Indian River Lagoon Hydrodynamics and Water Quality Model: Nutrient Storage and Transformations in Sediments

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INDIAN RIVER LAGOON HYDRODYNAMICS AND WATER QUALITY MODEL: NUTRIENT STORAGE AND TRANSFORMATIONS IN SEDIMENTS

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EXECUTIVE SUMMARY

Anthropogenic nutrient inputs into estuaries and coastal marshes can have a significant impact on biological productivity of the ecosystem. This influence is prevalent in estuaries adjacent to urban and agricultural activities. The waste materials discharged can enter the estuaries either through surface flow (stream and river) and subsurface flow (ground water). The nutrients discharged into estuaries can lead to nuisance algal blooms and/or depletion of dissolved oxygen in receiving waters. Majority of nutrients/contaminants accumulate in sediments.

Establishment of nutrient load reduction targets in the Indian River Lagoon (IRL) is an integral component of water quality management and the restoration of seagrasses. Increased nutrient loading to IRL is apparently causing a shift in the primary producers such as seagrasses to phytoplankton and algae. Nutrient load reduction can potentially reverse that trend, to attain and maintain a macrophyte-based estuarine system. Seagrasses and plankton derive nutrients from both external and internal sources. External sources can be decreased by overall reduction of inputs. Internal loads derived from bottom sediments are difficult to control and often ignored in overall management schemes. Aquatic systems that receive have received nutrient loads for long period of time accumulate nutrients in bottom sediments. These sediments become a potential source of nutrients to the overlying water column. Sediment bound nutrients are then released through mineralization of organic matter, followed by resuspension and diffusion of nutrients into the water column.

In order to predict the effects of different strategies of pollution reduction in IRL, it is essential to have an accurate understanding of the budgets of the affected pollutants. For IRL, the pollutants of most immediate concern are nitrogen (N) and phosphorus (P). Nitrogen and P are essential nutrients that often limit the rate of plankton primary production, the source of flocculent sediments. Although C, which is continually supplied through photosynthesis and removed through microbial respiration, is a major component of the flocculent organic sediment, it is not as important in eutrophication as N and P. Nevertheless, the rate of accumulation of flocculent sediments is determined by the balance between C fixation via algal photosynthesis and C mineralization through microbial respiration. Information on the C budget, then, could indicate the level of reduction of algal productivity required to cause the estuary to become a net exporter of C.

In recent years, it has become clear that nutrient processing by the aquatic biota and the biogeochemical processes in estuarine sediments can be a major factor in regulating water quality. The bottom sediments in IRL can function as a source or sink for the nutrients in the water column. The direction of nutrient flux between the sediment and overlying water column is dictated by the external inputs of the nutrients and biogeochemical processes in the sediments and water column. These processes include: photosynthetic C fixation, microbial decomposition of organic C, N transformations (ammonification, adsorption/desorption of ammonium, nitrification-denitrification, ammonia volatilization, dinitrogen fixation), and P transformations (mineralization of organic P, adsorption/desorption of P). The balance between these sources and sinks of nutrients can either augment or reduce the trophic state of the water.

Results presented in this report are part of a larger study designed to develop pollutant load reduction models for IRL. As a part of this large project, studies on biogeochemical processes in sediments regulating surface water quality were conducted with following objectives.

The objectives of this study were to:

- Characterize spatial and temporal variations in selected physico-chemical properties of IRL sediments, and determine inorganic and organic forms of C, N, and P in sediments.
- Determine the net flux of dissolved N, and P between the sediments and the overlying water column.
- Determine the relative importance of biological and physico-chemical factors regulating nitrogen transformations in sediments.
- Determine the relative importance of biological and physico-chemical factors regulating phosphorus transformations in sediments

The first objective was to characterize spatial and temporal variations in selected physico-chemical properties of IRL sediments.

- Sediment sampling stations were grouped into three zones: southern zone, central (mud) zone, and northern zone.
- Generally, muddy sediment deposits in the vicinity of Melbourne were found to have elevated concentrations of porewater ammonium N (NH_4-N) and dissolved reactive P (DRP), as well as total N and total P, relative to the other sampling stations. Ammonium N and DRP in this region averaged **7.0** and **0.7** mg L^{-1}, whereas TN and TP averaged **3957** and **839** mg kg^{-1}. Total P in the surface sediments of the southern stations was higher than most of the remaining stations, with the exception of the mud zone stations.
- Most of the sediment P **(78%)** was in the Ca and Mg-bound pool (apatite-P) and this is likely due to high calcium carbonate and low organic matter content of these sediments. More P was recovered in iron and aluminum bound P (non-apatite P) fractions in the mud zone sediments than either the northern or southern zone sediments. For mud sediments, approximately **7%** of the TP was recovered in the Fe and Al – bound fraction and 8% in the organic P fraction. For the northern and southern zone sandy sediments, only 2 – **4** % was recovered in these pools.
- Total N and P storage in the surface sediments (0-10cm) is approximately 41,000 and **33,000** metric tons **of** N and P, respectively.
- Porewater NH_4-N and DRP showed significant seasonality, with higher values in summer than winter months.

The second objective of the study was to determine the net flux of dissolved N, and P between the sediments and the overlying water column.

- The average flux from the sediment to the water column was **1.6** and **30** mg m^{-2} day^{-1} for DRP and NH_4-N and, respectively. This internal supply of N and P represents a long-term source of nutrients to the water column.

The third objective of the study was to determine the relative importance of biological and physico-chemical factors regulating nitrogen transformations in sediments.

- Ammonium is not strongly adsorbed on sediment cation exchange complex. Low adsorption coefficients of IRL sediments results in maintenance of high dissolved NH_4^+ concentrations in the sediment porewater.
- Mineralization of organic N under aerobic conditions was approximately two times faster than under anaerobic conditions.
- Mineralization rates of organic N were in the range of **0.2** to 8.5 mg $kg^{-1}day^{-1}$ under aerobic conditions and 0.3 to 4.3 mg kg^{-1} day^{-1} under anaerobic conditions.
- Potential nitrification rates were in the range of **1.3** to 9.9 mg kg^{-1} day^{-1} and the turnover times of the initial ammonium N were in the range of **4.1** to 6.5 days.
- Potential denitrification rates were in the range of 0.9 to 6.9 mg kg^{-1} day^{-1} and the turnover times of the added nitrate N were in the range of 0.3 to **3** days.
- Estimated biological nitrogen fixation in the water column was very low with an average rate of 0.016 mg L^{-1} year". Much of the nitrogen fixation was confined to epiphytic algae on seagrass leaves.

The fourth objective of the study was to determine the relative importance of biological and physico-chemical factor regulating phosphorus transformations in sediments.

- Mineralization rates of organic P were in the range of 0.3 to 5.9 mg $kg^{-1}day^{-1}$ under aerobic conditions and 0.8 to **12.4** mg kg^{-1} day^{-1} under anaerobic conditions.
- Soluble P release rates were affected by sediment redox conditions, with rates in the range of 0.004 to 0.03 mg kg^{-1} day^{-1} under aerobic conditions and 0.009 to 0.24 mg kg^{-1} day^{-1} under aerobic conditions.
- Phosphorus release rates correlated to total P and organic P, while the soluble P release rates correlated to oxalate extractable iron and aluminum in sediments.
- Phosphorus sorption in sediments was regulated by amorphous and poorly crystalline forms of iron.
- Lower P sorption capacity and adsorption coefficients were observed for sediments under anaerobic conditions than aerobic conditions.

Results obtained from the laboratory and field studies show that sediments are enriched with P as compared to N, suggesting the system may be limited by N availability. Data presented is based on a limited number of stations, though these results do provide a preliminary survey of the physical, chemical, and biological properties of sediments. Although the study shows some definitive conclusions, results can not be extrapolated spatially or temporally to the whole lagoon. Muddy sediments, uncharacteristic of most the lagoon, were found in the vicinity of Melbourne. These deposits were found to contain labile forms of N and P in excess of that found at the other sampling stations. Since sampling in this region was very limited, the true extent of these deposits remains unknown. Therefore, accurate mapping of the sediments, nutrient characterization and determination of nutrient exchange processes should he further investigated in this region of the lagoon. Additional research should focus improving the spatial and temporal resolution in the data, which will help to derive more reliable conclusions. Since the system is limited in N, future research should focus on developing a better understanding of the spatial and temporal variations in N transformations in sediment-water column of the lagoon as related to the water quality and seagrass productivity.

CHAPTER 1

1.1 Introduction

Anthropogenic nutrient inputs into estuaries and coastal marshes can have a significant impact on biological productivity of the ecosystem. This influence is prevalent in estuaries adjacent to urban and agricultural activities. The waste materials discharged can enter the estuaries either through surface flow (stream and river) and sub-surface flow (ground water). The nutrients discharged into estuaries can lead to nuisance algal blooms and/or depletion of dissolved oxygen in receiving waters.

In shallow estuaries, dissolved oxygen of the water column remains relatively high due to: **(1)** a low density of oxygen consuming organisms; **(2)** photosynthetic oxygen production by algae, and **(3)** wind induced mixing in the water column. Under most conditions, oxygen demand in the water column is low and demand is usually high in the bottom sediments, especially by the sediments having high organic matter content. The greater potential consumption of oxygen within the bottom sediments compared to renewal rate through the water column, results in the development of two distinctly different sediment layers: **(1)** an oxidized or aerobic surface layer where oxygen is present, and (2) an underlying reduced or anaerobic layer in which no free oxygen is present. Thickness of the oxidized sediment layer is determined by the net oxygen consumption rate by the sediment and the oxygen renewal rate through the water column. The thickness of this layer generally varies from a few millimeters in sediment of high biological activity where there is greater oxygen demand to 1 or 2 cm in sediments with low demand for oxygen. The redox potential (Eh) in the surface oxidized sediment layer is usually >300 mV and below this layer, the Eh gradually decreases depending on the organic matter content (electron donor) and the concentration of NO_3^-, ferric iron, manganic manganese and SO_4^{2-}, and HCO_3^- (electron acceptors).

The surface aerobic sediment layer is a potential zone for nitrification of NH_4-N and for precipitation of **P** as ferric phosphate. Under most conditions, this aerobic zone decreases the concentration of NH_4-N and dissolved **P** at the sediment-water interface, thus decreasing overall concentration in the water column. In shallow estuaries, surface aerobic layer can be disrupted during wind-induced resuspension or bioturbation.

Resuspension of surface sediments in shallow estuaries during periods of heavy wind can result in the overlying water. These conditions can significantly affect light penetration and influence productivity of seagrasses and other macrophytes. The exchange of biogenic elements between sediments and overlying water column has long been recognized as one of the principal factors regulating chemical and biological cycles in estuaries. However, the key biogeochemical processes regulating fluxes and nutrient availability to seagrasses and other vegetation have not been quantified.

Nitrogen in the sediments and the overlying water column is present in organic and inorganic forms with the organic form predominating. Organic N consists of compounds from amino acids, amines, proteins, and humic compounds with low N content. Inorganic

N forms consist of NH^{+}_{4}, NOy^{-}_{2} and $NO^{-}_{3}y$. In the water column, NH_4^+ and NO^{-}_{3} are present in sufficient concentrations to support the productivity of aquatic biota, while in sediments NO^{-}_{3} and NO^{-}_{2} occur in trace quantities. Ammonium N is the dominant inorganic form of N in the sediments. In estuaries, N is derived from: (1) external sources (rainfall, drainage water from vegetable farms and runoff from non-point source), and (2) internal sources such as biological N_2 fixation and N transformations in the sediments.

Nitrogen transformations and transport processes in the sediment profile regulate the role of sediments as a sink or source of N. Organic N in sediments is converted to NH_4^+ during the microbial breakdown of organic matter. The rate of NH^{+}_{4} accumulation is governed by the composition of organic matter and the availability of electron acceptors. Usually NH_4^+ concentrations in the sediment porewater are several-fold higher than the NH_4^+ concentrations in the overlying water column. Thus, NH_4^+ tends to diffuse from the sediment to the overlying water column in response to the concentration gradient. Ammonium N is also released into the water column during wind-driven sediment resuspension. Depending on the O_2 concentration of the water column and at the sediment-water interface, NH^{+}_{4} is rapidly converted to NO^{-}_{3}. Because of the high demand for electron acceptors in the sediments, NO^{-}_{3} diffuses back into'the sediment where it is readily converted to gaseous end products such as N_2O and N_2. These processes continuously deplete sediment N by converting organic forms of N to gaseous forms. Biological N_2 fixation in the water column and deposition of dead algal cells provide continuous inputs of N to the sediments. The balance between the internal inputs and outputs dictates the rate of sediment N accumulation. The kinetics of many of these processes and the interacting biogeochemical processes have not been evaluated for the Indian River Lagoon (IRL) sediments. Several reviews have discussed the significance of these processes in sediments and wetlands (Seitzinger, 1988).

Phosphorus dynamics in estuaries are very complicated because of complex biogeochemical reactions functioning in the water column and the bottom sediment. Estuaries typically accrete P and can develop sediment porewater concentrations several-fold higher than the P concentrations of the overlying water column. Phosphorus cycling in lakes has been extensively studied and sediments have been identified as a major component of the P cycle (Froelich, 1988).

Phosphorus in sediments is present in inorganic and organic forms. Inorganic P can be divided into: (1) porewater P, (2) exchangeable P, (3) non-apatite P (NAIP), and (4) apatite P (AIP). Non-apatite P refers to inorganic P associated with Fe and Al, while apatite P is associated with calcium P. The porewater and exchangeable P forms are readily available, while Fe/Al-bound P and Ca-bound P are slowly available. The stability of most of the P compounds in sediments is governed by the intensity of sediment anaerobiosis (measured as oxidation-reduction potential) and pH, and by associated cations. It is important to determine the different forms of P in estuaries sediments in order to establish the impact of sediments on P concentrations of the overlying water column.

Although organic P frequently comprises a major fraction of the P in sediments, very little is known of the nature and behavior of organic P. Deposition of dead algal cells is probably one of the major sources of organic P in surface sediments. Organic P is mineralized during microbial breakdown of organic matter, thus the kinetics of organic P mineralization need to be better understood.

Dissolved P concentration in the porewater is regulated by the P retention characteristics of the solid phases in the sediment. It is important to determine the phosphate adsorption (removal of P from solution and retention by solid phase) desorption (release of P from solid phase into solution) as they relate to sediment physico-chemical properties (Froelich, 1988). These processes play a significant role in transport of soluble P either by diffusion or release during sediment resuspension in the water column.

1.2 Statement of Problem

Establishment of nutrient load reduction targets in the Indian River Lagoon (IRL) is an integral component of water quality management and the restoration of seagrasses. Increased nutrient loading to IRL is apparently causing a shift in the primary producers such as seagrasses to phytoplankton and algae. Nutrient load reduction can potentially reverse that shift, to attain and maintain macrophyte-based estuarine system. Seagrasses and plankton derive nutrients from both external and internal sources. External sources can be decreased by overall reduction of inputs. Internal loads derived from bottom sediments are difficult to control and often ignored in overall management schemes. Aquatic systems which have received nutrient loads for long period of time, accumulate nutrients in bottom sediments. These sediments become a potential source of nutrients in the overlying water column. Sediment bound nutrients are released by resuspension and diffusion.

1.3 Need for Research

In order to predict the effects of different strategies of pollution reduction in IRL, it is essential to have an accurate understanding of the budgets of the affected pollutants. For IRL, the pollutants of most immediate concern are N and P. Nitrogen and P are essential nutrients that often limit the rate of plankton primary production, the source of flocculent sediments. Although C, which is continually supplied through photosynthesis and removed through microbial respiration, is a major component of the flocculent organic sediment, it is not as important in eutrophication as N and P. Nevertheless, the rate of accumulation of flocculent sediments is determined by the balance between C fixation via algal photosynthesis and C mineralization through microbial respiration. Information on the C budget, then, could indicate the level of reduction of algal productivity required to cause the estuary to become a net exporter of C.

In recent years, it has become clear that nutrient processing by the aquatic biota and the biogeochemical processes in estuarine sediments can be a major factor in regulating water quality. The bottom sediments in IRL can function as a source or sink for the nutrients in the water column. The direction of nutrient flux between the sediment and overlying water column is dictated by the external inputs of the nutrients and biogeochemical processes in the sediments and water column. These processes include:

photosynthetic C fixation, microbial decomposition of organic C, N transformations (ammonification, adsorption/desorption of ammonium, nitrification-&nitrification, ammonia volatilization, dinitrogen fixation), and P transformations (mineralization of organic P, adsorption/desorption of P). The balance between these sources and sinks of nutrients can either augment or reduce the trophic state of the water.

Results presented in this report are part of a larger study designed to develop pollutant load reduction models for IRL. As a part of this large project, studies on biogeochemical processes in sediments regulating surface water quality were conducted with following objectives.

1.4 Objectives

The objectives of this study were to:

- Characterize spatial and temporal variations in selected physico-chemical properties of IRL sediment.
- Determine inorganic and organic forms of C, N, and P in sediments.
- Determine the net flux of dissolved N, and P between the sediments and the overlying water column.
- Determine the relative importance of biological and physico-chemical factors regulating nitrogen transformations in sediments.
- Determine the relative importance of biological and physico-chemical factors regulating phosphorus transformations in sediments.

1.5 Report format

The objectives of this study were accomplished through a series of laboratory and field experiments. Results are presented in eight separate chapters. Chapter 2 and 3 present the results of spatial and temporal variations in selected physico-chemical properties of sediments. Chapter 4 discusses the result of N and P flux from sediments to overlying water column. Chapter 5, 6 and 7 present the results of N transformations in sediments, while Chapter 8 and 9 present the results of P transformations in sediments.

1.6 References

Froelich, P.N. 1988. Kinetics control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnol. Oceanogr. 33:649-668.

Seitzinger, S.P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. 33:702-724.

CHAPTER 2

SPATIAL DISTRIBUTION IN PHYSICO-CHEMICAL PROPERTIES OF INDIAN RIVER LAGOON

[Task 6.6 as per the contract]

2.1 Introduction

Bottom sediments appear to play a crucial role in internal nutrient cycling of shallow estuaries. The biogeochemical processes associated with cycling of nutrients can significantly impact the water quality of these ecosystems. Nutrient exchanges between the sediment and the water column of a shallow estuary are dependent on physical, chemical, and biological properties of the sediment. In order to understand the functional role of sediments as a source or sink for nutrients to the overlying water column, it is important to first characterize the sediments for total labile and non-labile nutrient fractions.

The purpose of this study was to determine: (1) the total storage of C, N, and P in the sediments, and (2) the spatial distribution of selected nutrients in porewater and solid phases.

2.1.1 Site Description

The Indian River Lagoon Estuary is a large, shallow, mesohaline lagoon. It is approximately 255 km in length and varies in width from 0.3 km to 9 km. The lagoon is shallow, with an average depth of approximately lm. It is bounded to the east by a barrier island, separating it from the Atlantic Ocean. It has been reported that it has the highest biodiversity of any estuary in North America and provides annual economic benefits to counties surrounding the lagoon estimated at approximately 700 million dollars. Loss of emergent vegetation is estimated at 75% since 1950 with 100% loss of seagrass beds in some locations. The seagrasses and emergent macrophytes of the Indian River Lagoon are critical ecosystem components in that they provide habitat for many species for at least some period of their life cycle (Virnstein et al., 1983; Gilmore et al., 1983). Circulation and flushing occur through freshwater inflows, tidal cycles through three inlets, and wind mixing. Overall flushing by tidal cycles is low, whereas flushing due to wind can be the principle source of flushing, according to simulation models (Sheng et al., 1994). Low flushing rates have obvious implications on nutrient loading, tending to exacerbate the effects of point and non-point loading.

One of the goals of the Surface Water Improvement and Management (SWIM) Plan for the Indian River Lagoon Estuary calls for the attainment and maintenance of water and sediment quality sufficient to support a healthy macrophyte-based estuarine lagoon system; or to Class III waters or better (SWIM, 1994), with emphasis on the reduction of excessive point and non-point source loading of nutrients. A major portion of nutrients loaded to this estuary can be retained by sediments. Once the external load criteria are met as a result of better control of point and non-point source inputs, internal sources (from bottom sediments) may maintain current water quality conditions. Thus, sediments can act as a source of nitrogen (N) and phosphorus (P) and therefore constitute a potential non-point source of nutrient loading to the Lagoon.

2.1.2 Objectives

The objectives of this task were to characterize the Indian River Lagoon sediments and water for selected physico-chemical parameters and to calculate total storages of N and P.

2.2 Materials and Methods

2.2.1 Sediment sampling

Twenty-four sediment sampling locations were selected based on the synoptic survey of 206 stations sampled by the Department of Coastal and Oceanographic Engineering at UF (Table 2.1, Fig 2.1). Stations were selected to encompass a range of seagrass densities and physical characteristics of sediments, while providing reasonable spatial coverage of the lagoon. Navigation to sampling stations was done using a GPS receiver equipped with a differential beacon receiver. Coordinates for both the spatial and temporal sampling should therefore be accurate to within approximately 5m.

Intact sediment cores were obtained by driving a 7cm ID polycarbonate core tube into the sediment. Samples were extruded in the field into 1L Ziplock™ (polyethylene) bags and immediately placed on ice. Each core was sectioned into a 0-10 cm and a 10–20 cm depth interval. The spatial sampling was performed during March 12-16, 1997 (stations 1 - 14, 22) and April 8, 1997 (stations 15 – 21, 23-24). Sediments were analyzed for selected physico-chemical properties, as shown in Fig. 2.2.

2.2.2 Water sampling

Surface water samples were collected from all stations during March 1997. Samples were collected 0.5 m below the water surface with an Alpha™ water sampler (Wildlife Supply Company, Saginaw, MI). Water samples were subdivided into four separate containers. Samples for DOC and DIC analysis were stored in 7 ml amber glass vials and kept on ice. Samples to be analyzed for total suspended solids were stored in 0.5 L polyethylene bottles. Samples to be analyzed for TKN and TP were acidified to pH 2 with trace-metal grade H_2SO_4 placed in 100 ml polyethylene bottles and stored on ice.

Table 2.1. Geographic coordinates of sediment sampling stations visited in the spatial and temporal studies of the Indian River Lagoon Estuary sediments. SWS = Department of Soil and Water Science, COE = Department of Coastal and Oceanographic Engineering. Horizontal datum is North American Datum 1927 (NAD27).

SWS Station	COE Station	Latitude	Longitude
1	3c	27' 31.544'	80'20.131'
2	5.5e	27° 41.455'	80° 23.354'
3	6.5a	27° 51.300'	80° 27.227'
4	7e	27° 51.476'	80° 29.011'
5	9a	27° 58.576'	80° 31.842'
6	9c	27° 58.524'	80° 31.947'
7	11b	28° 03.397'	80° 34.237'
8	11c	28° 03.285'	80° 34.577'
9	11d	28° 03.217'	80' 34.761'
10	14b	28° 08.323'	80° 36.484'
11	14c	28° 08.188'	80° 36.927'
12	14d	28° 08.040'	80° 37.125'
13	21a	28° 27.769'	80° 43.600'
14	21b	28° 27.728'	80° 44.116'
15	23a	28° 35.386'	80° 44.753'
16	23c	28° 35.229'	80° 45.585'
17	23e	28° 35.031'	80° 46.573'
18	27a	28° 41.890'	80° 47.046'
19	27d	28° 42.918'	80° 48.356'
20	27e	28° 43.376'	80° 48.915'
21	27f	28° 43.710'	80° 49.354'
22	33c	28° 21.972'	80° 38.282'
23	36a	28° 45.399'	80° 44.209'
24	36c	28° 44.926'	80° 44.500'

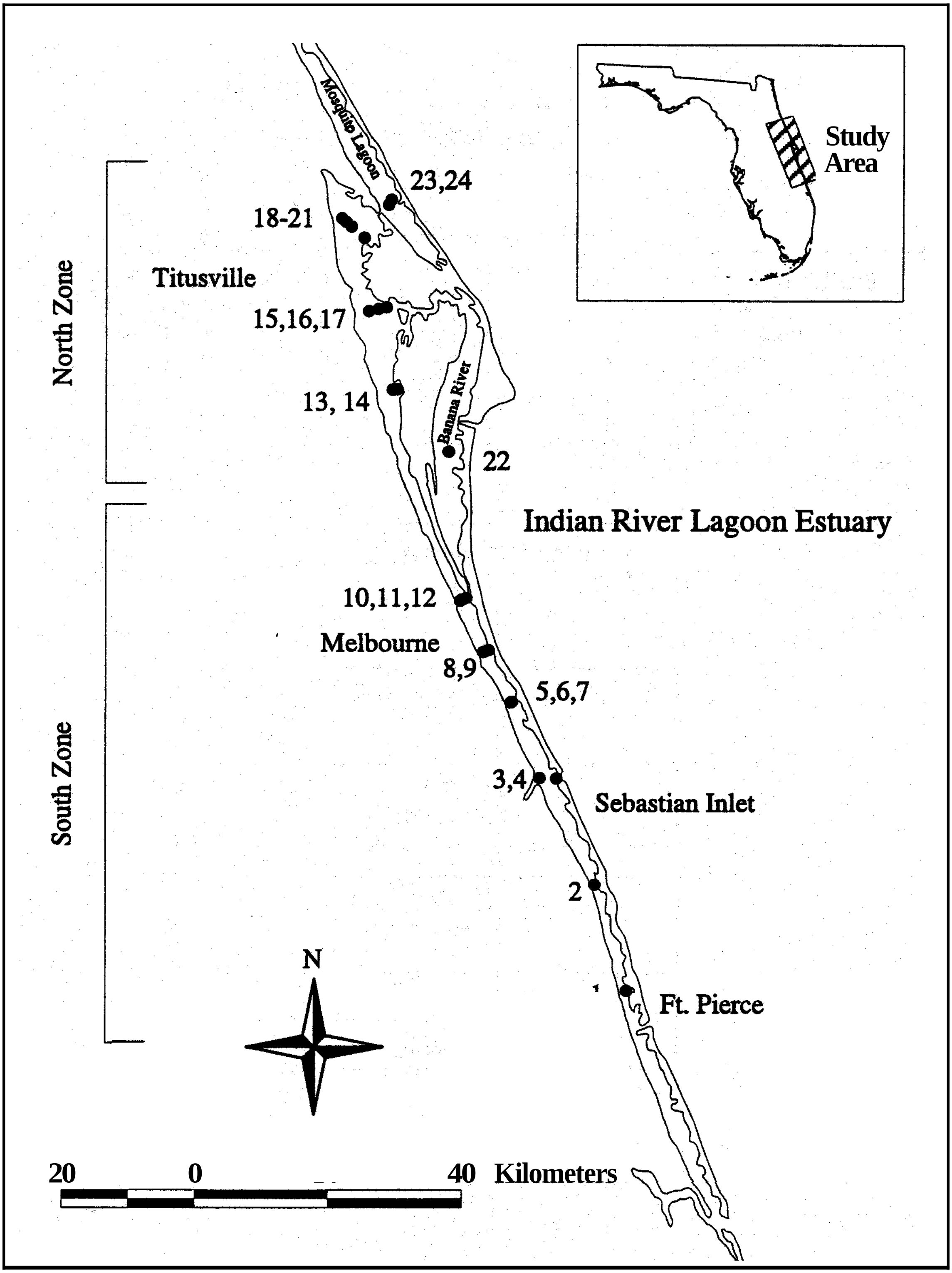


Figure 2.1. Location of sediment and water sampling stations used in the spatial and seasonal sampling of the Indian River Lagoon Estuary. Southern zone stations include stations 1-7, 10, and 12, while the northern zone stations include stations 13 – 24. The mud zone is represented by stations 8, 9, and 11.

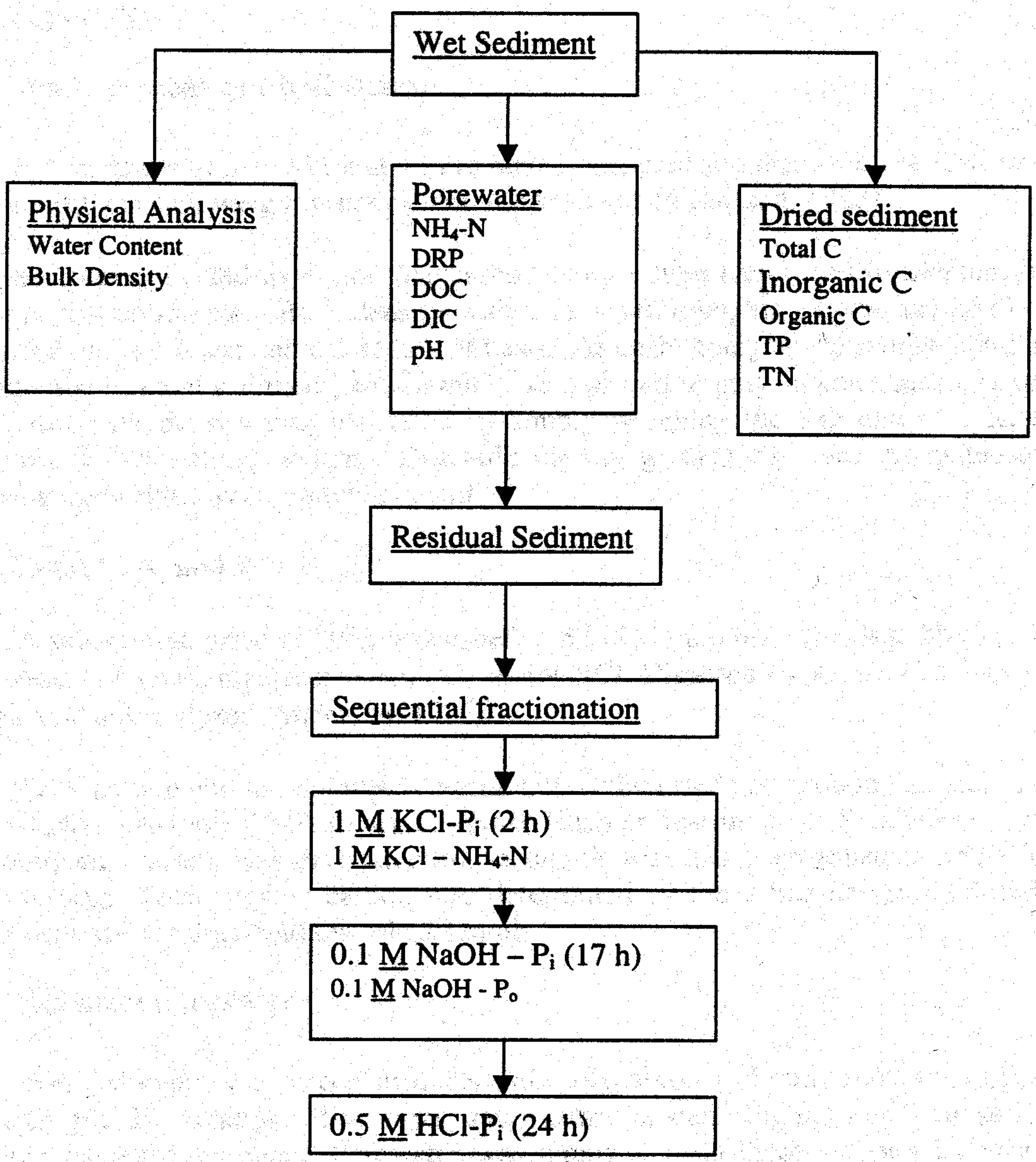


Figure 2.2. Schematic showing various physico-chemical properties measured on sediments collected from the Indian River Lagoon. Values in parentheses represent time of exposure to chemical extractants on a mechanical shaker.

Samples to be analyzed for DRP and NH_4-N were immediately field filtered through 0.45 µm polyethersulfone filters, acidified with trace-metal grade H_2SO_4 and stored in 20 ml polyethylene scintillation vials on ice. Water column pH, salinity, and temperature were recorded at each station with a Hydrolab Data Sonde 3™(Hydrolab Corp., Austin TX).

2.2.3 Water content and bulk density

A subsample of the sediment was removed, weighed and then dried at 70°C for 48 hours or until constant weight was recorded (Hakanson and Jansson, 1983).

Samples collected using the polycarbonate core tube were used to measure bulk density of the sediments. Bulk density within each stratigraphic section (sample) was determined on both a wet and dry sediment basis. As each stratigraphic sample contained a measured volume of sediment, and samples were placed in polyethylene bags of known weight, wet bulk density was measured by simply weighing the bag and sample, and subtracting the tare (bag) weight. Dry bulk density g (dry) cm^3 was computed after measuring dry weight/water weight content.

2.2.4 Total C, N, and P

A sub-sample dried at 70°C was ashed at 550°C in a muffle furnace. The ash was then digested at low temperature (≈100°C) in 6N HCl. Digested solutions were analyzed for P on an AutoAnalyzer (Anderson, 1976).

Total carbon and total N were determined on the dried and ground samples using a Carlo-Erba NA-1500 CNS Analyzer (Haak-Buchler Instruments, Saddlebrook, NJ). Total inorganic carbon was determined on a sample that had been ashed at 550°C in a muffle furnace. Total organic carbon was determined by the difference in total carbon content between the dried and the ashed sample.

2.2.5 Sediment porewater

Wet sediment was placed in a 250-mL polycarbonate bottle and centrifuged at 6000 rpm for 20 minutes. For some sand samples, centrifuging failed to separate porewater from the sediment. Porewater was removed from these samples by vacuum filtration. A sub-sample of the supernatant liquid was used to measure total organic and total inorganic C using a Dohrmann DC190 TOC analyzer (Rosemount Analytical, Santa Clara CA). The pH was measured on a separate fraction of the supernatant using an Orion Model SA720 pH meter (Orion Research Inc, Boston MA). A portion of the centrifuged supernatant liquid was filtered through a 0.45 µm polyethersulfone membrane filter and stored at 4°C until analyzed for ammonium N, nitrate + nitrite N, and soluble reactive P (SRP) on a Technicon AutoAnalyzer (Technicon Instruments Corp., Tarrytown NY).

2.2.6 KCl extractable P and NH_4-N (KCl-P_i and KCl -N)

Residual sediment after porewater removal was subjected to the following chemical extraction sequence. Exchangeable P and NH_4-N in the residual sediment were extracted with 1M KCl. Sediment suspensions were equilibrated for a period of **2** hours with the KCl solution by continuously shaking on a mechanical shaker, followed by centrifugation at **5000** rpm for **20** minutes. The average wet sediment : extractant ratio for all extractants used in the sequential fractionation was 1:15 for all samples except for stations 8, 9, and 11. These stations were mud sediments of considerably lower bulk density and a ratio of approximately 1:30 was used. The supematant solution was filtered through a **0.45** μm polyethersulfone membrane filter and the filtrate was acidified to pH **2.** Solutions were analyzed for SRP and NH_4-N. The residual sediment was **used** in the following sequential extraction.

2.2.7 Sodium hydroxide extractable P (NaOH-P_i and NaOH-P_o)

The residual sediment from the KCl extraction was extracted with 0.1 N NaOH on a mechanical shaker for 17 hours. The sediment suspensions were centrifuged at 5000 rpm. The supernatant solution was filtered through a **0.45** μm membrane filter. One sample was analyzed for SRP (NaOH-P_i) while a subsample was digested and analyzed for TP. The difference between the digested and undigested extract is assumed ***to*** be organic P associated with both living and dead organic P and associated fulvic and humic acids (NaOH-P_o). Inorganic P extracted with NaOH represents P associated with Fe and Al (NaOH-P_i).

2.2.8 Hydrochloric acid extractable P (HCl-P_i)

The residual sediment obtained from the above extractions was treated with 0.5M HCl and samples were allowed to equilibrate for a period of **24** hours by continuously shaking on a mechanical shaker, followed by centrifugation at 5000 rpm. The supernatant solution was filtered through a **0.45** μm membrane filter and the residual sediment was discarded. The filtered solutions were analyzed for **SRP** and will be referred to as HCl-P_i. This fraction represents Mg and Ca-bound P. The filtered solutions were analyzed for SRP by AutoAnalyzer and Ca, Mg, Fe and Al using Inductively Coupled Argon Plasma Spectroscopy (ICAP). Total organic P **(TP_o)** was determined by the difference between total P and the sum of the inorganic fractions (KCl-P_i + NaOH-P_i + HCl-P_i)

2.2.9 Analytical methods

References for the procedures used to measure the above parameters are given in Table **2.2.**

Table **2.2.** Analytical methods used for various physico-chemical parameters measured on IRL sediments and water.

Parameter	Reference
Sediment	
pH	Thomas, **1996.**
Water Content	Gardner, **1986.**
Bulk Density	Blake and Hartge, **1986.**
Porewater Soluble P	EPA **365.1**
Porewater Soluble Ammonium-N	EPA **350.1**
Ash Content	Nelson and Sommers, **1996.**
Total Carbon	Nelson and Sommers, **1996.**
Total Nitrogen	Nelson and Sommers, **1996.**
Total Phosphorus	Anderson, **1976**
Phosphorus Fractionation	Reddy et al. **1998**
KCl Extractable N	Mulvaney, **1996.**
HCL Extractable Cations	Soltanpour, **1996.**
Dissolved Organic Carbon	EPA **415.1**
Dissolved Inorganic Carbon	EPA **415.1**
Water	
Salinity	APHA **2520** B.
Temperature	EPA **170.1**
pH	EPA **150.1**
Dissolved Reactive P	EPA **365.1**
Ammonium-N	EPA **350.1**
Nitrate-N	EPA **353.2**
Dissolved Organic Carbon	EPA **415.1**
Dissolved Inorganic Carbon	EPA **415.1**
Total Organic Carbon	EPA **415.1**
Total Kjehdahl Nitrogen	EPA **351.2**
Total Phosphorus	EPA **351.2**
Soluble Organic Nitrogen	EPA **351.2**
Total Suspended Solids	EPA **160.1**

2.3 Results and Discussion

2.3.1 Dissolved nutrients

The sampling stations were subdivided into the northern stations **(13 - 24),** the mud stations **(8, 9,** and **11;** Melbourne area), and the southern stations **(1-7, 10** and **12)** for comparative purposes. This grouping was suggested primarily by the range of TP values observed in the spatial sampling, physical sediment characteristics, and location in the lagoon. Higher TP values were associated with sediments south of Melbourne. Also, the three mud stations **(8, 9,** and **11)** were distinctly different in most physico-chemical properties and thus justified their own separate consideration.

Porewater NH_4-N concentration was generally lower in the northern stations. For the whole lagoon, NH_4-N levels ranged from **0.3 – 10.4** mg L^{-1} for surface sediments, and **1.3 – 16.8** mg L^{-1} in **10-20** cm sediments (Table **2.3).** Central zone sediments (predominantly mud sediments) were slightly elevated, relative to the mean concentration of **4.7 (±2.5)** mg **NH_4-N** L^{-1} (Fig. **2.3** and Table **2.4).** In the northern zone, NH_4-N levels ranged from 0.3 – **10.4** mg L^{-1}, **as** compared to **2.3 – 7.3** mg L^{-1} in southern zone (Table **2.5** and **2.6).**

Dissolved reactive P (DRP) levels ranged from **0.015 – 1.28** mg L^{-1} in surface sediment and **0.012 – 4.3** mg L^{-1} in **10-20** cm sediments (Table **2.3).** Average DRP levels were **0.116, 0.71** and **0.215** mg L^{-1} in northern, mud, and southern zones, respectively (Tables **2.4 - 2.6,** Fig. **2.4).** The average DRP of the surficial (0 – **10** cm) sediment at the three mud stations was **0.71** mg DRP L^{-1} and was therefore considerably higher than the mean of all stations **(0.20 ±0.33** mg DRP L^{-1}) (Fig. **2.4).**

Dissolved organic (DOC) and dissolved inorganic C (DIC) showed no particular trend among the stations sampled. For all sampling stations other than the mud zone stations, the concentration of DIC and DOC in the surficial sediment was slightly higher than the lower sampling depth. The DOC values ranged from **14 - 77** mg L^{-1} in the surficial sediments, while DIC values ranged from **29 - 105** mg L^{-1} (Table **2.3 – 2.6).** Porewater pH showed minimal variability, ranging from **7.1 – 8.6** in surface sediments, and **8.3 – 8.6** in subsurface sediments (Tables **2.3 – 2.6).**

2.3.2 Bulk density and particle size distribution

Sediments were predominantly sandy, with low amounts of silt, clay, and organic matter. Bulk density values ranged from **0.29** to **1.55** g cm^{-3} (Table **2.7,** Fig. **2.5).** Mud deposits were observed in the region of the Eau Gallie Causeway and the Melbourne Causeway. Sediments at these stations were characterized by low bulk densities **(0.2 – 0.4** g cm^{-3}) and considerably higher total organic C (ca. **50** mg g^{-1}).

Table 2.3. Selected physico-chemical properties of Indian River Lagoon sediments in March 1997 (n = 24 stations).

	Porewater					
	pH	DRP	NH_4-N	TC	DIC	DOC
		mg L^{-1}				
0 - 10 cm						
Mean	8.22	0.223	4.80	83	54	28
Max.	8.66	1.280	10.44	174	105	77
Min.	7.14	0.015	0.29	44	29	14
Std. Dev.	0.29	0.349	2.63	29	21	15
C.V. (%)	4	157	55	35	39	54
10 - 20 cm						
Mean	8.45	0.376	4.25	75	47	28
Max.	8.85	4.325	16.78	189	148	77
Min.	8.23	0.012	1.29	38	24	7
Std. Dev.	0.17	1.009	3.91	34	29	15
C.V. (%)	2	268	92	45	62	54

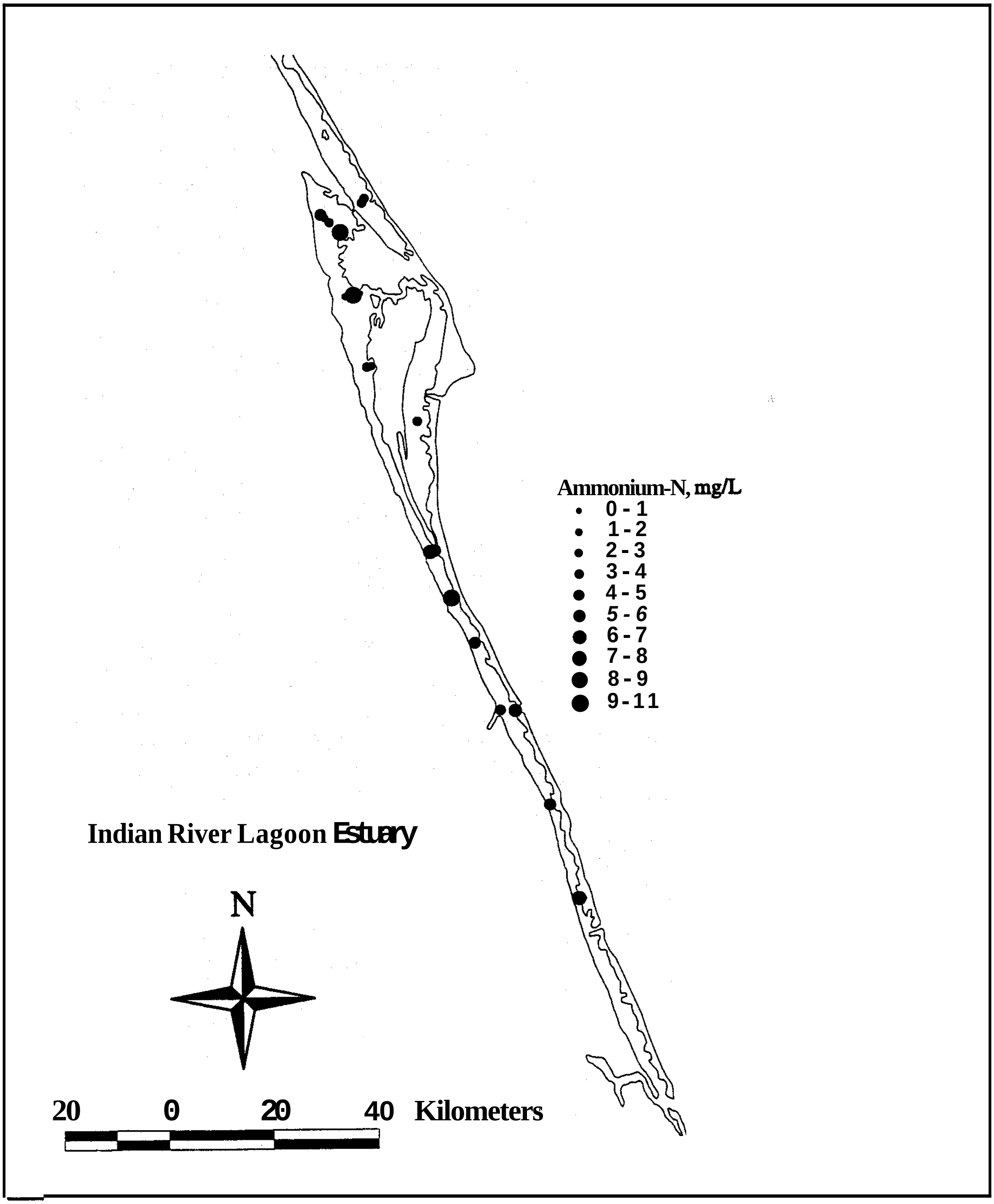


Figure 2.3 Spatial distribution of porewater ammonium-N of surficial (0-10 cm) sediment samples collected during March 1997 from the Indian River Lagoon Estuary.

Table 2.4. Selected physico-chemical properties of sediments obtained in March 1997, from the Indian River Lagoon stations characterized by surface deposits of mud (Stations 8, 9, 11).

	Sediment porewater					
	pH	DRP	NH_4-N	TC	DIC	DOC
	---------- mg L^{-1} ----------					
0 - 10 cm						
Mean	8.11	0.71	6.98	93.7	71.7	22.0
Min.	8.00	0.28	4.62	78.5	60.2	18.2
Max.	8.24	1.04	9.03	104.9	84.7	27.7
Std. Dev.	0.12	0.39	2.22	13.7	12.3	5.0
C.V. (%)	2	55	32	15	17	23
n	3	3	3	3	3	3
10 - 20 cm						
Mean	8.35	2.05	10.63	127.1	98.6	28.5
Min.	8.25	0.41	4.50	81.5	62.1	19.4
Max.	8.43	4.33	16.78	188.6	147.6	41.0
Std. Dev.	0.09	2.04	6.14	55.3	44.1	11.2
C.V. %	1	99	58	44	45	39

Table 2.5. Selected physico-chemical properties of sediments obtained in March 1997, from the northern Indian River Lagoon stations (Stations 13 - 24).

	Sediment porewater					
	pH	DRP	NH_4-N	TC	DIC	DOC
	---------- mg L^{-1} ----------					
0 - 10 cm						
Mean	8.19	0.1o	4.03	78.9	53.2	25.7
Min.	7.14	0.02	0.29	44.3	30.0	14.0
Max.	8.49	0.39	10.44	133.7	105.1	59.7
Std. Dev.	0.35	0.11	3.02	26.2	21.0	13.7
C.V. (%)	4	114	75	33	40	53
n	12	12	12	12	12	12
10 - 20 cm						
Mean	8.40	0.05	3.42	65.5	40.6	24.9
Min.	8.27	0.02	1.45	52.0	26.5	6.6
Max.	8.63	0.11	8.17	85.6	57.0	37.4
Std. Dev.	0.12	0.03	2.28	11.4	10.0	8.9
C.V. %	1	74	67	17	25	36
	8	8	8	8	8	8

Table 2.6. Selected physico-chemical properties of sediments obtained in March 1997, from southern Indian River Lagoon stations (Stations1-7, 10).

	Sediment porewater					
	pH	DRP	NH_4-N	TC	DIC	DOC
		---------- mg L^{-1} ----------				
0 - 10 cm						
Mean	8.32	0.23	5.15	84.4	50.0	34.4
Min.	8.04	0.02	2.32	49.8	29.2	18.6
Max.	8.66	1.28	7.28	174.4	97.1	77.3
Std. Dev.	0.24	0.44	1.64	38.4	21.5	19.4
C.V. (%)	3	193	32	46	43	56
n	8	8	8	8	8	8
10 - 20 cm						
Mean	8.55	0.08	2.68	65.0	34.2	31.0
Min.	8.23	0.01	1.29	37.9	24.3	10.4
Max.	8.85	0.39	5.77	106.7	59.0	77.2
Std. Dev.	0.19	0.13	1.52	22.8	10.8	21.7
C.V. (%)	2	158	57	35.0	31	70
n	8	8	8	8	8	8

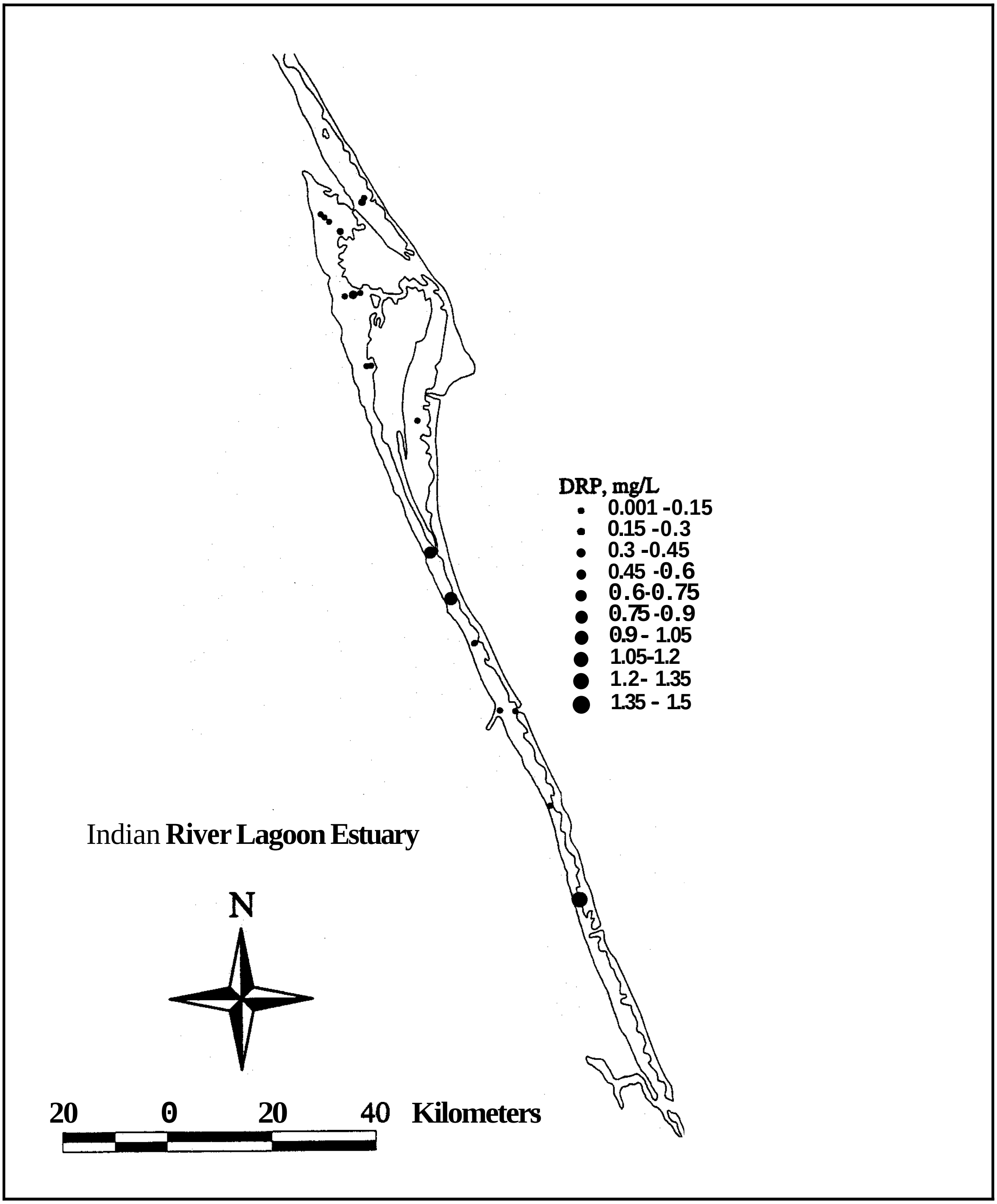


Figure **2.4** Spatial distribution of porewater dissolved reactive P (DRP) of surficial (0-10 cm) sediment samples collected during March 1997 from the Indian River Lagoon Estuary.

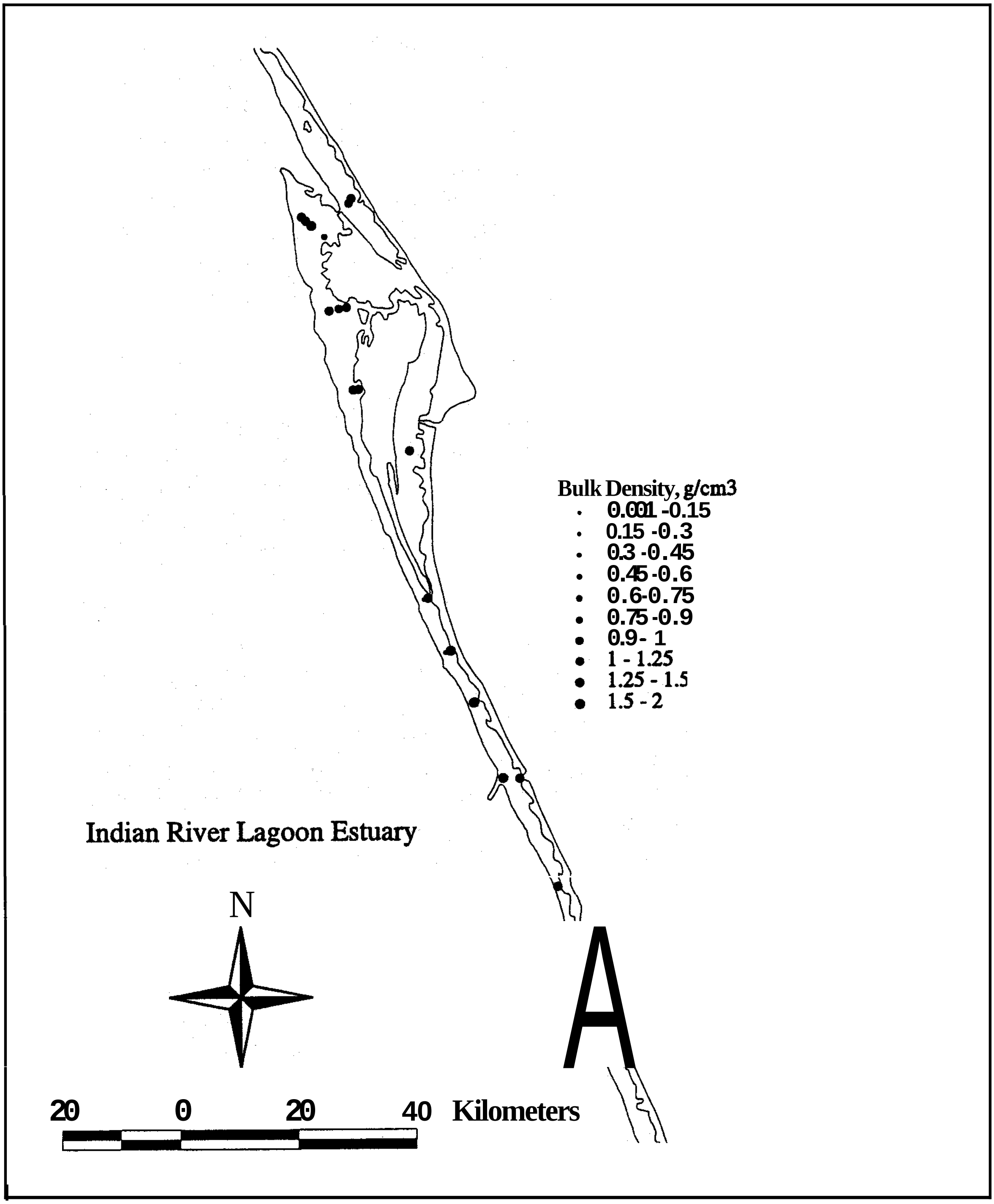


Figure **2.5** Spatial distribution of the dry bulk density of surficial (0-10 cm) sediment samples collected during March **1997** from the Indian River Lagoon Estuary.

2.3.3 Ash content and total carbon

Sediments contained very high mineral matter with values ranging from **82%** to almost **100%** in subsurface sediments (Table **2.7).** Total C content of sediments ranged from **1.1** to **70.6** g kg^{-1}, with approximately 50% in inorganic form (Table **2.7).** Mud sediments in central zone were high in total organic C (Table **2.9),** as compared to other stations (Tables **2.8 – 2.10,** Fig. **2.6).** Total C content of northern and southern zone sediments ranged from **1.1** to **56.3** g kg^{-1}, as compared to **45.7** to **70.6** g kg^{-1} in mud zone sediments (Table **2.8 - 2.10).**

2.3.4 Nitrogen

Total N content of sediments ranged from **30** to **4260** mg kg^{-1}, with high values observed in mud zone sediments (Table **2.7,** Fig. **2.7).** Sediments in central zone had high total N, followed by sediments in northern and southern zones (Tables **2.8 – 2.10).** Similar trends were also observed for exchangeable NH_4-N, with high values observed in mud zone sediments (Table **2.9).**

2.3.5 Phosphorus

Total P content ranged from **80** to **898** mg kg^{-1} in surface sediments (Table **2.11** Fig. **2.8).** Average total P content of **289, 839,** and **536** mg kg^{-1} was observed in northern, mud and southern zone sediments (Tables **2.12 – 2.14).** The surficial sediments north of Melbourne (Stations **13-24)** contained significantly higher total P than sediments from southern zone ($P = 0.005$). The ratio between total N and P is approximately **2,** suggesting enrichment of P and limitation of N. Phosphorus added to an ecosystem usually accumulates in sediments, since there is no gaseous loss mechanism, as compared to N. Total organic P was higher in mud zone sediments as compared to northern and southern zone sediments (Fig. **2.9).** These results were similar to total organic C content of sediments.

The principal pool of sedimentary P for all stations was Ca/Mg-bound P (HCl extractable) P, comprising on average **78%** of the total P (Figs. **2.10, 2.11).** For the stations characterized as sandy, the proportion increases to **87%.** Comparatively little P is in pools considered moderately labile. Though TP concentrations were lower in the northern stations, there was a slightly greater proportion in the exchangeable and Fe and Al-bound fractions, compared to the southern stations. For the mud stations, the

Table 2.7. Selected physico-chemical properties of Indian River Lagoon sediments in March 1997 (n = 24 stations).

	H_2O	Bulk Dens.	Ash	KCl-NH_4	TN	TC	TIC	TOC
	%	g cm^{-3}	%	------ mg kg^{-1} ------		--------- g kg^{-1} ---------		
0 - 10 cm								
Mean	33.0	1.21	96.6	9.5	858	19.8	10.1	10.1
Max.	75.3	1.55	99.5	41.0	4260	70.6	50.6	56.2
Min.	19.7	0.29	82.9	1.6	30	1.1	0.5	-0.5
Std. Dev.	16.9	0.40	4.6	11.2	1285	21.2	14.2	15.6
C.V. (%)	51	33	5	85	150	107	141	154
10 - 20 cm								
Mean	32.2	1.25	96.4	11.6	816	22.5	12.4	10.8
Max.	73.7	1.98	99.6	96.5	4180	72.4	43.4	59.8
Min.	19.8	0.29	81.5	1.0	40	1.7	0.5	0.7
Std. Dev.	16.7	0.44	4.6	22.5	1197	22.7	13.8	15.4
C.V. (%)	52	35	5	52	147	101	111	143

Table 2.8. Selected physico-chemical properties of sediments obtained in March 1997, from the northern zone of the Indian River Lagoon (stations 13-24).

	H20	Bulk Dens.	Ash	Exchangeable NH_4-N	TN	TC	TIC	TOC
	%	g cm^{-3}	%	---------- mg kg^{-1} ---------		---------- g kg^{-1} -----------		
0 – 10 cm								
Mean	28.8	1.28	97.8	6.6	532	13.0	7.5	6.1
Min.	20.4	0.69	93.6	1.6	30	1.3	0.5	-0.5
Max.	47.2	1.53	99.3	22.3	1870	45.3	41.4	17.5
Std. Dev.	8.4	0.26	1.8	6.2	578	12.6	11.9	5.8
C.V. %	29	20	2	95	109	97	159	95
n	12	12	12	12	12	12	11	12
10 – 20 cm								
Mean	25.9	1.44	98.1	4.4	406	12.5	7.8	5.7
Min.	21.5	1.04	94.4	1.0	90	2.0	0.7	0.9
Max.	32.5	1.98	99.4	16.2	1280	26.2	21.7	14.8
Std. Dev.	4.5	0.30	1.7	4.9	436	9.6	8.0	5.3
C.V. %	17	21	2	112	107	77	102	93
n	8	8	8	8	8	8	7	8

Table 2.9. Selected physico-chemical properties of sediments obtained in March 1997, from the Indian River Lagoon stations characterized by surface deposits of mud (Stations 8, 9, 11).

	H20	Bulk Dens.	Ash	Exchangeable **NH_4-N**	TN	TC	TIC	TOC
	%	g cm^{-3}	%	------- mg kg^{-1}---------		----------- g kg^{-1} -----------		
0 – 10 cm								
Mean	71.9	0.33	85.4	35.4	3957	5.9	1.1	4.8
Min.	67.9	0.29	82.9	31.2	3370	4.6	0.5	4.0
Max.	75.3	0.37	88.4	41.0	4260	7.1	2.2	5.6
Std. Dev.	3.8	0.04	2.8	5.0	508	1.3	0.9	0.8
C.V. %	**5**	12	3	14	13	21	86	17
n	3	3	3	3	3	3	3	3
10 – 20 cm								
Mean	67.7	0.39	87.1	51.4	3343	65.2	23.3	41.9
Min.	62.2	0.29	81.5	19.3	2660	60.4	2.9	29.0
Max.	73.7	0.49	90.1	96.5	4180	72.4	43.4	59.8
Std. Dev.	5.7	0.10	4.9	40.2	772	6.3	20.2	16.0
C.V. %	8	25	6	78	23	10	87	38
n	3	3	3	3	3	3	3	3

Table 2.10. Selected physico-chemical properties of sediments obtained in March 1997, from the southern zone of the Indian River Lagoon (stations 1-7, 10).

	H20	Bulk Dens.	Ash	**Exchangeable NH_4-N**	TN	TC	TIC	TOC
	%	g cm^{-3}	%	-------- mg kg^{-1}-------		----------- g kg^{-1} ------------		
0 – 10 cm								
Mean	24.7	1.42	98.7	4.9	286	16.9	13.8	3.1
Min.	19.7	1.15	97.5	1.6	50	1.1	0.5	0.6
Max.	33.2	1.55	99.5	10.9	700	56.3	50.6	7.1
Std. Dev.	4.9	0.13	0.8	3.4	253	20.1	19.4	2.3
C.V. (%)	20	9	1	70	88	119	140	75
n	8	8	8	8	8	8	8	8
10 - 20 cm								
Mean	25.3	1.37	98.3	3.9	279	16.5	12.2	4.3
Min.	19.8	1.09	95.8	1.2	40	1.7	0.5	0.7
Max.	39.6	1.52	99.6	7.9	820	42.9	39.9	11.7
Std. Dev.	6.4	0.15	1.3	2.6	260	16.8	14.9	4.1
C.V. (%)	26	11	1	66	93	102	122	96
n	8	8	8	8	8	8	8	8

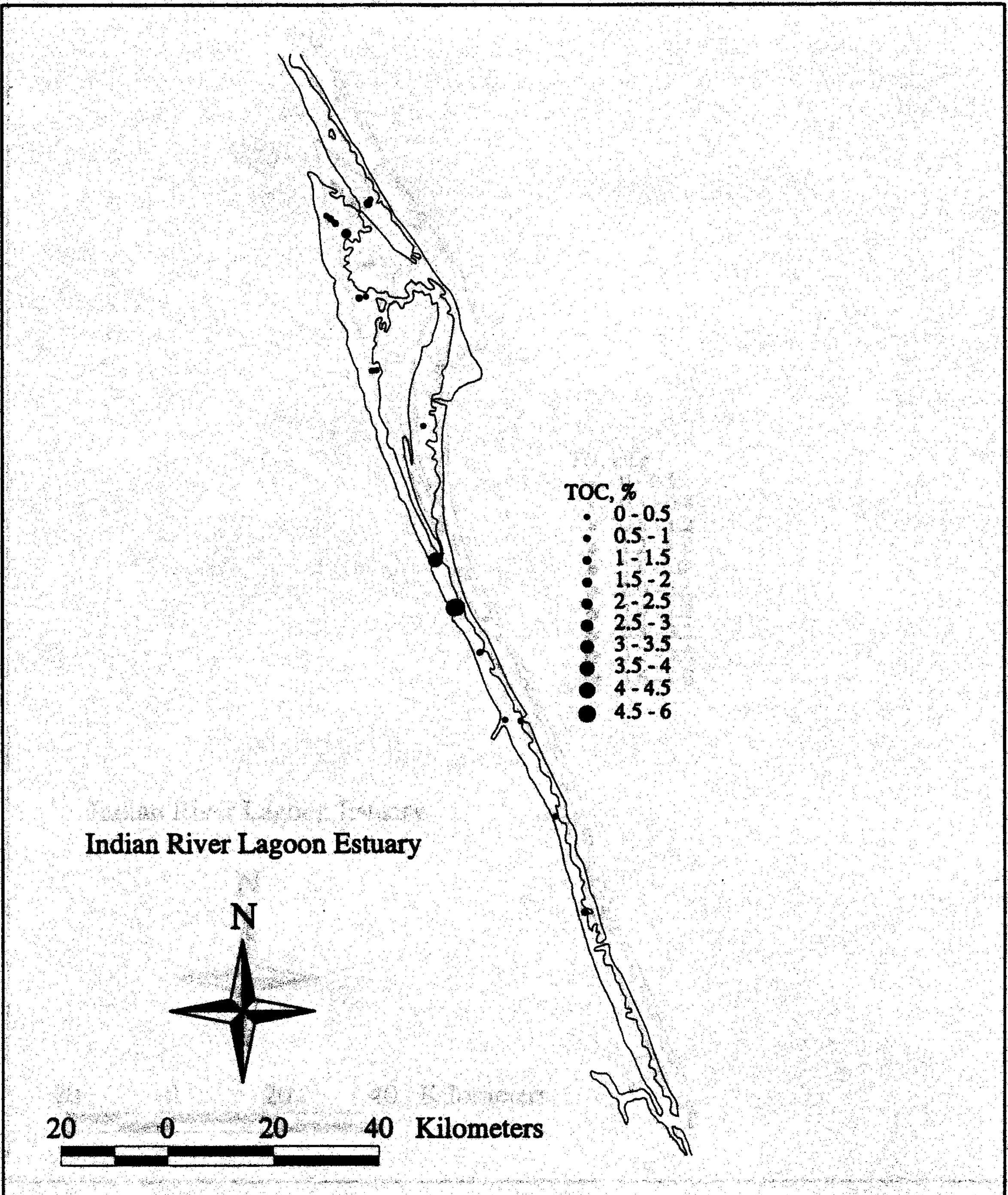


Figure 2.6 Spatial distribution of total organic carbon (TOC) of surficial (0-10 cm) sediment samples collected during March 1997 from the Indian River Lagoon Estuary.

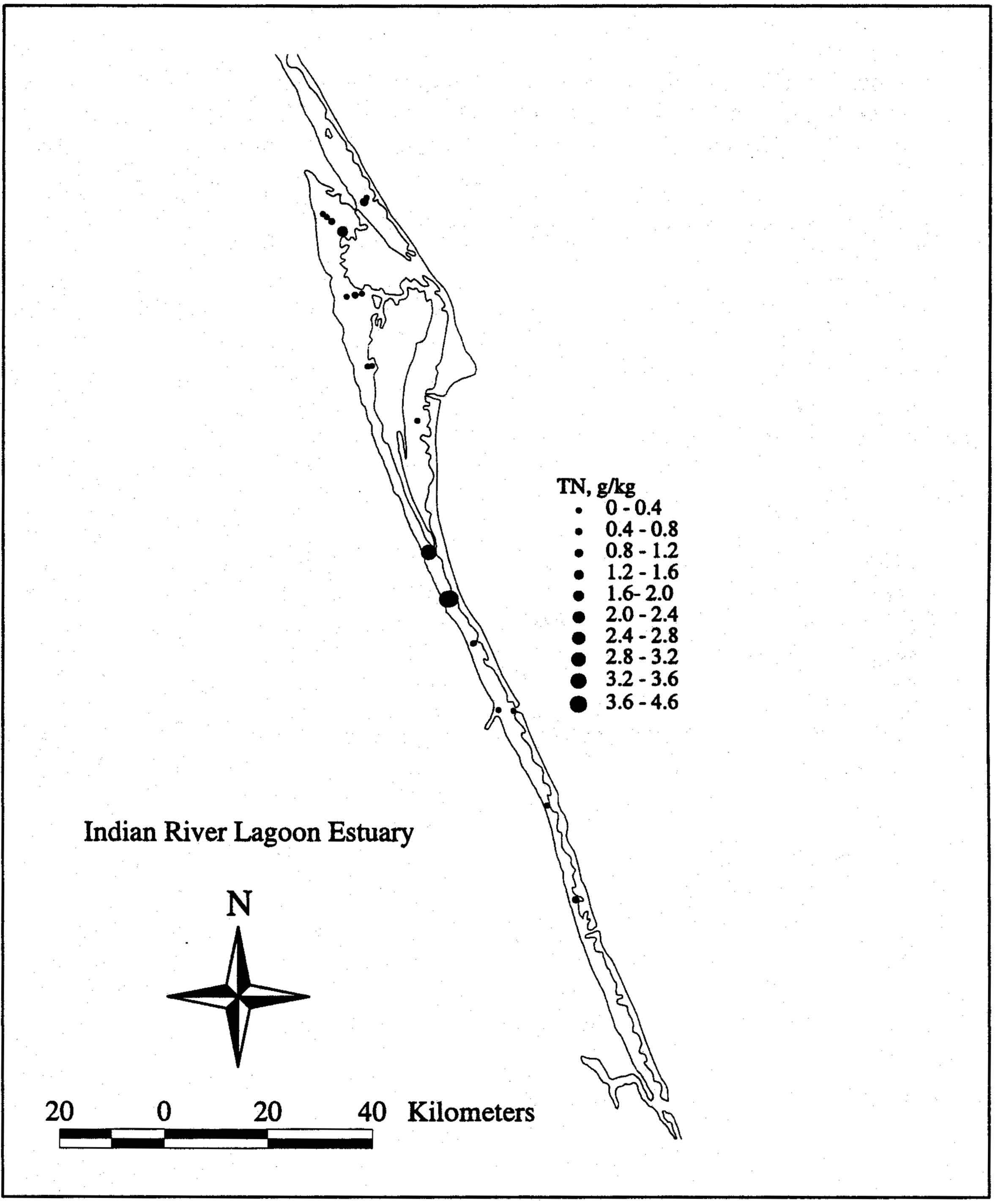


Figure 2.7 Spatial distribution of **total nitrogen (TN) of** surficial (0-10 cm) **sediment samples collected during March 1997 from the Indian River Lagoon Estuary.**

Table 2.11 Phosphorus forms of sediment obtained during March 1997 from the Indian River Lagoon. KCl-P_i = exchangeable inorganic P; NaOH-P_i = Fe/Al bound P; NaOH-P_o = alkali extractable organic P; HCl-P_i = Ca/Mg-bound P; Tp_i = total inorganic P; Tp_o = total organic P; TP = total P (n = 24).

	KCL-P_i	NaOH-P_i	NaOH-P_o	HCL-P_i	TP_i	TP_o	TP
	mg kg^{-1}						
0-10 cm							
Mean	1.35	11.6	13.9	332	345	91	436
Min.	0.30	0.8	0.6	18	20	-47	80
Max.	7.75	77.4	88.9	898	902	407	898
St. Dev.	1.76	20.3	23.8	276	284	134	288
CV %	130.7	174.5	171.2	83.2	82.3	147.8	32.1
n	23	23	23	23	23	23	23
10 – 20 cm							
Mean	1.50	9.3	9.7	310	321	67	388
Min.	0.26	0.4	0.7	36	38	-30	58
Max.	8.26	94.3	63.3	645	748	244	824
St. Dev.	1.91	22.2	17.9	224	235	81	255
CV %	127.3	238.6	184.4	72.2	16	-37	65.8
n	19	19	19	19	19	19	19

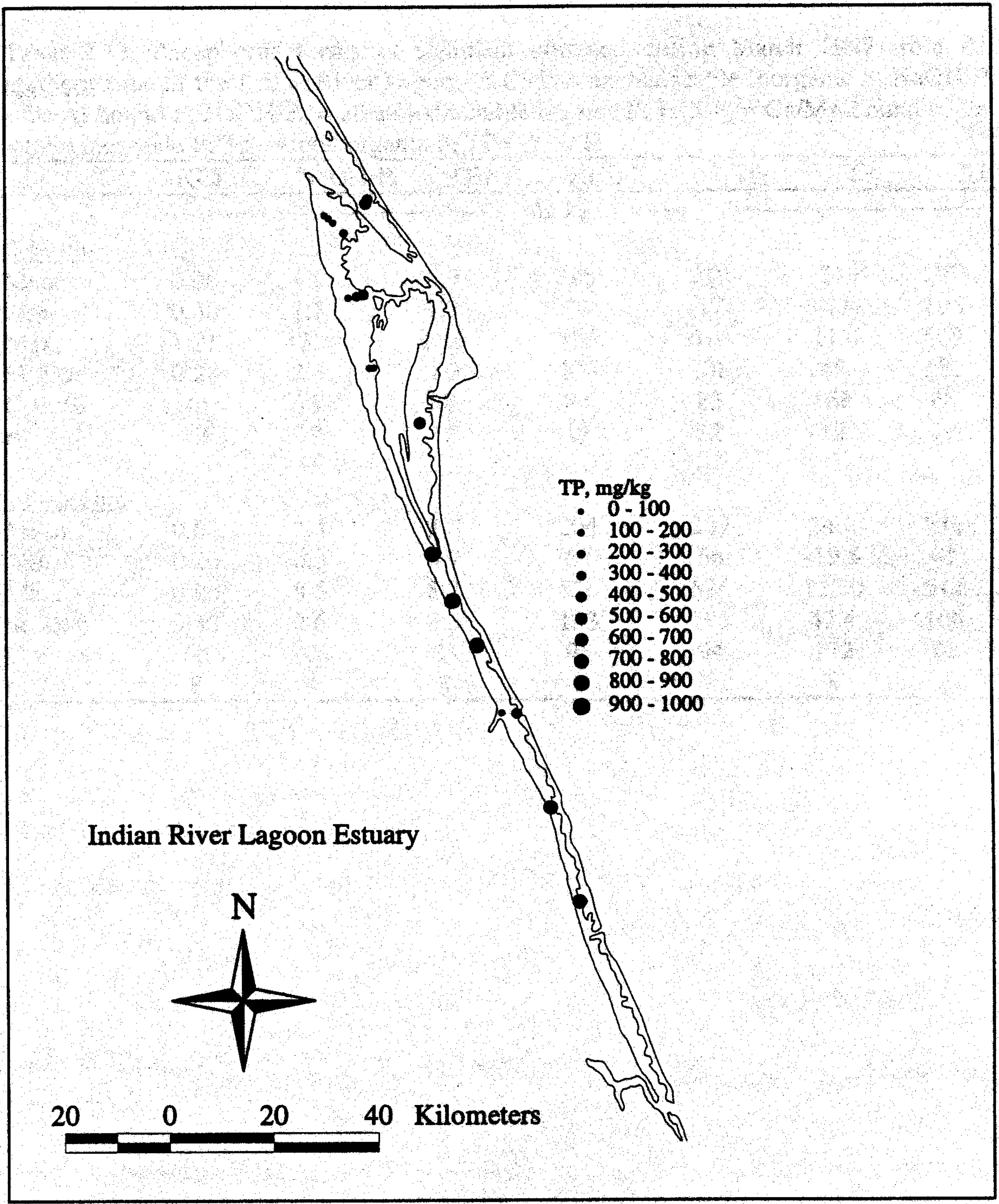


Figure 2.8 Spatial distribution of total phosphorus (TP) of surficial (0-10 cm) sediment samples collected during March 1997 from the Indian River Lagoon Estuary.

Table 2.12. Phosphorus forms of sediment obtained during March 1997 from the northern zone of the Indian River Lagoon. KCl-P_i = exchangeable inorganic P; NaOH-P_i = Fe/Al bound P; NaOH-P_o = alkali extractable organic P; HCl-P_i = Ca/Mg-bound P; Tp_i = total inorganic P; Tp_o = total organic P; TP = total P.

	KCL-P_i	NaOH-P_i	NaOH-P_o	HCL-P_i	TP_i	TP_o	TP
	---------- mg kg^{-1} ----------						
0-10 cm							
Mean	0.56	4.8	5.9	245	250	27	277
Min.	0.30	1.5	1.7	72	77	-47	105
Max.	1.01	13.1	15.5	596	610	113	562
St. Dev.	0.26	3.5	4.0	206	208	45	181
C.V. %	46	73	68	84	83	168	65
n	12	12	12	12	12	12	12
10 - 20 cm							
Mean	0.60	2.4	3.0	204	207	24.6	231
Min.	0.26	0.8	0.7	63	66	-19.5	81
Max.	0.96	8.6	8.2	526	528	122.0	517
St. Dev.	0.30	2.6	2.5	193	195	42.4	188
C.V. %	50	108	83	95	94	172	81
n	8	8	8	8	8	8	8

Table 2.13 Phosphorus forms of sediment obtained during March 1997 from the Indian River Lagoon stations characterized by surface deposits of mud (Stations 8, 9, 11). KCl-P_i = exchangeable inorganic P; NaOH-P_i = Fe/Al bound P; NaOH-P_o = alkali extractable organic P; HCl-P_i = Ca/Mg-bound P; Tp_i = total inorganic P; Tp_o = total organic P; TP = total P.

	KCL-P_i	NaOH-P_i	NaOH-P_o	HCL-P_i	TP_i	TP_o	TP
	mg kg^{-1}						
<u>0-10 cm</u>							
Mean	5.3	60.8	71.0	513	579	260	839
Min.	3.5	46.9	47.2	476	528	158	796
Max.	7.8	77.4	88.9	584	666	356	898
St. Dev.	2.2	15.4	21.5	62	76	99	52
C.V. %	41	25	30	12	13	38	6
n	3	3	3	3	3	3	3
<u>10 – 20 cm</u>							
Mean	5.0	47.6	45.5	453	506	187	693
Min.	2.9	12.4	19.0	335	350	76	595
Max.	8.3	94.3	63.3	645	748	244	824
St. Dev.	2.9	42.2	23.4	168	212	96	118
C.V. %	57	89	51	37	42	51	17
n	3	3	3	3	3	3	3

Table 2.14. Phosphorus forms of sediment obtained during March 1997 from the southern zone of the Indian River Lagoon. KCl-P_i = exchangeable inorganic P; NaOH-P_i = Fe/Al bound P; NaOH-P_o = alkali extractable organic P; HCl-P_i = Ca/Mg-bound P; Tp_i = total inorganic P; Tp, = total organic P; TP = total P.

	KCL-P_i	NaOH-P_i	NaOH-P_o	HCL-P_i	TP_i	TP_o	TP
	----------	----------	----------	mg kg^{-1}	----------	----------	----------
0-10 cm							
Mean	1.0	3.5	4.6	396	400	122	523
Min.	0.7	0.8	0.6	18	20	-23	80
Max.	2.5	12.1	15.3	898	902	407	886
St. Dev.	0.6	3.7	4.7	375	377	173	295
CV %	56	105	104	95	94	141	56
n	8	8	8	8	8	8	8
10 - 20 cm							
Mean	1.08	1.8	2.9	363	366	64	430
Min.	0.43	0.4	0.7	36	38	-30	58
Max.	2.38	4.4	6.1	603	609	196	689
St. Dev.	0.70	1.2	1.8	242	243	66	241
CV %	64	67	60	67	67	103	56
n	8	8	8	8	8	8	8

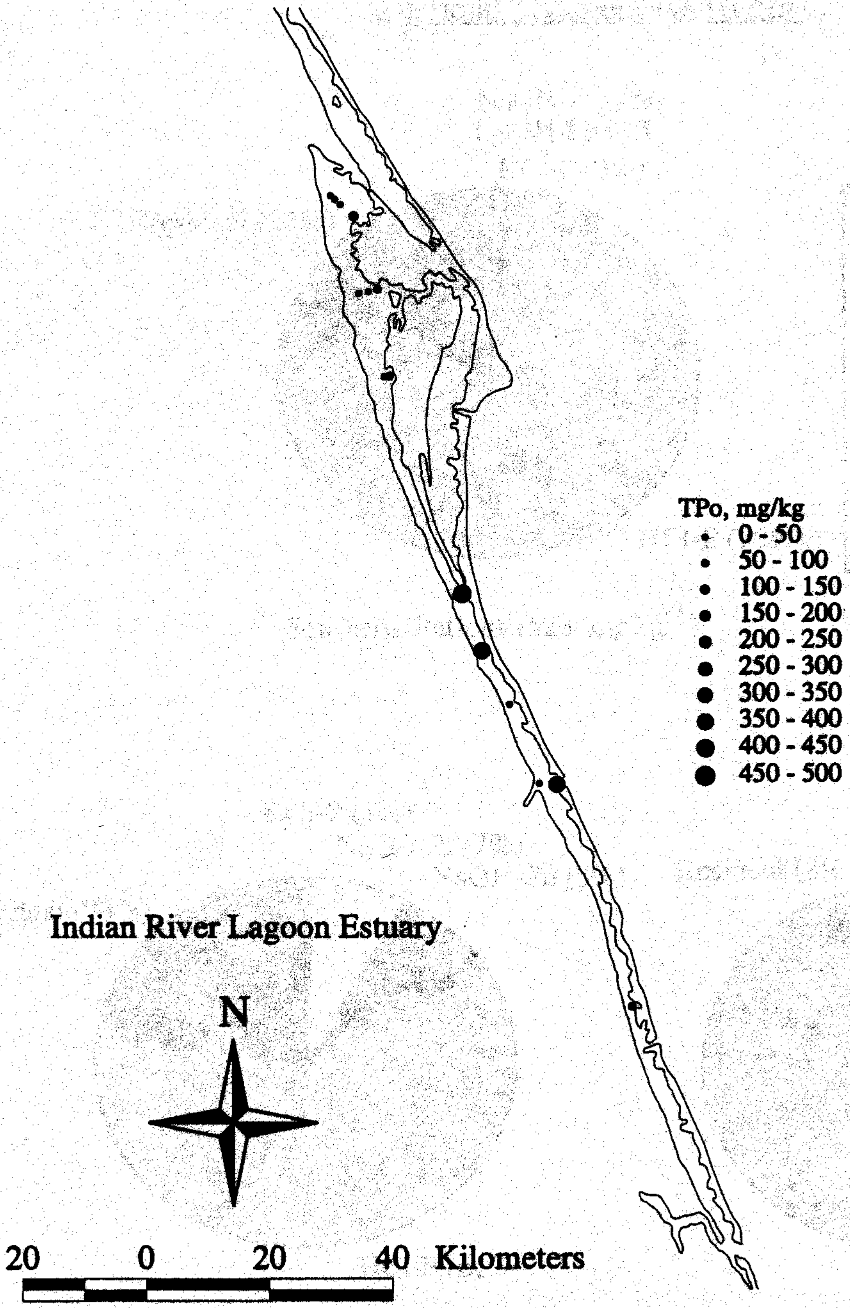
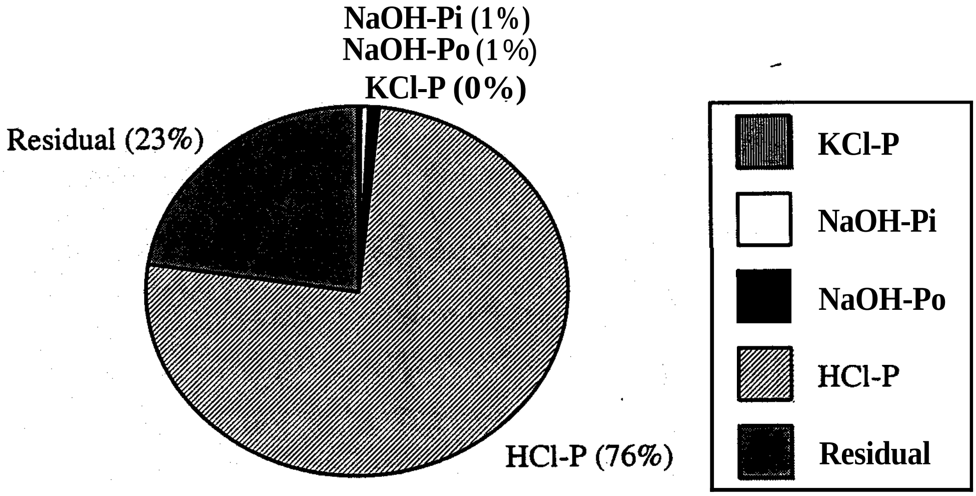
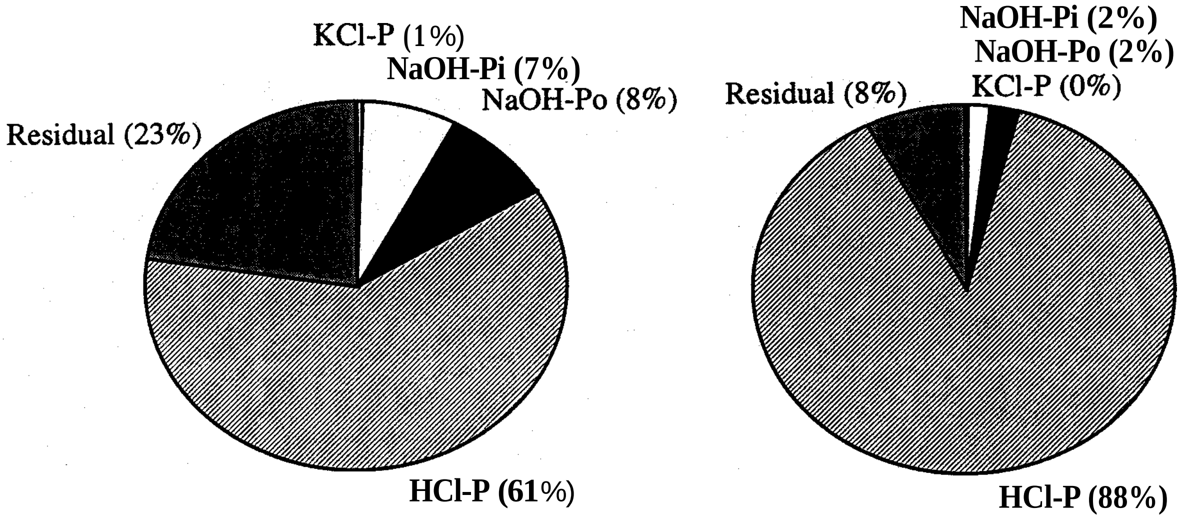


Figure 2.9. Spatial distribution of total organic P (TP_o) of surficial (0-10 cm) sediment samples collected during March 1997 from the Indian River Lagoon Estuary.

Surficial Sediment (0- 10 cm)



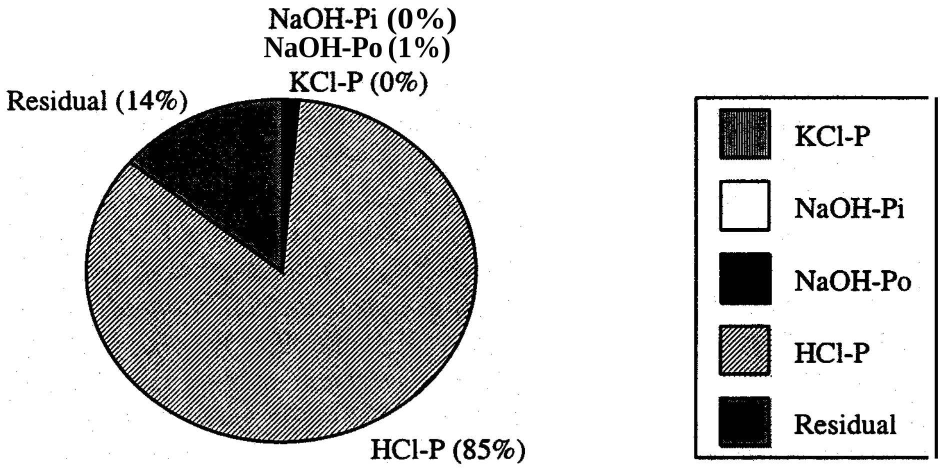
Southern Stations (523 mg kg^{-1})



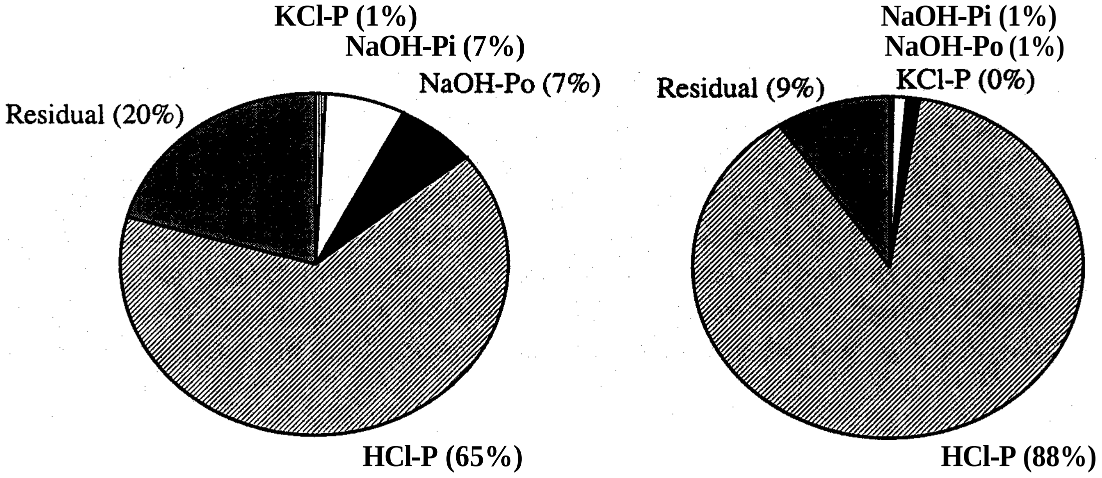
Mud Stations (839 mg kg^{-1}) Northern Stations (277 mg kg^{-1})

Figure 2.10. Labile and non-labile pools of P in the surface sediments of the Indian River Lagoon.

Deeper Sediment (10-20 cm)



Southern Stations (430 mg kg^{-1})



Mud Stations (693 mg kg^{-1})

Northern Stations (231 mg kg^{-1})

Figure 2.11. Labile and non-labile pools of P in the deeper sediments of the Indian River Lagoon.

moderately labile pool (KCl-P + $NaOH\text{-}P_i$ + $NaOH\text{-}P_o$) represented a substantially higher proportion of TP than the other surficial sediments, averaging 15% of total P (Table 2.13).

Sodium hydroxide extractable P was substantially higher for the three mud stations than the remaining stations. Both $NaOH\text{-}P_o$ and $NaOH\text{-}P_i$ represented approximately 8% of sediment TP, or combined represented 15% of TP. These values are in the range of values reported for the organic Histosols of the northern Everglades (Reddy et al. 1998). Typically, the $NaOH\text{-}P_i$ extract of Everglades surficial soils ranged from 10-24% of TP. The $NaOH\text{-}P_o$ extract of surficial Everglades soils ranged from 14 – 44% of TP which is considerably higher than that found in the Indian River Lagoon samples for this fraction. The other non-mud stations showed low recovery of P in this fraction, typically < 2% for both $NaOH\text{-}P_i$ and $NaOH\text{-}P_o$ fractions (Table 2.12 and 2.14). This was undoubtedly due to the low organic matter content of these samples. Both $NaOH\text{-}P_i$ and $NaOH\text{-}P_o$ were slightly higher on average for the northern stations, at both depths, than the southern stations. This is the reverse of the trend observed for the sediment TP content. However, there was no significant difference between the two groups (Student's t test, $a = 0.05$).

There were only slight differences with respect to the two sample depths, 0 –10 cm and 10 – 20 cm. On average, TP was slightly higher in the 0-10 cm depth interval (531 mg kg^{-1}) than in lower sediments (430 mg kg^{-1}) for the southern lagoon stations. Also, more P was recovered in the apatite pool in the deeper sediments. This could be due to diagenetic processes which sequester more P in apatitic mineral forms at this high pH (ca. 8.25) and calcium concentration at the greater sediment depths. There was very little difference in TP or fractionation results between the two depths for the northern lagoon stations. The mud stations also showed slightly higher TP values in the surficial sediments, compared to deeper sediment. It is possible that this reflects a changing depositional environment, i.e. the more recent sediments have a greater P content. There were no differences in the fractionation results between the two sediment layers for the mud stations.

One of the primary descriptors of sediment properties was the percent silt and clay content of the sediment. Silt and clay were positively correlated ($p<0.01$) with most of the P fractions, with the exception of Ca and Mg-bound P. Percent silt and clay were also significantly correlated with total N, total organic carbon, and 0.5M HCl-extractable metals (Ca, Mg, Fe, Al, and, Mn) (Tables 15-17). Conversely, the porewater analytes were not well correlated with silt and clay.

2.3.6 Variability of replicate cores

Two stations were selected for collecting replicate cores to test the precision of analytical and field collection techniques. Stations 4 and 24 were randomly selected from the 24 sampling stations. Three cores were taken at each of the stations during the March 1997 sediment sampling. Triplicate cores were also retrieved from stations 4 and 24 in June 1997, stations 4 and 18 in September 1997, stations 15 and 23 in December 1997,

Table 2.15. Selected cations extracted with 0.5M HCl from sediments obtained during March 1997 from the southern zone of the Indian River Lagoon.

	Ca	Mg	Mn	Al	Fe
	mg kg^{-1}				
0 - 10 cm					
Mean	31139	513	7.8	196	477
Min.	1106	41	0.4	2	0
Max.	133365	1178	17.2	610	1605
St. Dev.	46322	409	6.5	230	603
C.V. %	149	80	84	117	127
n	7	8	8	8	8
10 - 20 cm					
Mean	35904	866	13.6	384	777
Min.	2866	46	0.5	3	0
Max.	88010	2129	28.2	910	2137
St. Dev.	35660	710	10.2	338	706
C.V. %	99	82	75	88	91
n	6	8	8	8	8

Table 2.16. Selected cations extracted with 0.5M HCL from sediment obtained during March 1997 from Indian River Lagoon stations characterized by surface deposits of mud (Stations 8, 9, 11).

	Ca	Mg	Mn	Al	Fe
	------------------------	------------ mg kg^{-1}	------------	------------	------------
0 - 10 cm					
Mean	128817	6232	174	2797	7768
Min.	59076	5973	131	2669	6629
Max.	177140	6553	218	2891	9112
St. Dev.	61878	295	43	115	1254
C.V. %	48	5	25	4	16
n	3	3	3	3	3
10 - 20 cm					
Mean	96879	7382	176	3143	8343
Min.	39551	5245	106	2284	5205
Max.	179383	11192	308	4654	14137
St. Dev.	73237	3308	114	1313	5024
C.V. %	76	45	65	42	60
n	3	3	3	3	3

Table 2.17. Selected cations extracted with 0.5M HCl from sediments obtained during March 1997 from the northern zone of the Indian River Lagoon.

	Ca	Mg	Mn	Al	Fe
	------------------------	mg kg^{-1}	------------------------		
0 - 10 cm					
Mean	27118	944	7.2	271	432
Min.	2205	108	1.8	70	0
Max.	82599	4773	28.9	1168	2081
St. Dev.	26903	1334	7.7	315	553
C.V. %	99	141	107	116	128
n	11	11	11	11	12
10 - 20 cm					
Mean	40627	1065	7.9	279	461
Min.	3511	96	1.5	67	76
Max.	119008	4910	28.8	1118	1990
St. Dev.	39012	1701	9.6	374	663
C.V. %	96	160	121	134	144
n	8	8	8	8	8

and stations **5** and 18 in April **1998.** Variability results from the March spatial sampling are summarized for surface depths only (Tables **2.18 - 2.20).** Results for lower depths and the seasonally collected core samples are presented Appendix Tables **2.2** through **2.4.**

In most cases the variability between cores at the replicate stations was considerably lower than the overall spatial variability (Table **2.21).** Ammonium and **DRP** had relatively high variability between replicate cores. Variability in these two parameters probably occurs over relatively short spatial and temporal ranges. Sediment porewater concentration of NH_4-N and **DRP** has been shown to be highly dynamic, varying both of short spatial and temporal scales (Koch-Rose et al, **1994;** Montgomery et **al.,1979).** Water content and bulk density were measured with high precision. This is to be expected, since most of the stations sampled in the estuary were of uniformly sandy material. Most of the solid phase variables (TC, TIC, TOC, TN, KCl-N and TP) were measured with good precision. Station **4** showed low precision for TOC relative to the overall spatial sampling. This was primarily due to the very low TOC at this station. Total organic C was calculated **as** the difference between TC and TIC. Since TC was nearly equal to TIC, the difference was nearly zero for all three replications which in turn resulted in a high standard deviation, relative to the mean. The extractable P fractions (P_i-KCl, P_i-NaOH, P,-NaOH, and P_i-HCl) and TP showed good precision. **Total** organic P and residual P showed low precision. These two analytes **are** estimated by addition and difference (respectively) of the results obtained from separate sub-samples and therefore incorporate variability from both replicate sediment cores and replicate sub-samples from the same core.

2.3.7 Total storage of nitrogen and phosphorus in IRL sediment

The total mass of N and P stored in the surficial IRL sediments can be estimated by converting the N and P content to a volumetric basis (Fig. **2.12).** Average N and P storage in the surficial **0-10** cm sediment layer was **59 (±45)** and **47 (±33)** g m^{-2}, respectively. Storage in the deeper sediment layer **(10-20** cm) was slightly lower, at **57 (±48)** and **42 (±29)** g m^{-2} for N and P, respectively. If these values are extrapolated to the entire lagoon, an estimate of the total N and P storage can be determined. An areal extent of **700** km^2 was assumed for this analysis, which includes the region bounded to the north by the Haulover Canal and to the south, by Fort Pierce Inlet. This is the region that is represented by the **24** stations selected for this study. Using these assumptions and a limited number of samples, the total N and P storages in the upper **10** cm of sediment **are** **41,000** and **33,000** metric tons.

Table 2.18. Variability in physico-chemical properties of Indian River Lagoon surficial sediments in March 1997 among replicate cores.

	H_2O	Bulk Density	pH	DRP	NH_4-N	TC	DIC	DOC
Station	%	g cm^{-3}		mg L^{-1}				
24-I	42.8	0.91	8.24	0.215	3.13	69.1	53.2	15.9
24-II	35.8	1.11	8.49	0.163	2.85	66.7	52.7	14.0
24-III	33.3	1.11	8.52	0.108	3.10	67.5	54.4	13.1
Mean	37.3	1.0	8.42	0.162	3.03	67.8	53.4	14.3
Std. Dev.	4.9	0.11	0.15	0.054	0.15	1.2	0.9	1.5
C.V. %	13.2	10.9	1.8	33.0	5.1	1.8	1.6	10.2
4-I	21.0	1.51	8.33	0.015	3.35	49.8	29.2	20.6
4-II	21.2	1.53	8.36	0.082	6.13	60.9	37.4	23.5
4-III	20.7	1.51	8.30	0.018	3.77	49.8	29.6	20.2
Mean	21.0	1.52	8.33	0.038	4.42	53.5	32.1	21.4
Std. Dev.	0.3	0.01	0.03	0.038	1.50	6.4	4.6	1.8
C.V. %	1.4	0.8	0.4	98.7	34.0	11.9	14.4	8.3

Table 2.19. Variability in physico-chemical properties of Indian River Lagoon surficial sediments among replicate cores in March 1997.

	TP	Exchangeable NH_4-N	TN	TC	TIC	TOC
Station	mg kg^{-1}			%		
24-I	562	12.9	1500	2.71	0.98	1.72
24-II	525	1.1	1020	2.40	1.02	1.37
24-III	551	11.3	810	2.10	1.08	1.02
Mean	546	8.4	1110	2.40	1.03	1.37
Std. Dev.	19	6.4	354	0.30	0.05	0.35
CV, %	3.5	76.3	31.9	12.7	4.7	25.7
4-I	171	1.73	80	1.21	1.00	0.20
4-II	115	3.38	60	0.61	0.63	-0.02
4-III	119	1.87	70	0.91	1.03	-0.11
Mean	135	2.33	70	0.91	0.88	0.02
Std. Dev.	32	0.91	10	0.30	0.22	0.16
C.V. %	23.6	39.3	14.3	32.9	25.3	679.0

Table 2.20.Variability of results from the sequential P fractionation of Indian River Lagoon surficial sediments in March 1997.

Station	KCL-P_i	NaOH-P_i	NaOH-P_o	HCL-P_i	TP_i	TP
	-----	-----	----- mg kg^{-1}	-----	-----	-----
24-I	1.01	13.1	11.7	596	610	562
24-II	0.93	6.4	5.9	537	544	525
24-III	1.61	5.1	5.5	536	542	551
Mean	1.18	8.2	7.7	556	565	546
Std. Dev.	0.37	4.3	3.5	34	38	19
C.V. %	31.4	52.7	45.1	6.2	7	3.5
4-I	0.74	0.89	0.97	96	97	171
4-II	0.89	1.21	1.63	127	130	115
4-III	0.69	0.97	1.33	91	92	119
Mean	0.77	1.02	1.31	105	106	135
Std. Dev.	0.10	0.17	0.33	20	20	32
C.V. %	13.5	16.3	25.2	19	19	24

Table 2.21. A comparison of variability within each station to the variability observed among all stations visited during March 1997 in the Indian River Lagoon Estuary. Variability tabulated is for surficial (0-10 cm) sediments only.

Parameter	Variability within each station Station 4	 Station 24	Variability between all stations
	coefficient of variation (%)		
Water Content	1.4	13.2	51.2
Bulk Density	0.8	10.9	33.5
Porewater			
pH	0.4	1.8	3.6
DRP	98.7	33.0	156.1
NH_4-N	34.0	5.1	54.7
DOC	8.3	10.2	54.7
DIC	14.4	1.6	38.1
Phosphorus Fractionation			
P_i-KCL	13.5	31.4	130.7
P_i-NaOH	16.3	52.7	174.5
P_o-NaOH	25.2	45.1	171.2
P_i-HCL	19.1	6.2	83.2
TP_i	19.0	6.8	82.3
TP_o	157.1	-145.9	147.8
TP	23.6	3.5	66.1
Residual P	165.9	-115.8	165.0
Solid Phase			
TP	23.6	3.5	66.1
KCl-N	39.3	76.3	116.6
TN	14.3	31.9	145.8
TC	32.9	12.7	105.4
TIC	25.3	4.7	141.3
TOC	679.0	25.7	149.5

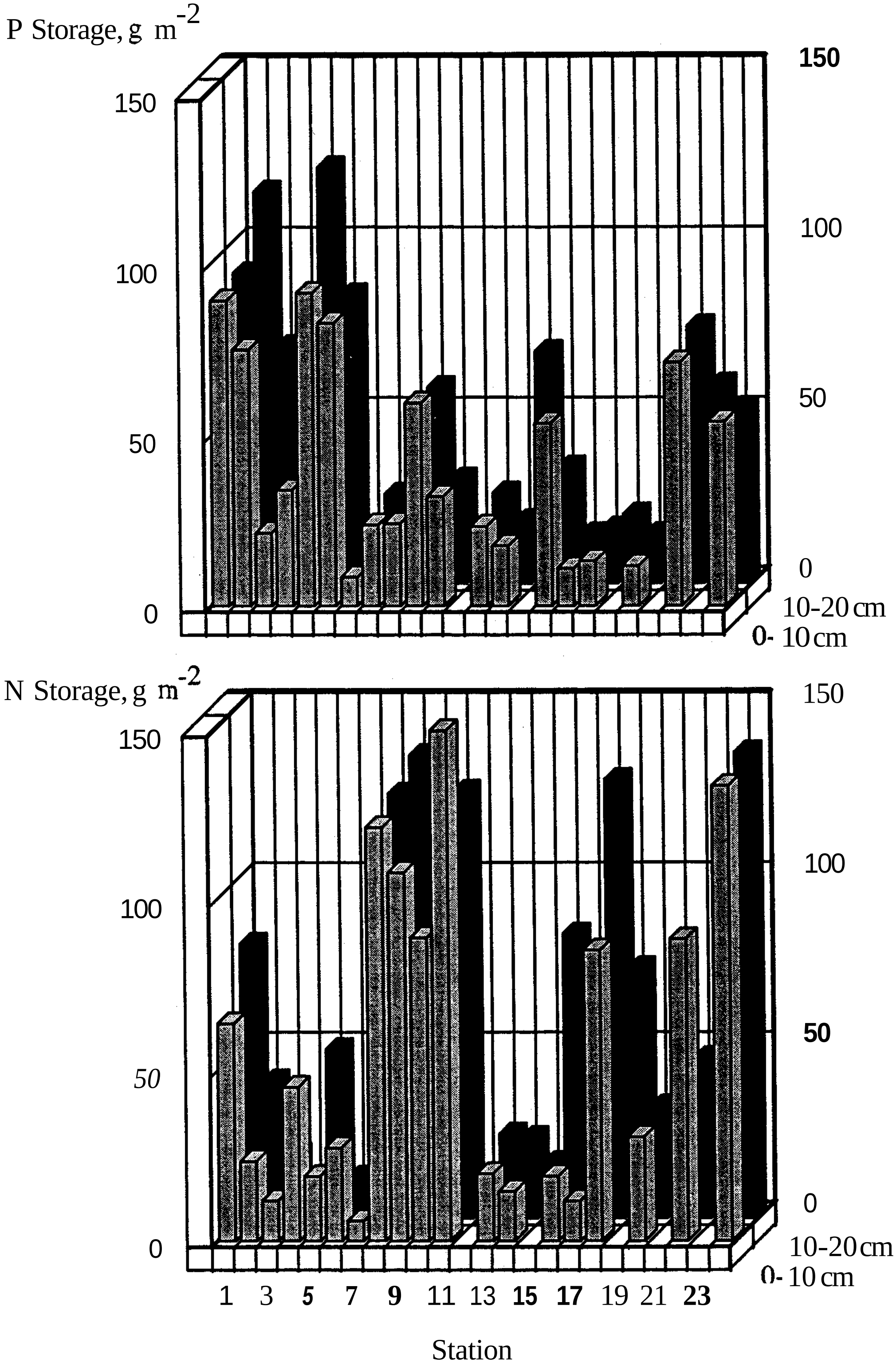


Figure 2.12. Storages of nitrogen and phosphorus in the surficial (0-10cm) and deeper (10-20 cm) sediments of the Indian River Lagoon.

2.3.8 Results of analysis of surface water samples

Water samples were collected from the **24** stations at the same time that the sediment samples were retrieved (Table **2.22** and **2.23;** Fig **2.13** and **2.14).** Water column temperature during the water and sediment sampling was approximately 25°C and varied little throughout the lagoon. Salinity ranged from a high of **37‰** at Station **3** (Sebastian Inlet) to a low of **16‰** at Station **12** (Melbourne area). Generally, salinity was high in the region between Fort Pierce Inlet and Sebastian Inlet and again in the extreme northern end of the lagoon. The average pH was near that of seawater, 8.06 **(±0.20).** Most of the organic nitrogen in the water column was in soluble form (SON), comprising on average 65% of the total water column total Kjeldahl nitrogen (TKN). Overall, TKN averaged **0.94 (±0.44)** mg $\mathbf{L^{-1}}$ for the **24** water samples collected. Organic nitrogen was considerably higher from Station **5** through Station **14** than either stations south of Sebastian Inlet or to the north of Titusville. Ammonium-N levels showed no trend with respect to location and varied from a low of **34** μ**g** $\mathbf{L^{-1}}$ at Station 8 to a high of **185** μ**g** $\mathbf{L^{-1}}$ at Station **20.** Soluble organic P was generally below the limit of detection, while TP averaged **57 (±22)** μg $\mathbf{L^{-1}}$. Dissolved reactive P accounts for approximately half of the water column TP, averaging **30 (±13)** μg $\mathbf{L^{-1}}$.

Physico-chemical properties of the surficial (0-10cm) sediments were not well correlated to the overlying water quality. Only a few of the parameters measured in the water column were correlated to sediment properties, and then only weakly (Table **2.24).** Hydrodynamic circulation patterns within the estuary likely result in spatial uncoupling between sediment processes, such as nutrient exchange, and the overlying water quality, thus resulting in low apparent correlation.

2.4 Conclusions

Sediment and water samples were collected in March and April of **1997** from twenty-four stations in the Indian River Lagoon. The stations encompassed the region of the lagoon bounded on the north by the Haulover Canal and to the south by Fort Pierce Inlet. The sediments and water were characterized for forms of N and P and other selected physico-chemical properties.

Generally, muddy sediment deposits in the vicinity of Melbourne were found to have elevated concentrations of porewater $\mathbf{NH_4}$**-N** and DRP, as well as total N and total P, relative to the other sampling stations. Ammonium N and DRP in this region averaged 7.0 and **0.7** mg $\mathbf{L^{-1}}$, whereas TN and TP averaged **3957** and **839** mg kg^{-1}. Total P in the surficial sediments of the southernmost stations (Stations 1 and **2)** was higher than most of the remaining stations, with the exception of the mud zone stations. The sediments were sequentially extracted to determine the major pools of sediment P. Most of the sediment P **(78%)**was in the Ca and Mg-bound pool and is thus not particularly labile.

Table 2.22. *Summary* of selected physico-chemical characteristics of Indian River Lagoon Estuary surface wat samples collected in March 1997.

	TSS	TOC	TKN	SON	T
	—— mg L^{-1} ——		——— µg L^{-1} ———		
Max.	57.8	28.3	1.82	1.32	105
Min.	4.4	2.3	0.30	0.00	31
Mean	18.0	12.0	0.90	0.61	57
Std. Dev.	12.7	5.3	0.40	0.40	22
C.V. %	71	44	47	0.07	38.

Table **2.23.** Correlation between selected physico-chemical parameters measured in the water column and surficial sediment properties during March 1997. Correlation coefficients reporte below are significant at the **0.05** level.

	Water Column Parameters				
	DRP	NH_4-N	TKN	TP	SON
Sediment					
BD					**-0.38**
DRP					
NH_4-N					
TC					
DIC					
DOC	**0.41**				
P_i-KCL					
KCl-N					
P_i-NaOH		**-0.36**			**0.41**
P_i-HCl					
P_o-NaOH					**0.41**
TP-NaOH		**-0.36**			**0.42**
TP_i	**0.37**				
TP					
TP_o					
Residual P					
TN		**-0.37**			**0.41**
TC					
TIC					
$NaHCO_3$-P					
TOC					**0.41**
Sand		**0.39**			**-0.41**
Silt		**-0.41**			**0.40**
Clay					**0.42**

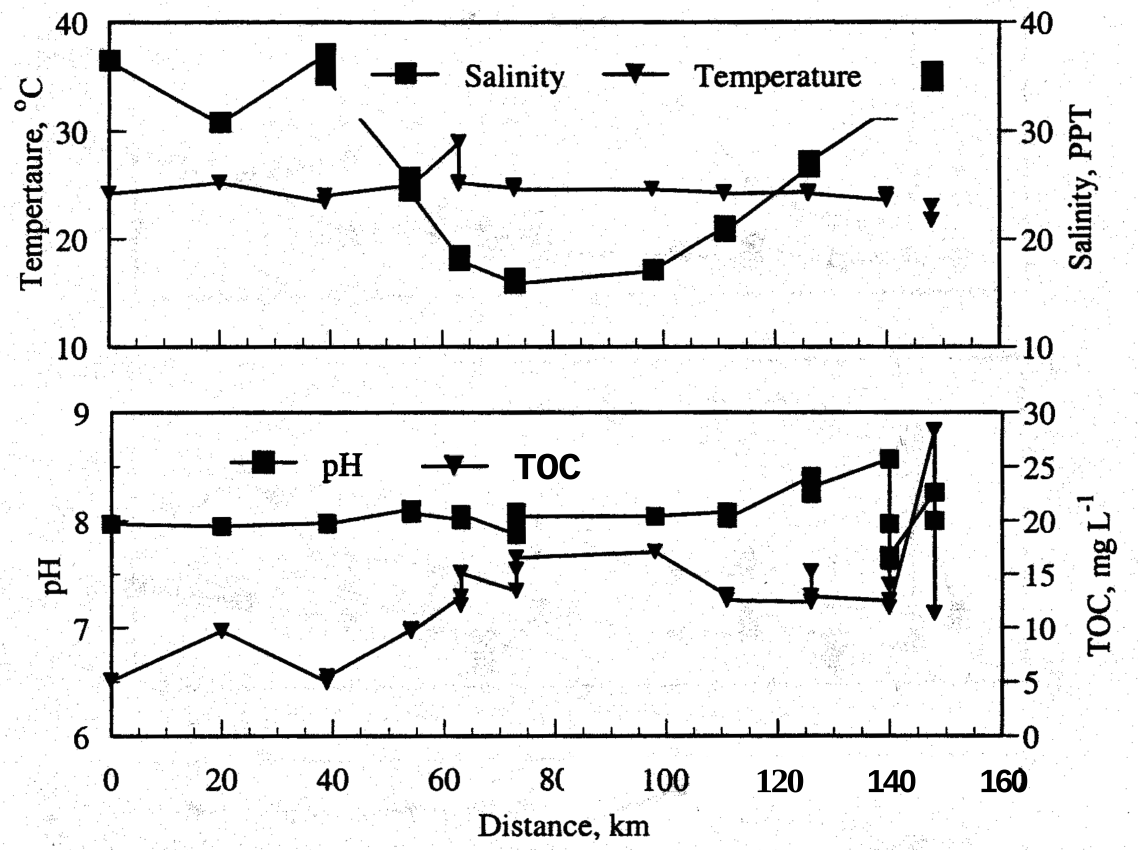


Figure 2.13. Selected physico-chemical properties of the water column of the Indian River Lagoon. Distance is measured from south to north, originating at Station 1 near Fort Pierce Inlet.

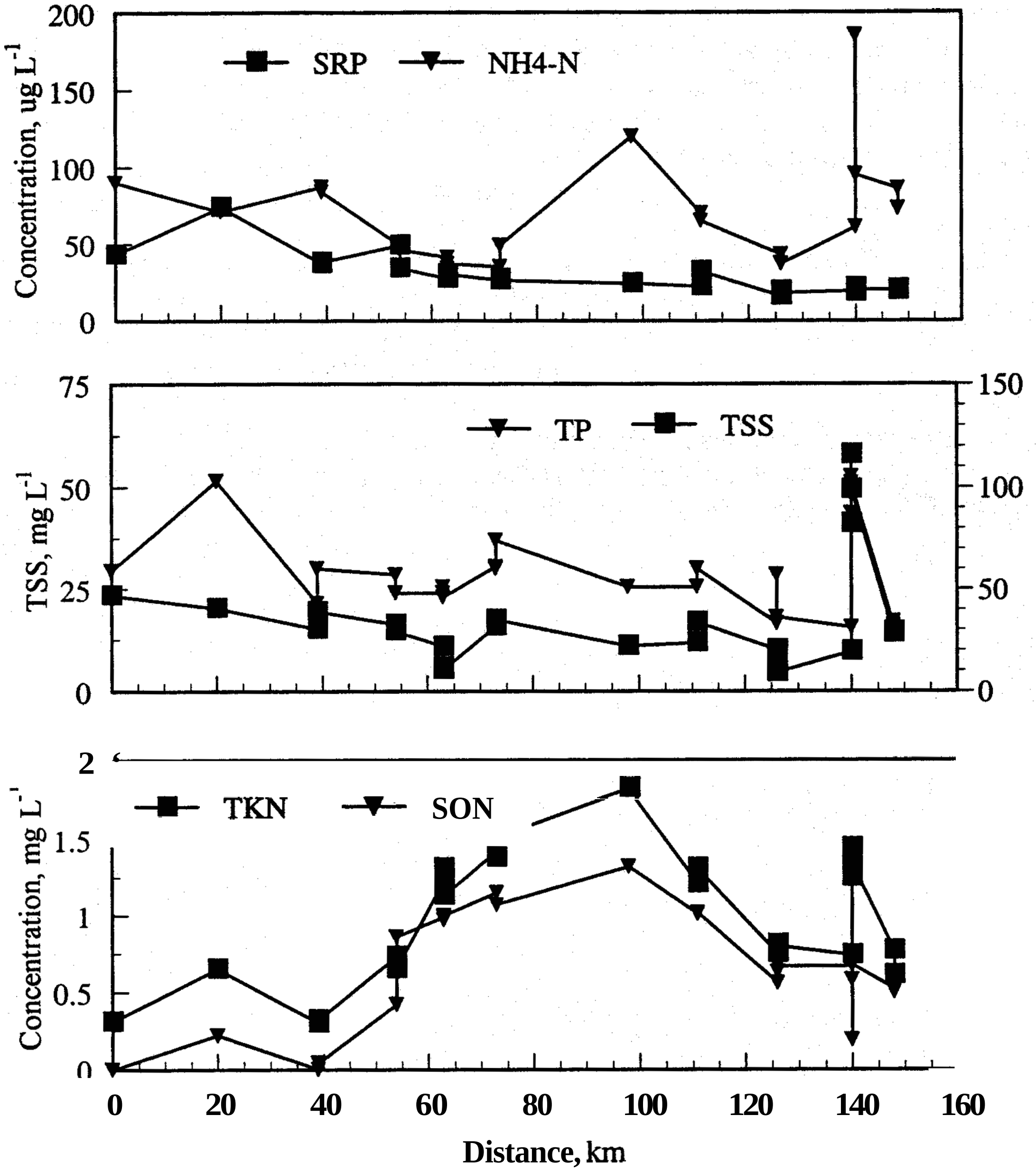


Figure 2.14. Selected physico-chemical properties of **the water column** of **the Indian River** Lagoon. **Distance is measured from south to north, originating at Station 1 near Fort Pierce Inlet.**

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Appendix 2.1. Results of physico-chemical analysis of Indian River Lagoon Estuary surface water samples collected in March 1997.

Station	Date & Time	Salinity	Temperature	pH	TOC	DOC	DIC	**SRP**	NH_4-N	NO_3-N	**TSS**	**TKN**	TP	SOP	**SON**
		PPT	°C		mg L^{-1}			µg L^{-1}			mg L^{-1}		µg L^{-1}		
I1	3/11/97 11:30	36.4	24.2	7.97	5.1	3.2	26.6	43	90	3	23.4	0.31	59	-14	-41
I2	3/11/97 14:30	30.7	25.2	7.95	9.7	10.9	29.2	74	71	ND	20.2	0.65	103	-11	222
I3	3/12/97 9:50	37.0	23.4	7.98	5.0	4.5	25.8	37	87	3	15.0	0.30	43	-11	-20
I4 **A**	3/12/97 10:28	35.1	24.0	7.97	5.5	2.5	27.0	38	84	**ND**	19.4	0.32	60	-12	39
I4 B					2.7	7.3	26.8	41	71	ND	19.4	0.35	31	10	70
I4 C					2.3	2.9	28.0	41	71	ND	20.6	0.37	57	-12	110
I5	3/12/97 12:13	25.6	25.0	8.11	9.8	12.6	28.7	49	49	**ND**	16.2	0.73	57	-13	421
I6	3/12/97 12:35	24.4	24.8	8.07	9.6	9.0	30.2	34	46	**ND**	14.6	0.65	48	-17	862
I7	3/12/97 14:00	18.3	28.9	8.01	12.9	15.9	30.5	27	41	**ND**	10.8	1.23	48	0	987
I8	3/12/97 14:46	17.9	25.1	8.06	12.1	11.7	29.4	28	34	**ND**	5.8	1.31	51	-4	965
I9	3/12/97 14:56	18.0	25.2	8.06	15.1	17.7	30.5	30	37	**ND**	5.2	1.13	46	0	1005
I10	3/12/97 17:00	15.9	24.7	7.87	13.4	14.0	31.1	26		ND	15.8	1.42	61	-17	
I11	3/12/97 17:15	16.2	24.9	8.08	15.4	11.5	28.8	27	35	ND	15.8	1.38	60	-15	1148
I12	3/12/97 18:00	15.8	24.6	8.04	16.5	11.7	28.6	26	49	**ND**	17.4	1.51	74	-17	1073
I13	3/13/97 14:30	21.1	24.3	8.08	13.0	13.1	32.2	22	70	12	11.8	1.21	51	19	1011
I14	3/13/97 14:50	20.6	24.2	8.02	12.6	14.5	31.3	32	65	12	16.8	1.31	60	-4	1016
I15	4/8/97 16:50	26.6	24.3	8.41	12.4	NA	29.8	16	43	**ND**	10.0	0.75	33	8	558
I16	4/8/97 17:20	26.8	24.2	8.25	15.2	**NA**	33.8	19	43	**ND**	9.0	0.81	57	7	630
I17	4/8/97 17:50	27.1	24.2	8.31	12.9	**NA**	31.0	18	37	**ND**	4.4	0.80	36	9	673
I18	4/8/97 13:10	31.9	23.6	8.57	12.5	**NA**	25.6	19	61	**ND**	9.6	0.74	31	**5**	668
I19	4/8/97 13:54	32.7	23.7	7.97	15.7	**NA**	37.8	18	61	6	41.0	1.25	87	6	580
I20	4/8/97 14:50	32.9	24.0	7.63	14.0	**NA**	37.6	21	185	6	57.8	1.44	105	3	194
I21	4/8/97 15:30	33.1	24.1	7.67	11.8	**NA**	37.9	20	95	6	49.4	1.34	102	11	680
I22	3/13/97 11:10	17.0	24.6	8.04	17.1	15.5	33.5	24	120	41	11.0	1.82	51	-7	1322
I23	4/8/97 11:30	35.3	23.0	8.26	28.3	**NA**	30.3	20	86	2	14.0	0.77	32	4	523
I24 I	4/8/97 9:22	34.5	21.7	8.00	11.3	**NA**	34.1	19	73	**ND**	14.4	0.61	34	4	501
I24 II					9.8	NA	34.4	19	61	ND	16.6	0.63	39	7	540
I24 III					**11.7**	**NA**	**33.8**	**19**	**70**	**6**	13.8	0.68	34	8	576

Appendix 2.2. Results of chemical fractionation of Indian River Lagoon sediments collected in March and April, 1997 (surficial sediments).

Field ID	Depth	Water Content	Bulk Density	pH	KCl-P_i	KCl-NH_4-N	NaOH-P_o	NaOH-P_i	HCl-P_i	TP	$NaHCO_3$-P_i	TN	TC	TIC	TOC
	(cm)	(%)	(g/cm^3)		(mg/kg)							(g/kg)			
11-A1	0-10	33.15	1.15	8.05	2.46	10.94	15.27	12.10	693	790	14.84	0.70	10.97	3.95	7.02
I2-A2	0-10	24.58	1.44	8.66	0.81	4.40	3.99	3.46	814	795	4.32	0.28	**8.85**	6.25	2.60
13-A1	0-10	20.36	1.47	**8.40**	0.71	1.98	0.62	0.78	89	474	5.52	0.13	39.75	38.33	1.42
14-A2	0-10	21.01	1.51	8.33	0.74	1.73	0.97	0.89	96	171	4.37	0.08	12.05	10.07	1.98
14-A4	0-11	21.22	1.53	8.36	0.89	3.38	1.63	1.21	127	115	3.98	0.06	9.12	10.32	ND
14-A3	0-12	20.65	1.51	8.30	0.69	1.87	1.33	0.97	91	119	4.53	0.07	6.08	6.31	ND
15-A1	0-10	26.39	1.38	8.29	0.90	8.54	6.51	3.72	898	886	2.07	0.36	4.93	0.86	4.07
16-A1	0-10	22.38	1.52	8.16	1.09	3.89	3.54	3.18	517	556	2.09	0.08	1.08	0.48	0.60
17-A1	0-10	19.74	1.55	8.04	0.69	1.55	1.51	2.13	41	80	0.97	0.05	1.44	0.49	0.95
18-A1	0-10	75.30	0.29	8.24	7.75	33.95	47.16	58.11	476	898	41.44	4.26	61.29	6.18	55.11
19-A1	0-10	72.43	0.32	8.08	3.48	31.18	76.87	46.91	478	796	53.93	4.24	70.57	25.51	45.06
110-A1	0-10	30.19	1.35	8.62	0.96	6.09	4.05	1.66	18	427	12.81	0.61	56.28	51.86	4.42
I11-A1	0-10	67.85	0.37	8.00	4.75	40.95	88.88	77.44	584	824	28.04	3.37	45.67	6.61	39.06
113-A1	0-10	22.12	1.46	8.32	0.55	1.65	2.80	2.45	111	183	0.71	0.17	2.39	0.48	1.91
114-A1	0-10	20.38	1.49	8.30	0.41	1.70	1.70	1.48	94	124	0.84	0.16	4.37	2.45	1.92
1-15	0-12	22.52	1.49	7.14	0.38	1.61	4.42	1.77	402	457	2.14	0.11	14.99	13.25	1.74
1-16	0-10	34.23	1.07	8.03	0.59	8.93	15.54	7.27	260	319	1.44	0.78	11.27	2.73	8.54
1-17	0-10	24.57	1.36	8.26	0.38	2.71	2.24	2.38	96	107	1.26	0.03	1.29	1.77	ND
1-18	0-10	47.17	0.69	8.18	0.86	22.32	6.86	6.64	114	235	1.12	1.87	18.91	1.58	17.39
1-19	0-10	27.03	1.53	8.23	0.31	5.21	4.09	3.40	88	133	2.60	0.48	7.34	1.67	5.67
1-20	0-10	24.04	1.37	8.31	0.30	9.47	7.02	4.28	77	105	1.76	0.24	5.96	0.00	5.96
1-21	0-10	26.03	1.33	8.33	0.37	2.14	4.74	4.48	72	113	1.21	0.32	5.77	1.55	4.22
122-A1	0-10	26.62	1.34	8.49	0.99	2.42	4.87	1.80	593	562	2.85	0.35	11.25	6.56	4.69
1-23	0-8.5	27.52	1.37	8.39	0.55	7.76	4.77	8.03	435	425	2.64	0.37	45.33	42.13	3.20
1-24-1	0-10	42.81	0.91	8.24	1.01	12.88	11.71	13.10	596	562	3.72	1.50	27.05	10.49	16.56
1-24-2	0-10	35.75	1.11	8.49	0.93	1.06	5.87	6.36	537	525	4.92	1.02	23.97	10.77	13.20
1-24-3	0-10	33.30	1.11	8.52	1.61	11.33	5.53	5.07	536	551	3.95	0.81	20.97	11.23	9.74

Appendix 2.3. Results of chemical fractionation of Indian River Lagoon sediments collected in March and April, 1997 (deeper sediments).

Field ID	Depth	Water Content	Bulk Density	pH	KCl-Pi	KCl-NH_4-N	NaOH-Po	NaOH-Pi	HCl-Pi	**TP**	$NaHCO_3$-Pi	TN	TC	TIC	TOC
	(cm)	(%)	(g/cm^3)					(mg/kg)					(g/kg)		
I1-B1	10-24	27.98	1.30	8.60	2.38	4.49	6.14	4.35	603	689	2.73	0.49	13.91	4.55	9.36
I2-B2	10-15	23.92	1.30	8.68	0.84	3.68	3.22	1.20	542	578	4.09	0.18	10.44	7.39	3.05
13-B1	10-15	20.42	1.31	8.38	0.43	1.35	0.71	0.43	77	164	4.52	0.09	42.38	40.26	2.12
I4-B2	10-18	26.01	1.50	8.85	0.93	3.37	1.70	2.01	151	226	2.06	0.30	14.28	10.44	3.84
I4-B3	12-17	21.06	1.59	8.47	0.47	2.30	1.86	0.83	90	114	4.06	0.12	17.41	12.91	4.50
I4-B4	11-19.5	32.69	1.24	8.99	0.56	2.97	1.56	1.89	174	192	3.97	0.37	17.57	8.33	9.24
I5-B 1	10-18	21.36	1.46	8.62	1.81	7.93	3.37	1.09	571	626	1.47	0.13	4.23	3.61	0.62
16-B1	10-20	23.00	1.52	8.48	0.58	1.97	2.71	2.04	575	547	2.16	0.18	2.38	0.50	1.88
17-B1	10-17	19.75	1.47	8.23	0.45	1.17	1.24	1.15	36	***58***	0.46	0.04	1.70	0.87	0.83
18-B1	10-20	73.69	0.29	8.43	8.26	96.49	63.30	94.33	***645***	824	65.29	4.18	62.72	3.56	59.16
19-B1	10-20	67.27	0.41	8.36	2.87	19.28	18.99	12.37	335	595	22.64	2.66	72.36	48.13	24.23
110-B1	10-20	39.64	1.09	8.54	1.22	7.57	4.37	1.95	349	549	13.93	0.82	42.87	32.51	10.36
I11-B1	10-20	62.24	0.49	8.25	3.92	38.35	54.25	36.05	380	662	25.27	3.19	60.41	26.33	34.08
I13-B1	10-12.5	22.64	1.98	8.32	0.45	3.10	1.42	1.40	89	118	0.65	0.10	2.03	0.67	1.36
I14-B1	10-20	21.45	1.46	8.39	0.40	0.97	1.39	0.77	99	121	0.25	0.10	3.71	2.65	1.06
1-16	10-13	22.24	1.73	8.27	0.36	2.72	2.20	0.88	187	310	3.72	0.11	22.61	21.92	0.69
1-17	10-18.5	24.07	1.32	8.43	0.26	1.14	0.72	1.44	86	84	1.08	0.09	5.32	4.17	1.15
1-18	10-20	31.33	1.17	8.31	0.95	16.18	3.72	3.43	***85***	113	2.23	0.73	10.43	2.27	8.16
1-20	10-16.5	23.15	1.45	8.50	0.44	4.73	1.59	2.07	63	81	1.62	0.21	7.82	0.00	7.82
122-B1	10-20	29.43	1.40	8.63	0.94	3.05	4.67	0.95	526	509	2.81	0.63	26.21	16.58	9.63
1-24-1	10-14	32.51	1.04	8.31	0.96	3.24	8.19	8.58	496	517	8.36	1.28	22.04	7.68	14.36
1-24-2	10-14	33.04	1.01	8.74	0.69	3.51	5.24	4.91	477	536	4.11	1.22	26.74	11.01	15.73
1-24-3	10-14	29.73	1.28	8.65	0.90	27.90	4.71	3.89	437	464	4.32	0.71	33.65	20.34	13.31

Appendix 2.4. Selected properties of surficial Indian River Lagoon sediments in March, 1997.

	Depth	Water Content	Bulk Density	pH	NH_4-N	DRP	DIC	DOC
Site	(cm)	(%)	(g/cm^3)		(mg/L)			
11-A1	0-10	33.15	1.15	8.05	7.284	1.28-	97.07	77.29
I2-A2	0-10	24.58	1.44	8.66	5.248	0.094	40.08	44.28
I3-A1	0-10	20.36	1.47	8.40	6.193	0.04	45.10	33.44
14-A2	0-10	21.01	1.51	8.33	3.347	0.015	29.19	20.64
14-A4	0-11	21.22	1.53	8.36	3.77	0.018	29.60	20.21
14-A3	0-12	20.65	1.51	8.30	6.132	0.082	37.40	23.47
15-A1	0-10	26.39	1.38	8.29	4.80	0.021	49.19	31.66
16-A1	0-10	22.38	1.52	8.16	5.527	0.015	40.73	18.57
17-A1	0-10	19.74	1.55	8.04	2.317	0.037	35.86	29.46
18-A1	0-10	75.30	0.29	8.24	9.026	1.04	84.73	20.16
19-A1	0-10	72.43	0.32	8.08	4.618	0.279	60.24	18.23
110-A1	0-10	30.19	1.35	8.62	6.459	0.31	62.79	19.49
I11-A1	0-10	67.85	0.37	8.00	7.283	0.808	70.11	27.74
113-A1	0-10	22.12	1.46	8.32	2.656	0.028	40.51	26.98
114-A1	0-10	20.38	1.49	8.30	3.225	0.015	30.26	33.82
1-15	0-12	22.52	1.49	7.14	0.293	0.027	30.02	14.23
1-16	0-10	34.23	1.07	8.03	9.303	0.387	105.1	21.43
1-17	0-10	24.57	1.36	8.26	1.088	0.052	49.83	14.02
1-18	0-10	47.17	0.69	8.18	10.439	0.204	73.95	59.74
1-19	0-10	27.03	1.53	8.23	3.769	0.022	51.34	25.46
1-20	0-10	24.04	1.37	8.31	2.133	0.024	42.88	17.11
1-21	0-10	26.03	1.33	8.33	5.214	0.103	59.51	16.44
122-A1	0-10	26.62	1.34	8.49	3.322	0.065	37.58	42.37
1-23	0-8.5	27.52	1.37	8.39	3.737	0.056	63.85	21.03
1-24-1	0-10	42.81	0.91	8.24	3.133	0.215	53.19	15.92
1-24-2	0-10	35.75	1.11	8.49	2.851	0.163	52.72	13.99
1-24-3	0-10	33.30	1.11	8.52	3.101	0.108	54.4	13.05

Table 2.5. Selected properties of surficial Indian River Lagoon sediments in March, 1997.

	Depth	PIP	POP	TP	PIN	PON	TN	TIC	TOC	TC
Site	(cm)		(mg/kg)			(mg/kg)			(g/kg)	
11-A1	0-10	707	83	791	10.94	689	700	3.95	7.02	10.97
E-A2	0-10	818	ND	795	4.40	276	280	6.25	2.60	8.85
I3-A1	0-10	90	384	474	1.98	128	130	38.33	1.42	39.75
I4-A2	0-10	97	74	171	1.73	78	80	10.07	1.98	12.05
14-A4	0-11	92	26	119	1.87	68	70	10.32	ND	9.12
I4-A3	0-12	130	ND	115	3.38	57	60	6.31	ND	6.08
15-A1	0-10	902	ND	886	8.54	351	360	0.86	4.07	4.93
16-A1	0-10	522	34	556	3.89	76	80	0.48	0.60	1.08
17-A1	0-10	44	36	80	1.55	48	50	0.49	0.95	1.44
18-A1	0-10	542	356	898	33.95	4226	4260	6.18	55.11	61.29
19-A1	0-10	528	268	796	31.18	4209	4240	25.51	45.06	70.57
110-A1	0-10	20	407	427	6.09	604	610	51.86	4.42	56.28
Ill-A1	0-10	666	158	824	40.95	3329	3370	6.61	39.06	45.67
113-A1	0-10	114	69	183	1.65	168	170	0.48	1.91	2.39
114-A1	0-10	96	28	124	1.70	158	160	2.45	1.92	4.37
1-15	0-12	404	53	457	1.61	108	110	13.25	1.74	14.99
1-16	0-10	268	50	319	8.93	771	780	2.73	8.54	11.27
1-17	0-10	99	8	107	2.77	27	30	1.77	ND	1.29
1-18	0-10	122	113	235	22.32	1848	1870	1.58	17.39	18.97
1-19	0-10	91	42	133	5.21	475	480	1.67	5.67	7.34
1-20	0-10	82	24	105	9.47	231	240	0.00	5.96	5.96
1-21	0-10	77	36	113	2.14	318	320	1.55	4.22	5.77
I22-A1	0-10	596	ND	562	2.42	348	350	6.56	4.69	11.25
1-23	0-8.5	444	ND	425	7.76	362	370	42.13	3.20	45.33
1-24-1	0-10	610	ND	562	12.88	1487	1500	10.49	16.56	27.05
1-24-2	0-10	544	ND	525	1.06	1019	1020	10.77	13.20	23.97
1-24-3	0-10	542	9	551	11.33	799	810	11.23	9.74	20.97

CHAPTER3

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TEMPORAL DISTRIBUTION OF NUTRIENTS IN INDIAN RIVER LAGOON SEDIMENTS

[Task 6.6 as per the contract]

3.1 Introduction

Bottom sediments appear to play a crucial role in internal nutrient cycling of shallow estuaries. The biogeochemical processes associated with cycling of nutrients can significantly impact the water quality of these ecosystems. Nutrient fluxes from sediment to the water column of a shallow estuary are dependent on physical, chemical, and biological properties of the sediment. In order to understand the functional role of sediments as a source or sink for nutrients to the overlying water column, it is important to first characterize the sediments for total labile and non-labile nutrient fractions, spatially, as well as temporally.

The sediments underlying lakes, wetlands, and estuaries are capable of pronounced seasonal changes with respect to the partitioning of key nutrients (Koch-Rose et al ., 1994; Moore et al. 1998; Reddy et al. 1996, Klump and Martens, 1981). Seasonal, or temporal, sampling can provide a more detailed description of how cyclical biogeochemical processes affect the mobility and availability of sediment nutrient pools.

3.1.1 Site Description

The Indian River Lagoon Estuary is a large, shallow, mesohaline lagoon. It is approximately 255 km in length and varies in width from 0.3 km to 9 km. The Lagoon is shallow, with an average depth of approximately 1m. It is bounded to the east by a barrier island, separating it from the Atlantic Ocean. It has been reported that it has the highest biodiversity of any estuary in North America and provides annual economic benefits to counties surrounding the lagoon estimated at approximately 700 million dollars. Loss of emergent vegetation is estimated at 75% since 1950 with 100% loss of seagrass beds in some locations. The seagrasses and emergent macrophytes of the Indian River Lagoon are critical ecosystem components in that they provide habitat for many species for at least some period of their life cycle (Virnstein et al., 1983; Gilmore et al., 1983). Circulation and flushing occur through freshwater inflows, tidal cycles through three inlets, and wind mixing. Overall flushing by tidal cycles is low, whereas flushing due to wind can be the principle source of flushing, according to simulation models (Sheng et al., 1994). Low flushing rates have obvious implications on nutrient loading, tending to exacerbate the effects of point and non-point loading.

One of the goals of the Surface Water Improvement and Management (SWIM) Plan for the Indian River Lagoon Estuary calls for the attainment and maintenance of water and sediment quality sufficient to support a healthy macrophyte-based estuarine lagoon system; or to Class III waters or better (SWIM, 1994), with emphasis on the reduction of excessive point and non-point source loading of nutrients. A major portion of nutrients loaded to this estuary can be retained by sediments. Once the external load criteria are met as a result of better control of point and non-point source inputs, internal sources (from bottom sediments) may maintain current water quality conditions. Thus, sediments can act as a source of nitrogen (N) and phosphorus (P) and therefore constitute a potential non-point source of nutrient loading to the Lagoon.

3.1.2 Objectives

The objective of this task was to determine if physico-chemical characteristics of the sediments of the Indian River Lagoon show any pattern of seasonal changes. A secondary objective was to obtain a better estimate of average sediment properties by repeated seasonal sampling.

3.2 Materials and methods

3.2.1 Sediment sampling

Sediment sampling was performed similarly to that described in the spatial sampling. However, only surficial (0 – 10cm) depths were collected for analysis. Dates of sampling were June 20, 1997, September 6, 1997, December 28, 1997, and April 24, 1998. Stations were selected to encompass a range of seagrass densities and physical characteristics of sediments, while providing reasonable coverage of the lagoon. Sampling stations were the same as those used in the initial sediment spatial characterization (Table 3.1). Navigation to sampling stations was done using a GPS receiver equipped with a differential beacon receiver. Re-acquisition of individual sampling stations for each seasonal sampling event should therefore be accurate to within approximately 5m.

Intact sediment cores were obtained by driving a 7cm ID polycarbonate core tube into the sediment. Sediment samples were extruded in the field into 1L Ziploc™ (polyethylene) bags and immediately placed on ice. Each core was sectioned into a 0-10 cm depth interval.

3.2.2 Chemical fractionation

The sediments were processed as in the spatial sampling, with several modifications. There was no sequential sediment P fractionation performed. Also, dried and ground sediment was extracted for particulate inorganic P (PIP) with 1M HCL. The sediment to solution ratio was 1:50 and the sediments were extracted for 2h while continuously shaking.

3.2.3 Analytical methods

The analytical methods used in this study are given in Table 3.2.

Table 3.1. Geographic coordinates of sediment sampling stations visited in the spatial and temporal studies of the Indian River Lagoon Estuary sediments. SWS = Department of Soil and Water Science, COE = Department of Coastal and Oceanographic Engineering. Horizontal datum is North American Datum 1927 (NAD27).

SWS Station	COE Station	Latitude	Longitude
1	3c	27' 31.544'	80' 20.131'
2	5.5e	27° 41.455'	80° 23.354'
3	6.5a	27° 51.300'	80° 27.227'
4	7e	27' 51.476'	80'29.011'
5	9a	27° 58.576'	80° 31.842'
6	9c	27'58.524'	80'31.947'
7	11b	28° 03.397'	80° 34.237'
8	11c	28° 03.285'	80° 34.577'
9	11d	28° 03.217'	80° 34.761'
10	14b	28° 08.323'	80° 36.484'
11	14c	28° 08.188'	80° 36.927'
12	14d	28° 08.040'	80° 37.125'
13	21a	28° 27.769'	80° 43.600'
14	21b	28'27.728'	80'44.116'
15	23a	28° 35.386'	80° 44.753'
16	23c	28° 35.229'	80° 45.585'
17	23e	28° 35.031'	80' 46.573'
18	27a	28° 41.890'	80° 47.046'
19	27d	28° 42.918'	80° 48.356'
20	27e	28° 43.376'	80° 48.915'
21	27f	28° 43.710'	80° 49.354'
22	33c	28° 21.972'	80° 38.282'
23	36a	28° 45.399'	80° 44.209'
24	36c	28° 44.926'	80° 44.500'

Table 3.2. Analytical methods used for various physico-chemical parameters measured on IRL sediments.

Parameter	Reference
pH	Thomas, 1996.
Water Content	Gardner, 1986.
Bulk Density	Blake and Hartge, 1986.
Porewater Soluble P	EPA 365.1
Porewater Soluble Ammonium-N	EPA 350.1
Ash Content	Nelson and Sommers, 1996.
Total Carbon	Nelson and Sommers, 1996.
Total Nitrogen	Nelson and Sommers, 1996.
Total Phosphorus	Anderson, 1976
Phosphorus Fractionation	Reddy et al. 1998
KCl Extractable N	Mulvaney, 1996.
HCL Extractable Cations	Soltanpour, 1996.
Dissolved Organic Carbon	EPA 415.1
Dissolved Inorganic Carbon	EPA 415.1

3.2.4. Statistical methods

The mean values of each season were compared using ANOVA. Variances of each analyte and season were compared to determine if the standard deviations of each population (season) were not significantly different using Cochran' C test. Data were transformed when necessary to satisfy normality and equal variance requirements. Differences were judged significant at $p < 0.05$. All statistical comparisons were performed with the statistical software Statgraphics Plus (Manugistics Inc., Rockville, MD). Some outliers in the original data were removed prior to statistical analysis. Far outliers tend to bias the dataset and can be removed using tests for their presence. In this case, an observation was considered an outlier if it exceeded the value of the third quartile $(Q_3) + 3*(Q_3-Q_1)$ (Tukey, 1977). The outliers are as follows: NH_4-N – Station 1 September 1997 (34.04 ppm), Station 8 September 1997 (138.8 ppm) Station 9 September 1997 (71.26 ppm) and Station 21 September 1997 (96.15 ppm). Dissolved reactive P was natural log transformed prior to statistical analysis to satisfy normality and equal variance requirements. When specific sediment zones were compared, exchangeable ammonium N was square-root transformed.

3.3 Results and Discussion

When all stations are considered together, ammonium-N and DRP showed the most pronounced seasonal changes of all analytes examined (Table 3.3). The June and September 1997 samples were significantly higher in porewater NH_4-N than the December 1997 and the April 1998 samples, even with high outliers removed from the data. There was however no significant difference between the June and September 1997 samples or the December 1997 and the April 1998 samples with respect to porewater NH_4-N levels. Higher concentrations in summer and fall are probably due to increased rates of mineralization of sediment organic matter during the wanner summer and early fall period. This is similar to soil and sediment porewater biogeochemical cycles observed in the Florida Everglades (Koch-Rose et al., 1994) and Lake Apopka, FL (Gale et al., 1992).

It is also possible that the assumed seasonal differences observed in this study are at least in part due to short-range spatial variability. Even though precise GPS methods were used to re-locate sampling stations, small-scale differences of perhaps several meters possibly occurred from one sampling event to the next. Montgomery, et al. (1979) documented relatively high short-range spatial heterogeneity among porewater collection devices in Indian River Lagoon sediments near Link Port. In their study, porewater DRP and NH_4-N were found to vary by as much as 40% within a 1 m^2 area.

Porewater DRP was significantly higher in June 1997 than all other periods. There was no difference between the DRP levels in the September 1997, the December 1997, and the April 1998 surficial sediment samples.

Table 3.3. Statistical comparison of all seasonally collected surficial sediment samples (0-10cm) retrieved from the Indian River Lagoon Estuary.

Season	DRP	NH_4-N	DOC	HCl-P	1M KCl-N
June 1997	a	a	b	b	b
September 1997	b	a	b	b	b
December 1997	b	b	b	b	b
April 1998	b	b	b	b	b

a and b = no significant difference within seasons sharing this letter.

When the data are re-analyzed by sediment zone (northern, mud, and southern stations), there are fewer seasonal differences. For the mud zone (stations **8, 9,** and **11),** no significant seasonal differences for any of the analytes evaluated were observed. This is probably due to the low number of observations per season **(3)** and the large variability within each season. There were large apparent seasonal changes in many of the sediment characteristics at Station **8.** However, this station seemed to be near the interface between muddy and sandy sediments. In March and September of **1997** and April of **1998,** muddy sediments were found at this station. On the two other sampling occasions, sediments were considerably more sandy. Therefore, the seasonal changes seen at this station are probably due more to differences in physical sediment characteristics than to seasonal effects (Figs. **3.1 – 3.5).**

Ammonium-N was the only analyte in the southern region of the estuary to show any significant differences, with respect to season. Porewater ammonium-N concentration was higher in June **1997** than in either December **1997** or April **1998.** For the northern region, exchangeable ammonium-N (KCl extractable N) was significantly higher in December **1997** than in April **1998.** Adsorption of NH_4-N to the predominately sandy sediments in this region of the estuary has been shown to be minimal (This report – Chapter 5). Using an average porewater **NH_4-N** concentration (March **1997)** of **4.2** mg L^{-1} in the surficial sediments of the northern stations, the molar ratio of sodium to ammonium is approximately **1400. This** suggests that virtually all of the cation exchange capacity of these sediments is dominated by sodium. Thus, the high sodium concentration in the brackish estuarine waters likely reduces any significant adsorption of ammonium on the sediment exchange complex. It is unlikely that exchangeable NH_4-N represents a significant pool of nitrogen, except perhaps in periods of very low salinity. Seasonal changes in exchangeable NH_4-N may therefore be related to salinity changes in this region caused by seasonal freshwater inputs and/or periods of **high** evaporation. Porewater DRP concentration was significantly lower for the northern stations in June **1997** than in all other seasons, averaging **0.128 (±0.116)** mg **L^{-1}**. Neither the mud nor the southern stations showed any significant seasonal effects with respect to porewater DRP concentrations.

Analyses of total organic C, total N and total P showed little seasonal variability (Figures **3.3 – 3.5).** These represent more stable pools of sediment nutrients and thus only small seasonal changes are to be expected. Characterization of Indian River Lagoon sediments for total nutrient analyses is therefore not dependent on time of sampling. This has implications for further sediment characterization studies in that the results from a more comprehensive sediment sampling are independent of time of sampling with respect to total C, N, and P storages.

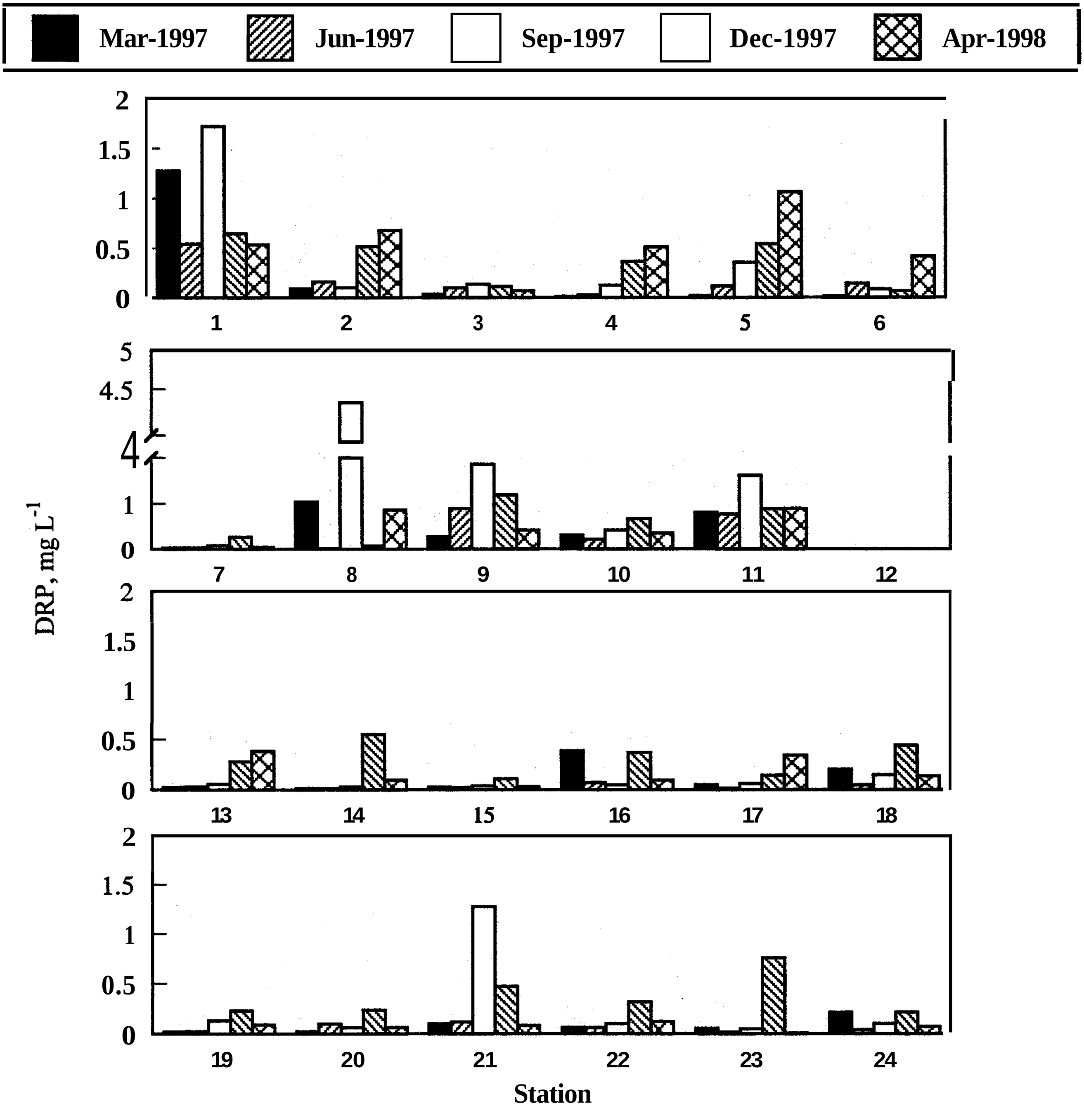

Figure 3.1. Seasonal changes in the porewater concentration of dissolved reactive P in the sediments of the Indian River Lagoon.

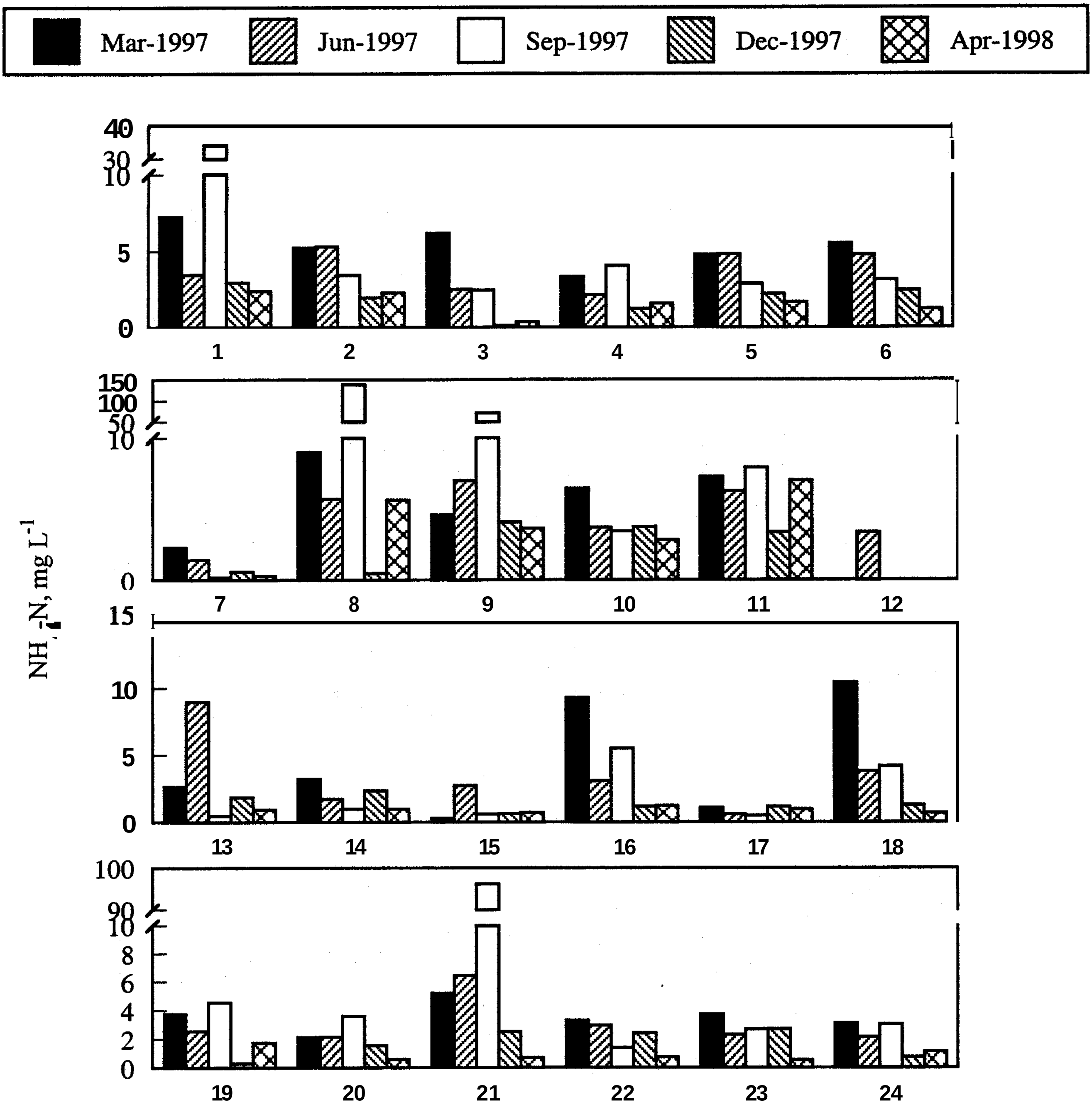

Figure 3.2. Seasonal changes in the porewater concentration of ammonium-N in the sediments of the Indian River Lagoon.

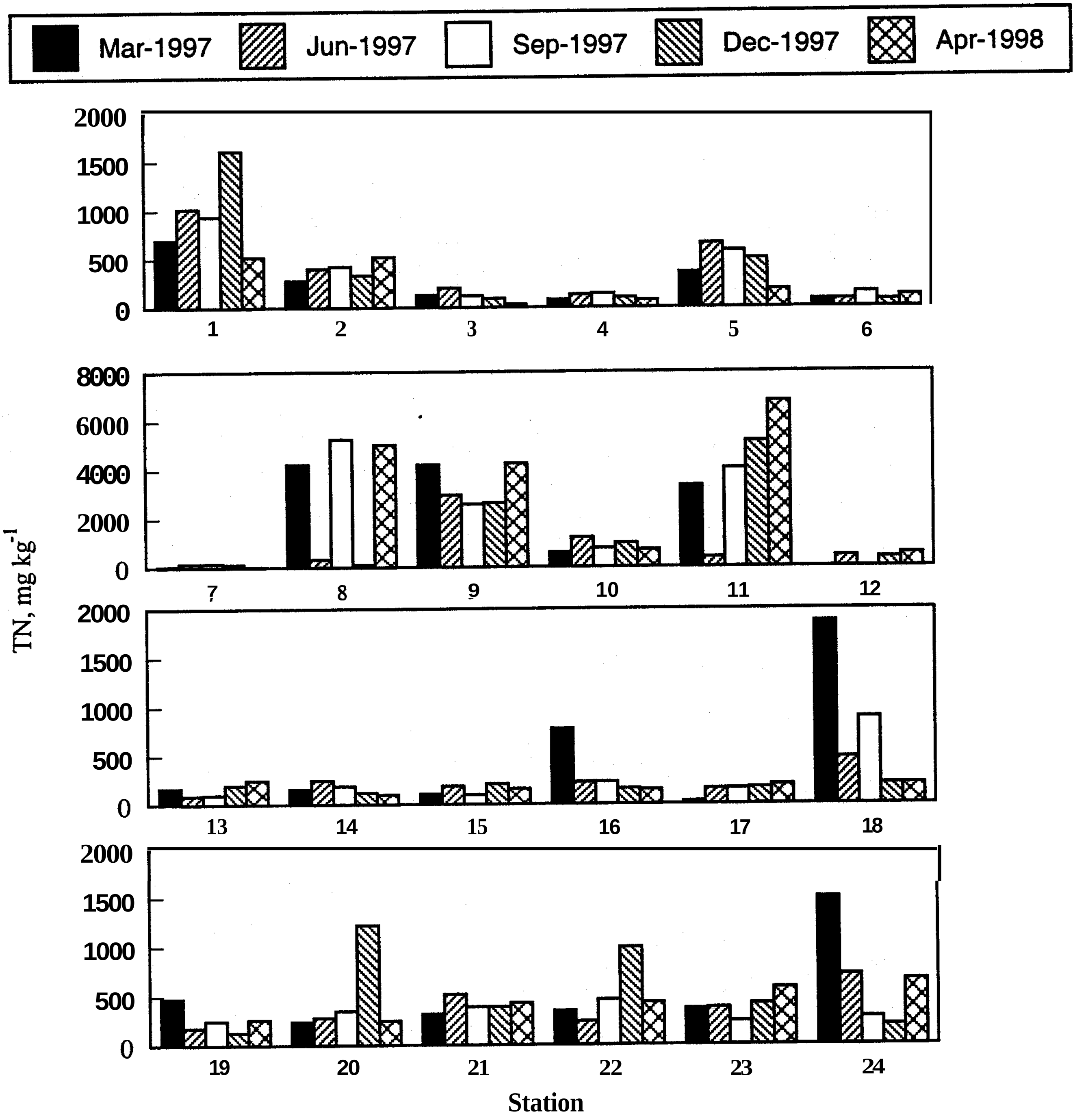

Figure 3.3. Seasonal changes in the total nitrogen content of the sediments of the Indian River Lagoon.

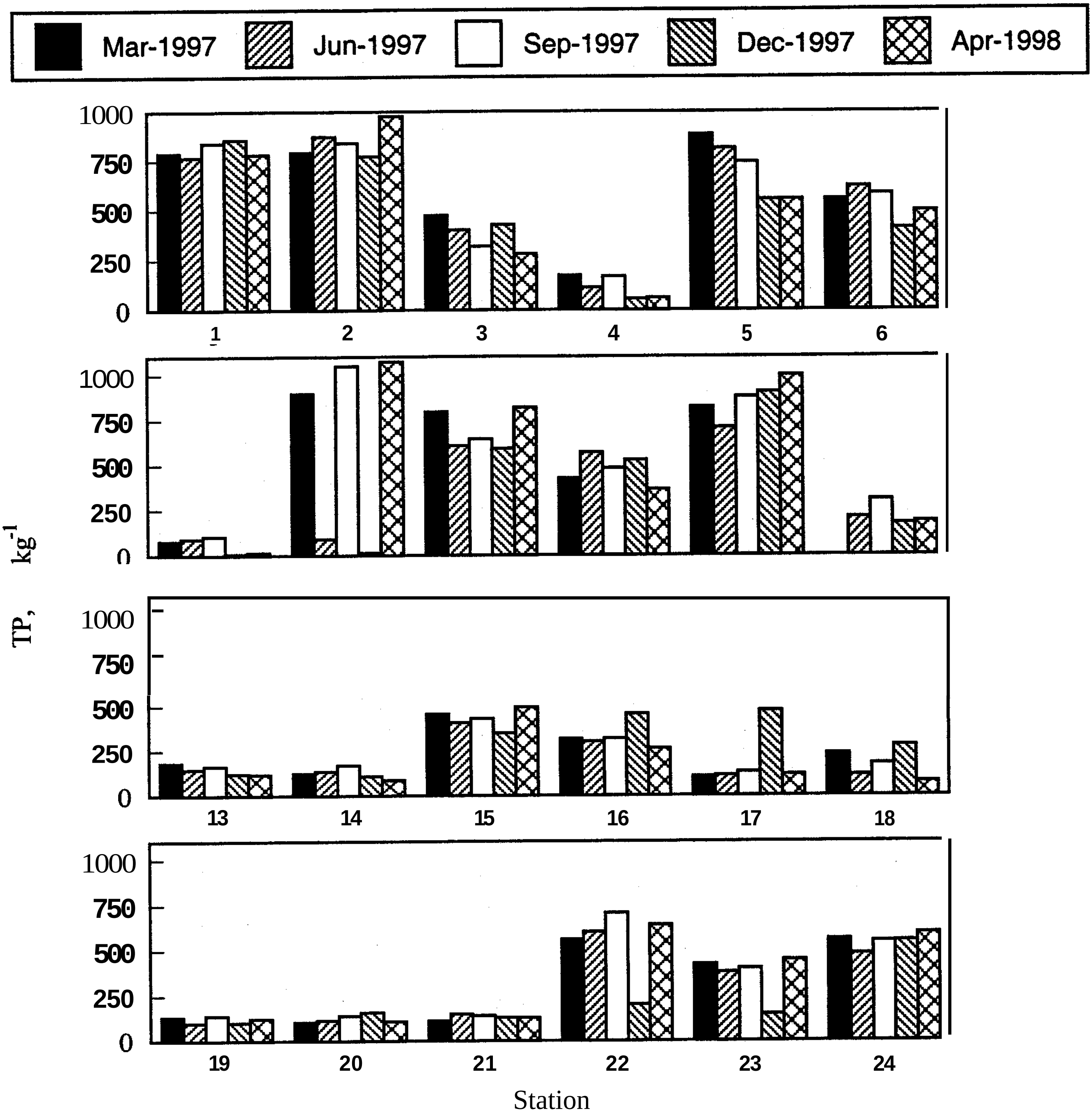

Figure **3.4.** Seasonal changes in the total phosphorus content **of** the sediments of the Indian River Lagoon.

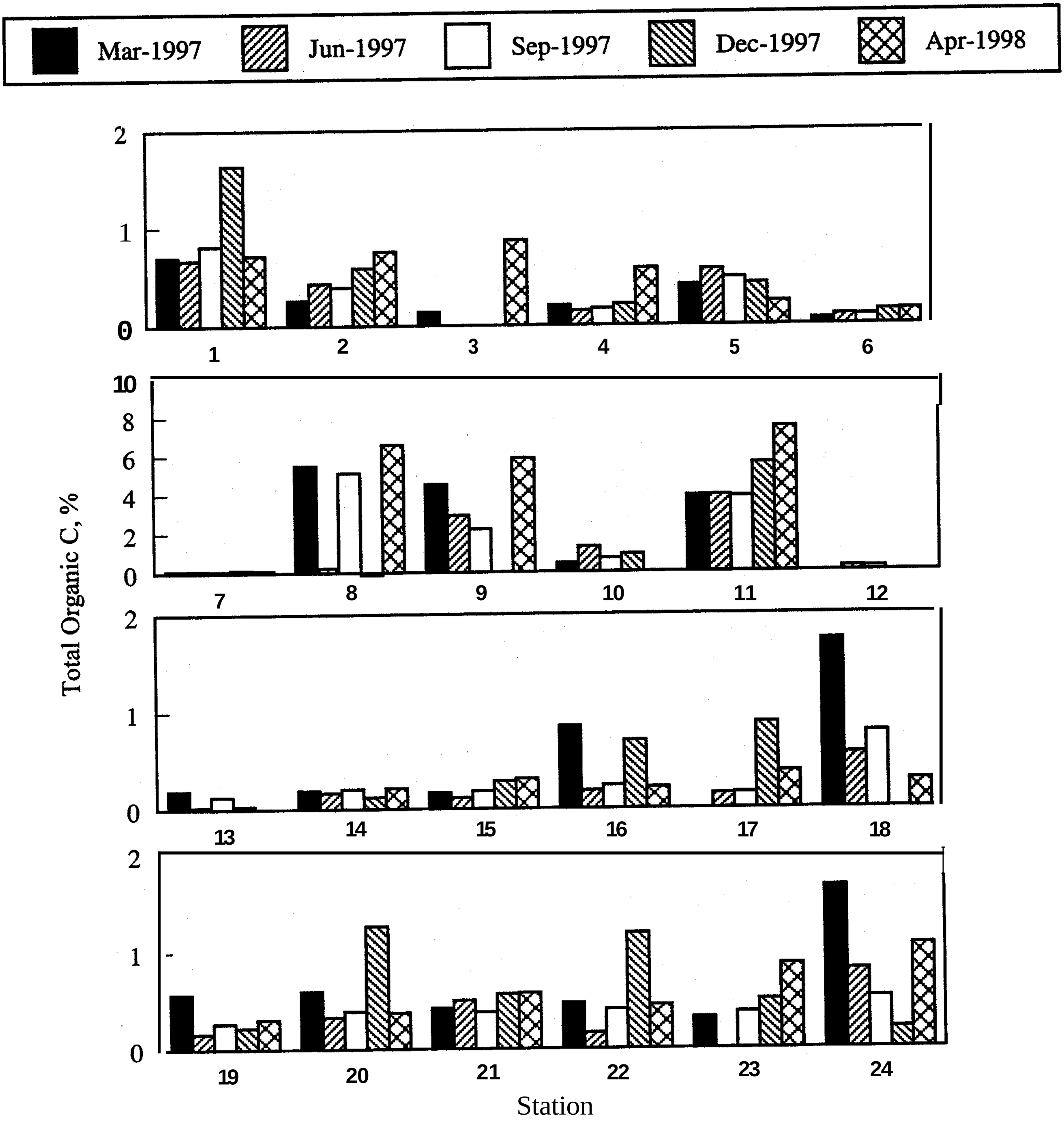

Figure 3.5. Seasonal changes in the total organic carbon content of the sediments of the Indian River Lagoon.

3.4 Seasonal averages

In all, the Indian River Lagoon sediments were sampled on five occasions, March **1997,** June **1997,** September **1997,** December **1997,** and April **1998.** Even though seasonal patterns were found to be largely insignificant, there were substantial differences between the sampling events. A single attempt at physico-chemical characterization of the sediments would therefore probably not approach the true mean value for most of the analytes measured in this study. Also, since most of the variation between seasons was not significant, the seasons can statistically be treated as replications, leading to a more accurate estimate of the true mean value of the sediment properties measured (Tables **3.4**-3.5).

Porewater NH_4-N ranged from a low of **0.11** mg L^{-1} to a maximum value of **138** mg L^{-1} at Station **8** in September of **1997.** All sediment zones (north, south, and mud) showed NH_4-N and DRP concentration maxima during this time period, though when considered individually, not all stations experienced concentration maxima during September. Approximately one third of the stations showed a pattern of increasing porewater concentration of both NH_4-N and DRP, from low in March, increasing to a maximum in September, then decreasing through April **1998.** This trend was particularly evident at the mud zone stations. Higher porewater nutrient concentrations at the end of the summer months are likely due to an increased rate of mineralization of sediment organic matter as a result of elevated water (and sediment) temperature. Porewater DRP ranged from **0.007** mg L^{-1} to a high of **4.427** mg L^{-1}, also at Station 8 during September of **1997.**

Dissolved organic carbon ranged from **106** mg L^{-1} at Station **13** in June of **1997** to **a** low of **4.7** at Station **4** in June **1997.** On average, DOC was lower in the mud zone **(22** mg L^{-1}) than the other two zones, even though total sediment organic carbon in this region was considerably higher, with an average TOC content of **4.1** %.

Total N content ranged from undetectable at Station **12** during September **1997** to a maximum of **6800** mg kg^{-1} at Station **11** in April **1998.** Sediments at Station **12** were composed almost entirely of shell fragments and typically had the highest total inorganic carbon content. Total P varied from a low of **10** mg kg^{-1} at Station **7** in December of **1997** to a high of **1074** mg kg^{-1} at Station 8 in April **1998.** However, all the mud zone stations in April of **1998** were quite similar with respect to TP content and were within approximately **200** mg kg^{-1} of one another.

Some lagoon-wide patterns were apparent with respect to nitrogen and phosphorus. Both total N and porewater NH_4-N were slightly higher at Station **1,** near Link Port and Fort Pierce Inlet. Stations **2** through **7** (slightly south of Sebastian Inlet to south Melbourne) were low in N; especially total N. The mud sediments in the Melboune area, Stations **8, 9,** and **11** were high both in terms of total N content and porewater NH_4-N. The stations between Melbourne and Titusville (Stations **13 –17)** were generally low in N. Station **18,** near the mouth of the Haulover Canal, was slightly higher in TN content than the rest of the stations along this transect (Stations **19 – 21).** Station **18** was located

Table 3.4a. Average of selected physico-chemical properties for the northern surficial Indian River Lagoon sediments observed for five sampling events.

	Depth	Water Content	Bulk Density	pH	NH_4-N	DRP	DOC
Station	(cm)	(%)	(g/cm^{-3})		———	(mg L^{-1})	———
13	0-10	21.86	1.59	8.07	2.98	0.16	40.7
14	0-10	22.32	1.56	8.12	1.86	0.14	25.4
15	0-10	24.15	1.56	8.10	1.00	0.05	19.7
16	0-10	25.86	1.47	8.11	4.07	0.21	21.5
17	0-10	22.90	1.54	8.15	0.69	0.14	17.0
18	0-10	36.22	1.16	8.09	4.12	0.15	48.3
19	0-10	25.91	1.52	8.23	3.02	0.15	22.9
20	0-10	28.52	1.40	8.23	2.17	0.11	19.1
21	0-10	26.56	1.48	8.21	22.24	0.47	33.9
22	0-10	26.55	1.46	8.27	1.83	0.11	34.2
23	0-10	30.15	1.36	8.08	2.16	0.03	26.2
24	0-10	33.96	1.26	8.05	2.00	0.10	37.6
Average		27.1	1.45	8.14	4.01	0.152	28.9
Std. Dev.		5.9	0.29	0.17	12.29	0.211	18.9
C.V.(%)		22	20	2	306	139	66
Max.		47.2	2.06	8.50	96.15	1.277	105.9
Min.		20.3	0.69	7.82	0.29	0.007	8.9

Table 3.4b. Average of selected physico-chemical properties for the central (mud zone) surficial Indian River Lagoon sediments observed for five sampling events.

	Depth	Water Content	Bulk Density	pH	NH_4-N	DRP	DOC
Station	(cm)	(%)	(g cm^{-3})		———	(mg L^{-1})	———
8		54.54	0.91	8.03	31.94	1.29	25.0
9		67.55	0.58	8.00	18.13	0.93	16.7
11		71.86	0.51	7.88	6.37	1.00	23.9
Average		64.6	0.66	7.97	18.81	1.069	21.9
Std. Dev.		18.8	0.47	0.26	38.48	1.095	8.5
C.V.(%)		29	71	3	205	102	39
Max.		79.6	1.52	8.30	138.83	4.427	43.3
Min.		19.6	0.23	7.54	0.48	0.017	11.4

Table 3.4c. Average of selected physico-chemical properties for the southern surficial Indian River Lagoon sediments observed for five sampling events.

	Depth	Water Content	Bulk Density	pH	NH_4-N	DRP	DOC
Station	(cm)	(%)	(g cm^{-3})		(mg L^{-1})		
1	(0-10)	38.26	1.09	7.94	10.04	0.95	37.6
2	(0-10)	26.99	1.41	8.36	3.66	0.31	24.9
3	(0-10)	16.83	1.79	8.35	2.33	0.09	18.5
4	(0-10)	19.87	1.69	8.19	2.48	0.21	22.2
5	(0-10)	27.06	1.43	8.06	3.28	0.42	23.9
6	(0-10)	21.88	1.63	8.13	3.44	0.15	21.7
7	(0-10)	18.71	1.72	8.00	0.98	0.09	22.2
10	(0-10)	39.28	1.14	8.27	4.05	0.40	17.7
12	(0-10)	29.50	1.21	8.19	3.37	0.14	9.0
Average		26.4	1.464	8.17	3.77	0.323	23.2
Std. Dev.		8.8	0.365	0.26	5.15	0.366	12.9
C.V.(%)		33	25	3	137	113	56
Max.		52.2	2.2	8.66	34.04	1.719	77.3
Min.		14.4	0.642	7.21	0.11	0.015	4.7

Table 3.5a. Average of selected physico-chemical properties for the northern surficial Indian River Lagoon sediments observed for five sampling events.

	Depth	TN	TP	HCl-P_i	TIC	TOC	TC
Station	(cm)	(mg kg^{-1})	(g cm^{-3})	(mg kg^{-1})	(g kg^{-1})		
13	0-10	162	147	106	0.17	0.09	0.26
14	0-10	164	125	112	0.23	0.18	0.41
15	0-10	154	428	395	1.22	0.22	1.44
16	0-10	320	296	268	0.82	0.22	1.04
17	0-10	136	114	104	0.19	0.17	0.36
18	0-10	934	153	112	0.39	0.93	1.32
19	0-10	312	125	100	0.17	0.37	0.54
20	0-10	422	135	97	0.27	0.58	0.80
21	0-10	416	136	94	0.24	0.48	0.72
22	0-10	336	613	568	0.59	0.34	0.93
23	0-10	474	438	400	2.62	0.53	3.15
24	0-10	800	562	495	1.53	1.06	2.59
Average		386	273	237	0.7	0.4	1.1
Std. Dev.		347	185	176	0.8	0.4	0.9
C.V.(%)		90	68	74	116	95	83
Max.		1870	707	591	4.1	1.7	4.5
Min.		30	77	77	0.0	0.0	0.1

Table 3.5b. Average of selected physico-chemical properties for the three Indian River Lagoon stations that were characterized by surficial deposits of mud. Values are average of five sampling events.

	Depth	TN	TP	HCl-P$_i$	TIC	TOC	TC
Station	(cm)	(mg kg^{-1})	(g cm^{-3})	(mg kg^{-1})	(g kg^{-1})		
8	0-10	3008	625	315	0.75	3.49	4.24
9	0-10	3354	692	421	3.72	3.93	7.65
11	0-10	3966	864	**544**	0.71	4.99	5.71
Average		3443	727	426	1.7	4.1	5.9
Std. Dev.		1980	319	171	1.7	2.2	2.4
C.V.(%)		58	44	40	100	53	40
Max.		6800	1074	579	5.2	7.5	8.3
Min.		110	14	52	0.3	0.00	0.9

Table 3.5c. Average of selected physico-chemical properties for the southern surficial Indian River Lagoon sediments observed for five sampling events.

	Depth	TN	TP	HCl-P$_i$	TIC	TOC	TC
Station	(cm)	(mg kg^{-1})	(g cm^{-3})	(mg kg^{-1})	(g kg^{-1})		
1	0-10	958	808	705	0.45	0.91	1.36
2	0-10	390	853	828	0.48	0.49	0.97
3	0-10	114	380	405	3.71	0.11	3.82
4	0-10	104	113	107	0.81	0.26	1.08
5	0-10	456	711	742	0.12	0.42	***0.55***
6	0-10	100	532	484	0.04	0.11	0.15
7	0-10	106	60	57	0.04	0.11	0.16
10	0-10	860	474	420	3.70	0.89	5.07
12	0-10	343	219	186	5.75	0.29	7.78
Average		382	467	437	1.3	0.4	2.1
Std. Dev.		363	290	280	1.8	0.4	2.5
C.V.(%)		95	62	64	138	98	118
Max.		1610	978	969	6.8	1.6	11.3
Min.		0	10	49	0.0	0.0	0.1

in a region of dense submerged aquatic vegetation. High average sediment TOC **(1.96%)** and low bulk density **(1.16** g cm^{-3}) suggest that decomposing vegetation may contribute to the somewhat elevated TN content at this station. Station **23** and **24,** located approximately 1000m east of the Haulover Canal, were similar in N content to the Stations 19 - **21.**

Total P showed very little seasonal effect. However, differences between stations and regions of the lagoon were striking. Stations **1** and **2** were relatively high in both TP and DRP. Stations **3** and **4,** in the vicinity of Sebastian Inlet and the San Sebastian River were low in P. Station 7 was lower in TP and DRP than any of the other stations. It is worth noting that Station 7 was lower in almost all sediment parameters than any other station within the lagoon. **The** average water content of the sediments at Station **7** was **19%**, indicating the very low porosity of fine, clean sand. Stations 8 – **11** were high in P forms and were very similar in TP content to Stations **1** and **2.** Stations **13 – 21** were similar in TP and **DRP** content, averaging approximately **150** mg kg^{-1} and 0.2 mg L^{-1}, respectively. Station **22** (Banana River) and Stations **23** and **24** (east of Haulover canal) were higher in TP content than the remaining stations in the northern lagoon, averaging approximately **400** mg kg^{-1}. It is unusual that TP content should vary dramatically from one side of the Haulover canal to the other, when **TN** levels **are** constant.

Indian River Lagoon sediments are similar in many respects to sandy sediments underlying the western side of Lake Okeechobee, Florida (Table **3.6). Bulk** density, total carbon content and results of the fractionation of sediment P **are** quite comparable, while the total nitrogen content of the lagoon sediment is dramatically lower. Also, the N : P ratio of Lake Okeechobee sand sediments approaches 10 **:1,** whereas the lagoon sediment N : P ratio is closer to **1** : **1.** This could be due to the nature of the allochthonous material entering both systems and may also suggest a long-term N limitation in the lagoon system.

3.4 Conclusions

Porewater NH_4-N and DRP showed some effect of season. When all stations are analyzed together, concentrations were significantly higher in the warmer summer months (June and September). When the stations are subdivided by sediment zone, north, mud and south, there are fewer significant differences with respect to season. This may due to the small number of stations (replications) for any one region and the high inherent small-scale spatial variability of these sediments. When the data are analyzed by sediment zone, porewater NH_4-N levels observed in the sediments of the southern stations were significantly higher for the summer sampling. Also, exchangeable N in the northern region was significantly higher in the winter, though the reason for this is unclear.

Table 3.6. A comparison of selected properties of the Indian River Lagoon (IRL) and Lake Okeechobee sand zone sediments. Values for the IRL are the average of five seasonally collected samples. Values for Lake Okeechobee are the result of a synoptic sediment characterization performed in the summer of 1988 (Reddy, et al., 1991). Values reported for the IRL NaOH-P_x are the result of fractionation performed on the March 1997 samples only.

Location	Bulk Density	TN	TP	HCl-P_i	NaOH-P_i	NaOH-P_o	TC
	g cm^{-3}	mg kg^{-1}					%
Northern IRL	1.45	386	273	237	4.8	5.9	1.13
Southern IRL	1.09	381	461	437	3.5	4.6	2.07
L. Okeechobee	0.81	1844	204	98	7.0	10	2.14

Considerable variability was seen between seasonal sampling events. Some of the variability is due to changing temperature regimes throughout the year, while an additional component of the overall variability probably is a result of small-scale spatial variability. In contrast to the sometimes large differences observed in porewater chemistry, TN, TP, and TC content at most stations was relatively constant.

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Appendix 3.2b. Selected properties of surficial **Indian** River **Lagoon** sediments in September 1997.

	Depth	PIP	POP	TP	PIN	PON	TN	TIC	TOC	TC
Station	(cm)		(mg/kg)			(mg/kg)			(g/kg)	
I-1	0-10	680	161	841	6.12	934	940	4.53	8.10	12.6
1-2	0-10	807	36	843	7.83	412	420	5.46	3.89	9.4
1-3	0-10	449	ND	318	3.64	116	120	55.65	-2.97	52.7
I-4A	0-10	110	57	167	2.01	138	140	5.27	1.65	6.9
I-4B	0-10	120	52	172	3.41	117	120	8.19	0.70	8.9
I-4C	0-10	104	102	206	3.41	77	80	4.44	0.91	5.4
1-5	0-10	799	ND	744	9.31	571	580	0.81	4.82	5.6
1-6	0-10	611	ND	582	1.61	148	150	0.40	0.94	1.3
1-7	0-10	61	43	104	2.35	158	160	0.65	0.93	1.6
I-8	0-10	52	997	1049	NA	5498	5280	2.70	51.15	53.9
I-9	0-10	386	260	646	NA	2635	2600	51.75	22.05	73.8
1-10	0-10	490	ND	482	9.24	761	770	39.71	6.81	46.5
I-11	0-10	497	382	879	63.98	4016	4080	11.27	38.62	49.9
1-12	0-10	164	144	308	6.98	#N/A	#N/A	47.00	1.94	48.9
1-13	0-10	96	68	164	2.55	97	100	1.04	1.26	2.3
1-14	0-10	105	66	171	2.20	188	190	3.32	2.04	5.4
1-15	0-10	449	ND	430	3.06	97	100	12.25	1.82	14.1
1-16	0-10	324	ND	318	2.97	227	230	3.94	2.36	6.3
1-17	0-10	82	50	132	1.89	158	160	1.91	1.58	3.5
I-18A	0-10	105	73	178	7.73	882	890	7.27	7.88	15.2
I-18B	0-10	86	95	181	6.77	1113	1120	7.09	11.98	19.1
I-18C	0-10	82	76	158	5.46	765	770	6.75	8.15	14.9
1-19	0-10	88	53	141	3.42	247	250	1.76	2.67	4.4
1-20	0-10	#N/A	#N/A	140	2.79	347	350	3.22	3.88	7.1
1-21	0-10	347	ND	141	-9.90	400	390	2.73	3.78	6.5
1-22	0-10	418	289	707	2.49	458	460	4.97	4.03	9.0
1-23	0-10	479	ND	400	6.43	234	240	25.05	3.72	28.8
1-24	0-10	477	74	551	4.89	275	280	13.67	5.26	18.9

Appendix 3.3a. Selected properties of surficial Indian River **Lagoon** sediments in December 1997. Nitrate was not detected in sediment porewater.

	Depth	Water Content	**Bulk** Density	pH	NH_4-N	**DRP**	**DOC**
Station	(cm)	(%)	(g/cm^3)			mg L^{-1}	
I 1	0-10	52.19	0.642	7.70	2.98	0.648	14.9
I 2	0-10	28.09	1.233	8.15	1.98	0.517	24.9
I 3	0-10	17.53	1.65	8.45	0.11	0.113	17.5
I 4	0-10	18.63	1.617	8.10	1.23	0.368	29.6
I 5	0-10	23.60	1.378	8.20	2.23	0.542	21.8
I 6	0-10	18.14	1.615	8.15	2.48	0.069	40.2
I 7	0-10	16.89	1.641	7.95	0.61	0.268	14.8
I 8	0-10	19.60	1.515	8.30	0.48	0.081	18.8
I 9	0-10	60.95	0.486	8.15	4.10	1.188	11.4
I10	0-10	43.04	1.011	8.20	3.76	0.670	18.7
I11	0-10	73.40	0.330	7.85	3.37	0.886	21.4
I12	0-10	27.60	1.076	8.29	No porewater		
I13	0-10	21.57	1.555	7.90	1.85	0.281	23.0
I14	0-10	21.26	1.492	8.05	2.35	0.548	22.9
I15a	0-10	25.21	1.515	8.03	0.64	0.109	26.3
I15b	0-10	24.54	1.476	8.24	1.17	0.370	19.9
I15c	0-10	24.20	1.534	8.18	1.17	0.144	18.5
I16	0-10	24.24	1.474	8.12	1.26	0.441	36.4
I17	0-10	21.73	1.533	8.25	0.30	0.231	21.3
I18	0-10	42.59	0.958	7.89	1.55	0.237	20.7
I19	0-10	26.44	1.452	8.18	2.51	0.473	21.9
I20	0-10	39.83	1.016	7.82	2.41	0.318	17.8
I21	0-10	25.57	1.417	8.05	2.70	0.759	24.4
I 22	0-10	24.99	1.319	8.2	0.73	0.218	28.3
I23a	0-10	38.69	0.996	7.86	1.55	0.023	19.0
I23b	0-10	28.01	1.400	7.82	2.80	0.040	28.2
I23c	0-10	23.68	1.458	8.02	2.41	0.023	27.6
I24	0-10	36.37	1.052	7.85	0.59	0.069	26.4

Appendix 3.3b. Selected properties of surficial Indian River Lagoon sediments in December 1997.

	Depth	PIP	POP	TP	PIN	PON	TN	TIC	TOC	TC
Station	(cm)		(mg/kg)			(mg/kg)			(g/kg)	
I1	0-10	738	120	858	24.2	1586	1610	4.10	16.39	20.5
I2	0-10	859	-86	773	10.8	319	330	3.28	5.85	9.1
I3	0-10	527	-100	426	2.0	88	90	26.18	-1.24	24.9
I4	0-10	49	6	54	3.8	96	100	5.14	2.10	7.2
I5	0-10	521	34	554	7.0	493	500	1.51	4.21	5.7
I6	0-10	329	80	409	4.3	66	70	0.38	1.42	1.8
I7	0-10	50	-40	10	3.9	126	130	0.30	1.45	1.8
I8	0-10	130	-116	14	6.3	104	110	10.55	-1.25	9.3
I9	0-10	388	205	593	1.6	2658	2660	50.99	31.65	82.6
I10	0-10	400	127	528	4.4	986	990	35.96	9.00	45.0
I11	0-10	586	320	906	41.3	5139	5180	5.08	55.95	61.0
I12	0-10	146	29	174	9.9	370	380	#N/A	#N/A	#N/A
I13	0-10	77	44	122	4.2	196	200	3.60	0.30	3.9
I14	0-10	95	13	108	3.1	117	120	0.41	1.21	1.6
I15a	0-10	321	29	350	3.5	207	210	15.57	2.85	18.4
I15b	0-10	494	-38	457	3.3	157	160	10.83	7.01	17.8
I15c	0-10	482	-7	475	1.4	169	170	5.43	8.85	14.3
I16	0-10	253	28	281	2.0	208	210	12.77	-4.18	8.6
I17	0-10	114	-12	103	1.3	129	130	1.31	2.20	3.5
I18	0-10	124	35	159	5.5	1215	1220	4.46	12.64	17.1
I19	0-10	109	21	130	1.1	389	390	1.81	5.65	7.5
I20	0-10	126	77	203	8.8	981	990	1.14	11.88	13.0
I21	0-10	99	49	148	2.8	417	420	1.66	5.05	6.7
I22	0-10	516	38	554	3.5	197	200	6.03	2.08	8.1
I23a	0-10	505	31	536	7.3	793	800	15.17	10.74	25.9
I23b	0-10	490	14	505	6.9	443	450	19.72	4.89	24.6
I23c	0-10	423	42	466	3.8	376	380	21.50	4.12	25.6
I24	0-10	588	29	617	7.0	843	850	10.71	10.87	21.6

Appendix 3.4a. Selected properties of surficial Indian River Lagoon sediments in April 1998.

	Depth	Water Content	Bulk Density	pH	NH_4-N	DRP	DOC
Station	(cm)	(%)	(g/cm^3)		(mg/L)		
I-1	0-10	28.6	1.83	7.90	2.408	0.537	18.08
1-2	0-10	26.8	1.87	8.10	2.303	0.679	16.44
1-3	0-10	15.7	2.19	7.94	0.366	0.072	6.19
I-4	0-10	20.6	2.03	7.73	1.570	0.511	22.81
I-5A	0-10	23.0	1.87	7.21	1.675	1.066	14.86
I-5B	0-10	22.5	1.98	7.41	2.617	0.808	13.86
I-5C	0-10	24.3	2.01	8.17	1.431	0.472	23.12
1-6	0-10	22.6	2.09	7.99	1.222	0.420	10.04
1-7	0-10	17.0	2.09	7.92	0.314	0.052	13.30
I-8	0-10	75.4	1.20	7.54	5.654	0.860	18.47
I-9	0-10	73.1	1.23	7.64	3.664	0.420	14.56
1-10	0-10	34.9	1.69	8.08	2.827	0.356	11.78
1-11	0-10	76.7	1.15	7.54	7.015	0.894	26.21
1-12	0-10	27.5	1.53	7.89	0.000	#N/A	#N/A
1-13	0-10	22.8	1.99	7.96	0.942	0.382	25.41
1-14	0-10	22.6	2.06	8.05	0.977	0.097	16.00
1-15	0-10	24.7	1.95	7.88	0.724	0.033	8.92
1-16	0-10	22.4	2.00	7.85	1.222	0.097	15.71
1-17	0-10	22.3	1.90	8.04	0.960	0.343	14.79
I-18A	0-10	24.3	1.86	8.37	0.681	0.136	16.69
I-18B	0-10	25.2	1.86	8.21	0.977	0.330	15.57
I-18C	0-10	35.8	1.55	7.76	2.513	0.110	66.65
1-19	0-10	23.5	1.91	8.40	1.727	0.091	13.96
1-20	0-10	24.9	1.93	8.23	0.576	0.065	22.39
1-21	0-10	27.2	1.85	8.31	0.698	0.084	16.81
1-22	0-10	26.8	1.85	7.98	0.733	0.123	51.76
1-23	0-10	32.9	1.72	7.95	0.523	0.007	41.96
1-24	0-10	29.9	1.82	7.91	1.134	0.072	60.54

Appendix 3.4b. Selected properties of surficial Indian River Lagoon sediments in April 1998.

	Depth	PIP	POP	TP	PIN	PON	TN	TIC	TOC	TC
Station	(cm)		(mg/kg)			(mg/kg)			(%)	
I-1	0-10	713	70	783	2.0	518	520	0.33	0.71	1.04
1-2	0-10	843	135	978	3.8	516	520	0.44	0.75	1.20
1-3	0-10	380	-101	279	0.4	30	30	2.61	0.87	3.47
1-4	0-10	149	-89	60	0.9	69	70	0.94	0.58	1.51
I-5A	0-10	969	-414	**555**	1.4	179	180	0.04	0.24	0.27
I-5B	0-10	944	-195	749	4.3	196	200	0.04	0.25	0.29
I-5C	0-10	759	-140	619	2.1	418	420	0.05	0.51	0.56
1-6	0-10	518	-23	495	0.8	119	120	0.03	0.15	0.18
1-7	0-10	54	-38	16	5.1	25	30	0.03	0.11	0.14
1-8	0-10	519	**555**	1074	29.4	5021	5050	1.01	6.57	7.59
I-9	0-10	485	334	819	20.1	4260	4280	1.85	5.86	7.71
1-10	0-10	372	-7	365	3.4	707	710	**#N/A**	**#N/A**	7.00
I-11	0-10	579	420	999	52.0	6748	6800	0.35	7.45	7.81
1-12	0-10	219	-34	185	1.0	549	550	**#N/A**	**#N/A**	11.28
1-13	0-10	134	-16	118	0.9	249	250	**#N/A**	**#N/A**	0.23
1-14	0-10	119	-32	87	4.1	96	100	0.29	0.21	0.50
1-15	0-10	440	54	494	0.6	159	160	1.01	0.31	1.32
1-16	0-10	253	9	262	0.3	150	150	1.22	0.22	1.44
1-17	0-10	121	-4	117	0.6	199	200	0.11	0.38	0.49
I-18A	0-10	105	-28	77	0.4	210	210	0.33	0.29	0.62
I-18B	0-10	138	281	419	0.5	249	250	0.16	0.44	0.60
I-18C	0-10	134	46	180	3.5	1036	1040	0.18	1.22	1.40
1-19	0-10	110	13	123	1.0	259	260	0.17	0.31	0.48
1-20	0-10	98	11	109	1.9	248	250	0.30	0.37	0.68
1-21	0-10	101	28	129	2.7	427	430	0.28	0.57	0.85
1-22	0-10	576	65	**641**	2.3	428	430	0.49	0.45	0.94
1-23	0-10	360	88	448	4.5	575	580	1.99	0.87	2.86
1-24	0-10	475	121	596	5.1	655	660	1.46	1.07	2.52

CHAPTER4
NUTRIENT EXCHANGE BETWEEN SEDIMENT AND OVERLYING WATER COLUMN
[Task **6.5** *as per the contract]*

4.1 Introduction

Estuarine sediments can function as sources or sinks for nitrogen (N) and phosphorus (P) to the overlying water column. Wind-induced mixing in estuaries can increase nutrient exchange across the sediment-water interface. The nutrient exchange is attributed to i) steady diffusive flux resulting from porewater concentration gradients established across the sediment-water interface and ii) wind-induced sediment resuspension into water column and subsequent nutrient release by suspended parties.

This has implications for environmental managers in that sediments underlying these ecosystems can potentially supply nutrients in excess of external, anthropogenic loading. Therefore, quantification of the magnitude of nutrient flux, especially N and P, from sediments can suggest the relative importance of controlling either internal or external nutrient loading.

Several methods have been used to determine the magnitude and direction of nutrient flux from sediments to the overlying water column. Physical law-based models of solute flux, such as Fick's First Law of Diffusion rely on close-interval estimation of porewater concentration gradients (Berner, 1980). The gradients are typically measured using finely sliced sediment samples or by using porewater equilibration devices (D'Angelo and Reddy, 1994a; Moore et al., 1998). Nutrient flux can also be determined using more direct approaches, such as by observing changes in water column concentrations inside *in situ* benthic chambers, or by measuring changes in water column concentrations in intact, incubated soil and sediment cores (Moore et al., 1998). The results from these approaches to flux measurement can be combined to provide a better estimate of the functional role of the sediments as a regulator of the overlying water quality. The three techniques have been combined and compared in a wide variety of ecosystems; in lakes (Sinke et al., 1990), open ocean (Devoe, 1987) nearshore marine (Hopkinson, 1987), and estuarine (Callender and Hammond, 1982) ecosystems. It is important to quantify the magnitude of this internal source of nutrient loading because it may maintain eutrophic conditions, even when external loads to an ecosystem are curtailed.

The objective of this study was to estimate the rate of nutrient exchange (NER) or flux of N and P from the sediment to the overlying water column.

4 2 Materials and Methods

4.2.1 Study site and sampling locations

Nutrient exchange rates were measured during May 1997, June 1998, May 1999, and December 1999 using two methods: Intact sediment cores and porewater equilibrators. Equilibrators and intact sediment cores were used to estimate the NER at a site approximately 5 km south of Melbourne during May 1997, approximately 13 km north of Sebastian Inlet in June 1998, and 10 km north of Titusville in May and December 1999. (Table 4.1) (Fig. 4.1). The 1997 NER site was located approximately 4 km south of the existing seasonal stations 7, 8, and 9 and within a few kilometers of stations 5 and 6 in the 1998 NER study. All locations coincided with the UF Coastal and Oceanographic Engineering episodic sites.

4.2.2 Intact sediment cores

Acrylic cores measuring 15.25 cm (6") ID by 50 cm in were used for the intact core study in 1997 and 1998. The cores for the two 1999 studies were polycarbonate 7 cm ID tubes. We found that the smaller polycarbonate tubes could be driven further into the sands that underlie most of the estuary. The cores were carefully driven into the sediment surface by a diver, capped on the bottom and top, and withdrawn from the sediment. The sediment cores were then returned to the laboratory and placed into a water bath. The overlying water was removed and filtered through 0.45μm filters and replaced. Approximately 20 cm of sediment was retrieved during both periods. The water column was treated with 0.033 g N-Serve per liter of floodwater for the June 1998 and the 1999 NER experiments. N-Serve is a nitrification inhibitor that prevents the formation of nitrate and subsequent diffusion into and denitrification losses in the sediment. The cores were kept in kept in the dark and were continuously bubbled with ambient air to maintain aerobic water column conditions. The experimental period lasted 14 days. Dissolved reactive P, NH_4-N, NO_3-N, (1998 only) dissolved O_2 , pH, and temperature were then measured for a period of two weeks.

4.2.3 Porewater equilibrators

Porewater equilibrators are a device commonly used to measure porewater vertical gradients of soluble species (Hesslein, 1976). The equilibrators are constructed of clear Lexan™ and have $8 cm^3$ chambers arranged vertically at an offset distance of 1 cm. The chambers were filled with deionized water, covered with a permeable 0.45 μm pore size membrane and then purged of all dissolved O_2 with N_2 gas. They were then taken to the field site, driven into the sediment, and withdrawn after an equilibration period of approximately two weeks. The cells were immediately sampled with a syringe. The samples were acidified with trace-metal grade H_2SO_4 and kept frozen until analyzed.

Table 4.1.Geographic location of the field experiments used to determine the nutrient exchange rates in the Indian River Lagoon Estuary. All coordinates are referenced to the North American Datum of 1927 (NAD27).

Station	Latitude	Longitude
May 1997		
Station A	27' 58.907'	80' 32.173'
Station B	27' 57.488'	80' 31.604'
Station C	27' 56.331'	80° 31.560'
June 1998		
Station A	27' 58.907'	80' 32.173'
Station B	27' 57.448'	80' 31.604'
Station C	27' 56.331'	80° 31.560'
May and December 1999		
Station A	28'41.117'	80'48.411

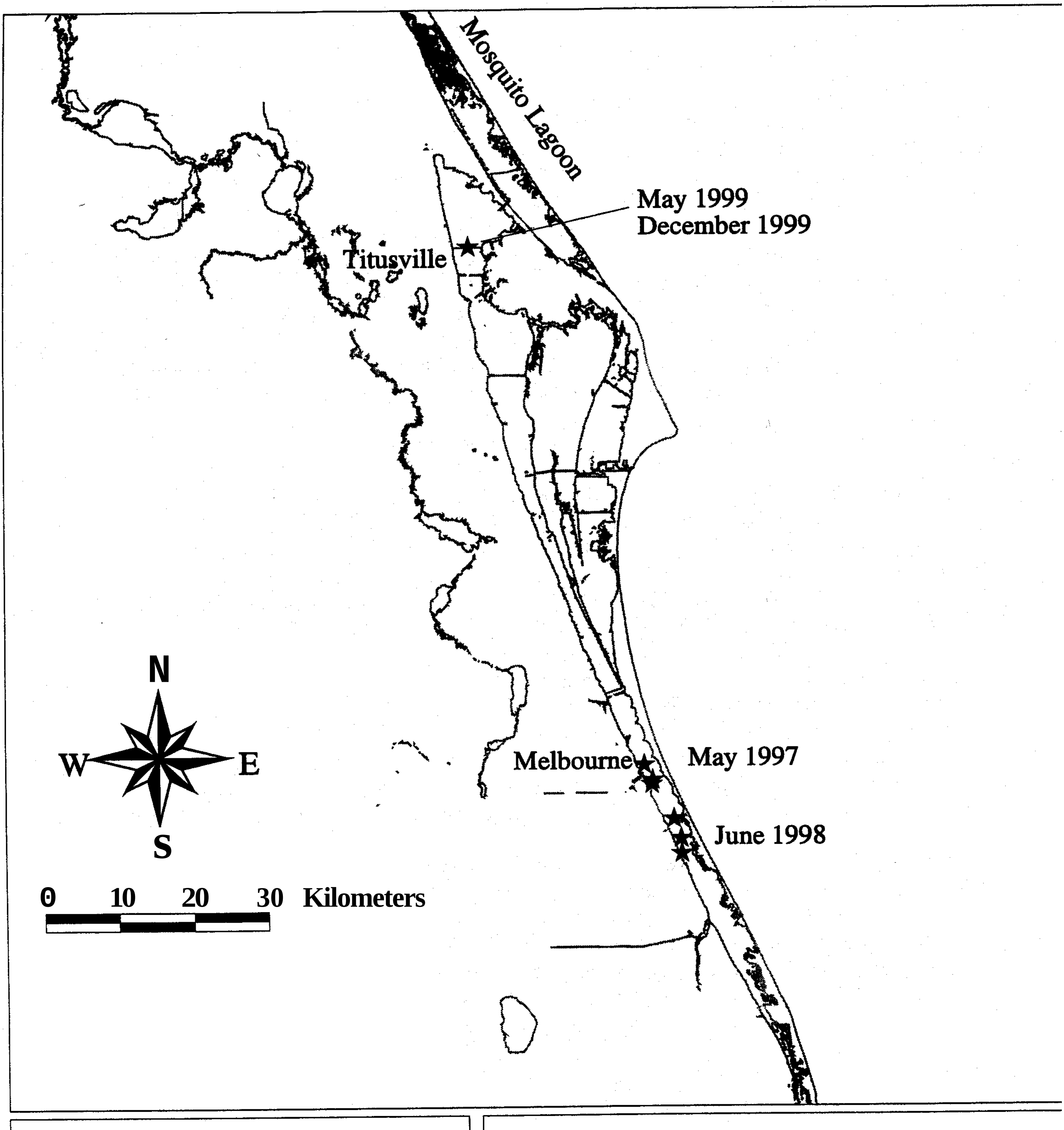


Figure 4.1. Location of the porewater equilibrato and intact core experiments.

The porewater equilibrators were deployed at all stations at the same time that the intact cores were retrieved. Seagrass coverage at the May 1997 stations was very low to non-existent. Seagrass coverage at Station A and B for the June 1998 study was high. Station C had no rooted seagrass, however there was significant drift algae, possibly *Gracilaria spp.* The 1999 study site had little or no seagrass present. Duplicate equilibrators and triplicate cores were used at each station in May 1997. Triplicate equilibrators were used at Station A in June 1998 and single equilibrators at the remaining stations. Triplicate equilibrators were used for the 1999 studies. All replicated equilibrators were placed within 0.5-m of each other. A Hydrolab DataSonde 3 (Hydrolab Corp., Austin TX) was installed for the two-week period that the porewater equilibrators were in place. The station designations were the same as those used by the Department of Coastal and Oceanographic Engineering at University of Florida.

4.2.4 Sediment Resuspension Experiments

Duplicate intact sediment cores were obtained on December 4, 1999 from a site located 10 km north of Titusville (28° 41.117' N. Lat., 80° 48.411' W. Long.) (Fig. 4.1). One intact sediment core overlain with 30 cm of water was used as a control, while the second core was used to simulate resuspension of surface sediments. Sediment resuspension was generated in Plexiglas cylinders (6.35 cm i.d., and 60 cm long) by oscillating grids (Fig. 4.2), an experimental setup similar to that described by Wolanski et al., (1989). Using this apparatus and an orbital speed of 180 rpm, the surface 0.5-cm of sediment was resuspended into the water column for 1 hour. During this period, water samples were obtained at the end of one hour resuspension and filtered through a 0.45 μm membrane filter. After one hour, sediment resuspension was stopped, and suspended sediment particles were allowed to settle. During sediment settling, water samples were obtained at selected time intervals for a period of 24 hours and analyzed for SRP, TP, NH_4-N and TKN using standard methods.

Sediment cores not used in resuspension experiments were sectioned into 0.5 cm depth increments to determine N and P gradients in the top 10 cm sediment. Particulate inorganic N (PIN) was determined by extracting sediments with 2 M KCl, followed by analysis of extracts for NH_4-N. Particulate organic N (PON) was determined from the difference between total N and PIN. Particulate inorganic P (PIP) was determined by extracting sediments with 1M HCl, followed by analysis of extracts for P. Particulate organic P (POP) was determined from the difference between total P and PIP.

4.2.5 Calculations

The NER was calculated using two techniques; vertical porewater concentration gradients and observed changes in the floodwater of intact sediment cores. Exchange rates were calculated from the concentration gradients measured with porewater equilibrators using Fick's First Law of Diffusion, which states that

$$J_i = \phi * D_s * \frac{\partial C}{\partial z} * 8.64(10^5)$$

Sediment Suspension Device

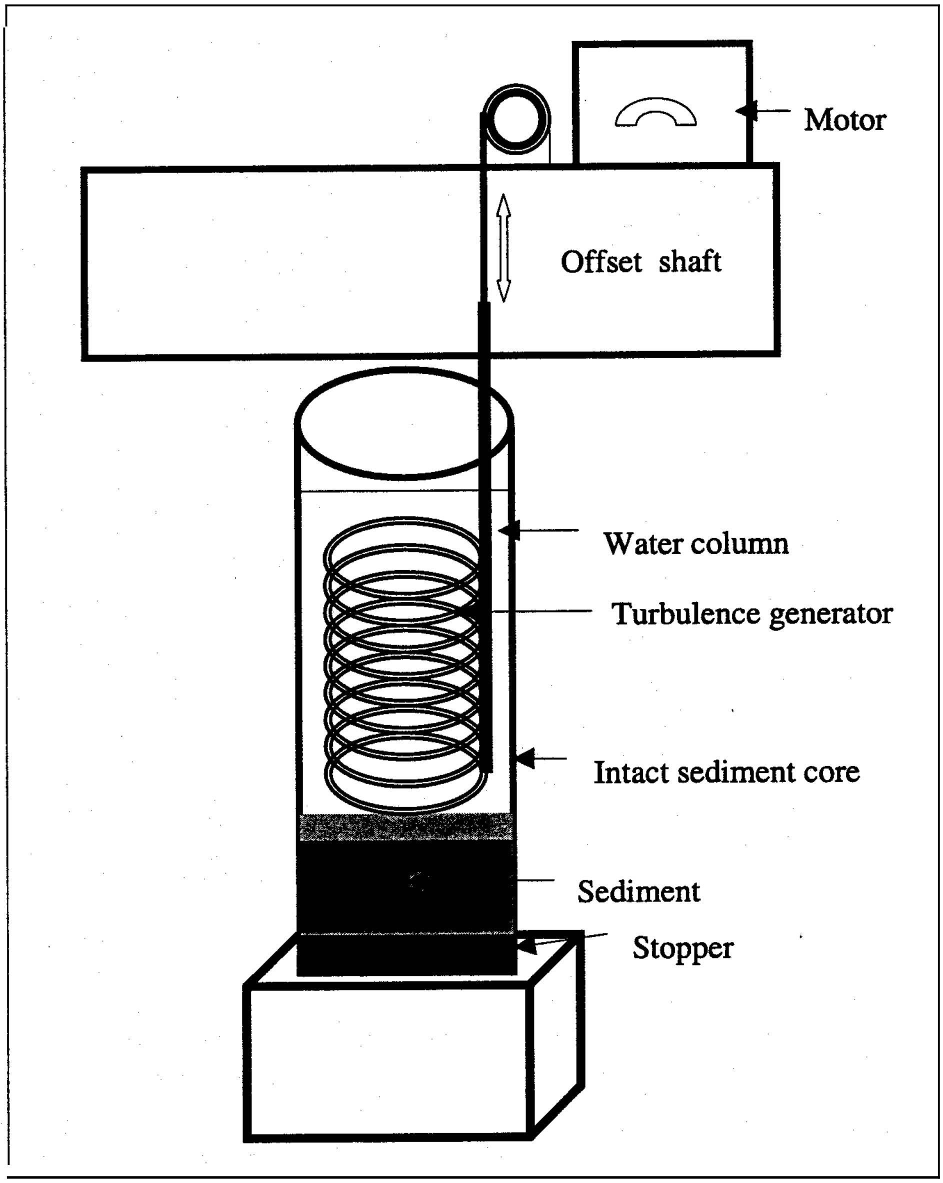


Figure 4.2. Experimental set-up used in sediment resuspension studies.

where

J = diffusive flux of component i, mg m $^{-2}$day^{-1}

ϕ = sediment porosity, cm^{3}cm^{-3}

D_S = sediment diffusion coefficient, cm^2 sec^{-1}

$\frac{\partial C}{\partial Z}$ = porewater concentration gradient, μg cm^{-4}

8.64(10^5) = **units** conversion

The average pH in the upper 10 cm of sediment during the **1997 NER** experiment was **7.8,** in the **1998** experiment, **7.6,** and in the **1999** experiments **7.7.** This was used to determine the diffusion coefficient in water. Since the speciation of the various forms of soluble P is pH dependent, **an** interpolated value of D_0 **was** used.

$$HPO_4^{2-} + H' \leftrightarrow H_2PO_4^{2-};\ Log\left(\frac{1}{K_a}\right)$$

Therefore, at an average porewater pH of 7.2 there should be approximately equal concentrations of HPO_4^{2-} and $H_2PO_4^{2-}$. Li and Gregory **(1974)** reported the diffusion coefficients of HPO_4^{2-} and $H_2PO_4^{-}$ in pure water **as 7.34 (10^{-6})** and **8.46 (10^{-6})** cm^2 sec^{-1}, respectively. At the pH of the study sites given above, the ratio of HPO_4^{2-} to $H_2PO_4^{2-}$ approaches one. Therefore, an average of the diffusion coefficients for the two species was used in the calculation of diffusive flux, **7.9 (10^{-6})** cm^2 sec^{-1}. The diffusion coefficient used for **NH_4-N** was **21.4(10^{-6})** cm^2 sec^{-1}. The diffusion coefficients were modified for the restrictive effect of sediment structure by dividing by the square of the sediment tortuosity. Sediment tortuosity (Θ^2) was calculated from a relationship developed by Sweerts et al. **(1991),** or

$$\Theta^2 = -0.47 \times \phi + 1.91$$

where ϕ is the sediment porosity. The sediment porosity was determined by % loss on drying of the sediment retrieved from respective stations.

Nutrient exchange rates measured in the intact cores were calculated by determining the slope of the concentration vs. time curve through linear regression, then multiplying by the floodwater volume to soil surface area ratio of the soil core (Gomez-Parra and Forja, **1993):**

$$J_i = \frac{dC}{dt} \times \frac{V}{A}$$

where

J_i = flux of component i, mg $m^{-2}day^{-1}$

C = Floodwater concentration, mg L^{-1}

V = Floodwater volume, L

A = Sediment surface area, m^2

t = time, days

4.2.6 Analytical methods

Dissolved O_2 was measured with a YSI Model 58 O_2 meter (Yellow Springs Instrument Company, Yellow Springs, OH) using EPA Method 360.1. Floodwater samples were analyzed for DRP and NH_4-N using a Technicon AutoAnalyzer (Technicon Instruments Corp., Tarrytown, NY), and EPA Methods 365.1 and 351.2, respectively. The pH was measured with a Fisher Scientific Accumet model 1002 pH meter (Fisher Scientific, Pittsburgh, PA). Sulfate was determined with a Dionex Series 4500i ion chromatograph (Dionex Corp., Sunnyvale, CA), using EPA Method 300.0. Porewater CH_4 and CO_2 were measured with a Shimadzu gas chromatograph Model 8A equipped with a thermal conductivity detector and a Porpak N 80/100 mesh column, using He as the carrier gas (Mindrup, 1978).

4.3 Results and Discussion

4.3.1 Porewater equilibrators

Selected physico-chemical parameters of water column including temperature, salinity, pH, and dissolved O_2 (DO) were measured at all sampling sites (Fig. 4.3-4.6). Dissolved O_2 showed typical diel patterns at all sites, while pH showed no diel fluctuations. Sediment porewater NH_4-N and DRP profiles are presented in figs. 4.7-4.10.

Ammonium-N increased from approximately 100 µg L^{-1} in the water column to a maximum of between 8 and 10 mg L^{-1}. for all but the December 1999 experiment. Porewater NH_4 levels were approx. 2 mg L^{-1} for that period, possibly due to the lower *in situ* temperature (Table 4.2). Ammonium concentration gradients showed maxima at a depth of approximately 10-cm. Sediment concentration profiles of DRP increased from near the limit of detection in the water column to a concentration maximum at approximately 5 to 7 cm beneath the sediment-water interface at all locations. The porewater DRP levels were in the range of 1 to 2 mg L^{-1} for the stations near Melbourne (1997 and 1998) and approximately 0.25 mg L^{-1} for the station north of Titusville (1999). Replicate equilibrators showed good overall agreement.

Carlson et al. (1983) measured porewater DRP and NH_4-N in the porewater of a mangrove-dominated overwash island located approximately 60 km south of the NER experiments conducted in this study and found them to be approximately 300 and 280 µg

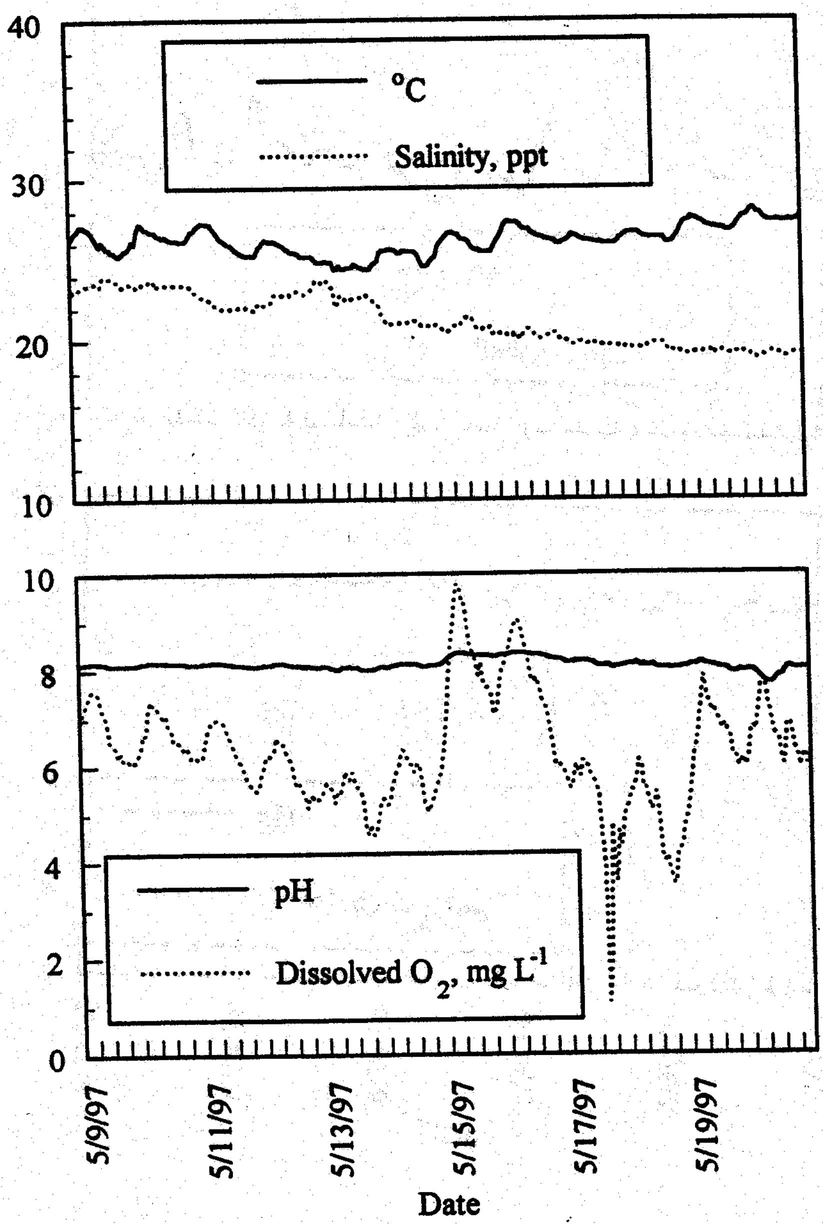


Figure 4.3. Selected physico-chemical parameters measured in the water column of the Indian River lagoon during the NER experiments in May 1997.

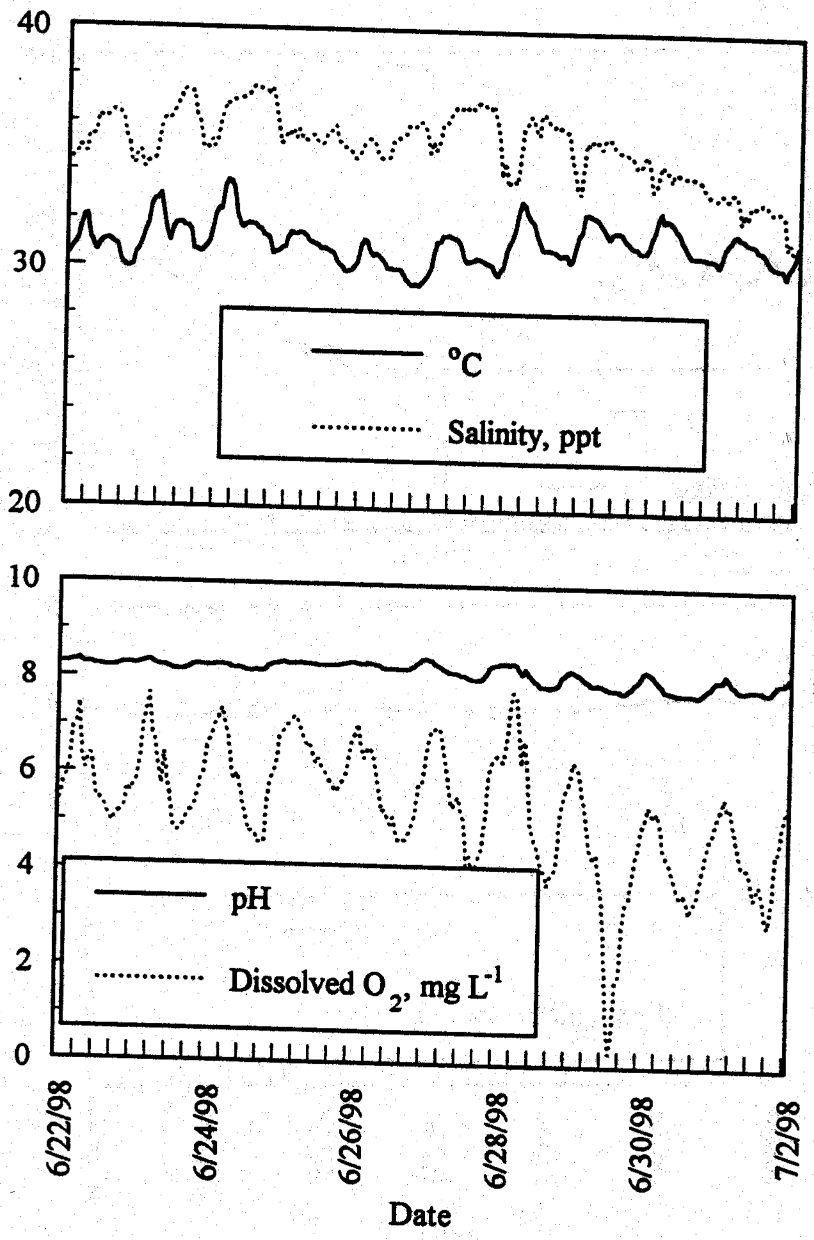


Figure 4-4. Selected physico-chemical parameters measured in the water column of the Indian River Lagoon during the NER experiments in June 1998.

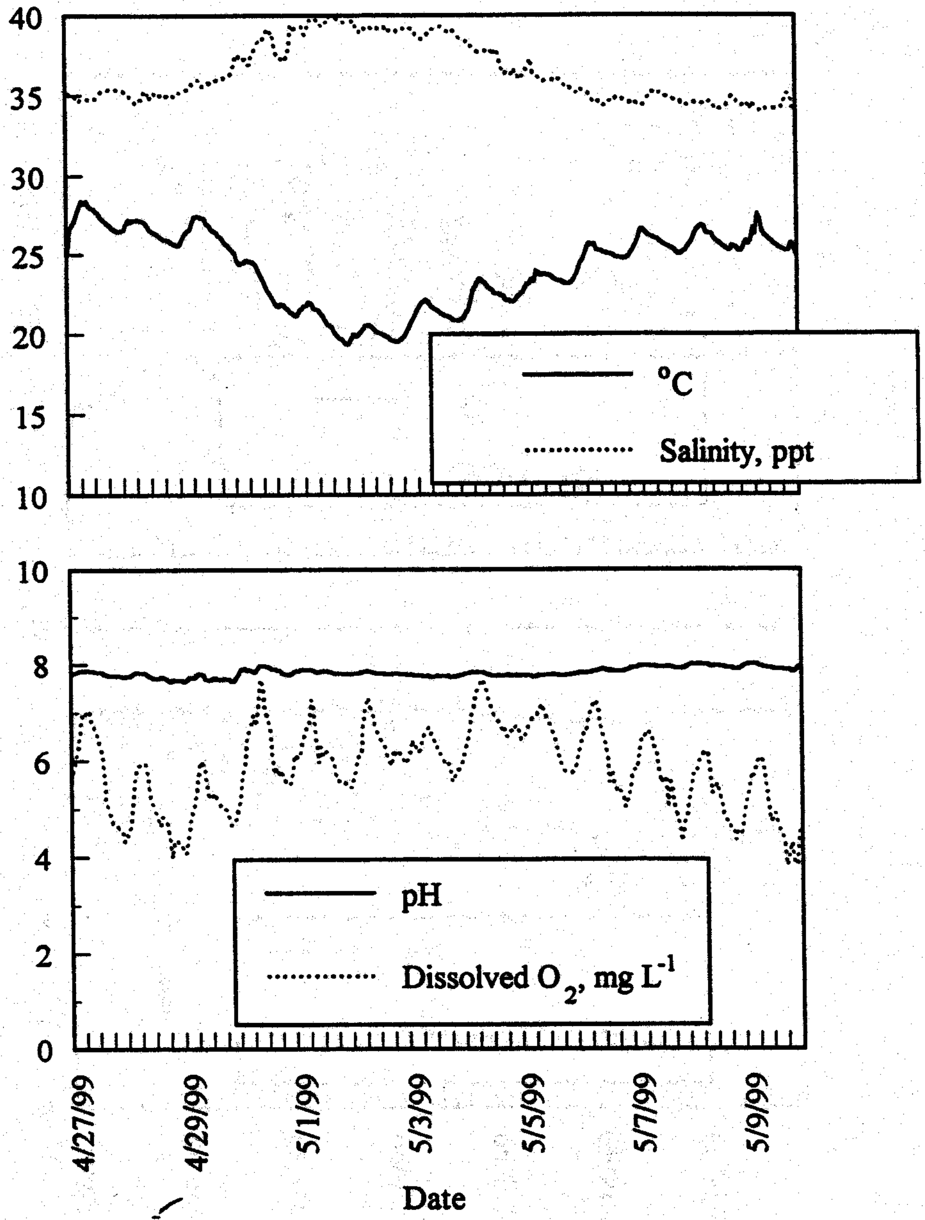


Figure 4-5. Selected physico-chemical parameters measured in the water column of the Indian River Lagoon during the NER experiments in May 1999.

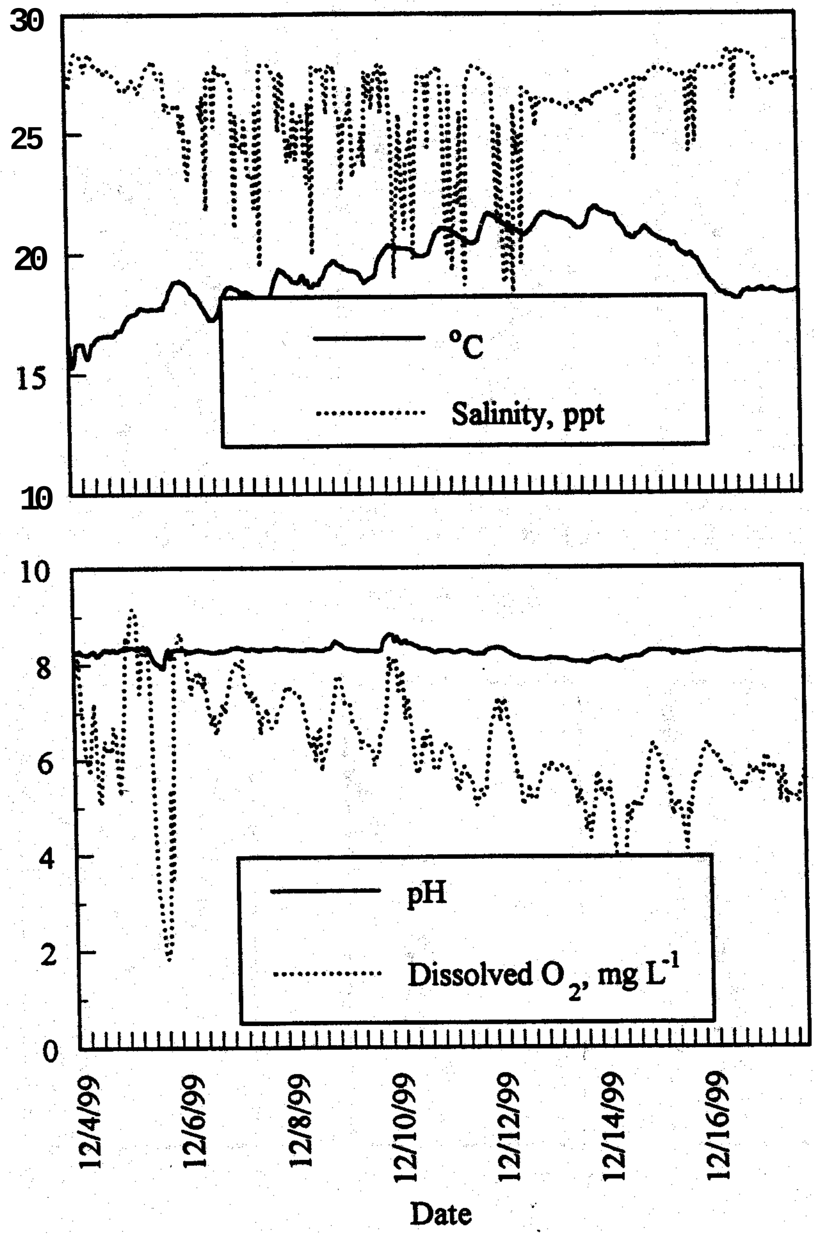


Figure 4.6. Selected physico-chemical parameters measured in the water column of the Indian River Lagoon during the NER experiments in December 1999.

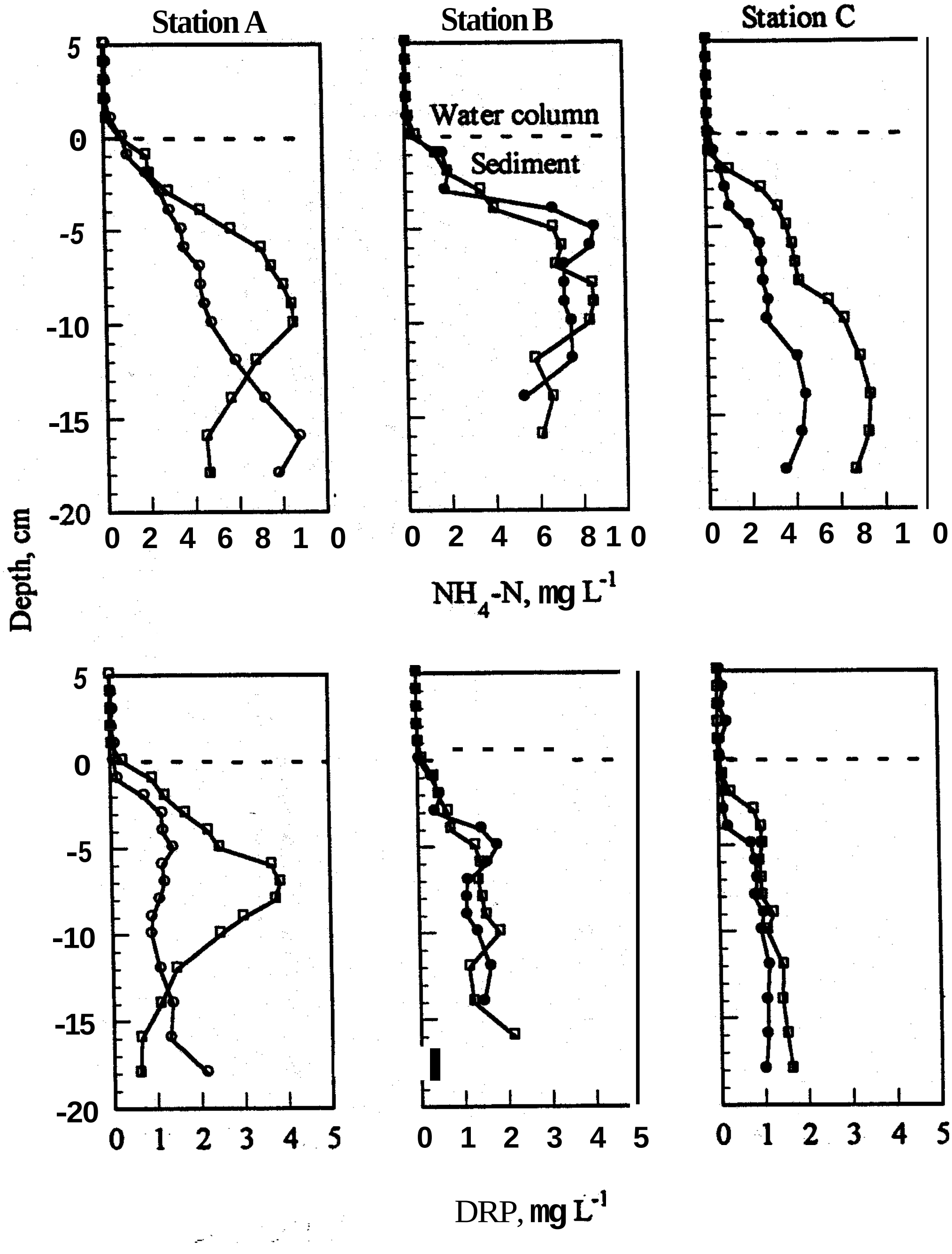


Figure 4-7. Porewater concentration profiles of DRP **and** NH$_4$-N **measured in the** Indian River Lagoon **in May 1997.**

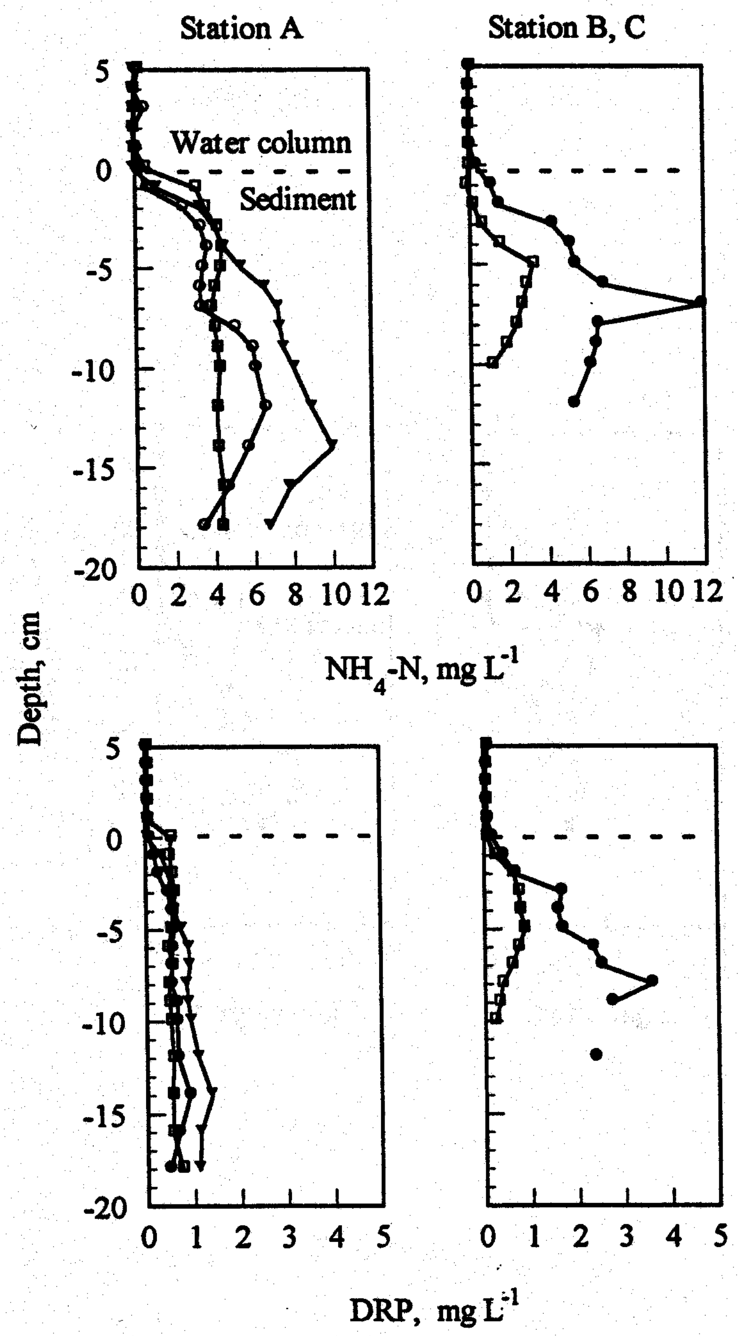


Figure 4-8. Porewater concentration profiles of DRP and NH$_4$-N measured in the Indian River Lagoon in June 1998.

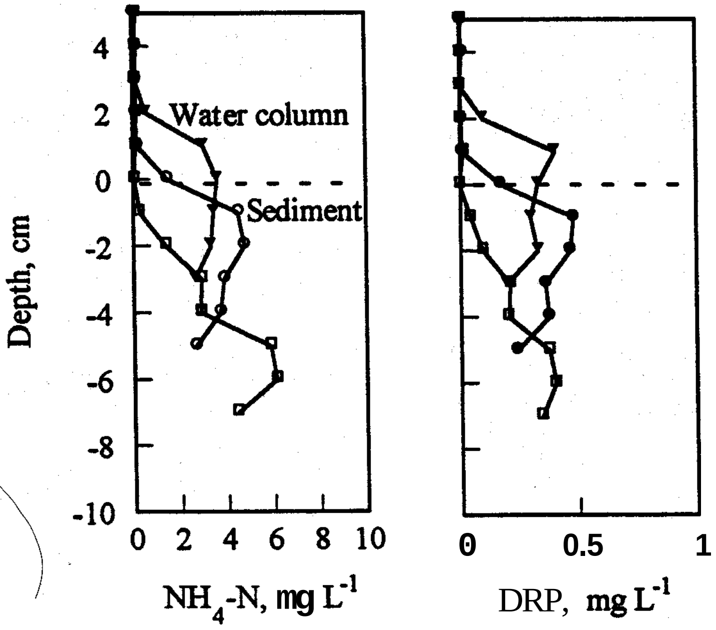


Figure 4-9. Porewater concentration profiles of DRP and NH_4-N measured in the Indian River lagoon in May 1999.

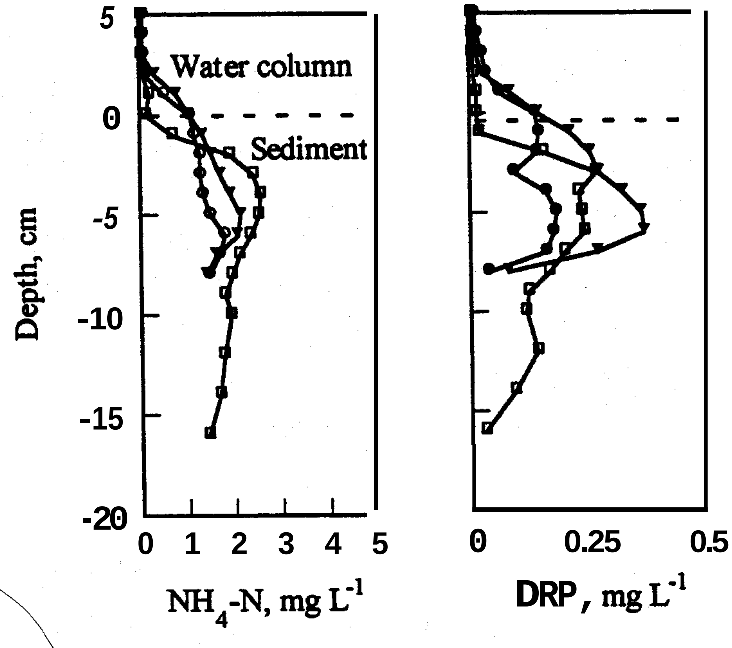


Figure **4-10.** Porewater concentration profiles **of** DRP and **NH_4-N** measured in the Indian River Lagoon in December **1999.**

Table 4.2. Selected physico-chemical parameters of experiments used to measure the nutrient exchange rates in the Indian River Lagoon Estuary.

May 1997	Equilibrators	Sediment Cores
Temperature, °C	26.7 (±0.8)	24.5 (±0.5)
Dissolved O_2, mg L^{-1}		6.25 (k0.93)
pH		7.76 (M.15)
June 1998		
Temperature, °C	31.1 (M.8)	20.2 (±0.9)
Dissolved O_2, mg L^{-1}		6.82 (±0.90)
pH		6.89 (M.16)
May 1999		
Temperature, °C	24.1 (±2.4)	21.0 (M.66)
Dissolved O_2, mg L^{-1}		6.24 (M.45)
pH		7.88 (M.06)
December 1999		
Temperature, °C	19.4 (±1.5)	20.3 (±0.2)
Dissolved O_2, mg L^{-1}		7.38 (M.84)
pH		7.94 (M.13)

L^{-1} at a depth of 10 cm. This is considerably lower than the results reported here and may reflect flushing of the porewater by tides, as speculated by the authors.

Montgomery et al. (1979) also found concentration maxima at a depth of approximately 10 cm below the sediment water interface. Their study site was also located approximately 60 km south of the 1997 and 1998 stations described in this study. They found maximum porewater concentration of NH_4-N and DRP of approximately 2000 μg L^{-1} and 620 μg L^{-1}, respectively, depending on season. It is worth noting that porewater NH_4-N and DRP levels at Station 1 (near the 1979 and 1983 study sites) were 7300 and 1300 μg L^{-1} in the surficial (0-10 cm) sediments during the March 1997 spatial sampling (this study). In both previous studies, porewater nutrient concentrations were considerably lower. This may be due to the inherent spatial heterogeneity of the sediments in the estuary, or to long-term changes in porewater chemistry.

Sulfate concentration in the water column during the 1997 NER experiment was 1300 mg L^{-1} and in the 1998 experiment, approximately 2500 mg L^{-1} (Fig. 4.11). Seawater has an approximate sulfate concentration of 2700 mg L^{-1} (Fig's. 4.11 and 4.14). The difference between the sulfate concentration observed at these two sites may be due to distance from Sebastian Inlet and the attendant difference in salinity at the two sites. The average salinity at the NER stations (1997) near Melbourne was 21 ppt (Fig. 4.3). The 1998 study site was located relatively close to Sebastian Inlet and had an average salinity of 35 ppt (Fig.4.4). Porewater SO_4 concentration at the NER site north of Titusville was approximately 3000 mg L^{-1} in May 1999 and 2000 mg L^{-1} the following December. Relatively high SO_4 levels in May were possibly due to the effects of a severe drought in the region. Sulfate concentration profiles during all experiments showed gradual gradients from the sediment-water interface to a generally constant concentration at a depth of approximately 5-cm (Figs. 4.6-4.9). The sulfate concentration profile at Station C during the 1997 experiment was nearly constant with respect to depth. This station also had low average dissolved inorganic carbon (DIC) in the 0- to 5-cm sediment depth interval, indicating lower benthic respiration at this station (Fig. 4.10). The sediment porewater concentration of DIC was approximately 10-fold greater at the NER stations in the Melbourne area, as compared to the Titusville station. Porewater concentration of DIC averaged approximately 75 mg L^{-1} at the 1997 and 1998 sites, but only 9 mg L^{-1} the Titusville station. This is likely due to the very low organic matter content of the sediments at the 1999 site. The average redox potential at a depth of 6-cm beneath the sediment-water interface was –194 mV (±39) in the sediment cores retrieved during the 1998 NER experiment, indicating moderately reducing conditions and absence of molecular oxygen. Therefore, sulfate was likely the dominant terminal electron acceptor. The dissolved inorganic carbon profiles and thus carbon mineralization are therefore largely due to sulfate respiration (McCaffrey, et al 1980, Kelley, et al 1990).

Even though the SO_4 concentration was in excess of 1000 mg L^{-1}, evidence of methanogenesis was detected at all sites (Fig's. 4.15-4.18). It is possible that CH_4 was actually produced below the region of sulfate reduction (and the depth of the porewater equilibrators) and diffused upwards. It is also possible that methanogenesis and sulfate reduction are occurring simultaneously in the same depth zone. It is generally regarded

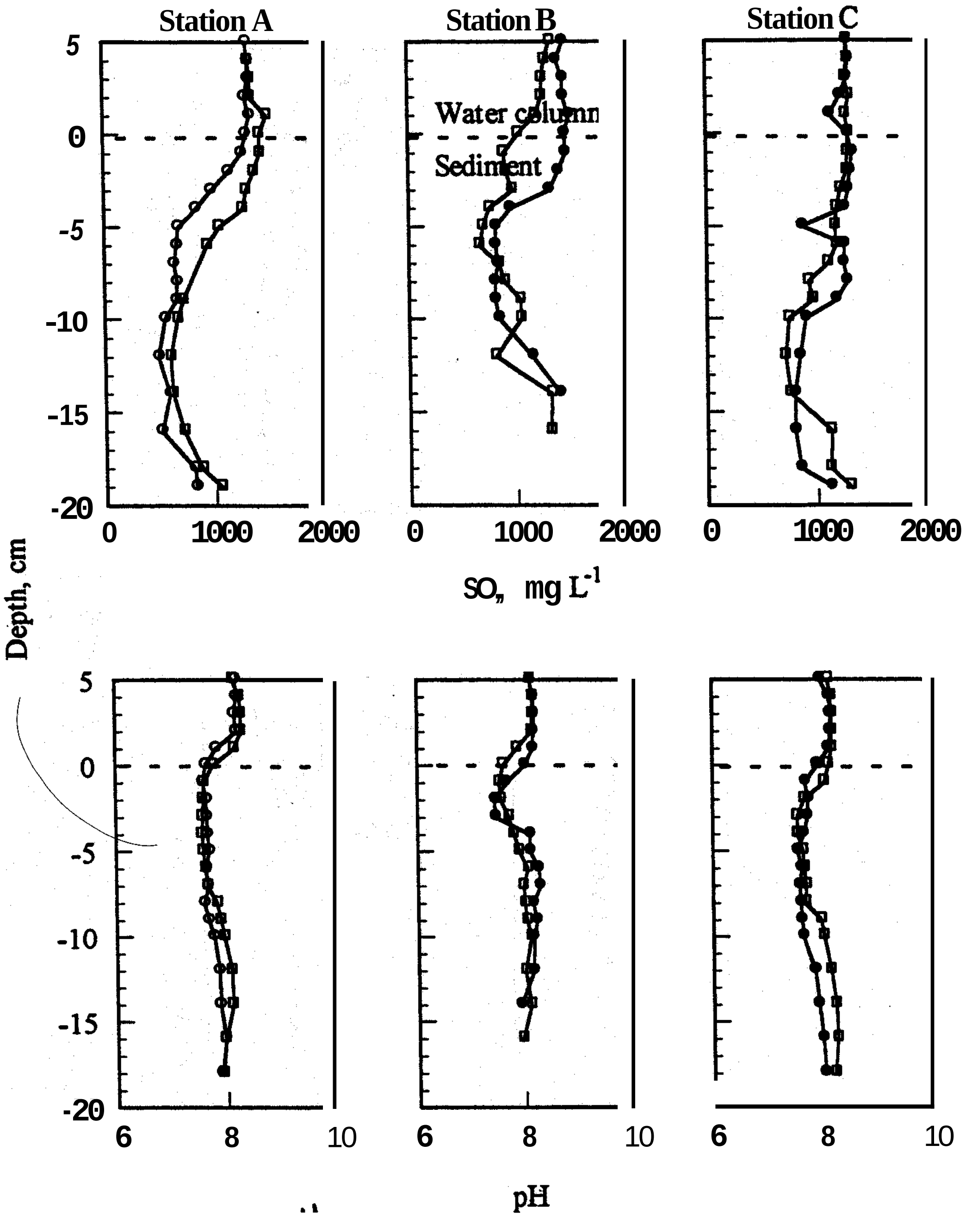


Figure 4-11. Porewater concentration profiles of sulfate and pH measured in the Indian River Lagoon in May 1997.

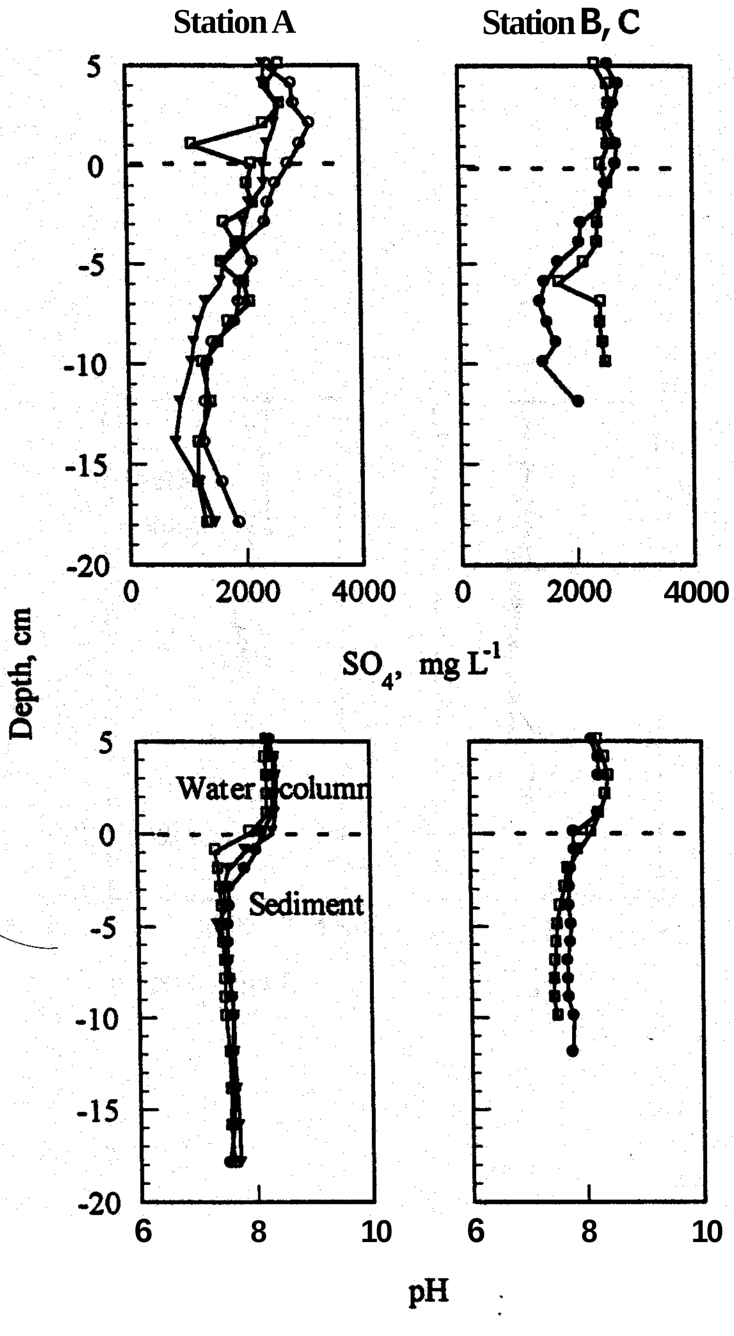


Figure 4-12. Porewater cancentration profiles of sulfate and pH measured in the Indian River Lagoon in June 1998.

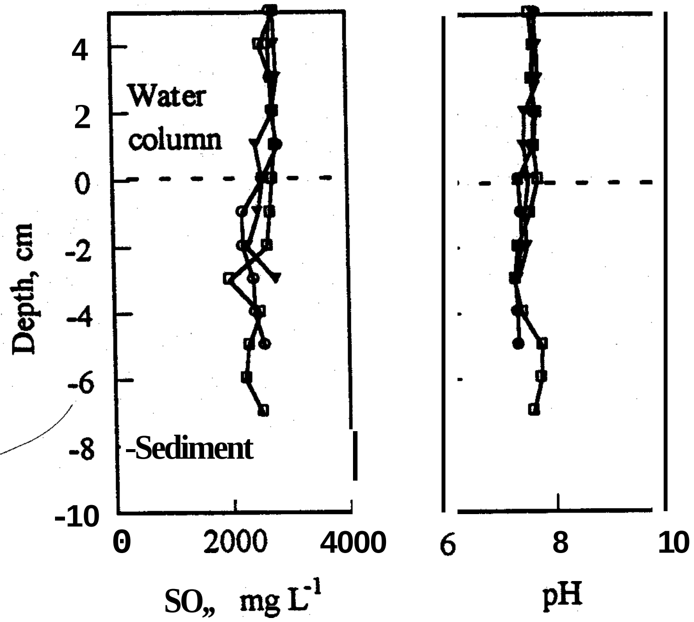


Figure 4-13. Porewater concentration profiles of sulfate and pH measured in the Indian River Lagoon in May 1999.

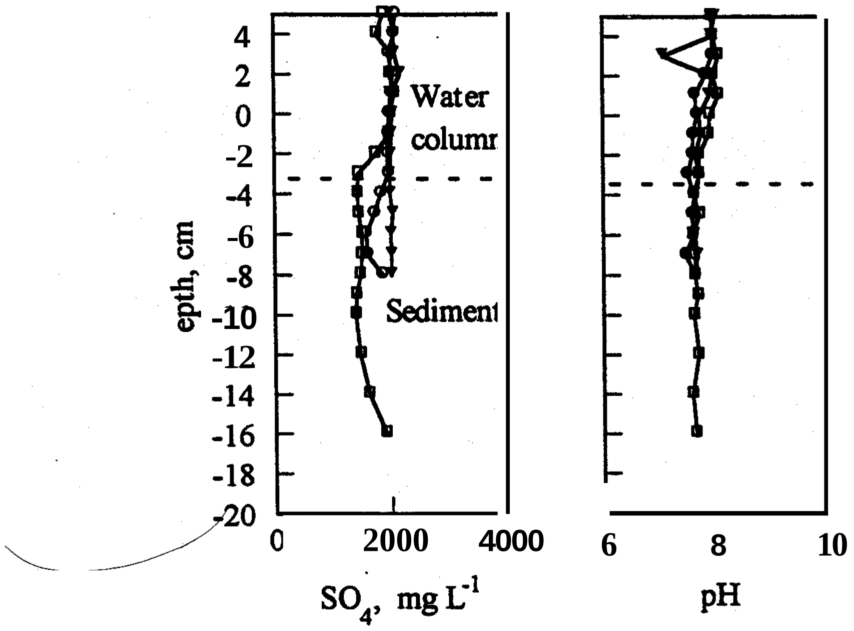


Figure 4-14. Porewater concentration profiles of sulfate and pH measured in the Indian River Lagoon in December 1999.

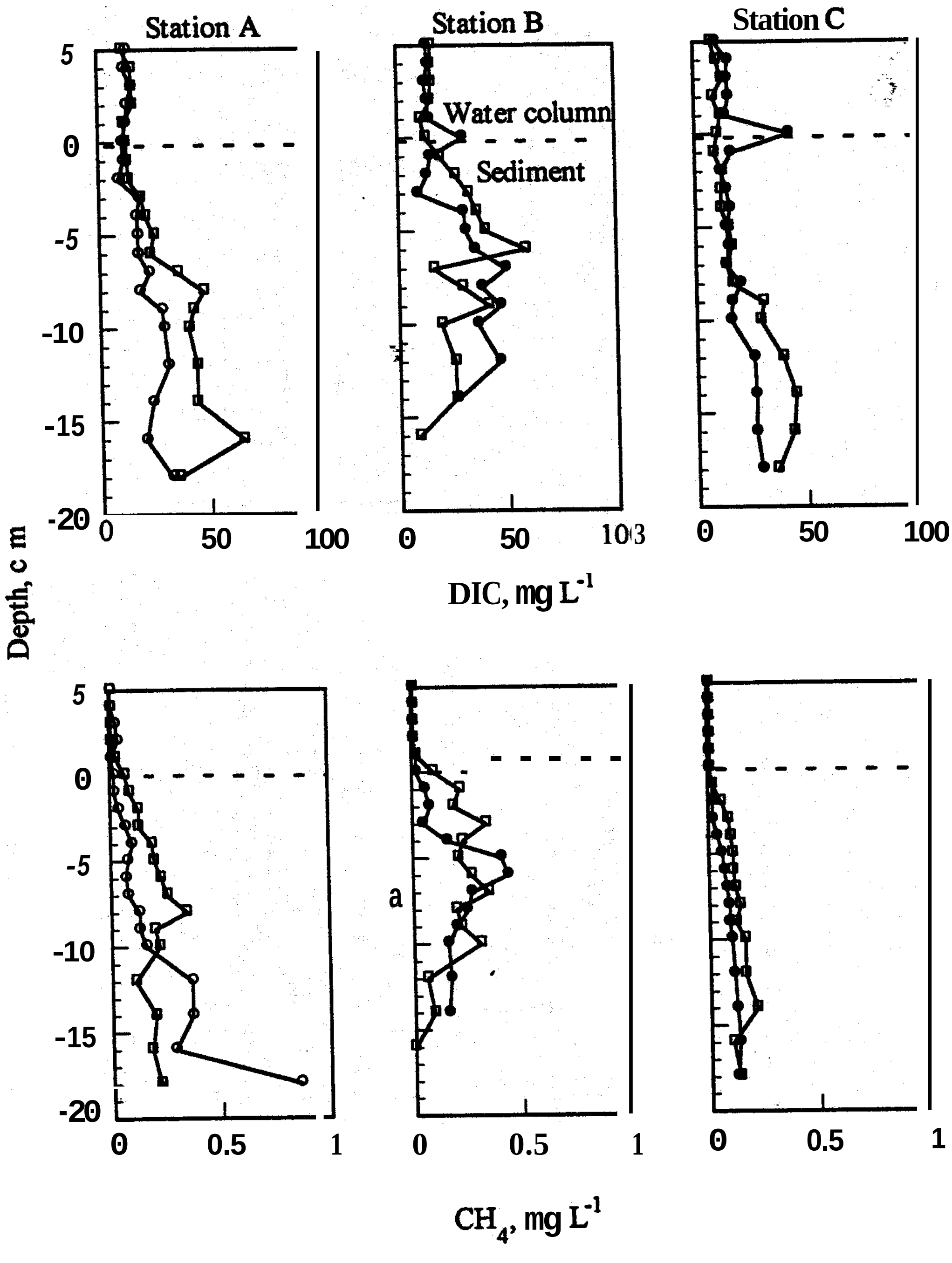


Figure 4-15. Porewater concentration profiles of dissolved inorganic carbon and methane measured in the Indian River Lagoon in May 1997.

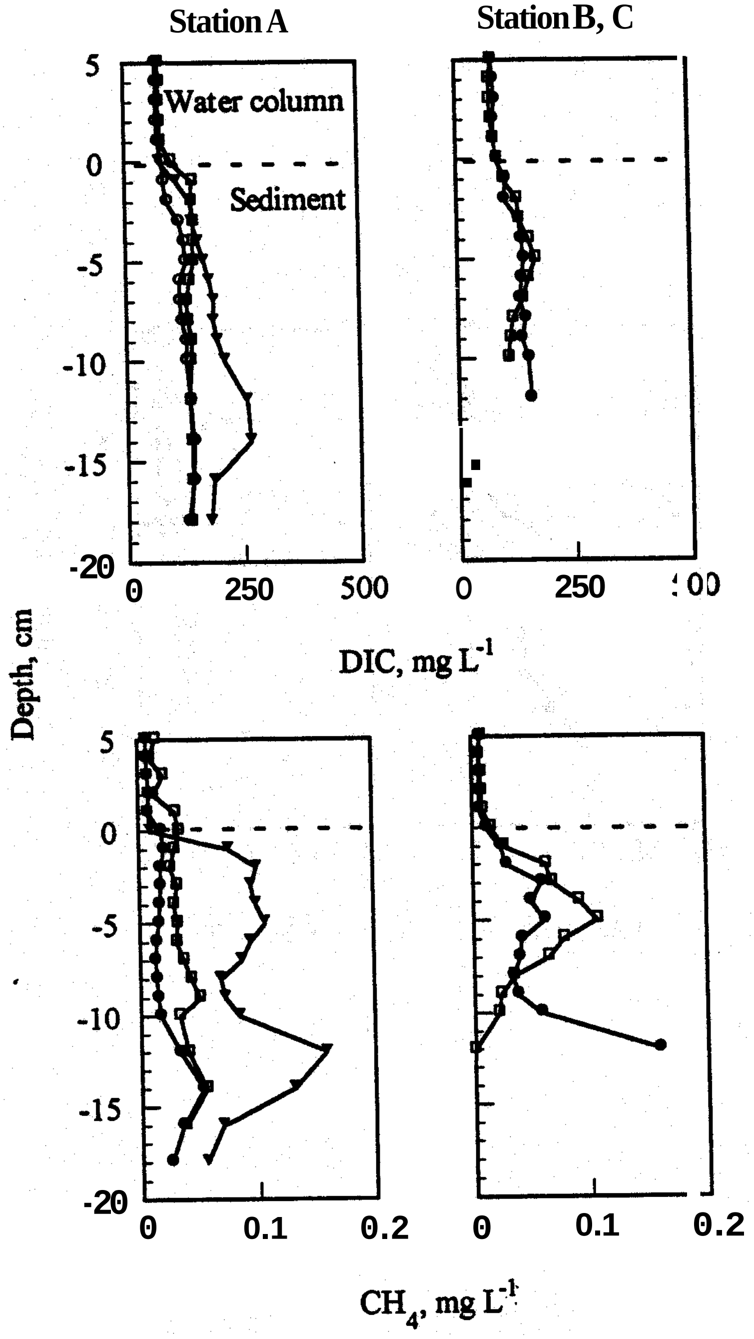


Figure 4-16. Porewater concentrations profiles of dissolved inorganic carbon and methane measured in the Indian River Lagoon in June 1998.

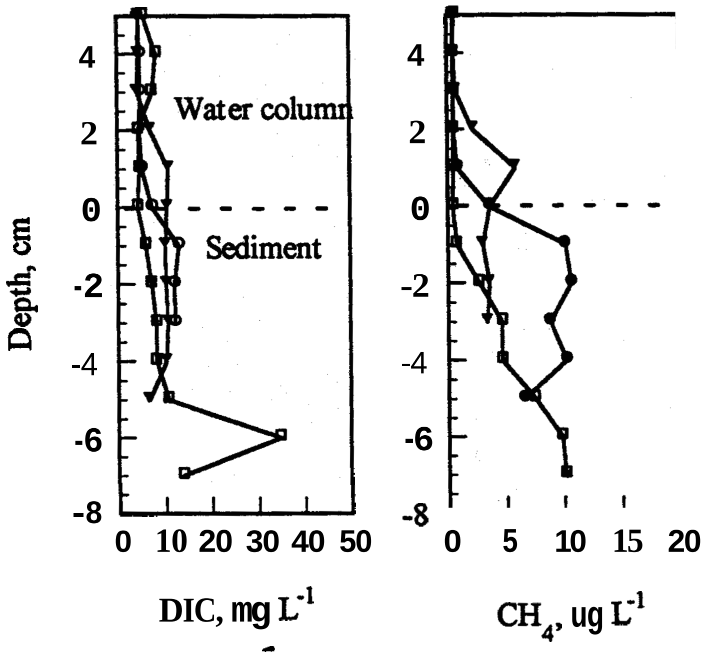


Figure 4-17. Porewater concentration profiles of dissolved inorganic carbon and methane measured in the Indian River Lagoon in May 1999.

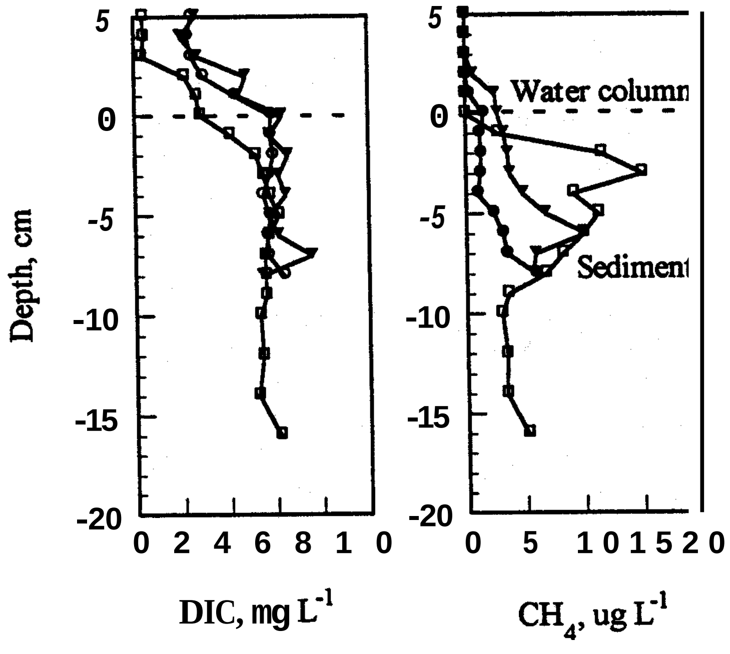


Figure 4-18. Porewater concentration profiles of dissolved inorganic carbon and methane measured in the Indian River Lagoon in December 1999.

that sulfate reducing bacteria will outcompete methanogens for substrate in freshwater systems, thereby gaining a competitive advantage. However, it has been shown that methanogens are able to utilize certain substrates found in estuarine sediments, such as methanol, trimethylamine and methionine, that are not utilized by SO_4 reducers (Oremland and Polcin, 1982).

Nitrogen and P flux from the sediment to the overlying water were calculated for all experimental periods, based on the concentration profiles observed in the porewater equilibrators (Table 4.3). Both P and N flux were higher at the locations more proximal to Melbourne. The P flux was generally in the range of 0.2 – 1.6 mg m^{-2} day" at the sites near Melbourne, compared to 0.05 – 0.10 mg m^{-2} day^{-1} at the Titusville site. Montgomery et al. (1979) calculated diffusive flux for Indian River Lagoon sediments 60 km south of the sites investigated here and reported N and P flux of 400 and 50 and mg m^{-2} day^{-1}, respectively. These are unrealistically high and may reflect an error in their calculation of the concentration gradients. Nitrogen flux as measured with the porewater equilibrators averaged approximately 6.5 mg m^{-2} day^{-1} at the Melbourne stations (1997 and 1998) and 2 mg m^{-2} day^{-1} at the Titusville site (1999).

4.3.2 Intact sediment cores

Water column DRP concentration gradually increased to approximately 0.2 mg L^{-1} at the 1997 and 1998 (Melbourne) stations over the duration of the experiment (Fig. 4.18). Phosphorus release form the sediments at the Titusville station was much lower; water column concentration only rose to approximately 20 μg L^{-1} over the 14-day incubation period. One core from Station A during the 1998 experiment showed considerably higher rate of P release. On closer examination, there appeared to be a mollusk or other small organism that had been crushed by the coring operation inside the core. This core was discarded from the flux computations. Interestingly, N flux did not appear to be affected. The same phenomenon was observed in one replication taken from Station C, therefore this core was also eliminated from the flux calculation.

The NH_4-N concentration increased for the first four days during the 1997 experiment to approximately 2 mg L^{-1}, then decreased to nearly undetectable levels within the 14 day period (Fig. 4.20) This is likely due to the establishment of a community of nitrifiying bacteria within the sediment core microcosms, and the subsequent oxidation of NH_4-N to NO_3-N. In the 1998 and 1999 experiments, a nitrification inhibitor was added to the water column of the sediment cores and NH_4-N continued to increase throughout the 14 day experimental period to approximately 2 mg L^{-1}, on average. Nitrate-N was near the limit of detection (approx. 10 μg L^{-1}) for all but two of the sediment cores for the entire experimental period, indicating the effectiveness of the inhibitor. One replication from Station A and Station C (1997) showed some evidence of water column nitrification after 14 days, with a final NO_3-N concentration of approximately 0.1 mg L^{-1}. Two cores from Station A (1998) showed considerable flux of NH_4-N to the overlying water while the remaining replication showed little or no increase in water column NH_4-N, indicating short-range spatial variability.

Table 4.3. Nutrient exchange rates (NER) estimated with porewater equilibrators and intact sediment cores in the Indian River Lagoon estuary. Values in parentheses represent one standard deviation.

	Nitrogen	Phosphorus	Location
Intact Cores	-------- mg m^{-2} day^{-1} --------		
Dec-99	17.6 (2.6)	ND	(10 km north of Titusville)
May-99	30.5 (7.8)	0.162 (0.104)	(10 km north of Titusville)
1998	36.3 (14.6)	1.537 (0.58)	(13km north of Sebastian Inlet)
1997	23.9 (47.2)	1.236 (1.72)	(10km south of Melbourne)
Equilibrators			
Dec-99	*0.85* (0.43)	0.038(0.02)	(10 km north of Titusville)
May-99	2.9 (0.601)	0.115 *(0.066)*	(10 km north of Titusville)
Jun-98	5.9 (0.09)	0.167 (0.14)	(13km north of Sebastian Inlet)
May-97	7.0 (4.1)	1.6 (0.42)	(10km south of Melbourne)

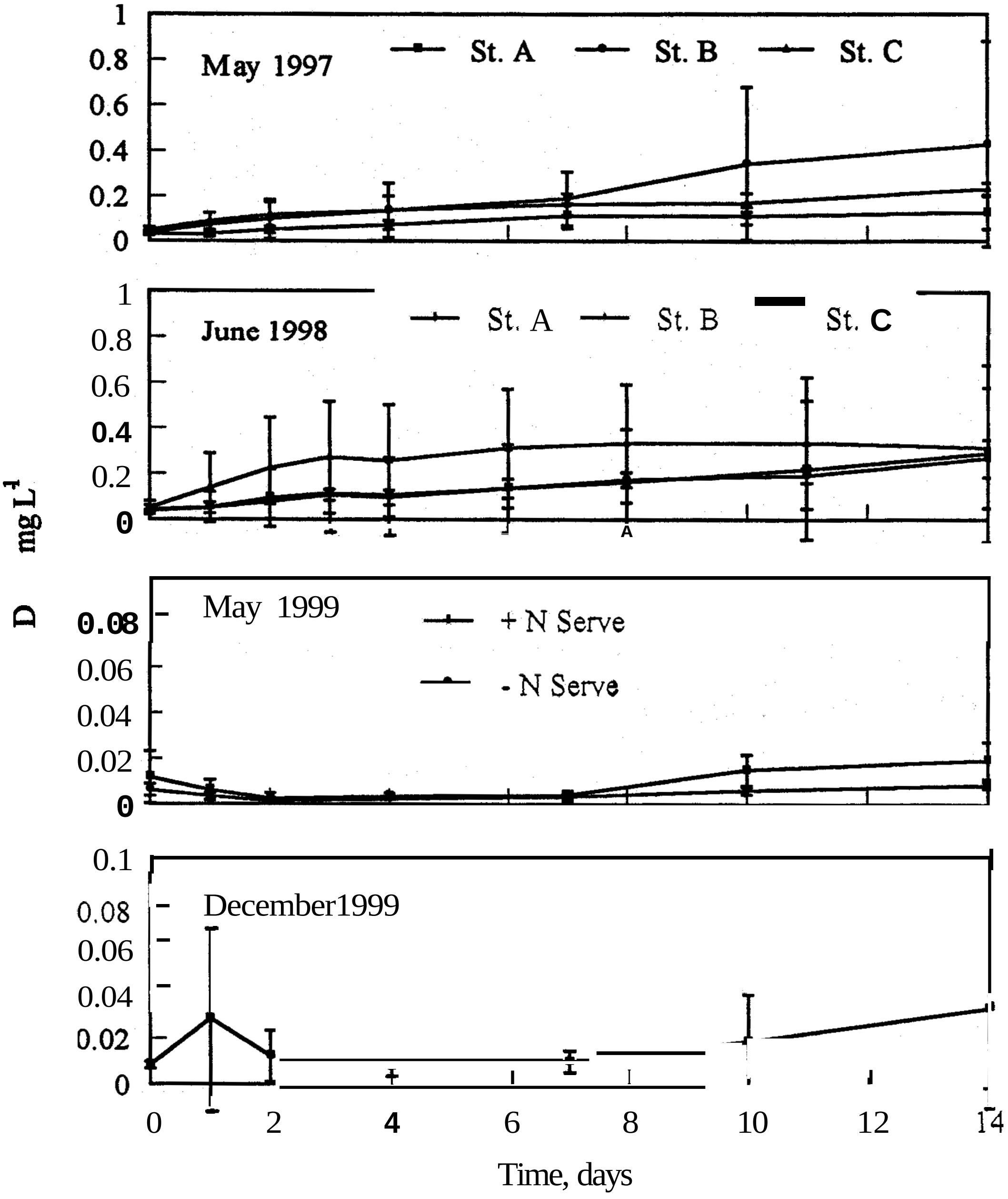
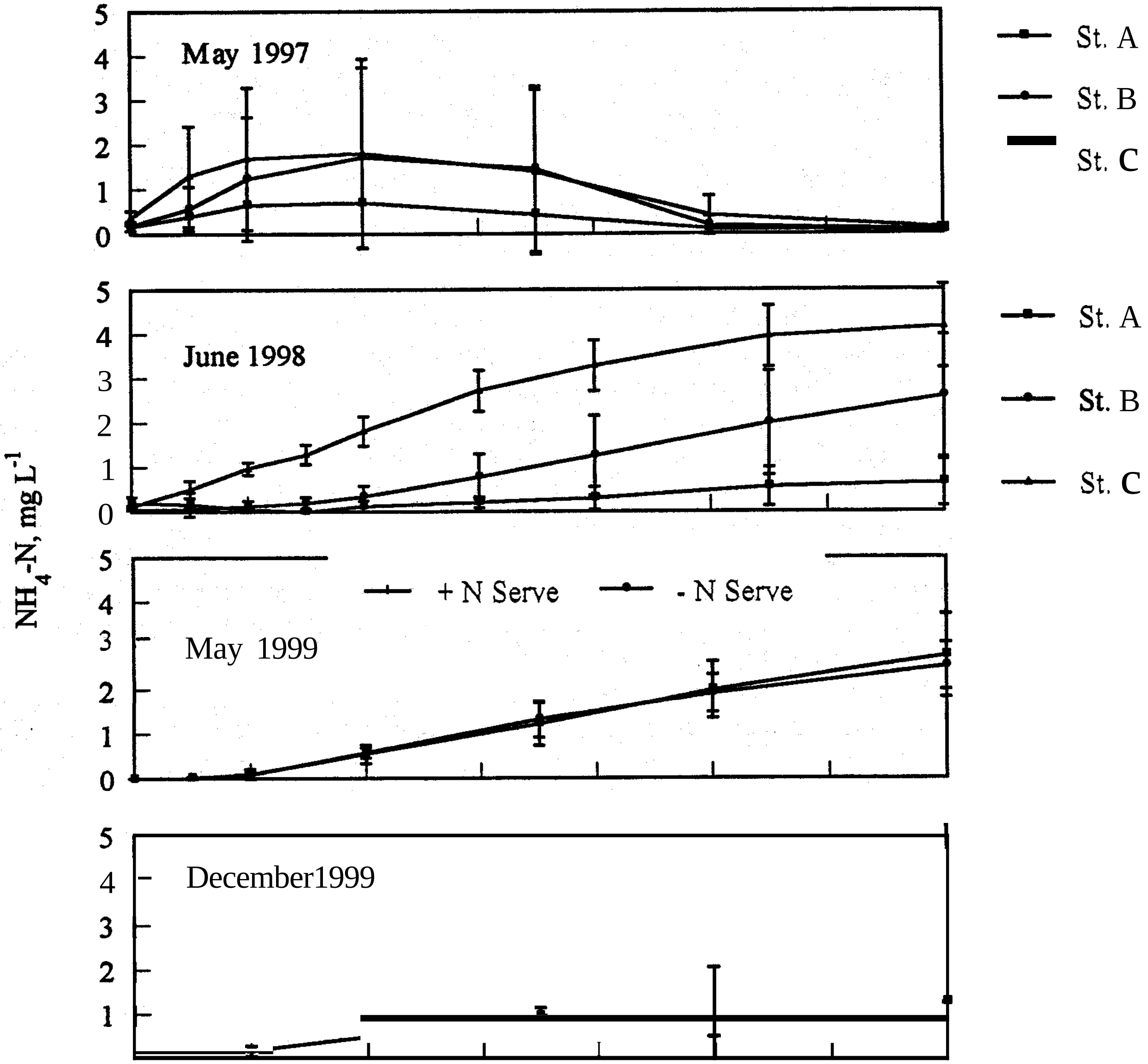


Figure 4.19 Dissolved reactive P concentration in the floodwater of intact sediment cores taken from the Indian River Lagoon. Three separate stations were used in each of the 1997 and 1998 studies, whereas a single station near the Haulover Canal was used for the 1999 experiments. Error bars represent the standard deviation of three replications for May 1997, June 1998, May 1999 and four replications for December 1999.


May 1997
June 1998
May 1999
December1999
St. A
St. B
St. C
+ N Serve
- N Serve
NH_4-N, mg L^{-1}
0
1
2
3
4
5

One core was kept with site water only (no sediment) to determine if the core systems themselves were responsible for some of the observed changes in water chemistry. Water column DRP and NH_4 showed very little change in concentration over the experimental period for these cores (data not shown).

Flux of both P and N using the two flux measurement techniques was greater at the **1997** study site (near Melbourne) than the **1998** site. Also, flux as measured with the intact sediment cores was in excess of that estimated from the concentration gradients (equilibrators) (Table **4.3).** The overall average flux using both techniques at all locations was **0.61** and **15.6** mg m^{-2} day^{-1} for **DRP** and NH_4-N, respectively. In all cases, flux estimated with the porewater equilibrators underestimated the flux calculated using the intact cores. Variability among the commonly used flux measurement techniques is well documented for a wide variety of ecosystems (Callender and Hammond, **1982;** Gomez-Parra and Forja, **1993;** Moore et al., **1998).** Factors affecting solute flux through sediment such as bioturbation, gas ebullition, formation and dissolution of mineral phases, water velocity at the sediment-water boundary layer and sediment structure complicate estimates of diffusive flux based on concentration gradients alone. However, estimates of flux based on porewater gradients do provide reasonable relative estimates when comparisons are made between locations or seasons, especially when issues such as small-scale variations in porewater chemistry are adequately addressed. Typically this is accomplished through replication. Further refinement of the estimate of the magnitude of sediment solute flux can be made by comparing the results from a variety of measurement techniques, such as was done in this study.

An estimate of the lagoon-wide loading of N and P from the sediment to the water column can be made by extrapolation using the flux results obtained in this study. If the average fluxes given above **(0.61** and **15.6** mg m^{-2} day" for DRP and NH_4-N, respectively) are multiplied by the area of the IRL estuary, an internal load of **425** and 11,000 kg day^{-1} is the result. This assumes a lagoon area of 700 km^2, which is the areal extent of the lagoon that is bounded to the north by the Haulover Canal and to the south by Fort Pierce Inlet. This area excludes Mosquito Lagoon and includes the Banana River. Of course, this estimate is based on only three sites where diffusive flux was measured and should therefore be used with caution. It does however provide an estimate of the importance of the sediments to the regulation of the nutrient status of the overlying water, and to their role in the overall Indian River Lagoon nutrient budget. Obviously, additional measurements of sedimentary flux of N and P are needed to further refine this estimate.

The differences observed in the results from both measurement techniques for the two experimental sites suggests that the sediments closer to Melbourne are contributing a higher sediment loading of N and P to the overlying water than the station near Titusville. Also, average porewater DRP and NH_4-N measured in the **1997** spatial sampling was greater for the mud sediments than either the sediments to the north or south of Melbourne. This indicates enhanced loading from this region. Further research involving the sediments in this region of the lagoon are necessary to determine if this trend continues as sampling stations become more proximal to Melbourne.

4.3.3 Resuspension Experiments

Distribution of PIN and PON in surface 10-cm sediment is shown in Fig. **4.20.** No distinct gradients in inorganic N were observed. However, particulate inorganic N (PIN) did increase slightly, from approximately 0.5 mg kg^{-1} at the surface, to 2 mg kg^{-1} at lower depth's. Though this fraction represents a potentially labile pool of N, it constitutes less than 0.5% of the sediment total nitrogen. Sharp gradients in organic N were noted in surface sediments, with maximum values at a depth of approximately **4 – 5** cm. These observations suggest some degree of organic matter burial, or accumulation in sub-surface sediments horizons. Of course, this represents a single point measurement (one core) at one location in the estuary. Sediment TP also showed increasing concentration with respect to depth, attaining maximum values of approximately 175 mg kg^{-1} at a depth of approximately 3-cm (Fig. **4.20).** On average, **90%** of sediment TP was in the form of particulate inorganic P **(PIP)** (Table **4.4). This** P fraction is the **sum** of exchangeable P (labile) and P associated with Ca and Mg minerals. Since exchangeable P was very low **(< 0.2%),** most of the sediment P at this station can be considered to be relatively immobile, especially at ambient Lagoon pH (ca. 8.0).

Resuspension of the surface 0.5-cm of sediment into the overlying water column resulted in rapid increase in PON and TKN, but slow release of **NH$_4$-N** (Fig. **4.22).** During the 1-hr resuspension period, ammonium N levels increased to approximately 0.1 mg L^{-1}, while TKN increased to 15 mg N L^{-1}. This effect was short-lived, as TKN levels decreased to **2.5** mg L^{-1} immediately following the resuspension period. TKN levels continued to decline over the **24-hr** experimental period, and were only slightly greater than the control core after **24-hrs.** This implies that nearly all of the nitrogen initially entrained via the resuspension apparatus was in a particulate form and therefore subject to rapid settling. Ammonium concentration in the resuspended core increased more gradually over the experimental period. At the end of the **24-hr** period, NH$_4$-N concentration in the resuspened core was **0.45** mg **L^{-1}** higher than the control core. This increase was likely due to: i.) entrainment of porefluid (containing elevated **NH$_4^+$)** into the water column ii.) desorption of N from the sediment exchange complex, and iii.) short-term mineralization of sediment organic N under the aerobic conditions of the water column. The purely physical action of porewater entrainment and liberation of the N in the exchangeable pool (i. and ii.) during the resuspension period could not have accounted for the increase in water column ammonium concentration. Total exchangeable N from the sediment extraction revealed that this pool is very small and could have accounted for a water column increase of only **2** μg **L^{-1}**. The difference between the two treatments may therefore be due to enhanced aerobic mineralization of organic N and aerobic conditions. The result observed in this study are in sharp contrast to a similar study on Lake Apopka, a hypereutrophic lake in central Florida. Reddy et al. (1996) demonstrated **an** immediate large increase in water column NH$_4$-N upon initiation of resuspension, with water column NH$_4$-N increasing from approximately 0.1 to 3.5 mg L^{-1} during the 1-hr resuspension period. The difference between the two studies is due to the nature of the sediment in the two ecosystems; Lake Apopka sediments are highly organic and nutrient enriched **(25** g N kg^{-1}), whereas the IRL sediments at **this** site are sandy and are relatively nutrient-poor (0.5 **g** N kg^{-1}).

Table 4.4. Selected physico-chemical properties of Indian River Lagoon sediment at a station approximately 10-km north of Titusville, FL. Core retrieved on December 4, 1999 from same location as cores used in resuspension experiment.

Parameter	Depth Interval 0 - 5 cm	5 - 10 cm
Bulk Density, g cm^{-3}	1.254	1.338
% Water, %	28.7	24.1
Exchangeable P, mg kg^{-1}	0.28	0.08
HCl-P, mg kg^{-1}	103	102
PIP, mg kg^{-1}	103	102
POP, mg kg^{-1}	8.4	25.5
TP, mg kg^{-1}	112	127
PIN, mg kg^{-1}	1.95	2.34
PON, mg kg^{-1}	608	449
TKN, mg kg^{-1}	610	452

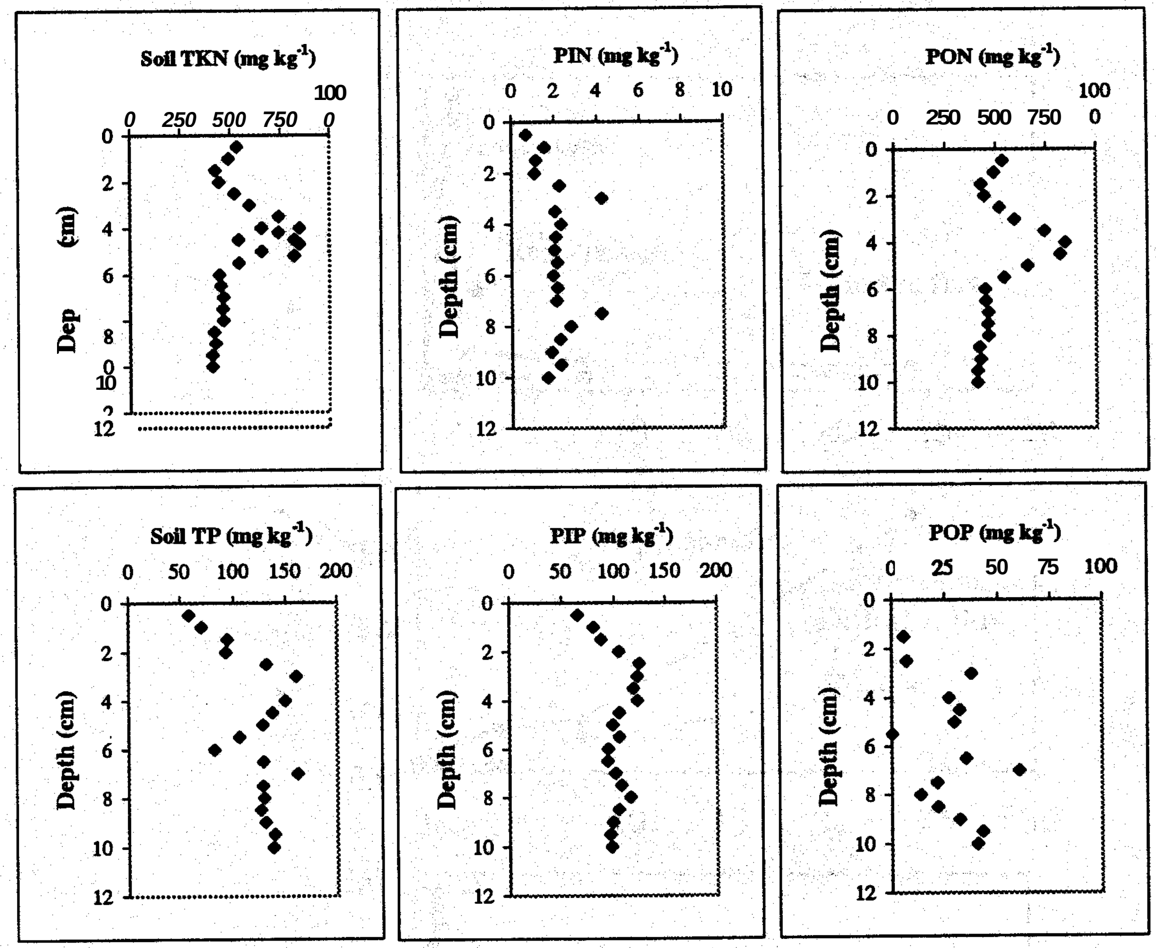


Figure 4.21. Distribution of nitrogen and phosphorus forms in sediment cores retrieved on December 1999 from a station approximately 10-km north of Titusville, Fl.

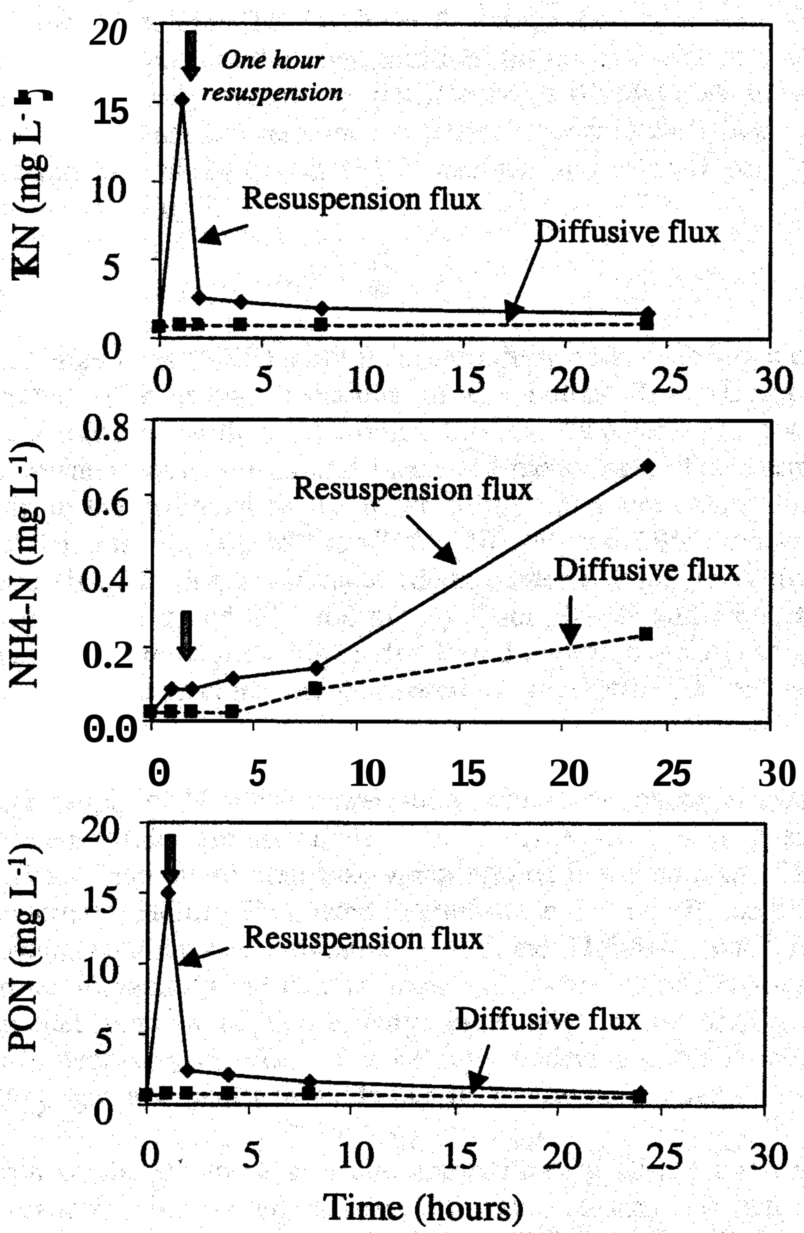


Fig. 4.22. Nitrogen release during and after sediment resuspension in cores obtained from a station located approximately 10km north of Titusville, Fl.

Total P levels showed a very similar pattern of resuspension-release kinetics, compared to the TKN data (Fig. 4.23). Water column TP concentration initially increased to **3.1** mg L^{-1} during resuspension, followed by rapid decrease to **0.18** mg L^{-1}. At the end of the experiment, water column TP levels in the suspended core were **0.11** mg L^{-1} greater than the control core. That the concentration did not decrease to pre-suspension levels in the **24-hr** period likely reflects the persistence of silt and clay-sized particulate matter in the water column that still remained unsettled. The soluble P data confirms this, as DRP levels at the end of 24-hrs in the suspended and control core were nearly identical, differing only by 2 μg L^{-1}.

4.4 Conclusions

Nutrient exchange rates (NER) were measured during May **1997,** June **1998,** May **1999** and December **1999** at two locations in the Indian River Lagoon south of Melbourne and one location north of Titusville, Florida. Two techniques were used to estimate NER, porewater equilibrators and intact sediment cores. The average nutrient flux (both sites) from the sediment to the water column measured using the porewater equilibrators was 0.5 and **4.2** mg m^{-2} day^{-1} for NH_4-N and **DRP,** respectively. The average flux **(three** sites) from the sediment to the water column measured using the intact sediment cores was **0.7** and **27.1** mg m^{-2} day^{-1} for NH_4-N and DRP, respectively. Measured flux was therefore slightly higher for P and approximately seven-fold higher for N in the intact sediment cores, as compared to the estimates derived form the porewater equilibrators.

This internal supply of N and P represents a long-term source of nutrients to the water column. When results are extrapolated to a large area, it is possible that it represents a significant internal nutrient load when viewed in the context of known point and non-point external loading. Estimated lagoon-wide N and P loading from the sediment to the water column was estimated as 425 and **11,000** kg day^{-1} for N and P, respectively. Further research is needed to more fully characterize nutrient exchange processes for broader regions of the estuary, especially in the region surrounding Melbourne. This is necessary in order to more fully understand the functional role of sediments in regulating water quality in the Indian River Lagoon Estuary.

Resuspension of the sediment at a site approximately **10-km** north of Titusville resulted in a short-term pronounced increase in water column TP and TKN. After cessation of the resuspension period, water column TKN and TP quickly decreased to near pre-resuspension levels (within 24-hr). Soluble P showed a rapid increase by approximately 10 μg L^{-1}, and then a return to background levels within 24-hrs. Ammonium-N increased more gradually over the entire experimental period, possibly due to increased aerobic mineralization of organic nitrogen. Most of the initial increase in total nutrients can be attributed to simple entrainment of sediment particles, which are then subject to settling after the episodic disturbance. It should be noted that the conditions invoked in this experiment were very extreme, requiring quite vigorous agitation of the water column in order to entrain 0.5-cm of the sandy sediment at this site.

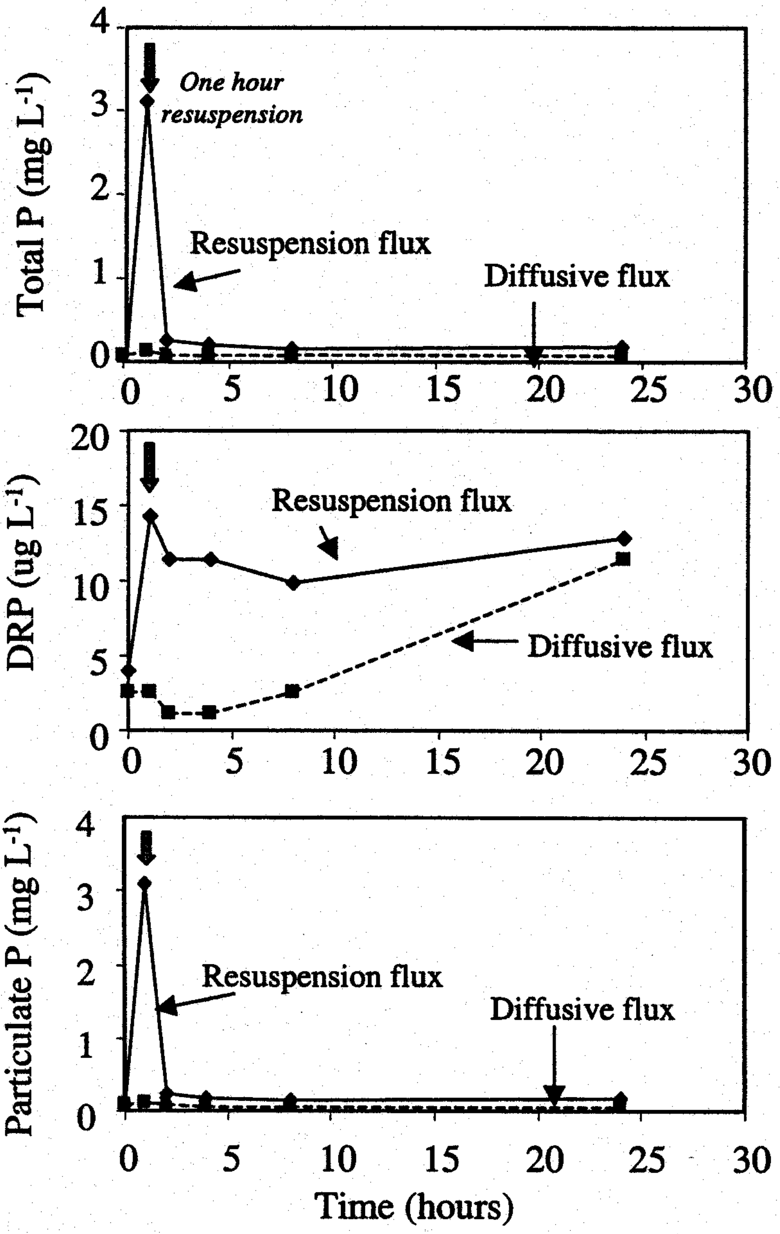


Fig. 4.23 Phosphorus release during and after sediment resuspension in cores obtained from a station located approximately 10 km north of Titusville, Fl.

As such, this experiment may overestimate the effect of an episodic sediment resuspension event in this region of the estuary.

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Appendix 4.1. Values used in the calculation of diffusive P flux using porewater equilibrators during the May 1997 and June 1998 NER experiment.

May 1997						
Station	A1	A2	B1	B2	C1	C2
Flux est. interval, cm	0-3	0-3	0-5	0-5	2-5	2-5
Gradient, mg L^{-1} cm^{-1}	-0.453	-0.389	-0.209	-0.346	-0.226	-0.197
Constant, cm^{2} day^{-1}	0.683	0.683	0.683	0.683	0.683	0.683
porosity, cm^{3} cm^{-3}	0.83	0.83	0.83	0.83	0.77	0.77
Adj const., cm^{2} day^{-1}	0.45	0.45	0.45	0.45	0.45	0.45
Flux, mg m^{-2} day^{-1}	1.69	1.45	0.77	1.28	0.76	0.67
June 1998						
Station	A1	A2	A3	B	C	
Flux est. interval, cm	0-5	0-5	0-6	0-5	0-8	
Gradient, mg L^{-1} cm^{-1}	0.006	0.108	0.123	0.161	0.388	
Constant, cm^{2} day^{-1}	0.68	0.68	0.68	0.68	0.68	
porosity, cm^{3} cm^{-3}	0.52	0.52	0.52	0.43	0.34	
Adj. const., cm^{2} day^{-1}	0.41	0.41	0.41	0.41	0.41	
Flux, mg m^{-2} day^{-1}	0.013	0.228	0.260	0.275	0.515	

Appendix 4.2. Values used in the calculation of diffusive N flux using porewater equilibrators during the May 1997 and June 1998 NER experiment.

May 1997

Station	A1	A2	B1	B2	C1	C2
Flux est. interval, cm	0-5	0-5	0-5	0-5	2-5	2-5
Gradient, mg L^{-1} cm^{-1}	-0.94	-0.56	-1.16	-1.62	-0.85	-0.41
Constant, cm^{2} sec^{-1}	1.98E-05	1.98E-05	1.98E-05	1.98E-05	1.98E-05	1.98E-05
porosity, cm^{3} cm^{-3}	0.83	0.83	0.83	0.83	0.77	0.77
Adj. const., cm^{2} sec^{-1}	1.30E-05	1.30E-05	1.30E-05	1.30E-05	1.28E-05	1.28E-05
Flux, mg m^{-2} day^{-1}	8.75	5.21	10.79	15.00	7.15	3.48

June 1998

Station	A1	A2	A3	B1	C1
Flux est. interval, cm	0-3	0-3	0-4	0-5	0-5
Gradient, mg L^{-1} cm^{-1}	1.13	1.10	1.21	0.63	1.15
Constant, cm^{2} sec^{-1}	1.98E-05	1.98E-05	1.98E-05	1.98E-05	1.98E-05
porosity, cm^{3} cm^{-3}	0.52	0.52	0.52	0.43	0.33
Adj. const., cm^{2} sec^{-1}	1.19E-05	1.19E-05	1.19E-05	1.16E-05	1.13E-05
Flux, mg m^{-2} day^{-1}	5.984	5.839	6.425	2.683	3.746

Appendix 4.3. Concentration profiles (mg L^{-1}) of DRP observed using porewater equilibrators in May 1997 and June 1998 in Indian River Lagoon sediment.

Depth	A1	A2	B1	B2	C1	c2
5	0.01	0.01	0.01	0.01	0.01	0.06
4	0.03	0.04	0.01	0.01	0.01	0.14
3	0.03	0.06	0.01	0.01	0.01	0.06
2	0.03	0.04	0.01	0.01	0.01	0.21
1	0.04	0.11	0.03	0.03	0.01	0.06
0	0.29	0.09	0.11	0.04	0.04	0.07
-1	0.97	0.16	0.37	0.31	0.11	0.09
-2	1.24	0.78	0.46	0.51	0.29	0.11
-3	1.71	1.18	0.69	0.39	0.82	0.13
-4	2.22	1.19	0.75	1.46	0.97	0.21
-5	2.48	1.42	1.30	1.80	0.99	0.74
-6	3.67	1.17	1.42	1.58	0.93	0.84
-7	3.86	1.22	1.37	1.12	0.97	0.88
-8	3.75	1.09	1.45	1.09	0.98	0.82
-9	3.00	0.92	1.53	1.10	1.23	1.01
-10	2.48	0.91	1.84	1.33	1.09	0.95
-12	1.47	1.09	1.13	1.62	1.43	1.12
-14	1.09	1.37	1.23	1.47	1.42	1.07
-16	0.64	1.32	2.14		1.52	1.07
-18	0.61	2.14			1.63	1.02
-20	0.68	1.19			0.79	0.97

June 1998	A1	A2	A3	B1	C1
5	0.055	0.041	0.057	0.074	0.100
4	0.060	0.042	0.055	0.062	0.057
3	0.061	0.044	0.057	0.057	0.055
2	0.064	0.048	0.057	0.061	0.057
1	0.068	0.061	0.059	0.061	0.092
0	0.548	0.095	0.059	0.072	0.183
-1	0.515	0.184	0.341	0.246	0.414
-2	0.565	0.258	0.486	0.625	0.658
-3	0.614	0.466	0.534	0.744	1.663
-4	0.586	0.549	0.601	0.771	1.580
-5	0.538	0.590	0.743	0.861	1.671
-6	0.476	0.561	0.900	0.730	2.333
-7	0.565	0.541	0.916	0.590	2.512
-8	0.484	0.534	0.847	0.381	3.588
-9	0.495	0.653	0.885	0.321	2.727
-10	0.522	0.648	0.939	0.221	
-12	0.561	0.665	1.097		2.369
-14	0.552	0.908	1.376		
-16	0.548	0.679	1.136		
-18	0.747	0.482	1.110		

Appendix 4.4. Concentration profiles of NH_4-N (mgL^{-1}) observed using porewater equilibrators in May 1997 and June 1998 in Indian River Lagoon sediment.

Depth						
May 1997	A1	A2	B1	B2	C1	c2
5	0.03	0.09	0.09	0.09	0.09	0.09
4	0.03	0.11	0.09	0.09	0.09	0.09
3	0.03	0.09	0.09	0.09	0.09	0.09
2	0.03	0.09	0.09	0.09	0.09	0.09
1	0.13	0.33	0.18	0.13	0.09	0.09
0	0.77	0.83	0.48	0.24	0.09	0.18
-1	1.93	1.07	1.37	1.72	0.13	0.38
-2	2.06	1.89	1.91	1.96	1.07	0.66
-3	2.92	2.56	3.45	1.80	2.51	0.88
-4	4.34	2.95	4.04	6.71	3.25	1.07
-5	5.72	3.48	6.71	8.59	3.64	1.96
-6	7.13	3.59	7.08	8.39	3.89	2.41
-7	7.55	4.29	6.81	7.20	4.04	2.51
-8	8.11	4.30	8.49	7.20	4.19	2.56
-9	8.49	4.47	8.52	7.20	5.52	2.77
-10	8.54	4.78	8.34	7.50	6.22	2.69
-12	6.81	5.87	5.82	7.53	6.91	4.09
-14	5.65	7.21	6.61	5.31	7.35	4.44
-16	4.50	8.79	6.10		7.25	4.26
-18	4.63	7.78			6.66	3.51
-20	4.63	6.81			5.01	2.46
June 1998	A1	A2	A3	B1	C1	
5	0.195	0.019	ND	0.031	ND	
4	0.001	ND	ND	ND	ND	
3	ND	0.445	ND	ND	ND	
2	ND	ND	ND	ND	ND	
1	0.001	0.074	ND	ND	0.001	
0	0.536	0.220	ND	ND	0.293	
-1	3.100	0.622	1.096	ND	1.060	
-2	3.556	2.408	3.283	0.148	1.461	
-3	4.146	3.296	4.049	0.604	4.196	
-4	4.389	3.624	4.499	1.498	5.108	
-5	4.328	3.405	5.374	3.230	5.381	
-6	4.012	3.271	6.565	2.883	6.803	
-7	3.842	3.296	7.234	2.628	11.890	
-8	4.024	5.009	7.331	2.336	6.530	
-9	4.146	5.933	7.538	1.826	6.438	
-10	4.255	6.067	8.048	1.097	6.129	
-12	4.121	6.553	8.935		5.272	
-14	4.146	5.654	9.969			
-16	4.383	4.621	7.769			
-18	4.316	3.344	6.711			

Appendix 4.5. Concentration profiles of SO_4 (mg L^{-1}) observed using porewater equilibrators in May 1997 and June 1998 in Indian River Lagoon sediment.

Depth						
May 1997	A1	A2	B1	B2	C1	c2
5		1303	1323	1443	1279	1283
4	1323	1321	1273	1383	1286	1295
3	1340	1320	1250	1441	1262	1283
2	1340	1290	1243	1440	1299	1212
1	1492	1331	1186	1495	1265	1120
0	1424	1295	1021	1453	1294	1284
-1	1427	1253	882	1460	1283	1329
-2	1366	1132	905	1390	1275	1306
-3	1295	975	967	1310	1214	1287
-4	1262	839	747	943	1178	1252
-5	1045	678	689	809	1162	866
-6	938	665	654	805	1174	1251
-7		639	836	821	1099	1244
-8		668	892	799	922	1278
-9	722	658	1037	801	961	1177
-10	671	555	1043	835	743	898
-12	604	494	805	1146	710	842
-14	623	594	1320	1399	754	797
-16	720	517	1313		1121	796
-18	881	813			1115	848
-20	1051	829			1296	1121
June 1998	A1	A2	A3	B1	C1	
5	2619	2408	2357	2354	2570	
4	2392	2835	2354	2556	2748	
3	2630	2873	2613	2589	2662	
2	2345	3143	2546	2487	2563	
1	1123	2976	2419	2563	2709	
0	2137	2763	2335	2430	2695	
-1	2052	2539	2351	2547	2516	
-2	2158	2406	2096	2432	2447	
-3	1658	2349	2000	2368	2091	
-4	1870	1970	1975	2360	2056	
-5	1605	2135	1647	2123	1697	
-6	1991	1918	1595	1705	1452	
-7	2084	1899	1330	2416	1368	
-8	1706	1825	1221	2403	1492	
-9	1546	1440	1128	2451	1647	
-10	1263	1358	1088	2495	1414	
-12	1407	1315	879		2028	
-14	1185	1288	793			
-16	1179	1583	1209			
-18	1320	1866	1466			

Appendix 4.6. Concentration profiles of DIC (mg L^{-1}) observed **using** porewater equilibrators in May 1997 **and** June 1998 in **Indian** River Lagoon sediment.

Depth						
May 1997	A1	***A2***	B1	B2	C1	c2
5	11	13	16	14	8	10
4	15	12	16	14	10	15
3	16	15	16	13	13	15
2	16	13	15	14	8	16
1	12	13	11	15	12	14
0	12	11	13	30	10	43
-1	13	12	20	15	9	16
-2	14	9	26	13	12	12
-3	19	18	33	9	12	14
-4	21	17	36	30	12	16
-5	25	18	40	31	15	14
-6	23	18	59	35	16	15
-7	36	23	16	49	14	14
-8	48	18	29	38	16	20
-9	43	28	41	47	30	16
-10	41	29	20	36	29	16
-12	**44**	31	26	46	39	26
-14	44	24	26	27	45	27
-16	65	20	9		43	26
-18	35	32			36	29
-20	49	33			27	20
June 1998	A1	***A2***	A3	B1	C1	
5	74	68	74	78	81	
4	7s	69	72	74	83	
3	74	68	73	74	86	
2	75	69	74	76	82	
1	77	71	75	82	82	
0	99	79	74	88	88	
-1	143	82	110	102	107	
-2	140	89	139	131	104	
-3	145	113	142	135	134	
-4	143	124	154	155	139	
-5	144	127	166	169	144	
-6	135	114	177	154	139	
-7	128	114	186	141	134	
-8	131	118	185	119	147	
-9	138	127	194	113	139	
-10	137	126	208	109	152	
-12	133	135	256		157	
-14	137	142	***264***			
-16	137	140	183			
-18	133	128	176			

Appendix 4.7. Concentration profiles of CH_4 (mg L^{-1}) observed using porewater equilibrators in May 1997 and June 1998 in Indian River Lagoon sediment.

Depth						
May 1997	A1	A2	B1	B2	C1	C2
5	0.01	0.01	0.01	0.01	0.01	0.01
4	0.01	0.01	0.01	0.01	0.01	0.01
3	0.01	0.03	0.01	0.01	0.01	0.01
2	0.01	0.04	0.01	0.01	0.01	0.01
1	0.03	0.01	0.02	0.02	0.01	0.01
0	0.07	0.02	0.1	0.02	0.01	0.01
-1	0.09	0.02	0.22	0.06	0.02	0.02
-2	0.13	0.04	0.19	0.08	0.06	0.02
-3	0.13	0.07	0.34	0.05	0.09	0.02
-4	0.19	0.1	0.23	0.16	0.1	0.04
-5	0.2	0.08	0.21	0.41	0.11	0.06
-6	0.23	0.07	0.27	0.44	0.11	0.07
-7	0.26	0.08	0.35	0.27	0.12	0.08
-8	0.35	0.13	0.2	0.25	0.14	0.09
-9	0.2	0.13	0.22	0.2	0.12	0.09
-10	0.22	0.16	0.31	0.16	0.16	0.1
-12	0.11	0.37	0.06	0.17	0.16	0.11
-14	0.2	0.37	0.09	0.16	0.21	0.12
-16	0.18	0.29	0		0.1	0.13
-18	0.22	0.86			0.13	0.12
-20	0.21	0.3			0.11	0.08
June 1998	A1	A2	A3	B1	C1	
5	0.015	0.007	0.007	0.008	0.007	
4	0.01	0.007	0.007	0.006	0.006	
3	0.021	0.008	0.008	0.008	0.006	
2	0.013	0.009	0.009	0.008	0.006	
1	0.031	0.008	0.008	0.009	0.006	
0	0.034	0.019	0.01	0.016	0.012	
-1	0.03	0.021	0.076	0.027	0.024	
-2	0.026	0.018	0.1	0.063	0.029	
-3	0.032	0.018	0.095	0.068	0.059	
-4	0.029	0.017	0.099	0.091	0.05	
-5	0.032	0.016	0.107	0.107	0.062	
-6	0.031	0.014	0.094	0.078	0.042	
-7	0.037	0.013	0.086	0.065	0.04	
-8	0.043	0.014	0.068	0.035	0.034	
-9	0.05	0.015	0.072	0.023	0.038	
-10	0.033	0.017	0.084	0.021	0.058	
-12	0.04	0.033	0.159	0	0.159	
-14	0.055	0.052	0.131			
-16	0.037	0.035	0.069			
-18		0.025	0.055			

Appendix 4.8. Concentration profiles of pH observed using porewater equilibrators in May 1997 and June 1998 in Indian River Lagoon sediment.

Depth May 1997	A1	A2	B1	B2	C1	c 2
5	8.14	8.19	8.11	8.11	8.09	7.95
4	8.26	8.2	8.15	8.17	8.15	8.11
3	8.28	8.16	8.15	8.18	8.16	8.13
2	8.28	8.19	8.13	8.17	8.16	8.13
1	8.15	7.83	7.85	8.15	8.16	8.1
0	7.77	7.64	7.59	8	8.1	7.9
-1	7.61	7.59	7.52	7.66	8.02	7.68
-2	7.59	7.65	7.55	7.44	7.66	7.74
-3	7.58	7.66	7.7	7.45	7.53	7.72
-4	7.57	7.67	7.79	8.1	7.54	7.65
-5	7.59	7.7	7.89	8.1	7.64	7.54
-6	7.63	7.64	8.05	8.26	7.66	7.61
-7	7.67	7.67	7.97	8.28	7.69	7.57
-8	7.83	7.61	8	8.15	7.68	7.59
-9	7.89	7.68	8.03	8.22	7.95	7.61
-10	7.95	7.77	8.11	8.16	8	7.64
-12	8.08	7.86	8	8.15	8.12	7.84
-14	8.09	7.87	8.1	7.91	8.21	7.9
-16	7.96	7.96	7.94		8.24	7.97
-18	7.91	7.89			8.19	8.01
-20	7.9	7.95			7.86	7.61
June 1998	A1	A2	A3	B1	C1	
5	8.22	8.29	8.22	8.2	8.11	
4	8.19	8.34	8.37	8.32	8.22	
3	8.22	8.35	8.39	8.39	8.23	
2	8.22	8.33	8.38	8.34		
1	8.22	8.3	8.37	8.23	8.21	
0	7.92	8.13	8.32	8.09	7.79	
-1	7.33	8.03	7.84	7.86	7.8	
-2	7.38	7.83	7.55	7.68	7.74	
-3	7.41	7.56	7.47	7.62	7.71	
-4	7.43	7.57	7.5	7.54	7.7	
-5	7.44	7.54	7.35	7.49	7.74	
-6	7.45	7.54	7.46	7.47	7.72	
-7	7.48	7.53	7.55	7.45	7.67	
-8	7.48	7.57	7.56	7.43	7.68	
-9	7.48	7.6	7.61	7.43	7.69	
-10	7.49	7.62	7.63	7.49	7.77	
-12	7.55	7.61	7.63		7.75	
-14	7.57	7.63	7.67			
-16	7.56	7.62	7.7			
-18	7.62	7.53	7.72			

Appendix 4.9. Concentration of NH_4-N in the water column of intact sediment cores retrieved from th
Indian River Lagoon Estuary.

	Station								
	A-1	A-2	A-3	B-1	B-3	C-1	c-2	c-3	
May 1997	mg L^{-1}								
0	0.147	0.193	0.147	0.258	0.110	0.361	0.221	0.519	
1	0.426	0.379	0.351	0.909	0.221	0.798	0.500	2.583	
2	0.816	0.528	0.574	2.211	0.258	0.928	0.621	3.513	
4	1.002	0.426	0.640	3.141	0.286	0.630	0.537	4.257	
7	0.574	0.249	0.454	2.769	0.137	0.202	0.435	3.513	
10	0.091	0.091	0.137	0.333	0.054	0.110	0.221	0.909	
14	0.082	0.054	0.054	0.110	0.054	0.091	0.137	0.193	
June 1998									
	A-1	A-2	A-3	B-1	B-2	B-3	C-1	c-2	c-3
0	0.341	0.08	0.153	0.062	0.031	0.104	0.104	0.122	0.122
1	0.001	0.457	0.001	0	0.092	0.062	0.353	0.718	0.408
2	0.092	0.001	0.049	0	0.232	0.122	0.912	1.125	0.852
3	0.001	0.001	0	0.043	0.274	0.244	1.216	1.52	1.095
4	0.244	0.11	0.001	0.062	0.487	0.445	1.581	2.195	1.642
6	0.062	0.305	0.214	0.183	1.046	1.089	2.559	3.222	2.347
8	0.031	0.293	0.536	0.256	1.441	2.037	2.979	3.939	2.918
11	0.062	0.669	0.906	0.657	2.371	2.906	3.574	4.729	3.514
14	0.037	0.967	0.912	1.046	2.979	3.72	3.58	5.24	3.653

Appendix 4.10. Concentration of soluble P in the water column of intact sediment cores retrieved from the Indian River Lagoon Estuary.

	Station								
	A- 1	A-2	A-3	B-1	B-3	**C**-1	c-2	c-3	
May 1997	mg L^{-1}								
0	0.024	0.032		0.041	0.026	0.052	0.034	0.058	
1	0.034	0.039	0.023	0.108	0.034	0.086	0.049	0.125	
2	0.063	0.052	0.034	0.158	0.036	0.112	0.062	0.175	
4	0.093	0.065	0.052	0.220	0.050	0.130	0.075	0.203	
7	0.171	0.099	0.062	0.272	0.103	0.164	0.112	0.209	
10	0.149	0.116	0.071	0.579	0.103	0.166	0.132	0.214	
14	0.207	0.104	0.067	0.746	0.108	0.222	0.209	0.261	
June 1998									
0	0.029	0.065	0.036	0.041	0.036	0.032	0.032	0.086	0.036
1	0.018	0.129	0.011	0.043	0.079	0.032	0.043	0.312	0.058
2	0.029	0.237	0.014	0.072	0.090	0.072	0.101	0.481	0.093
3	0.029	0.294	0.022	0.090	0.097	0.133	0.140	0.553	0.122
4	0.022	0.294	0.007	0.072	0.083	0.133	0.129	0.538	0.101
6	0.029	0.359	0.018	0.108	0.115	0.183	0.179	0.610	0.144
8	0.036	0.431	0.025	0.172	0.144	0.208	0.205	0.632	0.165
11	0.058	0.567	0.029	0.197	0.158	0.223	0.187	0.667	0.151
14	0.097	0.732	0.036	0.230	0.208	0.359	0.172	0.617	0.151

Appendix 4.3. Values used in the calculation of diffusive N flux using porewater equilibrators during the May 1999 and December 1999 NER experiment.

May 1999

Replication	I	II	III
Flux est. interval, cm	0-(-5)	+1-(-2)	+2-0
Gradient, mg L^{-1} cm^{-1}	-1.10123	-1.6784	-1.5225
Constant, cm^2 sec^{-1}	1.98E-05	1.98E-05	1.98E-05
porosity, cm^3 cm^{-3}	0.21	0.21	0.21
Adj. const., cm^2 sec^{-1}	1.09E-05	1.09E-05	1.09E-05
Flux, mg m^{-2} day^{-1}	2.217	3.379	3.065

December 1999

Replication	I	I	III
Flux est. interval, cm	0-4	2-(-1)	2-(-5)
Gradient, mg L^{-1} cm^{-1}	-0.65684	-0.35912	-0.24372
Constant, cm^2 sec^{-1}	1.98E-05	1.98E-05	1.98E-05
porosity, cm^3 cm^{-3}	0.21	0.21	0.21
Adj. const., cm^2 sec^{-1}	1.09E-05	1.09E-05	1.09E-05
Flux, mg m^{-2} day^{-1}	1.322	0.723	0.491

Appendix 4.4. Values used in the calculation of diffusive P flux using porewater equilibrators during the May 1999 and December 1999 NER experiment.

May 1999

Replication	I	II	III
Flux est. interval, cm	0-(-6)	+1-(-1)	+3-0
Gradient, mg L^{-1} cm^{-1}	-0.07121	-0.236	-0.1297
Constant, cm^{2} sec^{-1}	7.90E-06	7.90E-06	7.90E-06
porosity, cm^{3} cm^{-3}	0.21	0.21	0.21
Adj. const., cm^{2} sec^{-1}	4.36E-06	4.36E-06	4.36E-06
Flux, mg m^{-2} day^{-1}	0.056	0.187	0.103

December 1999

Replication	I	II	III
Flux est. interval, cm	0-3	2-(-1)	2-(-5)
Gradient, mg L^{-1} cm^{-1}	-0.090	-0.041	-0.048
Constant, cm^{2} sec^{-1}	7.90E-06	7.90E-06	7.90E-06
porosity, cm^{3} cm^{-3}	0.21	0.21	0.21
Adj. const., cm^{2} sec^{-1}	4.36E-06	4.36E-06	4.36E-06
Flux, mg m^{-2} day^{-1}	0.071	0.033	0.038

CHAPTER 5

MINERALIZATION OF ORGANIC NITROGEN IN SEDIMENTS
[Task 6.7 as per the contract]

5.1 Introduction

Nitrogen cycling between benthic sediments and the overlying water column regulates the productivity of estuary and the food chain. In many estuaries and other aquatic systems, N was shown to be limiting nutrients (Kemp et al., 1982; Nixon, 1981; D'Elia et al., 1986). In addition to anthropogenic N inputs, in many estuaries a significant portion of the recycled N is released from sediments to the overlying water column in the form of NH_4-N (Kemp et al., 1990; Roy et al., 1994). Similar observations were made in freshwater ecosystems (Reddy and Patrick, 1984; Reddy and D'Angelo, 1994). The coupled processes related to N cycling in benthic sediments and in the overlying water column are: (1) mineralization of organic N to NH_4^+, (2) nitrification of NH_4^+ to NO_3^- in aerobic environments, (3) denitrification of NO_3^- to N_2 in anaerobic environments, (4) adsorption/desorption of NH_4^+ in sediments, (5) NH_3 volatilization in the water column, and (6) assimilation of N species by plankton. These processes are coupled with two major exchange mechanisms, i.e., diffusion and resuspension. Because sediment functions as a major reservoir of N, the NH_4^+ is constantly regenerated in the sediments during decomposition of organic matter. Ammonium N produced undergoes ion exchange equilibrium between sediment solid phase and sediment porewater, thus resulting in an equilibrium concentration in the porewater.

Microbial oxidation of sediment organic matter during aerobic (O_2 as electron acceptor), facultative anaerobic (NO_3^- and Fe^{3+} as electron acceptors) and anaerobic (SO_4^{2-} and HCO_3^- as electron acceptors) respiration can result in breakdown of organic N compounds and release of NH_4-N. A significant portion of the organic matter produced in the photic zone of surface water is decomposed aerobically, while the settled organic matter undergoes anaerobic decomposition, depending on the availability of electron acceptors (Cappenberg and Prins, 1974; Jorgensen, 1982; Howarth and Teal, 1979).

Objective of this study was to determine the potential rates of organic N mineralization under aerobic and anaerobic conditions in estuarine sediments.

5.2 Materials and methods

5.2.1. Site Description

The Indian River Lagoon Estuary is a large, shallow, mesohaline lagoon. It is approximately 255 km in length and varies in width from 0.3 km to 9 km. The Lagoon is shallow, with an average depth of approximately 1m. It is bounded to the east by a barrier island, separating it from the Atlantic Ocean. It has been reported that it has the highest biodiversity of any estuary in North

America and provides annual economic benefits to counties surrounding the lagoon estimated at approximately 700 million dollars. Loss of emergent vegetation is estimated at 75% since 1950 with 100% loss of seagrass beds in some locations. The seagrasses and emergent macrophytes of the Indian River Lagoon are critical ecosystem components in that they provide habitat for many species for at least some period of their life cycle (Virnstein et al., 1983; Gilmore et al., 1983). Circulation and flushing occur through freshwater inflows, tidal cycles **through** three inlets, and wind mixing. Overall flushing by tidal cycles is low, whereas flushing due to wind can be the principle source of flushing, according to simulation models (Sheng et al., 1994). Low flushing rates have obvious implications on nutrient loading, tending to exacerbate the effects of point and non-point loading.

One of the goals of the Surface Water Improvement and Management (**SWIM**) Plan for the Indian River Lagoon Estuary calls for the attainment and maintenance of water and sediment quality sufficient to support a healthy macrophyte-based estuarine lagoon system; or to Class III waters or better (SWIM, 1994), with emphasis on the reduction of excessive point and non-point source loading of nutrients. A major portion of nutrients loaded to this estuary can be retained by sediments. Once the external load criteria **are** met as a result of better control of point and non-point source inputs, internal sources (from bottom sediments) may maintain current water quality conditions. Thus, sediments can act as a source of nitrogen (N) and phosphorus (P) and therefore constitute a potential non-point source of nutrient loading to the Lagoon.

5.2.2 Sediment sampling

Based on physico-chemical properties of sediments obtained from 24 stations, we have identified nine sites with a wide range in sediment physico-chemical properties (Fig. 5.1) (Table 5.1). Surface sediments obtained from these sites were used in laboratory experiments to determine potential rates of organic N mineralization under aerobic and anaerobic conditions.

5.2.3 Batch incubations

Aerobic conditions: Two-hundred grams of wet sediment and 0.8 L of filtered (**0.45** µm) estuary water (obtained from Station 17) was placed into nine continuously stirred, foil-covered 1-L reactors (Fig. 5.2). A #13 rubber stopper inserted into the **flask** was outfitted with 2 redox electrodes, a salt bridge, glass aeration inlet and outlet ports, and a glass pH electrode (Fig. 5.2). The sediment slurry was continuously **stirred** with a magnetic stir plate, and was continuously bubbled with laboratory air using **an** aquarium pump (approx. 280 mL minute-'), to maintain aerobic conditions. The air exiting from the flask was bubbled **through** 2 M H_2SO_4 to trap NH_3 evolved during volatilization. All incubations were conducted in the dark at 31°C (± 1C) in triplicate.

Samples of the sediment-water slurry were withdrawn at time = 0, 1, 2, 4, 8, and 16 days. They were immediately filtered through 0.45 µm polyestersulfone filters, acidified with concentrated H_2SO_4, and frozen until analyzed. Ammonium-N, **NO_3-N, NO_2-N,** DRP, pH, temperature, and redox potential were determined for each time step. Each station was replicated three times with the individual replications for each station performed approximately 16 days apart; i.e. all nine stations

Table 5.1 Geographic coordinates of sampling stations used in sediment sampling. Horizontal datum is North American Datum 1927 (NAD27).

Station	Latitude	Longitude
Southern zone		
I-1	27' 31.544’	80'20.131'
1-2	27' 41.455'	80° 23.354'
I-4	27' 51.476'	80° 29.011'
1-5	27' 58.576'	80' 31.842
Mud zone		
1-8	28' 03.285'	80' 34.577'
I-11	28'08.188'	80° 36.927'
Northern zone		
1-13	28' 27.769'	80' 43.600'
1-15	28° 35.386'	80° 44.753’
1-21	28' 43.710'	80° 49.354'

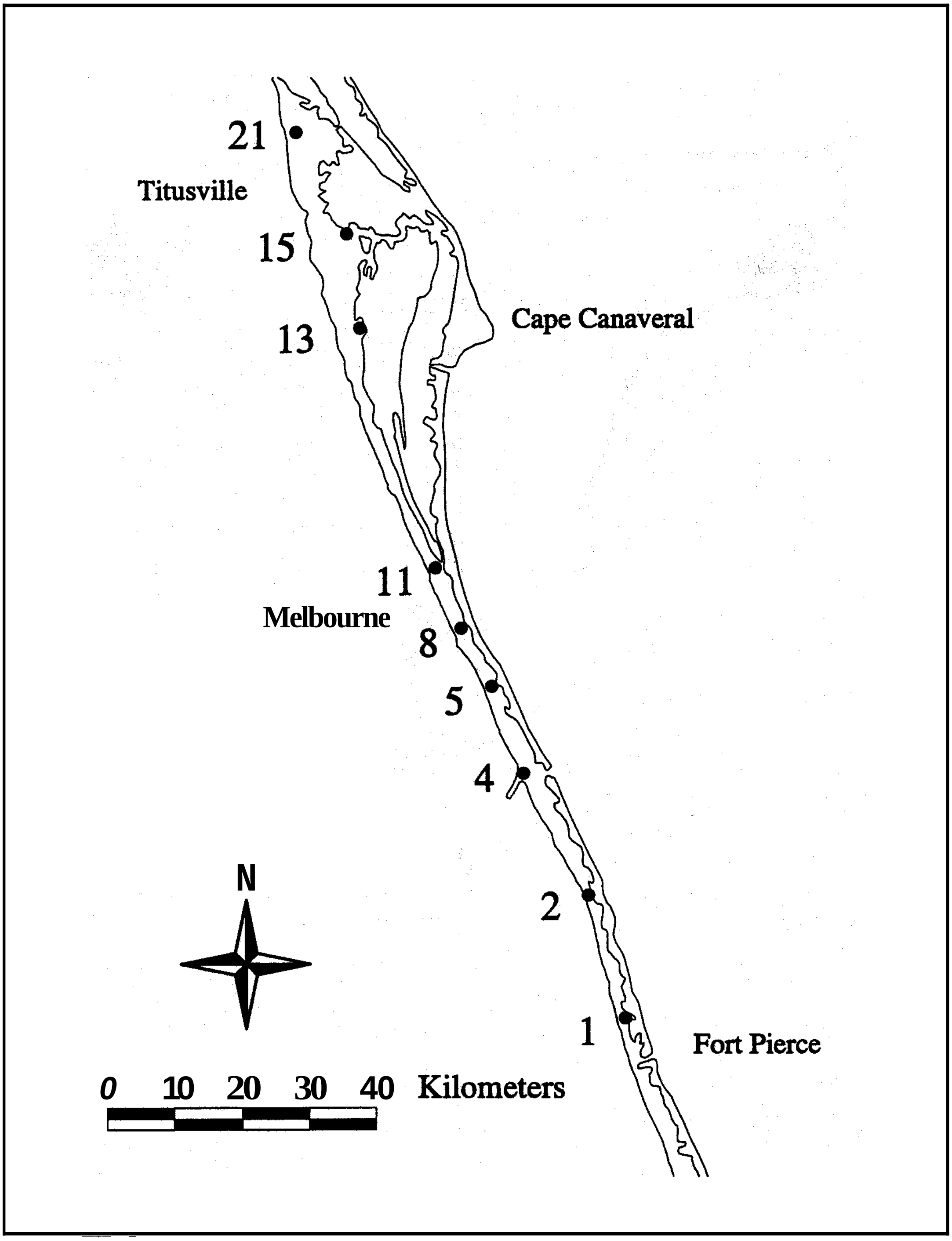

Fig. 5.1. Map showing the sampling stations

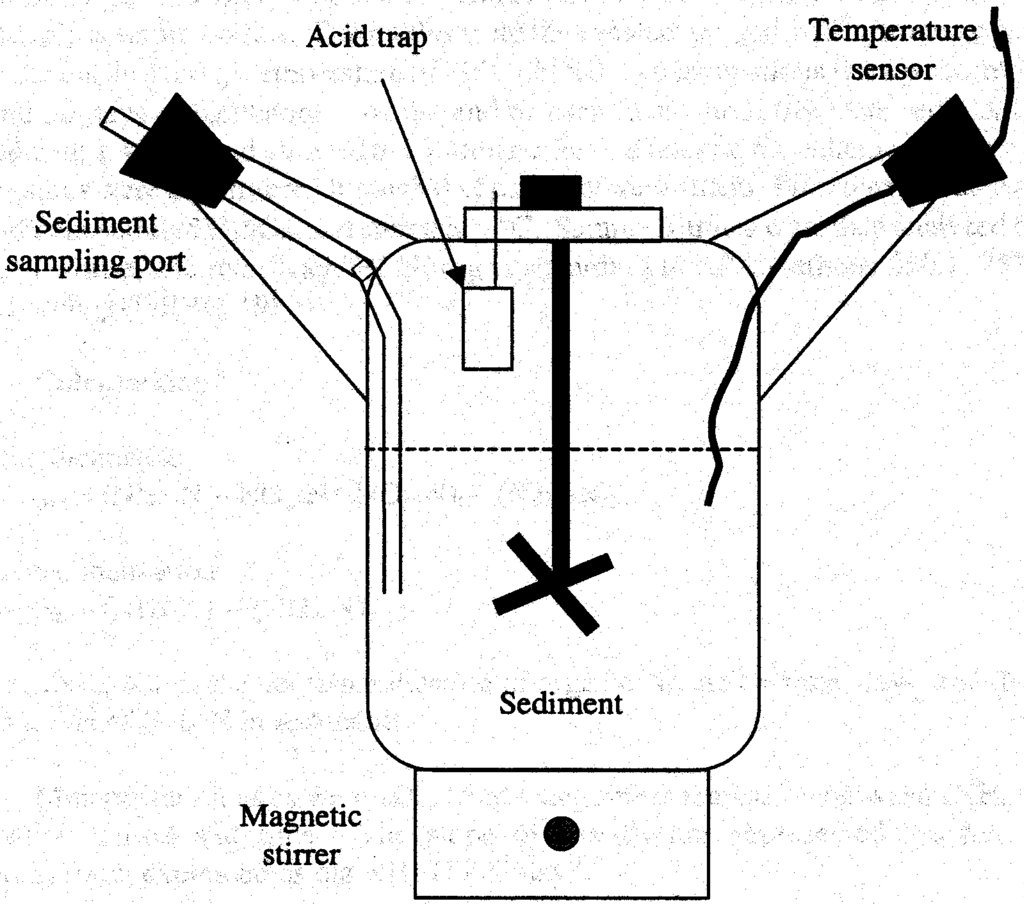

Fig. 5.2. Schematic showing the reactor set-up used for mineralization experiments conducted under aerobic conditions.

were incubated simultaneously for a single replication. Bulk surface (0-10 cm) sediment samples obtained for this experiment were collected on December 28, 1997, and the experiment commenced on February 16, 1998, ending April 8, 1998. The average pH and Eh during the course of the experiment was approximately 7.50 and 440 mV, respectively, for all stations and all replications (Table 5.2).

Anaerobic incubation: Surficial (0-10 cm) sediment samples collected from the IRL during the December 1997 were used to determine potential mineralization of organic N under anaerobic conditions. Approximately 10 g of wet sediment and 10 mL of unfiltered site water were placed into 160 mL glass serum bottles. The bottles were then sealed, purged with nitrogen gas, and incubated in the dark at an average temperature of 29°C (±1°C). All incubations were performed in 0, 3, 7, 15, 21, and 30 days of incubation. At the end of each incubation, triplicate sediment samples were treated with 1*M* KCl and allowed to equilibrate for one hour on a mechanical shaker. The sediment suspensions were then filtered through 0.45 μm membrane filters. Filtrates were then acidified with 1 drop of concentrated H_2SO_4, and stored at 4 °C. Sample filtrates were then analyzed for ammonium, nitrate + nitrite, and total Kjeldhal Nitrogen according to EPA methods 350.1, 353.2, and 351.2, respectively, (USEPA, 1983).

5.2.4 Calculations

Aerobic Incubation

$$(NH_4\text{-}N)_m = (NH_4\text{-}N + NO_2\text{-}N + NO_3\text{-}N)_t - (NH_4\text{-}N)_{t=o}$$

Anaerobic Incubation

$$(NH_4\text{-}N)_m = (NH_4\text{-}N)_t - (NH_4\text{-}N)_{t=o}$$

where: $(NH_4\text{-}N)_m$ is the net mineralization of organic N; and t = time, days; and $(NH_4\text{-}N)_{t=o}$ is the initial levels of NH_4-N in sediments.

Mineralization rates were calculated using linear regression between $(NH_4\text{-}N)_m$ at various incubation period and time. The slope of best-fit line represented the rate of organic N mineralization, expressed as mg NH_4-N kg^{-1} day''.

5.3 Results and Discussion

Sediments varied in total N content ranging from 100 to 5,180 mg N kg^{-1} (Table 5.1). Sediments in the mud zone showed a high degree of spatial variability. Total N content was low in sediments obtained from Station 8 during December, 1997 sampling as compared to previous sampling periods (Chapter 3). Sediments from Station 11 (mud zone) contained high levels of total N, reflecting the characteristics of mud zone sediments. Sediments in southern zone (Stations 1-5), and northern zone (Stations 13-21) contained low levels of total N (Table **5.2).** The particulate organic N (PON) accounted for >95% of the total N (Table **5.3).**

Table 5.2 Selected physico-chemical properties of sediments used in the study.

Sampling Station	pH	Total Organic C	Total N	Total P
		g kg^{-1}	---------------mg kg^{-1}---------------	
Southern zone				
I-1	7.7	16.4	1610	858
1-2	8.2	5.9	330	773
I-4	8.1	2.1	100	54
1-5	8.2	4.2	500	554
Mud zone				
1-8	8.3	---	110	14
I-11	7.9	56.0	5180	906
Northern zone				
1-13	7.9	0.3	200	122
1-15	8.2	6.2	180	427
1-21	8.1	5.1	420	148

Table 5.3 Mineralization of organic nitrogen in Indian River Lagoon sediments incubated under aerobic conditions (n=3). PON = Particulate Organic N. Specific rate = zero-order/Initial PON concentration.

Sampling Station	Initial Organic N	Mineralization Rate		
		zero-order		Specific rate
	mg kg^{-1}	mg kg^{-1} day^{-1}		day^{-1}
Southern zone				
I-1	1586	3.12	(0.27)	0.0020
1-2	319	1.04	(0.03)	0.0033
I-4	96	0.77	(0.06)	0.0080
1-5	493	2.10	(0.22)	0.0043
Mud zone				
1-8	104	1.15	(0.06)	0.0111
1-11	5,139	8.54	(1.55)	0.0017
Northern zone				
1-13	196	1.12	(0.07)	0.0057
1-15	178	0.83	(0.11)	0.0047
1-21	417	0.18	(0.06)	0.0004

Under aerobic conditions sediment NH_4-N concentration decreased rapidly followed by a concomitant increase in NO_3-N + NO_2-N over the period, due to nitrification (see Chapter **6**). However, NO_3-N + NO_2-N accumulation was much higher to account for nitrification only, suggesting mineralization of organic N. Aerobic mineralization rates were estimated from inorganic N accumulation measured and **16** day incubation period (Fig. **5.3**). Appropriate connections were made for NO_3-N derived during nitrification of initial NH_4-N. For all sediment samples, an initial lag-phase was observed in organic N mineralization, followed by a steady increase during **16** day incubation period (Fig. **5.3**). Aerobic mineralization rates were highest for sediments from Station **11.** Mineralization rates ranged from **0.77** to **3.12** mg N kg^{-1} day^{-1} for southern zone sediment, as compared to **0.18 – 1.12** mg N kg^{-1} day^{-1} for northern zone sediments (Table **5.3**). Mineralization rates increased with increase in particulate organic N (PON) (Table **5.3**). Mineralization rates normalized to PON, indicate highest rates in sediments obtained from Station 8, and lowest rates at Station **21.**

Anaerobic mineralization rates were measured from **NH_4-N** accumulation over **30** day incubation period (Fig. **5.4**). Increase in **NH_4-N** during **30** days showed a non-linear relationship with time for most sediments. Initial lag-phase was not observed in organic N mineralization. However, the rates presented in Table **5.4** represent the linear portion of the **NH_4^+** accumulation over time. Anaerobic mineralization rates also showed similar trends as those observed under aerobic conditions (Table **5.4**). Rates were approximately one-half to two-thirds of those observed under aerobic conditions (Fig. 5.5).

Organic N mineralization involves stepwise breakdown, with initial step involving enzymatic hydrolysis, followed by (i) hydrolytic deamination of amino acids and peptides, (ii) degradation of nucleotides, and (iii) metabolism of methylamines by methanogenic bacteria (King et al., **1983**). Often the limiting step in mineralization is the conversion of PON to soluble organic N **(SON).** The turnover times for SON, ranged from **14** to **166** days under aerobic conditions, **25** to **145** days under anaerobic conditions (Table 5.5). Organic N mineralization in sediments is influenced by a number of factors including the characteristics of planktonic biomass deposited on sediment surface, C/N ratio of organic substrate, and temperature. Mineralization of organic N in sediments regulates the porewater NH_4^+ concentration and **flux** of **NH_4^+** from sediment to overlying water column (Kemp et al., **1990**).

Results presented in this study show relative rates of potential sediment organic N mineralization under aerobic and anaerobic conditions. Additional studies are needed on the rate of PON deposition and temporal changes in N pools, in surface sediments. Low concentration of PON in the water column suggests low deposition rates. It is likely much of the decomposition of detrital planktonic biomass occurs in the water column before it is deposited on the sediments surface. Ammonium produced in the sediment during mineralization, is transformed into NO_3^- at the aerobic sediment-water interface or the water column and some of this **NH_4^+** is also used to support primary production in the water column.

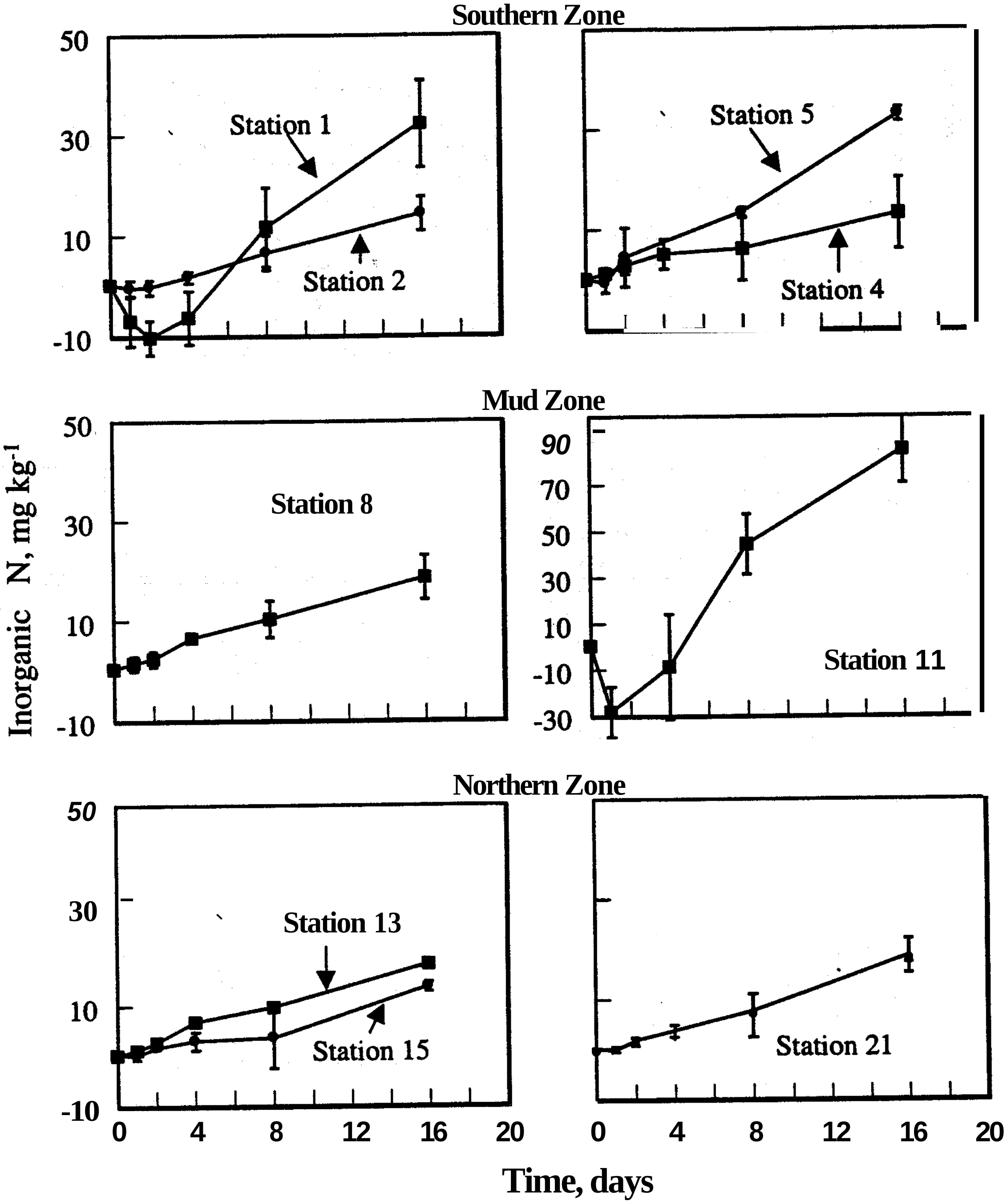

Fig. 5.3. Nitrate accumulation during mineralization of organic nitrogen under aerobic conditions.

Table 5.4 Mineralization of organic nitrogen in Indian River Lagoon sediments incubated under anaerobic conditions (n=3). Values shown in parenthesis are one standard deviation. PON = Particulate organic N. Specific rate = zero order rate/initial PON concentration.

Sampling Station	PON	Mineralization Rate	
		zero-order	Specific rate
	mg kg^{-1}	mg kg^{-1} day^{-1}	day^{-1}
southern zone			
I-1	1586	2.61 (0.12)	0.0016
I-2	319	0.65 (0.09)	0.002
I-4	96	0.30 (0.03)	0.0031
I-5	493	0.65 (0.03)	0.0013
Mud zone			
I-8	104	0.95 (0.20)	0.0091
I-11	5139	4.28 (0.25)	0.0008
Northern zone			
I-13	196	0.45 (0.05)	0.0023
I-15	178	0.66 (0.06)	0.0037
I-21	417	0.62 (0.06)	0.0015

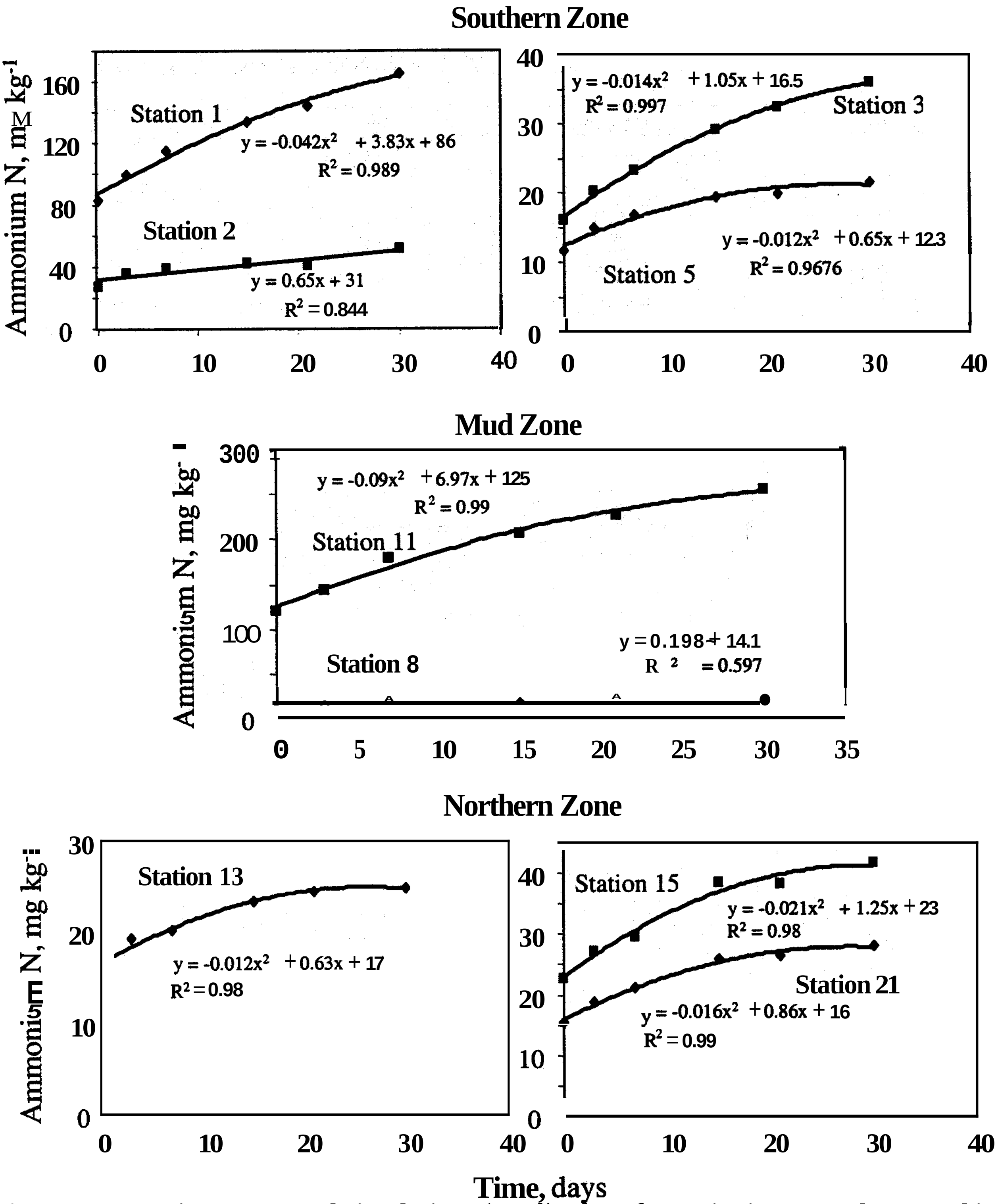

Fig. 5.4. **Ammonium N accumulation during mineralization of organic nitrogen under anaerobic conditions.**

Table 5.5 Specific mineralization rate of soluble (SON) of organic nitrogen in Indian River Lagoon sediments incubated under anaeobic conditions (n=3). Values shown in parenthesis are one standard deviation. PON = Particulate organic N.

Sampling Station	SON	Aerobic	Anaerobic
	mg kg^{-1}	---------------------day^{-1}	----------------
Southern zone			
I-1	65.8	0.047	0.040
1-2	51.6	0.020	0.013
I-4	43.0	0.018	0.007
1-5	43.1	0.049	0.015
Mud zone			
1-8	35.8	0.032	0.027
I-11	116.6	0.073	0.037
Northern zone			
1-13	27.1	0.041	0.017
1-15	28.8	0.029	0.023
1-21	31.3	0.006	0.020

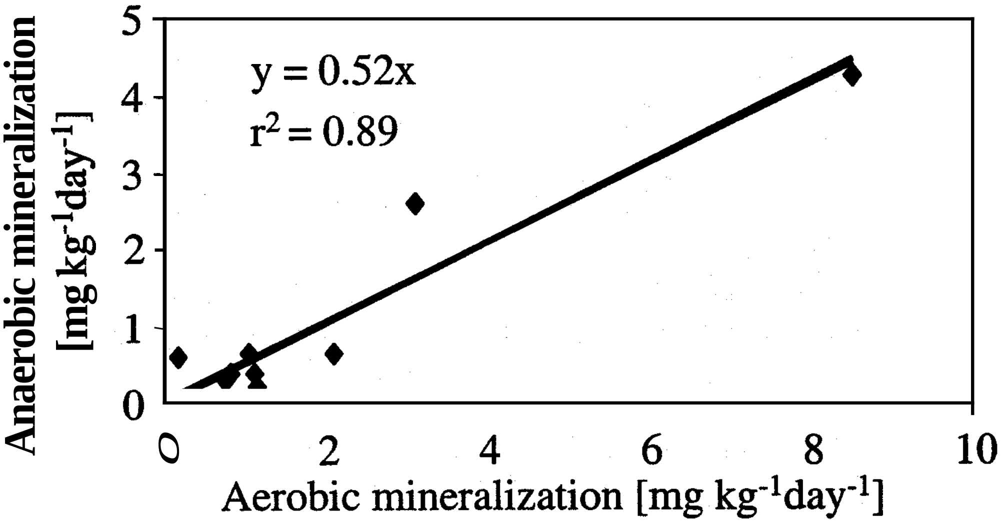

Fig. 5.5 Relationship between aerobic and anaerobic mineralization of organic nitrogen.

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CHAPTER 6

NITRIFICATION AND DENITRIFICATION IN SEDIMENTS

[Task 6.7 as per the contract]

6.1 Introduction

Ammonium N is added to aquatic systems either **through** anthropogenic inputs or by mineralization of organic N in sediments and water column. Nitrification is defined as the biological conversion of reduced N forms (NH_4-N) to more oxidized states (NO_3-N or NO_2-N). The nitrifying bacteria are confined largely to aerobic lithotrophs of the genera *Nitrosomonas* and ***Nitrobacter.*** Nitrification is a key process in the N budget of estuarine systems, since the NO< formed can be assimilated by many species. More importantly, nitrification provides the substrate (NO_3^-) for denitrification, a major N removal mechanism in estuaries (Henriksen and Kemp, 1988; Roy et al. 1994).

In estuaries, nitrification can occur: (1) in the water column (Dore and Karl, 1996), and (2) in the surface-oxidized sediments (Kemp et al., 1990). Nitrate formed during nitrification either in the water column or in the surface oxidized sediments can diffuse into anoxic zones of sediments and consumed by microbes as an alternate electron acceptor. Nitrate reduction is one of the major N removal mechanisms in estuaries (Jensen et al1994). Denitrification (a nitrate reduction mechanism) is a respiratory process where facultative anaerobic bacteria use NO_3^- (or NO_2^-), in the absence of O_2, as the terminal electron acceptor during the oxidation of organic **C,** resulting in the production of gaseous end products such as N_2O and N_2 which are lost to the atmosphere. **A** competing mechanism called dissimilatory NO_3^- reduction to ammonia (DNRA), is also a respiratory process used by facultative and obligate anaerobic bacteria which also use NO_3^- as the terminal electron acceptor (Tiedje, 1988). Both processes are beneficial to organisms living in anaerobic, electron-rich environments such as sediments, since N oxide compounds act as an electron sink, which coupled to electron transport phosphorylation, produces energy for the organisms. **A** third mechanism called assimilatory nitrate reduction conserves N within the estuaries, since the organisms responsible utilize N in protein synthesis and other anabolic processes.

Physical, chemical, and biological conditions in the sediment determine which N transformation predominates. For example, denitrifying organisms are selected for when anoxia is temporary, or when the concentration of electron acceptors (i.e. NO_3^-) is high, since their utilization of NO_3^- (instead of O_2) is a secondary process. On the other hand, organisms responsible for DNRA are selected for **C** and electron-rich environments that are continuously anoxic. Assimilatory NO_3^- reduction is repressed by large amounts of NH_4^+ which usually occur in anaerobic sediments. Numerous field and laboratory studies have confirmed that each of the NO_3 reduction processes occur in a variety of environments, including estuarine sediments (King and Nedwell, 1987; Rivera-Monroy and Twilley, 1996), marine sediments (Oremland et al., 1984; Seitzinger and Nixon, 1985; Sorensen, 1978 a,b,c; Henriksen and Kemp, 1988, Roy et al., 1996), and lake sediments (Kaspar, 1983,1985; D'Angelo and Reddy, 1993).

The coupled processes of nitrification and denitrification regulate the overall N loss from estuarine sediments. Ammonium N in the sediment porewater readily diffuses into the water column in response to concentration gradient, where it is either assimilated by algae or undergoes transformation. However, diffusive flux of NH_4^+ is regulated by the capacity of sediments to adsorb NH_4^+. Sediments with high cation exchange capacity can maintain low NH_4^+ levels in the porewater, thus, decreasing flux to overlying water column. A major portion of NH_4^+ can be readily oxidized at the sediment water interface. Nitrate formed in the surface aerobic sediment zone diffuses downward in response to concentration gradient and demand for electron acceptors, and readily reduced to N_2O and N_2 (Howarth et al., 1988; Kemp et al., 1990). Similar processes can function when bottom sediments are resuspended into the water column during heavy wind events. Ammonium adsorbed onto sediment particles is rapidly desorbed into the water column upon resuspension, and made available for uptake by plankton. Sediment bound NH_4^+ when exposed to oxygenated water column can also be oxidized to NO_3^-. In addition, relatively high pH conditions of water column (pH > 8.0) during active photosynthetic period can also result in the conversion of NH_4^+ to NH_3 and lost to the atmosphere. Thus, two processes regulate the fate of NH_4^+ in the sediment-water column, i.e. (1) nitrification-denitrification, and (2) NH_3 volatilization. For example, N losses due to denitrification may account for about 50% of anthropogenic inputs of N (Seitzinger, 1988). Similarly, in Chesapeake Bay sediments, Kemp et al. (1990) showed nitrification-denitrification as the major mechanism regulating N cycling processes and nutrient enrichment.

The objective of this study was to determine: (1) NH_4^+ sorption potential of sediments, and (2) potential rates of nitrification and denitrification in sediments of Indian River Lagoon as related to water quality.

6.2 Materials and Methods

6.2.1 Site Description

The Indian River Lagoon Estuary is a large, shallow, mesohaline lagoon. It is approximately 255 km in length and varies in width from 0.3 km to 9 km. The Lagoon is shallow, with an average depth of approximately 1m. It is bounded to the east by a barrier island, separating it from the Atlantic Ocean. It has been reported that it has the highest biodiversity of any estuary in North America and provides annual economic benefits to counties surrounding the lagoon estimated at approximately 700 million dollars. Loss of emergent vegetation is estimated at 75% since 1950 with 100% loss of seagrass beds in some locations. The seagrasses and emergent macrophytes of the Indian River Lagoon are critical ecosystem components in that they provide habitat for many species for at least some period of their life cycle (Virnstein et al., 1983; Gilmore et al., 1983). Circulation and flushing occur through freshwater inflows, tidal cycles through three inlets, and wind mixing. Overall flushing by tidal cycles is low, whereas flushing due to wind can be the principle source of flushing, according to simulation models (Sheng et al., 1994). Low flushing rates have obvious implications on nutrient loading, tending to exacerbate the effects of point and non-point loading.

One of the goals of the Surface Water Improvement and Management (SWIM) Plan for the Indian River Lagoon Estuary calls for the attainment and maintenance of water and sediment quality sufficient to support a healthy macrophyte-based estuarine lagoon system; or to Class III waters or better (SWIM, 1994), with emphasis on the reduction of excessive point and non-point source loading of nutrients. A major portion of nutrients loaded to this estuary can be retained by sediments. Once the external load criteria are met as a result of better control of point and non-point source inputs, internal sources (from bottom sediments) may maintain current water quality conditions. Thus, sediments can act as a source of nitrogen (N) and phosphorus (P) and therefore constitute a potential non-point source of nutrient loading to the Lagoon.

6.2.2 Sediment sampling

Based on analysis of sediment samples collected from **24** stations, we have identified nine stations with a wide range in sediment physico-chemical properties (Fig. **6.1).** Surface sediments **(0-10** cm) obtained from these sites were used in the following laboratory experiments.

6.2.3 Batch incubations

6.2.3.1 Ammonium Sorption by Sediments

Bulk sediments obtained from nine stations **(0-10** cm depth) were incubated under anaerobic conditions to determine the partitioning coefficient (K_d) between sorbed NH_4^+ and porewater NH_4^+. A known amount of sediments was placed in several *50* ml centrifuge tubes. Ten milliliters of 0, 5, 10, and 20 mg NH_4-N L^{-1} solution were added to each of three replications from the nine selected stations. The incubation stock solutions were prepared in a solution of **24** g NaCl + **5** g $MgCl_2$ per liter of deionized water to which was added varying volumes of 1000 mg NH_4-N L^{-1} as NH_4Cl solution, to achieve the concentrations listed above. The final dry sediment to solution ratio was approximately 1:10. Samples were shaken for a period of **24** hours at 25°C. After a **24**-hour equilibration period, sediment samples were centrifuged and the supernatant liquid was filtered through a **0.45** um membrane filter. Filtered solutions were analyzed for NH_4-N (EPA Method No. **350.1).** Ammonium not recovered in solution was assumed to be sorbed by the sediments.

Ammonium sorbed by sediment was calculated as follows:

$$S = [C_o V - C_{24} V]/M \qquad [1]$$

where: $S = NH_4^+$ sorbed to sediment, mg kg^{-1}; C_o = initial NH_4^+ in solution mg L^{-1}; C_{24} = concentration of NH_4^+ in solution after **24** hour equilibration period, mg L^{-1}; V = volume of solution, L; and M = dry weight of sediment, kg. The NH_4^+ adsorption coefficient was calculated as follows:

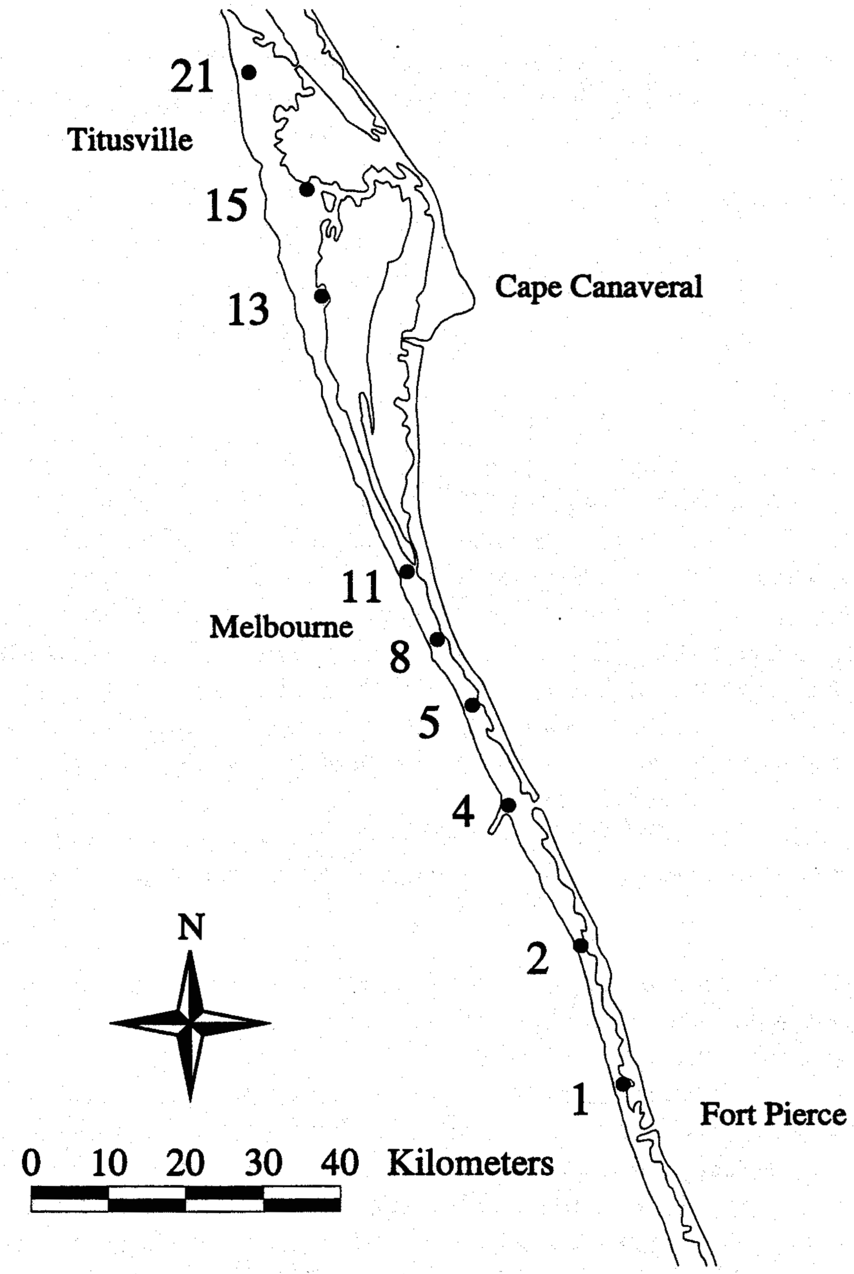


Fig. 6.1 Map of Indian River Lagoon showing sediment sampling stations.

$$S = K_D C_{24} - S_o \qquad [2]$$

where: K_D = adsorption coefficient, L kg^{-1}; $S_o = NH_4^+$ in sorbed phase at C_o; S and C_{24} are describe above. Adsorption coefficients were normalized to the amount of clay present in sediments.

$$K_{Dc} = K_D/f_c \qquad [3]$$

where: K_{Dc} = adsorption coefficients normalized to clay content; f_c = clay fraction in sediments.

6232 Nitrification

Laboratory experiments for nitrification were coupled with the mineralization experiments conducted under aerobic conditions (see Chapter **5).** Under aerobic conditions, mineralization of organic N results in conversion to NH_4^+, followed by subsequent conversion to NO_3^-. Two-hundred grams of wet sediment and **0.8** L of filtered **(0.45** µm) estuary water (obtained from Station **17)** was placed into nine continuously stirred, foil-covered **1** L reactors (Fig. **6.2).** A **#13** rubber stopper inserted into the top of the flask was outfitted with **2** platinum redox electrodes, a salt bridge, glass aeration inlet and outlet ports, and a glass pH electrode (Fig. **6.2).** The sediment slurry was continuously stirred with a magnetic stir plate, and was continuously bubbled with laboratory air using an aquarium pump (approx. **280 mL** minute-'), to maintain oxidized conditions favorable for nitrification. The air exiting from the flask was bubbled through **2** H_2SO_4 to monitor NH_3 volatilization processes. The incubation was conducted in the dark at **31°C** in triplicate.

Samples of the sediment-water slurry were withdrawn at time = 0, **1, 2, 4, 8,** and **16** days. They were immediately filtered through **0.45** um polyestersulfone filters, acidified with concentrated H_2SO_4, and frozen until analyzed. Ammonium-N, **NO_3-N,** NO_2-N, pH, temperature, and redox potential were determined for each time step. Each station was replicated in triplicate with the individual replications for each station performed approximately **16** days apart; i.e. all nine stations were incubated simultaneously for a single replication. Bulk surface **(0-10** cm) sediment samples obtained for this experiment was collected on December **28, 1997,** and the experiment commenced on February **16, 1998,** ending April **8, 1998.** The average incubation temperature for the first, second, and third replications was 30.0 **(±1.4), 30.6 (±1.7), 30.7 (21.9) °C,** respectively. The average pH and Eh during the course of the experiment was approximately **7.5** and **440** mV, respectively, for all stations and all replications.

Nitrification rates were calculated using linear regression between [NO_3-N + **NO_2-N]** concentrations measured at various sampling periods and time. The slope of best-fit line represented the rate of nitrification expressed as mg(NO_3 + **NO_2)-N** kg^{-1} day^{-1}. The rate was normalized to initial **NH_4-N** concentration of the sediment, expressed as first-order rate constants, as follows:

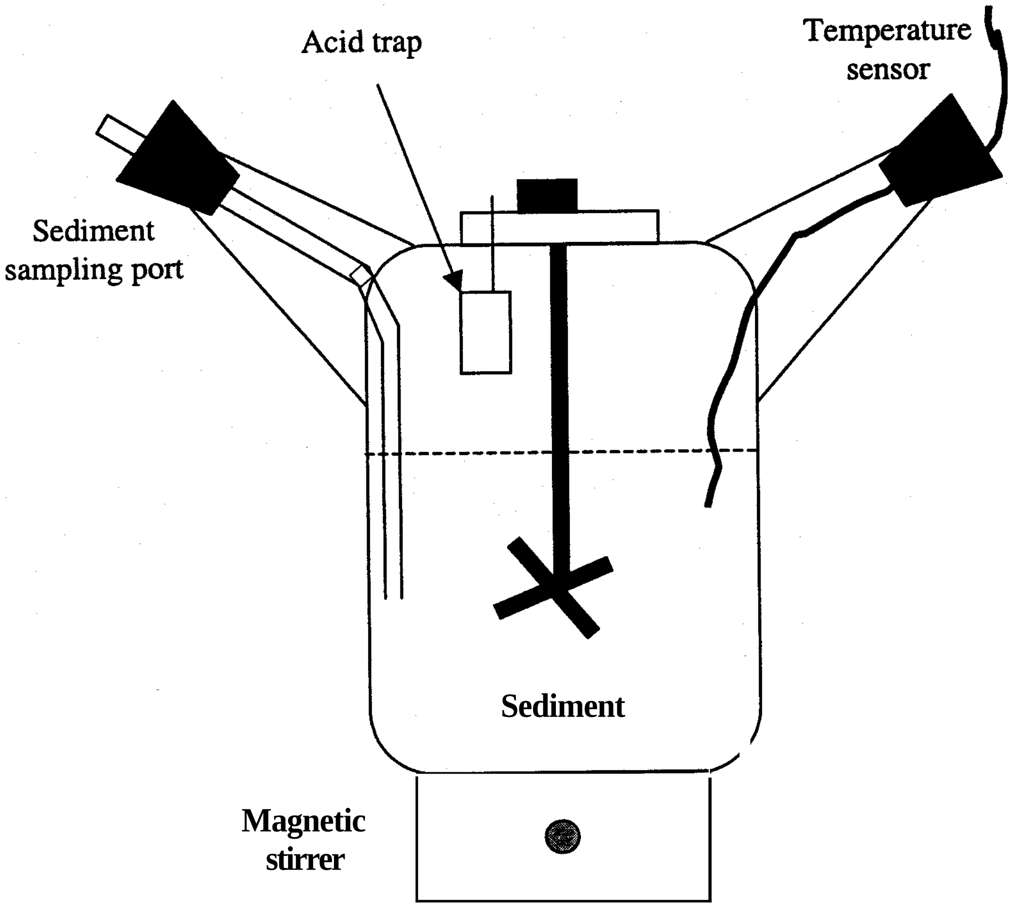


Fig. 6.2 Experimental reactors used in nitrification experiments.

Nitrification rate (day^{-1}) = (potential nitrification rate (mg kg^{-1} day^{-1})/ Initial NH_4-N concentration (mg kg^{-1})

6.2.3.3 Denitrification

Batch incubations were performed to determine the rate of denitrification, on sediments obtained at nine selected stations (Fig. 6.1). Fifty grams of wet sediment plus 50 ml of filtered estuary water was placed into 150 ml serum bottles. Each bottle was purged with N_2 gas to create anaerobic (oxygen free) conditions. Sediments were spiked with 0.5 ml of 100 mg NO_3-N L^{-1} to obtain a final concentration of approximately 1 mg NO_3-N L^{-1}. Nitrate used to spike the incubated samples was derived from KNO_3. Approximately 20% of the headspace volume was replaced with C_2H_2 in order to block the reduction of N_2O to N_2. High-purity acetylene was produced by reaction of CaC_2 with water. Samples were incubated in the dark at 25°C in an incubator/shaker. Headspace samples were withdrawn for analyses of N_2O at t = 0, 2, 4, 6, 8, 10, and 24 hours. The experiment commenced on March 23, 1998 and terminated on March 25, 1998. Nitrous oxide in the headspace samples was analyzed on a Shimadzu GC 14A gas chromatograph equipped with an electron capture detector.

Denitrification rates were calculated using linear regression between N_2O-N concentration measured at various sampling periods and time. The slope of best-fit line represented the rate of denitrification expressed as mg N kg^{-1} day^{-1}. The rate was normalized to initial NO_3-N concentrations of the sediment, and expressed as first-order rate constants as follows.

Denitrification rate (day^{-1}) = (potential denitrification rate (mg kg^{-1} day^{-1})/ Initial NO_3-N concentration (mg kg^{-1}).

6.3 Results and Discussion

6.3.1. Ammonium Adsorption

Selected characteristics of sediments (sampled in September, 1997) used NH_4^+ adsorption experiments are shown in Table 6.1. Sediment clay content was high in mud zone, as compared to northern or southern zones of the lagoon. Sediments sampled in December, 1997 were different in physico-chemical characteristics, especially at Stations 1 and 8, suggesting a high degree of spatial variability (Table 6.2). Sediments obtained December, 1997 were used in nitrification-denitrification experiments. Total N content of mud zone sediment was substantially higher than sediment of southern and northern zone sediments (Table 6.1). The total N content of mudzone sediment is in the same range as those reported for other estuaries (Simon and Kennedy, 1987). Adsorbed NH_4-N concentration (KCl-extractable NH_4-N) represent approximately 1-8% of total N.

Table 6.1 Selected physico-chemical properties of sediments used in NH_4^+ adsorption experiments. Sampling period = September, 1997. TOC = Total organic C; TN = Total nitrogen; and TP = total phosphorus.

Sampling Station	pH	Bulk Density	Clay content	TOC	TN	TP
		$g\ cm^{-3}$	%	$g\ kg^{-1}$	------------mg kg^{-1}------------	
Southern zone						
I-1	8.04	0.95	6.9	8.1	940	841
1-2	8.44	1.30	5.3	3.9	420	843
I-4	8.37	0.66	1.7	1.1	113	182
1-5	8.32	1.30	3.2	4.8	580	744
Mud zone						
1-8	7.79	0.23	17.0	51.1	5280	1049
1-11	8.01	0.32	27.9	38.6	4080	879
Northern zone						
1-13	8.04	1.56	1.6	1.3	100	164
1-15	8.12	1.50	2.6	1.9	100	430
1-21	8.20	1.46	4.4	3.8	390	141

Table 6.2 Selected physico-chemical properties of sediments used in nitrification and denitrification experiments. Sampling period = December, 1997. TOC = Total organic C: TN = total nitrogen; and TP = Total phosphorus.

Sampling Station	pH	Bulk Density	Porewater		Particulate		
			NH_4-N	DOC	TOC	TN	TP
		$g\ cm^{-3}$	----------mg L^{-1}-------		$g\ kg^{-1}$	----mg kg^{-1}--------	
Southern zone							
I-1	7.7	0.64	3.0	14.9	16.4	1610	858
1-2	8.2	1.23	2.0	24.9	5.9	330	773
I-4	8.1	1.62	0.1	29.6	2.1	100	54
I-5	8.2	1.38	2.2	21.8	4.2	500	554
Mud zone							
I-8	8.3	1.52	0.5	18.8	--	110	14
I-11	7.9	0.33	4.1	21.4	56.0	5180	906
Northern zone							
1-13	7.9	1.56	1.9	23.0	0.3	200	122
1-15	8.2	1.51	1.0	21.6	6.2	180	427
1-21	8.1	1.42	2.7	24.4	5.1	420	148

Relationship between NH_4^+ in dissolved and exchangeable pools is shown in Fig. **6.3.** Linear relationship was observed between these two pools for all sediments examined. The slope of linear regression, which represents the adsorption coefficient (K_D) (ratio between NH_4^+ adsorbed to NH_4^+ in solution). These values ranged from **2.2** to **7.8 L** kg^{-1} for mud zone sediments, as compared to **0.61** to **1.82 L** kg^{-1} for southern zone sediments, and **0.82** to **1.9 L** kg^{-1} for northern zone sediments (Table **6.3).** High K_D values were observed in sediment with high clay content. The K_D values assume equilibrium partitioning of NH_4^+ between solid and liquid phase during **24-hour** equilibrium period. Other researchers have reported values ranging from 0.8 to **4.9** L kg'' for marine sediments (Rosenfield, **1979;** Boatman and Murray, **1982;** Mackin and Aller, **1984).**

Adsorption coefficients (K_D values) were adjusted to variations in sediment bulk densities as follows:

$$K_D^* = K_D \, BD$$

Where K_D^* is the adsorption coefficient expressed as cm^3 cm^{-3} and BD in the bulk density, g cm^{-3}. The unitless adsorption coefficient, K_D^* ranged from **0.5** to **2.9,** with higher values found for mud zone sediment collected from Station 8 (Table **6.3).** For sediments obtained from the tidal Potomac River and estuary, Simon and Kennedy **(1987)** reported a value of **1.5.**

A number **of** factors regulate NH_4^+ adsorption by sediments, including clay content, cation exchange capacity, pH, Eh, and concentration of reduced cations such as Fe^{2+} and Mn^{2+}. In estuarine sediments the dominant cation occupying the cation exchange complex is Na^+, and simple exchange of Na^+ for NH_4^+ can result in low K_D values for NH_4^+

$$R\text{-}NH_4^+ + M^+ \rightarrow R - M^+ + NH_4^+$$

Where $[M^+]$ is a cation such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Fe^{2+}.

High pH conditions in sediments can result in deprotonation of adsorbed NH_4^+ by excess OH^- concentration (Simon and Kennedy, **1987)** as follows:

$$R - NH_4^+ + OH \rightarrow R - NH_3 + H20$$

Ammonium adsorption can play a significant role in sediments resuspended into water column during hydrodynamic events. The fine clay particles resuspended into water column generally have high cation exchange capacity, which may result in higher K_D values than those reported in this study. Additional studies should be conducted to determine short-term adsorption-desorption processes to more accurately represent sediment resuspension events. These studies should focus on fine sediments and kinetics of NH_4^+ sorption.

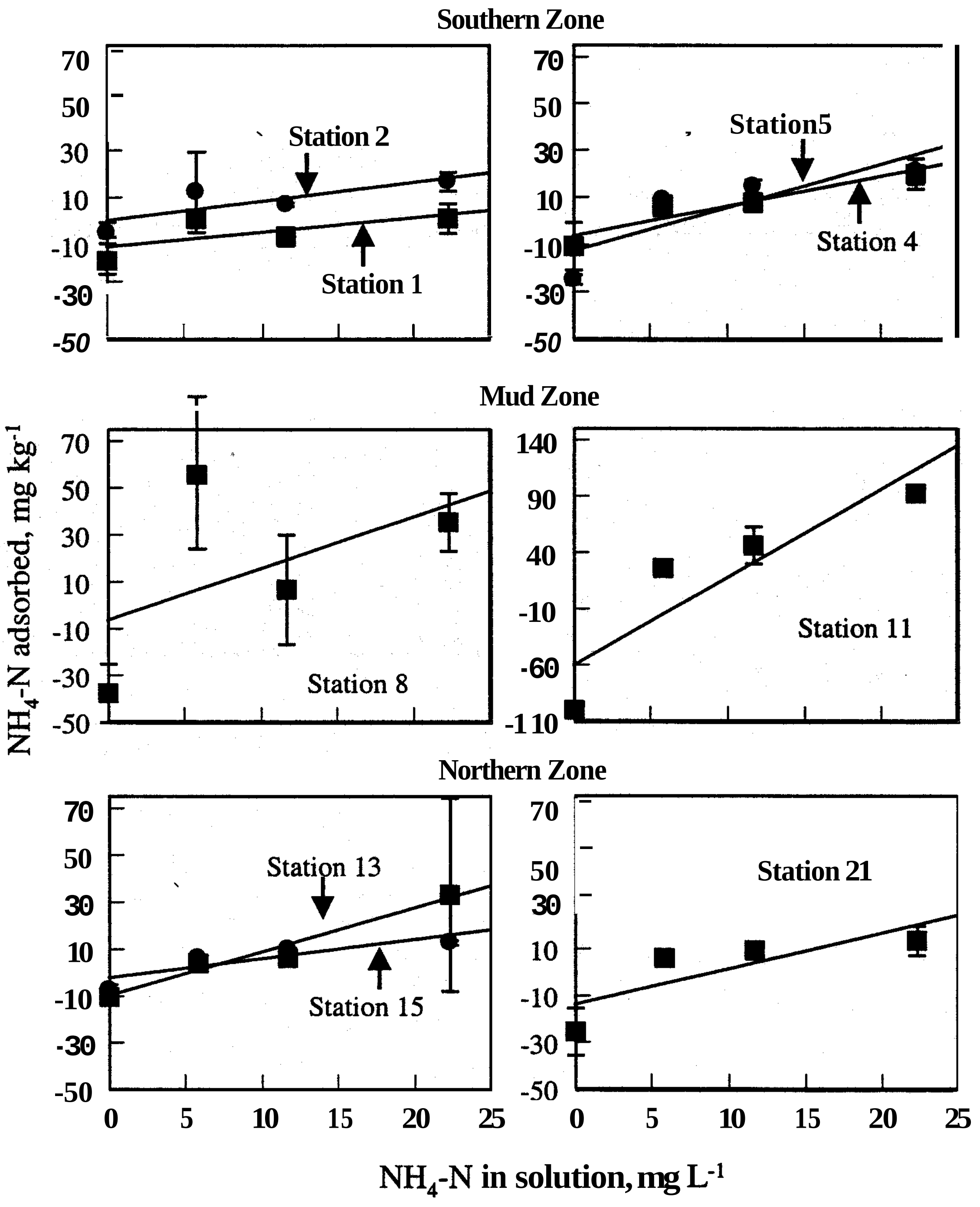


Fig. 6.3 Ammonium adsorption isotherms determined on IRL sediments.

Table 6.3 Ammonium adsorption coefficients measured under anaerobic conditions. K_{DC} = Adsorption coefficient normalized to clay content of sediments (n=3). Values in parenthesis represent the standard error of the estimate of the adsorption coefficient. K_D^* = unit less adsorption coefficient.

	Adsorption Coefficient			Adsorption	Coefficient
Sampling Station	K_D	Std.error	r^2	K_{DC}	K_D^*
	L kg^{-1}			L kg^{-1}	
Southern zone					
I-1	0.61	7.57	0.47	8.8	1.26
I-2	0.80	6.65	0.66	15.1	1.04
I-4	1.26	4.73	0.91	74.1	0.83
I-5	1.82	13.18	0.72	56.9	2.37
Mud zone					
I-8	2.18	42.5	0.27	12.8	0.50
I-11	7.78	44.5	0.81	27.9	2.49
Northern zone					
I-13	1.87	4.53	0.96	116.9	2.92
I-15	0.82	5.33	0.76	31.5	1.23
I-21	1.52	12.8	0.66	34.5	2.22

6.3.2 Nitrification

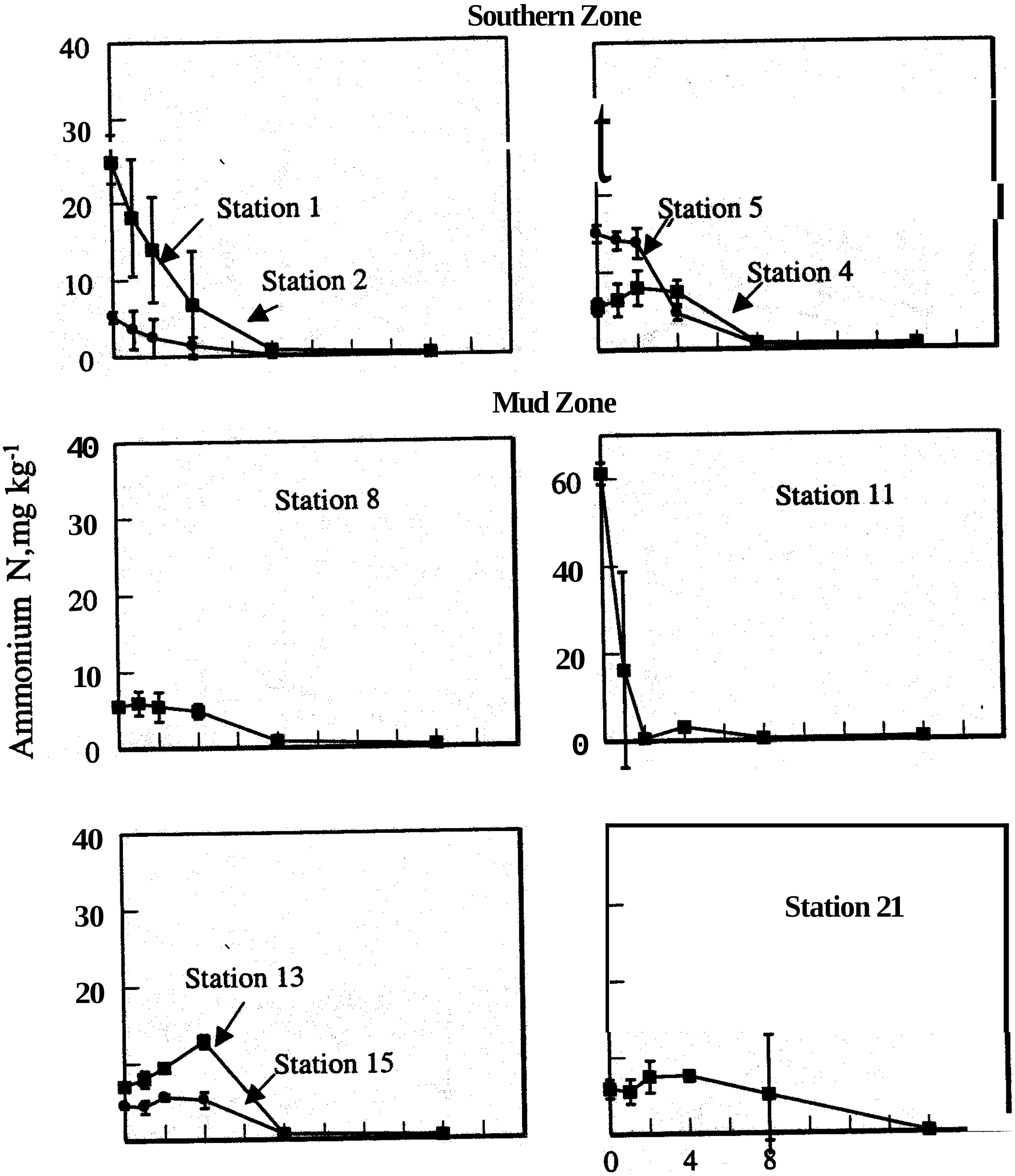
Ammonium-N concentration sediment porewater decreased rapidly from approximately **1** to **4** mg L^{-1} at the beginning of the incubation period to less than **0.10** mg L^{-1} by the end of 8 days (Fig. **6.4**). There was a concomitant increase in NO_2-N and NO_3-N over the period, due to nitrification (Fig. **6.5** and **6.6**). Nitrate accumulation increased up to 8 days, followed by rapid decrease by **16** days of incubation (Fig. **6.5**) A high degree of variability among replicates was noted among replicate incubations. Maximum NO_2^- concentrations were **<1** mg L^{-1}. Nitrate concentrations steadily increased throughout the incubation with maximum concentration up to 10 mg L^{-1} (Fig. **6.6**). Highest levels **of** NO_3^- accumulation was observed in sediment obtained from Station **11** of mud zone.

Potential nitrification rates were estimated by linear regression of $[NO_3^- + NO_2^-]$ –N with time, (Table **6.4**). Nitrification rates were influenced by initial NH_4^+ concentration of sediments. Rates were higher in sediments with high NH_4^+ concentrations (Table **6.4**). For example, NH_4^+ levels in sediments at Station **11** were highest, which resulted in high rates of potential nitrification rates. However, when rates normalized to initial NH_4^+ concentrations, they were approximately the same for all sampling stations, ranging from **0.154** to **0.241** day^{-1}. The turnover times for NH_4^+ levels ranged from **4.1** to 6.5 days.

Nitrification rates reported in Table **6.4** were converted on areal basis, for surface 1 cm sediment layer. We assume a maximum of l-cm surface sediment may be aerobic where nitrification can occur. Estimated potential rates of nitrification ranged from **56** to **97** pmol m^{-2} $hr^{-1}$for surface 1-cm aerobic sediment layer. For Chesapeake Bay sediments, Kemp et al (1990) reported potential nitrification rates in the range of 0 to 70 pmol m^{-2} hr^{-1}. Nitrification rates in Chesapeake Bay sediment exhibited a high degree of temporal variability, with negligible rates during summer months, and high rates during winter months (Kemp et al., **1990**). Decrease in summer nitrification rates were due to high sediment O_2 demand (Henriksen and Kemp, **1988;** Kemp et al., **1990**). Oxygen availiability was shown regulate nitrification in sediment (Rysgaard et al., **1994**). These studies suggest that similar temporal variations exist in IRL, and requires additional studies to establish these patterns. Other studies reported nitrification rates **46** pmol m^{-2} hr^{-1} in euphotic zone of North Pacific deep water (>4500 m).

6.3.3 Denitrification

Denitrification rates were estimated by acetylene blockage technique. Addition of acetylene blocks the enzyme system involved in the reduction of N20 to N_2, a final step in denitrification process. Thus, measurement of N_2O provides an evidence of denitrification in sediments (Fig. **6.7**). Negligible levels of NO_3^- were measured in sediments. Thus, to determine potential denitrification rates it was necessary to spike the sediments with NO_3^-. After spiking, initial NO_3^- levels in sediments ranged from **1.2** to



Southern Zone
40
30
20
10
0
Station 1
Station 2
Station 5
Station 4
Mud Zone
Ammonium N, mg kg-1
40
30
20
10
0
Station 8
60
40
20
0
Station 11
40
30
20
Station 13
Station 15
Station 21
0
4
8

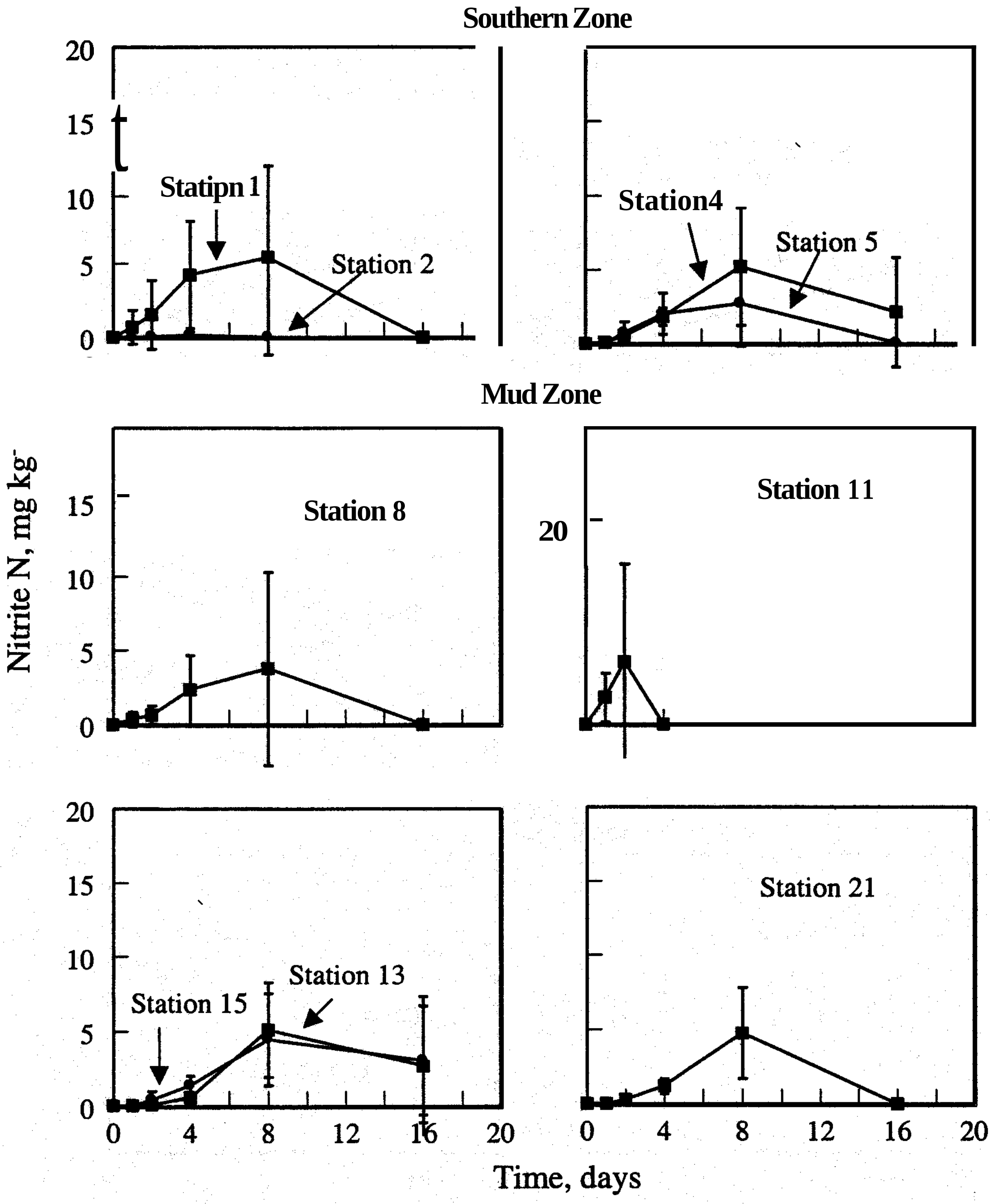


Fig. 6.5 Changes in NO_2-N concentration of sediments incubated under aerobic conditions.

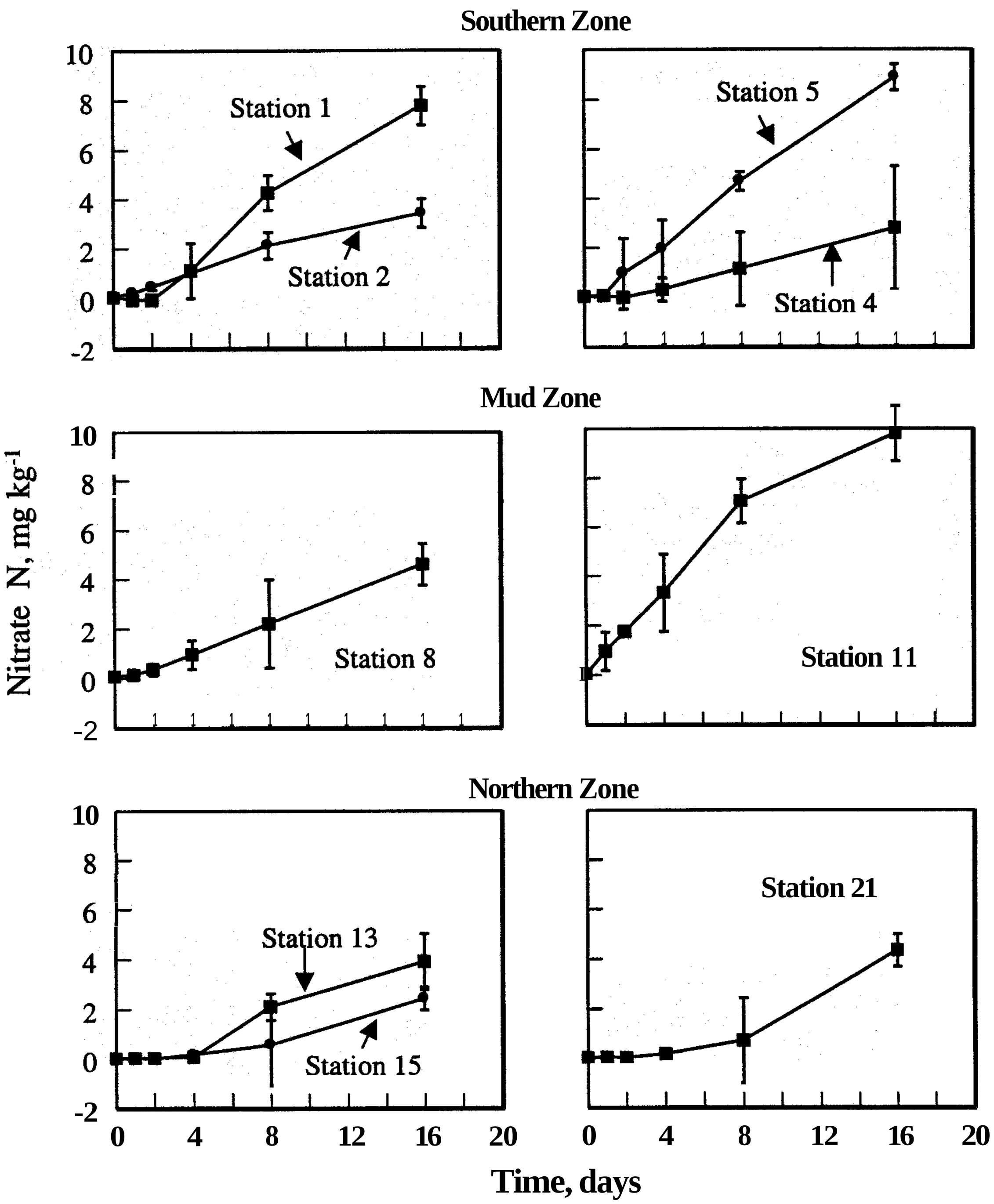


Fig. 6.6 Changes in NO_3-N concentration of sediments incubated under aerobic conditions.

Table 6.4 Nitrification rates in Indian River Lagoon Sediments (n=3). Values in parenthesis are one standard deviation. Specific rate = zero-order rate/initial NH_4-N.

Sampling Station	Initial Ammonium in sediments	Nitrification Rates		
		zero-order		Specific rate
	mg kg^{-1}	mg kg^{-1} day^{-1}		Day^{-1}
Southern zone				
I-1	28.8	4.44	(0.32)	0.154
I-2	6.2	1.27	(0.07)	0.204
I-4	6.6	1.25	(0.12)	0.190
I-5	17.8	3.21	(0.15)	0.180
Mud zone				
I-8	6.5	1.44	(0.13)	0.221
I-11	65.3	9.92	(0.79)	0.152
Northern zone				
I-13	8.3	1.89	(0.38)	0.226
I-15	5.3	1.27	(0.04)	0.241
I-21	7.0	1.68	(0.10)	0.240

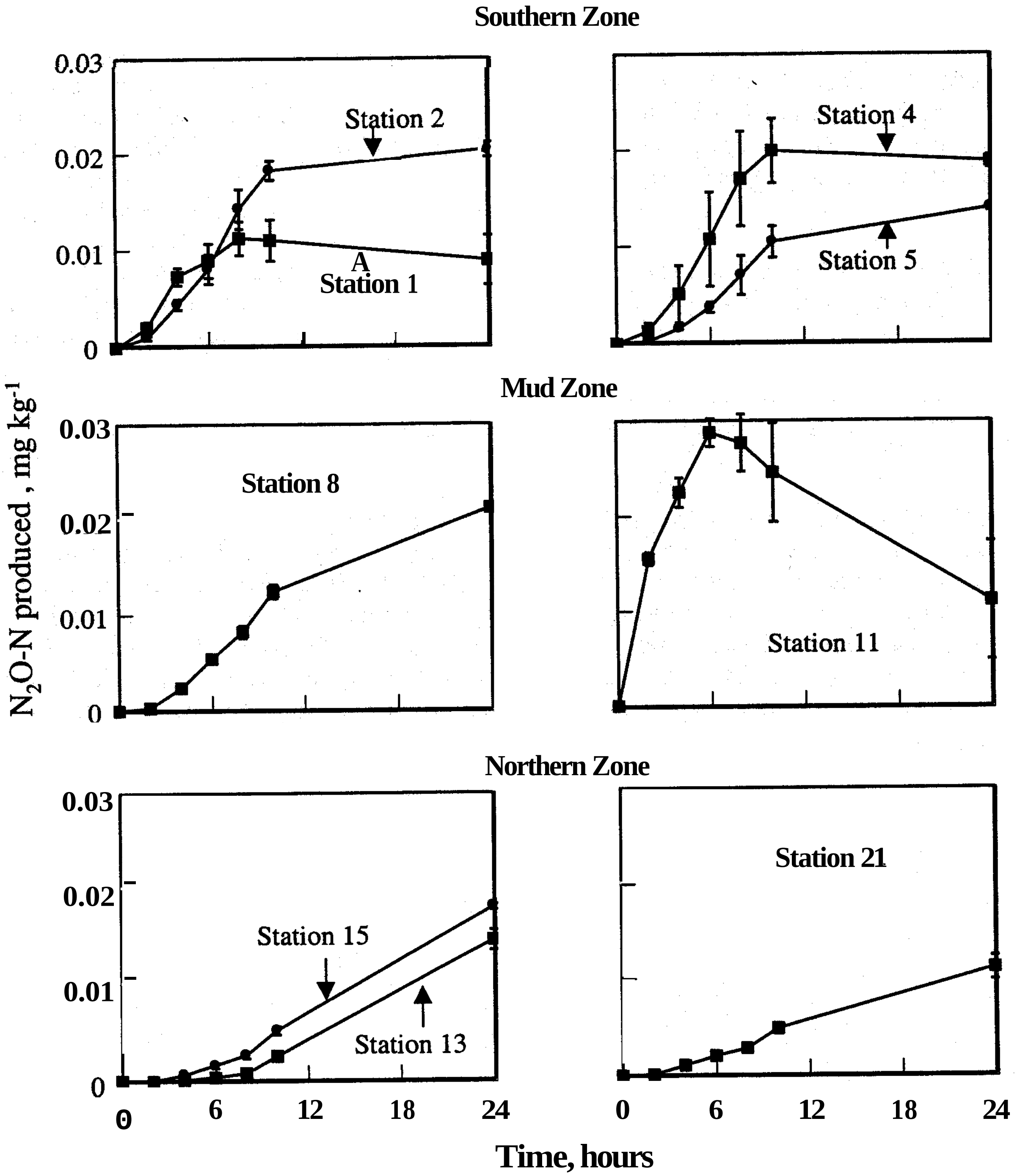


Fig. 6.7 Nitrous oxide production during denitrification process in sediments incubated under anaerobic conditions.

3.2 mg kg^{-1} (Table **6.5**). Potential denitrification rates ranged from **0.4** to **6.9** mg kg^{-1} day^{-1}, with high values reported for mud zone (Table *6.5*).

Several studies have indicated NO_3^- limitation for denitrification in both freshwater and estuarine systems (Koike and Sorensen, **1988;** D'Angelo and Reddy, **1993**). When denitrification rates were normalized to the initial NO_3^- concentrations the resulting rates ranged from 0.34 to 2.2 day^{-1} (Table *6.5*). These rates suggest NO_3^- turnover period of **11** to 70 hours, suggesting high demand for NO_3^-. In addition to NO_3^- concentration, denitrification rates are also regulated by the availability of dissolved organic C (DOC) (D'Angelo and Reddy, **1999**). However, for **IRL** sediments, denitrification rates were not correlated to DOC, suggesting recalcitrant nature of the organic carbon present in sediment porewater.

When denitrification and nitrification rates normalized to initial NO_3^- and NH_4^+ concentration were compared, the denitrification rates were approximately **8** to **16** times the nitrification rates in southern and mud zone sediments, and 1.5 to **3** times for northern zone sediments. These observations suggest that nitrification is the limiting process, and regulates the rate of denitrification in IRL sediments. The coupled nitrification-denitrification reactions can be a significant N loss mechanism in estuarine systems (Seitzinger, **1988**).

Results presented in this study show that NH_4^+ is not strongly adsorbed on sediment cation exchange complex. Low adsorption coefficients of IRL sediment results in maintenance of high dissolved NH_4^+ concentrations in the sediment porewater. Nitrification of NH_4^+ at the sediment-water interface functions as an effective sink for NH_4^+ removal. However, NO_3^- formed in the aerobic zone is rapidly removed through dentrification processes. It should be recognized that the rates of nitrification and denitrification represent potential rates, and do not provide any indication of temporal variations under field conditions.

Table 6.5 Denitrification rates in Indian River Lagoon sediments. Specific rate = zero-order rate/initial NO_3^- concentration.

Sampling Station	Initial Nitrate-N	Denitrification Rates	
		zero-order	Specific rate
	mg kg^{-1}	mg N_20 – N kg^{-1} day^{-1}	day^{-1}
Southern zone			
I-1	1.64	2.21	1.35
1-2	1.29	3.34	2.59
I-4	1.22	3.69	3.02
1-5	1.28	1.96	1.53
Mud zone			
I-8	1.22	2.27	1.86
I-11	3.19	6.93	2.17
Northern zone			
1-13	1.25	0.43	0.34
1-15	1.27	0.93	0.73
1-21	1.30	0.85	0.65

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CHAPTER 7

BIOLOGICAL NITROGEN FIXATION IN THE WATER COLUMN

[Task 6.7 as per contract]

7.1 Introduction

Biological nitrogen fixation (N_2 fixation) is the process by which bacteria are able to convert gaseous nitrogen (N_2) to reduced, organic nitrogen via the nitrogenase enzyme complex. Because N is a potentially limiting nutrient in aquatic ecosystems, N_2 fixation plays a critical role as a direct input of N for biotic growth. In aquatic systems, N_2 fixation can occur at various sites of bacterial growth, such as within the water column, within the sediments, or in periphyton coatings on benthic or submersed plant surfaces.

Several factors are known to affect the rate of N_2 fixation. In general, water column N_2 fixation rates are much lower than for sediment or benthic and plant surface fixation rates (Howarth et al., **1988).** In terms of nutrients, high water column N concentrations reduce N demand within the system resulting in lower rates of N_2 fixation (Home et al., **1979).** High phosphorus (P) loading, on the other hand, can cause the system to become more N-limited and, consequently, result in increased N_2 fixation rates (Flett et al., **1980;** Schindler, **1977;** Smith, **1990).** Other trace elements (e.g., molybdenum) can also serve to limit N_2 fixation because they are components of the nitrogenase enzyme (Howarth and Cole, **1985).**

The goal of this study is to assess the spatial trends of N_2 fixation within the Indian River Lagoon by measurement of potential N_2 fixation rates of the major sites of N_2 fixation (water column and plant surfaces) within the Lagoon ecosystem. Also, measurements of possible factors limiting N_2 fixation are being conducted to gain additional insight into the regulation of this process within the estuary.

7.2 Materials and Methods

7.2.1 Sampling

Water samples for N_2 fixation measurement were collected from nine Indian River Lagoon stations during July **2-3, 1998.** These sites were chosen to best describe the range of possible water column P concentrations within the lagoon. Three replicate water samples were collected from each station at 1-meter depth using an Alpha water sampler. Collected water samples were stored in amber bottles **(125 ml)** prior to the N_2 fixation assay. All samples assayed for N_2 fixation within five hours of collection. Following removal of one aliquot **(20 ml)** from each bottle for the N_2 fixation assay, the water samples were acidified **(0.125 ml** H_2SO_4) for subsequent nutrient analysis.

Submersed macrophyte samples for N_2 fixation measurements were collected at station **18** on July **3, 1998.** Bulk samples of three benthic macrophyte species (a seagrass, *Syringodium filiforme*; a green alga, *Caulerpa prolifera*; and a red alga, *Laurencia* sp.)

were collected from a water depth of approximately 1 meter. These samples were stored briefly in clear, rectangular, 40.8L Rubbermaid® containers prior to dissection and insertion into incubation vessels. Extreme care was taken during this process to avoid disturbance to the surficial periphyton coating. All collected samples were assayed for N_2 fixation within 2 hours of collection.

Batch Incubations

Measurements of potential N_2 fixation rate proceeded according to the following adaptation of the acetylene reduction (AR) method for aquatic N_2 fixation by Stal (1988). Water and plant samples were placed into 50-ml **Kimax™** screw-capped tubes. To allow insertion of syringe needles, the tubes are equipped with an open-top, septa (0.120" silicone with teflon liner) cap. Acetylene (–10% headspace volume, generated from CaC_2) was injected into each tube to initiate the AR incubation.

Water samples were incubated in tube racks floating directly in the Lagoon water exposed to ambient light and water temperature for approximately 4 hours. Separate 2-hour light and dark incubations were conducted on macrophyte samples to consider oxygenic photosynthesis effects on the nitrogenase enzyme. The dark incubation was conducted in sealed ice chests filled with Lagoon water while the light incubation samples were simultaneously incubated in a manner similar to the water samples. Following the incubation, a headspace sample from each tube was taken and injected into evacuated, 3-ml, crimp-top serum vials for transport to the laboratory.

Chemical Analysis

Collected gas samples were analyzed for ethylene using a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector (6 ft. Poropak-N column, 110°C injection, 80°C column). All gas samples were analyzed within 36 hours of collection.

Plant samples measured for AR were weighed prior to and following oven drying (70°C) to determine water content as well as dry mass of each sample. These dried plant samples were ground for nutrient analysis of total nitrogen (TN) and total carbon (TC) using a Carlo-Erba NA-1500 nitrogen analyzer. Ground plant samples were digested for total phosphorus (TP) according to the nitric/perchloric acid method (Kuo, 1996). Digests were then analyzed for ortho-P by the ascorbic acid method (4500-P-E, APHA, 1992).

7.3 Results and Discussion

Measured values of AR for the Indian River Lagoon sites studied are shown in Table 7.1. These data demonstrate that water column AR rates show no detectable spatial differences. These data also indicate that the majority of the Indian River Lagoon water column N_2 fixation occurs under light conditions (Station 18 light vs. dark). This pattern

Table 7.1. Measured rates of water column acetylene reduction (mean of 3 measurements) for selected Indian River Lagoon stations.

Station	**Acetylene Reduction Rate ($nmol\ l^{-1}\ hr^{-1}$)**
I18 Dark	0.07_{a}*
I18 Light	1.06_{b}
I1	0.70_{b}
I2	0.63_{b}
I4	1.13_{b}
I5	0.82_{b}
I8	0.65_{b}
I11	0.98_{b}
I13	1.16_{b}
I15	0.37_{b}
I21	0.39_{b}

* Means with the same subscript letters are not significantly different (One -Way ANOVA, $P<0.05$) within a column.

of fixation is typical of planktonic cyanobacteria whose nitrogenase activity is dependent on photosynthetically derived energy sources (Fay, 1992). Pooling the light incubation measurements results in an average AR rate of 0.78 nmol l^{-1} hr^{-1} for the estuary.

This rate of *AR* provides only a measure of the activity of the nitrogenase enzyme present in a given sample. To estimate the rate of N_2 fixation, then, it is necessary to convert measured *AR* rates to rates of actual N fixed. For most aquatic systems, a conversion ratio of 3:1 (moles of acetylene reduced to moles of N_2 fixed) has been generally accepted (Howarth et al., 1988). Using this ratio, and assuming an average daily reduction rate of half the maximal AR rate over an average, 12-hour day, we arrive at an estimated, average N_2 fixation rate for the estuary of 0.016 mg N l^{-1} yr^{-1}.

In terms of overall N_2 fixation rates, the water column values are low, but typical of those reported for estuaries (Howarth, 1988). These low rates appear even smaller when compared to those of the benthic plant biomass (Figure 7.1). Caution should be used when making such a comparison, however, as the rates of acetylene reduction in the water column are reported for only a representative water sample and do not represent an integrative measure of N_2 fixation on an areal basis. Similarly, rates of *AR* of the benthic plant biomass are reported on a dry weight basis. The benthic plant biomass AR data do, however, clearly demonstrate that significant N_2 fixation may potentially occur in association with benthic estuary surfaces, and that this potential varies greatly depending on the plant species. Using the *AR* values for S. *filiforme* and the above conversion procedure (but instead assuming the daily fixation rate equals the average of light and dark AR rates), we arrive at an annual N_2 fixation rate of 3.2 mg N g^{-1} yr^{-1}.

In the comparison of a washed and unwashed plant species (*Syringodium*), it appears that the observed N_2 fixation is due primarily to the periphyton coating on the benthic plant surface. In addition, unlike the water column fixation, the light dependence of N_2 fixation of the benthic plants was variable. In the case of the unknown red alga, higher acetylene reduction rates were observed in the dark incubation. This response indicates that, at least in some cases, the benthic plant N_2 fixation may be carried out by non-photosynthetic bacteria.

Tissue nutrient contents of the benthic plant samples appear inconclusive as an explanation of the observed differences in *AR* between plant species (Table 7.2). This uncertainty stems partly from a need to correct these nutrient concentration values for biomass ash content and also, from the fact that the values represent an integration of the plant and epiphyte biomass. Basing the nutrient contents on an ash-free basis would correct the erroneously low tissue TN and TP of the red alga, *Laurencia* sp., which possessed considerable amounts of mineral encrustation. Also, in the comparison of the nutrient content of the washed and unwashed S. *filiforme*, we see that the epiphyte biomass dilutes the tissue N and P concentrations of the substrate plant. As the epiphyte is the dominant N_2 fixer, the tissue content of the epiphyte biomass is undoubtedly a better predictor of the combined plant/epiphyte N_2 fixation rate.

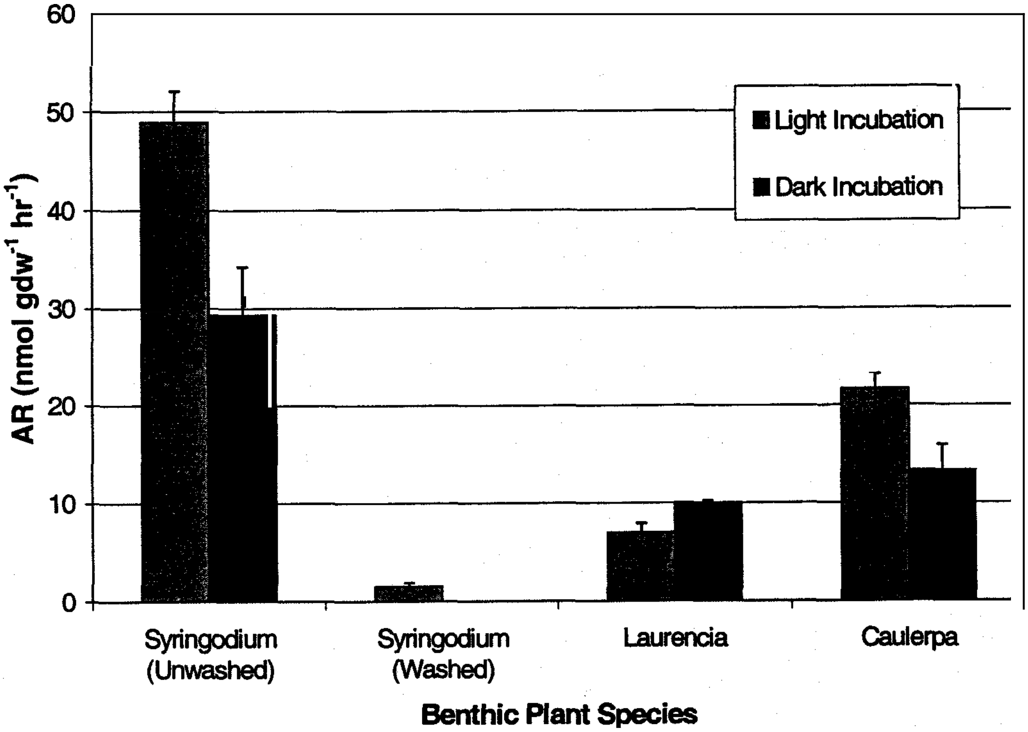

Figure 7.1. Measured values of acetylene reduction (*AR*) for three unidentified Indian River Lagoon benthic plant species collected at Station 18. Error bars represent the standard error of three measurements.

Table 7.2. Tissue nutrient contents for selected Indian River Lagoon benthic plant samples used in acetylene reduction assay. (TP=Total Phosphorus, TN=Total Nitrogen, TC=Total Carbon).

Unidentified Plant Species	TP (mg kg^{-1})	TN (%)	TC/TN
Syringodium filiforme (unwashed)	520.1_{b}	1.19_{a}	18.0_{b}
Syringodium filiforme (washed)	863.9_{c}	1.46_{b}	21.6_{c}
Laurencia sp.	69.6_{a}	0.43_{c}	$20.0_{b,c}$
Caulerpa prolifera	820.3_{c}	2.18_{d}	14.0_{a}

[*] Means with the same subscript letters are not significantly different (One-way ANOVA, P<0.05) within a column.

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CHAPTER 8

PHOSPHORUS MINERALIZATION IN SEDIMENTS

[Task 6.7 as per the contract]

8.1 Introduction

Phosphorus (P) in estuarine sediments is found in organic and inorganic forms and their relative proportions depend on the nature and origin of the sources. Phosphorus flushed into estuaries by their tributaries and P associated with living tissues or suspended organic matter/particulate in water column are the major *sources* of P in sediments. Organic P in sediments comprises up to 75% of total P (Sommers et al. 1972; Reddy and Ivanoff 1991), and occurs in varieties of forms including phospholipids, nucleic acids, inositol phosphates, sugar phosphates and polymeric P of high molecular weight compounds (Stewart and Tiessen, 1987). However, much of the organic P remains uncharacterized.

Microorganisms are principal decomposers of organic matter in aquatic ecosystems (Davelaar, 1993). They could play a critical role in the transformations and cycling of various nutrients including P. Sediment bacteria may catalyze the mineralization of organic P, transiently store P and release if redox conditions are not favorable (Gachter and Meyer, 1993). The utilization of organic P is preceded by release of inorganic P by means of phosphatases (Jansson, 1988). The amounts of phosphatases produced by microorganisms depend on energy sources and the amount of inorganic P. Factors including the forms of P compounds, accessibility of the compounds to the phosphatases and physico-chemical characteristics of sediments that affect the enzyme-substrate interaction may regulate the P mineralization. Though the availability of P is site specific, eutrophication due to its enrichment is a major concern in freshwater (Hecky and Kilham, 1988) as well as in coastal marine systems (Likens, 1972; D'Elia, 1987). Recent studies suggest that P may also limit productivity of oligotrophic marine habitats (Karl et al., 1995; Michaels et al., 1996). Since a major portion of sedimentary P is generally in organic form, its mineralization followed by release of inorganic P to water column is crucial to satisfy the P requirements in surfacewaters. The objectives of this study were to (1) determine the P mineralization rates of organic P under aerobic and anaerobic conditions and (2) estimate the effects of various sediment characteristics on the rates.

8.2 Materials and Methods

8.2.1 Site Description

Indian River Lagoon system is an integral component of water quality management and restoration of seagrass programs of the St. Johns River Water Management District, Florida. The Lagoon system comprises Mosquito Lagoon, Banana River Lagoon, Indian River Lagoon, and all the tributaries and drainage canals, which deliver freshwater to these lagoons. This lagoon system covers a distance of 251 km along the east central coast of Florida, extending southward from New Smyrna Beach

(Volusia County) to Hobe Sound (Martin County) (Figure **8.1).** The major sources of freshwater for this lagoon system are natural streams, runoff, and a number of wastewater treatment plants. Mosquito Lagoon has one direct connection to the Atlantic Ocean and a connection to the Indian River Lagoon through Haulover Canal, an intra-coastal waterway. The Banana River Lagoon has also some water exchange with the Atlantic Ocean via a system of locks at Port Canaveral, a home for commercial shipping and fishing, US naval submarines, support vessels for the Kennedy Space Center, and Canaveral Air Force Station. The Lagoon has also a connection with the Indian River Lagoon at the southern tip of Merritt Island. The Indian River Lagoon, however, has four connections to the Atlantic Ocean, namely, Sebastian Inlet, Fort Pierce Inlet, St. Lucie Inlet, and Jupiter Inlet via Hobe Sound. This lagoon system has a surfacewater area of **928** km^2 and an average depth of **1** m. Hydrodynamic energy is low in the northern part of the lagoon system (Mosquito Lagoon, the Banana River Lagoon, and the northern part of Indian River Lagoon) consequently, prone to stagnation and long pollutant residence times, though occasional flushing by large storms (Ryther **1985).** This lagoon system is a biogeographic transition zone with the highest species diversity of any estuary in North America, approximately 2,200 species, 35 of which are listed **as** endangered (Barile **1987).** There is a growing concern in the decline of biological integrity and slow transformation of the lagoon from macrophyte-based ecosystem to a phytoplankton based ecosystem due to poor sediment and water qualities because of nutrient overenrichment.

8.2.2 Sediment Sampling

Intact sediment cores of **0-10** cm depth were obtained from nine selected locations in Indian River lagoon (Figure **8.1;** Table **8.1).** The sediment samples were then immediately sieved through 5 mm-sieve and homogenized, and stored at 4°C until **used** in mineralization experiment.

8.2.3 Chemical Analysis

Total organic carbon (TOC) was determined from the difference of total carbon (TC) and total inorganic carbon (TIC). Total carbon was determined in sediments by CNS analyzer (Carlo Erba Model **NA-1500,** Milan, Italy) and TIC was determined in ash obtained after burning off organic matter at 550 °C in a muffle furnace for **5** hours.

Dry sediments (0.5 – **1.0** g finely ground) were extracted with 30 **mL 1** M HCl for 3 h. Thereafter, the samples were centrifuged at **5,000** g for **10** min and filtered through a **45** µm filter. The supernatants were saved for **SRP** and total P (TP) analysis. The residues of HCl extracts were extracted with 30 mL 0.5 M NaOH for **16** h. The extracts were centrifuged at 5,000 g for **10** min and filtered through a 0.45 µm filter. The supernatants were saved for further analysis. The residues were centrifuged again at 5,000 g for **10** min by adding 30 mL deionized water to wash out the remaining NaOH extracts. The residues were then analyzed for TP.

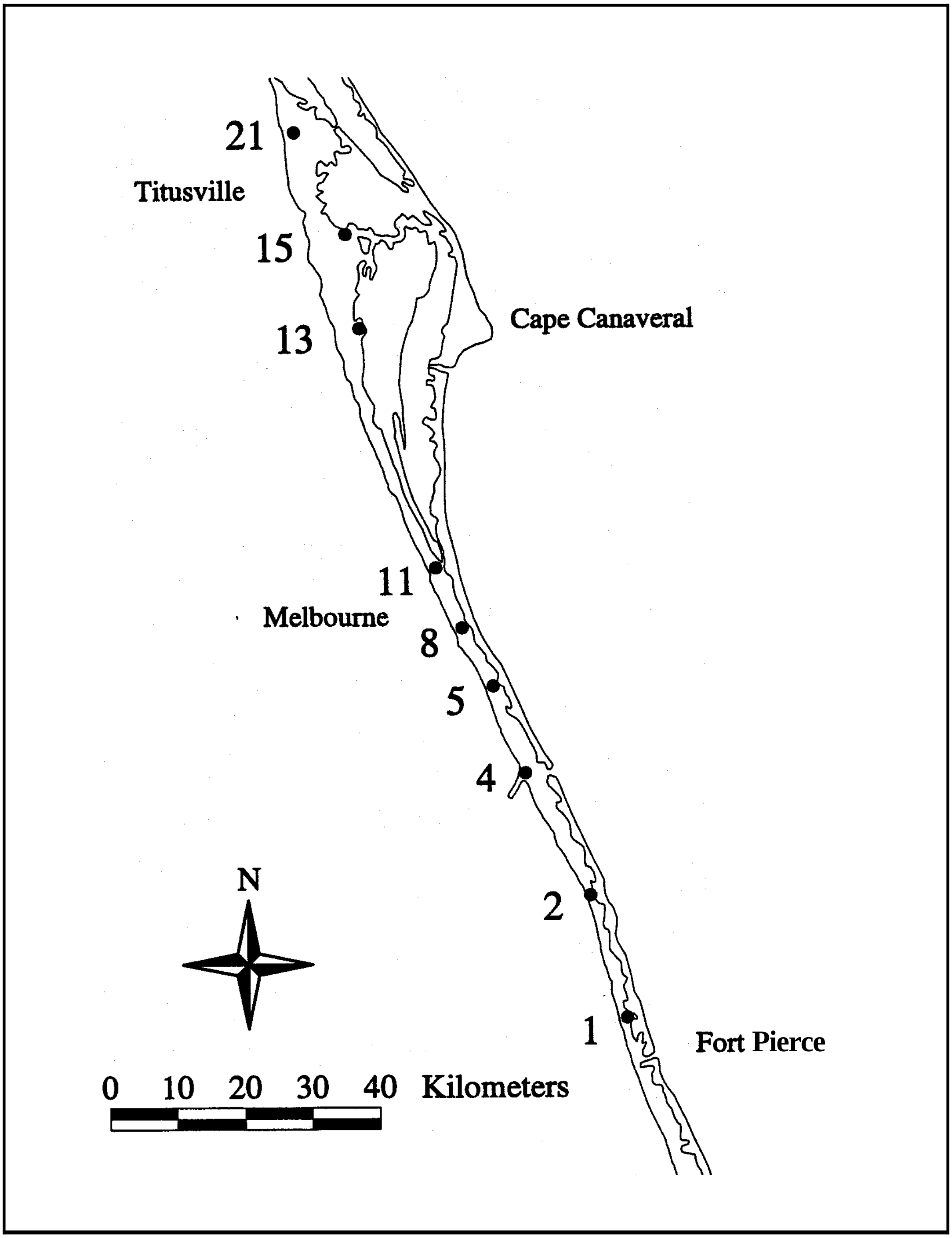

Fig. 8.1 Map of Indian River Lagoon showing sediment sampling stations.

Table 8.1 Coordinates of sampling stations in the Indian **River Lagoon system.**

Sampling station	Latitude	Longitude
I-1	27’ 31.544’N	80° 20.131’W
1-2	27° 41.455’N	80° 23.354’W
I-4	27° 51.476’N	80° 29.011’W
1-5	27° 58.576’N	80° 31.842’W
1-8	28° 03.285’N	80° 34.577’W
I-11	28° 08.188”	80° 36.927’W
1-13	28° 27.769”	80° 43.6’W
1-15	28° 35.386”	80° 44.753’W
1-21	28° 43.71’N	80° 49.354’W

A portion of the supernatant of NaOH extracts were acidified to 0.2 pH with few drops of concentrated H_2SO_4 (2 drops mL^{-1} sample) then centrifuged at 5,000 *g* and filtered through a **0.45** µm filter. The supernatants (fulvic acid fraction) were analyzed for TP and the precipitates (humic acid fraction) were discarded. However, P content in the precipitates were calculated from the difference between NaOH-TP and fulvic acid-TP. Soluble reactive P in all the extracts was determined using an automated ascorbic acid method (Method, **365.1,** EPA, **1983).** Total P was also determined by the above method after persulfate digestion. The total P (TP) in sediments was calculated by the addition of HCl-P, NaOH-P and residual P.

The residues of NaOH extracts were combusted at 550 °C in a muffle furnace for **4** h and the ash was dissolved in **6** M HCl (Anderson **1976).** The digestate was analyzed for P using an automated ascorbic acid method (Method **365.4,** EPA, **1983).** Total organic P **(TOP)** in sediments was estimated by subtracting water-, $NaHCO_3$- and HCl-extractable P (at incubation time zero) from **TP**.

8.2.4 Phosphorus Mineralization Experiments

To perform P mineralization under aerobic conditions, **5** g sediment was weighed in **a** 50-mL centrifuge tubes and 10 mL lagoon water (filtered through a **0.45** µm membrane filter) was added. Thereafter, the centrifuge tubes were incubated at 28 °C in a incubator shaker for 0, **7, 15, 35** and **50** days. To maintain aerobic conditions, the centrifuge tubes were opened once a day to let air in. Following the end of each mineralization period, the incubated sample were centrifuged at 5,000 g for **15** min and filtered through a **0.45** µm membrane filter. The filtrates were acidified with one drop of concentrated H_2SO_4 and stored at 4°C. The filtrates were then analyzed for SRP using the automated ascorbic acid method. Total P (TP) was also determined in the filtrates using the automated ascorbic acid method following the persulfate digestion (Method **365.4,** EPA **1983).** The sediment residues were subjected to sequential P extractions with 0.5 M $NaHCO_3$ followed by **1** M HCl. Soluble reactive P and TP were analyzed in both extracts as described above.

A similar set of experiment was carried out under anaerobic conditions to determine organic P mineralization under anaerobic conditions. Sediment (5 g) was placed in 50-mL centrifuge tubes and 10 mL filtered lagoon water was added. The centrifuge tubes were fitted with rubber septa and purged with N_2 gas to create anaerobic conditions. Thereafter, the centrifuge tubes were incubated **as** described above for aerobic conditions. To maintain anaerobic conditions, the centrifuge tubes were purged with N_2 gas once a day during the incubation period. The rest of the steps followed were the same as described above for aerobic experiment. The filtrates of water, $NaHCO_3$ and HCl extracts were then analyzed for SRP using the auto-analyzer as described above. Total P (TP) was also determined in the filtrates of water and $NaHCO_3$ extracts using the auto-analyzer followed by persulfate digestion **as** described above.

8.2.5 Release and Mineralization Rate Calculations

The water-soluble P release rate was obtained from a linear portion of the slope of the plot of SRP release over a period of incubation vs. incubation time.

To calculate P mineralization rate, an increase in SRP in water, 0.5 M NaHCO$_3$ and 1M HCl extracts over a period of incubation was plotted against the incubation time, and the slope of a linear portion of the curve was used as the rate in a particular sediment sample.

$\mathbf{SRP_{\Delta t}} = \Sigma SRP_t\,(H_2O + NaOH + HCl) - \Sigma \mathbf{SRP_0}\,(H_2O + NaOH + HCl)$
Where,
$\mathbf{SRP_{\Delta t}}$ = increase in SRP at incubation time t.
$\mathbf{\Sigma SRP_t}$ = sum of SRP at incubation time t.
ΣSRP_0 = sum of initial (i.e., at incubation time zero) SRP.

8.2.6 Data Analysis

Unless otherwise stated, all experiments were carried out in triplicates and means were reported. All the data were subjected to two-way-ANOVA using SAS Windows Version 6.12 (SAS Institute Inc., 1996). The difference in P mineralization rates were performed using Least Significant Difference (LSD) at $p<0.05$ level.

8.3 Results and Discussion

Phosphorus in various chemically defined pools is given in Appendix 8.1. The amounts of water- and NaHCO$_3$-extractable P were very low compared to HCl-extractable P. Unlike in water extracts, all the extracted P in NaHCO$_3$ extracts was SRP. This was expected because 0.5 M NaHCO$_3$ extracts mostly labile P, which could be hydrolyzed during the extraction process. In water extracts, however, TP was up to 13 times of SRP in sediments from some sites. Water extracts could contain soluble organic P including sugar phosphates and some DNA-P. Harrison (1987) also reported up to 20 times more organic P in water-soluble forms compared to inorganic P in some soils. Hydrochloric acid-extractable P represented from 46 to 96% of TP in the sediments (Table 8.2). The acid-extractable P may represent P associated with Ca, Mg, Fe and Al.

Sodium hydroxide-extractable P comprised only up to 22% of TP (Table 8.2). Fulvic acid P represented from 15-100% of NaOH-extractable P, while humic acid P comprised from 0-85%. This may indicate that a major fraction of NaOH-extractable P compounds had low molecular mass (3000 Da) in most of the sediment samples, thus relatively more bioavailable compared to humic acid P, i.e., microorganisms can actively decompose aquatic fulvic acid (Shin and Lim, 1998; Matsunaga et al., 1998). Residual P, possibly associated with highly recalcitrant materials, also represented up to 14% of TP.

Table 8.2 Physico-chemical characteristics of the sediments (n = 3).

Sampling station	Clay (%)	pH	TOC	$^{\Psi}$TP	HCl-P		NaOH-P	FA-P	HA-P	†TOP
					SRP	OP				
			mg k g^{-1}					% of NaOH-P		mg k g^{-1}
I-1	7.9	7.4	6900	899±14	719±17	74±6	57±4	99	1	205
I-2	3.0	7.5	7350	849±15	758±20	57±22	21±1	90	10	28
I-4	1.4	7.5	199	131±2	125±8	0	6±1	100	0	22
I-5	2.7	7.5	2840	826±89	767±65	13±59	35±4	83	17	55
I-8	1.6	7.9	2110	58±20	54±20	3±1	5±1	100	0	14
I-11	13.8	7.3	47900	942±80	615±60	0	209±18	15	85	465
I-13	1.1	7.8	2370	155±4	145±1	0	11±1	98	2	28
I-15	1.8	7.8	1450	499±2	470±10	18±11	7±4	53	47	48
I-21	2.9	7.5	3990	117±9	92±4	4±8	15±2	73	27	25

$^{\Psi}$: total P (HCl-P + NaOH-P + residue-P), P:HCl-P: HCl-extractable P, SRP: soluble reactive P, OP: organic P, NaOH-P: NaOH-extractable P, FA-P: fulvic acid P and HA-P: humic acid P.

The rates of water-soluble P release were significantly affected by redox conditions ($p<0.01$) (Table 8.3). The P release rate under anaerobic conditions was **0.069** mg kg^{-1} day^{-1} (mean value) whereas under aerobic conditions the rate was **0.014** mg kg^{-1} day^{-1} (mean value). The water-soluble P release in sediments was significantly correlated with oxalate-extractable- Al (ox-Al) and Fe (ox-Fe), HCl-extractable Mg, total organic C (TOC) and NaOH-extractable TP and OP contents under anaerobic conditions but not under aerobic conditions (Table **8.5)** though ox-Al and ox-Fe could explain **70%** of the variability in the P release rates (Table **8.7).** Under aerobic conditions, however, ox-Al alone explain **86%** of variability in the P release rates. The hydr(oxides) of both Fe and Al strongly adsorb P (Chambers et al., **1995;** Loeppert and Inskeep, **1996)** under aerobic conditions whereas the models implied that Al associated P tends to be released under both redox conditions. These observations may have **been** apparent due to higher pH. Though the role of Al in sediments is not clear yet, the release of Al associated P to water in Andisols has been reported (Negrin et al., **1996).** A significant correlation between P release rates and ox-Fe under anaerobic conditions is expected because of reduction of **Fe(III)** to **Fe(II).** The correlation between the rates and NaOH-TP and OP, and TOC may indicate, **as** expected, a major role of organic P in determining P release.

The rates of organic P mineralization were significantly affected by redox conditions **($p<0.01$)** (Table **8.4).** The P mineralization rate under anaerobic conditions was **4.59** mg kg^{-1} day^{-1} (mean value) whereas under aerobic conditions the rate was **2.97** mg kg^{-1} day^{-1} (mean value). Effects of redox conditions were expected on microbial activities (Stevenson, **1986;** Kleeberg and Dudel, **1997),** ultimately on **P** mineralization rates.

Though Dorioz et al. **(1998)** reported that TP was not a good indicator of bioavailability of P in sediments, both under aerobic (r = **0.83)** and anaerobic (r = **0.76)** conditions, P mineralization rates were correlated with **TP** (Table **8.6).** These observations were apparent may be because of a major portion of TP was HCl-extractable. Under anaerobic conditions, however, the rates were also correlated with fulvic acid P (r = **0.82).** The reason for the correlation between fulvic acid P and the P mineralization rates under anaerobic conditions is not known, however, fulvic acid associated P is considered to be labile (Bowman and Cole, **1978).** Total P explained **68%** of variability in the P mineralization rates under aerobic conditions whereas under anaerobic conditions, fulvic acid P explained **67%** of the variability (Table **8. 8).**

The amounts of inorganic P (water soluble Pi, **NaHCO3-P_i,** and HCl-P_i) released were more or less linearly correlated with duration of incubation under any redox conditions. However, the rates of release of inorganic P were higher in the first two weeks of incubation under both redox conditions (Appendix **8.1).** It is obvious that easily hydrolyzable P would be mineralized within the 1st or 2nd week of incubations so that the P mineralization rates were higher. However, a slow mineralization process seemed to occur as the duration of incubations increased.

Table 8.3 Water-soluble reactive P release rates in sediments under different redox conditions (n=3).

Sampling station	P release rates	
	aerobic	anaerobic
	------------mg kg^{-1} day^{-1}	-----------
I-1	0.004±0.0002	0.017fo.003
1-2	0.009±0.0005	0.020±0.0002
I-4	n.d.	n.d.
1-5	0.020±0.001	0.08fo.01
1-8	0.008	0.009
I-11	0.028±0.004	0.24±0.12
1-13	0.021±0.001	0.063fo.026
1-15	0.005kO.003	0.014fo.0002
I-21	0.014±0.0002	0.023k0.001

Table 8.4 Phosphorus mineralization rates in sediments under different redox conditions (n=3).

Sample I.D.	P mineralization rates	
	aerobic	anaerobic
	------------mg kg^{-1} day^{-1}	------------
I-1	5.3±0.5	12.4±2.9
I-2	5.9±1.5	5.6±1.2
I-4	1.0±0.1	3.4±0.7
I-5	3.9±1.1	4.2±1.2
I-8	1.3±0.6	1.0±0.1
I-11	2.8±0.2	5.5±2.2
I-13	0.6±0.2	0.9±0.1
I-15	4.8±1.1	5.3±3.1
I-21	0.3±0.1	0.8±0.7

Table 8.5 Correlation coefficient of water-soluble P release rates in sediments with selected chemical properties (N = 8).

chemical properties	P release rates	
	aerobic condition	anaerobic condition
ox-Fe	NS	0.88
ox-Al	NS	0.92
HCl-Mg	NS	0.89
NaOH-TP	NS	0.93
NaOH-OP	NS	0.94
TOC	NS	0.93

ox-: oxalate-extractable, HCl-: HCl-extractable, NaOH-: NaOH-extractable, TOC: total organic C and NS: not significant at $p \leq 0.05$ level.

Table 8.6 Correlation coefficient of P mineralization rates in sediments with selected chemical properties (N = 9).

chemical properties	P mineralization rates	
	aerobic condition	anaerobic condition
TP	0.83	0.76
FA-P	NS	0.82

TOP: total organic phosphorus (TP-SRP), FA-P: fulvic acid P and NS: not significant at $p \leq 0.05$ level.

Table 8.7 Multiple linear regression analysis of water-soluble P release rates and selected independent variables under different redox conditions ($N = 8$)

Redox condition	Fitted model equation	R^2 (%)	SE	DW	p-value
Aerobic	$P_{release} = 0.01138 + 0.00012[ox\text{-}Al] - 0.00003[ox\text{-}Fe]$	69.7	0.006	2.8	0.05
Anaerobic	$P_{release} = 0.0063 + 0.0002[ox\text{-}Al]$	85.6	0.03	1.7	0.001

R^2: equivalent to variability explain, SE: Standard Error of estimation, DW: Durbin-Watson statistic (value >1.4 indicates no auto-correlation in the residuals) and ox-: oxalate-extractable (mg kg^{-1}).

Table 8.8 Multiple linear regression analysis of P mineralization rates and selected independent variables under different redox conditions ($N = 9$)

Redox condition	Fitted model equation	R^2 (%)	SE	DW	p-value
Aerobic	$P_{minrlzn} = 0.553 + 0.005[TP]$	68.1	1.3	2.2	0.006
Anaerobic	$P_{minrlzn} = 0.71 + 0.17[FA\text{-}P]$	67.0	2.2	2.0	0.007

R^2: equivalent to variability explain, SE: Standard Error of estimation, DW: Durbin-Watson statistic (value >1.4 indicates no auto-correlation in the residuals), TP: total organic P (mg kg^{-1}) and FA-P: fulvic acid P.

In conclusion, water-soluble P release and P mineralization rates in estuarine sediment could be affected by redox conditions. The solubility of Al associated P at higher pH may play a major role in water-soluble P release under both aerobic and anaerobic conditions. Higher P mineralization rates under anaerobic conditions may have been due to P release from microorganisms. Amounts of organic P content in sediments seem to have a positive effect in P mineralization rates. The effect is more pronounced under anaerobic conditions than aerobic.

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ORPTION AND DESORPTION CHARACTERISTICS OF ESTUARINE SEDIMENTS

[Task 6.7 as per the contract]

9.1 Introduction

Phosphorus (P) occupies an important position in biological systems due to its key role in biochemical reactions. Phosphorus is a component of nucleic acids and nucleoside triphosphates, the basis of enzyme synthesis and energy transfer systems at the cellular level. Thus, P is one of the limiting nutrients and its adequate supply to biota is very important in regulating primary productivity. However, P is also a major contributor of eutrophication of surfacewater systems. Though there is a mark reduction of P reaching aquatic systems from point sources, non-point sources like agricultural runoff is still bringing a substantial amount of P into aquatic systems. Moreover, the knowledge about the role of sedimentary P in P enrichment of surface water is limited.

Understanding P sedimentation in ocean is important for both quantifying outputs in P cycle and controlling phosphogenesis. There is much interest in the capability of sediments to sequester P because of its effect on oceanic P budget (Ruttenberg and Berner 1993; Howarth et al. 1995) and productivity of estuaries (Caraco et al. 1990). Only a small portion of P is buried in sediments (Blazer 1986; Sundby et al. 1992; Anschutz et al. 1998). Sedimentary P can function as internal load to overlying water column for a long period (Lijklema 1993; Reddy et al. 1996).

The exchanges of nutrients across the sediment-water interface in shallow coastal and estuarine systems have been the focus of number of studies (Hargrave 1973; Callender and Hammond 1982; Koop et al. 1990). Depending on limnological conditions, sediments can function either as sources or sinks for P (Fisher et al. 1982; Sonzogni et al. 1982; Koop et al. 1990; Olila and Reddy 1995). The adsorption and desorption of P by sediments mainly depend on their physical, chemical and biological properties. In general, sediments retain inorganic P at considerably greater concentrations than those observed in sediment porewater, whereas at low water column P concentration, sediments function as a source of P (Froelich 1988; Afif et al. 1993; Ravan and Hossner 1993). In shallow lakes and lagoons, wind driven sediment resuspension is a common phenomenon (Reddy et al. 1996; Kleeberg and Dudel 1997). During this process, surface layers of anaerobic bottom sediments can be resuspended into aerobic water column and result in oxidation of ferrous ion followed by retention of P as ferric phosphate (Moore and Reddy 1994, Chambers et al. 1995). Phosphorus sorption phenomenon has received extensive research because of its functional role in maintaining bioavailable P pool for algal growth in aquatic systems and for higher plants in wetlands and terrestrial ecosystems. This study was conducted to (1) investigate the effects of various physico-chemical characteristics of estuarine sediments on their P sorption phenomena and (2) determine the capacity of sediment to function as sinks or sources for P to the overlying water column.

CHAPTER 9

PHOSPHORUS ADSORPTION AND DESORPTION CHARACTERISTICS OF ESTUARINE SEDIMENTS

[Task 6.7 as per the contract]

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9.2 Materials and Methods

9.2.1 Site Description

Indian River Lagoon system is an integral component of water quality management and restoration of seagrass programs of the St. Johns River Water Management District, Florida. The Lagoon system comprises Mosquito Lagoon, Banana River Lagoon, Indian River Lagoon, and all the tributaries and drainage canals, which deliver freshwater to these lagoons. This lagoon system covers a distance of 251 km along the east central coast of Florida, extending southward from New Smyma Beach (Volusia County) to Hobe Sound (Martin County) (Figure 9.1). The major sources of freshwater for this lagoon system are natural streams, runoff, and a number of wastewater treatment plants. Mosquito Lagoon has one direct connection to the Atlantic Ocean and a connection to the Indian River Lagoon through Haulover Canal, an intra-coastal waterway. The Banana River Lagoon has also some water exchange with the Atlantic Ocean via a system of locks at Port Canaveral, a home for commercial shipping and fishing, US naval submarines, support vessels for the Kennedy Space Center, and Canaveral Air Force Station. The Lagoon has also a connection with the Indian River Lagoon at the southern tip of Merritt Island. The Indian River Lagoon, however, has four connections to the Atlantic Ocean, namely, Sebastian Inlet, Fort Pierce Inlet, St. Lucie Inlet, and Jupiter Inlet via Hobe Sound. This lagoon system has a surfacewater area of 928 km^2 and an average depth of 1 m. Hydrodynamic energy is low in the northern part of the lagoon system (Mosquito Lagoon, the Banana River Lagoon, and the northern part of Indian River Lagoon) consequently, prone to stagnation and long pollutant residence times, though occasional flushing by large storms (Ryther 1985). This lagoon system is a biogeographic transition zone with the highest species diversity of any estuary in North America, approximately 2,200 species, 35 of which are listed as endangered (Barile 1987). There is a growing concern in the decline of biological integrity and slow transformation of the lagoon from macrophyte-based ecosystem to a phytoplankton based ecosystem due to poor sediment and water qualities because of nutrient overenrichment.

9.2.2 Sediment Sampling

Intact sediment cores of 0-10 cm depth were obtained from nine representative locations of the Indian River Lagoon system (Figure 9.1 and Table 9.1). The sediment samples were then immediately sieved through 5 mm-sieve and homogenized, and stored at 4 °C until used in sorption experiments.

9.2.3 Physico-chemical Analysis

The particle size distributions of the sediments were determined by pipette method as described by Gee and Bauder (1986).

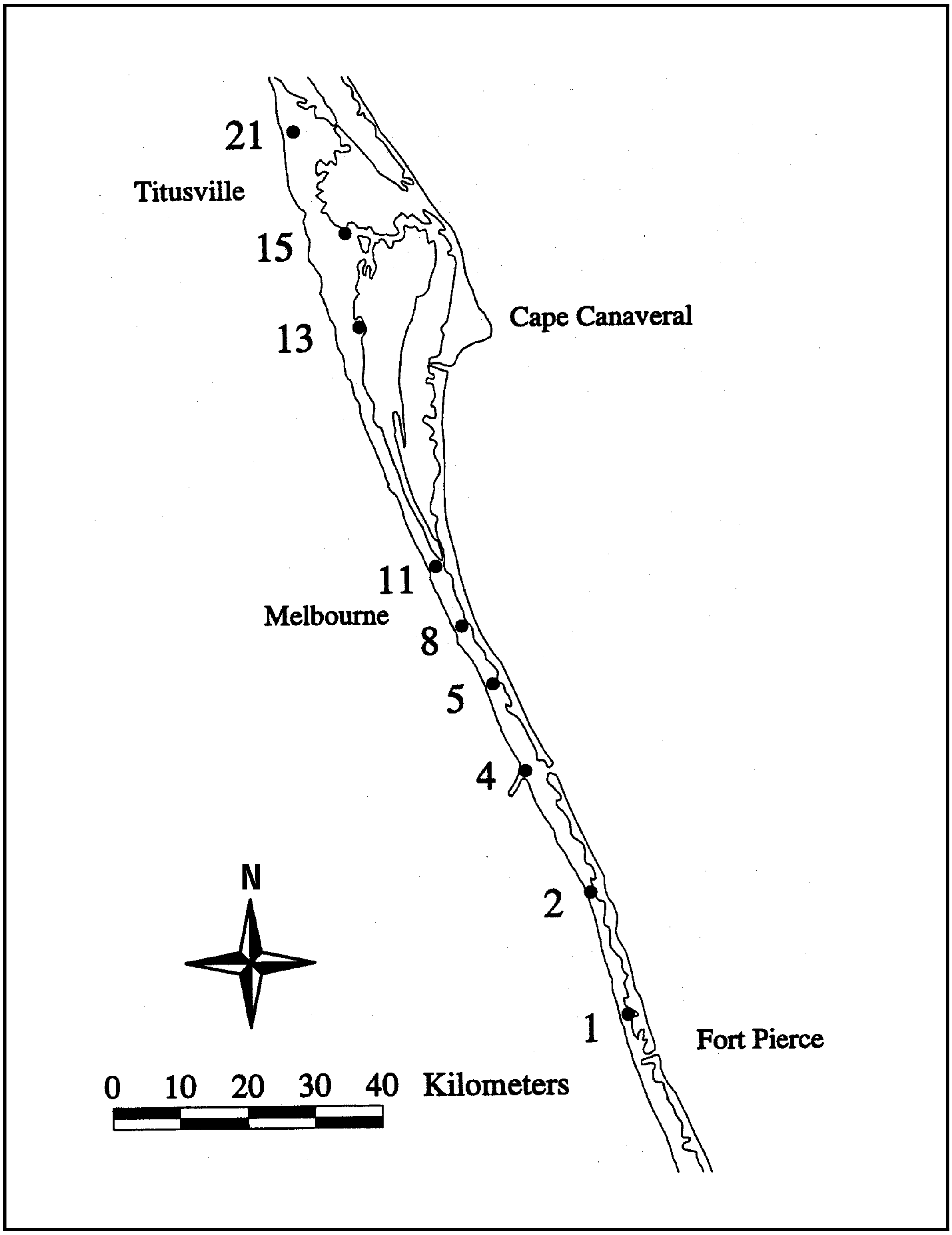

Fig. 9.1 Locations of sampling stations used in the study.

Table 9.1. Coordinates of the sampling stations in the Indian **River Lagoon system.**

Sites	Latitude	Longitude
I-1	27’ 31.544’N	80° 20.131’W
1-2	27° 41.455”	80’ 23.354’W
I-4	27° 51.476’N	80° 29.011’W
1-5	27° 58.576”	80° 31.842’W
1-8	28° 03.285”	80° 34.577’W
1-11	28° 08.188”	80° 36.927’W
1-13	28° 27.769”	80° 43.6’W
I-15	28° 35.386’N	80° 44.753’W
1-21	28° 43.71’N	80° 49.354’W

Amorphous and poorly crystalline Fe and Al (hydr)oxides were determined by oxalate method as described by Loeppert and Inskeep (1996). Sediment (1 g) was extracted with 0.175 M ammonium oxalate + 0.1 M oxalic acid at a sediment/solution ratio of 1:60 by shaking on a mechanical shaker for 4 hours. The suspensions were then centrifuged at 5,000 g for 15 min and filtered through a 0.45 μm membrane filter. The filtrates were analyzed for Fe and Al by inductively coupled argon plasma spectrometry (Model 61E, Thermo Jarrell Ash Co., MA, USA) at Analytical Research Laboratory, University of Florida, Florida. Moreover, oxalate-extractable P was determined in the filtrates using an automated ascorbic acid method as described for soluble reactive P (SRP) determination (Method 365.1, EPA 1983).

Total organic carbon (TOC) in sediments was determined from the difference in total carbon (TC) and total inorganic carbon (TIC). Total C was determined in sediments by CNS Analyzer (Carlo Erba Model NA-1500, Milan, Italy) and TIC was determined in ash obtained after burning off sediments at 550 °C in an oven for 5 hours.

Calcium (Ca) and magnesium (Mg) were extracted from sediments using 1 M HCl and analyzed by the inductively coupled argon plasma spectrometry. The HCl-extracts were also analyzed for SRP using the automated ascorbic acid method.

For Total P (TP) determination, 0.5 - 1.0 g finely ground dry sediments were combusted at 550 °C in a muffle furnace for 4 hours and the ash was dissolved in 6 M HCl (Anderson 1976). The digestate was analyzed for P using an automated ascorbic acid method (Method 365.4, EPA 1983).

9.2.4 Phosphorus Sorption Experiments

Batch incubation experiments were performed to determine P sorption characteristics of sediments under aerobic and anaerobic conditions. For incubation under aerobic conditions, 5 g (wet) sediment sample from each site was placed in 50-mL centrifuge tubes and treated with 10 mL of solution containing 0, 0.1, 0.2, 0.5, 1, 2, 5, 10, 25 and 50 mg P L^{-1} prepared in lagoon water (filtered through a 0.45 μm membrane filter). Thereafter, the tubes were shaken for 24-h equilibration using a mechanical shaker at 25±2 °C. The equilibrated samples were centrifuged at 5,000 g for 15 min and filtered through a 0.45 μm membrane filter. The filtrates were acidified with a drop of concentrated H_2SO_4 and stored at 4°C. Soluble reactive P was measured in the filtrates using the automated ascorbic acid method. Phosphorus not recovered in solutions was considered as the amount adsorbed by the sediments. The sediment residues were saved to perform P desorption experiment.

Another set of a similar experiment was conducted to study P adsorption by sediments under anaerobic conditions. Sediment samples (5 g) were weighed in 50-mL centrifuge tubes and 9.0 mL filtered lagoon water was added to each tube. Thereafter, the centrifuge tubes were fitted with rubber septa and purged with N_2 gas to create anaerobic conditions, and incubated in a water bath for 4 weeks at 25±2 "C. To maintain anaerobic conditions, the centrifuge tubes were purged once a week during the pre-incubation period. At the end of the pre-incubation, 1.0 mL of 0, 1, 2, 5, 10, 20, 50 and 100 mg P L^{-1} (to obtain the final concentrations 0, 0.1, 0.2, 0.5, 1, 2, 5 and 10 mg P L^{-1}) prepared in filtered lagoon water was added to the centrifuge tubes. The tubes were purged again with N_2 gas and shaken on a mechanical shaker for 24-h equilibration. Following the equilibration, the samples were centrifuged at 5,000 g for 15 min and filtered through a 0.45 µm membrane filter under a N_2 atmosphere. The filtrates were then acidified with a drop of concentrated H_2SO_4 and analyzed for SRP as described above. The sediment residues were saved for the desorption experiment.

Phosphorus desorption experiment was performed on sediment residues immediately after adsorption experiments. Sediment residues from aerobic adsorption experiments were equilibrated with 10 mL lagoon water (filtered through a 0.45 µm membrane filter) using a mechanical shaker for 24 hours at 25±2 °C. Thereafter, desorbed P was measured in filtrates as described in adsorption experiments after centrifuging the sample at 5,000 g for 15 min and filtering through a 0.45 µm membrane filter. The filtrates were acidified with concentrated H_2SO_4, and analyzed for SRP as described in the adsorption experiments. The difference in the amount of P adsorbed and amount of P recovered in solutions after equilibration was considered as the amount retained by the sediments (P_r) in relatively stable form. The retention of adsorbed P was calculated from the slope of P adsorbed (P_{ad}) vs. P_r plot (forced through origin). A similar set of experiment was also performed on the sediment residues immediately after anaerobic P adsorption experiments. Anaerobic conditions were maintained throughout the desorption experiment using N_2 gas as described previously.

9.2.5 Data Analysis

Unless otherwise stated, all experiments were conducted in triplicates and mean values were reported. The amount of P adsorbed per unit mass of sediment (S) were plotted against the concentration of P in solution (C) to determine the type of adsorption isotherm that exist between the equilibrium concentration of adsorptive and the quantity of adsorbate in the sediments. The P sorption characteristics of sediments were correlated with physico-chemical characteristics of sediments including clay content, oxalate-extractable Al and Fe, HCl-extractable Ca and Mg, and TOC to make inference about P adsorption and desorption phenomena in sediments. Statistical analysis was performed using Statgraphics plus version 3.1 (Statistical Graphics Corp. 1997).

9.2.6 Sorption Parameter Calculations

The total amount of P adsorbed on sediment can be calculated as follows:

$$S = S' + S_o \quad [1]$$

Where

S = total adsorbed P in sediment (mg kg^{-1})

S' = amount of added P retained by sediment (mg kg^{-1})

S_o = initial or native adsorbed P in sediment (mg kg^{-1})

Since at low equilibrium concentrations the relationship between S' and C (equilibrium concentrations) is typically linear (Rao and Davidson 1979), the S_o can be estimated by a least square fit using the following equation (Reddy et al. 1998):

$$S' = K_d * C_t - S_o \qquad [2]$$

Where

C_t = solution P concentration measured after 24-h equilibration (mg L^{-1})

By plotting the linear form of equation [2], i.e., S' vs. C_t, the intercept is equal to S_o and slope is equal to K_d, a linear adsorption coefficient estimated without taking into account of native adsorbed P (S_o).

A frequently used term in P sorption phenomena, equilibrium P concentration (EPC_o), can be defined **as the** concentration of P in solution where no net adsorption or desorption of P occurs, i.e., **S' = 0.**

Thus, by substituting the values of ***S'*** and C_t in equation [2], EPC_o can be calculated **as** follows:

$$EPC_o = S_o/K_d \qquad [3]$$

The P sorption parameters, sorption maxima (***S,***) and bonding energy constant (**k**) were estimated using Langmuir equation:

$$C_t/S = 1/k*S_{max} + C_t/S_{max} \qquad [4]$$

Where

S, = Sorption maximum (mg kg^{-1})

k = a constant related to bonding energy (L mg^{-1})

By plotting C_t/S vs. C_t, the slope is equal to $\mathbf{1/S_{max}}$ and the intercept is equal to $\mathbf{1/k*S_{max}}$.

Similarly, the P sorption parameter, namely, energy of adsorption (K_f) was calculated using Freundlich equation:

$$S = K_f C_t^{1/n} \qquad [5]$$

Where

K_f = adsorption energy (L kg^{-1})

n = correction factor

By plotting the linear form of equation [5], i.e., log **S** vs. Log C_t, the slope is equal to 1/n and the intercept is equal to **log K_f.**

9.3 Results and Discussion

Sediments from Site **11** had the highest oxalate-extractable Fe and Al content compared to other sites examined in this study (Table **9.2).** The oxalate-extractable Fe and Al represent amorphous and poorly crystalline forms (Loeppert and Inskeep **1996),** which are important in regulating P sorption (Reddy et al. **1998).** Despite the different ranges of oxalate-extractable Fe and Al contents, a linear relationship was observed between them with Fe to Al mass ratio ranging from **2.4** to **4.5** (Table **9.2). As** expected, a linear relationship was also observed between clay content, and oxalate-extractable Fe and Al because of the occurrence of Fe and Al oxides predominantly in clay (Bertsch and Bloom **1996;** Loeppert and Inskeep **1996).** The HCl-extractable Ca and **Mg** in Site **11** sediments were also highest compared to sediments from other sites (Table **9.2).** Though pH could vary under aerobic and anaerobic conditions and ultimately affect the P sorption phenomena in sediments, no significant changes in pH were observed between these conditions (Table **9.2).** The HCl-extractable P represented **24-90%** of TP, whereas oxalate-extractable P represented only **4-16 %** of TP in sediments (Table **9.2).**

Higher equilibrium P concentrations (EPC$_0$) were observed under anaerobic conditions compared to aerobic conditions (Table **9.3).** The EPC, is defined as the concentration in the sediment porewater, where adsorption equals desorption. The higher EPC, under anaerobic conditions were expected because of the reduction of **Fe(III)** to Fe(II) under anaerobic conditions and consequent release of Fe-bound P. Though higher EPC, values under anaerobic conditions were associated with higher oxalate-extractable Fe content of the sediments (Table **9.4),** some sediments had higher EPC, (Table **9.3)** in spite of a lower oxalate-extractable Fe content (Table **9.2).** A multiple linear regression analysis showed that total organic carbon (TOC) played a reverse role compared to Fe in determining EPC, under anaerobic conditions (Table **9.5).** This may imply that TOC adsorbs the P released by Fe and ultimately reduces the EPC,. Under aerobic conditions, however, EPC$_0$ can be estimated by oxalate-extractable Al and HCl-extractable Ca and **Mg** contents (Table **9.5).** A negative correlation of Mg with EPC$_0$ under aerobic conditions may indicate that Mg adsorbs P from solutions and contributes in lowering EPC,. Since there should be no behavioral difference between Ca and Mg under the given conditions, it indicates that every P compound in sediments maintains equilibrium independently with P in solutions, This may help to explain why Langmuir and Freundlich models, which are basically derived to describe sorption phenomena in homogeneous surfaces, could also successfully describe the phenomena in heterogeneous systems like soil and sediment. The maintenance of independent equilibrium by P compounds may suggest that the heterogeneous systems like soil and sediment simply behave as a mixture of homogeneous surfaces as far as their sorption characteristics are concerned.

All P sorption isotherms were L-shaped (Langmuir isotherms) regardless of the redox conditions (anaerobic or aerobic). The L-shaped isotherms indicated that high affinities of the sediment components for P at low P solution concentrations, however, the affinities decreased at high P solution concentrations as the adsorbent in sediments were saturated with P. In general, both under anaerobic and aerobic conditions, the P

Table 9.2. Selected physico-chemical characteristics of sediments (n=3).

sample	Oxalate-extractable				TOC	HCl-extractable			TP	Clay	pH	
ID	Al	Fe	P	Fe:Al		Ca	Mg	P			aerobic	anaerobic
	mg kg^{-1}				mg kg^{-1}					%		
I-1	308	1399	145	4.5	6900	18686	1295	681	899	7.9	7.2	7.2
I-2	186	775	64	4.2	7350	20148	829	813	849	3.0	7.5	7.4
1-4	45	191	15	4.2	1990	19648	105	102	131	1.4	8.1	7.8
I-5	134	495	42	3.7	2840	5466	630	771	826	2.7	7.3	7.4
1-8	58	196	13	3.4	2110	22478	144	36	58	1.6	8.0	7.8
1-11	1172	3863	260	3.3	47900	43185	4245	437	942	13.8	7.2	7.2
1-13	133	320	11	2.4	2370	1506	68	124	155	1.1	7.6	7.4
1-15	79	264	21	3.3	1450	30318	181	446	499	1.8	7.7	7.5
1-21	84	231	24	2.7	3990	7689	380	87	117	2.9	7.5	7.4

TOC: total organic C and TP: total P.

Table 9.3. Phosphorus adsorption characteristics of the sediments under different redox conditions (n = 3). Data were fitted to linear adsorption isotherm model: $S = K_d * C_t - S_o$.

Redox condition	sampling site	K_d	S_o	EPC,	r^2	Prange	N
Anaerobic		L kg^{-1}	mg kg^{-1}	mg L^{-1}		mg L^{-1}	
	I-1	2.3	-8.6	3.74	0.81	1.01-6.51	8
	1-2	14.7	-2.0	0.14	0.94	0.12-0.42	6
	I-4	5.5	-1.5	0.28	0.95	0.06-1.66	7
	1-5	14.8	-5.4	0.36	0.91	0.3-0.44	5
	1-8	17.6	-3.1	0.18	0.99	0.14-0.39	6
	1-11	14.4	-22.5	1.57	0.90	1.3-3.61	8
	1-13	2.7	-0.6	0.21	0.86	0.2-1.02	6
	1-15	9.9	-1.30	0.13	0.99	0.11-0.30	5
	1-21	7.8	-1.3	0.17	0.89	0.18-0.59	6
Aerobic							
	I-1	190.8	-1.5	0.01	0.70	0.008-0.01	3
	1-2	82.6	-0.6	0.01	0.65	0.03-0.06	6
	I-4	15.9	-2.9	0.19	0.96	0.17-0.29	5
	1-5	26.1	-0.4	0.01	0.84	0.07-0.43	7
	1-8	15.2	-1.2	0.08	0.95	0.08-0.34	6
	I-11	346.6	-4.3	0.01	0.66	0.02-0.04	6
	1-13	21.1	-1.3	0.06	1	0.05-0.10	4
	1-15	18.6	-1.6	0.08	0.96	0.07-0.31	6
	I-21	42.6	-0.9	0.02	0.91	0.03-0.08	5

K_d: linear adsorption coefficient, S_o: initial adsorbed P at C=O (-ve sign represents the desorbable P), EPC,: equilibrium P concentration, P range: solution P concentration range and N: number of data points.

Table **9.4.** Correlation coefficient of P sorption parameters of the sediments with the selected physico-chemical properties.

	S_{max}		EPC_o		K_f		P_r	
parameter	anaerobic	aerobic	*anaerobic	aerobic	anaerobic	aerobic	anaerobic	aerobic
ox-Fe	0.893	0.971	0.975	-0.422''	0.802	0.980	-0.501''	0.619'
ox-Al	0.880	0.960	0.979	-0.395''	0.815	0.970	-0.443''	0.555'
HCl-Ca	**0.791**	0.752	0.647	0.039''	0.647''	0.684	-0.081*	0.755
HCl-Mg	0.894	0.962	0.971	-0.446''	0.645''	0.970	-0.434''	0.601''
ox-Fe+ox-Al	0.890	0.967	0.976	-0.417''	0.813	0.982	-0.488''	0.605''
clay	0.891	0.965	0.972	-0.474''	0.781	0.986	-0.596''	0.681
TOC	0.901	0.943	0.975	-0.347''	0.673	0.942	-0.333''	0.542'

*: data from sample **I-1** not included, *: not significant at $p \leq 0.05$ level, ox-: oxalate-extractable (mg kg^{-1}), HCl-: HCl-extractable (mg kg^{-1}), clay: clay content (%) and TC: total C (mg kg^{-1}).

Table ***9.5.*** Multiple linear regression analysis of P sorption parameters and selected independent variables under different redox conditions **(N=9;** $p \leq 0.1$).

Redox condition	Fitted model equation	R^2 (%)	SE	DW
Anaerobic	EPC, = -0.231+ **0.004[ox-Fe] − 0.0003[TOC]**	87.4	0.496	2.8
	K_f = 6.7 − **0.016[Fe] +0.017[HCl-Mg]**	64.6	2.85	2.0
	S_{max} = 22.8 + 0.001[TOC]	81.2	8.89	1.9
	P_r = 90.0 − **0.04[ox-Fe] +0.0027[TOC]**	71.3	8.47	2.5
Aerobic	*EPC_o = 0.021 + **0.0004[ox-Al] + 0.000002[HCl-Ca]** − 0.0001[HCl-Mg]	93.5	0.011	1.9
	K_f = -114.6 + **0.413[ox-Fe]**	96.7	97.2	2.9
	S_{max} = 28.6 + 0.121[ox-Fe]	94.3	38.1	2.9
	P_r = 84.2 − **0.07[ox-Al]** + 0.021[ox-Fe] + **0.0003[HCl-Ca]**	81.5	3.36	2.6

R^2: equivalent to variability explain, SE: standard error of estimation, DW: Durbin-Watson statistic (value **>1.4** indicates no auto-correlation in the residuals), ox-Fe: oxalate-extractable Fe (mg kg^{-1}), ox-Al: oxalate-extractable Al (mg kg^{-1}), TOC: total organic carbon (mg kg^{-1}), HCl-Ca; 1 M HCl-extractable Ca (mg kg^{-1}), HCl-Mg: **1** M HCl-extractable Mg (mg kg^{-1}) and *: data from **1-4** was not used.

sorption isotherms were better fitted to Langmuir model than to Freundlich model, except for sediments with **high** oxalate-extractable Fe and Al. The above observations may suggest that oxalate-extractable Fe and Al play major roles in **P** sorption phenomena in estuarine sediments. This supports a view that non-silicates, especially freshly precipitated forms of Fe oxides possess high **P** sorption capacities (Efimov et al. **1996),** however, release **P** upon reduction of Fe(III) to Fe(II). An increase in distinctness of multiple slopes in Freundlich isotherms under aerobic conditions was observed corresponding to increasing in oxalate-extractable Fe and Al, and the HCl-extractable Mg (Figure **9.2).**

A lower **P** sorption maxima **(S,)** and adsorption coefficient **(K_f)** were observed under anaerobic conditions compared to aerobic conditions (Tables **9.6** and **9.7).** A reduction in both S, and **K_f** was expected under anaerobic conditions because of the desorption of **P** from Fe-P compounds due to the reduction of Fe(III) to Fe(II). A multiple linear regression analysis indicated that a dominant role of HCl-extractable Mg and oxalate-extractable Fe in determining **K_f** under anaerobic conditions whereas Fe was the dominating component under aerobic conditions (Table **9.5).** Though both Ca and Mg could play a significant role in determining **K_f** under anaerobic conditions, Mg showed a major role. The ratio of Ca to Mg was **high (>10),** i.e., the systems was relatively dominated with $CaCO_3$ compared to $MgCO_3$ that left Mg available for adsorption of **P.** Thus, a dominating role of Mg over Ca could be expected in determining **K_f** in these sediments under anaerobic conditions. Total organic C could explain **81%** of the variability in **,S** under anaerobic conditions, whereas oxalate-extractable Fe could explain **94%** of variability in S, under aerobic conditions.

Under anaerobic conditions, desorption of P was higher in sediments with high oxalate-extractable Fe compared to sediments with low oxalate-extractable Fe (Table 9.8), in other words, a negative correlation between oxalate-extractable Fe and **P** retained after desorption **(P_r)** under anaerobic conditions (Table **9.4).** In contrary, under aerobic conditions, sediments with high oxalate-extractable Fe desorbed virtually no **P,** i.e., a positive correlation between oxalate-extractable Fe and **P_r** (Table **9.4).** A multiple linear regression analysis also indicated that oxalate-extractable Fe was positively correlated with **P_r** under aerobic conditions and negatively correlated under anaerobic conditions (Table **9.5).** As expected under aerobic conditions, P_r was positively correlated to HCl-extractable Ca, surprisingly, however, it was negatively correlated oxalate-extractable Al.

This may indicate that **P** adsorbed on oxalate-extractable Al is not as stable as **P** adsorbed on oxalate-extractable Fe or HCl-extractable Ca. Under anaerobic conditions, TOC was positively correlated to **P_r,** it together with oxalate-extractable Fe could explain **71%** of variability in the **P_r.** This may explain the reason for higher **P_r** under anaerobic conditions in some sediments despite the higher oxalate-extractable Fe content (Table **9.8).** However, sediments containing low amount of oxalate-extractable Al and Fe, and HCl-extractable Ca and Mg did not show major difference in **P** retained under aerobic

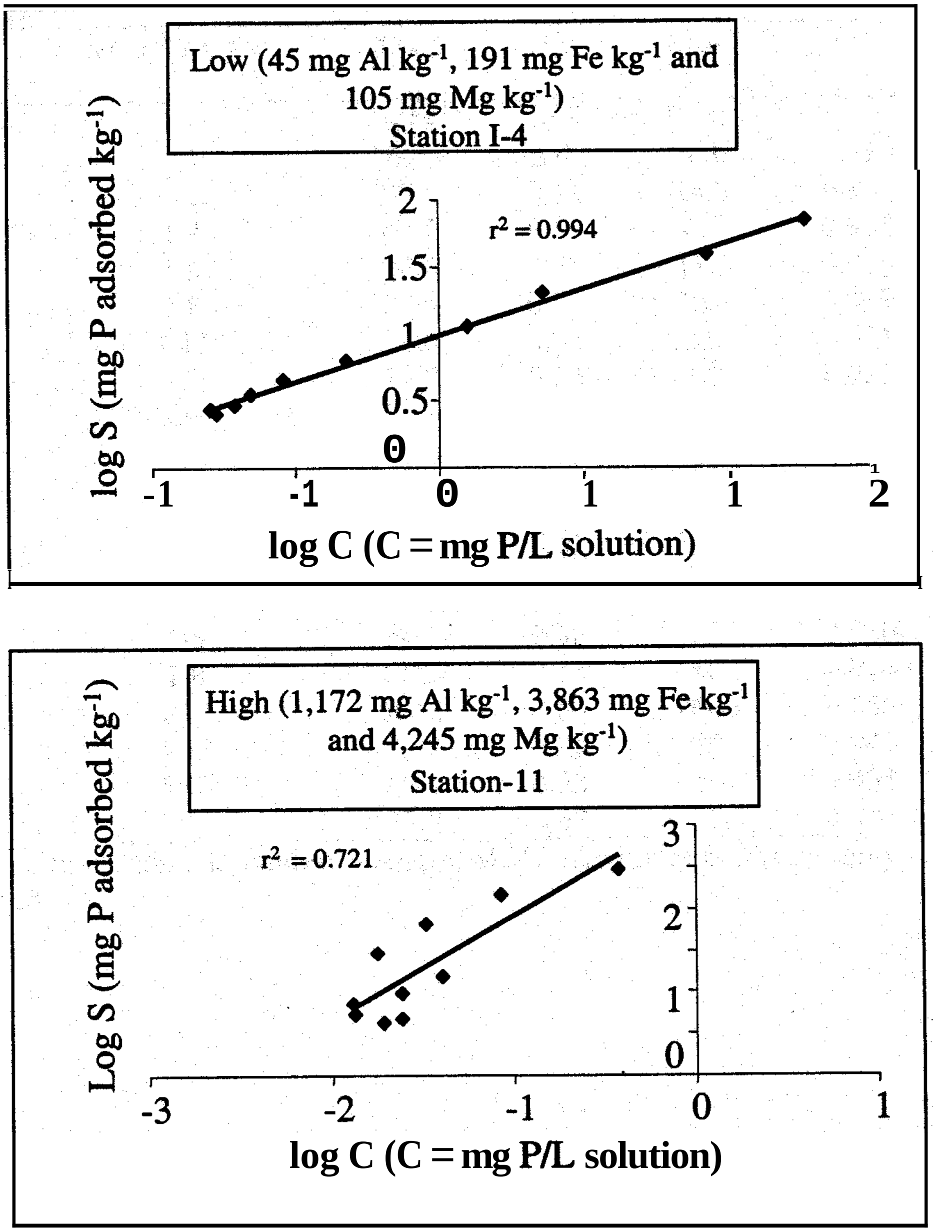

Fig. 9.2 Effect of oxalate-extractable Fe and Al, and HCl-extractable Mg on distinctness of multiple slopes in Freundlich plots under aerobic conditions.

Table 9.6. P sorption characteristics of sediments calculated by using Langmuir equation (n=3). Due to two slopes, one at lower and the other at higher P solution concentrations, the slope corresponding to higher P solution concentrations was used to calculate the parameters.

Redox condition	sampling site	*S_{max}	*k	MBC	*r^2	N
Anaerobic		mg kg^{-1}	L mg^{-1}	L kg^{-1}		
	I-1	n.d.	n.d.	n.d.	n.d.	
	1-2	30.8	0.61	18.9	0.997	5
	I-4	42.2	0.16	6.7	0.978	4
	1-5	24.6	0.71	17.4	0.969	8
	1-8	27.5	0.72	19.8	0.959	8
	I-1 1	74.6	0.03	2.5	0.971	3
	1-13	13.7	0.23	3.2	0.980	4
	1-15	24.1	0.44	10.6	0.988	8
	1-21	20.0	0.52	10.4	0.980	5
Aerobic						
	I-1	222.2	6.43	1429	0.869	5
	1-2	67.1	0.59	39	0.947	10
	I-4	85.5	0.16	14	0.907	10
	1-5	64.1	0.36	23	0,950	6
	1-8	108.7	0.15	16	0.974	8
	I-1 1	500.0	4.00	2000	0.950	4
	1-13	31.2	0.32	10	0.948	10
	1-15	67.6	0.23	16	0.935	10
	1-21	47.8	0.62	30	0.981	10

S_{max}: sorption maxima, k: binding strength, MBC: maximum buffer capacity and n.d.: not determined.

Table 9.7. P sorption characteristics of sediments calculated by Freundlich equation (n=3). Number of data points used (N): anaerobic=8, aerobic=10.

Redox condition	sampling site	n	K_f	r^2
Anaerobic			L kg^{-1}	
	I-1	n.d.	n.d.	0.350*
	I-2	1.26	10.2	0.960
	I-4	1.40	4.6	0.753
	I-5	1.89	9.0	0.982
	I-8	1.53	10.1	0.973
	I-11	1.10	14.7	0.724
	I-13	0.99	1.7	0.585
	I-15	1.32	6.4	0.980
	I-21	1.29	5.3	0.908
Aerobic				
	I-1	0.99	616	0.679
	I-2	1.60	29.3	0.791
	I-4	1.46	9.8	0.994
	I-5	1.35	8.9	0.795
	I-8	1.09	9.6	0.874
	I-11	0.79	1467	0.721
	I-13	2.05	5.8	0.987
	I-15	1.53	9.2	0.978
	I-21	1.82	10.7	0.948

n: correction factor, K_f = adsorption coefficient, n.d.: not determined and *: not significant at $p \leq 0.05$ level.

Table 9.8. Phosphorus retained by sediments after 24-h equilibration with lagoon water under different redox conditions (n=3). P_r = P adsorbed - P desorbed after 24-h equilibration. $P_r = P_{ad} * f$, where P_r is the P retained after 24-h desorption, P_{ad} is the P adsorbed after 24-h equilibration and f is the ratio of P_r/P_{ad}. Number of data points used: anaerobic=8, aerobic=10.

Redox condition	sampling site	Slope (f)	P_r
			% of P adsorbed
Anaerobic			
	I-1	0.503	50
	I-2	0.902	90
	I-4	0.842	84
	I-5	0.863	86
	I-8	0.929	93
	I-11	0.695	70
	I-13	0.707	71
	I-15	0.866	87
	I-21	0.871	87
Aerobic			
	I-1	0.992	99
	I-2	0.922	92
	I-4	0.917	92
	I-5	0.851	85
	I-8	0.963	96
	I-11	0.993	99
	1-13	0.821	82
	I-15	0.889	89
	I-21	0.865	87

and anaerobic conditions. The correlation among sorption parameters and selected physico-chemical properties of the sediments showed that all the physico-chemical properties behaved like Fe, i.e., differently under aerobic and anaerobic conditions, as far as their effects on P sorption parameters were concerned (Table 9.4 Since oxalate-extractable Fe was a dominating component in the sediments and had a linear correlation with the selected physico-chemical properties, the above observations were expected.

In conclusion, this study has shown that P sorptions phenomena in the lagoon sediments were controlled by amorphous and poorly crystalline forms of Fe. This statement is supported by highly significant correlation ($r>0.95$) between oxalate-extractable Fe in sediments, and EPC, under anaerobic conditions and P adsorption energy (K_f) under aerobic conditions. However, the capacity of sediments to retain P was correlated to both oxalate-extractable Fe and Al, and acid-extractable Ca and Mg.

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