NO}_3^-$  (30 July 1991).  $\text{NH}_4^+$  concentrations in cores enriched with  $^{15}\text{NH}_4^+$  declined with depth from  $60 \mu\text{g gdw}^{-1}$  in the upper 5 cm than to  $11 \mu\text{g gdw}^{-1}$  at 15-19 cm. Whereas,  $\text{NH}_4^+$  concentrations were more consistent with depth at  $30\text{-}40 \mu\text{g gdw}^{-1}$  in the  $^{15}\text{NO}_3^-$  enriched cores. The pattern of  $\text{NO}_3^-$  concentrations with depth were similar in both enrichments with values ranging from only 6 to  $8 \mu\text{g gdw}^{-1}$ . PN concentrations with depth were higher in the  $^{15}\text{NO}_3^-$  enriched cores than in the  $^{15}\text{NH}_4^+$  treatment, particularly in the top 5 cm (Fig. 5-3). This difference is reflected in the C:N ratios, which were lower in the  $^{15}\text{NO}_3^-$  enriched cores (Fig. 5-3). Bulk density was variable with depth in cores from both experiments. However, this difference was not significantly different with the exception of the value obtained in the top 4 cm (0.42) ( $p < 0.05$ ) in  $^{15}\text{NO}_3^-$  enrichment experiment. On average, bulk density values with depth were  $0.30$  and  $0.34 \text{ g cm}^{-3}$  in the  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  enrichment experiments, respectively.

**$^{15}\text{N}$  atom % enrichment.** Peak atom %  $^{15}\text{N}$  excess of the respective labeled isotope of  $^{15}\text{NH}_4^+$  (Fig. 5-4a) and  $^{15}\text{NO}_3^-$  (Fig. 5-4b) occurred at 4-8 cm depth. There was a significant difference ( $p < 0.05$ ) in enrichment with depth in both experiments (Fig. 5-4). In the  $^{15}\text{NH}_4^+$  enriched cores,  $^{15}\text{N}$  excess decreased with depth to minimum value of 1.75% at 16-20 cm (Fig. 5-4a). Variation in atom %  $^{15}\text{NO}_3^-$  excess with depth was different since concentrations generally increased with depth below depth of peak concentration and the lowest concentration occurred at surface (0-4 cm depth). Atom %  $^{15}\text{NH}_4^+$  excess was observed at all depths in the cores enriched with  $^{15}\text{NO}_3^-$ , although concentrations were low ( $< 2$ ) and showed no change with depth (Fig. 5-5).

$^{15}\text{N}_2$  production was not observed in the cores enriched with  $250 \mu\text{mol /core}$  of  $^{15}\text{NH}_4^+$  in any of the experiments performed in fringe, basin, or riverine mangroves. However, we measured  $^{15}\text{N}_2$  production in cores from the riverine mangrove enriched with  $450 \mu\text{mol } ^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  in July 1992. In this experiment denitrification rates in cores enriched with  $^{15}\text{NH}_4^+$  were  $4.4 \mu\text{mol m}^{-2} \text{ h}^{-1}$  on day one,  $2.4 \mu\text{mol m}^{-2} \text{ h}^{-1}$  on day three, and  $28.9 \mu\text{mol m}^{-2} \text{ h}^{-1}$  on day 5.  $^{15}\text{N}_2$  production was not observed on day eight (Fig. 5-6). Denitrification rates in cores treated with  $450 \mu\text{mol/core } ^{15}\text{NO}_3^-$  were 221.1



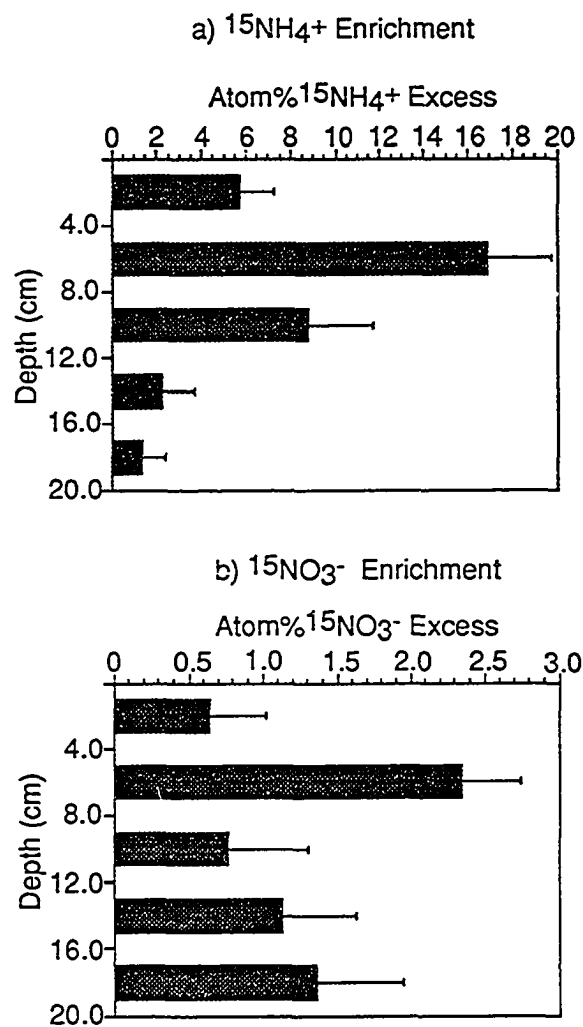


Figure 5-4. Mean Atom%  $^{15}\text{N}$  excess with depth in sediments from the riverine mangrove forest enriched with  $^{15}\text{NH}_4^+$  (24 July 1991) and  $^{15}\text{NO}_3^-$  (30 July 1991).

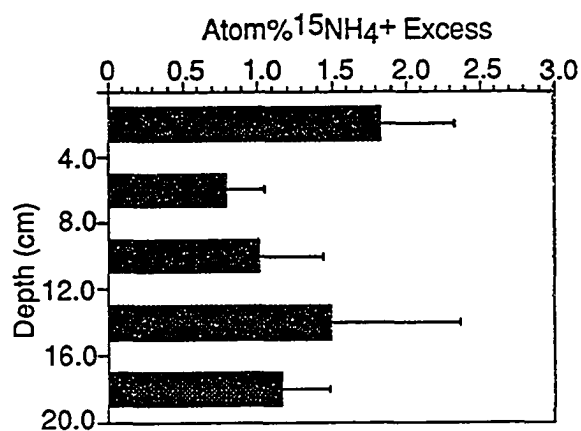


Figure 5-5. Mean Atom %  $^{15}\text{NH}_4^+$  excess with depth in sediment from the riverine mangrove forest enriched with  $^{15}\text{NO}_3^-$  (30 July 1991).

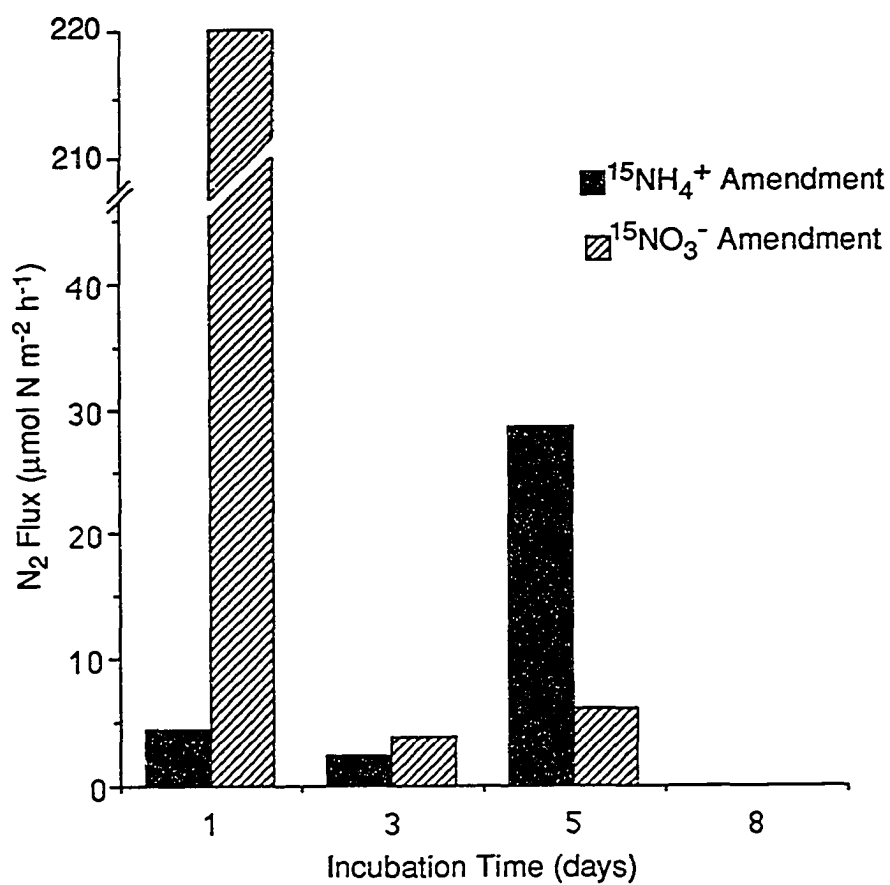


Figure 5-6. Denitrification rates ( $\mu\text{mol N m}^{-2} \text{ h}^{-1}$ ) in cores from the riverine forest (Boca Chica) amended with  $450 \mu\text{mol } ^{15}\text{NO}_3^-$  and  $^{15}\text{NH}_4^+$  and incubated for different days in July 1992.

$\mu\text{mol m}^{-2} \text{ h}^{-1}$  on day one,  $3.7 \mu\text{mol m}^{-2} \text{ h}^{-1}$  on day three, and  $6.0 \mu\text{mol m}^{-2} \text{ h}^{-1}$  on day five. As in the  $^{15}\text{NH}_4$  treatment, no  $^{15}\text{N}_2$  flux was measured at day eight of incubation (Fig. 5-6).

**Mass Balance. a) Coupled denitrification experiments.** Most of the added  $^{15}\text{N}$  was recovered in the sediment pool in all experiments (Table 5-2). The total recovery in the fringe mangrove in June 1990 ranged from 41.7 to 94.6 % (Table 5-2). Extracted  $^{15}\text{NH}_4^+$  content was initially the largest fraction of  $^{15}\text{N}$  excess ( $1623 \pm 231 \mu\text{g } ^{15}\text{N}$ ), but total  $^{15}\text{N}$  in this pool decreased after eight d ( $243 \pm 54 \mu\text{g } ^{15}\text{N}$ ). Most of the  $^{15}\text{N}$  was recovered in the sediment (68 %) at the end of the incubation.  $^{15}\text{NO}_3^-$  represented <1% of the added  $^{15}\text{N}$ . After a 10 d incubation in November 1990 the total recovery of  $^{15}\text{NH}_4^+$  applied was 67 and 94 % for the riverine and fringe mangroves, respectively (Table 5-2). The largest fraction of the added  $^{15}\text{N}$  was recovered in the sediment in both areas. Recovery in the sediment pool of the fringe mangrove was similar after one (95.2 %) and 10 days (93.7 %) of incubation; whereas in the riverine mangrove the percentage increased from 45.6 % to 67 % during the 10 d incubation. The recovery of  $^{15}\text{N}$  in the extracted-N pool in both mangroves ranged from 5 to 15% (Table 5-2). Total  $^{15}\text{N}$  recoveries in cores from the riverine and fringe mangroves in March 1991 (Table 5-2) were similar to those obtained in November 1990 after a 10 d incubation (one replicated core from the riverine mangrove was lost during incubation). In this experiment >80% of the added  $^{15}\text{N}$  was recovered in the sediment in the fringe mangrove and >50% in the riverine mangrove.  $^{15}\text{N}$  recoveries in the extracted pool for both mangroves were <1% for  $^{15}\text{NO}_3^-$  and <10% for  $^{15}\text{NH}_4^+$ .

The total recovery of  $^{15}\text{N}$  ranged from 36.2 to 58.4% in the basin mangrove, and from 49.3 to 89.8% in the fringe mangrove in May 1991 (Table 5-2).  $^{15}\text{N}$  recovery in the basin mangrove sediments increased from 25 % after one d of incubation to 57 % after eight d. Recovery of  $^{15}\text{N}$  in the extracted  $^{15}\text{NH}_4^+$  pool also decreased over time; from 10.5% after one d to 1.5% after eight d.  $^{15}\text{NO}_3^-$  in the sediment extracts was <0.1% (Table 5-2). Nearly 90 % of  $^{15}\text{N}$  was recovered after one d (90) of incubation in the fringe mangrove, but recovery was only 60 % in the eight-day core, exhibiting the spatial variation in  $^{15}\text{N}$  distribution. Recovery of extracted N and sediment pools over time was similar to values obtained in the fringe mangrove (Table 5-2). The distribution of  $^{15}\text{N}$

Table 5-2. Distribution of applied  $^{15}\text{N}$  ( $\mu\text{g}/\text{core}$ ) among various forms of nitrogen including nitrogen gas ( $\text{N}_2$ ), extractable N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ), sediment nitrogen and total  $^{15}\text{N}$  recovered at different times following enrichment as an average with depth ( $\approx 0\text{-}20$  cm) in cores from fringe, basin, and riverine mangroves.

Date	Season	Isotope	Time (d)	Applied N (μg/core)	N2	Extractable N		Sediment	Total
						NH4+	NO3-		
Fringe									
25 June 1990	Rainy	15NH4+	1	2970	0	1623	15	1057	2695
			3	2970	0	677	12	499	1188
			5	2970	0	519	9	1018	1546
			8	2970	0	243	0	1939	2182
29 November 1990	Norte	15NH4+	1	2970	0	86	54	257	2712
			10	2970	0	196	5	2466	2669
9 March 1991		15NH4+	10	2970	0	273	2	2325	2600
			10	2970	0	76	3	2262	2341
21 May 1991	Dry	15NH4+	1	2970	0	293	2	2262	2558
			3(2)	2970	0	149	0.6	1255	1405
			5(4)	2970	0	158	0.9	1752	1911
			8	2970	0	165	1.0	1545	1712
Basin									
21 May 1991	Dry	15NH4+	1	2970	0	300	2	730	1033
			3(2)	2970	0	181	2	1446	1630
			5(4)	2970	0	195	1	1362	1560
			8	2970	0	43	0.3	1622	1665
2 August 1991	Rainy	15NH4+	1	1485	0	27	3	1047	1080
			3	1485	0	5	1	1113	1120
			5	1485	0	-	-	1171	1171
			8(10)	1485	0	4	0.1	1335	1340
Riverine									
29 November 1990	Norte	15NH4+	1	2970	0	199	15	1083	1298
			10	2970	0	169	14	1716	1900
9 March 1991			10	2970	0	68	16	1386	1471
24 July 1991	Rainy	15NH4+	1	6682	28	3709	66	1535	5338
			3	6682	118	2766	121	2264	5269
			5	6682	406	1881	176	2295	4758
			8	6682	592	1710	93	3984	6289
30 July 1991	Rainy	15NO3-	1	6682	1444	262	78	1914	3698
			3	6682	2178	399	43	2735	5335
			5	6682	2250	170	37	1322	3779
			8	6682	2289	279	118	1285	3971

content in cores from the basin mangrove enriched with  $^{15}\text{NH}_4^+$  (250  $\mu\text{mol/core}$ ) in August 1991 (Table 5-2) was similar to recoveries measured in May 1991. Although  $^{15}\text{N}$  content in the overlying water was not determined in cores after 5 and 8 d incubation, concentrations in cores after 1 and 3 d indicate that  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  were negligible ( $<0.1\%$ ). Extractable  $^{15}\text{N}$  content was also small in all cores and represented  $<2\%$  of the  $^{15}\text{N}$  amendment.

**b) Coupled and direct denitrification experiment.** Recovery of  $^{15}\text{N}$  was higher in cores amended with  $^{15}\text{NH}_4^+$  than in cores with  $^{15}\text{NO}_3^-$ . Overall,  $^{15}\text{N}$  recovery ranged from 78 to 89 % in the  $^{15}\text{NH}_4^+$  amended cores.  $^{15}\text{NH}_4^+$  in the soil extracts was the largest fraction (55%) measured on day one, but it decreased during the incubation period (Table 5-2). Conversely, the recovery of  $^{15}\text{N}$  in the sediments increased from 23% of amendments on day one to almost 60% at the end of the incubation.  $^{15}\text{NO}_3^-$  content in the soil extracts increased from 67  $\mu\text{g}$  on day one to 176 on day five, to later decline to 93  $\mu\text{g}$ .  $^{15}\text{N}_2$  in the headspace also followed the same pattern; it increased from 29 to 933  $\mu\text{g}$  on day five. No  $^{15}\text{N}_2$  production was measured during day eight of the incubation. The percentage of  $^{15}\text{N}_2$  in the overlying and porewater for all cores was  $<1\%$ . Concentrations of  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  in the overlying water were not determined.

The recovery in the  $^{15}\text{NO}_3^-$  amended cores ranged from 25 -56 % (Table 5-2). The largest  $^{15}\text{N}$  fraction was always observed in the sediments where it ranged from 19% (8 d) to 41% (3 d). The second largest fraction was measured in the headspace after 1 d incubation, which declined from 22% to  $<2\%$  in the following 5 days.  $^{15}\text{N}_2$  concentrations in the pore and overlying water were  $<1\%$  of the total  $^{15}\text{N}$  recovered.  $^{15}\text{N}$  recoveries in the extractable- $\text{NH}_4^+$  were almost constant throughout the incubation (range: 2.5-4.2  $\mu\text{g}$ ) and  $^{15}\text{NO}_3^-$  recoveries in the soil extracts were  $<2\%$ . As in the  $^{15}\text{NH}_4^+$  amended cores,  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  dissolved in the overlying water were not determined.

### Discussion

The lack of  $^{15}\text{N}_2$  production in cores from the fringe, basin, and riverine mangroves amended with 200  $\mu\text{mol/core}$  of  $^{15}\text{NH}_4^+$ , along with the significant recovery of  $^{15}\text{N}$  in the sediment in most experiments, indicate that coupled denitrification was not an important nitrogen transformation throughout the 8 to

10 d incubations. The high recovery of  $^{15}\text{N}$  in the organic sediment pool indicates that immobilization can be the process that accounts for the loss of inorganic nitrogen in overlying water that is transported into mangroves by tides (Rivera et al. 1995). Nitrogen immobilization is the microbial conversion of inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) into organic forms (Rice and Tenore 1981; Rice 1982; Lindau 1994). This process is associated with the high nitrogen demand of microbes during initial decomposition of macrophyte litter. There are other specific mechanisms other than microbial absorption that account for reduction of inorganic nitrogen concentrations from tidal waters. The use of  $\text{N}^{15}$  tracer techniques in this study have established that very little of this loss of inorganic nitrogen is transformed to nitrogen gas in mangrove sediments.

The fate of inorganic nitrogen from tidal waters that is immobilized in mangrove sediments depends on time scales of sedimentary processes. The accumulation of litter contributes organic matter to the formation of wetland sediments. This process occurs on decadal time scales, and the nitrogen that is immobilized in the sediment can contribute to the burial of nitrogen in wetland ecosystems. However, some of this immobilized nitrogen in early stages of litter decomposition may be recycled by ammonification and utilized in plant uptake. Thus the measurements of inorganic nitrogen immobilization using  $^{15}\text{N}$  techniques refer to the accumulation of nitrogen in litter during early stages of decomposition. Studies of longer time scales are needed to determine how much of this nitrogen may contribute to the burial of nitrogen in wetland sediments.  $^{15}\text{N}_2$  production of labeled inorganic nitrogen, on the other hand, does not necessarily refer to nitrogen loss since net effect of this flux must be evaluated relative to nitrogen fixation. Reference to  $\text{N}^{15}$  immobilization and accumulation in our enrichment studies of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  does not necessarily imply nitrogen sinks, nor does  $\text{N}_2$  production from these amendments suggest net nitrogen loss from mangrove ecosystems.

The pattern of  $^{15}\text{N}$  immobilization in the sediment pool was consistent in most of the treatments with low nitrogen enrichment ( $<250 \mu\text{mol/core}$ ), although the coefficient of variation was large for the amount of atom %  $^{15}\text{N}$  excess in some of the measured pools (20-40%). Yet, we could not account for up to ~40% of the added  $^{15}\text{N}$  in some of the cores. We attributed this missing  $^{15}\text{N}$  to uptake by pneumatophores and algae attached to these aerial roots, which

were present in the cores. There is evidence that  $\text{NH}_4^+$  uptake by mangroves exceeds regeneration rates (Boto and Wellington 1984), and that extensive fine root development in mangrove seedlings occurs when supplied with  $\text{NO}_3^-$  (Boto et al. 1989). This process can be important since we averaged  $7 (\pm 2)$  (data not shown) pneumatophores in our experimental cores. In addition, information on N assimilation rates of the algal community associated with pneumatophores is practically nonexistent (Dor and Levy 1984), so it is difficult to assess their role in the nitrogen cycle in mangrove sediments. Another potential factor contributing to the unrecovered  $^{15}\text{N}$  is  $\text{NH}_4^+$  volatilization.  $\text{NH}_4^+$  volatilization has been reported in submerged tropical soils where  $\text{NH}_4^+$  losses can range from 3- 19% (Macrae and Ancajas 1970). Boto et al. (1985) estimated that  $\text{NH}_4^+$  volatilization in a mangrove sediment could account for N losses of 10 to 20%. Yet, Alongi et al. (1992) pointed out that although volatilization of  $\text{NH}_4^+$  occurs in mangrove sediments from Missionary Bay, Australia, it might be small since the pH range (6.5-8.2) was low. Most of the inorganic nitrogen in our study either remained in the sediment in the organic pool or was removed by plant uptake.

Sediments amended with  $^{15}\text{NO}_3^-$  in the riverine mangrove contained some  $^{15}\text{NH}_4^+$  (range: 170-399  $\mu\text{g } ^{15}\text{N}/\text{core}$ ) during the 8 d incubations. Dissimilatory reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  (DNRA) indicates that fermentative bacteria in sediments may have used  $\text{NO}_3^-$  as a terminal electron acceptor for energy production (Cole 1990). In some environments and under certain conditions, DNRA is quantitatively more important process than denitrification (Koike and Hattori 1978, Harris 1982, Nishio et al. 1982, Jørgensen and Sørensen 1985, Koike and Sørensen 1988, Sørensen 1987, Jørgensen and Sørensen 1988, Henrikson and Kemp 1988). Moreover, Smith and Delaune (1985) and Korom (1992) pointed out that DNRA generally conserves N within the system, in contrast to dissimilatory reduction to  $\text{N}_2$  that results in nitrogen loss. For example, Abd Aziz and Nedwell (1986) reported that in an unpolluted salt marsh sediment < 1% of the ammonified nitrogen mineralized from organic matter was nitrified and subsequently denitrified. Denitrification in this salt marsh accounted for <10% of  $\text{NO}_3^-$  reduction. This percentage is similar to the fate of  $\text{NO}_3^-$  observed in our experiments. Since  $\text{NH}_4^+$  formed through  $\text{NO}_3^-$  ammonification can be assimilated by heterotrophic bacteria and/or



plants, DNRA represents an effective mechanism to conserve N within mangrove ecosystems.

Although actual DNRA rates were not calculated in our cores, apparently this N pathway is important for nitrogen conservation in the riverine mangrove and probably for mangrove sediments in general. For example, Rivera-Monroy et al. (in review) also found evidence of DNRA in sediment cores enriched with  $^{15}\text{NO}_3^-$  from the fringe and basin mangrove in Estero Pargo. Alongi et al. (1992) mentioned in their review of the nitrogen cycle in tropical mangrove ecosystems that the only empirical data of DNRA was reported by Shaiful (1987) in Malaysia. He measured high rates ranging from 460 to 1340  $\mu\text{mol NO}_3^- \text{ reduced m}^{-2} \text{ h}^{-1}$ , which represented 89-94% of  $\text{NO}_3^-$  produced from nitrification. However, most of these rates are for  $\text{NO}_3^-$  uptake, and the specific transformation is unknown. However, N immobilization in sediments from mangrove forest in Boca Chica and Estero Pargo can be the result of simultaneous sedimentary bacteria uptake of both  $\text{NH}_4^+$  produced by DNRA and  $\text{NO}_3^-$  dissolved in the overlying and pore waters.

The few estimates of nitrification rates in mangrove sediments indicate that rates are very low (Alongi et al. 1992). Izumi et al. (1986) reported a nitrification rate of  $\sim 0.001 \mu\text{mol N g}^{-1} \text{ d}^{-1}$  in mangroves on Hinchinbrook Island, Australia. Similarly, Shaiful et al. (1986) measured rates ranging from 0.0 - 0.22  $\mu\text{mol N g}^{-1} \text{ d}^{-1}$  in Malaysian mangrove sediments. Alongi et al. (1992) proposed that nitrification might be limited in mangrove sediments due to the high concentration of tannins in pore waters (Boto et al 1989) that can inhibit the growth and activity of nitrifying bacteria. There was evidence that nitrification occurred in the sediment cores of our study in riverine mangrove when amended with higher concentrations of  $\text{NH}_4^+$  (450  $\mu\text{mol/core } ^{15}\text{NH}_4^+$ ). The occurrence of nitrification in this experiment was coupled to  $^{15}\text{N}_2$  production that declined from 28  $\mu\text{mol m}^{-2} \text{ h}^{-1}$  on day five to levels below detection at day eight of incubation. This sharp decline in denitrification rate and the inverse relationship (Fig. 5-7) between  $^{15}\text{N}$  content in the sediment and the extracted- $\text{NH}_4^+$  pools throughout the incubation strongly suggest that  $^{15}\text{NH}_4^+$  was gradually immobilized in the sediments and therefore not available for nitrification. Apparently, the elevated amendments of  $^{15}\text{NH}_4^+$  provided an

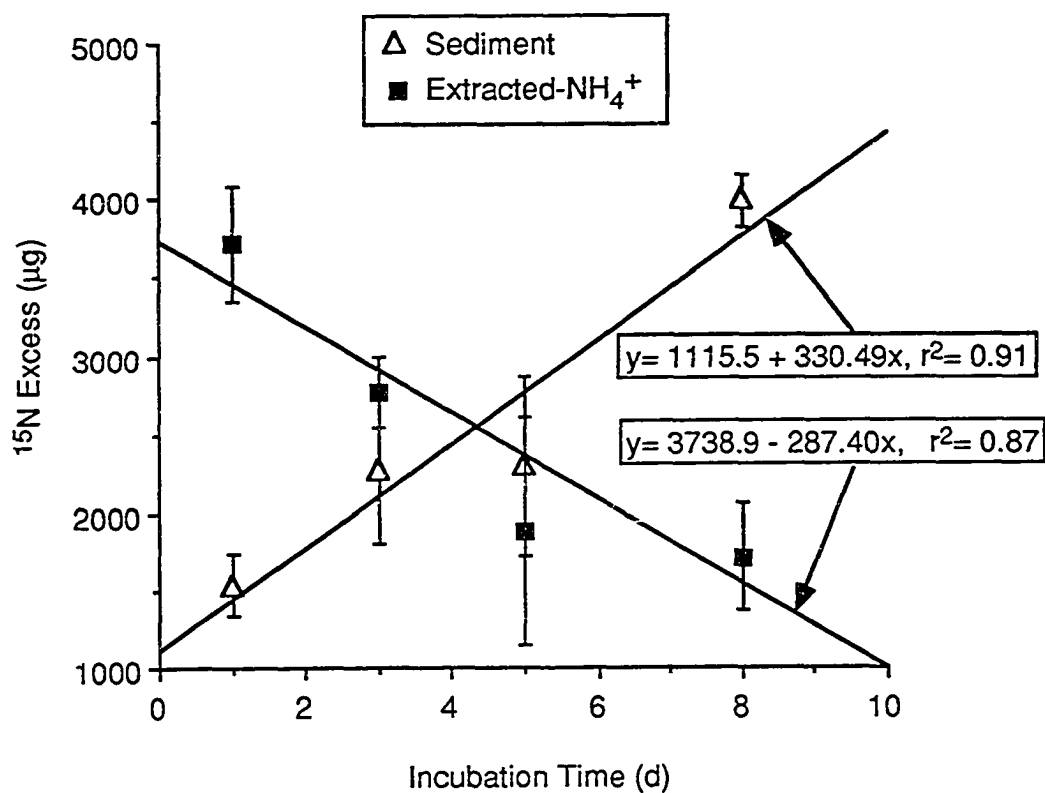


Figure 5-7. Regression curves between  $\mu\text{g } ^{15}\text{N}$  excess and incubation time (d) for sediments and extracted  $\text{NH}_4^+$  pools in cores from the riverine forest in July 1992. Cores were enriched with  $450 \mu\text{mol } ^{15}\text{NH}_4^+$  and incubated for 8 d.

excess supply of nitrogen for decomposition, plant root uptake, and nitrification. However, by day five most of the  $^{15}\text{N}$  was recovered in the sediment pool and there was little evidence of nitrification-denitrification. The inverse relationship between extractable  $\text{NH}_4^+$  and sediment N, along with lack of  $^{15}\text{N}_2$  production are indicative of this competition for available  $\text{NH}_4^+$  among decomposers, plant roots, and nitrifiers.

Limitation of nitrification as indicated by lack of  $^{15}\text{N}_2$  production could be related to low  $\text{NO}_3^-$  and  $\text{O}_2$  concentrations, which are "proximate" factors (Tiedje 1988) known to control this nitrogen transformation (Henrikensen and Kemp 1988). Overall, concentrations of inorganic nitrogen in sediments of mangrove ecosystems are very low. We measured mean  $\text{NO}_3^-$  concentrations from 0.1 to  $10 \mu\text{g gdw}^{-1}$  at the end of the experiments suggesting  $\text{NO}_3^-$  limitation (Boto 1992). In contrast,  $\text{O}_2$  may not have been limiting since cores amended with  $200 \mu\text{mol/core } ^{15}\text{NH}_4^+$  were incubated without overlying water, allowing  $\text{O}_2$  diffusion into the sediments (Kristensen et al. 1992). Another indication that  $\text{O}_2$  was not limiting is the atom %  $^{15}\text{NO}_3^-$  excess measured at all depths in cores from the riverine mangrove enriched with  $^{15}\text{NH}_4^+$  on July 24, 1991. Moreover, this  $^{15}\text{NO}_3^-$  excess measured down to 19 cm suggest that pneumatophores may be playing an important role in supplying  $\text{O}_2$  into deeper layers of the sediment as reported in other mangrove ecosystems (Scholander et al. 1955, Curran 1985, Nickerson and Thibodeau 1985, Andersen and Kristensen 1988, McKee et al. 1988).

Denitrification rates measured in cores from Boca Chica amended with  $^{15}\text{NO}_3^-$  also indicate that denitrification is  $\text{NO}_3^-$  limited. We measured a high denitrification rate ( $221.1 \mu\text{mol N m}^{-2} \text{ h}^{-2}$ ) on day one following amendments of  $450 \mu\text{mol/core } ^{15}\text{N}$  to riverine mangrove sediments. This rate rapidly declined by >90% after day 5 and by day 8 no  $^{15}\text{N}_2$  production was detected. This rapid shift in denitrification rate is probably a function of the lack of continued availability of substrate ( $\text{NO}_3^-$ ) in the sediment.  $^{15}\text{NO}_3^-$  enrichment experiments in the fringe mangrove in Estero Pargo (Rivera et al. in review) showed that denitrification was negligible at additions of 25 and  $100 \mu\text{mol/core } ^{15}\text{NO}_3^-$ ; yet denitrification rates of  $4\text{--}7 \mu\text{mol N m}^{-2} \text{ h}^{-1}$  were measured in sediment cores enriched with  $200 \mu\text{mol/core } ^{15}\text{NO}_3^-$ . They concluded that denitrification in mangrove sediments in fringe and basin mangrove is limited by

$\text{NO}_3^-$  supply. High demand for inorganic nitrogen due to assimilatory uptake by sedimentary microorganisms and pneumatophores (e. g. roots, benthic algae) restricts the availability of  $\text{NO}_3^-$  for denitrifiers. If excess  $\text{NO}_3^-$  is applied, there is a strong potential for dissimilatory reduction of  $\text{NO}_3^-$  to nitrogen gas in mangrove sediments. For example, King and Nedwell (1987) reported that sediments with higher  $\text{NO}_3^-$  concentrations exhibited higher rates of nitrate reduction. They proposed that over long time periods the denitrifying community in sediments from the Colne River Estuary, UK could be selectively modified (e. g. more denitrifying than nitrate-fermenting species) in response to increased  $\text{NO}_3^-$  input. Adaptations of the microflora to high  $\text{NO}_3^-$  concentrations have also been reported for mangrove sediments in Thailand, where the source of  $\text{NO}_3^-$  was from a sewage treatment plant (Nedwell 1975).

Nitrate diffusion from the water column may be the main source of nitrogen for denitrification in these mangrove sediments. Denitrification did not occur in cores from any of the mangrove sites amended with  $<200 \mu\text{mol/core } ^{15}\text{NH}_4^+$ , although low rates of  $^{15}\text{N}_2$  production were measured in cores amended with similar levels of  $^{15}\text{NO}_3^-$  (Rivera-Monroy et al. in review). In the fringe mangrove sediments of our study,  $^{15}\text{N}_2$  production from cores following amendments of  $450 \mu\text{mol } ^{15}\text{NO}_3^-$  was an order of magnitude higher compared to sediments with similar levels of enrichment with  $^{15}\text{NH}_4^+$ . When nitrogen is available for denitrification, higher rates of  $^{15}\text{N}_2$  production are associated with  $\text{NO}_3^-$  amendments rather than  $\text{NH}_4^+$  amendments. The preference of  $\text{NO}_3^-$  diffusion from overlying water rather than nitrification as major source of  $\text{NO}_3^-$  for denitrification has also been observed in several temperate estuarine and coastal ecosystems (Christensen et al. 1990, Nielsen 1992, Risgaard-Petersen et al. 1994).

Leaf litter of forest ecosystems influences soil fertility under the canopy by contributing to the C:N ratio of the organic matter. Leaf litter of woody vegetation in soils low in nitrogen will have higher C:N ratios than leaf litter in nitrogen rich sites (Vitousek 1982, Morris 1991). Leaf litter with high C:N ratios tend to favor net immobilization of nitrogen during decomposition in forest soils, while litter rich in nitrogen (low C:N) favor net mineralization (Alongi et al 1992, Kristensen et al 1992). Leaf litter of mangrove trees, particularly of the genus *Rhizophora*, are characterized by the low N concentrations and high C:N ratio

(Twilley et al. 1986, Steyer 1988, Lugo 1990). This low N content in mangrove litter is associated with high amounts of N retranslocated before leaf abscission (Vitousek 1984, Twilley et al. 1986, Steyer 1988). Thus C:N ratios of leaf litter from the canopy have been reported as >90 (Twilley et al. 1986). During initial stages of decomposition, nitrogen concentrations increase in this leaf litter resulting in the immobilization of N and reductions of C:N ratio to about 40 (Twilley et al. 1986, Robertson 1988). Our results of nitrogen transformations in mangrove sediments from Terminos Lagoon suggest that this nitrogen limitation in leaf litter can be supplied by both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the water column and sediments.

C:N ratios >20 in the mangrove sediments at Terminos Lagoon indicate that N is limiting microbial decomposition, causing N immobilization (or accumulation) by the bacteria and fungi during colonization phases of organic matter decomposition (Aulakah 1992). We were able to stimulate transformations of nitrification and denitrification in mangrove sediments in Terminos Lagoon by increasing levels of nitrogen enrichment. When 450  $\mu\text{mol/core}$  of  $^{15}\text{NH}_4^+$  and  $^{15}\text{NO}_3^-$  were added to sediments in a riverine mangrove, there was significant production of  $^{15}\text{N}_2$ . Low denitrification rates have been recorded in other forest soils and explained as a consequence of high soil C:N ratios. This suggest that nitrogen limitation in mangrove sediments may be an important process that controls the fate of inorganic nitrogen. Nitrogen immobilization can be high in mangrove sediments due to high rates of bacterial production, low  $\text{NH}_4^+$  flux across the sediment water interface, and the generally high C:N ratio of mangrove litter (Boto and Wellington 1984; Twilley et al. 1986; Twilley 1988; Steyer 1988; Kristensen et al. 1988; Kristensen et al. 1992).

There is evidence that bacterial biomass is high in mangrove sediments and can absorb significant amounts of carbon and nitrogen. Sander and Kalff (1993) reviewed bacterial production reported in 26 studies which included marine, river and lake environments, and found that the highest bacterial abundances ( $328.7 \times 10^{13} \text{ cells m}^{-2}$ ) and specific growth rates ( $5.5 \text{ d}^{-1}$ ) were reported for mangrove sediments. Although  $\text{NH}_4^+$  is the preferred form of nitrogen for microbial assimilation, most of the  $\text{NO}_3^-$  applied to mangrove sediments in our study was also recovered in the sediment pool. Microbial

assimilation of  $\text{NO}_3^-$  occurs when  $\text{NH}_4^+$  is not available at some microsites within heterogeneous soil environments (Rice and Tiedje 1989). This is important in mangrove forests since  $\text{NH}_4^+$  concentrations in sediments are generally low (Alongi et al. 1992).

Flux studies in mangrove sediments indicate that dissolved inorganic nitrogen in tidal waters and in deeper sediment layers are "trapped" in the first cm of the sediment surface (Kristensen et al. 1988, Boto and Wellington 1988, Boto et al. 1989, Rivera-Monroy et al. 1995). Rivera-Monroy et al. (1995) found that significant amounts of  $\text{NO}_3^- + \text{NO}_2^-$  and  $\text{NH}_4^+$  were removed by sediments in the same fringe mangrove site where we obtained our experimental cores. Sediment uptake of inorganic nitrogen occurred throughout the year, especially at the beginning of high river discharge. They concluded that this mangrove was a "sink" (Nixon and Lee 1986) of dissolved inorganic nitrogen since they assumed that most of the inorganic nitrogen was consequently lost from the mangrove forest through denitrification. Yet, as shown by our results and those of Rivera et. al. (in review) most of the inorganic nitrogen remains within the sediment. High inorganic nitrogen demand in mangrove sediments may regulate an efficient recycling of nitrogen that could serve as a mechanism for nutrient conservation (Twilley et al. 1986; Twilley 1988; Alongi 1988a, Alongi 1988b, Alongi 1989, Alongi et al. 1992).

The high denitrification rates observed in Puerto Rico by Corredor and Morrel (1994) clearly demonstrate that when C:N ratio of mangrove litter is reduced by the constant flooding with  $\text{NO}_3^-$ , a shift from  $\text{NO}_3^-$  ammonification to denitrification can occur as shown in temperate marshes (Abd Aziz and Nedwell 1986, King and Nedwell 1985, King and Nedwell 1987). Moreover, King and Nedwell (1987) pointed out that sedimentary bacteria in estuarine sediments responded to high  $\text{NO}_3^-$  levels in the water and became increasingly physiologically adapted to use  $\text{NO}_3^-$ . Changes in the bacterial composition and increasing adaptation to high  $\text{NO}_3^-$  concentration might be responsible for the high denitrification rates observed in the fringe mangrove forest in Puerto Rico. Given the positive correlation found between denitrification rates and nitrate concentrations shown by Rivera et. al. (in review), the fringe mangrove in Estero Pargo could also have the potential to denitrify large amount of  $\text{NO}_3^-$  as shown in other mangrove forests (Clough et al. 1983, Boto 1992; Corredor and

Morrel 1994). However, nitrogen demand during litter decomposition will have to be overcome before denitrification could be a dominant nitrogen transformation in these mangrove sediments.

The riverine mangrove at Boca Chica has a higher capacity for significant rates of denitrification than the fringe mangrove at Estero Pargo due to the strong influence of flood waters from the fluvial-deltaic Palizada River. Since Boca Chica is a small mouth (~ 150 m) connecting the Palizada River to Terminos Lagoon (Fig. 5-1), large amounts of dissolved inorganic nitrogen are received during high river discharge by the mangrove forests in this area. Vera-Herrera et al. (1988) reported concentrations of up to 24  $\mu\text{M}$   $\text{NO}_3^-$  and 115  $\mu\text{M}$   $\text{NH}_4^+$  in the Palizada River system during the rainy season. Also, Rivera-Monroy et al. (1995) measured  $\text{NO}_3^-$  concentration of up to 25  $\mu\text{M}$  in Estero Pargo during the rainy season. They pointed out that high  $\text{NO}_3^-$  concentrations were associated with high river discharge since the Palizada River plume in Terminos Lagoon could reach the mouth of Estero Pargo. Although riverine mangroves may have a large demand for inorganic nitrogen in sediment, higher concentrations of  $\text{NO}_3^-$  associated with river discharge indicate that denitrification can still be an important transformation of nitrogen in this mangrove. Flux studies are needed to compare the relative fate of inorganic nitrogen exchange with nitrogen transformations in mangrove sediments to compare with observations for the fringe mangrove at Terminos Lagoon.

Denitrification rates (both direct and coupled) reported for several mangrove forests are much lower than rates summarized for estuarine sediments in temperate ecosystems (Table 5-3). In contrast to the large number of denitrification estimates in the temperate coastal systems, denitrification rates in mangroves ecosystems are scarce, particularly under natural conditions. Most of the studies have focused in measuring direct denitrification in nutrient enriched mangrove ecosystems (Table 5-3). Nedwell (1975) reported denitrification rates from 78-261  $\mu\text{mol N m}^{-2} \text{ h}^{-1}$  in a small tidal river in Fiji where mangroves received  $\text{NO}_3^-$  discharge from a sewage plant. He found that about 90 % of the reduced  $\text{NO}_3^-$  was denitrified when  $\text{NO}_3^-$  concentrations were greater than 2.8  $\mu\text{M}$ . Similarly, Corredor and Morell (1994) estimated an average denitrification rate of 74.9  $\mu\text{mol N m}^{-2} \text{ h}^{-1}$  (range, 9.7- 183  $\mu\text{mol N m}^{-2} \text{ h}^{-1}$ ) in a fringe mangrove forest receiving effluents with high nitrate

Table 5-3. Denitrification rates (direct and coupled) in different types of mangroves based on different techniques (all rates expressed as  $\mu\text{mol N m}^{-2} \text{ h}^{-1}$ ).

Location	Mangrove	Method	Denitrification Rates			Reference
			Direct	Coupled <sup>¶</sup>	Total	
Fiji	nr	$\text{NO}_3^-$ Uptake	78 - 261			Nedwell (1975)
Australia	Basin	$\text{NO}_3^-$ Uptake	0.53 <sup>£</sup>			Iizumi (1986)
Puerto Rico	Fringe	Acetylene Blockage	9.7 - 183			Corredor & Morrel (1994)
Mexico	Fringe	$^{15}\text{N}$	0.08 - 9.4 <sup>a</sup>	0.0 <sup>b</sup>	0.08 - 9.4	Rivera-Monroy et. al (submitted) <sup>a</sup>
	Basin	$^{15}\text{N}$	1.9 - 4.5 <sup>a</sup>	0.0 <sup>b</sup>	1.9 - 4.5	This study <sup>b</sup>
	Riverine	$^{15}\text{N}$	3.7 - 221.1 <sup>b</sup>	2.4 - 28.9 <sup>b</sup>	6.1 - 250	

nr = not reported

¶ = Coupled nitrification-denitrification

£ = mean



concentrations (range, 200-1000  $\mu\text{M}$ ) from a sewage treatment plant in Puerto Rico. Direct denitrification rates in this mangrove compare with rates reported for site in Fiji (Nedwell 1975) and our rates in the riverine mangrove (Table 5-3). Upper estimates of direct denitrification rates in more oligotrophic basin and fringe mangroves in Terminos Lagoon and Hinchinbrook Island, Australia (Iizumi 1986) are much lower ( $0.08\text{--}9.4 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ ).

The variation in denitrification rates among studies of both estuarine and mangrove sediments can be related to levels  $\text{NO}_3^-$  enrichment. Rates of estuarine sediments range from 5 to  $250 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ , although in highly polluted estuarine sediments rates can be  $> 500 \mu\text{mol N m}^{-2} \text{ h}^{-1}$  (Seitzinger 1990). However, the response of denitrification to supply of  $\text{NO}_3^-$  may depend on the nitrogen demand by decomposers as indicated by C:N ratio of sediments. The presence of litter in these intertidal forested wetlands (mangroves) establishes different nutritional constraints on nitrogen transformations in sediments than observed in subtidal sediments. Thus rates of denitrification in mangroves are generally much lower than observed for most estuarine sediments. Further work is needed to determine at what particular combination (threshold) of  $\text{NO}_3^-$  concentrations and C:N ratios in sediments is required for denitrification to become a significant process in the nitrogen balance of mangrove ecosystems. This threshold value might determine if a mangrove forest will function as a nitrogen sink, associated with the production of  $\text{N}_2$ , or as a nitrogen transformer due to the absorption of inorganic nitrogen (by roots, algae, sedimentary bacteria) and its conversion to organic nitrogen (Nixon and Lee 1986). We hypothesize that the fate of inorganic nitrogen is significantly different among fringe, basin, and riverine mangroves given their differences in hydrology and supply of inorganic nitrogen to leaf litter.

### Conclusion

This is the first study comparing coupled nitrification-denitrification rates among basin, fringe, and riverine mangrove forests using  $^{15}\text{N}$  techniques in the neotropics. Results from 9 experiments in different seasons show that  $\text{NH}_4^+$  was readily immobilized in the sediment and not transformed to  $\text{N}_2$  through nitrification. Denitrification of  $\text{NH}_4^+$  occurred in the riverine mangrove only when  $450 \mu\text{mol NH}_4^+$  were added. This response suggests that for denitrification to occur N-demand by sedimentary bacteria have to be met first.

In addition, simultaneous studies of direct and coupled nitrification-denitrification in the riverine mangrove indicate that this type of mangrove might have a higher denitrification capacity (as reflected by high denitrification rates) than fringe and basin mangroves in Terminos Lagoon. Similar denitrification capacity has been reported in other mangroves where high levels of pollution were predominate (Nedwell 1975, Corredor and Morrel 1994). Further studies are needed to evaluate if denitrification rates in mangrove forest subjected to high  $\text{NO}_3^-$  concentrations ( $>25 \mu\text{M}$ ) can be sustained throughout the year (Clough et al. 1983, Boto 1992) and how they will affect mangrove structure and other components in the sediment (e.g. infauna, Boto 1992). Increasing agriculture and urban development in the upper watershed of Terminos Lagoon and Carmen Island will eventually affect nitrogen cycling in this complex estuarine system. Thus, coastal management plans in the region should consider the effect of increasing organic and inorganic nutrient concentrations on the structure and function of mangrove forests.

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## **CHAPTER 6**

### **A CONCEPTUAL MODEL OF NITROGEN CYCLING IN MANGROVE FORESTS: SUMMARY AND CONCLUSIONS**

#### **Introduction**

Conceptual model formulation is an important step toward understanding the behavior of an ecosystem (Odum 1983). Ultimately, it is through defining the boundaries of the system, categorizing its components, and identifying the relationships between these components, that we can establish meaningful relationships to answer specific questions related to a particular problem regarding the system (Odum 1983, Voinov & Akhremenkov 1990, Hanks & Ritchie 1991). Thus, the model and its objectives must be defined and bounded within a set of spatial, temporal, and structural constraints (Sklar et al. 1990). Translating a collection of hypotheses for ecological processes from a conceptual model into a mathematical representation of how the whole ecosystem works is an important step towards constructing computer models (Swartzman & Kaluzny 1987). Currently, conceptual and computer models are important tools to understand and manage a variety of ecosystems. Furthermore, conceptual models help to identify research needs. Since conceptual models are the first step towards building computer models, establishing the relationships between key components allow the evaluation of the parameters needed to simulate processes that regulate the behavior of the system.

The nitrogen cycle in wetland systems is more complex (Whitney et al. 1981, Howard-Williams & Downes 1993) than in terrestrial systems given the role hydrology plays in controlling nutrient exchanges and transformations (Mitsch 1988). Wetland areas are unique for sharing ecosystem properties with terrestrial and aquatic systems (Howard-Williams & Downes 1993). Also, given the ecosystem structure of wetlands, almost all processes in the nitrogen cycle can occur in close proximity, either spatially or temporally (Howard-Williams & Downes 1993). Although a number of simulation models of the nitrogen cycle have been developed for wetland ecosystems, including salt and fresh water marshes (Teal et al. 1979, Valiela & Teal 1979, Morris & Bowden 1986, Wiegert 1986), northern peatlands (Mitsch et al. 1982, Logofet & Alexandrov

1984), riparian wetlands (Mitsch 1988), there are no specific nitrogen models proposed for mangrove forests. This lack of modelling effort is surprising since mangroves are the dominant coastal wetlands in subtropical and tropical regions throughout the world (Duke 1992, Mitsch & Gosselink 1993). One of the major reasons for the lack of models in mangrove ecosystems is that a large number of nitrogen transformations involved in the nitrogen cycle (i. e. denitrification, nitrification, ammonification etc.) have just recently begun to be studied (Iizumi 1986, Shaiful et al. 1986, Corredor & Morell 1994, Chapter 2, Chapter 3, Chapter 4). This information has been identified as an important research priority necessary to explain the high primary productivity of mangrove forests (Lugo 1990) and their, sometimes, contradictory role as sinks or sources of nitrogen (Twilley 1988). Recently, Alongi (1992) published a nitrogen budget of a tropical mangrove forest in Australia. This is the first study in a mangrove ecosystem where actual rates of diverse nitrogen transformations (i.e. parameters) were available in a single location, thus allowing, using a mass balance approach, the construction of a nitrogen budget. However, they did not explicitly establish the relationships among variables responsible for such nitrogen transformations.

In this chapter, I present a conceptual model of relevant nitrogen transformations for mangrove forests in Terminos Lagoon, Mexico. This model includes the major transformations, pools of nitrogenous compounds and key forcing functions involved in the nitrogen cycle. This model is intended to be used as a generic, or "unit" model (Constanza et al. 1990) to describe different types of mangrove forests (e. g. fringe, basin, riverine) by changing specific parameters and the magnitude of the forcing functions controlling the state variables. Another objective of this model is to integrate the different rates obtained throughout this study (Chapter 2, 3, 4, and 5) in a general context to point out what parameters and interactions are needed to construct a computer model towards the goal of simulating specific natural fluctuations and coastal management scenarios in the Terminos Lagoon region (Fig. 6-1).

The model includes 8 major fluxes: nitrogen exchange at the mangrove-tidal creek boundary and its relationship with aquatic primary productivity, denitrification, nitrification, nitrogen fixation, dissimilatory nitrate reduction to ammonium (DNRA), ammonification, microbial immobilization, and mangroves

and algae uptake. Each flux is described in separate sections but within the context of the model. In each section I define the flux, establish its importance in relation to other variables and forcing functions, and briefly describe what information is known about the flux in mangroves in general. Finally, I present a summary and conclusions integrating results from Chapters 2, 3, 4, 5.

### Ecosystem Description

Terminos Lagoon is a, shallow (mean depth = 3.5 m), large coastal Lagoon (~1800 km<sup>2</sup>) in the state of Campeche, Mexico. The climate of the area is tropical with annual average air temperature ranging from 18 °C to 36 °C. Tides are mixed diurnal with a mean tidal range of about 0.5 m. Average annual precipitation (1680 mm yr<sup>-1</sup>) is seasonal, with a rainy season from June to October associated with frequent tropical convectional rains. The winter storm season is from November to February, with strong north winds and frontal rains. The dry season is from March to June. Peak river discharge occurs in the latter months of the rainy season from September to November. The lagoon is bordered almost completely by extensive mangrove swamps. Three species are dominant: *Rhizophora mangle* L., *Avicennia germinans* L., and *Laguncularia racemosa* Gaertn. f. (Day et al. 1987). Boca Chica and Estero Pargo are areas representative of basin, fringe, and riverine forests surrounding the lagoon (Fig. 6-1).

Boca Chica is continuously flooded with freshwater from the Palizada River in the rainy season during the period of high river flow, while in the dry season the forest floor is almost free of standing water (Day et al 1987). The riverine forest in this area is dominated by *Rhizophora mangle* in the periphery and by *Avicennia germinans* and *Laguncularia racemosa* in the inner forest. Accretion rates range from 1.3-4.4 mm y<sup>-1</sup>. C:N ratio in the sediments is 33 ± 1.7 (top 16 cm). Organic matter and total N accumulation rates are 409 and 5.8 g m<sup>-2</sup> yr<sup>-1</sup>, respectively (Lynch 1989). Soil salinities range from 25 - 42 ‰. Total aboveground net primary production (NPP) reported for this forest is 2458 g m<sup>-2</sup> yr<sup>-1</sup>.

Mangroves adjacent to the tidal creek in Estero Pargo are characteristic of fringe forests with regular tidal inundation, while the inland mangroves are characteristic of basin forests which are infrequently flooded (Day et al. 1982,

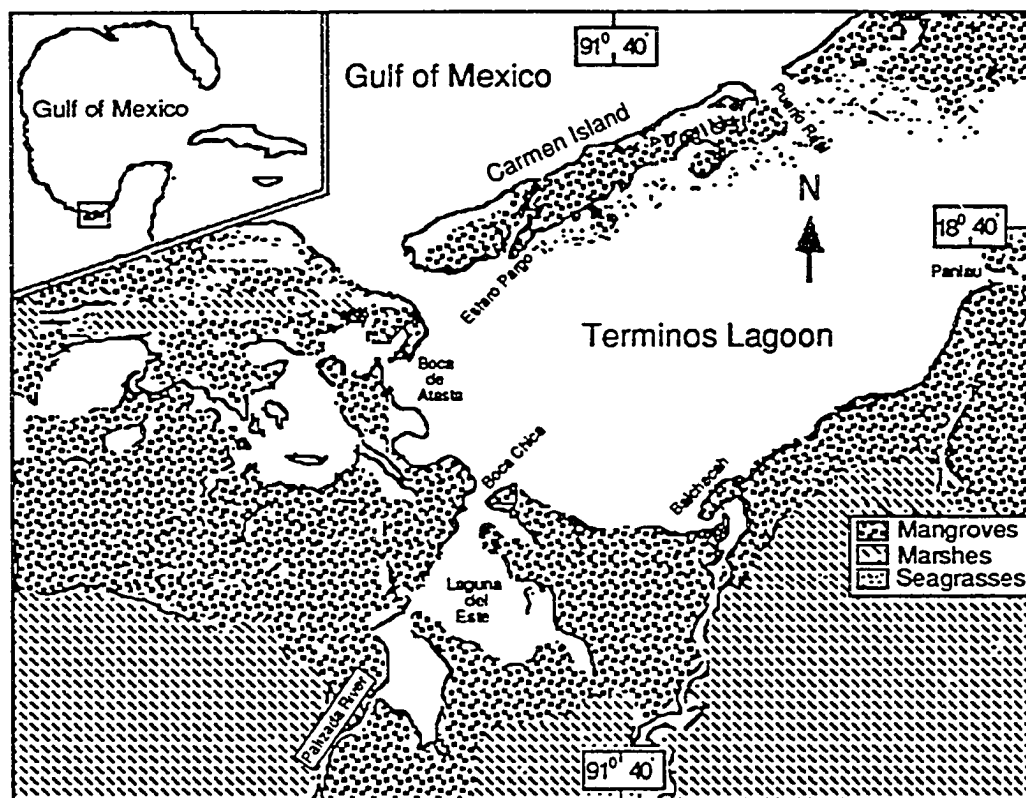


Figure 6-1. Map of Terminos Lagoon showing Estero Pargo and Boca Chica.

Lynch et al. 1989). The dominant species are *Avicennia germinans* followed by *Rhizophora mangle*. NPP estimated for the fringe forest is  $1606 \text{ g m}^{-2} \text{ yr}^{-1}$  (Day et al. 1988). Soil salinities in the fringe forest range from 30 to 35 ‰ and are controlled by the seasonal salinity of creek waters in Estero Pargo (Day et al., 1987). Salinities in the basin forest reach up to 90 ‰ in the dry season. Accretion rates reported for the fringe and basin forest are 2.9 and 1  $\text{mm yr}^{-1}$  (Lynch et al. 1989), respectively. C:N ratio in the sediment is  $25.1 \pm 1.5$  in the top 16 cm (Lynch 1989). Organic matter and TN accumulation rates are 270 and  $4.8 \text{ g m}^{-2} \text{ yr}^{-1}$ , respectively.

### Nitrogen Model

#### A) Model Description

Mitsch & Gosselink (1993) pointed out that hydrology is probably the single most important factor in the establishment and maintenance of wetlands processes. Flood duration and frequency regulate factors such pH and redox potential that in turn control several nitrogen transformations (Kadlec & Hammer 1988). Thus, any model describing nitrogen cycling in mangrove forests should consider hydroperiod (Mitsch 1988) as a key variable controlling fluxes of materials in and out of the system. In this conceptual model (Fig. 6-2) two hydroperiod components are considered as critical forcing functions: tides and surface inflows and outflows (e. g. river flooding). These two components reflect pulsing hydrological conditions (Odum 1971) which make mangrove forests one of the most productive wetlands in the world (Twilley et al. 1992). The frequency and duration of inundation regulates the amount of oxygen being diffused into the soil and as a consequence a "oxycline" (Gambrell & Patrick 1978) is developed at the surface of the soil at the soil-water interface (Mitsch and Gosselink 1993). Denitrification and other microbial mediated nitrogen transformations (i.e. dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$ , ammonification, nitrogen fixation) are strongly affected by the thickness of this layer. For example,  $\text{O}_2$  concentration in the sediments controls nitrification rates so this relationship is included in the model. Also,  $\text{O}_2$  is related to the decomposition of organic matter which influences partially the C:N ratio of the organic matter accumulated in the soil. C:N ratios of organic matter affect immobilization and, therefore, availability of dissolved inorganic nitrogen through microbial metabolism. In addition to  $\text{O}_2$  diffused into the sediment, either

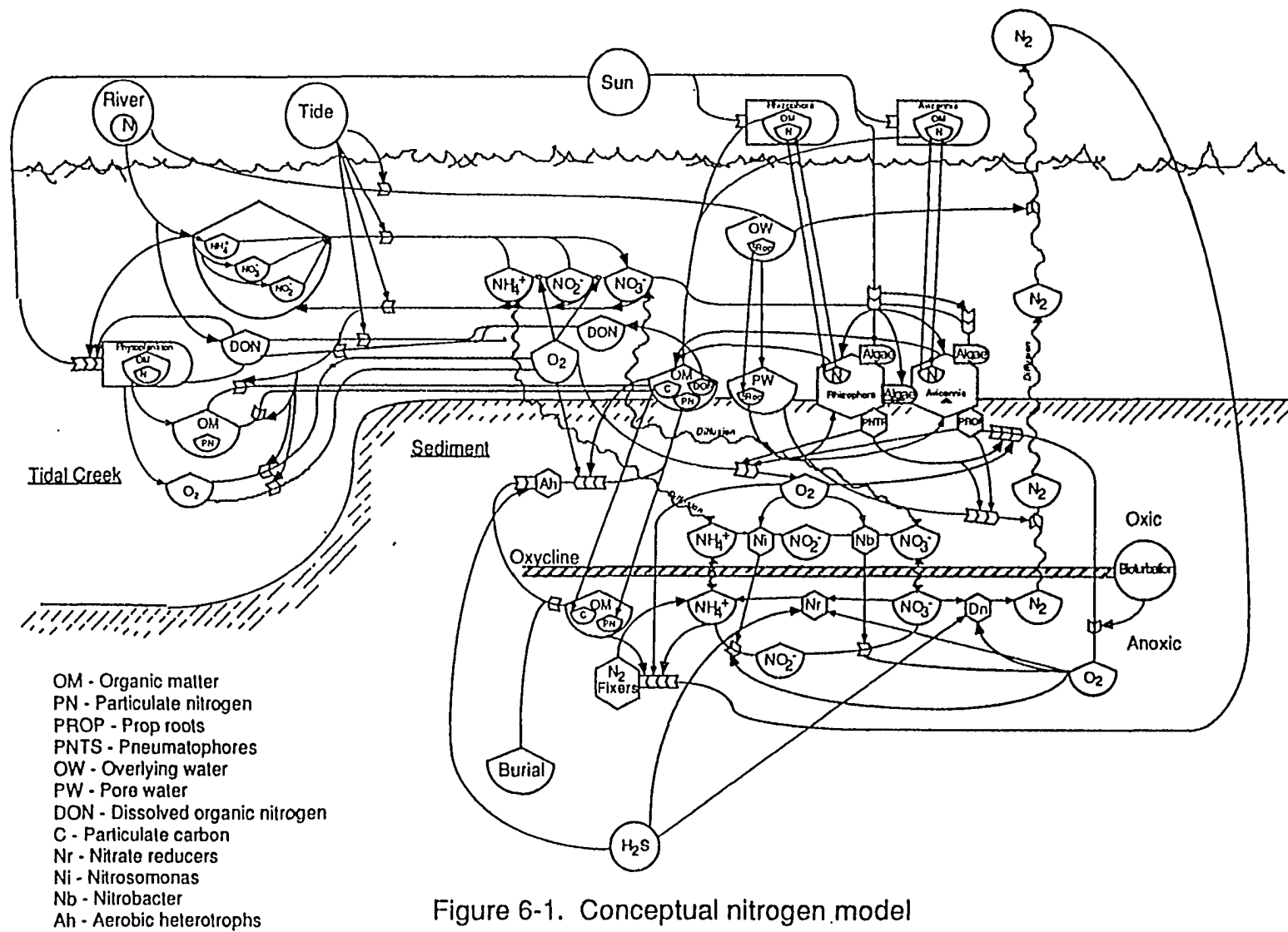


Figure 6-1. Conceptual nitrogen model



during dry or wet conditions, O<sub>2</sub> is transported into the sediment through aerenchymous tissue of stems and roots (Dacey 1980, Reedy et al. 1989). Nitrogen cycling in the sediments of wetlands is regulated by the transport of oxygen through the aerenchymous tissue and roots of wetland plants (e. g. Caffrey & Kemp 1991). Oxygen then diffuses outwards from the roots by radial oxygen loss to aerate the rhizosphere in the immediate vicinity of the root (Dunbabin et al. 1988, Reddy et al. 1989). Pneumatophores and prop roots of mangrove trees have a large percentage of aerenchyma tissue (Curran 1985, Andersen & Kristensen 1988) and are known to transport a significant amount of O<sub>2</sub> into the sediments (Scholander et al. 1955, Nickerson & Thibodeau 1985, McKee et al. 1988). The capacity of mangrove roots to transport O<sub>2</sub> into anaerobic sediments results in a mosaic of aerobic-anaerobic conditions with depth. N<sub>2</sub> loss may also be facilitated by transport upwards through pneumatophores as shown in other wetlands plants (Reddy et al. 1989). Thus, this model considers that in mangrove forests the nitrogen transformations are affected by the sharp gradients in dissolved O<sub>2</sub> that occur spatially both on horizontal and vertical scales.

O<sub>2</sub> concentrations are in turn influenced by bioturbation, benthic algae, and algae attached to prop roots (*Rizhophora mangle*) and pneumatophores (*Avicennia germinans*). Ventilation (including O<sub>2</sub> diffusion) of burrows is a major factor controlling biogeochemical processes occurring in mangrove sediments (Kristensen et al. 1988, Kristensen et al. 1992, Smith et al. 1991). The presence of plants can impose seasonal and diurnal cycles on denitrification activity due to O<sub>2</sub> production during photosynthesis by algae in the sediments and attached to roots. This is particularly important during high water levels inside the forest as shown in other coastal sediments (e.g. Nielsen et al. 1990, Risgaard-Petersen et al. 1994). Algae production inside mangrove forest is high (Dor & Levy 1984) and sometimes equivalent to mangrove litter productivity (Rodriguez & Stoner 1990).

Dissolved inorganic nitrogen (DIN= NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) concentrations in the flooding water and sediments are also influenced by plant uptake (mangroves + algae). This relationship is important to consider since DIN in water and sediments in non-polluted mangrove systems is generally low (Twilley 1988, Alongi et al. 1992). There is evidence that the rate of NH<sub>4</sub><sup>+</sup> uptake by

mangrove trees in productive areas appears to exceed regeneration rates (Boto & Wellington 1984) and that  $\text{NO}_3^-$  may play an important role in root development in early growth stages (Boto et al. 1985).  $\text{NH}_4^+$  adsorption by sediments is not considered in the model.

Soil salinity in the model is considered as an important factor influencing mangrove distribution along the tidal inundation gradient. Salt tolerances for each species will also determine above ground biomass and productivity which influences nutrient uptake.

Hydrological conditions and nitrogen transformations described in the model are contemplated within a time frame of hours and days.

#### B) Nitrogen transformations

1) Nitrogen exchange at the mangrove-tidal creek boundary and its relationship with aquatic primary productivity.

Nitrogen exchange at the mangrove-tidal creek boundary has a significant effect on nitrogen transformations inside the forest. For example DIN in the water column can supply  $\text{NH}_4^+$  and  $\text{NO}_3^-$  to denitrification. Thus, frequency and duration of inundation strongly control the interaction between DIN and denitrification. Nutrient exchange between mangroves and coastal waters is poorly understood. Results from different flux studies between mangroves and adjacent waters indicate that mangroves are balanced and there is no nitrogen lost from the system (Boto and Wellington 1988, Alongi et 1992). Apparently, mangroves export organic nitrogen (detritus, litter) (Twilley 1988) and import dissolved inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) (Boto et al. 1988, Chapter 1). Given this dual function, mangroves can be considered as nitrogen "transformers" (Twilley 1988, Mitsch & Gosselink 1993). However, this conclusion should be taken with caution since different methodologies were used in estimating current published fluxes, and no information from other environmental settings is available (Thom 1982, Thom 1984, Woodroffe 1992).

The humic substances that enter coastal and estuarine waters affect the plankton communities in diverse ways (Langis et al. 1986, Prakash et al. 1973). Thus, primary productivity of estuarine waters is linked to the relative inputs of autochthonous and allochthonous organic matter, particularly in areas of high river discharge (Prakash 1971). Phytoplankton primary productivity

rates in tropical coastal lagoons may be enhanced by mangrove forests located at the margin between terrestrial and marine systems (Morrel & Corredor 1993, Ricard 1984). These coastal systems receive nutrients, litter and dissolved organic matter from mangrove forests through the action of tidal inundation and river discharge, which influences phytoplankton and bacterial secondary production. Yet, it is not clear how nitrogen exported from mangroves forests enhances aquatic primary productivity. The nitrogen model shows the effect of DON and PN exported from mangroves on the aquatic primary productivity of adjacent estuarine waters. Turbidity and light are included and modeled in reference to their interaction with nitrogen exports.

## 2) Denitrification

Denitrification is the dissimilatory reduction of  $\text{NO}_3^-$  to gaseous products including  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  (Knowles 1982). It is a microbial process that occurs under anaerobic conditions and is influenced by organic carbon content, temperature, and soil pH (Godwin & Jones 1991). Denitrification is stimulated by flooded conditions. In the model (Fig. 6-2) denitrification is controlled by DIN levels, nitrifier and denitrifier densities, and  $\text{O}_2$  concentration. Coupled nitrification-denitrification and direct denitrification are considered in both the oxic and anoxic layers. Temperature is not included since temperature fluctuations in sediments in Boca Chica and Estero Pargo (and mangroves in general) are minor (range: 25-32 °C). Estimates of denitrification rates in mangrove sediments are scarce. Most of the data come from mangrove systems subjected to high  $\text{NO}_3^-$  enrichments (Nedwell 1975, Corredor and Morrel 1994). Currently, there are only 3 estimates in unpolluted mangrove systems (Iizumi et al. 1986, Chapter 3, Chapter 4).

## 3) Nitrification

Nitrification refers to the process of oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . It is a biological process and occurs under aerobic conditions. The main factors that limit nitrification are substrate  $\text{NH}_4^+$ ,  $\text{O}_2$ , soil pH,  $\text{H}_2\text{S}$ , and temperature. The nitrification step has been identified as the rate limiting step in the nitrogen cycle in several wetland studies and seems to be the case in mangrove forests. Hydroperiod allows for very efficient nitrification and ammonification. Nitrification is controlled by  $\text{O}_2$ , nitrifier density, and  $\text{NH}_4^+$  levels supplied by ammonification and  $\text{NH}_4^+$  diffused from the water column during high water

levels (Fig. 6-2). Nitrification can occur in the anoxic layer due to the  $O_2$  diffused throughout mangrove roots. Two estimates of rates in mangrove are currently reported in the literature (Iizumi 1986, Shaiful et al. 1986). Due to plant uptake and microbial immobilization, sediment  $NO_3^-$  concentrations are low. Tannins and  $H_2S$ , which are in high concentrations in mangrove sediments (Boto et al. 1989), can inhibit the growth and activity of nitrifying bacteria (Alongi et al. 1992) and therefore indirectly limit coupled nitrification-denitrification rates.

#### 4) Nitrogen fixation

Nitrogen fixation is the conversion of  $N_2$  gas to  $NH_4^+$  in the presence of the enzyme nitrogenase (Postgate 1982). It is performed by nonsymbiotic bacteria, by symbiotic bacteria of the genus *Rhizobium*, or by the actinomycetes. Nitrogen fixation generally provides only a small source of N to wetland systems (ca 5%) (Alongi et al. 1992). Among other factors regulating  $N_2$  fixation,  $O_2$ , inorganic nitrogen and organic substrate are the most important. These three factors are important considerations in the model.  $N_2$  fixation is the nitrogen transformation most studied in mangrove ecosystems. There are more than a dozen studies in different environmental settings (c. f. Alongi et al. 1992). Rates have been reported for anoxic sediments, litter, fresh and aged leaves, bark, live and dead roots, and creek banks without mangroves.

#### 5) Dissimilatory nitrate reduction to ammonium (DNRA)

DNRA occurs when  $NO_3^-$  is reduced to  $NO_2^-$ , which is subsequently reduced to  $NH_4^+$  in a respiratory process or a fermentative reaction (Koike & Sørensen 1988). DNRA and denitrification are influenced by the same factors but the dominance of denitrification depends on  $NO_3^-$  concentrations. Denitrification represents loss of nitrogen from the system whereas in DNRA the reduced nitrogen is recycled within the ecosystem rather than lost to the atmosphere (Herbert & Nedwell 1990). Denitrification becomes dominant as  $NO_3^-$  concentrations increase (King & Nedwell 1985). DNRA via nitrite is favored by low redox and high organic carbon content at the expense of denitrification. Although the importance of DNRA has been recognized in other wetland ecosystems, there is no data for mangrove sediments.

## 6) Ammonification

Ammonification is the production of  $\text{NH}_4^+$  through the deamination of organic nitrogen through bacterial activity (Henrikson and Kemp 1988).  $\text{NH}_4^+$  is the dominant N species released from coastal sediments after organic matter decomposition. If  $\text{O}_2$  is present,  $\text{NH}_4^+$  regenerated from benthic decomposition of organic matter or diffused from the overlying water, can be oxidized to  $\text{NO}_3^-$  (nitrification).  $\text{NO}_3^-$  produced, in turn, can be denitrified and lost from the system. This coupled nitrification-denitrification represents a sink that diverts N away from recycling pathways (Jenkins & Kemp 1984). Thus, ammonification and nitrification are favored by dry periods when oxygen concentrations in the sediment increase.

## 7) Microbial immobilization

Immobilization refers to the transformation of inorganic compounds to the organic state. Immobilization occurs when soil microorganisms assimilate inorganic N compounds and use them in the synthesis of the organic constituents of their cells. A balance exists between immobilization and ammonification. For example when organic matter with a high C:N ratio is added to the sediment, net immobilization is dominant. After some of the sediment carbon has been consumed by respiration, net mineralization may resume. In mangrove sediments low C:N ratios generally found in litterfall tend to favor N immobilization. The high production rates by mangrove forests (Lugo et al. 1990) result in an abundance of carbon providing an organic substrate for bacterial processes (Robertson et al. 1992). The highest bacterial abundance and specific growth rates in marine and estuarine systems are found in mangrove sediments (Sander & Kalff 1993). Alongi et al. (1992) suggested that  $\text{NH}_4^+$  immobilization was high in mangrove sediments due to the generally high C:N ratio of mangrove litter and high rate of bacterial production. This relationship is included in the model.

## 8) Mangrove and algae uptake

Plant growth is greatly affected by the supply of nitrogen. In general, nitrogen is taken up by wetland plants as  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Uptake as  $\text{NO}_3^-$  requires that the organism has the capacity to produce nitrate reductase. Preferential uptake of  $\text{NH}_4^+$  is likely in most rooted wetland plant species where, in spite of aerobic microzones,  $\text{NH}_4^+$  dominates the inorganic pool. The

concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are low in sediments where mangrove roots are present probably due to plant uptake (Alongi et al. 1992). Mangroves show little evidence of  $\text{NO}_3^-$  utilization, as measured as nitrate reductase activity, but when grown in  $\text{NO}_3^-$  this enzyme increased in the roots allowing for its utilization (Stewart & Orebamjo 1984). Boto et al. (1985) observed high root development in seedlings grown exclusively under  $\text{NO}_3^-$  fertilization. However, there is limited information on the nutritional status of mangrove forests and the effect of nitrogen limitation on growth rates in the field for specific species (Twilley et al. in prep.). Internal translocations of nitrogen have been suggested as important mechanisms for the conservation of N in mangrove forests (Twilley et al. 1986, Steyer 1988) and are responsible for the high C:N ratio of litterfall. According to Vernberg (1993) primary production in saline wetlands is nitrogen limited.

Nitrogen requirements for micro and macroalgae in mangrove sediments are not available (Cordeiro-Marino et al. 1992). Standing stocks of microalgae (chlorophyll *a*) in mangrove sediments are generally low ( $\leq 5 \mu\text{g chl a g dw}^{-1}$ , Alongi 1990). Limited chlorophyll *a* levels are attributed to low light intensity under the dense mangrove canopy (Alongi 1988a, Alongi 1988b) and the inhibitory effect of dissolved organic carbon in pore waters on benthic diatom growth (Cooksey & Cooksey 1978). In contrast to microalgae biomass, macroalgae biomass attached to pneumatophores and base of mangrove trees is high (Alongi & Sasekumar 1992). Dor and Levy (1984) reported that macroalgae productivity was 200 times higher than phytoplankton productivity in a mangrove forest of Sinai. Also, Rodriguez and Stoner (1990) found that epiphytic algae associated with *Rhizophora mangle* roots were as productive as mangrove trees. Although the importance of micro and macroalgae biomass and production have an important role in the nitrogen cycle of mangrove forests, there is no information on their nitrogen requirements and uptake rates. Uptake of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  by algae and light, as a forcing function, are represented in the model.

### Summary and Conclusions

1) Nitrogen exchange at the mangrove-tidal creek boundary and its relationship with aquatic primary productivity.

The fringe forest in Estero Pargo acts as a sink of inorganic nitrogen and as a source of dissolved and particulate nitrogen. There was a net import of dissolved inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^- + \text{NO}_2^-$ ) from the creek and basin forest, while particulate (PN) and dissolved organic nitrogen (DON) were exported to the creek and basin forest. The tidal creek was the principal source of  $\text{NH}_4^+$  and  $\text{NO}_3^- + \text{NO}_2^-$  to the fringe forest while the basin forest was the main source of total suspended sediments. Net export of PN occurred from the fringe forest to the tidal creek while less PN was exported to the basin forest. The exchange of nutrients among the tidal creek, the fringe, and basin forests in Estero Pargo is strongly influenced by seasonal weather forcing, such as winter storms, that can influence the magnitude and direction of water flow.

There was a net stimulation of net aquatic primary productivity (NAPP) after addition of different amounts of mangrove filtered surface water to water collected from Terminos Lagoon. Additions of filtered water had a variable effect on production rates, depending of the month. Results show that this stimulation occurs during all seasons where additions of low volumes of surface water stimulated productivity by more than 50%. High percentages of increase in net productivity were observed during high and low river discharge conditions indicating that drainage from mangrove forests could enhance water column primary productivity in adjacent estuarine waters throughout the year.

## 2) Denitrification

We did not observe coupled nitrification-denitrification in mangrove sediments from the fringe, basin or riverine forest in Terminos Lagoon after addition of  $^{15}\text{NH}_4^+$  to soil cores. This lack of  $\text{N}_2$  production was due to a lack of  $\text{NO}_3^-$  from nitrification. Yet, when higher  $\text{NH}_4^+$  concentrations were added to sediment from the riverine forest, coupled nitrification-denitrification did occur. This response suggests that denitrification takes place only after nitrogen demands by sedimentary bacteria are met. Addition of  $^{15}\text{NO}_3^-$  to measure direct denitrification in mangrove sediments in the rainy season resulted in similar denitrification rates in the basin and fringe forest and the highest rate in riverine forest after addition of higher  $^{15}\text{NO}_3^-$  concentrations. The high denitrification rates in the riverine forest observed 24 h after addition of  $^{15}\text{N}$  indicate that this type of forest has a large denitrification capacity, probably as

an adaptive response to high  $\text{NO}_3^-$  concentrations in flooding waters from the Palizada river during high river discharge.

We observed that some sediments amended with  $^{15}\text{NO}_3^-$  produced  $^{15}\text{NH}_4^+$ . This indicates that dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  took place. Since 1) DNRA is considered as an N transformation leading to the conservation of nitrogen within the system and, 2) a large percentage of the added  $^{15}\text{N}$  was stored in the sediments and not denitrified, mangroves in Terminos Lagoon may be very efficient in recycling and conserving nitrogen. Further evidence comes from the flume studies where  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were imported in the fringe forest throughout the year.

This study supports the evidence that 1) mangroves are efficient at retaining and recycling nitrogen throughout several processes that reduce export (Boto 1982, 1984, Twilley 1988) and 2) mangroves are nitrogen transformers importing dissolved inorganic nitrogen and exporting organic nitrogen which could increase primary productivity in adjacent coastal waters.

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## **APPENDIX**

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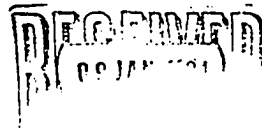
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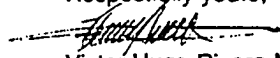
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Thank you very much for your attention to this matter.

I take the opportunity to wish you a happy new year.

Respectfully yours,

  
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## **VITA**

Victor Hugo Rivera Monroy was born in Mexico City in 1957 on April 4. He attended High School at the Centro de Estudios Científicos y Tecnológicos No. 2 of the Instituto Politécnico Nacional, graduating in 1975. He received his Bachelor in Biology, with emphasis in Hydrobiology and Ecosystem Analysis at the Department "El Hombre y su Ambiente" of the Autonomous Metropolitan University-Xochimilco in 1980. He worked 1980-1983 as a research associate and taught marine ecology in the same University. In the spring of 1983 he worked in the National Marine Mammal Program of the National Institute of Fisheries conducting research in the distribution and migration of the gray whale in Baja California, Mexico. In 1985 he entered the Masters Degree program at the Department of Marine Sciences, Louisiana State University, where he worked in coastal studies of phytoplankton production and nitrogen cycling. He obtained his Master of Science degree in Marine Sciences in 1988. He entered the Ph.D. program in the Department of Oceanography and Coastal Sciences, Louisiana State University in 1989 where he is currently a candidate for the Doctor of Philosophy degree.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

**Candidate:** Victor Hugo Rivera-Monroy

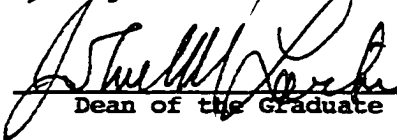
**Major Field:** Oceanography and Coastal Sciences

**Title of Dissertation:** Nitrogen Fluxes in Mangrove Sediments and their  
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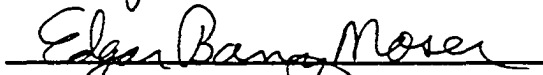
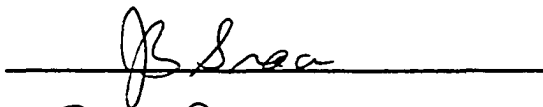


Major Professor and Chairman



Dean of the Graduate School

EXAMINING COMMITTEE:



Date of Examination:

October 28, 1994