THE SIGNIFICANCE OF AMMONIUM ADSORPTION IN LOWER LAGUNA MADRE (TEXAS) SEDIMENTS

A Dissertation

by

JEFFERY P. MORIN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2007

Major Subject: Oceanography

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Approved by:

Chair of Committee,	Luis Cifuentes
Committee Members,	George Jackson
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	Stephen Davis
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ABSTRACT

The Significance of Ammonium Adsorption in Lower Laguna Madre (Texas) Sediments.
(December 2007)
Jeffery P. Morin, B.S. Clemson University
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The work presented in this dissertation focuses on NH_4^+ in marine sediments and attempts to elucidate some of the specific pathways and processes affecting NH_4^+ in coastal marine regions. The majority of work was conducted in the Laguna Madre estuary. A major feature of the estuary is the Gulf Intracoastal Waterway (GIWW) connecting the Lower Laguna Madre to Baffin Bay. Establishment of the GIWW has altered the hydrodynamics of the estuary, reduced seagrass coverage and increased sediment mobility resulting in frequent maintenance by the U.S. Army Corp of Engineers. GIWW sediment relocation associated with dredging is investigated to determine potential influence of NH_4^+ release during resuspension. GIWW sediments are characterized by extremely high concentrations of porewater and exchangeable NH_4^+ as well as reducing ions (millimolar HS^-), and significant release hours to days after resuspension was observed during laboratory experiments. Using sediment NH_4^+ porewater and exchangeable quantities, release potentials are calculated for a dredging event conducted in 1989 and results indicate that potential release from the dredging event are comparable to monthly inputs from intact GIWW and seagrass sediments.

Reducing condition influence on NH_4^+ adsorption dynamics was tested through resuspension experiments over a wide range of initial bulk concentrations in laboratory determined redox conditions. Significant increase in NH_4^+ adsorption was observed in anoxic conditions. Calculations of the apparent partition coefficient (K*) were determined to be affected as well and implications to diagenetic models is explored.

Observations in the laboratory were tested in field monitoring. Analysis of wind measurements established strong potential for interaction with sediments over the collection period. Measurements of water column NH_4^+, total suspended solids, and chlorophyll exhibited highest concentrations and correlation in areas close to the GIWW. Concentration measurements were combined with flux measurements in a model system designed to integrate field observations. Several model cases were considered including and excluding sediment resuspension. Model simulations including sediment resuspension maintained water column concentrations similar to field observations.

DEDICATION

This work is dedicated to the people who have never given up on me. They are my mother, Lucy Morin, and friends Jennifer Wormuth, Deanna Wormuth, and Jennifer Ayers.

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CHAPTER I

INTRODUCTION

Nitrogen is essential in the elemental composition of proteins forming the basis for life. Proteins carry out catalytic reactions generating energy and form the building blocks for cell structure. The two chain-forming reactive groups involved (in terms of peptide formation) in the amino acid structure composing proteins are the carboxyl ($COOH^-$) and amide groups (NH_2^-). Nitrogen, making up a part of the amide structure, is also involved in many of the active sites in enzymes created by arrangement of the R groups of amino acids. In addition nitrogen is a component of the structural backbone required for the production of deoxyribonucleic acid (DNA). Uptake of nitrogen in the nature occurs primarily through absorption of the inorganic forms (NO_3^-, NO_2^-, and NH_4^+). Organismal adsorption strategies can influence survivability of species as well as influence dominant population distribution.

The availability of nitrogen can determine the productivity of living populations such as phytoplankton. Nitrogen in the biosphere occurs as gaseous N_2 in the atmosphere; however, a larger quantity of nitrogen exists in the lithosphere incorporated in continental materials. Stevenson (1962) reported that, "A considerable amount of the nitrogen in igneous and sedimentary rocks exists as ammonium ions held within the lattice structure of silicate minerals." The positive NH_4^+ ions act to neutralize negative

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This dissertation follows the style and format of Marine Chemistry.

charges on silicate minerals. Nitrogen incorporated in continental materials makes up the majority of available nitrogen on the planet. Nitrogen distribution has been reported by Hutchinson (1944) as the amount of nitrogen per cm^2 of Earth's crust (Table 1). Primary rocks (rocks formed before the advent of life and of irregular crystalline form or aggregates without cement) appear to contain a significant portion of terrestrial nitrogen. The weathering of these primary rocks and dissolution of minerals supplies nitrogen to the coastal ocean through river transport. Increases in nitrogen delivery to coastal ecosystems during high flow periods are well documented (Chen et al., 1997, Chen et al 2000, Brock, 2001). Investigations attempting to determine correlations between increased nutrient input and alterations in primary productivity refer to nutrient delivery in excess of that associated with normal weathering and dissolution in soils (McClelland et al., 1997; McClelland and Valiela, 1998). The nitrogen derived from weathering of soils and transport to coastal systems is the primary source making up non-anthropogenic input. The coastal systems involved in the investigations mentioned above also establish nitrogen as the limiting nutrient in marine phytoplankton productivity.

Nitrogen limitation in coastal marine ecosystems has been demonstrated previously (Ryther and Dunstan, 1971; Hofmann and Ambler, 1988, Howarth and Marino, 2006). The process of continental weathering can relieve limitation through the release of NH_4^+ to runoff and river transport. Oxidative conversion of NH_4^+ to NO_3^- through biological activity occurs before it reaches coastal systems. Delivery of dissolved inorganic nitrogen is incorporated into marine systems through absorption by

Table 1. Nitrogen distribution estimated by Hutchinson (Hutchinson, 1944) where values are presented as per square centimeter of earth's crust.

Nitrogen Distribution	g/cm^2
Primary rock	3.2×10^4
Atmospheric	755
Fossil nitrogen associated with reduced carbon in sediments	68 - 108
Nitrogen as nitrate in superficial deposits	5×10^{-5}

phytoplankton, utilized in heterotrophic production through incorporation or as a terminal electron acceptor (ultimately evolved as N_2), or transferred to the open ocean. Nitrogen fixed into organic matter through primary production is less likely to leave systems immediately and is usually deposited in the sedimentary environment where it is eventually remineralized to dissolved form and reincorporated (Hedges et al., 1988). This recycling is a significant obstacle to nitrogen transport to the open ocean (Christian et al., 1996). When water exchange with the outer ocean environment is low, high trapping efficiency of nutrients and organic matter is observed in estuarine systems (Nixon 1983). Depending on the size and residence time of the particular estuarine system, trapped materials can be recycled many times through incorporation in biological and chemical reactions, settling and sedimentation, followed by release through remineralization or dissolution. Such sediment processing can result in the preferential loss of N in coastal systems (Valuer et al. 1995, Christiansen et al. 1997, Twomey et al. 2005). The recycling of nitrogen and opportunity for conversion to a biologically–unavailable form (N_2) implies selective elimination of nitrogen in comparison to phosphorus in coastal systems before transport to the open ocean. Phosphorus in the form of ortho-phosphate is not converted to biologically unavailable forms and tends to remain in the marine environment. The availability of phosphorus can be more directly related to the anoxic state of the sedimentary environment (Chambers and Odum, 1990).

Organic matter transported to coastal systems (considered allocthonous) and that produced within the systems (considered autochthonous) are usually deposited in sediments in shallow estuaries characterized by high residence times. Different sources and fate of nitrogen in marine systems have been successfully determined through analysis of $\delta^{15}N$ values of estuarine organic matter (McClelland et al., 1997; Cifuentes et al., 1999). A large fraction of organic matter deposited in the sediment environment of estuaries and coastal systems is remineralized and can be returned through gradient-driven sediment flux (Simon, 1989; Fisher et al., 1992; Alvarez-Salgado et al., 1996; Tyrrell and Law, 1997). The process of remineralization through heterotrophic community activity occurs in sediments much as in the water column. In contrast, remineralized inorganic components generated in the sediments do not diffuse as rapidly due to restrictive flows in the sediment environment. For this reason, dissolved concentrations of inorganic species (i.e., NH_4^+, HPO_4^{-2}, $HCO_3^{\check{S}}$) can reach extremely high levels in sediments.

The capacity for sediment storage of remineralized N and P, as well as other ions, in dissolved and absorbed form creates a significant problem for estuarine eutrophication, and difficulties for regulatory assessment. Cappuyns et al. (2006) in a study of a dredged navigation channel in Northern Belgium refers to the sediments as a potential "chemical time bomb" due to availability of dissolved heavy metals and potential for total release and release days after initial resuspension. The gradient developed due to this intensification of porewater concentration results in flux of dissolved inorganic components through the sediment–water interface which can be described and quantified by Fickian kinetics (e.g., Jorgensen and Des Marias, 1990). Indeed this is the method of determining sediment–derived nutrient inputs to many systems where core concentration profiles are measured. The return of dissolved inorganic components from remineralized organic matter production has been shown to be capable of supplying the majority of demand in terms of primary production for some estuaries (McCarthy et al., 1977; Cowan et al., 1996).

Elevated ion concentrations (nutrients) result from metabolism and remineralization in sediment porewaters. Such high concentrations affect the adsorption tendencies on particulate surfaces: high concentrations favor adsorption in sediment environment and low concentrations in the water column favor release. The majority of particles delivered to marine systems are negative in charge. This is one explanation for the characteristic particle maximum at the head of many estuaries where the negative surface charge is neutralized by dissolved positive ions (in saline water). Elimination of repulsion allows for attraction through the formation of Van der Wals forces. One ubiquitous member of the materials delivered to coastal systems is the particles classified as clay minerals. Griffen et al. (1968) have estimated that 60% of marine sedimentary deposits are made up of materials in the size fraction < 2 µm. Of this fraction, clays make up 58% in the Atlantic Ocean and approximately 27% in the Gulf of Mexico. One extremely interesting characteristic of clay minerals is their ability to adsorb large amounts of positive ions from solution (indicated by high cation exchange capacity (CEC)). The importance of adsorption of dissolved components (specifically in these cases NH_4^+) in sedimentary environments has been established previously (Rosenfeld, 1979; Raaphorst and Malschaert, 1996), as well as the importance of this phenomenon to diagenetic models (Berner, 1976).

Cation exchange capacity (CEC) of clay minerals is dependent on the overall charge of the clay particle. Microbial reduction of structural iron in clay minerals has been observed (Stucki et al., 1987). These studies observed an overall increase in ferrous iron compared to total iron when weathered clay minerals were exposed to reductive conditions in controlled laboratory conditions. Alteration in CEC was then investigated in these "reduced" clays to determine if the change in clay particle charge might affect the adsorption characteristics. Khaled and Stucki (1991) have reported an approximate 30% increase in what is referred to as "fixed" K^+ content in the interlayers of the clays. The term "fixed" here refers to an increase in overall K^+ content in the particles which is unavailable for desorption. The adsorption of NH_4^+ (having similar ionic radius and equivalent charge to K^+) and concurrent absorption resulting in entrapment has been observed previously in soil investigations and is correlated with elevated concentrations of high CEC clays (Chen et al., 1989; Feigenbaum et al., 1994).

The adsorption of NH_4^+ on sediment particles has significant implications in nutrient management in coastal systems. Generally nutrient inputs and sinks in coastal systems includes sources such as freshwater, groundwater, and saline coastal water as well as sediment flux. The capacity for sediments to store and maintain a memory of past inputs can alter assessments of systems that assume constant rates of input. This idea has been implied previously as well (Froelich, 1988; Sundby et al., 1992). Considering the developing problems observed in coastal systems in the United States (Bricker et al., 1999) and elsewhere (Friedl et al., 1998), a complete understanding of nitrogen cycling in marine systems is desirable.

To apply effective management efforts to coastal systems in response to the increasing occurrence and severity of water quality decline, a complete understanding of nutrient dynamics is necessary (Clarke et al. 2006). Concern over nutrient inputs to estuarine environments is largely derived from nutritional limitation of phytoplankton communities and the resulting alterations observed when this basic control is removed. Remineralization of organic matter in undisturbed sediments creates pools of dissolved ions restricted to porewater and particle surfaces (adsorbed). Disruption the sedimentary environment can cause relatively rapid increases in water column nutrient concentrations through porewater injection and activation of sorptive surfaces.

This process can create periodic pulses of nutrients to the water column capable of relieving limitation, and maintaining productivity (Smith 2006). Periodic pulses of NH_4^+ were tested in a batch experiment of a prymnesiophycae culture (*Isochrysis galbana*) (Gentihomme and Rich 2001). The researchers determined that the cultured organism could adapt rapidly to the pulsed input. Rapid adaptation and uptake of nutrients has been observed in mesocosm studies from the Neuse River (North Carolina) where adaptation to a nutrient pulse was also implicated in community selection (Pinckney et al. 1999). Pulse type inputs of nutrients can be thought of as perturbations to steady state conditions. Perturbation driven shifts in stable communities involve changes in system level activity and alteration in system organization referred to as system “ascendancy” (Ulanowicz 1980). This type of shift has been observed in the Mondego estuary (Portugal) where pulsed nutrient inputs are implicated in a gradual shift in the system from a community dominated by rooted macrophytes (*Zostera noltii*) to a community dominated by green macroalgae (Patricio et al. 2004). Onuff (1994) noted a similar response in the Southern Laguna Madre.

Potential for sediment impact on biogeochemical cycling, nutrient limitation, primary productivity, and eutrophication in coastal systems is extensive. Understanding the mechanisms surrounding coastal sediment and nutrient dynamics is extremely important when recommendations are made for water quality associated regulation.

The following dissertation presents investigations conducted in the Lower Laguna Madre (LLM) estuary as well as work in the hypoxic region of the Mississippi plume-influenced Gulf of Mexico (GOM). The investigations begin with work conducted for the United States Army Corp of Engineers (Galveston District) who relocate large amounts of sediment performing dredge maintenance of the Gulf Intracoastal Waterway (GIWW). This work develops a modification to the traditional method of exchangeable NH_4^+ determination. It also provides an assessment of the potential for NH_4^+ release during dredging by considering the extremely high concentrations in channel porewaters.

During this investigation, observations of extremely reduced channel sediments with high clay fraction representation and high NH_4^+ concentrations led to the postulation that redox conditions in the sediments may have an important influence on the capacity for NH_4^+ particle adsorption. Under this hypothesis, experiments were designed to observe release of NH_4^+ as a function of reducing conditions and bulk concentration of NH_4^+ in solution. Sediments intended for resuspension were collected in the channel of the LLM as well as in the hypoxic region of the GOM. Controls conducted during sediment resuspension experiments highlighted a possible defect with the methods used by the Corp of Engineers to ascertain possible NH_4^+ release. In addition, laboratory experiments give strong indications that the redox characteristics of the resuspending medium influences the ultimate release of NH_4^+.

The final investigation chapter is a presentation of monitoring data over a transect established in the LLM and sampled in an attempt to correlate productivity and surface sediment resuspension. During previous samplings over the estuary, observations of a periodic nature in daily wind patterns led to the idea that, in the shallow Laguna Madre, diel sediment resuspension might be an important factor in nutrient delivery to this hypersaline system. A model of NH_4^+, NO_3^-, and algal biomass is used to test the hypothesis that resuspension of sediments as a possible source of nitrogen to the system.

The final chapter is a summary of the conclusions obtained through this research.

CHAPTER II

AMMONIUM RELEASE FROM RESUSPENDED SEDIMENTS IN THE LAGUNA MADRE ESTUARY*

1. Introduction

Microbially mediated redox reactions in estuarine sediments lead to the remineralization of organic matter and the recycling of nitrogen and phosphorus compounds (Fenchel and Blackburn, 1979). In the presence of oxygen, NH_4^+ released during remineralization of organic nitrogen compounds is oxidized to NO_2^- and NO_3^- through the biological process of nitrification. However, in anoxic coastal sediments, NH_4^+ can accumulate to millimolar concentrations in sediment porewaters. Estuarine sediments generally are in the pH range of 7 to 8, causing NH_4^+ to be the dominant form of ammonia. This positively–charged ion can participate in adsorption–desorption reactions with sediment solids followed by incorporation into the solid phase (absorption) (Rosenfeld, 1979; Froelich, 1988). This process has been suggested to be an important buffering mechanism for nutrient concentrations in estuaries (Pomeroy et al., 1965). Under high porewater NH_4^+ concentrations, the quantity of NH_4^+ maintained in the adsorbed phase is primarily limited by the cation exchange capacity of the sediments.

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Loosely bound NH_4^+ on clay minerals is referred to as the exchangeable fraction (Rosenfeld, 1979). This fraction has been defined as the amount released during a single 2 N KCl extraction (Rosenfeld, 1979; Mackin and Aller, 1984; Seitzinger et al., 1991). The measure of exchangeable NH_4^+ can be used to calculate a linear adsorption coefficient (K) for NH_4^+ using the relations described by Rosenfeld (1979). The adsorption coefficient is important in models of early diagenesis and nutrient cycling (Berner, 1976). Recently, the effectiveness of a one-step extraction determination of exchangeable NH_4^+ has been questioned when the extraction efficiency in some cases has been less than 50% (Laima, 1992).

Bottom sediments can supply a significant fraction of the nutrients required by primary producers in estuaries (Nixon, 1981; Rizzo, 1990). In shallow estuarine systems characterized by frequent resuspension of surficial sediments, desorption from suspended particles can also supply NH_4^+, delaying efforts to reduce the effects of eutrophication (Rizzo and Christian, 1996). Release of nutrients from resuspended porewater and sediment particles has been implicated in the stimulation of heterotrophic microplankton in estuarine waters (Wainright, 1987). Considering the capacity for elevated porewater nutrient concentrations, this effect is not surprising. Investigations of the extent and the geochemical mechanisms of nutrient release (Blackburn, 1997; Rutgers van der Loeff and Boudreau, 1997; Wainright and Hopkinson, 1997) have mainly concentrated on organic matter mineralization and mineral dissolution during periodic resuspension of surficial sediments.

Anthropogenic activities such as dredging in coastal regions results in the relocation of large volumes of anaerobic porewater and particles. The method used by the U.S. Army Corps of Engineers (COE) (responsible for the maintenance of coastal waterways in the U.S.) to assess the release of NH_4^+ during dredging involves mixing dredged sediments with overlying water at relatively high solid–to–solution ratios (1:5 v/v). At these high ratios, the potential NH_4^+ release may be underestimated. We have developed and tested an alternative methodology that may better simulate the conditions created during resuspension of sediments in coastal environments. Here we report the results along with a comparison of the two experimental approaches.

2. Methods

2.1. Study Area

Laguna Madre is a seasonally hypersaline and shallow (ca. 1 m) estuary located along the southern coast of Texas (Fig. 1). It is transversed from north to south by the Gulf Intracoastal Waterway (GIWW) which has an average depth of approximately 4 m. The GIWW was constructed to accommodate barge traffic from Port Isabel to Corpus Christi. Maintenance of the channel requires frequent dredging that relocates channel sediments to other regions of the estuary or to the side of the waterway. Barge traffic and high wind conditions can also cause additional and perhaps more frequent resuspension of channel sediments.

2.2. Sediment Collection

Sediments were collected from the GIWW channel along the northern and southern sections of the Laguna Madre using a 7 cm gravity corer and from shallow

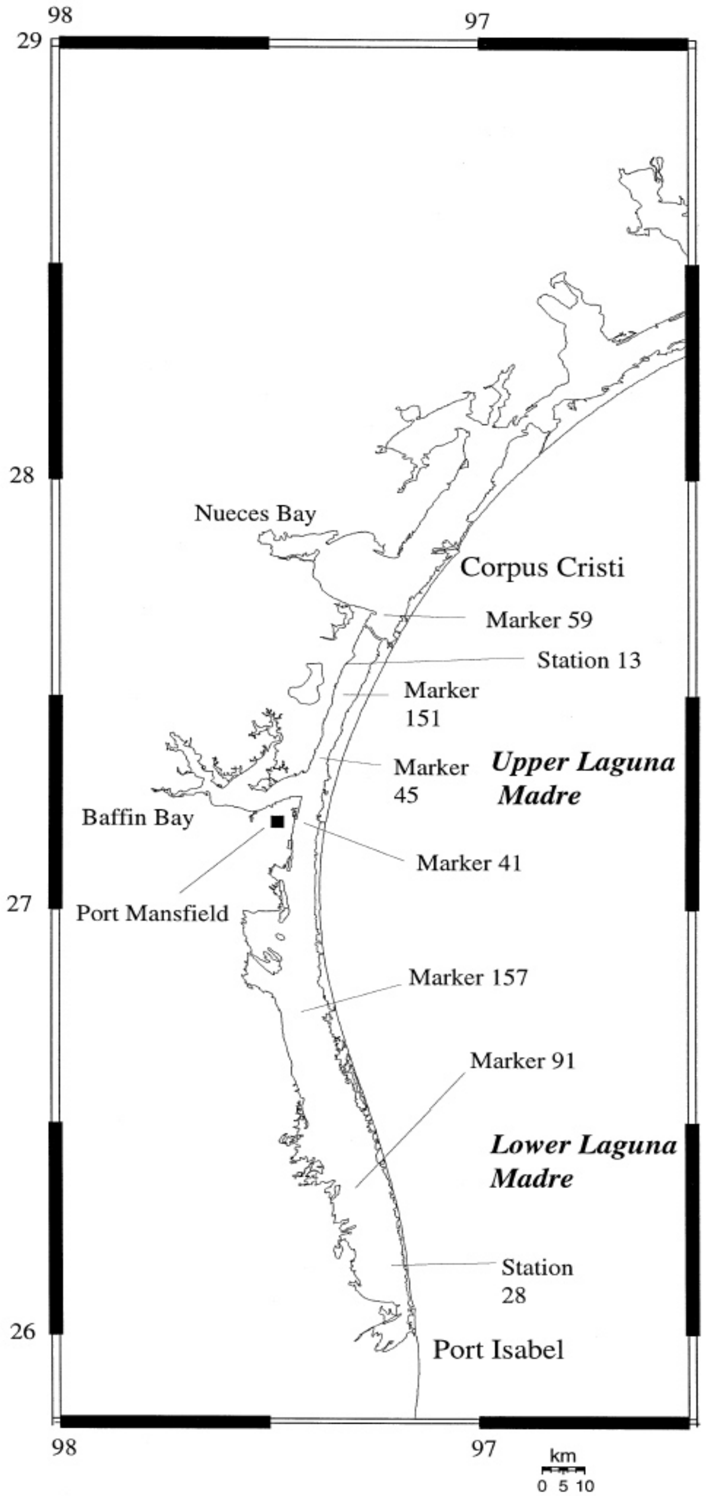


Fig. 1 The Laguna Madre estuary located in the southern region of Texas (USA). Markers in the Intracoastal waterway where sediment cores were taken are identified.

vegetation-free areas adjacent to the channel using a larger (30.5 cm diameter) hand-held corer (Fig. 1, Table 2). The top 10 cm of each sediment core were quickly homogenized, sealed in 1-liter Nalgene containers, cooled to 4°C, and transported to the laboratory in College Station, Texas. COE in the table refers to sites chosen by the Corp of Engineers, which were located in and around seagrass beds outside of the GIWW. Overlying water samples were collected in close proximity to each site for use in the resuspension experiments. The water was filtered into large Nalgene carboys through a 1.0 µm Milliguard cartridge filter in-line with a 142 mm, 0.2 µm membrane filter (Millipore) and kept cold during transport. All sediments and water samples were stored at 4°C.

Cores collected by divers from 12 stations in both upper and lower Laguna Madre were used to determine NH_4^+ gradients and fluxes. Sediment cores (7.0 cm diameter, 30 cm length) were taken both within grass-covered areas and in vegetation-free areas. The top 12 cm of each core was sectioned in 2 cm intervals. Two centimeter sections were also taken at 14, 20, 24, and 28 cm.

2.3. General Sediment Characterization

Porosity was measured from the weight loss of a known amount of wet sediment dried at 80°C to a constant value. The > 63 µm fraction was determined by wet sieving. Total carbon was determined by combustion using a Leco Organic Carbon analyzer. Organic carbon was determined after acidification with 10% HCl. Inorganic carbon was obtained by difference. Interstitial waters were collected by centrifuging approximately

Table 2. Sediment collection locations

NH_4^+ mixing experiment samples from Laguna Madre

Sediment Sample	Location	Location Description
1	Marker #91	GIWW Lower LM
2	Marker #157	GIWW Lower LM
3	Marker #41	GIWW Lower LM
4	Marker #45	GIWW Upper LM
5	Marker #59	GIWW Upper LM
6	Marker #151	GIWW Upper LM
7	COE Station #28	Top 2 cm Bare Sediment
8	COE Station #13	Top 2 cm Bare Sediment

Water samples collected in lower and upper Laguna Madre (LM) were filtered through a 0.2 µm filter immediately and stored for use in sediment resuspension experiments.

20 ml of sample at 3000 rpm for 1 hour in a fixed–angle centrifuge rotor. Porewater was drawn off with a 10 ml glass syringe and filtered through a 0.45 μm membrane filter into pre-cleaned 20 ml scintillation vials with Teflon caps, frozen and stored at –20°C. NH_4^+ concentrations in porewater and overlying water were determined spectrophotometrically (phenol blue method) (Strickland and Parsons, 1972).

2.4. Sediment NH_4^+ Extractions

Total extractable NH_4^+ (ΣNH_4^+) content was determined using a modification of a method used by Laima (1992). Ten grams of solid sediment (calculated from porosity) were centrifuged at 3000 rpm for 1 hour to remove most porewater. The supernatant was then drawn off and filtered through a 0.45 μm Millipore syringe filter. A 20 ml volume of 2 N KCl and 0.1% azide was then added to the sediment fraction and the mixture was homogenized in 250 ml centrifuge bottles using a bench-top rotary vortex mixer. The samples were shaken at 150 rpm overnight at 25°C, and then centrifuged. The supernatant was removed, filtered, frozen, and stored as above. This extraction procedure was repeated 5 times for each sample. The results were plotted as cumulative extracted NH_4^+ versus cumulative extraction volume. The observed asymptotic relationship can be described by:

$$[NH_4^+] = [NH_4^+]_{\max} (1 - e^{-k\upsilon}) \tag{1}$$

where $[NH_4^+]_{\max}$ is equal to the maximum cumulative amount of NH_4^+ or total extractable NH_4^+, k is a desorption constant, and υ is the cumulative volume. Total NH_4^+ was obtained by fitting a line described by Eqn (1) to the data and extrapolating the asymptote (average error approximately 5%; see discussion section that follows). The line fit was determined using a non-linear optimization routine in MATLAB™.

2.5. Sediment Resuspension Experiments

2.5.1. Closed System (Oxygen Not Maintained During Resuspension). Duplicate wet sediment subsamples containing 10.0, 1.0, and 0.1 g (d.wt. calculated from porosity) were resuspended in six 1-liter Erlenmeyer flasks containing 1000 ml of 0.1% azide amended overlying water of known NH_4^+ content. These sediment additions were made with wet sediment resulting in significant addition of porewater to each experiment. The 1-l flasks were sealed with rubber stoppers fitted with syringe needle ports, and the contents were stirred throughout the experiments (48 h). At intervals of 5, 15, 60, 120, 240, 720, 1440, 2160, and 2880 min, 10 ml of the sediment water mixture were removed for NH_4^+ analysis. All experiments were maintained at room temperature (approximately 23°C).

2.5.2. Open System (Oxygen Maintained During Resuspension). The open system experiments were done according to the U.S. Corps of Engineers (COE) method (Plumb, 1980). Sediment volumes of 100 ml were added to 400 ml overlying water in 500 ml Pyrex Erlenmeyer flasks. Each flask was sealed with a rubber stopper containing two syringe needle ports. One port was used to withdraw samples of the slurry. The other was connected to an air pump. Background samples were taken as above, prior to sediment addition. Sediment was maintained in suspension by shaking (150 rpm). After 1 h, the sediment slurry was allowed to settle. Samples were collected at 10, 20, 40, 60, and 1440 min as described by the COE method. Storage and nutrient analyses of the time series samples were performed as described.

2.6. Sampling during Dredge Operation

Samples were obtained in close vicinity to an active dredging operation being conducted near Port Mansfield, Texas in Lower Laguna Madre. The dredging operation was interrupted temporarily so that samples could be taken near the pipe carrying sediment. Samples were also collected approximately 30 m (near) and 300 m (far) from the opening of the pipe. Water volumes were collected and filtered for nutrient analysis as well as samples frozen for determination of total suspended solids. Samples collected for suspended solid analyses were later thawed, resuspended, and filtered onto pre-tared 47 mm GF/F filters. The filters were dried to constant weight.

3. Results

3.1. Sediment Characteristics

Sediments collected from the channel bottom had a significantly greater silt- and clay-size fraction than those from shallow vegetation-free areas outside the channel (Table 3). Sediments collected inside the channel were dark black in color, smelled of sulfide, had NH_4^+ concentrations on the order of mmol L^{-1} (an order of magnitude greater than outside the channel), and contained roughly twice as much organic carbon as non-channel sediments.

Table 3. Sediment physical characteristics and porewater concentrations.

Station	ϕ	< 63 µm (%)	Inorganic carbon (%)	Organic carbon (%)	Total carbon (%)	Porewater PO4 (mM)	Porewater NH_4^+ (mM)	Total NH_4^+ (µ mol g d.wt.–1)
Inner Channel								
Marker 151	*0.90*	81	1.18	4.53	5.71	0.03	3.85	32.50
Marker 157	*0.80*	99	2.60	1.00	3.59	0.11	1.73	11.61
Marker 45	*0.83*	65	1.84	1.59	3.42	0.06	2.90	15.80
Marker 59	*0.72*	60	0.36	0.93	1.28	0.12	3.62	8.04
Marker 91	*0.78*	91	2.40	1.06	3.45	0.02	2.07	10.90
Marker 41	*0.87*	94	2.44	2.37	4.81	0.04	2.66	20.60
Outer Channel								
Station 13 (N)	*0.47*	5	4.81	0.42	5.23	0.00	0.35	1.61
Station 28 (S)	*0.43*	6	1.24	0.52	1.76	0.00	0.45	2.70

(N) and (S) in the lower rows refer to the northern and southern sections of Laguna Madre.

3.2. Sediment NH_4^+ Extractions

Total sediment NH_4^+ is composed of the dissolved porewater fraction and that associated with the solid phase, determined as described in the extraction method. Fig. 2 present extraction results for sediments collected from the channel at Marker 45 in upper Laguna Madre, that are typical for all sediments. In order to establish goodness-of-fit for the analysis procedure, we calculated the sum of residuals (sum total difference between the measured points and equation predictions) for each sediment extraction. In all inner channel sediment extractions, the sum of residuals was less than 5% of the asymptotic maximum. The sum of residuals in one of the duplicate analyses for the outer sediment at Station 13 was 14% of the asymptotic maximum. The sediments collected outside the channel were, in general, not as well described by Eqn (1), though the summed residuals calculated for all outer sediment extractions, with the exception of Station 13, were at most 7% of the asymptotic value.

Total NH_4^+ (determined by multiple extractions) per gram (d.wt.) sediment (ΣNH_4^+) was much greater in sediments taken from the channel than in sediments taken outside of the channel (Table 3). The ΣNH_4^+ content of sediments inside and outside the GIWW were examined to assess the amount of NH_4^+ available for desorption and to evaluate what fraction of the total might be released during resuspension. Efficiencies for the first extraction did not exceed 50% for any sediment and were as low as 18% for the sandy sediment collected at Station 28 (Table 4). After the second extraction, only half of the yields exceeded 50% and the highest yield was 74% for one of the inner sediments. This suggests that single extraction determination of exchangeable NH_4^+ can

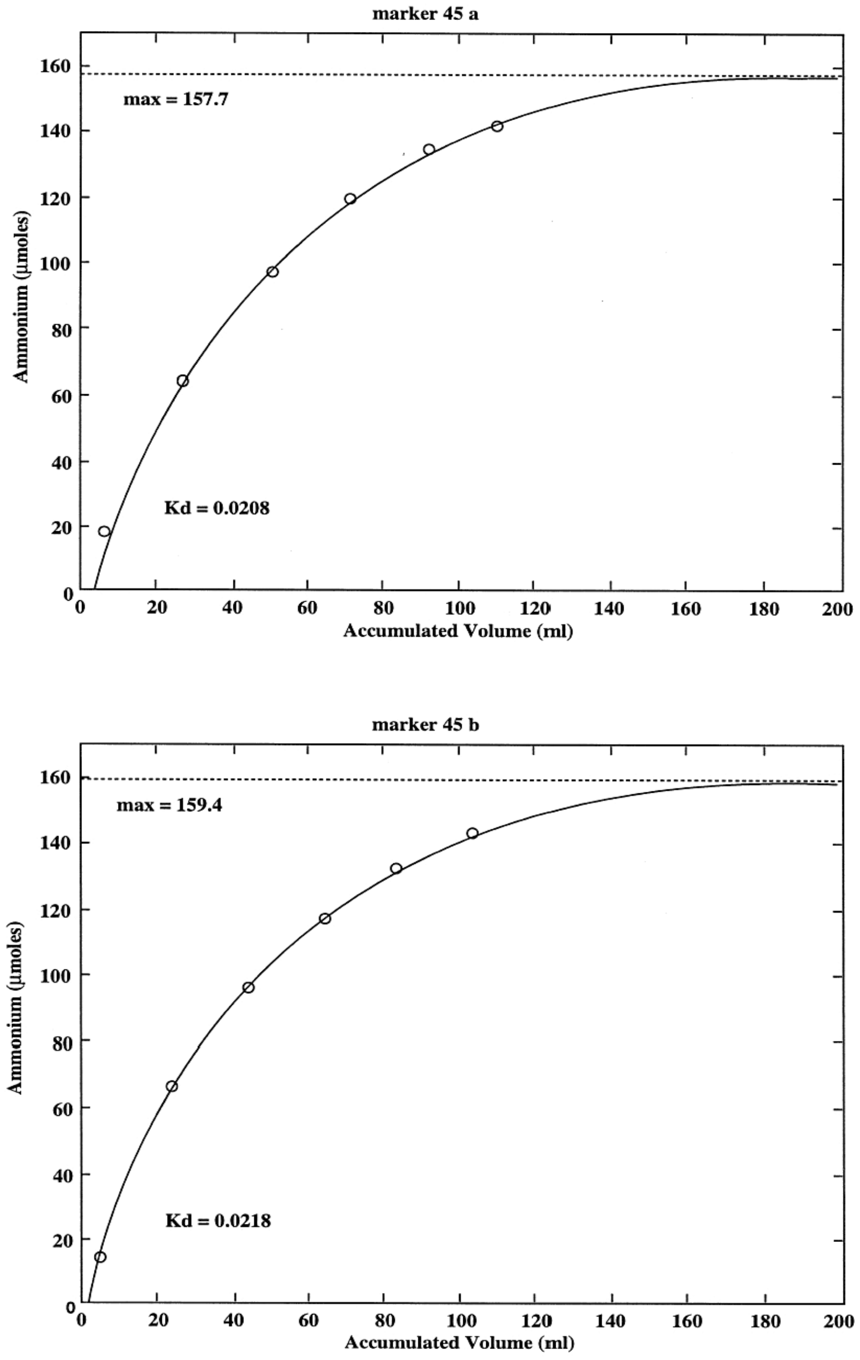


Fig. 2 (a and b) Replicate extractions of sediments collected at Marker 45 in the Laguna Madre Estuary (Texas). Accumulated volume of extract is compared to quantity of NH_4^+ collected. Equation fits approach the maximum (dotted lines) considered to be the total associated with the sediments.

Table 4. Yields of extractable NH_4^+ after one and two extractions in 2 N KCl with comparisons to the total NH_4^+ assessed using the multiple extraction technique with subsequent equation fitting

Station	Exchangeable ammonium							
	After first extraction (µmol g d.wt^{-1})	Percent of total	*K* (slope = 2.18)	After second extraction (µmol g d.wt^{-1})	Percent of total	*K* (slope = 3.53)	Total extractable NH_4^+ (µmol g d.wt^{-1})	*K* (slope = 7.96)
Inner Channel								
Marker 157	3.51	30.2	1.4	5.68	48.9	2.3	11.61	4.5
Marker 151	8.71	26.8	0.7	14.42	44.4	1.1	32.50	2.1
Marker 59	3.94	49.0	2.3	5.96	74.1	3.7	8.04	7.1
Marker 45	4.84	30.6	1.2	7.82	49.5	2.0	15.80	3.8
Marker 41	5.62	27.3	0.9	9.61	46.7	1.4	20.60	2.7
Marker 91	4.04	37.1	1.6	6.39	58.6	2.6	10.90	5.1
Outer Channel								
Station 13	0.75	46.6	6.7	1.05	65.2	10.8	1.61	20.9
Station 28	0.48	17.9	7.7	1.53	56.7	12.4	2.70	23.9

Linear diffusion coefficient (*K*) was calculated according to Mackin and Aller (1984) for each of the first two extractions and for the total.

lead to underestimation of particle associated NH_4^+. No correlation was obvious between extraction efficiency and the sediment porosity.

Following Rosenfeld (1979), NH_4^+ dissolved in porewaters was compared to the corresponding exchangeable NH_4^+ by plotting NH_4^+ (p.w.) against estimates of NH_4^+ (exch.) obtained with one extraction, two extractions, and total exchangeable NH_4^+ (Fig. 3). The slope of the regression line ranged from 2.18 for the first extraction to 7.96 for the total extractable NH_4^+ content, and *y*-intercepts were all negative. This result differs from earlier data (Rosenfeld, 1979; Boatman and Murray, 1982; Mackin and Aller, 1984), possibly because we did not attempt to remove organic matter. The slope of each regression line was used in the relationship of Mackin and Aller (1984) to determine the apparent adsorption coefficient (K^*):

$$K^* = \frac{\hat{C}_{\mathrm{N}}}{C_{\mathrm{N}}} \tag{2}$$

where $\hat{C}_{\mathrm{N}}$ is the sediment exchangeable NH_4^+ concentration (µmol g d.wt.$^{-1}$ sediment) and is the porewater concentration of NH_4^+ (mmol L^{-1}). Unit for K^* is ml porewater g d.wt.$^{-1}$. The linear adsorption coefficient can be calculated from the relationship of Krom and Berner (1980) using K^*, porosity, and sediment density ρ_{s} (2.65 g ml^{-1}).

$$K = \left(\frac{1 - \phi}{\phi}\right) \rho_{\mathrm{s}}\, K^* \tag{3}$$

The calculated adsorption coefficients were extremely variable and showed a strong

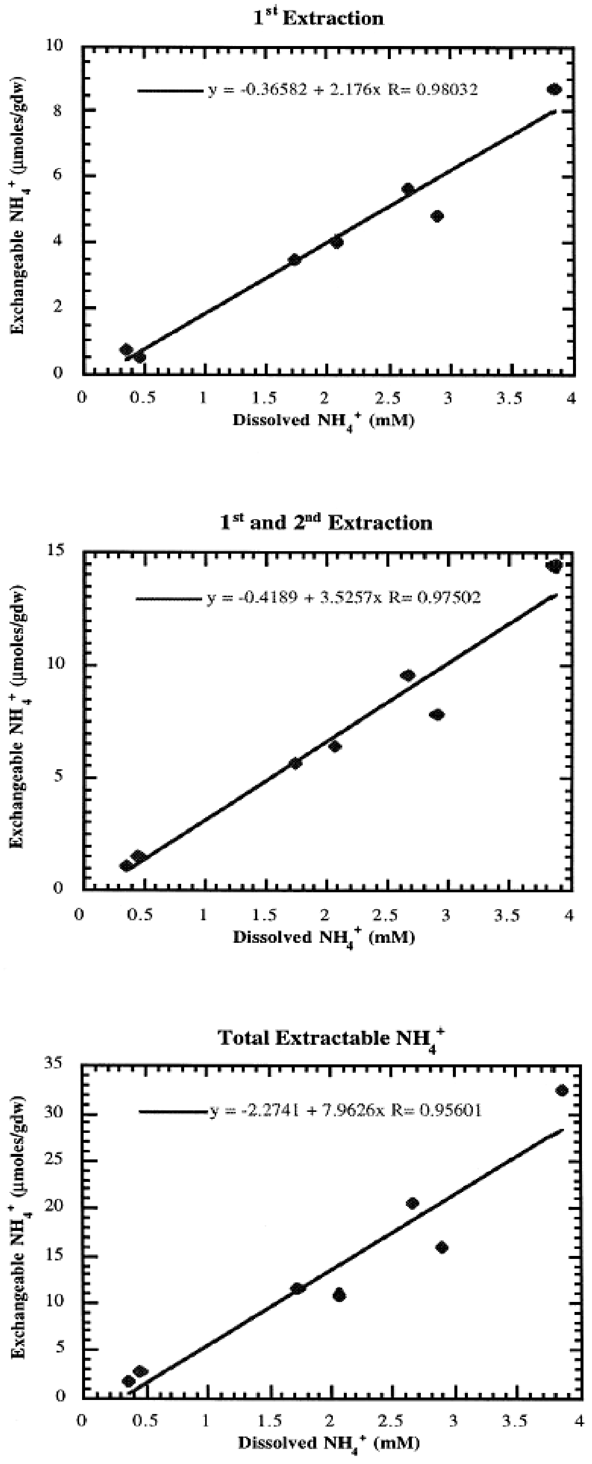


Fig. 3 Determination of apparent adsorption coefficient (K*) utilizing the bulk NH_4^+ (dissolved) concentration (millimolar) and exchangeable concentration determined through extraction.

dependence on the number of extractions. However, they were well within the range of adsorption coefficients measured in various coastal systems by Laima (1999).

3.3. Closed Experiments

Following sediment addition, NH_4^+ concentrations in the resuspension waters increased rapidly over the first 20 min of the closed experiments and then exhibited slow increases over the remainder of the experiment (Fig. 4). Background quantities of NH_4^+ in the overlying water were added to the porewater NH_4^+ to arrive at a seawater + porewater NH_4^+. This value represents the concentration of NH_4^+ expected immediately following resuspension. The NH_4^+ released after 5 min minus the background and porewater quantities is defined as 'fast release' NH_4^+. The total amount released at the end of the 48 h time period is defined as the total releasable NH_4^+. A 'slow release' fraction was determined by subtracting the fast release from the total. Desorbed NH_4^+ from the channel sediments generally exceeded the release from the sediments collected in vegetation-free areas of the Laguna Madre, with the exception of the 0.1 g addition for sediments collected at Marker 157. In the higher dilutions (1.0 and 10.0 g additions), Marker 157 sediments released more NH_4^+ g d.wt.$^{-1}$ than the vegetation-free areas sediments. Porewater concentrations of NH_4^+ in the Marker 157 sediments were the lowest of the sediments collected in the channel.

'Fast' and 'slow' release patterns shown in Fig. 4 indicate that significant release occurs after the first 2 h of resuspension. Averages of the fast and slow release fractions (g d.wt.$^{-1}$) for each experiment are given in Table 4. In general, the quantity of rapidly-

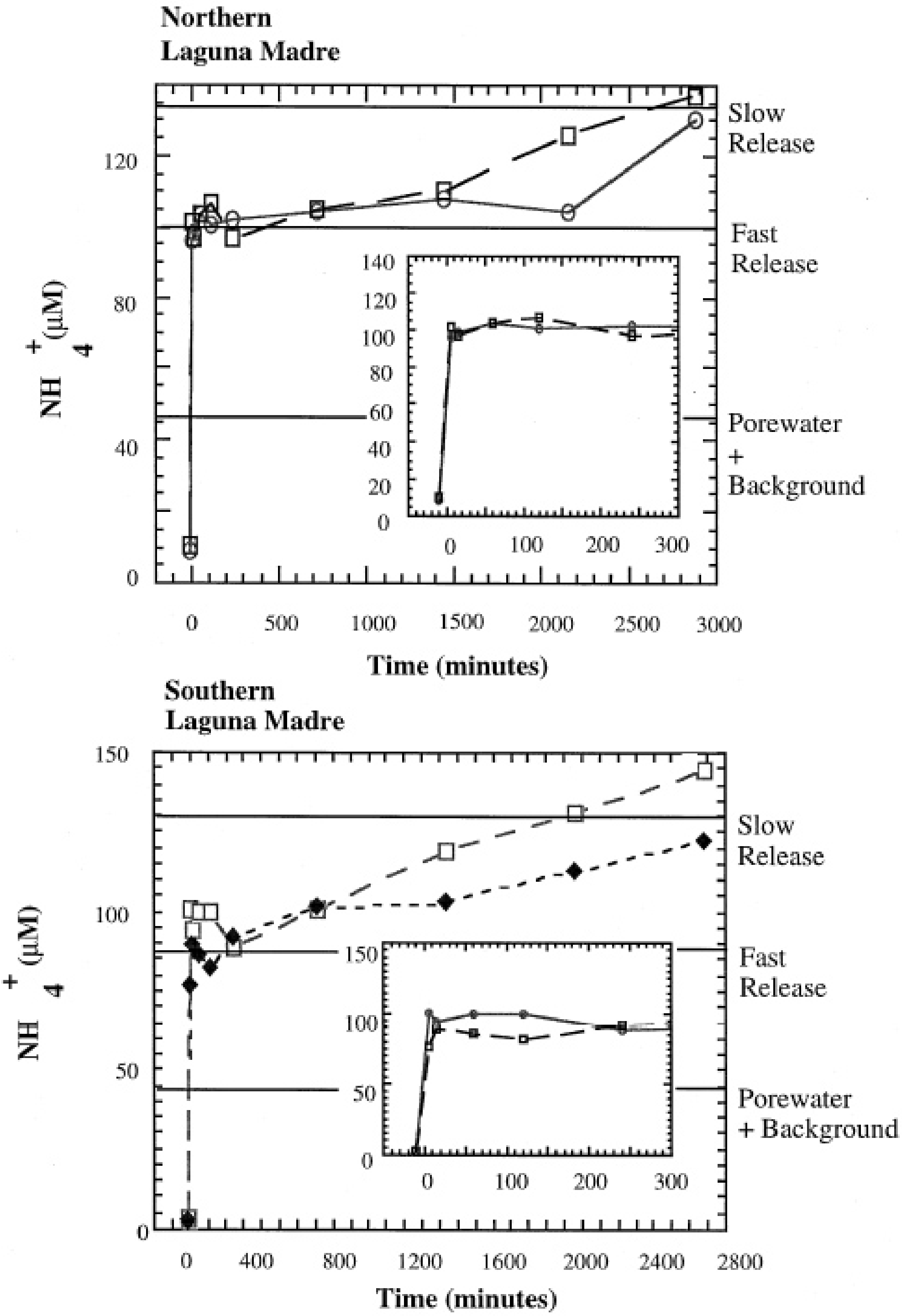


Fig. 4 Time course NH_4^+ concentrations determined for closed resuspension experiments on sediments collected in the Laguna Madre. Inset graphs display data from the first 300 minutes of the experiments.

Table 5. **Results for the closed experiments conducted by adding 0.1, 1.0, and 10.0 g of sediment by dry weight to 1 l volumes of overlying water.**

Location and sediment addition (g l^{-1})	Seawater initial concentration (µM)	Seawater + porewater NH_4^+ (µM)	Initial NH_4^+, t = 5 min (µM)	Fast release (µM)	NH_4^+ maximum (µM)	Slow release (µM)	Fast release (µmol g $d.wt.^{-1}$)	Slow release (µmol g $d.wt.^{-1}$)	Total NH_4^+ (µmol g $d.wt.^{-1}$)	Released as % of Total	Total release (µmol g $d.wt.^{-1}$)
Inner											
Marker 151									32.50		
0.1	7.5	8.8	7.9	–0.9	12.6	3.8	nd	37.8		116.39	37.83
1.0	11.6	24.9	45.1	20.2	57.2	12.1	20.2	12.1		99.39	32.30
10.0	11.3	144.0	325.6	181.7	373.5	47.9	18.2	1.8		70.63	22.96
Marker 157									11.61		
0.1	1.0	1.3	1.4	0.1	2.5	1.1	1.0	11.0		103.44	12.00
1.0	1.9	4.6	9.2	4.5	13.7	4.5	4.5	4.5		77.74	9.02
10.0	1.2	28.7	86.8	58.1	123.5	36.7	5.8	3.7		81.72	9.48
Marker 45									15.8		
0.1	4.2	4.8	7.1	2.3	9.5	2.5	22.8	24.9		301.39	47.62
1.0	3.4	8.8	21.3	12.5	29.6	8.3	12.5	8.3		131.85	20.83
10.0	3.9	57.8	150.7	92.9	218.8	68.1	9.3	6.8		101.90	16.10
Marker 59									8.04		
0.1	10.1	10.5	10.7	0.2	12.6	1.9	2.3	19.4		270.90	21.67
1.0	7.6	11.2	16.1	4.9	24.9	8.8	4.9	8.8		171.09	13.69
10.0	9.6	45.7	98.6	52.9	133.8	35.1	5.3	3.5		110.00	8.80
Marker 91									10.90		
0.1	3.3	3.6	5.3	1.7	6.8	1.5	17.3	15.3		298.79	32.57
1.0	2.2	5.2	10.8	5.7	18.5	7.7	5.7	7.7		122.40	13.34
10.0	3.1	32.3	95.3	63.0	133.2	37.9	6.3	3.8		92.64	10.10
Marker 41									20.60		
0.1	6.6	7.3	8.1	0.7	13.4	5.3	7.4	28.8		175.52	36.16
1.0	6.4	13.5	22.5	9.1	23.9	1.4	9.1	1.4		50.83	10.47
10.0	5.7	76.0	160.4	84.5	171.8	11.3	8.4	1.1		46.51	9.58
Outer											
Station 13									1.61		
0.1	7.2	7.2	7.8	0.6	8.9	1.1	6.4	11.1		1092.74	17.48
1.0	6.7	6.8	8.3	1.5	15.5	7.2	1.5	7.2		545.17	8.72
10.0	7.1	8.2	31.9	23.7	43.5	11.5	2.4	1.2		220.23	3.52
Station 28									2.70		
0.1	8.0	8.0	7.7	–0.4	9.9	2.2	nd	22.0		762.22	18.37
1.0	8.5	8.6	9.5	0.9	10.5	1.0	0.9	1.0		78.40	1.89
10.0	6.6	7.9	9.7	1.8	12.8	3.1	0.2	0.3		20.31	0.49

Total NH_4^+ refers to the quantity ascertained through the extraction procedure.

released NH_4^+ was dependent on the quantity of sediment added. The rapid release fraction for each sediment, however, did not increase in a manner directly proportional to the mass of sediments. In most cases the NH_4^+ g d.wt.$^{-1}$ release was greatest for the 0.1 g sediment addition. This relationship was also observed for the total released fraction and particularly for the slow release quantity. The last three columns of Table 5 display ΣNH_4^+ for each sediment (from above extractions), the maximum NH_4^+ measured for each experiment, and the fraction of the total NH_4^+ measured in the closed system experiments. The calculations of greater than 100% of the total NH_4^+ (porewater + extractable) determined for some sediments are attributed to the varying ratios of solid–to–solution and will be addressed in the discussion.

3.4. Open Experiments (Elutriate Test)

The dynamics of NH_4^+ release as a function of time for the open system experiments were very similar to those observed in the closed systems experiments. NH_4^+ concentrations rapidly increased initially, then showed a relatively small increase between the 60-min sample and the final sample taken at 24 h. This final increase in the nutrient concentration in the overlying water occurred after the sediments had settled, indicating that release of NH_4^+ can continue after particles have fallen out of the water column. The two graphs of Fig. 5 display typical results observed for release experiments carried out according to the Corps of Engineers elutriate method. In several of the experiments, the release after sediments had settled was in excess of 10% of the total release (Table 6). One exception to this was the results for Marker 151 sediments

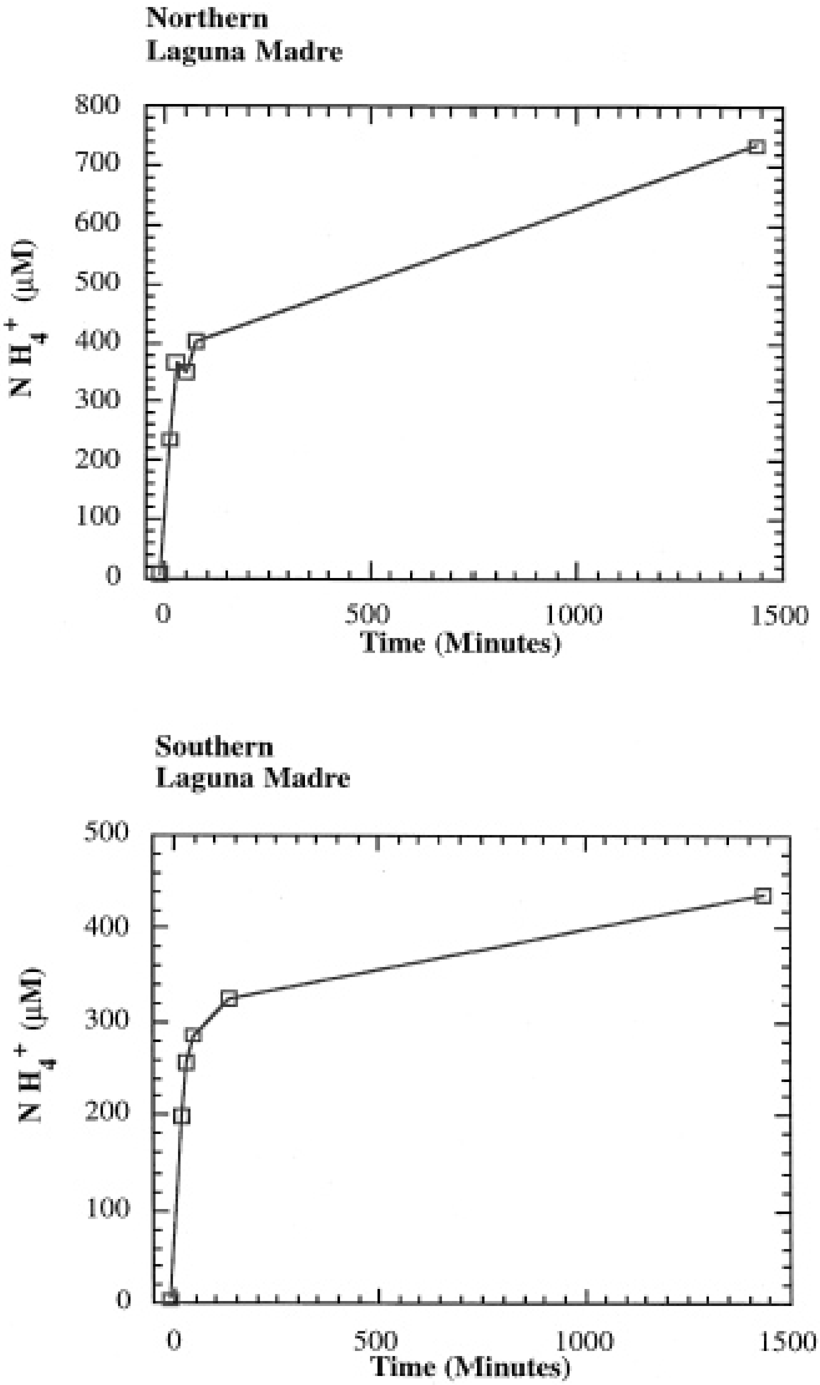


Fig. 5 NH_4^+ concentrations determined for open resuspension experiments carried out according to Corp of Engineers elutriate method.

Table 6. Results for the open, elutriate test.

Location	NH_4^+ maximum measured (µmol L^{-1})	Grams sediment added	µmol of NH_4^+ released	NH_4^+ released (µmol g d.wt.$^{-1}$)	Total NH_4^+ (µmol g d.wt.$^{-1}$)	Released as % of total
Inner Channel						
Marker 151	1449.30	26.75	528.45	19.75	32.50	60.78
Marker 157	692.32	52.00	169.67	3.26	11.60	28.13
Marker 45	929.80	45.19	305.03	6.75	15.80	42.72
Marker 59	1074.30	73.63	279.97	3.80	8.00	47.53
Marker 91	982.40	57.17	242.37	4.24	10.90	38.89
Marker 41	828.00	33.70	0.30	0.01	20.60	0.04
Outer Channel						
Station 13	705.60	139.54	186.43	1.34	1.60	83.50
Station 28	99.00	146.67	26.96	0.18	2.41	7.63

where NH_4^+ concentration decreased between the 1-h sample and the final sample. This station's sediments also had the highest release of NH_4^+ in the open experiments and were characterized by the highest ΣNH_4^+ content. NH_4^+ release from vegetation-free sediments in the elutriate experiments was more than an order of magnitude less than for the channel sediments. Final calculations of release (g d.wt.$^{-1}$) in the open experiments exhibited similar trends to the closed experiments. In both experiments, Marker 151 sediments had a very high release of NH_4^+, whereas sediments collected at Marker 157 and Marker 59 released the least. Marker 45 and 91 sediments released large fractions of the ΣNH_4^+ for both the open and closed experiments. Experiments where the largest fraction of ΣNH_4^+ was released were also characterized by the highest mass of sediments added. Sediment mass additions in the open experiments exceeded at least twice the mass addition in closed experiments. Porewater additions in open experiments also far exceeded the additions in the closed experiments and were considered in final calculations of NH_4^+ concentrations and fraction of ΣNH_4^+ release.

3.5. NH_4^+ Flux Determination and Sediment Plume Analysis

Sediment NH_4^+ profiles were determined in cores taken from seagrass beds and from vegetation-free areas. Flux estimates were calculated using Fick's first law along with modifications suggested by Boudreau (1996). Concentration gradients were calculated using the difference between concentrations of NH_4^+ in the overlying water and at 2 cm depth. The diffusivity was considered a function of porosity (ϕ) and adjusted using the reciprocal of $(1 - 1n(\phi^2))$. NH_4^+ flux estimates were all positive and ranged from 229 to 622 µmol m^{-2} day^{-1}

for vegetation-free areas and from 175 to 612 μmol m^{-2} day^{-1} in grass-covered regions. These estimates were used to calculate an aerial NH_4^+ flux from sediments in Southern Laguna Madre, considering a total sediment surface area of 487 km^2 and approximately 70% seagrass coverage. A conservative estimate of NH_4^+ flux will be presented in the discussion with calculations of potential release associated with a dredging event.

The graph in Fig. 6 displays the NH_4^+ concentration and suspended solid quantities measured at the three points during sediment plume sampling in February 1997. Both NH_4^+ and suspended solid concentration increase with distance from the dredge pipe. The increase in suspended solids with distance from the source was due to the interruption of sediment flow from the outlet during sampling, allowing the sediment plume to move with the water current away from the area of disposal. Concentrations of NH_4^+ increased from approximately 20 μmol L^{-1} near the dredge pipe terminus to over 130 μM in the sediment plume. It should be kept in mind that the higher concentration of particles also corresponds to an increase in distance from the dredge pipe, and thus an increase in the amount of time the sediments had been resuspended. This possibly also resulted in the loss of a significant amount of suspended sediment due to deposition.

4. Discussion

4.1. Comparison of Release Experiments

We found that our closed system experiments resulted in much greater release of NH_4^+ (g $d.wt.^{-1}$) when compared to the elutriate method. There are several differences

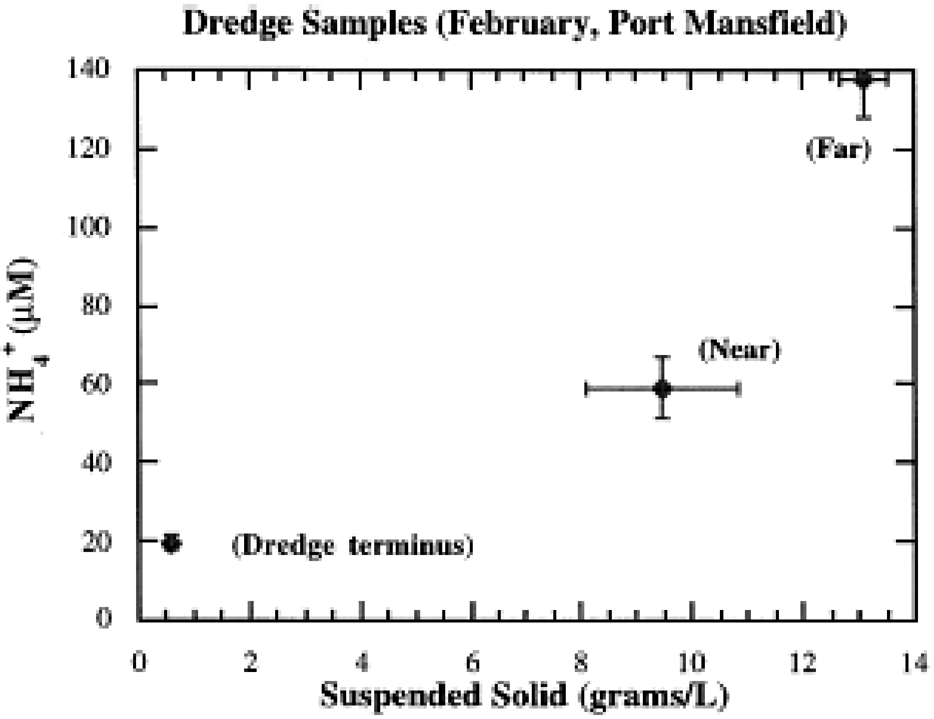


Fig. 6 Data collected during a dredging event in February 1997. The graph displays NH_4^+ concentrations vs. suspended particulate matter (SPM) at points 300 m from the dredge pipe (far), 30 m from the dredge pipe (near), and immediately adjacent to the pipe.

between the two methods that influence the results. First, the elutriate method involves constant aeration resulting in conversion of any easily oxidized compounds (e.g., HS^-). Second, according to the elutriate technique, agitation of the sediment water mixture is terminated after 1 h whereas sediment suspension is maintained in the closed system. Although these differences in methodology influenced the results, they are probably of secondary importance to the ratio of sediment added to overlying water outlined by each method.

Sediment (d.wt.) to volume ratios in elutriate experiments ranged from 52.4 to 249 g L^{-1}. In contrast, sediment (d.wt.) additions in closed experiments were 10, 1, and 0.1 g L^{-1}. Fig. 7 displays the final concentration (assumed to be the equilibrium concentration (μmol L^{-1})) measured at the end of all resuspension experiments for sediments collected at Marker 45. The equilibrium concentration is plotted against the amount of desorption available NH_4^+ (ΣNH_4^+). The graph resembles a Langmuir function with the closed experiment results found on the linear part of the curve, and elutriate experiment measurements closer to the saturation part of the curve. This type of relationship was observed for all sediments. A saturation function was fitted to the data and is represented by the dotted line in Fig. 7. The r^2 value for this curve was 0.998. Elutriate experiments were largely designed to imitate high sediment–to–water ratios inside dredge pipes. After sediments are expelled into open waters, the ratio of sediment–to–water volume rapidly decreases as the sediment plume moves away from the source. Thus, our closed system experiments may better represent conditions in open waters where sediment plume dilution and maintenance of small particles in suspension allows for greater nutrient release. It should also be noted that, with the exception of

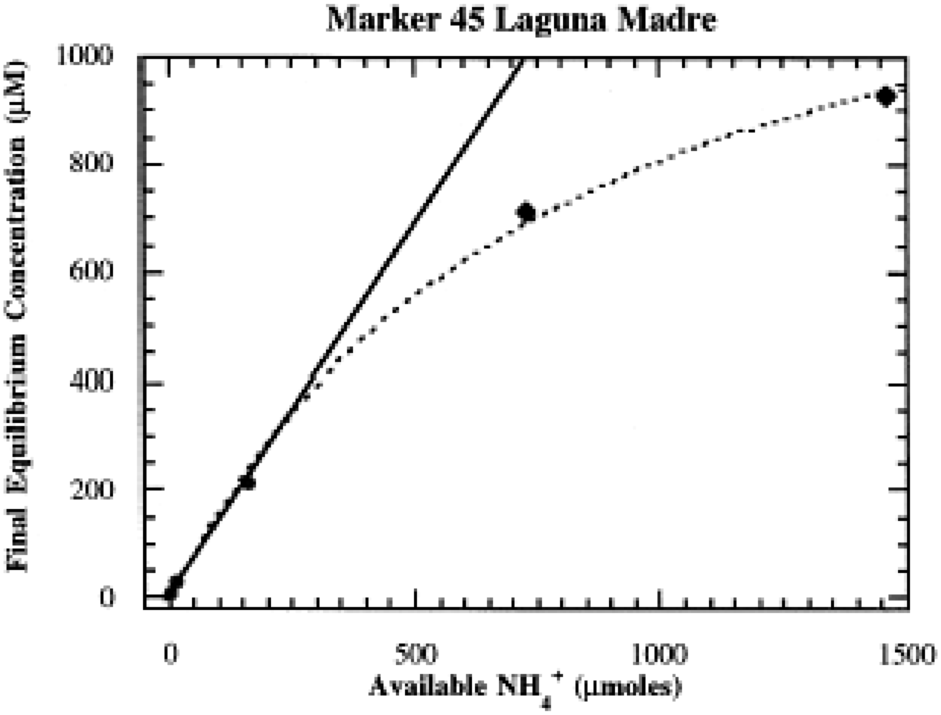


Fig. 7 Final measured NH_4^+ concentration vs. total extractable NH_4^+ (calculated as ΣNH_4^+ (gram d.wt.$^{-1}$) multiplied by dry weight added) for all resuspension experiments (open and closed) with Marker 45 sediments. Data collected from the closed experiments fall on the linear portion of the curve near the origin (filled circles) and open experiment results occur in the saturation portion (diamonds).

areas near the air–water interface, our closed experiments better simulate low oxygen conditions present during resuspension of anoxic sediments. Measurements taken in the field during a dredging event appear to support this conclusion. The data presented in Fig. 6 illustrate the release of NH_4^+ after the initial dilution of porewater. Instead of a linear increase in NH_4^+ with suspended particles, we observed more of an exponential relationship. This would seem to indicate that NH_4^+ release continues after porewater dilution. In both the elutriate and closed experiments large quantities of NH_4^+ associated with the 'fast' release of loosely bound ions were evident in the first 5 min of sediment resuspension. This fraction will be important in the early stages of particle resuspension. In addition, smaller particles capable of remaining in suspension for long time periods (on the order of hours) will continue to desorb NH_4^+ until removal by sedimentation.

4.2. Environmental Implications

A recent investigation by Blackburn (1997) using a simulation model of sediment resuspension concluded that resuspension of up to 2.4 cm of surficial sediment and porewater would have inconsequential effects on the overlying water nitrogen concentration, and thus no effect on primary producers in the water column. In a mesocosm experiment, Sloth et al. (1996) observed a slight increase in NH_4^+ concentrations when an estimated 6 mm of surficial sediments were resuspended. The liberated NH_4^+ nitrogen was assumed to be relatively rapidly absorbed by planktonic algae. The present investigation concentrates on the affect of large-scale dredging, which can relocate up to 1 m of sediment (Brown and

Kraus, 1996). A similar investigation conducted by Jones and Lee (1981) using the elutriate procedure on sediments collected in various dredging areas concluded that nutrient release would rarely have an adverse effect on water quality. These authors determined that the relatively short-lived duration of these events would prevent any significant effects on the dumpsite surroundings, though they admit that this conclusion should be evaluated on a site-by-site basis.

Using the data collected in the present study we calculated a potential release of NH_4^+ during dredging near Port Mansfield, Texas in 1989 (these calculations should be considered rough estimates of the conditions which actually occur during sediment relocation) in which 318,000 m^3 of sediment were dredged and deposited outside the channel (Militello and Kraus, 1994). The movement of this volume of sediment resulted in a release of approximately 5.3×10^8 L of porewater. An estimated release of NH_4^+ through porewater dilution and desorption of loosely bound ions can be calculated from these figures. The potential release in this relatively small area was in excess of 46 metric tons of NH_4^+ over a period of approximately 2 months. This estimate should be considered conservative in that the release of additional NH_4^+ associated with a slow release fraction could increase the potential release by one-third to 60 metric tons. For comparison, we used the sediment flux calculations described in the results to estimate NH_4^+ release for the entire lower Laguna Madre to be approximately 80 metric tons (monthly). This estimate is also conservative in that only molecular diffusion of NH_4^+ from sediments was considered and other factors, such as bioirrigation, were ignored but might be important (Aller, 1982). Due to the restricted circulation in the Laguna Madre, the impact of dredging on dissolved NH_4^+ will be largely confined to the region where the activities are taking place. Therefore comparisons with sediment fluxes over the entire area of the estuary may not be appropriate. Clearly, there exists a potential for significant refinement of these estimates through more direct observations of dredging and measurements of benthic fluxes. However, this study does demonstrate at least the potential for a substantial impact on availability of NH_4^+ in portions of the estuary on monthly time scales.

Alterations in the NH_4^+ concentration, specifically the ratio of available NH_4^+ to available NO_3^-, may influence the structure of the algal communities inhabiting the Laguna Madre. A phenomenon referred to as ‘the brown tide’ has been occurring in this South Texas estuarine system for the last 7 years. Street et al. (1997) described the brown tide event and isolated the organism responsible for the bloom. This organism is closely related to an organism associated with brown tide in Long Island Sound and Narragansett Bay (*Aureococcus anophagefferens*). Unlike the organism isolated in the northern Atlantic coastal systems, the Laguna Madre species cannot utilize nitrate as nitrogen source (DeYoe and Suttle, 1994). Lomas et al. (1996) have characterized the nitrogen uptake dynamics of the organism isolated from Long Island Sound and Narragansett Bay. The authors determined that *A. anophogefferens* is well adapted to low light environments and that, under these conditions, preferentially absorbs NH_4^+ as nitrogen source.

The onset of the brown tide in South Texas was associated with a large scale die-off of fish and benthos during severe freezes in the winter of 1989 (DeYoe and Suttle, 1994). This event caused NH_4^+ to increase to 69 μmol L^{-1} in Southern Laguna Madre and coincided with a collapse of the micro- and macro-zooplankton communities. These events taken together with the physiological characteristics of the Texas brown tide organism created favorable conditions for the mono-specific bloom. NH_4^+ inputs during dredging events combined with a reduction in light penetration could simulate the substrate alterations of the original event, at least in a localized fashion. Due to the geographical structure of the Laguna Madre estuary, nutrient concentration perturbations are not transported rapidly outside and eliminated. These localized alterations can persist, acting to exacerbate the brown tide bloom.

5. Conclusions

The current widely used open system elutriate method is probably not generally as good a predictor of NH_4^+ release from resuspended sediments as the more dilute solution, closed system technique presented here. Our technique also made it possible to discern the source of released NH_4^+ and the kinetics of the release process. It was found that about two thirds of NH_4^+ released from resuspended sediments is from desorption rather than simple dilution of porewaters. Results were substantially confirmed by direct observation of a dredging event. Although quite approximate, our model calculations raise the possibility that dredging activities in Laguna Madre could locally cause releases of NH_4^+ to the water column similar in magnitude to those from natural benthic fluxes.

CHAPTER III

AMMONIUM INTERACTIONS WITH COASTAL MARINE SEDIMENTS: INFLUENCE OF REDOX CONDITIONS ON K*

1. Introduction

Nitrogen release in the form of NH_4^+ (here, reference to ammonium includes the minor species ammonia NH_3) from estuarine and shallow coastal sediments has been linked to coastal productivity as well as nitrogen cycling in coastal regions. The relatively rapid deposition of organic matter in coastal regions is usually followed by slow decomposition and mineralization to elemental components. These components usually concentrate in marine sediments, creating a water column-favored flux gradient (Berner, 1976; Aller, 1982; Nixon, 1981; Rosenfeld, 1981). Sediment nitrogen flux has been determined to be a significant source of nitrogen nutrients for primary productivity in coastal regions (Nixon, 1981). The fact that coastal marine systems are primarily nitrogen-limited (Ryther and Dunstan, 1971), combined with recent increases in fertilizer utilization, nitrogen emission through fossil fuel burning, and worldwide per capita protein consumption, suggests that the eutrophication problems in existence today may be amplified in the near future (Nixon, 1995). This type of changing nutrient structure and concurrent alteration in ecosystems has been observed in the northwest Gulf of Mexico due to increased agricultural utilization of fertilizers and transport through the Mississippi River (Turner and Rabalais, 1991; Rabalais et al., 1996), as well as in the northwestern Black Sea where the Danube, Dniester, and Dnieper Rivers drain major agricultural basins (Friedl et al., 1998). Sediments may play a key role in changing nutrient dynamics due to their capacity for focusing nutrient concentrations.

Pulsed release of high concentrations of nutrients through particle and porewater resuspension has recently been investigated due to the capacity for release of significant quantities (e.g. Fanning et. al. 1989; Sloth et. al 1986; Blackburn, 1997; Pilskaln, 1998; Gentilhomme and Rich, 2001; Cartensen et. al., 2007). Mesocosm experiments conducted in a coastal system in Denmark support this proposition where resuspension of surficial sediments resulted in significant alterations in water column nutrient concentrations and stimulation of primary and secondary producers (Sloth et al., 1996). Oldham and Lavery (1999) observed a wind–induced doubling in NH_4^+ concentration in overlying waters of the Swan River estuary (Australia), but noted that the increase occurred prior to sediment resuspension. The increase in nutrient concentration was attributed to hydrodynamic forcing and injection of porewaters from the sediments. Water column nutrient profiles collected in the northern region of the Gulf of Mexico displayed high concentrations correlated with the occurrence of winter storms and high winds (Fanning et al., 1982). Episodic resuspension of sediments and interstitial waters specifically have the capacity for short-circuiting the denitrifying process through transport of NH_4^+ from anoxic conditions in sediments to overlying water where oxygen concentrations are not conducive to micro-aerophilic nitrifying bacteria. Nitrogen returned to the water column through this mechanism is less likely to be biologically altered ($NH_4^+ \rightarrow NO_2^-$) and provides nitrogen in a reduced form, which is incorporated more efficiently.

Significant resuspension of sediments also occurs due to human activity in coastal marine ecosystems (Lohrer and Wetz, 2003). A bottom water nephloid layer in the Gulf of

Maine has been partially attributed to bottom trawling activities (Pilskaln et al., 1998). The investigators in this study found that resuspension due to fishing reached up to 30 meters above the sediment–water interface and that nutrient profiles indicated short-term pulses of NH_4^+ and NO_2^- into the euphotic zone. Since trawling in this area takes place during the spring bloom, effects on phytoplankton uptake and productivity were not discernible from the normal bloom–inducing supply. Channel maintenance dredging of the coastal waterways is also capable of relocating hundreds of thousands of cubic meters of sediment and porewater (Brown and Kraus, 1996). A recent investigation conducted in the lower Laguna Madre determined that the quantity of sediment relocated over a one-month time period could potentially release amounts of NH_4^+ comparable to the monthly averaged sediment flux in the entire lower Laguna Madre (Morin and Morse, 1999). Resuspension experiments with the highly anoxic muds of the channel revealed that the quantity of NH_4^+ released was strongly dependent on the solid: solution ratio and that significant release of an absorbed NH_4^+ fraction could occur hours after initial resuspension. Extremely high concentrations of NH_4^+ were measured in the porewaters of the sediments taken from the channel in Laguna Madre (up to 3.85 mM) during this study. Excessive concentrations of NH_4^+ have been observed previously in a Mediterranean lagoon where onset of anoxia was correlated with rapid increases in and high concentrations of NH_4^+ (Souchu et al., 1998). The research conducted in the lower Laguna Madre also determined that a very large fraction of NH_4^+ could be particle bound (up to 32 μmol g d.wt.$^{-1}$). It was reasoned that the accumulation of NH_4^+ in the sediments could be related to high clay representation in the sediments of the Gulf Intracoastal Waterway channel.

Clay minerals are a ubiquitous component of marine sediments (up to 58% of North Atlantic sediments (Griffen et al., 1968)). This component of terrestrial soils is derived from continental weathering and is delivered to the coastal ocean through riverine transport and runoff. Clay minerals are known to have extremely high cation exchange capacities (e.g., montmorillonite (a smectite) has a CEC value 110 cmol kg^{-1}, vermiculite has a CEC value of 159 cmol kg^{-1} (Borchardt, 1989)). In a pure suspension of clays these values would equilibrate to 1.1 and 1.59 mmol gm^{-1} of cation adsorption. CEC of clay minerals is dependent on the overall charge of the clay particle. Microbial reduction of structural iron in clay minerals has been observed (Stucki et al., 1987). Alterations of CEC were then investigated in these "reduced" clays to determine if the change in clay particle charge might affect the adsorption characteristics. Khaled and Stucki (1991) have reported an approximate 30% increase in what is referred to as "fixed" K^+ content in the interlayers of the clays. The term "fixed" here refers to an increase in overall K^+ content in the particles which is unavailable for desorption.

This mechanism suggests significantly different solution dynamics for inorganic nitrogen dependent on the redox state of the sediments in which organic matter is remineralized. In addition, the potential for sediments to act in a buffering capacity to overlying water nutrient concentration change is dependent on the mobility of ions and thus the redox state of sediments. The idea that nutrient concentrations in shallow marine systems can be buffered by sediment–water interaction has been investigated previously (Pomeroy et al., 1965; Krom and Berner, 1980; Froelich, 1988; Sundby et al., 1992). These investigations generally employ an equilibrium-based buffering mechanism to describe the capacity for sediments to adsorb/desorb nutrients dependent on the solution concentration of the nutrient in question. This method involves resuspension of a fixed quantity of sediments into multiple containers with increasing concentrations of the ion of interest. Ion concentration is measured before sediment addition and after equilibration with solution.

The present work is an extension of the resuspension work carried out in the lower Laguna Madre and was designed to confirm a solution concentration control mechanism for NH_4^+ and to identify any possible relationship between the redox conditions and potential for NH_4^+ desorption.

2. Methods

2.1. Study Area

Two sites were chosen to investigate adsorption dynamics of NH_4^+ with marine sediments. A site in the northwestern Gulf of Mexico (Fig. 8) was chosen because of its position in the hypoxic zone. Periodic anoxia has been observed at this site and sulfide has been measured in the water overlying the sediment (unpublished data). The site is in close proximity to the Southwest Pass where the majority of the Mississippi River effluent enters the Gulf of Mexico. In order to establish that alteration in adsorption capacity was not site-specific, a collection site was established in the lower Laguna Madre of Texas (Fig. 9) near the area of interest for the original research mentioned above. These sediments also have a large representation of clay-sized components and exhibit extraordinary concentrations of NH_4^+. In terms of adsorption investigation, this site can be considered an extreme due to high solution concentrations of NH_4^+.

2.1.1. Lower Laguna Madre (LLM). Data in the text labeled LLM come from work done with sediments collected in the lower Laguna Madre (Fig. 9). The sediments were collected inside the Gulf Intracoastal Waterway (GIWW) channel at 26°10.75”N, 97°15.62”W at a water depth of approximately 4 meters. Laguna Madre is one of two negative estuaries that border the Gulf of Mexico. It is characterized by very low freshwater input and low yearly precipitation. Estimates of residence time for south Texas estuaries are in excess of 200 days and have been correlated with the geologic features and exceptionally low freshwater inflow (Solis and Powell, 1999). The samples collected and data presented here are from a station located in the lower Laguna Madre. Prior to the construction of the GIWW in 1949, lower Laguna Madre was separated from Baffin Bay and upper Laguna Madre by an approximately 20 km expanse of periodically flooded salt flat. Salinities in excess of 100 ppt were not uncommon in the area due to this isolation. The construction of the GIWW, along with the formation of the pass at Port Mansfield, Texas, altered the hydrography of the system by increasing flow into the lower estuary. This alteration in salinity regime has had relatively serious effects on the seagrass community in the area. The distribution of one specific species of seagrass, referred to as shoal grass (*Halodule wrightii*), has decreased from 82% coverage in 1965 to 33% in 1988 and total seagrass coverage has been significantly reduced in the southern part of lower Laguna Madre (Onuf, 1994).

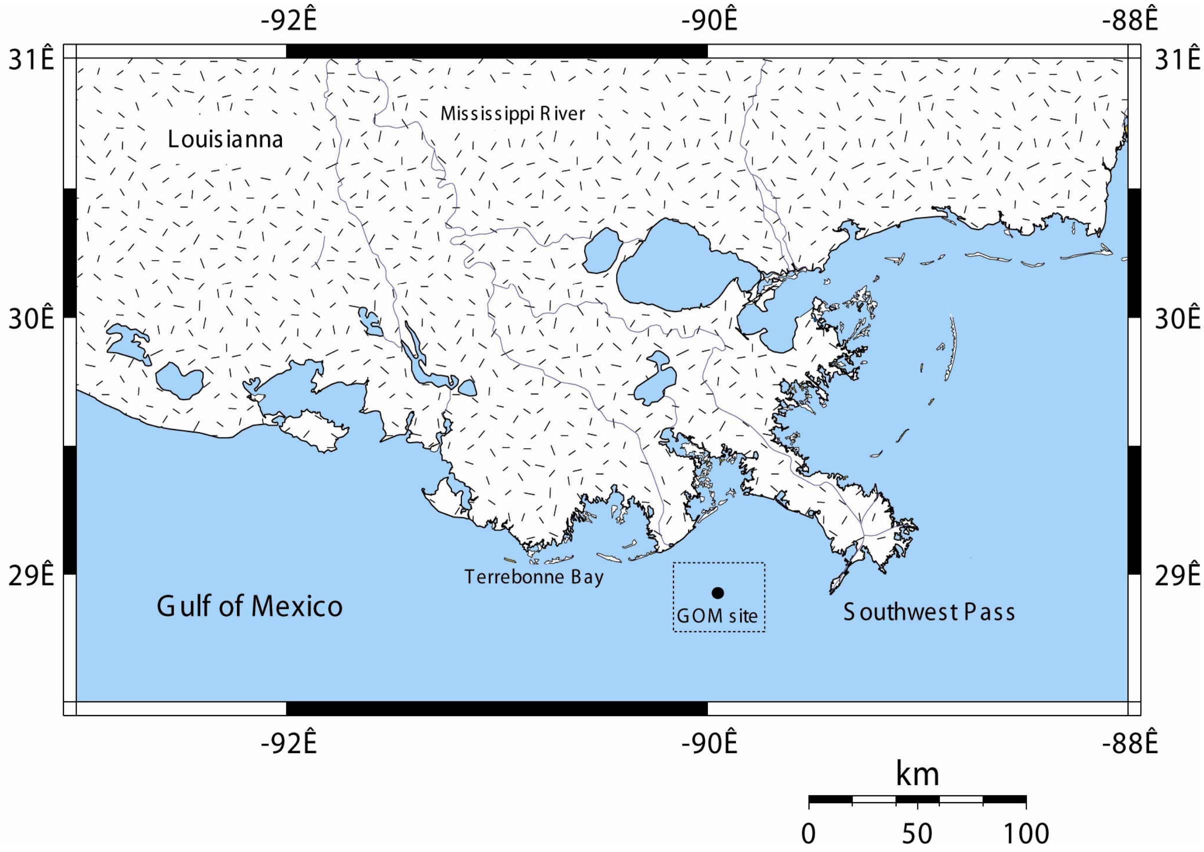


Fig. 8 North Central Gulf of Mexico (GOM) where sediment samples were collected for experiments and characterization.

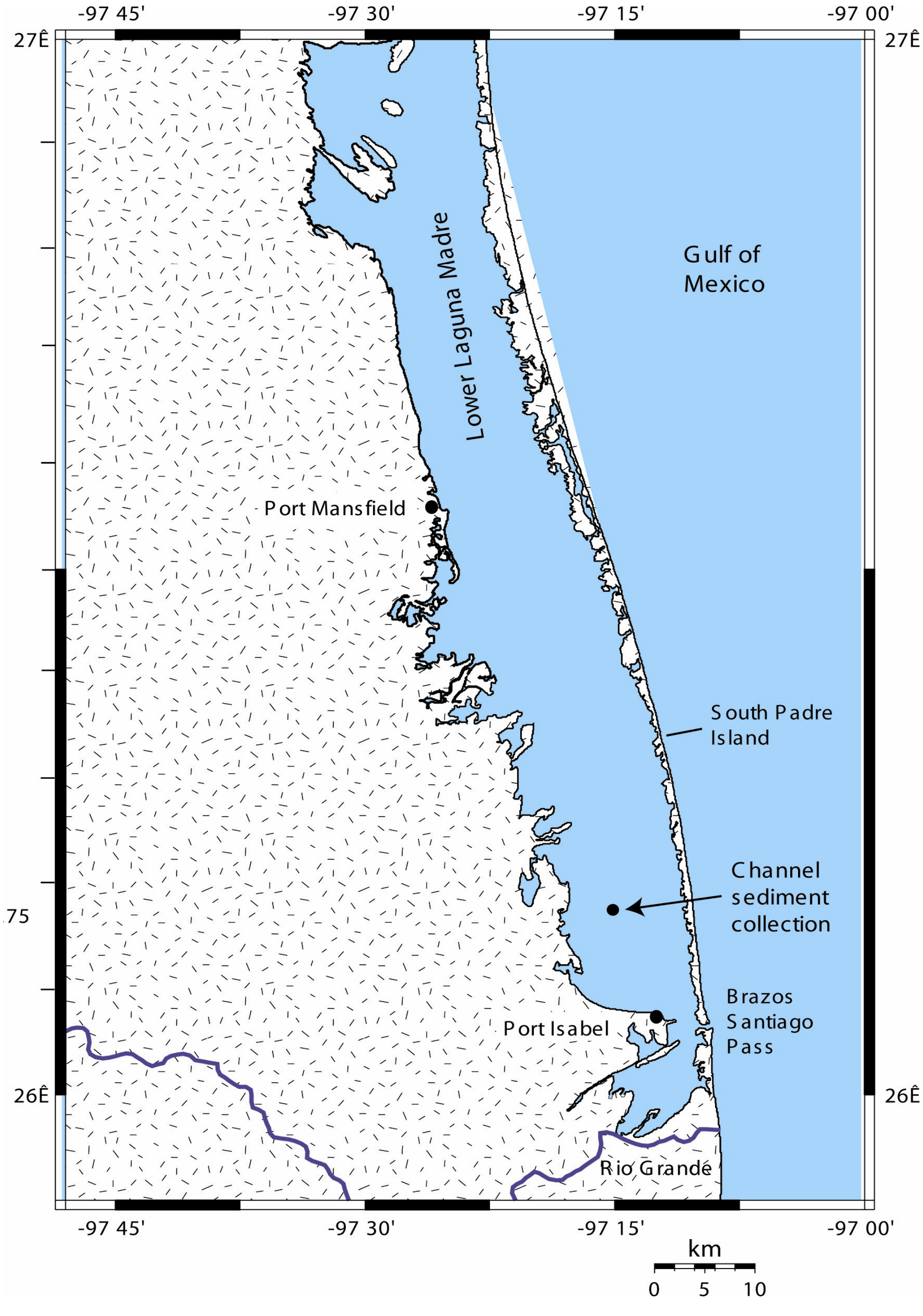


Fig. 9 Lower Laguna Madre (Texas) (LLM). Sediment collection site is represented by the black dot located in the lower portion of the figure. The site is located in the Gulf Intra coastal Water Way (GIWW).

The coastline of South Texas and Northern Mexico is primarily composed of bar–built islands enclosing lagoon-type estuaries. The lower Laguna Madre is one of the largest lagoon systems in the Gulf of Mexico. Sources of freshwater as well as river-borne continental sediment are limited to the Arroyo Colorado. Average flow rate for the Arroyo is approximately 5.8 $m^3 s^{-1}$, compared to the Colorado River, which delivers freshwater at a rate of 70.2 $m^3 s^{-1}$ to Matagorda Bay to the north (U.S.G.S. Water Quality and Stream Flow Database). The implication of this low addition rate of terrigenous material is that the sediments are relatively mature and weathered due to excessive residence time. Sediments in the bay are mostly sandy on the eastern side near the barrier island and silty to clayey sands and clayey silts in the deeper sections (Schroeder and Wiseman, 1999). Clay mineralogy of the majority of sediments in South Texas estuaries tends toward high representation of montmorillonite with lower concentrations of chlorite and illite (Schroeder and Wiseman, 1999).

The introduction of the GIWW in 1949 by the U.S. Army Corps of Engineers was designed to provide a conduit for industrial traffic along the southern coast of Texas. The channel is approximately 3 to 4 meters deep and 50 meters in width. Sediments taken from the channel during dredging are usually deposited on the west side of the north–south running channel. These areas are easily visible in satellite photographs (Fig. 10) appearing as circular island-type formations on the west side of the estuary. Sediment movement due to currents and wind resuspension result in gradual shoaling of the channel. These shoals slow barge traffic and must be removed periodically. Dredging activities are carried out on a biannual schedule. The process of removing and relocating channel sediments involves hundreds of thousands of cubic meters of sediments. The storage and ultimate fate of these sediments and their associated dissolved components are of paramount importance to the lower Laguna Madre.

2.1.2. Northern Gulf of Mexico (GOM). Site data labeled GOM in the text refer to a collection site located in the northern Gulf of Mexico delta area (Fig. 8). This area is dominated in terms of sedimentological features and water column structure by the Mississippi River and the buoyant fresh water plume that enters the gulf in this region. The abundant sediment delivery, combined with the salt and shale diapiric activity occurring in the continental slope, result in a large majority of the sediment remaining on the shelf in close proximity to the deltaic system itself. This is also the reason for the excessive thickness of Quaternary riverine deposits (in excess of 3000 meters) (Coleman et al., 1991) that makes up the current fan structure. This wedge of sediments overlays approximately 15 km of sediments deposited during the Mesozoic and Cenozoic periods. The depth of sediment and the aerial coverage (28,600 km^2) of the Mississippi Delta system make it one of the largest in the world and demonstrate the considerable amount of time that the river has been influencing the geologic structure of the northern Gulf of Mexico.

The GOM collection site is located 4 km due west of Southwest Pass where the Mississippi River flows into the Gulf (28°55.0” N, 90°00.00” W) in approximately 30 meters of water. The sediments deposited at this location are fine-grained, composed primarily of silt- and clay-sized particles characteristic of the sediments found in pro-delta regions associated with deltaic formations. Strong physical marine processes such as daily high energy wave exposure, tides, and littoral currents are virtually absent in the area resulting in rapid progradation of the deltaic complex (Coleman et al., 1991).

Fig. 10 Photograph taken from the space shuttle (Columbia) of the Lower Laguna Madre estuary. The Gulf Intracoastal Water Way (GIWW) can be seen as a line of islands stretching from Port Mansfield pass down to Port Isabel.

Along with freshwater and sediment, the Mississippi River delivers dissolved organic and inorganic compounds to the Gulf of Mexico. The Mississippi is the seventh largest river in the world in terms of sediment discharge (210 x 10^6 t yr^{-1}) (Milliman and Meade, 1983) (Fig. 11) and the Mississippi-Atchafalaya River system delivers 90% of all freshwater that enters the Gulf of Mexico (Dinnel and Wiseman, 1986). Approximately 0.11 x 10^{12} mol yr^{-1} of dissolved organic carbon along with 0.21 x 10^{12} mol/yr of particulate organic carbon are delivered annually through the Mississippi outflow (Trefry et al., 1994). Increasing utilization of nitrogen fertilizer in the agricultural Mississippi watershed following industrialization in the United States has led to consistent increases in inorganic nitrogen output to the Gulf of Mexico (Turner and Rabalais, 1991; Rabalais et al., 1996). Historical data show an increase from approximately 1000 kg N d^{-1} in the 1960s to well over 2000 kg N d^{-1} in the mid– to late–1980s (Bollinger et al., 1999). This consistent increase in nitrogen loading to the Northern Gulf of Mexico has been linked to an increase in total primary productivity in the region affected by the Mississippi River plume as well as a shift in phytoplankton species composition (Rabalais et al., 1996).

Concern recently has centered on the establishment of a yearly zone of hypoxia linked to transport and metabolism of increasing amounts of primary productivity to the area underlying the Mississippi plume. The formation of this "suffocating" zone has been presented in popular news magazines (Annin, 1999) as well as more scientific journals (Malakoff, 1998). The yearly reoccurrence of the zone of low oxygen initiated the development of the Nutrient Enhanced Coastal Ocean Productivity (NECOP) program through NOAA. The findings of this multidisciplinary study were organized

Fig. 11 Photograph taken from the space shuttle (Columbia) of the Mississippi Delta located in the north central section of the Gulf of Mexico. Sediment plume is visible and displays the western tendency of the riverine water mass.

and presented in a special edition of Estuaries (Estuaries, Vol. 17, No. 4, 1994). The fact that large sections of the benthic environment spreading westward from the plume covering an area estimated to exceed 9,500 km^2 (Rabalais et al., 1994) becomes hypoxic and in much of the area anoxic suggests that benthic respiration is dominated by anaerobic processes. This implies that the sediments and porewater chemistry are largely influenced by byproducts of anaerobic respiration.

2.2. Sediment Acquisition

Sediments for resuspension experiments and porewater profiles were collected in 7.5 cm Plexiglas coreliners and ranged between 30 and 60 cm in length. Sediment cores collected in the Laguna Madre were taken either by divers or by a smaller version of the Benthos gravity corer (in the channel). The cores were immediately taken to the University of Texas – Pan American Coastal Studies Laboratory on South Padre Island and processed. Sediments designated for laboratory resuspension experiments were sectioned in a glove bag under N_2 (top 10 cm homogenized) and stored in 1-liter Nalgene containers. These sediments were maintained at 15^oC until utilized in laboratory experiments. Cores designated for down-core profiles were sectioned immediately in an inert atmosphere glove bag at approximately 2–cm intervals down to 30 cm. Sediment sections were transferred to squeezer cups and placed on a modified Reeburgh-type interstitial water sampler (Reeburgh, 1967). This mechanism isolates porewater by squeezing the sediment under a latex membrane pressurized with N_2. Interstitial fluids were passed through a GF/C glass fiber filter and collected in 20 ml syringes. The samples were then filtered through 0.45 µm syringe filters into sample containers and frozen. Samples for solid analysis were sectioned and transferred under inert atmosphere to 30 ml Nalgene containers and stored at 15°C.

2.3. Porewater Concentration Analysis

Characterization measurements were made on cores and homogenized sediments collected at both sites. Down-core profiles for sediments from both sites of nutrients, dissolved organic carbon (DOC), organic carbon and nitrogen content of sediments, sulfide, sulfate, chloride, reduced iron (Fe^{+2}), porosity and grain size were determined. Methods and results are presented in Table 7. NH_4^+ (porewater and extracted) was determined manually via spectrophotometer according to the methods of Harwood and Kuhn (1970). Overlying water was collected at the time of sediment acquisition, filtered and stored at 4°C until utilized in resuspension experiments.

2.4. Resuspension Experiments

A modified shaker table was utilized to carry out the resuspension experiments (Fig. 12). Erlynmeyer flasks (500 ml) were secured to a Plexiglas platform and attached to the rotary devise on the table. The top panel in Fig. 12 shows an anoxic resuspension while the lower panel shows an oxic resuspension. A total of twelve flasks were used allowing for 6 resuspension concentrations of NH_4^+ to be carried out in duplicate. These concentrations were designed to create a range of adsorption conditions from 0 μmol L^{-1} bulk solution to saturating conditions. After porosity measurements the correct weight of sediment and porewater was calculated to achieve a final concentration of 10 grams

Table 7. Sediment components analyzed at the Gulf of Mexico (GOM) and Lower Laguna Madre (LLM) sites.

Component	Concentration unit	Concentration		Method
		GOM	LLM	
Grain Size				
Sand	%>63 μm	1.4	10.3	Wet sieve
Silt	%>2 and <63 μm	15.3	41.8	Folk, 1974
Clay	%<2 μm	83.3	47.9	Folk, 1974
Porosity (ϕ)	Volume fraction H_2O	0.75	0.81	Weight loss
Organic-C	Wt.% of dry solid	0.69	0.98	Carlo Erba
Organic-N	Wt.% of dry solid	0.08	0.13	Carlo Erba
C/N	Wt. ratio	8.21	7.69	-
SO_4^{-2}/Cl^-	Conc. ratio	0.047-0.053	0.04-0.05	Ion Chromatogram
ΣH_2S	μM	<5	<5-4800	Cline, 1969
Fe^{+2}	μM	2-43	2-10	Ferrozine, Gibbs, 1979
$NH_4^+ + NH_3$				
Porewater	mmol L^{-1}	0.3	6.5	Harwood and Kuhn,1970
Exchangeable	mmol g dw^{-1}	1.5	20.2	Morin and Morse, 1999
ΣPO_4	μmol L^{-1}	13-27	8-123	Parsons, 1984
DOC	mmol L^{-1}	3-11	1-14	High Temperature Combustion

Ranges of values are given for the top 10 cm of sediment based on profiles. A single value indicates a measured value for the homogenized sediment used in the resuspension.

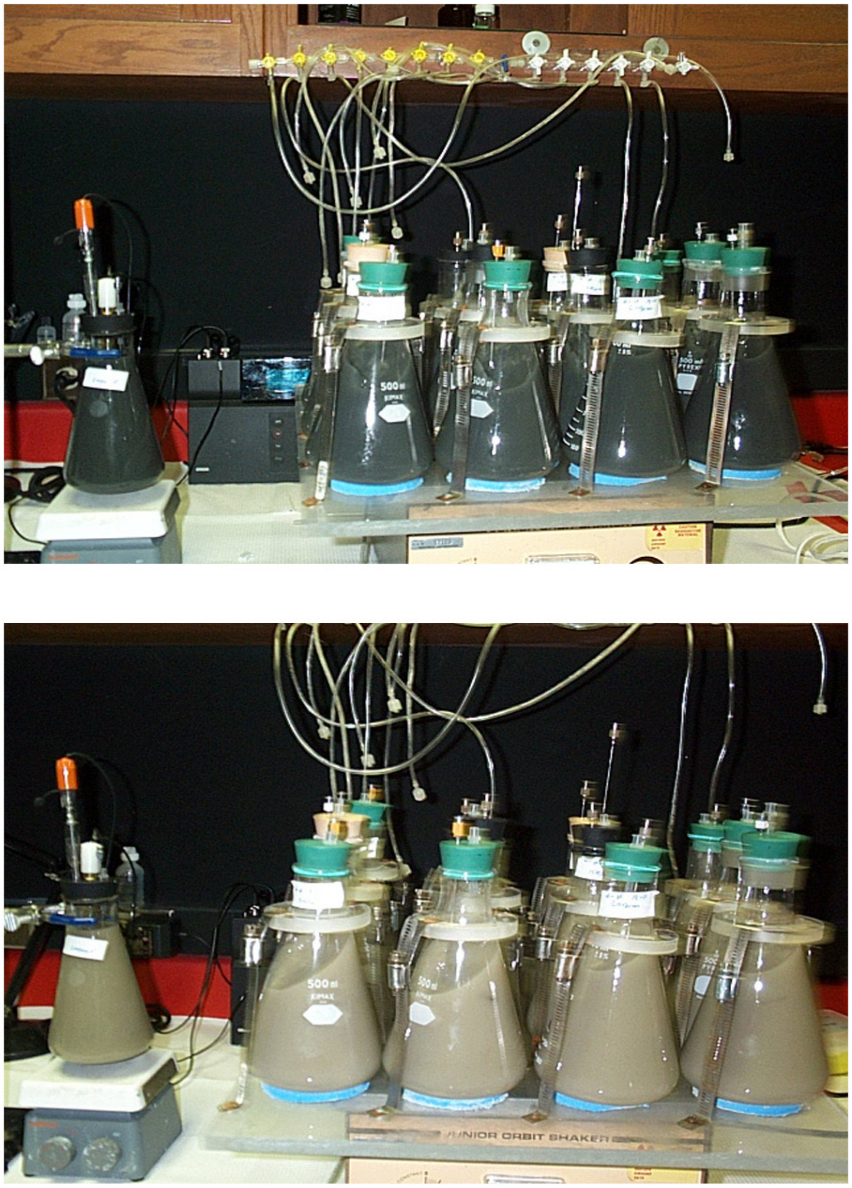


Fig. 12 Resuspension experiment design. The upper photograph is an anoxic resuspension and the lower is an oxic resuspension of the same sediments. The container on the left has a redox and pH electrode used to monitor experimental parameters.

sediment L^{-1}. In the upper photo of Fig. 12 an additional resuspension replicate (highest bulk concentration) is displayed with electrodes protruding from the stopper. Three electrodes were positioned below the suspension solution surface in order to monitor pH and redox potential during the resuspension experiments. Operation and calibration ofthese electrodes are discussed later.

Filtered (0.2 μm) overlying water collected at the core acquisition sites was the medium of resuspension in these experiments. The redox conditions were manipulated through addition of either oxygen or a reducing agent. Redox conditions for each treatment were as follows:

2.4.1. Anoxic. Anoxic conditions were produced according to Stucki et al. (1984). Dithionite was added to the solution prior to sediment resuspension at 500 mg $Na_2S_2O_4$ gm^{-1} sediment. This amount is at the upper range of what is normally used to prepare reduced pure clays. The dithionite was added in a bicarbonate/citrate buffer to neutralize pH changes. At this addition rate a reduction potential of –650 mV was generally achieved before sediment addition. This potential never exceeded –400 mV during the resuspension experiments. (Redox potential measurements were made with a platinum electrode, the construction of which will be discussed later.) The standard electrode potential for the redox couple $Fe^{+3} + e^{-} \rightarrow Fe^{+2}$ is –440 mV. The range of reduction potentials observed during the anoxic resuspension was generally well below the potential for ferric to ferrous iron.

2.4.2. Oxic. Filtered water utilized in oxic resuspension conditions was maintained at 15°C overnight with an air stone and pump. The resuspension water was well in excess of supersaturation at the start of each oxic experiment. Electrode potentials for the oxic experiments generally began around –50 mV but rapidly increased and stabilized at approximately +100 mV.

To all experiments, enough azide was added to give a final concentration of 0.1%. Azide was added to avoid the complications inherent in interpreting nitrogen data with active biological processes such as nitrification and denitrification. This would probably not have affected the anoxic experiments but potentially may have altered results from the oxic resuspensions. The experiments were sealed to minimize volatilization of NH_4^+ from solution. A control was also run parallel to the experiments in which resuspension medium was set up and sealed but no sediment was added. This control was sampled along with the resuspension duplicates. Sample volume was replaced by gas headspace using the attached 10 ml syringes (see Fig. 12). Approximately 5 ml of the resuspension slurry was removed, filtered through a 0.45 µm syringe filter into 20 ml scintillation vials, and frozen.

The purpose of the sediment resuspension experiments was to determine if the amount of NH_4^+ adsorbed from solution by resuspended sediments could be related to redox conditions (oxic versus anoxic). The sediments were resuspended in six increasing concentrations of NH_4^+ (in duplicate), the range of which varied between the two sites. Initial resuspension concentrations for GOM sediments were 0, 250, 500, 750, 1500 and 3000 µmol L^{-1}. Initial resuspension concentrations for LLM sediments was 0, 500, 750, 1500, 3000, and 6000 µmol L^{-1}.

After determining sediment addition rate from porosity (to achieve 10 gm L^{-1}), the predetermined amount was weighed into 50 ml centrifuge tubes. Approximately 20 ml of the resuspension medium was added to the tube and the mixture was vortexed prior to addition to the Erlenmeyer flask. Immediately following sediment addition, the Erlenmeyer flasks were sealed with rubber stoppers fitted with sample ports (also sealed with small viton stoppers). Samples for NH_4^+ concentration analysis were taken prior to addition and 5 minutes after addition. Further samples were taken periodically until the end of the experiment at 100 hours. These concentrations were examined to determine if equilibration was reached. In most cases NH_4^+ concentration changes at the end of the experiments were statistically unimportant compared to initial changes.

Two additional resuspensions were carried out at the greatest addition rate. One is visible in Fig. 12 with electrodes protruding from the rubber stopper. The other was used as a control as described above. A platinum electrode was constructed according to the design of Patrick et al. (1996). This electrode was used with a saturated calomel double junction reference electrode to obtain gross estimates of redox potential. The electrode was standardized at the beginning and end of each experiment using pH buffer solutions with addition of quinhydrone as suggested by Patrick. Anoxic experiments remained below –400 mV, while oxic experiments always reached values of at least +150 mV early in the experiments. The pH of the resuspension was monitored using a Corning pH electrode. The pH electrode was also calibrated at the beginning of each experiment and checked afterward for large drifts in calibration buffer readings. Calibration standards of 9.0, 7.0, and 4.0 pH units were used.

2.5. Extraction Procedure

At the conclusion of each experiment the shaker table was turned off and the sediments were allowed to settle while the duplicates were still sealed. The resuspension medium was drawn off with a vacuum trap and the sediments were collected in 50 ml centrifuge tubes. These were spun down (2500 rpm, 1 hour) and the resuspension medium was removed. Sediments were extracted with 2 N KCL to determine total NH_4^+ associated with sediment particles. The procedure for extraction was carried out according to Morin and Morse (1999). The sediments from the resuspension experiments were extracted five times with 20 ml of 2 N KCl. Accumulated NH_4^+ quantities and accumulated extraction volumes were recorded and plotted against each other. An exponential decrease in extracted NH_4^+ is observed and can be described by an exponential line equation. Line-fits were performed to predict the maximum amount of NH_4^+ generated by continual extractions.

3. Results

3.1. Site Sediment Characteristics

The sites chosen for experimentation are active depositional sites and are relatively productive in terms of sedimentary metabolism. Down-core porosity profiles of the sediments show a small range of values from approximately 0.7 to 0.85 and are indicative of sedimentary environments influenced by periodic mixing. Fall wind events at the GOM site and barge traffic combined with frequent wind events at the LLM site caused periodic resuspension and re-deposition of the surface sediments. The sediment porewaters are characterized by millimolar concentrations of dissolved organic carbon (DOC) and relatively high, down-core increasing profiles of NH_4^+ and HPO_4^{-2} except in the GOM HPO_4^{-2} profile. Metabolism during the sampling period (July for the LLM site and August for the GOM site) in the sediments appears to be driven primarily by sulfate reduction (see SO_4^{-2}:Cl^- ratio for core profiles above, Table 7).

The two sites were chosen as candidates for the resuspension experiments for several reasons. Both sites are historic sites where sediment cores have been taken and porewater profiles measured for several chemical species including DOC, NH_4^+, HPO_4^{-2}, HS^-, and DIC. During periods of maximum temperature (late summer) the sites have both been observed to be sources of NH_4^+ to the overlying water (unpublished data obtained with flux chambers). The high concentration of HS^- in the LLM site and profiles of oxygen tending toward bottom extinction along with high concentrations of dissolved iron in surficial sediments taken at the GOM site indicate that during much of the summer season the sediments are anoxic up to the sediment-water interface. In addition the grain size of both sites tends towards very small, high-surface area particles. Size fractioning of the LLM sediment revealed that approximately 60% of the particles were silt-size while approximately 40% were in the clay-size fraction (< 2 µm) (unpublished data). Both sediments are in regions known to have high representation of montmorillonite and are generally exposed to relatively high concentrations of metabolism byproducts.

Table 7 displays the results of analysis of the core profile and homogenized sediments that were taken from the top 10 cm of replicate cores at the site and used in the resuspension experiments. The two sites did not vary greatly in organic carbon and nitrogen content, but the C/N ratio for Laguna Madre was lower. This probably reflects the greater terrestrial inputs to the GOM deltaic site and the proximity of the channel in the Laguna Madre to highly productive seagrass beds and macrophytes. Interstitial NH_4^+ concentration in the Laguna Madre channel sediments was much greater that what was measured at the Gulf of Mexico sediments. The concentration of HPO_4^{-2} and DOC were also much greater in the Lower Laguna Madre channel than at the Gulf of Mexico location. This is reasonable considering the argument for the C/N ratio. The Lower Laguna Madre channel is very deep compared to the rest of the bay. It acts as a sediment trap catching resuspended sediments and sinking debris. This material would be much less worked over by secondary producers and creates a very high nutrient and DOC environment. The exchangeable NH_4^+ concentrations also reflect this. Sediment particles from the channel had over ten times more NH_4^+ associated with the particles. This means that quite possibly the particles in the Laguna Madre channel may be positioned differently on an adsorption isotherm than the Gulf of Mexico sediments.

3.2. Resuspension Experiments

Initial attempts at resuspension experiments provoked concern over the possibility that changes in NH_4^+ concentration observed during the duration of experiments may be partially due to volatilization. The pK value for NH_4^+ at the temperature the experiments (23.0°C) were carried out at is approximately 9.3. Seawater pH is close enough to this value to warrant concern over loss due to volatilization. Control experiments were carried out to find the extent to which volatilization might influence the final calculations (no sediment added). The controls were run in duplicate exactly like actual initial resuspension experiments (initial concentration 1500 μmol L^{-1} and 3000 μmol L^{-}). The flasks with overlying water and NH_4^+ were shaken at 125 rpm and bubbled with either chromatographic grade N_2 (anoxic experiment) or filtered air (oxic experiment). Experiments were originally slowly sparged to either retard atmospheric intrusion of the anoxic experiments or to insure oxic conditions in the oxic experiments. The top two diagrams in Fig. 13 display results from these experiments. Assuming no adsorption to the container, volatilization appears to be considerable in the time course of the experiments. Concentration changes (end concentration – beginning concentration) by the end of the control experiments compared to initial concentrations were 20.4% and 6.0% for oxic and anoxic controls, respectively, at 1500 μM addition and 5.0% and 3.5% for oxic and anoxic controls at 3000 μM addition. These values can be compared to concentration changes observed in the experimental results (presented later). At 1500 μmol L^{-1} initial concentration reductions of approximately 6.2% and 11.9% were observed for oxic and anoxic resuspensions, respectively, in lower Laguna Madre adsorption experiments. Changes of 6.33% and 9.79% were seen at 3000 μmol L^{-1} initial concentrations. After the control experiments were completed it was decided that the experiments should be sealed and parallel controls run simultaneously at the greatest addition rate. The diagram at the bottom of Fig. 13 shows the results of controls for the sealed lower Laguna Madre sediment resuspension experiments. The change from beginning to end in both the oxic and anoxic case is below 0.5% of the initial concentration. The overall change in concentration (calculated as the percentage standard deviation represents of the mean) was 0.4% and 0.6% for oxic and anoxic parallel controls.

The hypothesis that NH_4^+ adsorption may be linked to redox conditions is not a new idea. This phenomenon has been extensively researched in the soil literature due to the importance of cation exchange capacity to agricultural crop maintenance. In many cases this adsorption idea has been investigated because of the important role that K^+ plays in plant growth. Resuspension of collected sediments was performed at a concentration of 10 grams

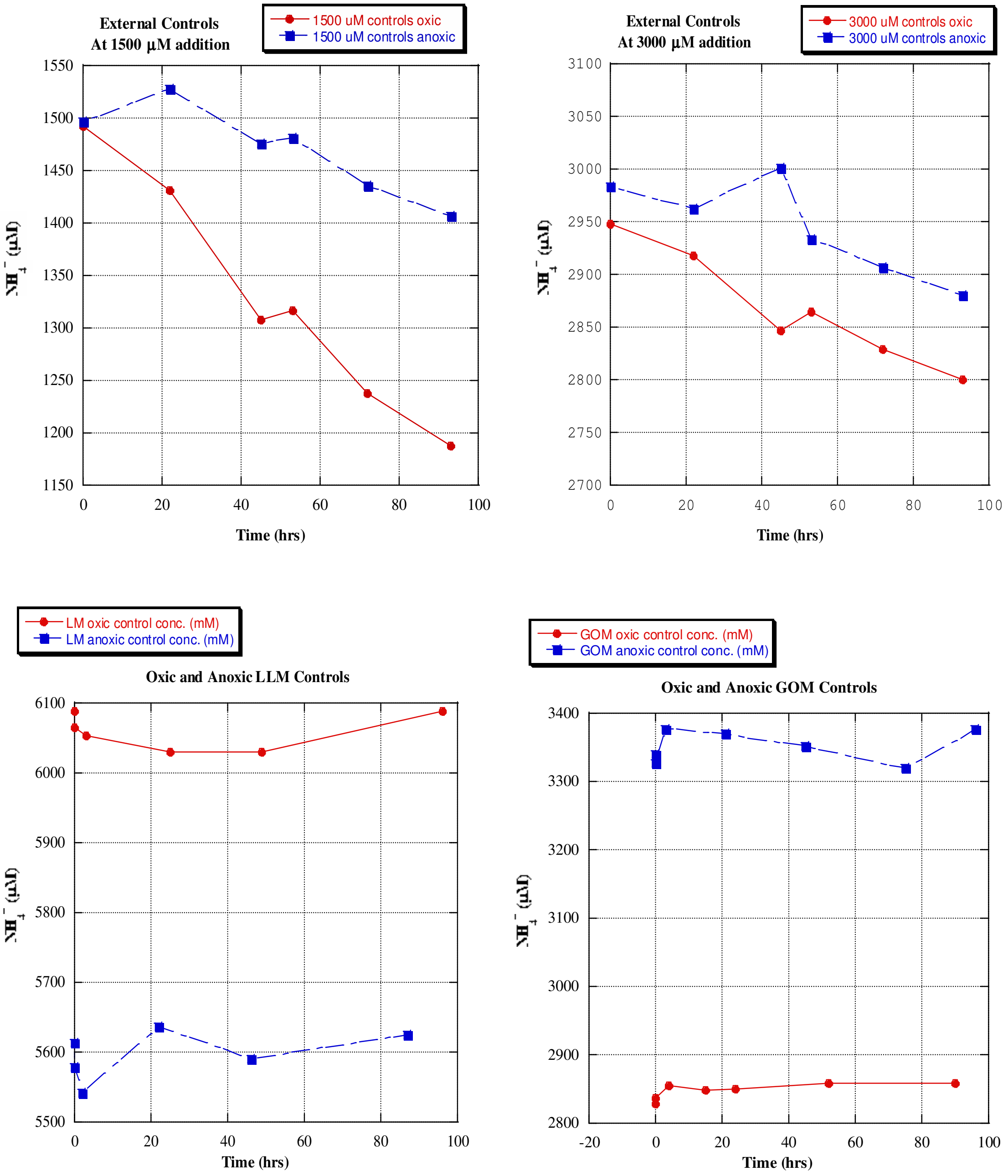


Fig. 13 Control experiments run prior to actual resuspensions (upper graphs, either bubbled with air (red) for the oxic simulation or chromatographic grade N_2 (blue) in the anoxic simulation). Control experiments run concurrently (parallel) with resuspension are displayed in the lower graph with the same color scheme.

(dry weight, calculated by porosity) in 1 liter. The redox conditions were controlled essentially through the addition of a buffered dithionite solution or saturation of resuspension fluid with oxygen. The electrode generally indicates a value of approximately –600 mV after buffered dithionite addition but before sediment addition. This value increased over the 96 hour course of the experiments to approximately –400 mV, probably due to some oxidation through oxic sediment components and inevitable leaks in the sealed replicates. Resuspension water in the anoxic case was initially heated and sparged with chromatographic grade N_2. This was done in order to eliminate as much O_2 from solution as possible. Unfortunately this also eliminated much of the carbonate in the solution, which generally buffers pH change. Variations in pH were part of the reasoning behind using a buffered solution of dithionite to control redox potential. Enough carbonate was added with the dithionite solution to resist large pH variations during the resuspension. The pH in the resuspensions was variable but did not vary by more than one pH unit during the experiment (Fig. 14). The anoxic resuspensions generally varied in the lower 7.0 range while the oxic resuspensions were less variable and ranged in the upper 7.0 range.

Addition of dithionite as reductant in the anoxic resuspension experiments was conducted according to pure clay mineral preparation techniques employed by Stucki et al. (1984). The reduction of structural iron in this investigation was found to occur rapidly and completely with the addition of a citrate/carbonate buffered solution of dithionite. Unfortunately this technique is also very useful in the removal of iron oxides in marine sediments and is the accepted technique for determining this important parameter (Raiswell et al., 1994). Particulate surface iron oxide formation could be important in resuspension experiments seeking to observe alterations in adsorption capacity of cations. In the

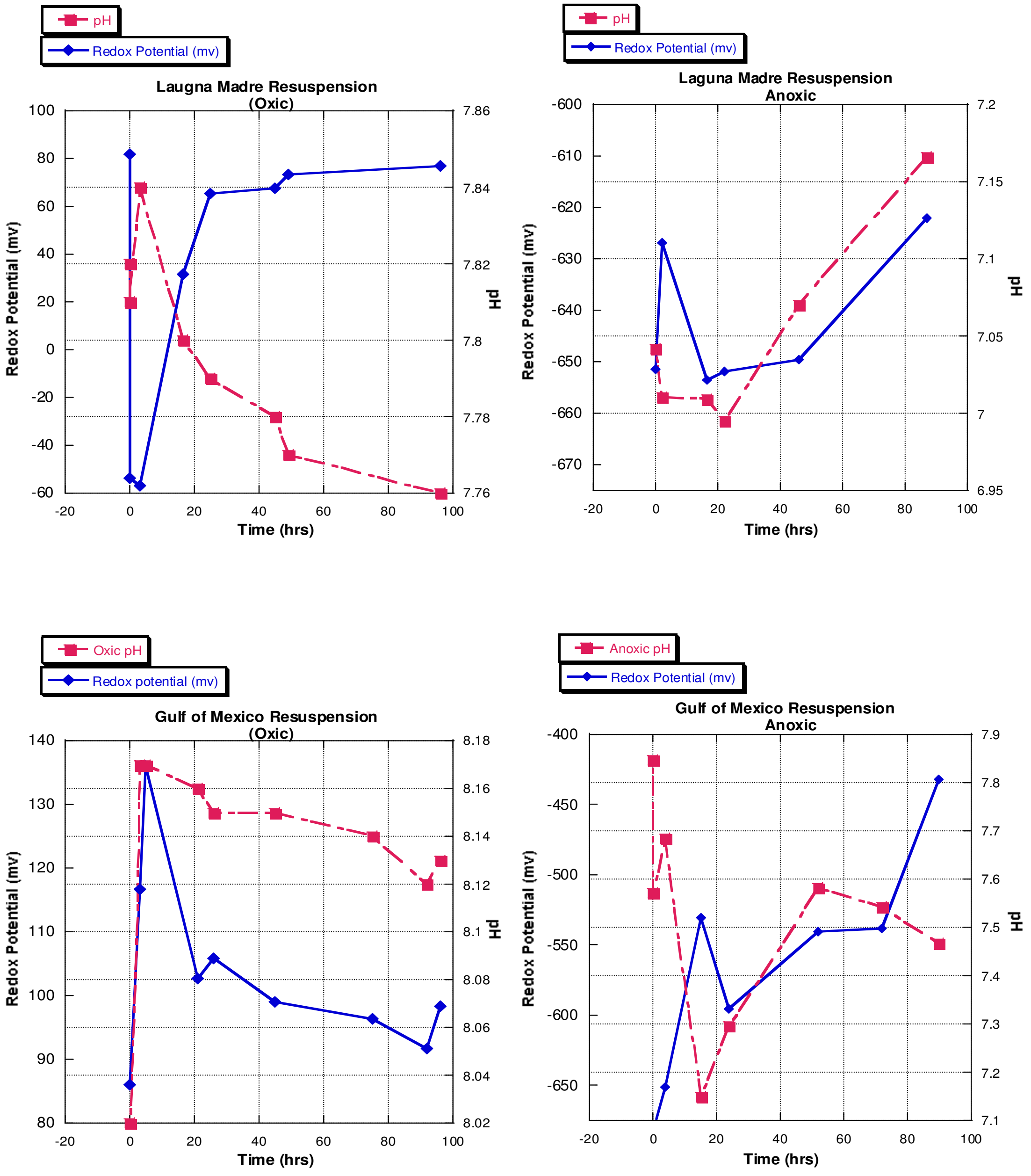


Fig. 14 Redox and pH measurements observed during the resuspension experiments. Determinations were made on the additional resuspension carried out simultaneously.

experiments described in this work dithionite was added to resuspensions of sediments that had previously been in moderately- to highly-reducing conditions. Sulfide (HS^-) concentrations in the Laguna Madre sediments are extremely high even at the sediment–water interface. High reductant concentrations would tend to preclude extensive coverage of the resuspended particles surface with iron oxide. This argument can be extended to the Gulf of Mexico site where high reduced iron concentrations were measured. This supposition is supported by the findings of Morse et al. (2002) who found that little Fe remains in the citrate dithionite-extracted reactive-Fe-phase of near surficial sediments in both of these environments. This argument is reasonable for the anoxic resuspensions performed during this investigation but does not pertain to the oxic resuspensions. Additions of oxygen to sediments with significant concentrations of porewater reactive iron could result in the rapid formation of iron oxide on the surface of resuspended sediments. This is not likely in the Laguna Madre sediments where reduced iron concentrations are extremely low and sulfide concentrations dominate the availability of iron. Reduced iron concentrations in the GOM sediment porewaters exceeded that of the LLM site. This implies that Fe was available for reaction in the oxic resuspension of these sediments. Reduced iron concentrations reached a maximum of approximately 40 μM in the down-core profiles. Sediment addition for this experiment was performed in an effort to achieve 10 grams solid sediment. This would result in an addition of at maximum 10 mls (considering porosity) of interstitial waters. Approximately 0.4 μmol L^{-1} of Fe would be available for oxide formation in this resuspension. The formation of an oxide mineral on the surface of the sediments could influence the results obtained from the analysis of this experiment.

3.3. Exchangeable Ammonium

At the end of each resuspension experiment the flasks were kept sealed and the particles were allowed to settle to the bottom. When the solution became clear the resuspension fluid was removed and the sediment water slurry was collected. It was observed that the anoxic experiments cleared faster than the oxic experiments. This probably reflects alterations in the clay particle charge between the two experiments. The sediment particles remaining after the cleared solution was drawn off were then extracted as described above (KCL extraction) to determine the particle associated NH_4^+ concentration per gram sediment (dry weight). These determinations are displayed in the column graph in Fig. 15. The solid blue columns represent the anoxic resuspension sediments and the red columns represent the sediments resuspended in oxic conditions. At each initial addition rate more NH_4^+ was associated with sediments in the anoxic case than in the oxic case for sediments from both sites. The upper graph displays the results from the LLM resuspensions and includes two extractions at the highest addition rate.

The additional sediments were resuspended in the replicate which was used to monitor the pH and redox conditions. The sediments in this replicate were kept in suspension with a stir bar instead of shaker table. Increased particle bound NH_4^+ was observed in this replicate at similar concentrations to the replicate on the shaker table. The two extractions are placed together at the highest initial NH_4^+ concentration on the x axis with the electrode replicate on the left. In both of these extractions (maximum addition concentration) more NH_4^+ was bound to anoxic sediments than on sediments resuspended in oxic overlying water. It is interesting that the quantity of surface bound NH_4^+ seems to be

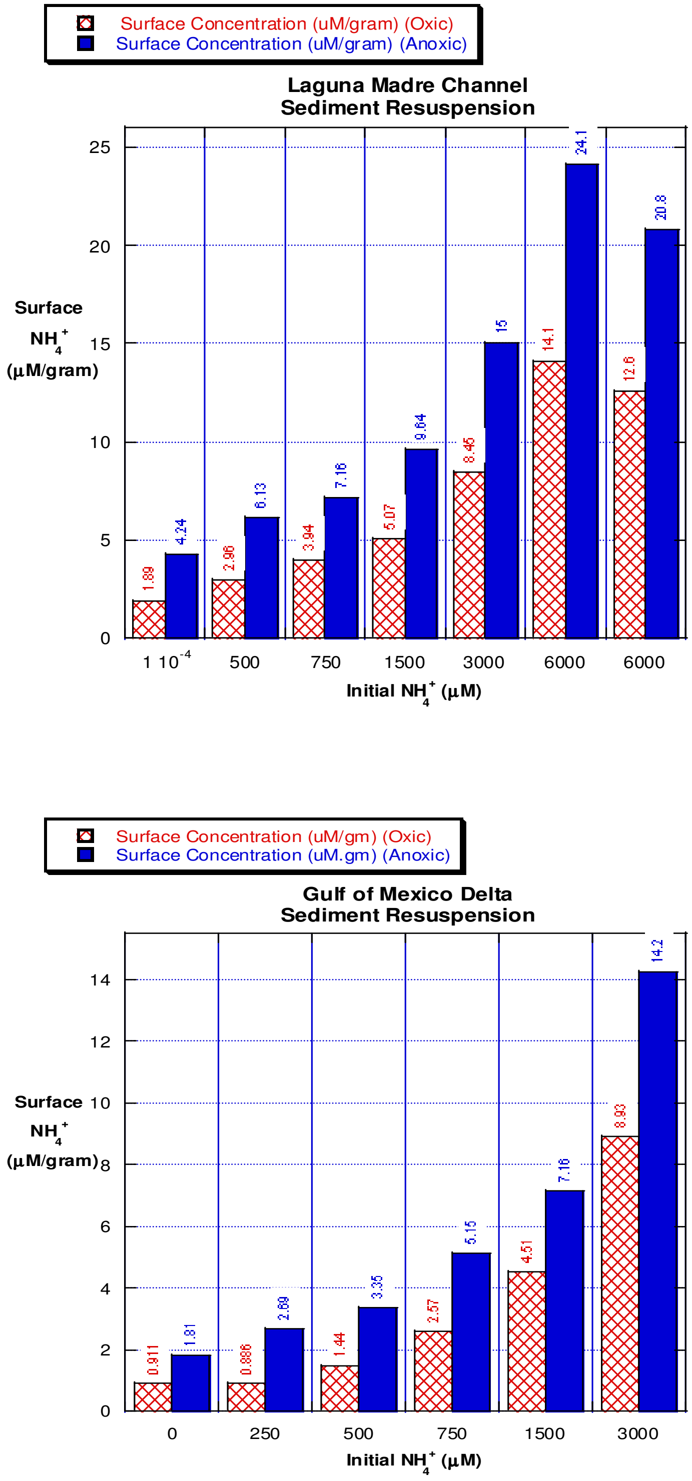


Fig. 15 Exchangeable NH_4^+ determined for oxic and anoxic experiments. Blue columns represent values obtained from reducing conditions and red columns represent oxidizing.

following an exponentially increasing relationship instead of saturation. An increase in particle bound NH_4^+ was also observed in the anoxic resuspension of GOM sediments compared to the oxic resuspension of these sediments. Boatman and Murray (1982) observed a similar relationship in sediments collected in Saanich Inlet, British Columbia. These authors determined that below 10 μmol L^{-1}, NH_4^+ was observed to adsorb in a linear fashion. The presented data appear to indicate an exponential relationship. This is possibly due to the fact that the adsorbed NH_4^+ data are plotted against the intended initial concentrations for the experiments. Since experiments were carried out separately (oxic versus anoxic) the initial NH_4^+ concentrations for each experiment varied. When the data are plotted against the measured initial concentrations a different relationship is observed. The data are plotted against the ideal initial concentration to illustrate the difference in common treatments. The column graph also shows what seems to be a decreasing difference between the amounts of NH_4^+ bound to sediments resuspended in anoxic conditions compared to oxic conditions.

For both sites, exchangeable NH_4^+ on sediments was greater by a factor of about 1.7 under reducing conditions as compared to oxic conditions and the data for the two sites overlap for similar redox conditions (Fig. 16). There is a linear relationship between the exchangeable concentrations of NH_4^+ (c = μmol g dw^{-1}) and the corresponding concentration in solution (m = μmol L^{-1}). The intercept for the relationships is very close to zero.

Reducing: $c = 2.01 + 0.0040m$ ($R^2 = 0.96$) (4)

Oxidizing: $c = 1.12 + 0.0023m$ ($R^2 = 0.98$) (5)

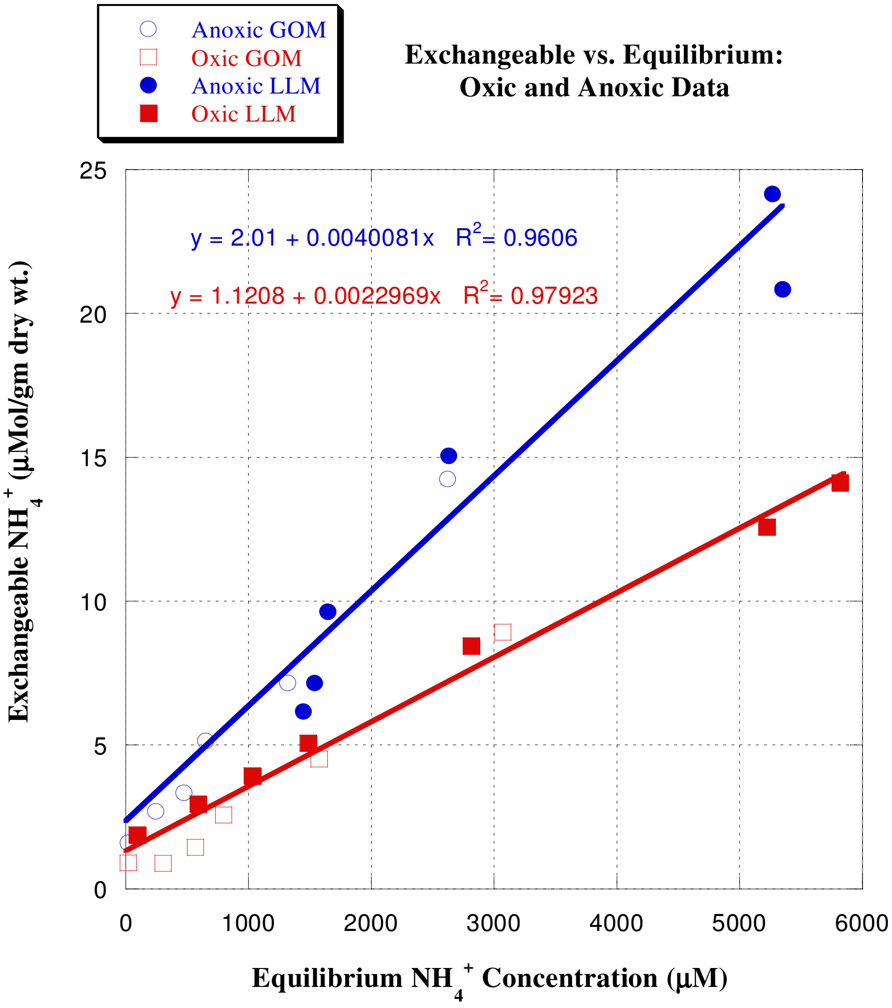


Fig. 16 Experimentally determined reducing (circles) and oxidizing (squares) exchangeable NH_4^+ concentrations plotted against equilibrium NH_4^+ concentrations along with linear regression curves for LLM (solid symbols) and GOM (open symbols) sediments.

Results indicate that the adsorption capacities of these sediments, collected in different marine environments (coastal vs. estuarine) are similar over a wide range of NH_4^+ concentrations. The effect of different redox conditions also is the same for sediments from the two sites. This may indicate that, for continentally derived marine sediments of similar grain size, the adsorptive behavior of NH_4^+ will be closer to the same during early diagenesis (Mackin and Aller, 1984), but differs significantly between oxidizing and reducing conditions.

Results for the resuspension experiment were utilized in generating relationships describing adsorption to the specific site sediments. Predicted concentrations of exchangeable NH_4^+ under reducing and oxidizing conditions, compared to values observed in the down core profiles for cores taken for the LLM and GOM sites are shown in Fig. 17. The predictions of exchangeable NH_4^+ are based on the equations derived above (4 and 5) where bulk concentrations of adsorbent (NH_4^+) is entered as m. The exchangeable concentration c is calculated and plotted. Prediction of exchangeable NH_4^+ concentrations from the reducing conditions in the above relationship agreed better with observed values than did predictions generated from the oxic experiments. This is reasonable given the characteristics of the sediments. The mean square error ($MSE= \Sigma(c_{predict} - c_{observed})^2/n$: where n is the number of determinations) is about four times greater for oxidizing versus reducing predictions at both sites (LLM $MSE_{ox}/MSE_{red} = 3.7$; GOM $MSE_{ox}/MSE_{red} = 4.3$). This is also a good indication in terms of the reproducibility of the method. The errors were very similar for each site though the GOM sediments had much less exchangeable NH_4^+ than the LLM sediments (1.5 vs. 20.2 μmol g dw^{-1}).

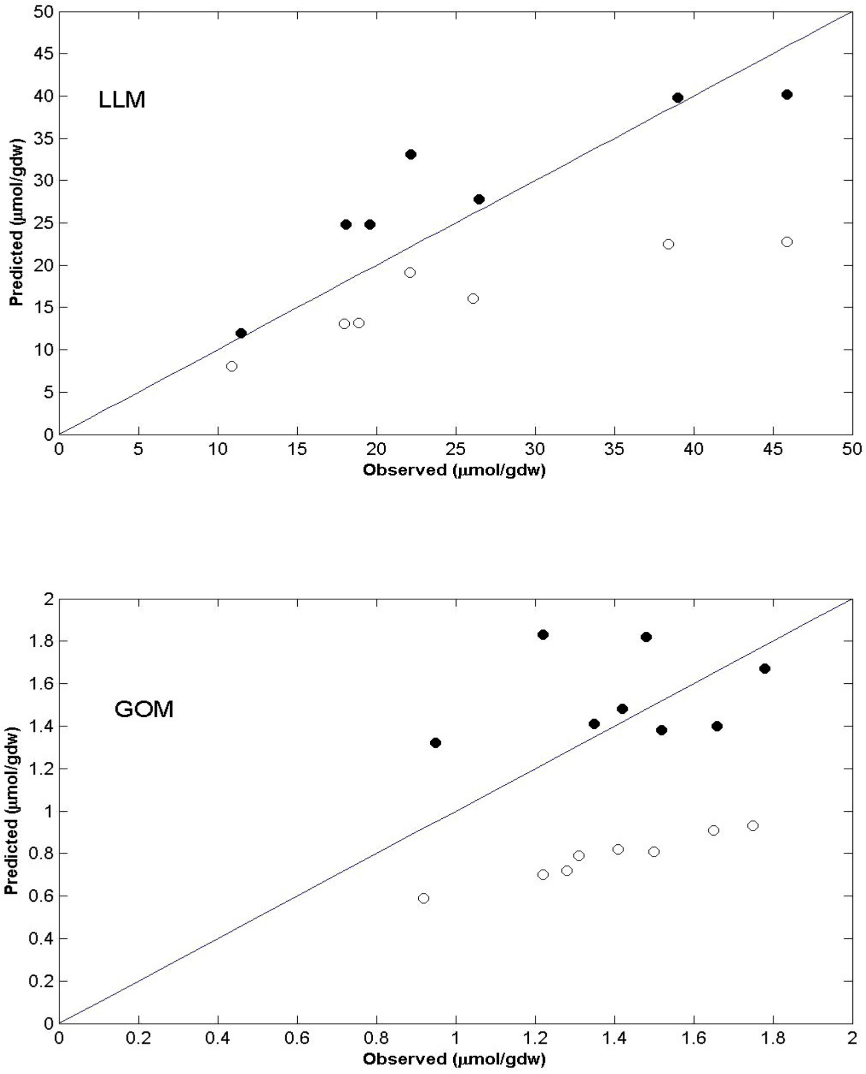


Fig. 17 Exchangeable NH_4^+ concentrations predicted from the down-core porewater concentrations using oxidizing (open circles) and reducing (solid circles) condition adsorption isotherms versus observed down-core exchangeable NH_4^+ concentrations. Solid line is for a 1:1 agreement.

4. Discussion

The cycling of nitrogen in marine systems is extremely complicated being dependent both on biological and purely chemical processes and is strongly linked to global cycling of the element. Considering the increasing frequency of hypoxic and anoxic observations in coastal marine systems, alterations to the adsorptive capacity of NH_4^+ in sediments may have a significant effect on our understanding of the cycling of nitrogen which is generally described through various diagenetic equations. The necessity to include the effects of adsorption in these formulations has been well established (Berner, 1976). Adsorption is generally represented as isotherms in these models and any alteration to the isotherms will have significant effects on the predictability of nitrogen cycling. Resuspension experiments in the presented investigation exhibited differences in the amount of the adsorbate NH_4^+ both added to solution and taken out of solution when sediments were resuspended in oxic versus anoxic suspensions. Solution concentration changes can be very difficult to interpret as was found in the control investigation during this study. The release of extremely high concentrations of NH_4^+ in resuspensions of LLM channel sediments at low initial solution additions is difficult to explain. Exchangeable concentrations associated with the sediments were also greater for the anoxic resuspensions. One parameter that was not investigated specifically during this study was the effect of organic matter. In a modeling investigation of minor cations, it was found that a clay-humic complex may exist in sediments and that this complex may significantly influence the adsorption of NH_4^+ (Boatman, 1985). This could explain the origin of the extreme release in this sediment. The same release was not observed in the GOM deltaic sediments. Clay–humic complexes in these sediments are probably highly site–specific and related to the refractive nature of the organic matter itself. The effect of oxidation-reduction reactions on clay-humic complexes is not well understood so speculation into this mechanism could be premature. The LLM site sediments did have slightly more organic matter associated with them (Table 7) but less clay–sized particles. Though solution concentration changes can be problematic, the exchangeable concentrations are more straightforward to interpret. These are also the means by which the affect on the predictability of adsorptive capacity were based.

One of the major points of interest in NH_4^+ exchange with sediments has been its influence on NH_4^+ transport in sediments and the related influence this has on benthic fluxes of NH_4^+. This process has consequently been incorporated in mathematical models describing early diagenesis, where it appears as a dimensionless adsorption coefficient K (Berner, 1981; Rosenfeld, 1982; Raaphorst and Malschaert, 1996). K is related to K* which is defined as the ratio of the exchangeable NH_4^+ in μmol g dw^{-1} to the concentration in solution in mmol L^{-1} units, by the relationship:

$$K = \left(\frac{1-\phi}{\phi}\right)\rho_s K^* \tag{6}$$

Where ϕ is the porosity of the sediments and ρ_s represents solid density (Mackin and Aller, 1984). K* has units of ml g dw^{-1} and has been referred to both as a sorption coefficient and a partition or distribution coefficient (eg. See discussion in Raaphorst and Malschaert, 1996).

There have been numerous determinations of K* and K that have addressed a variety of questions. These include the influence of temperature (Mackin and Aller, 1984; Raaphorst and Malschaert, 1996), salinity (Seitzinger, et. al., 1991), mineralogy (Rosenfeld, 1979; Boatman and Murray, 1982), grain size (Raaphorst and Malschaert, 1996), and organic matter concentration (Rosenfeld, 1979; Boatman and Murray, 1982; de Lang, 1992). In most studies a close to linear relationship has been found between solid-associated (or exchangeable) and dissolved NH_4^+. However, Raaphorst and Malschaert (1996) found nonlinear behavior at low dissolved NH_4^+ concentrations (< 40 μmol L^{-1}) and de Lange (1992) found exchangeable NH_4^+ correlated with organic matter concentrations, not with dissolved NH_4^+ in deep Atlantic Ocean sediments. Mackin and Aller (1984) concluded that most fine-grained terrigenous marine sediments have a closer to constant value of K = 1.3 ± 0.1. However, subsequent work has yielded a much wider range of values. It is also of note that, except for sediments with low organic matter content, exchangeable NH_4^+ has generally been found to be more strongly associated with organic matter than clay minerals.

Values of K* (Based on Eqn (4) and (5)) and K obtained in this study are given in Table 8. Note that porosity in the LLM sediments was about 0.90 and in GOM sediments porosity is 0.75. This results in major differences in K even though the values of K* are about the same for a given redox condition (density of 2.26 g cm^{-3} was used for the solid phase). Equation 6 can be solved for the pore water concentration:

$$C_{pw} = \left(\frac{1-\phi}{\phi}\right) \cdot \rho_s \left(\frac{C_{exch}}{K}\right) \qquad (7)$$

Where C_{pw} represents porewater concentration and C_{exch} represents the adsorbed fraction of NH_4^+ on the particles. Using values for marker 41 in the previous chapter the value of C_{pw}

was derived then subtracted from the value of C_{exch}. This procedure was reiterated a number of times to simulate resuspension of the particles in porewater free of NH_4^+. The exchangeable concentration was found to drop off exponentially with iterations of the equation approaching a value of 0. This relationship was found to be strongly dependent on the porosity utilized. When very high porosity values are utilized (i.e. 0.99) the decrease in exchangeable concentration is much slower and more linear. With reduced values of ϕ the loss of exchangeable NH_4^+ was much more rapid. In this analysis this would appear to be related to the mass being resuspended. Higher values of porosity would represent smaller mass fractions of particles, resulting lower release.

The reason for the major (factor of 2) difference in NH_4^+ adsorption under reducing and oxidizing conditions for both sediments studied is not known. A possible explanation may be associated with the fact that under oxidizing conditions acid volatile sulfide minerals which coat mineral grains can rapidly oxidize. However, such an explanation is not compatible with the general observation that, in sediments similar to the ones utilized in this study, exchangeable NH_4^+ is most strongly associated with organic matter. This investigation was not intended to present a simplified explanation of the processes of cation exchange in marine systems but to attempt to establish a controlled situation where specifically the effects of redox conditions on the particles could be investigated as to alteration in adsorption of NH_4^+. In the laboratory experiments, higher values for concentration decrease at the highest initial additions of NH_4^+ were associated with the anoxic resuspensions. In addition more exchangeable NH_4^+ was associated with sediments

Table 8. K* and K calculated from the results of this study.

Site	Oxidizing		Reducing	
	K*	K	K*	K
LLM	2.3	0.7	4.0	1.2
GOM	2.3	2.0	4.0	3.5

resuspended in anoxic conditions which had a direct effect on the constants calculated for the isotherm models presented. This observation has important practical implications. When modeling diagenetic behavior in sediments, the alteration observed and effect of K* values should be taken into account. Though the isotherms are useful and are utilized in the models for analyzing sediments, they do not take into account important parameters such as competition with other cations such as Ca^{+2} and K^{+}. In addition this investigation tended to ignore the important contribution of organic matter in overall adsorption, though the KCl extraction procedure is thought to be relatively specific to minerals in the sediments. The alterations observed here do indicate that this type of redox associated effect has the capacity to significantly change the model calculations in profiles predicted with models. The frequency of observations of extremely high concentrations of metabolic byproducts in sediments is increasing and is probably related to an overall increase in reduced oxygen conditions in coastal regions. It is evident that the relationship between redox state of sediments and adsorptive capacity must be understood if accurate estimates of nitrogen cycling in the marine environment are to be made.

CHAPTER IV

THE POTENTIAL IMPORTANCE OF WIND-INDUCED SEDIMENT RESUSPENSION TO WATER COLUMN PRIMARY PRODUCTION IN THE LAGUNA MADRE ESTUARY

1. Introduction

Coastal marine environments for the United States are an extremely important financial and aesthetic resource. They are a vital conduit for transportation and industry and approximately half of the current U.S population dwells within 50 miles of the coast line. Coastal environments provide a buffer zone for industry and agriculture, while also providing ecosystems for countless species of marine organisms. Estuarine environments in the United States comprise over 80% of the Atlantic coastline including the Gulf of Mexico and approximately 10% of the Pacific. Human interactions with these environments have resulted in perturbations with unpredictable long-range effects which are only now becoming apparent. Bricker et al. (1999), in a recent report to the National Ocean Service, have estimated that 65% of U.S. estuaries currently show signs of decreasing water quality and eutrophication. Human impact on coastal environments has become a major issue in the United States inspiring publications in non-traditional mediums (see Pinckney, 1999; Van Dolah, 2000), as well as initiating government policy reform (Rabalais, 2002). In southern Texas, construction of the Gulf Intracoastal Waterway (GIWW) has been associated with decreases in salinity and increases in turbidity in the lower Laguna Madre (Quammen, 1993;

Onuf, 1994). Estuary-wide alterations in hydrologic characteristics and light attenuation due to establishment and maintenance of the channel cutting through lower Laguna Madre have been indicated as the primary reason for drastic shifts in the seagrass community and a general reduction in seagrass distribution (Quammen and Onuf, 1993). Contributing to further light reduction in the Laguna Madre estuary is the Texas "brown tide" alga recently named *Aeroumbra lagunensis* (Deyoe et. al. 1997). This organism has been a persistent resident of the lower Texas estuary since 1993 (Buskey and Stockwell, 1993; Buskey et al., 1998).

Organic matter formed by phytoplankton in coastal systems usually is transported through particle settling to the sediments below, where it is eventually remineralized to inorganic components (CO_2, inorganic N, and P) (Hedges et al., 1988; Norrman et al., 1995). The sediments have the capacity to build concentrations of these inorganic components to levels greatly exceeding the overlying water concentration. This process of accumulation usually results in the flux of the remineralized components back to the water column where phytoplankton can again incorporate them in primary productivity (Nixon, 1981; Fisher et al., 1992; Cowan and Boynton, 1996). The process of nutrient recycling is important to coastal environments but not well understood. Christian et al. (1996), in their network analysis of several estuarine environments (including the Neuse River estuary, a rice field, and several lagoons in Spain), have determined that the ratio of nitrogen exported in dissolved or particulate form or dissipated through denitrification to imported dissolved nitrogen delivered into the studied environments is generally less than one and is related to residence time. Recycled nitrogen has been shown to be an important dissolved nitrogen source for phytoplankton productivity in the Mobile Bay estuary (Cowan et al., 1996), in the

Neuse River estuary where release during hypoxic conditions was investigated (Paerl et al., 1998), on the continental shelf off the southern Texas coast (Flint and Kamykowski, 1984), as well as many other coastal systems (Cowan et al., 1996; Gentilhomme and Rich, 2001). Many investigations into recycling of nitrogen concentrate on the process of sediment flux and characteristic variability and magnitude as important sources of nutrients for primary productivity, but perhaps more important may be the phenomena of pulsed release of nutrients due to porewater and particle relocation through the resuspension of sediments (Simon and Kennedy, 1987; Simon 1989; Lawrence et. al. 2004).

The fact that winds can be an important controlling force in water column turbidity in the shallow estuaries of the Gulf of Mexico is well documented (Shideler, 1980; Macintyre and Cullen, 1996; Booth et al., 2000). Wind-generated sediment resuspension has been found to be important in many other shallow coastal systems as well. In South San Francisco Bay, Schoellhamer (1996), using long-term backscatter data, has determined that seasonal wind patterns were correlated with increases in suspended sediment concentration and that the resuspension of fine-grained sediments during spring and summer resulted in transport to and deposition in the main channel. The same author observed correlations between the magnitudes of orbital velocity characteristic of wind-generated waves and concentrations of suspended solids in the water column of Tampa Bay, Florida (Schoellhamer, 1995). The process of sediment resuspension also results in the relocation or ejection of porewaters from sediments which are frequently characterized by high concentrations of dissolved components. Doubling of NH_4^+ concentration in bottom waters of the Swan River estuary (Australia) occurred preceding wind-induced critical bottom shear stress at which sediments are resuspended (Oldham, 1999). The increase in NH_4^+ was observed while water column HPO_4^{-2} and NO_3^- concentrations remained constant. In the Ria de Arousa (Spain) seasonal wind changes have been correlated with increased suspended matter concentrations and elevated seawater-atmosphere exchanges of CO_2 derived from sediments enriched in dissolved calcium carbonate ($CaCO_3$) (Roson et al., 1999). Similar results have been reported in the Ringkobing Fjord in Denmark where wind speeds generate resuspension potential in the estuary over 98% of the year and highly variable concentrations of organic matter and nutrients have been attributed to wind-induced bottom water circulation (Pedersen et al., 1995). The authors of this work suggest the results demonstrate a need for frequent monitoring of similar environments where eutrophication is of concern. The resuspension of sediments due to wind events in coastal systems has the potential to alter dissolved nutrient ratios on very short time scales relieving phytoplankton limitation. These events could have major impacts on bloom initiation and organic matter transport in coastal marine environments.

Physical factors such as winds have the potential to introduce sediments and associated nutrients to the water column in coastal systems more frequently than anthropogenic activity. Lund-Hansen et al (1997) have observed suspended solid loads associated with wind-induced resuspension in a Danish fjord and concluded that a minimum monitoring period of 12 – 24 hours was required to reveal the positive correlation between current shear stress and measured fluxes. Similar results were observed in another Danish estuary where observations of total N, P and suspended solids showed daily fluctuations associated with strong wind patterns (Pedersen et al. 1995). Wind measurements themselves have been shown to be reliable predictors of suspended solid concentrations (Banas et al. 2005, You 2005). Unlike anthropogenic resuspension activities which tend to be limited regionally to the area of activity, winds have the potential of influencing suspended particle load on a whole system scale. Wind-generated waves are very common to South Texas estuaries, including Corpus Christi Bay and Laguna Madre (Shideler, 1984; Onuf, 1994). Sediment plume distributions in Corpus Christi Bay and transport of sediments from the Nueces River have been linked to dominant wind direction and the wave activity generated from sustained winds (Shideler, 1980). The author of this work later determined that shifts in dominant wind direction in concert with the geographic structure of Nueces Bay acts as a release valve for sediments temporarily deposited in the Nueces Basin (Shideler, 1984). In addition, modal and mean diameters of resuspended particles were found to be highly correlated to wind speeds occurring 30 hours before sampling. Calculated settling velocity for the mean particles indicated that, in many cases, the particles require over 60 hours to settle 3 m, the general depth of the bay's interior.

Laguna Madre is an optimal system to investigate sediment impact on nitrogen dynamics for several reasons. It is located in the characteristically flat coastal plains of southern Texas. The topography, or lack thereof, means that daily winds interact strongly with the shallow estuary (average depth = 1 meter). Daily wind patterns in Lower Laguna Madre have been described as having a strong diurnal component (Teeter, 2002). A periodic cycle of sediment resuspension is often witnessed in the lower lagoon in the late spring and through the summer (personal observation). In addition, frequent introduction of weather fronts over the estuary are known to cause large resuspension events (Morton et al., 2000). Forcing due to winds in the area has been suggested to be the most important physical agent affecting the south Texas coast (Morton et al., 2000). The estimated freshwater residence time in Lower Laguna Madre is approximately one year (Solis and Powell, 1999). Nutrient input to the estuary is almost entirely derived from the sediments (Twilley et al., 1999). The fact that sediments in the lagoon are an extremely important source of nitrogen to the ecosystem is relatively well known, but no comparison of benthic flux versus resuspension release of nitrogen has been attempted. Establishing resuspension release of nitrogen in this relatively nitrogen-limited estuary would be of great importance due to the periodic nature of weather fronts in the area. Daily wind cycles generating sediment plumes in the system could result in frequent pulsing of nitrogen to the system.

2. Methods

2.1. Site Description

The Laguna Madre estuary, located in southern Texas (USA) (see Fig. 18 and Fig. 19), is one of the largest and ecologically unusual negative estuaries in the United States. It contains some of the most extensive and diverse seagrass beds including *Halodule wrightii* which supports one of the largest populations of redhead ducks (*Aythya americana*) in the world (Weller, 1964), and overall is an extremely productive ecosystem. This estuary also supports many commercially important species of shellfish and finfish. The estuary has formed over the last 18,000 years through drowning of Pleistocene deltaic sediments in the south and later Holocene sandy deposits in the north. Barrier island construction and subsequent restriction of the estuary has occurred over the last few thousand years. Local climate is semi-arid with increasing freshwater input deficits (precipitation–evaporation) from north to southwest (Solis and Powell, 1999). The lower estuary is 15 km in width at its widest and is greater than 160 km in length stretching from the southern extreme of Baffin Bay to the mouth of the Rio Grande River (at the U.S./Mexico border). The majority of the estuary is relatively shallow with an average depth of 1 meter except along the central axis where the Gulf Intracoastal Waterway (GIWW) transects the entire estuary and reaches a depth of 4 meters (approximately 50 m in width). The GIWW was established in the late 1940s when the land cut was constructed (U.S.A.C.E.) through wind/tidal flats which make up a large portion of the northern Laguna Madre (~ 20 km.). Connection of Baffin Bay and construction of the channel along the north-south axis of Laguna Madre changed the hydraulic dynamics of the estuary and initiated a decline in the normal hypersaline conditions (Quammen and Onuf, 1993). The subsequent decline in seagrass coverage and shifts in the resident populations of seagrass communities have been attributed to the reduction in estuarine salinity and increased light attenuation associated with turbidity (Onuf, 1994).

While freshwater input remains limited to precipitation and input from the Arroyo Colorado (5.8 $m^3 s^{-1}$), decreased residence time and decreased salinity have been caused by the connection of the lower Laguna Madre with Baffin Bay. Astronomical tides are small (< 30 cm), have a diurnal to semi-diurnal periodicity, and are generally strongest in the northern and southern extremes near passes (Port Mansfield and Brazos Santiago). Water level in the majority of the estuary is most dependent on meteorological conditions such as wind speed and barometric pressure (Gill et al., 1995). Southeasterly winds are most frequent and have helped to shape the dunes and wind/tidal flat in the north. Due to the average depth of the Laguna Madre and the distance of the majority of the estuary from ocean outlets, water circulation is more dependent on wind speed and the significant fetch along the north-south axis than tidal cycling. The circulation patterns are important factors in movement of resuspended sediment as well as supplying sediments to the eastern section of the estuary

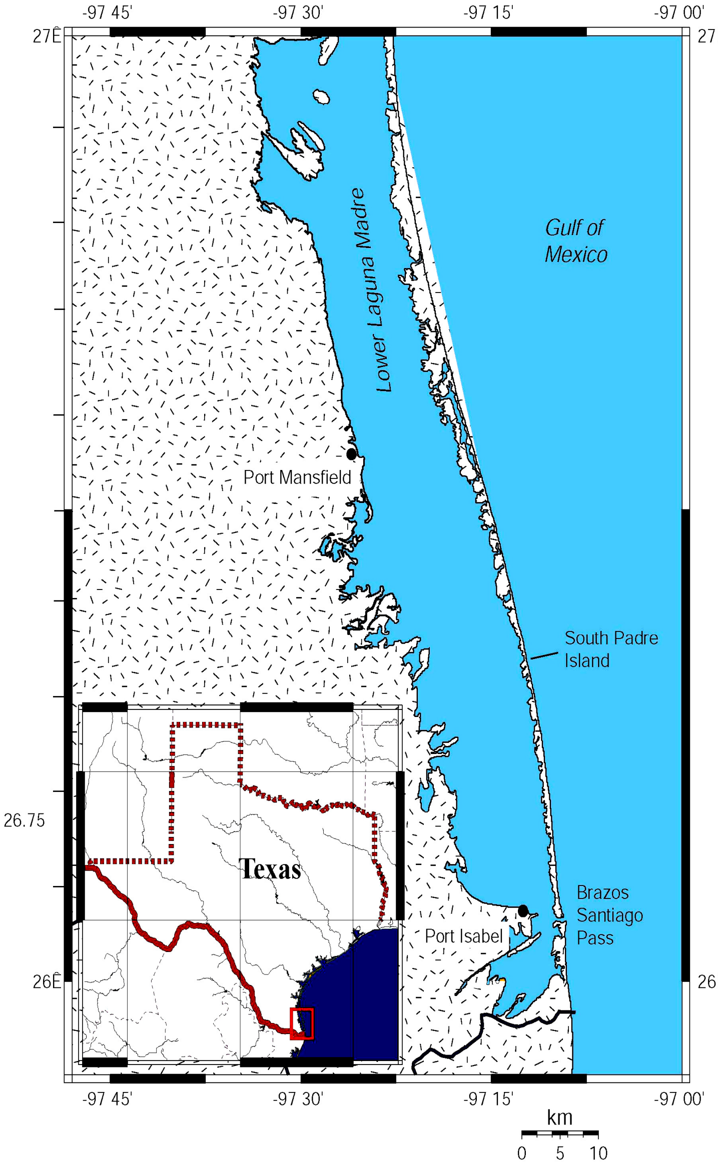


Fig. 18 Lower Laguna Madre (Texas).

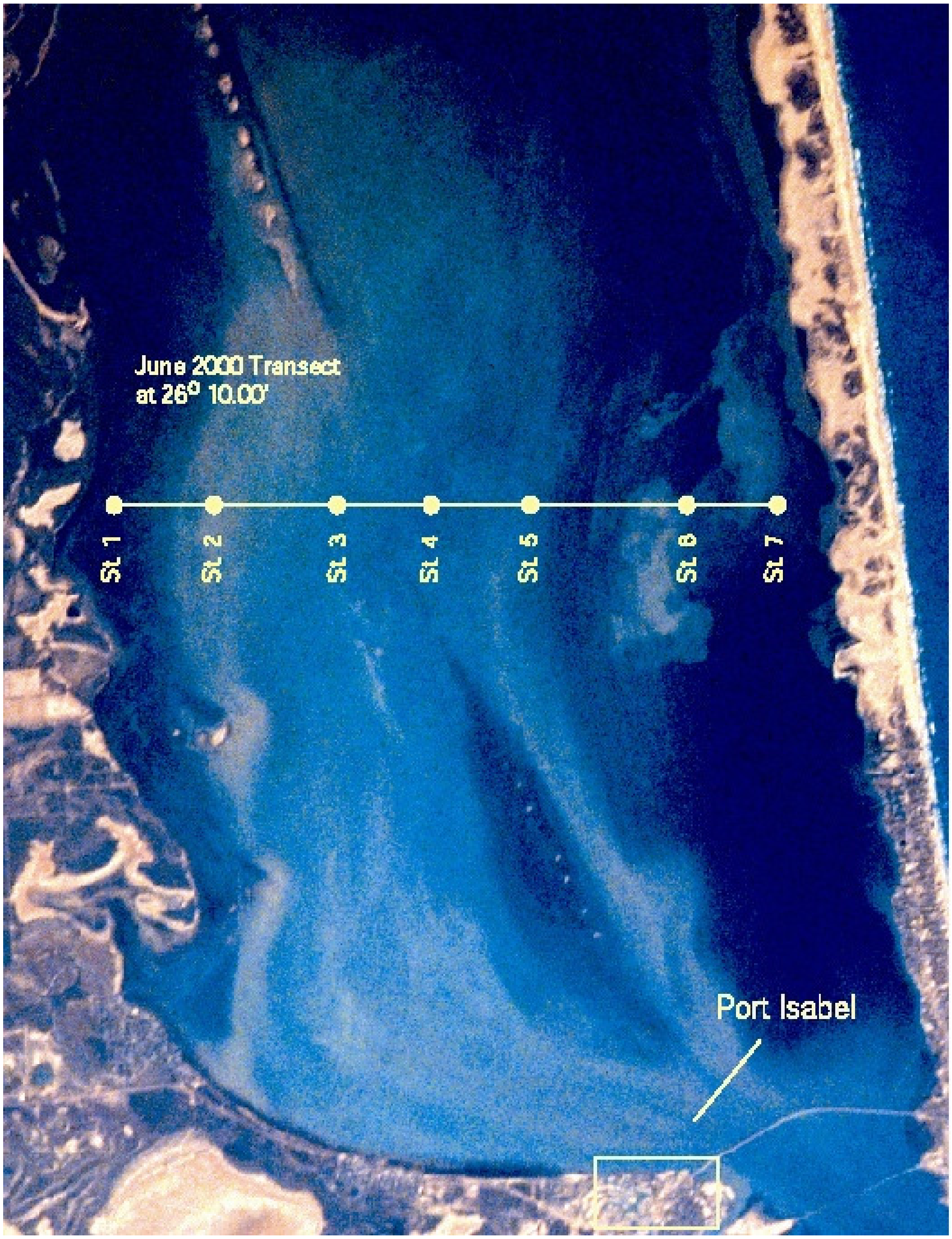


Fig. 19 Photo taken from the space shuttle (Columbia, May 1996) of the Lower Laguna Madre estuary. Station 1 was established in the western section of the estuary and Station 7 in the furthest extreme of the eastern section. Station locations were determined during the first cross transect sampling and were placed according to the location of the sediment plume at the time.

through aeolian transport of sand (Morton et al., 2000).

Morton et al. (2000) have made an extensive sediment budget for the Lower Laguna Madre and have concluded that the estuary is a net sink for sediments. Though significant influx of sediments from the north and south passes occurs, small organic detritus is the only fraction of the total input significantly exported through tidal outlets (Morton et al., 2001). Much of the material transported through tidal inflow is deposited in the dredged navigation channels. This material is generally removed during maintenance dredging operations. After tidal inputs, aeolian sediment transport is next in magnitude, followed by storm washover in the eastern regions of the estuary and upland runoff in the west. Sediment contribution from the Arroyo Colorado and authigenic mineral formation make up small fractions of the total input. On average, a little over 1,000,000 m^3 of sediment is transported to the lower Laguna Madre each year. This can be compared to the annual average sediment volume dredged from the GIWW of 1,600,000 m^3 (Morton et al., 2001). Much of this dredged material is removed from the southern section of the GIWW due to inputs from the movement of course grain sand into the estuary through the Brazos Santiago pass. The reason for this is the existence of a cross channel gyre in this area of the estuary which is induced by prevailing southeastern winds generating a plume of sediment which can be seen in satellite photographs (Militello and Kraus, 1994) (see Fig. 19, courtesy of Johnson Space Center, NASA, http://eol.jsc.nasa.gov/).

2.2. Sampling Sites

A 6.7 km station line was established at approximately 26° 10’ latitude (Fig. 19) across the Lower Laguna Madre transecting the GIWW during the summer of 2000 (June).

Stations were established as the most western at station 1 (transect start) and distributed at 572 m (station 2), 2,224 m (station 3), 3,252 m (station 4), 4,417 m (station 5), 5,790 m (station 6), and 6,677 m (station 7) from the transect start. Stations 4, 5, and 6 were chosen in what appeared to be a sediment plume related to the channel. This cross transect was within 10 nautical miles of Port Isabel allowing for rapid access by small boat while also being in an area of seagrass coverage. Water samples were collected using a 60 cm Norwell Teflon bailer, transferred to pre-cleaned and pre-rinsed 4–liter Nalgene carboys and stored temporarily on ice. The sampler is approximately 3.4 cm in diameter and allows for an integrated surface water sample. All sample processing was conducted on shore as quickly as possible. Flow-through cores were collected at the beginning of the investigation along the transect in areas of seagrass coverage (4 cores) to determine rates of nutrient flux from the sediments. Cores were collected in the channel (4) as well for flux comparison and quantification of dissolved material inputs and losses. The cores were sealed with overlying water and transported along with additional overlying water in 25–liter Nalgene containers to the University of Texas – Pan American's Coastal Studies Laboratory on South Padre Island where they were incubated under constant flow for a period of 48 hours. Utilization of these cores will be discussed below. Sediment cores for concentration profiles were also taken at this time in two locations. Cores were taken around a seagrass bed by divers using 7.5 cm polycarbonate push cores. Channel sediments were acquired using a modified gravity corer. Cores designated for down-core profiles were sectioned upon reaching the labs on South Padre Island in an inert atmosphere glove bag at approximately 2 cm intervals down to 30 cm. Sediment sections were transferred to squeezer cups and placed on a modified Reeburgh-type interstitial water sampler (Reeburgh, 1967). This mechanism isolates porewater by squeezing the sediment under a latex membrane pressurized with N_2. Interstitial fluids were passed through a GF/C glass fiber filter and collected in 20 ml syringes. The samples were then filtered through 0.45 μm syringe filters into sample containers and frozen. Samples for solid analysis were sectioned and transferred under inert atmosphere to 30 ml Nalgene containers and stored at 15°C. These cores were used to determine dissolved concentrations of NH_4^+ in the sediments and particle associated NH_4^+. Porewater concentrations were determined using the method of Slawk and MacIssac (1972) and sediment particle associated NH_4^+ was determined using the method of Morin and Morse (1999).

Seven stations were established along the transect and visited six times over a 60 hour period during daylight hours. Water column parameters, including dissolved O_2, salinity and temperature, were measured using a YSI water quality monitoring system. The salinity data sensor on the YSI sonde was calibrated each day with two YSI standard solutions (37.3 ppt. and 15.0 ppt.) at 25°C. The O_2 sensor was calibrated with O_2-saturated water and the pH sensor with standard buffers of 7.0 and 10.0.

2.3. Water Sample Processing and Analysis

2.3.1. TSS. A measured volume of surface water was passed through pre-weighed, GF/F (Whatman) filters (approx. 0.7 μm pore size). The filters were stored in mini-petri dishes and dried (60°C until no weight change) upon returning. The filters were again weighed and the suspended solids were calculated as the difference between the pre-tare and dry weight.

2.3.2. Nutrient Determination. Samples for dissolved nutrient concentration were passed through a 25 mm GF/F (Whatman) filter and collected in 30 ml Nalgene containers. These samples were immediately frozen on dry ice and kept frozen until analyzed. Water column nutrient concentrations were determined on a Technicon II Autoanalyzer.

The measurements of NO_3^-, NO_2^-, HPO_4^{-2}, and $Si(OH)_4(aq)$ were made according to the method of Atlas et al. (1971). Water column NH_4^+ concentrations were analyzed using the method of Slawk and MacIssac (1972). Nutrient samples were analyzed in duplicate and the average between the determinations is presented in the text.

2.3.3. Chlorophyll a. A measured volume of surface water was filtered onto a 25 mm GF/F (Whatman) filter and frozen on dry ice for acetone extraction and chlorophyll *a* concentration determination using a Turner model fluorometer. Frozen filters collected for chlorophyll *a* analysis were extracted in acetone overnight and measured according to the modified procedure of Welschmeyer (1994).

2.4. Uptake Bioassays

Simple bioassays were conducted in which whole water collected along the transect was placed in 1 l clear, polycarbonate bottles and incubated through one daylight cycle (Pinckney et al., 1999). Bioassays were spiked with a 20 μmol L^{-1} addition of NH_4^+ and 2 μmol L^{-1} HPO_4^{-2}, then incubated at the extremes of the transect for part of one daylight cycle (09:00 to 17:00). Nutrient and chlorophyll *a* samples were taken at the beginning (T_0) and end (T_{end}) of the incubations. These simple bioassays give an estimate as to whether a pulse of NH_4^+ and HPO_4^{-2} can be absorbed by the ambient phytoplankton community. Bioassays were conducted with whole water from the central channel (turbid zone) so that the determination of chlorophyll *a* and nutrient changes were due to the ambient community.

2.5. Flow-Through Cores

Rates of flux of dissolved components from the sediment to the water column were determined using flow-through core mechanisms (Fig. 20). These were constructed with moderate modification according to Miller-Way and Twilley (1996). The Plexiglas chamber was 11.0 cm in diameter and 40 cm in height. A sediment plug approximately 24 cm in depth was taken for incubation with approximately 16 cm of overlying water. Water for the flow-through operation was taken over the area where the sediment plugs were obtained. The water was first filtered through a 1.0 μm poresize cartridge filter (Millipore), then, passed through a 143 mm, 0.22 μm membrane filter. Overlying water was pumped through the chambers, flushing the headspace, via small Master-flex digital peristaltic pumps. Flow rates were approximately 7.0 ml min^{-1} through a head space volume of approximately 760 ml. Turnover time in the headspace was 1.75 hours. Circulation of headspace waters was continuous through a hanging stir bar and rotating magnet over the flow-through mechanism. Sediments in the chamber formed either a source or sink for dissolved components. Flux rates were calculated using the formulation:

$$\text{Flux} = (C_e - C_i) \times \text{flow rate (ml min}^{-1}) \qquad (8)$$

where C_e is the effluent concentration and C_i is the influent concentration (Miller-Way and Twilley, 1996).

After allowing sediments in the chambers to settle and the accumulation of dissolved

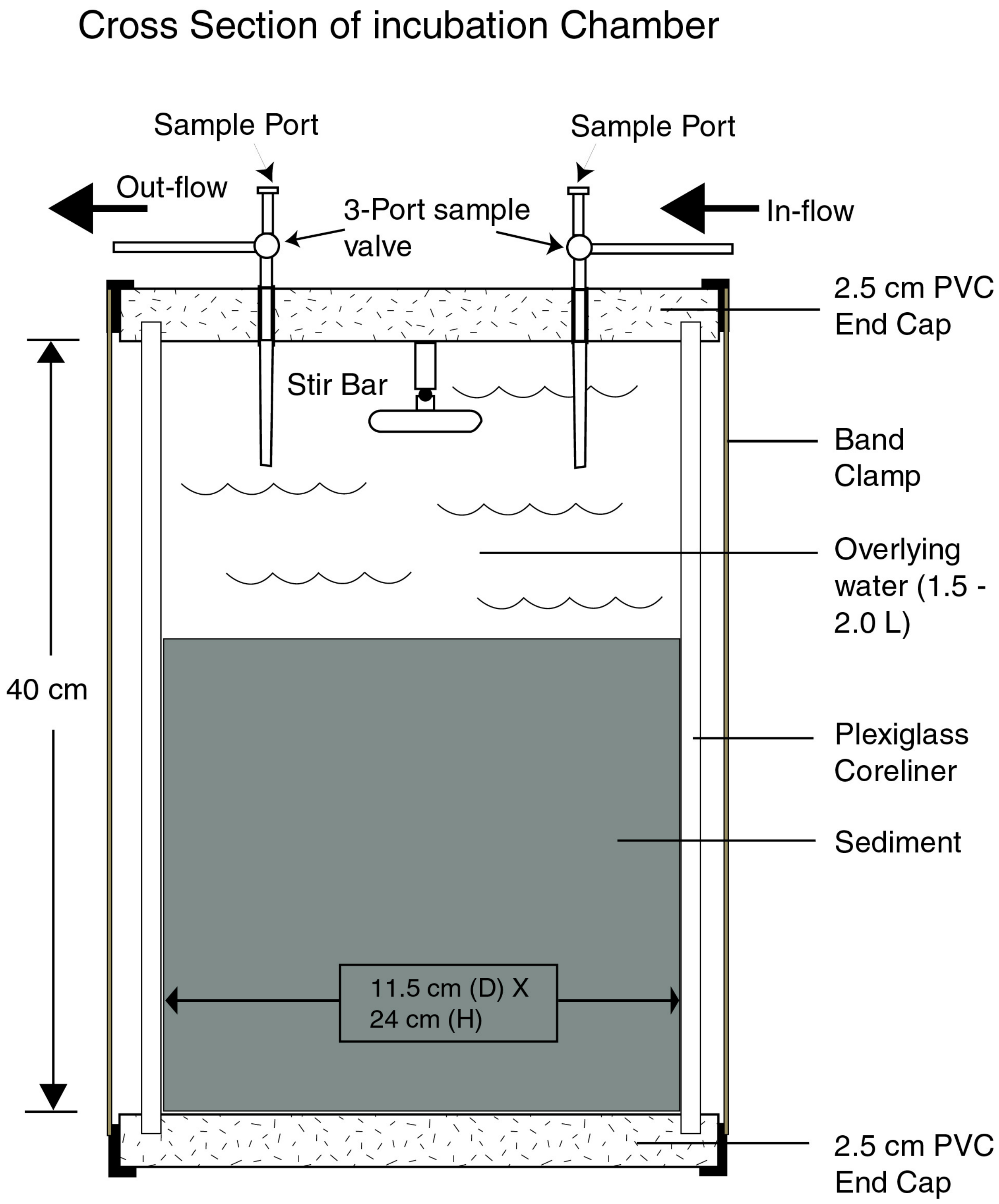


Fig. 20. Diagram of incubation chamber used to measure net sediment-water exchanges of nutrients. Sediment cores ranged around 24 cm. producing overlying water volumes approximately 1600 ml.

components in the head space due to exchange during transport to diffuse (approximately 4 hours) the outflow of each of the flux chambers was sampled. Samples were taken five times over a period of 48 hours. Measurements of O_2 utilized in O_2 consumption estimates were made using the Winkler titration method with modification of Carrit and Carpenter (1966). Dissolved O_2 was titrated using a Brinkman model 665 dosimat and model 682 titroprocessor on 60 ml samples of the chamber out-flows. The titration system employed a platinum electrode and thiosulfate as titrant. A KIO_3 standard was run in triplicate prior to analysis to acquire < 0.2% repeatability. Nutrient samples were filtered through 0.45 μm syringe filters and immediately frozen. Analysis was conducted as described for water column concentrations above. Flow-through water for DOC determination was filtered through pre-combusted (450°C, 2 hours) 13 mm GF/F glass fiber filters (0.7 μm, Whatman). The samples were collected in pre-combusted borosilicate scintillation vials with Teflon caps and frozen immediately. DOC analysis was accomplished on a Shimadzu TOC 5000 using the high temperature combustion technique of Susuki (1993).

2.6. Wind-Induced Resuspension

Surface waves can be generated by winds in estuaries if the wind speed is sustained and the fetch is long enough. Pond and Pickard (1983) define deep-water waves as those traveling in water with depth (d) greater than one half of the characteristic wavelength (L). When the average depth is less than one half the wavelength, surface water particles moving in an approximately circular path can potentially transfer energy to the bottom and possibly resuspend sediments. The critical wavelength (L_c) for potential resuspension would then be values greater than 2d. Wavelength is also related to wave period according to the formulation:

$$L = gT^2/2\pi \qquad (9)$$

where g represents the gravitational acceleration (9.8 m s^{-1}) and T is the wave period.

Booth et al. (2000) have used these formulations to establish a relationship between wind velocity and resultant wave period to predict potential energy transfer to sediments. The critical wind speed (U_c) for potential wave induced sediment interaction was defined in the investigation as:

$$U_c = [1.2\{4127(T_c^3/F)\}^{0.813}] \qquad (10)$$

where the critical wave period (T_c) comes from solving the above wavelength equation (9) for T:

$$T_c = (4\pi d/g)^{1/2} \qquad (11)$$

F represents the fetch of the water body and is determined by using the dominant wind direction. Booth et al. (2000) used 24-hour averaged wind vectors to calculate wind speeds in excess of the critical wind speed U_c in an analysis of Barataria Bay (Louisianna). This relationship was applied to wind velocity data acquired from NOAA's National Climate Data Center (NCDC) for the southern region of Lower Laguna Madre. The data were collected at the Port Isabel–Cameron County Airport located near the same latitude (26° 10’) as the established transect for this study and within 6 km of the western edge of the estuary.

3. Results

3.1. Wind Analysis

The results of the critical wind speed analysis considering 24-hr average wind vectors are shown in Fig. 21 for the year 2000. For this calculation the fetch (F) was considered to be most dependent on the north-south axis of the estuary (160 km) and the depth is set at 4 meters, the depth of the channel sediments. The velocity vectors in the upper graphs indicate that the fetch assumption is reasonable. The majority of winds in the study area appear to move from the north or south along the longest axis of the estuary. In the summer months, dominance of northerly moving winds is apparent. This is in good agreement with published observations (Teeter, 2002). If the average depth of the channel in the center of the Laguna Madre is considered to be 4 m, Eqn. 11 yields a value of 5.93 m s^{-1} as the critical wind speed for surface wave interaction with channel sediments. Channel depth was considered in the analysis to estimate potential for resuspension of sediments for which the majority of laboratory work was conducted. The velocity in excess of the critical wind speed U_c, is plotted in the lower graph (Fig. 20). Over 65% of the daily averaged wind vectors produced winds in excess of the calculated U_c. Many of these occurrences are concentrated in the summer and winter months primarily due to land-sea breeze and winter storms. The prevailing winds in the area appear to have the potential for playing a major role in the movement of sediments in the estuary.

Southerly winds dominate in the summer months over the estuary, but stronger winds with more variable direction occur in the winter months. Though the wind data establish

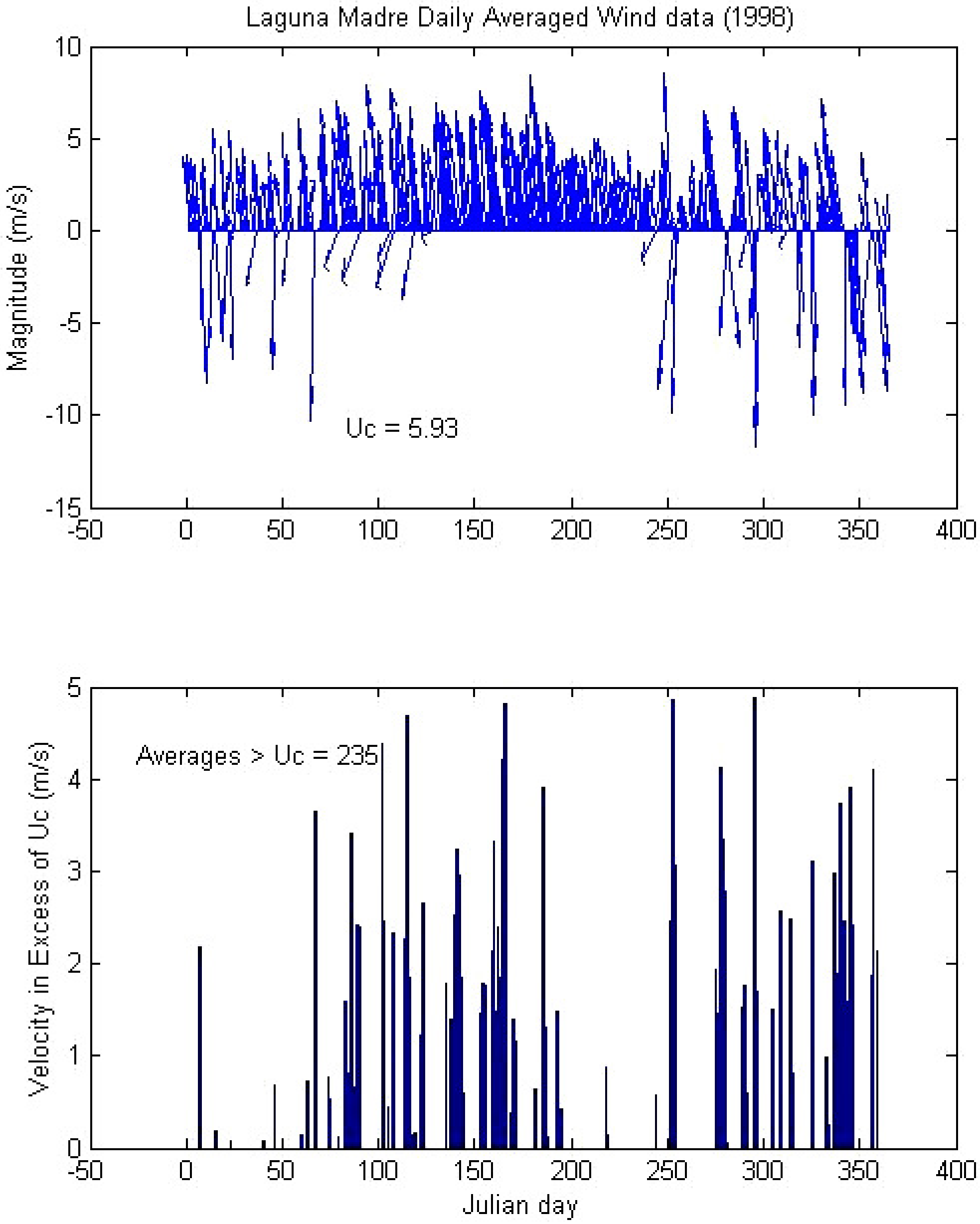


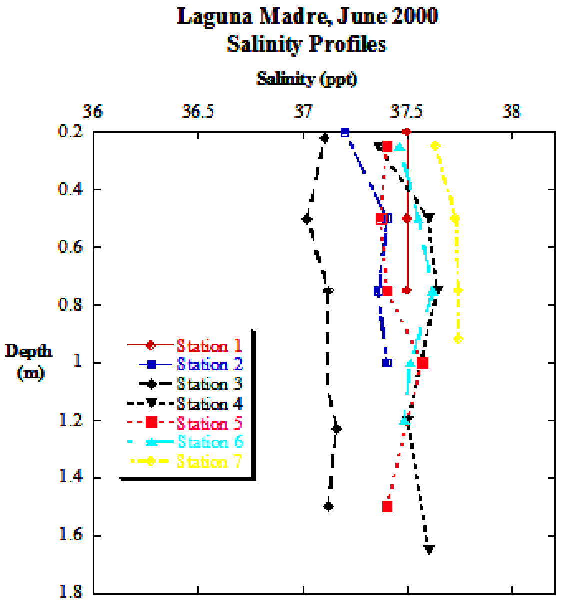
Fig. 21 **Analysis of wind measurements collected near the transect established in the lower Laguna Madre collected in 2000. The upper panel displays wind direction and magnitude. The lower panel shows the velocity in excess of critical velocity (Uc) calculated from CERC (1984).**

northerly moving winds as the predominant direction, the critical wind speed (U_c) was determined for additional wind directions in the estuary (varying fetch, F). If wind direction was predominantly toward the north east, then the effective fetch utilized in the calculation would be approximately 50 km with resulting critical wind speed value of 10.2 m s^{-1}. If the predominant winds were directly across the estuary the effective fetch would be approximately 23 km and the corresponding critical wind speed would be 16.1 m s^{-1}. Given these calculations for the north-south axis of the estuary, the magnitude of winds observed in the Lower Laguna Madre (Fig. 21) could potentially cause resuspension over much of the year.

3.2. Water Column Data

Observational evidence of sediment resuspension caused turbidity in the Lower Laguna Madre is obvious both from small boats in the estuary and from satellite photos (see Fig. 19). During the period of transect sampling, the central part of the estuary was always extremely turbid while the edges overlying sea grass beds were usually quite clear. The edge of the turbidity plume marked by a visible reduction in water clarity appeared to move slightly but to remain relatively constant. Where water clarity increased at the edges of the estuary, surface waves (and difficulty of water sampling) decreased. This may result from seagrasses which can act to dampen wave action and stabilize sediments in shallow environments (Fonesca et al., 1982; Fonesca et al., 1983).

Along the transect, the central region of the estuary is practically devoid of seagrass beds. Vertical profiles taken with the water quality monitor through the monitoring period showed very low variation, even at the edges (Station 1 and 7). Water column profiles of



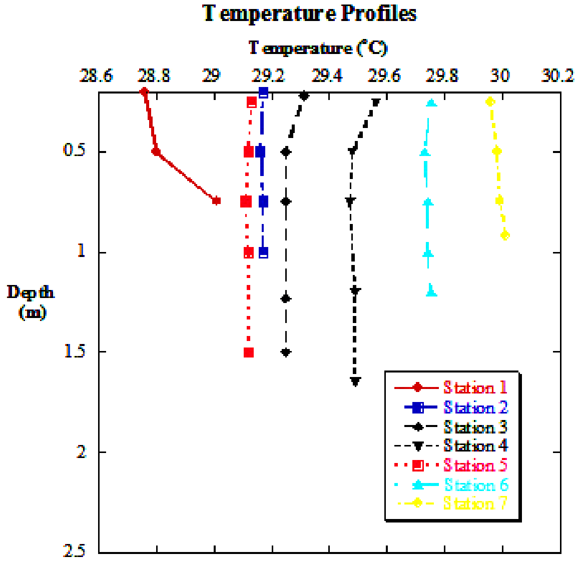


Fig. 22 Profiles of salinity (ppt) and temperature (^{o}C) taken over the Lower Laguna Madre transect.

salinity and temperature at each of the stations during the first sampling period are shown in Fig 22. These data reflect a well mixed water mass in the central regions of the estuary as is expected in shallow water systems such as the Laguna Madre. Slight stratification was indicated in the western section of the estuary (Station 1) in an area overlying seagrass beds. Water column parameters for the remainder of the sampling period exhibited almost identical profiles. Salinity ranged from 37.2 ppt to 37.8 ppt across the transect (lower salinities generally associated with western stations), but showed no relationship with depth. Temperatures were slightly in excess of 29.0°C and displayed almost no variation with some warming at the surface and a slight warming trend from east to west. Dissolved O_2 concentrations at the surface were always around 7.0 ml L^{-1} and only slightly decreased to approximately 6.4 ml L^{-1} with depth throughout the sampling period. The decrease in oxygen was observed in stations close to the central channel region probably due to high rates of oxygen flux into the sediments in these areas (see flow through core measurements). Channel sediments invariably are characterized by high concentrations of reducing constituents such as HS^- and Fe^{+2}.

Winds in the estuary during the sampling period were always evident, but seemed to increase through the daylight period. This observation is supported by data collected at the Laguna Madre presented in Fig. 23 where wind velocity data for the region are plotted against time in the upper graph. The sequence begins on June 19 at 08:00 and continues to morning on June 25. These particular wind measurements were acquired from The Conrad Blucher Institute, Division of Nearshore Research for a platform close to the transect (CBI ID 047, platform located at 26° 21’ N 97° 15’ W). A diurnal pattern of wind velocity maximum during the late afternoon to evening is apparent in this plot for the period of

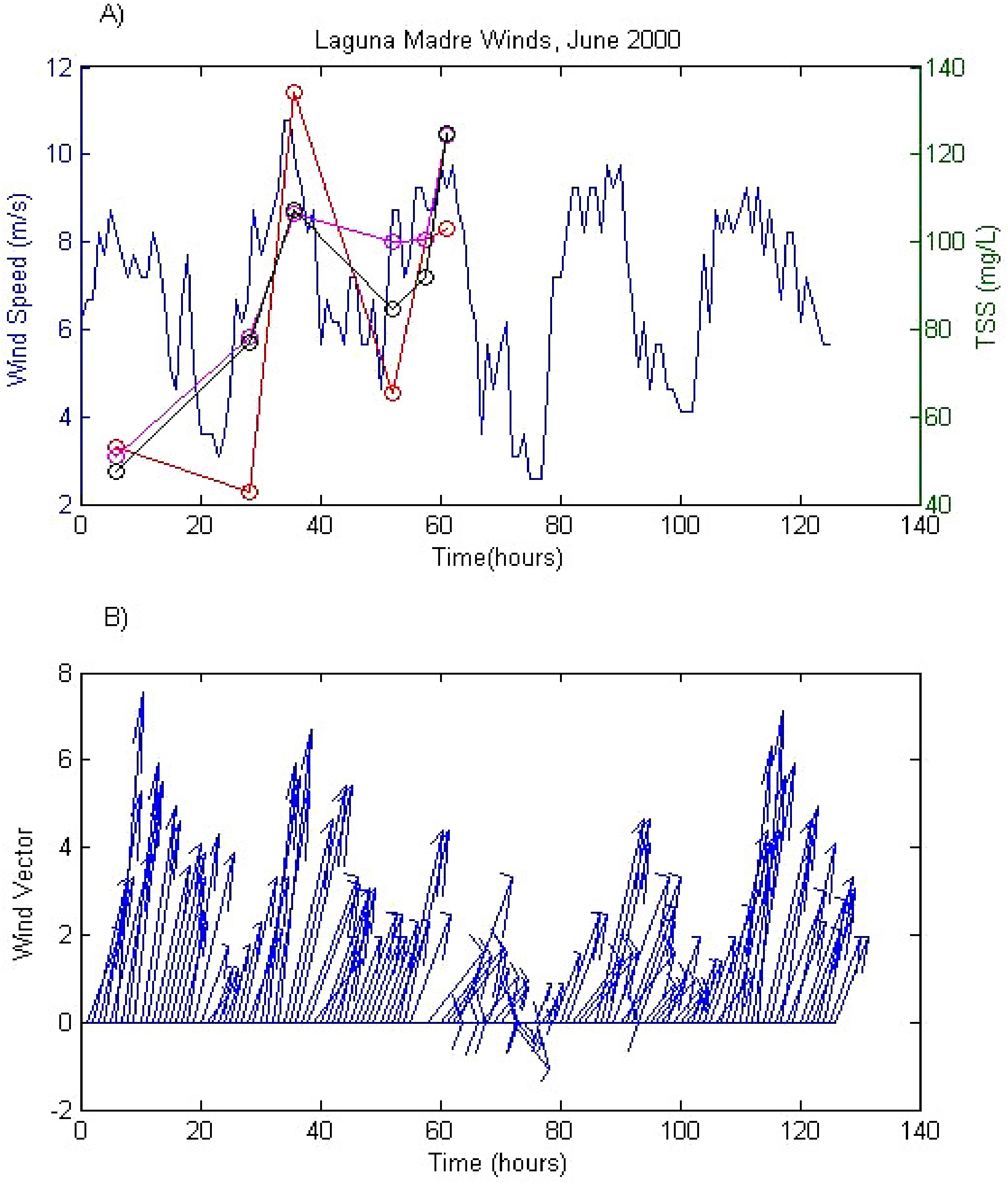


Fig. 23 TSS data plotted with wind data collected from 08:00, June 19 to 08:00 June25 (A). Three stations sediment data are displayed with wind magnitude data (o Station 3, o Station 4, o Station 5). The lower panel (B) displays the wind vector illustrating a predominance of northerly wind direction over the transect sampling period. Wind data collection begins on June 19, 2002.

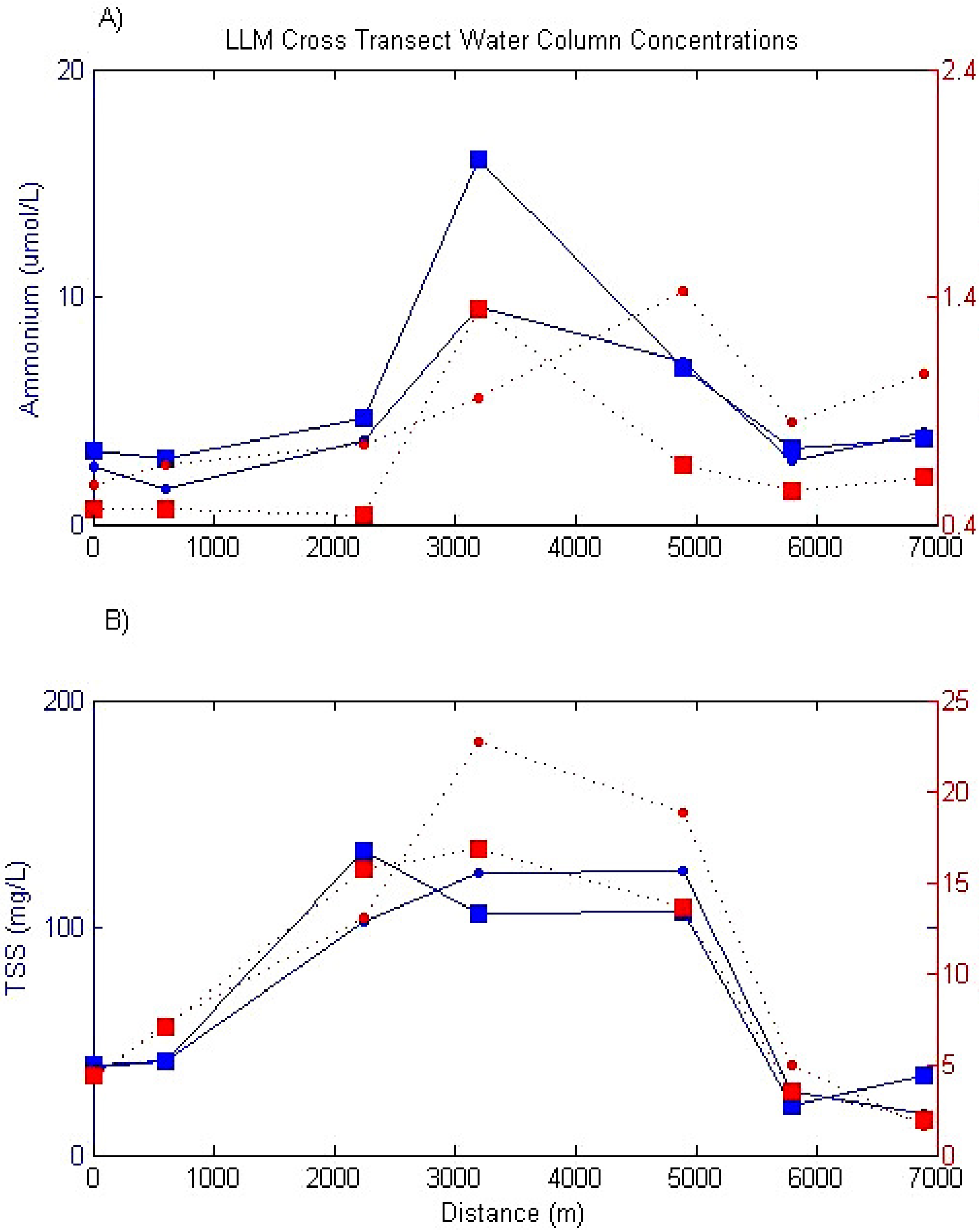


Fig. 24 NH$_4^+$ and HPO$_4^-$(a) and chlorophyll *a* and TSS (b) concentration measurements plotted along the sample transect. Blue symbols and lines in the upper panel represent NH$_4^+$ concentration and red represents HPO$_4^-$. Blue symbols and lines in the lower panel represent TSS concentrations and red represents chlorophyll a. Squares in both graphs are measurements from the afternoon hours of June 20, 2000, and circles represent data collected the next afternoon on June 21, 2000.

observation. In the lower graph the wind vector has been calculated for hourly wind observations at the Conrad Blucher meteorological station and plotted against the same time axis. Wind direction during the period was out of the southwest and follows the diurnal pattern evident in the average wind velocity plot. This direction is along the longest axis of the estuary and has the longest fetch for potential resuspension by surface waves. Turbidity as indicated by Total Suspended Solids (TSS) is also plotted on the upper wind velocity plot for the three stations located adjacent to the channel influenced region of the transect (Stations 3, 4 and 5). There was a turbidity maximum for each of these stations in the late afternoon slightly after a maximum in wind speed, producing measured peaks in TSS in excess of 120 mg L^{-1}. In contrast, the stations located at the outer edges of the transect and outside the persistent sediment plume associated with the channel region (Stations 1, 2, 6, and 7) exhibited lower variability in TSS (20 – 40 mg L^{-1}) over the same time period.

Cross transect concentrations of chlorophyll *a*, TSS and NH_4^+ displayed more temporal variation at stations near the channel (Fig. 24). This contrasts with the water quality monitoring data which showed very little variation in space and time. The plot shown in Fig. 24 contains data collected from the transect during the afternoon hours of June 20 and 21, but reflect the same trends seen in all measurements taken during the period the estuary was sampled. The measured parameters appear to covary and all transects taken during this monitoring effort showed approximately the same trends. Highest concentrations of each of the water column measurements occurred in the channel region of the estuary, while minimum levels of TSS, NH_4^+, and chlorophyll *a* were observed along the edges over the seagrass beds. The area over the channel was also the most active in terms of surface

Table 9. Nonparametric (Pearson's X^2 test) analysis of water column data.

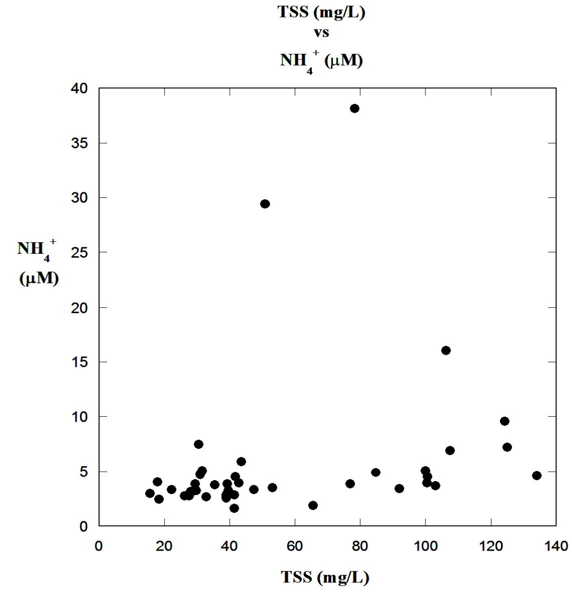
			TSS (mg/L)	**NH_4^+ (µM)**	**Chlorophyll *a* (µg/L)**
		p		0.001	< 0.001
All data (n = 42)	TSS (mg/L)	Correlation Coefficient		0.362**	0.700**
		p		0.001	< 0.001
	NH_4^+ (µM)	Correlation Coefficient	0.362**		0.303**
		p	0.001		0.005
	Chlorophyll *a* (µg/L)	Correlation Coefficient	0.700**	0.303**	
		p	< 0.001	0.005	
Without channel (n = 36)	TSS (mg/L)	Correlation Coefficient		0.266*	0.646**
		p		0.024	< 0.001
	NH_4^+ (µM)	Correlation Coefficient	0.266*		0.179
		p	0.024		
	Chlorophyll *a* (µg/L)	Correlation Coefficient	0.646**	0.179	
		p	< 0.001		

* Correlation is significant at the 0.05 level.

** Correlation is significant at the 0.01 level.

waves Data collected from all transect sampling (TSS, NH_4^+, and chlorophyll *a*) were compared to determine if significant relationships could be detected.. Environmental conditions in the 60 hour period in which the transect was established and monitored in the Lower Laguna Madre were better described as a continuing wind event. Nonparametric analyses (Peasons X^2 test, utilizing SPSS software) of the three water column parameters reveal significant correlations when all data are included (Table 9). This is somewhat surprising when plots of parameter comparisons are viewed. Fig. 25 displays NH_4^+ concentration compared to TSS in the upper plot and NH_4^+ compared to chlorophyll *a* in the lower. The total suspended solid measurements predominantly correspond with lower NH_4^+ concentrations, with three outlier values separate from the majority of observations in the upper range of NH_4^+ concentration. The higher values were measured at station 4 of the transect which is located in close vicinity to the Intracoastal Waterway channel.

The sediments in the channel exhibited the highest flux rates of NH_4^+, contributing water column input greater than an order of magnitude more NH_4^+ than the seagrass sediments (discussed later). This station was also deepest, and the majority of high TSS and chlorophyll *a* concentrations were measured in the water column overlying the channel sediments. The water column data collected at station 4 were removed and the reduced set reanalyzed to determine if correlation significance would increase. The results of these analyses are shown in the lower part of Table 9. All correlation significance decreased when this station was removed, lowering the relationship between TSS and NH_4^+ concentration to significance at p value 0.05 and making the relationship between chlorophyll *a* and NH_4^+



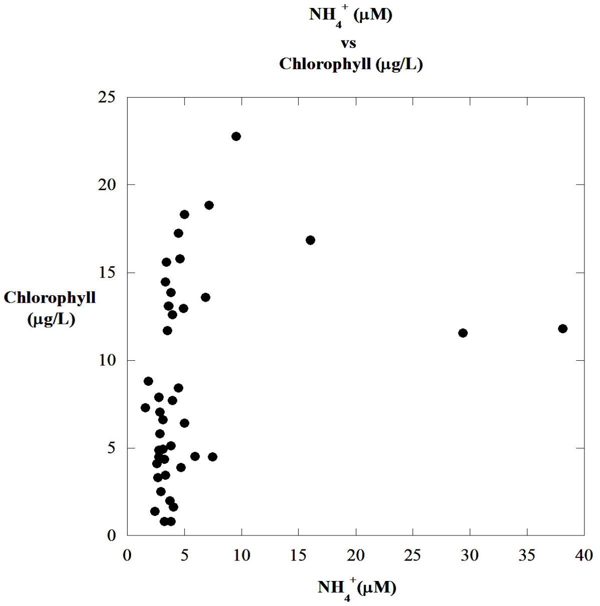


Fig. 25 Comparison of TSS (Total Suspended Solids), NH_4^+ and chlorophyll *a* concentrations. The upper panel displays NH_4^+ concentrations plotted against TSS, and the lower panel shows chlorophyll *a* concentrations plotted against NH_4^+.

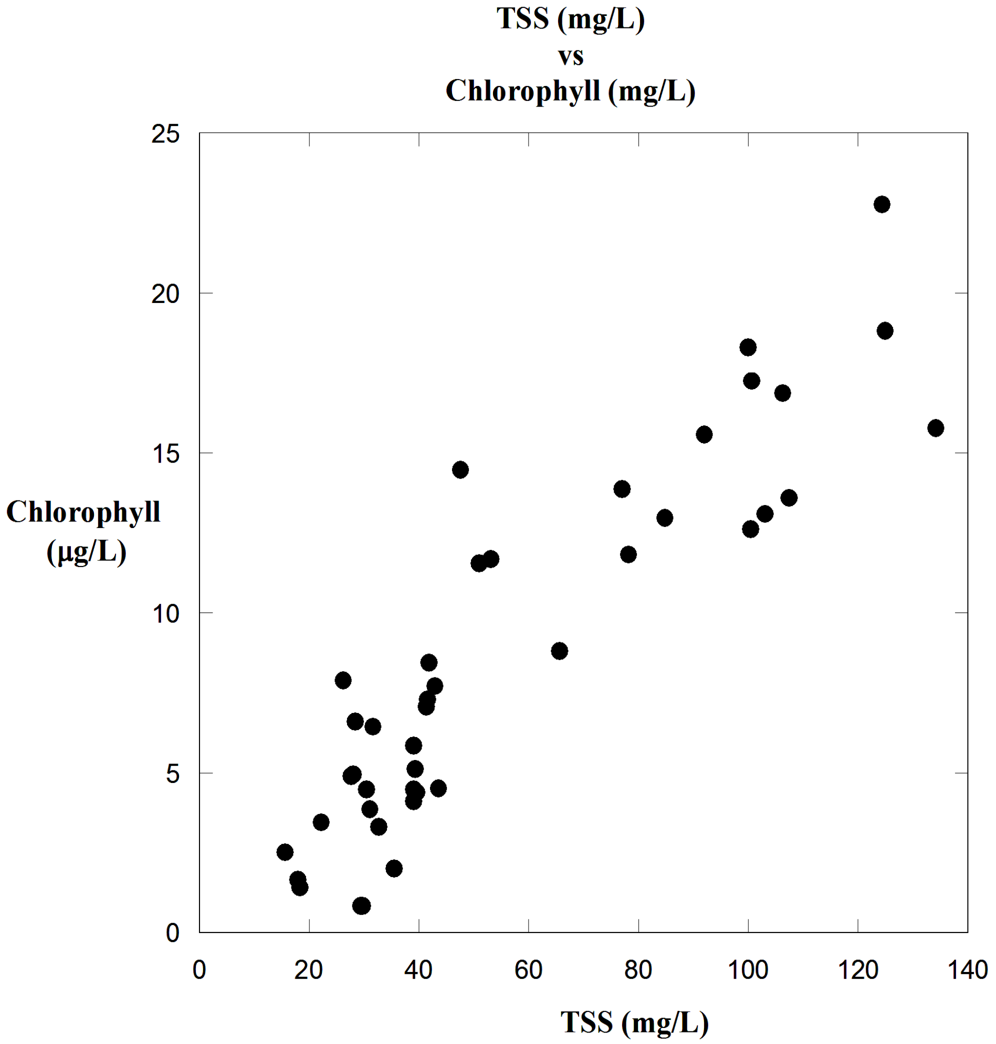


Fig. 26 Comparison of TSS and chlorophyll *a* concentration for all data collected over the sampling period.

insignificant. The correlation between TSS and chlorophyll *a* is reduced in significance with removal of the channel station data as well, but remains significant at p value 0.01. TSS and chlorophyll *a* concentrations are compared in Fig. 26 and display a strong relationship between the two parameters when all data are considered.

3.3 Bioassays

The resident water column phytoplankton community was capable of rapid uptake of a pulsed nutrient input, as is evidenced by the changes observed in NH_4^+, HPO_4^{-2}, NO_3^-, and $Si(OH)_4(aq)$ concentrations during the bioassay incubations (Fig. 27). Reductions in the NH_4^+ concentrations in the two incubations were 8.5 (A) and 15.6 (B) µmol L^{-1} while increases in chlorophyll *a* concentration were 12.6 and 18.5 µg L^{-1} (A and B respectively) over the incubation period in the two bioassays. In these incubations there were also reductions in $Si(OH)_4(aq)$ concentrations of 50 and 86 µmol L^{-1} indicating that the predominant species in the community was most likely diatoms (Fig. 27). Removal of HPO_4^{-2} during the incubation time period for bioassay A and B was 0.73 and 2.0 µmol L^{-1}. The corresponding N:P ratio of absorption for the incubations is 12.2 and 7.8. These values indicate growth in the bioassays was well below the Redfield ratio (16:1). Stoichiometric conversion of chlorophyll *a* increases to carbon, reflecting carbon incorporation by phytoplankton, was compared to NH_4^+ (N) uptake. The bioassays had uptake C: N ratios of 6.13 (A) and 4.94 (B), indicating phytoplankton growth close to Redfield ratio. Nitrate in both incubations did not vary, having start and end concentrations of approximately 0.5 µmol L^{-1}. Preparation of the bioassays did not include pre-filtration to remove predators so

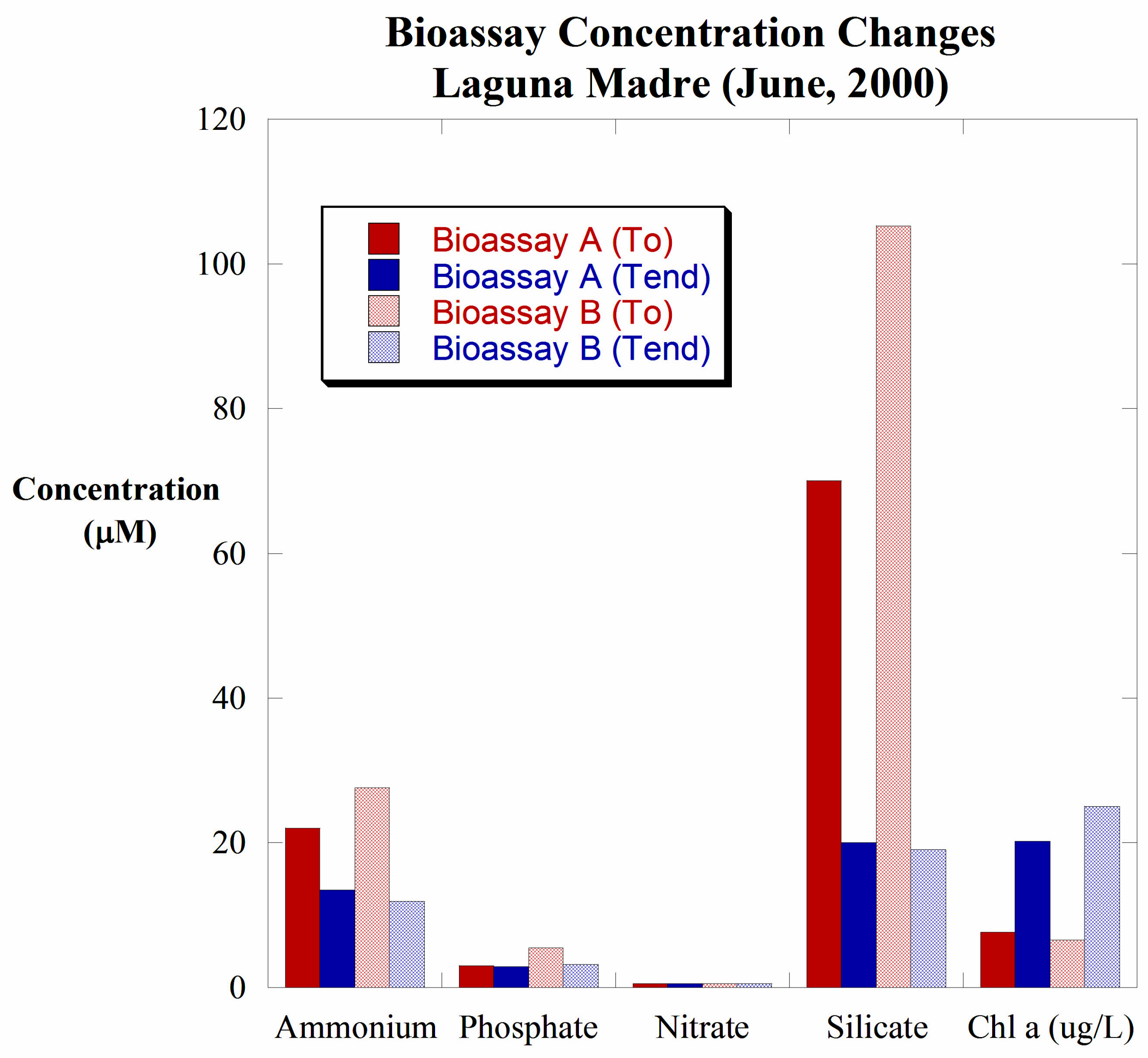


Fig. 27 Comparisons of beginning and ending concentrations for bioassays incubated at the extreme of the transect sampled in June. T_o in the legend refers to measurements made on samples taken after bioassays were spiked. T_{end} measurements were made at the end of the incubation period.

the decreases in the nutrients observed are a conservative estimate of the ambient phytoplankton population’s potential to alter water column nutrient concentrations. The reduction in concentration over this relatively short time span would suggest differing controls on concentrations of NH_4^+ and chlorophyll *a* in the estuary over the sampling period. This is also indicated when the water column measurements are plotted over time.

Shown in Fig. 28 (a – d) are the water column NH_4^+, TSS and chlorophyll *a* concentration for the stations 4 and 5. Both of these stations are in close proximity to the channel and are probably strongly influenced by resuspension of sediments in and immediately adjacent to the Intracoastal Waterway. At station 4 a negative correlation appears to exist between chlorophyll *a* concentration and NH_4^+ (Fig. 28 a), but the increase in chlorophyll *a* is also accompanied by an increasing concentration of TSS (Fig. 28 b). The increase in chlorophyll *a* could be due to growth or possibly increasing resuspension of bottom particles. At station 5 in this figure (Fig. 28 c and d) however, chlorophyll *a* concentrations do not change significantly until the end while TSS concentrations continually rise through the sampling period. Constant NH_4^+ concentrations were also observed through the sampling period at station 5. These observations indicate that the relationships between these parameters may be controlled on varying time scales and that continual resuspension events of particles over and over again from the sedimentary environment are not reflected in the observations.

Cross transect concentration plots (Fig. 24) reveal that the central region of the Lower Laguna Madre was characterized by the highest concentrations of NH_4^+, TSS, and chlorophyll *a* during the time period the estuary was sampled. Concentrations of NH_4^+, while

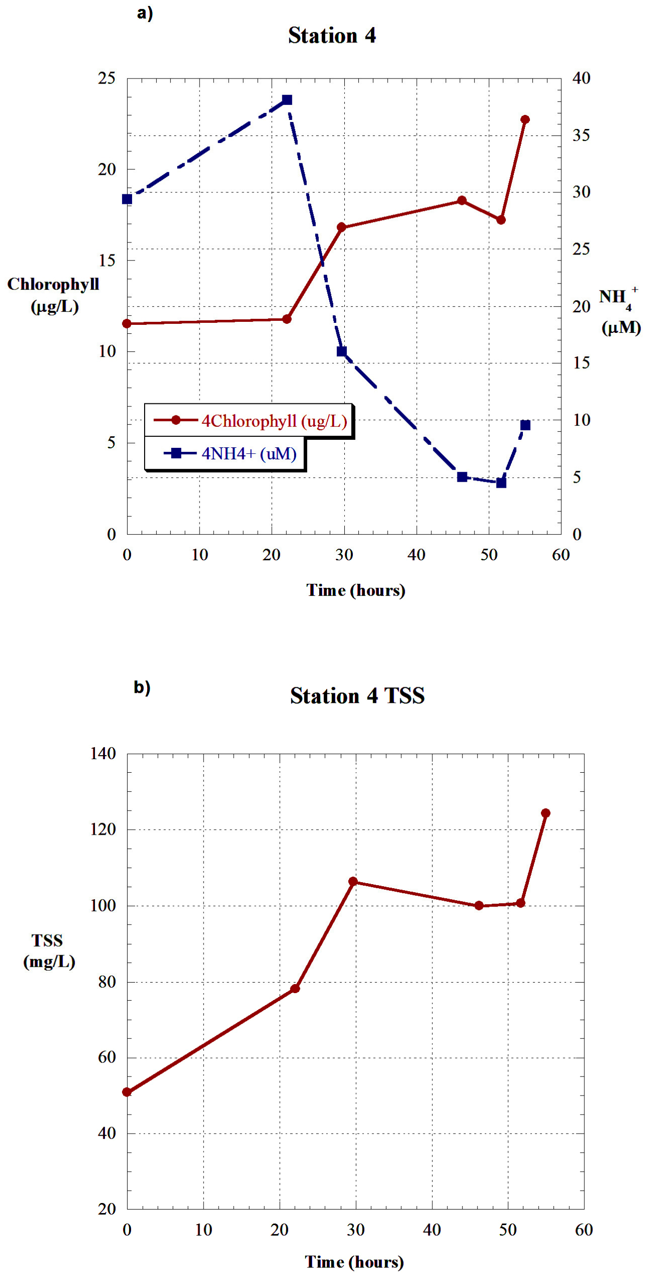
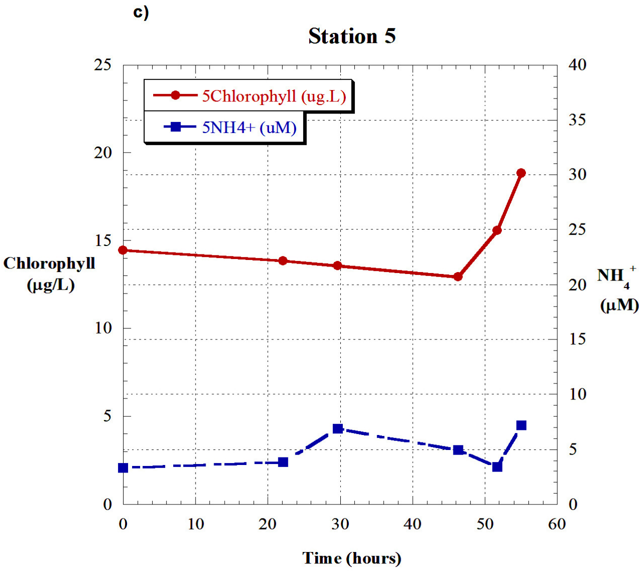


Fig. 28 (a and b) Water properties including total suspended solids (TSS), NH_4^+ and chlorophyll *a* measured for water samples collected at station 4 over the entire transect sample period.



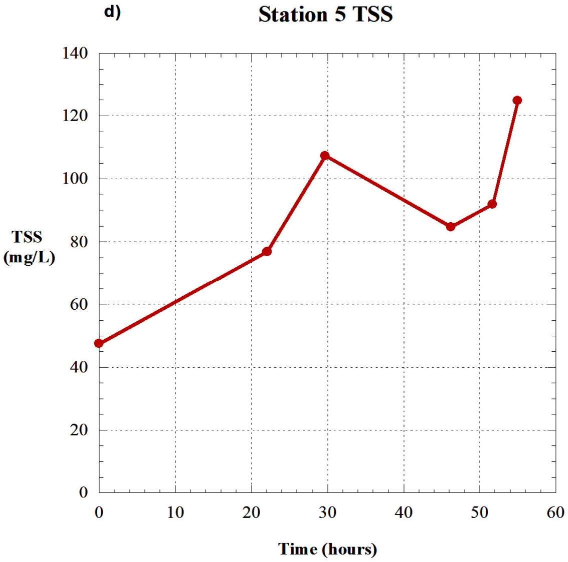


Fig. 28 (c and d) Water properties including total suspended solids (TSS), NH_4^+ and chlorophyll *a* measured for water samples collected at station 5 over the entire transect sample period.

centrally high in every transect sampling, appear to decrease rapidly at approximately 30 hours. At this point of decline in the NH_4^+ concentrations, chlorophyll *a* concentrations were almost simultaneously observed to begin rising at the central transect stations and continued to rise throughout the sampling period. TSS is also observed to begin an upward trend and also continued increasing through the sampling period. The observation could be due to absorption and subsequent growth by actively photosynthesizing water column phytoplankton, but is probably better explained by advection. The high concentrations of NH_4^+ in the channel vicinity of the transect as compared to the fringes indicates that a nutrient source influencing the central region may be an important factor affecting nitrogen availability in the estuary.

3.4. Sediment Flux Measurements (Flow-Through Cores)

Flux measurements were conducted from sediment cores taken along the estuary transect to determine the magnitude of their contribution (Table 10). The channel sediments appear to act as source for NH_4^+, HPO_4^{-2}, and $Si(OH)_4(aq)$ to the water column, while being a sink for O_2 and NO_3^-, which are consumed as terminal electron acceptors for sediment metabolism. Nitrate has been observed to decrease rapidly in down core profiles, usually disappearing within centimeters of the sediment water interface (Gardner et al. 2006). The N:P ratio of inorganic ion flux into the overlying water was extremely variable, ranging from 10.7 to 95.1 for seagrass cores and averaging 14.5 for the channel sediments. Unfortunately the wide variation in N:P flux ratio is probably due to removal of the cores from the estuary for measurement. No attempt was made to control O_2 concentration in the flow-through core

Table 10. Flux measurements in the Intracoastal Waterway channel and grass areas determined from core incubations.

Site	Oxygen µmol m^{-2} d^{-1}	DOC µmol m^{-2} d^{-1}	NH_4^+ µmol m^{-2} d^{-1}	HPO_4^- µmol m^{-2} d^{-1}	NO_3^- µmol m^{-2} d^{-1}	$HSiO_3^-$ µmol m^{-2} d^{-1}
Channel	-5119.7 (2931.7)	-175358.6 (62885.21)	6329.3 (1307.67)	421.8 (215.467)	-203.8 (186.42)	6115.0 (5927.2)
Grass (core 1)	-16240.1 (3220.3)	41079.0 (22894.4)	1277.0 (319.25)	12.49 (6.01)	-88.49 (23.42)	5593.8 (1700.4)
Grass (core 2)	-14296.8 (4219.7)	18801.0 (7029.05)	705.13 (310.46)	52.75 (31.92)	-135.26 (57.26)	13539.0 (4144.7)
Crass (core 3)	-13917.9 (3834.0)	14062.4 (10919.0)	724.78 (73.97)	32.83 (52.5)	-91.91 (52.6)	8308.7 (3355.62)
Grass (core 4)	-14574.4 (3046.2)	21060.0 (8287.7)	961.1 (449.05)	15.76 (34.14)	-106.68 (27.9)	10841.5 (4336.9)
Grass Average	-14757.3	23750.8	917.0	12.0	-105.6	9570.7

incubations which could alter flux of HPO_4^{-2} from the sediment by influencing the availability of amorphous iron hydroxide (FeOOH). The channel sediments themselves have above average concentrations of organic carbon (0.98%, see previous chapter) and extremely high concentrations of HS^- and NH_4^+. These dissolved constituents reach millimolar concentrations in core profiles within 2 cm of the sediment water interface (previous chapter). The presence of HS^-, a metabolic end-product and indicator of SO_4^{-2} reduction, in such high concentrations near the surface of the sediment suggests an organic carbon source rich in metabolizable organic matter. The channel sediments are not unusual in their organic carbon content and the possibility of DOC utilization in the sediments is reasonable. In addition, due to the rapid productivity of macro algae in the estuary, DOC concentrations in the water column can be very high (approximately 1,000 µmol L^{-1} measured during the flux measurements).

The channel sediments also appear to be a relatively major source of NH_4^+ and HPO_4^{-2} to the system having rates of 6,329 and 421 µmol m^{-2} d^{-1}, respectively. The N:P ratio of inorganic nutrient flux from the channel sediments is approximately 15 which is very close to Redfield and reflects returning inorganic nutrients from sediments with relatively fresh inputs of organic matter. Fluxes of NH_4^+ from the channel sediments were more than ten times greater than in the seagrass sediments. This result reflects both low concentrations in the sediments and the fact that the seagrasses themselves are capable of nitrogen acquisition both from the water column and through root systems in the sediment (Lee and Dunton, 1999). Down core profiles shown in Fig. 29 exhibit rapid increases in both dissolved and particle bound NH_4^+ (labeled extractable) for one seagrass and one channel core. Channel sediments without nitrogen absorbing seagrasses or microaerophilic conditions important to nitrification rapidly accumulate NH_4^+ in the down core profile and contain relatively large quantities of NH_4^+ associated with sediment particles. The seagrass sediment porewater NH_4^+ concentration on the other hand increases but over a much smaller range and the particle associated NH_4^+ is observed to decrease.

The flux rates measured during the monitoring period can be used with the approximate width of the estuary (10.8 km) at the transect location to calculate a daily input. Considering the channel to be 50 m in width and an average depth of 4.0 m, daily input to the central region of the estuary from channel sediments would result in a NH_4^+ concentration addition of 1.8 μmol L^{-1}. Similarly, considering the remainder of the cross estuary to be seagrass beds with an average depth of 1 m daily contribution from seagrass sediments would result in daily water column NH_4^+ addition of 0.917 μmol L^{-1}. These measurements can be compared to flux measurements determined in the second chapter of this document. Sediment flux estimations amounted to rates of up to 622 μmol m^{-2} d^{-1} in the seagrass areas. Water column concentrations measurements made during the transect monitoring were in excess of these values, suggesting that NH_4^+ is being derived from an alternative source in the Lower Laguna Madre. In addition bioassay NH_4^+ concentration decreases were 8.54 and 15.64 μmol L^{-1}, indicating that the resident phytoplankton community has the capacity to consume this input of nitrogen. Resuspension of channel and seagrass bed sediments would likely result in much different resultant concentrations. In addition the large amount of particle associated NH_4^+ could become a factor when the sediment particles are resuspended and the solid to solution ratio decreases drastically

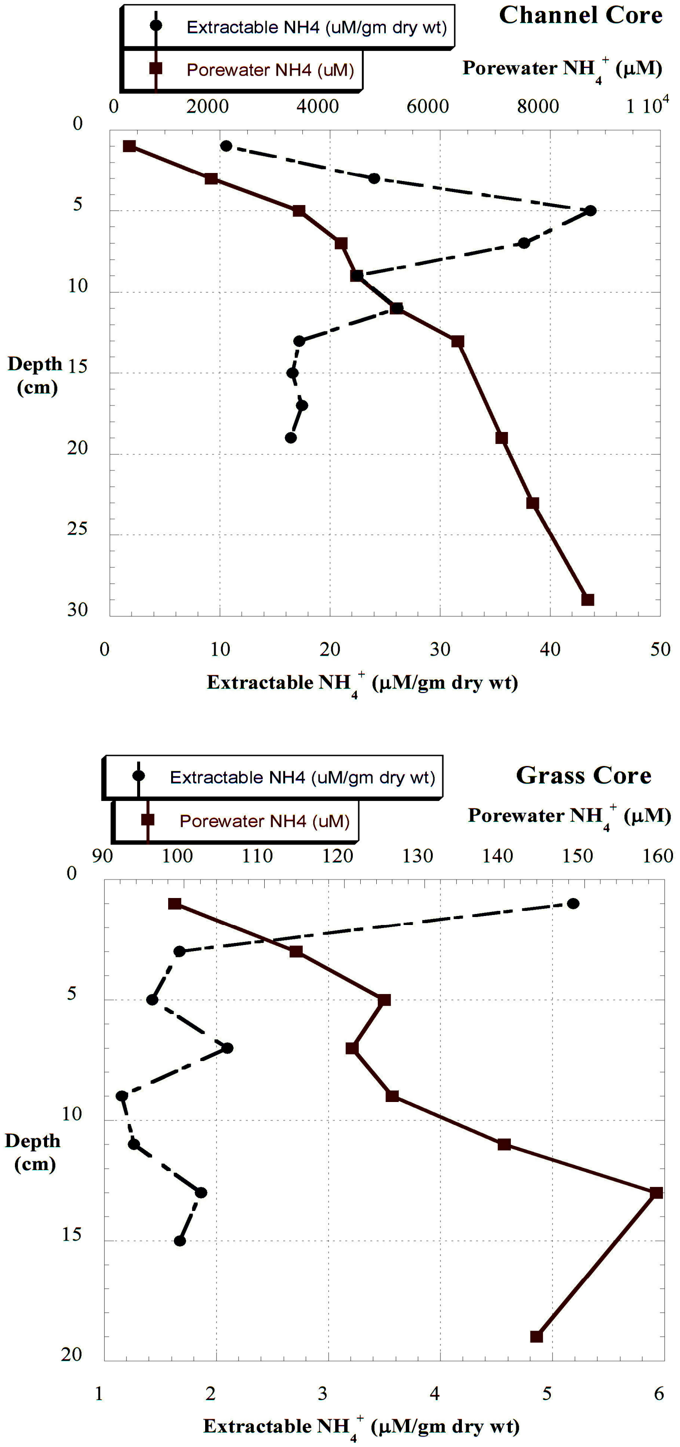


Fig. 29 Porewater and extractable NH_4^+ profiles from cores collected in Lower Laguna Madre. The lower graph displays data collected near a seagrass bed and the upper graph displays measurements in a channel core.

(Morin and Morse, 1999). In this scenario, NH_4^+ could be released over longer time frames dependent on the water column concentration and time of particle suspension.

4. Discussion

Wind induced wave action has been attributed to many important hydrologic processes in estuaries. Specifically sediment resuspension and resultant water column turbidity as well as dominant circulation patterns have been attributed to wind as a forcing agent. Correlations between wind velocity and nutrient inputs have been observed in the Ria de Arousa in North Western Spain where destabilization and destruction of thermal stability lead to biological activity in the surface waters (Alverez-Salgado et al., 1996). In Chesapeake Bay, Ward et al. (1984) have observed correlations between water column sediment concentrations and wind speed. The Gulf of Mexico is characterized by a relatively stable coastal environment and shallow estuaries. Studies linking wind velocity and water column sediment concentrations in Gulf of Mexico estuaries include Barataria Basin, Louisiana (Booth et al., 2000), Corpus Christi Bay, Texas (Shideler, 1980), and Laguna Madre, Texas (Morton et al., 2000). Historical wind velocity records collected near the transect established for this study in the Lower Laguna Madre were analyzed using the procedure described above (Critical wind speed determinations, CERC 1984) to determine if surface waves generated from winds could potentially interact with sediments and approximately how often. Winds are observed to originate primarily from the south in the region and to blow at speeds in excess of the critical wind speed calculated for the fetch and depth of the estuary for approximately 60 % of the year (Data collected for 1998). Wind measurements collected near the transect (at the Conrad Blucher platform) for the sampling period were also in excess of the critical wind speed and displayed an apparent 24 hour cycle. Visual evidence of turbidity existed throughout the sampling period as well.

It is not surprising to find high sediment loads in the regions adjacent and directly over the channel in the Laguna. This area is heavily trafficked by barges transporting materials from Corpus Christi, Texas to Brownsville, Texas. Though the channel is frequently cleared through dredging by the Army Corps of Engineers (Galveston District), shoaling in this area of the estuary is a significant problem (Morton et al., 2001). The channels themselves in Texas estuaries have altered the hydrography through increased volume of tidal prism, and alterations to circulation patterns (Channelization) (Solis 1999). Water "jetting" by propeller activity results in frequent resuspension of shallower sediments and consequently the formation of unconsolidated aggregations of particles on the bottom which resemble a nephloid layer (Osborne and Boak, 1999). This phenomenon has been seen both by divers in GIWW channel core acquisition and in channel cores themselves taken by other techniques. On the other hand the very presence of the sea grasses in the east and west extremes of the estuary away from the central channel region imply water clarity (Fonesca et al., 1983) and low nutrient concentration (Lee and Dunton, 1999).

Comparison of the water column properties determined along the transect in the Laguna Madre indicate that the relationship between these characteristics is extremely complicated. This is due primarily to the fact that resuspension is only the beginning of the process of component import into the water column. The factors dictating the fate of each of the parameters measured are quite different. Using the Stokes settling equation, a residence time for a particle resuspended to the top of a 1 m water column with an average grain-size of 35 μm would be approximately 16 minutes. Smaller particles less than 2 μm (approximate cut off for clays) could take hours to days to settle. Release of absorbed components (surface bound cations) continues as long as the concentrations thermodynamically favor release. Release of NH_4^+ hours after initial particle introduction to the water column was observed in resuspension experiments (see chap II). Complicating this further is the idea that resuspension of sediments results in the formation of unconsolidated surface layers of sediment which are more easily resuspended. Chlorophyll *a* containing phytoplankton particles in estuaries range in diameter from several to hundreds of micrometers , but are essentially hollow spheres with densities more reflective of marine waters. Resuspended algal structures settle at rates in the range of 1 – 10 m dy^{-1} (Smayda 1974). Resuspension of sediments can result in the introduction of resting state planktonic cells (cysts) which can become photosynthetically-competent and begin to proliferate, remaining in the water column for long periods of time. Dissolved components however, from desorption and dilution of interstitial waters do not settle from the water column. The fate of these components on short time scales is controlled in shallow, high residence time estuaries such as the Laguna Madre by biological factors (i.e., incorporation into organic matter, nitrification and denitrification). What can be concluded in looking at the parameter concentrations across the transect is that the central region of the estuary is strongly influenced by resuspension of sediment. All transects showed peak concentrations of the three determinations at the central portion of the estuary located proximal to the channel. Concentrations of NH_4^+ specifically showed a very narrow peak associated with the channel.

The N:P ratio for returning nutrients from the seagrass sediments was varied and ranged from 10 to 95 for the sea grass sediments acting as sources of the nutrients. This is not surprising considering the dynamics of phosphate reactions with amorphous iron hydroxide minerals in oxic environments. Seagrasses are capable of O_2 transport through root systems and thus can alter the chemistry temporally and spatially. The seagrass sediments also act as a sink for O_2 and NO_3^-, but contribute $Si(OH)_4(aq)$ to the water column. Seagrass beds act as filters in shallow marine systems, collecting particulate matter suspended in the water column. These sediments usually have very high concentrations of organic carbon and high heterotrophic metabolic rates making them prime sources for DOC in estuaries. The N:P ratio of sediment to water exchange for channel sediments was approximately 15, closer to Redfield and representative of relatively rapid Remineralization of recently incorporated nutrients. Dissolved concentrations in the water column however, exhibited dissolved N:P ratios well below Redfield except in isolated cases over the central region of the estuary. Dissolved ion and bioassay incorporation ratios imply that the Lower Laguna Madre estuary in primarily controlled by availability of nitrogen, consistent with previous observations (Pennock et. al. 1999). The exchange rates for the channel sediments were extremely high for NH_4^+ and HPO_4^{-2} (6,329 and 421 μmol m^{-2} d^{-1} respectively) in comparison to the seagrass beds. These values can be compared to July flux measurements made on the continental shelf off of Louisiana and influenced by the Mississippi river (Rowe et al., 2002). Rates of O_2 consumption during this investigation ranged between 820 and 11,000 μmol m^{-2} d^{-1} and NH_4^+ flux to the water column ranged between 2,000 and 4,000 μmol m^{-2} d^{-1} during what is described by the authors as a hypoxic event over the continental shelf area. The central region of the Laguna Madre acts as a trap for particulate material and an area of relatively efficient recycling, generating high porewater concentrations of remineralized organic matter.

Concentrations of NH_4^+ were high during the sampling period in June, 2000, exceeding 4.0 µmol L^{-1} in approximately 40% of the water column samples and always at the deepest region of the transect. Inorganic nitrogen in the form of NH_4^+ is frequently a component of nutrient pools in coastal regions due to the close coupling of sediments and water column. Sediment flux measurements of NH_4^+ can be used to determine the contribution the sediments make through diffusion. If we consider an average water column depth of 1 meter and use the average flux rate reported in the results for the seagrass cores, the amount of NH_4^+ addition expected to the water column from this process alone is 0.917 µmol L^{-1}. Using the channel flux rate and considering the channel to have an average depth of approximately 3.5 m we can calculate the expected contribution to be 1.8 µmol L^{-1}. The collected NH_4^+ and TSS data are plotted once again in Fig. 30 and shows that many of the data points collected exceed these values. Also plotted are isotherms generated from partition coefficients estimated in a previous study of the area (Morin and Morse, 1999). These curves correspond to what would be expected in the water column if all of the sediment were either of channel origin (top curve) or seagrass bed origin (bottom curve). As can be seen, more NH_4^+ was observed in the water column than would be expected from sediments from seagrass beds but less than if all of the sediment were from the channel. The NH_4^+ concentration observed in the water column could be a result of a mixture of resuspension along the transect. However, the peak in concentration occurs extremely locally around the channel possibly indicating much more contribution of channel sediments. Observations during the sampling would support this in that the most active area in the estuary during all transect samplings was located in the region of the channel. The GIWW

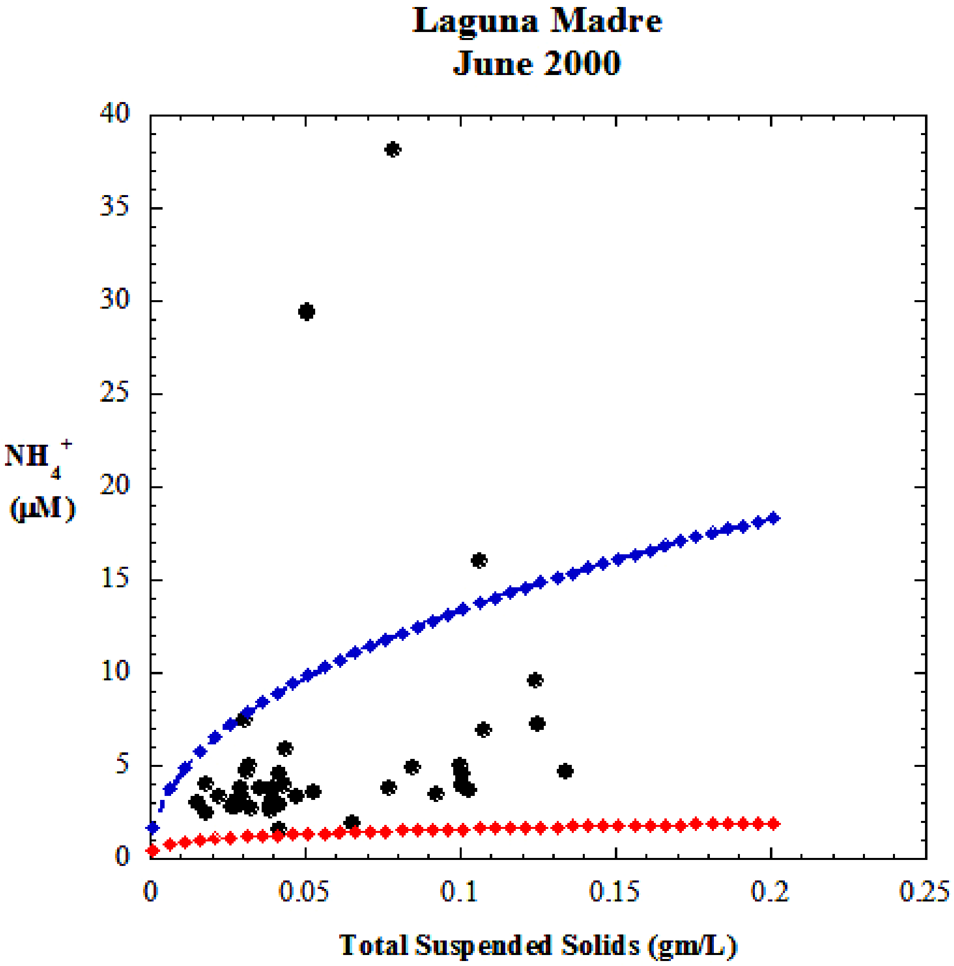


Fig. 30 TSS concentration plotted against NH_4^+ for all transect samples and isotherms calculated from resuspension experiments (red represents seagrass data and blue represents channel sediments) in chapter II.

region in the estuary is the deepest and the bare sediments in the area would not dampen wave activity as much as the seagrass beds. If we consider that the increase in chlorophyll *a* in the central region of the estuary over the time frame of the sampling could be due to active photosynthesis then an increase in carbon biomass attributed to phytoplankton production can be calculated. Gallegos and Vant (1996) give a range of chlorophyll to carbon ratios associated with actively growing phytoplankton in estuarine systems. A value of 50 for this ratio has been used in the literature and is within the range estimated by Gallegos and Vant (1996). Chlorophyll *a* concentration at the central station of the transect increased by 11.2μg L^{-1} over the 60 hour time period of sampling which would require the consumption of approximately 6.04 μmol L^{-1} of nitrogen from solution. This amount of nitrogen could not be supplied by simple sediment diffusion from either source (channel or seagrass sediment diffusion) over the time period of observation and implies the contribution of resuspended sediments and interstitial water.

The Laguna Madre data show a clear correlation between resuspended sediment and chlorophyll *a* concentrations. Resuspension of chlorophyll *a* containing cells has been reported previously in San Antonio Bay (Texas) and the cells resuspended were found to be photosynthetically competent (Macintyre and Cullen, 1996). Resuspension experiments conducted in the coastal region of the Southern Baltic also illustrate the importance of phytoplankton (as well as other members of the microbial food web) resuspension to water column production as well as taxonomic distribution of the water column community (Garstecki et al., 2002). This study presented evidence of increases in water column NH_4^+ concentration over an initial 12 hr time period followed by decrease. After the 12 hr peak in NH_4^+ concentration, picoautotroph abundance increased independent of seston concentration implying growth. Spiked bioassays conducted during this investigation in the Laguna Madre showed relatively rapid uptake of added nutrients, accumulation of chlorophyll *a*, and uptake of ambient $Si(OH)_4(aq)$. Water incubated in the uptake bioassays was collected in a relatively turbid portion of the estuary (within 1.5 km of the channel). The above mentioned investigation in San Antonio Bay determined that active cells were resuspended and that turbidity levels may facilitate photosynthetic activity by reducing photo-inhibition in the productivity–inhibition relationship. In this investigation as well as a similar study carried out in the Westerchelde estuary (Netherlands) temporal and spatial observations of phytoplankton distribution indicate that wind induced resuspension can explain much of the short term variability in both total number and community structure (Lucas et al., 2001; Lucas 2003; Macintyre and Cullen, 1996). Water column inorganic nutrient addition through wind induced wave resuspension of bottom sediments has been observed and is well established as a source comparable to yearly inputs of freshwater (Fanning et al., 1982; Lund-Hansen et al., 1997; Pedersen et al., 1995; Christiansen et al., 1997). The combination of competent cells along with significant dissolved inorganic nutrients creates the potential for bloom induction in estuaries. In addition, this mechanism could maintain bloom conditions through frequent pulsed release of inorganic nutrients.

A regionally germane example of a sustained phytoplankton bloom is the recent reappearance of the nuisance algal species *Aureoumbra lagunensis* in the Laguna Madre referred to as “brown tide”. This algal pelagophyte had almost completely disappeared from the Laguna Madre in 1997, but is currently approaching bloom concentrations (Buskey et al., 2001). The organism has not proven to be toxic to fish stocks in the estuary, but is of significant concern due to reduction in light levels and possible deleterious effects on the seagrass community. Before the 1997 reduction in the *A. lagunensis* population, the brown tide had bloomed continuously for eight years (Buskey and Stockwell, 1993; Whitledge, 1993). Above normal rainfall and a reduction in the average salinity (40 ppt to 20 ppt) during July of that year contributed to the temporary reduction.

An interesting characteristic of the organism responsible for the brown tide is an inability to utilize NO_3^- for cellular maintenance (Deyoe and Suttle, 1994). The organism appears to be capable of transporting NO_3^- across the cell membrane, but not capable of converting NO_3^- to NO_2^-. This means that the organism may depend exclusively on NH_4^+ as nitrogen source for the production of proteins. Optimal growth for the organism appears to occur at low light levels and relatively high salinity (> 30 ppt) (Lomas et al., 1996). The decline of brown tide in the Laguna Madre probably came about due to flushing of the estuary during high rainfall and an increase in ambient light levels. The return of the estuary to high salinity and low light levels seems to have recreated bloom conditions. Buskey et al. (2001) have speculated that a reservoir of resting *A. lagunensis* cells in the sediments of the estuary would make recovery of the bloom inevitable after elimination.

The phenomena of the reoccurrence and persistence of the brown tide organism necessitates the elucidation of a nitrogen source consistent and of a magnitude great enough to sustain the organism. The data collected during this investigation suggest that the sediments in the estuary may supply that nitrogen in a suitable form (as NH_4^+ N) for maintenance of the bloom. However, this investigation only sampled a small area of the estuary over a relatively short time period. The results suggest a mechanism for daily pulsed and consistent import of nitrogen as NH_4^+ into the Laguna Madre, but limited spatial and temporal sampling exclude conformation of any hypotheses. In addition the analysis of wind data only produces a potential for resuspension. Waves in shallow systems are very complex and may not strictly adhere to the theory utilized to establish the potential. For these reasons a clear diurnal pattern, though observed in the system, cannot be established. The Laguna Madre is a diverse and complex ecosystem, with characteristics approaching the extreme in terms of marine environments. The reappearance of the brown tide organism in the system suggests some reoccurrence of bloom favorable conditions. Investigations into these conditions and elucidation of the factors and their complex interplay will be tantamount to the understanding of what conditions lead to nuisance and toxic blooms in coastal marine systems.

CHAPTER V

MODEL ANALYSIS OF SEDIMENT NITROGEN AND ALGAL BIOMASS CONTRIBUTION TO THE LOWER LAGUNA MADRE THROUGH WIND-INDUCED SEDIMENT RESUSPENSION

1. Introduction

Nutrients exert fundamental control on primary productivity in all ecological systems. These nutrients are supplied by regenerative processes in the water column and sediments of marine systems, as well as through anthropogenic input and weathering of continental sources. The role of the benthos in supplying these nutrients is amplified in shallow systems such as the Laguna Madre estuary. Work in the previous chapters of this dissertation has shown that a significant fraction of nutrients is bound to the sediment in this system and could be released upon resuspension. Such resuspension can be driven by wind induced wave activity. In this chapter I will be exploring the interaction between the sediment and phytoplankton via nutrients through development of a simple mathematical model.

Wind activity is well established as a driving mechanism supplying nutrients in upwelling systems (Alverez-Salgado et al., 1996; Roson et al., 1999). Models of this process suggest that even daily variation in wind can be important in these systems (Wroblewski, 1977). Wind forcing is also important in shallow estuarine systems (Lund-Hansen et al., 1997; Ogilvie and Mitchell, 1998; Wainright, 1990). For example, wind induced variation in estuarine systems resuspension has been linked to variations in nutrient, turbidity and chlorophyll *a* concentrations in San Antonio Bay (Macintyre and Cullen, 1996). Episodic events such as strong winter storms can have even larger impacts on coastal systems both by increasing water column concentrations and affecting gross sedimentation rates (Gremare et. al., 2007). These variations have been observed on the order of hours and have been attributed to resuspension processes.

Short term variation in nutrient supply can have physiological affects on phytoplankton communities. Pinckney et al. (1999), using mesocosms positioned in the Nuese River estuary, observed rapid alterations in growth rate in phytoplankton communities associated with changing growth conditions such as pulsed nutrient inputs and fluctuating light due to turbidity. The Nuese River experiments were conducted in a mesocosm but similar results could occur with pulsed nutrient inputs in estuaries (Garstecki et al., 2002; Gentilhomme and Rich, 2001). In the Laguna Madre, the small alga *Aureoumbra lagunensis* (3- 5 µm) has been shown to increase cell volume and chlorophyll *a* content, as well as maintain total community representation in mesocosms in which NH_4^+ was added compared to mesocosms in which no nitrogen was added (DeYoe et. al., 2007).

Estuarine sediments generally have higher proportions of organic matter than open ocean sediments because of their shallow depths as well as reduced water column consumption. Regeneration in the sediments results in elevated interstitial concentrations of metabolic products (i.e. nutrients, DOC). Because estuarine sediments tend to lie in the euphotic zone, benthic algae establish communities and can take advantage of high nutrient concentrations. The sediments in estuarine systems also have higher mass fractions of continental materials (minerals). Particle size and mineralogical characteristics of the inorganic component of estuarine benthic sediments are highly regional. The particles making up the sedimentary environment can alter nutrient dynamics by surface adsorption (Krom and Berner, 1980; Mackin and Aller, 1984) and desorption. As a result, resuspension of particles with absorbed ions can result in release through desorption because of lower water column concentrations (See Chapter II).

Resuspension of sediments can affect the water column in several ways: nutrient release from resuspended particles, nutrient release from entrained interstitial waters, introduction of algal biomass from the sediments, as well as reduction in water transparency. All of these effects can alter primary productivity in estuarine environments. In addition, short term variations in nutrient, turbidity and phytoplankton distribution can be greatly altered through particle resuspension.

This chapter describes a simplified model system of phytoplankton, water column nutrients and suspended sediments whose properties change as a result of resuspension release, settling and biological growth. Resuspension has an imposed diurnal cycle. The goal of this model is to use information developed earlier (i.e. sediment flux rates, partition coefficients) as well as observations taken during field expeditions (concentrations of dissolved nutrients, Chlorophyll *a* and TSS) to determine the factors controlling phytoplankton growth and water column nutrient concentrations. The model consists of three state variables – concentrations of phytoplankton, NH_4^+ and NO_3^-. Two versions of the model (including and excluding resuspension) are used to investigate effects of particle and dissolved component resuspension into the water column. It will be shown that inclusion of resuspension in the model system can have a substantial impact on the maintenance of nutrient and chlorophyll *a* concentrations in the water column. In addition a single pulse input and time constant input of sediment is investigated to test the systems response to a rapid NH_4^+ input (as would be seen in a dredge event) and test the capacity of sustaining a phytoplankton community with constant NH_4^+ input.

2. Background

The phytoplankton concentration in this model is determined by a balance between algal growth, whose rate varies as a function of nitrogen concentration, and losses due to settling and grazing. Dissolved NH_4^+ is usually taken up in preference to NO_3^- by phytoplankton (Boyer et al., 1994; Elskens et al., 1997; Takahashi et al., 1995). In addition, ambient NH_4^+ concentrations exceeding 1-2 μmol L^{-1} can suppress NO_3^- uptake by phytoplankton (Glibert et al., 1982; McCarthy et al., 1977; Pennock, 1987) through inhibition of the nitrate reductase enzyme essential for NO_3^- assimilation (Packard and Blasco, 1974). The suppression of NO_3^- uptake has been mathematically described by Wroblewski (1977) using an exponential term dependent on NH_4^+ concentration and multiplied by the Monod relationship describing NO_3^- uptake. The absorption model utilized in the system described here was described by O'Neill et al. (1989) and has been incorporated by Cullen et al. (1993) in a generalized formulation of phytoplankton growth for biogeochemical models in the ocean.

Maximum specific growth rate (μ_{max}) for phytoplankton was measured by Liu et al. (2001) and was described as an upper bound on the true maximum growth rate for the resident phytoplankton community including the brown tide organism in the Laguna Madre estuary (0.697 d^{-1}). This number agrees well with other observations in the estuary (Deyoe and Suttle, 1994). In an investigation utilizing dilution experiments, similar growth rates were calculated (Buskey et al., 2001).

Removal of algal biomass from shallow water systems occurs through particle settling and grazing. Grazing can also act as an important source of nitrogen through inefficient feeding and release of dissolved nitrogen as NH_4^+. Though the Laguna Madre is undergoing a recovery from the brown tide alga, micro-zooplankton derived excretion is potentially an important source of dissolved inorganic nitrogen in the estuary. *Aureoumbra lagunensis* has been observed to produce exopolymeric secretions as a response to high salinity which can reduce grazing efficiency (Lui and Buskey, 2000, DeYoe et. al, 2007). The amount of dissolved nitrogen returned to the water column due to grazing related excretion is represented by a fraction of grazing (E). Lehrter et al. (1999) have estimated the assimilation efficiency of nitrogen by grazers in Mobile bay (Alabama) at approximately 0.7.

The concentration of NO_3^- in shallow systems is influenced by phytoplankton and seagrass uptake, sediment diffusion, and nitrification. Biological conversion of NH_4^+ to NO_3^- by coastal nitrifiers in marine waters has been observed at low light conditions associated with resuspension and increased turbidity (Berounsky and Nixon, 1993; Hunik et al., 1992; Law et al., 1991; Seitzinger, 1988). Water column nitrification is known to be inhibited by high light conditions, though estuarine ammonium oxidizers tend to be less affected than open ocean varieties. Approximately 55% of NO_2^- and NO_3^- entering Narragansett Bay is formed by nitrification (Berounsky and Nixon, 1993) as determined in direct measurements of surface waters. In the Narragansett Bay nitrification has been established to be more dependent on temperature than light levels. In the relatively shallow Neuse River estuary (North Carolina) rates of pelagic nitrification comparable to excretion release of DON and diffusive flux of NH_4^+ from the sediments are assumed in network analysis of the system (Christian et. al., 1992). Nitrification will largely be utilized to balance the flux rates of NO_3^- into the sediment in the model system presented in this work. In the lower Laguna Madre, sediment resuspension with subsequent reduction in light penetration into the water column probably favors this process. Shallow sediments can be a sink for NO_3^- through sediment directed diffusion associated with denitrification. Core incubations presented in Chapter IV indicated a significant flux of nitrate into the sediments associated with denitrification. Denitrification in the estuary occurs primarily in the sediments where lower oxygen concentrations favor the utilization of NO_3^- as terminal electron acceptor in organic matter mineralization. Detection of high concentrations of HS^- in the sediments during the monitoring period indicates nitrification favorable conditions.

Seagrasses are responsible for removal of dissolved inorganic nitrogen in the Laguna Madre as well. Seasonal biomass measurements for *Thallasia testudinum* (turtle grass) conducted in the Lower Laguna Madre display a range of between 78 and 160 g. dry wt. m^{-2} (Kaldy and Dunton, 2000). Maximum uptake rates for both NH_4^+ and NO_3^- were measured in the Laguna Madre estuary for *T. testudinum* by Lee and Dunton (1999). The authors determine uptake ranges of 8.3–16.5 μmol g. dry wt.$^{-1}$ h^{-1} for NH_4^+ and 3.4–6.5 μmol g. dry wt.$^{-1}$ h^{-1} for NO_3^-. Half saturations constants were estimated in this investigation as well and have ranges of 5.1–19.4 μmol L^{-1} for NH_4^+ and 2.2–38.5 μmol L^{-1} for NO_3^-.

Turbidity is an important water column property in the Laguna Madre (See Fig. 25, Chap. IV). There is reasonable correlation between turbidity in the sampled transect in the Laguna Madre estuary and chlorophyll *a* concentrations (r^2 = 0.90, Chapter IV). Turbidity resulting from resuspension of sediments in shallow waters affects biological processes such as phytoplankton growth and nitrification. Particles relocated from the benthic environment can alter systems chemically through the desorption of adsorbed ions as well as the release of ions through interstitial water injection. Intact sediments focus ions from organic matter decomposition such as nutrients, DOC, and HS^- due to limited exchange with overlying waters.

Significant resuspension of recently settled algal cells has been observed in the San Antonio Bay Estuary (Macintyre and Cullen, 1996) as well as other estuaries (Stearns et al., 1987). In terms of nutrients, Fanning et al. (1982) concluded that resuspension of as little as 1 mm of the sediments in the coastal regions in the Northern Gulf of Mexico could initiate a 100 to 200% increase in water column productivity. A diurnal pattern of sediment resuspension was correlated in a 1977 study with surface wave activity and it was found that currents and internal waves were much less effective in increasing water column sediment concentrations than wind induced waves (Lund-Hansen et al., 1999). Forced functions describing natural phenomena have been utilized in other ecosystem modeling attempts when a daily oscillation in forcing factors was represented (Burd and Dunton, 2001; Klump and Martens, 1989).

Particles in semi-consolidated form (as sediments) are exposed to interstitial fluids with limited exchange and elevated concentrations of metabolic byproducts (i.e. NH_4^+, HPO_4^{-2}, etc.). High concentrations of dissolved ions in bulk solution shift adsorption/desorption equilibrium towards adsorption of ions onto particle surface. Adsorption continues until equilibrium, when adsorption site saturation is reached. Radical displacement of the particles to the water column with lower bulk ion concentration (compared to interstitial fluids) shifts the equilibrium towards desorption. The adsorption/desorption process can be simply represented as:

$$SA \xleftrightarrow{adsorption/desorption} S + A$$

where S represents the adsorption site, A is the adsorbate (bulk concentration) and SA is the adsorbed ion on the site. The predominant direction of the reaction is determined by the concentration of reactants and products. Adsorption of ions on particle surfaces can be described mathematically by the Langmuir isotherm which can be represented by:

$$\frac{[SA]}{Mass} = S_T\left[\frac{k_{ads}[A]}{1+k_{ads}[A]}\right] \qquad (12)$$

where *Mass* represents mass of particles, S_T is the maximum concentration of adsorption sites gm sediment^{-1}, and k_{ads} is an adsorption coefficient. Ion desorption is dependent on multiple parameters including resuspended sediment mass, particle surface coverage, and bulk solution (dissolved) concentration of the free ion of interest ($\mathrm{NH_4^+}$ here).

2.1 Model Description

Phytoplankton biomass, dissolved N and suspended solid concentration are the components tracked in this model system. A graphical representation of the model system is presented in Fig. 31. The participants represented by the boxes and the relationships between them are intended to simulate a shallow estuarine system with limited water volume exchange such as the Laguna Madre Estuary. The growth limiting nutrient in the Laguna Madre and in the model system is nitrogen available in the dissolved forms of NH_4^+ and NO_3^-. This aspect of the model is established through bioassay and water column measurements made in the Laguna Madre during this study (see discussion Chapter IV, Pennock et. al. 1999).

Essentially the model system describes the dynamics of the state variables in a volume averaged over the width of the estuary (10.836 km at the transect sampled in Chapter IV). Total volume of the model domain is defined by considering it as a strip across the estuary with constant depth outside the Intracoastal Waterway (average depth 1 m, transecting this part of the estuary in the center) combined with a deeper section (50 m in width) in the central region (depth 4 m). Salinity profiles taken during the monitoring period of Laguna Madre (described in Chapter IV) which generated the data for parameterization showed no vertical density stratification across the estuary. The model domain simulates an established transect approximately 15 km from the pass located in the southern extreme of the estuary at Port Isabel, which is far removed from the only freshwater input from the Arroyo Colorado over 20 km north. The model domain is assumed to be well mixed so that changes in water column nutrient and algal biomass concentrations in the defined model are governed by the dominant processes in the Laguna Madre.

Estuarine concentration of NH_4^+ is controlled by biological as well as sediment processes. Sources of NH_4^+ include diffusion from the sediments and release by grazers. Biological uptake by both phytoplankton and seagrass represent sinks. These sources and sinks are represented mathematically in the model prediction presented. In addition, there is

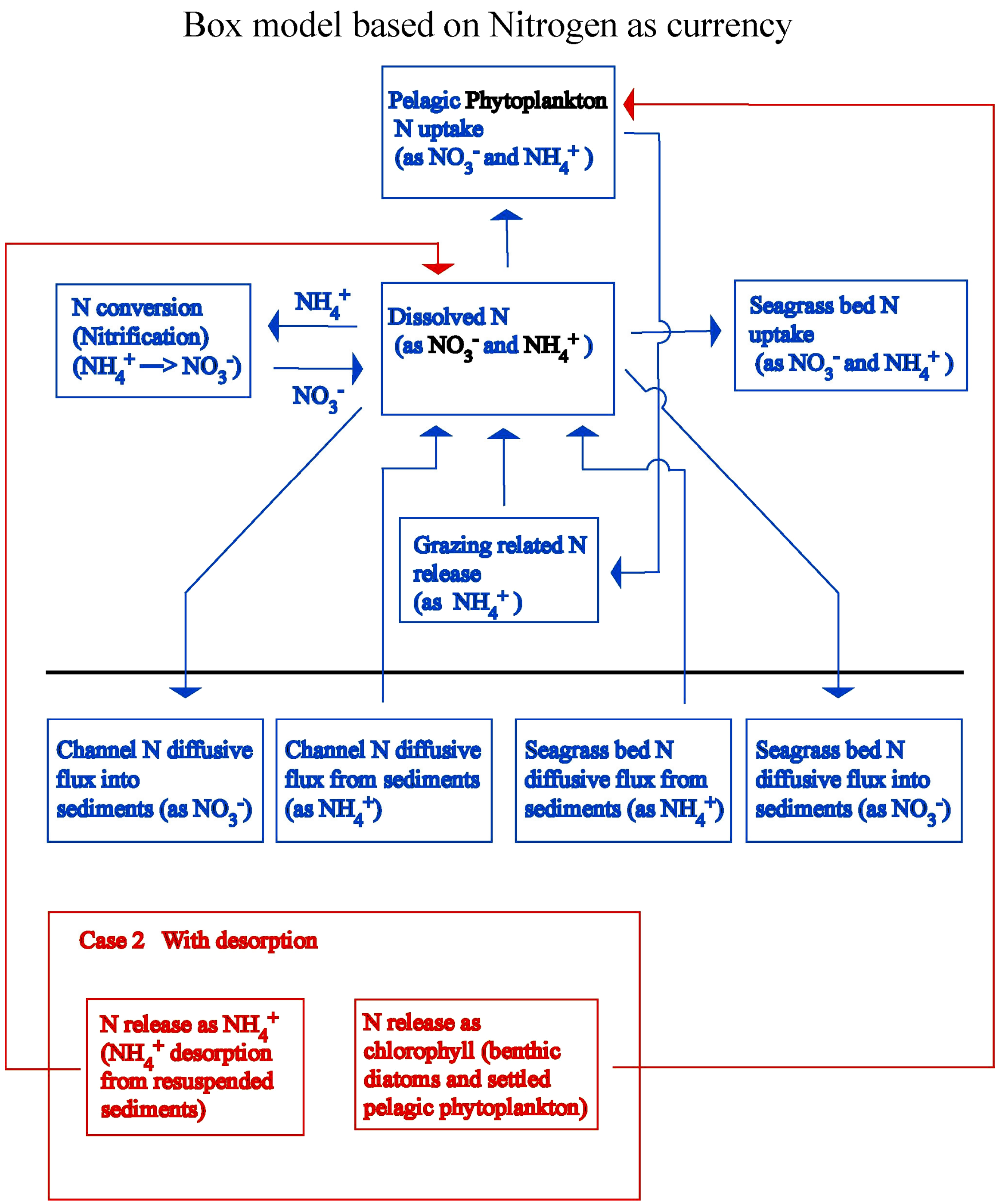


Fig. 31 Box description of the model approximation incorporating the measured parameters collected during the transect occupation. Blue represents the case 1 approximation not including resuspension of settled particles. Black labeled components are state variables. Red boxes and inputs represent the approximation including resuspension.

a term used to represent nitrification (conversion of NH_4^+ to NO_3^-) occurring in the water column. The importance of desorption of NH_4^+ from suspended particles as an input to the water column will be tested using imposed sediment resuspension rates. The model describing the three state variables can be modified to test the proposition that resuspension of particles is an important source of NH_4^+ and algal biomass to the Laguna Madre. Representation of resuspension of surficial sediments is accomplished through a vertical particle flux rate (R(t)) varied as a sinusoid. Particle removal (including phytoplankton) is accomplished with an imposed settling rate. This formulation imposes a diurnal periodicity to sediment resuspension and as a result, introduces periodic input of NH_4^+ and algal cells. Unfortunately the model will not include advection of dissolved and particulate materials. This is potentially a severe limitation considering the currents and winds in the Laguna Madre.

2.2 Model Equations

2.2.1 ***Phytoplankton Biomass (P).*** Symbol definitions are described in Table 11. All state variables are expressed in terms of nitrogen (µmol L^{-1}). The abundance of phytoplankton biomass is increased by nutrient-limited growth and lost to grazing and settling (Eqn. 13). Increase in phytoplankton nitrogen is governed by the specific growth rate (μ_{max}) considered here to be in the upper range of the true maximum growth rate for the resident phytoplankton community including the brown tide organism in the Laguna Madre estuary (0.028 h^{-1}). The growth rate is strongly influenced by a competitive relationship (NO_3^- vs. NH_4^+) describing uptake of dissolved inorganic nitrogen. Grazing and settling are

Table 11. Model Parameters.

Parameter	Description	Units		Ref.
State				
P	Phytoplankton	(μmol N L^{-1})		
C_{NH4}	Concentration of NH_4^+	(μmol N L^{-1})		
C_{NO3}	Concentration of NO_3^-	(μmol N L^{-1})		
Total				
	Width	m	10,900	
z	Depth	m	1	
I	Sediment-Water Interface Area	m^2	10,900	
T_{vol}	Total Volume	m^3	10,990	
Channel				
	Width	m	50	
I_{Ch}	Sediment-Water Interface Area	m^2	50	
F_{Ch}	Sediment NH_4^+ Flux	μmol m^{-2} h^{-1}	264(54)	This Study
D_{Ch}	Sediment NO_3^- Flux	μmol m^{-2} h^{-1}	-11.40	This Study
Seagrass				
	Width	m	10836	
I_{Sg}	Sediment-Water Interface Area	m^2	10836	
	Seagrass Coverage	%	70.5	Kaldy and Dunton (2000)
B_{Sg}	Biomass (*Thalassia testudinum*)	gm Dry Wt m^{-2}	119.0	Kaldy and Dunton (2000)
V_{NH4max}	Maximum Uptake of NH_4^+	μmol g^{-1} Dry Wt h^{-1}	16.50	Lee and Dunton (1999)
K_{NH4Sg}	Half Saturation for NH_4^+ Uptake	μmol L^{-1}	9.4	Lee and Dunton (1999)
V_{NO3max}	Maximum Uptake of NO_3^-	μmol g^{-1} Dry Wt h^{-1}	9.5	Lee and Dunton (1999)
K_{NO3Sg}	Half Saturation for NO_3^- Uptake	μmol L^{-1}	10	Lee and Dunton (1999)
F_{Sg}	Sediment NH_4^+ Flux	μmol m^{-2} h^{-1}	38.21	This Study
D_{Sg}	Sediment NO_3^- Flux	μmol m^{-2} h^{-1}	-9.67	This Study
Water Column				
k_{aNH4}	Half Saturation for Plankton NH_4^+ Uptake	μmol L^{-1}	3.3	Lomas et. al. (1996)
k_{aNO3}	Half Saturation for Plankton NO_3^- Uptake	μmol L^{-1}	2.14	Romeo and Fisher (1982)
μ_{max}	Plankton Maximum Specific Growth Rate	h^{-1}	0.028	Liu et al. (2001)
g	Plankton Predation Rate	h^{-1}	0.017	Buskey et al. (2000)
v	Settling velocity	cm h^{-1}	0.042	
E	NH_4^+ Excretion from Grazing	Fraction	0.3	Lehrter et al. (1999)
C_{chla}	Carbon/Chlorophyll	mg C mg Chl a^{-1}	40	Gallegos and Vant (1996)
V_{nitmax}	Community Nitrification	μmol m^{-2} h^{-1}	0.23	Berounsky and Nixon (1993)
k_{nit}	Half Saturation for Nitrification	μmol L^{-1}	1.21	Hunik et al. (1992)
Sediment Resuspension				
S_T	Maximum NH_4^+ Release	μmol gm^{-1}	20.2	Morin and Morse (2000)
k_{ads}	Half Saturation for NH_4^+ Release	μmol L^{-1}	2.1	Morin and Morse (2000)

both represented by constant specific loss rates taken from the literature, and are dependent only on the concentration of algal biomass (*P*).

The system is assumed to be nitrogen limited due to the size of the estuary and residence times estimated to be between 300 days to years. Growth on NO_3^- and NH_4^+ is described by a Monod type nutrient adsorption component (A) with substrate specific half saturation constant (k_{aNH4}, k_{aNO3}). This is a competitive inhibition formulation allowing for adjustment of the half-saturation constants (k_{aNH4}, k_{aNO3}) to describe the inhibition influence of NH_4^+.

The next two terms represent losses due to grazing (B) and settling (C). The loss to zooplankton grazing (*gP*) in the Eqn.13 is proportional to *P* and was taken from the growth and grazing investigation conducted by Buskey et al. in the Laguna Madre (2001). The loss of algal nitrogen through settling (*vP/z = sP)* is an average term derived from a settling rate of 1 m d^{-1}. The estuary has an average depth of 1 m resulting in a specific loss to settling of *s*=0.042 h^{-1} (=1 d^{-1}). Eqn. 15 gives the mathematical relationship representing the factors controlling the phytoplankton nitrogen concentration in the model.

$$\frac{dP}{dt} = \mu_{\max} P \left[\underbrace{\frac{\left(\frac{C_{NH_4}}{k_{aNH_4}}\right)}{1+\left(\frac{C_{NH_4}}{k_{aNH_4}}\right)+\left(\frac{C_{NO_3}}{k_{aNO_3}}\right)} + \frac{\left(\frac{C_{NO_3}}{k_{aNO_3}}\right)}{1+\left(\frac{C_{NO_3}}{k_{aNO_3}}\right)+\left(\frac{C_{NH_4}}{k_{aNH_4}}\right)}}_{\textbf{(A)}} \right] - \underbrace{gP}_{\textbf{(B)}} - \underbrace{\frac{vP}{z}}_{\textbf{(C)}} \tag{13}$$

The system of equations will be modified later to include an introduction of phytoplankton biomass (cells) through resuspension and desorption of NH_4^+ from resuspended sediments.

2.2.2 *Ammonium (C_{NH4}).* The concentration of NH_4^+ is increased through sediment flux, and excretion by grazers. Water column NH_4^+ is removed from the model through biological absorption by phytoplankton and seagrass, as well as by nitrification. The input flux rates (*F*) were measured for channel and seagrass sediments as described in the methods in Chapter IV (flow through core incubations) in the Lower Laguna Madre Estuary (Eqn. 14 D, E). These values are multiplied by the interface area (*I*) for each of the types of sediment (10,836 m^2 for seagrass and 50 m^2 for channel sediments). The rates are divided by the total volume (*T*) in the area described by the model. As has been described above, grazing release of NH_4^+ through inefficient consumption of algal material can impact dissolved concentrations. Returned nitrogen due to grazing is thus set at 30%, making grazing related dissolved nitrogen release comparable to NH_4^+ release from seagrass sediment flux in magnitude (F).

The remaining terms in Eqn. 14 are sinks for NH_4^+ in the system. The first sink represents phytoplankton uptake of NH_4^+ resulting in nitrogen transfer to the phytoplankton pool (G). The next sink is NH_4^+ uptake by seagrasses (H). A competitive inhibition formulation is used to describe dissolved nitrogen absorption for seagrass as well as for phytoplankton. Maximum seagrass NH_4^+ uptake rates (V_{Sg}) are averages of the ranges given in Lee and Dunton (1999). The half saturation constants (k_{Sg}) are adjustable within the range calculated by Lee and Dunton to determine an appropriate inhibition relationship between NH_4^+ and NO_3^-. The kinetic uptake values reported by Lee and Dunton are per unit dry weight for leaf biomass of seagrass. An average over the range is represented by (*B*) in the model and is multiplied by the uptake relationship to determine NH_4^+ removal per m^2. This quantity is then multiplied by the fraction of the sediment water interface covered by seagrass in the Lower Laguna Madre (70.5%, Quammen and Onuf, 1993). Total seagrass biomass and coverage are assumed constant.

The last term in the Eqn. 14 represents the conversion of NH_4^+ to NO_3^- through bacterial nitrification in the estuary. The process of ammonium oxidation is included as a saturation relationship with the maximum rate (V_{nitmax}) measured by Berounsky and Nixon (1993) and the half saturation constant (k_{nit}) being derived from the investigation of Hunik et al. (1992) on *Nitrosomonas europaea* (I).

$$\begin{aligned}\frac{dC_{NH_4}}{dt} = {} & \overset{\textbf{(D)}}{\left(\frac{F_{Ch} I_{Ch}}{T_{vol}}\right)} + \overset{\textbf{(E)}}{\left(\frac{F_{Sg} I_{Sg}}{T_{vol}}\right)} + \overset{\textbf{(F)}}{E(gP)} - \mu_{\max} P \overset{\textbf{(G)}}{\left[\frac{\left(\frac{C_{NH4}}{k_{aNH_4}}\right)}{1+\left(\frac{C_{NH4}}{k_{aNH_4}}\right)+\left(\frac{C_{NO_3}}{k_{aNO_3}}\right)}\right]} \\ & \underset{\textbf{(H)}}{-V_{Sg\max}\left[\frac{\left(\frac{C_{NH4}}{k_{SgNH_4}}\right)}{1+\left(\frac{C_{NH4}}{k_{SgNH_4}}\right)+\left(\frac{C_{NO3}}{k_{SgNO_3}}\right)}\right]\frac{B_{Sg} I_{Sg}}{T_{vol}}} \underset{\textbf{(I)}}{-V_{nit\max}\left[\frac{\frac{C_{NH4}}{k_{nit}}}{1+\frac{C_{NH4}}{k_{nit}}}\right]}\end{aligned} \tag{14}$$

Water column NH_4^+ concentration is also influenced by resuspension. Desorption of NH_4^+ from resuspended sediments introduces a potentially significant source of nitrogen to the water column in this shallow estuary. Desorption will be considered as the only input of nitrogen due to resuspension of surficial sediments while injection of porewater, an equally and possibly more significant input, will not be included.

2.2.3 ***Nitrate (*C_{NO3}*).*** Nitrate supplies an additional source of nitrogen to nutrient limited growth in the Laguna Madre estuary for phytoplankton and seagrass. This form of dissolved nitrogen is found in relatively low concentrations in the estuary (See Chapter IV), probably due to the importance of sediments in this shallow estuary. The equation describing the controlling factors associated with NO_3^- is presented below (Eqn. 15) and most of the terms have been described above for the sources and sinks in the representation. Rates of denitrification were calculated from the flow through core incubations as described above for the NH_4^+ flux rates. These rates are the result of direct measurements of nitrate uptake by the sedimiment cores chapter IV. It is important to keep in mind that the measurements are net measurements of nitrate change in the system and encompass all sedimentary processes influencing nitrate. This value is used to represent the net loss of nitrate to the sediments due to all involved processes not only denitrification. The values (D_{Ch}, D_{Sg}) were normalized to 1 m^2 and thus are multiplied by the appropriate interface value for either channel sediments or seagrass sediments. Water column nitrification represents the only source of NO_3^- to the volume defined by the box model. Terms for NO_3^- input and outputs have been described earlier. By mass balance considerations, the terms are: ammonium oxidation (J), denitrification in the seagrass bed and channel sediments (K, L), phytoplankton uptake (M), and seagrass uptake (N).

$$\begin{aligned}\frac{dC_{NO_3}}{dt} = {} & \overset{\textbf{(J)}}{V_{nit\max}\left[\frac{\frac{C_{NH_4}}{k_{nit}}}{1+\frac{C_{NH_4}}{k_{nit}}}\right]} - \overset{\textbf{(K)}}{\left(\frac{D_{Ch}I_{Ch}}{T_{vol}}\right)} - \overset{\textbf{(L)}}{\left(\frac{D_{Sg}I_{Sg}}{T_{vol}}\right)} - \overset{\textbf{(M)}}{\mu_{\max}P\left[\frac{\left(\frac{C_{NO_3}}{k_{aNO_3}}\right)}{1+\left(\frac{C_{NO_3}}{k_{aNO_3}}\right)+\left(\frac{C_{NH_4}}{k_{aNH_4}}\right)}\right]} \\ & \underset{\textbf{(N)}}{-V_{Sg\max}\left[\frac{\left(\frac{C_{NO_3}}{k_{Sg\,NO_3}}\right)}{1+\left(\frac{C_{NO_3}}{k_{SgNO_3}}\right)+\left(\frac{C_{NH_4}}{k_{SgNH_4}}\right)}\right]\frac{B_{Sg}I_{Sg}}{T_{vol}}}\end{aligned} \qquad (15)$$

Eqn. 15 is not directly influenced by the introduction of particles from the sediment, though NO_3^- is consumed by the sediments. However, introduction of NH_4^+ and algal N to the water column by resuspension acts as a nitrogen source and sink, indirectly effecting the NO_3^- concentration in the system.

2.3 Resuspension

This model was modified to test the effect of sediment resuspension and estimate the impact of desorbed NH_4^+ (from resuspended particles) and resuspended algal cells in the estuary. The term governing sediment particle introduction rate is:

$$R(t)\left[\text{mg L}^{-1}\text{ h}^{-1}\right] = 90 + \left(37.4 * \sin\left(\frac{t\pi}{12}\right)\right) \qquad (16)$$

where R is a time dependent resuspension rate (mg L^{-1} h^{-1}) that introduces a 24 hour cycle of resuspension into the system (Chapter IV). There is no mathematical derivation for this function, but it produces a resuspension rate averaging 90 mg L^{-1} h^{-1} and ranging between 52 and 128, generating sediment concentrations similar to the range observed during the data collection in Chapter IV. This flux rate defined by the function oscillates over a 24 hour period with amplitude of 37.4 mg L^{-1} h^{-1}. Resuspension is offset by particle sedimentation (vP/z). Settling is responsible for removal of algal biomass and particles from the water column at a rate of 1 d^{-1} (4.2 cm h^{-1}). This value can be compared to settling velocities for spheroid silica based particles. Particles of size 5µm, 50 µm and 100 µm will settle at rates of approximately 1.4, 11.1, and 27.0 cm h^{-1}. Coastal diatoms such as *Thallasiosira* generally reach diameters of between 50 and 100 µm, but are characterized by lower densities and generally exhibit mechanisms for sustaining suspension. Sediments in the Laguna Madre from both the channel and around seagrass beds display high < 63 µm fractions implying that these particles remain in the water column for hours after initial resuspension allowing for desorption of NH_4^+.

In this model system, resuspension adds algal N at a rate proportional to the sediment resuspension rate. This quantity is based on an estimated concentration of 500 mg chlorophyll *a* m^{-2} (Macintyre et al., 1996) in surficial sediments (5 mm). Chlorophyll concentration is converted to carbon using the conversion factor (C_{chla}) of 40 mg C mg chlorophyll a^{-1} (Gallegos and Vant, 1996). The Redfield ratio (Falkowski, 2000) is then utilized to calculate an algal concentration of chlorophyll *a* in nitrogen (µmol N mg^{-1}). This addition is made to Eqn. 13 as follows:

$$\frac{dP}{dt} = (A) - (B) - (C) + \boldsymbol{R(t)}\mathbf{*(0.00018}\ \boldsymbol{\mu mol\ Algal\ N/mg\ sediment}\mathbf{)} \qquad (17)$$

The addition of algal N follows the sinusoidal function described by Eqn. 16, but unlike NH_4^+ addition, the input of biomass is offset by the vertical flux (*vP/z*) back to the sediment environment. The observed range of suspended material concentration in the Laguna Madre during the period of sampling was approximately 50 to 140 mg L^{-1}. This range appears to be related to wind patterns in the area (see Fig. 23, Chap IV).

The diffusive flux of NH_4^+ to overlying waters is a significant source of nitrogen to this shallow negative estuary. Additionally, resuspension of surficial sediments could be important as a source of nitrogen through alteration in equilibrium relations between particle bound NH_4^+ and bulk solution concentration. The adsorption coefficient (k_{ads}) for the sediments and the maximum concentration of NH_4^+ bound to the particles was determined previously (Morin and Morse, 1999). In this work fast and slow release of NH_4^+ from resuspended sediments was measured in sediments collected from the channel and from grass beds in the Lower Laguna Madre. The NH_4^+ measured as fast release combined with the slow release per gram sediment is the maximum concentration (S_T) on the sediments.

Potential for NH_4^+ release in the model is described by the Langmuir relationship (Eqn. 12) and is governed by the bulk NH_4^+ concentration. Released NH_4^+ is the equilibrium-predicted difference between particle associated NH_4^+ (*SA*, as a function of bulk dissolved NH_4^+ concentration [*A*]) and the maximum value S_T. The equation describing NH_4^+ concentration becomes:

$$\frac{d\,C_{NH_4^+}}{dt} = (\mathrm{D}) + (\mathrm{E}) + (\mathrm{F}) - (\mathrm{G}) - (\mathrm{H}) - (\mathrm{I}) + S_T\left[1 - R(t)\left(\frac{k_{ads}\left[C_{NH4}\right]}{1 + k_{ads}\left[C_{NH4}\right]}\right)\right] \qquad (18)$$

Total release of NH_4^+ depends on the mass of particles resuspended in the water column. The desorption term is multiplied by the resuspension term (Eqn. 16) and added to the equation representing changes in the NH_4^+ concentration in the water column (Eqn. 14).

3. Results

Observational data and measured rates obtained from previous chapters and the current literature (see Table 11) were incorporated in the above model formulation to predict algal biomass and dissolved inorganic nitrogen (in the form of NH_4^+ and NO_3^-). Initial state variable concentrations will be set at 5.0 μmol L^{-1} NH_4^+, 0.5 μmol L^{-1} NO_3^-, and 7.0 μmol L^{-1} algal N. The model formulation will be presented in several configurations including an initial presentation of results using Eqns. 13, 14, and 15. The system will be shown to be stable, however the values for the state variables will not reflect observed values in the Laguna Madre. An additional source of N is introduced to the system next through constant sediment input. The addition of nitrogen will be through desorption of NH_4^+ from resuspended sediments and a sediment concentration dependent addition of algal N. Stable concentrations of algal biomass and dissolved N are established with the additional source of nitrogen. The constant input scenario will also be utilized to test the sensitivity of the model system to initial concentrations of phytoplankton biomass and NH_4^+. Model configuration will be further altered by introduction of sediments through a time varying sinusoidal function (Eqns. 15, 17 and 18). The two configurations including additional nitrogen will show that the system requires these inputs to sustain concentrations of the state variables at concentrations similar to observations and that sediment introduction with the time dependent function creates oscillating variability. Finally the oscillating function will be modified to include a relatively large pulse of nitrogen to the system to test stability and the effects of a large scale resuspension event adding only desorption related NH_4^+.

3.1 Model without Resuspension

The model will initially be presented without resuspension (Fig. 32). Starting concentrations of P, C_{NH4}, C_{NO3} are averages of measurements made in the Laguna Madre. In this configuration the concentration of algal N is controlled only by growth, grazing and settling. The initial rates for A, B, and C are 0.21, 0.25, and 0.63 μmol N L^{-1} h^{-1} with dissolved N concentration dependent growth rate of 0.014 h^{-1} Settling is the dominant removal term of the system, and controls the phytoplankton concentration by eliminating algal N rapidly from the system. Water column concentration of NH_4^+ also decreases rapidly, reaching a constant value soon after algal concentration stabilization. C_{NH4} is controlled by microbial nitrification, and consumption by phytoplankton and seagrass (0.045, 0.08, and 0.106 μmol N L^{-1} h^{-1} respectively), with input of 0.112 μmol N L^{-1} h^{-1}. Input is about equally controlled by water column favored diffusion and grazing-related excretion. While addition and removal of NH_4^+ related to phytoplankton uptake and grazing release is dependent on algal N, seagrass uptake is described by a constant rate and is dependent on the concentration of NH_4^+ only. Sediment diffusion contributes NH_4^+ to the system at rates unrelated to any of the state variables. These components of the C_{NH4} equation supply a stabilizing influence on the system. With the reduction of biomass from

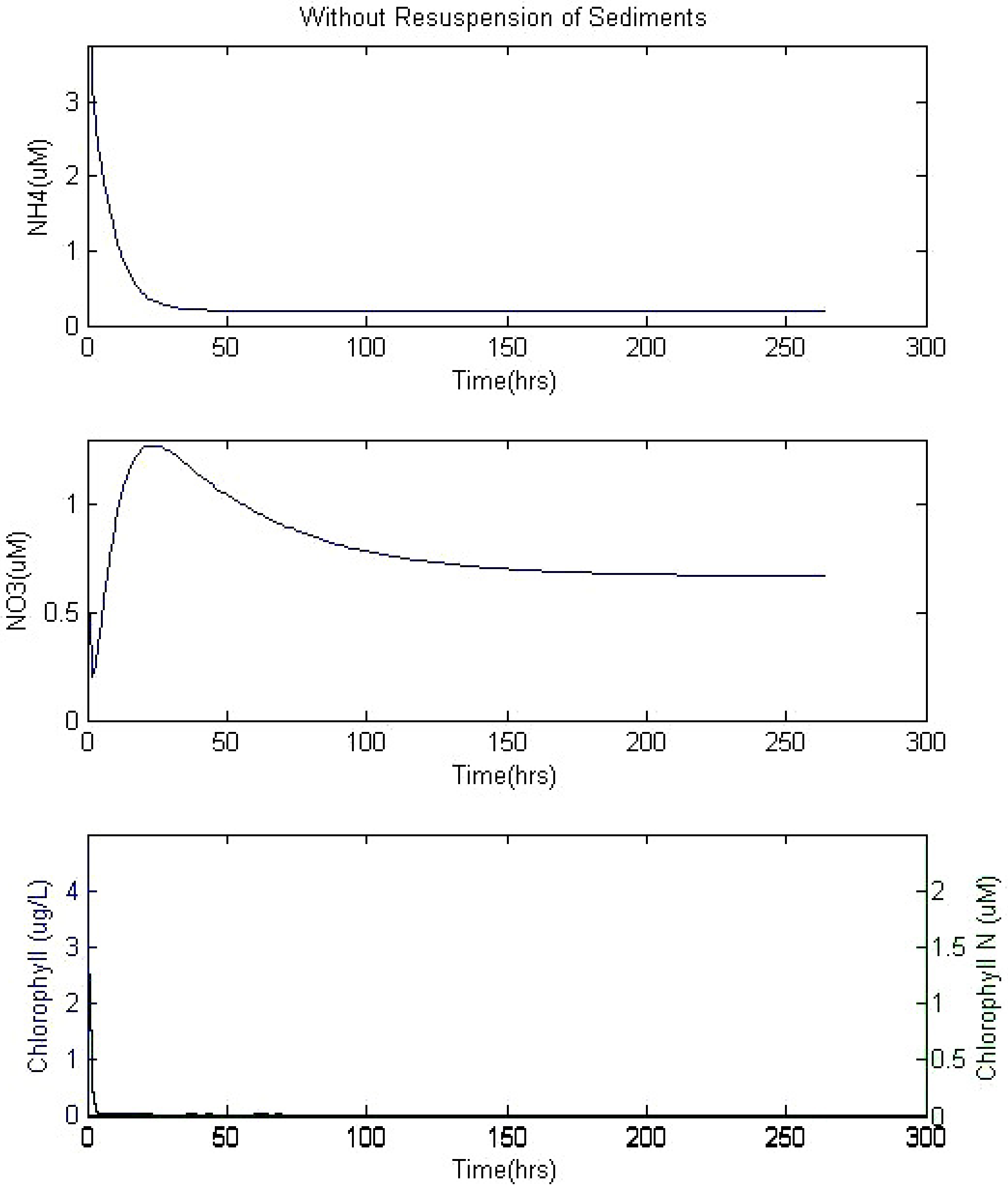


Fig. 32 Model approximation of phytoplankton and nutrient concentrations without resuspension of estuarine sediments.

the system, return of dissolved N through grazing-related excretion declines to 0.003 μmol N L^{-1} h^{-1} Absorption in early stages by phytoplankton and throughout by seagrass, and conversion of NH_4^+ to NO_3^- maintain very low levels of dissolved NH_4^+ in the system (approximately 0.2 μmol L^{-1}).

There is an initial decrease in NO_3^- concentration from algal uptake, followed by a significant increase as sediment-derived NH_4^+ is oxidized and algal N is removed from the system. Stable NO_3^- concentrations are observed at the highest concentration they will reach for all configurations of the model equations. Low concentrations of NH_4^+ in the system disable NH_4^+-induced inhibition of NO_3^- uptake by both phytoplankton and seagrasses. As with NH_4^+, constant consumption of NO_3^- occurring through NO_3^- dependent uptake (seagrass) and NH_4^+ concentration dependent nitrification, act to stabilize water column concentrations. At the stable NO_3^- and NH_4^+ concentrations reached in the simulation, dissolved nitrogen dependent μ_{max} for phytoplankton growth is reduced to 0.003 h^{-1}.

The absence of phytoplankton biomass in the water column significantly affects dissolved nutrients both as sink and as source. Phytoplankton biomass is lost from the system through grazing and settling, and added through growth. Without additional inputs, the sinks rapidly reduce the standing stock of phytoplankton. In simulations with a settling rate half the first value, phytoplankton and nutrient behave similarly, but phytoplankton take longer to reach very low stable concentrations. Further reduction (half again, 0.01 h^{-1}) of the settling rate resulted in phytoplankton concentrations sustained even longer, lasting through the first 50 hours, but ultimately declining to a stable low value. The slower decline of phytoplankton affects the dissolved inorganic nitrogen concentrations as well. When the settling rate is reduced by half, a reduction in $C_{NO_3^-}$ is observed from approximately 1.2 μmol L^{-1} to approximately 0.8 μmol L^{-1}. A similar reduction is observed in the $C_{NH_4^+}$. This reduction results in a phytoplankton μ_{max} of 0.002 h^{-1}. In each case the simulation eventually reached unchanging, very low concentrations reflecting the constant rates of grazing and settling for algal biomass and sediment diffusion and biological uptake for the dissolved inorganic concentrations.

3.2 Model with Constant Resuspension

Sediment resuspension was introduced at several constant rates (140, 90, and 45 mg L^{-1} h^{-1}). Results from the three rates are displayed in Fig. 33 . Constant input of sediment at 140 and 90 mg L^{-1} h^{-1} allow for sustained NH_4^+ and algal biomass concentrations in the system similar to concentrations observed in the Laguna Madre during the collection of monitoring data (Chap IV). At 140 mg L^{-1} h^{-1}, steady state NH_4^+ concentration is 2.7 μmol L^{-1} and algal biomass is 3.2 μg L^{-1} (1.6 μmol L^{-1}). Stable NH_4^+ concentration at the 90 mg sediment L^{-1} h^{-1} reaches 2.4 μmol L^{-1} and the corresponding algal biomass concentration is approximately 2.3 μg L^{-1} (1.0 μmol N L^{-1}).Calculations of desorption rate using the Langmuir formulation with the model constants results in NH_4^+ input of 0.040 μmol L^{-1} h^{-1} when sediment is added at the highest rate. At 90 mg L^{-1} h^{-1}, NH_4^+ is added at 0.025 μmol L^{-1} h^{-1} and at 45 mg L^{-1} h^{-1} the NH_4^+ the addition rate is 0.014. Desorption of NH_4^+ from resuspended sediments results in addition rates that are comparable to excretion and to the combined effect of water column favored diffusion from Laguna Madre seagrass and

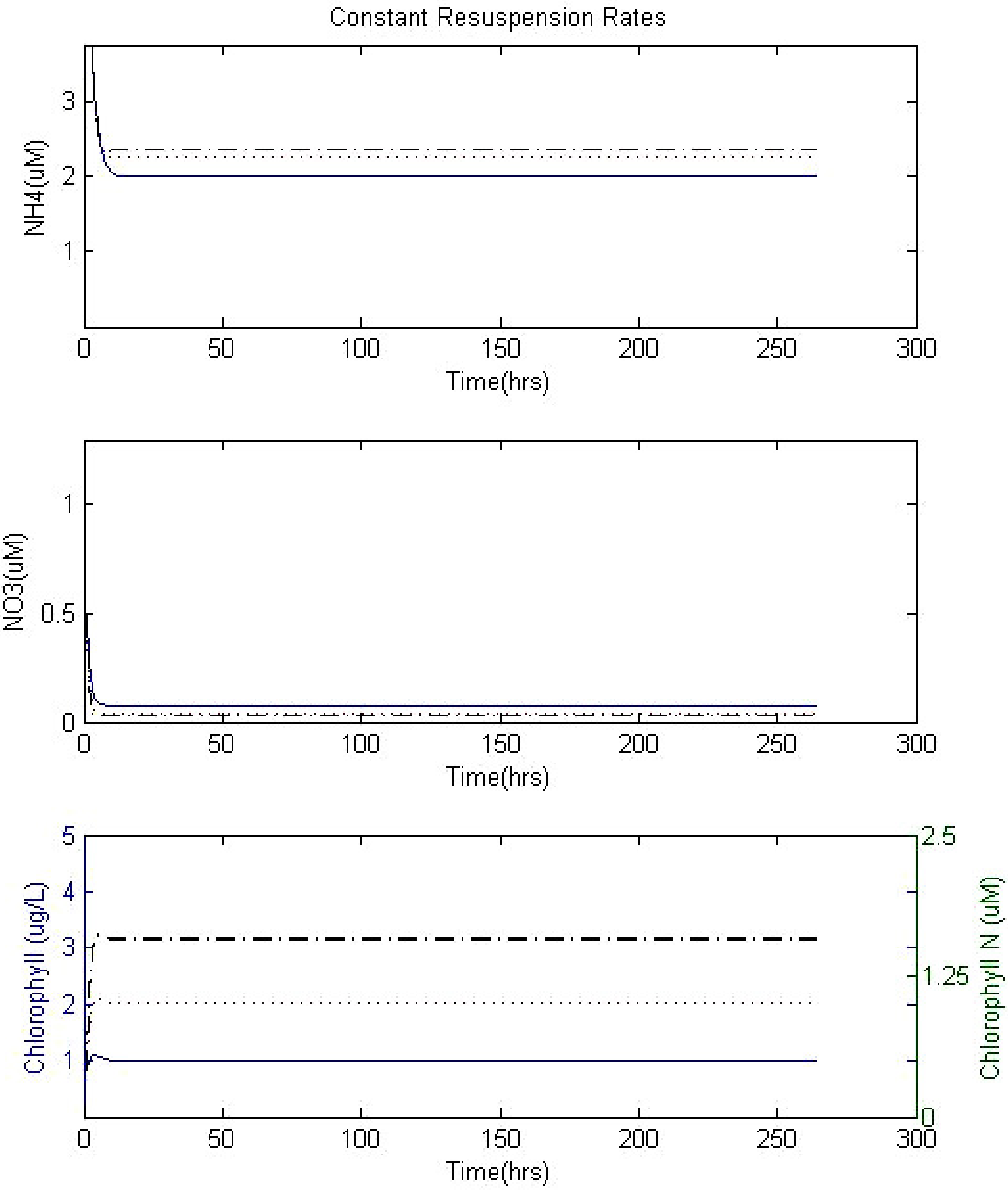


Fig. 33 State variable concentrations maintained when constant input of sediments is incorporated into the system. Solid lines represent 40 mg L^{-1} h^{-1}, dotted lines represent 90 mg L^{-1} h^{-1}, and dash dotted lines represent 140 mg L^{-1} h^{-1}.

channel sediments.

For stable concentrations to exist in the system, offsetting input and consumption rates must exist. The addition of algal N at the 140 mg addition rate is approximately 0.066 µmol N L^{-1} h^{-1} and at 90 mg sediment the addition rate is approximately 0.043 µmol N L^{-1} h^{-1}. Contribution of phytoplankton due to the growth term (A, Eqn. 13) at the stable algal N concentrations amounts to 0.022 and 0.016 µmol N L^{-1} h^{-1} (μ_{max} * P). Input of phytoplankton biomass through resuspension and growth exactly offset loss rates due to settling and grazing (0.088 and 0.059 µmol N L^{-1} h^{-1}).

It is interesting that a 35 % decrease in sediment addition to the system results in only a small decrease in the steady state NH_4^+ (from 2.4 to 2.2 µmol L^{-1}) but the reduction in algal N concentration is proportional to the change in input (3.2 to 2.3 µg L^{-1}, 1.61 to 1.16 µmol L^{-1}). The difference illustrates the importance of settling (and resuspension) to the system. While algal biomass is removed from the system through settling, NH_4^+ is not. This indicates that the reduction in rate of resuspension-derived NH_4^+ desorption is compensated by a reduction in biomass resulting in less removal of NH_4^+ through biological adsorption. Comparison of the magnitude of these numbers implies that while growth is important, settling on the short term controls variability.

3.3 Sensitivity to Initial Conditions

The model system appears to be very stable in a constant sediment input configuration (90 mg L^{-1} h^{-1}). In order to test the reliance of this stability on initial concentrations of NH_4^+ and algal N, starting values were varied over a reasonable range.

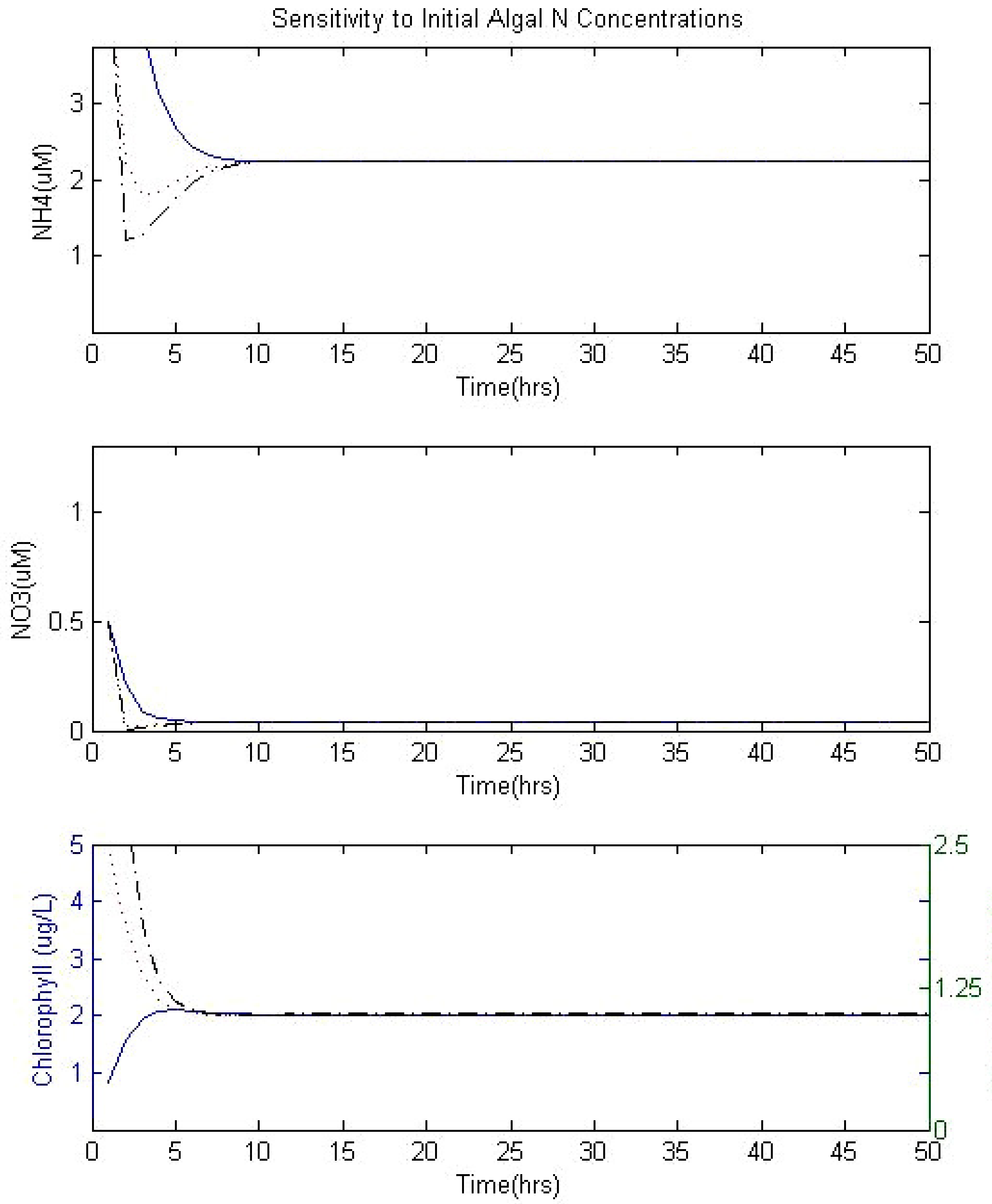


Fig. 34 Sensitivity determination of model system to varying initial concentration of algal N. Initial algal concentrations ranging between 1 μmol L^{-1} to 20 μmol L^{-1} N were tested utilizing the constant input configuration at 90 mg L^{-1} h^{-1} (solid line = 1 μmol L^{-1}, dotted line = 5.0 μmol L^{-1} and the dash dotted line = 10.0 μmol L^{-1})

When the model system is tested with initial NH_4^+ concentrations varying between 1.0 to 10.0 μmol L^{-1}, no change in final concentration was observed. Small changes in the first 10 hours of the test were observed, but over the duration of the model run, initial concentrations of NH_4^+ had no effect. This is most likely due to the stabilizing influence of seagrass uptake and nitrification which act as concentration dependent sinks to the NH_4^+ pool.

Initial algal concentrations had little influence on final concentrations as well, though the alteration in behavior in the first 10 hours was more pronounced. The predicted concentrations of algal N and dissolved inorganic N in the system are plotted in Fig. 34 for the range of initial concentrations tested 1.0 to 20.0 μg L^{-1} (0.5 to 10.0 μmol L^{-1}). The concentration of phytoplankton in the system reflects the results observed in the constant resuspension case, but approach the stable concentration slightly later. NO_3^- and NH_4^+ concentrations dip more rapidly depending on the initial concentration of algal N, but reach the stable concentration observed for constant input through sediment resuspension. Algal N in the water column both contributes and removes NH_4^+ from the system. At the highest test case (10 μmol L^{-1} N) consumption is greater amounting to a gross phytoplankton dependent NH_4^+ removal rate of 0.11 μmol L^{-1} h^{-1}.

3.4 Model with Oscillating Resuspension

When resuspension of bottom materials is included in the model system through the time dependent resuspension function (Eqn. 16, Fig. 35), there is a regular increase and decrease in the water column concentrations similar to the function describing resuspension (Fig. 36). Phytoplankton concentrations range from less than 2.0 μg L^{-1} to more than 4.0 μg

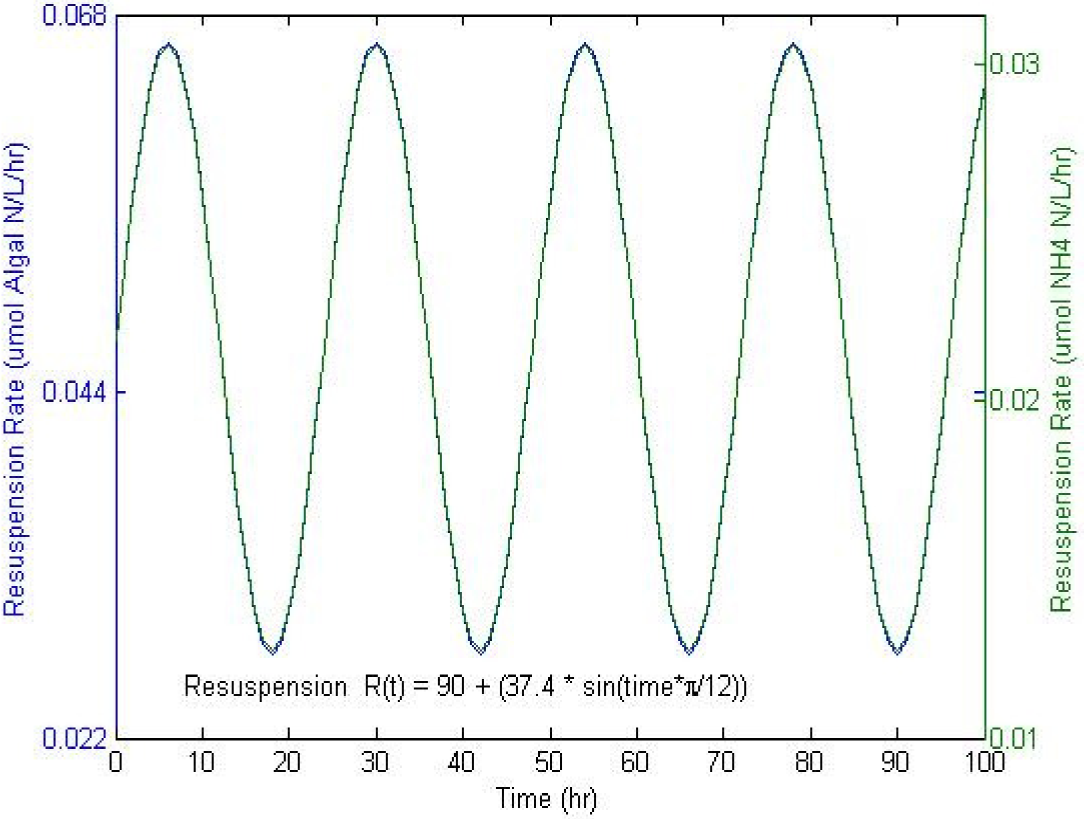


Fig. 35 The periodic function describes the rate of reintroduction of chlorophyll nitrogen and NH_4^+ through sediment resuspension. The function oscillates over a 24 hour cycle, reflecting the daily pattern of wind and resuspension in the Lower Laguna Madre during the summer.

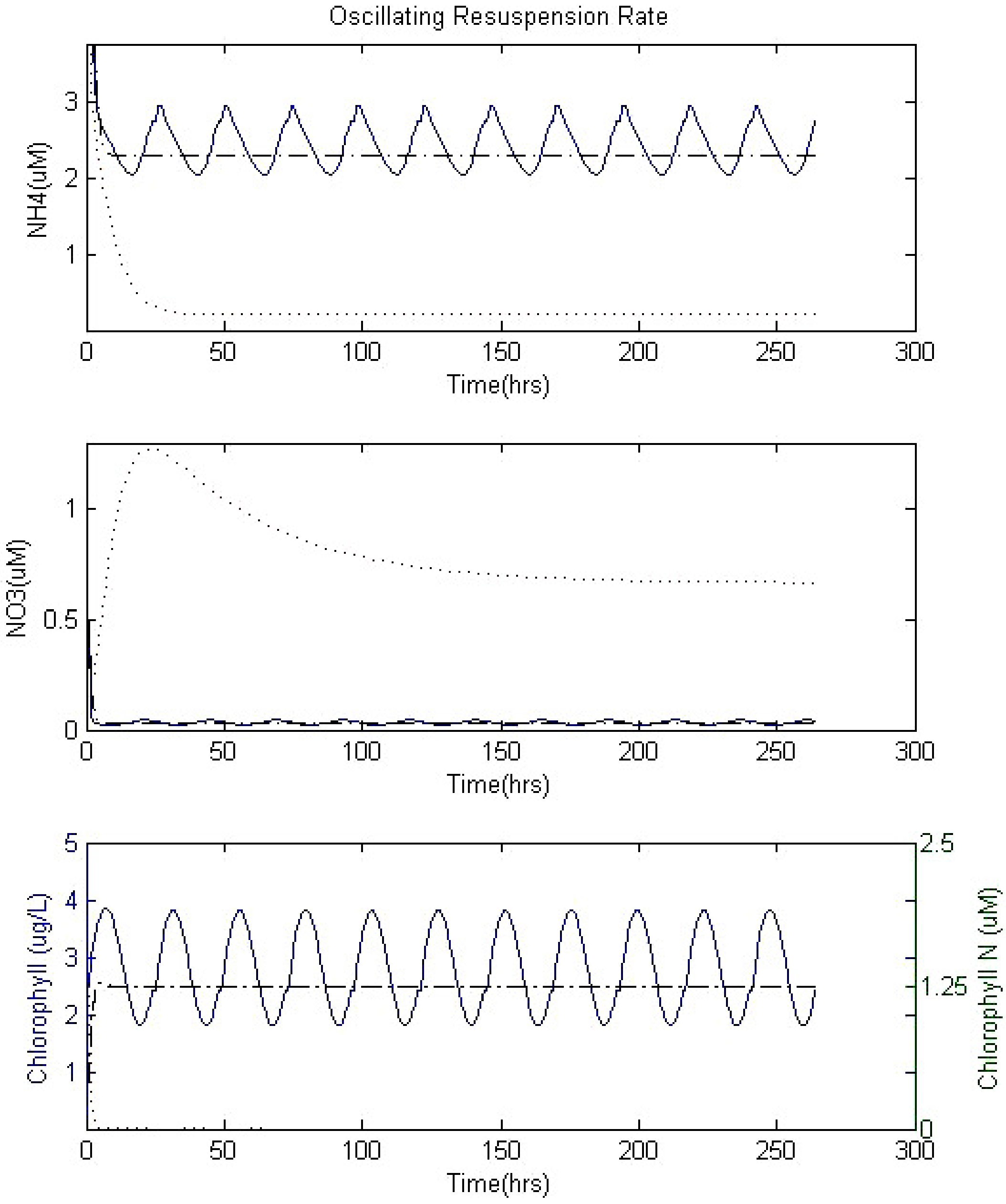


Fig. 36 Model prediction of dissolved N and algal N including the time forced resuspension function introducing nitrogen as chlorophyll N and dissolved N (NH_4^+) through sediment resuspension.

L^{-1} (1.0 to 2.0 µmol L^{-1}; For comparison see Fig. 24, Chapter IV). Algal biomass in the graph at the bottom of Fig. 36 has been converted to µg L^{-1} algal N from biomass using the ratios described above in order to make comparisons to observational data presented in Chapter IV. Algal biomass concentrations appear to reach maximum values following the peaks in the two inorganic nitrogen components implying inorganic nitrogen uptake, incorporation and growth. Dissolved inorganic nitrogen shows dependence on the concentration of algal N through a peak and rapid reduction once algal N concentration begins to increase. NO_3^- concentration peaks and begins reduction prior to that of NH_4^+ due to the inhibition relationship in the model formulation (Eqn 14, (A)) and the fact that resuspension does not directly contribute to this state variable. The reduction in inorganic nitrogen concentration initiated by sustained phytoplankton then contributes to a reduction in the phytoplankton growth rate. At this point settling is not offset by resuspension and once again becomes important, rapidly reducing the algal N concentration.

The average value of NO_3^- is significantly lower than the concentration reached in model runs without resuspension. This is reasonable given the increased algal standing stock, while input from NH_4^+ concentration dependent nitrification does not increase over initial conditions. At these increased dissolved nitrogen concentrations the algal growth rate increases to 0.012 d^{-1}, an approximate four fold increase over the configuration with no resuspension. Increased algal growth is primarily due to the increased input of NH_4^+ through resuspension and grazing release (resuspension 0.024 µmol L^{-1} h^{-1} and grazing release of 0.020 µmol L^{-1} h^{-1}; Sediment contribution through diffusion alone only contributes 0.040 µmol L^{-1} h^{-1}). This contributes to the higher oscillation of the algal

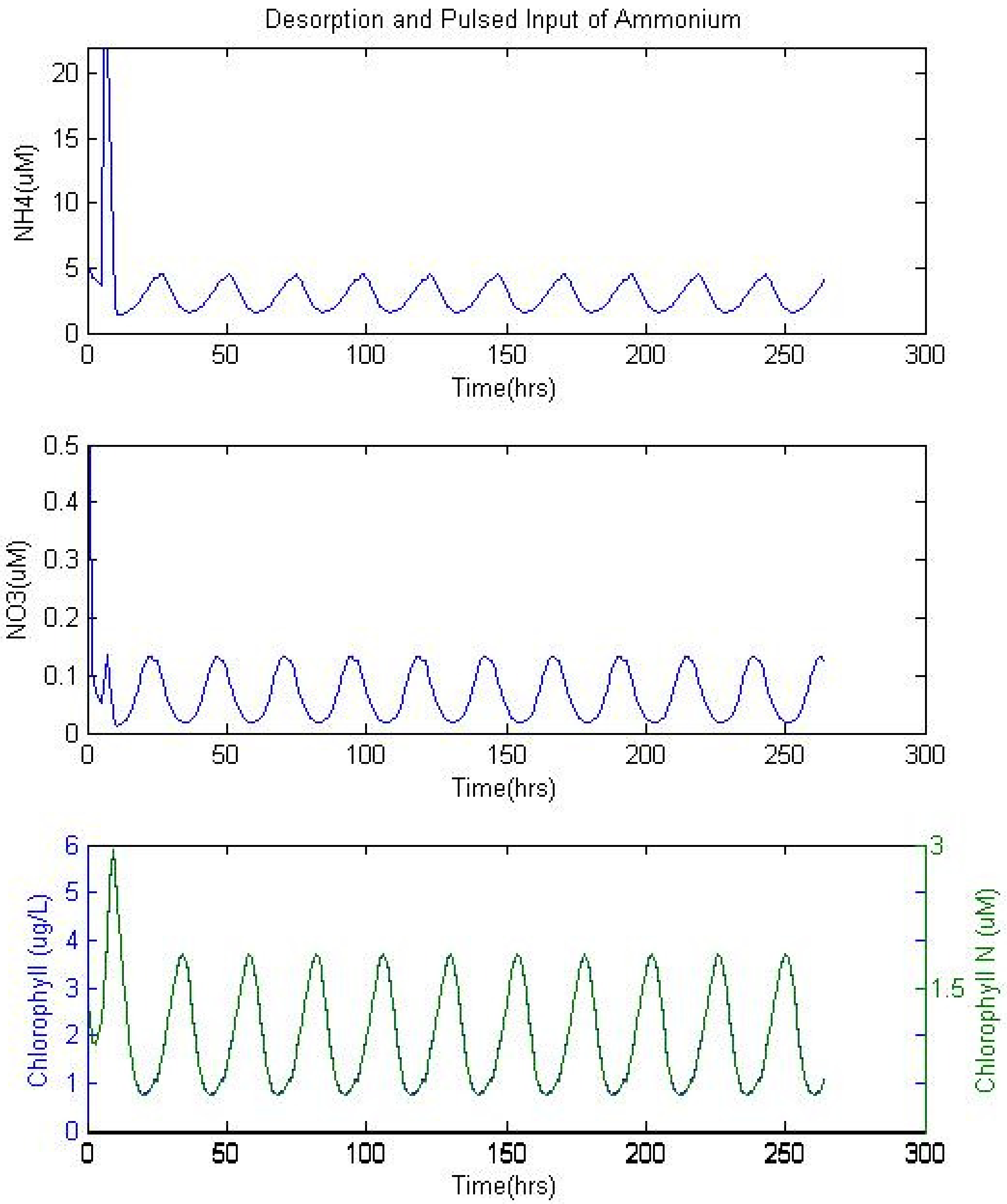


Fig. 37 Model prediction of state variables from simulations including resuspension and a pulsed input (over 12 hours) of sediment with concomitant release of NH_4^+ and algal N.

biomass value along with the 0.043 μmol L^{-1} h^{-1} biomass introduced through sediment resuspension (algal N and NH_4^+ input estimates for the average input at 90 mg L^{-1} hr^{-1}). Though resuspension itself is not responsible for sustained concentrations of the state variables in the system, it does introduce a time dependent oscillation. This type of variability in the state variables is more realistic in terms of reflecting field observations, but the system itself appears to respond reasonably (in terms of concentration ranges) to a constant input of sediments as well.

The model was intended to represent an average of the state variables over the transect in the Lower Laguna Madre. All concentrations varied regularly over defined ranges through the 250 h time period when time varying resuspension of algal cells and NH_4^+ was included. Desorption of NH_4^+ from resuspended sediments supplies a significant source of dissolved nitrogen for growth, but it appears that regular reintroduction of algal biomass is equally important to maintaining water column algal communities in the model. In addition, NH_4^+ returned to the system through grazing, also dependent on resuspension of algal cells, appears to supply dissolved nitrogen at a rate comparable to desorption. The entire system seemed to be relatively insensitive to initial concentrations. Altering these beginning values resulted in rapid establishment of regular variation over the presented ranges when resuspension is included or excluded.

3.5 Pulsed Sediment Input

The initial impetus for the project leading to this dissertation involved the determination of dredging impact on the Lower Laguna Madre. Relocation of channel sediments due to dredging activity rapidly increases suspended solids concentration in the water column resulting in a localized plume. Extremely high quantities of absorbed NH_4^+ have been observed in channel sediments with potential for significant alterations in water column concentrations (See Chapter II). In the estuary this would result in a pulse of nitrogen delivered to the system. An attempt to simulate a localized available nitrogen pulse was accomplished in the model essentially adding approximately 2500 mg L^{-1} h^{-1} of sediment to the water column over a 12 hour period. This would result in the input of approximately 1.1 μmol L^{-1} h^{-1} of NH_4^+ to the water column. Algal N is added with the pulse as has been the case for previous resuspension, at a rate of approximately 1.0 μmol L^{-1} h^{-1}. Fig. 37 displays the results of this simulation. The pulse in NH_4^+ concentration is seen in the first 12 hours of the simulation and the increase is reflected in both the water column nitrate and algal biomass state variables. The increase in NH_4^+ is observed to rapidly stimulate increased algal biomass, affecting the first cycle of resuspension, but essentially disappears after the first 24 hours. This is due to the offsetting influence of settling which limits the peak of algal N concentration and again rapidly reduces the algal N concentration to stable oscillating values. This type of rapid increase in phytoplankton biomass has been observed elsewhere (see Yeager, 2005) and was observed in this work during bioassay incubations (see Chapter IV). The model is strongly influenced by resuspension and settling which essentially allows for desorption of NH_4^+ with rapid elimination through algal biomass uptake. The results would suggest that the system described by the model is strongly influenced by the resuspension cycle and settling.

4. Discussion

Model predictions utilizing the original configuration of the system of equations with parameters both measured and taken from published reports indicates that NH_4^+ and algal biomass cannot be maintained in the system without an additional input of N. Inclusion of inorganic nutrient inputs in two configurations of the presented model system (constant and oscillating resuspension) produced varying outcomes in state variable concentrations. Constant introduction of sediment to the system of equation with corresponding desorption related NH_4^+ release and sediment concentration dependent input of algal N results in more reasonable sustained state variable concentrations. It was observed that algal N was more sensitive to alteration of the constant rate of sediment input than NH_4^+. This is attributed to the importance of settling in the system which is also primarily responsible for the elimination of algal N in the initial configuration without resuspension. When the system is configured with time varying introduction of sediments, NH_4^+, and algal N, sustained state variable values are also observed and oscillate around the values established at the 90 mg L^{-1} h^{-1} rate which reflects the average introduction rate established by Eqn. 16.

Concentrations of NO_3^- and NH_4^+ in the model runs including periodic resuspension oscillate regularly following the resuspension function (Eqn. 16) over relatively small ranges. This temporal variation in a cross transect water sampling would be difficult to identify given the possible introduction of error through acquisition and analysis and implies a close dependence on the parameterization of the model. Variation in the chlorophyll *a* concentration measured during the monitoring of the transect in the Lower Laguna Madre (displayed in Fig. 28, Chapter IV) for one central station ranged over approximately 12 μg L^-

^{1}. Conversely, variation at the transect extremes was much less (over approximately 2 μg L^{-1} at the east extreme and 5 μg L^{-1} at the west). Water column NH_4^+ concentrations observed during the monitoring period ranged over 30 μmol L^{-1} at the central station while transect extreme variations were as small as 2 μmol L^{-1}. The model NH_4^+ concentration varied by 2 μmol L^{-1} during the model system run, closer in behavior to the extreme stations.

The extreme ranges of values observed during the monitoring period were not seen in the model output. It has been stated that given the assumption of homogenous mixing in the system, values reflecting the extremes in the concentrations observed would not be expected. However model output more closely reflected observations at the farthest east and west stations located over the seagrass beds. This quite possibly is due to the assumption of an average value of algal biomass concentration in the surface sediments susceptible to resuspension. The channel structure being several meters deeper than the majority of the estuary probably acts as a sediment trap. Seagrasses also act to trap water column detritus but resuspension from the seagrass environment would probably be more difficult. This would imply a variable representation of phytoplankton biomass in the sediments dependent on the environment from which it was resuspended. This variation is not represented in the model.

A single growth maximum for the phytoplankton community was also employed in the model, supplying a rate dependent on one measurement. It would be unreasonable to assume that only one species of phytoplankton and one defined growth rate could govern primary productivity in the water column in the Lower Laguna Madre. This assumption was made to simplify the model system such that the effect of resuspension could be tested in a relatively constant background. The actual water column environment is much more complicated with species specific growth rates varying as a function of light, predation and nutrient concentration and relative ratio (i.e. N:P, Deyoe et. al., 2007). In addition rapid alterations in nutrient concentration and ratios can initiate relatively rapid responses in the phytoplankton community, selecting for specific species proliferation. One regime of phytoplankton growth and primary productivity found to be extremely important to shallow estuaries is found in the benthic environment (Macintyre et al., 1996). In the model presented here the formulation only allows for primary productivity or phytoplankton growth while the cells are resuspended. Given the depth of the estuary it is reasonable to assume that the benthic environment is exposed to euphotic conditions during much of the day. This would allow for a large increase in productivity and would be consistent with the assumption of photo competence upon resuspension.

Phytoplankton cells taken out of the water column system through settling are also assumed not to absorb dissolved nitrogen from the water column. The lack of resuspension of settled particles in the model system is observed to remove two potentially important sources of NH_4^+ to the system (grazing release and desorption). In addition the removal of suspended cells removes a sink for NO_3^-. Concentrations ranging around 0.1 μmol L^{-1} are maintained in the water column when resuspension is included in the model prediction results. When this sink is diminished, NO_3^- concentrations increase to values exceeding 0.8 μmol L^{-1}. In the model run cases excluding resuspension, seagrass uptake and sediment denitrification are the controlling sinks to the NO_3^- variable. Since these parameters have been set up as non-varying rates, the only factor governing the rate of NO_3^- removal in the water column is the concentration of NO_3^- itself. This allows for the establishment of a very constant concentration. Most biological processes operate contrary to this arrangement, allowing for physical forcing to introduce perturbation in the system controls.

Pulsed input of sediment with concurrent rapid input of algal biomass and NH_4^+ impacted the model system by rapidly increasing the state variables over one period of the sinusoidal function. The system was not affected by the pulse however in the long term. The pulse of available nitrogen and algal biomass was rapidly removed from the system, as would be the case when an episodic event resulted in localized increases in nutrients and particles as well as increasing gross sedimentation. The response of the system to the resuspension event would be greatly dependent on the subsequent water column concentration of sediment as well as the period over which the particles remained suspended. In laboratory experiments, the release of NH_4^+ was observed to increase over a period of sustained resuspension (Fast vs. Slow release, Chapter II). This highlights a weakness of this system in that it was parameterized with average values and somewhat adjusted (i.e. inorganic nitrogen concentration dependent inhibition growth rate determination) values to establish a stable system which could be tested.

An average value of input through sediment diffusion both from the seagrasses and the channel was utilized to establish a stable system. Average values were also utilized in terms of nutrient adsorption, growth rate and grazing related return of nitrogen for the system. These values were also observed to be extremely important determinants to the state variable interactions in the simulations. The model was intended as an integration of field measurements with current understanding of biochemical and desorption phenomena as an exercise to further elucidate the complex interactions in estuarine systems.

The Laguna Madre estuary is an extremely productive ecosystem considering the seagrass and macrophyte populations that exist. In addition the estuary has sustained a virtual monoculture of the brown tide organism for a number of years (cell counts approximately $1\mathrm{x}10^8$ ml^{-1} (Buskey et al., 2001)). The morphology of the estuary creates a low turnover, high recycling environment where nitrogen nutritional requirements must be derived from local sources. Sediments in estuarine systems are well established as regions of rapid nutrient regeneration, and have been established as primary to secondary sources of nitrogen driving productivity. The Laguna Madre is located in the lower region of Texas where topography is almost non-existent. Diurnal wind patterns have been observed in this region and are known to interact with the shallow environment to produce water column turbidity from sediment resuspension. Model predictions generated from the presented mathematical formulations indicate nitrogen release from resuspended sediments can sustain detectable levels of chlorophyll *a* and dissolved inorganic nitrogen. Resuspension of algal cells also allows for grazing release of NH_4^+ to the water column enhancing the effect of resuspension.

When the formulation is run without resuspension, predictions of algal biomass and NH_4^+ concentration reach undetectable levels within 50 hours of the model start. This conclusion is contrary to observational data presented in Chapter IV of this document. The results presented here indicate that observations in the estuary are more closely approximated when a resuspension function is included (given the limitations of utilizing average values for model parameterization) supplying a daily input of nitrogen through desorbed NH_4^+ and algal biomass. Of course the model is a simple representation of a very complicated system, but it has been shown through the model that the inclusion of resuspension has the potential to sustain nitrogen concentrations given the defined parameters of the model system.

CHAPTER VI

SUMMARY OF CONCLUSIONS

Prevailing wisdom is that nutrients supply in marine ecosystems is important in controlling primary production. Primary productivity in coastal marine ecosystems generally greatly exceeds that of the open oceans due to the proximity to continents and the dissolved nutrients delivered through rivers, ground waters and precipitation runoff. Dissolved nutrients essential for biological productivity are delivered to marine systems through this hydrologic cycle. Coastal systems also act as filters or processing zones attenuating much of the nutrients transported through the cycling of elements (Trimmer et al., 2000; Trimmer et al., 1998; Satula et al., 2004). In these studies, sediments were found to be the primary location where much of the organic matter produced in the coastal system and delivered from outside is processed.

The work presented in this dissertation focuses on NH_4^+ in marine sediments and attempts to elucidate some of the specific pathways and processes affecting NH_4^+ in coastal marine regions. From the observations obtained during the research and monitoring covered in this dissertation the following general conclusions can be drawn:

1. Dredging Impact Study

There is potential for significant release of NH_4^+ after initial resuspension of channel sediments. This conclusion resulted from resuspension experiments conducted with site sediment and subsequent monitoring of bulk NH_4^+ release over time. This was also supported by observations of pore water and fast NH_4^+ release during a dredging event. In 1989 approximately 318,000 m^3 of sediment were relocated from the Port Mansfield region. This movement could have released up to 46 metric tons of NH_4^+ over the two months of dredging. Such an input is significant compared to a monthly input of approximately 80 metric tons of NH_4^+ from sediment flux.

Corp of Engineer (COE) resuspension methodology introduces error in the estimation of potential release because of the use of very high sediment to solution ratios (represented in saturation portion of desorption isotherms). In addition, possible volatilization loss of NH_4^+ due to bubbling aeration of resuspension combined with the pH of resuspension solution may result in underestimation of potential release.

A new method for determining exchangeable NH_4^+ overcomes problems associated with single extractions of sediments (previously presented by (Laima, 1992)). The method is a multiple extraction procedure which shows that up to 75% of exchangeable NH_4^+ could be overlooked with a single extraction and that up to 50% could be missed with two extractions only.

2. Redox Manipulation of Resuspension Media

Reducing (anoxic) resuspension conditions affect cation (NH_4^+) adsorption behavior as was indicated by NH_4^+ solution concentration changes and particle associated exchangeable concentrations. Bulk NH_4^+ concentrations measured throughout resuspension showed saturation behavior but were difficult to interpret. Particle-associated or exchangeable concentrations showed consistently more adsorption in reducing conditions.

Alterations in adsorption behavior can be expressed in constant values associated with specific isotherm descriptions of NH_4^+ adsorption. When these experimentally determined constants are incorporated in models and utilized to predict measured exchangeable values, those determined in reducing conditions consistently fit observations more accurately.

Results were consistent between the Lower Laguna Madre and Gulf of Mexico. Analysis of K* revealed that the values of the partition coefficient were very similar for these two different marine systems.

3. LLM Monitoring Observations

Observations of water column parameters in a transect crossing the Gulf Intracoastal Water Way (GIWW) found highest concentrations of TSS, NH_4^+, and chlorophyll *a* in regions of the Lower Laguna Madre estuary closest to the GIWW. Transect extremes (farther from the GIWW or in seagrass beds) exhibited reduced concentrations. This observation was attributed to seagrasses resisting new sediment resuspension and trapping previously resuspended material.

Correlation analysis of TSS, NH_4^+, and chlorophyll *a* showed significant dependence between each of the three measured parameters. Elimination of the data collected in close proximity to the GIWW decreased overall statistical significance of these results.

Analysis of wind direction and speed data collected near the established transect confirmed potential for wind-generated wave interaction with the sediments for the majority of the collection period (one year). Only the potential for resuspension was established. Wind wave interactions in shallow estuaries are extremely complex, especially in systems as large as the Lower Laguna Madre. Though observations indicated a diurnal pattern of wind during the transect sampling period, a long term relationship was not established.

Spatial variation in measured water column parameters exceeded temporal variation over the period the estuary was sampled.

Bioassays conducted during the monitoring effort involving nutrient spikes (N and P) confirmed the potential for pulsed nutrient removal by the resident pelagic community.

4. Model Analysis of Conditions in the Lower Laguna Madre

A simplified Nutrient/Phytoplankton model system was generated to facilitate analysis of data collected in the Lower Laguna Madre estuary during the observation section of this work. Introduction of resuspension to the simplified model of the estuary allowed for maintenance of nitrogen in the system (in the form of NH_4^+ and algal biomass). Model runs excluding the resuspension function resulted in the loss of NH_4^+ and chlorophyll within two days of the model start.

The model system exhibited relative insensitivity to state variable initial conditions. Variation of these initial conditions always resulted in return to either stable oscillation (in the resuspension included case) or in near elimination of NH_4^+ and chlorophyll a (in the resuspension excluded case).

Stable, unvarying concentrations of model state variables are produced when resuspension is included as a source of nitrogen to the overlying water. When resuspension is included via an oscillating function designed to create a 24 hour signal, state variables oscillate with the resuspension input function. Though not necessary, the inclusion of varying input is probably more representative of estuarine conditions.

In addition to the oscillating input of sediments a pulse of nitrogen input was introduced to the system. The pulse was observed to be rapidly absorbed by the system further establishing the stable nature of the formulation.

Human interaction with coastal systems has led to unintended but deleterious effects (Bricker et al., 1999) through indirect agricultural practices (Rabalais et al., 1996) as well as direct alteration to coastal morphology (Onuf, 1994). In many cases alterations to coastal systems is necessary (Morton et al, 2001). The presented dissertation was intended mainly to address the behavior of regenerated NH_4^+ in marine sediments. Reasons have been given why this parameter is extremely important, specifically in coastal systems. Though conclusions have been drawn from the observations garnered from the research, only two sites were studied extensively. Much of the observed behavior of NH_4^+ in these two systems was consistent, but further research is necessary to establish the validity and implications of these findings.

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